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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.

Keywords: W-doped SBA-15 catalyst; Cyclopentene; Glutaraldehyde; Hydrogen peroxide; Selective oxidation

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_α 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_α radiation, operated at 40 mA and 40 kV. The laser Raman experiments were performed by using a Jobin Yvon Dilor Labram I Raman spectrometer 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 $\leqslant$ 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-

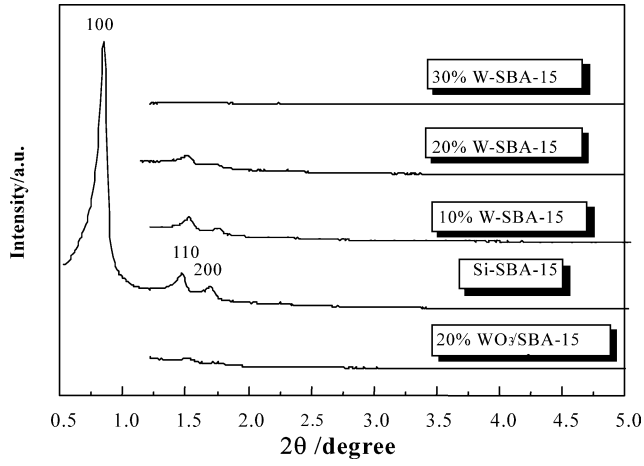

Fig. 1. XRD powder patterns of various samples.