Novel heterogeneous W-doped MCM-41 catalyst for highly selective oxidation of cyclopentene to glutaraldehyde by aqueous H$_2$O$_2$

Hao Chen, Wei-Lin Dai*, Jing-Fa Deng, and Kangnian Fan

Molecular Catalysis and Innovative Material Laboratory, Department of Chemistry, Fudan University, Shanghai 200433, P.R. China

Received 31 October 2001; accepted 14 January 2002

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$_2$O$_2$; 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$_2$O$_2$ 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 heterogeneous 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-H$_2$O) was
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 (NaWO₄·2H₂O, 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 NaWO₄·2H₂O. For purposes of comparison, theWO₃-supported catalysts were prepared through the conventional incipient wetness impregnation method as follows: 0.323 g of tungstic acid, denoted as Wo₃·H₂O, was dissolved in a solution of ammonium or oxalic acid. Into the stirred solution was dispersed different amounts of commercial SiO₂ 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 WO₃/SiO₂ or WO₃/MCM-41.

2.2. Catalyst characterization

X-ray powder diffraction (XRD) patterns were recorded on a Bruker D8 Advance spectrometer with Cu Kα 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 H₂O₂ 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 WO₃ at about 2θ = 23° were observed for W-MCM-41 (Si/W = 40) in the XRD patterns, meaning the absence of agglomerated crystalline WO₃ in the catalyst. Our results also showed that no agglomerated WO₃ 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 WO₃, as shown in figure 1(d).

Scanning electron microscopy with energy diffraction (SEM-EDX) also confirmed that no agglomerated WO₃ could be observed on the surface of W-MCM-41 sample (Si/W = 40) as shown in figure 2(a), while obvious agglomeration of WO₃ 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 WO₃ 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 WO₃, as shown in