

## EFFECT OF OXYGENATE IMPURITIES ON THE METHANOL DEHYDRATION TO DME OVER ORDERED MESOPOROUS $\gamma$ -ALUMINA AND HZSM-5

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### ABSTRACT

The catalytic performance of ordered mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and microporous HZSM-5 was tested during methanol dehydration to DME with co-fed oxygenate impurities: ethanol, isopropanol, water and propionic acid. The effect of reaction temperature on side reaction chemistry was evaluated for both catalysts. The catalysts were characterized by N<sub>2</sub> sorption, XRD, TEM, <sup>13</sup>C and <sup>27</sup>Al MAS NMR and propylamine/pyridine TPD/IR techniques. Dehydration of methanol to DME with selectivities above 99 % was achieved over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, with negligible accumulation of carbon species on the catalyst at 235 and 265 °C. On the contrary, further dehydration of DME to lower olefins and methane took place over HZSM-5 already at 235 °C. Accumulation of carbonaceous deposits and catalyst dealumination resulted in decrease of total pore volumes of up to 21 % and total acid sites of up to 18 %.

Keywords: methanol, dehydration, dimethyl ether, lower olefins.

### INTRODUCTION

Dimethyl ether (DME) is an established building block in the chemical industry, a complementary feedstock for production of C<sub>2</sub>-C<sub>4</sub> olefins [1] and an alternative for diesel fuel and liquefied petroleum gas [2]. DME can be produced from syngas via a two-stage (with methanol as the intermediate) or single stage process. The single-stage DME synthesis enables higher CO conversion. Since methanol purification via distillation is omitted in the single-stage DME process, investment costs are reduced by about 20 % and the energy efficiency is increased by about 3% [3]. The methanol dehydration reaction is catalyzed by Lewis acid-base pairs as present in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [4,5] or by Brønsted acid sites in zeolites. They are also known to catalyze further dehydration of DME to hydrocarbons [4]. This reaction decreases the DME selectivity and can result in catalyst deactivation due to pore blocking by carbonaceous deposits. In order to shed more light on the influence of impurities on catalysts' activity and stability in single stage DME synthesis, the effect of several oxygenates was investigated for the two most common solid acid catalysts for direct DME synthesis, namely  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM-5 zeolite.

### EXPERIMENTAL

Mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was synthesized according to the work of Morris et al. [6]. The HZSM-5 zeolite sample with a Si/Al ratio of 14.3 was kindly provided by Clariant. An ASAP 2000 apparatus was used for N<sub>2</sub> sorption analyses. Micropore volumes were derived from t-plots using model isotherms as reference that were calculated by the Harkins-Jura formula. The amounts of deposited carbon on spent catalyst samples were analyzed by a Vario Micro Cube CHNS elemental analyzer. DRIFT spectra were measured with a Magna-IR 560 spectrometer. Brønsted and Lewis acid site distribution was determined from FTIR spectra of adsorbed pyridine via integration of the IR bands at 1445 and 1545 cm<sup>-1</sup>. XRD patterns were recorded in sealed 0.5 mm glass capillaries on a Stoe STADI P transmission diffractometer using monochromatic Cu K<sub>α1</sub> radiation. Diffraction patterns were treated by Rietveld refinement. The solid-state NMR spectra were recorded on a Bruker Avance 500WB

spectrometer using a double-bearing standard MAS probe (DVT BL4). Morphological and structural characterization of catalysts was performed with a Hitachi H-7100 transmission electron microscope using an acceleration voltage of 100 kV. Methanol dehydration experiments were performed in an 8 mm (i.d.) stainless steel tubular reactor at 50 bar using one gram of catalyst at 235 and 265 °C. A HPLC pump was used to feed ultrapure methanol with a flowrate of 0.05 mL/min through an evaporator and into the reactor. The inlet composition was 28 % CO, 28 % H<sub>2</sub>, 5 % CO<sub>2</sub>, 4 % N<sub>2</sub> and 35 % methanol at a GHSV of 3600 h<sup>-1</sup>. The following concentrations (relative to methanol) of impurities were used: 100 ppm propionic acid (*PA*), 1 mol% ethanol (*EtOH*), 0.5 mol % iso-propanol (*IsoP*), and 10 mol% water (*H<sub>2</sub>O*). The product stream from the reactor was analyzed by GC.

## RESULTS AND DISCUSSION

Methanol conversions over microporous HZSM-5 and mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts are presented in Figure 1. With HZSM-5, time-averaged methanol conversions between 82 and 97 % were achieved. The values decreased slightly with increasing temperature, which indicates that the conversions are governed by the reaction equilibrium of methanol dehydration. In contrast, the methanol conversions were kinetically limited over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and far from equilibrium. That resulted in a substantial increase in conversion with increasing reaction temperature from 235 to 265 °C (Figure 1). Both types of catalysts exhibited stable methanol conversion during the course of our experiments, irrespective of the feed compositions.

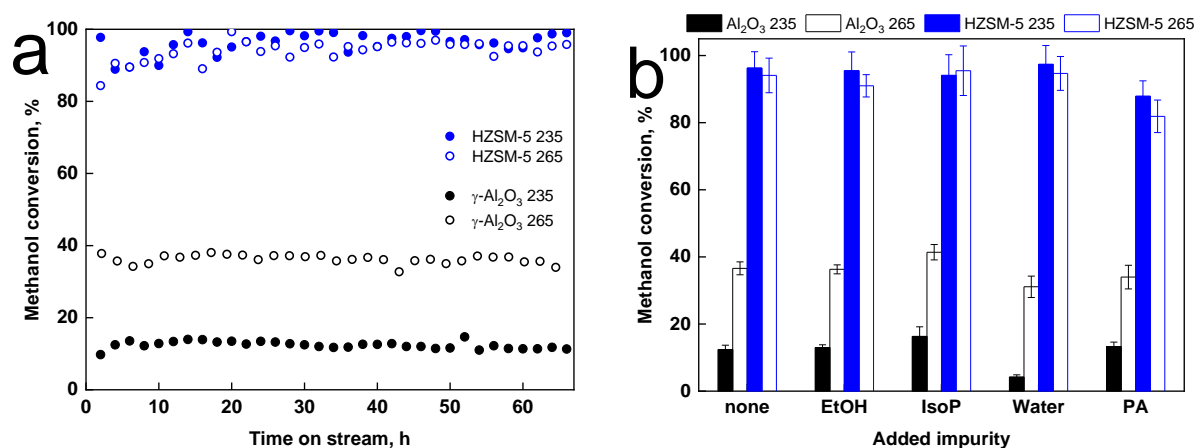


Figure 1. a) Methanol conversion over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM-5 catalysts at different temperatures as a function of time on stream for a pure methanol feed and b) average methanol conversion over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM-5 catalysts with different added impurities.

Methanol dehydration to DME over mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst occurs selectively under experimental conditions, i.e., no other reaction products than DME and water could be identified in the product gas stream. This applied for all investigated feed compositions, except the one containing ethanol as added impurity: 235 °C, trace amounts of methyl ethyl ether (0.2 % C based selectivity) were identified, along with DME and water as reaction products. Upon increasing the reaction temperature to 265 °C, also diethyl ether was found (C based selectivities of 0.7 % and 0.3 % for methyl ethyl and diethyl ether). This can be attributed to the moderate acid strength of the mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which provides preferentially Lewis acid sites that do not facilitate dehydration of alcohols or ethers to olefins. Co-feeding water with methanol (3.5 mol% based on the feed stream) resulted in a strong and instantaneous negative effect on the methanol dehydration activity over  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> at both tested reaction temperatures.

Ordered mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> with an acid site density of 162  $\mu$ mol/g was synthesized, which exhibited an ordered mesostructure with parallel cylindrical pores with an average diameter of 7.2 nm. Negligible morphological change of the ordered mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst after the catalytic tests (Figure 2) are obvious from the pore size distribution plots, the effect does not account for the reduced catalytic performance.

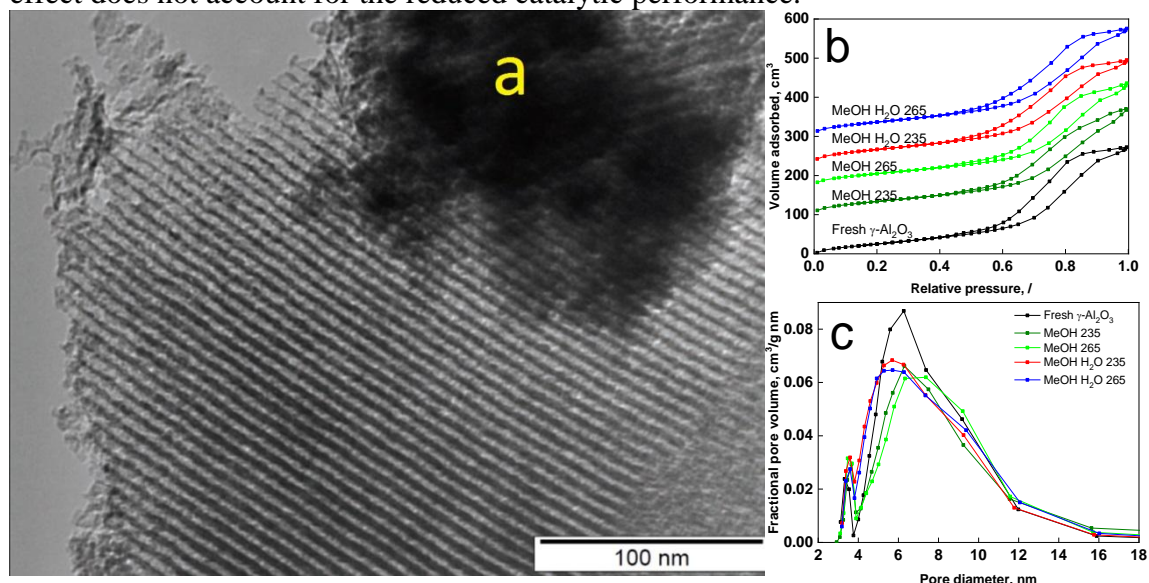


Figure 2. a) TEM micrograph of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst after 65 h of MeOH and EtOH dehydration reaction at 265 °C, b) N<sub>2</sub> sorption isotherms and c) pore size distributions of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts before and after methanol dehydration tests.

Products of methanol dehydration over HZSM-5 were primarily DME and water; in addition, side products, such as methane, ethane, ethylene, propane, propylene, and butane, were formed at low concentrations. This corresponds to a gradual transition towards methanol-to-olefin chemistry. Co-feeding ethanol resulted in formation of methyl ethyl ether, diethyl ether, and a slightly higher selectivity to C<sub>4</sub> hydrocarbons but did not result in a noticeable increase of C<sub>2</sub> selectivity. This shows that at the employed temperatures, the predominant source of C<sub>2</sub> products is methanol through dehydration of DME.

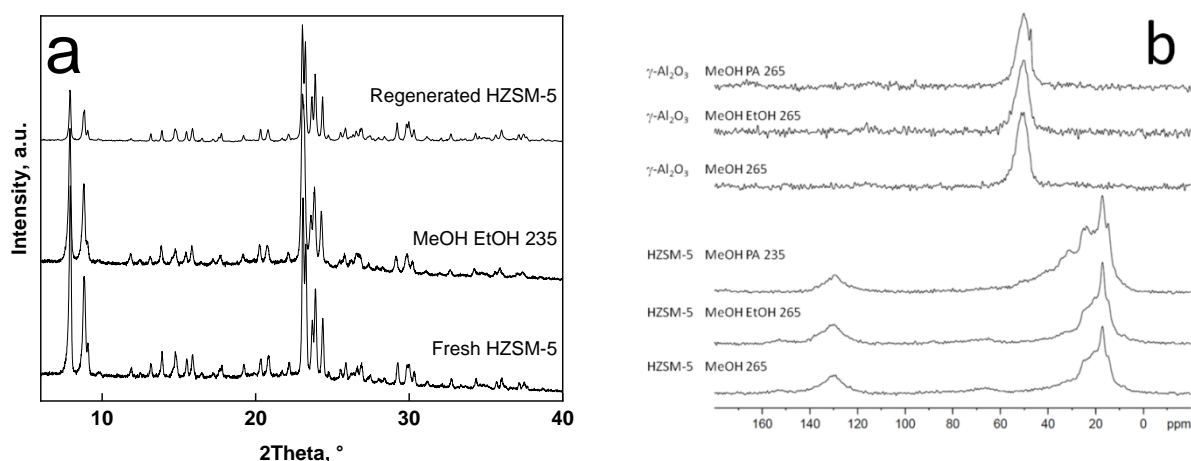


Figure 3. <sup>13</sup>C CP MAS NMR of various  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and HZSM-5 catalysts after the methanol dehydration reaction and b) XRD patterns of fresh, spent and regenerated HZSM-5 zeolite.

XRD analysis of HZSM-5 zeolite sample before and after reaction shows a pattern typical for MFI zeolite (Figure 3a). A slight shift of the diffraction peaks towards lower 2 theta values, as compared to the fresh material was observed. The reason for a unit cell

expansion were trapped hydrocarbons inside the pore system of the zeolite and causing swelling of the structure: unit cell volumes of fresh and spent HZSM-5 catalysts increased from 5398 Å<sup>3</sup> to 5449 Å<sup>3</sup>, which were calculated from cell parameters which had been derived by Rietveld refinements. Reversibility of this phenomenon was confirmed by gasification of carbonaceous deposits by heating in air at 550 °C for 1 h.

<sup>13</sup>C CP MAS NMR analysis was performed to obtain more insight into the nature of the carbonaceous deposits that had been accumulated over the catalyst surface during methanol dehydration. Spent  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts exhibit only one band at 50 ppm, characteristic of methoxy species [7] (Fig. 3b). On spent HZSM-5 catalysts, bands in the 120-140 ppm region, characteristic of sp<sup>2</sup> hybridized aromatic carbon were observed. Linear olefins also cause signals in the ranges of 120-140 and 15-30 ppm. Also several overlapping bands can be found at about 0-40 ppm. These signals are characteristic of aliphatic carbon species, namely from -CH<sub>2</sub> chain carbon (20 and 30 ppm) and terminal CH<sub>3</sub> groups (10 and 20 ppm).

## CONCLUSION

Stable catalytic performance of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> was maintained during 65 h of methanol dehydration to DME. Methanol conversions of about 15 and 35 % were achieved at 235 and 265 °C. Dehydration of methanol to DME occurs with selectivities of above 99 %. Co-feeding water at a concentration of 3.5 mol. % was found to have a highly detrimental and immediate effect on the catalytic activity, especially at 235 °C, where a 66 % decrease in methanol conversion was measured compared to a pure methanol feed. This was attributed to water causing excessive hydroxylation of the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> surface, which results in elimination of the catalytically relevant Lewis acid-base pairs. During the methanol dehydration reaction, elimination of metastable fivefold coordinated aluminium and its redistribution on tetrahedrally and octahedrally coordinated sites occurred. On the surface of spent  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples methoxy species and carbonate species were identified but no larger hydrocarbons. HZSM-5 zeolite was able to achieve and maintain equilibrium conversion of methanol to DME during 65 h of reaction. In addition, partial structural collapse and framework dealumination was observed to take place as a result of exposure to hydrothermal reaction conditions. This resulted in a decrease of up to 21 % of total pore volume and up to 18 % of total acid sites. Co-feeding of water did not exert any negative effect on the methanol dehydration activity, likely due to high conversions, which are very close to the equilibrium values. Further dehydration of DME to lower olefins and methane takes place over HZSM-5 already at 235 °C, resulting in DME selectivities between 94.9 and 97.8 %. Side products included C<sub>1</sub>-C<sub>4</sub> paraffins, olefins and ethers. In contrast to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, methoxy species could not be identified on the spent HZSM-5 catalysts.

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