



## Short Communication

Design of silica supported task-specific ionic liquid catalyst system for oxidation of cyclohexene to adipic acid with 30% H<sub>2</sub>O<sub>2</sub>

Majid Vafaezadeh, Mohammad Mahmoodi Hashemi\*, Mehdi Shakourian-Fard

Department of Chemistry, Sharif University of Technology, Tehran, Iran

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## ABSTRACT

1-Butyl-3-methylimidazolium tungstate ([BMIm]<sub>2</sub>WO<sub>4</sub>) ionic liquid supported onto silica sulphamic acid demonstrated desirable performance for oxidation of cyclohexene to adipic acid. Simple experimental procedure, easy product isolation, catalyst recovery and reusability are some attractive features of this protocol.

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## 1. Introduction

Adipic acid is one of the most important chemicals and typically is ranked in the top ten in the terms of volume used annually by chemical industries [1]. It is mainly used in the production of nylon-6,6, which is used in carpet fibers, tire reinforcements, upholstery and apparel [2,3]. The traditional route of preparation of adipic acid uses nitric acid oxidation of a mixture of cyclohexanone and/or cyclohexanol which are derived from benzene [1].

However, releasing of nitrous oxide (N<sub>2</sub>O) as a by-product, is thought to cause acid rain and ozone depletion that severely threaten the global pollution control [4]. Thus, the development of environmentally benign protocol seems to be crucial. Aqueous H<sub>2</sub>O<sub>2</sub> is a desirable oxidant because it is a relatively cheap reagent with water as the only by-product. Various routes for preparation of adipic acid using H<sub>2</sub>O<sub>2</sub> have been developed [5–10]. Although good to excellent yields were achieved in these methods, immiscibility of the hydrophobic reactants and aqueous oxidant phase in these reactions still is a common problem.

To overcome reagent incompatibility, Noyori et al. reported an oxidation method with aqueous H<sub>2</sub>O<sub>2</sub> in the presence of [CH<sub>3</sub>(n-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N<sup>+</sup>HSO<sub>4</sub><sup>-</sup>] as a phase transfer catalyst (PTC) with small amounts of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O [5,7]. However, relatively expensive quaternary ammonium compounds generally are not environmentally benign reagents. Using silica-bound peroxtungstate as a catalyst is another

approach for oxidation of cyclohexene to adipic acid [9]. But corrosive and toxic nature of applied sulphuric acid leads to environmental hazards and some operational problems.

Combination of ionic liquids in the form of multilayer adsorption with functionalized silica gel has attracted attentions to proceed organic reactions in water as an alternative reaction media [11–14]. Although, the deposition of hydrophobic ionic liquids in the form of a thin layer onto the solid supports is an interesting approach to minimize the amounts of applied expensive ionic liquid and facilitate transportation of organic reactants, however, when diffusion of both lipophilic organic compounds and polar substrates is considered, such protocols are not efficient enough. On the other hand, typically, the role of the ionic liquids in many organic transformations is only defined as an alternative reaction media and only few examples are given including functional ionic liquids (so called task-specific ionic liquids) [11,15]. Here, we found that the combination of a silica supported acid catalyst with hydrophilic task-specific ionic liquid, not only generates amphiphilic reaction environment [16,17], but also provides numerous nano-scale reactors [18] containing all necessary components for cyclohexene oxidation in an aqueous-organic process (solvent, acid sites and the catalyst precursor).

## 2. Experimental

## 2.1. Materials

All chemicals and solvents were purchased from the Fluka and Merck and used without further purification. <sup>1</sup>H and <sup>13</sup>C NMR spectra were determined on the Bruker DRX 500 MHz. Tungsten loading

\* Corresponding author. Tel.: +98 21 66005718; fax: +98 21 66029165.  
E-mail address: [mhashemi@sharif.edu](mailto:mhashemi@sharif.edu) (M.M. Hashemi).

measurement was performed using atomic absorption spectroscopy (GBC Avanta ver. 2.02). Thermogravimetric analysis was performed by TGA-Q50. FT-IR spectra were recorded with ABB Bomem MB100 Fourier Transform Infrared Analyzer. GC-MS was recorded by HP6860 with DB-5MS column, 30 m × 0.25 mm × 0.25 μm.

## 2.2. Preparation of silica sulphamic acid

Silica gel Davisil™ grade 635 (average pore diameter 60 Å, pore volume 0.75 cm<sup>3</sup>/g, surface area 480 m<sup>2</sup>/g) was activated by refluxing in 6 M hydrochloric acid for 24 h and then washed thoroughly with the deionized water to adjust the pH value of the solution to 6–7 and dried before undergoing chemical surface modifications. The activated silica gel (5.00 g) was mixed with (3-aminopropyl) trimethoxysilane (10 mmol ~ 1.75 mL) in dry toluene for 24 h. Then, the solid materials were filtered off and washed with hot toluene for 12 h in a continuous extraction apparatus (Soxhlet) and then dried in an oven at 100 °C over night to give 3-aminopropylsilica. To a mixture of 3-aminopropylsilica (5.00 g) in chloroform (20 mL) chlorosulphonic acid (1.00 g, 0.6 mL) was added dropwise at room temperature over 2 h. After addition was completed, the mixture was stirred for 2 h and HCl gas evolution was monitored with a pH paper indicator. Finally, the mixture was filtered and washed with ethanol (50 mL) and dried in vacuo at 50 °C to afford silica sulphamic acid [19].

## 2.3. Preparation of [BMIm]Br

1-Methylimidazole (20 mL, 0.252 mol, 1 eq.) was added to 1-bromobutane (29.9 mL, 0.277 mol, 1.1 eq.). The mixture was refluxed in toluene for 24 h. Then, it was cooled to room temperature and the toluene was decanted from the two layer mixture. The remaining viscous oil was crystallized from the minimum amount of acetonitrile, then it was dried in vacuo to afford [BMIm]Br [20].

## 2.4. Preparation of [BMIm]<sub>2</sub>WO<sub>4</sub>

The aqueous solution of 0.05 mol AgNO<sub>3</sub> (8.49 g) was added to the solution of 0.025 mol Na<sub>2</sub>WO<sub>4</sub> (8.25 g) to form Ag<sub>2</sub>WO<sub>4</sub>. The product was a precipitate as a pale yellow solid which was washed with deionized water for three times. Then an aqueous solution of 0.05 mol [BMIm]Br (10.96 g) was added to the freshly prepared Ag<sub>2</sub>WO<sub>4</sub> at room temperature. After 1 h stirring, the mixture was filtrated and the liquid was concentrated and dried in vacuo to afford [BMIm]<sub>2</sub>[WO<sub>4</sub>] as a colorless liquid [21]. [BMIm]<sub>2</sub>[WO<sub>4</sub>]: <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): 0.79 (t, J = 7 Hz, 3H), 1.14–1.19 (m, 2H), 1.66–1.72 (m, 2H), 3.65 (s, 3H), 4.19–4.22 (t, J = 7 Hz, 2H), 7.81 (s, 1H), 7.82 (s, 1H), 9.97 (s, 1H); <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>): δ = 14.17, 19.65, 32.48, 36.61, 49.36, 123.12, 124.55, 139.15.

## 2.5. Preparation of catalyst 1

Acetonitrile solution of [BMIm]<sub>2</sub>[WO<sub>4</sub>] (0.40 g of ionic liquid in 5 mL acetonitrile) was added dropwise to a mixture of 1.00 g of dried silica sulphamic acid in 40 mL acetonitrile at room temperature over 1 h. The reaction mixture was stirred for an additional 2 h and then the solvent was removed under reduced pressure to afford catalyst 1 as a white powder (40 wt.% [BMIm]<sub>2</sub>[WO<sub>4</sub>]/silica gel).

## 2.6. pH analysis of the catalyst 1

The catalyst 1 (0.50 g) was added to an aqueous solution of NaCl (25 mL, 1 M). The resulting mixture was stirred for 2 h after which the pH of solution decreased to 1.88. This is equal to a loading of 0.66 mmol H<sup>+</sup>/g [18].

## 2.7. General procedure for oxidation of a cyclohexene to adipic acid

A mixture of 1 mL cyclohexene (0.82 g, 10 mmol), 5.00 g (44 mmol) of 30% H<sub>2</sub>O<sub>2</sub> and 0.40 g of catalyst 1 was stirred at 75 °C in an oil bath for 18 h. (Note: Hydrogen peroxide is an explosive and oxidizer reagent. Therefore, particular care should be taken into consideration). The reaction progress was monitored by TLC. After the completion of the reaction, the slurry was filtrated and the catalyst was washed with ethanol and dried. The filtrate was concentrated and crystallized in ethyl acetate to afford pure adipic acid in 87% yield. Hexanedioic acid (Adipic acid): <sup>1</sup>H NMR (500 MHz, DMSO-d<sub>6</sub>): 1.45 (m, 4H), 2.45–2.46 (m, 4H), 11.93 (m, 2H); <sup>13</sup>C NMR (125 MHz, DMSO-d<sub>6</sub>): δ = 24.89, 34.24, 175.19.

## 3. Result and discussion

The catalyst 1 was prepared by impregnation of [BMIm]<sub>2</sub>WO<sub>4</sub> in the form of supported liquid phase (SLP) [22] onto the high surface area functionalized silica gel with the loading of 40 wt.% [BMIm]<sub>2</sub>WO<sub>4</sub>/silica gel. The schematic representation of the catalyst 1 is shown in Fig. 1. In this method, the ionic liquid is supported as a thin layer on the surface of the silica gel providing a suitable reaction media. Further, the ionic liquid could readily be recycled by simple filtration and does not need liquid processes which often use high volume of toxic organic solvents.

The structure of the catalyst 1 and [BMIm]<sub>2</sub>WO<sub>4</sub> was characterized by <sup>1</sup>H and <sup>13</sup>C NMR, FT-IR spectroscopy, ion-exchange pH analysis, atomic absorption spectroscopy (AA) and thermogravimetric analysis (TGA).

FT-IR spectroscopy was performed for [BMIm]<sub>2</sub>WO<sub>4</sub> and the catalyst 1 (Fig. 2). The characteristic band with a large absorption around 700 to 900 cm<sup>-1</sup> (Fig. 2a), was attributed to the W–O stretching frequency in WO<sub>4</sub><sup>2-</sup> species [23]. The presence of the organic groups on the surface of silica-gel was also confirmed by FT-IR spectroscopy, as shown in Fig. 2b. The main features of all silica-gel spectra were related to the inorganic backbone such as large broad stretching band at 3251 cm<sup>-1</sup>, which was attributed to the presence of the N–H bond stretching frequency of sulphonamide groups which has been overlapped with O–H stretching frequency of silanol group and/or the remaining water molecules. The corresponding bending frequency of N–H was observed at 1570 cm<sup>-1</sup>. Additionally, the peak at about 1164 cm<sup>-1</sup> is attributed to the typical symmetric stretching vibration of S=O bond of supported sulphonamide groups.

As discussed in the Experimental section, the proton capacity of the silica sulphamic acid was calculated to be 0.66 mmol H<sup>+</sup>.g<sup>-1</sup> using ion-exchange pH analysis. It is noteworthy that during the chlorosulphonic acid treatment, the unloaded surface OH groups

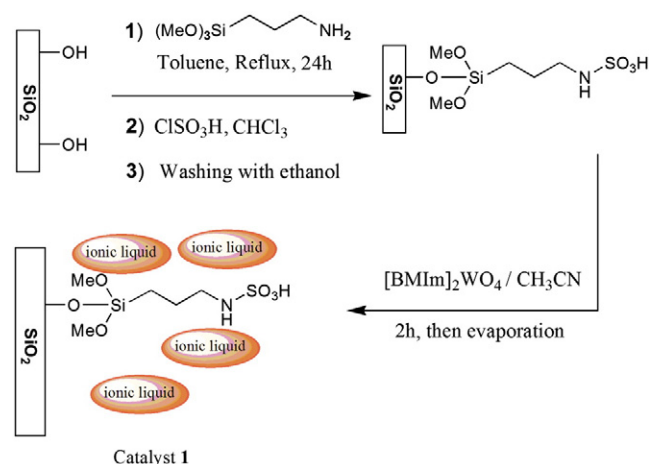


Fig. 1. The schematic illustration of the catalyst 1 preparation.

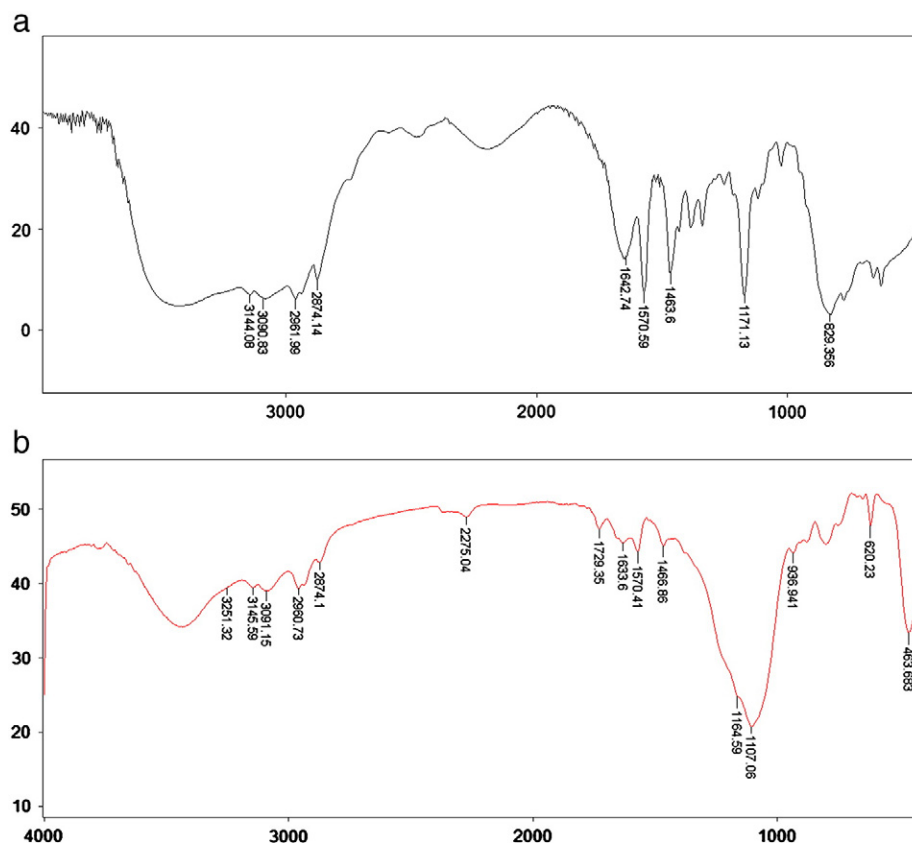


Fig. 2. FT-IR spectroscopy of [BMIm]<sub>2</sub>WO<sub>4</sub> (a) and the catalyst **1** (b).

could react with chlorosulphonic acid to form surface bonded sulphonic acid [24,25]. So, the acidity of the catalyst **1** for the oxidation process was supplied from two different sources, sulphamic acid and silica bonded sulphonic acid.

Atomic absorption spectroscopy was performed to determine the accurate loading of WO<sub>4</sub><sup>2-</sup> in catalyst **1**. According to the AA results, a loading at 0.52 mmol.g<sup>-1</sup> of WO<sub>4</sub><sup>2-</sup> was found in catalyst **1** (Fig. 2S of supporting information).

Thermogravimetric analysis (TGA) of the catalyst **1** was performed to prove its thermal stability (Fig. 3S of supporting information). The first weight loss curve around the 50 °C is attributed to residual physisorbed water and/or organic solvents, which was applied during the catalyst **1** preparation. The largest weight loss was occurred between 200 and 450 °C which is a characteristic of the surface functionalities and the ionic liquid decomposition that were overlapped with each other.

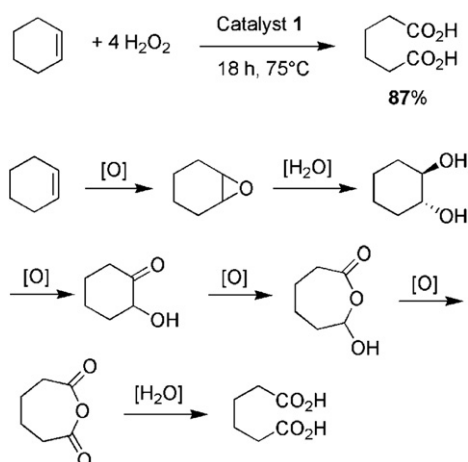
Conversion of cyclohexene to adipic acid in the presence of catalyst **1** theoretically needs 4 mol H<sub>2</sub>O<sub>2</sub> for four steps oxidation of 1 mol cyclohexene (Scheme 1). However, 4.4 mol of H<sub>2</sub>O<sub>2</sub> was used to ensure the complete conversion of cyclohexene [5].

As mentioned, [BMIm]<sub>2</sub>WO<sub>4</sub> provides an amphiphilic region on the surface of functionalized silica gel. This makes the catalyst **1** suitable for transportation of both hydrophobic and hydrophilic species in the interior of the catalyst **1** channels. Cyclohexene and the first intermediate (epoxide) are considered as hydrophobic species. Organic nature of N-butyl group of the imidazolium ring facilitates the diffusion of these compounds across the organomodified nanospace channels. On the other hand, the supported ionic liquid [BMIm]<sub>2</sub>WO<sub>4</sub> layer is a suitable environment for diffusion of more polar intermediates, product and aqueous H<sub>2</sub>O<sub>2</sub>. However, details of the reaction mechanism are not clear, but it seems that the reaction strongly takes place in the acidified supported ionic liquid layer.

Despite the role of the [BMIm]<sub>2</sub>WO<sub>4</sub> ionic liquid in balancing the polarity of the nano channels, the so called task-specific ionic liquid provides the catalyst precursor (WO<sub>4</sub><sup>2-</sup>) for oxidation of cyclohexene to adipic acid. So the catalytic precursors are in close proximity to the acidic sites and all of these are located in a thin layer of supported amphiphilic ionic liquid. Therefore, the catalyst **1** acts as numerous nanosize vessels with the same properties, in which each channel contains suitable solvent and catalyst species.

The activity of the catalyst **1** was investigated in oxidation of cyclohexene to adipic acid (Table 1). Our preliminary investigations showed that when the titled reaction was carried out the corresponding adipic acid was obtained in 87% yields within 98.1% selectivity determined by GC-MS (Table 1, entry 3) [26,27]. Increasing the molar ratio of H<sub>2</sub>O<sub>2</sub> to 6.0 mol per 1 mol of cyclohexene led to decrease the conversion of the cyclohexene to adipic acid (Table 1, entry 4). Further, increasing the amount of the catalyst to 0.55 g did not cause any major changes in the activity of the system. Only slightly superior conversion at similar reaction condition was observed (Table 1, entry 5). Therefore, the condition that which stated in the entry 3 of Table 1 was selected as the optimum condition.

The reusability is an important feature of heterogeneous catalysts. To investigate this issue, after the completion of the first run which affords the adipic acid in 87% yield (isolated yield), the catalyst was washed with ethanol and dried in vacuo for 3 h. The recovered catalyst **1** was subjected to another reaction cycle to yield 71% of adipic acid (Table 1, entry 6). In this case, the leaching of the ionic liquid was determined by <sup>1</sup>HNMR of crude product to approximately 2% (Fig. 4S of supporting information). Similarly, in another experiment, after the first reaction cycle, the catalyst **1** was washed with n-hexane. The yields of 79% for the second reaction cycle were obtained (Table 1, entry 7). These results are attributed to the unavoidable leaching of ionic liquid from the surface of silica gel during the



Scheme 1. Reaction pathway for oxidation of cyclohexene to adipic acid [5].

Table 1

The data of the catalytic performance in direct oxidation of cyclohexene to adipic acid at 75 °C.

Entry	Catalyst	Time (h)	Catalyst (g)	% Yield <sup>a</sup>
1	Catalyst 1	10	0.40	45
2	Catalyst 1	15	0.40	82
3	Catalyst 1	18	0.40	87 <sup>b</sup>
4	Catalyst 1	18	0.40	80 <sup>c</sup>
5	Catalyst 1	18	0.55	90
6	Catalyst 1	18	0.40	71 <sup>d</sup>
7	Catalyst 1	18	0.40	79 <sup>e</sup>
8	Silica sulphamic acid	18	0.24	N. R.
9	Silica@[BMIm] <sub>2</sub> WO <sub>4</sub>	18	0.40	N. R. <sup>f</sup>
10	[BMIm] <sub>2</sub> WO <sub>4</sub>	18	0.16	N. R.

<sup>a</sup> Yields refer to pure isolated product of adipic acid and gave satisfactory <sup>1</sup>HNMR and <sup>13</sup>CNMR spectra.

<sup>b</sup> The optimum reaction condition.

<sup>c</sup> Molar ratio of H<sub>2</sub>O<sub>2</sub>/CyH = 6.

<sup>d</sup> The catalyst washed with ethanol and was used in the second run.

<sup>e</sup> The catalyst washed with n-hexane and was used in the second run.

<sup>f</sup> The [BMIm]<sub>2</sub>WO<sub>4</sub> ionic liquid was supported onto the un-functionalized silica gel.

rigorous workup process and catalyst washing. More polar washing solvent (ethanol) leads to higher leaching of ionic liquid from the surface of the silica gel. In contrast, using n-hexane as washing solvent decreases the leaching of ionic liquid. Typically, when ionic liquids were supported in the form of physisorption methods, such as supported liquid phase (SLP), the maximum leaching of ionic liquids was observed [28]. In the next stage, background catalytic reactions were also explored. For the purpose of comparison, silica sulphamic acid not charged with ionic liquid and silica gel alone loaded with [BMIm]<sub>2</sub>WO<sub>4</sub> were examined under identical reaction conditions (Table 1, entries 8, 9). No adipic acid product was obtained in this reaction condition. Notably, no adipic acid product was obtained by using of homogeneous [BMIm]<sub>2</sub>WO<sub>4</sub> proving the crucial role of acidic media in obtaining catalytic activity toward oxidation of cyclohexene to adipic acid (Table 1, entry 10).

#### 4. Conclusion

In summary, we have developed a solvent and halide-free route to oxidation of cyclohexene to adipic acid. Safe, relatively clean and

operationally simple procedure is among the benefits of the current protocol. [BMIm]<sub>2</sub>WO<sub>4</sub> in combination with a heterogeneous acid catalyst results in an alternative reaction media and catalyst precursor which promotes the diffusion of both aqueous and organic reactants across the pores of the catalyst in the absence of any organic solvents and phase transfer catalysts. However, further developments of this novel concept are in progress in our laboratories.

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#### Appendix A. Supplementary data

Supplementary data (picture of the catalyst 1, thermogravimetric analysis, atomic absorption result of the catalyst 1, GC–MS analysis of adipic acid <sup>1</sup>H and <sup>13</sup>CNMR spectra of the ionic liquid and adipic acid) associated with this letter can be found in the online version. Supplementary data to this article can be found online at <http://dx.doi.org/10.1016/j.catcom.2012.04.031>.

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