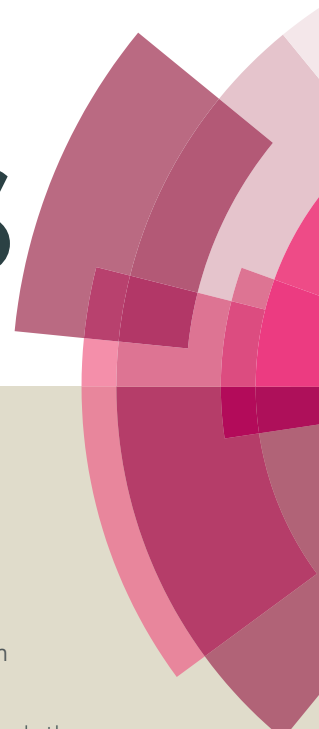


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ARTICLE TYPE

One pot oxidative cleavage of cyclohexene to adipic acid using silver tungstate nano-rods in Brønsted acidic ionic liquid

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A green and facile method for oxidation of cyclohexene to adipic acid is introduced using 30% H₂O₂ as oxidant. The catalytic system comprises small amounts of Ag₂WO₄ nano-rods and a Brønsted acidic ionic liquid (1,2-dimethyl-3-dodecylidazolium hydrogensulfate).

Adipic acid (1,6-hexanedioic acid) is an important building block which uses in the chemical industries for synthesise of polyamides, nylon-6,6, polyesters, polyurethane resins, as a plasticizer agent as well as an approved additive in fertilizers, lubricants, insecticides and in paper production.¹ This valuable compound which is ranked in top ten of the chemicals uses in the chemical industries mainly prepare *via* nitric acid oxidation of a cyclohexanone/cyclohexanol (KA oil) mixture in the presence of Cu^(II) and ammonium metavanadate catalysts.² Emissions of stoichiometric amounts of nitrous oxide (N₂O) accompanied by releasing of toxic copper^(II) as the reaction wastes are the major environmental drawback of the process. N₂O is a colorless greenhouse gas with a long atmospheric lifetime (approximately 120 years) and high heat trapping effects (about 310 times more powerful than CO₂ per molecule).³ It is also capable to destroy the ozone molecules and also contributes in acid rain.

Oxidative cleavage of cyclohexene with 30% hydrogen peroxide in an alternative way to avoid this “hazardous” synthetic pathway to reduce reaction wastes.⁴ In this method, hydrogen peroxide; the oxidant needs to be activated by using catalytic amount of a tungstate (WO₄²⁻) salt. The sources of the tungstate salt are mainly provided from sodium tungstate (Na₂WO₄·2H₂O),⁴ supported ammonium tungstate on the surface of the mesoporous materials,⁵ oxotungsten-containing SBA-15,⁶ surfactant-type peroxotungstates,⁷ mixture of H₂WO₄/H₂SO₄/H₃PO₄⁸ and H₃PW₁₂O₄₀.⁹ The use of H₂O₂ as a cheap oxidant with water as the sole by-product is a promising way. Unfortunately, in the hydrogen peroxide medium; reagents incompatibility including aqueous oxidant and organic substrate (cyclohexene) is the most challenging problem of the protocol. To overcome this drawback, recently we disclosed tungstate-based ionic liquids (ILs) for this reaction.¹⁰ Despite introducing both environmentally friendly reagents and improved efficiency, the catalytic systems based on tungstate-based ILs need for relatively high amounts of the expensive IL. Moreover, these methods did not show desirable reusability during the reaction which might be attributed to decomposition of the catalyst during the reaction.

Silver tungstate (Ag₂WO₄) is known as alternative oxide with various applications.¹¹ An interesting aspect of the Ag₂WO₄ is related to its crystalline structure. By exposure to the electron beams of an electronic microscope and under high vacuum, this compound undergo *in situ* nucleation of Ag filaments on the surface of the crystal.¹² Despite comprehensive structural studies, the catalytic properties of Ag₂WO₄ were not investigated well. In an interesting report, He and co-workers utilized Ag₂WO₄ as a bifunctional catalyst for the ligand-free carboxylation of terminal alkynes under atmospheric pressure of carbon dioxide at room temperature.¹³

Herein, we wish to introduce the application of Ag₂WO₄ for oxidation of cyclohexene to adipic acids in the presence of 1,2-dimethyl-3-dodecylidazolium hydrogensulfate (**IL 1**) as the catalyst. The applied IL provides the suitable acidic media which is necessary for the reaction. Moreover, it is miscible in both aqueous oxidant and organic phases of the starting materials.

The Brønsted acidic ionic liquid (BAIL) was prepared according to the known literature procedure with slight modifications.¹⁴ Ag₂WO₄ was simply synthesized by adding 0.009 M solution of Na₂WO₄·2H₂O to a freshly prepared 0.018 M solution of AgNO₃ at room temperature. After 1 h string at 1000 rpm, the precipitate was filtrated, washed with distilled water and dried in a dark place. FT-IR spectrum of Ag₂WO₄ showed a characteristic band with high intensity at 830 cm⁻¹ which is attributed to the W–O stretching frequencies^{12d} (See supporting information).

The Scanning electron microscopy (SEM) of Ag₂WO₄ is shown in Fig. 1. The as-synthesized Ag₂WO₄ crystals have a tetragonal needle/rod-like shape. A closer look on the crystalline structure of the Ag₂WO₄ rods reveals tiny particles on the surface (Fig. 1, a). This phenomenon may be attributed to the formation of [AgO₆] and metallic Ag *via* the nucleation and growth process from the various regions of the surface of Ag₂WO₄ during the exposure to electron beams of SEM microscope which proposed and identified by Longo *et al.*¹⁵ A uniform distributions of Ag and W atoms are observed in the structure of the Ag₂WO₄ in the elemental analysis maps for silver and tungsten (Fig. 1, b and c).

The activity of this catalytic system was tested for oxidative cleavage of cyclohexene to adipic acid (Table 1). In the acidic media, Ag₂WO₄ can slowly release WO₄²⁻ species during the reaction.¹⁶ The reaction comprises four steps oxidation and thus need at least four equivalents of H₂O₂. Routinely, 4.4 equivalents of hydrogen peroxide are used to ensure complete conversion of cyclohexene.

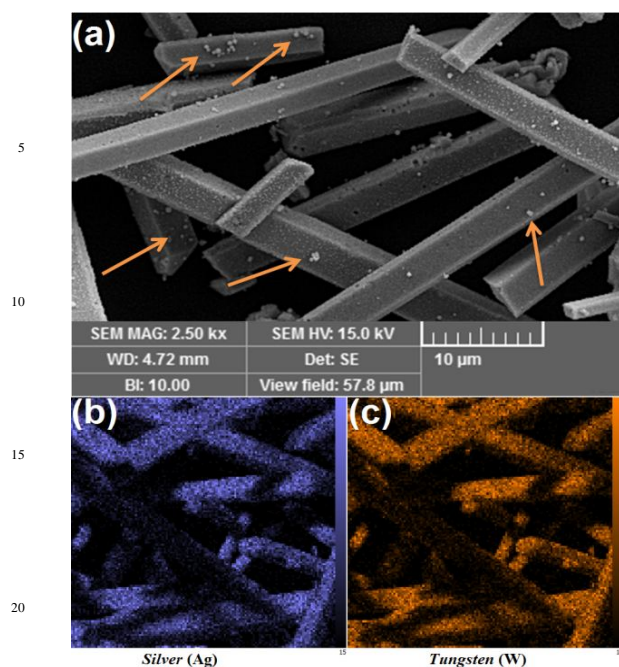


Fig. 1 Nucleation and growth of the silver particles on the surface of the Ag_2WO_4 after exposure to the SEM electron beam (a). Elemental distribution images for Ag (blue) and W (orange) utilizing SEM.

Table 1 The data of the catalytic performance for one pot oxidation of cyclohexene to adipic acid (AA).

Entry	Catalyst	IL	Temp. (°C)	Time (h)	AA (%) ^a
1	Ag_2WO_4	IL 1	r.t.	12	<5
2	Ag_2WO_4	IL 1	50	12	24
3	Ag_2WO_4	IL 1	75	12	57
4	Ag_2WO_4	IL 1	75	18	85
5	Ag_2WO_4	–	75	18	17 ^b
6	Ag_2WO_4	IL 1	75	18	70 ^c
7	Ag_2WO_4	–	75	18	–
8	–	IL 1	75	18	–
9	Ag_2WO_4	IL 1	75	18	89 ^d
10	Na_2WO_4	IL 1	75	18	84
11	CdWO_4	IL 1	75	18	67
12	Ag_2WO_4	[BMIm]HSO₄	75	18	73
13	Ag_2WO_4	[MOIm]HSO₄	75	18	80

^a Yields refer to isolated pure product of adipic acid and confirmed by ¹H NMR and ¹³C NMR. ^b 90 mg of H_2SO_4 was added in the absence of **IL 1**. ^c 6 equivalents of H_2O_2 was used as oxidant. ^d *t*-BuOOH was used as oxidant.

Since it would be wealthy that organic reactions conducted at ambient thermal condition, at the first step we set up an experiment at room temperature. However, no adipic acid product was obtained in this condition (Table 1, entry 1).

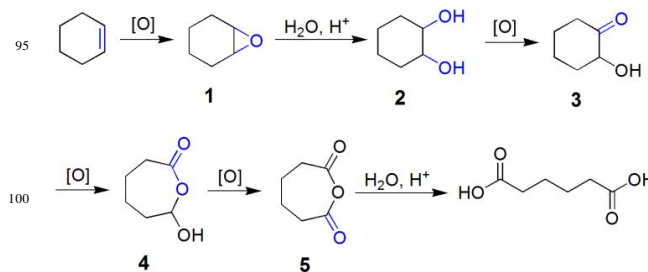
Increasing the reaction temperature to 50 °C for 12 h did not give a suitable yield of the adipic acid (Table 1, entry 2). It was found that when the reaction mixture was heated at 75 °C (at the reflux temperature of the reaction mixture), 57% of adipic acid was obtained (Table 1, entry 3). Hence, it was found that the reaction temperature is the key parameter for oxidation of cyclohexene to adipic acid in the current catalytic system. The highest yield of adipic acid was observed when the reaction was performed at 75 °C for 18 h (Table 1, entry 4) with more than 98% purity determined by gas chromatography (GC). Our further screening

revealed that 11% of 1,2-cyclohexanediol was also identified as the major intermediate at the end of reaction.

One of the roles of **IL 1** is providing a suitable acidic media for this reaction. The active catalytic species is monoprotonated peroxotungstate species which forms in a pH range 0.4–3.^{4,5} However, it was found that by replacement of **IL 1** by H_2SO_4 , despite providing suitable acidic medium for the reaction; the yield of the adipic acid was dropped to 17% which is attributed to poor miscibility of organic phase of starting materials and aqueous oxidant (Table 1, entry 5). Hence, in this method **IL 1** has dual catalytic functions: (i) providing acidic media for formation of monoprotonated peroxotungstate species in the reaction media and (ii) *N*-dodecyl hydrocarbon chain of **IL 1** provides a suitable balance between hydrophobicity/hydrophilicity for **IL 1**. In other words, the **IL 1** acts as a Brønsted acidic surfactant which is miscible in both organic and aqueous phases. Moreover, a significant decrease in adipic acid yield was observed when the amount of H_2O_2 reached to 6 equivalents which may be attributed to the effect of pH on the reaction efficiency at the higher ratio of hydrogen peroxide/cyclohexene. No adipic acid was obtained by using solely Ag_2WO_4 (Table 1, entry 7 or **IL 1** (Table 1, entry 8) at the optimized reaction conditions.

The effect of oxidant was also investigated for oxidation of cyclohexene to adipic acid. It was found that by using *t*-BuOOH, 89% of adipic acid could obtain in this condition (Table 1, entry 9). To make comparison with other sources of tungstate, the reaction was performed in the presence of Na_2WO_4 and CdWO_4 as catalyst (note: CdWO_4 is a toxic reagent. Therefore, particular care should be taken into consideration). The results indicated that Ag_2WO_4 has relatively identical efficiency compared to Na_2WO_4 (Table 1, entry 10) and superior activity to the CdWO_4 (Table 1, entry 11). To provide evidence about the effect of the imidazolium side-chain length on the reaction efficiency, the effect of various **IL** were studied at the next step (Table 1, entries 4, 12 and 13). It was found that by increasing the length of the *N*-alkyl in the imidazolium cation core of the **IL**, the yield of the adipic acid gradually increased. It can be concluded that the hydrophobic manner of the **IL** has a key role for improvement the product of adipic acid.

A proposed mechanism for oxidation of cyclohexene to adipic acid is shown in Scheme 1. The mechanism comprises (i) conversion of cyclohexene to 1,2-epoxycyclohexane **1** (ii) formation of 1,2-cyclohexanediol **2** (confirmed by GC) (iii) oxidation of the resulted diol to 2-hydroxycyclohexanone **3** and then 7-hydroxyoxepan-2-one **4**.



Scheme 1 Proposed mechanism for oxidation of cyclohexene to adipic acid.

Formation of the adipic anhydride **5** is the last intermediate which in the acidic media can readily undergo ring opening to produce adipic acid.

Table 2 provides comparison between our work and some of the previously reported methods for oxidation of cyclohexene to adipic acid using various oxidant and reaction condition parameters. From them, H₂O₂ is known as the most popular, cheap and green oxidant. Although the catalytic activity of SBA-15@Ti-Al in the presence of *t*-BuOOH as oxidant did not show suitable efficiency, InCl₃.*t*-BuOOH has relatively better catalytic activity at higher temperature (Table 2). RuCl₃/NaIO₄ seems to be the most efficient catalyst which can perform oxidation of cyclohexene to adipic acid at room temperature with short reaction time. However, the major drawback for this reaction is that RuCl₃ is a very expensive catalyst. Moreover the applied oxidant is not a green reagent. Consequently, the current work is ranked among the top of the most efficient and practical methods which have been introduced for synthesis of adipic acid *via* oxidative cleavage of cyclohexene.

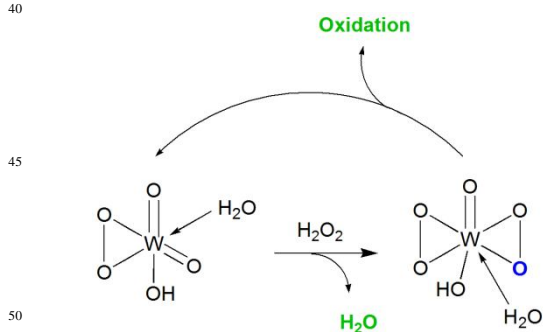
Table 2 Comparison among the results obtained from various methods for the oxidation of cyclohexene to adipic acid (AA).

Catalyst	Oxidant	Time(h)/Temp.(°C)	AA (%)	Ref.
Ag ₂ WO ₄ - IL 1	H ₂ O ₂	18 / 75	85	This work
[C ₁₆ H ₃₃ N(CH ₃) ₃] ₂ W ₂ O ₃ (O ₂) ₄	H ₂ O ₂	20 / 90	77.8	7
SSA@[BMIm]WO ₄ ²⁻	H ₂ O ₂	18 / 75	87 ^a	10a
SBA@Ti-Al	<i>t</i> -BuOOH	48 / 80	80	17
ML-101	H ₂ O ₂	8 / 70	90	18
InCl ₃	<i>t</i> -BuOOH	9 / 90	92	19
RuCl ₃	NaIO ₄	0.5 / r.t.	90	20

^a SSA is: Silica-sulfamic acid.

The possibility of reusability of the catalytic system was also investigated. In this regard, after the separation of adipic acid from the first reaction run, the remained solution was concentrated and subjected to another reaction at the optimized reaction condition (Table 1, entry 4). After the reaction termination and product isolation, 80% of pure adipic acid was obtained in this condition.

The aim of preparing of “2-CH₃” imidazolium ionic liquid is to prevent partially oxidation of the ionic liquid by H₂O₂ since the “2-H” position of the imidazolium specie is sensitive in the applied oxidizing condition. Details of the reaction mechanism are not clear. However, it is proposed that the active forms of catalyst are peroxotungstate species which were formed in the acidic media. It is believed that most of the catalyst could recover in the form of peroxotungstate. The proposed active form of the catalyst is shown in Scheme 2.



Scheme 2 The proposed active form of the catalyst in the acidic media.

FT-IR spectrum of the recovered Ag₂WO₄-**IL 1** was shown the distinct peak at 858 cm⁻¹ (see supporting information). This indicates the presence of the W–O bond which exists in both tungstate and peroxotungstate species.

Conclusions

The catalytic ability of Ag₂WO₄ was introduced for one pot oxidative cleavage of cyclohexene to adipic acid. It was shown that high yield of pure adipic acid could obtain at 75 °C in the presence of a Brønsted acidic ionic liquid (**IL 1**). Although ILs have some degree of environmental limitations for applications,²¹ this method was introduced as a significantly less hazardous protocol for replacement of the current synthetic procedures. The applied oxidant is cheap and commercially available with water as the sole by-product of the reaction. The reaction could conduct without special methodology or precautions. The reusability of the catalyst was also investigated and showed high efficiency for the recovered catalyst. Detail studies on the reaction mechanism, kinetic and applications of this catalytic system for oxidation of various organic compounds are ongoing in our laboratory.

Experimental

General

All chemicals and solvents were purchased from the Fluka and Merck and used without further purification. ¹H and ¹³C NMR spectra were determined on the Bruker DRX 500 MHz. 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. The Scanning electron microscopy (SEM) images were obtained by KYKY-EM 3200 with maximum acceleration voltage of the primary electron between 20 and 25 kV. The SEM samples were prepared by dispersion of the Ag₂WO₄ nano-rods on the surface of the gold film.

Preparation of **IL 1**

In a typical procedure, 20 mmol of 1,2-dimethylimidazol and 22 mmol of 1-bromododecane were refluxed in toluene for 8 h. The white precipitate was collected and washed separately with toluene and diethyl ether to produce 1,2-dimethyl-3-dodecylidazolium bromide. The anion exchange was performed by adding equimolar amount of H₂SO₄ in the super dry toluene. After 16 h, the solvent was evaporated and the **IL 1** was isolated as viscous oil and dried in oven in the presence of P₂O₅. ¹H NMR (500 MHz, CDCl₃): 0.86 (t, 3H), 1.22-1.27 (m, 18H), 1.73 (broad, 2H), 2.63 (s, 3H), 3.85 (s, 3H), 4.09 (t, 2H), 7.28 (s, 1H), 7.50 (s, 1H), 7.50-8.00 (broad, 1H). ¹³C NMR (125 MHz, CDCl₃): 11.39, 14.46, 23.02, 26.75, 29.42, 29.66, 29.74, 29.86, 29.93, 30.26, 32.24, 36.64, 49.41, 121.50, 123.55, 144.09.

Typical procedure for oxidation of cyclohexene to adipic acid:

A mixture of 50 mg Ag₂WO₄, 5.00 g of 30% H₂O₂ and 0.2 g of **IL 1** was added into a round-bottomed flask and stirred at room temperature for 10 min. Then, 1 mL cyclohexene (0.82 g~10 mmol) was added and the mixture was heated at 75 °C for 18 h.

At the end of reaction, the slurry was cooled to room temperature and then placed at 4 °C overnight. The resulting solid was collected *via* vacuum filtration and washed with small portion of cold water and dried to afford pure adipic acid in 85% yield. ¹H NMR (500 MHz, DMSO-d₆): 1.50 (t, 4H), 2.21 (t, 4H) and 12.00 (s, 2H). ¹³C NMR, DMSO-d₆): 24.9, 34.2, 175.2.

Notes and references

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† Electronic Supplementary Information (ESI) available: FT-IR of Ag₂WO₄, recovered Ag₂WO₄-IL I, Large-size SEM of Ag₂WO₄ and Large-size SEM of the elemental analysis of Ag₂WO₄ related to the Fig. 1.

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