

New green catalytic manufacture of glutaric acid from the oxidation of cyclopentane-1,2-diol with aqueous hydrogen peroxide

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Abstract

Selective oxidation of cyclopentane-1,2-diol to glutaric acid (GAC) over different kinds of materials has been carried out with aqueous hydrogen peroxide. The homogenous tungstic acid catalyst was tried first, which showed a yield of GAC as high as 91.2%. However, the separation, recovering and reusing of the homogeneous catalyst are very difficult, thus restricting its further application in industry. Then tungsten-containing mesoporous silica (W-MCM-41) was next tried as a heterogeneous catalyst. Although the activity was about 20% lower than that of the homogeneous one, it was much more easily to be separated, recovered and reused. It is interesting to find that the phase-transfer material shows the best performance in the reaction, during which the yields of GAC on $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_2\{\text{W}_2\text{O}_3[\text{O}_2]_4\}$ (CW) and $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_3\{\text{PO}_4[\text{WO}_3]_4\}$ (CPW) were 91.3 and 94.3%, respectively. These two materials demonstrated the characteristic features of “reaction-controlled phase-transfer”; the samples dissolved during the reaction and precipitated after the reaction. Therefore, these materials show the advantages of both homogeneous and heterogeneous catalysis and can easily be recovered and reused. The fresh samples and the recovered ones were all characterized by FT-IR, Raman, ³¹P NMR and XPS spectroscopy. The structures of these two materials all changed after the reaction, polymerizing by forming W–O_c–W (edge-sharing) bonds. XPS results revealed that the recovered samples of CW and CPW are all more stable than the corresponding fresh ones due to the changes of the coordination circumstances.

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1. Introduction

Dicarboxylic acids, including glutaric acid (GAC), adipic acid, trimethyladipic acid, and dodecanedioic acid, are essential feed-stocks for the manufacture of polyamides, polyesters, plasticizers, and lubricating oils [1]. The anhydrides, one of the monomers of LCD materials, can also be synthesized from dicarboxylic acids; however, there is no convenient method for the production of GAC yet, especially on a large-scale for industry. The current manufacture process is in multi-steps by oxidative cleavage of C–C bonds of mixtures containing the corresponding cyclic alcohols and ketones and their derivatives with nitric acid [2–4]. Noyori and co-workers [5,6] have developed a general method of synthesizing carboxylic acids,

including adipic acid and GAC, in which Na₂WO₄ and [CH₃(*n*-C₈H₁₇)₃N]HSO₄ were used as the oxidation and phase-transfer catalysts, respectively. The latter is quite expensive and cannot be easily separated and recovered. Thus, this process is impossible for large-scale industrial production of GAC.

In our previous work, a novel green process of synthesizing GAC from cyclopentene (CPE) with high GAC yield of 92.3% has been developed without using any kinds of solvents; in this process only 50% aqueous H₂O₂ solution and tungstic acid were used as the oxidant and the catalyst, respectively [7]. We also succeeded in the using of a phase-transfer material in synthesizing GAC from CPE; the yield is also very high (83.1%) [8]. However, the boiling point of CPE is 319 K, so it can easily evaporate and escape from the plant, thus resulting in the inevitable loss when in use and in great difficulties in its storage and transportation. Hence, the CPE process is inconvenient and not economic. Therefore, some other alternative derivatives from CPE can be chosen. It is found

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that cyclopentane-1,2-diol (CPDL), which can be easily obtained quantitatively from CPE with aqueous hydrogen peroxide, can be selected as a good substitute of CPE because of its high boiling-point as well as its excellent ability to mix with water when handed with aqueous hydrogen peroxide. In addition, CPDL is the main by-product in the process of glutaraldehyde from the selective oxidation of CPE, as reported in our previous work [10]. So the present process can be a good supplement for the previous glutaraldehyde process, thus making the whole process much economic and perfect, considering its abundant products and zero draining. In this research, three kinds of materials were tried in the novel process (homogeneous tungstic acid, heterogeneous WO_3/SiO_2 catalyst and tungsten-containing phase-transfer material). The recovering and reusing conditions of the heterogeneous and phase-transfer materials were also investigated. The fresh and recovered phase-transfer materials were all characterized by FT-IR, Raman, ^{31}P NMR and XPS spectroscopy to reveal the structure changes after the reaction.

2. Experimental

2.1. Preparation

2.1.1. Preparation of W-MCM-41

W-MCM-41 was synthesized via an in situ method according to the literature [9]. 12.4 g of cetylpridine bromide ($\text{CPBR}\cdot\text{H}_2\text{O}$) was added to 120 mL of HCl (5 M) to give a mixture. Next 22.4 mL of tetraethyl orthosilicate (TEOS) and different amounts of aqueous sodium tungstate solution ($\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$, 2H₂O, 0.2 M) were simultaneously and quickly added into the mixture under vigorously 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. The pure silica MCM-41 was synthesized by omitting the adding of $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$. For the purposes of comparison, the WO_3 -supported catalysts were prepared through the conventional incipient wetness impregnation method as follows: 0.23 g of ammonium tungstate ($(\text{NH}_4)_5\text{H}_5[\text{H}_2(\text{WO}_4)_6]\cdot\text{H}_2\text{O}$) was dissolved in a solution of ammonium. Into the stirred solution was dispersed 1 g of pure MCM-41 at 323 K. After the water evaporated completely, the dried solid was further calcined at 873 K in air for 4 h to obtain the $\text{WO}_3/\text{MCM-41}$. W-SBA-15 were also synthesized for comparison, according to the literature [10].

2.1.2. Preparation of the phase-transfer material

The phase-transfer material $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_3\{\text{PO}_4[\text{WO}_3]_4\}$ was prepared according to the procedure described previously [11,12]. A suspension of tungstic acid 2.5 g (10 mmol) in 7 mL of aqueous H_2O_2 (35%) was stirred and heated to 333 K until a colorless solution was obtained. The solution was filtered and then cooled to room temperature. After that, 40% (w/v) H_3PO_4 (0.62 mL, 2.5 mmol) was added to the solution, which was then diluted to 30 mL with distilled water. An amount equal to 1.80 g of cetylpyridiniumammonium

chloride (5 mmol) in dichloromethane (40 mL) was added dropwisely with stirring in 2 min, and the mixture was maintained for an additional 15 min. The organic phase was then separated, dried with anhydrous Na_2SO_4 , filtered and evaporated under atmospheric pressure at 323–333 K (water bath). At last, about 2.5 g (85%, based on the quaternary ammonium salt charged) of the dried yellow powder was obtained by further evacuation, which was labeled as CPW.

The phase-transfer material $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_2\{\text{W}_2\text{O}_3[\text{O}_2]_4\}$ was prepared according to the literature [13]: 1.65 g $\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}$ (5.0 mmol) was dissolved in 10 mL of water and 6.0 mL of H_2O_2 (30%) to obtain a yellow pellucid solution. Then hydrochloric acid was titrated to the solution until a pH of 2–2.5 was obtained. An amount equal to 3.58 g of cetylpyridiniumammonium chloride (10 mmol) in ethanol (10 mL) was added dropwisely under vigorous stirring, and a white precipitate formed simultaneously. The mixture was maintained for an additional 1 h, and then filtered and washed with distilled water. After the mixture was dried completely, the material $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_2\{\text{W}_2\text{O}_3[\text{O}_2]_4\}$ was obtained and labeled as CW.

$[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_7[\text{PW}_{11}\text{O}_{39}]$ (CPW11) was prepared also according to ref. [14]. Materials $[\pi\text{-C}_5\text{H}_5\text{NC}_{16}\text{H}_{33}]_3[\text{PW}_{12}\text{O}_{40}]$ (CPW12) and $[(\text{CH}_3)_3\text{NC}_{16}\text{H}_{33}]_3[\text{PW}_{12}\text{O}_{40}]$ (TPW12) were prepared according to ref. [8]. The recovered materials of CW and CPW are labeled as Re-CW and Re-CPW, respectively.

2.2. Catalytic oxidation of CPDL to GAC

A round-bottomed flask with a condensation tube was charged with the catalyst (0.1 mol WO_3), 50% H_2O_2 (19.5 mL) and CPDL (10 g). The flask was then placed in a water bath at 363 K with vigorous stirring for 8 h. After then, if necessary, the resulting suspension was centrifugated and the pellucid liquid was analyzed by titration with NaOH solution to get the yield of organic acid. The precipitated catalyst was recovered for further use.

The pellucid liquid was boiled up to bubbling to decompose the remaining peroxides (avoid explosion during vacuum distillation), until the amyllum-KI test is negative. Then small amounts of activated carbon were added and the mixture was stirred in a boiling water bath for 30 min. After filtering, the colorless solution was vacuum distilled and concentrated to remove most of the water. After that, the resulting solution was refrigerated at 273 K for 24 h and colorless GAC crystals were formed. After being filtered and washed with small amounts of ice water, the as-obtained crystals were dried at 363 K for 12 h for the future analysis. The filtrate can be further dehydrated to get more GAC crystals that can be mixed with those from the first step for the accurate analysis of pure GAC yield. The yield of GAC was determined with acid-base titration, while the purity of GAC was analyzed with melting point test, HPLC and GC (after esterification with methanol).

2.3. Characterization

The high-angle X-ray powder diffraction (H-XRD) patterns were recorded on a Bruker D8 Advance spectrometer with Cu

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