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Selective oxidation of alkenes using [bmim]₅[PW₁₁ZnO₃₉]·3H₂O hybrid catalyst

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Abstract The catalytic activity of $[bmim]_5[PW_{11}Z-nO_{39}]\cdot 3H_2O$ as a hybrid catalyst was studied in the oxidation of various alkenes in acetonitrile, using hydrogen peroxide as oxygen source. The effect of reaction parameters such as type of solvent and oxidant, amount of catalyst and oxidant, and temperature was also investigated. From our results, $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$ hybrid catalyst gave higher yields and selectivity in the oxidation of alkenes and was reused four times without loss of its catalytic activity.

Keywords Hybrid catalyst · Polyoxometalate · Oxidation · Ionic liquid · Alkenes

Introduction

Selective and efficient oxidation of hydrocarbons to useful corresponding organic compounds has received much attention in recent years. The conversion of raw materials like alkenes into industrial chemicals is one of the important applications of epoxidation reactions [1–3]. Detergents, surfactants, antistatic agents and corrosion protection agents, lubricating oils, textiles, and cosmetics

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M. Moghadam e-mail: moghadamm@sci.ui.ac.ir are technically vital products that obtained from the reaction of epoxides [4]. Indeed, pesticides, rubber promoters, chiral pharmaceuticals, and peroxy paints are produced from organic intermediates such as cyclooctene and cyclohexene oxides [5]. For this purpose, chemists have been used different homogenous and heterogeneous catalysts [6–8] and various oxidants such as PhIO, NaC1O, percarboxylic acids, molecular oxygen, and hydroperoxides [9–12]. Among these oxygen donors, the greener oxidants (O₂ and H₂O₂) are cheap, clean, and environmentally benign ones [13–18].

Polyoxometalates as a unique class of inorganic metaloxygen clusters bear many properties that make them attractive for applications in catalysis [19], electrochemistry [20], magnetism [21], optics [22], and medicine [23]. The catalytic activity of polyoxometalates has attracted much attention because their acidic and redox properties can be controlled by transition metal substitution and changing the type of the counter-cation [24–26]. The technologically significant aspect of polyoxometalates in catalysis is their specific stability toward oxygen donors such as O_2 and H_2O_2 . Therefore, various structures of polyoxometalates are useful for liquid phase oxidation of different organic substrates with hydrogen peroxide [27].

Ionic liquids (IL) have unique properties such as low melting point, negligible vapor pressure, high ionic conductivity and wide electrochemical stability [28]. These compounds are used in many fields including hybrid compounds synthesis, organic chemistry, electrochemistry, catalysis, physical chemistry, and engineering [29, 30].

The design, synthesis, characterization, and application of novel hybrid materials have established new area of research in chemistry and material science in order to obtain multifunctional structures with special property including catalytic, electronic, and optical properties [31,

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32]. In recent years, there have been an abiding research interest in synthesis of hybrid catalysts with polyoxometalates and room temperature ionic liquids due to their extensive applications in various fields such as catalysis, bio catalysis, thermally stable lubricants, hybrid inorganic–organic nanocompositse, electrochemistry, and photochemistry [33–35].

In continuation of our previous works on the investigation of catalytic activity of hybrid compounds [36–38], here, we wish to report the catalytic activity of [bmim]₅[PW₁₁Z nO_{39}]·3H₂O hybrid compound in the oxidation of alkenes with hydrogen peroxide (30 %) in acetonitrile as solvent (Scheme 1). The effect of different parameters such as solvent, oxidant, and temperature on the activity and selectivity of the catalyst was also studied (Scheme 1).

Experimental

General

All materials were commercial reagent grade and obtained from Merck and Fluka chemical companies. Alkenes were passed through a column containing active alumina to remove peroxidic impurities. The [bmim]₅[PW₁₁ZnO₃₉]·3H₂O (IL-POM(Zn)) hybrid catalyst was synthesized according to the published procedure [39] and its spectroscopic and analytic data are in according with the reported literature data. The UV-vis spectra were recorded from 200 to 800 nm on a 160 Shimadzu UV-vis spectrophotometer. FT-IR spectra (400-4,000 cm⁻¹) were recorded as KBr pallets using a JASCO 6300 spectrophotometer. Gas chromatography (GC) experiments were performed with a Shimadzu GC-16A instrument using a 2 m column packed with silicon DC-200 or Carbowax 20M. Hydration water contents were determined by thermogravimetric analysis on a Mettler TA4000 thermobalance instrument.

Typical procedure for oxidation of alkenes with hydrogen peroxide catalyzed by IL-POM

All reactions were carried out in a 25-mL glass reactor equipped with a reflux condenser. In a typical experiment, alkene (1 mmol), $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$ catalyst (0.05 mmol), acetonitrile (3 ml), and hydrogen peroxide (1 ml, 30 %) were mixed and stirred at 353 K. The reaction progress was monitored by GC. At the end of the



Scheme 1 Epoxidation of alkenes with H_2O_2 catalyzed by $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$

reaction, the reaction mixture was cooled to room temperature; the solvent was evaporated and n-hexane (10 mL) was added. The catalyst was filtrated and washed with n-hexane. The solvent was evaporated and the pure product was obtained by chromatography on a short column of silica gel.

Results and discussion

The catalytic activity of the prepared catalyst was tested using cyclooctene as reference alkene. In order to optimize the amount of $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$ hybrid catalyst, various amounts of catalyst were used for oxidation of cyclooctene. As shown in Fig. 1, the epoxide yield was 100 % in the presence of 0.05 mmol of hybrid catalyst under reflux conditions after 1 h.

For choosing the reaction media, various polar, non,polar coordinating, and protic solvents including CH_3CN , CH_2Cl_2 , EtOAc, MeOH, CHCl_3, *n*-C₆H₁₂, and H₂O/ CH₃CN were tested as reaction medium. The higher catalytic activity and solubility of the catalyst and substrate are the key factors for choosing the acetonitrile as the best solvent for epoxidation reaction. The results are summarized in Table 1.

Then, the effect of different oxidants on the catalytic activity of $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$ hybrid catalyst was studied in the epoxidation of cyclooctene. Different oxygen donors such as NaIO₄, Urea-H₂O₂ (UHP), *tert*-BuOOH, and H₂O₂ were also examined. The results, which are summarized in Table 2, showed that hydrogen peroxide is the best oxygen source.

In order to find the optimized amount of hydrogen peroxide, the oxidation of cyclooctene was carried out using different amounts of H_2O_2 (30 %) (0.2, 0.5, 0.8, and 1 ml). As shown in Fig. 2, the higher conversion was obtained when the reaction was carried out with 1 mL H_2O_2 (30 %).

The effect of reaction temperature on the oxidation of cyclooctene with H_2O_2 catalyzed by



Fig. 1 The effect of amount of $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$ catalyst on the epoxidation of cyclooctene after 1 h

Table 1 Effect of solvent on the oxidation of cyclooctene catalyzed by $[bmim]_5[PW_{11}ZnO_{39}] \cdot 3H_2O$

Row	Solvent	Conversion (%) ^a after 1 h			
1	CH ₃ CN	100			
2	CH_2Cl_2	27			
3	CHCl ₃	10			
4	H ₂ O/CH ₃ CN	51			
5	MeOH	38			
6	<i>n</i> -Hexane	Trace			
7	EtOAc	15			

Reaction conditions: cyclooctene (1 mmol), H_2O_2 (1 mL), catalyst (0.05 mmol), solvent (3 ml) under reflux conditions

^a GC yield

Table 2 Effect of oxidant type on the oxidation of cyclooctene catalyzed by $[\text{bmim}]_5[\text{PW}_{11}\text{ZnO}_{39}]$ ·3H₂O

Row	Oxidant	Conversion (%) ^a after 1 h			
1	H_2O_2	100			
2	NaIO ₄	15			
3	H ₂ O ₂ /Urea (UHP)	31			
4	tert-BuOOH	49			
5	No Oxidant	Trace			

Reaction conditions: cyclooctene (1 mmol), oxidant (10 mmol), catalyst (0.05 mmol), CH_3CN (3 mL) under reflux condition ^a GC yield

 $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$ was also investigated. It was observed that in the oxidation of cyclooctene with H_2O_2 catalyzed by $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$ at room temperature, small amounts of oxidation product was detected in the reaction mixture. While, by increasing the reaction temperature (reflux conditions), the conversion increased (Table 3).

Under the optimized conditions, which obtained for oxidation of cyclooctene, oxidation of different alkenes such as cyclohexene, styrene, α -methylstyrene, 1-heptene, 1-octene, and 1-dodecene were investigated. Different



Fig. 2 The effect of oxidant amount on the epoxidation of cyclooctene after 1 h $\,$

Table 3 Effect of temperature on the oxidation of cyclooctene catalyzed by [bmim]₅[PW₁₁ZnO₃₉]·3H₂O

Row	Temperature (°C)	Conversion (%) ^a after 1 h			
1	25	5			
2	40	14			
3	60	39			
4	Reflux	100			

Reaction conditions: cyclooctene (1 mmol), H_2O_2 (1 mL), catalyst (0.05 mmol), CH_3CN (3 ml)

^a GC yield

substrates were successfully oxidized to their oxidation products under reflux conditions (Table 4). It is clear that electron rich olefins are more reactive than electron poor ones. Also, it was found that the alkenes were not oxidized in the absence of catalyst or oxidant. In the case of cyclooctene, the cyclooctene oxide was the sole product with 100 % yield. Oxidation of cyclooctene in the presence of ionic liquid was carried out and the result indicated that ionic liquid alone was almost inactive. On the other hand, it was observed that the sodium and ammonium salts of polyoxometalate showed low catalytic activity in this oxidation reaction. It seems that a synergistic effect between the ionic liquid and the polyoxometalate due to nearing the size of two structures increased the catalytic activity of hybrid catalyst. In the oxidation of 6,6-dimethyl-2-methylene-bicyclo[3.1.1] heptane, the corresponding epoxide was produced in 93 % yield and 100 % selectivity. In the case of limonene, the ratio among 1,2-and 8,9epoxides was 6.1.

Interestingly, in the oxidation of styrene and α -methylstyrene, the major products were benzaldehyde and acetophenone, respectively. Oxidation of cyclohexene was accompanied by allylic oxidation. The notable feature of the catalytic oxidation with [bmim]₅[PW₁₁ZnO₃₉]·3H₂O is that non-activated terminal olefins such as 1-octene, 1-hexene could be transformed to their corresponding epoxides in good yields. These results show that the conjugation of aromatic ring with carbonyl group stabilizes the products.

Catalyst reusability

The reusability of the $[\text{bmim}]_5[\text{PW}_{11}\text{ZnO}_{39}]\cdot 3\text{H}_2\text{O}$ hybrid catalyst was examined using cyclooctene as model reaction. For each of the repeated reactions, the solvent was evaporated and *n*-hexane (10 mL) was added. The catalyst was filtrated, washed with *n*-hexane, dried at 50 °C, and reused in the next run. The results, Fig. 3, indicate that the $[\text{bmim}]_5[\text{PW}_{11}\text{ZnO}_{39}]\cdot 3\text{H}_2\text{O}$ can be recycled four consecutive times without a significant decrease in its activity.

Entry	Substrate	Products	Time (h)	Conversion ^a (%)	Selectivity ^b (%)	TOF (h ⁻¹)
1		o	1	100	100	20.00
2		$\bigcirc 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0$	1	94	 (1) 8 (2) 88 (3) 4 	18.80
3	X	o J	3	93	100	6.20
4		$\rightarrow \qquad \qquad$	4	98	 (1) 86 (2) 14 	4.90
5			4	91	(1) 31(2) 69	4.55
6			4	94	 (1) 12 (2) 88 	4.70
7		$\sim \sim \sim \circ$	1	74	100	14.80
8			1.5	68	100	9.07
9			3	88	100	5.87

Table 4 Epoxidation of alkenes with H₂O₂ catalyzed by [bmim]₅[PW₁₁ZnO₃₉]·3H₂O

Reaction conditions: alkene (1 mmol), H_2O_2 (1 mL), catalyst (0.05 mmol), CH_3CN (3 mL) under reflux conditions ^a GC yield



Fig. 3 The results of $[bmim]_5[PW_{11}ZnO_{39}]$ -3H₂O catalyst recovery in the oxidation of cyclooctene with hydrogen peroxide

Reaction mechanism consideration

A proposed reaction mechanism for styrene, as an example, was given in Scheme 2. In the first step, oxygen transfer from hydrogen peroxide to a $PW_{11}Zn$ cluster of IL-POM(Zn^{II}) occurred, leading to a higher valent transition metal-oxo compound (IL-POM–Zn^{III} = O). The next step is the formation of Zn^{III}-peroxocomplex under the interaction with H₂O₂. Afterward, styrene was bound with one of the metal-peroxo bonds to produce the peroxometallocycle (the third step). In the fourth step, the peroxometallocycle is broken and styrene oxide was produced [40–42]; simultaneously, the H₂O₂ is consumed, and the Zn^{III}-complex



Scheme 2 Proposed reaction mechanism for the reaction of oxidation of styrene with H_2O_2 to produce banzaldehyde catalyzed by $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O$

is reduced back to Zn^{II} -complex by the styrene. Therefore, the catalyst restores its initial state due to the loss of an oxygen atom [40]. A further nucleophilic attack of H_2O_2 on the styrene oxide leads to the final product, benzaldehyde (the fifth step) [43].

Conclusion

In conclusion, the oxidation of various alkenes with hydrogen peroxide in the presence of $[bmim]_5[PW_{11}Z-nO_{39}]\cdot 3H_2O$ hybrid catalyst was studied. Catalytic results indicated that the organic–inorganic hybrid catalyst, $[bmim]_5[PW_{11}ZnO_{39}]\cdot 3H_2O_2$, is a green, selective, and efficient catalyst for alkenes oxidation. Also this hybrid catalyst can be reused four times without a significant decrease in its activity.

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