Effect of SiO$_2$/Al$_2$O$_3$ Ratio on Micro-Mesopore Formation for Pt/Beta-MCM-41 via NaOH Treatment and the Catalytic Performance in N-heptane Hydro isomerization

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Abstract. Micro-mesoporous composite material Beta-MCM-41 (BM) were hydrothermally synthesized by treating parent beta with molar SiO$_2$/Al$_2$O$_3$ ratios of 12.5, 20 and 30 as precursors. The influence of SiO$_2$/Al$_2$O$_3$ ratio of zeolite beta on effective micro-mesoporous composite formation was studied by investigating the crystallinity, morphology, chemical composition, acidity and textural property of Beta-MCM-41 through XRD, nitrogen adsorption, SEM, TEM, NH$_3$-TPD, FTIR and Pyridine-FTIR. The catalytic performance was evaluated in terms of n-heptane hydro isomerization. The results demonstrated that Beta-MCM-41 supported Pt catalysts showed higher selectivity to isohexanes than Pt/Beta. It was attributed to the superiorities of the pore structure and mesoporous accelerated the diffusion of larger molecules of isohexanes.

1. Introduction
Because of environmental protection, reformulated gasoline’s must reduce aromatic and olefin content[1] and result in lowering octane rating. Isomerization of paraffin’s larger than C$_6$ is one way to improve octane without increased aromatic or olefin content. N-C$_7$ has a research octane rating of 0, while 2-methyl hexane and 2,3-dimethylpentane have research octane ratings of 53 and 93, respectively[2]. C$_7$ paraffin’s are relatively abundant in naphtha, and is usually used as the model reactant in this study[3]. No industrial hydro isomerization process exists for C$_7$ paraffin’s due to their high tendency to crack.[4]

Pt/Cl/alumina is the preferred catalyst for commercial C$_5$/C$_6$ isomerization. Pt/morden catalysts are also used[5], n-C$_7$ isomerization over Pt or Pd on morden[6], ZSM-5[6], β-zelite[7-8], Y zeolite[9-10], SAPO [11-13], SO$_4$$_2$/ZrO$_2$[14-15], and WO$_x$/ZrO$_2$[16] has been reported. Several patents covering isomerization of paraffin’s including C7 over catalysts based on amorphous alumina and silica-alumina

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supports have been granted [17]. Among them, the Pt/Beta catalyst is considered to be a promising candidate for hydro-isomerization of C7 hydrocarbon feedstocks [18-19]. However, the predominant presence of microspores in micro porous zeolites imposes diffusion limitations on reactions involving bulkier molecules that have the size larger than microspores[20]. To overcome this limitation, extensive efforts have been devoted to synthesis of zeolite nan crystals [21], large-pore zeolites and zeolite analogs, and ordered mesoporous materials[22].

Pure mesoporous silica does not have enough acidity, low thermal and hydrothermal stability. The development of composite micro/mesoporous materials [23-28] opens new perspectives to the improvement of hydro isomerization selectivity of zeolitic catalysts. These materials combine the advantages of both zeolites and mesoporous molecular sieves, especially, strong acidity, high thermal and hydrothermal stability and improved diffusivity of bulky molecules.

In this work, parent zeolite Beta with molar SiO2/Al2O3 ratios of 25-60 were treated by 1.5M NaOH at 40oC for 50 min to investigate the effect of SiO2/Al2O3 ratio of zeolite beta on the micro-mesoporous composite formation. To the best of our knowledge, through some on micr-o-mesoporous creation in Beta-MCM-41 have already been made, no systematic evaluation on the influence of SiO2/Al2O3 ratio of the zeolite beta on micro-mesoporous formation via alkaline treatment has been reported. The catalytic performances of Beta-MCM-41(BM), Beta and MCM-41 supported Pt were confirmed using n-heptane isomerization and distinctly enhanced catalytic performances are observed in BM isomerization on account of the development of mesoporosity.

2. Experimental

2.1. Materials
Cetyltrimethyl ammonium bromide (99%, CTAB), tetraethyl orthosilicate (99%, TEOS), NaOH(AR grade) and hexachloroplatinic acid (AR grade, H2PtCl6·6H2O) were purchased from Sino pharm Chemical Reagent Co. Ltd, People’s Republic of China. A commercial zeolite Beta, with nominal SiO2/Al2O3=25, 40 and 60 was provided by Nankai University Catalyst Co. All reagents were used as received without further purification.

2.2. Preparation of Supports

2.2.1 Synthesis of Beta-MCM-41. The Beta/MCM-41 composite (BM) was prepared using beta zeolite as silica-alumina source according to a modified method of Zhang et al [29]. A typical synthesis procedure was as follows: 9.6 g of Beta zeolite (SiO2/Al2O3=25, 40, 60) was dispersed in 72 ml NaOH solutions (1.5M) follower stirred for 50 min at 40 oC. Then, 74 g (14 wt% aqueous solution of CTAB) was added to this solution at 0.86 ml/min. The pH of the mixture was adjusted to 9.6 by dropwise addition of 50 wt% aqueous CH3COOH with vigorous stirring. After additional stirring for 15 min, the mixture was loaded into an autoclave and hydrothermally treated at 100 °C for 48 h. The resulting material was filtered, rinsed with deionized water and dried in air at 100 °C for 12 h. Finally, the as-synthesized product was calcined at 550 °C in air for 12 h to remove the organic species in the pores. The resulting sample is designated as BM (n), where n denotes the SiO2/Al2O3 ratios of zeolites beta used for s silica-alumina source.

2.2.2 Synthesis of MCM-41. MCM-41 used in this work was synthesized using a method described elsewhere. First, 0.8 g CTAB was mixed with 39 g water and 4.0 g of 2 M NaOH solution. To this solution 3.8 g TEOS was added at room temperature and stirred for 30-60 min. The mixture was then placed in an oven at 100 °C for 72 h. The solid product was recovered by filtration on a Buchner funnel, washed with distilled water repeatedly, dried in air at ambient temperature, and calcined at 550 oC in air for 6 h.
All prepared samples (BM and Beta) were ion exchanged three times with 1.0 M of NH4Cl solution at 80 °C for 1h and finally washed with distilled water. The ion-exchanged products were dried at 110 °C for 3 h and then claimed at 550 °C for 5 h to obtain the final products.

2.3. Preparation of Catalysts
Platinum supported catalysts with 0.4 wt% Pt loading were prepared by incipient wetness impregnation using aqueous H2PtCl6·6H2O solution on the acidic forms of the supports (BM, Beta and MCM-41). The impregnated catalysts were dried at 110 °C for 12 h and claimed at 400 °C for 4 h.

2.4. Catalytic Test

![Process flow diagram of hydro isomerization](image)

**Figure 1.** Process flow diagram of hydro isomerization

Hydro isomerization of n-heptane was carried out on an atmospheric fixed-bed flow reactor loaded with 0.5 g of the granular catalyst (0.25-0.42 mm) and is shown in Fig.1. Before reaction, the catalyst was reduced in-situ under H2 flow at 400 °C for 4 h. The typical reaction conditions contain: reaction temperature 240°C, weight hourly space velocity (WHSV) 2.46 h⁻¹, molar ratio of H2 to n-heptane 6.0 and time on stream (TOS) 120 min. The products were analyzed online with a gas chromatograph (Techcomp GC-7900) equipped with a TM-1 capillary column(50m×0.25mm×0.5μm)and FID.

2.5. Characterization
The supports and catalysts were characterized by a variety of methods. Power X-ray diffraction (XRD) on an X’Pert PRO MPD diffractometer (Philips, Netherland) using a 142 Cu Kα radiation (λ = 0.1540 nm) at 40 kV and 40 mA.

Nitrogen physisorption was performed at -196oC using a Micrometrics ASAP 2020M static volumetric analyzer. The samples were degassed at 300 °C overnight before sorption measurements.
The surface area was calculated using the BET method based on adsorption data in the partial pressure range 0.05-0.2. The pore-size distribution for mesopore was analyzed from desorption branch of the isotherm by the Barrett Joyner-Helena (BJH) method and the pore-size distribution for microspore was analyzed by HK method.

Fourier transform infrared (FT-IR) spectra were recorded by a Nicolet 6700 spectrometer equipped with a MCT liquid nitrogen cooled detector and a KBr beam splitter. The spectra of the samples were recorded by accumulating 64 scans at 4 cm⁻¹ resolution.

Pyridine adsorption (Py-FTIR) spectra were recorded on a NEXUS FTIR (Thermo Fisher Scientific, 166USA) using pyridine as a probe molecule to examine the nature of surface acid sites. Prior to measurement, the samples were degassed for 2 h in a vacuum at 573 K to ensure the moisture removal. The pyridine adsorption was conducted in a drying oven for 24 h in vacuum. The FT-IR spectra were finally recorded from 4000 to 400 cm⁻¹ using the average record of 64 times scanning.

Scanning electron microscopy (SEM) images were obtained with a Sirion 200 (FEI) instrument. High resolution transmission electron microscopy (HR-TEM) images were recorded on a JEM-2100 equipment (JEOL) at 200 kV.

Ammonia temperature programmed desorption (NH3-TPD) was performed on ChemBET-3000 TPR/TPD, Quanta chrome instruments. Typically, 150 mg of sample particles (20-40 mesh) was pretreated at 520 °C for 1 h in He flow (100 mL min⁻¹) and was subsequently cooled to the adsorption temperature of 100 oC. After contact of sample with the gas mixture of NH3: He (10.24 vol.% of ammonia) at the rate of 90 mL min⁻¹ for 10 min, He flow was passed through the sample to remove weakly adsorbed NH3 molecules for 10 min. Finally, the He flow (100 mL min⁻¹) was passed through the sample with increasing temperatures up to 500 °C at the rate of 10 °C/min.

3. Results And Discussion

3.1. Structure of Supports

XRD patterns for various catalysts are illustrated in Fig.2. In the large angle region of 5-50o (Fig, 2a), it can be seen that the three samples with different SiO₂/Al₂O₃ ratios possesses very intense XRD peaks at 7.6o and 22.4o[2, 30], suggesting a crystallinity retention of the BEA phase in the hydrothermal synthesis of the composite molecular sieves. The hydrothermal step in the presence of CTAB leads to the assembling of these dissolved species into the mesoporous phase, which depending on the degree dissolved of zeolite dissolution[31]. At lower framework SiO₂/Al₂O₃ ratios, the relatively high Al content inhibits Si extraction[32-33]. Therefore, the increase of SiO₂/Al₂O₃ ratio led to a signification drop in peak intensity, and at the highest concentration of BM (60), only traces of BEA structure were observed. BM (25) gave two distinct featured peaks, indicating only a small fraction of silicon is removed and formed the composite molecular sieves through the hydrothermal process. On the other hand, as shown in (Fig. 2b), the MCM-41 sample showed an intense XRD peak at 2θ=2.26 corresponding to the (100) plane, and a series of overlapping peaks for the (110), (200) plane. The XRD pattern indicates that this material has a well-ordered mesoporous structure, which belongs to the hexagonal symmetry [34]. BM gave the distinct peaks for (100) reflections, and with the increase of SiO₂/Al₂O₃ ratio, the intensities increased accordingly, indicating that the stronger desalination for Beta zeolite that caused more destruction of the micro-structure is favorable to the formation of larger and more ordered MCM41 mesopores.
3.2. Porous Properties of the Supports

The porous properties of the catalysts were examined by N₂ adsorption-desorption isotherms. The N₂-physisorption isotherms and the corresponding BJH pore size distributions of various catalysts are showed in (Figs.3a) and (Figs.3b), respectively. It can be seen that all BM composites exhibit a typical irreversible type IV isotherm[35], well express H₁ hysteresis loops, at relative pressures P/P₀ of 0.45-1.0.

The condensation step on the isotherm is characteristic of capillary condensation of framework-confined mesoporous and the mesopores became richer with the increase of SiO₂/Al₂O₃ ratio. This observation corresponds well to that in the XRD patterns in Fig 2b. Corresponding the pore size distribution reveals

| Samples   | S_BET(m²g⁻¹) | V_p(cm³g⁻¹) | V_mes(cm³g⁻¹) | V_mic(cm³g⁻¹) | V_mic/V_mes | d_BJH(nm) |
|-----------|--------------|-------------|---------------|---------------|-------------|------------|
| Beta      | 513          | 0.48        | 0.17          | 0.31          | 1.82        | 3.74       |
| BM(25)    | 633          | 0.68        | 0.41          | 0.27          | 0.66        | 4.29       |
| BM(40)    | 706          | 0.76        | 0.54          | 0.22          | 0.41        | 4.34       |
| BM(60)    | 832          | 0.90        | 0.65          | 0.25          | 0.39        | 5.98       |
| MCM-41    | 1327         | 0.96        | 0.91          | 0.05          | 0.055       | 2.04       |

a Calculated by the BET method.
b The total pore volume was obtained at a relative pressure of 0.98.
c Calculated using the BJH method.
d Calculated using the t-plot method.
Mesopore diameter calculated using the BJH method. That there is a mean diameter around 3.0 nm in the composite [36-37]. It can be seen that MCM-41 show a very small hysteresis loop, showed a smaller diameter (2.5 nm). In contrast, the Beta zeolite manifest their microporpus properties with type I adsorption/desorption isotherm with a steep rise at \( p/p_0 < 0.01 \), whereas no mesopores are detected in the Beta zeolite.

![Figure 3.](image)

**Figure 3.** (a) N2 adsorption/desorption isotherms of catalyst supports, and (b) BJH pore size distribution curves of catalyst support

The textural and structural properties are shown in Table 1. Compared to the Beta zeolite (\( V_{tb} = 0.48 \text{cm}^3 \text{g}^{-1} \)), the MCM-41 and BM supports possess high surface areas and pore volumes which are consistent with the reported observations on mesoporous materials. MCM-41 has mesoporous (\( V_{mes} = 0.96 \text{cm}^3 \text{g}^{-1} \)) after the removal of tailback copolymers (the microstructure template) that have been inserted into silicate wall.

3.3. Morphology of the Supports

Figure 4 shows the scanning electron microscopy images of the parent Beta, MCM-41, Beta/MCM-41 composite. The parent zeolite Beta appear like discrete particles with sizes up to several \( \mu \text{m} \). Irregular amorphous particles can be assigned to mesoporous MCM-41 aggregates with fine particle size of smaller than 1 \( \mu \text{m} \), while the Beta/MCM-41 composite shows spherically agglomerated particles. The Beta/MCM-41 composite material obtained by alkaline dissolution of Beta shows unique aggregated crystals, zeolite Beta and MCM-41 uniformly distributed and closely touched. This suggests that the dissolution of Beta crystals and the assembly process of MCM-41 probably occurred simultaneously.
Figure 4. HRSEM micrographs of sample (a) Beta; (b) MCM-41; (c) BM(40); (d) BM(60)

This would be beneficial for the incorporation of more zeolitic structural units in the pore wall of MCM-41.

HRTEM image of MCM-41 and BM are shown in Fig 5. The TEM of MCM-41 shows well-ordered hexagonal arrays of mesopores and confirm its 2D hexagonal structure with p6 mm symmetry. Meanwhile, the TEM images of BM exhibit show the same mesopores channels as MCM-41, which confirm that both MCM-41 and BM possess the 2D hexagonal p6 mm symmetry. Both the pore channels and the hexagonal symmetry can be clearly identified in the different areas of the images.
3.4. FTIR Spectra of the Supports

The infrared spectra were shown in Fig. 6. All supports have very similar IR spectra. The strong broaden peak near 1090 cm\(^{-1}\) absorption peak corresponds to the Si-O-Si bond symmetric stretching vibration, while in the vicinity of 461 cm\(^{-1}\) and 800 cm\(^{-1}\) attributable to Si-O-Si bending vibration and symmetric stretching vibrations. Two bands centered at ~520 and 570 cm\(^{-1}\) are typical vibration modes for zeolite Beta (six-or five membered rings of T-O-T(T=Si or Al) in micro porous zeolites) [38]. Similar to the SiO\(_2\)-based mesoporous materials MCM-41, the framework vibration spectrum of BM (40) consists of bands centered at ~461, 800, and 1090 cm\(^{-1}\). Two bands centered at ~520 and 570 cm\(^{-1}\) are observed in the FT-IR spectra of BM (40) and Beta. These results may indicate that BM has the same structural unit as Beta zeolite. In other words, there are some Beta zeolite primary units in the BM material.

The FTIR spectra of pyridine adsorbed on various supports are shown in Fig. 7 (1400-1700 cm\(^{-1}\) zone). The typical bands can be seen at 1636 cm\(^{-1}\), 1597 cm\(^{-1}\) and 1544 cm\(^{-1}\), which are assigned to structural OH\(^{-}\) ion vibration indicative of the interaction of pyridine with Bronzed acid sites (PyH\(_{+}\)). The band at 1455 cm\(^{-1}\) is assigned to pyridine interaction with Lewis acid sites (PyL) of the framework aluminum, and 1490 cm\(^{-1}\) for pyridine interacting with Bronzed and Lewis sites[39]. Quantitative evaluation of the pyridine ring vibrations revealed that the concentrations of pyridinium ions and Lewis acid-coordinated pyridine varied considerably. The MCM-41 exhibits only Lewis acidity and no Bronzed acid sites are formed. In contrast, bands at 1544 and 1636 cm\(^{-1}\) are observed in the spectra of the Pt/Beta and Pt/BM catalysts, suggesting that there are Bronzed acid sites in these samples. Meanwhile, for Pt/BM catalysts,
At lower framework SiO$_2$/Al$_2$O$_3$ ratios, the relatively high Al content can prevent the removal of silicon led to higher concentrations of Bronzed and Lewis acid sites. With SiO$_2$/Al$_2$O$_3$ ratios of zeolites beta

Figure 6. FTIR spectra of various supports

Figure 7. FTIR spectra of pyridine adsorbed on various supports
Increasing, the concentrations of Bronzed and Lewis acid sites decrease. This result is consistent with XRD.

3.5. NH₃-TPD
The acidity of the H-form samples are characterized by NH₃-TPD. One dispersed peak in a very large temperature range for all samples. Fig. 8 depicts the profiles obtained with various supports. Evidently, the amount of acid sites on BM sample is larger than MCM-41 and is smaller than on the Beta sample. BM possess a smaller amount of acid sites due to the non-acidity of MCM41. The amount of acid sites increase gradually in the order BM(25)> BM(40)> BM(60).

Figure 8. NH₃-TPD profiles of various catalytic

3.6. Catalytic Performance for the N-heptane of the Hydro isomerization
Table 2 compares the catalytic activities of various catalysts for the hydro isomerization of n-heptane. It can be seen that Pt/Beta alone showed a high conversion of n-heptane of 81.86%, but with a low selectivity to isomerization of 41.34% and a high cracking selectivity 58.66%. After the modification of Beta by hydrothermal compositing with MCM-41, all the resulting catalysts showed an increase in selectivity to isomerization, while the conversion decreased to some extent. For Pt/BM, the selectivity to isoheptanes increased with the SiO₂/Al₂O₃ ratios, but with a sharp reduction of conversion. In detail, Pt/BM (40) exhibited moderate selectivity to isomerization (83.95%) and conversion of n-heptad (66.14%), but Pt/BM (60) showed a much lowered conversion (55.76%), 86.11% of isomerized selectivity, Pt/BM (25) showed a much lowered isomerized selectivity (80.64%), 74% of conversion. Pt/BM (40) is considered to be a promising catalyst because it provided a very high selectivity to isomerization of 83.95% while the conversion kept at 66.14%. The MCM-41 supported catalyst exhibited a lower isomerized conversion than the BM-supported catalyst, although it had larger surface area and pore volume. This is probably due to the weaker acidity of the pure silicon MCM-41. Pt/zeolite is the typical functional catalyst for the hydro isomerization of alkanes[39]. Regarding the zeolite support, both acidity and pore structure play important roles [40-42]. Generally speaking, the conversion
of alkane depends largely on the acidity of zeolite and the selectivity to isomerization is highly influenced by the channel structure in zeolite [43-44]. In this study, the mesopores introduced into Beta zeolite by hydrothermal compositing with MCM-41 are considered to be helpful to speed up the transmission of the formed isomerized heptane’s with larger molecular sizes, and to shorten the residence time for the intermediate carbocation’s on acid sites to avoid further cracking [45]. Thus the result lead to higher selectivity to isomerization. For Pt/BM catalysts, the increase of the selectivity to isooctanes with the increase of MCM-41 mesopores (Fig.2b) further demonstrates that the mesopores contribute greatly to the fast diffusion of the larger molecules of isooctanes. Meanwhile, the decrease of conversion is most related to the decrease of the amount of acid sites, especially the strong acid sites, due to those treatments (Fig. 8) [46-47]. Compared to Pt/ (BM), Pt/BM (40) had much higher selectivity to isomerization coupled with a considerable conversion. This arises from the high number of MCM41-structured mesopores of the BM(40) composite connecting with the micro-channels of Beta zeolite [48].

| TABLE 2. Catalytic activities of various catalysts for hydro isomerization of n-heptane |
|-----------------------------------------------|----------|----------|----------|----------|----------|
|                                | Pt/Beta | Pt/BM(25) | Pt/BM(40) | Pt/BM(60) | Pt/MCM-41 |
| dimethylmethane                | 20.61   | 6.25      | 4.97      | 1.83      | 0         |
| iso-butane                     | 27.30   | 8.08      | 5.65      | 5.92      | 0         |
| 2-methylhexane                 | 10.88   | 22.45     | 22.17     | 15.83     | 0.23      |
| 3-methylhexane                 | 12.84   | 22.49     | 21.52     | 17.65     | 0.31      |
| 3-ethylpentane                 | 0.82    | 1.45      | 1.15      | 1.65      | 0.13      |
| 2,2-dimethylpentene            | 1.91    | 2.72      | 3.08      | 1.82      | 0         |
| 2,3-dimethylpentene            | 3.39    | 4.93      | 4.05      | 4.65      | 0.95      |
| 2,4-dimethylpentene            | 2.96    | 4.49      | 4.33      | 4.34      | 0         |
| 3,3-dimethylpentene            | 0.74    | 0.90      | 0.10      | 1.27      | 0         |
| 2,2,3-trimethylbutane          | 0.23    | 0.24      | 0.12      | 0.80      | 0         |
| n-heptane                      | 18.32   | 26        | 32.86     | 44.24     | 99.23     |
| Isomerization (%)              | 81.68   | 74        | 66.14     | 55.76     | 0.765     |
| Mono-is heptane (%)            | 24.54   | 46.39     | 44.84     | 35.13     | 0.67      |
| multi-isooctanes (%)           | 9.23    | 13.28     | 11.68     | 12.88     | 0.095     |
| Selectivity (%)                | 41.34   | 80.64     | 83.95     | 86.11     | 100       |
| Yield (%)                      | 33.76   | 59.67     | 55.52     | 48.01     | 0.65      |
| Crashing (%)                   | 58.66   | 19.36     | 16.06     | 13.89     | 0         |

4. Conclusion
In this study, Beta-MCM-41 composite molecular sieves were hydrothermally synthesized and used as supports to prepare functional catalysts Pt/BM for the hydro isomerization of n-heptane. The catalyst/BM (40) is much more selective for isomerization products than the counterparts using Beta, MCM41 as the supports. At the reaction temperature of 240 °C, molar ratio of H2 to n-heptane 6 and WHSV 2.46h⁻¹, Pt/BM (40) exhibits a very high selectivity to isomerization of 83.95% with a considerably high conversion of 66.14%. The promoted selectivity to isomerization mainly arises from the adequate MCM41-structured mesoporous connecting with zeolite channels, which favors the diffusion of the larger molecules of isooctanes.

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