Novel heterogeneous W-doped MCM-41 catalyst for highly selective oxidation of cyclopentene to glutaraldehyde by aqueous H_2O_2

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W-doped MCM-41 (W-MCM-41) has been reported as a novel heterogeneous catalyst for the selective oxidation of cyclopentene to prepare glutaraldehyde with environmentally benign aqueous hydrogen peroxide. It is found that tungsten species could stably exist in the silica-based matrix of MCM-41 up to a Si/W molar ratio of 40 by means of X-ray diffraction, laser Raman spectroscopy, scanning electron microscopy, etc. Proper content of tungsten species, high specific surface area and large mean pore size of the W-MCM-41 account mainly for its high catalytic activity in comparison with other W-containing heterogeneous catalysts. Complete conversion of cyclopentene and very high yield of glutaraldehyde (~72%) are obtained over the W-MCM-41 catalyst with an Si/W molar ratio of 40. Furthermore, almost no tungsten species are leached into the reaction solution, enabling the catalyst to be employed for many reaction cycles without obvious degeneration. The correlation of the catalytic behavior with the special structural characteristics of the W-MCM-41 catalyst is also discussed through various characterization methods.

KEY WORDS: cyclopentene; glutaraldehyde; H_2O_2; MCM-41; tungsten.

1. Introduction

Glutaraldehyde (GA) has been used extensively for disinfection and sterilization in many areas. However, the commercial preparation method from propenal is now being restricted by its complicated preparation process and expensive raw materials [1,2], resulting in the high price of GA and constraining its wide use in other fields such as the tanning process of leather, environmental protection, etc. The preparation of GA in a more convenient and economical way has been an important objective for many researchers. An alternative way to produce GA is from the selective oxidation of cyclopentene (CPE) with environmentally benign aqueous H_2O_2 as the oxidant, since a great quantity of CPE could be easily obtained by the selective hydrogenation of cyclopentadiene. The direct synthesis of GA from CPE appears to be an attractive way of utilizing cyclopentadiene, a main by-product of the C-5 fraction in the petrochemical industry [3,4]. Recently, several W-containing homogeneous catalysts have been reported as good catalysts for GA preparation [4–7]. But the difficulty of separating and recovering the catalysts from the product mixture in the homogeneous process made them impractical for industrial production processes. One of the most promising approaches is to design the heterogeneous W-containing catalyst. Although two heterogeneous W-containing catalysts (WO_3/SiO_2 and $WO_3/TiO_2{-}SiO_2$) reported in our previous work [8,9] presented good catalytic activity in the preparation of GA, the conversion of CPE was not complete (~85%) and the leaching of tungsten species could not be neglected. The concentration of the leached tungsten in the product mixture is relatively high (~10 ppm), which will inevitably bring pollution by heavy metals to the product. In addition, the yield of GA (~63%) is not high enough to be useful in industry over all of the reported heterogeneous W-containing catalysts. The previous work also showed that high specific surface area and large pore size of the support could be helpful to the catalytic performance of GA preparation. Since MCM-41 has a regular pore system with a large pore size between 2 and 10 nm and high specific surface area up to $1500\,m^2\,g^{-1}$, it may be possible to prepare W-doped MCM-41 (W-MCM-41) as a heterogeneous catalyst with better catalytic behavior for GA preparation [10]. Here we report a novel process using W-MCM-41 as a heterogeneous catalyst in the preparation of GA. The as-prepared W-MCM-41 heterogeneous catalyst showed much higher activity and selectivity in the oxidation of CPE for the production of GA. The conversion of CPE was 100%, and the yield of GA was 72%, about 10% higher than that of $WO_3/TiO_2{-}SiO_2$. Moreover, the leaching of tungsten was extremely low (<1 ppm), which made it possible for this catalyst to be a promising candidate for industrial production of GA.

2. Experimental

2.1. Catalyst preparation

The W-doped MCM-41 was synthesized as follows: 12.4 g of cetylpyridine bromide ($CPBR{\cdot}H_2O$) was

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added to 120 ml of HCl (5 M) to give a mixture. 22.4 ml of tetraethyl orthosilicate (TEOS) and different amounts of aqueous sodium tungstate solution ($NaWO_4 \cdot 2H_2O$, 0.2 M) were simultaneously and quickly added into the mixture under vigorous stirring to give a pale-yellow gel. After vigorous stirring for 1 h, the gel was aged at 323 K under moderate stirring for 24 h, and then filtered and washed with distilled water. The precipitate was dried at 393 K and calcined at 873 K in air to obtain the W-MCM-41 for further characterization and catalytic activity test. The pure silica MCM-41 was synthesized by omitting the addition of the $NaWO_4 \cdot 2H_2O$. For purposes of comparison, the WO_3-supported catalysts were prepared through the conventional incipient wetness impregnation method as follows: 0.323 g of tungstic acid, denoted as $WO_3 \cdot H_2O$, was dissolved in a solution of ammonium or oxalic acid. Into the stirred solution was dispersed different amounts of commercial SiO_2 or pure silica MCM-41 at 353 K. After the water evaporated completely, the dried solid was further calcined at 872 K in air for 2 h to obtain the WO_3/SiO_2 or WO_3/MCM-41.

2.2. *Catalyst characterization*

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance spectrometer with Cu K_α radiation, which was operated at 40 mA and 40 kV. The laser Raman spectra were recorded by using a Jobin Yvon Dilor Labram I Raman spectrometer equipped with a holographic notch filter, a CCD detector and an He–Ne laser radiating at 632.8 nm. The specific surface areas and mean pore diameters of the catalysts were measured and calculated according to the BET method by a Micromeritics Tristar BET spectrometer with liquid nitrogen at 77 K. Scanning electron micrographs were obtained using a Philips XL 30 spectrometer. The samples were deposited on a sample holder with an adhesive carbon tape and sputtered with a thin film of gold.

2.3. *Activity test*

The activity test was performed at 308 K for 24 h with vigorous stirring in a closed 50 ml regular glass reactor using 50 wt% aqueous H_2O_2 as oxygen-donor and *tert*-butanol (*t*-BuOH) as the solvent. The reaction products were analyzed by the GC-MS method. Details can be found elsewhere [9].

3. Results and discussion

3.1. *Structural characteristic of the catalysts*

As shown in figure 1(b), the XRD pattern of W-MCM-41 (Si/W = 40) shows three well-defined sharp Bragg peaks indexed as (100), (110) and (200), respectively, characteristic of MCM-41 materials [10,11]. XRD patterns of the pure MCM-41 are also shown in figure 1(a). No obvious difference could be observed from these two samples, suggesting that the characteristic mesoporous structure was well preserved after introducing tungsten into pure MCM-41. Except for the three peaks at low diffraction angles, no peaks attributed to the crystalline WO_3 at about $2\theta = 23^\circ$ were observed for W-MCM-41 (Si/W = 40) in the XRD patterns, meaning the absence of agglomerated crystalline WO_3 in the catalyst. Our results also showed that no agglomerated WO_3 could be detected by XRD in a wide range of Si/W ratio from 100 to 40. Further decrease of the Si/W ratio will lead to the collapse of the mesoporous structure and the appearance of crystalline WO_3, as shown in figure l(d).

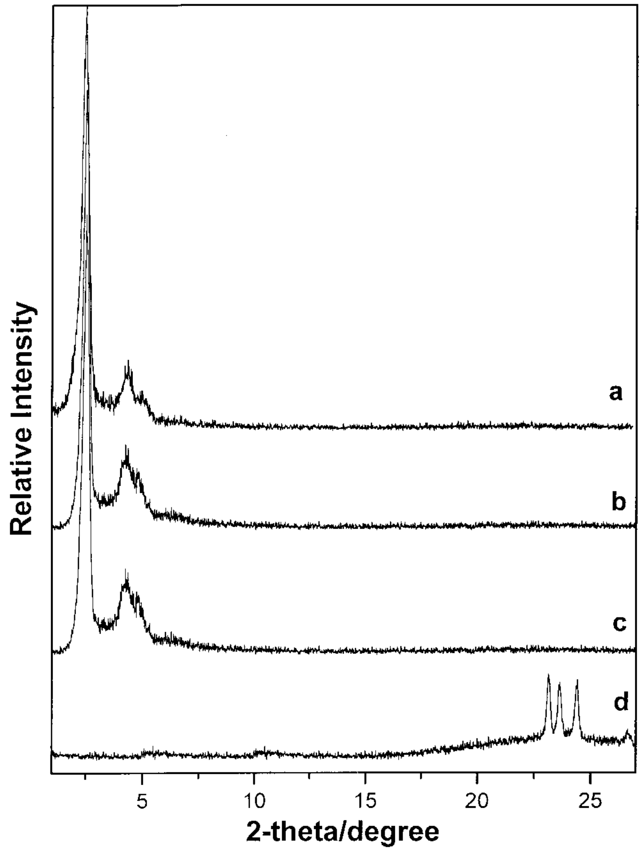

Figure 1. XRD patterns of pure MCM-41 and W-MCM-41. (a) Pure MCM-41; (b) W-MCM-41, Si/W = 40; (c) W-MCM-41, Si/W = 40 after 10 reaction cycles; (d) W-MCM-41, Si/W = 30.

Scanning electron microscopy with energy diffraction (SEM-EDX) also confirmed that no agglomerated WO_3 could be observed on the surface of W-MCM-41 sample (Si/W = 40) as shown in figure 2(a), while obvious agglomeration of WO_3 takes place on the sample surface with low Si/W ratio of 30, as also shown in figure 2(b). In other words, excess content of tungsten species will lead to the agglomeration of WO_3 on the surface of W-MCM-41 samples. Similar results were also observed in the confocal microscope laser Raman spectra of the sample as shown in figure 3. In comparison with the standard octahedral crystalline WO_3, as shown in

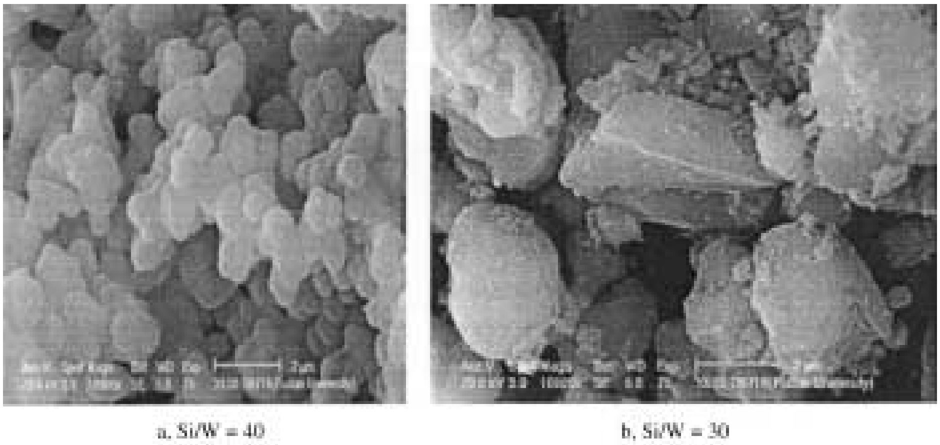
a. Si/W = 40
b. Si/W = 30

Figure 2. Scanning electron micrographs of W-MCM-41. (a) Si/W = 40; (b) Si/W = 30.

figure 3(f), no Raman bands attributed to the octahedral crystalline WO_3, at *ca.* 804, 714, 327 and 267 cm^{-1} [12] were observed for W-MCM-41 (Si/W = 40, see figure 3(b)). The Raman bands in figure 3(b) were very similar to those of the pure MCM-41, as also shown in figure 3(a). Figure 3(d) showed the Raman spectra of a W-MCM-41 sample with much higher content of tungsten species (Si/W = 30). Obvious Raman bands assigned to crystalline WO_3 could be detected, illustrating that certain high content of tungsten species would result in the agglomeration of microcrystalline WO_3 on the surface. Hence, a proper content of tungsten species was necessary for its high dispersion and the stability of the special mesoporous structure of MCM-41.

The FTIR spectra of the samples were shown in figure 4. For the pure MCM-41, no typical band peaked at 963 cm^{-1} was observed, which was assigned to the Si–O–W vibration mode present in the framework of MCM-41 [13]. When tungsten was doped in the MCM-41 sample, a band appeared at about 963 cm^{-1} in the FTIR spectra, indicating that tungsten species was incorporated into the framework of MCM-41 to form the Si–O–W bond. Similar assignments had been made for Ti- and V-containing molecular sieves reported by Alba *et al.* [14] and Thangaraj *et al.* [15]. When the Si/W ratio was as high as 30, the collapsed mesoporous structure of the W-MCM-41 framework made the WO_x species only present on the matrix surface, evidenced by the absence of the FTIR band peaked at 963 cm^{-1} of the sample.

3.2. Catalytic performance of different catalysts

The results of the selective oxidation of CPE to GA over several W-containing catalysts were listed in tables 1 and 2. As shown in table 1, the GA yield was strongly

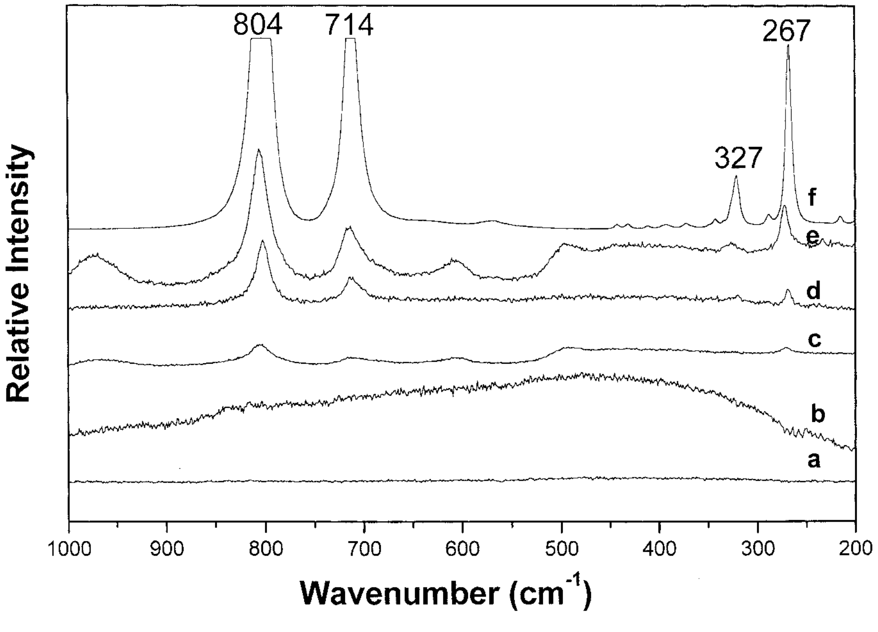

Figure 3. Raman spectra of W-MCM-41 and WO_3/MCM-41 samples with different ratios of Si/W. (a) Pure MCM-41; (b) W-MCM-41, Si/W = 40; (c) WO_3/MCM-41, Si/W = 40; (d) W-MCM-41, Si/W = 30; (e) WO_3/MCM-41, Si/W = 30; (f) pure WO_3.

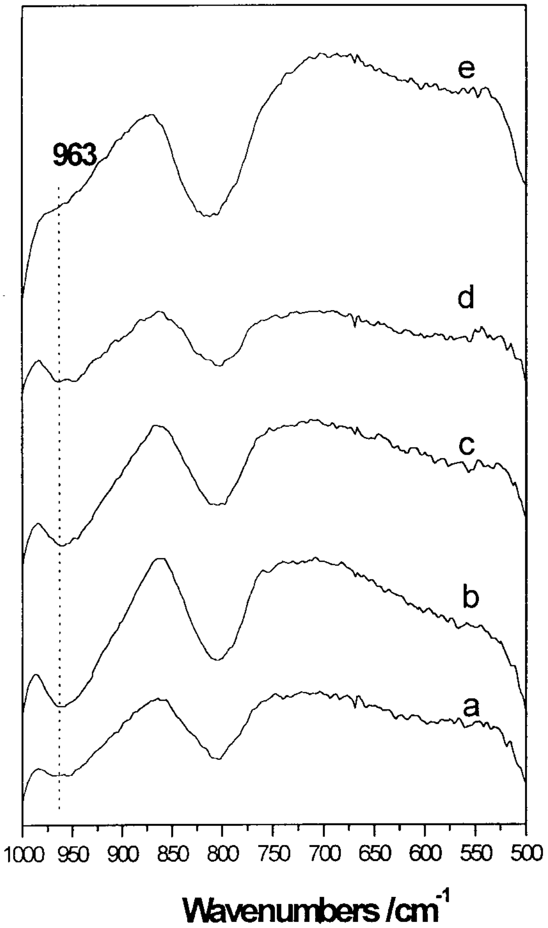

Figure 4. FTIR spectra of MCM-41 with structural Si/W molar ratio as: (a) ∞; (b) 50; (c) 40; (d) 35; (e) 30.

Table 1
Effects of the content of the tungsten species on the catalytic behavior of W-MCM-41 catalysts

Si/W (mol/mol)	CPE conversion (%)	H_2O_2 conversion (%)	GA yield
77	90	95	59
63	100	100	63
50	100	100	66
40	100	100	72
30	45	51	21

Reaction time: 24 h; reaction temperature: 35 °C; the molar ratio of H_2O_2/CPE = 2; the volume ratio of *t*-BuOH/CPE = 10.

dependent on the content of the tungsten species in the W-doped MCM-41 samples, which revealed that the optimum catalyst in the present reaction was the W-MCM-41 with an Si/W ratio of 40. When the Si/W ratio was higher than 40, low yield of GA was obtained. Otherwise, if the Si/W ratio was as low as 30, inevitable agglomeration of WO_3 and the corresponding collapse of the mesoporous structure of the W-MCM-41 led not only to the lower CPE conversion but also to lower GA yield, as shown in figure 1(d). In order to investigate the stability and duration of active W-species on the W-MCM-41 (Si/W = 40) catalyst, the leaching of W-species into the product mixture and the content of tungsten remaining in the catalyst were also determined after 10 reaction cycles. No detectable leaching of W-species or obvious loss of tungsten in the W-MCM-41 samples could be found, meaning the presence of strong interaction between tungsten species and the silica-based matrix. The mesoporous structure of the catalyst still remained after 10 reaction cycles as shown in figure 1(c). In addition, another experiment was carried out to test whether this novel W-MCM-41 catalyst was actually a heterogeneous catalyst. When the reaction over W-MCM-41 catalyst had been carried out for 10 h, the catalyst was removed through simple filtration and the reaction solution was stirred for another 14 h. No detectable increase of GA yield and CPE conversion in the 14 hours of reaction were observed, indicating that the trace amount of leached W species had almost no detectable catalytic effect on the reaction.

It was very interesting to find that the calcined W-MCM-41 (Si/W = 40) also showed the best activity and selectivity when compared with other kinds of W-containing heterogeneous catalysts, as shown in table 2. To the best of our knowledge about the heterogeneous W-containing catalysts, our novel W-MCM-41 catalyst exhibited the highest CPE conversion (100%) and GA

Table 2
Catalytic behavior of various W-containing catalysts

Sample	S_{BET} ($m^2 g^{-1}$)	Pore diameter (nm)	CPE conversion (%)	GA yield (%)	Leached W (ppm)
Si-MCM-41	1152	2.5	0	0	0
(a) W-MCM-41	1100	2.6	100	72	0.8
(b) WO_3/MCM-41	1060	2.4	100	66	4
(c) WO_3/SiO_2^{α}	900	0.5	51	15	30
(d) WO_3/SiO_2^{β}	230	3.0	83	48	70
(e) WO_3	–	–	2	0	0

Reaction time: 24 h; reaction temperature: 35 °C; the molar ratio of H_2O_2/CPE = 2; the volume ratio of *t*-BuOH/CPE = 10. (a) Si/W = 40. (b)–(d) Prepared through incipient wetness impregnation with W-containing solution. The molar ratios of Si/W were also equal to 40. SiO_2^{α} and SiO_2^{β} are commercial products. (e) Crystalline WO_3 obtained by the calcination of $WO_3 \cdot H_2O$ at 873 K for 2 h. For (a)–(e) the reactions were carried out over the catalysts containing the same amounts of W for the purpose of comparison.

yield (~72%), and seemed to be a promising candidate for its application in industry. When WO_3/SiO_2 or WO_3/MCM-41 was used as the catalyst, certain catalytic activities were also observed, but the activities were less than that of the W-MCM-41 counterparts. A blank experiment with pure silica MCM-41 as catalyst showed that no transformation of CPE to GA could be observed. Furthermore, unsupported completely crystalline WO_3 catalyst showed almost no catalytic activity toward the reaction. The great difference in the catalytic performance suggested that the presence of the completely or partly dispersed tungsten species on or in the silica matrix was necessary for the reaction.

4. Discussion

Although WO_3/MCM-41 has high surface area and large pore diameter compared with those of W-MCM-41, obvious differences in their catalytic behaviors were observed. First, higher yield of GA was obtained over W-MCM-41 (72%) than over WO_3/MCM-41 (66%); second, after the WO_3/MCM-41 catalyst had been employed for three cycles, obvious degeneration of activity was observed, while W-MCM-41 showed no obvious degeneration of activity even after 10 reaction cycles; third, the leaching of tungsten species from W-MCM-41 (0.8 ppm) is much lower than that from WO_3/MCM-41 (4 ppm).

In addition, the color of W-MCM-41 catalyst was white, indicating that tungsten species was highly imbedded in the matrix. In contrast, the color of WO_3/MCM-41 was yellow, suggesting that some WO_3 was agglomerated on its surface. Raman spectroscopy verified this assumption. As shown in figure 3, there were very obvious differences between the Raman patterns of W-MCM-41 and WO_3/MCM-41 with the same Si/W ratio. The WO_3/MCM-41 samples gave more visible and stronger Raman bands than their W-MCM-41 counterparts, indicating that the W species in W-MCM-41 were more highly dispersed than in their WO_3/MCM-41 counterparts. Thus, the difference of the catalytic characters between these two kinds of catalyst could be understood by considering that W species were more highly dispersed in W-MCM-41 than in WO_3/MCM-41, leading to the stronger interaction of WO_x species with the silica matrix and therefore reducing the leaching of W species into the reaction mixture.

For the purpose of comparison, the reaction was also carried out over the catalyst of tungsten oxides supported on two kinds of commercial silica. SiO_2^{α} has high BET area but small pore size, while SiO_2^{β} has large pore size but low BET area. Despite the high specific surface area of the SiO_2^{α} support of WO_3/SiO_2^{α} (900 $m^2\,g^{-1}$) and the large pore size of the SiO_2^{β} support of WO_3/SiO_2^{β} (3.0 nm), very low yields of GA over these two catalysts were obtained, as listed in table 2. The low catalytic activity of the oxidation reaction over catalysts from WO_3/SiO_2^{α} and WO_3/SiO_2^{β} could be easily explained by the absence of their large pore diameter (0.3 nm) and high specific surface area (230 $m^2\,g^{-1}$), respectively. As we know, for the oxidation of bulky CPE, a large pore size of the catalyst was certainly desired. Meanwhile it was not surprising that the small specific surface area of WO_3/SiO_2^{β} would undoubtedly account for its low catalytic activity and for its lack of active centers. Therefore, the high specific surface area (~1100 $m^2\,g^{-1}$) and large pore diameter (~2.6 nm) of the W-MCM-41 were confirmed to be another important factor for its high catalytic activity.

5. Conclusions

The W-MCM-41 catalyst exhibited the highest activity and selectivity in the selective oxidation of CPE to GA. The convenient separation of the W-MCM-41 catalyst from the reaction products mixture and its longer lifetime make it more feasible than the corresponding homogeneous catalysts when applied for industrial use. Moreover, the cheap and plentiful raw materials used in this novel process (one is cyclopentene, originating from a petrochemical by-product, and the other is an environmentally benign aqueous H_2O_2 oxidant) make this process more competitive than the traditional one. Detailed studies on the oxidation mechanism during this novel process are continuing.

Acknowledgments

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