

Abstract

Development of sustainable and environmentally friendly chemical processes is of vital importance nowadays. Although there is a palette of different synthetic methods for the formation of epoxides, sulphoxides and sulphones, from both economic and environmental points of view, a direct oxidation with a simple oxidant is highly appreciated.

The main goals of the thesis were design and synthesis of novel titanium containing zeolitic materials with the ability to catalyse selective oxidation of sterically demanding organic compounds, particularly epoxidation of cyclic olefins and terpenes and oxidation of bulky thioethers to corresponding sulphoxides and sulphones with hydrogen peroxide as the oxidant.

Two novel extra-large pore titanosilicates were prepared by means of hydrothermal synthesis (Ti-**CFI**, Ti-**UTL**), three large-pore titanosilicates (Ti-**CON**, Ti-**AFI**, Ti-**IFR**) were prepared using two step deboronation – liquid phase titanium impregnation procedure and two groups of lamellar materials were prepared. One group was based on modified nanosheet TS-1; the other was prepared from Ti-IPC-1P lamellar precursor, which was prepared by means of top-down transformation of Ti-**UTL**. Last but not least, the Ti-**UTL** was transformed into new titanosilicates Ti-IPC-2 (**OKO** structure) and Ti-IPC-4 (**PCR** structure) by means of ADOR transformation. This is the first example of an ADOR transformation of a titanosilicate material. Especially Ti-**UTL** based pillared materials (denoted Ti-IPC-1PI) are purely mesoporous, possessing titanium sites located on the surface of crystalline layers and thus providing a synergy of both crystalline titanosilicate zeolites and mesoporous molecular sieves. So-called silica-titania pillaring post-synthesis modification (applied on both groups of layered titanosilicates) was developed to boost number of active titanium centres.

The structure, morphology and texture of the materials were investigated by powder XRD analysis, nitrogen and argon physisorption and SEM. The character and amount of the titanium active sites were investigated by diffuse reflectance UV/Vis spectroscopy and XRF or ICP-OES elemental analysis. Catalytic activity of the prepared materials was investigated in selective oxidation of various sterically demanding substrates.

The silica-titania pillared Ti-IPC-1PITi catalyst provided cyclooctene conversion 26% and cyclooctene oxide yield 19.5% after 1 h of the reaction being the most active of all the prepared materials and one of the most active catalysts reported for epoxidation of bulky olefins with hydrogen peroxide.

High epoxide selectivity (95-97% at 10% conversion) and high yield of the cyclodecene oxide (TS-1-PITi 15%, Ti-IPC-1PITi 23% after 4 h) were achieved also in epoxidation of cyclodecene using the silica-titania pillared materials. Contrary, conventional TS-1 provided yield below 1%.

The Ti-IPC-1PISi catalyst exhibited an order of magnitude higher activity in both methylphenyl sulphide (MPS) and diphenyl sulphide oxidations (e.g. MPS oxidation: TON = 1418 vs. TON (TS-1-PISi) = 151, both after 30 min).

We conclude the catalysts with most open structures and therefore the lowest diffusion limitations and sufficient amount of the titanium centres (Ti-IPC-1PITi and TS-1-PITi) provided the highest yields as well as the selectivity. Simple silica-titania pillaring treatment improves the catalyst performance dramatically.