

## Abstract

Due to the presence of small structural units (e.g., D4R, D3R), the frameworks of germanosilicate zeolites are generally characterized by high pore volumes and multidimensional/extra-large pore systems, making them especially suitable in processing bulky molecules (in particular, involved in biomass-derived compounds valorization). However, weak acidity, low hydrothermal stability and high cost of Ge significantly limit the practical use of Ge-containing zeolites.

This thesis is aimed at design of sustainable germanosilicate zeolite-based catalysts of modifiable chemical composition and tunable porosity for relevant acid-catalyzed reactions, such as ketalization of polyols, epoxidation of olefins, Baeyer-Villiger oxidation of cyclic ketones and Meerwein-Ponndorf-Verley reduction of aldehydes.

Germanosilicate zeolites of different structures, including medium-pore **ITH**, large pore **IWW**, extra-large pore **UTL** and **\*CTH**, were thoroughly characterized using a combination of techniques (i.e., XRD, physisorption, electron microscopy, chemical analysis, among others) and subjected to different post-synthesis modifications to address synthesis-structure-activity relationships in the designed germanosilicate-zeolite based catalysts.

In ketalization of glycerol to solketal, weak acid centers of **IWW** and **UTL** germanosilicates were found as active sites capable to selective catalyze the targeted reaction. Noticeably, large pore **IWW** catalyst was shown featuring both Lewis and Brønsted acidity, while extra-large pore **UTL** zeolite was found to possess exclusively Ge-associated Lewis acid centers. Water-induced formation of Brønsted acid sites in **IWW** germanosilicate was verified using FTIR-monitored dose-by-dose water adsorption, followed by probing acid sites with pyridine.

To tailor germanosilicate zeolite-based catalysts with different nature of acid sites, post-synthesis isomorphous substitution of Ge with different tetravalent elements (e.g., Ti, Sn, Zr) coupled with Ge recovery and recycling was elaborated. Up to 94 % of Ge was recovered from

germanosilicate zeolites of different structures (**ITH**, **IWW** and **UTL**) under optimized leaching conditions (i.e., pH, T, duration of the treatment). The method of Ge-containing leaching solution separation from parent zeolite (i.e., *filtration* or *microfiltration*) was shown as a useful tool to direct the phase selectivity of zeolite formation upon Ge recycling. In particular, *microfiltration* yielded GeO<sub>2</sub> as a versatile Ge source for the synthesis of different zeolites (exemplified for **ITH**, **IWW** and **UTL**). In turn, *filtration* produced GeO<sub>2</sub> containing trace amounts of initial zeolite, thus favoring seed-assisted crystallization of parent zeolite, albeit possessing larger crystals, independently on the re-synthesis conditions applied.

Subsequent metalation of degermanated large pore (**IWW**) and extra-large pore (**UTL**, **\*CTH**) zeolites gave rise to Lewis acid solids of variable nature, proven as active and selective catalysts in model reactions, such as epoxidation of 1-octene for Ti-substituted zeolites, Baeyer-Villiger oxidation of cyclohexanone for Sn-containing materials and Meerwein-Ponndorf-Verley reduction of furfural for Sn- and Zr-substituted zeolites.

Water-induced disassembly of **UTL** germanosilicate in combination with Ge-for-Al isomorphous substitution was developed, optimized and proved as an efficient method for controllable alternation of both structural and acidic properties of zeolite catalysts. In particular, de-intercalation and rearrangement processes competing upon **UTL** disassembly, were efficiently regulated by adjusting water-to-zeolite ratio and concentration of framework-building Al ions in water-methanol medium. Unprecedentedly, Al-assisted rearrangement under slow deintercalation conditions allowed to achieve the cycled structural transformation of **UTL** (D4R interlayer units) → Al-**OKO** (S4R) → Al-**UTL** (D4R).

The synthetic methods designed in this thesis are envisaged to pave the way towards new nanoporous materials expanding the scope of highly active and selective heterogeneous catalysts engineered for specific application.