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Impact of post-synthetic treatments on unidirectional H-ZSM-22 zeolite catalyst: Towards improved clean MTG catalytic process

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In the present study, a series of H-ZSM-22 mesoporous catalysts resulting from three different desilication treatments (NaOH treatment, treatment using mixtures of NaOH/CTAB and using mixtures of NaOH/TBAOH) and sequential acid leaching over two different (commercial and lab-made) microporous ZSM-22, were tested in the conversion of methanol to hydrocarbons. The influence of the post-synthetic treatments on the catalytic lifetime and product distribution was examined. The influence of the starting catalysts on the change in the catalyst properties was also reflected in the catalytic behaviour. An increase of about 10 times in total methanol conversion capacity with respect to the untreated catalyst was reached after the CTAB/NaOH and acid treatment over the commercial material, whereas a 17-fold increase in conversion capacity was achieved for the lab-made catalysts treated with NaOH and acid. The yield towards the aromatic-free C_{5+} alkene fraction was slightly increased after the post-synthetic treatments, up to 58% of clean gasoline product precursors. The correlations between porosity, acidity and total conversion capacity suggested a more efficient use of the hierarchical catalyst particle as a result of a synergetic effect of mesopore formation, enhanced accessibility to the micropores and acid sites, and increased adsorption and transport properties. Mechanistic information extracted from the analysis of the C_3/C_2 and ethene/2M2B ratios, suggested that the improved catalyst properties allow a longer propagation of the olefin cycle with reaction time.

1. Introduction

The conversion of methanol to hydrocarbons (MTH) constitutes the last stage of the route to produce high-value petrochemical products from low valuable feedstock as natural gas, coal or biomass via syngas [1–3], and represents a real alternative to the most used processes which exploit the dwindling global oil reserves to produce energy carriers [4]. The MTH reaction proceed over acidic zeolite or zeotype materials, known as shape selective catalysts, since they are able to discriminate reactants, products and reaction intermediates based on their molecular size [5]. The acid sites responsible for the methanol conversion are located inside the pores and channels of the zeolite crystal and catalyse the multiple reactions of the MTH process, which can be tuned to produce gasoline-rich or olefin-rich products by choosing the appropriate catalyst architecture, composition and reaction conditions [2,6,7]. Currently, with the rise of oil prices, intense commercialization efforts are ongoing for ZSM-5 based methanol to gasoline (MTG) and SAPO-34 based methanol to olefins (MTO) technologies [1].

The major drawback of the existing ZSM-5 based MTG process is the content of carcinogenic aromatic compounds in the produced gasoline, which is high considering the environmental restrictions on the composition of transportation fuels. However, recent investigations have shown that this problem can be surpassed by using H-ZSM-22 as the active catalyst for the process. The ZSM-22 zeolite with TON topology has a one directional pore structure comprising non-intersecting 10-ring channels [8]. Due to this specific pore architecture, it possess unique shape selective properties and is able to selectively yield a product mixture that is intermediate to that found for SAPO-34 and ZSM-5, being rich in C_{5+} branched alkanes and alkenes and virtually without aromatics [9]. The mechanistic interpretation is based on the fact that the aromatic molecules only participate in one of the cycles of the MTH dual cycle mechanism and, by using H-ZSM-22, the aromatic cycle can be suppressed, thus producing a product virtually free of aromatics [2,10,11]. Therefore, the H-ZSM-22-based MTH product might meet the present fuel demands and might be suitable as gasoline after hydrogenation. Alternatively, the alkene rich product might be utilized as an alkylation feedstock to increase the carbon number and

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provide saturation. Currently, however, the process is far from becoming a commercial reality, owing the short lifetime or rapid deactivation by coke deposition, resulting in a limited methanol conversion capacity for the H-ZSM-22 catalyst [2,9].

Since H-ZSM-22 has one-directional non-interconnected channels, its acid sites are only accessible by the rare ends of the crystals. This gives rise to molecular transport limitations within the zeolite micropores. This weakness can be overcome by introducing a secondary network of pores within the existing micropore system of the zeolite, i.e. producing mesoporous zeolites. As pointed out by the numerous literature reviews, several synthetic approaches have been developed to overcome the diffusion limitations and to obtain improved catalysts for different processes [12–19]. The so-called hierarchical materials have shorter diffusion pathways for the reaction intermediates and products and allow catalytic reactions proceed on the mesopore surface and in the pore mouths. Concerning the MTH reaction, most of the research has been dedicated to obtain mesoporous ZSM-5 zeolites by desilication with alkaline treatment [20,21], surfactant-assisted solutions [22–24], or different processes [25,26]. The general effect of the mesoporosity is an increased lifetime. This is attributed to a more efficient use of the catalyst crystal which results in an increased resistance towards coking, lower rates of coke formation or formation of coke species mainly on the external surface of the catalyst. Additionally, a significant increase in the propene and C_{5+} selectivities was demonstrated in MTG or MTO studies over ZSM-5 [20,26]. The influence of the connectivity and location of the mesopores and acidity modifications on the catalytic properties is, however, still under debate [26–28].

Intuitively, the introduction of mesoporosity lead to a superior catalytic performance for zeolites which are more predisposed to suffer from diffusion limitations, such as one-dimensional systems with medium sized pores. This has been demonstrated with TON zeolite catalysts in isomerization and cracking reactions, for which pore mouth catalysis plays a significant role [29–33]. However, to the best of our knowledge, very few studies compare mesoporous and microporous H-ZSM-22 catalysts in the MTG reaction. We have previously conducted time- and space-resolved high energy *operando* XRD measurements to evaluate differences in activity and deactivation behaviour between two such catalysts during MTH reaction and found that methanol appears to be the main source of coke and that the formation of deactivating species is independent of the co-presence of products in the TON topology [34]. In a very recent study, Dyballa et al. focused on the MTO conversion over mesoporous ZSM-22 zeolite synthesized by alkaline desilication and subsequent acid treatment [35]. It was found that the lifetime was enhanced by a factor of 2 for the mesoporous catalysts with an optimal Brønsted acidity, accompanied by a highest propene selectivity of 48%. Furthermore, the product spectrum obtained for the purely microporous and the mesoporous catalyst was very similar, suggesting that the 10-ring pore system governs the shape selective properties of the H-ZSM-22 catalyst in MTO.

An extensive characterization study of mesoporous ZSM-22 zeolites prepared from two different parent materials by three different desilication approaches (using NaOH, mixtures of CTAB/NaOH and mixtures of TBAOH/NaOH) followed by acid leaching is presented in the complementary article [36]. The decisive effect of the morphology of the starting material and of the different desilication agents on the mesopore creation, and also the need of the acid washing step to improve the accessibility to the acidic sites in the zeolites were highlighted. In this contribution, we investigate the MTG catalyst performance of the same materials. Two different H-ZSM-22 samples were used as starting materials with the aim to correlate the properties of the starting material with the resulting catalyst performance seen for the treated material. One catalyst sample derived from each post-synthetic approach was chosen. These samples showed generally higher surface area, larger micropore volume and more accessible acid sites. First, we will recapitulate the most relevant results from the characterization study. Second, the changes in catalyst lifetime and product distribution will be examined. In the last part of this contribution, we aim to elucidate the causes of the significant improvement in catalyst performance observed for the hierarchical catalyst by analysing the porosity and acidity features and also the diffusion properties and degree of accessibility to the micropore volume and acid sites.

2. Experimental section

2.1. Catalyst preparation

In this study, two microporous H-ZSM-22 catalyst samples will be compared with their desilicated and acid-washed (mesoporous) counterparts. The parent commercial H-ZSM-22 (supplied by Zeolyst International) and the lab-made H-ZSM-22 (synthesized following the procedure described elsewhere [9]) catalysts are coded *c*-ZSM-22 and *m*-ZSM-22, respectively. The mesoporous zeolites were prepared by three desilication approaches, described previously in the complementary article [36]. The same sample codes will be used throughout the present work. For clarification, the post-synthetic treatments and sample codes are summarized in Table S1, and comprises: treatment with NaOH (0.2 M, 80 °C, 2 h, 33 g of zeolite per liter of solution), treatment with a mixture of NaOH/CTAB (0.25 M NaOH and 0.05 M CTAB, 80 °C, 24 h, 50 g l^{-1}), and treatment with a mixture of NaOH/TBAOH (0.12 M NaOH and 0.08 M TBAOH, 65 or 80 °C, 0.5 h, 30 g l^{-1}). Each desilication approach was followed by acid washing in HCl (0.1 M, 65 °C, 6 h, 10 g l^{-1}). The treated materials are coded with the suffix *-at1-HCl*, *-ats1-HCl* and *-tba1(2)-HCl*, respectively. The parent commercial zeolite was also treated with HCl at the same conditions (*c*-ZSM-22-*HCl*), for comparative purposes. All the zeolites were ion exchanged with 1 M NH_4NO_3 solution for 3 × 2 h at 75 °C, followed by calcination in static air at 550 °C for 2 h to obtain the protonated form.

2.2. Characterization methods

The crystallinity and purity of the catalysts were checked with PXRD. The Si/Al ratio was determined by elemental analysis using a MP-AES instrument. The size and morphology of the zeolite particles were analysed by TEM. The surface area, pore volume and pore size distribution were determined from N_2 physisorption. The amount of oxidable coke of the spent catalysts was analysed by TGA. The nature and accessibility of acid sites were investigated using FTIR spectroscopy with CO and pyridine as probe molecules. The accessibility and diffusion properties were investigated with time-dependent uptake of toluene monitored by IR. Experimental details are given in the Supporting Information.

2.3. Catalytic testing

All the catalytic tests were performed at ambient pressure using 50 mg of sample in a fixed-bed quartz reactor with 10 mm outer diameter, 7 mm inner diameter. The protonated zeolite was pressed into wafers, crushed and sieved to obtain particles in the 250–420 μm range. Before each catalytic experiment the samples were calcined in situ in a flow of pure oxygen at 550 °C for 1 h. Methanol (BDH Laboratory Supplies, > 99.8%) was fed by passing He through a saturation evaporator kept at 20 °C (p_{MeOH} = 130 mbar). Catalytic tests were performed at 400 °C and a weight hourly space velocity (WHSV) of 2 g feed per g catalyst per hour. The product stream was analysed online using an automatic injection Gas Chromatograph (GC) connected to the reactor outlet by a heated transfer line. An Agilent 6890N Gas Chromatograph with FID, equipped with a HP-PLOT Q capillary column (15 m, 0.320 mm i.d. film thickness 20 μm) was used for the analysis. The temperature of the GC oven was programmed between 90 and 270 °C with a heating rate of 20 °C/min (hold time of 5 min at 90 °C and at 220 °C and 9 min at 270 °C).