

Abstract

Zeolites represent an important class of heterogeneous catalysts. They possess distinctive textural properties and adjustable acidity, allowing them to effectively catalyze a wide variety of chemical reactions. Utilization of germanium in the synthesis of zeolites opened up a notable expansion of their structural diversity. Ge introduction into zeolites has led to the successful preparation of numerous unique structures characterized by large and extra-large pores. Moreover, taking advantage of the hydrolytic instability of the Ge-O bonds, germanosilicates have been employed for: i) the top-down synthesis of novel zeolite structures through the innovative ADOR (Assembly-Disassembly-Organization-Reassembly) synthetic approach, ii) the isomorphous substitution of germanium with elements such as aluminum (Al), gallium (Ga), titanium (Ti), and tin (Sn) to generate diverse acid functionalities within the zeolite framework. In theory, the ADOR synthetic approach can be employed for a wide range of zeolites, encompassing both structural and chemical diversity. However, in practice, this synthetic strategy has been successfully implemented only for several germanosilicates as well as titano- or alumino- germanosilicate UTL zeolite. This limitation has restricted the catalytic potential of ADORable zeolites to a certain extent, thereby narrowing the scope of reactions that can be catalyzed by these acid materials.

The main objective of this thesis is to synthesize a series of Lewis acid zeolite catalysts by bottom-up synthesis and following top-down modification of tetravalent element-substituted germanosilicates of different structures (UTL, IWR, IWW, and UOV). Another objective of the thesis is the application of thus prepared zeolites as catalysts in model reactions (epoxidation of alkenes for Ti-containing catalysts and citronellal transformation for Sn-containing catalysts) to demonstrate the relation between the characteristics of materials controlled by synthesis design and the catalytic behavior. The last objective is to understand the structural stabilization of OSDA-free germanosilicate zeolites with low Si/Ge ratios. Using UWY germanosilicate zeolite, which is characterized by D4R units occupying 2D directions, allows the study of the rates between Ge deintercalation and Si reintercalation.

The key accomplishments of this thesis can be summarized as follows:

Isomorphous incorporation of tetravalent elements during the Assembly step of UTL (Ti-containing system) and IWW, IWR, and UOV (Sn-containing systems) germanosilicate zeolites,

followed by their structural transformation *via* Disassembly-Organization-Reassembly steps has resulted in a set of Ti-containing isorecticular zeolites with variable pore sizes and new Sn-containing catalysts with 12- and 8-ring pores.

ADOR transformation of Ti-containing germanosilicate UTL zeolite resulted in the isorecticular zeolites, denoted as Ti-IPC-n ($n = 2, 4, 6, 7$), which exhibited similarity in their structure of the layers but with variations in their micropore sizes ranging from approximately 0.4 to 0.9 nm. Alternatively, Ti was introduced into already prepared IPC-n zeolites post-synthetically. The investigated catalysts had comparable amounts of framework Ti sites ranging from 0.15 to 0.17 mmol/g. However, there was a systematic decrease in their micropore sizes, following the sequence: Ti-UTL > Ti-IPC-7 > Ti-IPC-2 > Ti-IPC-6 > Ti-IPC-4. In the epoxidation reaction using cyclohexene and 1-hexene, synthesized Ti-containing catalysts proved to be active compared to Ti-free germanosilicates. The TOF number decreased with the decrease in the micropore volume. At the same time, a decrease in the selectivity toward both target epoxides was also observed.

The second part is devoted to the preparation of Sn-containing zeolites. In this part, Sn was successfully incorporated into zeolites with UOV, IWW, and IWR topologies. The ADOR transformation method was further applied resulting in the production of the respective Sn-IPC-12, Sn-IPC-18, and Sn-IPC-17. XRD, TEM, nitrogen physisorption, and spectroscopic techniques were employed to evaluate the structural, textural, and acidic properties of the newly synthesized Sn-containing ADORable zeolites. The configuration of Sn acid sites (open/ closed) within the zeolite frameworks showed a variation upon the ADOR transformation. Notably, a significant increase in the proportion of defective Sn sites with hydrolyzed Sn-O-Si bonds was observed in the ADOR IPC-n zeolites when compared to the parent Sn-containing germanosilicate zeolites. Also, results showed modifications in the pore architectures, with the ADOR IPC-n zeolites displaying parallel or intersecting 12- and 8-ring pores, in contrast to the parent Sn-containing germanosilicate zeolites which featured intersecting 12- and 10-ring pores. The catalytic performance of Sn-containing zeolites was evaluated in the citronellal transformation. Consequently, considering the modified configuration of Sn acid sites (the increase of the proportion of the defective sites) after the ADOR process and the switch in the pore systems, all catalysts showed a change in the selectivity during the conversion of citronellal. In comparison to

the reference 12-ring Sn-BEA catalyst and the parent Sn-UOV, Sn-IWW, Sn-IWR zeolites featuring intersecting 12- and 10-ring pores, ADOR materials exhibited a distinctive propensity for the selective reduction of citronellal in the MPV reaction, displaying a selectivity range of 55–60% at 15% conversion, as opposed to the 2–5% selectivity observed with the mentioned reference catalysts. Conversely, Sn-BEA, Sn-UOV, Sn-IWW, and Sn-IWR zeolites exhibited a preference for the generation of isopulegol isomers via the intramolecular cyclization route, showing a higher selectivity range of 90–95%.

The structural fragility of germanosilicate zeolites can be fortified through isomorphous substitution, wherein Ge atoms are replaced by Si atoms. Comprehensive investigations into the hydrolysis of germanosilicate zeolites, conducted both in pure water and acidic solutions, have unveiled a two-step sequential mechanism common to both cases. This process involves the deintercalation of Ge atoms from the zeolite framework, leading to the creation of silanol nests. Subsequently, a Si re-intercalation process ensues, occupying the vacated positions through condensation with hydroxyl groups present within the silanol nests. The relative rates of these dynamic processes are influenced upon several factors, including temperature, pH, and the water-to-zeolite ratio. In this context, two extreme ways may occur structural collapse or preservation depending on the disparity in rates between Ge deintercalation ($r(\text{GeD})$) and Si reinsertion ($r(\text{SiR})$). The method reported for the stabilization of UWY germanosilicate in aqueous environment by adjusting the factors mentioned above ensured the mobility balance between Ge removal and Si occupation. Insights on XRD patterns and time-resolved spectra showed dynamic alterations occurring in the state of zeolite framework atoms during exposure to an aqueous medium, while maintaining an apparent preservation of structural integrity. The suggested approach for handling Ge deintercalation and Si reinsertion demonstrated effectiveness for UWY zeolite which offers a controllable method for structurally stabilizing germanosilicate materials that may be inherently unstable.