

Preparation of Hierarchical Mesoporous MFI-Type Zeolite Using Cost-Effective and Sustainable Hard Template

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Abstract

The preparation of hierarchical mesoporous zeolites has lately become one of the principal focuses in the catalysis field. In this work, hierarchical mesoporous ZSM-5 zeolite (HM-ZSM-5) was successfully synthesized using soluble starch as a cheap mesoprogen. Techniques such as XRD, N₂ adsorption, FT-IR and TGA have been conducted to study the structural characteristics of the synthesized mesoporous ZSM-5 zeolite. The XRD and FTIR results verified the formation of aluminosilicate with MFI framework topology. Nitrogen isotherm of the HM-ZSM-5 sample showed a broad hysteresis loop can be in the relative vapor pressure range of 0.4-1.0 bar corroborating the generation of hierarchical mesoporosity in the synthesized zeolite sample. Additionally, the BJH pore-size distributions of HM-ZSM-5 confirmed the presence of hierarchical mesoporosity. The prepared HM-ZSM-5 sample has high thermal stability comparable to that of the conventional microporous counterpart. In light of its excellent properties including hierarchical porosity, large surface area as well as high thermal stability, HM-ZSM-5 can be deemed as a potentially promising catalyst with efficient mass-transfer, reduced diffusion limitation and improved resistance against coke deactivation.

Keywords: ZSM-5; Hierarchical zeolites; Hard template; Starch

Introduction

Over the past decades, zeolites have been *extensively* used as efficient heterogeneous acid catalysts for a wide variety of important processes in the oil refining and petrochemicals industries [1-8]. These processes include fluid catalytic cracking (FCC), hydrocracking, xylene

isomerization, alkylation of aromatics, reforming, linear paraffin isomerization and methanol-to-hydrocarbon conversions. The outstanding performance of zeolites as heterogeneous catalysts mainly originates from their strong Brønsted acidity and excellent shape selectivity [3,9].

In spite of the advantages offered by zeolite microporosity in terms of the extremely high surface area and the unique shape selective properties, the sole presence of micropores induces severe mass transport limitations [8,9]. It causes inefficient utilization of the internal voids of zeolite [10-18]. The access of the bulky reactant molecules to the catalytically active sites located within them is hampered, thus the conversion of bulky reactants takes place only over the active sites located on the outer surfaces of the zeolite [8,9,19,20]. Additionally, it may also cause fast deactivation of the catalyst by pore plugging by carbonaceous residue (coke) [8,20].

In recent years, *two different strategies have been described* in the literature to improve mass transfer in zeolite pores and increase accessibility to the catalytic active sites (see Figure 2). The first strategy is to shorten the diffusion path length for reactants and products via decreasing the crystal size of zeolite, the so-called nanosized zeolite crystals or nano-zeolites [3,18]. Although, nano-zeolites have been found to have superior catalytic performance, particularly when dealing with bulky molecules, and higher resistance against deactivation by coke formation as compared to their conventional micrometre-sized counterparts [21-25], their high *synthesis cost and the problems* encountered in their efficient separation *from reaction media* severely restrict their practical utility on a large-scale [3,18,26].

The second strategy involves the introduction of a *secondary mesoporous system* i.e. pores with diameters ranging from 2.0 and 50 nm, inside the microporous zeolite crystals [3,8,18,19]. The term hierarchical zeolites is commonly used in the literature to describe this type of zeolites because they have two levels of porosities; a supplementary mesoporosity in addition to the original zeolite microporosity and thus having a hierarchy of pore sizes [3,8,27]. *Hierarchically structured zeolite has gained enormous and increasing interest during recent years because they combine the positive aspects* found in both microporous zeolites (shape-selectivity, strong acidity, high hydrothermal stability) and mesoporous materials (efficient mass-transfer, reduced diffusion limitation and improved resistance against coke deactivation) in one material. These properties make these materials suitable for catalytic applications which are beyond the reach of the conventional microporous zeolites or mesoporous materials [3,8,18,27]. Throughout the last several years, mesostructured zeolites have proven to be highly efficient catalysts in a large variety of reactions, including selective hydrogenation [28], alkylation of benzene [29], conversion of methanol to hydrocarbon [30], xylene

isomerization [31,32], hydrocracking [33] and fluid catalytic cracking [34].

Over the past few years, several methods for the preparation of hierarchical meso-structured zeolites have been reported. Generally, these methods can be categorized into three classes namely, assembly, demetallization and mixed methods. In the assembly methods, also called 'bottom-up' or 'constructive' methods, the mesoporous system is generated by mean of the self-assembly of nano-sized zeolite crystals in the presence of a sacrificial mesopore directing agent [8]. In the demetallization methods, also called 'top-down' or 'destructive' methods, *mesoporosity is generated into* pre-existing microporous zeolites through the selective extraction of framework Si or Al atoms [8] and [35]. The third approach for the formation of hierarchically structured zeolites is the mixed methods or the zeolite recrystallization approach which is a combination of the above mentioned two methods. This route *involves two steps*: partial dissolution of a pre-synthesized microporous zeolite in an alkaline solution followed by the reassembling of the zeolitic fragments into a mesoporous structure in the presence of a surfactant [8] and [36].

In this work, hierarchical mesoporous ZSM-5 zeolite (HM-ZSM-5) was synthesized through the hard-template using starch as the mesoporous template. The structural characteristics of the HM-ZSM-5 were investigated by X-ray powder diffraction (XRD), N₂ sorption isotherm, Fourier Transform-Infrared Spectroscopy (FTIR) and thermal gravimetric analysis.

Experimental

Preparation of Hierarchical Mesoporous ZSM-5

A hierarchical mesoporous ZSM-5 (HM-ZSM-5) was synthesized using the tradition hydrothermal method [37]. Starch was used as a cheap mesopore template for modifying the pores of the catalyst. A typical synthesis was carried out as follows. In a 50 ml propylene bottle; 0.083 g of NaAlO₂ (Si/Al=20) was dissolved in 4.8 g TPAOH solution under vigorous stirring for 1 h to obtain a clear aluminate solution. 10.8 g deionized water and 0.032 g NaOH were added to solution under stirring then 4.2 g TEOS was added dropwise into the resulting solution. The mixture was stirred for 4 hours at 353 °K in an oil bath to obtain a uniform sol-gel, and then 3.5 g starch was added and stirred over night at 353 °K. Finally, the mixture was crystallized in a Teflon lined stainless steel autoclave at 453 °K for 48 h. The solid product was

separated by centrifugation, washed to neutral with deionized water several times, dried overnight at 373 °K and finally calcined in air at 873 °K for 10 h.

The H-form ZSM-5 sample was obtained as follows. Calcined ZSM-5 sample was put in 1 mol/L NH₄OH aqueous solution (with solid to liquid ratio of 1:40) and stirred for 6 h at 353°K. Then, the NH₄-type ZSM-5 was separated and washed by deionized after three times of ion-exchange. Finally, the solid was dried overnight at 373°K and calcined in air at 873°K for 3 h.

Catalyst Characterization

Powder X-ray diffraction (PXRD) patterns were recorded on a Bruker AXS D8-ADVANCE diffractometer using a filtered CuK α radiation source ($\lambda = 1.54056 \text{ \AA}$) operated at 40 kV and 30 mA. Diffraction data were collected in the 2θ range of 3-40° with a 0.02° 2θ step size and 0.4 s count time. The surface characteristics of the prepared samples were determined from N₂ adsorption-desorption isotherms measured at liquid nitrogen temperature (-196°C) using a Quantachrome Nova 3200 S instrument. Before the measurements, the samples were degassed at 573°K under vacuum overnight to remove any guest molecule from catalyst surface and pores. The

specific surface area was evaluated using the BET method applied to the range of relative pressures between 0.05 and 0.15. The total pore volume was calculated using single-point adsorption method at a relative pressure of $P/P^0 = 0.95$. Fourier transform infrared (FT-IR) spectra were obtained on an ATI unicam (Mattson 936) Bench Top spectrometer with pressed KBr pellets in the range of 4000-400 cm⁻¹.

Results and discussion

XRD

In the current investigation, hierarchical mesoporous ZSM-5 zeolites were synthesized using the co-templates of TPAOH and starch by adding starch in the conventional ZSM-5 synthetic gel. X-ray diffraction (XRD) diffractograms of the as-obtained HM-ZSM-5 sample is shown in Figure 1. The pattern of the micro-ZSM-5 sample prepared without the addition of starch is also given in the same figure for the sake of comparison. Both samples displayed diffraction lines at 2θ of 7.86°, 8.78°, 14.78°, 23.18°, 23.90° and 24.40° which can be readily attributed to ZSM-5 zeolite (JCPDS no. 43-0321), suggesting that the two samples have the MFI framework topology.

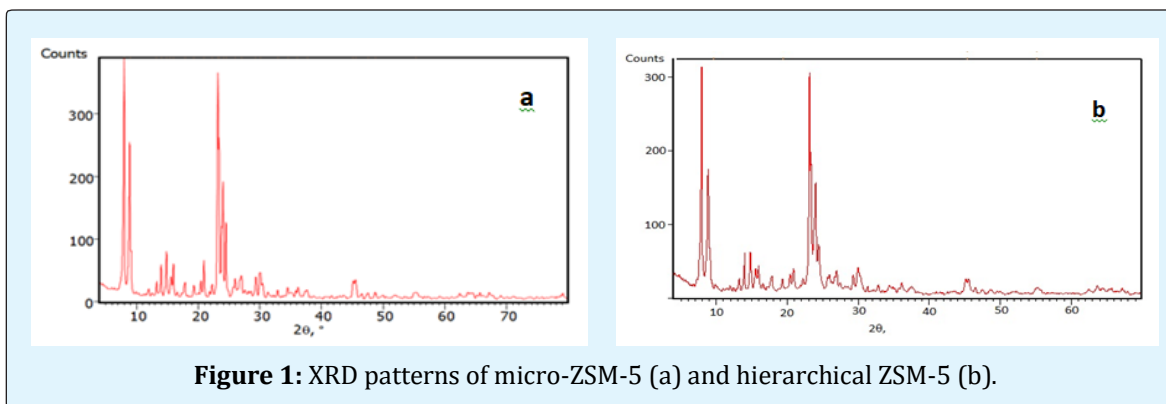


Figure 1: XRD patterns of micro-ZSM-5 (a) and hierarchical ZSM-5 (b).

FTIR

FT-IR spectra of the hierarchical and microporous ZSM- zeolite samples are depicted in Figure 2. The FTIR spectrum displayed a band at 3445 cm⁻¹ that can be assigned to stretching siloxane groups or O-H stretching of adsorbed water molecules [38,39]. The band at 1644 cm⁻¹ can be indexed to physically adsorbed water [38]. The symmetric stretching of the siloxane groups appeared at 792 cm⁻¹ [40]. The bands located at 545 and 447 cm⁻¹ are due to double five ring asymmetric stretching vibration and Si-O-Si bending mode [38,39], respectively. The two peaks at 1225 and 1102 cm⁻¹ stand for the external and

internal asymmetric stretching vibration of the siloxane groups [38,40]. The FTIR spectra of the samples verified the formation of aluminosilicate MFI structure, in line with XRD results.

SSA

In order to fully understand the porous features of the synthesized zeolites, nitrogen sorption analysis at -196°C was conducted and the obtained isotherms are illustrated in Figure 3 together with the Barrett-Joyner-Halenda (BJH) pore size distribution plots. As is shown in Fig. 3a, micro-ZSM-5 sample presented a typical type I isotherm

characteristic of microporous materials according to IUPAC classification of adsorption isotherms. This was further confirmed by the BJH pore size distribution plot (Fig. 3b), where no peak can be observed in the

mesoporous range, indicating the sole presence of microporosity in the micro-ZSM-5 sample prepared without the addition of starch in the synthesis gel. The micro-ZSM-5 has BET specific

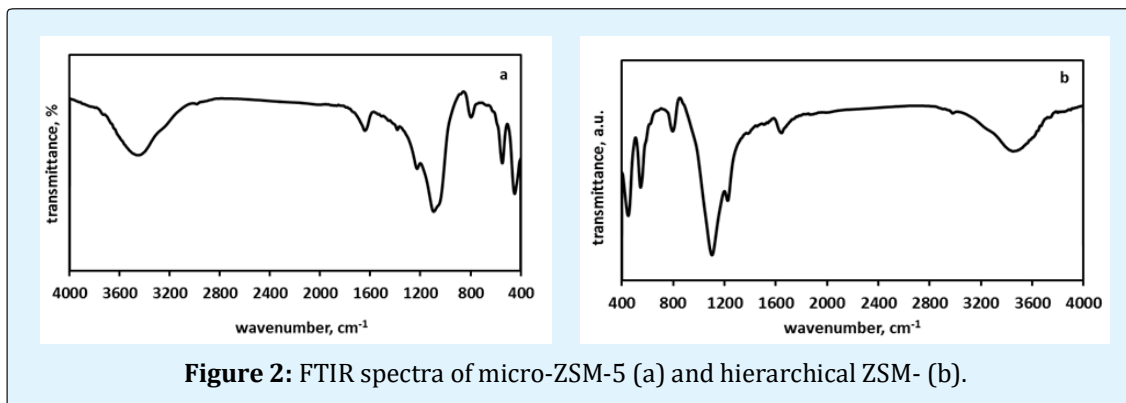


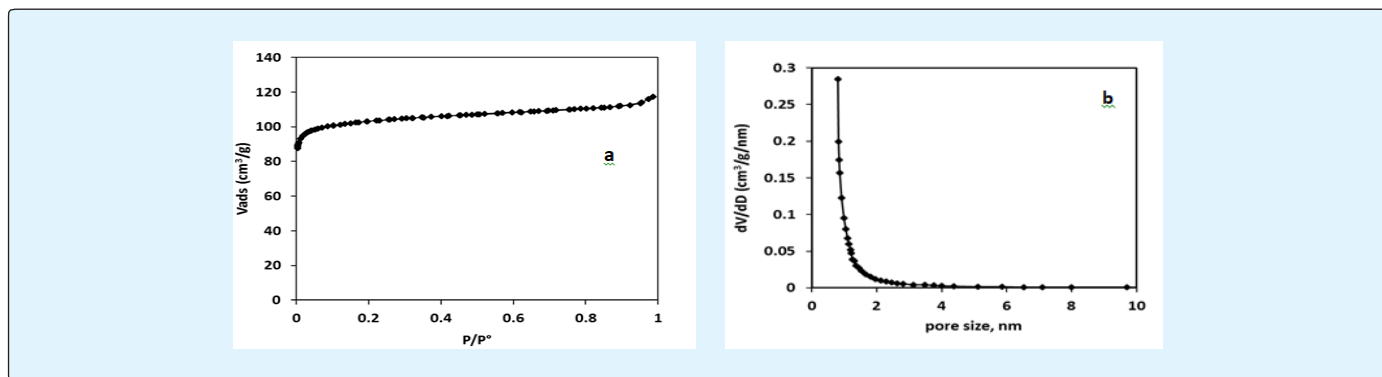
Figure 2: FTIR spectra of micro-ZSM-5 (a) and hierarchical ZSM-5 (b).

Surface area and total pore volume of about 311 m²g⁻¹ and 0.15 cm³g⁻¹, respectively, with low mesoporous surface area and pore volume of 31 m²g⁻¹ and 0.015 cm³g⁻¹, respectively. On the other hand, the obtained adsorption isotherm of the hierarchical ZSM-5 sample (Fig. 3c) can be deemed as an intermediate between Type-I and Type-IV isotherms, based on the IUPAC classification of sorption isotherms, indicating the coexistence of both micro- and mesoporosity. The amount of adsorbed nitrogen was found to increase dramatically in the low relative vapor pressure region of the isotherm demonstrating the existence of microporosity. Additionally, broad hysteresis loop can be also seen in the relative vapor pressure range of 0.4-1.0 bar, thus corroborating the generation of hierarchical mesoporosity in zeolites by employing starch as a mesopore-forming template. Additionally, the BJH pore-size distributions of HM-ZSM-5 (Fig. 3d) confirmed the presence of hierarchical mesoporosity.

The hierarchical sample displayed much larger mesoporous surface area (409 m²g⁻¹) and pore volume (0.315 cm³g⁻¹) as compared to the conventional micro-ZSM-5. The hierarchical sample displayed much larger mesoporous pore volumes (0.173 cm³g⁻¹) as compared to the conventional micro-ZSM-5 (0.015 cm³g⁻¹).

The Thermal Gravimetric Analysis (TGA)

The thermal gravimetric analysis (TGA) of hierarchical and microporous ZSM-5 zeolite samples under N₂ gas flow was conducted to study the effect of introducing mesoporosity on the thermal stability of the obtained hierarchical zeolite and the results are shown in Figure 4. As can be seen in this figure both samples have almost the same thermal stabilities, in other words the introduction of secondary mesoporous system has no adverse effect on the thermal stability of zeolite.



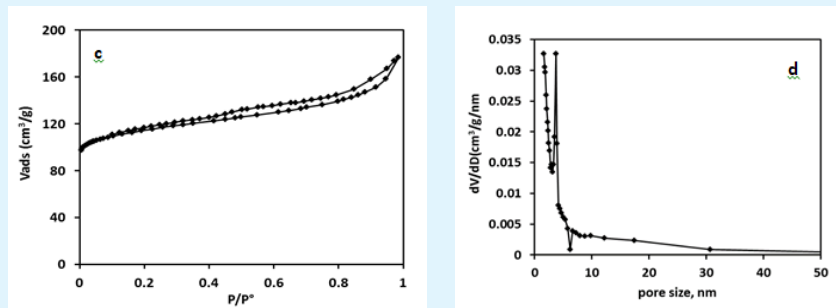


Figure 3: Nitrogen adsorption isotherms and BJH pore size distribution curves of micro-ZSM-5 (a,b) and hierarchical ZSM-5 (c,d).

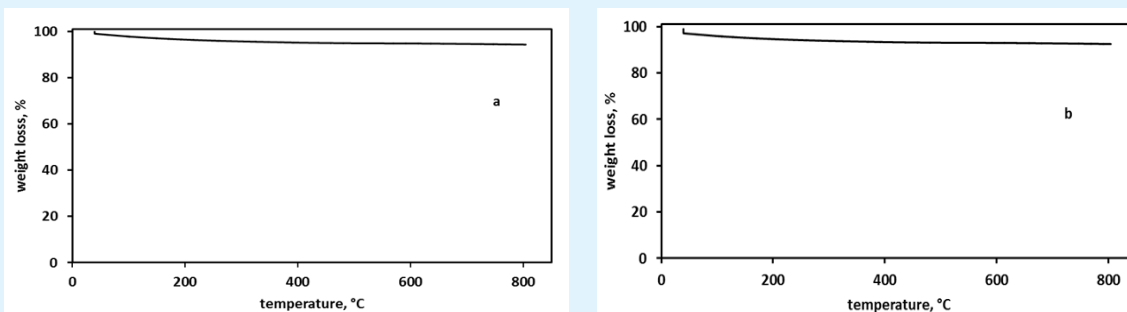


Figure 4: TGA curves of micro-ZSM-5 (a) and hierarchical ZSM-5 (b).

Conclusions

In the present work, we report the synthesis of hierarchical mesoporous ZSM-5 zeolite through the hard-template approach using soluble starch as a cheap, sustainable and available mesoprogen. The obtained hierarchical mesoporous ZSM-5 zeolite exhibited high surface area, hierarchical porosity, and excellent thermal stability. These properties make HM-ZSM-5 suitable for catalytic applications which are beyond the reach of the conventional microporous zeolites.

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