Research Note

Novel efficient and green approach to the synthesis of glutaraldehyde over highly active W-doped SBA-15 catalyst

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Abstract

In the present work, we demonstrate for the first time the use of W-doped SBA-15 catalyst prepared by a novel in situ synthesis method as highly efficient catalyst for the direct production of glutaraldehyde via selective oxidation of cyclopentene by using non-aqueous hydrogen peroxide as the green oxidant. It is suggested that the presence of a high surface concentraiton of WO_x species dispersed on well ordered hexagonal pore walls of SBA-15 support is essential to the superior performance of the catalyst for the selective oxidation of cyclopentene. © 2004 Elsevier Inc. All rights reserved.

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1. Introduction

Glutaraldehyde (GA) has been extensively used for purposes of disinfection and sterilization in many fields. Currently, the commercial production of GA is mainly based on a multi-step process using expensive propenal and vinyl ethyl ether as starting materials [1,2], which however results in extremely high cost of GA. Thus, the potential applications of GA in wider fields such as the tanning process of leather, environmental protection, water treatment or oil field are greatly compromised. It is therefore highly attractive to develop a new convenient and economical process that allows the direct and low cost production of GA. An alternative way to produce GA is the one-step route through the selective oxidation of cyclopentene (CPE) by using O_3 or H_2O_2 as the oxidant, since a great quantity of CPE could be easily obtained by the selective hydrogenation of cyclopentadiene (CPD), which can be easily obtained from the decomposition of dicyclopentadiene (DCPD), a main by-product from the C-5 fraction in the petrochemical or coking industry [3,4]. From the environmental and economical point of view, the most ideal oxidant would be molecular oxygen. To our knowledge, however, a satisfactory conversion of CPE to GA by aerobic oxidation is not reported yet [5].

Of particular interest is the use of H_2O_2 as an environmentally-friendly oxidant for the liquid-phase reaction [6–8], since it can reach an atom efficiency of 47% for the oxidation of organic compounds with water being the only co-product. Since Furukawa et al. reported an interesting one-step route for the synthesis of GA by the selective oxidation of CPE in a non-aqueous H_2O_2 system in 1987 [3], great efforts have been dedicated to investigating the non-aqueous system in which various solvents, such as dimethyl phosphite-methyl (DMPM), trimethyl phosphate (TMP), tributyl phosphate (TBP) and butyl acetate, were used while the catalysts employed were mainly homogeneous systems based on molybdenum or tungsten compounds [3,9–12]. Recently, a high GA yield of ca. 79% was achieved by aqueous hydrogen peroxide oxidation of CPE

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using homogeneous tungstic acid as an efficient catalyst [4]. Unfortunately, the GA yield did not exceed 80% over all mentioned homogenous catalytic systems.

Up to now, only very few heterogeneous W-containing catalysts (WO_3/SiO_2, WO_3/TiO_2–SiO_2 and W-MCM-41) have been proposed for the aqueous hydrogen peroxide system [13–17], where the GA yield (72%) achieved is far satisfactory for industrial application. However, all these works have showed a substantial formation of cyclopentane-1,2-diol (> 15%) [4] due to the reaction of the intermediate (CPE oxide) with H_2O. Thus, it appears that decreasing water content in the reaction mixture may be beneficial for enhancing the GA yield. On the other hand, it is known that SBA-15, a new type of ordered mesoporous material achieved by using a triblock copolymer as template under strongly acidic conditions, may be a promising candidate in catalysis since it possesses a high surface area (600–1000 $m^2\,g^{-1}$) and uniform tubular channels with tunable pore diameters in the range of 5–30 nm, significantly larger than those of MCM-41 [18,19]. To the best of our knowledge, there are no reports on the synthesis of W-doped SBA-15, which may show excellent catalytic performance for the preparation of GA in the anhydrous H_2O_2 system. Herein we demonstrate for the first time the use of a novel W-doped SBA-15 material as highly efficient catalyst for the high yield production of GA up to 91% by an anhydrous H_2O_2 oxidation of CPE in the presence of TBP.

2. Experimental

2.1. Catalyst preparation

Typical procedure for the synthesis of W-doped SBA-15 catalyst is as following: 5 g of Pluronic P123 triblock polymer ($EO_{20}PO_{70}EO_{20}$, $Mav = 5800$, Aldrich) and 28 g of distilled water were added to 150 mL of 2 M HCl and stirred for 4 h at 313 K. After that, 10 g of $Si(OC_2H_5)_4$ (TEOS) was added to the above mixture, and stirred for 30 min. Then 13 mL aqueous solution of sodium tungstate ($Na_2WO_4 \cdot 2H_2O$, 0.2 M) was added. The mixture was aged at 313 K under moderate stirring for 24 h, and then crystallized at 368 K for 3 d. The solid product was filtered, washed with distilled water, and dried at room temperature. Finally, it was calcined at 873 K in air for 5 h to remove the template and was used as catalyst without any further treatment.

2.2. Characterizations and activity test

The low-angle X-ray powder diffraction patterns were recorded on Rigaku D/max-rB diffractometer with Cu-K$_\alpha$ radiation, operated at 60 mA and 40 kV. The high-angle X-ray powder diffraction patterns were recorded on a Bruker D8 advance diffractometer with Cu-K$_\alpha$ radiation, operated at 40 mA and 40 kV. The laser Raman experiments were performed by using a Jobin Yvon Dilor Labram I Raman spec-

trometer equipped with a holographic notch filter, a CCD detector and He–Ne laser radiating at 632.8 nm. The specific surface areas, the pore volumes and mean pore diameters of the catalysts were measured and calculated according to the BET method on a Micromeritics Tristar ASAP 2000 apparatus at 77 K. Scanning electron micrographs were obtained using a Philips XL 30 apparatus. The samples were deposited on a sample holder with an adhesive carbon tape and sputtered with a thin film of gold. Transmission electron micrographs (TEM) were obtained on a Joel JEM 2010 scan-transmission electron microscope. The samples were supported on carbon-coated copper grids for the experiment. The FT-IR spectra were obtained with a Nicolet Model 205 spectrometer, using KBr pellet technique. The tungsten content was determined by inductively coupled Argon plasma (ICP, IRIS Intrepid, Thermo Elemental Company) after solubilization of the samples in HF:HCl solutions.

The activity test was performed at 308 K for 12 h with magnetic stirring in a closed 100 mL regular glass reactor using anhydrous H_2O_2 as oxygen-donor and TBP as solvent. The quantitative analysis of the reaction products was performed by using GC method, and the identification of different products in the reaction mixture was determined by means of GC-MS. Details can be found elsewhere [15,16].

3. Results and discussion

3.1. Characterization

The low-angle powder XRD patterns of W-doped SBA-15 samples with different tungsten contents are shown in Fig. 1. The W-doped SBA-15 material with WO_3 content ⩽ 20 wt% displays three well resolved peaks indexed to (100), (110) and (200) reflections of the hexagonal space group *p6mm*. The existence of (200) peak indicates the maintenance of well-defined hexagonal porosity in the present W-doped material. Further increase of WO_3 content up to 30% will lead to a partial collapse of the mesoporous struc-
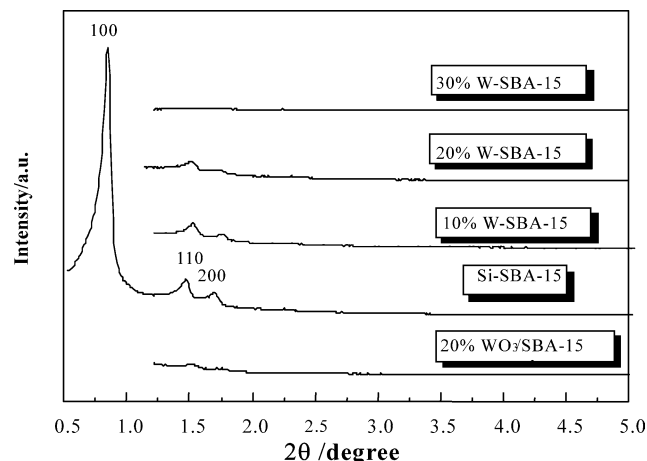

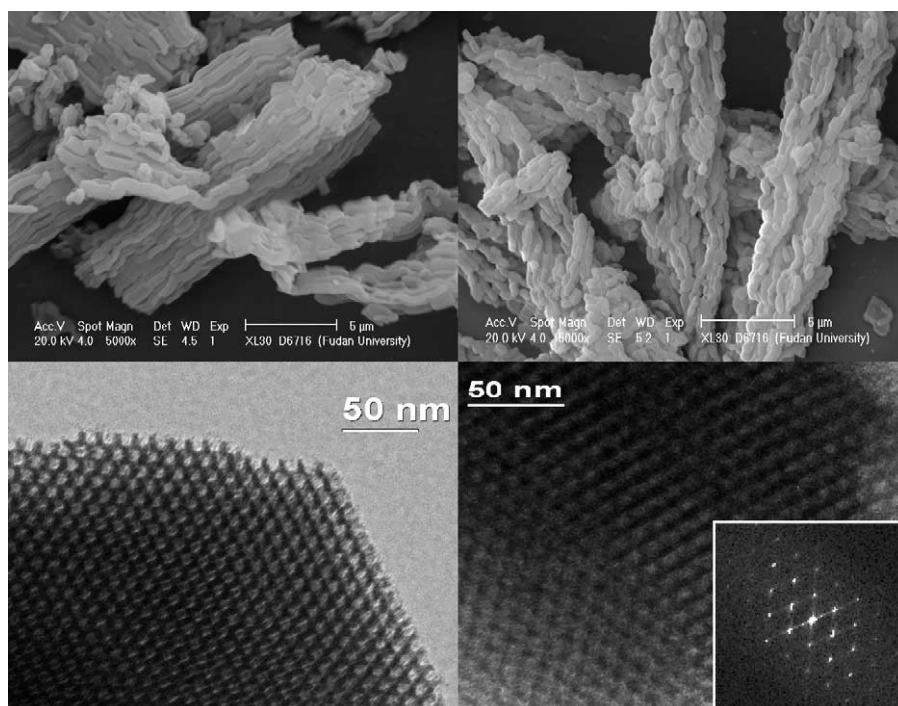Fig. 1. XRD powder patterns of various samples.

Fig. 2. SEM/TEM photos of blank and W-doped SBA-15 material. SEM photos of pure (a) and W-doped SBA-15 (b); TEM photos of pure (c) and W-doped SBA-15 (d) (insert: the electron diffraction pattern).
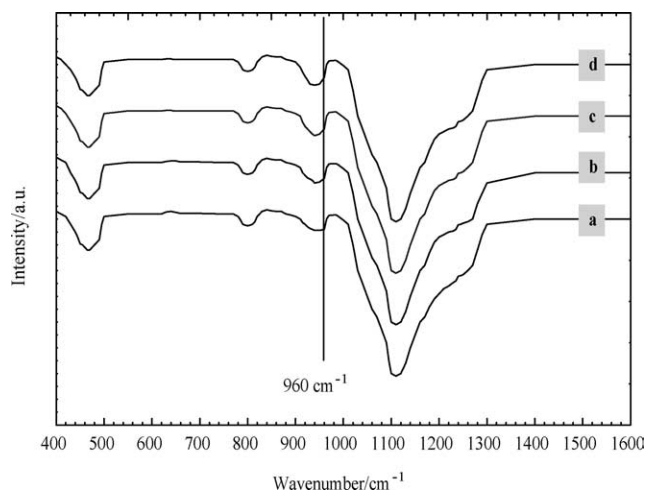

Fig. 3. FT-IR spectra of W-doped SBA-15 catalysts with different content of WO_3: (a), Si-SBA-15; (b), 10 wt%; (c), 20 wt%; (d), 30 wt% W-doped SBA-15.

Fig. 4. Raman spectra of various W-doped SBA-15 catalysts.

ture. The supported WO_3/SBA-15 (20 wt%) sample prepared via incipient wetness impregnation also displays an intense reflection corresponding to the (100) plane; however, the (110) and (200) planes could not be easily identified. This is a clear indication that the W-doped SBA-15 catalyst prepared through in situ synthesis method shows much better uniform mesoporous structure than the traditional impregnated one. Typical morphology of the W-doped SBA-15 (20%) is further attested through SEM and TEM, as can be seen in Fig. 2. Very clear and perfect morphology, as well as the ordered hexagonal structure for the W-doped SBA-15
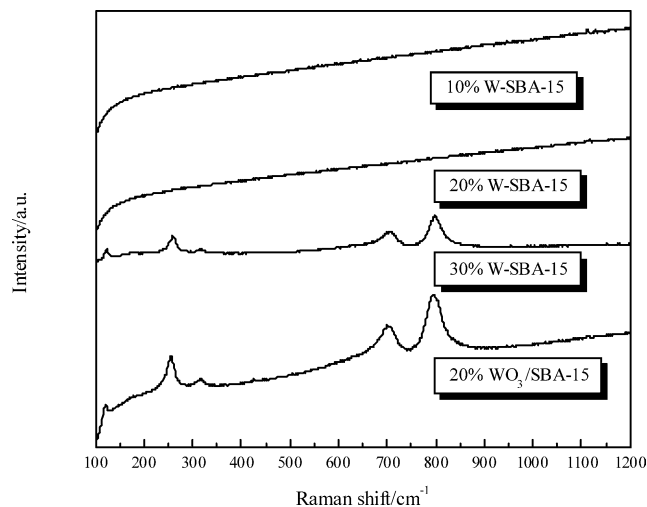
materials, is being observed. FT-IR spectrum of the W-doped SBA-15 (20%, refer to Fig. 3) shows typical absorption band at 963 cm^{-1}, a feature that tungsten species are incorporated into the inner framework of SBA-15. Similar assignments have also been made for W-containing MCM-41 [16]. It should also be noted that the as-prepared novel W-doped SBA-15 material is very thermally stable up to 973 K as confirmed by DTA.

The surface state of WO_3 species was also investigated by using the confocal microprobe Laser Raman spectra, as shown in Fig. 4. No Raman bands attributed to the octahedral crystalline WO_3, at e.g. 804, 714, 327 and 267 cm^{-1} are

Table 1
Catalytic performance of various W-containing catalysts

Sample	S_{BET} $(m^2\,g^{-1})$	Pore diameter (nm)	Conversion (%)		Yield (%)		TOF (h^{-1})
			H_2O_2	CPE	GA	Diol	
10% WO$_3$-SBA-15	623	4.1	87.0	91.9	79.7	5.3	2.0
20% WO$_3$-SBA-15	571	4.3	90.7	100	91.1	4.3	2.2
30% WO$_3$-SBA-15	411	4.3	84.9	90.3	77.7	6.5	2.0
20% WO$_3$/SBA-15[a]	385	4.7	86.8	90.8	75.5	5.9	2.0
WO$_3$[b]	–	–	17.3	16.2	9.9	1.0	0.2
20% WO$_3$/SiO$_2$[a,c]	293	1.2	77.9	79.8	65.8	6.1	1.8
20% WO$_3$/MCM-41[a]	850	2.7	84.6	86.1	72.0	5.9	1.9

Reaction time: 12 h, reaction temperature: 308 K, the molar ratio of CPE:H$_2$O$_2$:WO$_3$ = 100:210:4, the volume ratio of TBP/CPE = 7.5.
  [a] Prepared through incipient wetness impregnation with tungstic acid and oxalic acid solution.
  [b] Crystalline WO$_3$.
  [c] Commercial product.

observed for 10 and 20% W-doped SBA-15, very similar to those of pure SBA-15 (not shown here). Fig. 4 also shows the Raman spectra of samples of 30% W-doped SBA-15 and 20% WO$_3$/SBA-15 supported catalyst for comparison. Obvious Raman bands ascribed to crystalline WO$_3$ could be detected in the figure with respect to these two samples, illustrating that the loading of excess content of tungsten species would result in the agglomeration of WO$_3$ on the surface. However, the supported catalyst shows much stronger peak intensity than that of 30% W-doped SBA-15. In comparison, the 20% counterpart prepared through in situ synthesis method presents no Raman bands of crystalline WO$_3$. That is a clear indication that the WO$_3$ species are well dispersed in the framework of SBA-15 material for the in situ synthesized catalysts. Hence, the loading of tungsten species with a suitable content lower than 20% is necessary for obtaining a high dispersion of WO$_x$ species incorporated in the mesoporous framework, which consists very well with the result obtained from XRD.

3.2. Catalytic activity test

The catalytic performances over various W-containing catalysts with different tungsten contents are shown in Table 1. For the purpose of comparison, the catalysts used in these experiments possess the same amounts of tungsten. As shown in Table 1, unsupported crystalline WO$_3$ shows little activity towards the title reaction, while those catalysts with tugsten species well-dispersed on/in different supports show essential activity and selectivity to the cleavage reaction. This result suggests that the WO$_3$ species incorporated within the uniform framework of mesoporous materials, such as SBA-15 and MCM-41, act as the active centers for the selective oxidation of CPE. The TOF values (also shown in Table 1) unambiguously verified the above conclusion. It is also found that the tungsten content, the support and the preparation method, all influence the catalytic performance intensively.

When other supports are tried, much lower GA yield is obtained over the commercial silica support than that of MCM-41 and SBA-15, which can be easily ascribed

to its low specific surface area and small pore diameter. Considering the different preparation methods, W-doped SBA-15 shows much higher activity and selectivity than WO$_3$/SBA-15 and WO$_3$/MCM-41, respectively, indicating that the in situ synthesis method for the preparation of W-doped SBA-15 is more suitable for achieving a higher dispersion of active tungsten species than the incipient wetness impregnation. When WO$_3$ content is lower than 20%, low GA yield is obtained, which is probably due to a lower surface concentration of active centers as well as the negative diffusional effect due to the presence of excess amounts of catalysts in the reaction system. At the case where the WO$_3$ content is well above 20%, inevitable collapse of the mesoporous structure of the W-doped SBA-15 occurs which leads to the decrease of GA yield. Although a reletively high GA yield ($\sim$ 85%) can also be obtained over the homogeneous tungstic acid catalyst in the anhydrous H$_2$O$_2$/TBP system, the difficulty for the separation and recovery of the catalyst hampers its further industrial application.

In addition, the chemical and structural properties of the tungsten species presented on the SBA-15 samples have been characterized by using combined spectroscopic techniques of BET, FT-IR, and Raman spectroscopy. The introduction of tungstic species onto the inner walls of SBA-15 can provide catalysts with a high concentration of accessible, isolated, and structurally well-defined active sites for the oxidative cleavage of CPE. Moreover, it is conceivable that the large pore diameters of the SBA-15 materials (5–30 nm) can make it easy to discharge the produced GA to the outside of the pores, thus preventing the subsequent deep oxidation. Hence, the highly dispersed nature of the tungsten species, as well as the unique mesoporous structure (with extremely large pore diameters) of the SBA-15 support, has been considered to contribute for the improved catalytic activity in the selective oxidation of CPE over the present mesoporous W-doped SBA-15 catalyst.

It should also be noted that the leaching of tungsten species is very small ($<$ 1 ppm) and the high catalytic activity is almost kept at its initial state even after 6 reaction cycles, suggesting its high stability in the present anhydrous H$_2$O$_2$-TBP system. The 20 wt% W-doped SBA-15 catalyst

shows 100% CPE conversion and 91.1% GA yield, much higher (> 12%) than those previously reported in aqueous system and about twice higher than those reported in homogeneous anhydrous system. This result shows attractive potential to extend this novel process to a number of other important oxidation reactions. The advantages compared to previous ones may be as follows. Firstly, the extremely high yield of GA decreases the cost of the raw material remarkably; secondly, the yield of the main byproduct, cyclopentane-1,2-diol, is only 4.3%, which can be easily separated from the mixture by distillation; thirdly, the heterogeneous catalyst can be conveniently separated from the products by simple filtration; finally, GA with high purity (Medical Grade) can be easily obtained through decompressed rectification, due to the big difference of boiling point between GA and TBP ($\sim 100\,^\circ$C). It is found that GA is thermally very unstable, especially in aqueous state, thus making it very difficult for the dehydration through decompressed rectification if high purity is required. That is the main reason why the aqueous process has not been commercialized. Moreover, the novel anhydrous system is also fit for the oxidative cleavage of other cycloalkenes to the corresponding dialdehydes, i.e. if cyclopentene is replaced by cyclohexene in the above reaction, the hexandial yield is 62%, much higher than those reported earlier ($\sim 47\%$). Detailed work concerning the selective oxidation of other olefins and the mechanism at molecular level is being under way.

4. Conclusions

In conclusion, the heterogeneous W-doped SBA-15 catalyst exhibits an excellent activity and selectivity for the selective transformation of CPE to GA in the non-aqueous H_2O_2/TBP system. An easy separation of both the W-doped SBA-15 catalyst and GA from the reaction mixture, as well as the easy recyclability of the catalyst, makes the present heterogeneously anhydrous process particular attractive for practical applications.

References

[1] S.P. Gorman, E.M. Scott, A.D. Russell, J. Appl. Bacteriol. 48 (1980) 161.
[2] F.M. Collins, J. Appl. Bacteriol. 61 (1986) 247.
[3] H. Furukawa, E. Nishikawa, T. Koyama, JP 6219546, 1987.
[4] J.F. Deng, X.H. Xu, H.Y. Chen, A.R. Jiang, Tetrahedron 48 (1992) 3503.
[5] R.A. Sheldon, J.K. Kochi, Metal-Catalyzed Oxidations of Organic Compounds, Academic Press, New York, 1981.
[6] C.W. Jones, Applications of Hydrogen Peroxide and Derivatives, Royal Society of Chemistry, Cambridge, 1999.
[7] G. Strukul (Ed.), Catalytic Oxidations with Hydrogen Peroxide as Oxidant, Kluwer Academic, Dordrecht, 1992.
[8] R. Noyori, M. Aoki, K. Sato, Chem. Commun. 16 (2003) 1977.
[9] H. Furukawa, E. Nishikawa, T. Koyama, JP 6219546, 6219548, 1987.
[10] H. Furukawa, T. Nakamura, H. Inagaki, E. Nishikawa, C. Imai, M. Misono, Chem. Lett. 5 (1988) 877.
[11] Nissan Chem. Indust. Ltd., JP 5707434, 1982.
[12] Nippon Oil Co. Let., JP 95921, 1982.
[13] R.H. Jin, X. Xia, W.L. Dai, J.F. Deng, H.X. Li, Catal. Lett. 62 (1999) 201.
[14] R.H. Jin, H.X. Li, J.F. Deng, J. Catal. 203 (2001) 75.
[15] H. Chen, W.L. Dai, J.F. Deng, K.N. Fan, Catal. Lett. 81 (2002) 131.
[16] W.L. Dai, H. Chen, Y. Cao, H.X. Li, S.H. Xie, K.N. Fan, Chem. Commun. 7 (2003) 892.
[17] F. Somma, G. Strukul, J. Catal. 227 (2004) 344.
[18] D.Y. Zhao, J.L. Feng, Q.S. Huo, N. Melosh, G.H. Fredrickson, B.F. Chmelka, G.D. Stucky, Science 279 (1998) 548.
[19] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olsen, E.W. Sheppard, S.B. Mccullen, J.B. Higgins, J.L. Schlenker, J. Am. Chem. Soc. 114 (1992) 10834.