Hydrocracking in Al-MCM-41: diffusion effect

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Abstract

The effects of wall defects on the molecular diffusion and hydrocracking ability of mesoporous MCM-41 materials having particulate and hierarchical tubular morphologies with various extents of structural defects have been studied. The diffusion properties of the MCM-41 materials were investigated by ¹H pulsed-field-gradient NMR self-diffusion measurements of cyclohexane, whereas the catalytic performances of the aluminosilicate MCM-41 were evaluated using 1,3,5-triisopropylbenzene cracking as the test reaction. ³¹P MAS NMR of the adsorbed trimethylphosphine oxide probe molecules confirmed the existence of active sites in the Al-MCM-41 samples, whose acid distribution were evaluated in conjunction with elemental analyses. It was found that, the Al-MCM-41 sample with tubules-within-tubule (TWT) morphology showed superior catalytic activity and tolerance for deactivation during hydrocracking reaction compared to the particulate morphology sample having the same Al content. The TWT Al-MCM-41 sample, which has more extensive structural defects than the particulate Al-MCM-41, was also found to have higher cyclohexane diffusivity. It is conclusive that, the structural defects possessed by these unique Al-MCM-41 materials synthesized by the ‘delayed neutralization method’ effectively provoke interchannel connections, which facilitate transport of the adsorbate molecules, thus promote the catalytic activity of the catalysts.

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1. Introduction

The molecular transport phenomena in porous materials improvise an ideal system for the investigation of restricted diffusion, which has always

been an important issue in guest/host chemistry. However, the related guest–host interactions and microscopic processes involved during chemical reactions are still not well understood. Thus, further investigations of chemistry in confined space are demanded, especially for catalytic reactions during which molecular transports are constrained by and/or associated with local properties of the porous supports.

The MCM-41 materials, comprised by a hexagonal array of uniform mesoporous channels

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with tunable pore size (1.5–20.0 nm), are known to possess high surface area ($\sim 1000 \text{ m}^2/\text{g}$), high hydrocarbon sorption capacities ($>0.7 \text{ ml/g}$), and high thermal and hydrothermal stability [1,2]. These unique properties render their potential applications, for examples, as the media or supports for electronic/optical devices, sorption/separation processes or catalytic reactions [3–5]. In terms of their potential applications as catalysts, Al-MCM-41 materials, being less acidic than most microporous zeolites [6], are most suitable for catalytic reactions either require only weak acid sites or involve large organic molecules ($>0.7 \text{ nm}$) for which most acidic zeolite catalysts are not feasible [7–10].

Acidity and mass transport property are known to dictate the overall catalytic performance (e.g., activity, deactivation rate etc.) of a catalyst. While the former is mainly related to the distribution and concentration of the framework Al species, the latter is generally manipulated by the aperture and pore structure. Thus, in view of promoting the catalytic performance for an Al-MCM-41 sample with a given Al content, it is desirable to increase the interchannel accessibility, which may be favorable for the transport of reagents and products within the intraparticle voids.

Previously, Mou and co-workers [11] introduced a convenient ‘delayed neutralization’ method for the alkaline synthesis of siliceous and aluminosilicate MCM-41. By careful control of surfactant-water content under gradual acidification condition, ordered MCM-41 molecular sieve with a hollow tubules-within-tubule (TWT) hierarchical structure could be obtained [12–14]. Based on their N_2 adsorption/desorption studies (at 77 K), the authors further demonstrated that these Al-MCM-41 materials exhibit pronounced type-H4 hysteresis loop located at $0.5 \leq p/p_0 \leq 1.0$, revealing the presence of structural defect holes amid the nanochannels. Moreover, while these wall defect holes are normally irregular in shape and sizes (typically $\approx 5\text{--}30 \text{ nm}$), they also depend largely on the morphology of the synthesized materials. Consequently, the extent of the structural wall defects can be manipulated by the water content during synthesis [15]. Using ethylbenzene dehydrogenation as test reaction, Wong et al. [16] fur-

ther showed that the TWT Al-MCM-41 catalyst revealed a higher catalytic activity than the conventional Al-MCM-41 with particulate morphology. The authors ascribed their results to the intimate co-existence of meso- and macropores in the TWT sample, which affords better interchannel molecular diffusion than the defect-free catalytic support. Nonetheless, such argument demands further justification.

In continuation of the previous studies made by Mou and his co-workers [15,16], the objective of this study is thus to further verify the effects of structural wall defects on mass transport properties and catalytic activity of the Al-MCM-41 catalysts. Pulsed-field-gradient (PFG) NMR self-diffusion measurement is known as the most powerful technique to study the transport phenomena of porous materials, such as zeolites and molecular sieves [17,18]. Recently, similar studies have been extended to mesoporous MCM-41 using various probe molecules, such as water, cyclohexane and *n*-hexane [19–23]. In this work, the molecular transport properties of Al-MCM-41 catalysts having different morphology and extent of structural defects were examined by the ^1H PFG NMR self-diffusion coefficient of cyclohexane. Whereas their catalytic performance were evaluated using 1,3,5-triisopropylbenzene cracking as the test reaction.

2. Experimental

2.1. Materials

Three different mesoporous MCM-41 molecular sieve samples having the same average pore size (2.6 nm) were examined in this study, namely the siliceous MCM-41 (denoted as SM) and aluminosilicate MCM-41 with particulate (denoted as M37) and hierarchical TWT (denoted as TM37). Their fundamental properties characterized by Lin et al. using a variety of techniques [15]. More specifically, the XRD patterns, N_2 adsorption-desorption isotherms (77 K), and microtome TEM micrographs obtained from samples SM, TM37, and M37 (previously denoted as Samples II, III, and IV, respectively) have been unraveled in Figs.

1A,B and 2 of Ref. [15], respectively. The physical properties of the samples are summarized below:

- (1) Samples SM ($\text{Si}/\text{Al} = \infty$) and M37 ($\text{Si}/\text{Al} = 37$), which were both synthesized using the ‘delayed neutralization’ method [11], possess the conventional particulate morphology and an averaged particle size of $\approx 0.3 \mu\text{m}$. Whereas sample TM37 ($\text{Si}/\text{Al} = 37$), which possesses the tubular morphology (particle size $\approx 0.7 \times 3.5 \mu\text{m}$), was synthesized under ‘gradual acidification’ condition [12–14].
- (2) All samples exhibit similar type-H4 N_2 adsorption–desorption isotherms with sharp inflection point at $p/p_0 = 0.32$ (which correspond to a common average pore size of $\approx 2.6 \text{ nm}$, as calculated by the Barrett–Joyner–Halenda or the so-called BJH method). In particular, an additional hysteresis loop exists at p/p_0 between 0.5 and 1.0, whose size decreases in the order: sample TM37 ($150 \text{ cm}^3/\text{g STP}$) > M37 ($50 \text{ cm}^3/\text{g STP}$) > SM ($16 \text{ cm}^3/\text{g STP}$). This is parallel with the extent of structural defects formed in the MCM-41 hexagonal channel matrix, as evidenced by the microtome TEM results. The formation of these structural defects is mainly provoked by the ‘delayed neutralization’ procedure applied during sample synthesis.
- (3) The amount and extent of the structural defect holes (typically 5–30 nm in size) in the framework of MCM-41 depend mainly on the amount of incorporated aluminum and water content and hence can be controlled (within a certain range) by varying the synthesis conditions [15].
- (4) Comparing to SM and M37, sample TM37 was found to possess more extensive structural defects, which may provoke interchannel connections.

2.2. Hydrocracking reaction

1,3,5-Triisopropylbenzene (1,3,5-TiPB) cracking reaction was used as a test reaction, which was conducted in a continuous flow, fixed-bed flow reactor under the conditions: temperature (T_r) = 573 K; weight hourly space velocity (WHSV) = 15.25

h^{-1} ; pressure = 1 atm; carrier gas, N_2 ; $\text{N}_2/\text{feed} = 2.0 \text{ mol/mol}$, and time-on-stream (TOS) = 6 h. Typically, $\approx 1 \text{ g}$ of pelletized ($\approx 40 \text{ MPa}$) MCM-41 sample (10–20 mesh) was used. A small amount of quartz sand (20–30 mesh) was packed on top of the catalyst in the reactor column to ensure adequate pre-heating of the reactant. Prior to the reaction, the catalyst was first activated at 723 K in air for 8 h then cooled under N_2 stream down to the desired reaction temperature. The composition of the reactor effluents was analyzed by gas chromatography (Shimadzu GC-9A) using a packed column (5% SP-1200 + 1.75% Bentone 34 on 100/120 Supelcoport, 6 ft). All products were identified using internal standard method. Upon completion of the experiment, the catalyst was purged with N_2 at T_r for 0.5 h to remove unreacted residues. Then, the reactor system was brought down to 473 K and maintained at the same temperature for over 6 h before it was finally cooled down to room temperature (298 K).

2.3. Catalyst characterization

The coke contents of the spent catalysts were determined by thermogravimetric analyses (TGA, Netzsch TG209). Typically, $\approx 10 \text{ mg}$ of spent sample was heated at a rate of 10 K/min under dry air up to 1173 K. Sample coke content was determined by the weight loss between the temperature range of 573–973 K. The acidity of the Al-MCM-41 samples was characterized by means of ^{31}P MAS NMR of adsorbed trimethylphosphine oxide (TMPO) as probe molecules [24–30]. Prior to the adsorption of TMPO, sample was first subjected to dehydration at 623 K under vacuum ($<10^{-5} \text{ Torr}$; $1 \text{ Torr} = 133.3 \text{ N m}^{-2}$) for more than 24 h. Then, a known amount of dry TMPO (dissolved in dry CH_2Cl_2) was added into the sample vessel, the mixture was agitated overnight under N_2 on an ultrasonic shaker. After the removal of solvent by evacuation, the sample tube was then transferred into a glovebox (under N_2 environment) in which the sample loaded with TMPO was placed into a ZrO_2 MAS rotor (4 mm o.d.) and sealed by gastight Kel-F cap. ^{31}P MAS NMR experiments were performed on a Bruker MSL-500P NMR spectrometer operated at resonance

frequency of 202.46 MHz and a sample-spinning rate of 10 kHz. A single-pulse sequence with pulse-width of 2 μ s ($\approx \pi/5$ pulse) and a recycle delay of 5 s were used. ^1H MAS NMR spectra were acquired at 500.13 MHz and a sample-spinning rate of 5 kHz using a rotor-synchronized spin-echo pulse sequence with a $\pi/2$ pulse of 4.5 μ s and a recycle delay of 15 s. Tetramethylsilane (TMS) and 85% H_3PO_4 aqueous solution were used as the external references for ^1H and ^{31}P chemical shifts, respectively. All spectral analyses were performed using Bruker Winfit software. Diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) experiments were carried out using Bruker IFS-28 FTIR spectrometer. Sample was dehydrated in situ at 673 K for at least 0.5 h before each experiment.

Elemental analysis by ICP (Jarrell-Ash, ICAP9000) was performed to correlate the loading the probe molecules with the amount of acid sites on each sample. Typically, ≈ 0.1 g of the adsorbate loaded sample was dissolved in 10 ml of a HF , HNO_3 , and HCl mixture and then added to 60 ml of a saturated boric acid solution at room temperature. The amount of P, Al, and Si elements were then determined using the respective commercial standards. The ^{31}P resonance arising from TMPO adsorbed on bridging hydroxyls (or Brønsted sites) were renormalized after deducting the contribution from the physisorbed TMPO. The concentration of each acid site can then be determined by assuming that each TMPO occupy only one acid (Al) site [30].

2.4. NMR self-diffusion measurements

Variable temperature ^1H PFG NMR measurements were also performed on the Bruker MSL-500P NMR spectrometer operating at a frequency of 500.13 MHz using a diffusion probe (sample cell o.d. 10 mm). The PFG set-up is capable of producing a maximum magnetic field gradient of 1.0 kG/cm. Sample was first subjected to dehydration by gradual heating (1 K/min) from room temperature up to 623 K then maintained at the same temperature for at least 30 h under vacuum. High purity cyclohexane was degassed by the conventional freeze-pump-thaw method. Then, a known

amount of cyclohexane (3.7 mmol cyclohexane/g sample) was adsorbed onto the MCM-41 sample followed by careful sealing of the sample cell with a mini-torch while trapping the adsorbate at the bottom of the sample cell by liquid N_2 . The sealed sample was then placed at room temperature for at least 3 days to ensure a homogeneous adsorption. All diffusion measurements were performed by a pulsed-field-gradient stimulated echo (PFGSTE) pulse sequence [17] using gradient pulse width (δ), observation time (Δ), and relaxation delay of 400 μ s, 10 ms, and 4 s, respectively. Considering that cyclohexane can be frozen below its bulk freezing point (279.6 K) when adsorbed in mesoporous MCM-41 [31], the measurements were deliberately made within the temperature range of 280–310 K.

3. Results and discussion

3.1. Acidity characterization

Solid-state ^1H MAS NMR and DRIFT spectroscopy are commonly used for the determination of the types of hydroxyl groups in dehydrated zeolites and molecular sieves. Typically, the ^1H MAS NMR resonance of hydroxyl protons in aluminosilicate materials spanned over a range of chemical shift from 0 to 7 ppm. In terms of their local structure types, ^1H NMR signals of the silanol groups (SiOH) normally have chemical shifts of 1.2–2.2 ppm, the hydroxyl protons on extra-framework aluminum species (AlOH) should appear at chemical shifts of 2.6–3.6 ppm, whereas the bridging hydroxyl groups (SiOHAl) cover the range 3.6–7.0 ppm [32]. The bridging OH groups, which act as the proton donor (Brønsted acid) sites, are responsible for the ability of zeolites or molecular sieves to catalyze chemical reactions [33]. On the other hand, in the case of IR measurements, the absorption peaks at 3740, 3650, and 3600 cm^{-1} can be assigned to hydroxyl vibration (O-H stretching) bands of SiOH , AlOH , and SiOHAl groups, respectively [34,35].

However, the ^1H MAS NMR spectra obtained from the two dehydrated Al-MCM-41 (M37 and TM37) samples failed to observe the resonance

Fig. 1. (a) ^1H and (b) ^{31}P MAS NMR spectra obtained from Al-MCM-41 samples (Si/Al=37) with particulate (M37) and tubular (TM37) morphologies. The asterisks represent spinning sidebands. The dashed curves indicate deconvolution results using Gaussian lineshape function.

signals arise from the zeolite-like acid sites, which presumably should appear in the chemical shift range 3.6–7.0 ppm. As can be seen in Fig. 1(a), both spectra reveal only the presence of non-acidic silanol groups. Similarly, the observed DRIFT spectra (Fig. 2) for the dehydrated samples M37 and TM37 also showed only the SiOH absorption band at 3740 cm^{-1} . These results indicate that the local environments of the tubular (TM37) and particulate (M37) Al-MCM-41 samples are rather similar. Nevertheless, the absence of signals associated with bridging OH groups in the ^1H NMR and IR spectra deserve further investigation.

To further investigate the types and distribution of acid sites in the Al-MCM-41 samples, we invoked ^{31}P MAS NMR measurements [24–30] using trimethylphosphine oxides (TMPO) as the probe molecules. It has been proposed that, upon adsorbing TMPO on an acid catalyst, the guest molecules may readily interact with acid sites to form hydrogen-bonded complexes. The TMPO/Brønsted-acid complexes are provoked by bonding of TMPOH^+ with bridging oxygen [28]. Conse-

Fig. 2. IR spectra obtained from (a) SM, (b) M37, and (c) TM37 MCM-41 samples.

quently, the ^{31}P chemical shifts arising from this protonated TMPO species tend to move toward downfield as the degree of proton transfer increases. Thus, ^{31}P NMR resonance peaks with higher chemical shifts should arise from stronger protonic acid species with shorter H–O bonds and hence acid sites with greater acid strength.

The ^{31}P MAS NMR spectra of TMPO adsorbed on the tubular and particulate Al-MCM-41 samples are shown in Fig. 1(b). The fact that both spectra exhibit analogous overlapped resonance peaks indicates the distribution of acid sites in samples M37 and TM37 having the same Si/Al ratio are quite similar, regardless of the difference in their morphology. Subsequent spectra analysis by Gaussian deconvolution revealed the existence of three major resonance peaks at 69, 64 and 48 ppm. The former two peaks can be assigned to TMPO associated with different acid sites, whereas the peak at 48 ppm is due to the physisorbed TMPO [24–30]. Further studies in conjunction with ICP elemental analyses render quantitative determination of the distribution and concentration of acid sites for each sample. This can be readily done by first deducting the physisorbed TMPO from the known amount of TMPO loaded in the sample, followed by renormalizing the peak areas of the ^{31}P resonance responsible for TMPO

Table 1
Acidic and catalytic properties of Al-MCM-41 (Si/Al = 37) samples

Samples	Fresh		After 1,3,5-TiPB cracking reaction				
	Acid sites distribution ^a		Coke content ^b	Deactivation parameters ^c			
	69 ppm	64 ppm		X_0	κ	α^d	$X_0 + \kappa^e$
M37	0.12	0.15	4.2	22.8	30.5	0.47	53.3
TM37	0.13	0.16	3.2	34.0	30.4	0.39	64.4

^a Based on the ^{31}P NMR chemical shift (in ppm) assignments; in unit of mmole acid sites per gram catalyst.

^b Obtained from the spent catalysts by TGA, in unit of wt.%.

^c Results obtained from data fitting of Eq. (3).

^d In unit of h^{-1} .

^e Represents initial conversion (TOS = 0 h); in unit of wt.%.

adsorbed on acid sites to 100%. As the result, the concentration of acid sites can be determined, as depicted in Table 1. It is indicative that the two samples with TWT and particulate morphologies have nearly the same acidity.

It is noted that, while acidity of a catalyst can be achieved by isomorphous substitutions of framework Si by Al atoms during synthesis, the origins of acidity and the related roles played by the framework Al remain controversial. The fact that signals arising from the Al–OH and Al–OH–Si species were invisible on the corresponding IR and ^1H MAS NMR spectra indicating that the silanol groups may be associated with the three-coordinated Al to reveal acidity [36]. As the basic adsorbate molecules interact with the silanol groups of the Al-MCM-41 adsorbent, they may donate extra electrons to the oxygen atoms on the silanol groups and thus promoting the coordination of the slightly negative charged oxygen with the adjacent three-coordinated Al^{3+} sites. Consequently, acid sites analogous to the bridging hydroxyl groups (SiOHAl) in zeolitic materials may be formed. The results in Fig. 1(b) and Table 1 indeed reveal that, there are two types of acid sites. Our recent ^{27}Al MAS NMR experiments on a series of Al-MCM-41 samples saturated with water and acetylacetone provided further supporting evidences [37]. Presumably, those sites with weaker acidic strengths should be originated from silanol groups interacting with the adjacent to three-coordinated framework Al. Whereas sites with stronger acidic strengths should arise from the interaction of silanols with surface Al species.

3.2. NMR self-diffusion of cyclohexane

The effects of structural defects on diffusive properties of siliceous MCM-41 and aluminosilicate MCM-41 samples having different morphologies and extents of structural defects were studied by variable temperature ^1H NMR self-diffusion measurements using cyclohexane as probe molecule. It is noted that, the diffusing molecules should experience rapid exchange between intraparticle channels and interparticle voids, especially within the temperature range (280–310 K) examined. Furthermore, owing to the random orientation of the MCM-41 particles, the observed diffusivity is therefore a weighted average for cyclohexane molecules in the intraparticle channels (D) and interparticle space (D_1) and hence should be classified as quasi-isotropic rather than anisotropic diffusion [23]. The diffusion of cyclohexane in MCM-41 materials can therefore be described by the ‘two-region approximation model’ proposed by Kärger et al. [17,38]. In the case of measurements made by ^1H PFGSTE NMR pulse sequence and assuming that $D_1 \gg D$, the decay (Ψ) of the NMR signal obtained from the stimulated echo can be simplified as [17]:

$$\Psi(\Delta, \delta g) = \exp\{-\gamma^2 \delta^2 g^2 \Delta [D + p_1 D_1 / (\gamma^2 \delta^2 g^2 \tau p_1 D_1 + 1)]\} \quad (1)$$

where Δ is the observation time; δ and g respectively represent the pulse width and strength of magnetic field gradient pulse; γ is the gyromagnetic

ratio of the proton nucleus; p_1 denotes the relative number of molecules in the interparticle region, and τ is the mean residence time of cyclohexane within the intraparticle channels.

Accordingly, the intraparticle self-diffusion coefficients (D), mean residence times (τ) and long-range diffusivities ($p_1 D_1$) of cyclohexane at different temperatures can be obtained by data fitting to the observed echo attenuation curve, as in Eq. (1); the results are depicted in Table 2. Both values of D and $p_1 D_1$ are observed to increase with increasing temperature, as expected. The intraparticle diffusivities of cyclohexane in various MCM-41 samples were also found to obey the Arrhenius relation:

$$D = D_{\infty} \exp(-E/RT) \quad (2)$$

where D_{∞} is the pre-exponential factor and R is the gas constant. The results of the fittings are shown in Fig. 3 and Table 2. The activation energy values (E) correspond to intraparticle diffusion of cyclohexane in MCM-41 are in good agreement with the results obtained by Gjerdåker et al. [22]. The authors reported an E value of 24 and 21 kJ/mol for cyclohexane confined in MCM-41 with particulate and silica rope morphologies, respectively.

Fig. 3. Arrhenius plot showing the temperature dependence of intraparticle diffusivity of cyclohexane obtained from various MCM-41 samples by means of ^1H PFG NMR self-diffusion measurements. The solid lines are calculated using Eq. (2).

3.3. 1,3,5-TiPB cracking reaction

To investigate the effects of structural defects on the catalytic performance of TWT and particulate Al-MCM-41 catalysts, 1,3,5-TiPB cracking reaction was used as the test reaction. The catalytic activity of the each Al-MCM-41 catalyst was assessed by the observed conversion of 1,3,5-TiPB,

Table 2

List of activation energies (E) and NMR diffusion parameters for various MCM-41 samples measured by ^1H PFG NMR of cyclohexane

Samples	E (kJ/mol) ^a	Diffusion parameters ^b			
		T (K)	D ($\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$)	τ (ms)	$p_1 D_1$ ($\times 10^{-8} \text{ m}^2 \text{ s}^{-1}$)
SM	21	281	1.7	5.9	0.9
		286	2.2	4.0	2.0
		298	3.1	3.4	3.3
		308	3.9	3.0	3.2
M37	26	281	2.9	2.4	3.3
		286	4.0	1.9	4.2
		298	4.9	1.8	6.8
		308	7.6	1.8	9.0
TM37	15	281	3.7	5.0	1.9
		286	5.8	7.7	1.8
		298	6.8	6.1	2.2
		308	7.8	5.9	2.7

^a Values (± 3 kJ/mol) obtained from fitting of Eq. (2).

^b Obtained by data fitting to Eq. (1).

Fig. 4. Variations of 1,3,5-TiPB conversion against reaction time-on-stream (TOS) during cracking reaction over various MCM-41 samples. The solid curves were calculated using Eq. (3).

which may be catalyzed to form mainly mono- and di-substituted isopropylbenzene. The standard reaction was carried out at 573 K with a fixed WSHV = 15.25 h⁻¹ for TOS = 0–6 h. In terms of their major product yields, both TWT and particulate Al-MCM-41 catalysts disclosed the same order: *m*-DiPB > *p*-DiPB > cumene > *o*-DiPB > propene ≫ benzene. Only trace amount of benzene was observed.

The variation of 1,3,5-TiPB conversions versus TOS during cracking reaction over samples M37 and TM37 are shown in Fig. 4. The solid curves in Fig. 4 are the results of fittings by an exponential function:

$$X_t = X_0 + ke^{-\alpha t} \quad (3)$$

where X_t represents the conversion at a given time (TOS) t , X_0 and k are constants, and the exponent α is the parameter representing the deactivation rate. The results of the fittings are depicted in Table 1.

An apparent increase in 1,3,5-TiPB initial conversion, $X_0 + k$ (Table 1), for sample TM37 having the tubular morphology than sample M37 with particulate morphology is evident. However, an opposite trend is observed for the deactivation rate (α). Coking is the prominent cause for the deactivation of the catalysts. The coke contents obtained by TGA for the spent samples (TOS = 6 h) TM37

Fig. 5. Variations of DiPB isomer selectivity against reaction time-on-stream (TOS) during cracking reaction over various Al-MCM-41 samples. The solid curves represent empirical fittings to the experimental data.

and M37 were 3.2 and 4.2 wt.%, respectively. This is in line with the trend for the observed deactivation rate, indicating that sample TM37, which possesses more structural defects, is more resistant to coking and deactivation than sample M37.

Fig. 5 shows the variations of selectivity of major products, i.e., DiPB isomers, versus TOS during 1,3,5-TiPB cracking reaction over samples TM37 and M37. It is indicative that the selectivities for the *p*- and *o*-DiPB isomers are much lower than that of *m*-DiPB. The observed selectivity in terms of yield *m*-/*p*-DiPB ratio ~4 is in accordance with the thermodynamic equilibrium distribution. Moreover, for both *p*- and *o*-DiPB isomers, their respective selectivity variation curves for samples TM37 and M37 are not only nearly coincide but also appear to be independent with time-on-stream. In contrast, the observed selectivity for *m*-DiPB, which decreases slowly with increasing reaction time, is notably higher for sample TM37 than M37.

3.4. Effects of structural defects on diffusion and hydrocracking

As shown in Table 2, the observed intraparticle self-diffusion coefficients (D) of cyclohexane in

various MCM-41 samples (at constant temperature) follow the order: TM37 > M37 > SM, which is in parallel with the extents of structural defects observed in the samples. However, no apparent trend can be deduced from the activation energies observed. By comparing the results obtained from the Al-MCM-41 samples with particulate (M37) and tubular (TM37) morphologies, it is conclusive that the two samples which possess nearly the same acidic properties (see Table 1) exhibit marked differences in their transport properties. Thus, the presence of structural defects rather than the framework Al species are responsible for the observed diffusivity enhancement. A rough estimation based on the Einstein's relation [17]:

$$\langle l^2 \tau \rangle = 6D\tau \quad (4)$$

also reveals that, the mean displacement, $\langle l^2 \tau \rangle^{1/2}$, of cyclohexane molecule in sample TM37 at room temperature is $\approx 5 \mu\text{m}$, which is comparable to its particle size ($0.7 \times 3.5 \mu\text{m}$). That the estimated mean displacement value is analogous to the average particle size justifies the analyses of D values by the 'two-region approximation' diffusion model.

In view of the catalytic performance of Al-MCM-41 samples during 1,3,5-TiPB cracking reaction, we have shown that the sample TM37 which possesses the tubular morphology is more superior than sample M37 with particulate morphology. As described earlier, the observed catalytic activity, *m*-DiPB selectivity and tolerance to coking and deactivation for sample TM37 are indeed much better than M37. Yet, the two Al-MCM-41 catalysts have similar distribution and concentration of acid sites, as revealed by ^{31}P MAS NMR of the adsorbed TMPO probe molecules. In this context, diffusion limitation obviously plays the key role in terms of the overall performance of the reaction process. The structural defects present on the Al-MCM-41 catalysts examined in this study thus have definite effects on the catalytic features during hydrocracking reaction. This is mainly facilitated by the interconnected mesoporous channels caused by the wall defects, which effectively promote the accessibility of active sites for the reactants and also ease the diffusion of the products out of the channels of the Al-MCM-41 sample. As the result, the occurrence

of side-reactions and coke formation are greatly reduced.

Thus, sample TM37, which possesses the hierarchical TWT morphology and more extensive structural defects, resulted in a superior catalytic performance than the sample M37 during 1,3,5-TiPB cracking reaction. Our results therefore provide supports to the argument that the pore structure and topology of a catalyst may have strong influences on diffusion of reactants, reaction intermediates and products, and consequently, on activity and selectivity during catalytic reactions. The intimate co-existence of meso- and macropores, which afford interchannel molecular diffusion in the Al-MCM-41 materials, should be advantageous to catalytic applications. In addition to the hydrocracking reaction studied here, other reactions such as ring opening, dealkylation, and transalkylation are the interesting candidates for the catalytic applications of these mesoporous aluminosilicate Al-MCM-41 that contain structural defects. Our ability in controlling the formation and concentration of such defects further render potential applications which need to be exploited further.

4. Conclusions

We have demonstrated that, the structural wall defects possess by the Al-MCM-41 samples uniquely synthesized by the 'delayed neutralization method' provoke interchannel pathways that are favorable for molecular transport. In turn, the catalytic activity and tolerance for coke formation are notably enhanced during hydrocracking reaction. In particular, the sample with special hierarchical tubular morphology having more extensive defects reveals superior catalytic performance during 1,3,5-TiPB cracking than the particulate sample having nearly the same acidic properties. The advantages of the structural defects on the Al-MCM-41 samples reporting here toward some of the prominent properties of a potential catalyst (in this case, more so for catalyzing large molecules), namely suitable pore size, high surface area, high thermal/hydrothermal stability, high catalytic activity, high selectivity, fast adsorbate diffusion, and

resistant to coking/deactivation, can thus be inferred.

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References

- [1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, *Nature* 359 (1992) 710.
- [2] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.-W. Chu, D.H. Olson, E.W. Sheppard, S.B. McGullen, J.B. Higgins, J.L. Schlenker, *J. Am. Chem. Soc.* 114 (1992) 10834.
- [3] A. Corma, *Chem. Rev.* 97 (1997) 2373.
- [4] F. Marlow, M.D. McGehee, D. Zhao, B.F. Chmelka, G.D. Stucky, *Adv. Mater.* 11 (1999) 632.
- [5] S. Mann, G.A. Ozin, *Nature* 382 (1996) 313.
- [6] M. Trombetta, G. Busca, S. Rossini, V. Piccoli, U. Cornaro, A. Guercio, R. Catani, R.J. Willey, *J. Catal.* 179 (1998) 581.
- [7] K.M. Reddy, C. Song, *Catal. Lett.* 36 (1996) 103.
- [8] K.M. Reddy, C. Song, *Catal. Today* 31 (1996) 137.
- [9] A. Ghanbari-Siahkali, A. Philippou, J. Dwyer, M.W. Anderson, *Appl. Catal. A* 192 (2000) 57.
- [10] J.Y. Ying, C.P. Mehnert, M.S. Wong, *Angew. Chem. Int. Ed.* 38 (1999) 56.
- [11] H.P. Lin, S. Cheng, C.Y. Mou, *Micropor. Mater.* 10 (1996) 111.
- [12] H.P. Lin, C.Y. Mou, *Science* 273 (1996) 765.
- [13] H.P. Lin, S. Cheng, C.Y. Mou, *Chem. Mater.* 10 (1998) 581.
- [14] C.Y. Mou, H.P. Lin, *Pure Appl. Chem.* 72 (2000) 137.
- [15] H.P. Lin, S.T. Wong, C.Y. Mou, C.Y. Tang, *J. Phys. Chem. B* 104 (2000) 8967.
- [16] S.T. Wong, H.P. Lin, C.Y. Mou, *Appl. Catal. A* 198 (2000) 103.
- [17] J. Kärger, D.M. Ruthven, *Diffusion in Zeolite and Other Microporous Solids*, Wiley, New York, 1992.
- [18] U. Schemmert, J. Kärger, J. Weitkamp, *Micropor. Mesopor. Mater.* 32 (1999) 101.
- [19] F. Courivaud, E.W. Hansen, S. Kolboe, A. Karlsson, M. Stöcker, *Micropor. Mesopor. Mater.* 37 (2000) 223.
- [20] F. Courivaud, E.W. Hansen, A. Karlsson, S. Kolboe, M. Stöcker, *Micropor. Mesopor. Mater.* 35–36 (2000) 327.
- [21] F. Stallmach, J. Kärger, C. Krause, M. Jeschke, U. Oberhagemann, *J. Am. Chem. Soc.* 122 (2000) 9237.
- [22] L. Gerdäker, D.W. Aksnes, G.H. Sørland, M. Stöcker, *Micropor. Mesopor. Mater.* 42 (2001) 89.
- [23] F. Stallmach, A. Gräser, J. Kärger, C. Krause, M. Jeschke, U. Oberhagemann, S. Spange, *Micropor. Mesopor. Mater.* 44–45 (2001) 745.
- [24] L. Baltusis, J.S. Frye, G.E. Maciel, *J. Am. Chem. Soc.* 108 (1986) 7119.
- [25] J.H. Lunsford, *Top. Catal.* 4 (1997) 91.
- [26] K.J. Sutovich, A.W. Peters, E.F. Rakiewicz, R.F. Wormsbecher, S.M. Mattingly, K.T. Mueller, *J. Catal.* 183 (1999) 155.
- [27] J.P. Osegovic, R.S. Drago, *J. Phys. Chem. B* 104 (2000) 147.
- [28] E.F. Rakiewicz, A.W. Peters, R.F. Wormsbecher, K.J. Sutovich, K.T. Mueller, *J. Phys. Chem. B* 102 (1998) 2890.
- [29] W.H. Chen, T.C. Tsai, S.J. Jong, Q. Zhao, C.T. Tsai, I. Wang, H.K. Lee, S.B. Liu, *J. Mol. Catal. A* 181 (2002) 41.
- [30] Q. Zhao, W.H. Chen, S.J. Huang, Y.C. Wu, H.K. Lee, S.B. Liu, *J. Phys. Chem. B* 106 (2002) 4462.
- [31] D.W. Aksnes, L. Gerdäker, *J. Mol. Struct.* 475 (1999) 27.
- [32] M. Hunger, *Cat. Rev.—Sci. Eng.* 39 (1997) 345.
- [33] N.Y. Chen, W.E. Garwood, F.G. Dwyer, *Selective Catalysis in Industrial Applications*, Marcel Dekker, New York, 1989.
- [34] A. Auroux, V. Bolis, P. Wierzbowski, P.C. Gravelle, J.C. Védrine, *J. Chem. Soc. Faraday Trans. I* 75 (1979) 2544.
- [35] J.C. Védrine, A. Auroux, V. Bolis, P. Dejaifve, C. Nacache, P. Wierzbowski, E.G. Derouane, J.B. Nagy, J.P. Gilson, J.H.C. Van Hooff, J.P. Van de Berg, J. Wolthuisen, *J. Catal.* 59 (1979) 248.
- [36] M. Trombetta, G. Busca, M. Lenarda, L. Storaro, M. Pavan, *Appl. Catal. A* 182 (1999) 225.
- [37] Q. Zhao, W.H. Chen, S.J. Huang, Y.C. Wu, H.K. Lee, S.B. Liu, *Stud. Surf. Sci. Catal.* 141 (2002) 453.
- [38] J. Kärger, H. Pfeifer, W. Heink, *Adv. Magn. Res.* 12 (1988) 1.