http://dx.doi.org/10.5012/bkcs.2012.33.9.2961

Mesoporous Carbon as a Metal-Free Catalyst for the Reduction of Nitroaromatics with Hydrazine Hydrate

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Received August 19, 2011, Accepted June 8, 2012

Mesoporous carbons with tailored pore size were prepared by using sucrose as the carbon source and silicas as the templates. The silica templates were obtained from a hydroxypropyl-β-cyclodextrin-silica hybrids using ammonium perchlorate oxidation at different temperatures to remove the organic matter. The structures and surface chemistry properties of these carbon materials were characterized by N_2 adsorption, TEM, SEM and FTIR measurements. The catalytic performances of these carbon materials were investigated through the reduction of nitroaromatic using hydrazine hydrate as the reducing agent. Compared with other carbon materials, such as active carbon, and carbon materials from the silica templates obtained by using calcination to remove the organic matter, these carbon materials exhibited much higher catalytic activity, no obvious deactivation was observed after recycling the catalyst four times. Higher surface area and pore volume, and the presence of abundant surface oxygen-containing functional groups, which originate from the special preparation process of carbon material, are likely responsible for the high catalytic property of these mesoporous carbon materials.

Key Words : Mesoporous carbon, Hydroxypropyl-β-cyclodextrin, Metal-free catalyst, Silica, Nitroaromatic

Introduction

Mesoporous carbons (MCs) with high surface area, large pore volume, well-tailored pore size, benign chemical inertness and conductivity are extensively applied in many fields of science and technology. Recently, with the rapid development of novel means for the preparation of various mesoporous silica materials, much effort has been devoted to the synthesis of various silica-based MCs with attractive characteristics of structure and application, for instance, Lu *et al.*[1] developed a new method to synthesize an ordered structural SBA-15 by $KMnO_4$ oxidation to remove organic template at a low temperature. Using this silica as the template, MC with thick pore walls and relatively small mesoporous can be casted, which could be a candidate as molecular sieve type adsorbent and catalyst support. Vinu *et al.*[2] reported the synthesis and characterization of carbon nanocage using three dimensional large cage type face centered cubic *Fm3m* mesoporous silica material (KIT-5) as the template, and this carbon nanocage exhibited superior adsorption capacities to biomolecules such as catechin, histidine and vitamin E in their aqueous solutions.

Currently, the carbon materials with high surface areas and well developed porosities have attracted increasing attention in the field of catalysis.[3-10] As known, nitroaromatics can be easily reduced to the corresponding aromatic amines using hydrazine hydrate as a benign reductant and metals as well as carbons as the effective catalysts.[11-15] The reduction of nitroaromatics is recognized to be one of the most important chemical transformation in synthetic organic chemistry, mainly due to the fact that the amino group serves as an useful site for further derivatization.[16] The aromatic amines are also widely used as important intermediates for polymers, photographic materials, pharmaceuticals, agrochemicals, dyes and antioxidants. Nevertheless, the broad application of this catalytic method is restricted by the relatively high cost of the metal catalysts and the pollution of metals to product and environment.

Recently, Xu *et al.*[17,18] described the use of fullerenes as nonmetal catalysts for the reduction of nitrobenzene to aniline with hydrazine hydrate under light irradiation at room temperature with high yields and selectivity. However, it is inconvenient because of the light irradiation conditions required in this reaction process and relatively high cost of fullerenes. Our groups reported previously about carbon materials synthesized from the direct carbonization of β-HPCD/silica composites could catalyze the reduction, but, the reaction rate is slower.[19] Therefore, it is necessary to develop a highly efficient, economical and environmental friendly catalytic system to reduce nitroaromatics with hydrazine hydrate for applications both in academic laboratories and in industry.

According to our previous report,[20] mesoporous silicas was prepared by using NH_4ClO_4/HNO_3 oxidation to remove organic template at different temperatures from hydroxypropyl-β-cyclodextrin (β-HPCD)/silica composite. These silicas have rich surface silanol groups and thus can easily form intermolecular hydrogen bond with various carbon resources such as sucrose, fulfuryl alcohol and phenolic resin, which is advantageous to preparation of nanostructure

carbons with nanocasting technology. Therefore, in this paper, we presented the synthesis and characterization of MCs with high surface area and large pore volume using the mesoporous silicas as the hard templates. These carbon materials have high catalytic activity for the reduction of nitroaromatics to the corresponding aromatic amines with hydrazine hydrate under mild reaction conditions.

Experimental Section

Synthesis of Mesoporous Silica Templates. The mesoporous silica materials were synthesized using our previous procedure.[20] In brief, a certain amount of β-HPCD and tetraethyl orthosilicate (TEOS) were dissolved in an aqueous pH 2.0 sulfuric acid solution under stirring vigorously at room temperature, leading to a composition of gel in molar ratios of 1 TEOS:0.069 β-HPCD:0.0018 H_2SO_4:15 H_2O. After evaporation and dry, the obtained composite was treated with NH_4ClO_4/HNO_3 solution at room temperature (rt) or x °C (x = 60, 80 and 100, respectively) for 12 h in a Teflon autoclave to remove the organic matter. Thus, the obtained silicas were termed as Si-rt or Si-x (where x denotes the oxidation temperature with NH_4ClO_4/HNO_3 solution).

Synthesis of MCs. MCs were prepared by using an nanocasting procedure with the above-mentioned mesostructure silicas Si-rt or Si-x as the hard templates and sucrose as the carbon precursor. Correspondingly, these products were designated as MC-rt or MC-x. In a typical synthesis, 0.50 g of sucrose, 2.5 g of deionized water and 0.05 g of concentrated H_2SO_4 were mixed under stirring to form a homogeneous solution, then 1 g of the Si-rt or Si-x material was added into the solution. The resulting mixture was kept in an oven for 6 h at 100 °C; subsequently, the oven temperature was raised to 160 °C for another 6 h. These steps were repeated once to ensure the complete filling of carbon precursor mixture in the channels of hard template silica. Then the resultant powders were carbonized at 900 °C under a N_2 flow, the temperature was raised to 500 °C in 4 h and kept constant for 5 h, after that the temperature was increased to 900 °C in 7 h, and maintained for 4 h. The MC-rt or MC-x was recovered after the dissolution of the silica frameworks in a 40 wt % solution of hydrofluoric acid by filtration, washed several times with deionized water and dried at 120 °C. A similar program was used for synthesis of MC-cal with Si-cal obtained by calcination at 600 °C for removing organic matter.

Characterization. The samples were characterized by N_2 adsorption, Fourier transform infrared spectrometer (FTIR), scanning and transmission electron microscopy (SEM and TEM) imaging techniques. N_2 adsorption isotherms were measured using a Micromeritics ASAP2020 adsorption analyzer under liquid N_2 temperature. Prior to the measurements, the samples were degassed for 6 h in the degas port of the adsorption apparatus at 350 °C. The surface areas (S_{BET}) were calculated using the Brunauer-Emmett-Teller (BET) method based on adsorption data in the relative pressure (P/P_0) range 0.05-0.3, the total pore volumes (V_t) were determined based on the amount of the N_2 adsorbed at a relative pressure of 0.992 (P/P_0), and the PSDs were derived from the desorption branches of isotherms by using the Barrett-Joyner-Halenda (BJH) model. The micropore volumes were calculated based on the empirical *t*-plot method. FTIR spectra were collected on a Nicolet Fourier spectrophotometer (Avatar360E.S.P.) using KBr pellets of the solid samples. SEM images were recorded using a Quanta 200 environmental scanning electron microscope. Samples were mounted using conductive carbon double-sided sticky tape. A thin (*ca.* 10 nm) coating of gold sputter was deposited onto the samples to reduce the effects of charging. TEM experiments were conducted on a JEM 2100 electron microscope operating at 200 kV. The samples for TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid.

Catalytic Properties. Herein, the reduction of *p*-nitrotoluene with 80% hydrazine hydrate was used as a model reaction to evaluate the catalytic properties of synthesized MCs. The reduction of *p*-nitrotoluene was carried out following our previous procedure for investigating other carbon materials synthesized from the direct carbonization of β-HPCD/silica composites.[19] The progress of the reaction was tracked by the thin layer chromatography (TLC). After the reduction, the catalyst was separated by filtration, and washed repeatedly with ethanol and then dried for recycle. The filtrate was condensed and dried at 35 °C in a vacuum. The structure of the product was identified by liquid nuclear magnetic resonance (NMR) spectrum and melting point measurement.

Results and Discussion

Synthesis and Characterization of MCs. The porous characteristics of the MCs were investigated by N_2 adsorption. As can be seen from Figure 1, the sample MC-cal synthesized from Si-cal exhibits type I+IV isotherm with a small hysteresis loop, implying the co-presence of micropores and mesopores;[21] the PSD curve calculated from the desorption branch with the BJH method shows that the MC-cal sample exhibits only broad and weak peak centered at 3.9 nm. The samples of the MC-rt and MC-x present type IV isotherms with quite significant H2-type hysteresis loops, which is a characteristic of mesoporous materials with "ink-bottle" type pores,[21] and the PSD curves exhibit sharp peaks centered at 3.9, 3.3, 3.3 and 3.7 nm, respectively. Besides, as can be seen in Table 1, the BET surface area and total pore volume of MC-cal are much lower than those of MC-rt or MC-x samples. Concerning the influence of the temperature required for removing β-HPCD with NH_4ClO_4 on the structure of the carbons, one can be seen from Table 1 that the total pore volumes of carbons increase with the rise of temperature, but their BET surface areas are not in positive correlation with the temperature, which decrease in the order MC-60 > MC-80 > MC-rt > MC-100. It is noteworthy that MC-cal and MC-100 have a portion of micropores; moreover, the micropore volume (0.20 cm^3g^{-1}) and micropore

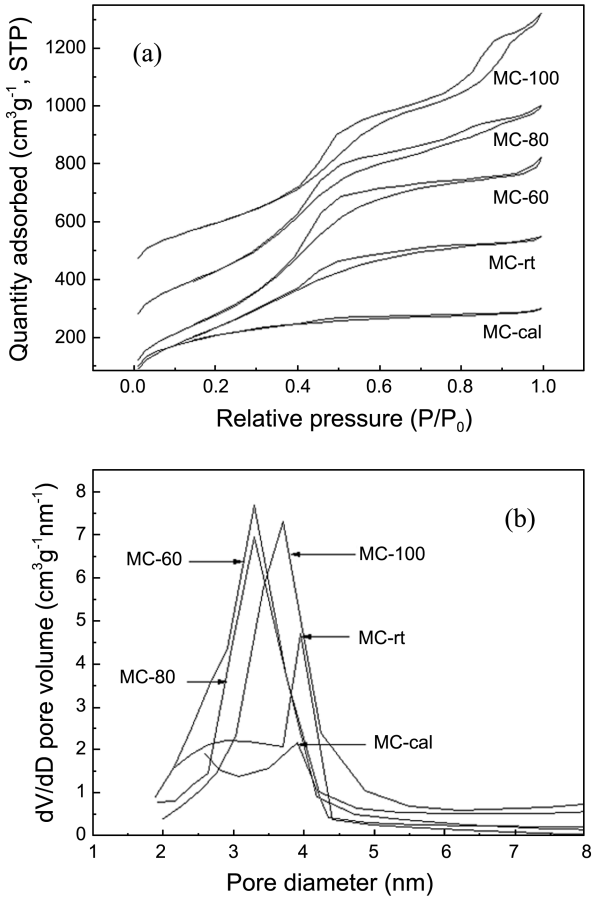


Figure 1. N_2 adsorption-desorption isotherms (a) and BJH desorption PSDs (b) of MCs prepared with different silica templates.

Table 1. Textural parameters of various MC samples[a]

Sample	S_{BET} (m^2 g^{-1})	S_{mic} (m^2 g^{-1})	V_{tot} (cm^3 g^{-1})	V_{mic} (cm^3 g^{-1})	V_{mes} (cm^3/g^{-1})	D_{BJH} (nm)
MC-cal	562	376	0.38	0.20	0.18	3.9
MC-rt	1240	-	1.33	-	1.33	3.9
MC-60	1430	-	1.52	-	1.52	3.3
MC-80	1407	-	1.58	-	1.58	3.3
MC-100	1222	154	1.74	0.07	1.67	3.7

[a]S_{BET}, specific surface area, was calculated by the BET method; S_{mic}, micropore area, was calculated by *t*-plot method; V_{tot}, total pore volume, was evaluated at $P/P_0 = 0.99$; V_{mic}, micropore volume, was calculated by the *t*-plot method; D_{BJH}, pore diameter, was calculated from the desorption branch by the BJH method.

area (376 m^2g^{-1}) of the former are evidently higher than those (0.07 cm^3g^{-1} and 154 m^2g^{-1}) of the latter, which may be mainly attributed to the structures of the silica templates. The *d*-spacing of Si-cal is larger but its pore diameter is smaller than that of Si-100,[20] with the result that Si-cal has a higher ratio between wall thickness and pore size, and the corresponding carbon MC-cal replicated from this template has thinner pore wall and thus easily collapse, which creates an opportunity for the formation of a more pronounced micropore system in this carbon wall.

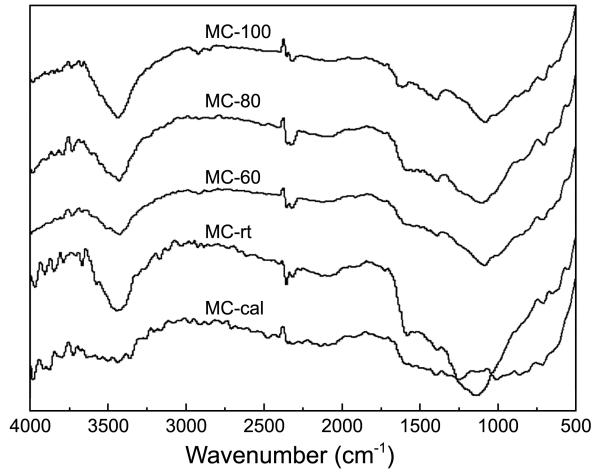


Figure 2. FTIR spectra of various MCs prepared with different silica templates.

Figure 2 shows the FTIR spectra of various carbon materials. Compared with the MC-cal sample, two broad bands centered at 3450 and 1150 cm^{-1} are evidenced for samples MC-rt~100, the former are caused by stretching vibration mode of O-H from hydroxyl, phenolic, and carboxylic groups, the latter can be attributed to C-O stretching,[9] suggesting that there are quite an amount of oxygen-containing functional groups in samples synthesized by using NH_4ClO_4 oxidation to remove β-HPCD.

The nature of framework structures and the surface morphologies of the obtained carbon materials were investigated from TEM and SEM images, respectively. Figure 3(a) and (b) reveal the existence of the disordered but uniform-size wormlike pore channels in representative example MC-rt and MC-cal, indicating that these carbon samples maintain the initial structural features of the silica templates. Figure 3(c) and (d) show the SEM images observed for MC-rt and

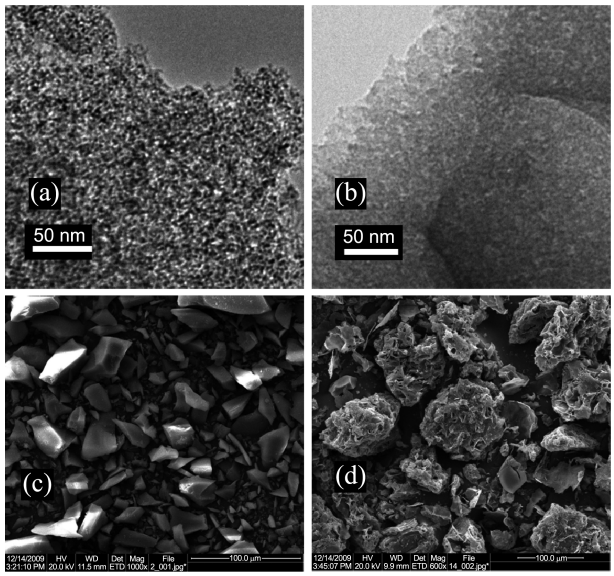


Figure 3. Representative TEM images of carbon materials MC-rt (a) and MC-cal (b). Representative SEM images of MC-rt (c) and MC-cal (d).

Table 2. Reduction of *p*-nitrotoluene with hydrazine hydrate in the presence of MC catalysts[a]

Sample	Time[b] (min)	Yield[c] (%)
Without any catalysts	720	None
Absence of hydrazine hydrate	720	None
Activated carbon	720	None
MC-cal	480	71.68 ± 0.12
MC-rt	30	88.48 ± 0.17
MC-60	240	85.23 ± 0.11
MC-80	300	83.72 ± 0.21
MC-100	380	82.95 ± 0.25

[a]Reaction conditions: the mixture of 5 mmol of *p*-nitrotoluene, 40 mg of catalyst and 20 mL of ethanol was heated at reflux temperature, then 15 mmol of hydrazine hydrate was added by dropwise into the flask while stirring. [b]From addition of hydrazine hydrate to the end of reaction. [c]The isolated yield of *p*-methylaniline.

Table 3. Reduction of *p*-nitrotoluene to aniline with carbon catalysts prepared with oxidated silica at room temperature[a]

Repetitions of catalyst	Dosage of catalyst (mg)	Mole ratio of material[b]	Time[c] (min)	Yield (%)
1	20	1:3	60	73
1	40	1:2	30	68
1	40	1:3	30	88
1	40	1:4	30	87
2	40	1:3	30	87
3	40	1:3	30	86
4	40	1:3	75	87
5	40	1:3	80	73
6	40	1:4	60	72

[a]Reaction conditions: 5 mmol of *p*-nitrotoluene, 20 mL of ethanol, reaction temperature 85 °C, a certain amount of hydrazine hydrate added dropwise in 20 min, and stirring speed 500 rpm. [b]Mole ratio of *p*-nitrotoluene and hydrazine hydrate. [c]Time from addition of hydrazine hydrate to the stop of reaction.

MC-cal. Since the samples were crushed for SEM analysis, the MC-rt demonstrates largely smooth granular carpolite-like morphology with particle size at the micrometer scale, which indicates that the original samples were essentially monoliths in nature. The MC-cal material takes on a hollow, tremella-like morphology with curly flakes inside.

Catalytic Properties. It can be seen clearly from Table 2 that all carbon samples can catalyze the reduction of *p*-nitrotoluene to *p*-methylaniline by hydrazine hydrate. To our surprise, compared with other carbon samples, the MC-rt can catalyze completely this reduction within the shortest time (30 min) under the same conditions, and the yield of *p*-methylaniline is highest (88%), suggesting that the MC-rt is the most ideal catalyst in all the synthesized carbons for the reduction, and its activity is even better than that of MC synthesized from the direct carbonization of *β*-HPCD/silica composites reported previously.[19] To further investigate the influences of the amounts of hydrazine hydrate and MC-rt catalyst on the reduction process, we devised a series of experiments as seen in Table 3. The theoretical molar ratio of hydrazine hydrate to nitrotoluene is 1.5:1 (see Eq. (1)); however, this reaction is accompanied by a slower decomposition of hydrazine hydrate to N_2 and NH_3 (see Eq. (2)); therefore, the reaction is carried out completely with enough amount of hydrazine hydrate. As can be seen from Table 3, with the increase of molar ratios of hydrazine hydrate to *p*-nitrotoluene, the yield of targeted compoud is improved gradually; but, the yield is not obviously increased when the molar ratio of reagent is higher than 3 under the same conditions, even if the reaction is fully carried out within the same time. In summary, when the reaction system is 8 catalyst: 3 hydrazine hydrate: 1 *p*-nitrotoluene: 4 ethanol (g/mol/mol/mL) at reflux temperature, MC-rt has the highest catalytic result (Table 3); moreover, it still kept high activity after being reused for 4 times through a simple filtration, washing with ethanol and drying. Though activated carbon used as a high frequency material can also catalyze the reduction of nitroaromatics with hydrazine hydrate, some metals or metal salts are indispensable in this system.[22-25] When we used the same amount of activated carbon instead of MC for the reduction of *p*-nitrotoluene under the same conditions, no *p*-methylaniline was found in the reaction mixture (see Table 2). These results indicated the synthesized MC-rt is better metal-free catalyst for the reduction of *p*-nitrotoluene with hydrazine hydrate.

$$2\ p\text{-}CH_3C_6H_4NO_2 + 3\ H_4N_2 \rightarrow 2\ p\text{-}CH_3C_6H_4NH_2 + 4\ H_2O + 3\ N_2 \quad (1)$$

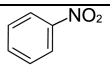
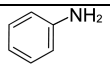
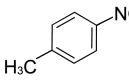
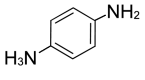
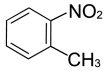
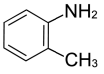
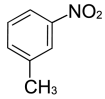
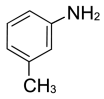
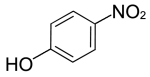
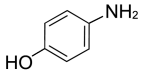
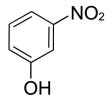
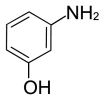
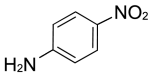
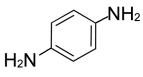
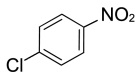
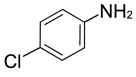
$$3\ N_2H_4 \rightarrow 4\ NH_3 + N_2 \quad (2)$$

MC-rt should also be able to catalyze the reduction of other nitroaromatics by hydrazine hydrate. We expanded reaction to the reduction of various substituted nitroaromatics in the same condition. The results shown in Table 4 indicate that the key advantages of this catalyst are shorter reaction times, higher yield and simple workup.

As is well known, hydrazine hydrate is a two-electron reducing agent,[26,27] and the reduction of nitroaromatic is an initial four-electron process, proceeding first to aromatic hydroxylamine, which is further reduced to aromatic amine in a subsequent two-electron process.[28] The synthesized MC, serves as an adsorbent, gathers nitroaromatic and hydrazine hydrate together by using its large surface area. This adsorption provides a reducing potential and a pool of electrons from many adsorbed hydrazine hydrates, thus making the initial four-electron process possible even though each individual hydrazine hydrate is a two-electron donor.[28] Therefore, it is crucial that the adsorbability of synthesized MC to nitroaromatic and hydrazine hydrate. Compared with MC-cal, MC-rt~100 have higher surface areas and larger pore volumes, which are beneficial for their adsorption performance to nitroaromatic and hydrazine hydrate; moreover, these carbon materials have some active oxygen-containing functional groups, all of which may be contribute to better catalytic properties for the reduction of nitroaromatic.

It was reported previously that some active oxygen-containing functional groups on the active materials could be eliminated by the heat treatment.[29] In our case, it can be seen

Table 4. Reduction of nitroaromatic compounds with hydrazine hydrate in the presence of MC-rt catalyst[a]

Entry	Substrate	Product	Time[b] (min)	Yield[c] (%)
1			30	91
2			30	88
3			45	82
4			30	90
5			40	89
6			45	85
7			70	81
8			30	93

[a]Reaction conditions: the mixture of 5 mmol of substrate, 40 mg of catalyst and 20 mL of ethanol was heated under refluxing temperature, then 15 mmol of hydrazine hydrate was added by dropwise into the flask while stirring. [b]From addition of hydrazine hydrate to the end of reaction. [c]The isolated yields.

from Table 2 that the catalytic activity of MC-rt~100 samples decreases gradually with the increase of treating temperature for removing β-HPCD with NH_4ClO_4, suggesting that the catalytic activity of these carbon materials may be correlated to the silica templates. The surface silanol groups on templates, which easily form intermolecular hydrogen bond with carbon resources, are decreased with the increase of treating temperature for removing β-HPCD with NH_4ClO_4, and thus affect the active sites of carbon materials in the course of preparation with nanocasting technology.

Conclusions

Mesoporous carbon materials, prepared from β-HPCD-based silicas as inorganic templates synthesized by using NH_4ClO_4 oxidation to remove β-HPCD, could be used as highly active and recyclable catalysts for the reduction of nitroaromatic with hydrazine hydrate under relatively mild reaction conditions, which may be due to many good characteristics of the MC such as higher surface area, larger pore volume and abundant active oxygen-containing functional groups. We believe that this novel metal-free catalytic system will attract considerable attention because of its some potential benefits, such as low cost, high catalytic activity, easily tailored properties and low environmental impact.

Acknowledgments. This work was supported by the NSF of China (20972090, 41030105) and the Fundamental Research Project for the Central Universities in China (GK200901010). The authors are also grateful to Dr. Kai-Qiang Liu for TEM measurements.

References

1. Lu, A. H.; Li, W. C.; Schmidt, W.; Schüth, F. *J. Mater. Chem*. **2006**, *16*, 3396.
2. Vinu, A.; Miyahara, M.; Sivamurugan, V.; Mori, T.; Ariga, K. *J. Mater. Chem*. **2005**, *15*, 5122.
3. Lu, A. H.; Schmidt, W.; Matoussevitch, N.; Spliethoff, B.; Tesche, B.; Bill, E.; Kiefer, W.; Schüth, F. *Angew. Chem. Int. Ed.* **2004**, *43*, 4303.
4. Joo, S. H.; Choi, S. J.; Oh, I.; Kwak, J.; Liu, Z.; Terasaki, O.; Ryoo, R. *Nature* **2001**, *412*, 169.
5. Su, F. B.; Zeng, J. H.; Bao, X. Y.; Yu, Y. S.; Lee, J. Y.; Zhao, X. S. *Chem. Mater*. **2005**, *17*, 3960.
6. Cui, X. Z.; Shi, J. L.; Zhang, L. X.; Ruan, M. L.; Gao, J. H. *Carbon* **2009**, *47*, 186.
7. Cui, X. Z.; Cui, F. M.; He, Q. J.; Guo, L. M.; Ruan, M. L.; Shi, J. L. *Fuel* **2010**, *89*, 372.
8. Zhang, J.; Liu, X.; Blume, R.; Zhang, A. H.; Schlögl, R.; Su, D. S. *Science* **2008**, *322*, 73.
9. Liu, G.; Liu, Y.; Zhang, X. Y.; Yuan, X. L.; Zhang, M.; Zhang, W. X.; Jia, M. J. *J. Colloid Interface Sci.* **2010**, *342*, 467.
10. Zhou, J. H.; He, J. P.; Wang, T.; Chen, X.; Sun, D. *Electrochim. Acta* **2009**, *54*, 3103.
11. Pietra, S.; Res, M. *Ann. Chim*. **1958**, *48*, 299.
12. Entwistle, I. D.; Jackson, A. E.; Johnstone, R. A. W.; Telford, R. P. *J. Chem. Soc*. **1977**, *1*, 443.
13. Furst, A.; Berlo, R. C.; Hootom, S. *Chem. Rev*. **1965**, *65*, 51.
14. Lee, H. R.; Ryoo, E. S.; Shin, D. H. *Taehan Hwhakhoe Chi*. **1988**, *32*, 607.
15. Han, B. H.; Shin, D. H. *Bull. Korean Chem. Soc.* **1985**, *6*, 320.
16. Kumarraja, M.; Pitchumani, K. *Appl. Catal. A: Gen*. **2004**, *265*, 135.
17. Li, B. J.; Xu, Z. J. *Am. Chem. Soc*. **2009**, *131*, 16380.
18. Niemeyer, J.; Erker, G. *ChemCatChem* **2010**, *2*, 499.
19. Wang, H. C.; Li, B. L.; Li, J. T.; Lin, P.; Bian, X. B.; Li, J.; Zhang, B.; Wan, Z. X. *Appl. Surf. Sci*. **2011**, *257*, 4325.
20. Wang, H. C.; Li, J. T.; Lin, P.; Li, X. B.; Bian, X. B.; Wang, X. M.; Li, B. L. *Micropor. Mesopor. Mater*. **2010**, *134*, 175.
21. Sing, K. S. W.; Everett, D. H.; Haul, R. A. W.; Moscou, L.; Pierotti, R. A.; Rouquerol, J.; Siemieniewska, T. *Pure Appl. Chem*. **1985**, *57*, 603.
22. Hirashima, O.; Manabe, T. *Chem. Lett*. **1975**, *3*, 259.
23. Clive, D. L. J.; Angoh, A. G.; Sharon, B. M. *J. Org. Chem.* **1987**, *52*, 1339.
24. Hine, J.; Hahn, S.; Miles, D. E.; Ahn, K. *J. Org. Chem*. **1985**, *50*, 5092.
25. Park, M. K.; Jang, D. G.; Han, B. H. *Bull. Korean Chem. Soc*. **1991**, *12*, 709.
26. Corey, E. J.; Mock, W. L.; Pasto, D. J. *Tetrahedron Lett*. **1961**, *11*, 347.
27. Corey, E. J.; Mock, W. L.; Pasto, D. J. *J. Am. Chem. Soc.* **1961**, *83*, 2957.
28. Larsen, J. W.; Freund1, M.; Kim, K. Y.; Sidovar, M.; Stuart, J. L. *Carbon* **2000**, *38*, 655.
29. Pigamo, A.; Besson, M.; Blanc, B.; Gallezot, P.; Blackburn, A.; Kozynchenko, O.; Tennison, S.; Crezee, E.; Kapteijn, F. *Carbon* **2002**, *40*, 1267.