



Short communication

Aluminated hierarchical silicalite-2 particles: Catalyst with remarkably increased lifetime for methanol to hydrocarbons



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ABSTRACT

Aluminated hierarchical silicalite-2 with both large particle size and high external surface area was prepared by aluminating silicalite-2 under the protection of TBA⁺ cations in a mild alkaline solution. The textural and acidic properties of thus formed material (Z11-*meso*) were characterized by SEM, TEM, XRD, N₂ adsorption, FTIR, NH₃-TPD, and ²⁷Al NMR spectroscopy. The resulting hierarchical Z11-*meso* contained mainly tetrahedral coordinated aluminum species with low Brønsted/Lewis ratio (B/L) while preserved the zeolitic structure. Owing to the high external surface area (S_{ext}), hierarchical porous structures and low B/L ratio, Z11-*meso* outperformed the microporous ZSM-11 counterparts in methanol to hydrocarbons in terms of both activity and stability.

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1. Introduction

As one of the most promising routes from methane to value-added chemicals, methanol to hydrocarbon (MTH) process has been rapidly developed after its first exploration in 1970s [1–3]. Though several MTH processes such as methanol to gasoline (MTG), methanol to propylene (MTP) and methanol to olefin (MTO) have been successfully commercialized, fast deactivation due to coke deposit on the catalyst surface still restricts the practical application of these processes [4–6].

Recent developments on MTH process have verified that methylbenzenes and corresponding cyclic compounds are not only the key reaction centers but also the potential coke precursors [3]. These large molecules easily deposit on the external surface or in the channels. The coking rate and the stability of the catalyst are strongly influenced by the intrinsic properties of zeolites such as topology and acidity. Zeolites with smaller pore size or cavities and stronger Brønsted acidity strength show faster coking rates [7,8]. Therefore, great efforts have been devoted to the synthesis of zeolites with large-pore and/or hierarchical porosity, and moderate acidity [4,9–12]. The hierarchical zeolite aggregates, which combine the advantages of not only reserving increased external surface for improved coke tolerance but also solving the difficulty in separation owing to larger secondary particle size [12, 13], have been developed rapidly. Zeolites obtained by direct crystallization usually have higher B/L especially in high-silicon system [14]. The obtained strong Brønsted acid sites could be weakened by atoms modification such as phosphorus or boron introduction, showing good anti-

coking capability and exhibiting a remarkable enhancement of catalytic stability and favorable selectivity [15,16]. Therefore, research focusing on the synthesis of zeolites with suitable acidity and textural properties which may reduce the coke deposit and prolong the lifetime is of profound significance in MTH process.

We herein propose a facile procedure to obtain the hierarchical Z11 aggregates with large external surface area (>300 m² g⁻¹) by two-step synthesis strategy instead of traditionally direct synthesis. To curtail the difficulty of filtration/separation problems, a non-alumina silicalite-2 with larger macro-size was prepared in the TBAOH-TEOS-H₂O system and used as a carrier [17], and then aluminating of the carrier was undertaken with the protection of TBA⁺ cations in a mild alkaline solution without excessive silicon extraction [18]. This strategy led to preserved zeolite structure and zeolitic acidity with low B/L. Besides, the catalytic performance in MTH process on this aluminated hierarchical Z11 has been explored.

2. Experimental

2.1. The synthesis of Z11-*meso*

1 g of silicalite-2 was uniformly dispersed in 20 mL of 0.1 M pre-heated alkaline solution at 60 °C. The alkaline solution contained NaOH, TBAOH and Al(NO₃)₃ (SiO₂/Al₂O₃ = 100 and 400, [TBAOH]/[OH⁻] = 0.2). After 30 min-stirring, the mixture was quickly cooled to room temperature and washed to neutral. The final products in H-form with different SiO₂/Al₂O₃ were labeled as Z11-*meso*-100/Z11-*meso*-400. For comparison, two microporous Z11 materials (Z11-Micron, S_{ext} = 30 m² g⁻¹ and Z11-Con, S_{ext} = 116 m² g⁻¹) and a

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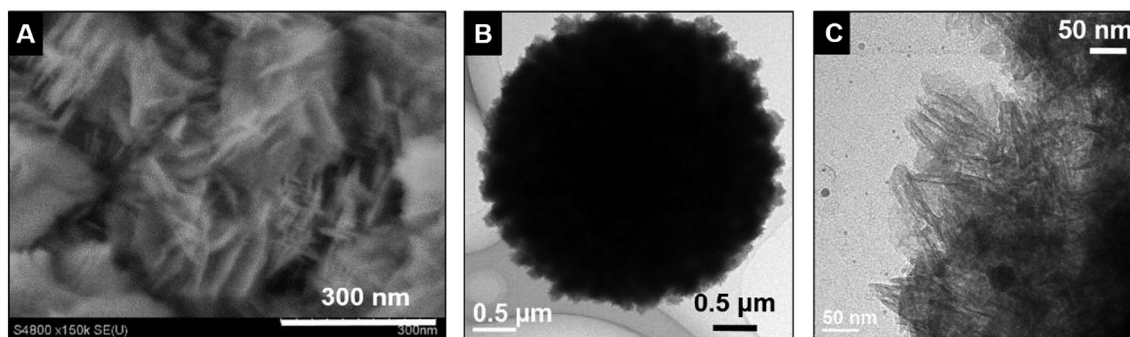


Fig. 1. The SEM image (A) and TEM images of Z11-meso-100 (B&C).

mesoporous nano-sized sample (Z11-Nano, $S_{\text{ext}} = 305 \text{ m}^2 \text{ g}^{-1}$) were also prepared according to literature (ESI).

2.2. Catalyst Characterization and catalytic tests

The powder X-ray diffraction (XRD) patterns were collected on a Bruker-D8-Advance powder diffractometer using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.154184 \text{ nm}$). Scanning electron microscopy (SEM) was performed on a HITACHI-S4800 microscope. The $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratios were quantified by inductively coupled plasma atomic emission spectroscopy. N_2 -adsorption-desorption isotherms were recorded with a Quantachrome-Autosorb-3B system. ^{27}Al MAS NMR spectra were measured on a VARIAN-VNMRS-400WB. Infrared spectra were recorded using a Nicolet iS50 FTIR spectrometer. Temperature programmed desorption of NH_3 (NH_3 -TPD) profiles were obtained on a XQ-TP5080 adsorption apparatus. The catalytic tests of these samples for MTH process and 1,3,5-triisopropylbenzene (TIPB) cracking were detailed in the ESI.

3. Results and discussions

Fig. 1 shows the SEM and TEM images of aluminated silicate-2 with $\text{SiO}_2/\text{Al}_2\text{O}_3 = 100$, namely, Z11-meso-100. The aluminated sample showed the similar morphology (Fig. 1A and B) as the pristine material with uniform spheres in about 5–15 μm (Fig. S1B). These spherical particles are secondary aggregates in size of 300–500 nm (Fig. S1C) composed of primary nano-sized lamellas in 5–10 nm (Fig. 1C). XRD patterns of Silicalite-2, Z11-meso and Z11-Nano samples presented in Fig. S2 indicate their small size of primary particles [4,12]. Their similar relative crystallinity (Table 1) varying from 92.6 to 95.3% implies that little influence occurred on zeolitic structure during the aluminations.

The textural properties of all samples are summarized in Table 1. Silicalite-2 exhibits the combined type I and IV isotherm (Fig. S3) which is known as fingerprints of a hierarchical porous system, possessing a BET specific surface area and porosity of $313 \text{ m}^2 \text{ g}^{-1}$ and $0.76 \text{ cm}^3 \text{ g}^{-1}$, respectively. After aluminations the resulting Z11-meso

materials have larger surface area but slightly decreased microporosity, likely attributing to the collapse of the microspores and simultaneously the formation of mesopores by the controllable extraction of framework silicon in basic conditions [19]. Pore size distribution (PSD) curves (Fig. 2) of silicalite-2 and Z11-meso samples show two broad distributions centered at around 8–9 nm and ~50 nm, which are related to the framing interspace of nano-lamellas and intercrystalline porosity of the secondary particles as shown by SEM and TEM images. Somewhat similar PSD is also observed for Z11-Nano while dominated microporosity is found for both Z11-Micron and Z11-Con.

The acidity of these materials was characterized by pyridine adsorption infrared spectroscopy (Py-IR, Fig. 3) and NH_3 -TPD profiles (Fig. S4 & Table S1). Neither pyridine nor NH_3 adsorption was found on silicalite-2 due to the absence of aluminum. The aluminated materials exhibit weak bands at 1540 cm^{-1} but strong bands at 1453 cm^{-1} in Py-IR spectra. In contrast, strong bands at 1540 cm^{-1} are observed for the microporous Z11s. These results point to the presence of less amount of BAs in Z11-meso compared with microporous Z11s, which is likely associated to the partially tetrahedral coordination of the “re-inserted” aluminum based on the ^{27}Al MAS NMR spectroscopy (Fig. S5) [18,20].

The catalytic properties of thus obtained Z11-meso samples were tested in MTH process by adopting the widely used MTH reaction conditions (Fig. S6). We roughly calculated the turnover frequency (TOF) of each catalyst by taking account of the total amount of B and L acids. The results shown in Fig. 4 indicate the microporous Z11-micron, Con, and Nano showed very similar initial activity, with about $1.5 \text{ mol}_{\text{methanol}}/(\text{mmol}_{\text{B+L}} \cdot \text{h})$. Silicalite-2 without aluminum did not show methanol conversion (not shown). Introducing minute amount of Al onto silicalite-2 (Z11-meso-400) remarkably increased the MTH activity, which was about $4 \text{ mol}_{\text{methanol}}/(\text{mmol}_{\text{B+L}} \cdot \text{h})$. Further increase of Al loading led to decrease of initial activity of Z11-meso-100 to $2 \text{ mol}_{\text{methanol}}/(\text{mmol}_{\text{B+L}} \cdot \text{h})$, while was still higher than microporous ones with similar $\text{SiO}_2/\text{Al}_2\text{O}_3$ ratio. The higher initial TOFs of both Z11-meso samples than those of the microporous Z11 materials points to the beneficial effect of mesoporosity on MTH reaction. The mesoporous

Table 1
The zeolitic/textural properties of the samples and the product distribution in MTH process.

Samples	Relative Crystallinity ¹ %	$\text{SiO}_2/\text{Al}_2\text{O}_3$	S_{BET}^2 $\text{m}^2 \text{ g}^{-1}$	S_{ext}^3 $\text{m}^2 \text{ g}^{-1}$	V_{mic}^3 $\text{cm}^3 \text{ g}^{-1}$	V_{total}^3 $\text{cm}^3 \text{ g}^{-1}$	total acid sites ⁴ $\mu\text{mol py g}^{-1}$	Lewis acid sites $\mu\text{mol py g}^{-1}$	Brønsted acid sites $\mu\text{mol py g}^{-1}$	B/L	$\frac{C_2}{C_2^s}$	$\frac{C_1+C_2}{C_2}$
Silicalite-2	95.3	6640	576	313	0.12	0.76	/	/	/	/	/	/
Z11-meso-400	93.5	357	582	337	0.12	0.85	47	28	19	0.71	/	/
Z11-meso-100	92.6	107	595	357	0.11	0.88	111	57	54	0.95	7.70	11.55
Z11-Nano	90.1	93	545	305	0.10	0.75	154	18	136	7.41	7.03	10.64
Z11-Micron	96.8	101	368	30	0.14	0.20	139	12	127	10.72	4.51	6.25
Z11-Con	95.6	110	416	116	0.14	0.47	148	13	135	10.06	5.14	7.59

¹ calculated from $2\theta = 23^\circ\text{--}25^\circ$ in XRD patterns using an ordinary ZSM-11 sample.

² calculated by the Brunauer-Emmett-Teller method.

³ calculated by the t -plot method.

⁴ determined by pyridine-adsorption-FTIR.

⁵ molar ratios.

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