Properties and reactivity of zinc-folded sheet mesoporous materials

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Abstract Mesoporous material incorporating zinc with different Si/Zn ratios = 95, 65, and 20 have been synthesized by intercalating kanemite using cetyltrimethylammonium bromide as the intercalating agent and zinc nitrate. The resulting materials were characterized by different techniques such as: inductively coupled plasma technique, XRD, Brunauer-Emmett-Teller, and a temperature-programmed-desorption of pyridine. The catalytic performance was studied in the vapor phase *tert*butylation of anisole with *tert*-butanol at different temperatures under atmospheric pressure. The results indicate that Zn-FSM-16 (20) was found to be more active than its relatives. The major products are found to be 4-*tert*-butyl anisole (4-TBA), 2-*tert*butyl anisole (2-TBA) and 2,4 di-*tert*-butyl-anisole (2,4-DTBA).

Keywords Zinc mesoporous · Kanemite · Tert-butylation · Anisole synthesis

Introduction

Folded sheet mesoporous material (FSM-16) was first synthesized by intercalation of a layered sodium silicate kanemite with long-chain cetyltrimethylammonium (CTMA) ions at 343 K followed by adjustment of the pH of the suspension to 8.5 and then calcination of the resulting CTMA–kanemite complex at 823 K in air [1]. FSM-16 materials, which are analogous to the most extensively studied MCM-41 (hexagonal, p6 mm) materials, have gained much attention because of their high surface areas and pore volumes [2–4]. They possess a hexagonal array of channels

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with narrow pore size distributions. On the other hand, FSM-16 materials are formed via a folded sheet mechanism in which the condensation of the reactive silanol groups present on the adjacent silicate layers in CTMA-kanemite complex leads to the formation of a hexagonal array of channels with uniform pore size [2]. This mechanism is further substantiated by in situ energy dispersive X-ray diffraction (EDXRD) measurements [5]. It is noteworthy that in comparison to MCM-41 materials, FSM-16 materials exhibit improved thermal stability, which is one of the key requirements for potential catalytic applications. This observed thermal stability can be attributed to their thicker pore walls. In fact, FSM-16 materials have widely been used as hosts to immobilize enzymes [6] and metal complexes [7–10]. Photofunctional [Ru (bpy)₃]Cl₂/FSM-16 materials are currently under increased investigation for the high potential they offer in the photooxidation of benzene to phenol [11]. FSM-16 materials are also known to be effective catalysts for reactions such as photometathesis of propene [12, 13] and Beckmann rearrangement of cyclohexanone oxime to ε -caprolactum [14]. Recently, the preparations of Pt, Rh, Fe, and Ga nanoparticles in FSM-16 have also been reported [15–18]. The acidic properties of FSM-16 materials and their applications in acidcatalyzed reactions have been reported [18-20]. Fe-modified FSM-16 has also been reported to possess high Brønsted acidity [21]. On the other hand, Friedel-Crafts reactions comprise a very important class of reactions that are of common use in organic chemistry. These reactions are habitually catalyzed by Lewis acids in the liquid phase and the substitution of liquid acids by solid acid catalysts is a challenging task [22-26]. The alkylation of anisole with tert-butanol (TBA) is a reaction of industrial importance as alkoxy benzenes are used as antioxidants, dye developers, and stabilizers for fats, oils, plastic, rubber, etc. [9]. Only a few reports are available in the literature. The alkylation of anisole using *tert*-butanol to yield 4-*tert*-butyl anisole was reported in the presence of $ZrCl_4$ [10], trifluoroacetic acid [11], and *tert*-butyl acetate was used as an alkylating agent in presence of H_2SO_4 . Yadav et al. [12] studied the same reaction using methyl-tert-butyl ether over solid acid catalysts and reported that DTP/K10 as more active. The same reaction was also reported over AlMCM-41 and H₃PW₁₂O₄₀ supported on AlMCM-41 molecular sieves [13, 14]. In the present study, we have reported the synthesis and characterization of zinc-incorporated folded sheet mesoporous material with different Si/Zn ratios = 95, 65, and 20, and their application in the alkylation ofanisole using tert-butanol reaction under vapor phase condition.

Experimental

Synthesis of the catalysts

Hydrothermal syntheses of mesoporous zinc-folded sheet mesoporous materials with different Si/Zn ratios were carried out using the typical procedure: kanemite (2.2 g) was added into a beaker containing a mixture of CTMABr (0.79 g) and 38.0 ml of deionized water and stirred for 45 min. A zinc nitrate (0.23 g) was then added dropwise into the above mixture and this mixture was stirred for another

45 min. The resultant mixture was transferred into a stainless-steel autoclave (60 ml) and heated to 373 K for 24 h under static conditions. The resultant product was filtered, washed thoroughly with deionized water, dried at 333 K, and then calcined at 973 K in air for 12 h.

Characterization techniques

The X-ray diffraction (XRD) patterns of samples were recorded with a powder XRD instrument (Rigaku D/max 2500PC) with Cu K α radiation ($\lambda = 0.154$ 18 nm). It was operated at 40 kV and 50 mA. The experimental conditions correspond to a step width of 0.02° and a scan speed of 1°/min. The diffraction patterns were recorded in the 2θ range of 1–10°. Specific surface area and pore size were measured by using a NOVA2000e analytical system made by Quantachrome Corporation (USA). The specific surface area was calculated by Brunauer-Emmett-Teller (BET) method. Pore size distribution and pore volume were calculated by Barrett-Joyner-Halenda (BJH) method. The zinc content in the samples was determined by inductively coupled plasma (ICP) technique (Vista-MAX, Varian). The density and strength of the acid sites of the different zinc-folded sheet mesoporous material were determined by the temperature-programmed desorption (TPD) of pyridine. About 100 mg of the materials were evacuated for 3 h at 523 K under vacuum ($p < 10^{-5}$ kPa). Afterwards, the samples were cooled to room temperature under dry nitrogen followed by exposure to a stream of pyridine in nitrogen for 30 min. Subsequently, the physisorbed pyridine was removed by heating the sample to 393 K for 2 h in a nitrogen flow. The temperatureprogrammed desorption (TPD) of pyridine was performed by heating the sample in a nitrogen flow (50 ml/min) from 393 to 873 K with a rate of 10 K/min using a high-resolution thermogravimetric analyzer coupled with a mass spectrometer (SETARAM setsys 16MS). The observed weight loss was used to quantify the number of acid sites assuming that each mole of pyridine corresponds to 1 mol. of protons.

Catalytic testing

Tertiarybutylation of anisole was carried out in a fixed-bed, vertical flow-type reactor made up of a Borosil glass tube 40 cm in length and 2 cm in internal diameter. The catalyst (0.5 g), diluted with a fourfold amount of porcelain beads of equal size, was loaded at the center of the reactor and supported on either side with a thin layer of quartz wool. The reactor was heated to the requisite temperature with the help of a tubular furnace controlled by a digital temperature controller indicator. The catalyst was activated at 773 K for 5 h in a flow of dry air before the reaction were conducted. Reactants were introduced into the reactor using a syringe pump. The bottom of the reactor was connected to a coiled condenser and a receiver to collect the products. The products were chilled, collected, and analyzed by GC (Perkin-Elmer, Elite 5MS capillary column) and the products were confirmed with GC–MS (HP-5973) analysis.

Results

Characterization of the samples

The small-angle X-ray diffraction patterns of Zn-folded sheet mesoporous material (Si/Zn = 95, 65, 20) are shown in Fig. 1. The unit-cell parameter (a_o) values calculated from the peak with (hkl) = (100) using the equation $a_o = 2d_{100}/\sqrt{3}$ are summarized in Table 1. The Zn-FSM-16 (95) sample gives a very strong (100) peak corresponding to the ordered hexagonal mesoporous structure. However, when the zinc content ratio decreased from 65 to 20, the intensities of the long-range ordered peaks were gradually reduced. However, compared with the pattern of the typical FSM-16 mesoporous molecular sieve [1], it can be noted that the d₁₀₀ spacing in Zn-folded sheet mesoporous material is significantly larger than FSM-16 (for both assynthesized and calcined samples) shows the incorporation of zinc in the FSM-16 structure. At the same time, no diffraction lines corresponding to bulk zinc species



Fig. 1 XRD patterns of Zn-folded sheet mesoporous materials in the domain of $1-10^{\circ}$ (2 θ): **a** Zn-FSM-16 (95), **b** Zn-FSM-16 (65), **c** Zn-FSM-16 (20)

Samples	Chemical analysis		$S_{\rm BET}~({ m m}^2~{ m g}^{-1})$	Pore volume $(cm^3 g^{-1})$	Pore diameter (nm)	
	Si/Zn (gel)	Si/Zn				
Zn-FSM-16	20	18.9	639	0.66	2.7	
Zn-FSM-16	65	62.7	905	0.88	2.5	
Zn-FSM-16	95	93.8	1,026	0.98	2.4	

Table 1 Physicochemical properties of different Zn-folded sheet mesoporous materials



Fig. 2 XRD patterns of the Zn-FSM-16 materials in the domain of 10–80° (2 θ): **a** Zn-FSM-16 (95), **b** Zn-FSM-16 (65), **c** Zn-FSM-16 (20)

could be observed in the $10-80^{\circ}$ (2θ) (Fig. 2). The zinc content in Zn-folded sheet mesoporous materials is increased with zinc content in the synthesis gel (Table 1). The specific surface areas and pore size distributions and pore volumes calculated by BET and BJH methods are summarized in Table 1. From this table, we can conclude that the specific surface area and pore volume of the resulting samples gradually decreased as the zinc content increased, and the pore size is in the range of 2.4–2.7 nm. Besides, the acid site distribution and acid amounts of Zn-folded sheet mesoporous material were determined using temperature-programmed-desorption (TPD) of pyridine and the data are collected in Table 2. Weak (423 and 633 K), moderate (633–743 K), and strong (>743 K) acid sites are found in all samples. The weak acid sites originate probably from the incorporation of zinc atoms into the FSM-16 walls. It is interesting to note that the number of weak acids sites decreases with increasing Si/Zn ratio. It should be noted that the total

Table 2 Density and strength of acid sites of Zn-folded sheet mesoporous catalysts with different Si/Zn ratios (Si/Zn = 95, 65, 20)

Samples	Acid sites (mmol/g)						
	Weak (423–633 K)	Medium (633–743)	Strong (>743)	Total (medium and strong acid sites)			
Zn-FSM-16 (20)	0.539	0.191	0.224	0.415			
Zn-FSM-16 (65)	0.601	0.123	0.179	0.302			
Zn-FSM-16 (95)	0.748	0.107	0.145	0.252			

number of acid sites (medium and strong acid sites) of Zn-FSM-16 (20) is higher than that of Zn-FSM-16 (65) and Zn-FSM-16 (95).

Catalytic activity

The vapor phase tert-butylation of anisole over Zn-folded sheet mesoporous material was carried out at 423, 473, and 523 K with molar ratio ANS/TBA = 3and WHSV of 3.5 h^{-1} . The results are presented in Table 3 and Fig. 3. The major product was 2-tert-butyl anisole (2-TBA), 4-tert-butyl anisole (4-TBA) and 2,4ditert-butyl anisole (2,4-DTBA). In addition to 3-tert-butyl anisole (3-TBA), dimerized and oligomerized butenes were also obtained. The conversion increases from 423 to 473 K, but decreases after that for all the catalysts. The decrease in conversion is due to oligomerization of butenes that block the active sites of coke. Although the same trend in conversion is observed over all the catalysts, the activity of the catalyst followed the order Zn-FSM-16 (20) > Zn-FSM-16 (65) > Zn-FSM-16 (95). Therefore, it is suggested that the density of acid sites on the catalyst surface is an important factor for tert-butylation. So far, another factor to be considered is hydrophobic and hydrophilic properties of the catalysts [27]. Since Zn-folded sheet mesoporous material with high Si/Zn ratio is more hydrophobic than those with less Si/Zn ratios, the former catalysts can exhibit high activity with reactants, which are hydrophobic. Therefore, in reaction with Zn-folded sheet mesoporous material, acid strength, hydrophilic and hydrophobic properties are also important in addition to the density of acid sites in accounting for the activity of the catalyst. The selectivity to 4-TBA increases with increase in temperature over all the catalysts. The Zn-FSM-16 (20) gives higher selectivity than other catalysts. The selectivity to 2-TBA decreases with increase in temperature, The selectivity to 2,4-DTBA display similar tendency as that of 2-TBA supporting again steric obstacle for substitution at the ortho position with respect to o-methyl grouping of 4-TBA.

Samples	Temperature (K)	Conversion (%)	Selectivity (%)			
			2-TBA	4-TBA	2,4-DTBA	Others
Zn-FSM-16 (95)	423	65.6	10.7	53.9	16.6	18.8
	473	70.3	9.8	58.6	15.7	15.9
	523	55.2	8.2	64.4	11.6	15.8
Zn-FSM-16 (65)	423	69.5	11.6	58.2	19.3	10.9
	473	75.3	10.4	61.6	17.6	10.4
	523	66.5	7.7	67.5	13.8	11.0
Zn-FSM-16 (20)	423	74.5	13.2	57.4	23.8	5.6
	473	80.3	12.8	64.7	19.3	3.2
	523	72.5	9.6	69.3	15.7	5.4

Table 3 The conversion and the selectivity of *tert*-butylation of anisole Zn-FSM-16 catalysts at different temperatures: 423, 473, and 523 K with molar ratio ANS/TBA = 3, WHSV 3.5 h^{-1} and time on stream = 2)

TBA tert-butyl anisole; DTBA di-tert-butyl anisole



Fig. 3 Effect of reaction temperature on anisole conversion over different Zn-folded sheet mesoporous catalysts with different Si/Zn ratio (reaction conditions: WHSV of 3.5 h^{-1} , molar ratio ANS/TBA = 3 and time on stream = 2)

The selectivity to 2,4-DTBA also follows similar tendency for zinc-folded sheet mesoporous materials with Si/Zn = 65, 95 as that of Zn-FSM-16 (20). From this study, it is concluded that the best temperature is found to be 473 K, as it provides high conversion and selectivity in comparison to higher temperature.

The effect of time on stream and the activity of catalyst Zn-FSM-16 (20) was studied at 473 K with ANS/TBA molar ratio = 3 and WHSV $3.5 h^{-1}$. The results are illustrated in Fig. 4. The conversion of anisole decreases with an increase in time on stream. This is due to coke formation. The catalyst appeared slightly black after 5 h of time on stream. The selectivity of 4-TBA increases it is due to gradual decrease in its conversion to 2,4-DTBA. As expected, the selectivity of 2,4-DTBA also decreases with an increase in time on stream. The selectivity of 2-TBA explains high augmentation with time on stream. It is also due to gradual decrease in its conversion to 2,4-DTBA with increase in time on stream. The enhanced *p*-selectivity with time can be accounted in terms of coke induced *p*-selectivity. During time on stream, the coke formed over the catalysts block the pores and the narrow pore size, which favors para products.

The effect of WHSV on the conversion of anisole of selectivity of the products was studied over Zn-FSM-16 (20) at 473 K, at 3.5, 4.5, and 5.5 h^{-1} with ANS/TBA molar ratio = 3 and shown in Fig. 5. The conversion decreases with an increase in WHSV. The selectivity 2-TBA is not much varied irrespective of the magnitude of increase in WHSV. The selectivity to 4-TBA increases with increase WHSV due to reduced conversion of it to 2,4-DTBA. If the selectivity to 2-TBA, 4-TBA, and 2,4-DTBA is carefully analyzed, it will be evident that 2-TBA may not be making important contribution of 2,4-DTBA as the selectivity of it is very less.



Fig. 4 Effect of time on stream on anisole conversion and product selectivity over Zn-FSM-16 (20) catalyst (reaction conditions: $T_R = 473$ K, molar ratio ANS/TBA = 3, WHSV of 3.5 h⁻¹)



Fig. 5 Effect of a weight hourly space velocity (WHSV) on anisole conversion and product selectivity over Zn-FSM-16 (20) catalyst (reaction conditions: molar ratio ANS/TBA = 3, $T_{\rm R}$ = 473 K and time on stream = 2)



Fig. 6 Effect of molar ratio ANS/TBA on anisole conversion and product selectivity over Zn-FSM-16 (20) catalyst (reaction conditions: $T_{\rm R} = 473$ K, WHSV of 3.5 h⁻¹ and time on stream = 2)

The conversion of anisole was studied at 473 K over Zn-FSM-16 (15) with the different ANS/TBA molar ratio = 1, 2, 3, and WHSV 3.5 h^{-1} . The results are illustrated in Fig. 6. Since the reaction involves the formation of *tert*-butyl cation on the catalyst surface the conversion increases with an increase in the tertiary butyl alcohol in the feed. If the difference in conversion between one, two, and three is compared, the former gives more increase in conversion than the latter. The selectivity to 2-TBA decreases but that of 2,4-DTBA increase with increases in the *tert*-butanol content in the feed. The 2-TBA might also be converted to 2,4-DTB and the selectivity to 4-TBA decreases with the increase in the *tert*-butanol content in the feed.

Conclusions

Zn-folded sheet mesoporous material with different Si/Zn ratios = 95, 65, and 20 and with high specific surface area were successfully synthesized. After the synthesized sample was calcined at 813 K in air for 6 h, the template was effectively removed. The Si/Zn molar ratio is a key factor influencing the textural properties and structural regularity of Zn-FSM-16 materials. The results of catalytic performance indicate that zinc-FSM-16 (20) was found to be more active than its relatives and the major products are found to be 4-*tert*-butyl anisole (4-TBA), 2-*tert*-butyl anisole (2-TBA), and 2,4 di-*tert*-butyl-anisole (2,4-DTBA).

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