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Short communication

A practicable mesostructured MFI zeolitic catalyst for large molecule reactions

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ABSTRACT

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1. Introduction

Zeolites as catalysts have been considered as one of the major accomplishments in petroleum refining and petrochemistry. However, the conversion of heavy oil and large molecules requires largemolecule pore-structured zeolitic catalysts. The current experiments in developing of new mesoporous or hierarchical zeolites are making the refining of catalytic processes possible. Compared with conventional zeolites, the mesoporous zeolites with higher external surface area have greatly improved the accessibility of large molecules into active sites, the reaction rates of diffusion-limited reactions and the selectivity of the target molecules, and decreased deactivation probability caused by coking. Alkylation of aromatics is a very important Friedel-Crafts reaction, in which benzylation of aromatics by benzyl chloride or benzyl alcohol is an essential reaction in the fine chemicals industry [1]. Earlier studies have shown that HY and HB zeolites with larger 12-ring microporous channels exhibit catalytic activity to a certain extent in benzylation reaction. But both zeolites could be rapidly deactivated owing to diffusional limitation caused by the microporous network. Moreover, ZSM-5 zeolite shows poor activity owing to the narrow 10ring microporous networks [2,3].

To overcome the diffusion limitations presented in conventional zeolites, the basic strategy is to reduce the zeolitic crystal size [4] or introduce mesopores into microporous zeolitic crystals [5–8]. As a result, the distribution, nature, number and strength of acid sites can be changed, which are the critical factors determining catalytic

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behaviors of mesoporous zeolites. In previous studies, we have systematically demonstrated the corresponding change of acidic properties owing to the introduction of mesoporous in the microspherical MFI mesoporous zeolites (MMZ-5) [7]. MMZ-5 zeolites showed an enhanced catalytic activity in the liquid-phase benzylation of p-xylene with benzyl chloride, but the improved role of porosity and acidity in the benzylation of aromatics has not been discussed in detail. This manuscript will systematically evaluate the catalytic reactivity of the MMZ-5 zeolites in the benzylation of different aromatics (*i.e.* benzene, toluene, mesitylene and anisole) with benzyl chloride and assess the relative impacts between the porosity, acidity, and catalytic performance of the MMZ-5 zeolites in order to optimize the performance of these zeolites as effective catalysts in the benzylation of aromatics.

A microspherical mesostructured zeolite (MMZ-5) with MFI-topological frameworks is employed. In-situ FT-IR

spectra of pyridine and 2, 6-di-tert-butylpyridine have indicated that almost all of the acid sites are located on

the zeolitic external surface, which are favorable for access of reactive large molecules. This key effect, along

with the reduced diffusion and steric limitation, has been proposed to be main the reason for the enhanced

catalytic activity, selectivity and stability exhibited in benzylation of aromatics with benzyl chloride. The need for optimized characterization of the mesoporous surface acidity for different aromatics is highlighted.

2. Experimental

MMZ-5 zeolites were synthesized according to the procedure in reference [7], only all the samples were amplified in 5 L autoclave. The samples were designated as MMZ-5-n (n = 1-5) with different mesoporosity and Si/Al ratio. The microporous ZSM-5 zeolite (denoted as ZSM-5-0) used as the reference sample was synthesized by using the fumed silica as silica source under the same procedure. In these samples, MMZ-5-0,-1,-2,-3 have very similar Si/Al ratio, but other two samples have lower Si/Al ratio than them. The mesoporosity and Si/Al ratio of the sample can be adjusted by the synthesis method described in reference [7]. All the samples were transferred into H⁺ forms by using ion exchange for three times at 353 K with 0.5 M NH₄NO₃ aqueous solution and followed by calcination in air at 823 K for 5 h.







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 Table 1

 Acidity of MMZ-5 zeolite catalysts^a.

Samples	Tomporaturo	FTIR-Py		FTIR-DTBPy	Brönsted acid sites (%)		
	remperature	L _{Py} (µmol/g)	B _{Py} (μmol/g)	B _{DTBPy} (μmol/g)	Internal	External	
ZSM-5-0	423	4	85	1	98.8	1.2	
	523	2	83	-			
	623	1	75	-			
MMZ-5-1	423	20	76	36	52.6	47.4	
	523	14	69	18			
	623	10	63	10			
MMZ-5-2	423	25	73	65	11.0	89.0	
	523	20	62	58			
	623	15	44	52			
MMZ-5-3	423	21	72	50	30.6	69.4	
	523	15	71	41			
	623	12	65	32			
MMZ-5-4	423	30	77	67	13.0	87.0	
	523	22	66	57			
	623	13	57	36			
MMZ-5-5	423	27	104	40	61.5	38.5	
	523	16	95	30			
	623	12	80	17			

^a Py-IR spectra and DTBPy-IR spectra of the zeolite samples were supported as Fig. S3 and Fig. S4.

The concentration of total Brönsted and Lewis acid sites of the samples was calculated from peaks intensities at 1545 cm⁻¹ (PyH⁺) and at 1455 cm⁻¹ (PyL) in the Py-IR spectra. The concentration of external Brönsted acid sites was determined by peak intensity at 1616 cm⁻¹ (DTBPyH⁺) in DTBPy-IR spectra.

The liquid phase benzylation of different aromatics with benzyl chloride (BC) was conducted in a 50 ml three-necked flask equipped with a reflux condenser. The aromatics and BC (26 mmol) in a required molar ratio of 13:1 were added to the system including the catalyst (0.15 g), while the excess of aromatics was applied as a solvent. The reaction mixture was continuously stirred under the reaction temperature. The reactants and products were withdrawn periodically to be analyzed on a gas chromatograph which was equipped with a FID detector and a 60 m HP-5 capillary column.

3. Results and discussion

3.1. Porosity and acidity of the samples

All the as-synthesized samples have well-resolved XRD characteristic peaks of MFI structure (Fig. S1) and contain very small crystalline grains of 20–30 nm (Table S1). The BET surface area and the external surface area for MMZ-5 zeolites obviously increase owing to their nanocrystalline feature and the presence of mesopores centered at 3–7 nm (Fig. S2b). The BET surface area and the external surface area of MMZ-5-2 zeolite reached 544 m²/g and 327 m²/g, respectively, which are 1.3 and 8.8 times the value of ZSM-5-0 zeolite.

The acidic properties of the samples are investigated by FTIR spectroscopy of adsorbed molecules (Py and DTBPy). A higher concentration of Lewis acid sites is observed for all MMZ-5 zeolites compared to ZEM-5-0 zeolite (Table 1), and these Lewis acid sites are predominantly

3.2. Catalytic activity

The benzylation of aromatics with benzyl chloride (BC) is totally in accordance with the classical mechanism of Friedel–Crafts reaction and presented in Scheme 1. The catalytic results of the samples are summarized in Table 2. The apparent rate data for the benzylation of aromatics in excess of aromatics over the zeolite catalysts could be fitted well to a pseudo-first order rate law:

$$\ln(1/(1-x)) = k_a(t-t_0),$$

where k_a is an apparent rate constant, x is the fractional conversion of benzyl chloride, t is reaction time, and t_0 is the induction period corresponding to the time required to reach the reaction temperature.

A plot of $\ln (1 / (1 - x))$ versus $(t - t_0)$ gives a linear graph over the range of BC conversion. The apparent rate constant k_a of the samples can be easily obtained. All MMZ-5-n catalysts have much higher BC conversion than ZSM-5-0. In benzylation of benzene and toluene, MMZ-5-2 zeolite has the highest catalytic activity, over which BC conversions reach 13.8% and 47.2% for benzene and toluene, respectively. The apparent rate constant for MMZ-5-2 is 31.0 times and 43.3 times that of ZSM-5-0. Interestingly, BC conversion can reach above 90% for all the MMZ-5 zeolites in benzylation of mesitylene and anisole. The apparent rate constants for zeolite MMZ-5-3 are 252.1 × 10⁴ min⁻¹ for mesitylene and 282.7 × 10⁴ min⁻¹ for anisole, which are 1.5 times and 1.1 times that for MMZ-5-2, respectively.

In general, Lewis and Brönsted acid sites in the catalysts play a major role in the production of the electrophile $(C_6H_5CH_2^+)$, which transition stage is very critical in the reactions [2,11,12]. After the acid sites interact with BC to produce the electrophile $(C_6H_5CH_2^+)$, the generated electrophilic species attack the benzene rings, resulting in the formation of the benzylated aromatics. Obviously, with the increase of the electron-donating ability of the substituents in benzen ring, the conversion of BC increases on the all ZSM-5 catalysts. The reactivities of these aromatics with BC are in the following order: anisole > mesitylene > toluene > benzene. The MMZ-5-n catalysts possess significantly more external acid sites (L_{Pv} and B_{DBTPv}), which are responsible for a much higher catalytic activity of these zeolite catalysts in benzylation of different aromatics without diffusion and/or steric limitation. As a result, MMZ-5-2 and MMZ-5-4 catalysts have higher activity in benzylation of benzene or toluene because of their significantly more strong acid sites (65 µmol/g and 67 µmol/g), although they have the different Si/Al ratio. By comparing the activities of MMZ-5-3 and MMZ-5-5, it is further confirmed that the number of external Brönsted acid sites, especially strong Brönsted acid sites, can influence the activity of the zeolite catalysts. This conclusion is also approved in benzylations of anisole and mesitylene. However, MMZ-5-3 shows the best catalytic activity among all the MMZ-5-n zeolite catalysts in these reactions although the amount of external acid sites is lower than that of MMZ-5-2 or MMZ-5-4. This could be assigned to



Scheme 1. Benzylation reaction scheme of aromatics with benzyl chloride.

Table 2				
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Run	Catalyst	Substrate					Reaction time (h)	Conv. BC (%)	C (%) $k_a(\times 10^4 \mathrm{min}^{-1})$	Monobenzylated aromatics distribution (%)		
		\mathbb{R}^1	\mathbb{R}^2	R ³	\mathbb{R}^4	R ⁵				0-	m-	p-
1	ZSM-5-0	Н	Н	Н	Н	Н	8	0.6	0.1			
2		CH ₃	Н	Н	Н	Н	8	1.2	0.3	42.5	7.8	49.8
3		CH ₃	Н	CH_3	Н	CH_3	8	1.7	0.4			
4		OCH ₃	Н	Н	Н	Н	8	1.9	0.4	47.1	0.3	52.6
5	MMZ-5-1	Н	Н	Н	Н	Н	8	4.0	0.8			
6		CH ₃	Н	Н	Н	Н	8	16.1	3.6	42.0	8.4	49.6
7		CH ₃	Н	CH_3	Н	CH_3	4	90.1	90.7			
8		OCH_3	Н	Н	Н	Н	4	92.7	142.6	47.0	0.3	52.7
9	MMZ-5-2	Н	Н	Н	Н	Н	8	13.8	3.1			
10		CH ₃	Н	Н	Н	Н	8	47.2	13.0	42.7	8.0	49.3
11		CH ₃	Н	CH_3	Н	CH_3	4	97.8	167.8			
12		OCH ₃	Н	Н	Н	Н	4	99.7	252.3	46.9	0.3	52.8
13	MMZ-5-3	Н	Н	Н	Н	Н	8	9.0	2.0			
14		CH ₃	Н	Н	Н	Н	8	36.1	9.2	42.4	7.5	50.1
15		CH ₃	Н	CH_3	Н	CH_3	4	99.8	252.1			
16		OCH ₃	Н	Н	Н	Н	4	99.9	282.7	47.7	0.2	52.1
17	MMZ-5-4	Н	Н	Н	Н	Н	8	10.0	2.2			
18		CH ₃	Н	Н	Н	Н	8	42.5	11.4	43.0	7.1	49.9
19		CH ₃	Н	CH_3	Н	CH_3	4	93.2	105.7			
20		OCH ₃	Н	Н	Н	Н	4	97.3	152.6	47.6	0.4	52.0
21	MMZ-5-5	Н	Н	Н	Н	Н	8	5.7	1.3			
22		CH ₃	Н	Н	Н	Н	8	26.9	6.5	42.5	7.6	49.9
23		CH ₃	Н	CH_3	Н	CH_3	4	90.7	95.2			
24		OCH ₃	Н	Н	Н	Н	4	95.9	146.6	47.4	0.3	52.3
		. ,										

the following points: (i) the aromatic substrates (anisole and mesitylene) with higher electron density can be strongly adsorbed on the acid surface of the catalysts leading to a poison effect and a steric hindrance [13,14]. (ii) Brönsted acid sites are easy to interact with the lone electron pairs of methoxyl of anisole, resulting in the weaker nucleophilicity of benzene rings and a lower catalytic activity. The results indicate that the heterogeneous catalysis is still a complex system and the relationship between reactivity and acidity is hardly described quantitatively.

MMZ-5-3 zeolite used in benzylation of toluene was recycled for three more times. The results show that the MMZ-5-3 zeolite catalyst could be used repeatedly in the benzylation process without significant loss in its catalytic activity (Fig. S5). Other mesoporous MMZ-5 catalysts have same reusability as MMZ-5-3 in these reactions. This clearly indicates the efficiency of MMZ-5 zeolite catalyst for the reactions of larger molecules.

4. Conclusion

Significantly higher availability of acid sites (above 90%), along with the sufficient reaction voids for large molecules reaction, make the zeolites to exhibit a notably enhanced catalytic activity and stability in the benzylation of different aromatics with benzyl chloride (BC). The high concentration of strong acid sites on the MMZ-5 zeolites is more favorable to the conversion of the aromatics. These results suggest that the MMZ-5-n zeolites could, with the optimization of porosity and acidity, become a practical zeolitic acid catalyst for large molecule reactions.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx. doi.org/10.1016/j.catcom.2016.02.010.

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