Preparation and Analysis of Transition Metal Chromium-Doped Mesoporous Silica

Longjiang Liu¹,², a, Pengzhi Xiang¹,², Yao Huang¹,² and Fang Tang¹,²

¹Yunnan Open University Kunming, 650500, China
²Yunnan Vocational&Technical College of National Defense Industry, Kunming, 650500, China

a421369414@qq.com

Abstract. Cr-doped mesoporous silicas with a two-dimensional hexagonal mesopore structure as well as with a cubic mesoporous framework have been synthesized by using 1-hexadecyl-3-methylimidazolium chloride as structure directing agent template and tetraethylorthosilicate (TEOS) and Cr (NO₃)₃·9H₂O as precursors via hydrothermal synthesis method under alkaline conditions. The effects of the concentration of chromate on hexagonal mesophase and the reaction time on cubic mesophase were discussed in detail. The samples were characterized by X-ray diffraction and thermogravimetry (TG) techniques. The results show that the template has been completely removed when the sample is calcined at 550 °C; the ordered long-range mesostructure with hexagonal and cubic phases can be obtained by adding appropriate amount of chromium salt.

1. Introduction

A new M41S type series silicon oxide (aluminum) group ordered mesoporous molecular sieves have been synthesized successfully by the American Mobil Company using the alkyl quaternary ammonium salt cationic surfactant as a template since 1992 [1-2]. These materials possess a porous system consisting of hexagonally arranged channels with diameters varying from 1.5 to 10 nm. MCM-41S type has attracted the attention of scientists due to its elevated specific surface area, high thermal and hydrothermal stability, possibility of controlling its pore size and its hydrophobicity and acidity. These characteristics have made MCM-41S type a promising material as catalyst and/or support and to be used in industrial processes of adsorption, ion exchange, and environmental control, and so on [3]. Through various chemical or physical methods, researchers assemble or introduce a variety of catalyst components into the pore channels, pore walls or pore wall framework of mesoporous materials to achieve a high degree of dispersion and fixation of the catalyst, finally an efficient catalyst material with mesoporous material as support was obtained. These composite mesoporous catalysts not only have high catalytic efficiency and good activity, but also are easier to recycle and reuse, especially in chemical reactions involving large volumes of molecules. However, most of them are modified by hydrothermal synthesis, in which the metal is directly doped into the silica matrix, and the structure and properties of the molecular sieves are modulated by synthesizing the doped materials, so that they have a wide range of potential applications in many fields such as catalysis, adsorption, light, electricity, magnetism, etc. [4].
At present, Cr, V, Mn, Fe and other metals [5, 6, 7] are doped in mesoporous materials. However, in the reported metal-doped MCM-41S type materials, the templating agents used are mostly ionic quaternary amine salts, such as CTAB [8-9]. Whereas, it is still worthwhile to explore new template to optimize the structure of doped type mesoporous phase. In this work, a long-chain ionic liquid, 1-hexadecane-3-methylimidazole (C_{16}mimCl), was used as the structure directing agent to synthesize hexagonal and cubic silicon dioxide chromium-doped under alkaline conditions, the hexagonal and cubic dioxide doped with chromium are studied. The effect of doping with different amounts of chromium on the ordered hexagonal mesoporous materials and the effect of different crystallization time on the cubic mesoporous phase were discussed.

2. Experimental

2.1. Reagents and instruments
The reagents used were all analytical grade. Orthosilicate (TEOS), sodium hydroxide (NaOH), 1-chlorohexadecane, and 1-methylimidazole. JJ-1 timing electric mixer (Zhengzhou Du Fu Instrument factory), muffle furnace, constant temperature magnetic stirrer, oven, etc.

2.2. Characterization of the sample
The small angle test was performed with the Rigaku TTR III type target X-ray diffractometer. The test conditions were Cu target, KA wire, tube voltage 40 kV, tube current 200 mA, and scanning speed 1°/min. The thermogravimetry was tested by the German NETZSCH STA449F3 comprehensive thermal analyzer.

2.3. Synthesis of samples
The mesoporous silica chromium-doped were prepared according to the references [10-11]. Specific steps are as follows: Hexagonal mesoporous silica chromium-doped was synthesized by firstly dissolving C_{16}mimCl and NaOH in water and stirring, heating to 45°C, then adding the required chromium salt and ethyl orthosilicate in order, adjusting the pH=9, and mixing the mixture at 45°C. After stirring at 45°C for 1 h, it was transferred to a stainless steel autoclave lined with polytetrafluoroethylene and crystallized at 100°C for 3 days. The crystallized mixture was filtered, washed with distilled water, dried at room temperature for 24 h, and then calcined at 550°C for 5 h at a heating rate of 2°C/min to obtain a doped mesoporous product after removing the template. At the same time, by adjusting the initial silicon-chromium molar ratio, the purpose is to explore the effect of doping with different amounts of chromium on the mesoporous phase structure. The synthesis of cubic mesoporous silica chromium-doped is quite similar to the synthesis of hexagonal mesoporous silica chromium-doped. The difference is that the pH of the mesoporous silica does not need to be adjusted. The effects of crystallization time on the cubic mesoporous phase were explored by changing the crystallization time to 1day, 3d ays and 5days, respectively.

3. Results and discussion

3.1. Structural characteristics of mesoporous phases
XRD analysis of the as synthesized samples indicated that the mesoporous MCM-41 type molecular sieves may be obtained by doping Cr into the silica matrix using C_{16}mimCl as a template. Figure 1 is the XRD diffraction patterns of hexagonal silica with a n (Cr)/n(Si) molar ratio of 0.01 after calcination. It can be seen from Figure 1 (a) that the diffraction peaks of silica Cr-doped are very obvious characteristic diffraction peaks at at 2θ angles in the range of 2°~6°, which is indexed to (100), (110) and (200) crystal plane, respectively. According to the Bragg diffraction equation 2d_{hkl}sinθ_{hkl} = nλ, the The interplanar spacings d_{100}, d_{110}, d_{200} are 3.798, 2.209, and 1.898 nm, which are consistent with those reported in the literature [1, 2]. These characteristic diffraction peaks can be
attributed to the typical hexagonal mesoporous phase structure, indicating that the sample has good long-range ordered. It is shown that the amphiphilic ionic liquid C_{16}mimCl template is used as the guide agent, and the hexagonal mesoporous phase structure has not been destroyed when the appropriate amount of chromium salt is doped into the silica matrix. The XRD spectra of cubic silica with a n (Cr)/n(Si) molar ratio of 0.01 after calcination is shown in Figure 1(b). It can be seen from Figure 1(b) that in the range of 2θ=2°~6°, there are four distinct characteristic diffraction peaks indexed to (211), (220), (322) and (422) crystal plane, indicating that the synthesized silica Cr-doped has a highly ordered cubic mesoporous structure, which is consistent with the literature reported and can be considered as having a cubic mesoporous phase structure. [9, 12]. According to the Bragg diffraction equation \(2d_{hkl} \sin \theta_{hkl} = n \lambda\), the cubic silica Cr-doped of the interplanar spacings \(d_{211}, d_{220}, d_{322}, d_{422}\) are 3.559, 3.072, 1.905 and 1.740 nm in turn.

Figure 1. XRD patterns of hexagonalCr-MCM-41 and cubicCr-MCM-48 after calcinations [n(Cr)/n(Si) = 0.01]

3.2. Effect of doping with different amounts of Cr on hexagonal mesoporous phases

Fig. 2 is an hexagonal mesoporous silica XRD spectrum of different amounts of chromium doped. It can also be clearly seen from the spectrum that the (100), (110) and (200) characteristic diffraction peaks are in the presence of the samples when n(Cr)/n (Si) is in the range of 0.01-0.02, these peaks are special intense and clearly visible. With the increase of the amount of chromium, when the n (Cr)/n(Si) is up to 0.10, no diffraction peaks were observed, indicating that within 72h synthesis, the hexagonal arrangement of the mesopores in these materials is less ordered compared to pure silica. According to the calculation formula of the hexagonal unit cell parameters, it is found that their unit cell parameters increase sequentially with n (Cr)/n (Si) from 0.00 to 0.02, which are 4.23, 4.38, and 4.43 nm corresponding to \(d_{100}\) crystal plane, respectively. The parameter \(a_0\) is also seen to show a tendency to increase with the amounts of chromium doped, which has been attributed to the increase in the wall thickness of the mesopores[3]. It shows that the incorporation of chromium has an effect on the order of the sample, but it still maintains a highly ordered hexagonal structure by adding appropriate amount...
of chromium salt. It can also be observed from the figure, the above results show that chromium ions have partially entered into the pore wall or skeleton of the mesopore silica.

Figure 2. XRD patterns of Cr-MCM-41 doped chromium with different molar ratios of n(Cr)/n(Si)

3.3. Effect of different crystallization time on cubic phase structure

In order to investigate the effect of crystallization time on the phase structure of cubic mesoporous materials. The n(Cr)/n(Si) mole ratio is 0.01, the reaction mixture are crystallized at 100°C for (1 day, 3 days, 5 days), respectively. Figure 3 shows the XRD spectra of cubic mesoporous materials at different crystallization times. It can also be seen from the figure 3(b) that the samples crystallized for 3d have a highly ordered cubic mesoporous phase structure, the main characteristic diffraction peaks are clearly discernible, the structure of the product channels and pore walls were improved. However, when the crystallization time is shortened (1 day) or increased (5 days), it is clearly observed that the degree of order is greatly reduced in figure 3(a) and figure 3(c), the characteristic diffraction peaks attributed to (211), (220), (322) and (422) crystal plane disappear, this is due to the collapse of some pores caused by the addition of chromium. When the crystallization time was extended to 5d, it was found that the order of the sample was significantly similarity compared to that of 3d. It can also be concluded that prolonging the appropriate time is greatly beneficial for the order of the Cr-doped cubic phase structure and the promotion of the pore structure. The results show that three-day crystallization is the best time, highly ordered cubic mesoporous phase can be synthesized via hydrothermal synthesis procedure.
3.4. **TG analysis of precursor thermal decomposition behavior**

In order to study whether the template can be completely removed after calcination, thermogravimetric analysis was adopted. Thermogravimetric analysis of the as synthesized samples presented a TG curve typical of mesoporous materials (Figure 4). Figure 4 is a thermogravimetric analysis chart of the sample of the cubic silica Cr-doped after calcining at 550°C for 5h. The figure is a thermogravimetric analysis curve from room temperature to 800°C, and the heating rate is 10°C/min. It can be seen from the figure that the sample is slowly weightless before 250°C, which is mainly the removal of adsorbed water and solvents; and the rapid weightlessness is after 300~500°C, which is the oxidative decomposition of organic templates. The weight loss is mainly concentrated in the temperature range of 200-500°C, and the weight loss rate is 50.9%, and the weight loss is mainly organic template, which indicates that the content of template is high. When the temperature rises to 550°C, the weight loss of the sample is hardly changed, indicating that the organic template had been completely removed. The remaining part corresponds to organic material whose mass loss is related to three exothermal stages[3]: (a) between 100-250°C: decomposition of the surfactant; (b) between 250-500°C: breaking of the hydrocarbon chain, and (c) between 500-800°C: combustion of the surfactant and water loss associated with condensation of silanol groups. It can be seen from the TG diagram that the calcination temperature and time of the organic template during removal are important factors affecting the ordered structure of the mesoporous materials.
4. Conclusion
Cr-doped silica with hexagonal and cubic mesoporous phase structure were synthesized under alkaline conditions via hydrothermal synthesis procedure using ionic liquid as template. The results show that this novel C_{16}mimCl template has obvious advantages for fabrication of the doped mesoporous phase structures, especially the hexagonal mesoporous phase. At the same time, the phase structure can be optimized and the order of the pore structure can be improved by changing some synthesis conditions.

Acknowledgements
This research has been supported by the Youth Project for Applied Basic Research in Yunnan Province (Project No.: 2012FD065), the Scientific Research Fund Project of Yunnan Provincial Department of Education (Project Number: 2012Y504 and 2011Y425), and supported by the research team of Yunnan Open University (Hybrid Functional Materials Research Team)

References
[1] C. T. Kresge, M. E. Leonowicz, W. J. Roth, et al. Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism, Nature., 359 (1992) 710-712
[2] J. S. Beck, J. C. Vartuli, W. J. Roth, et al. A new family of mesoporous molecular sieves prepared with liquid crystal templates, J. Am. Chem. Soc., 114 (1992)10834-10843
[3] R.A.A. Melo, M.V. Giotto, J. Rocha et al. MCM-41 ordered mesoporous molecular sieves synthesis and characterization, Mater. Res.,2 (1999)173-179
[4] K. Parida, K. Mishra, G. I. DASH, Adsorption of toxic metal ion Cr(VI) from aqueous state by TiO_{2}-MCM-41: equilibrium and kinetic studies, J. Hazard. Mater., 241-242(2012) 395-403
[5] Y. F. Shao, L. Z. Wang, et al. Synthesis and characterization of high hydrothermally stable Cr-MCM-48, Microporous Mesoporous Mater., 109 (2008) 271-277
[6] Y. F. Shao, L. Z. Wang, et al. The photoluminescence of rhodamine B encapsulated in

Figure 4. TG curve of cubic silica Cr-doped precursor at heating rate of 20°C/ min
mesoporous Si-MCM-48, Ce-MCM-48, Fe-MCM-48 and Cr-MCM-48 molecular sieves, J. Photochem. Photobiol. A, 180 (2006) 59-64.

[7] L. Mino, C. Barzan, G.A. Martino, et al. Photoinduced ethylene polymerization on the CrVI/SiO2 phillips catalyst, J. Phys. Chem. C, 2019, 123 (2019) 8145-8152

[8] D.R. Hua, S.L. CHEN, Z. ZHOU, et al. Synthesis of mesoporous MCM-48 molecular sieves of high quality in a fluorine-containing system, J. Fuel Cell Sci. Technol., 40 (2012) 564-568

[9] J. J. Wang, J. M. Lu, J. H. Yang, et al. Synthesis of ordered MCM-48 by introducing economical anionic surfactant as co-template, Mater. Lett., 78 (2012) 395-403

[10] T. W. Wang, H. Kape, M. Antoniett, et al. Templating behavior of a long-chain ionic liquid in the hydrothermal synthesis of mesoporous silica, Langmuir, 23 (2007) 1489-1495

[11] L. J. Liu, T. W. Wang, L. Liu, et al. Synthesis of Fe-, Co- and Ni-Containing MCM-48 using long-chain ionic liquid template, Chin. J. Inorg. Chem., 25 (2009) 693-6