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Comparison of mesoporous SSZ-13 and SAPO-34 zeolite catalysts for the methanol-to-olefins reaction

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ABSTRACT

Several approaches to improve the catalytic performance of SSZ-13 and SAPO-34 for application as acid catalysts in the methanol-to-olefins (MTO) reaction were explored. Silylation of mesoporous SSZ-13 with a Si/Al ratio of 20 zeolite resulted in increased lifetime in the MTO reaction. Lowering the acidity of SSZ-13 by increasing the Si/Al ratio to 50 also increased the lifetime. The generation of additional mesoporosity in SSZ-13 with a Si/Al ratio of 50 by use of the organosilane octadecyl-(3-trimethoxysilylpropyl)-ammonium chloride (TPOAC) only resulted in a minor improvement of the lifetime. Attempts to synthesize mesoporous SSZ-13 at high Si/Al ratios by use of $(C_{22}H_{45}{-}N^{+}(CH_3)_2{-}C_4H_8{-}N^{+}(CH_3)_2{-}C_4H_9)Br_2$ $(C_{22\text{-}4\text{-}4}Br_2)$ were unsuccessful, and instead ZSM-5 zeolite was obtained. Similarly, SAPO-34 could not be made hierarchical by using $C_{22\text{-}4\text{-}4}Br_2$ as a mesoporogen. In this case, other AlPO-phases were obtained. Mesoporous SAPO-34 was synthesized by using TPOAC in the synthesis gel. The additional intracrystalline mesoporosity did not lower the deactivation rate of SAPO-34 as was earlier observed for SSZ-13. The total methanol conversion capacity per acid site for microporous and mesoporous SAPO-34 were however comparable. The lower acidity of the acid sites in SAPO-34 led to the complete utilization of the micropore space. This is to be contrasted to SSZ-13 zeolite, for which the increased rate of coke formation results in more extensive coking deactivation and underutilization of the micropore space.

1. Introduction

Light olefins are key chemical intermediates in the petrochemical industry, which are usually produced through non-catalytic cracking of petroleum feedstock. With the growing importance of alternative feedstocks, most notably cheap natural gas and coal, there is now growing interest in methanol as a chemical intermediate of the synthesis of olefins. The methanol-to-olefins (MTO) reaction has been intensively studied in the last decades [1–5]. HSAPO-34, a silicoaluminophosphate having the chabazite (CHA) pore topology is the commercial catalyst for the MTO reaction. The relatively low acidity of silicoaluminophosphates and the combination of large cavities with a diameter of 9.4 Å, which stabilize the methylated benzene catalytic intermediates, with small 8-ring pore openings (3.8 Å) result in high selectivity to light olefins, typically above 80%. An inherent drawback of HSAPO-34 as MTO catalyst, which is typical for methanol-to-hydrocarbons (MTH) conversion reactions in zeolites, is deactivation due to formation of carbonaceous deposits. This requires intermittent regeneration of the catalyst in commercial operation. In China, the MTO process is being commercialized on a large scale as part of chemical plants that convert cheap coal via gasification to syngas followed by methanol manufacture, light olefin and polymer production [6]. Catalyst deactivation is delt with by carrying out the MTO reaction in a fluidized bed with a regenerator in which part of the coke is burnt. This capital-intensive process would benefit from catalysts with a longer lifetime, because the size of the regeneration section could be reduced [7].

Recently, we have been shown that the introduction of mesopores in HSSZ-13 crystals results in a substantial decrease of the negative effect of coke formation [8,9]. Further characterization of mesoporous and conventional HSSZ-13 showed that the better accessibility of the micropores results in more complete utilization of the micropore space for the MTO reaction. For the synthesis of mesoporous HSSZ-13, we were inspired by the approaches developed by the Ryoo group [10–12]. We employed a combination of a structure-directing agent (SDA) for CHA formation (trimethyladamantanammonium hydroxide) with a mesopore-generating template $C_{22}H_{45}{-}N^{+}(CH_3)_2{-}C_4H_8{-}N^{+}(CH_3)_2{-}C_4H_9)Br_2$, identified by predictive computational modeling. Our approach was recently

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shown to be more generally applicable for a wide range of zeolites [13]. When applied in the MTO reaction the presence of interconnected micro- and mesoporosity in HSSZ-13 substantially increases the total methanol conversion capacity [8,9]. The mesoporous HSSZ-13 zeolites exhibited a much greater lifetime than conventional HSSZ-13 in the MTO reaction at nearly similar light olefins yield. The increased lifetime is explained by better utilization of the micropore space. There are two competing effects of the introduction of mesoporosity: (i) increased accessibility of the micropore space and, accordingly, better utilization of the micropore space and (ii) increased rate of coke formation with increasing external surface (increasing mesopore volume). Due to the fast coke built-up in HSSZ-13, most of the coke forms in the external region of the zeolite. Maximum catalyst lifetime was obtained at a relatively low mesoporogen/SDA ratio.

In this work, we investigate further issues related to mesoporous CHA zeolites for the MTO reaction. First, we explore the possibility to further improve the catalytic performance of HSSZ-13 zeolite for the MTO reaction. Two approaches were followed, i.e. decreasing the Al content of the zeolite framework so as to lower the density of Brønsted acid sites and the rate of coking [14–16] and by silylating the acid groups at or close to the external zeolite surface. Second, we attempted to synthesize mesoporous HSAPO-34 using the mesoporogen successfully employed for synthesis of mesoporous HSSZ-13, $C_{22}H_{45}{-}N^+(CH_3)_2{-}C_4H_8{-}N^+(CH_3)_2{-}C_4H_9)Br_2$. For comparison, we also used an amphiphlic organosilane, which has been shown to induce mesopores for AlPO-5 and AlPO-11 molecular sieves [12].

2. Experimental

2.1. Synthesis of materials

2.1.1. Template synthesis

$C_{22-4-4}Br_2$: The surfactant ($C_{22}H_{45}{-}N^+(CH_3)_2{-}C_4H_8{-}N^+(CH_3)_2{-}C_4H_9)Br_2$ was synthesized following a published procedure [9]. First, 4.1 g (0.01 mol) 1-bromodocosane (Aldrich, 96%) was dissolved in 20 ml toluene and added dropwise into the 20 ml solution of 10.3 g (0.07 mol) *N,N,N′*,N′-tetramethyl-1,4-butanediamine (Aldrich, 98%) in acetonitrile. The resulting solution was stirred for 3 h at room temperature and then mixed at 70 °C under reflux overnight. After cooling to room temperature, the solution was kept in a refrigerator at 4 °C for 1 h, filtered and washed with diethyl ether. The resulting solid was dried in a vacuum oven at room temperature. The product was $(C_{22}H_{45}{-}N^+(CH_3)_2{-}C_4H_8{-}N(CH_3)_2)Br$. Second, 3.7 g (0.007 mol) $(C_{22}H_{45}{-}N^+(CH_3)_2{-}C_4H_8{-}N(CH_3)_2)Br$ and 1.96 g (0.014 mol) 1-bromobutane (Aldrich, 98%) were dissolved in 110 ml of acetonitrile and then stirred in a reflux condenser at 70 °C overnight. Next, the solid product was quenched in refrigerator at 4 °C for 1 h, filtered, washed with diethyl ether and dried in a vacuum oven at room temperature. The resulting product was $(C_{22}H_{45}{-}N^+(CH_3)_2{-}C_4H_8{-}N^+(CH_3)_2{-}C_4H_9)Br_2$ (denoted as $C_{22-4-4}Br_2$).

2.1.2. Synthesis of molecular sieves

SSZ-13(50): SSZ-13 was synthesized as described in literature [17]. An amount of 2 g of a 1 M NaOH solution, 4 g 0.5 M *N,N,N*-trimethyl-1-adamantanammonium hydroxide (TMAdOH, SACHEM, 25%) and 2 g deionized water were mixed together. 0.05 g aluminum hydroxide (Sigma Aldrich) was added to this solution under vigorous stirring. After 30 min, 0.24 g fumed silica (Sigma) was added. The resulting mixture was stirred at room temperature to obtain a homogeneous gel with the composition 20 TMAdOH: 10 Na_2O: Al_2O_3: 100 SiO_2: 4400 H_2O, which was then transferred into a Teflon-lined autoclave and kept in an oven at 160 °C for 4 days. The zeolite product was filtered, dried and calcined at 550 °C for 10 h in static air. The proton form of the zeolite was obtained by triple ion exchange of the calcined zeolite with 1 M NH_4NO_3 at 70 °C for 2 h followed by calcination in static air at 550 °C for 4 h.

Meso-Zeo(50, C_{22-4-4}): A zeolite with Si/Al = 50 was synthesized in the same manner as SSZ-13 by combining $C_{22-4-4}Br_2$ and TMAdOH as templates. The starting molar gel composition was 10 TMAdOH: 5$C_{22-4-4}Br_2$: 10 Na_2O: Al_2O_3: 100 SiO_2: 5000 H_2O, which was subjected to crystallization in a Teflon-lined stainless-steel autoclave at 160 °C for 6 days. After crystallization, the solid product was collected by filtration, washed with deionized water, and dried at 110 °C. The zeolites were finally calcined at 550 °C for 10 h in static air. The proton forms of the zeolites were obtained by triple ion exchange of the calcined form with 1 M NH_4NO_3 at 70 °C and calcination at 550 °C for 4 h in static air.

Meso-Zeo(50, TPOAC): A mesoporous zeolite was synthesized by using octadecyl-(3-trimethoxysilylpropyl)-ammonium chloride (TPOAC, ABCR) as a mesopore-directing organosilane surfactant. The gel molar composition was 4 TPOAC: 20 TMdAOH: 10 Na_2O: Al_2O_3: 100 SiO_2: 4400 H_2O. The mixture was stirred further at room temperature until a homogeneous gel was obtained. The resulting gel was transferred into a Teflon-lined stainless steel autoclave and kept at 160 °C for 6 days. Thereafter, the solid material was recovered by filtration. The catalysts were finally calcined at 550 °C for 10 h in static air. The proton form of the zeolite was obtained by triple ion exchange of the calcined form with 1 M NH_4NO_3 at 70 °C and calcination at 550 °C for 4 h in static air.

Meso-SSZ-13(C_{22-4-4}, 0.17)-sil: A mesoporous SSZ-13 with Si/Al = 20 synthesized by $C_{22-4-4}Br_2$ and TMAdOH as templates was treated with TEOS to deactivate the external surface [18]. To this purpose, 1 g dehydrated SSZ-13(C_{22-4-4}, 0.17) [8] in its proton form was suspended in a mixture of 50 ml *n*-hexane and 0.15 ml TEOS at 50 °C for 1 h. The silylated product was centrifuged, dried at 110 °C, and calcined in air in two steps: the temperature was increased to 120 °C at the rate of 5° min^{-1} for 2 h, and went to 550 °C at 0.2 °C min^{-1} for 4 h.

SAPO-34: SAPO-34 was synthesized according to a procedure described in a patent assigned to the Union Carbide Corporation [19]. Example 35 was followed in this work. To this end, aluminum isopropoxide, Ludox HS-30, orthophosphoric acid, and tetraethyl ammonium hydroxide (TEAOH) were used to obtain a homogeneous gel with the composition 2 TEAOH: 0.3 SiO_2: Al_2O_3: P_2O_5: 50 H_2O. This gel was placed in a Teflon-lined autoclave and kept in oven at 200 °C for 5 days. Afterwards, the solid material was recovered by filtration.

Meso-SAPO: Mesoporous SAPO zeolites were synthesized by addition of octadecyl-(3-trimethoxysilylpropyl)-ammonium chloride (TPOAC, ABCR) as a mesopore-directing organosilane surfactant to the synthesis gel of SAPO-34. Two samples were prepared. In the first one, the silica source was stoichiometrically replaced by TPOAC so that a molar gel composition of 0.3 TPOAC: 2 TEAOH: Al_2O_3: P_2O_5: 50 H_2O was used. This sample is denoted by meso-SAPO(TPOAC, ∞), the infinity sign indicating the molar TPOAC/Si ratio. The other sample denoted by meso-SAPO(TPOAC, 0.04) was obtained by addition of a small amount of TPOAC to the synthesis of SAPO-34. The gel composition was 0.012 TPOAC: 2 TEAOH: 0.3 SiO_2: Al_2O_3: P_2O_5: 50 H_2O.

Meso-SAPO(C_{22-4-4}, n): In this case, 50% and 100% of the TEAOH compound in the standard SAPO-34 synthesis was replaced by $C_{22-4-4}Br_2$. The gel compositions were $C_{22-4-4}Br_2$: 0.3 SiO_2: Al_2O_3: P_2O_5: 50 H_2O: 2$NH_3{\cdot}H_2O$ and TEAOH: 0.5 $C_{22-4-4}Br_2$: 0.3 SiO_2: Al_2O_3: P_2O_5: 50 H_2O: $NH_3{\cdot}H_2O$, respectively. The synthesis procedure for these two zeolites is similar to conventional SAPO-34. The zeolites are denoted as meso-SAPO(C_{22-4-4}, n), where n refers to the fraction of TEAOH replaced by $C_{22-4-4}Br_2$ in the synthesis gel. All the materials were finally calcined at 550 °C for 5 h in static air before further use.