

## Short Communication

## Simple and green oxidation of cyclohexene to adipic acid with an efficient and durable silica-functionalized ammonium tungstate catalyst



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## ARTICLE INFO

## Article history:

Received 2 August 2013

Received in revised form 28 September 2013

Accepted 2 October 2013

Available online 11 October 2013

## Keywords:

Adipic acid

Green oxidation

Hydrogen peroxide

Silica-functionalized ammonium tungstate

N<sub>2</sub>O

## ABSTRACT

A novel silica-functionalized ammonium tungstate interphase catalyst has been reported as a non-nitric acid route for adipic acid production from one-pot oxidative cleavage of 30% hydrogen peroxide and catalytic amounts of p-toluenesulfonic acid (PTSA). The catalyst has been simply prepared by commercially available starting material. The structure of the catalyst has been investigated using FT-IR spectroscopy, atomic absorption, TEM, SEM and XRD analysis. The catalyst has shown good to high activity even up to 10 runs of reaction. Simple preparation of the catalyst, avoids using harmful phase transfer catalyst (PTC) and/or chlorinated additives are among the other benefits of this work.

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## 1. Introduction

Adipic acid (1,6-hexanedioic acid) is a very important raw material which is used in the chemical industries [1]. It is mainly used in the manufacture of nylon-6,6 as a precursor for synthetic fibers, tire reinforcements, plastics, urethane foams, elastomers, and synthetic lubricants [1,2]. The current industrial method for adipic acid production is oxidation of a cyclohexanone/cyclohexanol (so-called KA oil) mixture with nitric acid [1]. Emission of huge volume of environmentally harmful gas, nitrous oxide (N<sub>2</sub>O), is the major drawback of this process. N<sub>2</sub>O is a greenhouse gas with 120 years life-time in atmosphere [3,4]. Owing to the strong IR absorption, the ability of N<sub>2</sub>O on warming the atmosphere is about 310 times higher than that of carbon dioxide (CO<sub>2</sub>) [4]. The nitric oxide (NO) which is produced from the N<sub>2</sub>O decomposition can destroy ozone molecules in a series of reactions. Additionally, N<sub>2</sub>O is a harmful gas which forms acid rains.

One-step oxidative cleavage of cyclohexene to adipic acid with H<sub>2</sub>O<sub>2</sub> has been introduced as a green alternative to adipic acid [5]. In this method, in order to overcome organic starting material and aqueous oxidant incompatibility and accelerate the reaction; quaternary ammonium salt has been employed as a phase transfer

catalyst (PTC) into the reaction mixture. Although H<sub>2</sub>O<sub>2</sub> is a cheap oxidant with water as the sole by-product, the relatively expensive applied quaternary ammonium compounds generally are not environmentally benign reagents. Another limitation of this process is the cost of the applied oxidant (H<sub>2</sub>O<sub>2</sub>) which is relatively higher than O<sub>2</sub> in the traditional nitric acid oxidation route. However, applying recoverable catalyst accompanied by environmentally benign protocols would significantly cover the cost of adipic acid production with H<sub>2</sub>O<sub>2</sub> as oxidant.

In this regard, various methods have been developed to improve the cyclohexene oxidation reaction such as using of surfactant-type peroxotungstate and peroxomolybdates [6], H<sub>2</sub>WO<sub>4</sub>/H<sub>2</sub>SO<sub>4</sub>/H<sub>3</sub>PO<sub>4</sub> mixture [7], ionic liquids [8,9], MIL-101 metal-organic framework [10] complexes derived from heteropoly acid and glycine [11] and Ti-ALISA mesostructured catalysts [12].

However, uses of relatively expensive and corrosive reagents, difficulties in catalyst recovery as well as catalysts degradation and/or deactivation are among the drawbacks of these methodologies. Hence, this oxidation reaction still requires further improvement in the point of reducing hazardous reagents, improving catalyst recovery and simplifying the overall process.

In the current study, we designed an interphase (organic-inorganic hybrid) catalyst for oxidation of cyclohexene to adipic acid. The catalyst comprises alkyl ammonium groups which covalently anchored on the surface of the silica gel. The surface functionalities provide the WO<sub>4</sub><sup>2-</sup> species which is necessary for oxidation. Additionally, the functionalized porous material acts as quasi-homogenous system with a large area of amphiphilic surface for better mass transfer of

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organic starting material and aqueous oxidant. In other words, the surface-bonded ammonium groups act as heterogenized PTC and therefore there is no need to use harmful organic additive(s) to overcome reagent phase incompatibility.

## 2. Results and discussion

The catalyst was easily prepared by commercially available starting materials (Scheme 1). The material **A** was prepared by grafting the 2-[2-(3-Trimethoxysilylpropylamino)ethylamino] ethylamine precursor onto the high surface area silica gel (see electronic supplementary information for details of the experimental procedure). Trifluoromethanesulfonic acid treatment of **A** produces surface-bonded ammonium triflate **B**. The catalyst **1** is prepared by subsequent anion exchange of the material **B** with an aqueous solution of  $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$  at room temperature.

To investigate the structure of the functionalized materials, comparative FT-IR spectra of the pure silica, material **A** and the catalyst **1** are shown in Fig. 1. The top spectrum is for pure silica, while the next two are for intermediate **A** and the final catalyst, which show important differences relative to the silica. The characteristic bands of the **A** are at 2922 and 2855  $\text{cm}^{-1}$  which is attributed to C–H and N–H stretching frequencies of the surface alkyl amine functionalities. In the case of the catalyst **1**, a very important characteristic band was observed at 875  $\text{cm}^{-1}$  which belongs to the W–O stretching frequency [8,9] and proves the presence of the  $\text{WO}_4^{2-}$  species in the catalyst. It is worth mentioning that the bands around 1470 and 1740  $\text{cm}^{-1}$  in both of **A** and catalyst **1** are attributed to the N–H bending frequencies of the surface-bonded amine and/or ammonium functionalities.

Atomic absorption analysis was performed to determine the accurate loading of  $\text{WO}_4^{2-}$  in the catalyst. The result indicates that the loading of  $\text{WO}_4^{2-}$  in the catalyst **1** is 1.02  $\text{mmol} \cdot \text{g}^{-1}$ .

XRD analysis of the pure silica, material **A** and catalyst **1** is shown in Fig. 2. The diffraction peak which appeared at about 25° in all of the structures is attributed to the amorphous silica gel [13]. This observation proves that no essential changes in topological structure of the silica gel occurred during the grafting process, chlorosulfonic acid treatment and anion exchange of the **B**. In the case of catalyst **1**, the decrease of the intensity may be interpreted by the formation of hydrogen bond between  $\text{WO}_4^{2-}$  and surface ammonium functionalities [14]. Our explanation about the peaks which are observed at nearly 10 and 60° is that they may be attributed to the silica-bonded ammonium tungstate species in catalyst **1**. TEM and SEM of the catalyst are provided in the Supplementary data.

The activity of catalyst **1** was investigated in oxidation of cyclohexene to adipic acid (Table 1). Typically, conversion of cyclohexene to adipic acid theoretically needs 4 moles  $\text{H}_2\text{O}_2$  for four step oxidation (Scheme 2). However, 4.4 moles of hydrogen peroxide was used to ensure the complete conversion of cyclohexene [5]. Worthy of note is that the activity of the  $\text{WO}_4^{2-}$  species in oxidation of cyclohexene to adipic acid strongly depends on the acidity of the reaction media [15]. At the first

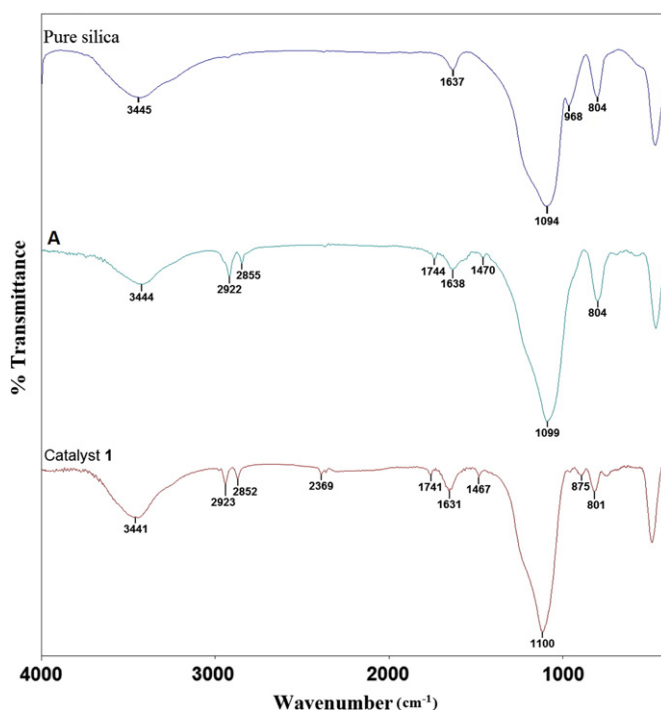
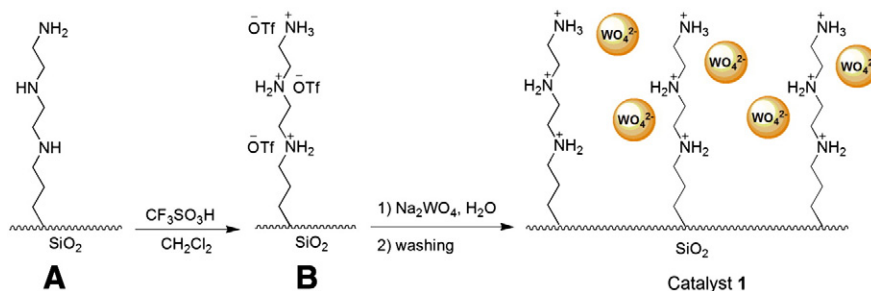


Fig. 1. FT-IR spectroscopy of the pure silica, material **A** and catalyst **1**.

step, the efficiency of catalyst **1** was investigated for oxidation of cyclohexene to adipic acid in the presence of 200 mg of HCl and  $\text{H}_2\text{SO}_4$ . The results indicated that in these cases the corresponding adipic acid can be obtained in 29% and 47% (Table 1, entries 1 and 2).

The yield of the reaction significantly increases to 64% when *p*-toluenesulfonic acid (PTSA) was used (Table 1, entry 3). The increase in the reaction yield may be attributed to better miscibility of the organic acid into both starting material/intermediates and aqueous oxidant.

Oxidation of the cyclohexane to adipic acid is also a temperature-dependent reaction with two distinct thermal steps [16]. To improve the yield of the reaction we considered this issue and the reaction was performed into two thermal steps. For this purpose, the mixture was first heated at 73 °C (near the boiling point of the cyclohexene–water mixture) to convert cyclohexene into 1,2-cyclohexanediol [16]. After 5 h, the flask immediately transfers into the second oil bath which its temperature was adjusted at 87 °C and was heated for 15 h. In this condition the pure adipic acid was obtained in 84% yield (Table 1, entry 4) and 99% selectivity (determined by gas chromatography (GC)) toward other dicarboxylic acids which might be produced from some rearrangement reactions [16]. Increasing the amount of  $\text{H}_2\text{O}_2$  to



Scheme 1. Schematic illustration of catalyst **1** preparation.

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