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Dicationic Ionic Liquids/Heteropoly AcidComposites as Heterogeneous Catalysts for Cyclohexene Oxidation with Molecular Oxygen under Solventfree Condition: Insights from Theory and Experiments

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Graphical Abstract



Highlights

- Dicationic ionic liquids/heteropoly acid composites as heterogeneous catalysts.
- Molecular oxygen and cyclohexene oxidation under solvent-free conditions.
- DIL-L/W composite as the best catalyst and 96% conversion of cyclohexene.
- Semi-empirical method and the interaction energy of TPA with DILs.

Abstract

This study describes solvent-free oxidation of cyclohexene using dicationic ionic liquids (DIL)/heteropoly acid (HPA) composites with molecular oxygen. Structural characterization of the DIL/HPA composites was carried out by different techniques such as ICP, FT-IR, ¹H NMR, BET, TGA, XRD, FESEM, EDX and TEM. Characterization results confirmed that heteropoly acids i.e., tungstophosphoric (H₃PW₁₂O₄₀, TPA) and molybdophosphoric acid (H₃PMo₁₂O₄₀, MPA) were incorporated with DILs without distortion of the Keggin structure of the heteropoly acids. Two different dicationic ionic liquids with linear and aromatic linkage, DIL-L and DIL-A, were prepared and applied for synthesis of the composites. Effective parameters including the effect of temperature, time, oxygen pressure, amount of the selected catalyst, i.e., DIL-L/tungstophosphoric acid was thoroughly investigated. The catalyst was found to be stable and recyclable. The main product of the reaction was cyclohexene-2-one (Cy-one) at 70 °C and 15 bar oxygen pressure after 6 h. Additionally, theoretical calculations at the PM6 semi-empirical method was performed on DILs/HPA complexes with different number of DIL molecules to explore the capacity of HPA in interaction with DILs and obtained the orientations of DILs around the Keggin oxoanion of the HPA. The calculations showed that the maximum number of DIL molecules around the $[H_2PW_{12}O_{40}]^-$ oxoanion was five and the interaction of DIL-L with the oxoanion was stronger than that of DIL-A which was in agreement with the experimental data.

Keywords: Oxidation; Cyclohexene; Heteropolyacid; Dicationic ionic liquid; Bis(imidazolium)compounds; Heterogeneous catalyst.

1. Introduction

Oxidation of unsaturated hydrocarbons on the allylic and the double bond positions are very important transformations in synthetic organic chemistry because of the importance of the products as valuable commercial intermediates [1-3].

Cyclohexene as an important petrochemical resource, in the oxidation process could undergo provoking olefinic oxidation at the double bond in addition to allylic oxidation. Therefore, it is reasonable to expect that due to the tendency of the oxidant for the allylic position as well as for the double bond position in the reaction medium, the reaction will end up with the formation of the allylic oxidation products, i.e., 2-cyclohexen-1-one (Cy-one) and 2cyclohexen-1-ol (Cy-ol) [1,4-8], or epoxidation products i.e., cyclohexene epoxide and 1,2cyclohexanediol (CyH-diol) [9,10]. It is known that the type of oxidant used in the reaction could conduct the reaction to the specific products [11-13]. It is believed that by using hydrogen peroxide, NaOCl, KHSO₅ and PhIO the oxidation occurs at the double bond position, and by using the bulky oxidants such as tert-butyl hydroperoxide (TBHP) because of the steric hindrance of the bulky *tert*-butyl group, the oxidation would occur at the allylic position of the cyclohexene [14-16]. Mechanistically, there is a hypothesis that allylic oxidation occurs through a free-radical chain reaction route [17]. Reported data in the literatures [18-20] have emphasized that the metallic species which are in a low oxidation state follow up the free-radical pathway. On the other hand, the oxometallic reagents with higher oxidation states, such as the catalyst reported in this work, i.e., W=O or Mo=O are prone to facilitate the double bond oxidation because these type of transition metals by having empty d-orbitals could accept electron pairs from oxidant (hydrogen peroxide, molecular oxygen, etc) and increasing the electrophilic nature of the oxidant and becoming liable to be attacked by the π -electrons of the olefinic substrate [21].

It should be mentioned that in the cases where one observes the allylic and double bond oxidation products both mechanisms could occur simultaneously.

The basic feature of the parameters that govern the regioselectivity of a catalyst is a fundamental question. To best of our knowledge, in the oxidation of cyclohexene the key reactions to be mentioned are the allylic and double bond oxidation. Different catalysts give different ratio of allylic and double bond oxidation products, and the ratio of C-H/double bond oxidation is more than one in most cases. The present paper addresses the regioselectivity problem by shifting this ratio to one extreme, i.e., predominantly oxidizing the allylic position. In this respect, we decided to monitor the effect of environment of Keggin oxoanion on its catalytic performance [18]. It should be mentioned that many Keggin oxoanion-based ionic hybrid composites have been used as heterogeneous catalysts. For example, Wang and his co-workers used a family of HPA/dicationic-IL composites as reusable catalysts for hydroxylation of benzene [22] and esterification [23]. Moreover, Leng, et al., have used a mesoporous amphiphilic HPA/dicationic-IL as a highly efficient epoxidation catalyst [24]. However, dissolution of HPA-IL composites in some common oxidants such as H_2O_2 is a drawback for these hybrid composites as desirable liquid-solid heterogeneous catalysts in oxidation reactions [25, 26].

In this context, we had this in mind to disperse polyoxometalates of the used heteropoly acids without losing a large extent of their oxidative sites by supporting them on a solid support [19,20,27]. Therefore, we precipitated the water soluble tungstophosphoric and molybdophosphoric acids with two different dicationic ionic liquids (DILs), **1** and **2**. We think that a uniform dispersion of the oxoanions between the DILs and increasing their hydrophobicity might be considered as the main reason responsible for the high catalytic performance of the prepared catalysts.

Our semi-empirical calculations have shown that each oxoanion unit could hold maximum of five DIL molecules electrostatically around itself and the interaction of DIL-L with the $[H_2PW_{12}O_{40}]$ oxoanion was stronger than that of DIL-A.

2.Experimental

1. Materials

Triphenylphosphine was obtained from Fluka. Bromine and 1,4-dibromobutane were purchased from Sigma-Aldrich. All other necessary chemicals such as 1,4bis(hydroxymethyl)benzene, silica-gel, 1-methylimidazole, tungstophosphoric acid (TPA), molybdophosphoric acid(MPA) and cyclohexene were purchased from Merck Company. Molecular oxygen (99.99 %) was obtained from Argon Company (Iran). All solvents used in this study such as CCl₄, EtOH and acetonitrile were analytical grade.

2.2. Characterization Techniques

The products were characterized by FT-IR, ¹H NMR, GC, GC-MS, FESEM-EDX, TEM, BET, ICP-OES and XRD techniques which they are described in the supporting information.

2.3. Preparation of the Catalysts

2.3.1. Synthesis of 1,4-Bis(bromomethyl)benzene, 3,3'-(Butane-1,4-diyl)bis(1-methyl-1Himidazol-3-ium) bromide and 3,3'-(1,4-Phenylenebis(methylene))bis(1-methyl-1H-imidazol-3ium) bromide

The procedures for synthesis of 1,4-Bis(bromomethyl)benzene,3,3'-(Butane-1,4diyl)bis(1-methyl-1H-imidazol-3-ium) bromide and 3,3'-(1,4-Phenylenebis(methylene))bis(1methyl-1H-imidazol-3-ium) bromide have been described in the supporting information, and structures of both products were confirmed by FT-IR and ¹H NMR techniques (Figs S1-S3).

Henceforth, the 3,3'-(butane-1,4-diyl)bis(1-methyl-1H-imidazol-3-ium) dibromide and 3,3'-(1,4-phenylenebis(methylene))bis(1-methyl-1H-imidazol-3-ium) dibromide are denoted as **DIL-L** (1) and **DIL-A** (2), respectively (Scheme 1).

(*a***)**



DIL-L = 3,3'-(Butane-1,4-diyl)bis(1-methyl-1H-imidazol-3-ium) dibromide



DIL-A= 3,3'-(1,4-Phenylenebis(methylene))bis(1-methyl-1H-imidazol-3-ium) dibromide

Scheme 1. Preparation of the (a) DIL-L (1) and (b) DIL-A (2).

2.3.2. Preparation of 3,3'-(Butane-1,4-diyl)bis(1-methyl-1H-imidazol-3-ium)/Heteropoly acid and 3,3'-(1,4-Phenylenebis(methylene))bis(1-methyl-1H-imidazol-3-ium)/Heteropoly acid Composites [DIL-L/W(Mo) and DIL-A/W(Mo)]

For preparation of DIL-L/tungstophosphoric acid (DIL-L/TPA), and DIL-L/molybdophosphoric acid (DIL-L/MPA) catalysts, 0.1 g (0.263 mmol) of DIL-L was dissolve in 2 mL of DI water and an aqueous solution of 0.076 g (0.026 mmol) [or 0.15 g (0.05 mmol), or 0.3 g (0.1 mmol)] TPA or 0.048 g (0.02 mmol) [or 0.096 g (0.05 mmol)] MPA in 2 mL of DI water was slowly added to it. Then, the solid was separated by filtration, dried at room

temperature and renamed hereafter as DIL-L/W(x) or DIL-L/Mo(x), respectively; the number in parenthesis shows the weight percentage of the metal in the catalyst.

To prepare DIL-A/tungstophosphoric acid (DIL-A/TPA) and DIL-A/molybdophosphoric acid (DIL-A/MPA) catalysts, 0.1 g (0.234 mmol) of DIL-A was dissolved in 2 mL of DI water and an aqueous solution of 0.067 g (0.026 mmol) [or 0.134g (0.05 mmol)] TPA or 0.085 g (0.05 mmol) MPA in 2 mL of DI water was slowly added to it. The resulting solid was separated by filtration, dried at ambient temperature and renamed hereafter as DIL-A/W(x) or DIL-A/Mo(x), respectively; the number in parenthesis shows the weight percentage of the metal in the catalyst (Scheme 2).

2.3.3. General Procedure for Oxidation of Cyclohexene

A 50 mL titanium batch reactor was charged with cyclohexene (2 mL) and the catalyst (20 mg). The desired pressure (15 bar) was provided with oxygen and the selected temperature was set [28]. Reaction was carried out under solvent-free condition at the selected temperature. After performing the reaction for the preset time and cooling the reactor, the mass balance was checked. Then, after separating the catalyst products were analyzed quantitatively by GC using p-xylene as internal standard. The yield of 2-cyclohexene-1-one was defined as the ratio of theweight of 2-cyclohexene-1-one, as determined by GC, to the weight of 2-cyclohexene-1-one theoretically produced upon oxidation of cyclohexene; the products were identified by GC-Mass (Scheme 3).



Scheme 2. Synthesis of DIL-L/W(Mo) and DIL-A/W(Mo).



Scheme 3. Oxidation of cyclohexene in the presence of DIL-L/W composite.

3. Results and Discussion

3.1. Characterization of the Synthesized Catalysts

In the next sections we will show that the DIL-L/W(33) was the preferred catalyst on the basis of the conversion, selectivity and cost-effective. Therefore, we mainly concentrated on characterization of this catalyst. The DIL-L/W(33) catalyst was prepared by electrostatic interactions between the DIL-L and the oxoanion of the TPA $[PW_{12}O_{40}]^n$. Scheme 2 shows the synthetic route for formation of the $[DIL]_n^{2+}[H_mPM_{12}O_{40}]^n$. The metal content of the catalyst before and after the catalytic reaction was measured by atomic absorption spectroscopy ICP-OES; as shown in the reusability experiments and in agreement with data of FESEM and XRD analysis, the catalyst probably reaches to its best TPA/DIL ratio, and in this process loses a fraction of ionic liquid which affects on the reusability of the catalystby becoming less hydrophilic and in a way its contact with cyclohexene decreases. The EDX data and EDX mapping show the presence of metal ions, phosphorous and nitrogen in the fresh and reused catalyst (Fig. 1).

The FESEM images of the fresh DIL-L/W(33) catalyst and after 4 runs are shown in Fig. 1 with four different magnifications and particle size distribution histogram of 200 nm scale. According to these images, the fresh catalyst (Fig. 1a) is composed of spherical nanoparticles with an average size of around 35 nm. The morphology of the catalyst after 4 runs completely changes, and in agreement with XRD of the reused catalyst (Fig. 3g), crystallinity of the catalyst improved to a large extent.



Fig. 1. FESEM images of (a) fresh DIL-L/W(33) and reused DIL-L/W(33) at magnification of 200 nm, 500 nm and 1 μ m and EDX confirmation of the presence of W element and elemental mapping images (inset).

The companionship of phosphotungstate anion with DIL-L and formation of the DIL-L/W as catalyst was confirmed by EDX analysis. According to the elemental mapping analysis the elements of C, N, O, Br, P and W have been discovered with a homogeneous distribution of P and W on the catalyst (Fig. 1).

The significant stretching vibrations of the prepared catalyst and its components have been helpful for identification of the catalyst. Fig. 2 shows the IR spectra of the DIL-L, TPA, DIL-L/W(33) and reused DIL-L/W(33) catalyst after four runs; we have also measured the IR spectra of the DIL-A/W(Mo) composites which are shown in Fig. S4. In the spectrum of DIL-L the broad peak at 3500 cm⁻¹ is attributed to the –OH stretching of the moisture presents in the hydrophilic DIL-L, and the peaks at 3145 and 3073 cm⁻¹ are assigned to the C-H stretching of the imidazolium rings. Also the peaks in the region of 2862-3000 cm⁻¹ are attributed to the aliphatic stretching vibrations. Moreover, the peaks at 1632, 1577 cm⁻¹ and 1158 cm⁻¹ were ascribed to the breathing vibrations of C=N and C-H out-of-plane bending vibrations of the imidazolium rings, respectively (Fig. 2a). TPA has four characteristic bands which are appeared in the range of 800-1100 cm⁻¹. These peaks have been observed at 804, 891, 982 and 1079 cm⁻¹that are attributed to edge shared oxygen (W-O_c-W), corner shared asymmetric oxygen(W-O_b-W), terminal asymmetric oxygen (W=O_d) and terminal asymmetric oxygen (P-O_d), respectively (Fig. 2b) [24]. For DIL-L/W(33) catalyst these peaks are located at 803, 895, 976 and 1078 cm⁻¹, so that the red shift observed in the peak corresponding to W=O_d bond probably suggests the existence of an electrostaticinteraction between oxygen of the W=O_d bond in the Keggin oxoanion with the positive charge of the imidazolium ring of the surrounding ionic liquids [29, 30].



Fig. 2. FT-IR spectra of (a) DIL-L, (b) TPA, (c) DIL-L/W, (d) reused DIL-L/W, (e) MPA and (f) DIL-L/Mo.

The XRD patterns of the pure H₃PW₁₂O₄₀ (TPA), DIL-L and DIL-L/W catalysts with different molar ratios of TPA are illustrated in Fig. 3. Clearly one could see that H₃PW₁₂O₄₀ displayed a set of well resolved sharp diffraction peaks, Fig. 3b. As mentioned, we prepared three different samples of the catalyst with different ratios of DIL-L/TPA (33, 46 and 57 wt% of the metal), Figs.(3d-f). As can be seen, obviously by decreasing the amount of TPA in the composite the crystallinity of the composite increases, and more interesting in Fig. 3g which belongs to the reused catalyst the crystallinity has improved a large extent; .What do we understand from these changes? We think by decreasing the amount of TPA in the composite,

the ratio of oxoanion and the ionic liquid reaches to the optimum value to form a thermodynamically stable crystal.



Fig. 3. XRD pattern of (a) DIL-L (support), (b) TPA, (c) a+b, (d) DIL-L/W(33), (e) DIL-L/W(46), (f) DIL-L/W(57) and (g) reused DIL-L/W(33).

The TEM images of the DIL-L/W(33) catalyst sample are presented in Fig. 4 which shows a 2D microstructure composed of nanoparticles. The approximately spherical nanoparticles were compact and did not show any porous network.



Fig. 4. TEM images of DIL-L/W(33) at different magnifications.

The specific surface area of 30 (m²/g), pore volume of 0.126 (cm³/g) and pore diameter of 2.5 nm for the DIL-L/W(33) catalyst was obtained using nitrogen adsorption-desorption isotherm (Table 1) which indicates the presence of macropores in the prepared catalyst, and reasonable surface area of the catalyst might be due to nano-size of the crystalline composite (Fig. 5). Moreover, the nanoparticles became smaller after a few runs of oxidation reaction because of leaching of TPA from the catalyst.

Table 1. Textural Properties of DIL-L/W(33)						
Catalyst	$S_{BET} (m^2/g)$	V_{pore} (cm ³ /g)	D _{pore} (nm)			
DIL-L/W(33)	30	0.126	2.5			



Fig. 5. N₂ adsorption (▲) and desorption (■) isotherm of DIL-L/W(33) and dBJH-Plot pore size distribution (inset).

The thermogravimetric curve of the DIL-L/W(33) catalyst has been depicted in Fig. S5.

3.2. Theoretical Calculations

In this part, theoretical calculations were used to explore the capacity of the oxoanion to be surrounded by the DIL molecules. The TPA is a strong acid with three acidic hydrogen atoms which could produce three anionic forms such as TPA⁻, TPA²⁻ and TPA³⁻in aqueous solution. The pK_a values of the TPA are 1.6, 3.54 and 7.16, respectively [31]. Therefore, it is expected that the dominant anionic form of TPA in water is TPA⁻. There were a few questions that we were encourage for performing the following calculations in this work including (1) to obtain the correct orientation of DILs around TPA⁻ oxoanion (2) calculating the maximum number of interacting DILs and (3) predicting the change in the interaction energy per each DIL unit that interacting with the TPA⁻ oxoanion. The semi-empirical PM6 method [32] was used for the

optimization of the structures and the calculations of the interaction energies. The reason for choosing of this method was the size of TPA⁻ oxoanion and the size of the DIL molecules. The composite of TPA⁻ with different number of DIL molecules were optimized, separately. Fig. 6 displays the optimized structures of $[(DIL-L)_n/TPA^-; n=4, 5 \text{ and } 7]$ composites. The other optimized structures of the [(DIL-L)_{n=1-3}/TPA⁻] composites have been shown in Fig. S6. The optimized structures of the $[(DIL-L)_{n=1-3}/TPA^{-}]$ show that the DIL-L molecule prefers to have a conformer with the two imidazolium rings near the TPA⁻ oxoanion to create desire electrostatic interactions with the oxygen atoms of the oxoanion. By adding the 4th DIL-L to [(DIL-L)₃/TPA⁻] to form [(DIL-L)₄/TPA⁻] it also acts like other DILs. The optimized structure of [(DIL-L)₅/TPA⁻] shows that two of the DIL-Ls have vertical positions relative to the TPA⁻. The trend of increasing the number of DILs was continued and our calculations showed that by increasing the number of DILs molecules the oxoanion loses some of its electrostatic interactions with the previously anchored DILs to open room for other DIL molecules while keeping three DIL molecules very close to it. The optimized structure of the [(DIL-L)7/TPA-] shows four DIL-Ls in vertical orientation relative to TPA⁻ and the other three DIL molecules had maximum interactions with oxoanion (Fig. 6c). It is interesting to notice that the distance between two of them and the TPA⁻ oxoanion is considerably higher than the others.



Fig. 6. The optimized structures of $[(DIL-L)_n/TPA^-; (a) n=4, (b) n=5 and (c) n=7].$

Similar calculations were performed on $[(DIL-A)_{n=1-5}/TPA^-]$ structures and their optimized structures have been demonstrated in Fig. S7. It should be mentioned that the presence of the aromatic linkage between two imidazolium rings in the DIL-A reduces the flexibility of the molecule for the interaction with the TPA⁻. Comparison of the optimized structure of the $[(DIL-L)_2/TPA^-]$ with that of $[(DIL-A)_2/TPA^-]$ confirmed this prediction. The orientation of the DILs relative to TPA⁻oxoanion in the optimized structure i.e., $[(DIL-A)_4/TPA^-]$ is considerably different from that observed in the optimized structure of the $[(DIL-L)_4/TPA^-]$ composite. One of the DILs has vertical orientation relative to TPA⁻ in $[(DIL-A)_4/TPA^-]$ unlike to what is seen in the $[(DIL-L)_4/TPA^-]$. Generally, electrostatic interaction of the DILs with TPA⁻in the vertical position was lower than this interaction with the conformer that the two imidazolium rings facing the TPA⁻ oxoanion. Moreover, similar calculations were performed on TPA²⁻ and TPA³⁻ and the same optimized structures were obtained for the interaction of different numbers of DIL-L or DIL-A molecules which show that the optimized structures are independent of the charge on TPA oxoanion (not reported).

In these calculations the interaction energy between the TPA⁻ and different numbers of DILs was obtained using the following equation:

$\Delta E = E_{\text{complex}} - E_{\text{TPA}} - E_{\text{DILs}}$

Where E_{complex} is the total electronic energy of TPA⁻ interacting with DILs, E_{TPA} is the electronic energy of the oxoanion and E_{DILs} is the total electronic energy of DILs, interacting with each other in the absence of TPA⁻. Fig. 7 demonstrates the variation of the interaction energy per each DIL unit ($\Delta E/n$) versus the number of DILs for both DIL-L and DIL-A. It can be seen that by increasing the number of DILs, the value of ($\Delta E/n$) becomes more positive for both DIL-L and DIL-A molecules. In regard to Fig. 7, there are two important points that should be emphasized:

(1) the interaction of TPA⁻ with DIL-L is stronger than that of DIL-A (2) the interaction of TPA⁻ reaches to a saturated value of around n=6 and n=5 for $[(DIL-L)_n/TPA^-]$ and $[(DIL-A)_n/TPA^-]$, respectively.



Fig. 7. Variation of the interaction energy/DIL unit ($\Delta E/n$).

3.3. Catalytic Performance of the Prepared Catalysts

The effect of temperature on the oxidation of cyclohexene over the various prepared catalysts was studied by changing the temperature from 60 °C to 100 °C while the other parameters were fixed. The results of oxidation with molecular oxygen in regard to conversion and selectivity are summarized in Fig. 8. At 60 °C, the catalysts containing molybdenum did not react with cyclohexene although the catalysts containing tungsten show a moderate conversion

and selectivity to 2-cyclohexene-1-one; less than 2% cyclohexene oxide was detected at this temperature. In the other extreme, i.e., at 100 °C the catalysts having phosphomolybdate demonstrated an excellent conversion and selectivity to 2-cyclohexene-1-one but the catalysts containing TPA undergoover-oxidation. This could be due to the higher activity of the tungstophosphoric acid among the Keggin series of HPAs. Moreover, at 70 °C only the DIL-L/W shows considerable selectivity to the main product. At 80 °C all of the catalysts exhibited a high conversion and selectivity.



Fig. 8. Influence of the reaction temperature on the cyclohexene oxidation. Reaction conditions: cyclohexene 2 mL; different catalysts DIL-L/W(Mo)(46) and DIL-A/W(Mo)(46) 20 mg; 15 bar O_2 ; 6 h under solvent free.

As shown in the Fig. 9, the time of the reaction evidently had a significant effect on the DIL-L/W(Mo)(46) and DIL-A/W(Mo)(46) catalytic selectivity of the reaction although the conversion was high in all of the reactions specially for DIL-L/W and DIL-A/W catalysts. When employing the DIL-L/W(46) catalyst for 4 h, a desirable conversion of cyclohexene was achieved with 98% total selectivity for 2-cyclohexene-1-one such that the yield of this product was over 90%. By increasing the time of reaction to 8 h, clearly the DIL-L/W catalyst exhibited the best performance. Finally, on the basis of the presented data the 6 h was chosen as the optimum time for the reaction.



DIL-L/Mo= L-Mo DIL-L/W= L-W DIL-A/Mo= A-Mo DIL-A/W= A-W

Fig. 9. Influence of the reaction time on the cyclohexene oxidation. Reaction conditions: cyclohexene 2 mL; different catalyst (DIL-L/W(Mo)(46) and DIL-A/W(Mo)(46) 20 mg; 15 bar O_2 ; under solvent free.

On the basis of the presented data we did choose the DIL-L/W as the selected catalyst. In this respect to demonstrate the effect of the weight percentage of the phosphotungstate in the DIL-L/W catalyst for oxidation of cyclohexene, the amount of TPA was varied from 33 wt% to 57 wt% while the other parameters were kept constant. The results on the conversion of cyclohexene and selectivity to 2-cyclohexene-1-one are summarized in Table 2. Clearly, by increasing the percentage of TPA in the composite of the DIL-L/W catalyst the conversion starts decreasing which might be related to agglomeration of the catalyst.

Fig. 10 demonstrates the effect of the initial oxygen pressure on the oxidation of cyclohexene over the DIL-L/W(33) catalyst. It is clear that by increasing the initial O_2 pressure conversion increased but the selectivity to the main product decreased to some extent. In this respect, one could imagine that the reaction site has changed toward the oxidation of the double bond position. Also by increasing the pressure from 15 to 20 bars, conversion decreased which might be ascribed to the "saturation" of the exposed catalytic sites at higher O_2 pressures [5,33,34]. Therefore, by considering the conversion of cyclohexene and the selectivity for 2-cyclohexene-1-one, 15 bar was chosen as the optimal initial oxygen pressure.

Entry	Catalyst	Т	W	Conv.	Selectivity (%)		
		(°C)	(wt%)	.(%)	Cy-ol	CyH-diol	Cy-one
1	DIL-L	80	-	34	2	2	96
2	DIL-L/W	80	57	84	-	6	94
3	DIL-L/W	80	46	89	-	17	83
4	DIL-L/W	80	33	94	5	-	95
5	DIL-L/W*	80	33	21	14	41	45
6	DIL-L/W**	80	33	N.R.	*	*	*
7	DIL-L/W	70	33	96	-	14	86

Table 2. Influence of the weight percent of tungsten in DIL-L/W and reaction media on cyclohexene oxidation

Reaction condition: cyclohexene 2 mL; catalyst 20 mg; 15 bar O₂; 6 h; 80 °C and 70 °C under solvent free condition.

*In the presence of acetonitrile 5 mL

**In the presence of acetic acid 5 mL



Fig. 10. Influence of the O_2 pressure on the cyclohexene oxidation. Reaction conditions: cyclohexene 2 mL; DIL-L/W(33) 20 mg; 70 °C under solvent free; 6 h.

The effect of amount of catalyst for oxidation of cyclohexene was studied by varying the amount of DIL-L/W(33) catalyst from 10-30 mg while the other parameters were fixed (Fig. 11).



Fig. 11. Influence of the catalyst amount on the cyclohexene oxidation. Reaction conditions: cyclohexene 2 mL; 15 bar O_2 ; 6 h under solvent free,70 °C.

The results reveal the increase of conversion when the amount of catalyst was 20 mg and by enhancing its amount to 30 mg no remarkable change was observed in the conversion of the reaction. Therefore, 20 mg of the catalyst was taken as optimum amount of the catalyst.

The effect of solvent on the oxidation of cyclohexene over the DIL-L/W catalyst was studied to reach to a better understanding of the catalytic system. The used HPAs are soluble in water but they precipitate in the presence of the dicationic ionic liquids prepared in this work which it could mean that in this trend the hydrophilicity of the HPA has decreased to a large extent and perhaps should be more compatible with the cyclohexene as a hydrophobic substrate. If this is true one would expect that by increasing the polarity of the media the interaction between the substrate and the catalyst should decrease appreciably. In this respect, acetonitrile and glacial acetic acid were chosen as the media of the oxidation reaction. In each case, the oxidation reaction was performed by 5 mL solvent and 2 mL cyclohexene while other parameters were fixed and similar to solvent-free reactions. As shown in Table 2 (entries 5 and 6) the reaction did not occur in acetic acid, and the conversion and selectivity were unsatisfactory when the reaction was performed in acetonitrile.

And finally, in this catalytic reaction the formation of peroxo species of the metal (W or Mo) is proposed as the key intermediate in the first step. In the second step, coordination of the double bond to metal causes oxidation of the cyclohexene in different positions. Perhaps the water that might be present in the catalyst converts the produced cyclohexene epoxide with the help of acidic property of the TPA to 1,2-cyclohexanediol.

3.4. Reusability of the Catalyst

The reusability of the catalyst was examined by recovering the catalyst from the reaction mixture and used in the next run. Before using the catalyst in the next run, it was washed with ethanol, dried at60 °C for overnight and then used as the catalyst under similar conditions. The DIL-L/W(33) catalyst was recycled for 4 runs and as shown in Fig. 12, the conversion of the reaction in the4th run decreased to 70%. As mentioned in section 3.1, the catalyst after 4 runs loses some of the ionic liquid component and reaches to a better crystallinity and in this respect the activity of the catalyst decreased appreciably which could not be due to the leaching of tungsten but might be attributed to structural changes of the catalyst.



Fig. 12. Reusability of the DIL-L/W(33) catalyst.

Different catalytic systems such as Au/Silica [5], Au/HNTs [35], Cr-MCM-41 [36], PS-DA-Cu [37] and Fe₃O₄@SiO₂-CoO [38] are few examples of the catalysts which have been reported for oxidation of cyclohexene under solvent-free conditions with O₂ as the oxidant. The data in the Table 3 compare the activity of the DIL-L/W catalyst and other catalysts reported in the literature. Perhaps, the catalysts exhibited in the present work could be appropriate catalysts for producing 2-cyclohexene-1-one.

Table 3	. Comparison	of DIL-L/W	and DIL-A	/W catal	ytic performance	with some	previously
reported	catalyst in cyc	clohexene oxid	lation.				
			Po.	Temp.	Reaction time	Conversion	

Entry	Catalyst		Temp. (°C)	Reaction time (h)	Conversion (%)	Ref.
1	Cu-MOF ^a	1	80	15	14.6	[39]
2	GNPs/TChD ^b	17	80	8	87	[6]
3	Au-bentonite ^c	8	80	10	53	[5]
4	Au-silica ^c	13	80	8	92	[5]
5	Au/La-OMS-2 ^d	4	80	24	48	[40]
6	Au/HNTs ^e	4	80	12	29.5	[35]
7	Fe ₃ O ₄ @SiO ₂ -CoO ^f *	3	75	6	96.5	[38]
8	P-Salen-BsdB18C6-(Co-Na) ^g	1	70	12	91.4	[41]
9	[NSP]@MWNTs ^h	1	70	8	68.6	[42]
10	Cr-MCM-41 ⁱ	1	70	24	52	[36]
11	PS-DA-Cu ^j	1	70	10	51.9	[37]

12	DIL-L/W(33) ^{.k}	15	70	6	96	This work
13	DIL-A/W(33) ^{.k}	15	70	8	93	This work

* In the presence of solvent (cyclohexane)

Reaction conditions:

- ^a catalyst, 50 mg; cyclohexene, 5 mL; oxygen balloon
- ^b catalyst, 50 mg; cyclohexene, 20 mL
- ^c catalyst, 50 mg; cyclohexene, 10 mL
- ^d catalyst, 200 mg; cyclohexene, 20 mL
- ^e catalyst, 200 mg; cyclohexene, 20 mL
- ^f catalyst, 0.004 mol Co; cyclohexene, 2 mmol
- ^g catalyst, 1.5 mg; cyclohexene, 2 mL
- ^h catalyst, 1.2×10^{-5} mol; cyclohexene, 10 mL
- ⁱ catalyst, 20 mg; cyclohexene, 1 g; glass reactor equipped with oxygen balloon
- ^j catalyst, 2 mg; cyclohexene, 2 mL; glass reactor
- ^k catalyst, 20 mg; cyclohexene, 2 mL, titanium batch reactor

4. CONCLUSION

On the basis of two dicationic ionic liquids and tungstophosphoric and molybdophosphoric acids, different catalysts were prepared and characterized by FESEM-EDX, XRD, TGA, BET and FT-IR techniques. The catalytic activity of the prepared catalysts with molecular oxygen as oxidant for oxidation of cyclohexene was studied. The catalyst DIL-L/W(33 wt%) was found to have a desirable catalytic activity for oxidation of cyclohexene. By considering various parameters the reaction conditions were optimized. The maximum conversion of cyclohexene was 96% and selectivity for the main product i.e., 2-cyclohexene-1-one was 86%. Moreover, we have made efforts to elucidate the structure of DIL-L/W nanocomposite and calculate the interaction energy of tungstophosphoric acid with DIL-L on the basis of semi-empirical method.

Supporting Information

Additional experimental data including some FT-IR and ¹H NMR spectra, TGA curve, and the optimized structure of prepared catalysts

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