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Novel economic and green approach to the synthesis of highly active W-MCM41 catalyst in oxidative cleavage of cyclopentene

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A highly active and perfectly structured W-MCM41 catalyst for the oxidative cleavage of cyclopentene to glutaraldehyde was synthesized through a novel economic and green synthetic method by using Na_2SiO_3 as the Si source and $CH_3COOC_2H_5$ as the hydrolyzer.

MCM41, first reported by Mobil in 1992,[1,2]which shows not only very large specific area of up to 1500 m^2 g^{-1}, but also uniform dimensional and hexagonally shaped pores indexed in the space group *p6m*, is widely studied in many fields. Metal ion-containing MCM41, possessing regular nano-ordered mesopores and high density of isolated active sites, has attracted much attention as a new host of oxidation catalysts, especially for liquid-phase oxidation reactions because convenient diffusion of relatively bulky molecules can be expected. Many researchers reported the synthesis and characterizations of metal ion-containing MCM41, and some of these materials, e.g., Ti-, Fe- and V-MCM41, presented peculiar catalytic characters for the reaction of larger molecules.[3–9]Only one study has been reported on the synthesis and characterization of W-MCM41 using a different method,[10,11]but the details about the location and the leaching behavior of active tungsten components are still not clear. On the other hand, the promising catalytic character of W-MCM41 is limited by a shortage of suitable synthesis methods reported in the literature; in all cases, the source of the silica for the synthesis is the costly organic silica precursor, ethyl silicate (TEOS). The use of expensive ethyl silicate limits synthesis of W-MCM41 on a large scale in industry. Using a convenient and cheap inorganic silica precursor in place of an organic one may be a very important improvement to the synthesis of the W-MCM41. Furthermore, almost every process for the synthesis of MCM41 needs strong acid—HCl as hydrolyzer, which will bring about considerable pollution to the circumstance and inevitable corrosion to the equipment when applied to large scale production. Herein we report for the first time the synthesis of W-MCM41 using inorganic silicate as the silica precursor and ethyl acetate as the hydrolyzer. The as-synthesized W-MCM41 is found to show perfect uniform dimensional and hexagonal structure which has not been reported yet and extremely high catalytic activity towards the oxidative cleavage of cyclopentene (CPE) to prepare glutaraldehyde (GA), a very important chemical used as disinfectant and germicide widely. It is well known that the commercial process for GA production is an acrolein route, in which the high price of the raw materials restricts its wide application. The new route using CPE as the raw material, aqueous H_2O_2 as the oxidant and supported WO_3 as the catalyst developed by our group is not yet ready for industry owing to the leaching of active components and the expensive raw materials needed in the synthesis of the catalyst.[12–15]In the present work, the as-prepared W-MCM41 exhibits excellent anti-leaching properties towards the targeted reaction.

A typical synthesis is as follows: to the stirred water at 358 K are added 5.825 g of sodium silicate, denoted as $Na_2SiO_3{\cdot}9H_2O$, and 2.45 g of cetyltrimethyl-ammonium bromide (CTMAB), to obtain an aqueous solution, then 2 ml of sodium tungstate solution ($Na_2WO_4{\cdot}2H_2O$, 0.2 mmol g^{-1}) is mixed with the above solution. Under vigorous stirring, 7.5 ml of ethyl acetate is rapidly added into the solution one time. After vigorous stirring for 6 min, the obtained mixture is stirred moderately for 24 h at 358 K and then centrifuged to obtain the solid. After washing with de-ionized water 3 times, the solid is air-dried and then calcined in air at 873 K for 2 h to remove the template, CTMAB. It should be also noted that this kind of W-MCM41 material is very stable after the removal of the template. Changing the amount of the sodium silicate or sodium tungstate initially added can obtain a series of samples with different molar ratios of Si to W. In this procedure, ethyl acetate is employed as the acid-producing precursor instead of the conventional strong acid, such as HCl, employed by other authors in their work. When the ethyl acetate is mixed with water at a certain temperature, ethyl acetate will hydrolyze to produce acetic acid, a mild acid. So this synthesis occurs under mild acidic conditions and is environmentally friendly. No noxious substances are needed and no toxic waste is generated. Hence, it can be called a green process.

As confirmed by the ICP-AES (Jarrell-As Atom Scan 2000), the as-synthesized W-MCM41 sample consists of only three elements: Si, O and W. The residue Na is too low to be detected ($<$ 0.01 mass%). The XRD (Bruker Advance D8) pattern of the W-MCM41 shows three well-defined sharp Bragg peaks indexed as (100), (110) and (200), respectively, characteristic of MCM41 materials. In all the XRD patterns of the sample with Si/W ratios larger than 30, no peaks corresponding to the crystalline WO_3 are observed, meaning that tungsten oxide is highly dispersed in the silica matrix.

The typical structure of the W-MCM41 was further attested through TEM (Jeol JEM2010) as shown in Figure 1, a very clear and perfectly ordered hexagonal structure of the pores of the W-MCM41 is observed. To the best of our knowledge, the extremely long range ordered mesoporous structure of W-MCM41 is reported for the first time.

The FT-IR (Nicolet Model 205) spectrum of the W-MCM41 showed the typical band peak at 963 cm^{-1}, indicating that the tungsten species was incorporated into the inner framework of MCM41. Similar assignments had been made for Ti- and V-containing molecular sieves.[7,8] When the Si/W ratio was as high as 27, the collapsed mesoporous structure of W-MCM41 framework resulted in the WO_x species being present only on the matrix surface, as evidenced by the absence of the FT-IR band peak at 963 cm^{-1} of the sample. In the mild acidic synthesis situation, the tungsten exists with low polymerization, which may make the tungsten oxide easy to be dispersed and incorporated into the matrix composed of tetragonal SiO_4. Raman (JY Super LabRam) and DR UV-VIS (Jasco V-550) spectra also support this suggestion since no absorption band corresponding to crystalline WO_3 appeared.

It is very interesting to find that the as-synthesized W-MCM41 sample shows extremely high activity and selectivity toward the cleavage reaction of CPE by using aqueous H_2O_2 as the oxidant, different from that reported previously,[9,10] which only showed a hydroxylation effect towards the oxidation

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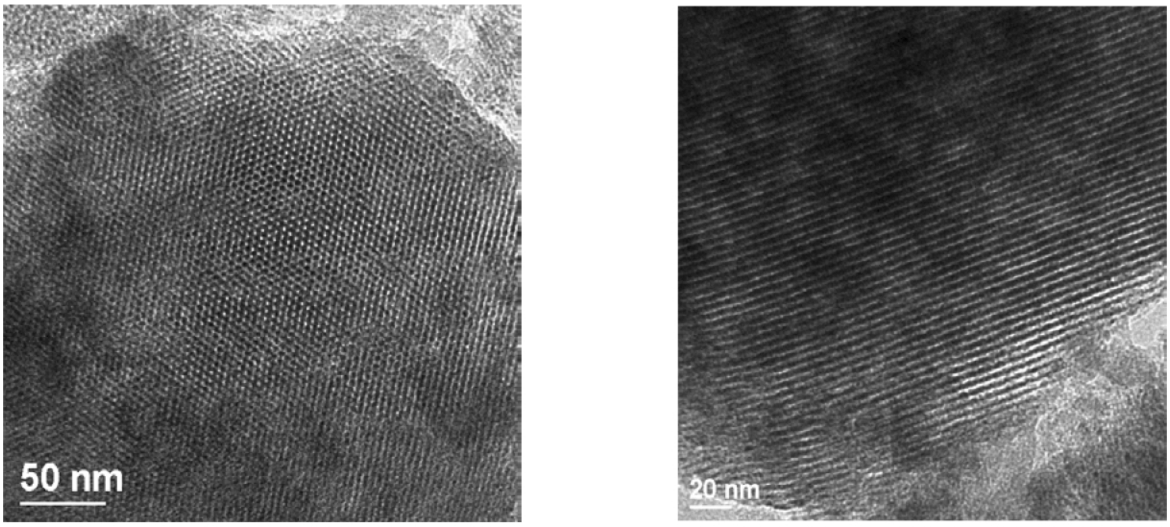

(a) (b)

Fig. 1 HRTEM images of W-MCM41 samples (a), taken with the electronic beam parallel to the pore direction; (b) taken with the electronic beam perpendicular to the pore direction.

Table 1 Catalytic behaviour of various W-containing catalysts

Sample	S_{BET}/m^2 g^{-1}	Pore diameter/nm	CPE conv./%	H_2O_2 conv./%	GA Yield/%	TOF[e]/h^{-1}	Leached W/ppm
Si-MCM41	1152	2.5	0	0	0	0	0
[a]WO_3	–	–	1.5	0.1	0	0.04	0
[b]WO_3/SiO_2*	200	1.0	51	72	15	1.4	4
[c]WO_3/SiO_2**	230	3.0	83	90	48	2.2	70
[d]W-MCM41	1100	2.6	100	100	71	3.2	0.8

Reaction time: 24 h, reaction temperature: 35 °C, the mole ratio of H_2O_2 : CPE : WO_3 = 2 : 1 : 0.016, the volume ratio of t-BuOH/CPE = 10.[a] crystalline WO_3 [b] prepared through incipient wetness impregnation with ammonium tungstate solution (* and** are commercial products of silica). [c] prepared through incipient wetness impregnation with ammonium tungstate solution (* and** are commercial products of silica). [d] Si/W = 32. [e] TOF: moles of CPE converted per mole of WO_3 in the catalyst per hour.

reaction of cyclohexene in a H_2O_2–HAc medium. As shown in Table 1, the W-MCM41 gives 100% conversion of CPE and 71% selectivity towards GA, much higher than that over WO_3 and WO_3/SiO_2 catalysts, showing attractive potential for practical applications. As also shown in Table 1, unsupported WO_3 shows little activity towards the title reaction, suggesting that the WO_x species incorporated into the uniform framework of mesoporous materials, such as MCM41, shows essential activity and selectivity towards the cleavage reaction. The TOF values shown in Table1 unambiguously verified the conclusion. The high specific surface area (~ 1100 m^2 g^{-1}) and ordered large pore diameter (~ 2.6 nm) of the W-MCM41 were affirmed to be important factors for its high catalytic activity as compared to the supports from commercial silica. Another outstanding property of this novel catalyst is its good stability and reproducibility. It can be reused after washing with acetone at 35 °C and dried at 120 °C. No loss of activity and selectivity or the collapse of its mesporous structure were observed after 7 runs. We verified that the reaction did not occur in the absence of catalyst and it was not the result of homogeneous catalysis by leached active sites. The leached WO_x species after 7 runs was lower than 1 ppm, which could also be confirmed by the elemental analysis of W in the used catalyst after 7 runs.

The present results confirm that WO_x species incorporated into framework of MCM41 materials are efficient catalytic sites for cleavage reaction of alkenes. Preliminary characterization results suggest that the novel synthesis method leads to a uniform distribution of the WO_x active sites throughout the mesoporous structure of MCM41 without any conglomeration. This novel W-MCM41 catalyst is an efficient, selective and recyclable catalyst for the production of GA by the selective oxidation of CPE using H_2O_2 as the oxidant. Thus, efficient WO_x sites can be created by a simplified hydrothermal method and the highly selective and recyclable catalyst does not need any expensive organic precursors or toxic materials.

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Notes and References

1. C. T. Kresge, M. E. Leonowicz, W. J. Roth, J. C. Vartuli and J. S. Beck, *Nature*, 1992, **359**, 710.
2. J. S. Beck, J. C. Vartuli, W. J. Roth, M. E. Leonowicz, C. T. Kresge, K. D. Smith, C. T.-W. Chu, D. H. Olson, E. W. Sheppard, S. B. McCullen, J. B. Higgins and J. L. Schlenker, *J. Am. Chem. Soc.*, 1992, **114**, 10834.
3. A. Sayari, *Chem. Mater.*, 1996, 1840.
4. A. Corma, M. T. Navarro and J. Perez-Pariente, *J. Chem. Soc. Chem. Commun.*, 1994, 149.
5. J. M. Thomas, *Nature*, 1994, **368**, 289.
6. P. T. Tanev, M. Chibwe and T. J. Pinnavaia, *Nature*, 1994, **368**, 321.
7. M. D. Alba, Z. Luan and J. Klinowski, *J. Phys. Chem.*, 1996, **100**, 178.
8. A. Thangaraj, R. Kumar and P. Ratnasamy, *Appl. Catal.*, 1990, **57**, L-1.
9. Y. Wang, Q. Zhang, T. Shishido and K. Takehira, *J. Catal.*, 2002, **209**, 186.
10. Z. Zhang, J. Suo, X. Zhang and S. Li, *Chem. Commun.*, 1998, 241.
11. Z. Zhang, J. Suo, X. Zhang and S. Li, *Appl. Catal. A.*, 1999, **179**, 11.
12. R. Jin, X. Xin, D. Xue and J. F. Deng, *Chem. Lett.*, 1999, 371.
13. R. Jin, X. Xin, W. L. Dai, J. F. Deng and H. X. Li, *Catal. Lett.*, 1999, **62**, 201.
14. H. Chen, W. L. Dai, J. F. Deng and K. N. Fan, *Catal. Lett.*, 2002, **81**, 131.
15. R. Jin, H. X. Li and J. F. Deng, *J. Catal.*, 2001, **203**, 75.