Applied Catalysis A: General 391 (2011) 254–260

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

Novel extruded fixed-bed MTO catalysts with high olefin selectivity and high resistance against coke deactivation

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ARTICLE INFO

Article history:
Received 8 January 2010
Received in revised form 23 April 2010
Accepted 24 May 2010
Available online 1 June 2010

Submitted for the Special Issue "Recent Developments in Model Catalysis—Closing the Gap to Technical Applications" in honour of Prof. Helmut Knözinger's 75th birthday.

Keywords:
MTO (methanol to olefins)
ZSM-5
Coke deactivation
Extrusion
Aluminium phosphate

ABSTRACT

This report describes the catalytic performances of $AlPO_4$/ZSM-5 extrudates in comparison to conventional alumina- and silica-bound extrudates in the fixed-bed MTO (methanol to olefins) conversion. The novel $AlPO_4$/ZSM-5 extrudates are produced with an aluminium phosphate binder which undergoes a phase transition into an $AlPO_4$-tridymite phase upon calcination of the greenbodies. The finished $AlPO_4$/ZSM-5 extrudates are macroporous and mechanically very stable. In contrast to alumina, this novel matrix does not exhibit catalytic self-activity, and it does not release aluminium which is incorporated in the zeolite lattice. At temperatures above 400 °C, $AlPO_4$/ZSM-5 extrudates show superior activity, propylene selectivity and stability. The coke deactivation of $AlPO_4$/ZSM-5 extrudates can further be reduced dramatically, if a pre-reactor is installed upstream, where an equilibrium mixture of dimethyl ether (DME), methanol and water ($X_{MeOH} = 87.7\%$ at 275 °C) is produced. In contrast, the insertion of the DME pre-reactor has no significant effect on the coke resistance when extrudates with alumina- or silica-matrices are used.

1. Introduction

The conversion of methanol to the important intermediates ethylene and propylene represents a synthesis gas-based manufacturing route which is independent on oil resources. Therefore, the MTO process has been investigated since decades. Numerous studies have been published concerning the mechanism and, in particular, on the formation on the first C–C bond. Meanwhile, the so-called "hydrocarbon pool mechanism" suggested by Dahl and Kolboe is most widely accepted [1–3]. Furthermore, many different acidic catalysts, mostly zeolites, have been tested; an overview on these studies has been given by Stöcker [4]. Industrially applied so far are only ZSM-5 and SAPO-34. The latter is used as a spray-dried catalyst in the MTO process with fluidised bed reactor and regenerator developed by UOP/Hydro [5]. ZSM-5 is employed in the Lurgi fixed-bed MTP-process (methanol to propylene) in the form of extrudates bound with γ-alumina [6]. Roughly, the MTO reaction network consists of two parts: (i) the equilibrium reaction of methanol to dimethyl ether (DME) and water, and (ii) formation of hydrocarbons and water. All reactions are highly exothermic. In the Lurgi-process, the formation of DME at a methanol conversion level of about 99% is performed in a pre-reactor in order to spread the release of heat. To cope with the rapid coke deactivation of the γ-Al_2O_3/ZSM-5 catalysts, three further reactors with up to four stages each are employed for the formation of hydrocarbons from DME and methanol. These parallel reactors are operated in swing mode, that is, one of the reactors always has to be off-line while the coke on the deactivated catalyst inside is burnt off [7,8]. Obviously, coke deactivation still is an important issue in all processes where methanol is to be converted to hydrocarbons.

In this contribution, it will be shown that the binder used for shaping of the catalyst plays a decisive role for the MTO-performance. We will compare extruded ZSM-5 catalysts produced with different binders. Besides conventional alumina and silica, we used an aluminium phosphate hydrate binder which transforms into an $AlPO_4$-sintermatrix with tridymite structure upon calcination of the greenbodies. Details on the preparation and characterisation of $AlPO_4$/ZSM-5 extrudates have been published earlier [9,10]. In [10], the following characteristics of the $AlPO_4$-bound extrudates have been demonstrated:

- This matrix exhibits a negligible surface area. Hence, catalytic self-activity is negligible as well.

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doi:10.1016/j.apcata.2010.05.035

Table 1
ZSM-5 samples used to produce extruded catalysts.

Manufacturer	Manufacturer labelling	Si/Al ratio	Crystal diameter	Cation
Süd-Chemie	SM55	25	4–5 μm	NH_4^+
ExxonMobil	AT 298-391	30	0.3–0.8 μm	TPA^+/H^+
Zeochem	PZ-2/100	50 ± 8	0.5–2 μm	Na^+
Zeochem	PZ-2/500H	250 ± 35	0.5–2 μm	H^+
Zeochem	PZ-2/900	≥450	2–5 μm	Na^+

- The pore size distribution can be tailored through the choice of the size of the embedded particles and their amount in the extrudates. At zeolite concentrations of 50% (m/m) or higher, the mean pore diameter of the matrix (D_{pore}) depends on the zeolite crystal size, only, and amounts to $D_{\text{pore}} \approx 0.25 \cdot D_{\text{particle}}$. Hence, an entirely macroporous matrix can be produced if zeolite crystals are extruded which exhibit diameters of 200 nm or larger.
- Despite their macroporosity, extrudates with $AlPO_4$-sintermatrix are mechanically much more stable than alumina- or silica-bound extrudates because the bonding forces of the sinter necks are much stronger than van der Waals or electrostatic interactions in particulate matrices.
- Other than conventional matrices on alumina basis, the $AlPO_4$-matrix does not cause any alumination of the zeolite framework.

All these features are important in the context of MTO. It will be shown in this contribution that $AlPO_4$/ZSM-5 extrudates exhibit superior activity, propylene selectivity and coke resistance.

2. Experimental

2.1. Catalysts

All extrudates used in this study were of cylindrical shape with a diameter of 2 mm and a length of 5 mm. This report focuses on samples consisting of ZSM-5 and matrix in a mass ratio of 1:1 on dry basis. Other compositions have been inspected as well, but the zeolite content predominantly determines the activity and the mechanical stability of the extrudates, whereas the effect on selectivity and coking rate is minor. All samples of zeolite ZSM-5 were of commercial origin (Table 1). Binder materials were pseudo-boehmite (Sasol, Pural SB1), silica gel (Grace, Perkasil SM 604) and aluminium phosphate hydrate (Fluka, Riedel-de Haen). During calcination at 550 °C for 3 h, these binders form porous matrices consisting of γ-Al_2O_3 (AO), SiO_2 (SO) or $AlPO_4$ (AP) with the crystal structure of tridymite, respectively. In the following, the denotation of the catalysts reveals the matrix type and the Si/Al ratio of the embedded zeolite. For instance, AP250 denotes extrudates composed of $AlPO_4$-matrix and zeolite ZSM-5 with an atomic ratio Si/Al = 250. Irrespective of the cation present in the original ZSM-5 employed, all extrudates were exposed to at least one ion exchange at 80 °C with an aqueous solution of ammonium nitrate (2 mol/L, 100 mL per 10 g of extrudates), each followed by a further calcination at 550 °C to remove ammonia. A detailed description of the preparation of the extrudates has been reported elsewhere [10].

2.2. Characterization

The characterization of the catalysts using scanning electron microscopy, X-ray diffraction, nitrogen adsorption (BET), temperature programmed desorption of ammonia and measurements of the bulk crush strengths has been reported before [10]. Here, we only show mercury intrusion plots which characterise the pore size distributions of the matrices. These measurements were taken on an Autopore III (Micromeritics). The instrument allows for operating pressures up to 4000 bar, corresponding to a minimum pore diameter of 3 nm. Hence, the micropores of the zeolite are not detected.

2.3. MTO processing and data evaluation

MTO experiments were carried out in a continuous flow reaction unit with an isothermal fixed-bed tubular reactor (L = 350 mm, D_i = 16 mm). The voids between the extrudates were filled with silicon carbide particles (SiC, D_{particle} = 0.2 mm) to ensure a good heat transfer and to establish plug flow conditions. The volume up- and downflow to the catalyst bed was also filled with SiC (D_{particle} = 1 mm). The temperature in the bed was controlled with a coaxial thermocouple (Ni/Cr–Ni). Reaction temperatures were adjusted between 320 °C and 500 °C. At a fixed total pressure of 1.65 bar and a methanol fraction of 21.5% (v/v), weight hourly space velocities (WHSV) were varied between 2 h^{-1} and 60 h^{-1}. Note that the WHSV is related to the zeolite rather than to the total catalyst mass:

$$\text{WHSV} = \frac{\dot{m}_{\text{MeOH}}}{m_{\text{zeolite}}} \ (\text{h}^{-1}) \tag{1}$$

In some experiments, a second reactor of identical shape was used upflow to the MTO reactor in order to convert methanol to DME. The DME-reactor was filled with 8 g of γ-Al_2O_3 extrudates (without zeolite). At a constant temperature of 275 °C, the equilibrium conversion of methanol of 87.7% could be achieved. The products were analyzed on-line with a GC-FID (Agilent, capillary column: Varian, CP-PoraBond Q). Prior to the GC-analysis, an internal standard (50 mL/min, 0.5% neopentane in nitrogen) was fed to the reactor effluent. The feed composition could be analyzed by by-passing the reactor. Downstream to reactor(s) and GC-analysis, a catalytic afterburner (L = 408 mm, d_i = 106 mm, Cu/Mn-oxide catalyst) was installed. There, organic reaction products, unconverted reactants and internal GC-standard (neopentane) were combusted with air (6 l/min NTP) at 425 °C. In combination with a CO/CO_2 on-line analysis by means of IR (Hartmann & Braun, Uras 10E), the afterburner allows for a continuous monitoring of the carbon balance.

Because of the fast equilibrium reaction of methanol to DME, those two species can be lumped together to one educt. The conversion in the MTO is then defined as:

$$X_{\text{MeOH/DME}} = \frac{(\dot{n}_{\text{MeOH},0} - \dot{n}_{\text{MeOH}}) \cdot z_{\text{MeOH}} - \dot{n}_{\text{DME}} \cdot z_{\text{DME}}}{\dot{n}_{\text{MeOH},0} \cdot z_{\text{MeOH}}} \tag{2}$$

with z_i = carbon number of species i. The reactor selectivity to species i (${}^{R}S_i$) was calculated according to:

$${}^{R}S_i = \frac{\dot{n}_i \cdot z_i}{(\dot{n}_{\text{MeOH},0} - \dot{n}_{\text{MeOH}}) \cdot z_{\text{MeOH}} - \dot{n}_{\text{DME}} \cdot z_{\text{DME}}}. \tag{3}$$

It should be noticed that the major by-product water is not considered in this way as it does not contain a carbon atom.

By means of test experiments at varied feed flow velocity (and constant WHSV) it could be assured that external transport was not rate influencing. However, pore diffusion resistances may be effective at least at temperatures of 400 °C and higher as was indicated by experiments with particle fractions made of crushed extrudates. In order to obtain quantitative values, the Weisz moduli (Ψ) and the