Zeolites for high selective C-O bond formation

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1. Introduction
Zeolites by definition are microporous crystalline aluminosilicate materials with accessible porosity. Their permanent porosity, various pore structure geometries, good mechanical and thermal properties made them one of the most important class of heterogeneous catalysts in chemical and petrochemical industry over the last 70 years [1]. Most of the industrial zeolite applications as catalysts benefit of the acid/base properties and shape selectivity. On the other hand, fossil fuels derived building blocks like ethylene or propylene often required selective oxo-functionalization A major breakthrough towards redox catalysts occurred with the discovery of the TS-1 (titano-silicate 1 zeolite) by Taramasso in early 80’s [2], in which isolated Ti⁴⁺ species were isomorphously substituted in the silica zeolite matrix. The success of TS-1 attracted significant attention in the last decades to introduce new Ti zeolite materials that could offer new opportunities for industrially selective oxidations. Beginning of 2000’s Tatsumi first reported the synthesis of Ti-MWW zeolite and claimed improved catalytic performance in epoxidation of linear alkenes like 1-hexene [3,4]. The layered structure with 2D pores allows several modifications that results in different packings and interlayer distances and tuning of the zeolite activity and accessibility [5] which make it a very interesting oxidation catalyst resulting in a family of Ti-zeolite structures, who could combine redox properties with acid base catalysis.

2. Results and discussion
The properties of the Ti-MWW product as a function of the synthesis route and relation to solvent properties and process conditions will be discussed taking several industrial relevant chemical transformation as examples. In a first example the potential of Ti-MWW zeolite for the olefin epoxidation with hydrogen peroxide will be discussed (Figure 1). For propylene epoxidation, first plants based on the HPPO technology went on stream in 2008 in Ulsan (100 kt/a) SKC (based on Evonik/Uhde technology) and Antwerp (300 kt/a) BASF/DOW technology. BASF/DOW HPPO technology is the most utilized with more than 60 % of the PO HPPO based capacity. The HPPO processes currently on the market are all using a TS-1(titanium silicalite-1) zeolite as epoxidation catalyst and possible developments of the HPPO process in view of new zeolitic materials like for example Ti-MWW would be discussed as well as potential of expanding the concept to other linear olefins.

![Figure 1. HPPO process scheme](image-url)
In addition to redox function of Ti-MWW, acid functionality could be added through introduction of B in the Ti-MWW structure. This could allow one step synthesis as described in Figure 2, involving epoxidation with epoxide ring opening and consecutive methylation of making 2-methoxy cyclohexanol from cyclohexene as a route for guajacol.

3. Conclusions
Selective oxidation is one route to produce valuable building blocks for production of bulk or fine chemicals. Higher selectivities are often difficult to be achieved in oxidation reactions due to competitive total oxidation, or over-run reactions due to free radical formation. Use of Ti-containing zeolites allowed development of high selective oxidation processes that operate under mild conditions. These allows a better valorization of the starting raw materials and least waste formation. As example, the HPPO process has clear advantages in comparison to the competing PO manufacturing technologies in terms of energy consumption, eco-efficiency (water is the main by-product) and costs [6]. Further improvement of the process was demonstrated by using a new type of titanium silicate zeolite based on a Ti-MWW. Cascade type of reactions could be another type of example for more efficient processes by reducing the need of intermediate product separation and purification.

References