Mesoporous Basic Catalysts

DOI: 10.1002/anie.200800034

One-Pot Synthesis of Potassium-Functionalized Mesoporous γ-Alumina: A Solid Superbase**

Lin Bing Sun, Jing Yang, Jia Hui Kou, Fang Na Gu, Yuan Chun, Ying Wang, Jian Hua Zhu, and Zhi Gang Zou*

The synthesis of mesoporous superbases is a challenge for chemists owing to their wide range of potential applications in green chemistry and the difficulties inherent in their preparation. Mesoporous superbasic materials are extremely desirable for use in environmentally benign and economical chemical processes as they can catalyze diverse reactions under mild conditions,[1,2] therefore many attempts have been made to prepare mesoporous solid bases, for example, by incorporating nitrogen-containing species into mesoporous silica[3,4] and by grafting organic bases onto mesoporous silica.[5,6] Owing to the reaction of these strongly basic species with silica, however, most of the solid bases reported to date are relatively weak, which suggests that it is difficult to generate superbasicity on mesoporous silica.[7,8] In contrast to silica, alumina, especially that of the γ-type, is a well-known support for a variety of solid strong bases,[9–11] which means that the occurrence of mesoporous aluminas affords a good opportunity to prepare mesoporous superbasic materials.[12–14] Unfortunately, the stability of mesoporous aluminas is relatively poor and structural damage occurs to a greater or lesser extent even if post-synthesis modification is performed carefully. This drawback hinders the application of mesoporous aluminas in preparing solid superbases and other functional materials.

Table 1: Physicochemical characteristics of MA-γ and KMA-γ samples.

Sample	K/Al[a]	S_{BET}[b] [m^2 g^{-1}]	V_p[b] [cm^3 g^{-1}]	D_p[b] [nm]	Base strength [H_-]	Basicity [mmol g^{-1}]	1-Hexene isomerization Conversion [%]	*cis/trans*
MA-γ	0	334	0.393	3.8	<9.3	0.30	1.6	0.8
KMA(0.05)-γ	0.05	281	0.354	3.8	22.5	1.03	2.0	1.2
KMA(0.11)-γ	0.11	186	0.266	4.1	27.0	1.78	7.6	2.0
KMA(0.18)-γ	0.18	154	0.241	4.3	27.0	2.44	20.0	4.4
KMA(0.27)-γ	0.27	121	0.191	4.5	27.0	3.25	34.8	4.0

[a] Atomic ratio, detected by ICP. [b] S_{BET}: BET specific surface area; V_p: pore volume; D_p: average pore diameter.

Herein we report a new strategy for the one-pot synthesis of potassium-functionalized mesoporous γ-alumina that involves the use of K_2CO_3 to adjust the pH value of the reaction system such that the base precursor KNO_3 is produced in situ by hydrolysis of $Al(NO_3)_3$. KNO_3 is decomposed to the strongly basic species K_2O on the γ-Al_2O_3 that is also formed in situ during the same calcination process. This strategy allows the synthesis and modification of mesoporous alumina in a one-pot process, avoids post-treatment framework damage, and saves time and energy. The basic materials obtained exhibit a well-defined mesoporous structure and superbasicity and are active in 1-hexene isomerization, which means that they are valuable candidates for selective adsorption and catalysis involving strong solid bases.

The synthetic process is shown schematically in Figure S1 in the Supporting Information. KNO_3-coated mesoporous boehmite (AlOOH) with a K/Al atomic ratio (n) of between 0 and 0.27 (Table 1) is obtained initially (denoted as MA-B ($n=0$) or KMA(n)-B ($n>0$)). The formation of both KNO_3 and boehmite is crucial for subsequent generation of the superbase as they are precursors of K_2O[8,11] and γ-Al_2O_3,[15,16] respectively. The conversion of KNO_3 and boehmite occurs in the subsequent calcination step, where KNO_3 is decomposed to the strongly basic species K_2O on the γ-Al_2O_3 formed in situ. The resulting products are denoted as MA-γ ($n=0$) or KMA(n)-γ ($n>0$).

Figure 1 depicts the N_2 adsorption/desorption isotherms and pore-size distributions of KMA-γ samples. The isotherms are classical type-IV isotherms with little or no additional uptake at high partial pressures. Each of the isotherms has a clear hysteresis loop, which indicates the mesoporosity of the materials. All samples display narrow and uniform pore-size distributions and the pore diameter tends to increase with increasing potassium content. This tendency is also suggested by the average pore diameters listed in Table 1, which imply the preference of potassium species for occupying the small pores in mesoporous alumina. Table 1 also shows the

---

[*] L. B. Sun, J. Yang, F. N. Gu, Prof. Y. Chun, Prof. J. H. Zhu
Key Laboratory of Mesoscopic Chemistry of MOE
School of Chemistry and Chemical Engineering
Nanjing University, Nanjing 210093 (China)
Fax: (+86) 25-8331-7761
J. H. Kou, Prof. Y. Wang, Prof. Z. G. Zou
Ecomaterials and Renewable Energy Research Center (ERERC)
Nanjing University, Nanjing 210093 (China)

[**] The NSF of China (20673053 and 20773061), the National Basic Research Program of China (2007CB613301), the 863 projects of the Chinese Scientific Committee, and the Analysis Center of Nanjing University are acknowledged for their financial support of this research.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

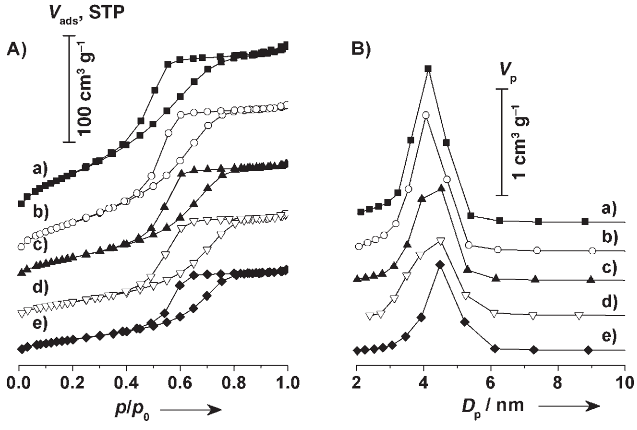

Figure 1. A) N_2 adsorption/desorption isotherms and B) pore-size distributions of a) MA-γ, b) KMA(0.05)-γ, c) KMA(0.11)-γ, d) KMA(0.18)-γ, and e) KMA(0.27)-γ. The curves are offset for clarity.

variation of the surface area and pore volume of KMA-γ samples—an increase in potassium content leads to a decrease in the surface areas and pore volumes.

The representative low-angle X-ray diffraction (XRD) pattern of KMA-γ samples (Figure 2A) shows a single diffraction line. This pattern is characteristic of a mesoporous structure with no long-range order in the pore arrangement and is similar to that observed for mesoporous aluminas obtained by hydrothermal synthesis and microwave heating.[13,16] The peak intensity of KMA-γ is stronger than that of its precursor before calcination (KMA-B), thus implying that the formation of γ-Al_2O_3 and K_2O does not affect the mesoporous structure.

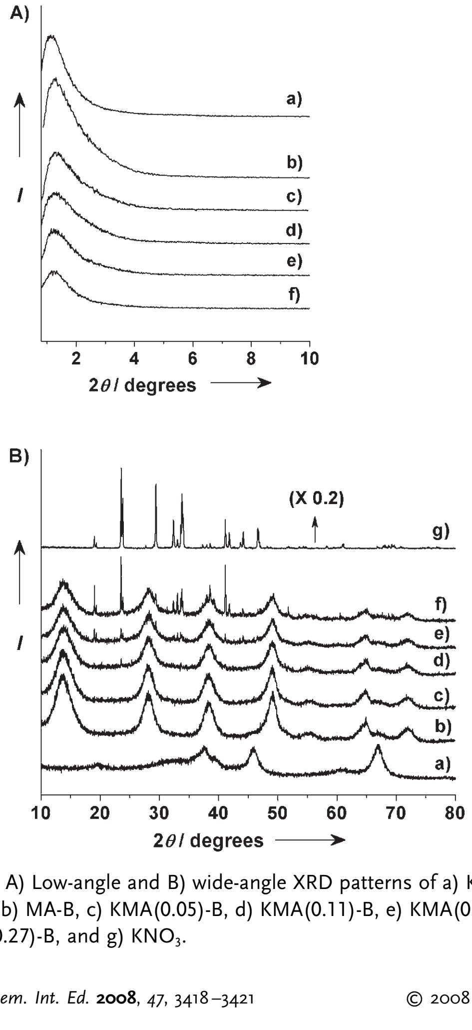

Figure 2. A) Low-angle and B) wide-angle XRD patterns of a) KMA-(0.27)-γ, b) MA-B, c) KMA(0.05)-B, d) KMA(0.11)-B, e) KMA(0.18)-B, f) KMA(0.27)-B, and g) KNO_3.

The TEM image shown in Figure 3 indicates the presence of a wormhole-like framework, which is consistent with the low-angle XRD results. Although long-range packing order is absent, the channels in the network have a regular diameter, as shown by the TEM image, which is in agreement with the pore-size distribution data (Figure 1B). The local element composition, as determined by energy-dispersive X-ray (EDX) analysis (data not shown), verifies the presence of potassium and aluminum in the sample, and the resultant K/Al atomic ratios are similar even though several random areas were selected for EDX analysis; this suggests a homogeneous distribution of potassium species on the mesoporous alumina.

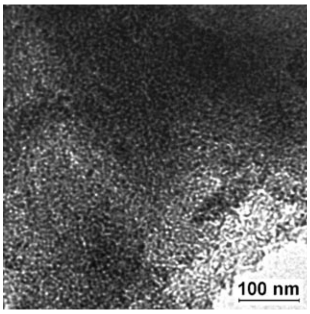

Figure 3. TEM image of KMA(0.18)-γ.

The base strength and amount of basic sites of the KMA-γ samples were initially determined from their Hammett indicators and a basicity titration, respectively. A base strength (H_-) of less than 9.3 was found for bare MA-γ, whereas the introduction of a small amount of potassium species (K/Al = 0.05) increased the base strength to 22.5. Dramatically, basic sites with a high base strength of 27.0 were found for KMA-γ samples with a K/Al ratio of between 0.11 and 0.27. Materials with a base strength higher than 26.5 can be regarded as solid superbases according to Tanabe's definition,[17] which means that these compounds are solid superbases. The introduction of potassium species also increases the amount of basic sites in the composite—number of basic sites in MA-γ, KMA(0.05)-γ, KMA(0.11)-γ, KMA(0.18)-γ, and KMA(0.27)-γ is 0.30, 1.03, 1.78, 2.44, and 3.25 mmol g^{-1}, respectively.

The results of CO_2-temperature programmed desorption (CO_2-TPD; Figure 4) confirm the generation of unusually strong basic sites in these KMA-γ samples. Bare mesoporous alumina (MA-γ) has a low ability to adsorb CO_2, which means that only a single desorption occurs around 100 °C in the CO_2-TPD profile. The introduction of potassium species enhances the basicity of the sample, which causes both the amount of CO_2 desorbed and the desorption temperature to increase. Thus, an abundant CO_2 desorption at about 200 °C (with a shoulder at 360 °C) along with a broad peak centered at 600 °C

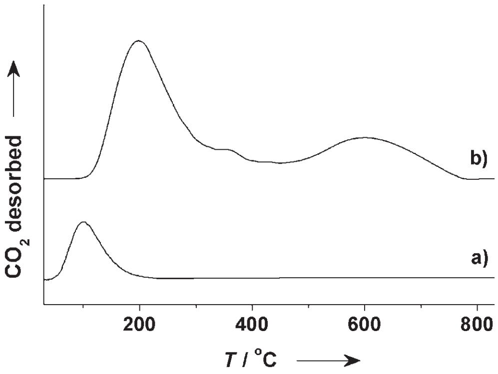

Figure 4. CO_2-TPD profiles of a) MA-γ and b) KMA(0.18)-γ.

appear in the CO_2-TPD profile. The latter desorption of CO_2 clearly provides further evidence for the strong basicity of the KMA-γ sample.

Double-bond isomerization of alkenes at low temperature is a well-known reaction for characterizing solid superbases.[1,11,18] We therefore performed the isomerization of 1-hexene at 40 °C to probe the superbasicity of our KMA-γ samples. The conversion of 1-hexene is low (1.6 %) on bare MA-γ and the *cis/trans* ratio is less than one (Table 1). The introduction of potassium species improves both the 1-hexene conversion and *cis/trans* ratio, and the highest *cis/trans* ratio of 4.4 is provided by KMA(0.18)-γ. This result implies the existence of unusually strong basic sites,[11,18] consistent with the base strength and CO_2-TPD measurements. This is the first report of mesoporous solid superbases synthesized by an energy- and time-saving direct method.

Two main factors are responsible for the successful synthesis of mesoporous solid superbases (KMA-γ) by this one-pot method. The first factor is the flexible reactivity of K_2CO_3, which plays a double role in this synthetic process by adjusting the pH value of the system, and thereby promoting the hydrolysis of $Al(NO_3)_3$, and at the same time producing the base precursor KNO_3. This step results in KNO_3-coated mesoporous boehmite (KMA-B; see Figure S1 in the Supporting Information), as demonstrated by the wide-angle XRD patterns (Figure 2B; JCPDS No. 21-1307). The FTIR spectra (see Figure S2 in the Supporting Information) display bands at 1765, 1384, and 826 cm^{-1}, which can be assigned to the nitrate anion,[19] as well as bands at 3301, 3094, 1156, 1073, and 741 cm^{-1}, which can be assigned to Al–OH stretching and bending vibrations,[20] thereby confirming the production of KNO_3 and boehmite.

The second factor is the multiple role of the calcination process, in which the conversion of both KNO_3 and boehmite takes place and the strongly basic K_2O species are directly coated onto the γ-Al_2O_3 formed in situ. This situation differs from the in situ coating method,[21] where the base precursor is coated onto an assembled mesoporous silica. Figure 2B (curve a) shows a typical wide-angle XRD pattern of γ-Al_2O_3 (JCPDS No. 10-0425) without the diffraction line of KNO_3, thereby confirming the decomposition of KNO_3. In addition, no K_2O diffraction lines can be identified for the KMA-γ samples, which is indicative of the good dispersion of K_2O and no particle formation on the mesoporous γ-Al_2O_3 support. As seen in Figure S2 (Supporting Information), the FTIR spectra also provide evidence for γ-Al_2O_3 formation and KNO_3 decomposition. Moreover, the bands at 1550, 1411, and 1005 cm^{-1} are observed, which originate from the adsorption of atmospheric CO_2 on the strongly basic sites of KMA-γ samples.[22] Thermogravimetry–mass spectrometry (TG-MS; Figure S3 in the Supporting Information) can be used to follow the detailed conversion process from KMA-B into KMA-γ. The dehydration of boehmite to γ-Al_2O_3 ($2\,AlOOH \rightarrow Al_2O_3 + H_2O$) occurs in the temperature range 150–500 °C.[23] Most of the supported KNO_3 is decomposed at 500 and 640 °C, with some decomposition occurring at 300 °C. This reaction mainly produces NO and O_2 rather than NO_2 ($2\,KNO_3 \rightarrow K_2O + 2\,NO + 1.5\,O_2$).

The formation of γ-Al_2O_3 in situ is important for the decomposition of supported KNO_3 and the resultant superbasicity. An amorphous Al_2O_3-supported KNO_3 sample, with the same potassium content as KMA(0.18)-B, was prepared for comparison. Only part of the KNO_3 can be decomposed on this amorphous Al_2O_3 under the same conditions, and the residual KNO_3 is apparent in the XRD and FTIR spectra (Figure S4 in the Supporting Information). Similar results were also observed for a sample of KNO_3 supported on amorphous Al_2O_3 with a mesoporous structure. This sample was found to have a base strength of 22.5 rather than 27.0. These differences can be attributed to the inherent properties of the two aluminas. The potassium cation of KNO_3 can insert into the octahedral vacant sites on the surface of γ-Al_2O_3,[10] which leads to a strong host–guest interaction. This interaction means that KNO_3 tends to disperse dissociatively,[24] which weakens the bond between the potassium cation and the nitrate anion. These nitrate species start to decompose during thermal treatment and create strongly basic sites on the surface of γ-Al_2O_3, thereby generating superbasicity for these KMA-γ samples. The amorphous Al_2O_3 sample does not contain such vacant sites for K^+ ion insertion, which means that KNO_3 decomposition and superbasicity generation is much more difficult.

Apart from saving time and energy, the present one-pot synthesis plays an important role in the fabrication of superbasic materials with good mesostructures. Mesoporous aluminas are less stable than their silica analogues and their mesoporous structure is easily damaged by post-synthesis modification. A potassium-modified mesoporous γ-Al_2O_3 sample was therefore prepared by conventional wet impregnation for comparison. As can be seen from the low-angle XRD pattern (Figure S5 A in the Supporting Information), the diffraction line of the impregnated sample is very weak. The N_2 adsorption data (Figure S5 B in the Supporting Information) show uptake at high partial pressures along with a smaller hysteresis loop than for the compound obtained from the one-pot method. Furthermore, the pore volume of the sample prepared by wet impregnation (0.187 $cm^3\,g^{-1}$) is lower than that of the one-pot sample (0.241 $cm^3\,g^{-1}$). This one-pot method therefore allows the mesoporous alumina to maintain its structure, while wet impregnation results in considerable structural damage.

The isomerization of 1-hexene was also conducted with the impregnated sample. The results showed that 15.2 % of 1-

hexene could be converted, which is less than that with the one-pot sample with the same K/Al ratio (KMA(0.18)-γ: 20.0%; Table 1). The *cis*/*trans* ratio of 3.0 obtained with the impregnated sample is also much lower than that with KMA(0.18)-γ (4.4; Table 1). The relatively low activity of the impregnated sample is probably due to its poor mesostructure.

In summary, a novel superbasic material, namely potassium-modified mesoporous γ-alumina, has been successfully synthesized by a one-pot method. Performing both the synthesis and modification in a one-pot process produces mesoporous superbases with narrow and uniform pore-size distributions. These solid superbases are efficient catalysts for the isomerization of 1-hexene and are also promising candidates for selective adsorption and catalysis involving strongly basic materials. This strategy may open up a route for the design and synthesis of new functional materials.

Experimental Section

The potassium-functionalized mesoporous alumina was synthesized as follows. $Al(NO_3)_3\cdot 9H_2O$ (0.1 mol) was dissolved in water (17.0 g) and blended with the triblock copolymer P123 (6.38 g; $(EO_{20}PO_{70}EO_{20})$). The resulting mixture was stirred at 40 °C for 36 h to form a clear sol and aged statically for another 6 h. An aqueous K_2CO_3 solution (40 wt.%) containing 0.15 mol of potassium was added dropwise to the clear sol with slow stirring. The temperature of the mixture was then increased to 100 °C for 24 h under static conditions to produce mesoporous alumina with boehmite walls. The resultant solid was washed with 60, 80, 100, 120, or 200 mL of water to vary the potassium content of the product. The surfactant was removed by extraction with ethanol to give the mesoporous boehmite-supported KNO_3 with K/Al atomic ratios (n) of 0.27, 0.18, 0.11, 0.05, and 0, respectively (Table 1). The resulting samples were denoted as MA-B ($n=0$) or KMA(n)-B ($n>0$). Calcination of the composite was carried out in a stream of nitrogen by heating the sample to 600 °C at a rate of $2\,°C\,min^{-1}$ and maintaining the final temperature for 2 h. The resultant mesoporous γ-Al_2O_3-supported K_2O was denoted as MA-γ ($n=0$) or KMA(n)-γ ($n>0$).

The structure of the materials was characterized by XRD, TEM, and N_2 adsorption methods. XRD patterns were recorded with a Rigaku D/max-rA system using $Cu_{K\alpha}$ radiation in the 2θ range 0.6–10° or 10–80° at 40 kV and 40 mA. TEM and EDX analyses were performed with a FEI Tecnai G^2 20 S-TWIN electron microscope operating at 200 kV. The N_2 adsorption/desorption isotherms were measured using a Micromeritics ASAP 2020 system at −196 °C; the samples were previously outgassed at 300 °C for 4 h. The Brunauer–Emmett–Teller (BET) surface area was calculated from the adsorption data in the relative pressure range 0.04–0.20, and the total pore volume was determined from the amount adsorbed at a relative pressure of about 0.99. The pore diameter was calculated from the desorption branch by the Barrett–Joyner–Halenda (BJH) method.

FTIR measurements were performed with a Bruker 22 FTIR spectrometer by the KBr pellet technique. The elemental composition of the samples was determined with a J-A1100 inductively coupled plasma-optical emission spectrometer (ICP-OES). TG-MS analysis was conducted on a thermobalance (STA-499C, NETZSCH) coupled with a mass analyzer (QUADSTAR-422, PFEIFFER). The sample was heated from 25 to 900 °C at a rate of $8\,°C\,min^{-1}$ in a continuous flow of argon ($30\,mL\,min^{-1}$).

In a typical CO_2-TPD experiment, the sample was activated at 600 °C for 2 h prior to the adsorption of CO_2 at 25 °C. After purging the physically adsorbed CO_2 at 25 °C, the sample was heated to 900 °C at a rate of $8\,°C\,min^{-1}$, and the CO_2 liberated was detected by a mass analyzer (the mass signal at m/z 44 was used to determine the amount of CO_2 desorbed). The base strength (H_-) of the sample was determined from a series of Hammett indicators.[21] To measure the basicity, the activated sample (50 mg) was shaken in aqueous HCl (10 mL; 0.05 M) for 24 h and the slurry was separated by centrifugation. The acid remaining in the liquid phase was titrated with aqueous NaOH (0.02 M).

The isomerization of 1-hexene was conducted in a conventional flow reactor.[11] N_2 was used as the carrier gas with a flow rate of $20\,mL\,min^{-1}$. A sample pellet (50 mg) with 20–40 mesh was activated at 600 °C for 2 h and then cooled to the reaction temperature of 40 °C. 1-Hexene was introduced with a syringe pump with a space velocity of $0.1\,h^{-1}$ and the reaction mixture was analyzed by on-line GC (Varian 3700).

Received: January 4, 2008

Keywords: aluminosilicates · basicity · heterogeneous catalysis · mesoporous materials · template synthesis

---

[1] J. Weitkamp, M. Hunger, U. Rymsa, *Microporous Mesoporous Mater.* **2001**, *48*, 255.

[2] T. Seki, S. Ikeda, M. Onaka, *Microporous Mesoporous Mater.* **2006**, *96*, 121.

[3] Y. Xia, R. Mokaya, *Angew. Chem.* **2003**, *115*, 2743; *Angew. Chem. Int. Ed.* **2003**, *42*, 2639.

[4] J. Wang, Q. Liu, *Microporous Mesoporous Mater.* **2005**, *83*, 225.

[5] D. J. Macquarrie, D. B. Jackson, S. Tailland, K. A. Utting, *J. Mater. Chem.* **2001**, *11*, 1843.

[6] X. Wang, K. S. K. Lin, J. C. C. Chan, S. Cheng, *J. Phys. Chem. B* **2005**, *109*, 1763.

[7] K. R. Kloetstra, M. van Laren, H. van Bekkum, *J. Chem. Soc. Faraday Trans.* **1997**, *93*, 1211.

[8] Z. Y. Wu, Q. Jiang, Y. M. Wang, H. J. Wang, L. B. Sun, L. Y. Shi, J. H. Xu, Y. Wang, Y. Chun, J. H. Zhu, *Chem. Mater.* **2006**, *18*, 4600.

[9] Y. Ono, *J. Catal.* **2003**, *216*, 406.

[10] J. H. Zhu, Y. Wang, Y. Chun, X. S. Wang, *J. Chem. Soc. Faraday Trans.* **1998**, *94*, 1163.

[11] Y. Wang, W. Y. Huang, Y. Chun, J. R. Xia, J. H. Zhu, *Chem. Mater.* **2001**, *13*, 670.

[12] P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka, G. D. Stucky, *Nature* **1998**, *396*, 152.

[13] Z. Zhang, T. J. Pinnavaia, *J. Am. Chem. Soc.* **2002**, *124*, 12294.

[14] J. Cejka, *Appl. Catal. A* **2003**, *254*, 327.

[15] R. W. Hicks, T. J. Pinnavaia, *Chem. Mater.* **2003**, *15*, 78.

[16] T.-Z. Ren, Z.-Y. Yuan, B.-L. Su, *Langmuir* **2004**, *20*, 1531.

[17] K. Tanabe, R. Noyari, *Chokyo-san, Chokyo-enki*, Kodansha, Tokyo, **1980**, p. 114.

[18] H. Hattori, *Chem. Rev.* **1995**, *95*, 537.

[19] L. B. Sun, Y. Chun, F. N. Gu, M. B. Yue, Q. Yu, Y. Wang, J. H. Zhu, *Mater. Lett.* **2007**, *61*, 2130.

[20] S. Music, D. Dragcevic, S. Popovic, N. Vdovic, *Mater. Chem. Phys.* **1999**, *59*, 12.

[21] Y. L. Wei, Y. M. Wang, J. H. Zhu, Z. Y. Wu, *Adv. Mater.* **2003**, *15*, 1943.

[22] V. K. Diez, C. R. Apesteguia, J. I. Di Cosimo, *J. Catal.* **2006**, *240*, 235.

[23] C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli, J. S. Beck, *Nature* **1992**, *359*, 710.

[24] T. Yamaguchi, J. H. Zhu, Y. Wang, M. Komatsu, M. Ookawa, *Chem. Lett.* **1997**, 989.