

Abstract

Zeolites are crystalline aluminosilicates and environmentally friendly solid acid catalysts thanks to their non-toxicity, large surface area, excellent (hydro)thermal stability, and tunable acidity. Traditionally, zeolite catalysts are applied in industrial processes related to petrochemistry, but several studies have recently shown their high potential in fine chemicals production and volatile organic compounds (VOCs) elimination. Advanced materials based on newly developed layered and nanosized zeolites have exhibited further fascinating properties, e.g., a short diffusion pathway, tunable structure and morphology. However, the limited correlation between key parameters of zeolite synthesis and their properties (structural, textural, acidic) and catalytic performance, especially for new layered and nanosized zeolites, hinders the development and application of zeolite catalysts.

Considering the above, this thesis focused on the preparation of several sets of specific zeolite catalysts to gain further insights into the relationship between key properties of zeolites (structure, morphology, chemical composition, accessibility to acid sites or other functional groups, and organization of layers, among others) and their performance as catalysts, supports for other active phases or nanosized components of colloidal systems.

The structural, morphological and textural properties of these materials were characterized by XRD, electron microscopy and N₂ adsorption. The nature, number and location of catalytic active sites were investigated by ICP-OES, ²⁷Al NMR, FTIR with different probe molecules, diffuse reflectance UV/Vis, XPS, TG and TPD techniques. Catalytic performance over the developed catalysts was assessed in gas phase and liquid phase reactions, including ethanol dehydration, toluene alkylation, VOCs catalytic oxidation, tetrahydropyranlation of alcohols and p-xylene acylation.

The main achievements of this thesis are the following: (1) design of a group of isorecticular Al-IPC zeolites with gradually varied micropore size but with the same morphology, Al content and concentration of acid sites by selecting an appropriate set of synthesis parameters; as a unique set of model catalysts (lattice parameters can be adjusted independently of most other properties), these isorecticular Al-IPC zeolites revealed a clear pore size-activity relationship in ethanol dehydration and tetrahydropyranlation reactions; (2) comparative analysis of the textural and catalytic properties of one-dimensional-pore zeolites synthesized using direct and post-synthetic

alumination techniques; this strategy enabled us to optimize the incorporation of Al into zeolite frameworks typically considered Al-poor (e.g., **AFI** type); (3) correlation between the aggregation-resistant properties of nanosized zeolites prepared by surface modification of respective nanocrystals and the nature (density, polarity and size) of the functionalization agent. Compared with non-modified nanocrystals, materials containing optimized surface protection groups showed improved stability against aggregation both in suspension and under harsh catalytic conditions; (4) preparation of **MWW** zeolites with different layer arrangements (MCM-22/36/56) and chemical composition ($\text{Si/Al} = 12 - 50$) to understand the role of zeolites as supports in the elimination of VOCs; in particular, the Al content in the support significantly affects the dispersion and reducibility of the active phase (cobalt oxide) and thus the catalytic activity in toluene and propane oxidation reactions; the MCM-22 material with minimized external surface area and appropriate composition ($\text{Si/Al} = 50$) exhibited the highest catalytic activity for toluene and propane oxidation (the temperatures for 90% hydrocarbon conversion were 307 and 295 °C, respectively), demonstrating the high potential of this composite catalyst for its application in VOCs elimination.

Overall, (1) the catalytic activity studies over Al-IPC-n zeolites showed that both ethanol dehydration and tetrahydropyranlation of alcohols proportionally increased with pore size and concentration of external acid sites, thus demonstrating the potential of **UTL**-derived isorecticular zeolites as model catalysts to further our understanding of catalyst pore size-activity relationships. In addition, (2) the results from toluene alkylation demonstrated that post-synthetic isomorphous substitution of Al-poor one-dimension large pore zeolite can be used to efficiently tune the chemical composition of one-dimensional large-pore zeolites, thereby generating Al-enriched zeolite materials for appropriate catalytic applications. Furthermore, (3) surface silylation of **MFI**-nanosized zeolites reduced their aggregation and improved their catalytic activity, hence partly solving their underlying activity and stability issues and enabling their application to a wider range of catalytic processes. Lastly, (4) the catalytic activity of cobalt-containing **MWW** zeolites in toluene and propane oxidation reactions increases with the Si/Al of the **MWW** supports and consequently with the dispersion and reducibility of the cobalt species. Thus, assessing the effects of specific properties of zeolites as supports on the dispersion and reducibility of the catalytic active phase and on the corresponding catalytic activity is crucial for the design of zeolite-supported catalysts with high activity in VOCs elimination.