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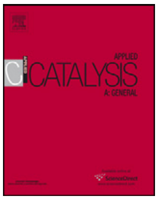

Shape selective methanol to olefins over highly thermostable DDR catalysts

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ABSTRACT

ZSM-58, having a DDR topology, is shown to be a very attractive catalyst for the direct formation of propylene and ethylene via conversion of methanol. A performance similar to the state of the art SAPO-34 catalysts is achieved, while no olefins longer than C_4 are formed. In addition, ZSM-58 has a much higher thermostability than SAPO catalysts.

Mainly propylene, ethylene and linear butenes (trans-but-2-ene and butadiene) are formed when materials with the DDR topology are used as catalysts during the MTO process. The ratio propylene/ethylene can be tuned by changing the reaction conditions or the degree of catalyst coking. An optimum in performance, in terms of stability and selectivity, is found for catalysts containing one acid site (one Al) per accessible cavity. Deactivation of the catalysts takes place due to formation of coke and homogeneous blocking of the catalysts porosity. Activity is fully recovered after regeneration in air.

1. Introduction

Light olefins, namely propylene and ethylene, are among the most demanded raw materials in the chemical industry. Their overall demand, especially that of propylene is forecasted to keep rising during the next decades [1]. Traditionally, they have been produced at very large scale in steam cracking, a non-catalytic process. These processes are robust but the selectivity is modest. Therefore, it is not surprising that catalytic processes to supply these chemicals are of high interest for both industry and academia. FCC (fluid catalytic cracking) processes have been adapted by modifying the catalysts, increasing the production of lower olefins, in particular propylene. Several other approaches appear to be promising. Catalytic dehydrogenation of lower paraffins [2], direct or oxidative, modifications in the catalytic cracking and the direct conversion of methanol to olefins have been proposed as possible processes. The latter, the so-called methanol to olefins (MTO) process has attracted the attention of researchers during the last four decades [3]. Methanol can be made either from syngas (from natural gas or coal) or even via fermentation. Subsequently it can be catalytically processed to gasoline (methanol-to-gasoline, MTG) or to olefins (MTO). The MTG process was initially designed as an alternative to Fischer–Tropsch-synthesis, but with the development of new small pore zeolites, more specifically silico-alumino-phosphates like SAPO-34, it was discovered that ethylene and propylene can be selectively produced.

Most of the open MTO literature deals with the use of either ZSM-5 or SAPO-34 catalysts, while only recently the use of other zeolites like ZSM-11, ZSM-22, SAPO-5, SAPO-11, SAPO-18 and SAPO-35 has been reported [4–6].

It is claimed that the mild acidity of SAPO-34 together with its CHA topology are responsible for the high selectivity of the material towards the formation of ethylene and propylene [3]. This is probably the reason why mainly silico-alumino-phosphates have been explored. However, not much is known about materials with similar topologies containing only Si and Al. From the application viewpoint, it would be desirable to produce a catalyst with a higher thermal stability, since during the MTO process regeneration of the catalysts at high-temperatures in the presence of air is an integral part of the operation and silico-alumino-phosphates have a limited thermal stability compared to silico-aluminate systems [7].

A possible candidate is ZSM-58, a silico-aluminate with low aluminium content, having a DDR topology firstly synthesized by Exxon Mobil [8,9]. The structure of DDR consists of window-connected cages, in contrast to zeolite frameworks, which makes this material a member of the group of clathrasils. The crystal structure is built by corner-sharing SiO_4 tetrahedra that are connected to pseudohexagonal layers of face-sharing pentagonal dodecahedra (5^{12} cages). These layers are stacked in an *ABCABC* sequence and are interconnected by additional SiO_4 tetrahedra that form six-membered rings between the layers. Thus, two new types of

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cages arise, a small decahedron, $4^3 5^6 6^1$ cage, and a large 19-hedron, $4^3 5^{12} 6^1 8^3$ cage. By connecting the 19-hedra cavities through a single 8-ring with an aperture of 4.4 Å × 3.6 Å, a two-dimensional porous system is formed, which is accessible to small molecules after thermal treatment at 773 K [10,11].

The selective adsorption of propylene over propane and trans-2-butene and butadiene over other butane and butene isomers together with the high uptakes of ethylene on the all-silica DD3R were firstly reported by our group by studying single component adsorption using a Tapered Element Oscillating Microbalance (TEOM) [12–14]. Olson et al. [15] studied the sorption properties of some 8-ring zeolites, among which ZSM-58, in which the high selectivity for propylene was also suggested from single component adsorption. Later we reported the first propane–propylene mixture separation using DDR in a packed bed adsorption operation [16].

Up to now, little is known about the catalytic properties of ZSM-58 in the open literature, to the best of our knowledge only its use in the catalytic cracking of *n*-octane in its acidic form [17] and the application of the Mn exchanged form in the catalytic oxidation of *n*-hexane [18] have been reported.

In this work we present the application of ZSM-58 for the direct synthesis of olefins via methanol conversion. The performance of this DDR-structure type catalyst is comparable in terms of activity to the best SAPO-34 catalysts, it shows high selectivities to propylene and ethylene, while no product longer than linear butenes is formed. Moreover, the ratio propylene/ethylene can be tuned either by changing the reaction temperature or by controlling the coke level in the catalyst.

2. Experimental

2.1. General

All chemicals were obtained from Sigma–Aldrich and were used without further purification. Scanning Electron Microscopy (SEM) was measured in a JEOL JSM 6500F setup coupled to an Energy Dispersive Spectrometer (EDS) for micro-analysis.

Nitrogen adsorption at 77 K in a Quantachrome Autosorb-6B unit gas adsorption analyzer was used to determine the textural properties as BET surface area between 0.05 and 0.15 relative pressures and pore volume at 0.95 relative pressure. The *t*-plot was used to calculate the external surface area of the catalyst particles (calculated as the surface area of pores larger than micropores). The crystalline structures were analyzed by X-ray diffraction (XRD) using a Bruker-AXS D5005 with CuKα radiation. Thermogravimetric analysis (TGA) was performed by means of a Mettler Toledo TGA/SDTA851e, on samples of 10 mg under flowing 60 ml/min of air at a heating rate of 10 K/min up to 873 K.

Elemental analysis was carried out by means of inductively coupled plasma optical emission spectroscopy (ICP-OES). The samples were digested in duplo in an aqueous mixture of 1% HF and 1.25% H_2SO_4 and analyzed with an ICP-OES Perkin Elmer Optima 3000dv in order to determine the amount of Si and Al present in the structure.

DRIFT spectra were recorded in a Bruker model IFS66 spectrometer, equipped with a high-temperature cell with CaF_2 windows. The spectra were recorded after accumulation of 128 scans and a resolution of 4 cm^{-1}. A flow of helium at 10 ml/min was maintained during the measurements. Before collecting the spectra the different samples were pretreated in a helium flow at 393 K for 30 min. KBr was used as background.

The acid site concentration was determined using temperature-programmed desorption of ammonia (NH_3-TPD). NH_3-TPD was carried out on a Micromeritics TPR/TPD 2900 apparatus equipped with a thermal conductivity detector (TCD). Approximately 25 mg of each sample was pretreated at 923 K and rapidly cooled to 473 K followed by loading with ammonia applying a flow of 30 mL (STP)/min for about 10 min. A helium flow of 50 mL/min was applied for 10 min to remove weakly adsorbed NH_3. The adsorption process was repeated 3 times. After the loading procedure, a linear temperature program was started (473–973 K at 10 K/min) in a flow of He (50 ml/min), and the ammonia desorption was followed by the TCD.

2.2. Synthesis of the catalysts

For the synthesis of ZSM-58 [19], first the structure directing agent (SDA), methyltropinium iodide (MTI), was prepared by adding 25.1 g methyl iodide (99 wt.%) dropwise to a solution of 25.0 g tropine (98 wt.%) in 100 g ethanol at 273 K under stirring and keeping the suspension under reflux for 72 h. After cooling and filtration, the resulting crystalline MTI was washed with 100 g ethanol and dried at 353 K.

The molar ratio of the synthesis mixture was MTI:SiO_2:Al_2O_3:Na_2O:H_2O = 17.5:70:x:11.5:2800. It was prepared as follows: 10 g of Ludox HS-40 was added to a solution of 4.7 g MTI and 8.7 g demineralised H_2O and stand overnight while stirring (solution A). 0.78 g sodium hydroxide and the corresponding amount of sodium aluminate (Al_2O_3: 50–56, Na_2O: 40–45 wt%) were dissolved in 33.3 g H_2O (solution B). The resulting solution (A + B) is stirred for 30 min, placed in a teflon lined autoclave and heated under hydrothermal conditions (autogenous pressure) to 433 K for 3–7 days depending on the Al content (the higher the Al content the longer the synthesis time, i.e. 4 days synthesis for Si/Al = 392 and 7 days for Si/Al = 80). The as synthesized materials were calcined (2 K/min) at 973 K for 10 h in a static oven.

A commercial ZSM-5 from Zeolyst International (CBV28014, SiO_2/Al_2O_3 = 560) was used as benchmark catalyst.

2.3. Experimental setup

Experiments were carried out with a 1/4 in. stainless steel reactor with a length of 6 cm. 100 mg of catalyst particles (pelleted zeolite, crushed and sieved to a size of 0.75–1 mm) was placed in the reactor between quartz wool plugs for packing purpose and gas distribution. An ISCO liquid pump was used to feed the liquid to the reactor system.

In a typical experiment, the liquid feed stream (methanol or methanol + water) was pumped to the reaction section located in a heated chamber (373 K) to evaporate the liquid while diluting it with N_2. In this chamber all valves and reactor oven were located to avoid condensation. The temperature of the reactor was varied between 573 and 723 K in the different experiments. The product mixture was analyzed online with an Interscience Compact GC over a 60 m RTX®-1 (1% diphenyl-, 99% dimethylpolysiloxane) column.

Conversion (%) was calculated as follows:

$$X = 100 \times \frac{N_{\mathrm{MeOH_{in}}} - N_{\mathrm{MeOH_{out}}}}{N_{\mathrm{MeOH_{in}}}}$$

The overall olefin selectivity (%) was based on the carbon atoms in the products and calculated as follows:

$$S = 100 \times \frac{2N_{\mathrm{C_2H_4}} + 3N_{\mathrm{C_3H_6}} + 4N_{\mathrm{C_4H_8}}}{N_{\mathrm{MeOH_{in}}} - N_{\mathrm{MeOH_{out}}}}$$

With N_i being the number of moles.

Similarly that for the individual olefins is defined. The yield (%) of olefin *i* is then simply the product of conversion and its selectivity:

$$Y_i = \frac{S_i X}{100}$$