Synthesis of hierarchical porous materials with ZSM-5 structures via template-free sol–gel method

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Abstract

Interests are focused on preparation of hierarchical porous materials with zeolite structures by using soft or rigid templates in order to solve diffusion and mass transfer limitations resulting from the small pore sizes of zeolites. Here we develop a convenient template-free sol–gel method to synthesize hierarchical porous materials with ZSM-5 structures. This method involves hydrothermal recrystallization of the xerogel converted from uniform ZSM-5 sol by a vacuum drying process. By utilizing this method we can manipulate the size of zeolite nanocrystals as building units of porous structures based on controlling temperature of recrystallization, consequently obtain hierarchical porous materials with different intercrystalline pore sizes and ZSM-5 structures.

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1. Introduction

Zeolites have been applied widely on many industrial processes such as adsorption and catalysis due to their high surface area, adsorption capacity, ion-exchange capacity and regular arrays of channels and cavities (3–15 Å). Their intricate channel structures allow the zeolites to present different types of shape selectivity, i.e., product, reactant, and transition state, which can be used to direct a given catalytic reaction toward the desired product avoiding undesired side reactions [1]. However, their small pore size brings diffusion and mass transfer limitations, which can be solved by using zeolite nanocrystals [2]. Unfortunately, nanozeolites cannot be used directly due to the much higher pressure drops in packed-bed reactors and difficulty of separation [3]. Currently, interests are focused on preparation of hierarchical porous materials with zeolite structures.

ZSM-5 zeolite as one of the most famous solid acid catalysts has been used to achieve the “greening” of process technology by replacing many hazardous acidic catalysts such as HF, HCl and H\textsubscript{2}SO\textsubscript{4} [4]. However, conventional ZSM-5 has an intercrossing pore network composed of straight channels and zigzag channels with pore sizes of \textasciitilde 0.55 nm [5]. The small pore size of ZSM-5 limits its application on the reactions involving large molecules. Therefore, synthesis of hierarchical porous structure ZSM-5 has attracted much attention. Other than steaming and acid-leaching dealumination method which often generates mesopores or macropores with wide size distribution, several strategies for the synthesis of hierarchical porous materials with ZSM-5 structures have been described in the literatures. Generally, soft [6] or rigid [7] templates are necessary for the formation of mesopores and macropores with narrow size distribution within those reported materials. Those methods can be also described as assembly of zeolite structures in the present of templates. In our previous work [8,9], we developed a template-free sol–gel method to synthesize mesoporous materials. Here,
we synthesize hierarchical porous materials with ZSM-5 structures via a modified sol–gel method without using any templates.

2. Experimental

2.1. Materials preparation

Hierarchical porous materials with ZSM-5 structures were synthesized by a three-step procedure. The first step consists of the preparation of ZSM-5 precursor sol. In a typical synthesis, 25.4 g of 20% aqueous solution of TPAOH was added to the mixture of 20.8 g of TEOS and 0.4 g of Al(i-OPr)₃ under vigorous stirring at 273 K to obtain a turbid solution with molar composition of 1.0TEOS: 0.02Al(i-OPr)₃: 0.25TPAOH: 11.3H₂O. Clear ZSM-5 precursor sol containing a little floccule was obtained by stirring the turbid solution at 323 K for 48 h. In the second step, the ZSM-5 precursor sol filtrated floccule was dried at 303 K in a vacuum box retaining the vacuum value of 6.65 kPa until it became xerogel. The silica content in the xerogel was about 7.7 mol/g. The third step involves the recrystallization of the xerogel. The mixture of xerogel and water (1Si: 150 water, molar ratio) was transferred into Teflon-lined stainless steel autoclaves and carried out hydrothermal synthesis at a certain temperature for 24 h. Finally, the solid products were filtered, washed, dried at 303 K in a vacuum box and calcined at 823 K in air for 6 h. The obtained hierarchical porous materials were named as HPM-X, where X indicates the temperature of recrystallization. For comparison, the direct-calcined xerogel (DCX) was also prepared.

2.2. Characterization

A N₄ plus laser-scattering particle meter (Coulter company, detection range: 3–3000 nm) was used to measure particle size distribution of ZSM-5 precursor sol. Drops of the sol were diluted in the sample cuvette with water to give the appropriate intensity for measurement. N₂ adsorption/desorption isotherms of samples were measured on a Coulter Omnisorp-100CX apparatus at 77 K. The solid samples were first degassed at 623 K under high vacuum (1.33×10⁻⁴ Pa) for at least 3 h to remove adsorbed impurities in pores of samples before isotherms were recorded. Mesopore and micropore size distributions were determined by BJH method from desorption branch and HK method from adsorption branch, respectively. XRD characterization was performed with a Rigaku D/max-2500PC using a copper target at 40 kV and 100 mA. IR spectra were recorded by using a Nicolet Impact 410 FTIR spectrometer. The mixture of sample and KBr was pressed into a thin wafer before IR measurement. All the IR spectra were measured in the following conditions: scan 32 times, resolution 4 cm⁻¹. SEM images of samples were made using a Quanta 200 FEG (FEI company) scanning electron microscope.

3. Results and discussion

3.1. Particle size distribution of ZSM-5 precursor sol

Fig. 1 shows particle size distribution of ZSM-5 precursor sol. ZSM-5 precursor sol has a very uniform particle size distribution. The size of about 85% sol particles centralizes in 12 nm, which is similar with the result of de Moor et al. [10]. They observed two types of precursor particles (2.8 nm sized primary units and ~10 nm aggregates) in MFI zeolite synthesis system by using small-angle X-ray scattering technology.

3.2. Texture properties of different samples

Fig. 2(a) shows N₂ adsorption/desorption isotherms of the calcined samples prepared under different conditions. The isotherms’ shape of HPM-80 is ascribed to a composite of types I and IV, corresponding to microporous and mesoporous materials [11], respectively. As the temperature of recrystallization increases, the type of isotherms has a tendency towards a composite of types I and II, which indicates that HPM-100 and HPM-130 are composites containing micropores and macropores [11]. The type of their loops can be ascribed to type H1, which is often associated with porous materials which consist of agglomerates or compacts of uniform spheres in fairly regular array according to interpretation of IUPAC [11]. The calculation results of HK method (Table 1) show that the samples after recrystallization have similar micropore size distribution centralizing in 0.53–0.54 nm, which corresponds to the channel opening size of ZSM-5. Compared with the sample after recrystallization, the adsorption isotherm of DCX is a type III isotherm. Namely, DCX does not contain ZSM-5 structures. The surface area and pore volume of DCX are also much less than those of the samples after recrystallization (Table 1). We presume that the pore walls of the xerogel collapse during calcination.
because of its low thermal stability. HPM-X obtained after the recrystallization of the xerogel have high thermal stability because of the existence of ZSM-5 structures within them. The calculation result of BJH method shows that HPM-80 has uniform mesopore size distribution centralizing in 4.5 nm (Fig. 2(b)). Table 1 shows that the surface area and pore volume of the recrystallized sample decrease as the temperature of recrystallization increases.

Obviously, the formation of more ordered zeolite structures results in the decrease of porosity of the sample prepared at higher temperature. And the degree of this decrease is reduced gradually, which is also similar with the change rule of zeolite crystalline ordering.

![Graph](image1.png)

| Sample no. | \( S_{\text{BET}} \) (m\(^2\)/g) | \( V_{\text{micro}} \) (cm\(^3\)/g) | Micropore size (nm) | \( V_{\text{meso/macro}} \) (cm\(^3\)/g) |
|------------|----------------------------------|-----------------------------------|---------------------|----------------------------------|
| HPM-80     | 560.8                            | 0.25                              | 0.53                | 0.70                             |
| HPM-100    | 464.9\(^a\)                      | 0.19                              | 0.54                | 0.56                             |
| HPM-130    | 431.1\(^a\)                      | 0.16                              | 0.54                | 0.55                             |
| DCX        | 4.4                              | –                                 | –                   | 0.05                             |

\(^a\) For HPM-100 and HPM-130, we use Langmuir surface area because their BET C value is negative and unreasonable.

![Graph](image2.png)

![Graph](image3.png)

![Graph](image4.png)

Fig. 2. (a) \( \text{N}_2 \) adsorption/desorption isotherms of different samples and (b) mesopore size distribution of HPM-80.

Fig. 3. The powder XRD patterns of different samples.

Fig. 4. FTIR spectra of different samples.
3.3. Powder XRD, FTIR and SEM results

Fig. 3 shows powder XRD patterns of samples synthesized at different conditions. The powder XRD patterns of HPM-100 and HPM-130 in the 2θ range of 5°–50° show some diffraction peaks which can be assigned to those of ZSM-5 zeolite according to standard power XRD data [12]. Only a wide diffraction peak located between 15° and 30° is observed for the XRD pattern of HPM-80, which indicates that the crystalline ordering of HPM-80 is less than 4–5 unit cells or 8–10 nm [13]. Fig. 4 shows FTIR spectra of different samples. Compared with the IR spectrum of DCX, those of the samples after recrystallization contain silanol stretching band [14] at 950–960 cm⁻¹ and double ring vibrations band [15] at 550–560 cm⁻¹ (positions marked by black arrows). For HPM-80 the appearance of the 550–560 cm⁻¹ band is indicative of the atomic ordering of ZSM-5, even though its ordering is not enough to be detected by X-ray diffraction method. SEM image (Fig. 5(a)) of HPM-80 shows it has interconnected porous structures from agglomerating of spherical zeolite particles with size of less than 10 nm. As the temperature of recrystallization increases, agglomerated ZSM-5 nanoparticles become 30 nm (Fig. 5(b)) and 200 nm (SEM image omitted in this paper) in size within HPM-100 and HPM-130, respectively.

3.4. Formation mechanism of the hierarchical porous materials

Based on our experimental data and previous study [9], we have proposed possible formation mechanism of hierarchical porous materials. Uniform pores form via close packing of uniform ZSM-5 precursor sol particles (~12 nm) due to the evaporation of solvents as the dispersion media of them during vacuum drying process. During hydrothermal recrystallization these nanoparticles start to change into ZSM-5 nanocrystals, and intergrowth of nearby nanocrystals forms the walls of porous structures. Since uniform zeolite nanocrystals are as building units of porous structures, intercrystalline pore sizes also have narrow distribution and increase accordingly as the increase of nanocrystal size. Therefore, we can obtain micro/mesopore composites (HPM-80) or micro/macropore composites (HPM-100 and HPM-130) by adjusting the temperature of recrystallization.

Though a few template-free methods [16,17] have been reported to prepare hierarchical porous materials with zeolite structures, it is difficult to obtain satisfying hierarchical porous materials by using reported methods. Naik et al. [16] used template-free dry gel conversion method under controlled humidity to try to synthesize hierarchical porous materials, but their products had very little mesoporosity and homogeneity. In our experiment, the preparation of precursor sol and vacuum drying process play important roles of ensuring the formation of uniform sol particles and close packing of them to form uniform porous structures within xerogel, respectively. And this uniformity is kept into the final hierarchical porous materials.

4. Conclusions

We develop a convenient template-free sol–gel method to synthesize hierarchical porous materials with ZSM-5 structures. By utilizing this method we can manipulate the size of zeolite nanocrystals as building units of porous structures based on controlling temperature of recrystallization, consequently obtain hierarchical porous materials with different intercrystalline pore sizes and ZSM-5 structures. Furthermore, we also synthesized a series of mesoporous materials with ZSM-5 structures via the above-mentioned sol–gel method by using polyol as medium of recrystallization, which will be reported in subsequent papers. Work has also been undertaken to further understand the formation mechanism of these materials and test their performances.

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References

[1] A. Corma, Chem. Rev. 97 (1997) 2373.
[2] M.A. Camblor, A. Corma, S. Valencia, Micropor. Mesopor. Mater. 25 (1998) 59.
[3] L. Tosheva, V.P. Valtchev, Chem. Mater. 17 (2005) 2494.
[4] B.K. Marcus, W.E. Cormier, Chem. Eng. Prog. 95 (1999) 47.
[5] W. Song, R.E. Justice, C.A. Jones, V.H. Grassian, S.C. Larsen, Langmuir 20 (2004) 8301.
[6] S.J. Lee, D.F. Shantz, Chem. Mater. 17 (2005) 409.
[7] A.G. Dong, Y.J. Wang, Y. Tang, N. Ren, Y.H. Zhang, Z. Gao, Chem. Mater. 14 (2002) 3217.
[8] N. Yao, G.X. Xiong, Y.H. Zhang, M.Y. He, W.S. Yang, Catal. Today 68 (2001) 97.
[9] N. Yao, G.X. Xiong, M.Y. He, S.S. Sheng, W.S. Yang, X.H. Bao, Chem. Mater. 14 (2002) 122.
[10] P.E.A. de Moor, T.P.M. Beelen, R.A. van Santen, J. Phys. Chem. B 103 (1999) 1639.
[11] K.S.W. Sing, D.H. Everett, R.A.W. Haul, L. Moscou, R.A. Pierotti, J. Rouquerol, T. Siemieniewska, Pure Appl. Chem. 57 (1985) 603.
[12] M.M.J. Treacy, J.B. Higgins, R. von Ballmoos, Zeolite 16 (1996) 330.
[13] S.L. Burkett, M.E. Davis, J. Phys. Chem. 98 (1994) 4647.
[14] R. Ravishankar, C. Kirschhock, B.J. Schoeman, P. Vanoppen, P.J. Grobet, S. Storck, W.F. Maier, J.A. Martens, F.C. De Schryver, P.A. Jacobs, J. Phys. Chem. B 102 (1998) 2633.
[15] J.C. Jansen, F.J. van der Gaag, H. van Bekkum, Zeolite 4 (1984) 369.
[16] S.P. Naik, A.S.T. Chiang, R.W. Thompson, J. Phys. Chem. B 107 (2003) 7006.
[17] B.T. Holland, Micropor. Mesopor. Mater. 89 (2006) 291.