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Journal of Catalysis 231 (2005) 194–200
JOURNAL OF CATALYSIS
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The methanol-to-olefins conversion over zeolite-coated ceramic foams

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Received 12 November 2004; revised 29 December 2004; accepted 13 January 2005

Abstract

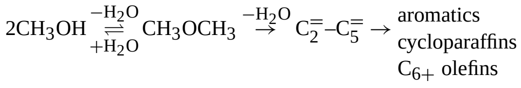
The use of ZSM-5-coated ceramic foam packing in the conversion of methanol to olefins showed substantial activity and selectivity improvements as compared with conventional extruded zeolite pellets. The formation of propylene was particularly favored over the coated foams. At 380 °C the amount of ethylene and propylene produced per unit volume of reactor packing was 2.5 times higher over the zeolite-coated foams than over pellets. However, at a lower temperature (320 °C) and higher space velocities the zeolite-coated foams were less active than the zeolite pellets. This behavior could be explained by the autocatalytic hydrocarbon pool mechanism. The species involved in the autocatalytic process, which are in equilibrium with the products, were decomposed and flushed off when the space velocity was high or the characteristic size of the catalyst bulk was too small. Thus the zeolite coat has to be optimized to ensure simultaneously a high effectiveness factor and sufficient buildup of catalytic species.

Keywords: MTO; Methanol conversion; Olefin; Hydrocarbon pool; Ceramic foam; ZSM-5; Zeolite washcoat; Structured packing; Propylene

1. Introduction

The conversion of methanol to hydrocarbons over zeolite catalysts is an alternative technology for the manufacture of petrochemicals and gasoline from feedstock other than oil, such as natural gas, coal, or biomass. A large research effort has been dedicated in the last decades to understanding the reaction mechanism, the kinetics, the influence of process parameters, the coking process, and the role of the zeolite catalyst [1–3].

The classical representation of the reaction path in the conversion of methanol to hydrocarbons comprises several consecutive reaction steps (Scheme 1), the first being the fast equilibration of methanol with its dehydration product, the dimethylether [1]. In the next step the equilibrium mixture of oxygenates is converted to light olefins. Most researchers agree that this reaction proceeds mainly autocatalytically, after the C–C–coupling has produced some light olefins. The oxygenates are considered to be bound by the previously formed olefins [4] or by a so-called hydrocarbon pool consisting of polymethylated benzenes, residing in the micropores of the zeolite lattice [5]. The light olefins are subsequently formed by cracking. For the hydrocarbon pool mechanism very convincing evidence was accumulated in the literature [5–7]. The formation of paraffins, aromatics, and higher olefins proceeds through homologation and cyclization of the light olefins. The coke, which deactivates the catalyst, probably results from the polymerization of the aromatic species contained in the hydrocarbon pool inside the micropores [8]. The conversion of methanol to hydrocarbons (MTH) can be driven toward preferential olefin production (MTO) or gasoline production (MTG) by an appropriate



$$2CH_3OH \underset{+H_2O}{\overset{-H_2O}{\rightleftarrows}} CH_3OCH_3 \xrightarrow{-H_2O} C_2^{=}\text{–}C_5^{=} \rightarrow \begin{array}{l}\text{paraffins}\\ \text{aromatics}\\ \text{cycloparaffins}\\ C_{6+}\ \text{olefins}\end{array}$$

Scheme 1.

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doi:10.1016/j.jcat.2005.01.016

choice of the catalyst/carrier system and operating conditions.

The present work is an investigation of the possibility of increasing the production of light olefins in the MTO operation mode by a convenient catalyst design. According to the reaction pathway in Scheme 1, the yield of the light olefins as intermediate products is controlled by the contact time of the reactants with the catalyst. In other words, the light olefins have to be quickly removed from the catalyst to prevent them from reacting further. As the catalytic reactor is a hierarchic system, the time needed by molecules to arrive or to leave the active centers consists of three components: (1) the time in the gas phase of the reactor (the space time); (2) the time spent in the catalyst bulk phase (grain diffusion); and (3) the time within the micropores in the zeolite crystal. Regarding the first time component, the yield of light olefins has indeed been shown to pass a maximum, whereas their selectivity continuously decreased with increasing reactor space time [9]. The third time component can be varied by means of the zeolite crystal size. Prinz and Riekert [10] have shown that the olefin selectivity increased with decreasing crystal size of the zeolite ZSM-5. Lowering the characteristic size of the catalyst bulk phase should also produce an increase in the selectivity of light olefins. However, a packing of small particles yields a high pressure drop. An alternative is to use the zeolite in the form of a coat supported on a low-pressure-drop carrier. Such an attempt was reported by Schulz et al. [11], who used fused silica spheres coated with a thin layer of HZSM-5 zeolite for the conversion of methanol to hydrocarbons.

On the basis of these considerations, a new type of MTO catalyst, consisting of a ceramic foam monolith coated with zeolite, was developed. The ceramic foams are open, tridimensionally reticulated structures build of ceramic struts that encompass polyhedric cells. The cells communicate through polygonal windows [12]. A picture of a ceramic foam carrier is shown in Fig. 1. The unconventional carrier was selected because of several considerable advantages: high porosity and permeability for gas flow, radial mixing, turbulent flow, and high geometric surface area. The mechanical strength of the ceramic foams is high enough to allow their use as catalyst carriers: their compressive strength usually amounts to 1–2 MPa (about 10–20 $\mathrm{kg/cm^2}$). The characteristic dimension of the catalyst bulk—the coat thickness—can be varied independently of the cell size of the foam. This makes it possible to decouple the hydrodynamics of the flow from the internal mass transfer characteristics of the catalyst. The foam packing can be operated at higher gas velocities required for low space-time without a considerable pressure drop. It was essential to choose a zeolite type that would ensure good stability against coking, as the fixed-bed operation requires. For this reason HZSM-5 was chosen as a catalyst. The zeolite crystals were uniform in size, which was about 500 nm. This size was chosen as a compromise between the need for a small crystal size, as shown before, and the necessity to minimize reactions on the outer, nonselective crystal surface.

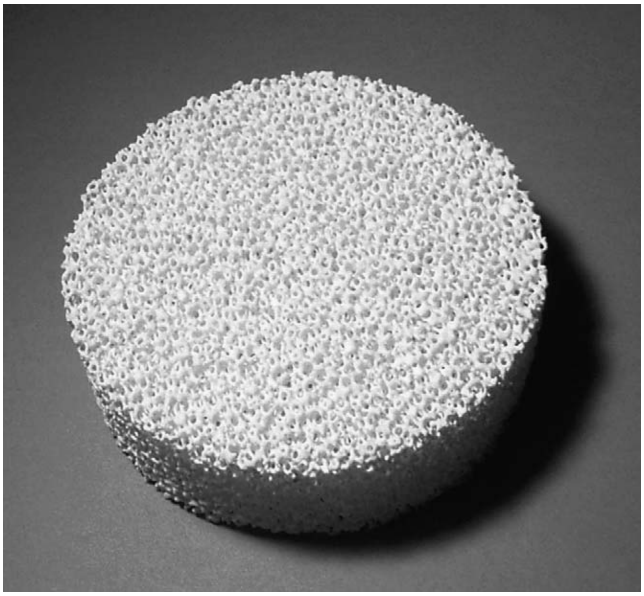

Fig. 1. Photograph of an open cell ceramic foam piece.

To assess the changes and improvements driven by the new catalyst form, the performances of the zeolite coated foam packing were compared with those of conventional extruded zeolite particles, which is one of the usual catalyst formulations for a packed bed.

2. Experimental

2.1. Preparation and characterization of the catalysts

The foam was specially designed for use as an inert catalyst carrier. It was manufactured by the polymer foam replication method without any ingredients that could interfere catalytically with the reaction studied [13]. It consisted of α-alumina bound with mullite and had a pore count of 45 PPI. The foam was pre-cut in cylindrical pieces 14 mm in diameter and 10 mm in length, to match the inner diameter of the reactor tube. The zeolite coat was applied to the foam carrier by the washcoating technique described in [14]. The coat thickness could be arbitrarily changed by the zeolite content of the coating slurry. The zeolite was ZSM-5, with a Si/Al ratio of 32 and a crystal size of 500 nm. After coating and calcination at 550 °C to remove the template, the zeolite changed to the H-form by an ion exchange with NH_4NO_3 (1.5 M, 3 h, 50 °C) followed by another calcination at 550 °C. The amount of zeolite loaded was determined by measuring the BET “surface area” (Micromeritics ASAP 2010, argon as a probe), by taking into account that the surface area of the carrier was negligible in comparison with that of the zeolite.

The cylindrical pellets (2-mm diameter, 7-mm length) were prepared from the same zeolite by extrusion with