Journal of Molecular Catalysis A: Chemical 188 (2002) 225–231

JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL

www.elsevier.com/locate/molcata

A novel preparation method of ZnO/MCM-41 for hydrogenation of methyl benzoate

Weijing Lu, Guanzhong Lu*, Yong Luo, Aiping Chen

Research Institute of Industrial Catalysis, East China University of Science and Technology,
Shanghai 200237, PR China

Received 15 January 2002; accepted 6 June 2002

Abstract

A series of supported ZnO catalysts were prepared by a novel method, hydrothermal-impregnation–precipitation (HIP). The activities of catalysts were tested for hydrogenation of methyl benzoate (MB). ZnO supported on MCM-41 behaves much higher activity than that on γ-Al_2O_3, β-zeolite and SiO_2. Changing the loading of ZnO on MCM-41 can adjust the depth of hydrogenation of MB, and high loading of ZnO is available for the hydrogenolysis of MB to benzene. XRD, FT-IR and N_2 absorption were used to reveal that zinc oxide incorporated into the pore channels of MCM-41 in single or double molecular ZnO layer. After supporting 10%ZnO on MCM-41 by HIP, the structure of MCM-41 is unchanged, its pore diameter decreases from 3.14 to 2.62 nm.

Keywords: Hydrothermal-impregnation–precipitation; ZnO/MCM-41; Hydrogenation; Methyl benzoate; Hydrogenolysis

1. Introduction

Mesoporous molecular sieves such as MCM-41 [1] are among the best candidates as a support material for the metal clusters, due to their sizable pores ranging from 1.5 to >10 nm. In view of the general interest in the properties and application of the metal/mesoporous materials, much effort has recently been expended in incorporating metals into the pores of MCM-41, of which there are each assimilated intact [2], directly (one-step) synthesis [3], ion exchange [4], graft [5], multi-step anchoring [6], coordinative anchoring [7], reductive solid-state ion exchange (RSSIE) [8], incipient wetness impregnation [9], atom-planting [10], organically modified [11], etc. These methods are suitable for only a small amount of supported metals or metal oxides [12,13], but it is difficult to incorporate the compound of large size or high loading into the pores of MCM-41, especially metal oxides. Here, a new method, hydrothermal-impregnation–precipitation (HIP) is proposed to prepare ZnO/MCM-41. Little reference can be found in the literature about this technique of incorporating metal oxide into the channels of molecular sieves.

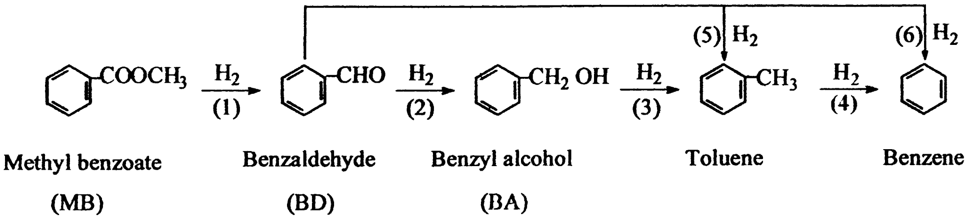
The catalytic activity of ZnO/MCM-41 was evaluated by using the hydrogenation of methyl benzoate (MB) as a model reaction. The processes of multi-step hydrogenation of MB can be described

---

[*] Corresponding author. Fax: +86-21-6425-3703.
E-mail address: gzhlu@ecust.edu.cn (G. Lu).

1381-1169/02/$ – see front matter © 2002 Elsevier Science B.V. All rights reserved.
PII: S1381-1169(02)00335-7

as follows:



2. Experimental

2.1. Preparation of catalysts

A 10%ZnO/MCM-41 was prepared by HIP: MCM-41, solution of $Zn(NO_3)_2$ and urea (urea/zinc = 2/1 (atoms)) dissolved in de-ionized water, were added into an Teflon-lined stainless steel autoclave, stirred at 80–85 °C under 4 kg cm^{-2} for 10 h, then cooled and filtered. The solid obtained was dried at 110 °C for 14 h and calcined from 110 to 500 °C at the rate of 8 °C min^{-1}, then kept at 500 °C for 2 h. Then the catalyst was crushed to 0.45–0.90 mm. The loading of ZnO was 10 or 20%. Using the methods of preparing catalyst as mentioned, ZnO was supported on β-zeolite (Si/Al = 39.5 (atoms), Wenzhou Huahua Catalysts Co., China), γ-Al_2O_3 and SiO_2. 10%ZnO/MCM-41 (P) was prepared by precipitation: MCM-41 powder was added into the solution of zinc nitrate dissolved in de-ionized water at 65 °C under stirring, then ammonia was dropped slowly into the solution until pH = 9.0, the mixture solution was stirred continually for 1 h at 65 °C. The following operating procedures were the same as HIP processes. The catalysts prepared and their data of BET surface area are presented in Table 1.

Table 1
The BET surface area of ZnO supported catalysts

Catalyst	BET surface area ($m^2 g^{-1}$)	Method of preparation
10%ZnO/MCM-41	648.5	HIP
20%ZnO/MCM-41	321.8	HIP
10%ZnO/MCM-41 (P)	259.2	Precipitation
10%ZnO/β-zeolite	204.9	HIP
10%ZnO/γ-Al_2O_3	67.1	HIP
10%ZnO/SiO_2	167.4	HIP

MCM-41 was synthesized hydrothermally with tetraethylorthosilicate (TEOS) and surfactant CTMABr [14]. TEOS was mixed with a solution containing the surfactant CTMABr and ethylamine (EA). The composition of matrix gel was 1 TEOS:0.2 CTMABr:0.6 EA:150 H_2O (weight). After stirred at ambient temperature for 3 h, the gel was transferred into Teflon-lined stainless steel autoclave and kept at 100 °C for 48 h under autogenous pressure. The crystalline product was filtered, washed, air-dried overnight, and finally calcined in air at 550 °C for 6 h.

2.2. Activity testing of catalysts

The hydrogenation of MB over zinc substrate catalysts was carried out in the fixed-bed reactor at 320–420 °C under atmospheric pressure for 12 h. A 5.0 ml catalyst was packed in the silica glass reactor (i.d. 20 mm) and some quartz sands were placed on the catalyst. LHSV of MB was 0.36 h^{-1} and GHSV of H_2 was 787 h^{-1}. After the reaction temperature was kept on stable for 1 h, the reaction products in the outlet of reactor was collected for 1 h, then it was analyzed by a gas chromatograph (PE Autosystem XL), in which 25 m × 0.32 mm (Ø) capillary column with 5% methyl phenyl silicone and the flame ionization detector were used.

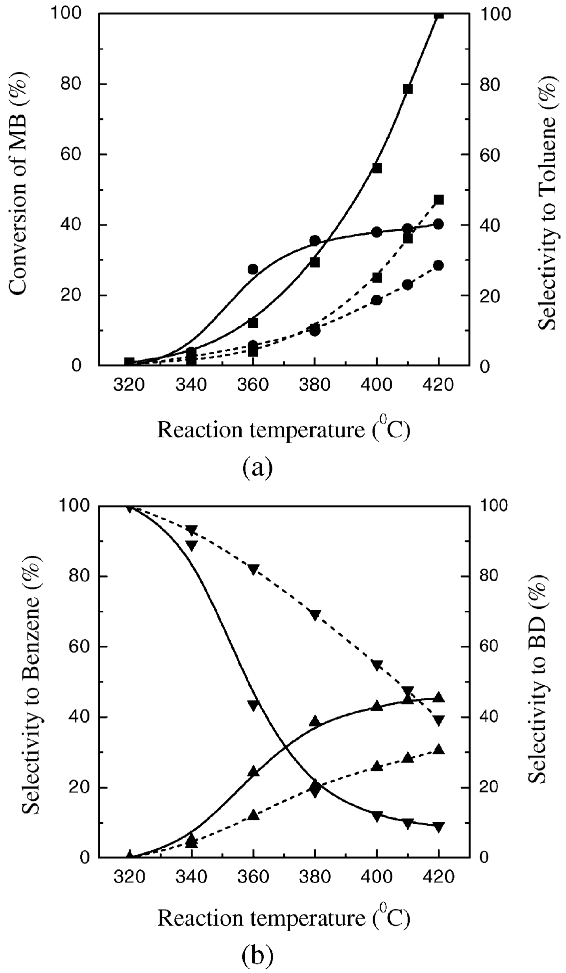
2.3. Catalyst characterization

X-ray powder diffraction (XRD) data were recorded by Riguku D-MAX RB diffractometer (Japan) with Ni filter and Cu Kα radiation. FT-IR spectra were obtained at room temperature with an instrument of Magna-IR550 (Nicolet, USA). The pore size distribution and the BET surface area were obtained by N_2 adsorption isotherms measured at −196 °C with an instrument of ASAP2010 (Micromeritics, USA).

3. Results and discussion

3.1. *Catalytic performance of ZnO/MCM-41 catalyst*

The catalytic performances of 10%ZnO/MCM-41 and 10%ZnO/MCM-41 (P) catalysts for hydrogenation of MB are presented in Fig. 1. At 420 °C, the former prepared by HIP behaves much higher conversion of MB (100%), selectivity to toluene (40.2%) and benzene (45.3%) than the latter prepared by precipitation, corresponding 47.2, 28.6 and 30.5%. For the selectivity to benzaldehyde (BD), the situation is reversed. It is 39.4% over 10%ZnO/MCM-41 (P), and 9.2% over 10%ZnO/MCM-41. This shows that 10%ZnO/MCM-41 (P) catalyst prepared by precipitation exhibits higher activity for the first-step hydrogenation of MB than the catalyst prepared by HIP.



(a)

(b)

Fig. 1. Catalytic performance of 10%ZnO/MCM-41 catalyst prepared by HIP (—) or precipitation (- - - -). (a) Conversion of MB (■), and selectivity to toluene (●); (b) selectivity to benzene (▲), and selectivity to BD (▼).

The catalytic activity of MCM-41 is low for hydrogenation of MB. The conversion of MB, the selectivity to benzoic acid and toluene are 1.8, 66.7 and 33.3%, respectively and BD was not detected out.

3.2. *Effect of the support on performance of ZnO catalyst*

The results of hydrogenation of MB over 10%ZnO supported catalysts prepared with the HIP method are shown in Figs. 2 and 3. It shows that the conversion of MB over 10%ZnO/MCM-41 is higher than that over 10%ZnO/γ-Al$_2$O$_3$ at >383 °C and over 10%ZnO/β-zeolite at >361 °C (Fig. 2). The conversion of MB over 10%ZnO/SiO$_2$ is lowest. At 420 °C, 100% conversion of MB is obtained over 10%ZnO/MCM-41, while 67.9, 61.5 and 32.5% is over 10%ZnO/γ-Al$_2$O$_3$, 10%ZnO/β-zeolite and 10%ZnO/SiO$_2$, respectively. Using 10%ZnO/MCM-41 catalyst, the higher selectivity to toluene (40.2%) and benzene (45.3%) can be obtained also; using 10%ZnO/γ-Al$_2$O$_3$, 5.2 and 11.0% (Fig. 3),

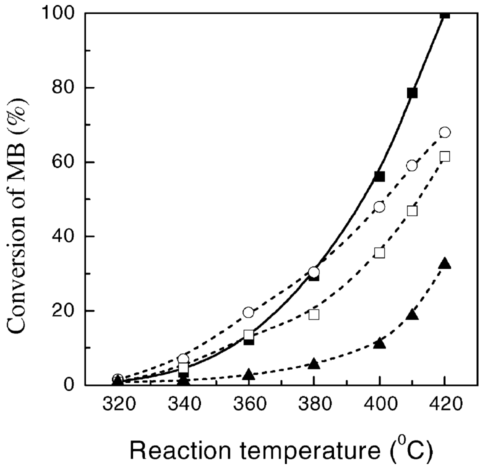


Fig. 2. Catalytic performance of 10%ZnO supported on MCM-41(■); γ-Al$_2$O$_3$ (○); β-zeolite (□); SiO$_2$ (▲).

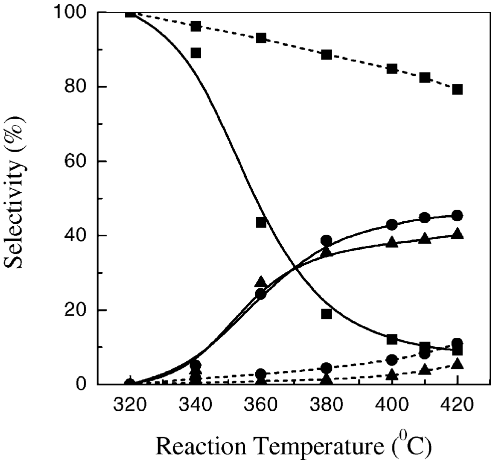


Fig. 3. Catalytic performance of 10%ZnO/MCM-41 (—) and 10%ZnO/γ-Al_2O_3 (- - - -): selectivity to BD (■); selectivity to toluene (▲); selectivity to benzene (●).

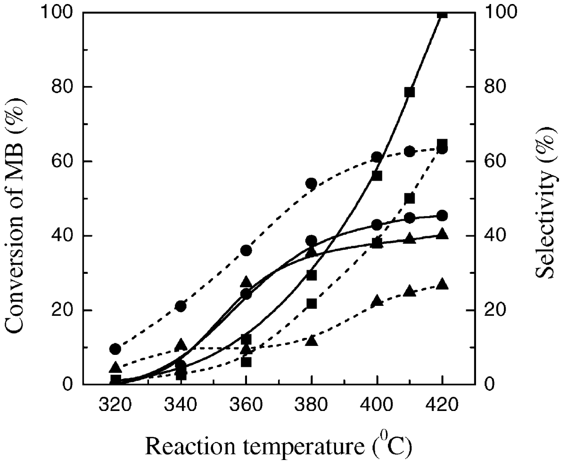


Fig. 4. Catalytic performance of 10%Zn/MCM-41 (—); 20%ZnO/MCM-41 (- - - -): conversion of MB (■); selectivity to toluene (▲); selectivity to benzene (●).

respectively. For 10%ZnO/β-zeolite and 10%ZnO/SiO_2, toluene and benzene in the reaction products can be detected hardly. For the selectivity to BD, 9.2% over 10%ZnO/MCM-41 and 79.3% over 10%ZnO/γ-Al_2O_3 have been obtained at 420 °C (Fig. 3). Those results indicate that using MCM-41 as the support of ZnO presents the higher activity for hydrogenation of MB to toluene and benzene; for hydrogenation of MB to BD, γ-Al_2O_3 should be selected perfectly as the support. It is to say, changing the support of ZnO catalyst can control the selectivity to product for hydrogenation of MB.

For the selectivity to benzyl alcohol (BA), the situation of 10%ZnO/MCM-41 is similar to that of 10%ZnO/γ-Al_2O_3, which is 0–5%.

3.3. Effect of the loading of ZnO on MCM-41

The performances of 10%ZnO/MCM-41 and 20%ZnO/MCM-41 for hydrogenation of MB are shown in Fig. 4. It is shows that, 10%ZnO catalyst has higher conversion of MB and selectivity to toluene than 20%ZnO catalyst but the selectivity to benzene over 20%ZnO is higher than that over 10%ZnO and the selectivity of BD and BA are very low for two catalysts.

The results show that, changing the loading of ZnO on MCM-41 can adjust the depth of hydrogenation of MB, and high loading of ZnO is available for the hydrogenolysis of MB to benzene.

3.4. Catalyst characterization

3.4.1. XRD

The XRD spectra of MCM-41, 10%ZnO/MCM-41, 10%ZnO/MCM-41 (P), and 10%ZnO/MCM-41 (used) are shown in Fig. 5. The XRD spectrum of MCM-41 is the same as results reported by Karlsson et al. [15] and Grünm et al. [16]. There are (1 0 0), (1 1 0) and (2 0 0) diffraction peaks of MCM-41 in the XRD spectra of 10%ZnO/MCM-41 and 10%ZnO/MCM-41 (P), in which the intensity of (1 0 0) peak is almost the same as that of MCM-41, the (1 1 0) and (2 0 0) peaks of 10%ZnO/MCM-41 and 10%ZnO/MCM-41 (P) are weaker than that of MCM-41. This indicates that some changes of crystal order of MCM-41 have taken place, but the frame structure is almost unchanged, after supporting ZnO on MCM-41 by HIP or precipitation process.

A 10%ZnO/MCM-41 (used) has been used in hydrogenation for 12 h, and its XRD spectrum is almost the same as that of 10%ZnO/MCM-41 (see Fig. 5b and c). This indicates that the frame structure and crystalline order of MCM-41 in 10%ZnO/MCM-41 is unchanged after being used for 12 h.

In the XRD spectrum of 10%ZnO/MCM-41, the diffraction peaks of ZnO phase have not been

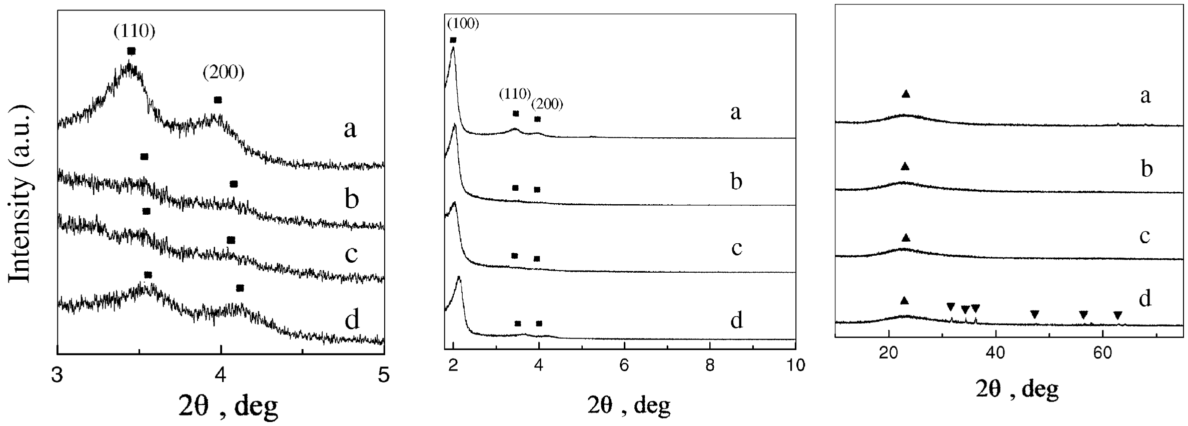


Fig. 5. XRD patterns of MCM-41 (a); 10%ZnO/MCM-41 (b); 10%ZnO/MCM-41 (used) (c); 10%ZnO/MCM-41 (P) (d); MCM-41 (■); ZnO (▼); SiO_2 (▲).

observed, even if the loading of ZnO reaches 20% (not shown in Fig. 5). But in the XRD spectrum of 10%ZnO/MCM-41 (P) prepared by precipitation, the ZnO peaks are still observed obviously (Fig. 5d). The results of XRD study indicate that ZnO is highly dispersed in 10–20%ZnO/MCM-41 prepared by HIP, in which ZnO has entered into the pore of MCM-41.

3.4.2. FT-IR

IR spectra of 10%ZnO/MCM-41 and MCM-41 are presented in Fig. 6. IR spectrum of MCM-41 is similar to that reported in [18,19], in which there are the bands of 461.3, 799.8, 954.2 and 1078.5 cm^{-1}. In IR spectrum of 10%ZnO/MCM-41 sample, there is the absorption bands at 474.3 cm^{-1} that can be attributed to ZnO [17], other than the bands of MCM-41. From the results of Fig. 6, we can see, the framework structure of MCM-41 has been unchanged in the HIP processes of preparing catalyst.

3.4.3. N_2 adsorption

The data in Table 1 show that the surface area of 10%ZnO/MCM-41 (648.5 $m^2\,g^{-1}$) is much larger than that of 20%ZnO/MCM-41 (321.8 $m^2\,g^{-1}$), which means higher loading of ZnO might obstruct the channels of MCM-41, resulting in the decrease of its surface area and catalytic activity (Fig. 4).

The surface area of 10%ZnO/MCM-41 (648.5 $m^2\,g^{-1}$) is much larger than that of 10%ZnO/MCM-41 (P) (259.2 $m^2\,g^{-1}$). This indicates ZnO in 10%ZnO/MCM-41 has entered into the pores of MCM-41 by HIP and is high dispersion in catalyst. ZnO supported on MCM-41 by precipitation maybe coat on the mouths of pore canals, which results in its surface area decreasing and the size of ZnO particles increasing. This opinion has been confirmed by the results of XRD in Fig. 5. So it is understandable that 10%ZnO/MCM-41 catalyst exhibits much higher activity than 10%ZnO/MCM-41 (P) (Fig. 1).

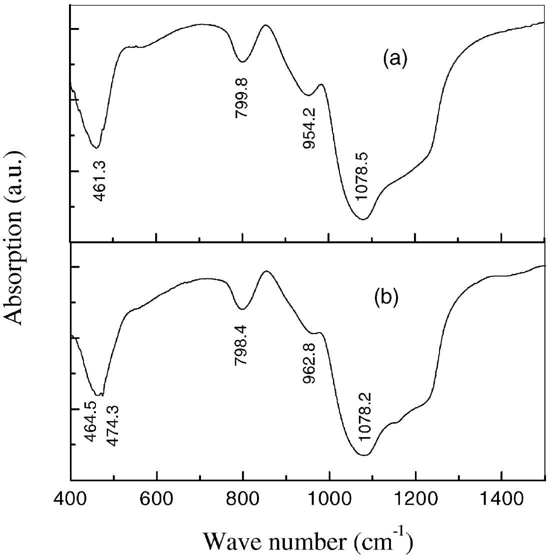


Fig. 6. IR spectra of MCM-41 (a); 10%ZnO/MCM-41 (b).

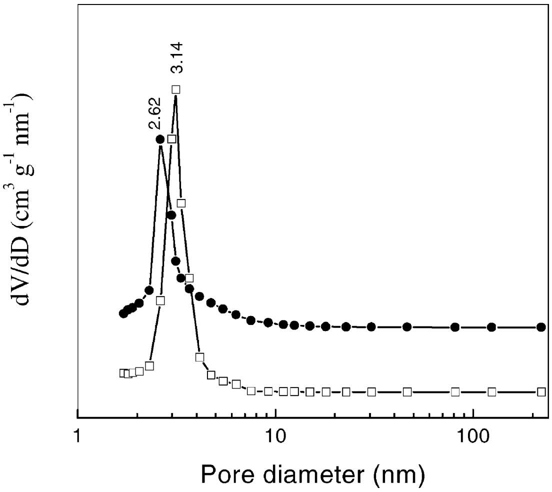


Fig. 7. Pore-size distribution of 10%ZnO/MCM-41 (●); MCM-41 (□).

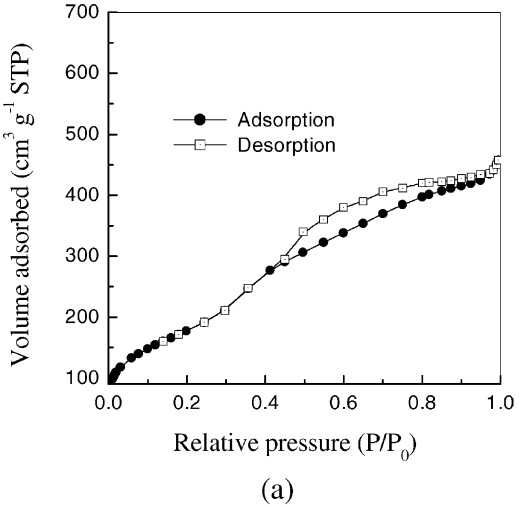
For 10%ZnO/γ-Al_2O_3, 10%ZnO/β-zeolite and 10%ZnO/SiO_2 prepared by HIP, their surface areas are much smaller than that of 10%ZnO/MCM-41. Low surface area leads to low catalytic activity.

The pore size distribution and feature parameters of 10%ZnO/MCM-41 and MCM-41 is presented in Fig. 7 and Table 2. A 10%ZnO/MCM-41 has a narrow pore size distribution as MCM-41 sample did. According to the data of pore diameter and ZnO crystallite (the radius of Zn^{2+} and O^{2-} is 0.074 nm and 0.132 nm, respectively), thickness of ZnO layer should be calculated and is about 0.26 or 0.52 nm, which ZnO is supported on the wall of channels of MCM-41 in single or double molecular layer, to realize the molecular assembly of oxide into the pore of MCM-41 by HIP. This shows that the HIP method is suitable for ZnO supported on MCM-41.

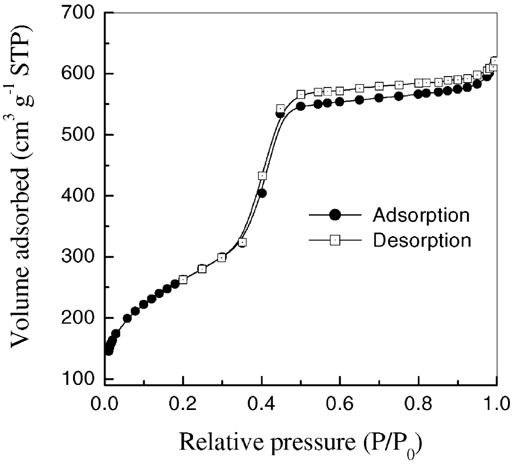
The N_2 adsorption/desorption isotherms of 10%ZnO/MCM-41 and MCM-41 are shown in Fig. 8. Both 10%ZnO/MCM-41 and MCM-41 give the type IV of isotherm, the typical curve of mesoporous solids [20]. For the hysteresis loop, 10%ZnO/MCM-41 (type B) is different to MCM-41 (type A) [21]. At high pressure ($P/P_0 > 0.5$), the desorption branch of the isotherm in 10%ZnO/MCM-41 gives a larger degree of channel blocking than that of MCM-41.

Table 2
The pore parameters of 10%ZnO/MCM-41 and MCM-41

	10%ZnO/MCM-41	MCM-41
BET surface area (m^2 g^{-1})	648.5	955.1
Average pore sizes (nm)	2.62	3.14
Volume of pore (cm^3 STP g^{-1})	149.0	219.4
FWHM (full-width at half-maximum) (nm)	0.64	0.71



(a)



(b)

Fig. 8. Adsorption/desorption isotherms of N_2 of 10%ZnO/MCM-41 (a); MCM-41 (b).

4. Conclusions

The HIP is useful method to introducing ZnO into the channels of MCM-41, to realize the molecular assembly of oxide into the pore of MCM-41. The thickness of ZnO layer in the pores of MCM-41 is about single or double molecular ZnO. The structure of MCM-41 is unchanged in the progress of HIP. After supporting 10%ZnO on MCM-41 by HIP, the pore diameter and BET surface area of MCM-41 decreases from 3.14 to 2.62 nm and 955.1 to 648.5 $m^2\,g^{-1}$, respectively.

For the hydrogenation of MB, ZnO/MCM-41 is a useful catalyst, and changing the loading of ZnO on MCM-41 can adjust the depth of hydrogenation of MB, and high loading of ZnO is available for the hydrogenolysis of MB to benzene. At 420 °C, 100% conversion of MB and 40.2 and 45.3% selectivity to toluene and benzene are obtained over 10%ZnO/MCM-41; using γ-Al_2O_3, β-zeolite and SiO_2 as the support, the conversion of MB are 67.9, 61.5 and 32.5%, respectively.

References

[1] C.T. Kresge, M.E. Leonowicz, W.J. Roth, J.C. Vartuli, J.S. Beck, Nature 359 (1992) 710.
[2] W. Zhou, J.M. Thomas, D.S. Shephard, B.F.G. Johnson, D. Ozkaya, T. Maschmeyer, R.G. Bell, Q. Ge, Science 280 (1998) 705.
[3] S.K. Badamali, A. Sakthivel, P. Selvam, Catal. Today 63 (2000) 291.
[4] B. Winfried, P. Andreas, M. Dieter, Coll. Surf. A 158 (1999) 235.
[5] S. Kowalak, K. Stawinski, A. Mackowiak, Micro. Meso. Mater. 44-45 (2001) 283.
[6] G.J. Kim, D.W. Park, Catal. Today 63 (2000) 537.
[7] A. Ortlam, M. Wark, G. Schulz-Ekloff, J. Rathousky, A. Zukal, Stud. Surf. Sci. Catal. 117 (1998) 357.
[8] Y. Neinska, V. Mavrodinova, Ch. Minchev, R.M. Mihalyi, Stud. Surf. Sci. Catal. 125 (1999) 37.
[9] U. Junges, F. Schuth, G. Schmid, Y. Uchida, R. Schlogl, Ber. Bunsen-Ges. 101 (1997) 1631.
[10] P. Wu, M. Iwamoto, J. Chem. Soc., Faraday Trans. 94 (1998) 2871.
[11] A. Bhaumik, T. Tatsumi, J. Catal. 189 (2000) 31.
[12] W.Z. Zhang, M. Froeba, J.L. Wang, P.T. Tanev, J. Wong, T.J. Pinnavaia, J. Am. Chem. Soc. 118 (1996) 9164.
[13] T. Klimova, E. Rodriguez, M. Martinez, J. Ramirez, Micro. Meso. Mater. 44-45 (2001) 357.
[14] Y. Luo, G.Z. Lu, J.Z. Wang, Y.L. Guo, Y.S. Wang, Acta Chim. Sinica. 59 (2001) 1401.
[15] A. Karlsson, M. Stöcker, R. Schmidt, Micro. Meso. Mater. 27 (1999) 181.
[16] M. Grünm, K.K. Unger, A. Matsumoto, K. Tsutsumi, Micro. Meso. Mater. 27 (1999) 207.
[17] Sadler Research Laboratories Inc., Inorganics IR Grating Spectra, Vol. 4, Philadelphia, PA, USA, 1972, Y913K.
[18] G. Gu, P.P. Ong, C. Chu, J. Phys. Chem. Solids 60 (1999) 943.
[19] C.Y. Chem, H.X. Li, M.E. Davis, Micro. Matter. 2 (1993) 17.
[20] S.J. Gregg, K.S.W. Sing (Eds.), Adsorption, Surface Area and Porosity, Academic Press, New York, 2nd Edition, 1982, p. 111.
[21] S.J. Gregg, K.S.W. Sing (Eds.), Adsorption, Surface Area and Porosity, Academic Press, New York, 2nd Edition, 1982, p. 116.