Synthesis of AlMCM-41 mesoporous molecular sieves with high stability

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Abstract: Mesoporous molecular sieves AlMCM-41 were synthesized by static hydrothermal crystallization using cetyltrimethylammonium bromide as template, water glass as silica source and pseudoboehmite as aluminum source. The XRD results showed that the prepared AlMCM-41 mesoporous molecular sieves had high relative crystallinity and long-range order. The relative crystallinity was greater than 27% after calcination at 900 °C for 2 hours and was still greater than 14% after ageing in steam at 800 °C for 2 hours. The results indicated that both thermal and hydrothermal stabilities of the mesoporous molecular sieves AlMCM-41 were good.

Key words: Pseudo-boehmite, hydrothermal synthesis, AlMCM-41, thermal stability, hydrothermal stability

1 Introduction

Since mesoporous molecular sieve M41S was synthesized (Kresge et al, 1992; Beck et al, 1992), the synthesis of acidic mesoporous molecular sieves with high crystallinity and long-range order, has been the focus of scientific research. Synthesis of the aluminum-containing MCM-41, i.e. AlMCM-41, is the way to improve the acidity of MCM-41. Different aluminum sources have different characteristics, sizes, concentrations and degrees of hydrolyzation, which will influence entry of aluminum into the framework and its positions in the framework. The hydrothermal stabilities and acidities of mesoporous molecular sieves AlMCM-41 prepared from different aluminum sources are greatly different (Biz et al, 1999; Sakthivel et al, 2003), so the selection of aluminum source is crucial. So far, according to the literature, the mesoporous molecular sieves usually use sodium metaaluminate, aluminum isopropoxide (Sakthivel et al, 2003), aluminum sulfate (Gao et al, 1998) and aluminum chloride (Fang et al, 2005) etc. as aluminum source. Unfortunately, although the acidity of mesoporous molecular sieves AlMCM-41 was improved, the thermal and hydrothermal stabilities decreased greatly. In our previous work, AlMCM-41 was synthesized by using hydrate of γ - Al_2O_3 as aluminum source (Huang et al, 2005; Huang et al, 2006) and the composite AlMCM-41/ γ - Al_2O_3 was obtained. The thermal stability of MCM-41 was improved. Until now, there has been no report on the synthesis of AlMCM-41 by using pseudoboehmite as aluminum source.

2 Experimental

First hexadecyltrimethyl ammonium bromide (CTAB, analytical pure, Beijing Chemical Reagents Company) was dissolved in distilled water and stirred in a water bath at 40 °C for one hour, then pseudoboehmite (industrial product, with Al_2O_3 content of 76.4 mol%, Research Institute of Shandong Aluminum Co. Ltd) was added and stirred, finally water glass (industrial product, modulus 3.4, the Catalyst Plant of PetroChina Lanzhou Petrochemical Company) was added and stirred to form a homogeneous colloid. The pH of the solution was adjusted to about 10 with dilute sulfuric acid (analytical pure, Beijing Chemical Reagents Company) and stirred for half an hour, after ageing, the gel was enclosed in a pressure vessel of stainless steel to crystallize hydrothermally at 150 °C for a specific time. The crystals were filtered, washed with water, dried and then calcined at 550 °C in air for 6 hours to remove the organic template, and then the mesoporous molecular sieves AlMCM-41 were obtained. The molar composition of the gel was as follows: $1(\text{SiO}_2):0.2(\text{CTAB}):n(\text{Al}_2\text{O}_3):40\text{H}_2\text{O}$ ($n=0.01, 0.02, 0.04, 0.1$). When aluminum sulfate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, analytical pure) was used as aluminum source, the steps were the same as above, only substituting aluminum sulfate for pseudoboehmite.

X-ray diffraction (XRD) measurements were performed on a Shimadzu XRD-6000 X-ray diffractometer using Ni-filtered CuK α radiation operated at 40 kV and 30 mA. The 2θ angles in the low angle range of 1.6° – 6° were scanned at a speed of $1^\circ/\text{min}$ with the slit parameters of $\text{DS} = 0.5^\circ$, $\text{SS} = 1^\circ$ and $\text{RS} = 0.30 \text{ mm}$. The crystallinity of MCM-41 as the reference material was taken as 100%. The relative crystallinity of AlMCM-41 could be obtained by comparing the intensities of the diffraction peaks at $2\theta = 2.3^\circ$ with those

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of the reference material.

The thermal and hydrothermal stabilities of the obtained mesoporous molecular sieves AIMCM-41 were investigated. The thermal stability was investigated with XRD after the AIMCM-41 was calcined at 900 °C for 2 hours. And the hydrothermal stability was investigated after the AIMCM-41 was aged in steam at 800 °C for 2 hours.

3 Results and discussion

Mesoporous molecular sieves AIMCM-41 were synthesized by using aluminum sulfate or pseudoboehmite as aluminum source and characterized with XRD. The results are shown in Fig. 1 and Table 1. Fig. 1 shows their XRD patterns and Table 1 shows their compositions and relative crystallinities.

Fig. 1 XRD patterns of AIMCM-41 synthesized by using pseudoboehmite or aluminum sulfate as aluminum source

- (1) Run 1- synthesized by using pseudoboehmite
- (2) Run 2- synthesized by using pseudoboehmite
- (3) Run 3- synthesized by using pseudoboehmite
- (4) Run 4- synthesized by using pseudoboehmite
- (5) Run 5- synthesized by using aluminum sulfate
- (6) Run 6- synthesized by using aluminum sulfate
- (7) Run 7- synthesized by using aluminum sulfate

Fig. 1 shows that mesoporous molecular sieves AIMCM-41 synthesized by using two different aluminum sources all had a strong diffraction peak at around 2.3 °, which accorded with the XRD patterns of MCM-41 reported by Beck, et al. (1992), corresponding to the (100) plane characteristic peak. In addition, there were a few weak diffraction peaks at 4-6 °, corresponding to the (110), (200) and (300) characteristic peaks, showing that both aluminum sources could be used to synthesize AIMCM-41. Moreover, at the same $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio the mesoporous molecular sieves AIMCM-41 synthesized by using pseudoboehmite had stronger characteristic diffraction peaks than those using aluminum sulfate. This might be related to the characteristics of aluminum sources. Table 1 indicated that the relative crystallinities of the mesoporous molecular sieves AIMCM-41 synthesized by using the two aluminum sources were all high and no difference was observed when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was 100, but when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio decreased to 50, 25 and 10, respectively, the relative crystallinity of the molecular sieves AIMCM-41 synthesized by using pseudoboehmite was still high while the relative crystallinity synthesized by using aluminum sulfate decreased gradually. In addition, there was no characteristic peak of AIMCM-41 when the $\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio was 10. In contrast, the relative crystallinity of the molecular sieves synthesized by using pseudoboehmite was 125.3%, showing that AIMCM-41 using pseudoboehmite as aluminum source had very good relative crystallinity. The reason might be that the solubility of pseudoboehmite was lower than other aluminum sources such as aluminum sulfate. Pseudoboehmite dissolved in water could provide $\text{Al}(\text{OH})_4^-$ buffer the increase in the pH of the mother liquor (Panias et al, 2001) and facilitate the aggregation of silicate (Gao et al, 1999), so increasing the relative crystallinity of the molecular sieves AIMCM-41 synthesized using pseudoboehmite as the aluminum source.

The thermal and hydrothermal stabilities of the mesoporous molecular sieves AIMCM-41 synthesized as above were investigated. For thermal stabilities the samples were calcined at 900 °C for 2 hours and for hydrothermal stabilities the samples were aged in steam at 800 °C for 2

Table 1 Influence of aluminum source and gel composition on crystallization of AIMCM-41

Run	Aluminum source	Gel composition, $n_{\text{mol}}/n_{\text{mol}}$			pH value	Relative crystallinity %
		$\text{SiO}_2/\text{Al}_2\text{O}_3$	CTAB/ SiO_2	$\text{H}_2\text{O}/\text{SiO}_2$		
1	Pseudoboehmite	100	0.2	40	10	147.0
2	Pseudoboehmite	50	0.2	40	10	145.0
3	Pseudoboehmite	25	0.2	40	10	143.7
4	Pseudoboehmite	10	0.2	40	10	125.3
5	Aluminum sulfate	100	0.2	40	10	132.2
6	Aluminum sulfate	50	0.2	40	10	87.1
7	Aluminum sulfate	25	0.2	40	10	52.1

hours. The XRD patterns of the treated samples are shown in Fig. 2 and Fig. 3, and the relative crystallinities are listed in Table 2.

Fig. 2 shows that the XRD characteristic peaks of the AIMCM-41 obtained in run 6 and run 7 almost disappeared after calcination, indicating that the structure of AIMCM-41 synthesized by using aluminum sulfate as aluminum source almost collapsed, while the characteristic XRD peaks of the AIMCM-41 obtained in runs 1-4 by using pseudoboehmite as aluminum source all remained intact. Table 2 also shows that the relative crystallinity of the AIMCM-41 obtained in run 6 was only 3.1% after thermal treatment, and that in run 7 was zero after thermal treatment. However the relative crystallinity of the AIMCM-41 obtained in runs 1-4 by using pseudoboehmite as aluminum source was all greater than 27%, indicating these mesoporous molecular sieves had

good thermal stabilities. Fig. 3 shows that the characteristic XRD peaks of the MCM-41 obtained in runs 1-4, using pseudoboehmite as aluminum source, all remained strong after ageing in steam at 800 °C, but the XRD characteristic peaks of the MCM-41 obtained in runs 5-7, using aluminum sulfate as aluminum source, almost disappeared after ageing in steam at 800 °C. The results in Table 2 also show that the hydrothermal stability of run 5 was low although its thermal stability was good. For example, relative crystallinity of the AIMCM-41 obtained in run 5 was 28.4% after thermal treatment, but the relative crystallinity was only 2.8% after hydrothermal treatment. These results indicated that the mesoporous molecular sieves AIMCM-41 synthesized by using pseudoboehmite had very good thermal and hydrothermal stabilities compared with the AIMCM-41 synthesized by using aluminum sulfate.

Fig. 2 XRD patterns of AIMCM-41 molecular sieves after 2 hours of thermal treatment at 900 °C
(1)-(7) are AIMCM-41 obtained in run 1-run 7 respectively in Table 1

Fig. 3 XRD patterns of AIMCM-41 molecular sieves after 2 hours of hydrothermal treatment (i.e. ageing) in steam at 800 °C
(1)- (7) are AIMCM-41 obtained in run 1 - run 7 respectively in Table 1

Table 2 Relative crystallinity of AIMCM-41 before and after thermal and hydrothermal treatment

Sample	Relative crystallinity, %		
	Fresh AIMCM-41	After thermal treatment	After hydrothermal treatment
1	147.0	36.5	14.2
2	145.0	41.5	20.6
3	143.7	27.6	30.2
4	125.3	34.7	27.9
5	132.2	28.4	2.8
6	87.1	3.1	0
7	52.1	0	0

Notes: Samples 1- 7 are AIMCM-41 obtained in Run 1 - Run 7 respectively in Table 1

4 Conclusions

Mesoporous molecular sieves AlMCM-41 with high stability were synthesized by using pseudoboehmite as aluminum source and water glass as silicon source. The AlMCM-41 sieves had higher structure stabilities and long-range order. After 2 hours of thermal treatment at 900 °C, the relative crystallinity was greater than 27%, and the relative crystallinity was still greater than 14% even after 2 hours of aging in steam at 800 °C, much greater than that of AlMCM-41 samples synthesized by using aluminum sulfate as aluminum source.

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