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Prohlášení

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Abstract

Noble metals are widely used in industry due to their excellent catalytic and optical properties. Because of limited reserves and high prices, it is desired to make effective use of every atom. It has been possible in recent years to produce subnanometer clusters or even isolated atoms, despite their low resistance against sintering. Furthermore, it has been recently established that the encapsulation of single atoms and subnanometer noble metal clusters can be achieved via trapping at metal oxides, ranging from two-dimensional layered materials to the void space within the pores of zeolites. However, neither the atomistic mechanisms of atom/cluster trapping, nor the means by which they may be optimized are known. Furthermore, the relationship between the physical and electronic state of trapped atoms/clusters and their reactive properties in catalysis are currently only weakly understood.

In this thesis, we used theoretical methods ranging from global structure optimization to kinetic Monte Carlo to identify the roles of cluster size, charge state, and the present and type of common adsorbents on the stability, catalytic and optical properties of subnanometre-sized noble metal clusters trapped at metal oxides. This thesis takes the form of three sections: (1) Structure, stability, and migration dynamics of zeolite-encapsulated platinum/gold clusters, (2) Stability and optical properties of zeolite-encapsulated silver clusters, (3) Electronic structure effects on promoting CO oxidation catalysis on palladium particles in hectorite. The main findings of these topics are summarized below.

(1) High stability of platinum (Pt) atoms have been proposed inside high-silica zeolites. We probed the potential energy surface for Pt in siliceous zeolite with framework topology of LTA. We found that single Pt atom spontaneously causes local defect formation in the siliceous framework, trapping Pt in the six-ring. This preference for six-rings is general across several frameworks, leading to a deep kinetic trap which severely

hinders migration through the zeolite pore system. The adsorption of common reducing adsorbates (CO , H_2) on the single Pt atom weakens the binding, reduces the migration barrier, destabilizes the six-ring trapping site, and thereby promotes cluster growth. Conversely, framework heteroatom substituents aluminium and boron significantly increase the binding between Pt atom and zeolite framework. We propose that by altering the Si/Al ratio in the zeolite framework, the kinetic trapping ability of the zeolite framework to the single Pt atom may be tuned. This work provides an atomistic picture of the dynamics of the single metal atom in high-silica zeolites, which represents the fundamental basis for understanding the deactivation of subnanometer catalysts.

(2) Subnanometer silver (Ag) encapsulated in zeolite pores has been shown experimentally to exhibit remarkable luminescent properties. The cluster size, charge state, and ligand environments are important to the stability of the whole system. All the above factors are likely to affect the optical properties of the encapsulated subnanometer silver as well. However, the cluster size, charge state, electronic structure, and ligand environments of encapsulated subnanometer Ag are not yet well understood. In particular, there remain questions over the location and degree of hydration of these particles. We studied the stability of silver clusters incorporated into the sodalite cages of a partially Ag-substituted sodium-form zeolite with FAU topology, as a function of charge states, cluster sizes, and the number of attached water molecules. We found that the triangular Ag_3 and tetrahedral Ag_4 with one and two positive charges, respectively, are the most stable configurations. When multiple water molecules are bonded to Ag_3 or Ag_4 , the structure becomes energetically unfavorable, and thus we may rule out highly coordinated Ag clusters inside the sodalite cage. A correction method is used to associate energetics with higher-level method, and it is found that a simple correction to the results of density functional theory within the generalized gradient approximation (GGA) functional can yield accurate optical properties to coupled cluster level, which greatly simplifies the task of modelling encapsulated silver clusters for future work.

(3) Charge transfer between noble metal nanoparticles and their support can affect the catalytic activity, morphology, and stability of the nanoparticles. Due to the gain or loss of electrons, the adsorption energy of the reactants and the desorption energy of the products will vary considerably compared to the neutral nanoparticles of the same size. It was reported that palladium (Pd) nanoparticles sandwiched between negatively charged clay nanosheets had better performance for carbon monoxide oxidation than that of the same size Pd nanoparticles supported on the external surfaces of hectorite or on a conventional Al_2O_3 support. Via atomistic modelling at the density functional level, we identify a correlation between improved catalytic performance of the positively charged palladium nanoparticles and a decrease in CO desorption energy, which was not shared with oxygen adsorption energies. It is rationalised that a decrease in CO binding reduces CO poisoning at high coverages, and thus charging maintains a surface better organised for CO oxidation catalysis. Such a finding may be generalised to other charge-pinned noble metal particles for the optimisation of catalysis via surface charge-transfer mechanisms.

Keywords: global structure optimization, kinetic Monte Carlo, density functional theory, zeolites, noble metal clusters, single-atom catalysts, sintering resistance, encapsulation, excitation energy

Abstrakt

Vzácné kovy se často využívají průmyslově, zejména kvůli svým mimořádným katalytickým a optickým vlastnostem. Vzhledem k jejich nízkému výskytu a s tím související vysoké ceně, je třeba maximalizovat využití každého jednotlivého atomu vzácného kovu. V poslední době se podařilo připravit subnanometrové klastry nebo dokonce izolované atomy, a to navzdory veliké tendenci těchto kovů aglomerovat do větších celků. Rovněž bylo ukázáno, že rezistence vůči aglomeraci je posílena jsou-li kovové atomy nebo klastry zachyceny v oxidické matici, například ve vrstevnatých dvourozměrných materiálech nebo v kanálech zeolitů. Detailní pochopení mechanismu záchytu a stabilizace kovů a kovových klastrů není znám a není tedy ani jasné, jakým způsobem je možné optimalizovat vlastnosti těchto materiálů. Stejně tak vztah mezi elektronovou strukturou kovů/kovových klastrů zachycených v matici a jejich katalytickými vlastnostmi je znám pouze částečně.

V této práci jsme použili širokou škálu teoretických metod od globální optimalizace až po kinetické Monte Carlo abychom identifikovali vliv velikosti kovového klastru, jeho náboje a typu adsorbentu na stabilitu, katalytické vlastnosti a optické vlastnosti kovových nanočástic. Práce je rozdělena do tří sekcí: (1) Struktura, stabilita a migrace platinových a zlatých klastrů zachycených v zeolitové matici. (2) Stabilita a optické vlastnosti stříbrných klastrů zachycených v zeolitové matici. (3) Vliv elektronové struktury paládiových nanočástic v hectoritu na katalytickou oxidaci CO. Níže uvádíme hlavní teze disertační práce.

(1) Pro vysokosilikátové zeolity byla nalezena vysoká stabilita izolovaných Pt atomů. Povrch potenciální energie řídící difuzi Pt atomů byl zkonstruován pro silikátový zeolit se strukturou LTA. Izolovaný Pt atom reaguje se zeolitovou mříží a dojde k tvorbě lokálního defektu, ve kterém je Pt atom zachycen v šestičlenném kruhu LTA. Preference atomů Pt se vázat v šestičlenném kruhu byla nalezena i pro jiné struktury zeolitů. Zachycení Pt v

šestičlenném kruhu vede ke vzniku kinetické bariéry, která výrazně omezí migraci atomů Pt. Adsorpce běžných redukčních adsorbátů (H_2 či CO) na izolovaném atomu vede k oslabení vazby Pt k zeolitu a tím i ke snížení aktivační energie pro difuzi Pt a v konečném důsledku vede k aglomeraci atomů Pt ve větší celky. Přítomnost heteroatomů (Al a B) v zeolitové mříži vede k výraznému posílení vazby mezi Pt a zeolitem. Proto navrhuje, že rezistence izolovaných atomů Pt vůči aglomeraci může být významně snížena vhodnou volbou Si/Al poměru zeolitu. Tato část práce představuje mechanismus a dynamiku migrace Pt atomů ve vysokosilikátových zeolitech a přináší důležité závěry k pochopení mechanismu aglomerace atomů Pt ve větší celky v zeolitech.

(2) V uplynulých letech byly experimentálně demonstrovány vynikající luminiscenční vlastnosti subnanometrových klastrů stříbra zachycených v zeolitech. Stabilita takových klastrů závisí mimo jiné i na velikosti klastru, jeho náboji a přítomnosti adsorbátů. Stejně faktory ovlivňují i luminiscenční vlastnosti stříbrných klastrů. Vzhledem k velikosti těchto klastrů je řada experimentálních charakteristik pouze přibližná: velikost klastrů, náboj a koncentrace a uspořádání adsorbátů na povrchu Ag klastrů. Zejména se vedou spory o polohu klastrů v zeolitové struktuře a o stupni hydratace těchto klastrů. V práci se zabýváme studiem stability stříbrných klastrů inkorporovaných do sodalitových klecí v sodné formě zeolitu FAU, kde část kationtů Na je nahrazena kationty Ag. Stabilitu studujeme v závislosti na velikosti stříbrných klastrů, jejich náboje, a počtu vod adsorbovaných na povrchu klastru. Zjistili jsme že trigonální Ag_3^+ a tetrahedrální Ag_4^{2+} klastry jsou nejstabilnější. Vzhledem k omezenému prostoru sodalitové klece je vazba vody na tyto klastry energeticky nevýhodná a tudíž přítomnost hydratovaných stříbrných klastrů v sodalitových klecích je nepravděpodobná. Vzhledem k nepřesnostem v popisu optických vlastností kovových klastrů na úrovni DFT metody jsme na základě přesných *ab initio* výpočtů našli korekci pro GGA funkcionály, která umožňuje spolehlivý popis elektronických stavů stříbrných klastrů.

(3) Přenos náboje mezi Pd nanočásticemi a maticí (na které jsou dispergovány) vede k

ovlivnění morfologie a stability nanočástic a ke změně jejich katalytických vlastností. V důsledku přenosu elektronů z nebo na Pd nanočástici se ve srovnání s neutrální Pd nanočásticí dramaticky mění adsorpční energie reaktantů i produktů. Bylo známo, že Pd nanočástice umístěné mezi záporně nabitou tenkou (nanometrovou) vrstvou jílu vykazují vyšší katalytickou aktivitu v oxidaci CO než Pd nanočástice o stejné velikosti dispergované na externím povrchu hectoritu či konvečním Al_2O_3 . Naše modelování na úrovni metody funkcionálu hustoty ukázalo, že vzrůst katalytické aktivity v závislosti na kladném náboji nanočástice je způsoben snížením desorpční energie CO, která se tak stala menší než desorpční energie O_2 . Z toho důvodu dochází u kladně nabitých Pd nanočástic ke snížení pokrytí povrchu molekulami CO, které u vysokých pokrytí vede až k “otrávení” povrchu katalyzátoru. Tento závěr může mít obecnější platnost a modulace náboje nanočástic vzácných kovů způsobená interakcí s adsorbentem může být využita pro optimalizaci katalytických vlastností v důsledku kontrolovaného přenosu náboje mezi nanočásticí a adsorbentem.

Klíčová slova: globální optimalizace, kinetické Monte Carlo, metody funkcionálu hustoty, zeolity, klastry vzácných kovů, katalýza jednotlivými atomy, odolnost vůči aglomeraci, záchyt klastrů v matici, excitační energie

List of the abbreviations

2D	two dimensional
3D	three dimensional
BBU	basic building unit
bcc	body-centered cubic
CBU	composite building unit
CCSD	coupled-cluster with single and double excitations
CHA	Chabazite
CI-NEB	climbing image nudged elastic band
COF	covalent organic framework
d4r	double four-ring
d6r	double six-ring
DFT	density functional theory
DOS	density of state
EOM- CCSD	Equation-of-Motion CCSD
EXAFS	extended x-ray-absorption fine-structure
FAU	Faujasite
GGA	generalized gradient approximation
hcp	hexagonal close packing
kMC	kinetic Monte Carlo
LDA	local-density approximation
LTA	Linde type A
MC	Monte Carlo
MD	molecular dynamics
MEP	minimum-energy path
MOF	metal-organic framework
NEB	nudged elastic band
PBE	Perdew–Burke–Ernzerhof
pDOS	projected density of state

PES	potential-energy surface
QTAIM	quantum theory of atoms in molecules
SBU	secondary building unit
SCF	self-consistent-field
sod	sodalite
TST	transition state theory
TDDFT	time-dependent density functional theory

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1 Introduction

Catalysis plays a crucial role in our daily life. Around 90% of commercial chemicals are produced by methods including at least one catalytic step.¹ A catalyst speeds up a chemical reaction by lowering the required energy to reach the transition state.²⁻³ With the application of catalytic technology, raw materials can be converted into products or energy more efficiently and economically and catalysts are widely used in the chemical industry,⁴ food processing,⁵ pharmaceutical industry,⁶⁻⁷ energy transformation⁸ and other fields.⁹ Transition metals have been widely used as catalysts.¹⁰⁻¹¹ The reason is that transition metal atoms can be in various oxidation states, so they can gain or lose electrons from the reagents. For example, the Haber-Bosch process using iron as the catalyst enables human beings to effectively convert nitrogen (N_2) and hydrogen (H_2) to ammonia (NH_3), which allows people to produce plant fertilizers in large quantities, thus providing enough food to people for the population explosion.¹² Another example is the conversion of crude oil to useful petrochemicals via fluid catalytic cracking (FCC).¹³⁻¹⁴ The solid acids, including zeolites, can reduce the temperature for FCC, and even drive selectivity towards particular desired products.¹⁵⁻¹⁷

Metals are not only in the form of bulk but can be nanostructured into particles. According to the size, metals can be divided into bulk, or bulk-like particles ($> 100 \text{ nm}$), nanoparticles ($1 - 100 \text{ nm}$), and subnanometer particles ($< 1 \text{ nm}$).¹⁸ Its structure morphology, electronic structure, and optical properties are closely related to particle size, and therefore particle size can be a useful handle to tune reactive or catalytic properties of noble metals.¹⁹⁻²¹ The stacking structure of atoms changes significantly with the decrease in particle size.²² For bulk and larger nanoparticles, gold, for example, has a face-centered cubic (fcc) structure. When the particle size is small enough, there exist the body-centered cubic (bcc) and hexagonal close packing (hcp) structure.²³ For Au structure with only six atoms. The planar configuration is preferred. The structural

transition from 2D to 3D occurs on the size of seven atoms.²⁴ With the decrease of particle size, and thus the change in structure, the surface area per unit volume or weight increases rapidly.²⁵⁻²⁶ For example, when the particle size of a Pt nanoparticle decreases from 2.4 to 0.8 nm, the fraction of surface atoms increases from 52 % to 92 %, and the fraction of Pt low-coordinated metal atoms at edges and corners increases from 27 % to 92 %.²⁵ These highly unsaturated atoms serve as adsorption sites, and the increase of unsaturated atoms can lead to an increase in catalytic activity. A classic example of particle size effects in noble metal catalysis is observed for Au. For a long time, Au was regarded as the least reactive metal toward atoms or molecules at the interface with a gas or a liquid.²⁷ By contrast, Au nanoparticles with a size of 3-5 nm, deposited on metal oxides (α -Fe₂O₃, Co₃O₄, and NiO) show high activity for CO oxidation at temperatures as low as -70 °C.²⁸⁻²⁹

The electronic structure of the metal particles is also closely related to the size of the particles.²⁵ The electronic energy levels of bulk metals are so close that they form a continuous energy band. For small nanoparticles and clusters, in which there are insufficient atoms to provide the necessary number of states to build a complete continuous band, the electronic states are discrete and molecule-like. This transition from band-like to molecule-like occurs when the size of the nanoparticles is around 1 to 3 nm, depending on the metal.^{19, 22, 30-32} The change of the electronic structure has a significant impact on the orbital hybridization and charge transfer between nanoparticles and the reactants, thus changing adsorption, activation, and desorption energy, which in turn affects particle activity as a catalyst. For example, the electron affinity energy of Ag nanoparticles with a mean cluster radius of 5 - 9 Å is much larger than that of bulk, which promotes O₂ dissociation on Ag nanoparticles.³³ Besides the excellent catalytic properties of Ag nanoparticles, the subnanometer Ag particle (only a few atoms) shows remarkable luminescence properties.³⁴⁻³⁷ The size and charge state of subnanometer Ag particles have a significant influence on the emission colors and brightness.

The novel catalytic, electronic, and optical properties mentioned above come from metal particles in the range of a few nanometers or even less than 1 nm. However, the surface free energy of metal particles increases significantly with the decrease of particle size. The separated metal particles have a strong tendency to aggregate into large particles to reduce the surface free energy of metal particles. To maintain the special catalytic, electronic and optical properties, the cluster must be protected against aggregation.

There are two main recognized mechanisms for the sintering of nanoparticles: Ostwald ripening and particle migration and coalescence.³⁸ Ostwald ripening is a surface energy-driven process in which atoms leave smaller particles and form bonds with larger particles. In order to reduce the difference in surface diffusion energy among particles, the size of metal particles should be controlled in a narrow range, which thereby inhibits the Ostwald ripening process. Particle migration and coalescence³⁹ is another agglomeration process in which small nanoparticles undergo a Brownian-like motion on the support surface and coalesce into large nanoparticles.

Without additional stabilization, metal atoms or nanoparticles tend to be mobile on the support surface and grow to large nanoparticles, as their high cohesive energies dictate that the final thermodynamic product is a metal particle of maximum size.⁴⁰ There are several methods for the stabilization of ultrasmall metal clusters and single atoms, including steric, charge-based, and ligand protection. For steric stabilization, metal particles can be encapsulated into the cages or channels of porous materials (such as zeolites,⁴¹⁻⁴³ metal-organic frameworks,⁴⁴⁻⁴⁵ or covalent organic frameworks⁴⁶⁻⁴⁸) or be encapsulated between the layers of layered materials (such as layered double hydroxides),⁴⁹⁻⁵⁰ thereby prohibiting the movement of metal particles and limiting their direct interaction and thus growth. By adding charge to the nanoparticle, the Coulomb repulsion makes nanoparticles separate.⁵¹ By attaching organic ligands to the nanoparticle surface, ligands can provide coordination protection to avoid nanoparticles contracting each other.⁵²⁻⁵³

Zeolites are a promising class of support materials to sterically stabilize metal subnanoparticles against sintering.^{42, 54} Zeolites are a family of microporous crystalline aluminosilicates,⁵⁵ which have various cages, cavities, and channels that enable encapsulating subnanometer particles with different diameters. In addition to the diversity of cage and channel structures, zeolites are also materials with high thermal stability. The decomposition temperature for low silica zeolites is about 700 °C. For the pure silicious zeolite, such as silicalite, is stable up to 1300 °C.⁵⁶ The high thermal stability enables zeolites to react under severe conditions of gas-phase and liquid phases. Furthermore, the synthetic process of zeolite is a mature technology. Therefore, the cost of large-scale popularization and application is reduced.

There are currently three main methods to encapsulate metal atoms in zeolite pores: i) wet-impregnation, ii) ion-exchange and iii) one-pot synthesis. Impregnation is a widely used method because of its easy implementation, low costs, applicability to a wide range of materials, and the limited amount of waste.⁵⁷⁻⁶¹ In this method, the zeolite is mixed with a precursor-containing solution. The precursor is introduced into the pores via capillary action. The solvent is then removed with evaporation or other methods. The dried product is further processed (e.g., calculation and/or reduction) to obtain the desired metal encapsulated materials. However, because most metal species are located on or near the surface, the distribution of metal atoms is uneven, and their thermal stability is low. In addition, the only force is the capillary action which results in low encapsulation efficiency. Ion-exchange is one of the most important techniques to modify zeolites. Ion-exchange method typically uses Al-containing zeolites to accommodate metal particles.⁶²⁻⁶⁵ For example, a Pt tetra-ammine ion, $[\text{Pt}(\text{NH}_3)_4]^{2+}$, can be exchanged with two Na^+ ions in the zeolite. With the calcination step, the ammine ligands are decomposed by heating in O_2 , and the naked Pt^{2+} ion forms bonds with oxygen atoms in the framework.⁶⁶ Because of its easy implementation, low cost, and moderate encapsulation efficiency, this method has been widely used to encapsulate metal particles into the zeolite framework. In

the one-pot synthesis, metal precursors are encapsulated into the zeolite framework during the crystallization process.⁶⁷⁻⁷² The structure is then calcined. Using the one-pot synthesis method, the size of metal species can be kept in the subnanometer scale range. The one-pot synthesis method can also reduce the amount of metal particles on the external surface after the calcination and/ or reduction steps.⁷³

It is well known that metal nanoparticles trapped in zeolite cages show high stability.⁷⁴⁻⁷⁶ In recent research, single Pt atoms in high Si/Al ratio CHA zeolite were found to have surprisingly high stability in O₂ in addition to reversible redispersion via redox cycling.⁷⁷⁻⁷⁸ The high stability of single Pt atoms in O₂ does not derive primarily from the physical blocking of the cagelike structure. The exact binding sites for the high stability of single Pt atoms in CHA that allow suppression of the Ostwald ripening sintering remains unclear. We manage to explain how single Pt atoms may be stabilized within high-silica zeolite by using basin-hopping global geometry optimization to identify low-energy structures and calculate migration barriers between representative local minima.

In addition to the unknown binding site, how gas molecules (e.g. CO, H₂) affect nanoparticles sintering and redispersion is also not very clear.⁷⁹⁻⁸⁰ For Pt nanoparticles encapsulated in high silicious CHA zeolite, it can be decomposed into small nanoparticles or subnanometer particles under the O₂ atmosphere at 650 °C. By contrast, the disintegrated small particles can aggregate into large particles under the H₂ atmosphere at 400 °C.⁷⁸ By controlling the temperature and atmosphere, the small nanoparticles (1 - 2 nm) can be decomposed into single platinum atoms, and vice versa. This kind of dynamic transformation has also been found in supported Au and Cu nanoparticles.⁸¹⁻⁸² We use the kinetic Monte Carlo method to assess the extent to which temperature and reduction atmosphere (CO and H₂) affect the stability and migration of single Pt atoms in high-silica zeolite.

Apart from the special binding sites and adsorbed gas molecules, the charge states and ligand environments are also important to the stability of zeolite encapsulated metal

nanoparticles. The morphology and stability of metal nanoparticles vary with the charges on the metal nanoparticles.⁸³⁻⁸⁴ The morphology of Ag_3 in the vacuum phase is an isosceles triangle. By contrast, Ag_3^+ is an equilateral triangle structure in the vacuum phase.⁸⁵ The ligand environments, such as water molecules, are another factor determining the morphology and stability of metal nanoparticles.⁸⁶⁻⁸⁷ To study the charge states and ligand environment effects on the stability of zeolite encapsulated metal particles are more complex as the metal particle and ligand environment also interact with the zeolite framework. Even though the instrumental analysis can provide some information, the analysis of such subnanometer metals is challenging because of the sensitivity of few atoms metal clusters and zeolite frameworks radiation damage caused by high-energy beam probes used in high-resolution technologies, such as high-resolution transmission electron microscopy.⁸⁸⁻⁹⁰ Computational studies are helpful to further understand the size, morphology, ligand effects, and electronic state of the subnanometer metal particles.⁹¹⁻⁹² In this work, various theoretical methods are employed to explain the effects of cluster size, charge states, and ligand environments on the stability and properties of encapsulated metal atoms and particles.

2 Model and Methods

2.1 Model

2.1.1 Zeolite

Zeolites are microporous crystalline aluminosilicates.⁹³ The basic building unit is TO_4 tetrahedra ($T = \text{Si}, \text{Al}$). By sharing corner oxygen atoms, they can form a wide range of framework topologies. For the pure silicious structure, the combination of SiO_4 units can build an uncharged structure. When the Al atom is incorporated into the framework, compared with the four valence electrons of Si, the three valence electrons of Al lead the framework to become negatively charged. Extra-framework cations (inorganic or organic) are required to balance the charge to maintain the neutrality of the whole framework. The chemical composition of zeolite can be described as $M_{n/m}^{m+} \cdot [\text{Si}_{1-n}\text{Al}_n\text{O}_2] \cdot n\text{H}_2\text{O}$, where $M_{n/m}^{m+}$, $[\text{Si}_{1-n}\text{Al}_n\text{O}_2]$ and $n\text{H}_2\text{O}$ are extra-framework cations, zeolite framework, and sorbed phase, respectively. The sorbed phase exists because of the hydrophilicity of Al-containing zeolites and it can be removed by thermal treatment. The extra-framework cations are ion-exchangeable and produce abundant ion-exchange chemistry of zeolites. The distribution of the cations controls the electric fields in the pores of the zeolite. By changing ion's type and amount, we can replace the atom with a different valence electron atom in the zeolite framework, and then change the adsorption and catalytic performance in a more subtle way than a simple molecular sieve.

The amount of Al incorporated into the zeolite framework can be varied within a wide range ($\text{Si}/\text{Al} = 1$ to ∞). Lowenstein⁹⁴ proposed that the lowest limit of $\text{Si}/\text{Al} = 1$ of the zeolite frameworks because the negative charged AlO_4^- tetrahedra cannot bond together due to the electrostatic repulsions. However, some aluminosilicate structures which disobey the Lowenstein rule have been reported, such as zeolite stilbite⁹⁵ and aluminate sodalites⁹⁶. Based on Si/Al ratio, zeolite can be divided into low silica ($\text{Si}/\text{Al} \leq 2$),

intermediate silica ($2 < \text{Si}/\text{Al} \leq 5$), and high silica ($5 < \text{Si}/\text{Al}$). Cation concentration, siting, and exchange selectivity vary significantly with Si/Al ratios and play an important role in adsorption, catalysis, and ion-exchange applications.

The negative charge is related to the $[\text{AlO}_4]^-$ tetrahedron and is mainly located at the oxygen atoms ($\text{O}^{\delta-}$) surrounding the aluminum atoms. If the negative charge is compensated by proton, protons are always bound to one of these framework oxygen atoms (Si-O-Al-OH-Si) forming representative Brønsted acid. The concentration of the acid site decreases with an increase in Si/Al ratio, and the acid strength and proton activity coefficient increase with the decrease of Al content.⁵⁶ This kind of Brønsted acidic site plays an important role in heterogeneous catalysts, such as zeolite Y and ZSM-5 used as the catalysts in the fluid catalytic cracking process for the gasoline production in refineries.

Basic building units TO_4 are too simple to represent the structural characteristics of zeolites. Therefore, researchers have put forward some higher-order building units, such as secondary building units (SBU), composite building units (CBU), and natural tiles.

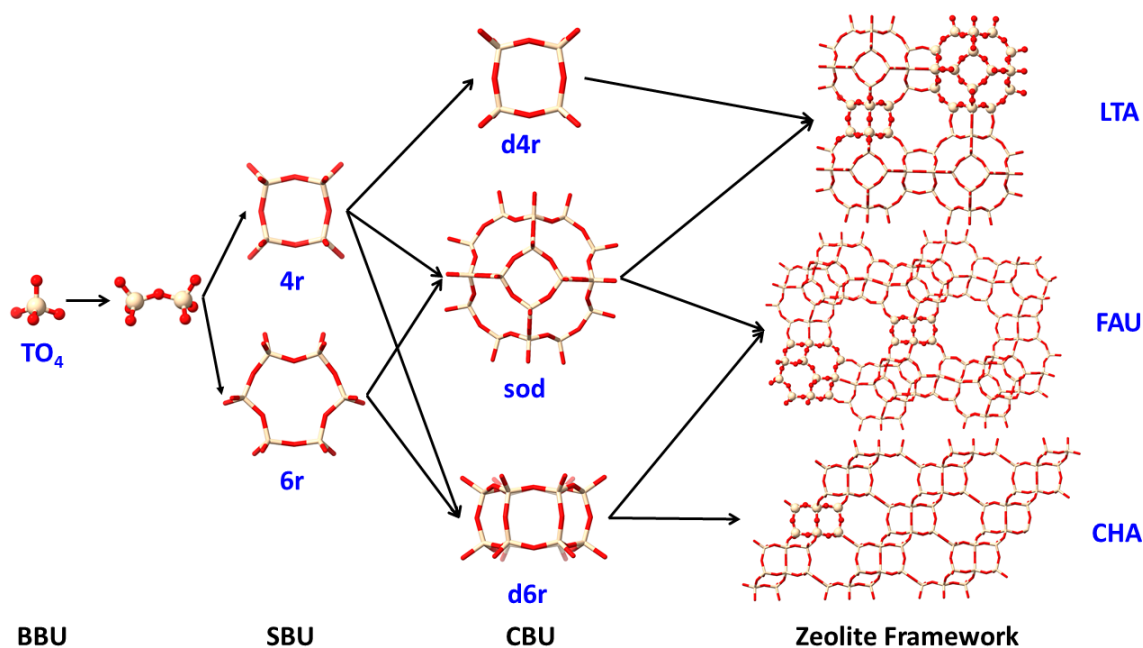


Figure 1 The process of building a zeolite framework.

SBU were introduced by Walter M. Meier⁹⁷ and Joseph V. Smith⁹⁸. The original idea of introducing SBUs is that the whole frame could be built by using one SBU. SBUs are non-chiral units with up to 16 T-atoms. Four-ring and six-ring are the most common SBUs. Due to the increasing complexity of the new zeolites discovered in the past decade, it is no longer possible to describe all framework structures with one SBU. Two or more SBUs are needed to describe zeolites. Up to now, as of October 2021, there are 255 zeolite framework codes. It is, however, not sufficient to describe the zeolite framework with SBUs. Therefore, CBUs are used to describe the zeolite framework. CBUs represent the common structural characteristics, for example, cages, channels, chains, and layers, existing in more than one zeolite topology. **Figure 1** shows three composite building units: d4r, d6r, and sod. Besides these three types, there are many composite building units, such as d8r, lta or cha.

a) Linde Type A

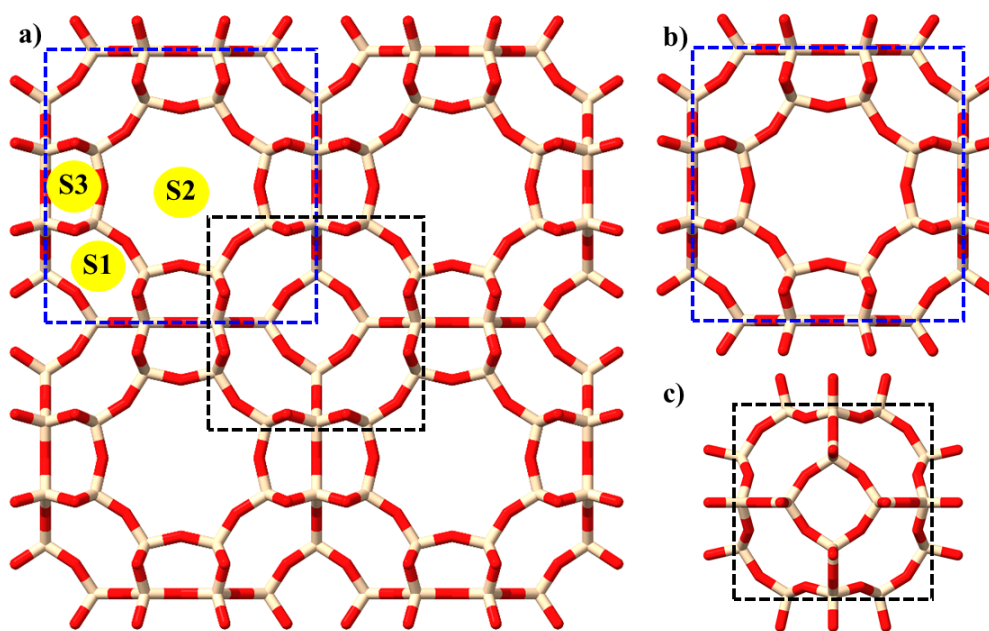


Figure 2 (a) LTA framework with three crystallographic sites S1 (the six-ring), S2 (the eight-ring) and S3 (the four-ring); (b) α cage of LTA; (c) β cage of LTA.

The Linde type A (LTA) zeolite (**Figure 2**), also known as zeolite A, does not exist in nature and was synthesized by the hydrothermal crystallization process.⁹⁹ LTA was first discovered at the Union Carbide Corporation Laboratories in the 1950s.¹⁰⁰ It is synthesized with a Si/Al ratio of about 1 to 6. Pure silica LTA was first reported by Corma et al.¹⁰¹ There are hundreds of thousands of tons of LTA zeolite produced for the application of water softening,¹⁰² industrial gas drying,¹⁰³ gas separation¹⁰⁴.

LTA zeolite framework is built with the sodalite cage (or β cage) consisting of 24 T atoms connected through the double four-ring. In the process, it creates an α cavity but is also known as an α cage due to historical reasons.¹⁰⁵ α cages are connected to each other through the eight-ring. The free diameter of the eight-ring channel is about 4 Å, so an open zeolite framework is formed, and its volume fraction is about 47 %.¹⁰⁶ LTA has a three-dimensional pore system molecules in which no molecules larger than water are accessible to all three directions.

In the LTA framework, besides proton, metal cations, such as Li^+ , Na^+ , K^+ , and Ca^{2+} , can balance the framework's negative charge. Instead of binding to the single O atom in the zeolite framework, these cations stay in the space above the rings. There are three cation sites: as shown in **Figure 2**, S1 (above the center of the six-ring), S2 (above the center of the eight-ring), and S3 (above the center of the four-ring). Sites S1, S2, and S3 can accommodate 8, 3, and 12 cations in each α cage, respectively. Cations tend to prefer sites S1, then S2, and then S3. Because S2 is close to the center of the eight-ring, cations occupying the S2 position will influence molecules' diffusion.

b) Faujasite

Faujasite (FAU) is a natural zeolite (**Figure 3**). The name Faujasite was firstly used by Damour (1842) to describe a mineral crystal which was previously considered apophyllite at Sasbach, Kaiserstuhl, West Germany.¹⁰⁷ FAU is widely used as a fluid catalytic cracking catalyst, which converts the high-boiling fractions of petroleum crude

oil into more valuable gasoline, diesel oil, and other products.¹⁴

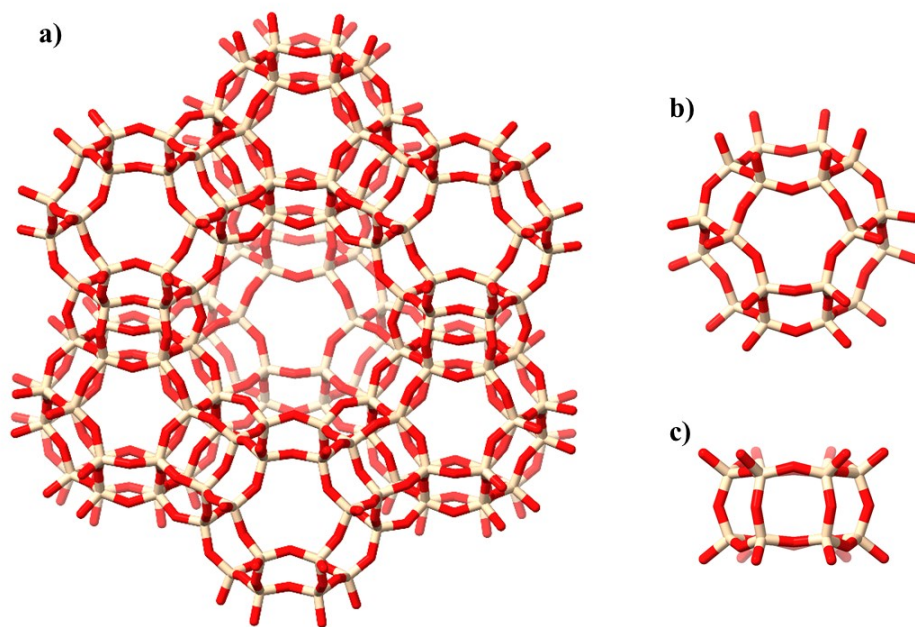


Figure 3 (a) FAU framework; (b) β cage; (c) d6r

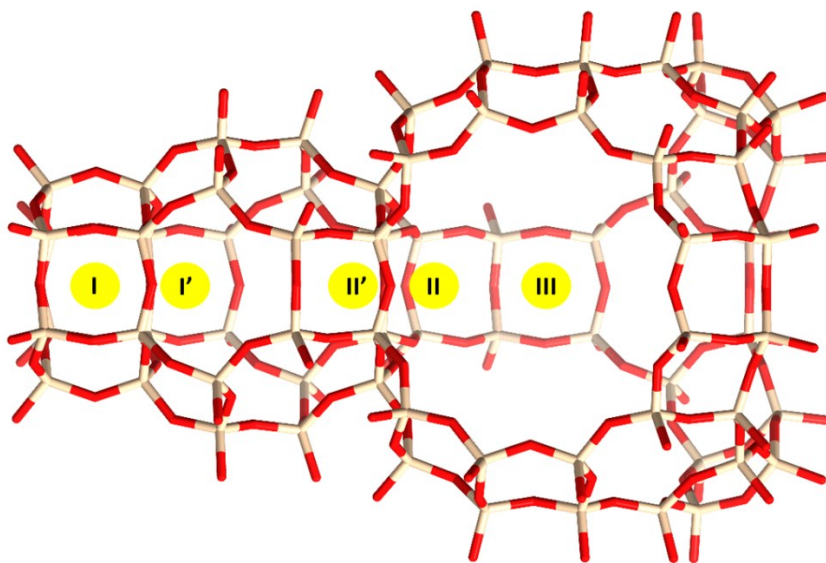


Figure 4 Cation sites in FAU.

The framework of FAU is composed of linking sodalite cages (or β cages) via a double six-ring (d6r). In this process, it produces a large cavity called a "supercage", which can

be accessed through a three-dimensional 12-ring. Every FAU unit cell has 16 d6r, eight sodalite cages, and eight supercages.

When Al appears in the FAU framework, FAU has more cation sites than that of LTA. All the possible cation sites show in **Figure 4**. Site I is in or near the center of the d6r. Site I' is in the sodalite cage and above the center of the six-ring of d6r. Site II' is also in the sodalite cage but above the six-ring connecting to the supercage. Site II and III are in the supercage and above six-ring and four-ring, respectively. For every FAU unit cell, it contains 16 I, 32 I', 32 II', 32 II, and 96 III cation sites, respectively.

2.1.2 Slab and cluster

Crystal surfaces play an important role in many chemical and physical processes. In order to simulate the electronic structure and catalytic performance of crystal surface, slab and cluster models are widely used. In the slab model, the surface is modeled by a periodic 3D structure, which contains a crystal slab separated by vacuum regions to keep the periodicity in this direction. The vacuum area needs to be wide enough to avoid the interactions between the slab and its upper and lower virtual copies (**Figure 5**). In addition, the slab model must be thick enough to reproduce the bulk-like behavior of the slab center area to avoid unphysical interactions between the top and bottom surfaces of the slab model. When slab models are used to study the catalytic reaction on the surface, in order to investigate the coverage effect, the unit cell of the slab needs to extend laterally, so as to avoid the adsorbed species interacting directly with their images in adjacent cells or indirectly through changes in the electronic structure of the surface.

The cluster model is another option to investigate surface adsorption reactions under low coverage. To use clusters to simulate surfaces, there are several rules to follow:¹⁰⁸

- (i) Except for corners and edges, atoms on the cluster surface should be equivalent to atoms on the crystal surface;

(ii) The coordination of the cluster surface atoms (except for corners and edges) is close to that of atoms on the crystal surface;

(iii) Stoichiometry of the bulk crystal is reflected by the cluster.

Although cluster models eliminate the issues related to the direct and indirect interactions between adjacent slabs, the size, and shape of the cluster must be carefully selected due to the inevitable boundary effects.¹⁰⁹ The atoms of the boundary cluster deviate from the lattice positions, and the electron density distribution on the boundary atoms is different from that of the perfect crystal.

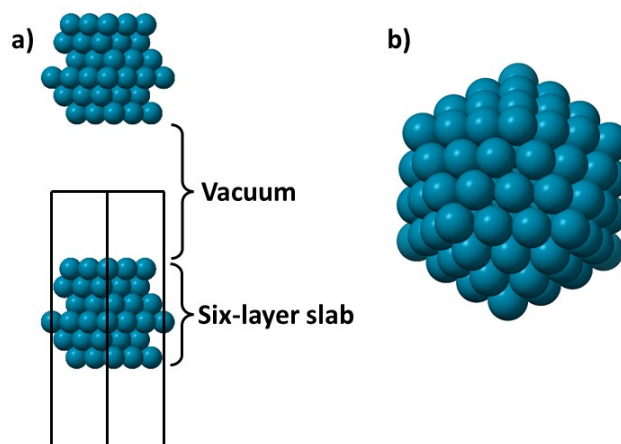


Figure 5 a) Slab model of Pd with six-layer. The black line is the shape of the unit cell of the slab model; b) Cluster model of Pd with 147 atoms.

2.2 Methods

Solid-state materials consist of a large number of atoms. One of the key issues in materials research is to understand the relationship between material structure and properties. Physical properties (optical properties, thermal properties, magnetic properties, mechanical properties) of materials are closely related to the electronic properties of the system. Therefore, investigating electronic properties is an effective way to understand the properties of a material at the atomic scale. Up to now, many methods are being

proposed to study material properties at the atomic scale, such as Hartree–Fock, and Density Functional Theory.

For a multi-particle interacting system composed of a large number of atoms, the motion of electrons and nucleus can be described by the Schrödinger equation:

$$\hat{H}\Psi=E\Psi \quad (1)$$

where $\hat{H}$, Ψ and E are Hamiltonian, wavefunction, and total energy of the system, respectively. When the nuclei and electrons are considered to be point masses and ignore spin-orbit and relativistic interactions, the Hamiltonian operator is

$$\begin{aligned} \hat{H} = & -\frac{\hbar^2}{2} \sum_{\alpha} \frac{1}{m_{\alpha}} \nabla_{\alpha}^2 - \frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 + \sum_{\alpha} \sum_{\beta > \alpha} \frac{Z_{\alpha} Z_{\beta} e^2}{4\pi\epsilon_0 r_{\alpha\beta}} \\ & - \sum_{\alpha} \sum_i \frac{Z_{\alpha} e^2}{4\pi\epsilon_0 r_{i\alpha}} + \sum_j \sum_{i > j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \end{aligned} \quad (2)$$

where α and β refer to nuclei and i and j refer to electrons, respectively. The first and the second term in the equation is the operator of nuclear and electron kinetic energy, respectively. The third term is the repulsion energy between the nuclei α and β with a distance $r_{\alpha\beta}$ and atomic numbers Z_{α} and Z_{β} , respectively. The fourth term is the attraction energy between electron i and nucleus α with a distance of $r_{i\alpha}$. The last term is the repulsion energy between electron i and j with a distance of r_{ij} .

Although the Schrödinger equation can accurately reflect the movement of microscopic particles, any material is composed of a large number of particles. Furthermore, the interaction between electrons is complicated. It is impossible to solve the Schrödinger equation of the multi-particle system. Therefore, it is necessary to introduce approximate methods to solve this many-body problem. Born-Oppenheimer approximation is one of the approximation methods.

2.2.1 Born-Oppenheimer approximation

The proton to electron mass ratio is 1836. The mass of the nucleus is much heavier than that of the electron ($M/m_e \approx 10^3 \sim 10^5$). The motion of the nucleus is more slowly compared with that of electrons, and we can consider the electrons in the material to be moving in the field of fixed nuclei. The approximation of separating electronic and nuclear is called the Born-Oppenheimer approximation.¹¹⁰ With this approximation, the kinetic energy of nuclei is zero and the repulsion between nuclei can be considered constant. The remaining three terms are called the electronic Hamiltonian.

$$\hat{H} = -\frac{\hbar^2}{2m_e} \sum_i \nabla_i^2 - \sum_a \sum_i \frac{Z_a e^2}{4\pi\epsilon_0 r_{ia}} + \sum_j \sum_{i>j} \frac{e^2}{4\pi\epsilon_0 r_{ij}} \quad (3)$$

Although the Born-Oppenheimer approximation greatly simplifies the calculation, the Schrödinger equation can only be solved exactly for the H_2^+ molecule and similar one-electron system (eg. He^+ and Li^{2+}). For more electron systems, the interaction between electron and electron makes the solution of the Schrödinger equation still a many-body problem. To solve the Schrödinger equation, more approximations should be used. One of the most important methods is Hartree-Fock.

2.2.2 Hartree-Fock theory

We define the spin-orbital as a wave function for an electron. Before considering the form of the exact wave function for a fully interacting many-electron system, we consider a system without electron-electron interaction. Its Hamiltonian operator is

$$\hat{H} = \sum_{i=1}^N \hat{h}(i) \quad (4)$$

where $\hat{h}(i)$ is the Hamiltonian operator of kinetic energy and potential energy of the i th electron. The wave function Ψ^{HP} is a product of spin-orbital χ for each electron

$$\Psi^{HP}(x_1, x_2, \dots, x_N) = \chi_1(x_1)\chi_2(x_2)\cdots\chi_N(x_N) \quad (5)$$

where the three spatial coordinate r_i and the one spin coordinate s_i denote collectively by x_i . Equation 5 is known as the Hartree product.¹¹¹ Total energy for this system is

$$E = \varepsilon_i + \varepsilon_j + \cdots + \varepsilon_k \quad (6)$$

It is well known that electrons are indistinguishable. In the Hartree product, it specifies that electrons are distinguishable as electron-one occupying spin-orbital χ_i , electron-two occupying χ_j , and so on. Furthermore, electron wave functions are antisymmetric, and the sign of the wave function will change with the interchange of space or spin coordinates of any two electrons. These two problems can be fixed by introducing Slater determinant¹¹²

$$\Psi(x_1, x_2, \cdots, x_N) = (N!)^{-1/2} \begin{vmatrix} \chi_i(x_1) & \chi_j(x_1) & \cdots & \chi_k(x_1) \\ \chi_i(x_2) & \chi_j(x_2) & \cdots & \chi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \chi_i(x_N) & \chi_j(x_N) & \cdots & \chi_k(x_N) \end{vmatrix} \quad (7)$$

where $(N!)^{-1/2}$ is the normalization factor. Slater determination represents N spin orbitals are occupied by N electrons without specifying between electron and spin-orbital. The rows are labeled by electrons and the columns are labeled by spin orbitals. The Slater determination satisfied the requirement of electrons: the antisymmetry principle and no equal electron occupying the same spin-orbital. A short-hand notation for the Slater determinant is

$$\Psi(x_1, x_2, \cdots, x_N) = |\chi_i \chi_j \cdots \chi_k\rangle \quad (8)$$

Based on the variational principle, the best wave function will minimize the electron energy

$$E_0 = \langle \Psi_0 | \hat{H} | \Psi_0 \rangle \quad (9)$$

By choosing the spin-orbital, we can minimize the energy and derive an equation, also called the Hartree-Fock equation

$$\hat{f}(i)\chi(x_i) = \varepsilon_i\chi(x_i) \quad (10)$$

where $f(i)$ is the one-electron operator and called the Fock operator

$$\hat{f}(i) = -\frac{1}{2}\nabla_i^2 - \sum_{A=1}^M \frac{Z_A}{r_{iA}} + v^{\text{HF}}(i) \quad (11)$$

where $-\frac{1}{2}\nabla_i^2$ and $-\sum_{A=1}^M \frac{Z_A}{r_{iA}}$ is the kinetic and potential energy for one electron, respectively. The most important part for the Fock operator is $v^{\text{HF}}(i)$, which is an average potential experienced by the i th electron due to the presence of the other electrons. With this average potential, the complicated many-body problem is simplified to the one-electron problem.

The first two terms in equation 11 are the one-electron operator $\hat{h}$, and the third term is the two-electron operator. The two-electron operator can be further divided into Coulomb operator and exchange operator: $\hat{u} = \hat{J} + \hat{K}$. The Coulomb operator $\hat{J}$ is defined as

$$\hat{J}_j(x_1) = \int |\chi_j(x_2)|^2 \frac{1}{r_{12}} dx_2 \quad (12)$$

It represents the potential experienced by one electron at the position x_1 due to the average charge distribution of another electron in spin-orbit χ_j . The exchange operator does not have the classical interpretation. It comes from the antisymmetric nature of the Slater determinant and can be written as

$$\hat{K}_j(x_1)\chi_i(x_1) = \int \chi_j^*(x_2) \frac{1}{r_{12}} \chi_i(x_2) dx_2 \chi_j(x_1) \quad (13)$$

The Hartree-Fock energy is

$$E_{\text{HF}} = \sum_i^N \langle \chi_i | \hat{h} | \chi_i \rangle + \frac{1}{2} \sum_i^N \sum_j^N \langle \chi_i \chi_j | \chi_i \chi_j \rangle - \langle \chi_i \chi_j | \chi_j \chi_i \rangle \quad (14)$$

The Hartree-Fock equation 10 will be solved iteratively, and this procedure is called the self-consistent-field (SCF) method. The process for the SCF is as follows. First, based on the input data, it can make an initial guess of the spin orbitals. Then, the average field can be calculated. By solving the eigenvalue equation, it can get a new set of spin orbitals.

With these new spin orbitals, the new average field is updated to be used to solve the Hartree-Fock equation again. This procedure is repeated until the self-consistency is reached. Then we get a set of orthonormal Hartree-Fock spin orbitals with orbital energies.

2.2.3 Electron-Correlation methods

In the HF method, the real electron-electron interaction is treated as an average interaction. This means the HF method cannot correctly describe how electrons affect other electrons, which is known as the electron correlation. When a sufficiently large basis set is used to solve the Hartree-Fock equation, the HF wave function can account for about 99 % of the total energy, but the remaining 1 % energy (electron correlation energy) is also very important to describe the chemical phenomena. For example, without considering electron correlation, the HF method predicts qualitatively incorrect results in the ordering of the ionization potentials of N_2 .¹¹³ There are several methods to consider electron correlation, such as configuration interaction (CI), Møller–Plesset (MP) perturbation theory, the coupled-cluster (CC) method.

a) Excited determinants

Before introducing the electron-correlation methods, we need to introduce the concept of excited determinant which is used in the CI and CC methods. The HF procedure produces a set of N spin orbitals. The lower energy spin orbitals occupied with electrons are called the occupied spin orbitals. While the remaining higher energy spin-orbital without electron occupying is called the unoccupied spin orbitals (**Figure 6**). The HF ground state determinant is the best approximation to the ground state in the form of a single determinant. However, there are many determinants that could be formed from the N spin orbitals. A convenient way to describe other determinants is to regard the HF ground state determinant as the reference state and to classify other possible determinants according to their difference with the reference state. For example, by removing electrons

from occupied orbitals to the virtual orbitals, the occupied spin orbitals are replaced with the virtual spin orbitals in the new determinant. The determinants except the ground state are considered the excited determinants. A singly excited determinant is that an electron in the occupied spin orbitals has been promoted to a virtual spin-orbital. A doubly excited determinant is that two electrons in the occupied spin orbitals have been promoted to two virtual spin orbitals, respectively. It is similar to triply excited determinant, quadruply excited determinant. These excited determinants can be used in linear combination with the ground state determinant for a more accurate description of the ground state or any excited state of the system.

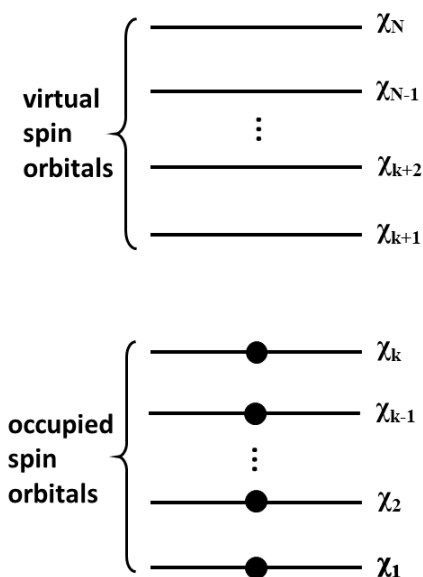


Figure 6 A pictorial representation of the HF ground state determinant, $|\chi_1\chi_2\ldots\chi_{k-1}\chi_k\rangle$. The black circles denote electrons.

b) Møller–Plesset (MP) perturbation theory

In the Møller–Plesset (MP) perturbation theory, the Hamiltonian of the system is divided into two parts: the unperturbed part and the perturbed part. Hamiltonian of the unperturbed part is taken as the sum of the one-electron Fock operator. Hamiltonian of the perturbed part is defined as the difference between the true electronic Hamiltonian

and the unperturbed Hamiltonian. When only considering the first-order correction, the total energy is the HF energy. To improve the HF energy, the second-order energy correction should be considered. The total electronic energy is $E^{(0)} + E^{(1)} + E^{(2)} = E_{\text{HF}} + E^{(2)}$ and this calculation is named MP2 or MPPT(2), where the 2 indicates inclusion of second-order energy corrections. $E^{(0)}$, $E^{(1)}$, $E^{(2)}$ are zero-, first- and second-order energy correction, respectively. MP2 calculation is faster than that of CI calculation and is supported by most ab initio programs.

c) Coupled-Cluster method

The Coupled Cluster (CC) method is a widely used method to include the electron correlation effect. The fundamental equation of the CC method is

$$\Psi_{\text{CC}} = e^{\hat{T}} \Psi_{\text{HF}} \quad (15)$$

where Ψ_{CC} is the ground state electronic wave function, Ψ_{HF} is the ground state HF wave function and the exponential operator $e^{\hat{T}}$ is a Talyor series expansion

$$e^{\hat{T}} = 1 + \hat{T} + \frac{\hat{T}^2}{2!} + \frac{\hat{T}^3}{3!} + \cdots = \sum_{k=0}^{\infty} \frac{\hat{T}^k}{k!} \quad (16)$$

where the excitation operator $\hat{T}$ is

$$\hat{T} = \hat{T}_1 + \hat{T}_2 + \cdots + \hat{T}_n \quad (17)$$

The one-particle excitation operator $\hat{T}_1$ and the two-particle excitation operator $\hat{T}_2$ are defined by

$$\hat{T}_1 \Psi_{\text{HF}} = \sum_i^{\text{occ}} \sum_a^{\text{vir}} t_i^a \Psi_i^a \quad (18)$$

$$\hat{T}_2 \Psi_{\text{HF}} = \sum_{i < j}^{\text{occ}} \sum_{a < b}^{\text{vir}} t_{ij}^{ab} \Psi_{ij}^{ab} \quad (19)$$

where t_i^a and t_{ij}^{ab} is the coefficient. Ψ_i^a is a singly excited determinant with the occupied spin-orbital i replaced by the virtual spin-orbital a . Ψ_{ij}^{ab} is a doubly excited determinant with the occupied spin orbitals i and j replaced by the virtual spin orbitals a and b .

Instead of including all the excitation operators ($\hat{T}_1, \hat{T}_2, \hat{T}_3 \dots$), the approximation to the excitation operator $\hat{T}$ is to include some of the important contribution operators. Including only the $\hat{T}_1$ operator cannot bring any improvement over HF, because the matrix elements between the HF and the single excited states is zero. The lowest level of approximation is $\hat{T}_2$.¹¹⁴ The approximation ($\hat{T} \approx \hat{T}_2$) gives the coupled-cluster doubles (CCD) method with an equation

$$\Psi_{\text{CCD}} = e^{\hat{T}_2} \Psi_{\text{HF}} \quad (20)$$

The next step to improve the CCD method is to include the operate $\hat{T}_1$ and take $\hat{T} = \hat{T}_1 + \hat{T}_2$ and this is known as the CC singles and doubles (CCSD) method, which is only slightly more expensive than CCD and yields better results.

2.2.4 Density functional theory

In the Hartree-Fock method, the wave function Ψ is the central quantity, which determines all the information of the system at the specific state. However, the wave function is very complex, which is depending on $4N$ (each electron has three space and one spin coordinates) variables. The Hamilton operator $\hat{H}$ (equation 3) contains operators related to one electron or two electrons at a time and has nothing to do with the size of the system. In 1964, Pierre Hohenberg and Walter Kohn proved that electron density uniquely determines the Hamiltonian operator, thus determining all properties of the system.¹¹⁵ Rather than the complicated wave function ($4N$ variables), we can use the electron probability $\rho(r)$, a quantity that depends on the three spatial variables, to solve the Schrödinger equation. The electron probability density $\rho(r)$ is defined as

$$\rho(r) = N \int \cdots \int |\Psi(x_1, x_2, \cdots, x_N)|^2 ds_1 dx_2 \cdots dx_N \quad (21)$$

It indicates the probability of finding any of the N electrons in volume element dr_1 with arbitrary spin, while the other $N-1$ electrons have arbitrary positions and spin in the state indicated by Ψ .

Pierre Hohenberg and Walter Kohn also proved that the ground-state energy, wave function, and all other electronic properties are uniquely determined by the ground-state electron probability density $\rho_0(r)$. The subscript 0 indicates the ground state. The functional relation can be written as

$$E_0 = E_0[\rho_0] \quad (22)$$

The formula for the total electronic energy is

$$E_0[\rho_0] = T[\rho_0] + E_{Ne}[\rho_0] + E_{ee}[\rho_0] \quad (23)$$

where these three terms are kinetic energy of electrons, attraction energy between the nuclei and electrons, and repulsion energy between electrons, respectively.

Pierre Hohenberg and Walter Kohn neither told us how to calculate E_0 from ρ_0 nor told us how to find ρ_0 without first finding the wave function. In 1965, Kohn and Sham proposed a method for finding ρ_0 and for finding E_0 from ρ_0 .¹¹⁶ Kohn and Sham put forward a fictitious reference system (denoted by the subscript s) that electrons have no interaction with each other but they experience external potential-energy function $v_s(r_i)$. The selection of the potential-energy function $v_s(r_i)$ must ensure that the ground-state electron probability density $\rho_s(r)$ of the fictitious reference system is equal to the ground-state electron density $\rho_0(r)$ of the system we are studying ($\rho_s(r) = \rho_0(r)$).

Similar to the Hartree-Fock method, for a non-interacting reference system, the Hamiltonian operator of the reference system is

$$\hat{H}_s = -\frac{1}{2} \sum_i^N \nabla_i^2 + \sum_i^N v_s(r_i) \quad (24)$$

The ground state wave function of the noninteracting system can be represented by a Slater determinant

$$\Theta_s(x_1, x_2, \dots, x_N) = (N!)^{-1/2} \begin{vmatrix} \varphi_i(x_1) & \varphi_j(x_1) & \cdots & \varphi_k(x_1) \\ \varphi_i(x_2) & \varphi_j(x_2) & \cdots & \varphi_k(x_2) \\ \vdots & \vdots & & \vdots \\ \varphi_i(x_N) & \varphi_j(x_N) & \cdots & \varphi_k(x_N) \end{vmatrix} \quad (25)$$

where φ_i is the Kohn-Sham orbital, which is determined by

$$\hat{f}^{KS} \varphi_i = \epsilon_i^{KS} \varphi_i \quad (26)$$

where $\hat{f}^{KS}$ and ϵ_i^{KS} are Kohn-Sham operator and Kohn-Sham orbital energy, respectively.

The Kohn-Sham operator is defined as

$$\hat{f}^{KS} = -\frac{1}{2} \nabla^2 + v_s(r) \quad (27)$$

By solving the one-electron equation **27** iteratively, we can get the Kohn-Sham orbital.

Then the ground-state electron probability density is determined with

$$\rho_s(r) = \sum_i^N |\varphi_i|^2 = \rho_0(r) \quad (28)$$

As $\rho_s(r) = \rho_0(r)$, in short, in the following section, we only use ρ . A general electronic energy equation is

$$E_{DFT}[\rho] = T_s[\rho] + E_{ne}[\rho] + J_s[\rho] + E_{xc}[\rho] \quad (29)$$

where $T_s[\rho]$ is the electronic kinetic energy of the noninteracting reference system. $E_{ne}[\rho]$ is the potential energy due to the nuclei-electron attraction. $J_s[\rho]$ is the classical Coulomb interaction of electron cloud. $E_{xc}[\rho]$ part is known as the exchange-correlation energy functional and is defined as

$$E_{xc}[\rho] = (T[\rho] - T_s[\rho]) + (E_{ee}[\rho] - J_s[\rho]) \quad (30)$$

The first parenthesis part represents the kinetic correlation energy due to the electronic kinetic energy difference between the real system and the noninteracting system, and the second parenthesis part is considered the potential correlation and exchange energy. The

only unknown term is the $E_{xc}[\rho]$. By now, the exact form of $E_{xc}[\rho]$ is not known. The key to the DFT calculation is to obtain a good approximation to $E_{xc}[\rho]$.

2.2.5 Functionals for exchange and correlation

a) Local density approximation

Local density approximation (LDA) is one of the famous approximation methods for finding the approximate exchange-correlation functional $E_{xc}[\rho]$. The central idea of this approximation is a hypothetical homogeneous electron gas, in which electrons move on a positive background charge distribution. When the electron probability density ρ varies very slowly with the position, the homogeneous electron gas model is used to derive the exchange-correlation energy equation. The volume V of electron gas and the number of electrons N are considered to be infinity, and the density of electrons, $N/V = \rho$, has a constant value everywhere. The E_{XC} can be written as

$$E_{XC}^{LDA}[\rho(r)] = \int \rho(r) \epsilon_{XC}(\rho(r)) dr \quad (31)$$

where $\epsilon_{XC}(\rho(r))$ is the exchange-correlation energy of each particle in the electronic gas with uniform density $\rho(r)$. The $\epsilon_{XC}(\rho(r))$ is usually separated into the exchange ($\epsilon_X(\rho(r))$) and correlation ($\epsilon_C(\rho(r))$) parts as,

$$\epsilon_{XC}(\rho(r)) = \epsilon_X(\rho(r)) + \epsilon_C(\rho(r)) \quad (32)$$

For the homogeneous electron gas, the exchange part is completely known. It is

$$\epsilon_X(\rho(r)) = -\frac{3}{4} \left(\frac{3\rho(r)}{\pi} \right)^{1/3} \quad (33)$$

There is no explicit expression for the correlation part. However, with the homogeneous electron gas model, the analytic expression of the correlation energy is available. One of the most widely used $\epsilon_C(\rho(r))$ is developed by Vosko, Wilk, and Nusair in 1980, which is known as the correlation functional VWN.¹¹⁷ Another widely used correlation functional is developed by Perdew and Wang in 1992.¹¹⁸

LDA is used because it is inexpensive, and it can give a reasonable molecular geometry and vibrational frequencies. LDA cannot reproduce the energy-related properties, such as binding energies, ionization potentials, and the intermolecular dispersion interaction. The electron probability density of the real system is varying with the distance between the reference electron and the other electron. In order to make the energy-related properties more accurate, the electron density gradient should be considered when establishing E_{xc} functional.

b) Generalized gradient approximation

To consider the variation of electron density with position, the gradients of electron density are included in the integrand. The equation of exchange-correlation functional including electron density gradient is

$$E_{xc}^{GGA}[\rho(r)] = \int f(\rho(r), \nabla\rho(r)) dr \quad (34)$$

where f is the functional of the electron density and their gradients. E_{xc}^{GGA} is usually divided into the exchange and the correlation parts

$$E_{xc}^{GGA} = E_x^{GGA} + E_c^{GGA} \quad (35)$$

Some commonly used GGA exchange functionals E_x^{GGA} are Perdew and Wang's 1986 functionals, denoted as PW86 or PWx86,¹¹⁹ Becke's 1988 functional, denoted as B88, Bx88,¹²⁰ Perdew and Wang's 1991 exchange functional, denoted as PWx91,¹¹⁸ and the Perdew–Burke–Ernzerhof exchange functional, denoted as PBE.¹²¹ The commonly used GGA correlation functionals E_c^{GGA} contain the Lee–Yang–Parr functional,¹²² denoted as LYP, the Perdew 1986 correlation functional, denoted as P86 or Pc86,¹²³ the Perdew–Wang 1991 correlation functional, denoted as PW91,¹²⁴ and the Perdew–Burke–Ernzerhof correlation functional, denoted as PBE.¹²¹ Each exchange functional could be combined with any of the correlation functionals. The PBE exchange and correlation functional is widely used in DFT calculations of solids.¹²⁵

Even GGA functionals are very widely used as a very successful improvement over the LDA for structural properties. When the electronic structure is calculated by GGA functional, the band gap of some materials may be underestimated by more than 50%. It is necessary to introduce new E_{xc} functionals to make the electronic structure closer to the experimental values.

c) Hybrid functionals

In exchange-correlation functional, the contribution of the exchange part is significantly larger in absolute value than the corresponding correlation effects.¹²⁶ Therefore, an accurate expression of the exchange functional is conducive to obtaining meaningful results from the DFT. One of the methods to find the equation of the accurate exchange energy is using the exchange energy of HF method but replacing the Hartree–Fock orbitals with the Kohn–Sham orbitals (E_X^{HF}).¹²⁷ The PBE0 functional¹²⁸⁻¹²⁹ is a widely used hybrid extension of PBE and includes 25% of E_X^{HF} . The equation of PBE0 exchange-correlation functional is

$$E_{xc}^{PBE0} = \frac{1}{4} E_X^{HF} + \frac{3}{4} E_X^{PBE} + E_C^{PBE} \quad (36)$$

where E_X^{HF} is the Hartree–Fock exchange functional with Kohn–Sham orbitals, E_X^{PBE} is the PBE exchange functional, and E_C^{PBE} is the PBE correlation functional.

The Heyd–Scuseria–Ernzerhof (HSE)¹³⁰⁻¹³¹ exchange-correlation functional is also widely used in condensed matter calculation. The exchange energy in HSE is separated into contributions due to short-range (SR) and long-range (LR) parts of the Coulomb interaction. The separation of the SR and LR part is based on the equation here:

$$\frac{1}{r} = SR + LR = \frac{1 - \text{erf}(\eta r)}{r} + \frac{\text{erf}(\eta r)}{r} \quad (37)$$

where erf is the error function and η is the screen parameter to control the definition of two ranges.¹³² The first and the second part in the right equation of 37 controls the SR and LR, respectively. The equation for HSE exchange-correlation functional is

$$E_{XC}^{HSE} = \alpha E_X^{HF,SR}(\eta) + (1 - \alpha) E_X^{PBE,SR}(\eta) + E_X^{PBE,LR}(\eta) + E_C^{PBE} \quad (38)$$

In the widely used HSE03 and HSE06 functional, the η is 0.3 and 0.2 $\text{\AA}^{-1}$, respectively.^{131, 133}

d) Dispersion interactions

The mean-field electronic structure methods such as Hartree-Fock and Kohn-Sham density functional theory cannot describe long-range electronic correlation effects, so they cannot include the dispersion interaction.¹³⁴⁻¹³⁵ Dispersion is a short-ranged weak interaction, but the dispersion force increases as the molecular size or atoms per unit cell increases.¹³⁶ Therefore, as the system becomes larger, it becomes more and more important. The widely used strategy is proposed by Grimme¹³⁷⁻¹³⁸ to include dispersion by additive empirical terms

$$E^{DFT-D3} = E^{DFT} + E_{Disp}^{D3(BJ)} \quad (39)$$

The dispersion energy is calculated via a damped pairwise London-type correction¹³⁹:

$$E_{Disp}^{D3(BJ)} = - \sum_{AB} \sum_{n=6,8} \sum_g s_n \left(\frac{C_n^{AB}}{R_{AB,g}^n + f_{d,n}} \right) \quad (40)$$

where C_n^{AB} is the n th order dispersion coefficients of a pair of atoms A and B. s_n is a scale factor for the individual multipolar contributions. The damping function $f_{d,n}$ is important to reduce double-counting of short/medium range correlation and to include the correct asymptotic long-range correlation. The default damping function is the so-called Becke-Johnson (BJ) function.¹⁴⁰

$$f_{d,n}^{BJ} = a_1 R_0 + a_2 \quad (41)$$

where a_1 and a_2 are functional-specific parameters and $R_0 = \sqrt{\frac{C_6^{AB}}{C_8^{AB}}}$ is an effective radius.

2.2.6 Time-Dependent density functional theory

DFT was initially developed as a time-independent ground-state theory. The Runge-Gross theorem¹⁴¹ pointed out that the one-to-one correspondence between an external potential and the electron density is valid in time-dependent and time-independent cases. To treat electronically excited states, DFT is extended to account for the time-dependent nature of the electromagnetic waves. This leads to Time-Dependent density functional theory (TD-DFT), which is a method to solve the Time-Dependent Schrodinger equation. One of the most widely used TDDFT methods is the linear response TDDFT (LR-TDDFT). In LR-TDDFT, a weak oscillating time-dependent spatially uniform electric field is applied to the ground state electronic density. It is found the effect of the applied field on the ground-state electronic density depends on a sum of terms involving the energy difference between the excited electronic state and the ground electronic state, where these energies difference are calculated at the same configuration. LR-TDDFT can not only calculate the energy difference between the excited electronic state and the ground electronic state but also calculate the strength of the electronic absorption to special states, which can predict the electronic absorption spectrum. LR-TDDFT performs quite well for vertical electronic excitation energy calculation with an error in the range of 0.1 to 0.5 eV when appropriate exchange-correlation functional is used¹⁴².

2.2.7 Electron population analysis

a) Bader charge analysis

The properties of chemicals and materials often relate to atoms gaining or losing electrons. Theoretical calculations can provide information on the electron distribution which can be used to estimate the electronic charge. Richard Bader developed a method to divide molecules into atoms and this method is called the Quantum Theory of Atoms in Molecules (QTAIM).¹⁴³⁻¹⁴⁵ In QTAIM, the only parameter that defines an atom is the electron density. An atom can be defined as a region of a real space, which is bounded by

the surface without flux in the gradient vector field of ρ and this surface is named the zero-flux surface. Then, the electron density within the zero-flux surface is integrated to get the total number of electrons in one atom. The difference between the number of neutral atom electrons and the calculated electron is the obtained or lost electron number.

b) Density of states

The density of states (DOS) describes the number of states per unit energy and per unit volume. The definition equation of 3D density of states is

$$D(E) = \frac{1}{V} \frac{dN}{dE} \quad (42)$$

where V , N and E are the total volume, the total number of states within energy E and energy, respectively. The integral of $D(E)$ gives the total number of electrons in a special energy unit. The DOS is often used to analyze the electronic structure, such as the width of the energy band gap and the change of the energy states of doping.

2.2.8 Geometry optimization

The geometry of a molecule or a material structure with N nuclei is defined by $3N$ independent nuclear coordinates $R_1, R_2, \dots, R_{3N}$. The total electronic energy E is a function of the coordinates. The function E gives the potential-energy surface (PES) of a structure. The PES is high-dimensional, and each point on PES represents a configuration. The first partial derivatives of E with respect to each of its variables constitute a vector, which is called the gradient of E . Any point on the PES with zero gradients is called a stationary point. Structure optimization is a term for finding the stationary points of the function E . A stationary point is not sure of a minimum. It may also be a maximum or a saddle point. To guarantee the stationary point is a minimum, all the second derivative values of the function E must be positive. There are a large number of minima on the PES. The minimum point with the lowest energy value of all the minima is the global minimum, while all the other minima are the local minima. In order to identify the

configurations corresponding to minimum points on the PES, we use the optimization method. The optimization method can be divided into local optimization methods and global optimization methods. There are many methods used for structure optimization and we will concentrate on those approaches that are most commonly used.

a) Local optimization

The methods that are widely used in local structure optimization are the steepest descent and the conjugate gradient method. These methods change atom coordinates gradually so as to move the system closer to the minimum point. The starting configuration for each optimization iteration is the configuration obtained from the previous step. The initial configuration of the system is provided by the user.

a.1) Steepest descent method

In the steepest descent method, the total energy E and the first derivative of the total energy (∇E) are calculated from the initial configuration. The vector direction of ∇E is the greatest increase rate of E . In the steepest descent method, each optimization step is carried out in the direction where E descends fastest, which means that each step is in the direction of $-\nabla E$. The direction of the gradient is determined by the largest interatomic forces and so the steepest descent method is a good method for optimizing the highest energy configurations. This method is generally robust even when the initial configuration is far from the minimum. However, with more steps of optimization, the steepest descent method can be very inefficient as the optimization process approaches the minimum (small ∇E value). The optimization process may oscillate around the minimum. So, the steepest descent method can be used to optimize the configuration at the beginning of the optimization process. When the configuration is close to the minimum and the ∇E value is small. Other optimization methods should be used to increase the optimization efficiency.

a.2) Conjugate gradient method

The conjugate gradient method tries to improve the steepest descent method by performing each search not along the current gradient but along a line that is constructed conjugate to the previous search direction. The first step of the conjugate gradient method is the same as the steepest descent step, calculating the total energy E and the first derivative of the total energy (∇E) of the configuration. In the subsequent step, the conjugate gradient method moves in a direction v_k from point x_k where v_k is computed from the gradient at the point x_k and the previous direction vector v_{k-1} . The conjugate method has better convergence characteristics than the steepest descent method, but the conjugate gradient method can only use to find local minimum configuration.

b) Global optimization

Because of the high dimension of PES, global structure search is a difficult task. Up to now, a lot of methods have been proposed to fix the tough problem, such as Simulated Annealing,¹⁴⁶⁻¹⁴⁷ Random Sampling,¹⁴⁸⁻¹⁵¹ Basin Hopping,¹⁵²⁻¹⁵⁴ Evolutionary Algorithms,¹⁵⁵⁻¹⁵⁷ Particle Swarm Optimization,¹⁵⁸ and Artificial Bee Colony.¹⁵⁹⁻¹⁶¹ In our work, we mainly use the Basin Hopping (BH) method. We will firstly introduce the BH method.

b.1) Basin hopping

On PES, different minima are separated by the energy barrier. The Basin hopping method transforms the PES (**Figure 7**) which the only obstacle is the energy difference between minima without changing the energy of local minima.

The energy landscape is sampled with the Monte Carlo simulation method, which is a computational algorithm that relies on repeated random sampling to obtain numerical results. For our case, at each step, the coordinates of one or a few atoms are randomly moved by a random number within $[-1,1]$ times the maximum possible displacement. The newly generated structure is locally optimized. The Metropolis criterion is used to decide whether to accept the optimized new structure or not. If the new structure has lower

energy, this structure is accepted. If the new structure is higher in energy than the previous structure, the Boltzmann factor $e^{\frac{-(E_N - E_P)}{k_B T}}$ (where E_n and E_P are the energy of the current and the last previous step configuration, respectively. k_B and T are the Boltzmann constant and temperature, respectively) is calculated and compared with a random number between 0 and 1. If the Boltzmann factor is larger than the random number, this new geometry is accepted. Otherwise, the new structure is discarded, and a new structure is generated based on the previous structure. This Metropolis procedure¹⁶² ensures that the configuration in the ensemble obeys Boltzmann distribution, while sometimes accepting new structures with high energy increases the possibility of escaping from the local minimum. This iteration process continues until the number of accepted structures reached the preset numbers.

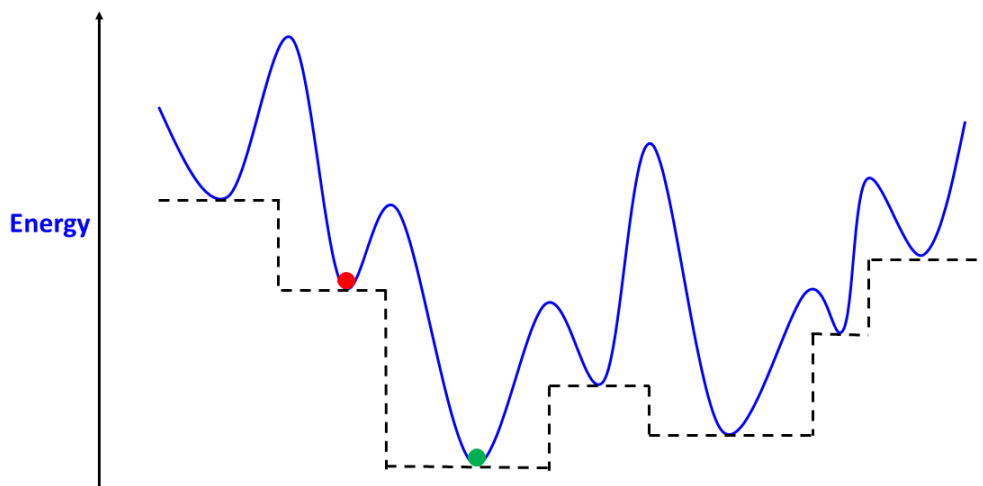


Figure 7 A diagram of the original one-dimensional PES (blue line) and the transformed PES (the black dashed line). The green and red circles are the global minimum and local minimum, respectively.

b.2) Ab Initio molecular dynamics

Molecular dynamics (MD) can also be used to search for the PES. In atoms, nuclei are heavy enough ($10^3 \sim 10^5$ times that of the electron) that they behave as classical particles, so we can simulate the dynamics of nuclei by solving Newton's equations of motion. In molecular dynamics, the simulation begins with a configuration, mostly a minimum

configuration, and then assigns a set of velocities to each atom, which is randomly selected from a Maxwell distribution at high temperature. The elevated temperature increases the probability of climbing over potential energy barriers to reach new regions of the PES that may contain lower-energy minima than the current region. As the initial position and velocity of each atom are known, we can apply Newton's second law to each atom, where the force on atom i is calculated as $F_{x,i} = -\partial E / \partial x_i$. The energy E is obtained from the electronic structure method.¹⁶³⁻¹⁶⁴ The integration of Newton's second law gets the position of each atom at the times Δt , $2\Delta t$, $3\Delta t$, ..., where the time step Δt is typically 10^{-15} s. The atomic positions propagate in time and thus generate a trajectory that contains the configurations.

MD simulations require small time steps. A typical time step is about 1 fs and a simulation with 10^6 steps covers 10^{-9} s. For light atoms, such as hydrogen, in order to get accurate enough data, the time step may be even less than 1 fs. One million steps are already a considerable amount of calculation, and typical simulation times are in picoseconds or nanoseconds which is quite short as many interesting phenomena (such as chemical reactions) happen in the order of milliseconds or seconds. Other methods need to be introduced to study the phenomena that require long-time simulation.

2.2.9 Transition state theory

Transition state is a first-order saddle point on the PES and has only one imaginary vibrational frequency. It is the maximum point on a minimum-energy path (MEP) between two local minima. The energy difference between the transition state and local minimum is the energy barrier. By searching for the transition state, the difficulty of transformation between different local minima is evaluated. In our research, we use the climbing image nudged elastic band (CI-NEB) and Dimer method to search for the transition state.

c.1) Climbing image nudged elastic band

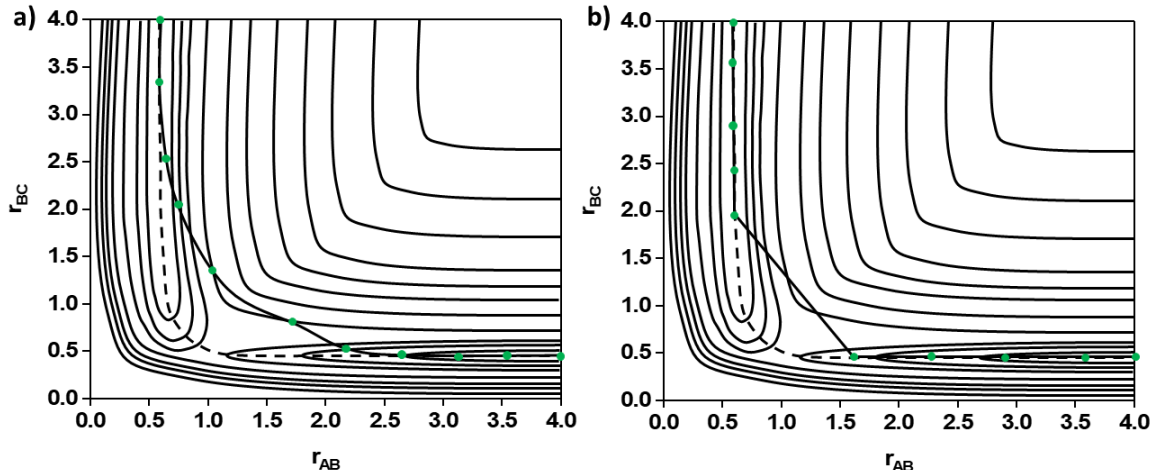


Figure 8 A contour plot of the potential energy surface, in which an atom B can form a chemical bond with either atom A or atom C. The horizontal and vertical axis gives the distance of A-B and B-C, respectively. a) The plane elastic band with constant $k = 1.0$ is represented by a circle connected by a solid line. It cuts the corner, leading to an overestimation of the saddle point energy. b) The plane elastic band with constant $k = 0.1$. The images slide from the barrier area to the minimum, thus reducing the resolution of the path in the most important area. This is known as sliding down. Reproduced with permission.¹⁶⁷ Copyright 1998, World Scientific Publishing Co. Pte. Ltd.

A series of $N-1$ structures or images are generated between the initial (R_1) and the final structures (R_N) and this kind of method are called the chain-of-state method.¹⁶⁵ By optimizing all the images with an approximate method, we can get not only the saddle point but also an approximation of the whole reaction path. The plain elastic band method introduces a function (“elastic band”) (equation 43) that is composed of two terms: one is the sum of energies of all images (the first term on the right side of equation 43 and the other term is to keep the distribution of images along with the MEP (the second term in the right side of equation 43. Images are coupled together by a virtual spring with a spring constant k .

$$S(R_1, R_2, \dots, R_N) = \sum_{i=1}^{N-1} E(R_i) + \sum_{i=1}^N \frac{k}{2} (R_i - R_{i-1})^2 \quad (43)$$

where R_i and R_{i-1} denote the coordinate of i and $i-1$ image, respectively. Instead of optimizing each image individually, the function S is optimized in which all the images are optimized together at every step. In the process of minimization of function S , it may have cut corners (**Figure 8a**) or sliding down (**Figure 8b**) problems due to the improper value of the spring constant k .¹⁶⁶⁻¹⁶⁷ These problems can be solved by generating more images, but the optimization efficiency will be low.

Another widely used method is “nudging” the elastic band,¹⁶⁸⁻¹⁶⁹ which is using only the perpendicular component of the spring force (first term in equation 44) and only the component of the spring force parallel to the tangent of the path (second term in equation 44).

$$F_i = -\nabla E(R_i)_\perp + F_i^S \parallel \quad (44)$$

where F_i is the total force on each image i . $E(R_i)$ is the energy of the i image. According to the force in equations 44, an optimization algorithm is used to move the images.

The climbing image NEB (CI-NEB)¹⁷⁰⁻¹⁷¹ method is a small modification of the NEB method. The major difference between CI-NEB, and NEB lies in the definition of stress at the highest energy point. In CI-NEB, the highest energy point will not be subjected to the spring force of the adjacent point, so as to avoid being pulled away from the transitional state. Moreover, the sign of the potential component parallel to the path direction is reversed, which makes this image climb to the transition state along the path in the direction of increasing energy. The CI-NEB method only needs a few images and can accurately locate the transition state, which makes CI-NEB the widely used method for finding the transition state.

c.2) Dimer

Dimer¹⁷²⁻¹⁷⁴ is another efficient method to search for the transition state on the potential energy surface. A dimer is defined by two points R_1 and R_2 in configurational space, whose energy and force are E_1 and E_2 , and F_1 and F_2 , respectively. The distance between

these two initial structures is $2\Delta R$ and ΔR is a constant. The middle point of these two points is R , and its force is $F(R) = (F_1 + F_2)/2$. Total energy of Dimer is $E = (E_1 + E_2)/2$. For a dimer method, it has two types of motion: rotation of the dimer and translation of the dimer. The dimer method involves two steps. First, the middle point R is fixed and is set as the axis. The dimer axis is rotated into the lowest curvature mode of the potential energy at the middle point. Then the dimer translates on the potential energy surface by a certain step to move to the saddle point. The dimer method uses fewer configurations than the CI-NEB method and does not need to calculate the Hessian, which increases its efficiency. When the guess configuration is far away from the transition state configuration, the dimer method is inefficient. It's better to do the CI-NEB calculation first, and then use the dimer method to refine the configuration found in CI-NEB method.

2.2.10 Kinetic Monte Carlo

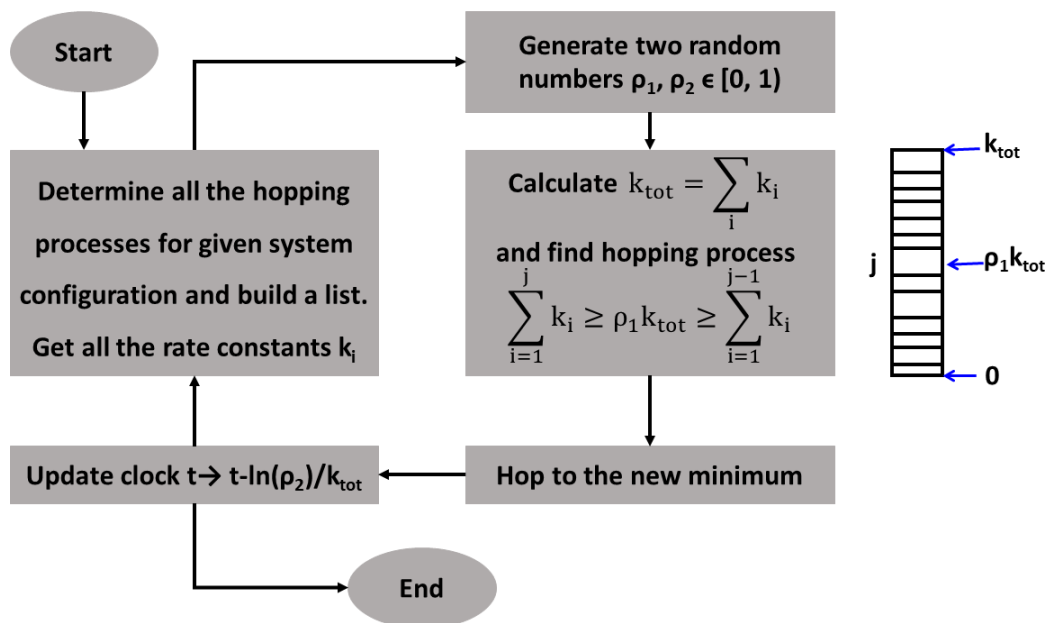


Figure 9 Flow chart illustrating the basic steps of kinetic Monte Carlo. The loop starts with the determination of all the minima and hops between different minima. The loop is terminated if a preset step has been reached. Reproduced with permission.¹⁷⁸ Copyright 2012, Wiley-VCH Verlag & Co. KGaA.

When we carry out a molecular dynamic calculation, a large fraction of time is spent on the local minimum. It vibrates in the local minimum until it gets enough energy to jump over the energy barrier and transform to another local minimum. It is a rare event¹⁷⁵ to go from one local minimum to another. If we want to have a proper understanding of what is happening in the system (such as diffusion, chemical reaction), it requires us to track its time evolution in at least one time span which includes several rare events to adjacent minima. The time span is in the order of several microseconds or more. MD is not a good choice for this kind of long-time simulation. kinetic Monte Carlo¹⁷⁶⁻¹⁷⁷ is a widely used method for studying the long-time evolution of the rare-event system.

Using the Basin Hopping method and transition state theory, we can obtain minima and barrier values between different minima. Then the rate constant k_i , which gives the average escape rate of jumping from current state i to other states, can be calculated by equation 45:

$$k_i = \frac{k_B T}{h} \frac{Z_i^*}{Z_i} e^{\frac{-\Delta E_i^*}{k_B T}} \quad (45)$$

where k_i is the rate constant within the harmonic approximation. k_B , T , and h are the Boltzmann constant, temperature, and Plank constant, respectively. In order to evaluate the effect of temperature on promoting atoms reaching equilibration, the different temperature value is used in different kMC process. ΔE_i^* is the static barrier value. Z_i^* and Z_i is the partition function for the transition state and the initial state i . For the process we considered, there are no translations and rotations as the vibrational modes that derive from the translational and rotational modes are low-frequency modes that are not important for our work. Therefore, only the vibrational partition function is used for the partition function part:

$$Z_i = \prod_{a=1}^{3n-6} \frac{1}{1 - e^{\frac{-E_a}{k_B T}}} \quad (46)$$

where a is the number of vibrational normal modes. To avoid the disproportionate errors resulting from the inaccurately approximated low-frequency modes, when the effect of the vibrational partition function is not significant, Z_i^*/Z_i is considered as 1.

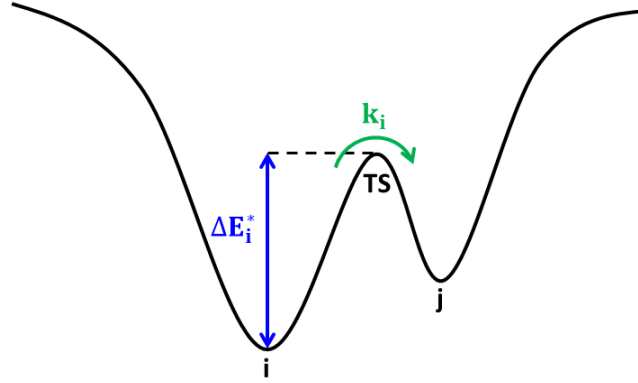


Figure 10 Schematic representation of the local minimum (i and j), migration barrier ΔE_i^* and rate constant k_i .

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With the rate constant, we can make a list of all possible hop processes for the system to escape from the current state i . The total rate constant is

$$k_{\text{tot}} = \sum_i k_i \quad (47)$$

Then we can find which minimum to hop from the present minimum i by

$$\sum_{i=1}^j k_i \geq \rho_1 k_{\text{tot}} \geq \sum_{i=1}^{j-1} k_i \quad (48)$$

where ρ_1 is a random number in the range of $[0,1)$.

The probability that the system escapes from state i to other states after a short time Δt is $1 - \exp(-k_i \Delta t)$. The connected probability distribution function for the time of the escape $p_i(\Delta t)$ is the time derivative of $1 - \exp(-k_i \Delta t)$ and is a Poisson distribution

$$p_i(\Delta t) = k_i \exp(-k_i \Delta t) \quad (49)$$

The average escape time is weighted by the Poisson distribution which is achieved by advancing the system through equation 50

$$\Delta t_{\text{escape}} = - \frac{\ln(\rho_2)}{k_i} \quad (50)$$

where ρ_2 is a random number in the range of $[0,1)$. The loop of hopping to other states and time updating process starts a new cycle from the new site. The loop terminates when the maximum number of steps is reached.

3 Results and Discussion

3.1 Effects on the stability of zeolite encapsulated subnanometer metals

Due to the limited reserves and annual production of noble metals,¹⁷⁹ it is desirable to use every atom to its highest capacity. In principle, single atom catalysts achieve the goal of maximizing the use of every atom, avoiding the waste of precious metals that is incurred in nanoparticles, in which many atoms are not exposed to the surface.¹⁸⁰⁻¹⁸¹ Single atom or subnanometer particles have also been shown to exhibit relatively higher catalytic activity than nanoparticles of the same composition, under some conditions. For example, the size-selected Pt₁₀ cluster deposited on amorphous alumina demonstrates to have CO oxidation reaction turnover rates as high as 3000 CO₂ molecules per cluster per second at 300 K, outperforming bulk Pt.¹⁸² However, due to the high surface free energy of single atoms and subnanometer particles, they have a strong tendency to form large particles which reduces the available metal surface area.^{32, 183}

The main challenge for the usage of subnanometer particles as catalysts in industry is to find strategies to inhibit the agglomeration process. One of the widely used methods is to physically trap these particles in the pores or channels of porous materials.¹⁸⁴⁻¹⁸⁵ Zeolites are one of the porous materials that have been widely used as metal carriers.^{18, 42, 54, 186} It is believed that the pores which form within the rigid zeolite frameworks are one of the reasons that prevent the sintering of metal particles, i.e. the framework provides a physical barrier to diffusion and growth beyond the size of the pore. But the structure of zeolite frameworks and the role of heteroatoms (Al) on the growth and migration of metal particles are not completely clear. Besides the carrier, the role of adsorbates and metal element identity on the stability of zeolite encapsulated metals is also incompletely understood. In this work, the unbiased density functional global optimization method, combined with nudged elastic band calculations and kinetic Monte Carlo simulations,

was used to identify the local minima and energetic barriers between local minima to evaluate the binding and migration of single and subnanometer metals in the Linde type A (LTA) zeolite.

3.1.1 Single Pt atom in silicious LTA

To find the local minima of single platinum (Pt) atoms encapsulated in pure silicon Linde type A (LTA) zeolite, the basin-hopping method, combined with DFT utilizing GGA-PBE functional and Grimme's D3 dispersion correction, was employed. In the searching process, several new local minimum structures were generated. The traditional cation sites S1, S2, and S3 of zeolite LTA, in which the metal lies in the center of the six, eight and four rings, respectively, with a small displacement into the cage, were found to be insufficient to label all the local minimum structures. The naming system was thus extended, based on the traditional cation sites. When the metal is in the plane of the six-ring, eight-ring or four-ring, it belongs to the S1, S2 or S3 sites, respectively (**Figure 11**). When it is outside the rings, the naming system is based on the ring and oxygen (O) atoms in the framework. If an atom is bound to the O atom shared by the six-ring and the four-ring, the name of this kind of site is denoted S1/S3. In the same manner, S1/S2 and S2/S3 sites are defined. As LTA contains an α and a β cage in the unit cell, some sites can exist in either cage. To distinguish the α and β cage S1/S3 sites, for example, the cage symbol is added as the subscript (S1/S3 $_{\alpha}$ and S1/S3 $_{\beta}$). Sites in which the metal atom occupies the face of a ring and induces the local breakage of a framework Si-O bond is denoted with an asterisk. For example, a broken six-ring site is denoted S1*, to distinguish it from the similar unbroken six-ring structure, S1. There are two symmetry inequivalent structures in which the metal atom is bound to the eight-ring, based on the S2 site. Firstly, S2₄, in which the metal atoms bind to two O atoms belonging to the four-ring and eight-ring, and secondly, S2₆, binding to two O atoms belonging to the six-ring and eight-ring. When reductive atmospheres, such as H₂, adsorbed on single Pt atom, there are two similar sites at the four-ring (S3). The site that metal atoms bind to two O

atoms belonging to the four-ring and six-ring (eight-ring) is named as S3-1 (S3-2) (**Figure 11**).

The strength of the binding of the metal atom or subnanometer cluster to the framework is estimated via the incorporation energy according to equation **51**

$$E_{\text{inc}}(M_n) = E_{M_n@LTA} - E_{LTA} - n \times E_{M_1(\text{vacuo})} \quad (51)$$

where n is the number of metal atoms. $E_{M_n@LTA}$ is the total energy of optimized structure after single metal atom or subnanometer particle is encapsulated into zeolite LTA. E_{LTA} is the total energy of an optimized empty zeolite framework. $E_{M_1(\text{vacuo})}$ is the energy of single metal atom in the vacuum phase.

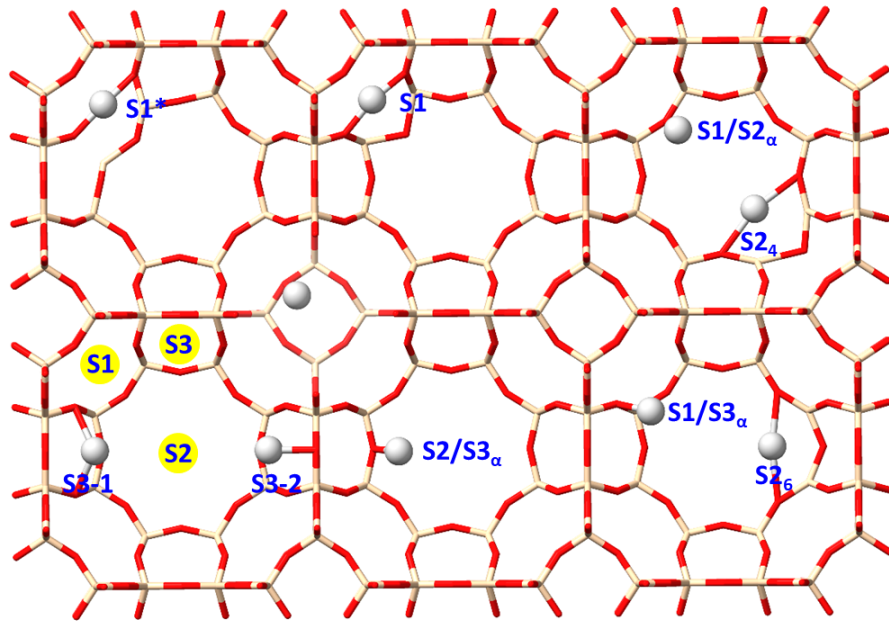


Figure 11 The structure of the LTA zeolite, which consists of a three-dimensional cubic grid of α -cages, connected by eight-rings, and smaller, β -cages, which are connected to α -cages via six-rings. Traditional metal binding sites S1, S2 and S3 are shown in yellow shadow. Binding sites of metal atoms, the silver color ball, are shown schematically.

First, we performed a global optimization at density functional level (PBE-D3), of the Pt atom in siliceous LTA. This provides the baseline knowledge of the binding sites for Pt and allows for the calculation of atom migration energies throughout the LTA pore

system. The most important structure is the Pt atom trapped in the broken six-ring (**Figure 12**, S1*). This S1* structure is the global minimum structure for single Pt atom in pure silicious LTA zeolite. To the best of our knowledge, only Liu .et.al⁷¹ reported that they observed single Pt atom trapped in the six-ring experimentally. This kind of six-ring broken structure has never been reported in the previous research. The sub-lowest energy structure is also a six-ring structure (S1), which has 0.31 eV higher than the global minimum structure S1*. There is no bond broken and the Pt atom stays in the distorted six-ring. Structure S1* and S1 are confirmed to be stable with higher quality hybrid and meta-GGA functional calculations. In addition to the six-ring, the eight-ring is also found to be a reasonable energetic trap for single Pt atom. The energy of structure S2₄ is 0.53 eV higher than that of the global minimum structure S1* and 0.58 eV lower than that of the similar eight-ring structure S2₆ (**Figure 12**).

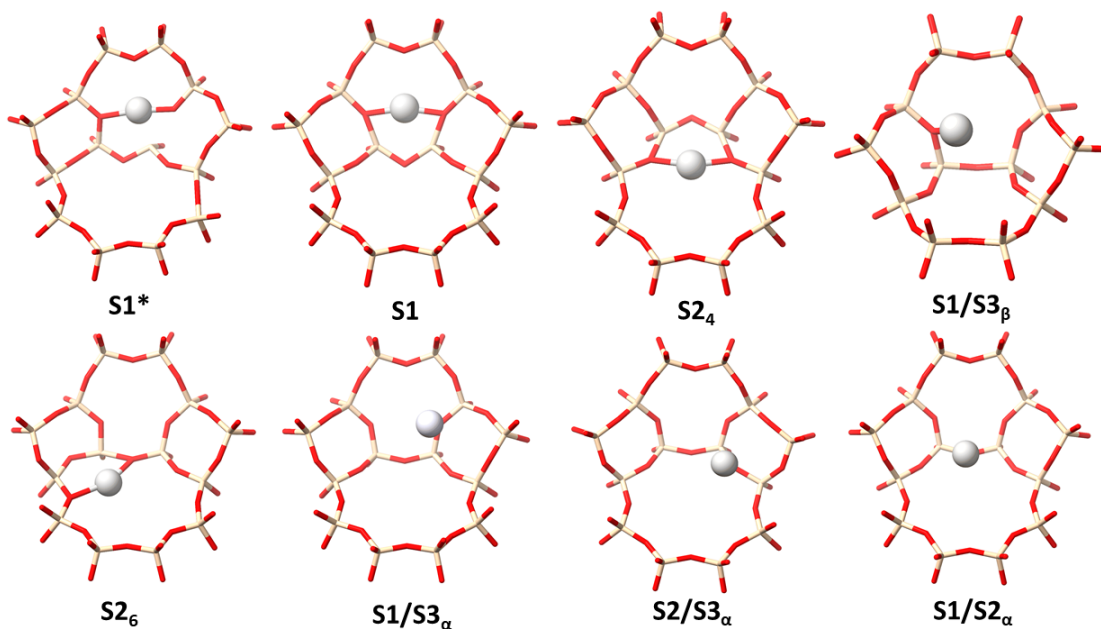


Figure 12 Minimum structures of single Pt atom in LTA zeolite. Si: yellow; red: O: read; Pt: silver

Besides the ring structures, there are also non-ring structure (**Figure 12**). We found that the energy of single Pt atom in the β cage is lower than that of single Pt atom in a similar position in the α cage. This is reasonable as Pt atoms in the β cage, the small space, have

Table 1 Incorporation energies and charge accumulation on Pt for minima of single Pt atom encapsulated in silicious LTA.

Site	E_{inc} (eV)	Charge accumulation on Pt (e)
S1*	-2.39	-0.16
S1	-2.08	-0.18
S2 ₄	-1.86	-0.14
S1/S3 _{β}	-1.44	-0.07
S2 ₆	-1.28	-0.10
S1/S3 _{α}	-1.22	-0.07
S2/S3 _{α}	-1.15	-0.07
S1/S2 _{α}	-1.06	-0.05

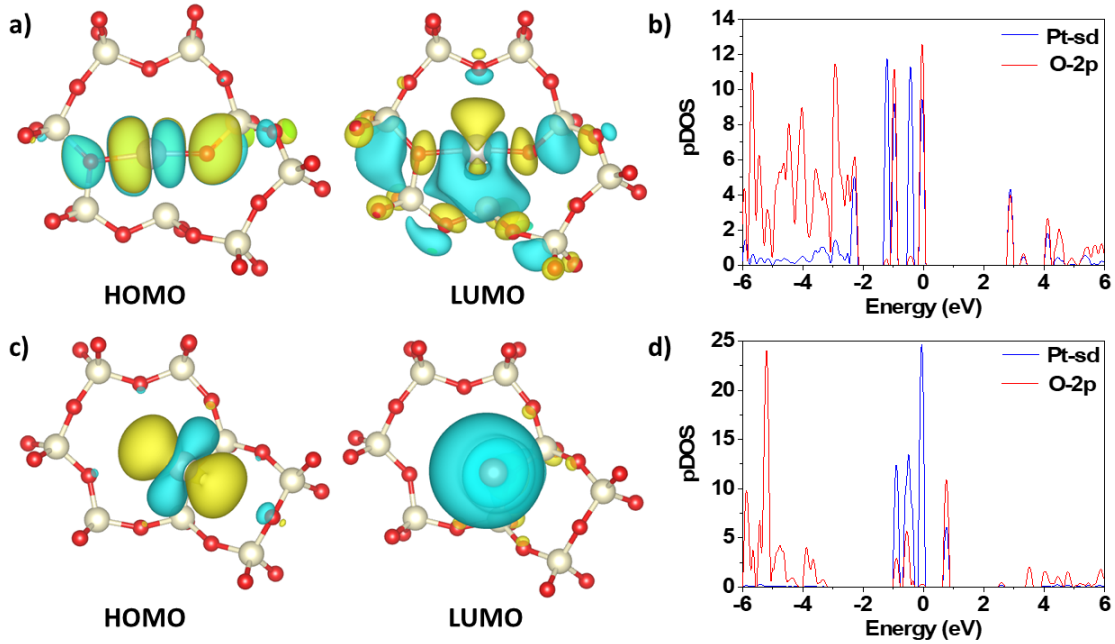


Figure 13 The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of S1* structure (a) and its projected density of states (b); The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of S1/S3_α structure (c) and its projected density of states (d). Si: yellow; red: O; read; Pt: silver.

more dispersion effect than that in the α cage. For example, when dispersion is considered, the energy difference between S1/S3_α and S1/S3_β is 0.22 eV. When the dispersion effect is not included, the energy difference is reduced to 0.09 eV. The energetics of each site are given in **Table 1**. The energies of all the non-ring α cage

structures (S1/S3_α, S2/S3_α, and S1/S2_α) are found to be substantially higher than those of ring structures. The energetic priority of these three α cage non-ring sites is S1/S3_α > S2/S3_α > S1/S2_α. The energy difference of these three sites is within 0.20 eV. All the non-ring site structures form one bond with O atoms that are shared by two rings. Hence, they are similar in stability, but, as they are undercoordinated to oxygen with respect to the ring-sites, they are energetically uncompetitive.

To investigate the stability of the global minimum, and compare between ring sites and non-ring sites, we explored the electronic structure of each configuration. **Figure 13** shows an exemplary comparison, with projected density of state (pDOS), between global minimum structure S1* and non-ring structure S1/S3_α. For S1*, the hybridization between Pt sd state and O 2p state leads to a large band gap, which explains the stability. The highest occupied molecular orbital (HOMO) consists of a hybrid between a d orbital of Pt and the O 2p orbitals of both oxygen atoms to which it is bound, giving rise to a three-center molecular orbital centered on Pt (**Figure 13a**). The lowest unoccupied molecular orbital (LUMO) consists of a broadly delocalized orbital between the Pt atom, the undercoordinated silicon atom and the oxygen atoms in the vicinity. By contrast, the HOMO of S1/S3_α is mainly on the Pt atom and the LUMO of S1/S3_α is determined by the Pt atom and oxygen atom bound to Pt atom. The pDOS of S1/S3_α shows an unfilled sd state at +0.76 eV and thus a much smaller band gap, concomitant with the weaker bonding. This is quite different from the pDOS of S1*, which indicates the different stability of structure S1* and S1/S3_α.

In all sites considered, negative charge is transferred from zeolite framework to the Pt atom leading to a partially anionic Pt^{δ-} species (**Table 1**). For ring sites, there is more framework charge transferring to the Pt atom than that of the non-ring sites. The six-ring sites have the most charge transfer, around -0.2 electrons to the Pt atom. This is in opposition to the traditional binding modes of single metal atoms to Al sites in zeolites, in which the atom become oxidized. This is examined in detail in section 3.1.7. Hence,

when binding to siliceous zeolites, or silicon-rich regions of the crystal, the metal can switch from partially oxidized to partially reduced, while maintaining stable bonds to the framework. This is likely to be relevant for catalysis, where the charge state of the metal can control reactivity.

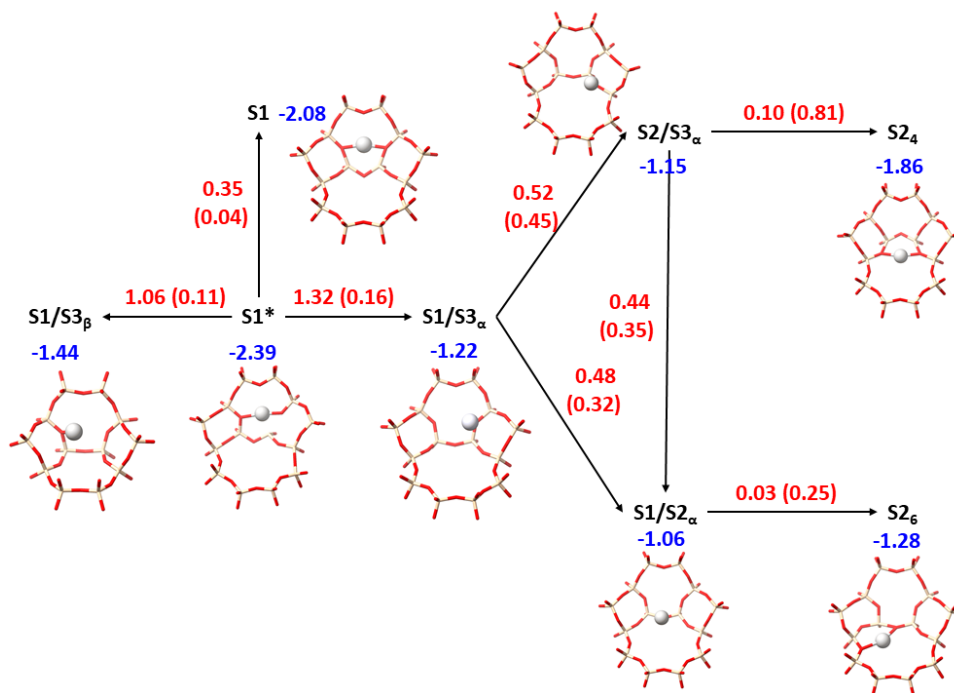


Figure 14 Incorporation energy (blue) and single Pt atom migration barrier (red) between different sites. Reverse barriers are in the parenthesis. Si: yellow; red: O; read; Pt: silver.

Sintering resistance is governed not only by the stability of the local minimum, but the ease with which the atom may leave and migrate around the zeolite pore system. To examine the migration properties, we calculated migration barriers for the single Pt atom and connected all pathways which connect minima via a single transition state into a complete kinetic map of the potential energy surface (**Figure 14**). Important barriers include those which lead into and out of the global minimum (S1*). We observe that moving from S1* to the adjacent site in the α cage (S1/S3_α) or the β cage (S1/S3_β) are 1.34 and 1.07 eV, respectively. This kind of barrier is high enough to severely hinder single Pt atom migrating outside of the six-ring trap. Barriers for the atom to return from

$S1/S3_\alpha$ and $S1/S3_\beta$ to the six-ring are only 0.16 and 0.11 eV, respectively. The high escape barrier and the lower reverse barrier indicate that the six-ring is a good kinetic local trap for the Pt atom. An alternative migration path is from $S1^*$ to the $S1$ site. This elementary step involves the closure of the broken six-ring and healing of the defect, with the concomitant energy penalty of 0.31 eV. The barrier to this framework healing step is low (0.35 eV), but the backward barrier is negligible (0.04 eV). Hence, the chance of occupation of the $S1$ site is likely to be quite low. $S1^*$ is the dominating six-ring structure.

When the Pt atom moves outside of the six-ring trap, because of the strong interaction between single Pt atom and O atoms in the framework, the Pt atom hops between non-ring sites. Barriers for atom migration from $S1/S3_\alpha$ to $S2/S3_\alpha$, $S1/S3_\alpha$ to $S1/S2_\alpha$, and $S2/S3_\alpha$ to $S1/S2_\alpha$ are 0.52, 0.48, and 0.44 eV, respectively. All these barriers are lower than that of escape from the broken six-ring trap, suggesting that leaving the trap site is the kinetically dominant step for atom migration.

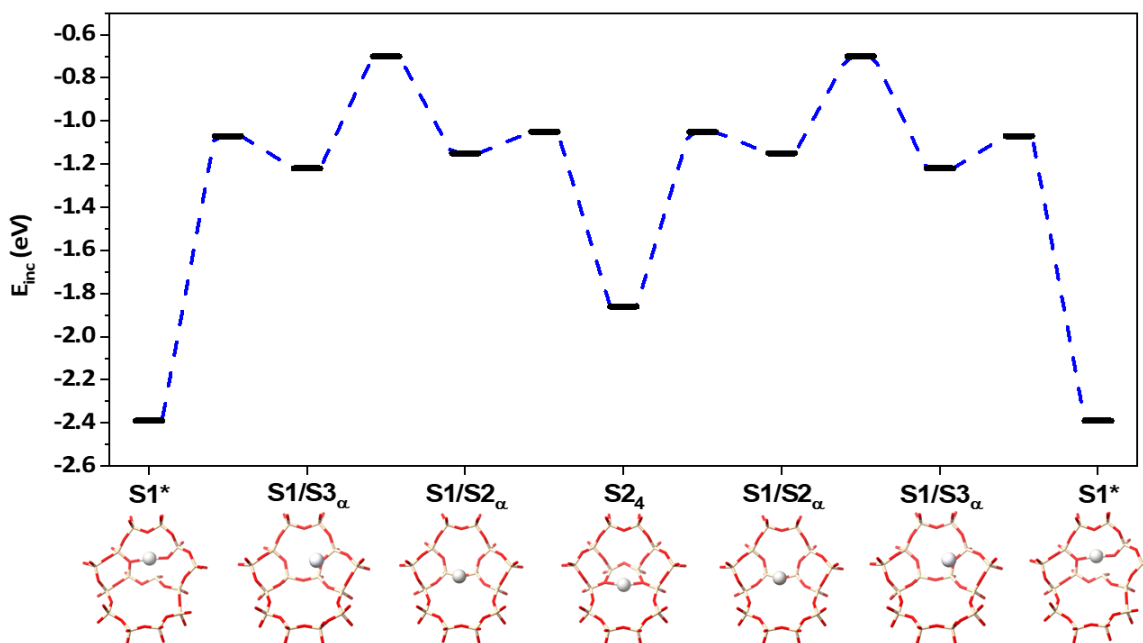


Figure 15 The global barrier for single Pt atom migrates from $S1^*$ to another $S1^*$ in the adjacent α cage by crossing through eight-ring sites $S2_4$. Si: yellow; red: O; read: Pt; silver.

By combining elementary steps together, we can generate longer pathways which represent potential diffusion routes through the zeolite pore system. One such pathway involves the migration of Pt from an S1* site in one LTA cage, through the α cage, then through the eight-ring, which acts as a window, connecting adjacent α cages, followed by migration to the S1* site in the next α cage (**Figure 15**). This pathway is symmetric, and moves the Pt atom one unit cell, between two identical global minimum sites. The global migration barrier for this process (from S1* to S1*) is 1.69 eV. Hence, six-ring is not only a global minimum, but a deep kinetic trap for single Pt atoms in high silicious LTA zeolite, and is likely to hinder diffusion severely.

3.1.2 The six-ring trap

In order to clarify whether the six-ring trap applies to other six-ring containing zeolites, several other topological zeolite frameworks (CHA, FAU, RHO, and SOD) were tested with placing one Pt atom in the six-ring or sites adjacent to the six-ring. Incorporation energy and Bader charges were calculated to analyze the stability. The results show in **Table 2** and **Figure 16**.

Table 2 Incorporation energy and charge accumulation on Pt atom for six-ring and non-six-ring structures.

Zeolite	Six-ring site		Non-ring site	
	Incorporation energy (eV)	Bader charge (e)	Incorporation energy (eV)	Bader charge (e)
RHO	-2.10	-0.17	-1.22	-0.05
SOD	-2.30	-0.17	-1.49	-0.05
LTA	-2.39	-0.16	-1.44	-0.07
FAU	-2.39	-0.18	-1.39	-0.05
CHA	-2.46	-0.18	-1.35	-0.06

For all the structures, the energy of the six-ring structure is at least 0.88 eV lower than that of non-six-ring structures. For zeolite RHO and SOD, when Pt atom is confined in the six-ring, the six-ring is not broken. The only six-ring structure is similar to S1 of zeolite LTA. When one Pt atom is trapped in zeolite FAU or CHA, they have a broken

six-ring structure. As shown in **Figure 16**, six-ring structures have lower incorporation energy than that non-broken six-ring structures. It has the same energy trend as found in zeolite LTA. When single Pt atom is in the six-ring, a charge transfer of at least 0.16 e is found between the Pt atom and zeolite framework (**Table 2**). When the Pt atom is not in the six-ring, even though it forms a bond with the O atom, the charge transfer is quite small (no more than 0.07 e). Hence, we conclude that the findings in LTA are generalizable to other six-ring containing zeolite topologies.

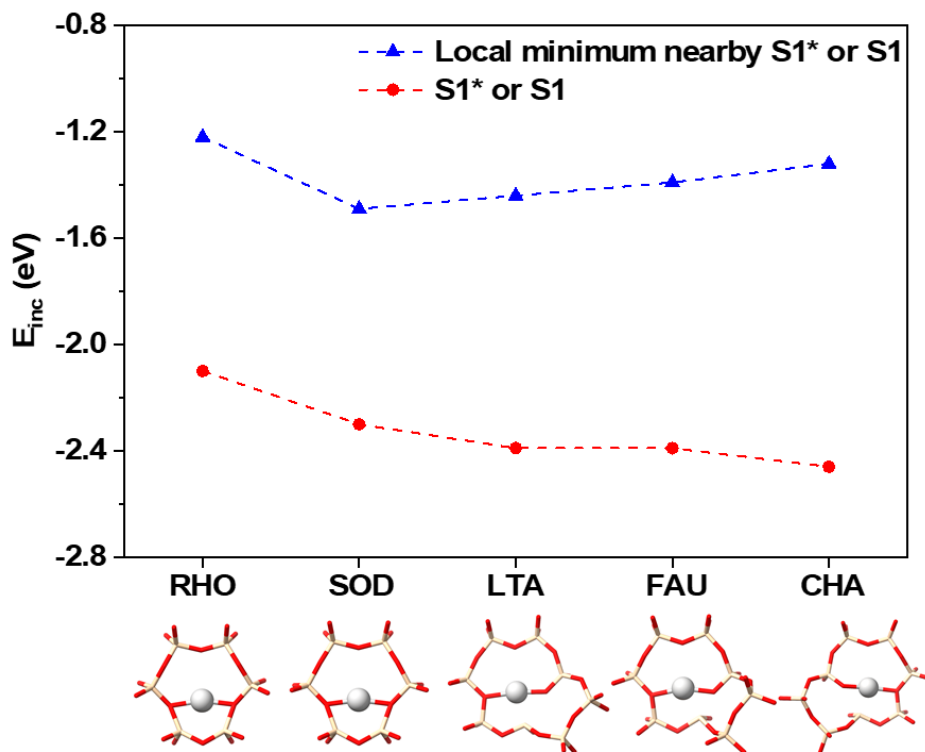


Figure 16 Incorporation energy for one Pt atom in six-ring sites and non-ring sites of various six-ring containing zeolite. Si: yellow; red: O: read; Pt: silver.

3.1.3 Kinetic behavior of single Pt atom in silicious LTA

It is found that single Pt atom can be trapped in the plane of six-ring with one Si-O bond broken and this is the global minimum structure, with difficult barriers to leave the site. This is, however, a conclusion only from static calculations. Under realistic experimental

conditions, the interaction between metal and zeolite framework is a dynamic process in which elevated temperatures will play a role. To understand the dynamic behavior of single Pt atom is important to comprehend the activation processes prior to Ostwald ripening and thus growth of Pt clusters. Hence, we developed a kinetic Monto Carlo (kMC) model to sample the migration kinetics of Pt atoms in LTA. Simulations were run in a regime in which single atoms exist and Pt is unable to interact with other Pt atoms or clusters. This is therefore an approximation for the kinetics of an atom in the infinitely dilute limit, and thus is not valid for the processes of cluster formation and growth, which will occur according to mechanisms and energetics that are so far unexplored.

The Boltzmann-weighted occupation distributions were calculated with equation **52**:

$$p_i = e^{-E_i/(k_B T)} / \sum_i e^{-E_i/(k_B T)} \quad (52)$$

where E_i is the incorporation energy of the minimum structure. k_B and T are Boltzmann's constant and temperature, respectively. As the reaction network contains no (non-frustrated) translations, rotations or desorption steps, the partition functions are modelled by the vibrational partition function. The denominator of equation **52** is the partition function for the sum of all vibrational normal modes.

Table 3 Boltzmann population and occupation lifetime of one Pt atom encapsulated in silicious LTA.

Site	Boltzmann Population (%)				Occupation Lifetime (s)	
	300 K	500 K	800 K	1000 K	800 K	1000 K
S1*	99.9	99.9	98.9	97.1	2.57×10^{-9}	2.79×10^{-10}
S1	6.17×10^{-4}	7.48×10^{-2}	0.11	0.266	2.87×10^{-11}	7.63×10^{-12}
S2₄	1.24×10^{-7}	4.52×10^{-4}	0.045	2.07×10^{-1}	1.61×10^{-6}	5.86×10^{-8}
S2₆	2.22×10^{-17}	6.42×10^{-10}	1.00×10^{-5}	2.46×10^{-4}	5.56×10^{-10}	8.77×10^{-11}
S1/S2_α	4.46×10^{-21}	3.88×10^{-12}	4.11×10^{-7}	1.91×10^{-5}	2.29×10^{-11}	6.50×10^{-12}
S1/S3_α	2.18×10^{-18}	1.59×10^{-10}	4.18×10^{-6}	1.23×10^{-4}	1.60×10^{-10}	2.96×10^{-11}
S1/S3_β	1.08×10^{-14}	2.63×10^{-8}	1.02×10^{-4}	1.58×10^{-3}	7.88×10^{-11}	1.72×10^{-11}
S2/S3_α	1.45×10^{-19}	3.14×10^{-11}	1.52×10^{-6}	5.44×10^{-5}	6.26×10^{-11}	1.43×10^{-11}

The Boltzmann-weighted occupation distributions is first considered to predict the occupation probabilities of all minima as a function of temperature. Boltzmann population values (**Table 3** and **Figure 17a**) demonstrate that the S1* site is the dominant occupation site across the full synthesis and catalytic temperature range.^{18, 71-72, 74, 77-79, 187-}

188

As shown in **Figure 14**, each minimum site is linked with one or several minimum sites. The kMC simulation was carried out to evaluate the equilibration time of the system, which is defined as the simulation time required for the occupation probabilities to converge to the Boltzmann populations to within a tolerance of 0.1 % (**Figure 17b** and **c**). After equilibration, the average occupation lifetimes of each site can be extracted at the given temperature. At 300 and 500 K, it was found to be impossible to reach the equilibration time within our maximum simulation steps (2.4 billion). We were thus limited to simulations at elevated temperatures. At 800 and 1000 K, the equilibration time was found to be 2.36 ms and 15.7 μ s, respectively (**Table 3**). These times are considerably shorter than the laboratory timescale, which indicates that the system quickly reaches the equilibration at these temperatures. By sampling the full configuration space of the potential energy surface ergodically within such short times, it is reasonable to assume that the single Pt atom will likely migrate across several LTA cages, and locate any nearby Pt atoms and clusters. We do not expect therefore that the trap sites in LTA are sufficient to overcome sintering and particle growth at such high temperatures and remain observable in experiment. However, at lower temperatures, where equilibration was not possible, this cannot be ruled out.

Considering the occupation lifetimes, it is interesting to note that the eight-ring site S24 is the longest-lived minimum, with an occupation lifetime of 1.61 μ s at 800 K and 58.6 ns at 1000 K (**Table 3**). This is a metastable local minimum, 0.51 eV higher in energy than the ground state. However, all barriers to leave the S24 site are high, and therefore, upon reaching it, Pt atoms will likely be trapped for long timescales. This site is also a local

minimum along the pathway between cages (**Figure 15**) and so kinetic trapping in the eight-ring is significant to the overall diffusion process for Pt. The next long-lived site is S1* with an occupation lifetime of nanosecond timescale (2.57 ns (800 K) and 0.28 ns (1000 K)). The reduced lifetime of this site is due to the fast interchange between S1 and S1*, which is essentially a ring opening, ring closing process, with no migration of the Pt atom. All other sites are kinetically insignificant in the range of considered temperatures. Hence, single Pt atom is predicted to occupy primarily six and eight-ring sites. It is notable that the timescales for six and eight ring occupation are significantly outside the range of ab initio molecular dynamical simulations, which necessitates the use of discretized simulation methods such as kMC.

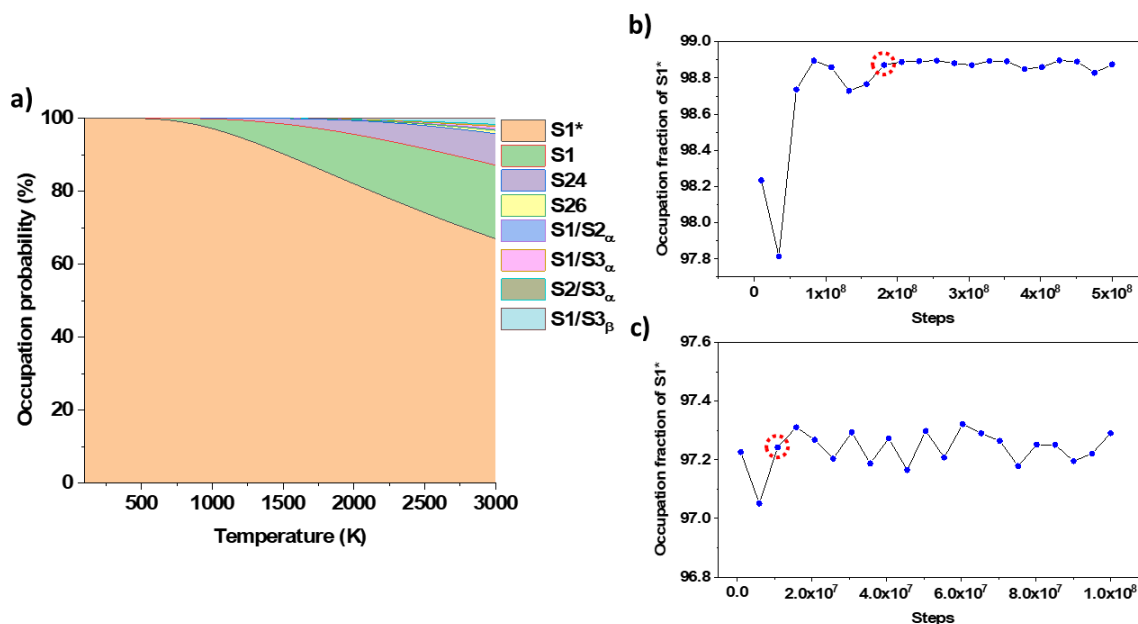


Figure 17 (a) Boltzmann-weighted occupation distributions of the minima for the temperature from 100 to 3000 K. Occupation percentage of the global minimum structure (S1*) from kinetic Monte Carlo simulations at 800 (b) and 1000 K (c) with various simulation durations. Red circles mark the number of steps required to reach equilibration, from which the equilibration time for the system is calculated – defined as the length of time required to reach a converged occupation percentage.

3.1.4 CO adsorbed single Pt atom in silicious LTA

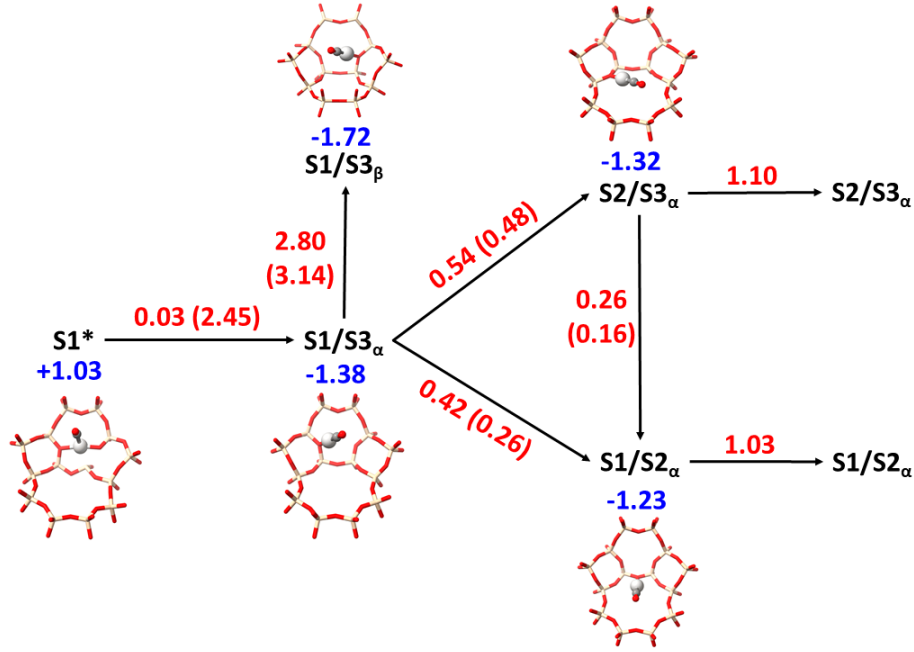


Figure 18 Diagram of local minima and barriers on the potential energy surface of PtCO@LTA. Incorporation energy and elementary step barriers are shown in blue and red, respectively. Reverse barriers are in the parentheses.

To continue towards a model of the single atom catalyst material under realistic conditions, we next elucidate the role of common reducing adsorbates on the binding and migration of Pt. The local minima and migration barriers of a single CO molecule adsorbed on Pt@LTA was first considered. The incorporation energy of PtCO in LTA is calculated with equation 53

$$E_{\text{inc}}(\text{PtCO}) = E_{\text{PtCO@LTA}} - E_{\text{LTA}} - E_{\text{PtCO(vacuo)}} \quad (53)$$

where $E_{\text{PtCO@LTA}}$ is the total energy of the optimized structure after one PtCO is encapsulated into zeolite LTA. E_{LTA} is the total energy of the optimized empty zeolite framework. $E_{\text{PtCO(vacuo)}}$ is the energy of the PtCO in the vacuum phase.

When a single CO molecule is adsorbed on the Pt atom, it significantly influences the energetics of Pt in zeolite. It is notable that the S1* site is destabilized (**Figure 18**). While it remains a local minimum, it is more than 2 eV higher in energy than the new global

minimum (S1/S3) and is even endothermic with respect to PtCO detachment and diffusion out of the zeolite entirely. Furthermore, the barrier for single Pt atom migration from S1* to S1/S3 $_{\alpha}$ is negligible and the reverse barrier is 2.45 eV, which indicates that the S1* minimum is impossible to exist. Hence, the adsorption of CO destroys the special stabilization of the six-ring site. Even though the incorporation energy of the β cage structure S1/S3 $_{\beta}$ is 0.34 eV lower than that of the similar α cage structure S1/S3 $_{\alpha}$, the six-ring does not allow PtCO to pass through to reach the S1/S3 $_{\beta}$ minimum, with a barrier of 2.80 eV. Hence, it can be excluded from consideration, and we neglect it in the following kMC simulation and discussion.

All the ring sites (S1, S2 $_4$, and S2 $_6$), except S1*, are no longer minimum structure when CO is adsorbed on the Pt atom. This simplifies the potential energy surface, reducing the number of nodes, and therefore potential kinetic traps for diffusion. The effective barrier for PtCO migrating among the LTA pores, according to the route from global minimum to another global minimum via the eight-ring window is 1.16 eV, which is 0.53 eV lower than that of Pt@LTA. Hence, the presence of CO molecules enhances the diffusion of Pt in the zeolite framework.

To explain why the ring sites are energetically unfavorable, the electric structure of the ring and non-ring structures are studied. When CO is adsorbed on Pt atom at S1*, there is no additional extra electronic stabilization afforded by the CO molecule. The Pt d band is filled, so interaction via electron donation from the 2 π molecule orbital into the Pt d band is not net bonding. There is no obvious electronic structure difference between the before and after CO adsorbed Pt-sd state (**Figure 19b**), which indicates the weak interaction between the Pt atom and CO molecule. By contrast, when CO is adsorbed on a Pt atom at the more stable S1/S3 $_{\alpha}$ site, due to the hybridization between the 2 π orbital of CO and 5d orbital of Pt atom, the unfilled orbital of the bare Pt atom near the Fermi energy is filled, leading to a large band gap (**Figure 19d**).

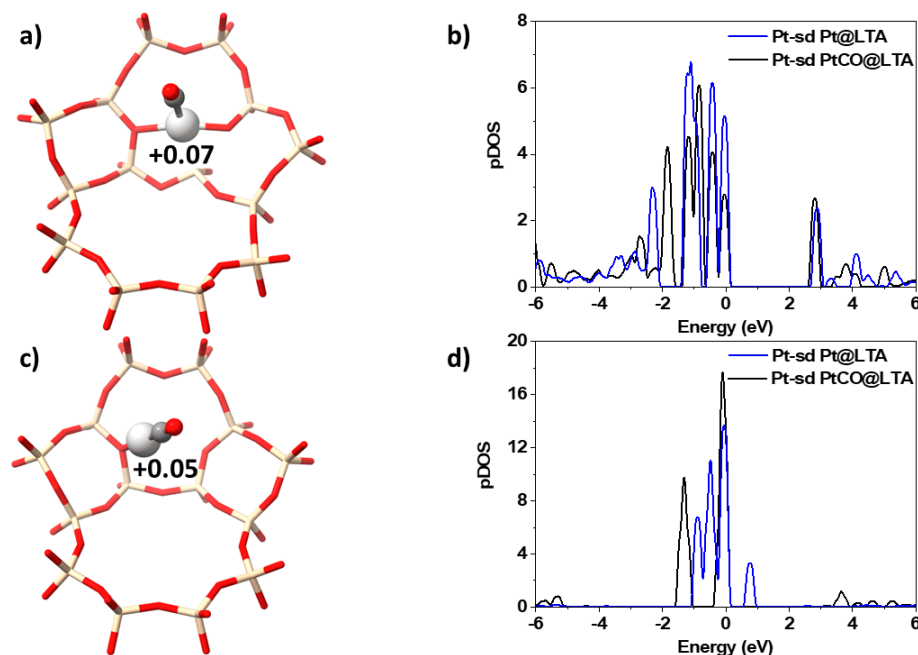


Figure 19 (a) Structure and charge accumulation on Pt atom charge of S1*. (b) The projected density of states for Pt atom at S1* before and after adsorption of CO molecule (b); (c) Structure and charge accumulation on Pt atom of S1/S3_α. (d) The projected density of states for Pt atom at S1/S3_α before and after adsorption of CO molecule.

Table 4 Boltzmann population and occupation lifetime of PtCO@LTA.

Site	Boltzmann Population (%)			Occupation Lifetime (s)		
	300 K	500 K	800 K	300 K	500 K	800 K
S1*	0	0	0	0	0	0
S1/S3 _α	90.82	78.18	65.27	1.82×10^{-4}	2.59×10^{-7}	6.04×10^{-9}
S2/S3 _α	8.91	19.41	27.33	3.76×10^{-7}	6.67×10^{-9}	6.72×10^{-10}
S1/S2 _α	0.27	2.40	7.40	7.65×10^{-9}	5.99×10^{-10}	1.32×10^{-10}

The effect of CO adsorption, and the flattening the potential energy surface which results, is determined numerically by kMC simulation. First it is notable that equilibration can be reached for lower temperatures than in the case of Pt@LTA, which is a stiffer, more hindered potential energy surface. As shown in **Table 4**, for all temperatures considered, the six-ring site S1* is not preferred to be occupied, which is consistent with the static calculations.

While the global minimum (S1/S3_α) is the most highly populated site, it decreases more quickly than that of the global minimum Pt@LTA structure (S1*) with increasing temperature. Hence it is likely that a non-negligible occupation of sub-optimal sites is likely. However, as the surface is easier to explore than for Pt, the equilibrium times are shorter. At 300 K, equilibrium is reached within 0.09 s, which is shorter than the laboratory timescale. By comparing with bare zeolite encapsulated single Pt atom at 800 K, the presence of CO molecule speeds up equilibration by about 80 times. The global minimum site S1/S3_α has the longest occupation lifetime in all the simulated time ranges. At 800 K, its occupation lifetime is 6.04 ns, which is more than 250 times shorter than the longest lived bare Pt site (S2₄) at the same temperature. Therefore, the presence of CO molecule not only simplifies the landscape for Pt migration, reduces barriers, and destroys the special trap site of S1*, but it speeds up diffusion and equilibration greatly.

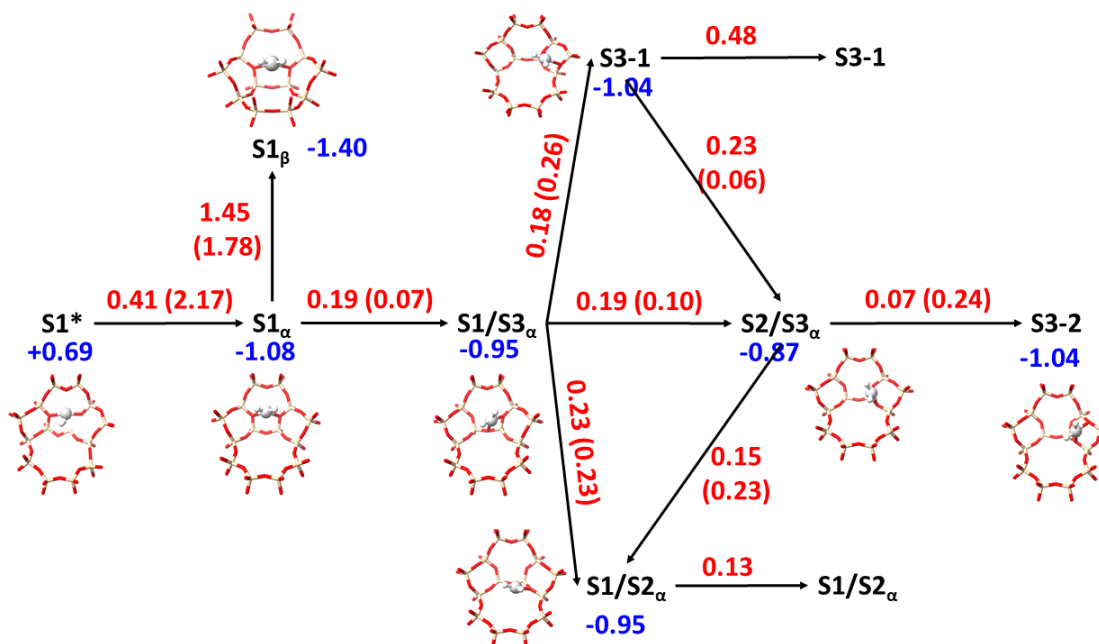


Figure 20 Diagram of local minima and barriers on the potential energy surface of PtH₂@LTA. Incorporation energy and elementary step barriers are shown in blue and red, respectively. Reverse barriers are in the parentheses.

In addition to CO, H₂ is another widely used reductive atmosphere in experiment.¹⁸⁹ Hydrogen is both a common byproduct of the dehydrogenation reactions that noble metals such as Pt catalyze in industrial and experimental processes, and a common reductant in the redox cycles used to grow and redisperse Pt particles inside zeolites during fundamental studies of particle sintering.^{78, 187, 190}

The introduction of H₂ to zeolite encapsulated single Pt atom leads to the dissociation of H₂ at some site and forms several new minima structures (S1_α, S1_β, S3-1, and S3-2; **Figure 20**). When located at the six-ring, PtH₂ occupies sites that are close to the traditional S1 cation sites: above the ring, displaced into a cage, either α or β. The subscript α or β is therefore added to the S1 label to indicate the cage where PtH₂ is located. The ring is not broken, and the H-H bond is dissociated, forming a Pt hydride. S3-1 and S3-2 are structures in which PtH₂ lies above the four-ring (the S3 cation site) and is bonded to O atoms belonging to either the four- and six-ring or four- and eight-ring, respectively. The incorporation energy is calculated with equation 54:

$$E_{\text{inc}}(\text{PtH}_2) = E_{\text{PtH}_2 @ \text{LTA}} - E_{\text{LTA}} - E_{\text{PtH}_2 (\text{vacuo})} \quad (54)$$

where $E_{\text{PtH}_2 @ \text{LTA}}$ is the total energy of the optimized structure after one PtH₂ entity is encapsulated into zeolite LTA. E_{LTA} is the total energy of the optimized empty zeolite framework. $E_{\text{PtH}_2 (\text{vacuo})}$ is the energy of the PtH₂ in the vacuum phase.

The incorporation energy of the global minimum PtH₂@LTA structure is -1.08 eV (**Figure 20**), which is less than that of Pt@LTA (-2.39 eV) and PtCO@LTA (-1.38 eV). H₂ molecule dissociates on the non-ring site Pt atom, forming a stable hydride product, but cannot adsorb on the ring site Pt atom (S1*, S1, S2₄ and S2₆). When H₂ interacts with the Pt atom at S1* (**Figure 21a**), the H-H bond is 0.757 Å, which is an extension of just 0.007 Å with respect to the vacuum phase H₂ molecule. The minimum distance between Pt and H atom is 2.759 Å, which indicates the weakness of the interaction between the S1* site Pt atom and the H₂ molecule. This is because the ring site Pt atom, such as S1*,

has a closed d band. The H₂ molecule therefore cannot form a bond to Pt. In the pDOS (**Figure 21b**), there is no electronic structure difference of Pt-sd state at S1* between the presence of H₂ molecule and absence of H₂ molecule. By contrast, when H₂ is adsorbed on the non-ring site Pt atom, such as S1/S3_α, the d state of the Pt atom hybridizes with the hydrogen electronic states (**Figure 21d**), forming a covalent bond. The H-H bond is broken, with an H-H distance of 1.947 Å. Therefore, overall, the presence of the H₂ molecule makes the most stable bare Pt structure (S1*) energetically unfavorable.

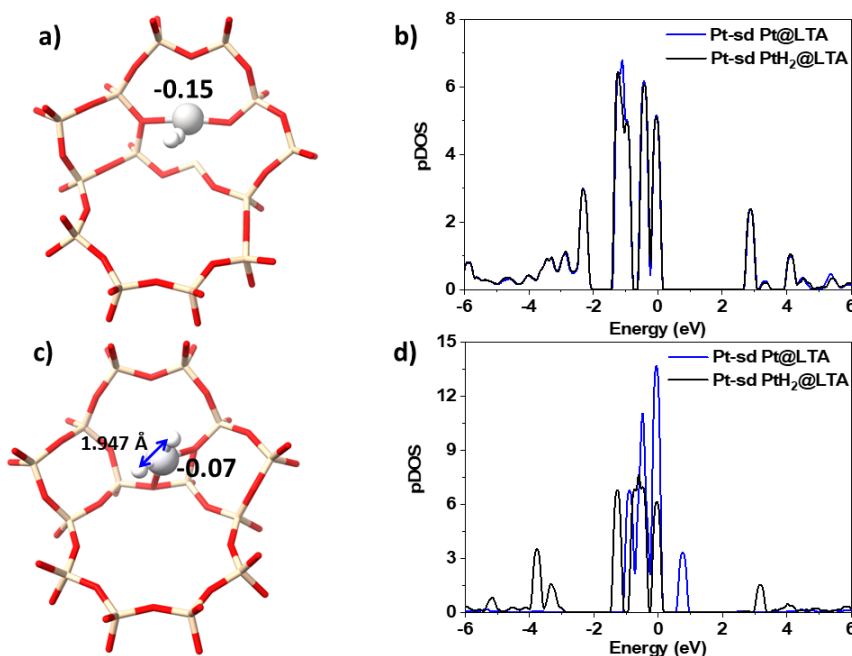


Figure 21 (a) Structure and charge accumulation on Pt atom of S1*. (b) The projected density of states for Pt atom at S1* before and after the presence of H₂ molecule; (c) Structure and charge accumulation on Pt atom of S1/S3_α. (d) The projected density of states for Pt atom at S1/S3_α before and after adsorption of H₂ molecule.

The lowest effective barrier for PtH₂ migration between α cages is calculated to be 0.52 eV, according to the pathway (S1_α → S1/S3_α → S3-1 → S3-1 → S1/S3_α → S1_α), which is much lower than for Pt@LTA (1.69 eV) and PtCO@LTA (1.16 eV). The incorporation of H₂ makes the ring sites unfavorable and the potential energy surface flattens, which is beneficial for the diffusion of PtH₂ among cages. Hydrogen is known to induce sintering and growth of Pt particles in zeolites, however, this is primarily due to hydrogen as a

reductant, in which H₂ reduces the oxidized M⁺ or M²⁺ cations that are bound to Al sites. In the current case, Pt is nearly neutral, and there are no anionic framework sites. As a result, H₂ is not acting as a strong reductant, but rather a competitive ligand to the framework. The mechanism by which it induces migration, and thus sintering is not the same as for metal cations on anionic charged sites, but the resulting behavior of Pt is similar.

The degree of H₂ adsorption on flattening the potential energy surface is determined by kMC simulation. Due to the steric constraint of the six-ring, the barrier for PtH₂ to move from α to β cage is 1.45 eV. The high migration barrier hinders PtH₂ migration into the β cage and so the S1 β site is deemed inaccessible, and is not considered in the calculation of Boltzmann population and kMC simulation. As shown in **Table 5**, the equilibration time at 300, 500 and 800 K is 72.3, 2.22, and 0.32 μ s, respectively. The equilibration time is more than 100 times shorter than that of the PtCO structure in all the corresponding temperatures. For the PtH₂ structure, the longest-lived site is S3-2 with 173 ns at 300 K, which is three orders of magnitude shorter than that of the longest-lived PtCO structure (S1/S3 α) at 300 K. At 800 K, the occupation lifetime of S3-2 site reduces to 0.2 ns, but it is still 30 times shorter than that of the longest-lived PtCO structure at the same temperature. Hence, H₂ molecule is much more efficient in promoting the diffusion of Pt atoms than the CO molecule.

Table 5 Boltzmann population and occupation lifetime of PtH₂@LTA.

Site	Boltzmann Population (%)			Occupation Lifetime (s)		
	300 K	500 K	800 K	300 K	500 K	800 K
S1*	2.71 $\times 10^{-28}$	1.19 $\times 10^{-16}$	3.79 $\times 10^{-10}$	0	0	0
S1α	69.50	52.75	40.48	2.50 $\times 10^{-8}$	7.94 $\times 10^{-10}$	9.43 $\times 10^{-11}$
S1/S3α	0.45	2.58	6.14	2.34 $\times 10^{-10}$	4.19 $\times 10^{-11}$	1.12 $\times 10^{-11}$
S3-1	14.78	20.84	22.66	8.97 $\times 10^{-8}$	1.33 $\times 10^{-9}$	1.01 $\times 10^{-10}$
S2/S3α	0.02	0.40	1.92	8.51 $\times 10^{-11}$	1.67 $\times 10^{-11}$	5.32 $\times 10^{-12}$
S1/S2α	0.45	2.58	6.14	2.35 $\times 10^{-9}$	1.64 $\times 10^{-10}$	2.70 $\times 10^{-11}$
S3-2	14.78	20.84	22.66	1.73 $\times 10^{-7}$	2.53 $\times 10^{-9}$	1.96 $\times 10^{-10}$

3.1.6 Au@LTA

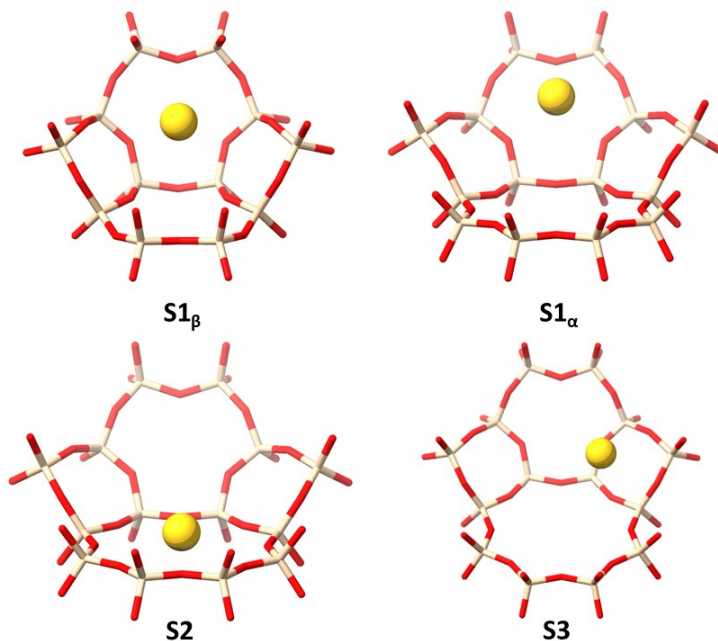


Figure 22 Minimum structures for one Au atom encapsulated in LTA zeolite

Gold (Au) is another common metal of choice for subnanometre cluster and single atom catalysis.¹⁹¹ Small gold clusters were one of the earliest examples of enhancing catalytic activity via control of cluster size at the atomic level.^{19, 192} As an expensive precious metal, the economic benefits of optimizing atom efficiency are pronounced. Therefore, in our study, we consider the effect of changing the metal atom that is encapsulated into the zeolite pore, by selecting Au. Isolated Au has a $d^{10}s^1$ electronic configuration and is different to the isolated Pt (d^9s^1) which has an unfilled d orbital.

We perform a global structure optimization via a basin hopping algorithm, at the DFT level with the PBE-D3 exchange correlation functional, as in the case of Pt@LTA. It was found that the Au atom binds very weakly to the framework, and has a less rich potential energy surface than does Pt. Au lies in the traditional cation sites, S1, S2 and S3 (**Figure 22**). Considering the six-ring, there are two possible structures depending on the position of Au atoms in the α or β cage, and thus the notation for these two structures are $S1_\alpha$ and $S1_\beta$, respectively.

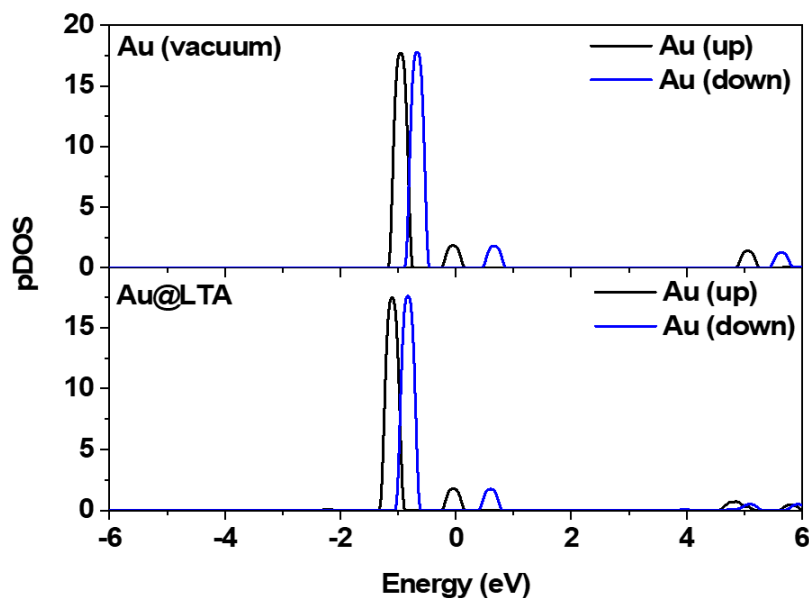


Figure 23 Projected density of states of single Au atom in vacuum phase and encapsulated in LTA at $S1_{\beta}$. Spin up and spin down are depicted by black and blue lines, respectively.

Table 6 Incorporation energies and charge accumulation on Au atom for low-lying minima of Au@LTA. Reverse barriers are in parentheses

Site	E_{inc} (eV)	Charge accumulation on Au (e^-)
$S1_{\beta}$	-0.58	+0.02
S2	-0.41	+0.04
$S1_{\alpha}$	-0.38	+0.02
S3	-0.33	+0.03

The Au atom in the β cage and at the site above the six-ring is the global minimum structure (**Figure 22**, $S1_{\beta}$). The sub-lowest energy structure is the Au atom in the S2 site, with 0.17 eV higher than the global minimum structure. The third lowest energy structure is the Au atom at the $S1_{\alpha}$ site, and it is 0.20 eV higher than the global minimum structure. This is again different to Pt atom in LTA, for which both six-ring sites have lower energy than all non-six-ring sites. The energy difference between $S1_{\alpha}$ and $S1_{\beta}$ is mainly governed by dispersion, as the β cage is smaller, with a volume of 718.4 Å³ as compared with the α cage (974.8 Å³). The total incorporation energies are weak, with the global minimum at only -0.58 eV (-2.39 eV for Pt@LTA). The weak interaction between single

Au atom and zeolite framework is further indicated in the electronic pDOS. As shown in **Figure 23**, there is negligible difference between the DOS of single Au atom in vacuum phase and single Au atom encapsulated in silicious LTA at the S1 $_{\beta}$ site. The Au is largely unperturbed by the presence of the framework, which acts less as a chemically reactive ligand, as in the case of Pt, but rather as a confining physical cage.

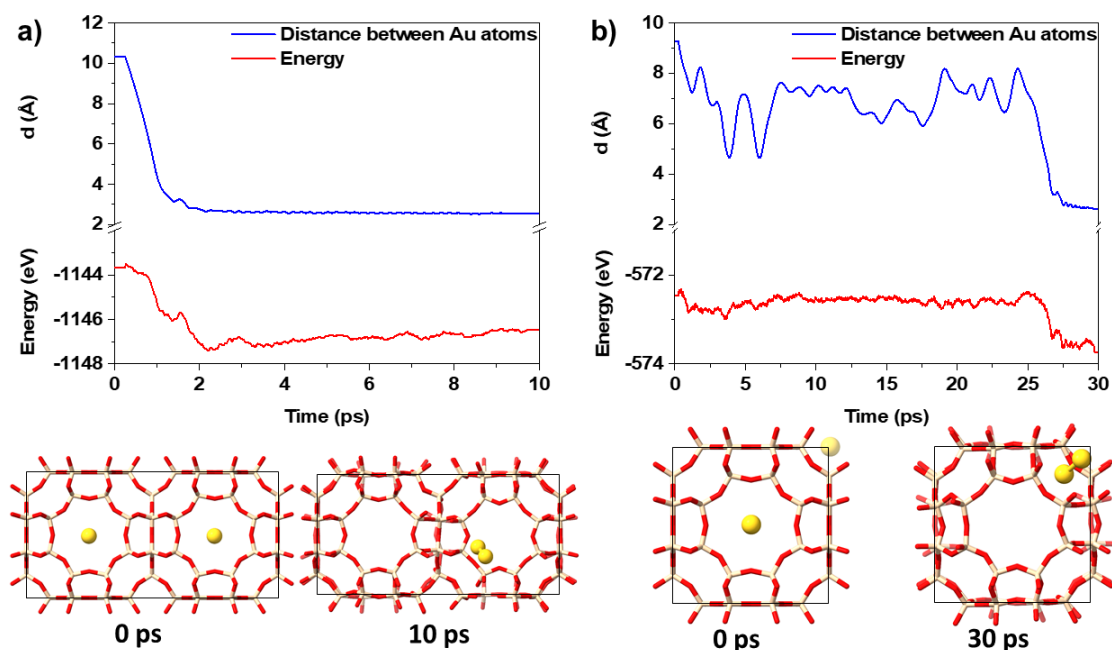


Figure 24 Ab Initio molecular dynamics simulations in the NVT ensemble were run at an elevated temperature of 450 K, with a timestep of 0.5 fs for two initial configurations, a) Au atoms located in adjacent α -cages; b) Au atoms located in adjacent α and β -cages.

The barriers for single Au atom migrating are found to be no more than 0.10 eV for single Au atom migration around and between adjacent α cages. Hence, single Au atom almost moves freely in the α cage and between different adjacent α cages. This is further illustrated via ab Initio molecular dynamics simulations in the NVT ensemble at a temperature of 450 K (**Figure 24a**). In **Figure 24a**, two Au atoms were placed in the centres of adjacent α cages and the simulation was begun. Within 2 ps a dimer had formed, which persisted for the remaining duration of the simulation. A second scenario was attempted, in which two Au atoms were placed in adjacent α and β cages (**Figure**

24b). The athermal migration barrier for a single Au atom between these sites is 1.04 eV in one direction and 1.24 eV in the reverse direction. Hence, this is a relatively high barrier, which may be expected to suppress Au atoms from forming a dimer. However, during the simulation, the two separated Au atoms formed a dimer in the β cage within 30 ps. This is because when the two atoms lie either side of the six-ring, at a short distance apart, they can interact. The formation of the relatively strong Au-Au bond allows the atom to overcome the barrier to diffuse through the six-ring, and move into the β cage, forming a dimer. This cooperativity ensures that clustering is allowed, even in the regions of configuration space where migration of single atoms is hindered. However, diffusion of the dimer out of the β cage is suppressed, and not observed on the timescale of the simulation.

3.1.7 Different behavior of single Pt and Au atom

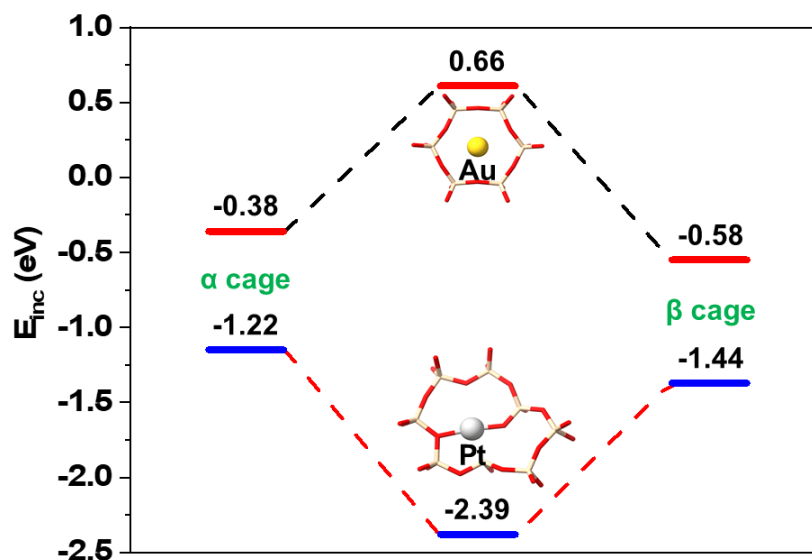


Figure 25 Barriers for single Au atom and single Pt atom migration between the α cage and the β cage.

In the previous part, it was shown that the six-ring is a good kinetic trap for single Pt atom encapsulated in pure silicious six-ring containing zeolite, while the six-ring trap does not exist for single Au atoms, which prefer to lie above unbroken rings, and are weakly bound. As shown in **Figure 25**, for the process of crossing through the six-ring,

Au atoms show quite different behavior to Pt atoms. The plane of the six-ring is the transition state for intra-cage migration, and the Au atom does not break the six-ring in passing through it. By contrast, the Pt atom can be trapped in the plane of the six-ring and this structure is the global minimum structure. Hence, this trapping site is implicated in the high stability of Pt atoms in high silica zeolites, and shows the importance of the metal element choice. The finding that Pt atoms may be effectively trapped in siliceous frameworks is not simply generalizable to other metals, due to the different chemical relationship between the metal atoms and the framework.

3.1.8 Subnanometer Pt in LTA

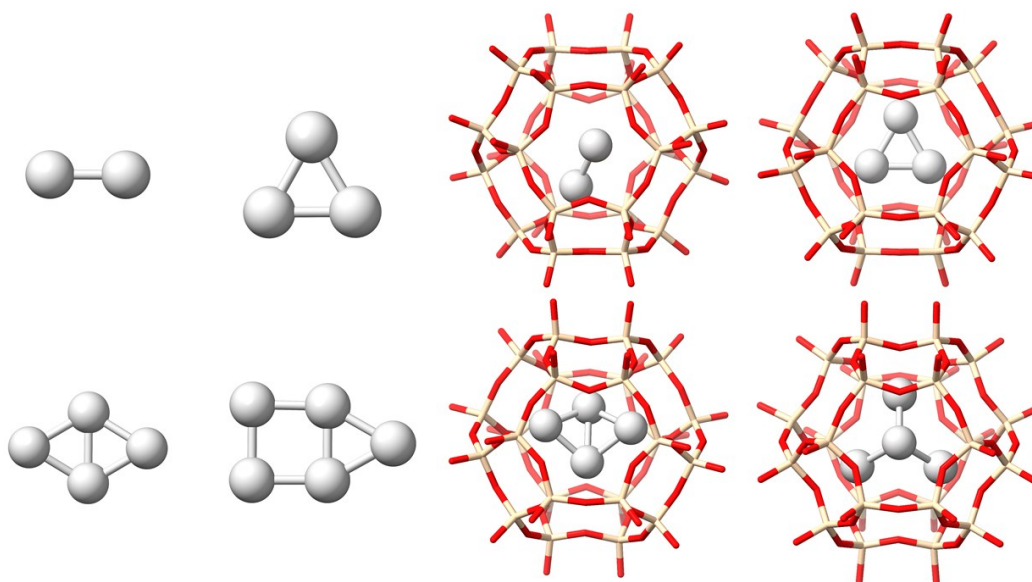


Figure 26 Global minimum structures of Pt_n in vacuum phase and encapsulated into the zeolite. Si: yellow; red: O; read; Pt: silver.

Apart from the single Pt atom, subnanometer Pt particles also widely exist in zeolites, and their formation is the next step along the pathway towards sintering and deactivation. Having considered the stability of the single atoms, and the kinetics of their migration in the low Pt concentration limit, it is informative to next study the nature of zeolite-encapsulated subnanometer Pt particles. Here, the basin-hopping global optimization

method is again used to search for local minima of zeolite LTA encapsulated subnanometer clusters with Pt atoms numbers ranging from two to five. The encapsulation energy and cohesive energy were calculated with equation here:

$$E_{\text{enc}}(\text{Pt}_n) = E_{\text{Pt}_n @ \text{LTA}} - E_{\text{LTA}} - E_{\text{Pt}_n(\text{vacuo})} \quad (55)$$

$$E_{\text{coh}}(\text{Pt}_n) = E_{\text{enc}}(\text{Pt}_n) - n \times E_{\text{inc}}(\text{Pt}_1) \quad (56)$$

where $E_{\text{Pt}_n @ \text{LTA}}$ is the total energy of the optimized structure after one Pt_n is encapsulated into zeolite LTA. E_{LTA} is the total energy of the optimized empty zeolite framework. $E_{\text{Pt}_n(\text{vacuo})}$ is the energy of the Pt_n in the vacuum phase. $E_{\text{inc}}(\text{Pt}_n)$ is the incorporation energy of Pt_n and $E_{\text{inc}}(\text{Pt}_1)$ is the incorporation energy of Pt atom at S1*.

Table 7 Encapsulation energy, cohesive energy, magnetization, and structural properties of encapsulated $\text{Pt}_n @ \text{LTA}$ and isolated Pt_n clusters (in parenthesis), with $1 < n < 6$.

Pt_n	E_{enc} (eV)	$E_{\text{coh/atom}}$ (eV)	Magnetization (μ_B)	$\langle r_{\text{Pt-O}} \rangle$ (Å)	$\langle r_{\text{Pt-Pt}} \rangle$ (Å)
2	-1.54	-0.67(-2.30)	2.00 (2.00)	2.271	2.325(2.318)
3	-3.11	-1.51(-2.87)	0.00(1.99)	2.493	2.475(2.483)
4	-3.27	-1.62(-3.20)	2.00(3.98)	2.214	2.526(2.503)
5	-3.46	-1.76(-3.46)	2.00(2.00)	2.236	2.575(2.460)

With global optimization calculation, it is found that the β cage encapsulated subnanometer clusters Pt_n ($n= 2-5$) are the most stable structures (**Figure 26**). For the platinum dimer, trimer and tetramer structure, the global minimum structure is a configuration that similar to the vacuum phase configurations, but the Pt-Pt bond is elongated due to the interaction with the framework (**Table 7**). When the platinum atom number increases to five, the most stable cluster structure is compact and situated within the β cage, which is quite different to the vacuum phase lowest pentameric structure. The global minimum vacuum phase Pt_5 cluster is a configuration of the capped square, while the β cage encapsulated Pt_5 cluster adopts a trigonal bipyramidal configuration. This configuration makes the Pt_5 cluster form the most bonds with the zeolite framework. The encapsulated cluster undergoes a 2D to 3D transition when the number of Pt atoms

reaches five due to the narrow space of the β cage. It should be noted that none of the global lowest structures contain Pt atoms located within six-ring or eight-ring. The trapping propensity of the ring is lost in the presence of other Pt atoms and therefore ring trap is a special effect for single Pt atoms.

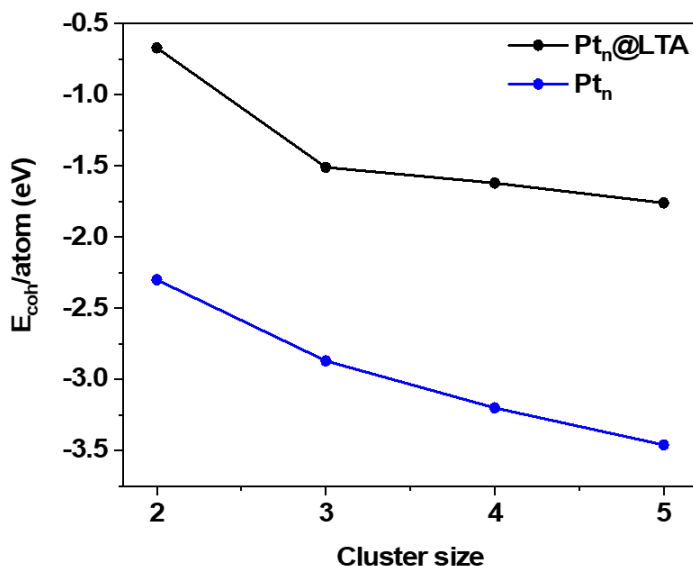


Figure 27 Cohesive energy of vacuum phase and zeolite encapsulated Pt_n .

The encapsulation energy values (**Table 7**) show that it is energetically preferable to introduce the already formed clusters into the zeolite framework. For all the cluster ranges ($1 < n < 6$), the encapsulation energy is negative which suggests that the encapsulated cluster is more stable than that in the vacuum phase. The absolute value of cohesive energy per atom increases monotonically with the cluster size in both encapsulated structure and vacuum phase structure (**Figure 27**). Therefore, there is still a thermodynamic driving force to promote cluster growth even encapsulated in the zeolite. Compared with isolated clusters, the growth tendency of encapsulated particles is much smaller, but the growth is favorable for all cluster sizes. The most stable Pt atom in the S1* site is lost and forms a large cluster, which is energetically favorable. Therefore, it is obvious that in high silica zeolite, the thermodynamic preference of subnanometer particle sintering has not been overcome but rather decreased, and the stability of single

atoms is contingent on slow kinetics of diffusion and thereby growth, which are ensured by the strong bonds to oxygen atoms in small rings, and the large escape barriers.

3.1.9 $\text{Pt}_n(\text{CO})_m@LTA$

CO was found to release the Pt atom from the framework and enhance migration. However, the role of CO on Pt cluster structure and growth is still under debate. CO has been shown by some authors to facilitate the dissociation of small Pt clusters, by acting as a substituting reducing ligand for other Pt atoms.⁸⁰ It has also been shown to induce growth of clusters.^{79, 193} These two observations may be in alignment, if growth is a kinetically hindered process, in which the splitting of small clusters allows single atoms (or smaller clusters) to migrate and locate larger clusters, as in an Ostwald ripening process. We explore the energetic characteristics of partially CO-covered Pt clusters via the binding and dissociation energies according to various decomposition channels, including release of Pt, CO, and PtCO from the cluster. By comparing the findings for vacuum phase and zeolite encapsulated $\text{Pt}_5(\text{CO})_m$ ($m = 1$ to 6) clusters, we may also isolate the confinement effect.

The global minimum structures of $\text{Pt}_5(\text{CO})_m$ in vacuum phase are shown in **Figure 28**. 2D to 3D configuration transformation happens when the presence of CO molecules number is three. When Pt/CO ratio is greater than or equal to one, Pt_5 forms a compact structure to form more Pt-Pt bonds.

Considering the dissociation energies, due to the higher relative strength of the Pt-Pt bond, the dissociation of the CO molecule from the metal cluster is the preferred channel over the full range of CO loading. At low CO loading, the trend is unchanging. CO removal is the easiest around 2.9 eV, followed by PtCO, around 3.1 eV. Removal of a Pt atom is heavily disfavoured, at around 4.4 eV. Once the CO/Pt ratio reaches 1, there is a change in trend. The cluster is overburdened with CO, and the lateral repulsion between CO molecules becomes significant. Thus, dissociation channels which reduce the CO loading

on the parent cluster become easy to achieve, and the opposite is true for Pt loss, which increases the CO/Pt ratio.

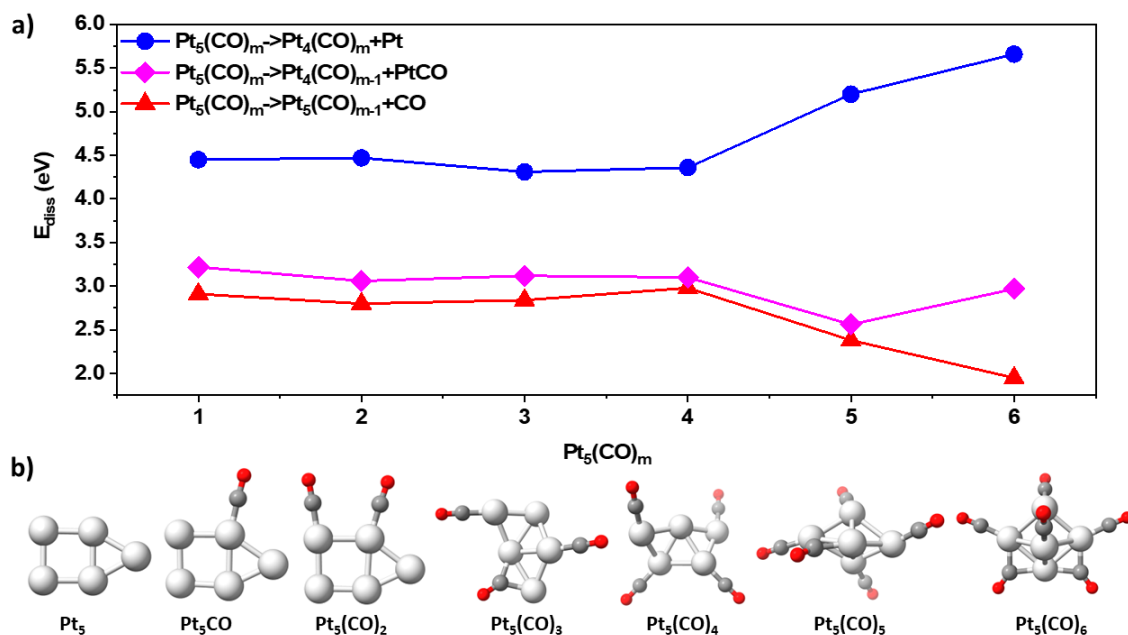


Figure 28 (a) Dissociation energy for CO, Pt, and PtCO separated from vacuum phase $\text{Pt}_5(\text{CO})_m$ cluster; (b) Global minimum structures of vacuum phase $\text{Pt}_5(\text{CO})_m$ cluster.

For the cluster bound inside the zeolite pore, the global lowest α cage structure is a capped square Pt_5 cluster above the four-ring, with two bonds to the framework (**Figure 29b**, $\text{Pt}_5@LTA$). When one CO molecule is adsorbed to the Pt_5 cluster, one of the bond between the Pt cluster and zeolite framework breaks. Once the CO/Pt ratio reaches one, the direct, covalent interaction between cluster and framework is lost, and the cluster becomes a fully CO-ligated particle, inside the pore space of the cage.

The dissociation energy trends are very different inside the pore than in the vacuum phase (**Figure 29a**). Inside the zeolite, dissociation to release PtCO is more favorable for zeolite encapsulated $\text{Pt}_5(\text{CO})_m$ except $\text{Pt}_5(\text{CO})_6$. Due to the overloading of CO molecules on $\text{Pt}_5(\text{CO})_6$, losing CO is energetically favorable for this cluster. Dissociation of single Pt atom from the $\text{Pt}_5(\text{CO})_m$ cluster is still unfavorable in all the CO molecule number ranges but is no longer the least stable dissociation product, owing to the strong binding of single

Pt atoms to the framework. Loss of CO is the least favorable reaction, as CO does not interact strongly with the zeolite. Hence, inside the framework, we expect the loss of PtCO to be a significant contributor to dissociation products. These products remain endothermic, but for highly decorated clusters, are below 2 eV, and are therefore potentially accessible transient species at elevated temperatures. PtCO, as shown in a previous section is highly mobile, and represents a good energetic compromise between binding strength to the framework and to the Pt cluster.

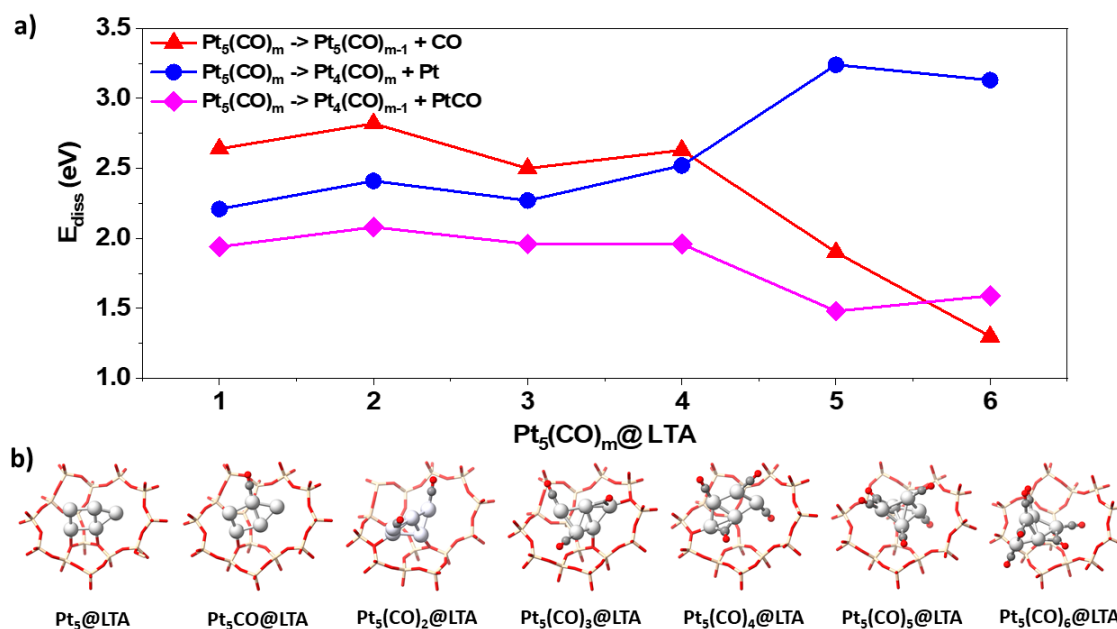


Figure 29 (a) Dissociation energy for CO, Pt, and PtCO separated from zeolite encapsulated $Pt_5(CO)_m$ cluster; (b) Minimum structures of zeolite encapsulated $Pt_5(CO)_m$ cluster.

3.1.10 The effect of functional group

In the previous part, the zeolite is a pure silicious. To study the effect of heteroatom on stabilizing single Pt atoms in the zeolite framework, one silicon atom in pure silicious LTA was replaced by one aluminum (Al) or boron (B) atom. For each Al (B) atom in the framework, there is an anion charge in the pores. Here the proton was used to compensate for the charge. Hence, our model remains one in which metal is introduced as a neutral

metal atom, rather than as a charge-compensating cation via ion-exchange, which has been studied by other authors.^{66, 194} This is a model relevant for reducing conditions, in which the interaction between metal and hydrogen, and between neutral metal and anionic sites are currently unknown.

a) Pt@Al-LTA

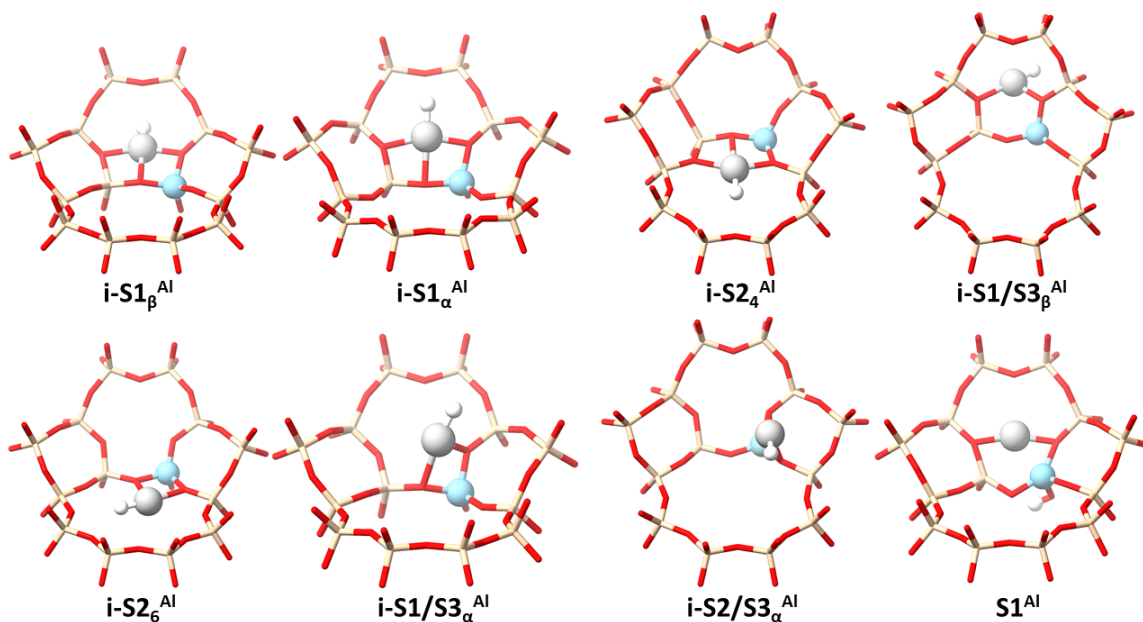


Figure 30 Local minimum structures for single Pt atom in Al-LTA. Al: sky blue; Si: yellow; red: O; read; Pt: silver; H: white.

The present of Al atom in zeolite framework turns neutral silicious LTA zeolite into a Brønsted acidic zeolite. The potential energy surface of single Pt atom encapsulated in the Al atom substituted LTA zeolite was searched by the bashing hopping method, combined with structure optimization by DFT (PBE-D3). It is found that single Pt atom in the six-ring with Al is the global minimum structure (**Figure 30**, $i\text{-S1}\beta^{\text{Al}}$). A new symbol ($i\text{-S1}\beta^{\text{Al}}$) was used to represent the global minimum structure, in which the prefix “i-” indicates that Pt atom is inserted into the O-H bond, the superscript “Al” indicates that Pt atom binding to O atoms directly bonded to Al and the subscript β indicates the slight displacement of Pt into the β cage. The proton prefers to locate on Pt atom, even

when Pt atom is located in the six-ring. In this way, Pt can share the positive charge with the proton as it forms a $\text{PtH}^{\delta+}$ entity. The incorporation energy for $\text{i-S1}_{\beta}^{\text{Al}}$ is -3.27 eV, which is -0.88 eV lower than that of single Pt atom in the six-ring of pure silicious LTA (S1^*). Hence, binding to the Al site is preferred over pinning in the siliceous six-ring, even under reducing conditions in which the Al charge is satisfied by H. There is also a similar six-ring structure that Pt is slightly displaced into the α cage ($\text{i-S1}_{\alpha}^{\text{Al}}$), rather than β cage. It has 0.17 eV higher than the global minimum structure ($\text{i-S1}_{\beta}^{\text{Al}}$). Similar to the pure siliceous structure, there are also two eight-ring structures (i-S2_4 and i-S2_6). Pt inserts into the O-H bond in both of these structures. They all have larger incorporation energy than the pure silicious similar structure. There are two factors for this additional stabilization. One is Pt insertion into the O-H bond and the other is the heteroatom. The single Pt atom binding to O atoms linked to Al but not inserted into the O-H bond is less stable than the inserted structures, while Pt bound to framework oxygen atoms which are not connected to Al, have the same incorporation energies as in the siliceous model, indicating that the stabilizing effect of nearby Al is a short-range effect.

Table 8 Incorporation energy and charge accumulation on Pt for single Pt atom in Al-LTA.

Site	E_{inc} (eV)	Charge accumulation on Pt (e)
$\text{i-S1}_{\beta}^{\text{Al}}$	-3.27	+0.39
$\text{i-S1}_{\alpha}^{\text{Al}}$	-3.10	+0.37
$\text{i-S2}_4^{\text{Al}}$	-3.04	+0.43
$\text{i-S1/S3}_{\beta}^{\text{Al}}$	-2.83	+0.43
$\text{i-S2}_6^{\text{Al}}$	-2.78	+0.48
$\text{i-S1/S3}_{\alpha}^{\text{Al}}$	-2.75	+0.46
$\text{i-S2/S3}_{\alpha}^{\text{Al}}$	-2.60	+0.46
S1^{Al}	-2.57	-0.24

Quite different to single Pt atom in silicious zeolite, instead of gaining electrons, the Bader charge calculation (**Table 8**) shows Pt atom becomes positively charged, by 0.39 electrons when Pt atom is bound to O atoms linked to Al in the global minimum structure ($\text{i-S1}_{\beta}^{\text{Al}}$). When Pt and H are separated from each other, Pt is partially negatively charged,

which is similar to Pt in the pure silicious LTA zeolite. This implies that the charge state of the Pt atom is drastically changed, depending on the location inside the zeolite crystal. In Si-rich regions, where Pt must occupy siliceous six-rings, it is partially anionic, and when it is in the more stable, but infrequent Al-rich regions, it will be cationic, to a degree controlled by the presence or absence of other charge compensating cations (such as protons).

The migration barrier of single Pt atom is also influenced by heteroatoms and protons. For migration out of the global minimum site ($i\text{-S1}_\beta^{\text{Al}}$) to the nearby α cage site ($i\text{-S1/S3}_\alpha^{\text{Al}}$). First, the single Pt atom crosses the six-ring to $i\text{-S1}_\alpha^{\text{Al}}$, then the PtH entity migrates out of the six-ring to $i\text{-S1/S3}_\alpha^{\text{Al}}$. Barriers for these two-step processes are 0.32 and 0.38 eV, respectively. The total barrier for migrating from the six-ring is 0.55 eV, which is much lower than that of the similar process in pure silicious LTA (1.32 eV). The effective barrier for single Pt atom to migrate from one zeolite cage to an adjacent one is 1.12 eV, which is 0.57 eV lower than that of a pure silicious LTA framework (1.69 eV). Overall, migration of single Pt atom among Al-adjacent sites is easier than that among pure silicious sites. Introducing Al to the zeolite framework increases its binding but decreases its migration barrier locally.

b) Pt@B-LTA

When one silicon atom was substituted with one born (B) atom and proton was used to balance the charge, instead of forming BO_4H , it forms a trigonal BO_3 structure and a silanol structure on the adjacent silicon.¹⁹⁵⁻¹⁹⁶ The six-ring containing B atom is broken before the encapsulation of single Pt atom. Therefore, when silicon is replaced with boron, it becomes a Lewis acid zeolite. The potential energy surface of single Pt atom encapsulated in the one B atom substituted LTA zeolite was searched by the global optimizing strategy similar to Pt@Al-LTA. The global minimum structure is single Pt atom trapped in the broken six-ring and inserted into the O-H bond ($i\text{-S1}^*$) (**Figure 31**). Its incorporation energy is -2.90 eV, which is between the incorporation energy value of

Pt@LTA (-2.39 eV) and Pt@Al-LTA (-3.29 eV). Other low-energy sites follow a similar sequence as Pt@LTA and Pt@Al-LTA. Structures with Pt insertion into the O-H bond are always more favorable than that binding to the silanol group without insertion. The charge state on the Pt atom is similar to that of Pt@Al-LTA.

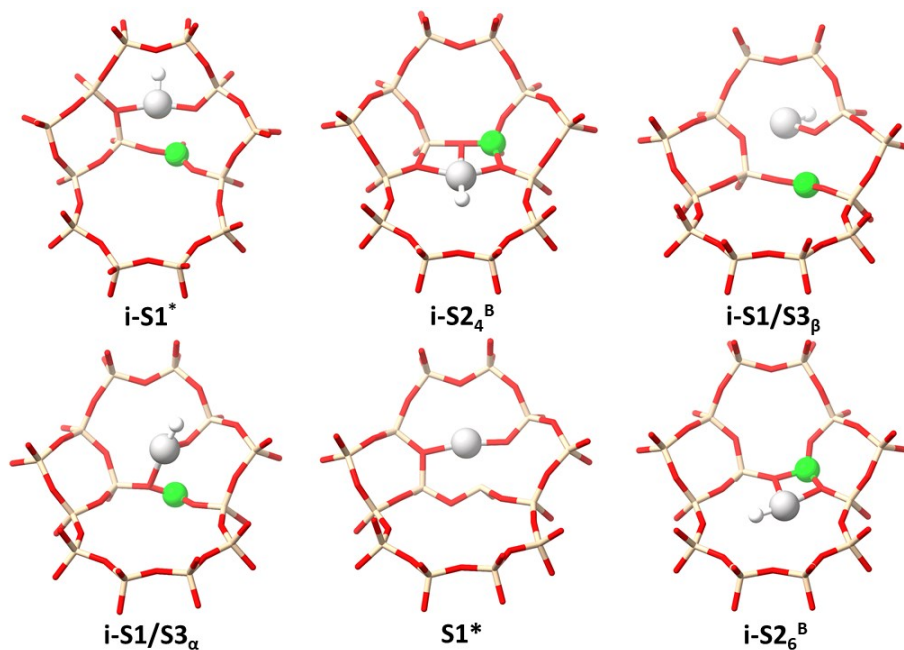


Figure 31 Local minimum structures for single Pt atom in B-LTA

Table 9 Incorporation energy and charge accumulation on Pt for single Pt atom in B-LTA

Site	E_{inc} (eV)	Charge accumulation on Pt (e^-)
i-S1*	-2.90	+0.38
i-S2 ₄ ^B	-2.63	+0.44
i-S1/S3 _β	-2.51	+0.37
i-S1/S3 _α	-2.43	+0.39
S1*	-2.42	-0.16
i-S2 ₆ ^B	-2.32	+0.46

The barrier for single Pt atom migrating from six-ring (i-S1*) to α cage or β cage are 0.57 and 0.45 eV, respectively. This barrier value is similar to that of Pt@Al-LTA (0.55 eV) and lower than that of Pt@LTA (1.32 eV). The barrier for single Pt atom migration from the i-S1* site to another i-S1* site in the adjacent α cage is 1.17 eV, which is similar to the analogous barrier in Pt@Al-LTA (1.12 eV) and lower than that of Pt@LTA (1.69 eV).

It is similar to Al that introducing B atom to zeolite framework increases its binding but decreases its migration barrier locally, but the effect is weaker than that of Al.

3.1.11 Si/Al (B) ratio

In a purely silicious six-ring containing zeolite, the six-ring is a good kinetic trap for single Pt atoms. When heteroatoms are introduced into the framework, six-ring with Al (B) is no longer a good local trap for single Pt atoms. However, the fact that it is easier for Pt to diffuse among sites which have more stable binding modes (in the Al (B)-rich zeolite) means that the global migration energetics goes through a maximum. For diffusion between Al (B)-rich cages, the effective barrier is 1.12 eV (1.17 eV). For the same process in the siliceous zeolite, it is 1.69 eV. For an intermediate system, with Al (B)-rich cages connected via siliceous cages, the effective barrier is 2.57 eV (2.20 eV) (**Figure 32**). This is due to the combination of increased energetic cost to go from low energy Al sites to higher energy Si sites, and the high barrier of moving across the siliceous cage. Hence, not only the six-ring but also Si/Al (B) ratio plays an important role in preventing single Pt atom migration and sintering. This provides new insights into the ability of zeolite to trap single Pt atoms in high silicious zeolite.

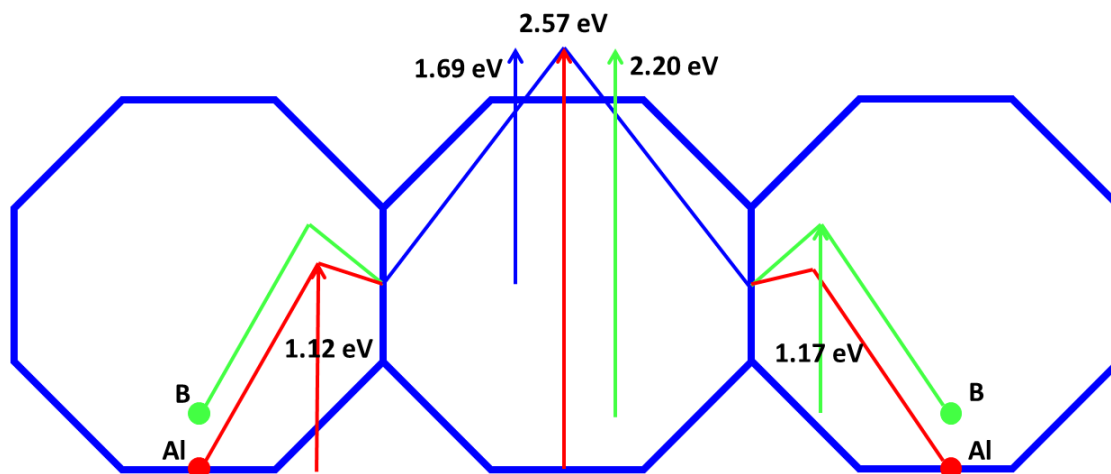


Figure 32 Diagram of the effective barrier for single Pt atom migrating from the global minimum site, crossing through a pure silicious α cage to another global minimum site.

3.1.12 Summary

In this chapter, we use theoretical method to try to explain the experimentally reported unusual stability of high silicious zeolite-encapsulated single Pt and subnanometer Pt. The six-ring, a secondary building unit, provides an ideal environment for trapping single Pt atom. For the pure silicious six-ring, one Si-O bond in the six-ring is broken to adapt the trap of single Pt atom and O-Pt-O covalent bonds are formed to stabilize the single Pt atom. The high escape barrier ensures high kinetic stability to hinder Pt sintering. By contrast, zeolite-encapsulated Au atoms shows quite different behavior. Due to the weak interaction between the Au atom and the zeolite framework, Au atoms move freely among α cages. The adsorption of the reductive adsorbates CO and H₂ not only weakens the interaction between Pt atoms and the zeolite framework but changes the energetic sequence of local minima. The reductive adsorbates reduce the stability of the ring sites with respect to non-ring sites, flatten the potential energy surface of migration, and thereby accelerate the diffusion of the PtX (X = CO, H₂), especially the H₂ molecule.

The ring trap can be destroyed not only by reductive adsorbates, but also by high loading of Pt atoms. The special trap does not work for the cluster as the Pt-Pt bond is much stronger than that of Pt-O. For all the considered cluster sizes Pt_n (1 < n < 6), clusters encapsulated in the β cage are energetically preferred. The dissociation of zeolite encapsulated Pt₅ cluster, the reverse process of cluster growth, is much more difficult, but is enhanced by the presence of CO, which provides dissociation channels via PtCO moieties, which are mobile.

The presence of a framework heteroatom is another factor that is important to the stability of zeolite encapsulated metals. When heteroatoms (Al or B) are introduced to the framework, the binding between Pt atom and zeolite framework is enhanced but the migration barrier is decreased. By altering Si/Al (B) ratio in the zeolite framework, the sintering resistance ability may be maximized. Overall, the possibility to sustain

significant populations of single atoms in zeolites may be achievable via kinetic trapping into metastable states provided the appropriate choice of metal element, and is therefore observed under low metal mass loadings and moderate temperatures. This work has contributed to the atomistic understanding of this stabilization, and probed the mechanisms of migration, diffusion and dissociation, and the various factors which affect them.

3.2 Theoretical study zeolite encapsulated sub-nanometer silver

While noble metal clusters are often employed for the enhancement of atom efficiency in traditional catalytic processes (for example oxidation and reduction chemistry of hydrocarbons),¹⁹⁷⁻¹⁹⁹ subnanometre metal particles have also been employed for their valuable optical properties, in particular silver clusters, which show molecular-like characteristics, that is, the discrete energy levels with optical transitions of absorption and emission in the ultraviolet-visible range.^{85, 200-201} The size and charge of clusters have a significant influence on the color and brightness of luminescence.^{92, 202-203} As described in the previous section, the encapsulation or trapping of these particles within a solid framework is important for stabilization of the particles against sintering, and thus maintenance of their unique size-dependent properties. Nevertheless, a lack of understanding of the local structure and environments of encapsulated clusters currently hinders the rational design and direct synthesis of small silver clusters with specific functions. In the following study, we use DFT and Post-Hartree-Fock methods to study small silver clusters, Ag₃ and Ag₄, encapsulated in a realistic model zeolite, in order to clarify the influence of cluster size, charge state and crucially, presence of ligands (water) on the stability of the clusters and their excitation properties.

In our simulations, we chose FAU zeolite framework topology as the model, because it has a higher photoluminescence quantum yield than other types of zeolite framework, and is commonly studied experimentally in combination with Ag clusters.²⁰⁴ For every periodic cell, it contains 48 T sites with 35 Si and 13 Al atoms (**Figure 33a**), respectively, and thus a Si/Al ratio of 2.7, which is appropriate for a model of the common experimentally synthesized Na-Y form of FAU. Due to the presence of Al atoms in the zeolite framework, it has 13 negative charges which are compensated by Na⁺ cations that can only occupy the well-defined extra-framework sites in FAU. There are 4, 8, 8 and 8

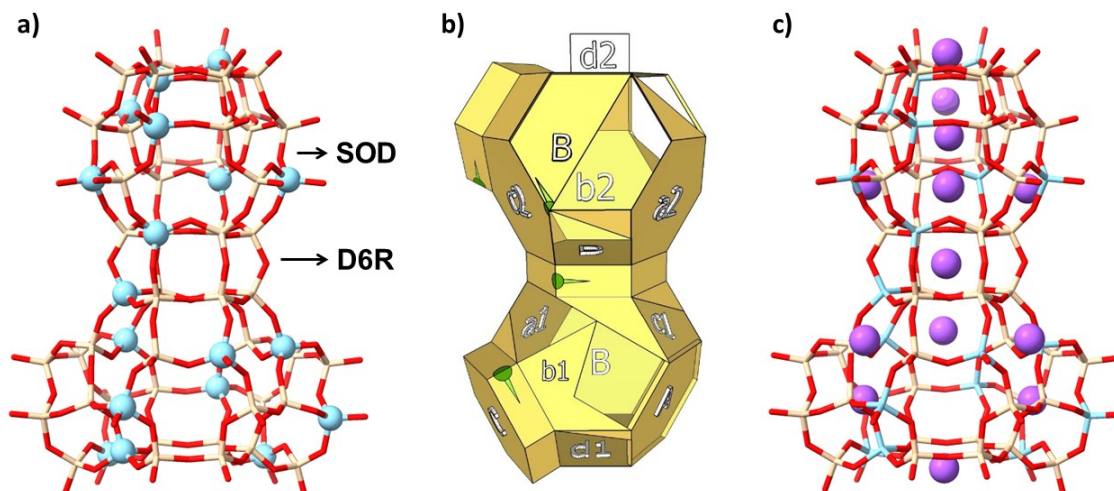
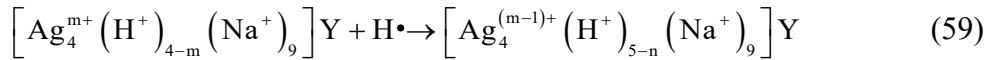
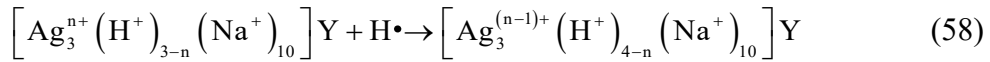


Figure 33 a) FAU zeolite framework used for this simulation. b) Graphical representation of FAU, with the definition of D6Rs (A, B, C, and D) and sites II (a₁, a₂, b₁, b₂, c₁, c₂, d₁, and d₂). The green needle on each D6R indicates the first oxygen atom for each D6R, and the tip of the needle indicates the numbering direction. c) The Na⁺ distribution with configuration of BCDA₁A₂8II. O: red; Si: white yellow; Al: sky blue; Na: pink

cation sites of type I, I', II and II', respectively.²⁰⁵ The definition of these cation sites is given in the model part of this thesis (section 2.1.1). We introduce a new notation for the cation sites developed by a colleague, Jan Hermann, which simplifies the description of cation locations in a reduced FAU unit cell. As shown in **Figure 33b**, there are four D6R units X (denoted by A, B, C, and D), and two sodalite (SOD) cages i (denoted by 1 and 2). Cation sites I and I' are denoted by X and X_i, respectively. Sites II are named according to the D6R in the opposite position to the six-ring occupied by the cation. A symbol x_i is used, where x is the lowercase of the symbol of D6R, and the subscript denotes the number of the SOD cage (either 1 or 2). For example, the configuration of 13 Na⁺ (assuming that D6R of A is empty and the A₁ and A₂ site is occupied with two Na⁺ cations, respectively.) is BCDA₁A₂8II (**Figure 33c**). 8II is a shorthand for the full occupation of II sites (a₁a₂b₁b₂c₁c₂d₁d₂). The shorthand 8II can be “divided” to denote some empty II sites. Thus, moving the cations in the configuration above, e. g., from a₁ to D₁ and from D to D₂ would result in the configuration BCA₁A₂D₁D₂8II/a₁. In the

following work, hydrogen, in the form of protons will additionally be included into the cell, as a result of chemical reduction processes described below. The naming convention of hydrogen is defined according to the name of the D6R (A, B, C, and D) and the number of O atoms (1 to 6) in the D6R to which H is bonded (**Figure 33b**).

Any of the Na^+ cations in FAU can be ion-exchanged with Ag^+ cations. The amount of silver loading can be adjusted by changing the amount of ion-exchanged Na^+ cations. Here, we consider one, three, and four Ag^+ cation exchanged structures. The ion-exchanged Ag^+ cations may undergo a self-assembly process to form silver clusters via an energy-driven activation such as heat-treatment, photon activation, and X-ray irradiation.^{37, 89, 206-209} This agglomeration may be induced by partial reduction. When a water molecule is involved in the reduction process, the water molecule is decomposed and an oxygen molecule is released in the following reactions²¹⁰⁻²¹²:



where for the purposes of this work, we focus on trimeric and tetrameric silver, and thus n and m range from 0 to 3 and 0 to 4, respectively. Y represents the negative charged framework FAU with a charge number of 13. For equation **57**, it is an endothermic reaction and the least energy required for the bond dissociation is $+336 \text{ kJ mol}^{-1}$, which is calculated from the average energy required for the dissociation of O-H bond ($+461 \text{ kJ mol}^{-1}$) and the formation of oxygen molecule (-498 kJ mol^{-1}).²¹³ Equations **58** and **59** are exothermic reactions. The total energy of the products used in equations **58** and **59** are calculated with DFT method with PBE functional and Grimme's D3 dispersion correction. In the following section, we determine the low energy configurations of Ag_3 and Ag_4 for a variety of charge states, and identify the effect of charge on the global stability and the structure of these clusters, which is summarized in **Figure 37**.

3.2.1 Stability of Na-Y

To determine the ground state energy of the baseline, pre-substitution model of FAU with 13 Na⁺, we calculated all possibilities of two Na⁺ cations occupying the I' site. As shown in **Table 10**, Na⁺ cations in the distribution of BCDA₁A₂8II have the lowest energy (**Figure 33c**). The energy difference between Na⁺ cations at BCDA₁A₂8II and ACDB₁B₂8II is small as both D6R A and B have four Al atoms. Therefore, we use the FAU configuration with 13 Na⁺ cations at BCDA₁A₂8II sites as our research model.

Table 10 Relative energy of Na⁺ cations occupying different cation sites.

13 Na ⁺	E (kJ mol ⁻¹)	n(Al)*
BCDA ₁ A ₂ 8II	0.00	4
ACDB ₁ B ₂ 8II	1.22	4
ABDC ₁ C ₂ 8II	15.66	3
ABCD ₁ D ₂ 8II	27.86	2

*n(Al) is the number of Al in the D6R occupied by Na⁺ cation at the I' site.

3.2.2 Stability of Ag⁺ exchanged Na-Y

a) Single Ag⁺ exchanged Na-Y

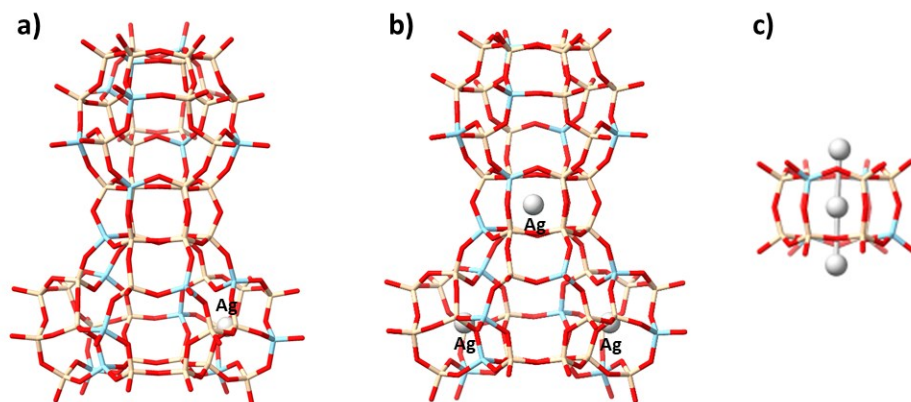


Figure 34 a) The lowest energy one Ag⁺ configuration with Ag⁺ occupying the D6R B. b) The lowest energy three isolated Ag⁺ configuration with Ag⁺ occupying the D6R B, C and D, respectively. c) The lowest energy three Ag⁺ configuration with a linear Ag₃³⁺ crossing through the D6R A. O: red; Si: white yellow; Al: sky blue; Ag: white gray.

The sodium ions are removed for ease of viewing.

Before determining the stability of the trimeric and tetrameric Ag clusters, we first consider the scenario in which one Na^+ cation is replaced with one Ag^+ cation. **Table 11** shows that the B site is the ground state location for Ag^+ (**Figure 34a**), which is due to this site containing the highest number of Al atoms locally. Indeed, the energetic trend closely follows the number of neighboring Al atoms, as the interaction between the negatively charged framework and positively charged Ag ions is primarily electrostatic in nature.

Table 11 Relative energy of $[\text{AgNa}_{12}]^{13+}\text{Y}$ structures.

Ag^+	12 Na^+	E (kJ mol ⁻¹)	n (Al)*
B(I)	CDA ₁ A ₂ 8II	0.00	4
C(I)	BDA ₁ A ₂ 8II	2.16	3
D(I)	BCA ₁ A ₂ 8II	2.53	2
A₁(I')	BCDA ₂ 8II	18.27	2
a₂(II)	BCDA ₁ A ₂ 8II/a ₂	19.50	2
b₁(II)	BCDA ₁ A ₂ 8II/b ₁	20.32	2
A₂(I')	BCDA ₁ 8II	20.99	2
a₁(II)	BCDA ₁ A ₂ 8II/a ₁	21.69	2
c₁(II)	BCDA ₁ A ₂ 8II/c ₁	24.18	2
d₁(II)	BCDA ₁ A ₂ 8II/d ₁	24.71	1
b₂(II)	BCDA ₁ A ₂ 8II/b ₂	26.64	2
c₂(II)	BCDA ₁ A ₂ 8II/c ₂	26.67	1
d₂(II)	BCDA ₁ A ₂ 8II/d ₂	27.12	1

* n(Al) is the number of Al atoms that connect to O atoms binding to Ag^+ cation

b) Triple Ag^+ cations exchanged Na-Y

b.1) Stability of $[\text{Ag}_3\text{Na}_{10}]^{13+}\text{Y}$ structures

For the encapsulation of three silver cations, several configurations are possible, which can be resolved into two main classes: isolated Ag^+ ions, and linear Ag_3^{3+} trimers. The latter are denoted in **Table 12** by square brackets (e.g. $[\text{D}_1\text{DD}_2]$). The configuration of the most stable structure has three Ag^+ in three separated D6R (B, C, and D) (**Figure 34b**).

When three Ag^+ cations at the I and I' site form a linear configuration, it is more than 100 kJ mol^{-1} more unstable than the most stable configuration. The lowest linear configuration shows in **Figure 34c** with Ag^+ occupying the A, A_1 and A_2 sites. The reason for the high instability is that cations occupying both I and I' sites have stronger electrostatic repulsion. Thus, we can rule out clustering for the 3+ charge state of Ag_3 .

Table 12 Relative energy of $[\text{Ag}_3\text{Na}_{10}]^{13+}\text{Y}$ structures

3 Ag^+	10 Na^+	r <Ag-Ag> (Å)	E (kJ mol^{-1})
BCD	-A ₁ A ₂ 8II	-	0.00
ABD	-C ₁ C ₂ 8II	-	14.26
ABC	-D ₁ D ₂ 8II	-	30.51
A ₁ A ₂ B	CD-8II	-	37.08
b ₁ Ab ₂	CDB ₁ B ₂ 8II/b ₁ b ₂	-	41.94
[A ₁ AA ₂]	BCD-8II/d ₂	3.228	100.07
[A ₁ AA ₂]	BC-8II	3.253	134.18
[A ₁ AA ₂]	CDB ₁ B ₂ 8II/b ₁ b ₂	2.996	161.29
[D ₁ DD ₂]	ABC-8II/b ₂	3.191	168.07
[C ₁ CC ₂]	BD-8II	3.189	203.08
[D ₁ DD ₂]	BCA ₁ A ₂ 8II/b ₁ b ₂	3.019	211.13

b.2) Stability of $[\text{Ag}_3\text{HNa}_{10}]^{13+}\text{Y}$ structures

Upon subsequent reduction by water via equation **57** and **58**, Ag_3 may adopt the Ag_3^{2+} state, while one negative charge on the framework is compensated by a hydrogen atom. The reference configuration is the lowest energy structure in **Table 12** with one H atom bound to the D₂ oxygen atom. We observe that in this charge state, there is an additional possible silver configuration, the trigonal cluster in the SOD cage, as well as the previously observed linear cluster across through the D₆R, and isolated atoms encapsulated in different D₆Rs. Trigonal clusters are energetically favorable by more than 60 kJ mol^{-1} to the most stable separated-ion configuration. The lowest trigonal silver cluster configuration is shown in **Figure 35a**. The linear silver configuration is much more unstable than the trigonal configurations. The lowest energy linear silver

configuration crossing through the D6R A is demonstrated in **Figure 35b**, with one Ag-Ag bond 0.704 Å longer than the longest Ag-Ag bond in the lowest energy 3+ linear silver configuration crossing the D6R A.

Table 13 Relative energy of $[\text{Ag}_3\text{HNa}_{10}]^{13+}\text{Y}$ structures

Ag_3^{2+}	10 Na^+	H^+	$r <\text{Ag-Ag}> (\text{\AA})$	$E (\text{kJ mol}^{-1})$
(a ₂ B ₂ D ₂)	ABC-8II/a ₂	D ₂	2.800	-160.20
(B ₂ C ₂ D ₂)	ABC-8II/a ₂	D ₂	2.799	-154.01
(a ₂ A ₂ B ₂)	ABC-8II/a ₂	D ₂	3.204	-128.91
(A ₂ B ₂ D ₂)	BCD-8II/d ₂	D ₂	2.843	-97.36
(a ₂ A ₂ B ₂)	BCD-8II/a ₂	A ₆	3.146	-75.17
(A ₂ B ₂ D ₂)	BCD-8II/d ₂	A ₆	2.816	-71.24
(A ₂ B ₂ D ₂)	BCD-8II/a ₂	A ₆	2.818	-66.70
[A ₁ AA ₂]	BCD-8II/d ₂	D ₂	3.585	-8.28
BCD	-A ₁ A ₂ 8II	D ₂		0.00
BCD	-A ₁ A ₂ 8II	B ₁		16.33
ABC	-D ₁ D ₂ 8II	D ₂		83.04
ABC	-D ₁ D ₂ 8II	A ₆		86.78
[A ₁ AA ₂]	BC-8II	A ₆	3.669	87.18
BCD	-A ₁ A ₂ 8II	A ₆		93.03

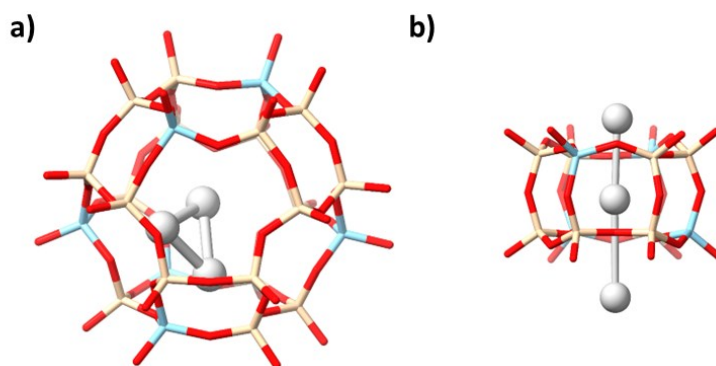


Figure 35 a) The trigonal silver cluster Ag_3^{2+} encapsulated in SOD cage with silver at the a₂, B₂ and D₂ site. b) The lowest linear silver configuration Ag_3^{2+} crossing through the D6R A. O: red; Si: white yellow; Al: sky blue; Ag: white gray. The sodium ions are removed for ease of viewing.

b.3) Stability of $[\text{Ag}_3\text{H}_2\text{Na}_{10}]^{13+}\text{Y}$ structures

For Ag^{3+} , the reference configuration is the most stable structure in **Table 12** with two hydrogen atoms adsorbed to D₂ and A₃ oxygen atoms, respectively. Trimeric clusters

remain the most stable configurations, while the relative energy of the most stable configuration in **Table 13** is more than twice times of that in **Table 12**, which implies that there is a significant overall stabilization upon reduction from Ag_3^{2+} to Ag_3^+ . The average Ag-Ag bond length of the most stable configuration is about 0.1 Å shorter than that in **Table 13**, as are the average bond lengths for the linear trimers, which is in accord with the enhanced stability. The most stable trigonal silver configuration and the linear silver configuration are shown in **Figure 36a** and **36b**, respectively.

Table 14 Relative energy of $[\text{Ag}_3\text{H}_2\text{Na}_{10}]^{13+}\text{Y}$ structures

Ag_3^+	10 Na^+	2 H^+	$r <\text{Ag-Ag}> (\text{\AA})$	$E (\text{kJ mol}^{-1})$
($\text{A}_2\text{B}_2\text{C}_2$)	BCD-8II/a ₂	A_3D_2	2.708	-365.52
($\text{A}_2\text{B}_2\text{C}_2$)	BCD-8II/a ₂	A_3A_6	2.700	-331.10
($\text{A}_2\text{B}_2\text{C}_2$)	BCD-8II/a ₂	A_6D_2	2.698	-330.98
($\text{a}_2\text{A}_2\text{B}_2$)	BCD-8II/a ₂	A_3A_6	2.674	-318.73
BCD	- $\text{A}_1\text{A}_28\text{II}$	A_3D_2		0.00
[A_1AA_2]	BCD-8II/d ₂	A_3A_6	2.800	9.65

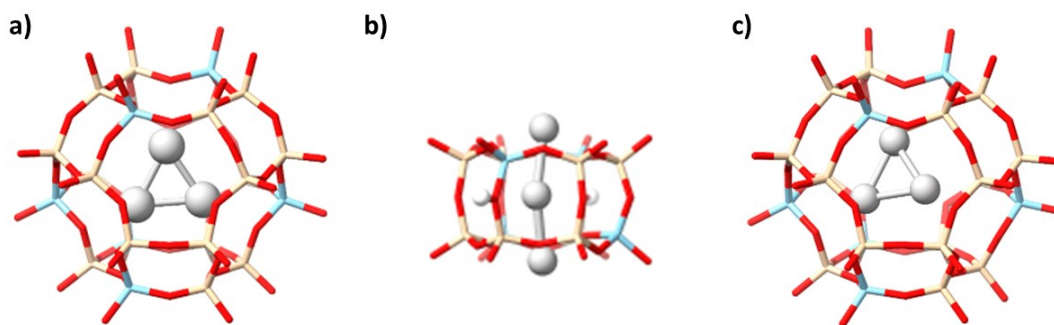


Figure 36 a) The trigonal silver cluster Ag_3^+ encapsulated in SOD cage with silver at the A_2 , B_2 and C_2 site. b) The linear silver configuration Ag_3^+ crossing through the D6R A. c) The fully reduced trigonal silver cluster encapsulated in SOD cage with silver at the A_2 , B_2 and C_2 site. O: red; Si: white yellow; Al: sky blue; Ag: white gray. The sodium ions are removed for ease of viewing.

b.4) Stability of $[\text{Ag}_3\text{H}_3\text{Na}_{10}]^{13+}\text{Y}$ structures

Finally, we consider the fully reduced configuration, Ag_3 . The most stable configuration is shown in **Figure 36c**. This cluster continues the trend of preference towards trimeric

clusters in reduced states, but the overall stability is reduced with respect to Ag_3^+ , implying that further reduction from Ag_3^{3+} is endothermic. The energetic trends are highlighted in **Figure 37a**.

Table 15 Relative energy of $[\text{Ag}_3\text{H}_3\text{Na}_{10}]^{13+}\text{Y}$ structures

Ag_3	10 Na^+	3 H^+	$r <\text{Ag-Ag}> (\text{\AA})$	$E (\text{kJ mol}^{-1})$
$(\text{A}_2\text{B}_2\text{C}_2)$	BCD-8II/a ₂	$\text{D}_2\text{A}_3\text{C}_6$	2.699	-343.39
$(\text{A}_2\text{B}_2\text{D}_2)$	BCD-8II/a ₂	$\text{D}_2\text{A}_3\text{C}_6$	2.708	-337.18
BCD	-A ₁ A ₂ 8II	$\text{D}_2\text{A}_3\text{C}_6$		0.00

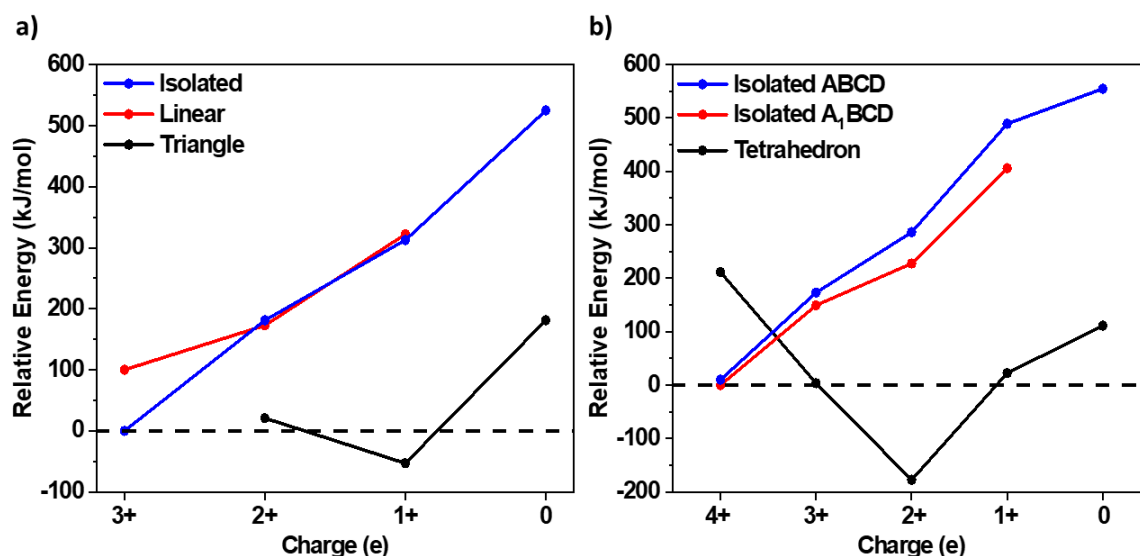


Figure 37 a) Relative energy of three silver encapsulated in FAU with different charge states. The isolated silver cations encapsulated in three different D6Rs (B, C, and D) with three positive charges were set as the reference configuration. b) Relative energy of four silver encapsulated in FAU with different charge states. The isolated silver cations encapsulated in three different D6Rs (B, C, and D) and the I' cation site A₁ with four positive charges were set as the reference configuration.

For the non-reduced configuration, the isolated configuration has lower energy than the linear configuration. So, there is no driving force for separated silver cations to form a linear Ag_3^{3+} cluster. The doubly reduced trigonal silver cluster is the most stable configuration. The singly reduced trigonal silver cluster is 73.8 kJ mol^{-1} higher than that of the doubly reduced silver cluster. The fully reduced trigonal silver cluster and partially

reduced isolated and linear configuration have more than $172.7 \text{ kJ mol}^{-1}$ higher energy than the reference non-reduced configuration and $225.7 \text{ kJ mol}^{-1}$ higher energy than the doubly reduced silver cluster. So, the process of silver cations reduction is as follows: 1) Before reduction, the isolated silver cations are the most stable configuration, 2) The energetically favorable structure in the singly reduced reaction is a trigonal silver cluster encapsulated in the SOD, which is slightly endothermic, 3) The process of forming a trigonal silver cluster with one positive charge is an exothermic reaction, and 4) The cluster prefers the Ag_3^+ state overall.

c) Quadruple Ag^+ cation-exchanged Na-FAU

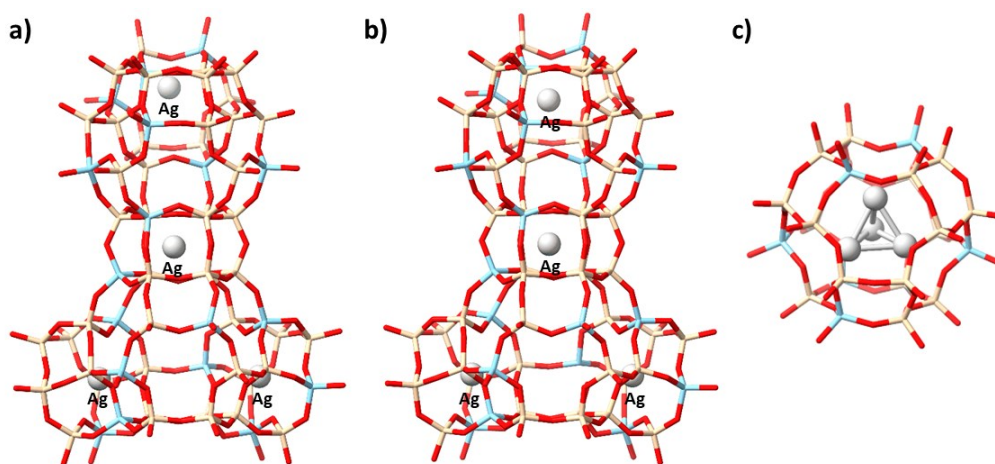


Figure 38 a) Isolated four Ag^+ configurations with Ag^+ at the A1, B, C and D site. b) Isolated four Ag^+ configurations with Ag^+ at the A, B, C and D site. c) The tetrahedral silver cluster Ag_4^{2+} encapsulated in SOD cage two. O: red; Si: white yellow; Al: sky blue; Ag: white gray. The sodium ions are removed for ease of viewing.

Experimental studies have suggested that tetrameric silver clusters may be the primary source of optical activity inside Na-zeolites such as Na-Y and Na-A. Hence, we additionally consider the structures and energetic stability of encapsulated Ag in a variety of oxidation states. We compare isolated (4 Ag^+) configurations with each other (**Table 16**), and with tetrahedral structures of all oxidation states. For isolated, non-reduced cations, the most stable arrangement is one in which all three Ag^+ ions are bound to three

different D6Rs (B, C, and D) and the fourth Ag^+ occupies the I' (A_1) site (**Figure 38a**). However, the energy difference between the lowest isolated configuration and other configurations is within 11 kJ mol^{-1} , which is less than that of isolated three Ag^+ configurations, suggesting a closer competition between isomers. The A_1BCD configuration is found not to be stable for all oxidation states, and no local minimum was observed for the neutral state. Hence, we also consider an alternative configuration, ABCD (**Figure 38b**), which does give a local minimum for the fully reduced state.

Table 16 Relative energy of $[\text{Ag}_4\text{Na}_9]^{13+}\text{Y}$ structures

4 Ag^+	9 Na^+	E (kJ mol^{-1})
A_1BCD	$-\text{A}_28\text{II}$	0.00
A_2BCD	$-\text{A}_18\text{II}$	3.03
b_1BCD	$-\text{A}_1\text{A}_28\text{II}/\text{b}_1$	3.46
a_2BCD	$-\text{A}_1\text{A}_28\text{II}/\text{a}_2$	3.94
a_1BCD	$-\text{A}_1\text{A}_28\text{II}/\text{a}_1$	4.96
c_1BCD	$-\text{A}_1\text{A}_28\text{II}/\text{c}_1$	7.38
d_1BCD	$-\text{A}_1\text{A}_28\text{II}/\text{d}_1$	8.31
b_2BCD	$-\text{A}_1\text{A}_28\text{II}/\text{b}_2$	9.41
c_2BCD	$-\text{A}_1\text{A}_28\text{II}/\text{c}_2$	9.55
ABCD	$-\text{A}_28\text{II}$	9.76
d_2BCD	$-\text{A}_1\text{A}_28\text{II}/\text{d}_2$	10.57

The relative energy of three types of configurations (two types of isolated configurations and a tetrahedral silver cluster encapsulated in SOD with different charge states) is shown in **Figure 37b**. For all oxidation states, isolated Ag^+ at ABCD sites is higher in energy than that of A_1BCD sites, and no significant structural changes occur upon reduction. For the non-reduced configurations, the isolated configuration is more energetically favorable than the tetrahedral structure, which is more than 200 kJ mol^{-1} higher than the isolated configurations. The tetrahedral structure is unable to exist in the non-reduced condition. With the decrease of oxidation state, the tetrahedral structure is more energetically favorable than that of the isolated configurations. The lowest energy configuration is a tetrahedral structure encapsulated in the SOD (**Figure 38c**) with two positive charges and

the formation of this tetrahedral structure is an exothermic reaction. For the tetrahedral structure, all reactions to leave the 2+ state are endothermic. Furthermore, while the energies of reduction of encapsulated Ag_3 and Ag_4 are governed by different equations (equation 58 and 59), and thus do not take into account the relative stabilities of the 3 Ag or 4 Ag initial states, it is of note that the formation of a tetrahedral Ag_4^{2+} structure releases more than three times more energy than that of forming the Ag_3^+ trigonal cluster. Hence, we may conclude that this is a strongly favorable reaction, and under the conditions in which sufficient Ag is present locally to form Ag_4^{2+} , it is a reasonable species to anticipate experimentally.

3.2.3 Electronic structure

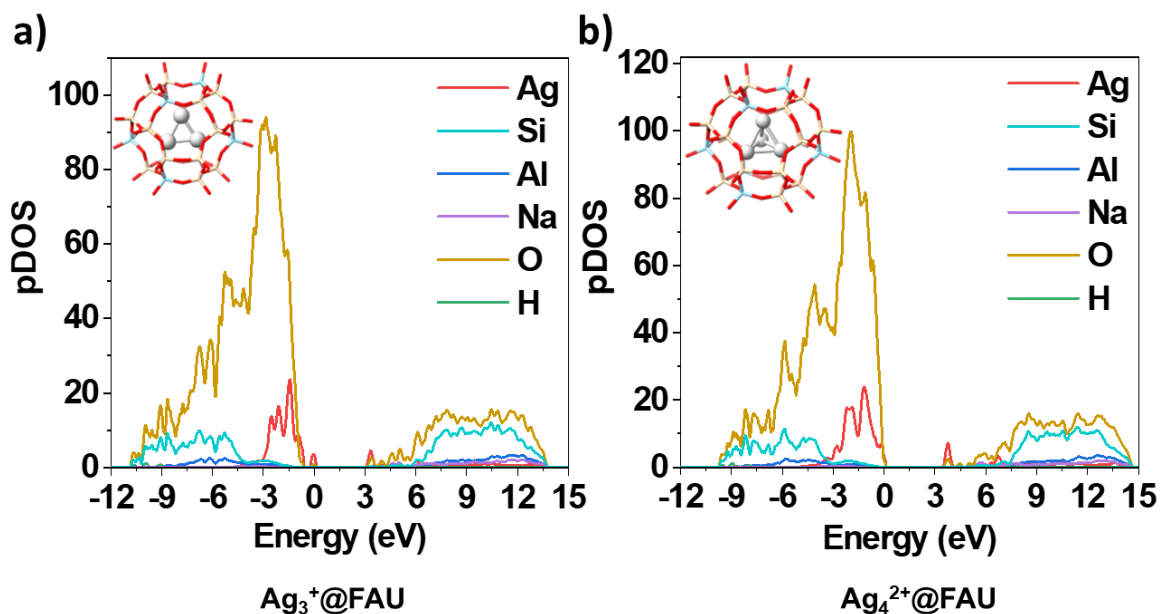


Figure 39 Projected density of state of the lowest energy configuration calculated with PBE functional: a) $\text{Ag}_3^+@FAU$ and b) $\text{Ag}_4^{2+}@FAU$

The particular stability of the Ag_3^+ and Ag_4^{2+} clusters can be explained in terms of superatom electronic shell closing effects. For simplicity, the lowest energy configuration of the trigonal silver cluster with one positive charge and tetrahedral silver cluster with two positive charges encapsulated into FAU is named as $\text{Ag}_3^+@FAU$ and $\text{Ag}_4^{2+}@FAU$,

respectively. We calculated the projected density of states of these $\text{Ag}_3^+\text{@FAU}$ and $\text{Ag}_4^{2+}\text{@FAU}$ near the Fermi energy, and the projections onto atomic types are shown in **Figure 39**. The bandgaps for both $\text{Ag}_3^+\text{@FAU}$ and $\text{Ag}_4^{2+}\text{@FAU}$ are wide, at 3.32 and 3.73 eV, respectively, and consist primarily of contributions from the Ag atoms at the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), with some contribution from the zeolite framework oxygens to which the Ag atoms are bound. These large bandgaps are indicative of a stable electronic configuration, which can be further investigated from the perspective of the HOMO and LUMO. The valence region of the gas phase Ag_3^+ cluster (**Figure 40a**), which has D_{3h} symmetry, consists of a singly degenerate a-type orbital and a doubly degenerate pair of e-type orbitals, which are filled with two silver 5s electrons, thus filling the a state, and leaving the e-pair empty. The band gap is thus the energy spacing between a and e states on the silver cluster. For the Ag_4^{2+} cluster (**Figure 40b**), with T_d symmetry, the valence region is an a state and a triply degenerate t state, which again is empty. This filling of the a state is the reason for the high stability of those particular charge states for Ag_3^+ and Ag_4^{2+} , respectively. We note that the clusters are only very mildly perturbed away from the gas phase structures upon encapsulation into FAU, and thus, the electronic structures are only weakly affected. Hence, the retention of high geometric symmetry leads to the same oxidation state preference. The HOMO and LUMO orbitals for the entire system appear as S-type and P-type superatomic orbitals (**Figure 40c** and **40d**), respectively, due to the dominance of the silver superatom electronic states derived from a and e (t) in Ag_3 (Ag_4), for the combined cluster@zeolite system. The lowest excitation is thus from the S-type orbital located primarily on Ag to the P-type orbital located primarily on Ag.

3.2.4 Water ligand effect

Several researchers have recently proposed that few water molecules coexist with the silver cluster inside the SOD cage of FAU/LTA.^{34, 91, 214-217} The emission color was observed to change with the hydration and dehydration of the silver exchanged zeolite,

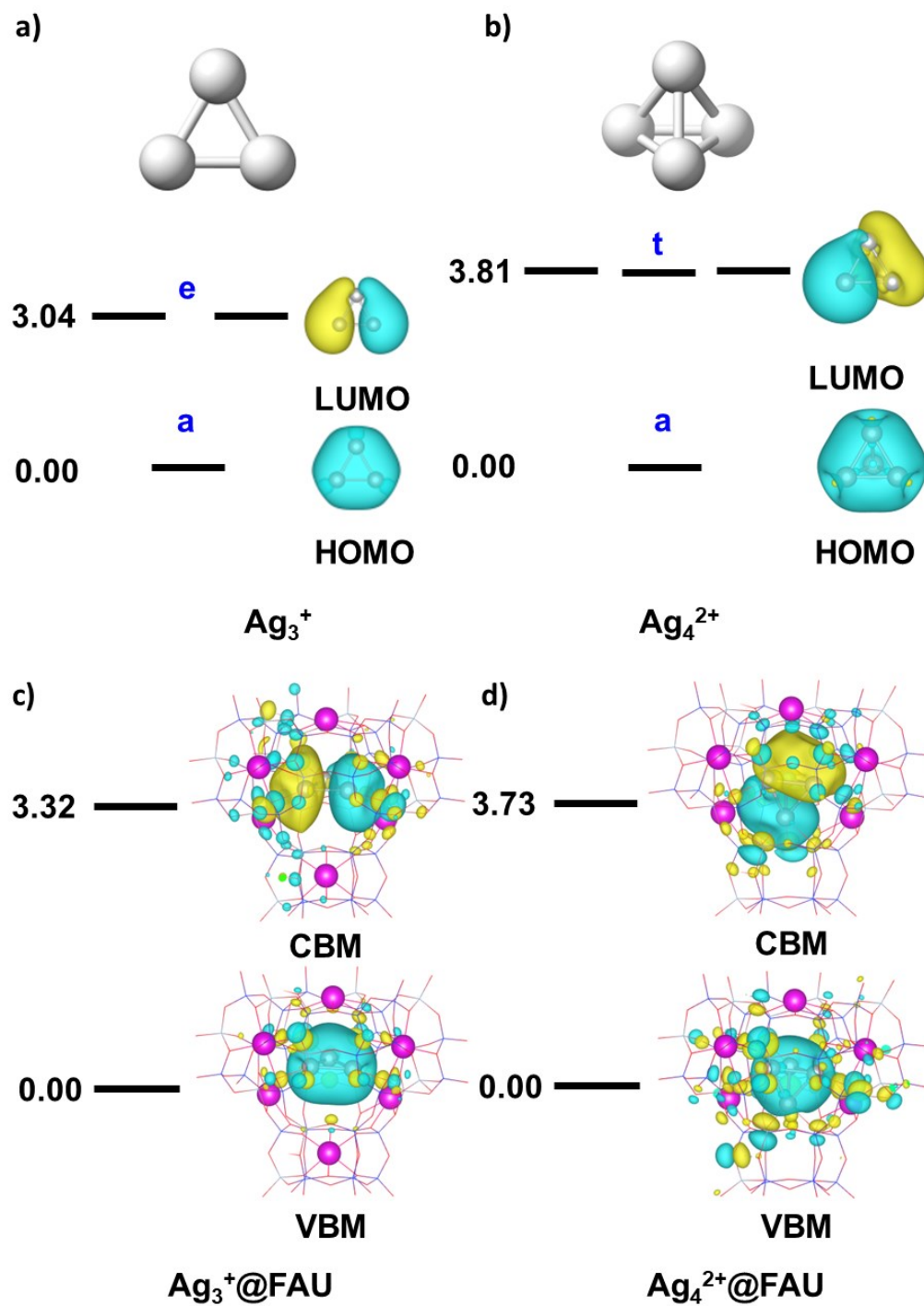


Figure 40 Structure and electronic orbital of vacuum phase silver cluster Ag_3^+ (a) and Ag_4^{2+} (b). The vacuum phase silver cluster was optimized with second-order Møller–Plesset perturbation theory method (MP2). Orbital of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) for $\text{Ag}_3^+@FAU$ (c) and $\text{Ag}_4^{2+}@FAU$ (d). O: red; Si: blue; Al: sky blue; Na: pink; Ag: white gray.

and even the luminescence was quenched during the dehydration process. Hence, we further consider the case of silver clusters with various loadings of water molecules. The incorporation energy is calculated with equation 60:

$$E_{\text{inc}} \{[\text{Ag}_i(\text{H}_2\text{O})_j]^{k+} @ \text{FAU}\} = E_{[\text{Ag}_i(\text{H}_2\text{O})_j]^{k+} @ \text{FAU}} - E_{\text{Ag}_i^{k+} @ \text{FAU}} - j \times E_{\text{H}_2\text{O}(\text{vacuo})} \quad (60)$$

where i is the number of Ag atoms, j is the number of water molecules in zeolite FAU and k is the number of charge state of the cluster. $E_{[\text{Ag}_i(\text{H}_2\text{O})_j]^{k+} @ \text{FAU}}$ is the total energy of zeolite FAU encapsulated subnanometer Ag with j water molecules at positive charge state k . $E_{[\text{Ag}_i^{k+} @ \text{FAU}]}$ is the total energy of zeolite FAU encapsulated subnanometer Ag without water molecules. $E_{\text{H}_2\text{O}(\text{vacuo})}$ is the energy of single water molecule in vacuum phase. All the energy values are calculated with GGA-PBE functional with D3 dispersion correction.

Figure 41 shows the incorporation energy of $\text{Ag}_3^+ @ \text{FAU}$ with one to four water molecules. While the total incorporation energies are always negative, and thus favorable with respect to the separated $\text{Ag}_3^+ @ \text{FAU}$ and vacuum phase H_2O molecules, we observe that for all cases, incorporation of water molecules in another SOD is always more energetically favorable than that of silver clusters and water molecules in the same SOD. Water forms a hydrogen bonded cluster which interact with the framework via hydrogen bond. Due to the high stiffness of the SOD cage, water molecules were not found to increase the optimal SOD volume to a sufficient degree to allow for their co-incorporation with silver clusters to become favorable. **Figure 42** shows the incorporation energy of $\text{Ag}_4^+ @ \text{FAU}$ with one to four water molecules. Again, water molecules and silver clusters in separated SOD cages have lower energy than that in the same SOD cage. Due to the increased crowding of the pore space for the tetramer, the energy gap between the best configurations with water in the same cage and water in a separate cage is larger for Ag_4 than Ag_3 .

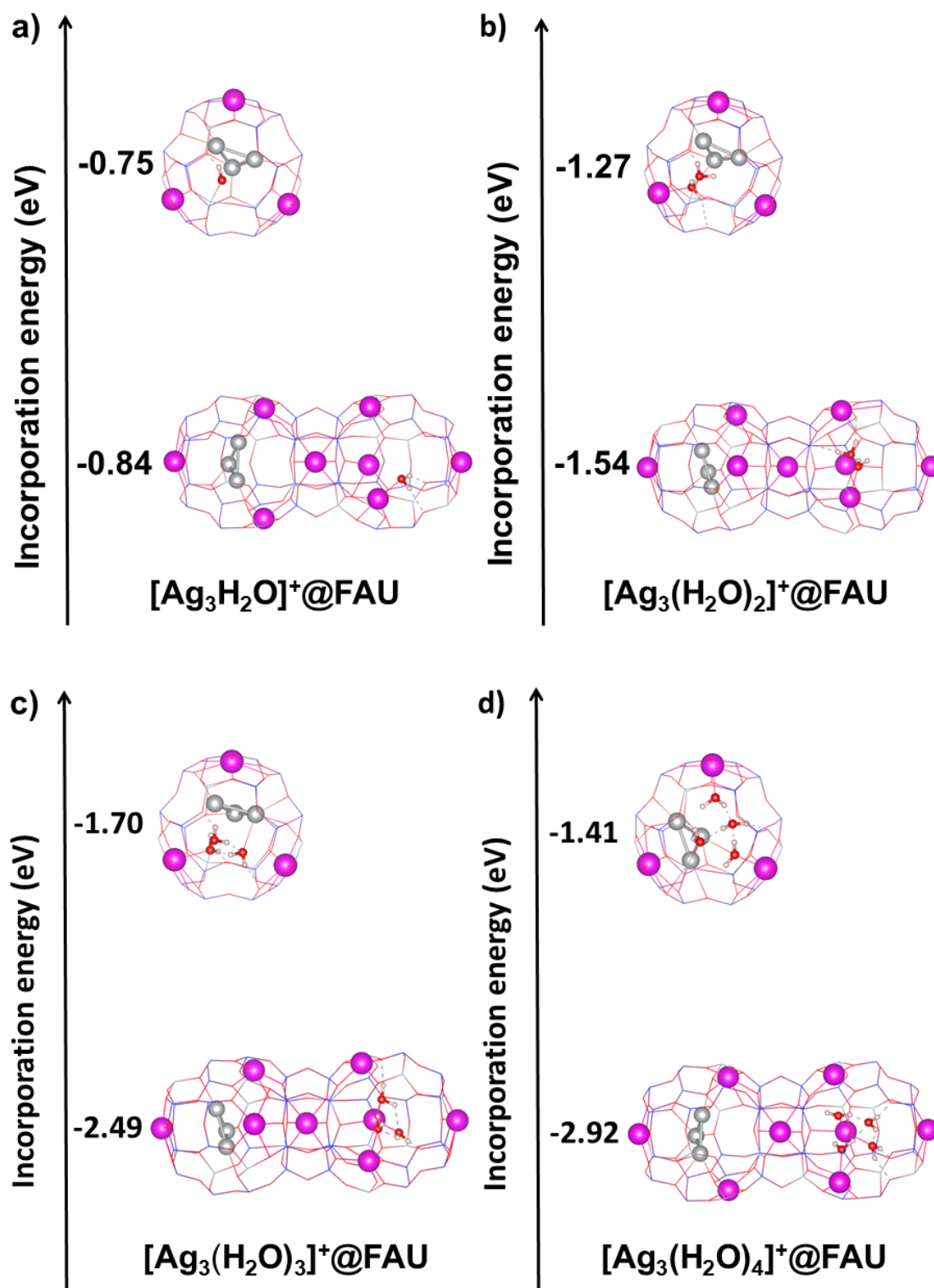


Figure 41 Incorporation energy of three silver atom clusters with one to four water molecules in the same and different SOD. Silver color ball: Ag; Pink color ball: Na.

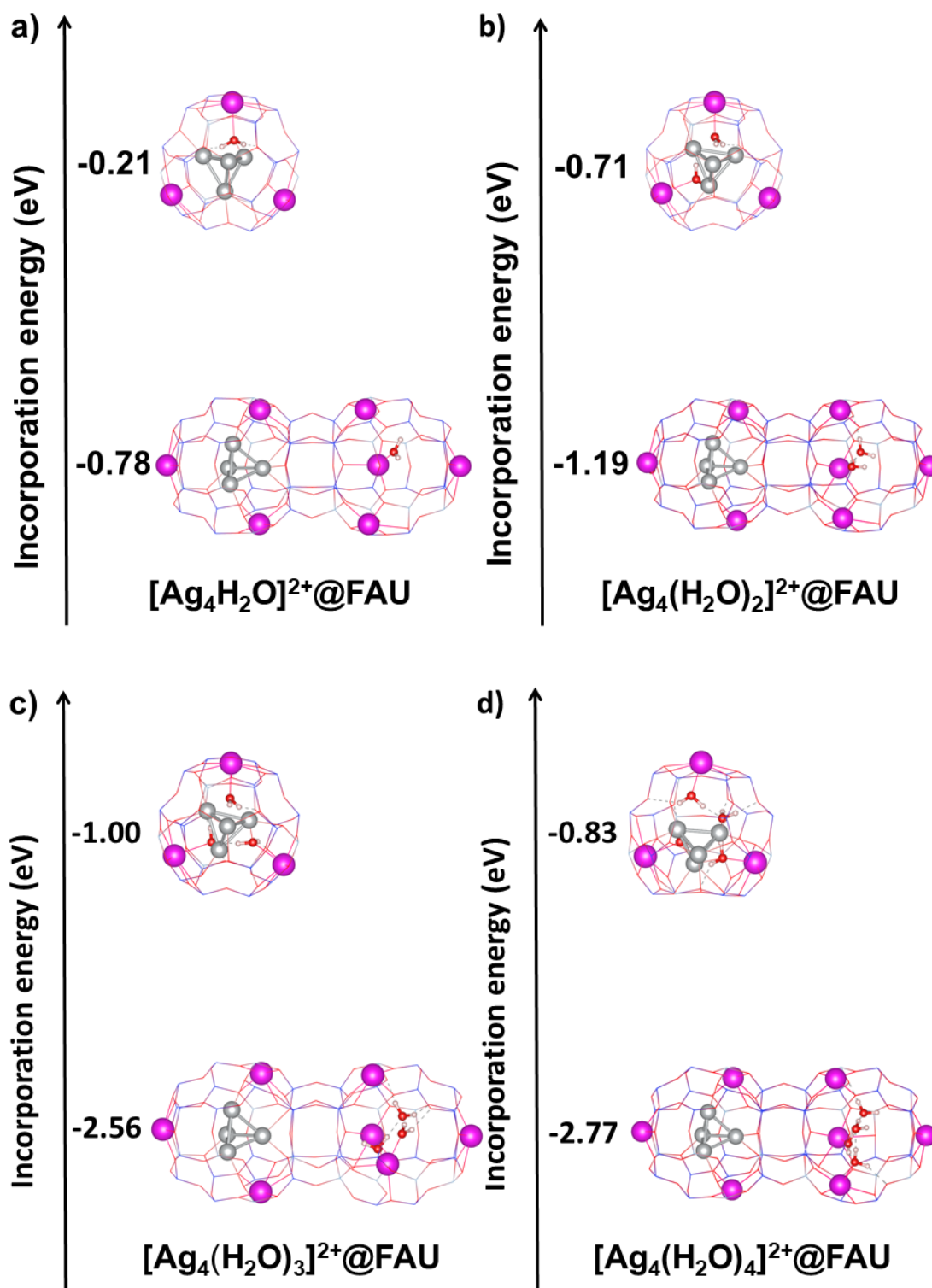


Figure 42 Incorporation energy of four silver atom clusters with one to four water molecules in the same and different SOD. Silver color ball: Ag; Pink color ball: Na.

For the case of one and two water molecules per cluster, silver clusters and water molecules may be possible to coexist in the same SOD cage to a small fractional occupation. It is, however, very unlikely that a silver cluster coexists with three or four water molecules in one SOD. We therefore must conclude that the role of water on the optical properties of encapsulated Ag clusters is not achieved via direct bonding to Ag inside the SOD cage, as predicted.

3.2.5 Excitation energies

In section 3.4.3, we have demonstrated that the orbitals of vacuum phase and encapsulated subnanometer Ag are similar. The lowest excitation both comes from electrons of S-type orbital to P-type orbital. Hence, we may probe the excitation energies according to this transition by a variety of methods, and determine an accurate excitation energy for the cluster, as a function of encapsulating environment and water loading. In this manner, we can isolate the effect of ligand binding upon the cluster on its optical properties.

Firstly, we determine the appropriate estimation method for the primary excitation. We select three methods to estimate the S→P transition: First, the HOMO-LUMO gap (H-L), which is determined via ground state DFT calculation. The second method is the singlet-triplet energy gap (S-T), which is determined again via DFT, by comparison of the vertical excitation of one electron from the closed shell singlet ground state to the first excited state. The third method is the most sophisticated, via calculation of the excitation energy via TDDFT or EOM-CCSD.

Next, we determine the value of the correction necessary to reach coupled cluster level from lower level methods, which will allow us to transfer from the smaller system of the vacuum phase cluster, to larger, more complex systems of zeolite-encapsulated clusters. In addition, we compare levels of DFT theory for reproducing the coupled cluster excitation energies. In **Table 17**, the excitation energies of the vacuum phase clusters are

shown for four clusters, the hydrated and unhydrated trimer and tetramer with all three excitation energy metrics, and two DFT methods, the GGA exchanged correlation functional PBE, and the related hybrid functional HSE03.

As expected, the excitation energy calculated with hybrid functional HSE03 is closest to the couple cluster level excitation energy, with an average energy difference of 0.12 eV across the series. The excitation energy difference increases to 0.65 eV when the excitation energy is calculated with PBE functional, but remains consistent.

Table 17 The Homo-LUMO gap (H-L), singlet-triplet energy gap (S-T) and excitation energy (TDDFT or EOMCCSD) of the vacuum phase cluster calculated with Gaussian code.

Cluster	PBE			HSE03			EOMCCSD (eV)
	H-L (eV)	S-T (eV)	TDDFT (eV)	H-L (eV)	S-T (eV)	TDDFT (eV)	
Ag_3^+	3.12	2.99	3.72	3.93	3.01	4.07	4.09
$[\text{Ag}_3(\text{H}_2\text{O})_3]^+$	3.74	3.65	4.12	4.50	3.65	4.49	4.59
Ag_4^{2+}	3.91	3.76	4.27	4.82	3.88	4.79	4.98
$[\text{Ag}_4(\text{H}_2\text{O})_4]^{2+}$	4.36	4.40	4.38	5.42	4.46	5.23	5.42

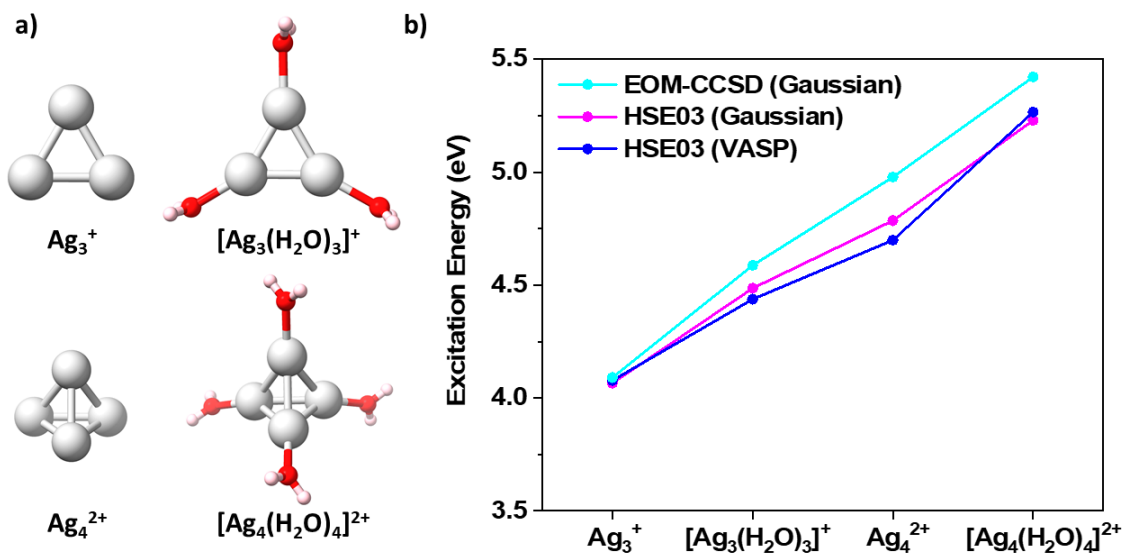


Figure 43 a) Configuration of the positively charged silver cluster with and without water ligand. The vacuum phase silver cluster was optimized with second-order Møller–Plesset perturbation theory method (MP2). b) Excitation energy calculated with TDDFT or EOMCCSD method.

In order to transfer to the periodic zeolite model, we recalculated these excitations in the periodic code VASP. The H-L, S-T and excitation energy (TDDFT) of the silver clusters were calculated by putting silver clusters in a cubic box with parameter of 20 Å. The results are shown in **Table 18**. The average excitation energy difference between the hybrid functional (HSE03) values calculated with Gaussian code and VASP code is 0.03 eV, which agrees very well between these two codes. Hence, there is good transferability between the codes, and we may use the coupled cluster values from one code to correct the periodic DFT values from another.

Figure 43b demonstrates the excitation energy calculated with Gaussian and VASP code. The average excitation energy difference between the hybrid functional calculated with VASP code and the EOMCCSD value is 0.15 eV. By adding a correction (0.15 eV) to the excitation energy calculated with VASP code, we can achieve a pseudo coupled cluster level excitation energy that is valid for the positively charged clusters. The average excitation energy difference between PBE functional and EOMCCSD method increases to 0.79 eV. Hence, the PBE functional can also be used to calculate the excitation energy by adding the above correction to obtain the pseudo couple cluster level excitation energy. Different DFT methods give different corrections, but both tested methods provide a consistent correction.

Table 18 The Homo-LUMO gap (H-L), singlet-triplet energy gap (S-T) and excitation energy (TDDFT or EOMCCSD) of the vacuum phase cluster calculated with the VASP code

Cluster	PBE			HSE03		
	H-L (eV)	S-T (eV)	TDDFT (eV)	H-L (eV)	S-T (eV)	TDDFT (eV)
Ag_3^+	3.04	2.89	3.50	3.56	2.89	4.08
$[\text{Ag}_3(\text{H}_2\text{O})_3]^+$	3.61	3.41	3.92	4.09	3.51	4.44
Ag_4^{2+}	3.81	3.66	4.06	4.43	3.74	4.70
$[\text{Ag}_4(\text{H}_2\text{O})_4]^{2+}$	4.42	4.29	4.44	5.02	4.31	5.27

The excitation energy calculation with TDDFT method is fairly resource-consuming, especially for a large system using a hybrid functional. However, the cheaper, ground

state metrics for excitation energy also provide a consistent correction to CCSD. H-L and S-T calculated with PBE functional give a correction of 1.05 and 1.21 eV, respectively. The average difference reduces to 0.49 and 1.16 eV, respectively, if the H-L and S-T are calculated with the hybrid functional. To finally confirm that the correction scheme is general and applies across functionals, metrics and clusters, we applied that appropriate corrections to each, and the values are reported in **Table 19**. For all the values in the **Table 19**, the largest difference comes from $(\text{Ag}_4\text{H}_2\text{O})^{2+}@\text{FAU}$ with a difference of 0.27 eV between different catalogues. As shown in the benchmark paper of TDDFT method, this value is within the error of excitation energy calculation with TDDFT method.²¹⁸⁻²¹⁹ Hence, the correction method is acceptable for estimating the excitation energy of subnanometer Ag encapsulated zeolite in the further work. This implies that a simple calculation of the H-L gap with a GGA method is sufficient to reproduce CCSD excitation energies for this system, which dramatically reduces the computational expense in exploring the optical properties of confined silver clusters.

Table 19 The corrected values to the couple cluster level calculated with VASP code

Structure	PBE			HSE03			Average (eV)
	H-L (eV)	S-T (eV)	TDDFT (eV)	H-L (eV)	S-T (eV)	TDDFT (eV)	
$\text{Ag}_3^+@\text{FAU}$	4.37	4.39	4.28	4.35	4.39	4.15	4.32
$(\text{Ag}_3\text{H}_2\text{O})^+@\text{FAU}$	4.31	4.32	4.42	4.31	4.33	4.38	4.35
$[\text{Ag}_3(\text{H}_2\text{O})_2]^+@\text{FAU}$	3.99	4.03	4.07	4.01	4.05	4.08	4.04
$\text{Ag}_4^{2+}@\text{FAU}$	4.78	4.79	4.67	4.92	4.92	4.86	4.82
$(\text{Ag}_4\text{H}_2\text{O})^{2+}@\text{FAU}$	4.13	4.19	4.11	4.32	4.38	4.29	4.24
$[\text{Ag}_4(\text{H}_2\text{O})_2]^{2+}@\text{FAU}$	4.17	4.25	4.16	4.32	4.41	4.27	4.26

The addition of water to the cluster inside the zeolite is found to generally reduce the excitation energies, while binding of water to the vacuum cluster increases the excitation energies.^{206, 217} This can be rationalized by consideration of the different manner in which water interacts with the cluster in the two environments. In the vacuum, water binds strongly to the metal atoms, via formation of Ag-O_w bonds. In the zeolite, the cluster is

repulsive to water, and water interacts with silver primarily by Ag-H close contact. Water prefers to bond to framework oxygen atoms, extra-framework Na cations, or other water molecules in place of Ag. As shown in **Figures 41** and **42**, the confinement effect of the sodalite cage makes such interactions energetically unfavourable. The exception is in the case of addition of the first water molecule to Ag_3 . In this situation there is sufficient space for the water molecule to interact favorably with the cluster, and thus the excitation increases, in the same manner as the free clusters.

To explain the effect of water molecules on the electronic structure of subnanometer Ag, the lowest energy tetrahedral Ag_4 structure with and without H_2O molecules were chosen as representative systems. Compared with the projected density of states of the configuration without water molecules (**Figure 44a**), the electronic structure of tetrahedral Ag_4 with two water molecules in the same SOD cage has one more peak near the Fermi level (**Figure 44b**), which leads to a narrowing of the band gap (3.12 eV) than that of encapsulated bare tetrahedral Ag_4 (3.73 eV).

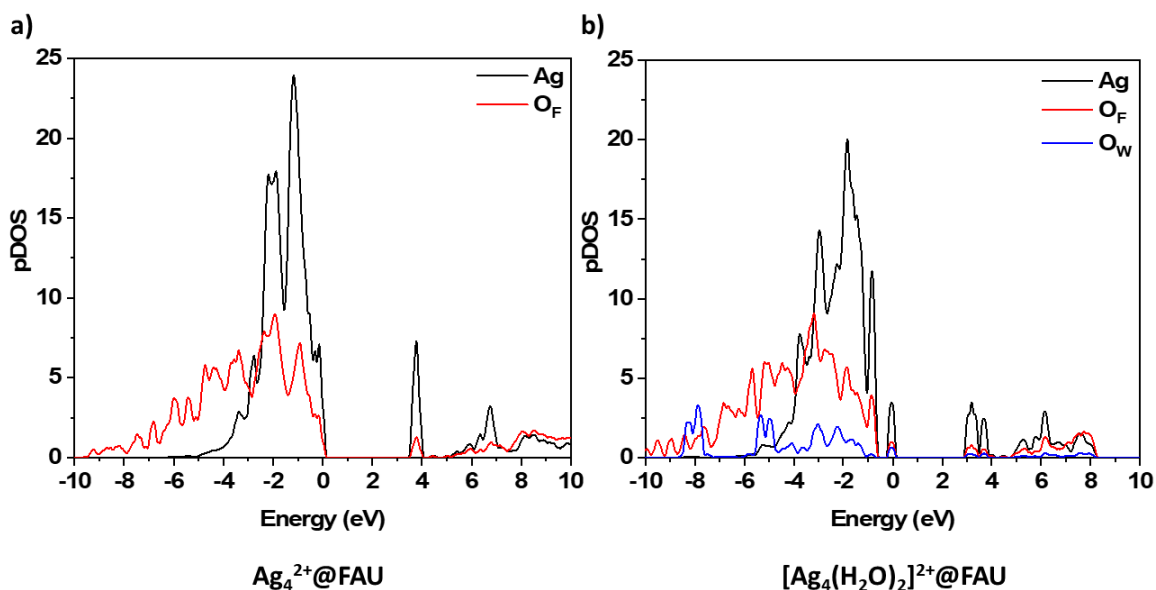


Figure 44 Projected density of states of the lowest energy tetrahedral silver cluster without water molecules (a) and with two water molecules (b) calculated with PBE functional.

The excitation energies of the clusters are thus found to be comprised of a sensitive combination of cluster size, water loading, water orientation and free volume inside the zeolite. These factors are likely to be further complicated by aluminum distributions and potentially defects.

3.2.6 Summary

We investigated the stability of zeolite-encapsulated silver clusters of two sizes, motivated by experiment, over a range of oxidation charge states. The trigonal structure of three silver atoms and the tetrahedral structure of four silver atoms encapsulated in the SOD is most stable, with one positive charge and two positive charge states, respectively, due to superatom shell closing effects. The optical properties of these two configurations mainly depend on the atoms of silver clusters and to a lesser extent, the directly bound oxygen atoms of the zeolite framework or the oxygen atoms of the water molecules. When water molecules are bonded to silver clusters, the excitation energy is reduced and the absorption spectrum is red-shifted, however, the direct incorporation of substantial quantities of water to Ag clusters inside SOD is found to be energetically forbidden. We further observe, that for the dominant electronic transition for Ag clusters in FAU, calculations of acceptable accuracy may be obtained with simple ground state proxies for the excitation, such as the HOMO-LUMO gap, which will be useful for the reduction of computational cost of future studies in this area.

3.3 Sintering-resistant clay-intercalated Pd nanoparticles

An alternative method for stabilizing noble metal clusters and nanoparticles against sintering is incorporation into the interlayer galleries of layered materials consisting of charged two-dimensional nanosheets, including layered double hydroxides²²⁰⁻²²⁶ and layered silicates (clays)²²⁷⁻²³². Synthesis of composite catalytic materials comprised of nanometer scale metal particles and nanosheets can be achieved straightforwardly via nematic swelling of the initial stacked layered material, followed by intercalation of metal particles, and subsequent condensation.²³³⁻²³⁵ By control of the charge density in the layers, the charge state of the metallic particle can be controlled, while the electrostatic pinning between charged metal particle and oppositely charged layer is understood to contribute to enhanced stability, and thus a resistance to sintering. A clear benefit to such a method over zeolite encapsulation is that particles may be grown to controlled sizes that are larger than the typical zeolite pore diameter (~ 1 nm), and do not suffer from issues of hindered penetration into the crystal.

Synthetic hectorite has been shown to be an amenable layered silicate clay for the stabilization of metal nanoparticles, including palladium and iron oxide.²³⁶⁻²³⁸ Experimental data suggests that not only does the hectorite nanosheet allow for the growth and entrapment of monodisperse Pd particles of around 3.5 nm, with ordered separation of 50 nm between particles, but that the particles show high catalytic activity for the oxidation of carbon monoxide and the partial oxidation of methane, with an earlier onset temperature than that of commercially available alumina-based catalysts.⁴⁹ In the following study, we investigate several hypotheses regarding the origin of the high activity of Pd, based on a DFT model of a charged Pd nanoparticle.

3.3.1 Choice of model

The metallic particles of interest have diameters of 3.5 nm, and so are unfeasible to realize directly with periodic DFT methods. Hence, we select a representative model: the

1.5 nm icosahedral cluster, Pd₁₄₇. This particle retains the pseudo-spherical shape of the experimentally synthesized particles, and contains the relevant {111} and {100} microfacets likely to be present in a 3.5 nm Pd particle. However, in order to identify the effects of local undercoordination and cluster curvature on the adsorption properties of Pd, we first compare the adsorption energy for CO with a {111} slab model.

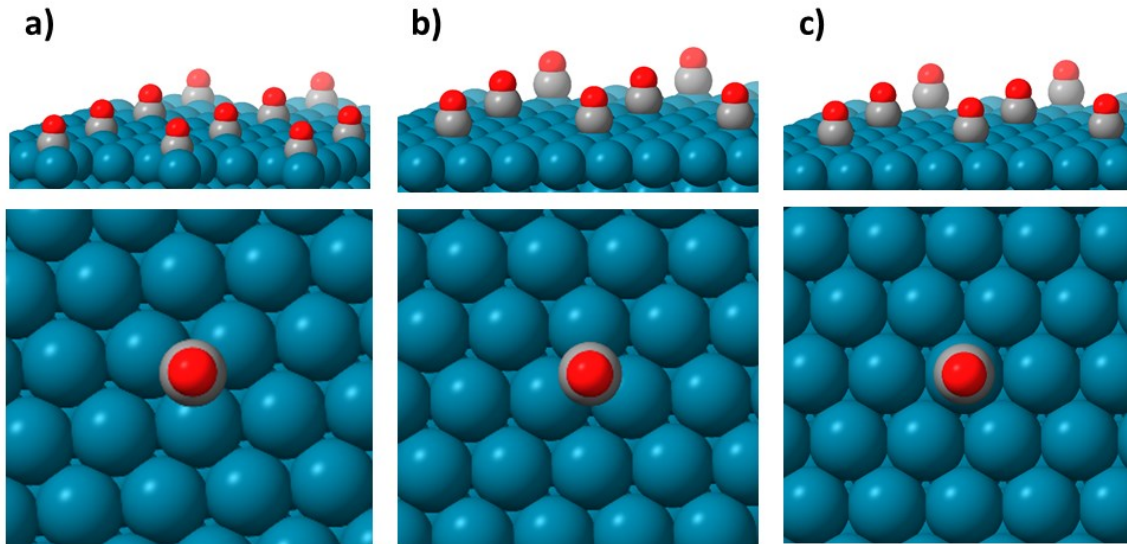


Figure 45 The adsorption of CO molecule on the fcc (a), hcp (b), and top (c) sites of the Pd(111) slab at coverage of 1/9.

A single CO molecule was adsorbed upon four different sites (fcc, hcp, top site and bridge site) of a 3x3 supercell Pd(111) slab comprised of six Pd layers, giving rise to a surface coverage of 1/9. The adsorption energy, defined as equation 61,

$$E_{\text{ads}(\text{slab})} = E_{\text{tot}(\text{slab})} - E_{\text{slab}} - E_{\text{CO}(\text{vacuo})} \quad (61)$$

where $E_{\text{ads}(\text{slab})}$ is the adsorption energy of CO molecules adsorbed on the slab surface. $E_{\text{tot}(\text{slab})}$ is the total energy of CO molecules adsorbed on Pd slab. E_{slab} is the energy of optimized bare Pd slab. $E_{\text{CO}(\text{vacuo})}$ is the energy of isolated CO molecule in vacuum phase. The adsorption energy was found to be -2.58, -2.54, and -1.95 eV, for the fcc, hcp and top sites, respectively (**Figure 45**). The bridge site was not observed to be a stable local minimum, with a barrierless conversion to a nearby top or hollow site upon local geometry optimization. Thus, the hcp three-fold hollow site was determined to be the

stable mode for low coverage CO. The priority of the adsorbing sites agrees with the previous research.²³⁹⁻²⁴⁰

For these and subsequent calculations, we applied the PBE exchange correlation function with Grimme's D3 dispersion correction. By comparison to the existing literature, we find the adsorption energy at low coverage to be in-line with other GGA DFT studies, excluding the dispersion correction (**Figure 46a**). The extrapolation of the previous data to the coverage of 1/9 is -2.27 eV, which agrees reasonably with our data without dispersion and dipole correction (-2.15 eV). **Figure 46b** shows the effect of the dispersion correction to be stabilizing by around 0.2 eV for all adsorption modes of CO. The dipole correction, included to ensure an accurate representation of the electrostatic field for the cell also contributes to the stabilization of CO at the surface, by around 0.1 eV.

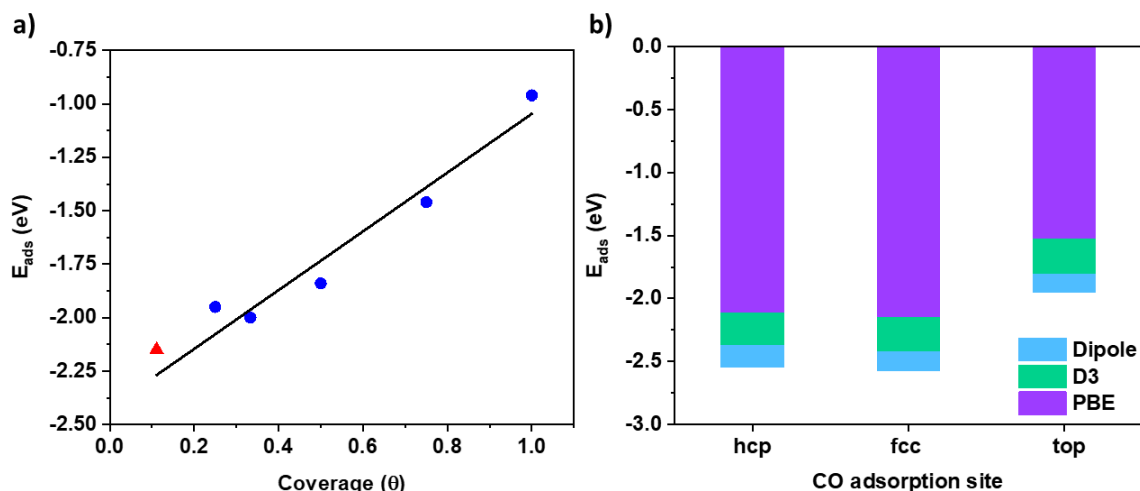


Figure 46 (a) The adsorption energy at different coverage rate reported by Duan et. al (blue point). The black line is the linear fitting of Duan's results. The red triangle is the adsorption energy in this thesis without dispersion and dipole correction. (b) Energetic contribution to CO adsorption energy at different adsorption sites.

The bond length of C-O after adsorption on the three sites are 1.191, 1.191, and 1.158 Å, for hcp, fcc and atop, respectively. It is known that at high coverage, the preferred occupation site of CO on Pd(111) changes from a hollow to the top site, however, in our

investigations, we consider low coverages that never exceed 0.6. Hence, only the hollow sites are considered in the following research.

3.3.2 Pd₁₄₇ nanoparticle

The nanoparticle we considered for the study contains 147 Pd atoms with a diameter of 1.5 nm (**Figure 47**). The adsorption energy of CO and oxygen atoms are calculated according to equation **62** and **63**.

$$E_{\text{ads}(\text{CO})} = E_{\text{CO@Pd}_{147}} - E_{\text{Pd}_{147}} - E_{\text{CO}(\text{vacuo})} \quad (62)$$

$$E_{\text{ads}(\text{O})} = E_{\text{O@Pd}_{147}} - E_{\text{Pd}_{147}} - \frac{1}{2} E_{\text{O}_2(\text{vacuo})} \quad (63)$$

where $E_{\text{CO@Pd}_{147}}$ and $E_{\text{O@Pd}_{147}}$ are the total energy of isolated CO or oxygen atom adsorbed on Pd₁₄₇, respectively. $E_{\text{Pd}_{147}}$ is the total energy of the optimized Pd₁₄₇. $E_{\text{CO}(\text{vacuo})}$ and $E_{\text{O}_2(\text{vacuo})}$ are the energy of CO or O₂ in vacuum phase, respectively. The adsorption energy of CO molecule on fcc and hcp sites of the (111) microfacets are found to be -2.51 and -2.63 eV, respectively. The hcp site therefore remains energetically more favorable than the fcc site for the nanoparticle Pd₁₄₇. Compared with the Pd(111) slab, it was found that the adsorption on the nanoparticle was only very moderately enhanced for the hcp sites, by less than 0.1 eV. Hence the (111) microfacets upon the 1.5 nm nanoparticle are a reasonable approximation to the extended Pd surface. Adsorption to the highly undercoordinated microfacet edge sites and vertices will be stronger than to the edges, but for a 3.5 nm particle, these sites make up only a small fraction of available sites, so we exclude them from our model. CO oxidation involves the reaction of adsorbed CO and dissociative adsorbed oxygen in the form of atoms on Pd(111). The adsorption energies of the oxygen atom on the fcc and hcp sites are calculated to be -1.57 and -1.62 eV, respectively. Hence, the two species may competitively bind to the surface during reaction conditions. Only CO molecule and oxygen atom adsorbed on the hcp site are considered in the following research.

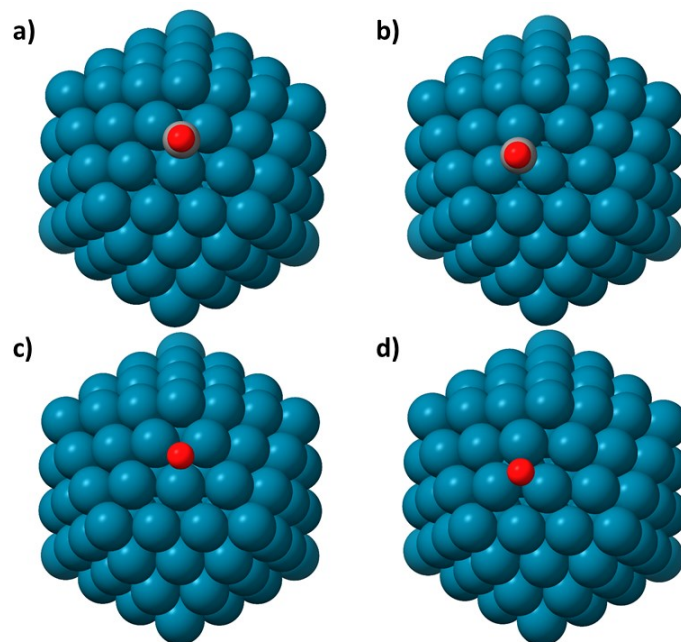


Figure 47 The adsorption of CO molecule at fcc (a) and hcp (b) sites on the nanoparticle Pd₁₄₇. The adsorption of the oxygen atom on the nanoparticle Pd₁₄₇ at fcc (c) and hcp (d) sites

3.3.3 Positive charge effect

As the nanoparticles pinned upon hectorite nanosheets contain a net positive charge, one hypothesis for the enhancement of catalytic activity is that additional charge weakens the binding of CO, thus reducing the propensity towards poisoning under CO-rich conditions.

In order to study the effect of electric charge on the oxidation of carbon monoxide, both CO and atomic oxygen were adsorbed on the hcp site of the nanoparticle Pd₁₄₇ {111} microfacets. In the range of charge states (0 to 7+) under consideration, the adsorption energy for the CO molecule decreased linearly with the increase of positive charge on the nanoparticle Pd₁₄₇, while the adsorption energy of the oxygen atom remains almost unchanged (**Figure 48a**). With the decrease in CO adsorption energy, the average bond length of Pd-C increased from 2.057 to 2.066 Å, and the bond length of C-O decreased from 1.197 to 1.187 Å (**Figure 48b**). The average distance between Pd and oxygen atom decreased from 1.995 to 1.981 Å.

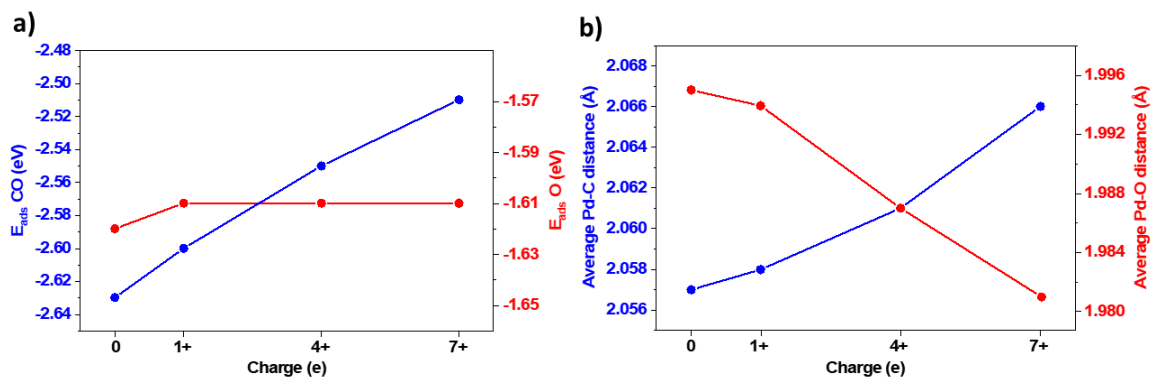


Figure 48 a) The functional relationship between the low coverage adsorption energies of CO (blue) and O (red) and the charge of nanoparticles. b) The average bond length of Pd-C (blue) and Pd-O (red) as a function of the charge on the nanoparticle.

To find out the mechanism behind the charge state and bond length variation, we calculated the electronic density of states. The electronic structure of the vacuum phase isolated CO molecule is shown in **Figure 49a**. The highest occupied molecular orbital is the 5σ lone pair orbital, which is mainly centered on the carbon atom. The 2π orbital is the lowest unoccupied molecular orbital, which is a strongly antibonding orbital. When the CO molecule interacts with the filled d orbital metals, the 2π orbital energy is low enough, and it can be used as a good acceptor orbital for d electrons.²⁴¹ When CO molecules were adsorbed on the Pd nanoparticle, the lone pair electron on the carbon atom forms a σ bond with Pd atoms, and the Pd atom donates its valence d electrons to the 2π orbital of the CO molecule. Compared with isolated CO molecules, the adsorption of CO molecules on the surface of the Pd nanoparticle leads to the downward shift of the energy state of the CO molecule (**Figure 49b**). The increase of the positive charge of the Pd nanoparticle induces the relative upward shift of the electronic state of the CO molecule with respect to Fermi energy (**Figure 49c**). Quite different to the adsorbed CO molecule, as shown in **Figure 49d**, there is no obvious difference between the pDOS of oxygen atom on the neutral and positive charged Pd₁₄₇, which agrees with the negligible change of the adsorption energy in increasing positive charge on Pd₁₄₇. Hence, while CO

remains the preferred adsorbate for the charge range considered, the reduction in adsorption energy is likely to weaken the propensity towards poisoning and may enhance catalytic activity for CO oxidation.

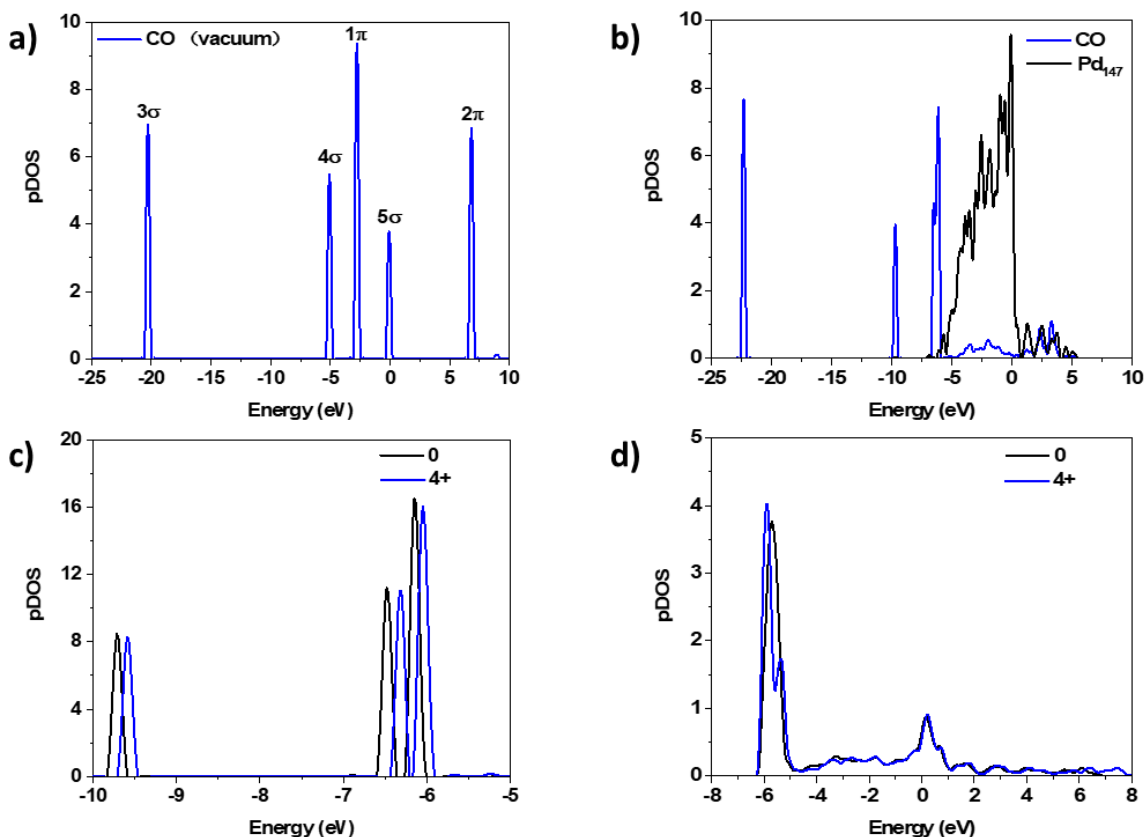


Figure 49 a) Projected density of states of an isolated CO molecule in vacuum phase. b) Projected density of states of CO molecule adsorbed on neutral Pd₁₄₇ cluster at low coverage. The blue and black lines are CO and Pd, respectively. c) Projected density of states of CO molecule adsorbed on the neutral and positively charged Pd₁₄₇ cluster. d) Projected density of states of oxygen atom on neutral and positively charged Pd₁₄₇ cluster.

3.3.4 Coverage effects

When more molecules are adsorbed on a metal surface, with the decreased intermolecular distance, the lateral interaction becomes an important factor affecting the adsorption energy.²⁴² A second hypothesis for the charge-induced enhancement of catalytic activity was considered: that increasing charge may induce a stronger coverage-driven

destabilization of CO than of O, leading to reduced poisoning on the surface of the nanoparticle.

To investigate this, we studied the influence of particle charge on the lateral effect between adsorbents. The coverage dependence of CO and O adsorption was studied by the adsorption on the surface of the Pd nanoparticle with a coverage range from 0.1 to 0.6 (between one and six adsorbates) with adsorbates bound to the hcp sites. This is the maximum coverage of a microfacet that is possible before interactions with the edge sites become unavoidable.

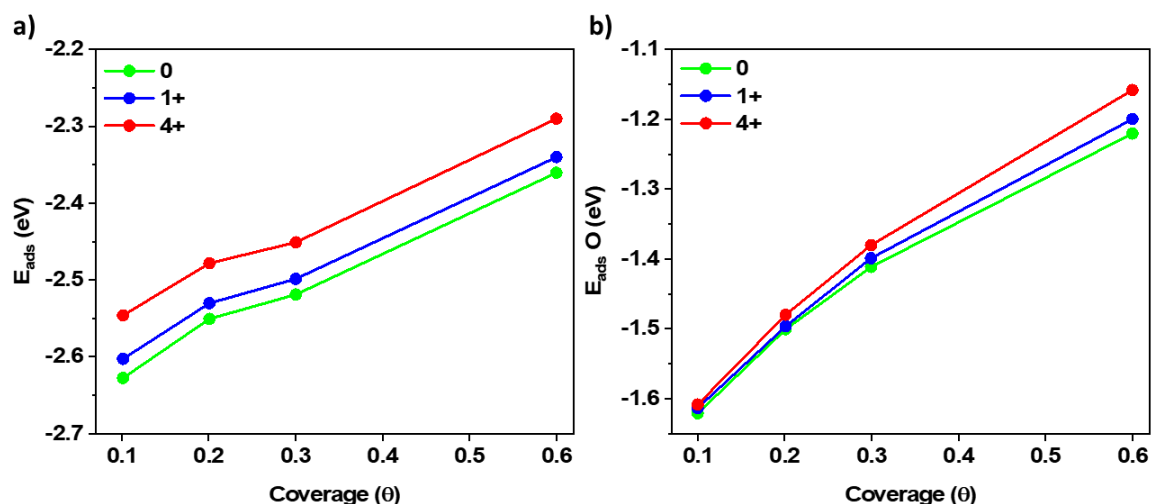


Figure 50 Coverage dependence of CO (a) and O (b) adsorption energy as a function of the charge on Pd₁₄₇.

For the neutral cluster, the coverage effect is to destabilize adsorption in a near-linear fashion for both CO and O (**Figure 50**). The destabilization is more pronounced for O than CO, which implying that at high coverages, CO poisoning is likely to be slightly worsened.

The charge on the nanoparticle Pd₁₄₇ increases from 1+ to 4+. In the whole coverage range of CO molecules, adsorption energy decreases with the increase of the charge of the Pd nanoparticle (**Figure 50a**), suggesting that the charged particle is less able to sustain high coverages than the neutral particle, which is in line with the prediction that overall, poisoning may be partially mitigated by increased particle charge. However, the

coverage trend for destabilization of oxygen adsorption is actually more pronounced than that of CO molecules (**Figure 50b**), and the adsorption energies of CO remain significantly higher than oxygen across the full range of coverages and charges studied. Therefore, the more charge and coverage rate on the surface of the Pd nanoparticle, the greater the destabilization of CO molecules and oxygen atoms, but it is unlikely that coverage effects are a major factor in enhancing catalytic activity on the charged cluster.

3.3.5 Charge effect on the diffusion of adsorbed CO and oxygen atom

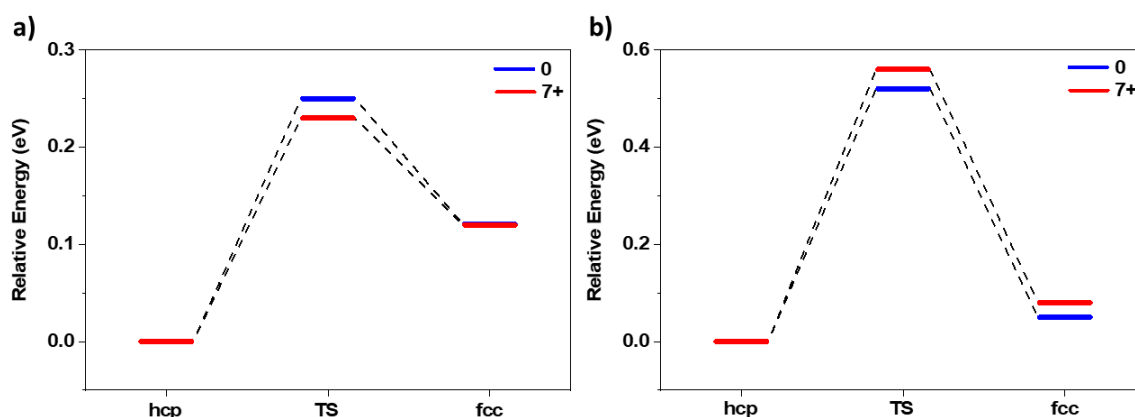


Figure 51 Migration barriers of CO molecule (a) and oxygen atom (b) from hcp site to fcc site on the neutral and positively charged Pd₁₄₇ at coverage of 1/9.

The diffusion of adsorbed CO molecules and oxygen atoms on the surface of the support is also important to CO oxidation as the oxidation process involves the migration of CO molecules and oxygen atoms to meet and react on the surface. To study the effect of positively charged cluster on the diffusion of CO molecule and oxygen atom, the migration barrier for single CO molecule and isolated oxygen atom between the hcp and fcc site at different charge states was calculated. As shown in **Figure 51a**, on the neutral Pd₁₄₇, the migration barrier of CO molecule is 0.25 eV, which is sufficiently low that the diffusion of the adsorbed CO molecule is not hindered. For the positively charged Pd₁₄₇, the migration barrier reduces to 0.23 eV. As the barrier is low and the difference is small, any promotion effect of charging is negligible. The migration barrier of the oxygen atom

on Pd₁₄₇ is more than twice that of CO molecules (**Figure 51b**). The effect of charge on the migration is again negligible, with the barrier difference between the neutral and positively charged nanoparticle being within 0.1 eV for both CO molecule and oxygen atom. Hence, the observed enhancement of positively charged nanoparticles on CO oxidation is not the result of a change in the diffusion barrier.

3.3.6 Summary

A theoretical work was done to try to explain the experimental observed high catalytic CO oxidation of Pd nanoparticles sandwiched between negatively charged clay nanosheets. Due to the large size (around 3.5 nm) of the encapsulated Pd nanoparticles reported in experiment, it is not suitable for DFT simulation. To compare the adsorption energy of slab model and the small nanoparticle model, we find that the Pd nanoparticle with 1.5 nm is an acceptable balance between the representation of the experimental reported nanoparticle and the feasibility of DFT simulation. The 1.5 nm Pd nanoparticle was used to study the effect of charge on the adsorption energy, the coverage rate, and the diffusion of adsorbed CO molecules and oxygen atoms. The adsorption energy of CO molecule decreases with the increase of charges on Pd nanoparticle, while oxygen adsorption is largely unaffected. This reduction of CO adsorption reduces the possibility of poisoning the surface, potentially leading to the enhancement of CO oxidation by reduction of poisoning. Other factors, such as coverage dependence and diffusion barriers were considered, but found to have little effect. For both neutral and charged Pd₁₄₇, the adsorption energy of CO molecules and oxygen atoms reduces as coverage and charge number increases, with the reduction trend being more pronounced for oxygen atoms. The diffusion barrier for CO molecule adsorbed on the neutral and charged Pd₁₄₇ is sufficiently low, both on neutral and charged nanoparticles, that the diffusion is not hindered by the barrier. Our findings contribute to a basic understanding of the role of nanoparticle charges in CO oxidation.

4 Conclusions

The purpose of this thesis is to investigate the role of cluster size, metal identity, charge state, and the existence and type of common adsorbents on the stability and optical or catalytic properties of encapsulated noble metals by theoretical methods. Three different topics were considered to study these factors, such as, the reason for the high stability and the effect of reductive adsorbents on the stability of single Pt atoms encapsulated in high silicious zeolite LTA; the cluster size, charge state, and ligand environment on the stability and optical properties of subnanometer Ag encapsulated in zeolite FAU and the effect of charge transfer between the Pd nanoparticles and negatively charged clay nanosheet on the performance of CO oxidation. These results reported in this thesis have deepened the understanding of above effects on the stability, optical and catalytic properties of encapsulated noble metals. The main results of this thesis are briefly described as follows:

Using the unbiased global structure prediction method, the special local structure (six-ring) where zeolite can effectively trap and stabilize single Pt atoms is confirmed. The six-ring provides a position to trap single Pt atoms, forming in-plane O–Pt–O complexes with one Si–O bond broken to maximize Pt–O bonding and charge transfer to Pt, leading to highly accessible and stable metal centers. This explains the experimental finding that high silicious zeolite encapsulated single Pt atoms show remarkable stability. The six-ring trap is a general trap for six-ring contain zeolites. Framework heteroatom (Al) provides an additional binding effect with Pt atom inserting into the O–H bond to form the $\text{PtH}^{\delta+}$ entity to compensate for the framework negative charge. But the trapping ability of Al six-ring is weakened compared to that of the pure silicious six-ring. The binding energy and migration barriers vary with the Si/Al ratio, which indicates that there is an optimal Si/Al ratio of the zeolite framework for maximizing single Pt atoms sintering resistance ability.

The ring trap can be energetically unfavorable or destroyed by introducing reductive

adsorbents or increasing Pt atoms loading. The adsorption of reductive adsorbates (CO and H₂) changes the energetic sequence of minimum structures, makes PtX (X = CO or H₂) entity easily diffuse in pores, and speeds up the system to equilibrium. CO molecules destroy the ring site minimum structures, while the H₂ molecule cannot adsorb on the ring site Pt atom but dissociates on the non-ring site Pt atoms and generates new minimum structures. H₂ molecules are more effective in weakening the Pt atom binding and promoting Pt atom diffusion than that of CO molecules. CO molecules can also assist the dissociation of zeolite encapsulated Pt₅ cluster by releasing PtCO entity. In addition to the reductive adsorbents, when more Pt atoms coexist, the six-ring trap does not survive. Even though the sintering tendency is suppressed for the encapsulated cluster, there remains the thermodynamic driving force for the cluster growth. The six-ring trap is a kinetic trap, rather than the thermodynamic sink, due to the energetic preference for forming more Pt-Pt bond than Pt-O bond. Hence, the maximum sintering resistance ability of single Pt atoms can be achieved by choosing special zeolite frameworks (with six-ring), optimizing Si/Al ratio, and limiting Pt atom mass loading.

The Pt (d⁹s¹) atom was replaced by Au (d¹⁰s¹) atom to study metal identity. There are high barrier (> 1 eV) for single Pt and Au atoms crossing through the silicious six-ring. The behavior of zeolite encapsulated single Au atom is quite different from that of single Pt atoms in the six-ring plane. It is the global minimum structure for single Pt atom in the six-ring, while it is a transition state for single Au atom in the six-ring plane. Another difference is that the Au atom cannot break the zeolite framework due to the weak interaction with the framework O atoms. This weak interaction makes Au atoms move freely among pores and can agglomerate to large cluster until the cluster size is comparable to that of the cage. Hence, the electronic structure of metals is important to the stability of encapsulated metal atoms. The metal can be trapped either via strong, covalent bonding, or via physical encapsulation in the pore, depending on electronic state. In addition to the special structure of the carrier, reaction atmospheres and electronic

structure of metals, the charge states and ligand environments are also important to the stability of encapsulated subnanometer metals. These effects on the stability of subnanometer metals were investigated with the subnanometer Ag encapsulated in partially Ag substituted sodium FAU. The results show that the configurations for triple and quadruple silver are trigonal and tetrahedral silver clusters encapsulated in the SOD cage with one and two positive charges, respectively. With the increase of water molecules, the structure becomes more and more unfavorable when water molecules are used as ligands for the SOD cage encapsulated silver clusters. Furthermore, due to the narrow space of SOD cage, the energy of structures with water molecules in another empty SOD cage is always lower than that of water molecules liganded Ag clusters. The optical properties of the most stable bare and water liganded Ag₃ and Ag₄ were studied with DFT and TDDFT method with the GGA and HSE03 functional. The results of the hybrid functional are close to the experimental results. A correction method is used to make the results calculated with DFT-GGA to the coupled-cluster level, which greatly reduces the resource requirement for the future similar work, especially for large systems. Lastly, the charge transfer between the support and the novel metals are also important to the stability and catalytic performance of encapsulated nanoparticles. The reason for the enhanced performance of carbon monoxide oxidation by Pd nanoparticles encapsulated in the negatively charged clay nanosheets was investigated with DFT. The Pd nanoparticles demonstrate positive charges when sandwiched between negatively charged clay nanosheets. The loss of d electrons in the Pd cluster leads to less electron back donation to the 2π orbital of CO molecules, thus weakening the Pd-C bond. This promotes the migration of adsorbed CO to combine with adsorbed O atoms on the surface of the Pd clusters. It also reduces the chance of CO poisoning the surface of the Pd clusters as the energy required for the desorption is lower than the neutral nanoparticles. When the coverage rate of CO or oxidation atoms on the surface of the Pd cluster increases, the adsorption energy of CO and oxygen atoms decreases more obviously than the low mass

loading. The idea of charge-controlled adsorbate loading is general, and may be extended to other catalytic systems.

This thesis provides detailed information for the factors, such as carrier structure and components, metal identity, cluster size, charge state, ligand environment and charge transfer, that affect the stability and optical or catalytic properties at the atomic level. These findings can be used as reference for the design of stable single atom catalysts, subnanometer silver based luminescent materials, or improving catalytic performance of noble metal nanoparticles.

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At this point, my graduation thesis has been basically completed, and my doctoral studies have come to an end. Looking back on the past years of doctoral study, I have a lot of feelings.

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List of Publications

1. **Hou, D.**; Grajciar, L.; Nachtigall, P.; Heard, C. J., Origin of the Unusual Stability of Zeolite-Encapsulated Sub-Nanometer Platinum. *ACS Catal.* **2020**, 10 (19), 11057-11068.
2. **Hou, D.**; Heard, C. J., Migration of zeolite-encapsulated Pt and Au under reducing environments. *Catal. Sci. Technol.* **2022**, 12 (5), 1598-1609.
3. **Hou, D.**, Hermann J., Nachtigall P., Heard, C. J., Optical properties of zeolite encapsulated sub-nanometer silver: A theoretical investigation. (Preparing for submission)
4. Ament, K.; Köwitsch, N.; **Hou, D.**; Götsch, T.; Kröhnert, J.; Heard, C. J.; Trunschke, A.; Lunkenbein, T.; Armbrüster, M.; Breu, J., Nanoparticles Supported on Sub-Nanometer Oxide Films: Scaling Model Systems to Bulk Materials. *Angew. Chem. Int. Ed.* **2021**, 60 (11), 5890-5897.