On the synthesis of highly acidic nanolayered ZSM-5

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ABSTRACT

Nanolayered ZSM-5 zeolites were synthesized at high framework Al content. Crystallization of ZSM-5 zeolite synthesis gel at Si/Al ratio of 20 at 423 K using $C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-R$ (R = hexyl or propyl) as structure-directing agents resulted in amorphous product. When the hydrothermal synthesis was carried out at 443 K instead of 423 K, crystalline nanolayered ZSM-5 zeolites were obtained. By replacing the hexyl end group by propyl, the crystallization rate increased due to increased occupancy of the intersections of the MFI framework by quaternary ammonium centers. Optimized hydrothermal synthesis at Si/Al = 20 (443 K, NaF addition) with this surfactant resulted in highly crystalline nanolayered ZSM-5 zeolite. Not all Al atoms are built into the zeolite framework, which limits the overall Brønsted acidity. The catalytic performance in *n*-heptane hydroisomerization of the various zeolites trends well with the Brønsted acid site density. The product distribution during *n*-heptane hydroisomerization points to an increased rate of product desorption (higher isomers' selectivities and increased selectivity of dibranched isomers). The nanolayered ZSM-5 zeolites outperform bulk ZSM-5 zeolite in the methanol-to-hydrocarbons reaction in terms of the methanol conversion capacity.

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1. Introduction

Zeolites are crystalline microporous aluminosilicates, which have been widely used as acidic catalysts for hydrocarbon conversion reactions since the early 1960s [1–3]. Their usefulness as catalysts for size- and shape-selective hydrocarbon conversion stems from the strong Brønsted acid sites that are mainly located in the micropores [4]. The Brønsted acid sites of zeolites arise from the Al^{3+} substitutions for tetrahedral Si^{4+} in the crystalline silica framework. For high-silica zeolites, the total Brønsted acidity can be directly related to the framework Si/Al ratio [5]. Despite these favorable properties, the location of the acid sites in pores typically smaller than 1 nm embedded in zeolite crystals with dimensions of several microns may result in mass transport limitations during catalytic reactions [6]. Various strategies can be applied to overcome these limitations; they include reducing the size of the zeolite crystals [7], delaminating zeolite frameworks [8], synthesizing zeolites with extra-large pores [9–11], and introducing additional mesoporosity in zeolite crystals [12–16]. Considerable attention has been given to the latter approach; such zeolites are generally known as hierarchical zeolites, emphasizing the presence of interconnected micro- and mesopore systems. The approach of

Ryoo and co-workers to use diquaternary ammonium-type surfactants to synthesize nanolayered ZSM-5 zeolite was a breakthrough [17]. The thickness of these ZSM-5 layers can be controlled by varying the number of ammonium groups in the hydrophilic head group of the multiquaternary ammonium-type surfactants [17–19]. Several recent studies highlight the promise of such nanostructured zeolites in catalysis [20–23].

The synthesis of nanolayered ZSM-5 with diquaternary ammonium surfactants (*e.g.*, $C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}Br_2$, abbreviated to $C_{22-6-6}\cdot Br_2$) requires longer crystallization times than synthesis of bulk ZSM-5 with tetrapropylammonium as the structure-directing agent. The crystallization time increases when the Si/Al ratio of the synthesis gel is decreased. The initial work of the Ryoo group reported nanolayered zeolite synthesized at Si/Al ratios around 50. We found that decreasing the Si/Al below 40 predominantly resulted in amorphous aluminosilicates product [25]. Ryoo and co-workers mentioned that the synthesis of nanolayered ZSM-5 at low Si/Al ratio did not result in a fully crystalline product, even not if the synthesis was prolonged to two weeks [18]. It has been speculated that the structure-directing agent decomposes during such prolonged hydrothermal treatment. One solution to overcome slow nucleation is to use bulk ZSM-5 seeds [24]. In this way, hierarchical ZSM-5 zeolite with a sponge-like mesostructure can be obtained, even at relatively high Al content.

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In the present work, we explored the synthesis of nanolayered ZSM-5 zeolite by use of diquaternary ammonium surfactants of the Ryoo type [17] with the aim to obtain crystalline acidic zeolites at a target Si/Al ratio of 20. The starting point of this study was the realization that the hexyl end group of the diquaternary $C_{22-6-6}·Br_2$ surfactant is too bulky to allow for complete filling of all intersections of nanolayered ZSM-5 (Fig. 1). This limits the charge compensation of the negative framework by the surfactant and helps to explain why crystallization of nanolayered ZSM-5 at low Si/Al ratio is very slow. When the hexyl end group is replaced by a propyl end group, complete filling of intersections of the final zeolites is in principle possible as shown in Fig. 1. In addition to varying the structure of the diquaternary ammonium surfactant, we used NaF as an additive to the synthesis gel to accelerate crystallization. The resulting nanolayered zeolites were characterized by XRD, SEM, TEM, Ar physisorption, and UV-Raman and ^{27}Al and ^{29}Si NMR spectroscopy. The acidic properties of the zeolites were determined by IR spectroscopy using carbon monoxide, pyridine, and 2,4,6-collidine as probe molecules. The catalytic performance of the nanolayered zeolites was compared with a bulk ZSM-5 zeolite in *n*-heptane hydroisomerization and methanol conversion reactions.

2. Experimental procedures

2.1. Synthesis of surfactants

$[C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}]Br_2$ (denoted as $C_{22-6-6}·Br_2$): For synthesis of $C_{22-6-6}·Br_2$, we followed the procedure outlined before [17,26]. 3.9 g (0.01 mol) of 1-bromodocosane (TCI, 98%) was dissolved in 50 ml toluene (Biosolve, 99.5%) and added dropwise into a mixture of 50 ml acetonitrile (Biosolve, 99.8%) and 21.4 ml (0.1 mol) N,N,N′,N′-Tetramethyl-1,6-hexanediamine. The reaction was refluxed in an oil bath at 343 K for 12 h. The solution was cooled to room temperature, which led to the precipitation of a white solid. The suspension was further cooled at 277 K for 1 h. The white solid (N-(6-(dimethylamino)hexyl)-N,N-dimethyldocosan-1-aminium bromide; $C_{22-6}·Br$) was filtered and washed with diethyl ether (Biosolve, 99.5%).

5.6 g of $C_{22-6}·Br$ and 3.4 g of 1-bromohexane (Aldrich, 98%) were dissolved in 100 ml acetonitrile and 10 ml ethanol (Biosolve, 99.8%). The resulting solution was refluxed at 343 K for 12 h. After cooling to room temperature, the white solid ($C_{22-6-6}·Br_2$) was filtered and washed with diethyl ether. The product was dried overnight at 323 K under vacuum.

$[C_{22}H_{45}-N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_3H_7]Br_2$ (denoted as $C_{22-6-3}·Br_2$): We first prepared $C_{22-6}·Br$ as outlined above.

Then, 5.6 g of $C_{22-6}·Br$ and 2.5 g of 1-bromopropane (Aldrich, 99%) were dissolved in 100 ml acetonitrile and 10 ml ethanol. The solution was refluxed in an oil bath at 343 K for 12 h. After cooling to room temperature, the white solid ($C_{22-6-3}·Br_2$) was filtered and washed with diethyl ether. The product was dried overnight at 323 K under vacuum.

2.2. Synthesis of materials

2.2.1. Synthesis of nanolayered ZSM-5 zeolites

1.4 g of $C_{22-6-6}·Br_2$ was dissolved in 7.8 ml deionized water at 333 K. 0.21 g of NaOH (Merck, 99%) was added to the clear template solution, followed by stirring at 323 K for 4 h. A second solution was made by mixing 0.1 g $Al(OH)_3$ (Aldrich, reagent grade), 10 ml deionized water, and 5.54 ml TEOS (Merck, 99%) for 1 h. After cooling the solution with the surfactant to room temperature, the silica solution was added dropwise under vigorous stirring. This resulted in a white suspension. The suspension was stirred for 1 h in an open vessel at room temperature. The resulting gel was transferred to a Teflon-lined stainless steel autoclave. The autoclave was heated under rotation (60 rpm) at 423 or 443 K for 5 days. In some cases, 0.1 g NaF (Merck, 99.5%) was added along with $Al(OH)_3$ to the starting gel. The synthesis of nanolayered ZSM-5 zeolites with a Si/Al ratio of 50 was done in a similar manner as described above. Bulk ZSM-5 (ZSM-5-bulk) was synthesized with tetrapropylammonium hydroxide (Merck, 40%) as the structure-directing agent. The details of the zeolite syntheses are collected in Table 1. In all cases, a white solid was recovered from the autoclave by filtration. The solid was washed with copious amounts of deionized water, followed by drying overnight at 383 K. The yields of the syntheses that yielded predominantly ZSM-5 zeolites are listed in Table S1.

2.2.2. Post-treatment of zeolites

The organics were removed from the as-synthesized zeolites by calcination in flowing air. The zeolite sample was placed in an oven. The temperature was increased at a heating rate of 1 K min^{-1} to 823 K followed by an isothermal period of 6 h. The proton forms of the zeolites were obtained by triple ion-exchange of the calcined zeolite with a 1 M NH_4NO_3 solution at 353 K for 2 h and intermediate calcination in air at 823 K for 4 h. The zeolites are denoted as follows: ZSM-5(x, y, T) with x representing the terminated group of surfactants, y the Si/Al ratio in the starting gel, and T the temperature of hydrothermal synthesis step. The zeolites synthesized with promoter NaF are denoted by ZSM-5-F(x, y, T).

2.3. Catalyst characterization

2.3.1. Basic characterization

X-ray diffraction patterns were recorded on a Bruker D4 Endeavor diffractometer using Cu Kα radiation in the 2θ range 5–60°. Elemental analyses were carried out by ICP-OES, and
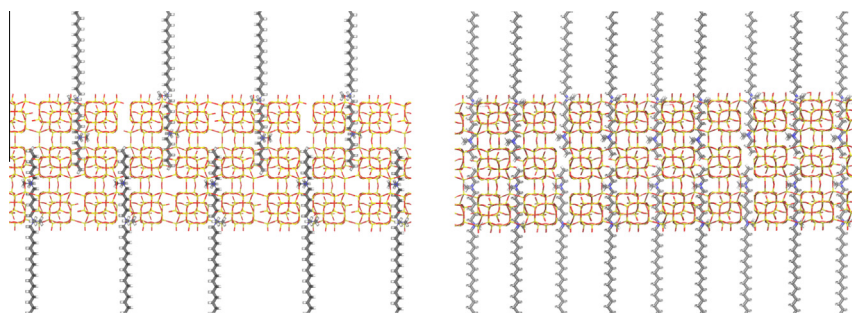
Fig. 1. Minimum-energy configuration of (left) $C_{16}H_{33}N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_6H_{13}$ and (right) $C_{16}H_{33}N^+(CH_3)_2-C_6H_{12}-N^+(CH_3)_2-C_3H_7$ in a nanolayered silicalite-1 framework (the dimension in the *b*-direction is approximately 2.4 nm; only diquaternary surfactants in which at least one quaternary ammonium is embedded in the zeolite are shown; simulations done with the CVFF forcefield in Materials Studio).