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Dehydroaromatization of methane under non-oxidative conditions over bifunctional Mo/ITQ-2 catalysts

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Abstract

Bifunctional Mo/ITQ-2 catalysts have been used for the methane dehydroaromatization (MDA) reaction. The Si/Al ratio, and thus the Brønsted acidity, of the zeolite affected the conversion, the formation rate of aromatics, and the selectivity to the different products (CO, C_2, benzene, toluene, and naphthalene). Maximum activity and aromatics productivity were obtained for the zeolite with the lowest Si/Al ratio (Si/Al = 15) presenting the highest Brønsted acidity, while maximum benzene selectivity ($\sim$70%) occurred for the zeolite with Si/Al = 25. The selectivity to naphthalene increased with decreasing the Si/Al ratio, that is, with increasing the density of surface Brønsted acid sites. At comparable Si/Al ratio, Mo/MCM-22 was more active and selective to benzene than Mo/ITQ-2. Reduction of surface acidity in ITQ-2 by treatment with oxalic acid significantly reduced the formation of naphthalene, resulting in enhanced benzene selectivity ($\sim$75%). The acid-treated ITQ-2 was even more selective to benzene than the Mo/MCM-22 catalyst ($\sim$65%). Molecular dynamics simulations were performed at the MDA reaction temperature (973 K) to study the diffusion of naphthalene in the two independent pore systems of MCM-22. The theoretical results allowed explaining the differences in selectivity between the two zeolite structures and the effect of surface dealumination in ITQ-2.

Keywords: Methane dehydroaromatization; Bifunctional catalyst; Molybdenum; Delaminated zeolite; ITQ-2; Molecular dynamics simulation

1. Introduction

The direct conversion of methane to fuels and high-value chemicals still remains as one of the most important challenges in the field of heterogeneous catalysis [1]. Recently, Wang et al. [2] reported the direct conversion of methane under non-oxidative conditions into aromatics and hydrogen over a Mo/HZSM-5 catalyst. Since then, numerous studies have been devoted to the methane dehydroaromatization (MDA) process, with special emphasis into the optimization of the catalyst system and reaction conditions, the nature of active sites and reaction mechanisms, the interactions between the transition metal(s) and the zeolite support, and the role of carbonaceous deposits in the reaction [3].

A relevant aspect of the MDA reaction is the templating role of the zeolite micropores in determining the product selectivity, as recently reviewed by Shu and Ichikawa [4]. Indeed, although under typical MDA reaction conditions (973 K, 1 atm) naphthalene is the thermodynamically favored product, the Mo/HZSM-5 catalyst promoted the selective formation of benzene owing to the shape selectivity imposed by the 10 member-ring (10 MR) channels, which prevent the formation of the bulkier naphthalene molecule [5]. Recently, Mo/HMCM-22 catalysts have been found to produce higher yields of benzene and to exhibit better coke tolerance in comparison with Mo/HZSM-5 at comparable reaction conditions [6,7]. These properties were related to the particular topology of the MCM-22 zeolite. On one hand, the lower size of the pore entrances in MCM-22 (0.40 nm × 0.59 nm in the sinusoidal interlayer 10 MR system, and 0.40 nm × 0.54 nm in the channel containing the 12 MR supercages) with respect to ZSM-5 (0.53 nm × 0.56 nm in the straight channel running parallel to [0 1 0] and 0.51 nm × 0.55 nm in the sinusoidal channel running parallel to [1 0 0]) may favor the formation of benzene in detriment of the bulkier naphthalene product. On

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the other hand, the better coke tolerance was ascribed to the presence of the large 12 MR cavities in MCM-22 acting as a trap for coke molecules.

Recently, a new material, called ITQ-2, has been prepared in our laboratories by delamination of the layered precursor of MCM-22 [8]. The delaminated zeolite is mostly formed by single layers organized in a ''house of card''-type structure having a very high external surface area. ITQ-2 consists of thin sheets 2.5 nm in height presenting a hexagonal array of ''cups'' (0.7 nm × 0.7 nm) that penetrate into the sheet from both sides connected by a double 6 MR window. These ''cups'' are the hemicavities related to the 12 MR supercages present in MCM-22 and which act as a coke trap during the MDA reaction. The sheets contain the 10 MR sinusoidal channel system of 0.40 nm × 0.59 nm size that is also present in MCM-22 and which is apparently responsible for the high selectivity of benzene displayed by Mo/HMCM-22 catalysts.

In view of this, in this work we have studied the possibilities of using the delaminated ITQ-2 zeolite as the acidic component of Mo-based MDA catalysts. The influence of the zeolite Si/Al ratio and of the surface dealumination on the activity and selectivity will be addressed. The catalytic properties of Mo/ITQ-2 will be compared with those of Mo/MCM-22 with the same Si/Al ratio. A thorough Molecular Dynamics simulation study of the diffusion of naphthalene at the MDA reaction temperature (973 K) in the two independent pore systems of MCM-22 has also been carried out. The results obtained allow accounting for the differences in selectivity found between the ITQ-2 and MCM-22 zeolites, as well as for the effects of the selective dealumination of the ITQ-2 external surface on product selectivity.

2. Experimental

2.1. Preparation of catalysts

The layered precursor of MCM-22, denoted as MCM-22(P), was synthesized using hexamethylenimine (HMI), silica (Aerosil 200, Degussa), sodium aluminate (56% Al_2O_3, 37% Na_2O, Carlo Erba), sodium hydroxide (98%, Prolabo) and deionized water, following the procedure reported in [8]. Thus, a gel of the following molar composition:

$SiO_2{:}xAl_2O_3{:}0.10OH{:}0.18\ Na{:}44.9\ H_2O{:}0.50HMI$

was prepared and crystallized in Teflon-lined stainless steel autoclaves at 423 K for 9 days. The concentration of Al in the synthesis gel was varied to obtain samples with Si/Al ratios of 15, 25, and 50. After crystallization, the solids were washed with deionized water and dried at 373 K to produce the layered precursor MCM-22(P). Then, the MCM-22(P) was swelled by mixing the solid with an aqueous solution of hexadecyltrimethylammonium bromide (CTABr) and an aqueous solution of tetrapropylammonium hydroxide (TPAOH, 40 wt.%), and the resulting solution was refluxed for 16 h at 353 K. The layers were forced apart by placing the slurry in an ultrasound bath (50 W, 40 kHz) for 1 h. Separation of the solids was done by acidification with concentrated hydrochloric acid (HCl, 37%) until the pH was below 2, followed by centrifugation. Calcination of the materials at 813 K yielded the ITQ-2 samples with different Si/Al ratios. These samples were denoted as I2-*y*, where *y* is the Si/Al ratio in the synthesis gel. A MCM-22 sample with Si/Al ratio of 15 was also prepared by calcination of the layered MCM-22(P) precursor (Si/Al = 15) at 853 K for 3 h. This sample was denoted as M22-15.

The calcined ITQ-2 sample with Si/Al ratio of 15 was submitted to a surface dealumination process with a 1.5 M aqueous solution of oxalic acid (99%, Fluka) at reflux and 343 K during 1.5 h using a liquid/solid ratio of 12 cm^3/g. After cooling at room temperature, the solid was filtered, extensively washed with deionized water, dried at 373 K, and finally calcined in a muffle at 773 K for 6 h. The acid-treated sample was denoted as I2-15-ox.

Molybdenum-containing catalysts were prepared by incipient wetness impregnation of the zeolite supports with an aqueous solution of ammonium heptamolybdate (Merck) to obtain a concentration of Mo in the final catalysts of 3 wt.%. After impregnation the materials were dried at 373 K and then calcined in a muffle oven at 773 K for 6 h.

2.2. Characterization of the materials

Powder X-ray diffraction was performed in a Philips X'pert diffractometer using monochromatized Cu Kα radiation to verify the quality of the synthesized zeolites. Textural properties of the zeolites and Mo-containing catalysts were obtained from the nitrogen adsorption isotherms measured at 77 K in a Micromeritics ASAP 2000 equipment. Surface areas were calculated by the BET method; micropore area and micropore volume were derived from the corresponding *t*-plots. External surface areas were then obtained by difference between the BET values and the micropore areas. Prior to the adsorption measurements the samples were degassed at 673 K and vacuum overnight.

X-ray photoelectron spectra (XPS) were acquired in a VG-Escalab-210 spectrometer using the Mg Kα radiation (1253.6 eV) operated at 20 mA, 10 kV, and a pass energy of the analyzer of 50 eV. The binding energy (BE) data were referenced to C 1s (284.5 eV). ^{27}Al solid-state nuclear magnetic resonance (NMR) spectra were recorded at room temperature in a Bruker AV400 spectrometer working at 104.2 MHz, using a 4 mm Bruker BL4 probe. Samples were packed into zirconia rotors and spun at the magic angle spinning (MAS) at rates of ca. 12 kHz. The ^{27}Al spectra were acquired with pulses of 0.5 μs corresponding to a flip angle of $\pi/20$ and were referred to a 0.1 M aqueous solution of $Al(NO_3)_3$.