



Green epoxidation of cyclooctene with molecular oxygen over an ecofriendly heterogeneous polyoxometalate-gold catalyst Au/BW₁₁/Al₂O₃*

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Abstract: An ecofriendly heterogeneous polyoxometalate (POM)-gold catalyst Au/BW₁₁/Al₂O₃ was synthesized and used for solvent-free epoxidation of cyclooctene under mild reaction conditions using molecular oxygen as an oxidant and t-butyl hydroperoxide (TBHP) as an initiator. The catalyst was characterized by Fourier transform infrared spectroscopy (FT-IR), scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDX), X-ray diffraction (XRD), induced coupled plasma optical emission spectrometry (ICP-OES), and Brunauer-Emmett-Teller (BET). The catalyst showed good conversion and high selectivity without use of solvents or environmentally harmful oxidants. Moreover, the catalyst is recyclable up to three cycles with no significant loss in selectivity towards epoxide.

Key words: Nano gold, Polyoxometalates (POMs), POM-gold catalyst, Cyclooctene epoxidation, Molecular oxygen
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1 Introduction

From synthetic organic chemistry and chemical industry perspectives, the epoxidation of olefins including cyclooctene requires no acknowledgment since epoxides are essential raw materials for epoxy resins, paints, and surfactants (Zhao *et al.*, 2008). They are hard to replace as intermediates in many organic syntheses (Mizuno *et al.*, 2005) as the

nucleophilic ring-opening contributes to a diversity of functional products ranging from small molecules (Jacobsen *et al.*, 1999; Pastor and Yus, 2005) to large polymers and oligomers (Matlock *et al.*, 1999; Petrovic, 2008; Endo and Sudo, 2009).

However, olefin epoxidation has always been a great challenge in many domains (Bawaked *et al.*, 2011a). Firstly, a variety of oxidants has been engaged for the catalytic liquid-phase oxidation processes, and some of them lead to toxic and environmentally unacceptable by-products. The principal features that make an oxidant appealing are the percentage of active oxygen and the selectivity which comes with it, as well as cost effectiveness and environmental safety. The active oxygen contents of many oxidants are modest (approx. 30%) (Mizuno and Kamata, 2011). In terms of availability, molecular oxygen and H₂O₂, with low price, ease of

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handling, absence of toxic waste, and high content of active oxygen species (O_2 : 100%; H_2O_2 : 47%), are the most reasonable oxidants (Sheldon, 1991). Moreover, the concept of “green chemistry” has been affiliated to this sort of catalytic oxidation, which makes use of molecular oxygen straight from the air (Du *et al.*, 2011; Wang *et al.*, 2012; Tang *et al.*, 2013).

Unfortunately, molecular oxygen is quite unreactive toward olefin epoxidation with the catalysts reported (Huber *et al.*, 2014) under relatively mild conditions (Villanneau *et al.*, 2014). Consequently, high temperatures are needed, which cause a chance of complete oxidation of the olefins to CO_2 or other by-products, and hence little success has been accomplished for the selective epoxidation of olefins with O_2 in the liquid phase (Tang *et al.*, 2004) because of possible catalyst deactivation and difficulty in C–H bond/ O_2 activation.

Secondly, the design and preparation of a highly active catalyst is a key point in olefin epoxidation. Cyclooctene epoxidation is a probe in search of an active catalyst for olefin epoxidation. Various types of catalysts have been employed for this purpose such as framework substituted zeolites (van der Waal *et al.*, 1998; Wu *et al.*, 2001), layered hydrotalcites (Ueno *et al.*, 1998), mixed oxides (Gan *et al.*, 2005; Somma *et al.*, 2006), porous material encapsulated metal complexes like Mn(salen)/NaY (Wang *et al.*, 2002), supported porphyrins (Brulé and de Miguel, 2006), and base catalysts like Mg, Al-layered double hydroxide (LDH), and $[CO_3]^{2-}$ (Yamaguchi *et al.*, 1999). Polyoxometalates (POMs) have acquired considerable attention during the last couple of decades, since they stand as a significant family of inorganic materials offering a variety of composition with unique properties and structures for potential applications in numerous fields like materials science, catalysis, biology, and medicine (Pope and Müller, 2001; Coronado *et al.*, 2005; Yamase, 2005; Proust *et al.*, 2008; Wang *et al.*, 2010; Cronin and Muller, 2012). Many kinds of POMs have been employed for olefin epoxidation recently such as $Y_4[PMo_{11}VO_{40}]$ and $Y_4K[PW_{10}V_2O_{40}]$ (Nomiya *et al.*, 2001), $K_8[SiW_{11}O_{39}]$ (Moghadam *et al.*, 2010), PW_{11} (Shringarpure and Patel, 2011), and PMo_{11} (Pathan and Patel, 2011).

POMs comprise a large class of metal-oxygen anions including group V and VI transition metals (Pope, 1983). Transition metal ions generally involved in forming the molecular structural framework of

POMs are W (VI), Mo (VI), V (V), Nb (V), Ta (V), and Ti (IV) (Gómez-Romero *et al.*, 2005). These ions or their local MO_x coordination polyhedra are called addenda ions, generally containing MO_6 octahedra, but MO_5 and MO_4 elements are rarely found. The Keggin heteropolyanions of formula $[X^{n+}M_{12}O_{40}]^{(8-n)-}$ are widely studied, where $M=W$ (VI) or Mo (VI). The heteroatom, X^{n+} , can be one of the *p* block elements (Hill and Prosser-McCartha, 1995). Specifically, POMs have done marvels in catalysis, owing to their inherent acidity, tunable oxidation states, ability to activate many oxidants, and oxidative stability (Pope and Müller, 2001). POMs are regarded as soluble analogues of metal oxides and employed in acid and oxidative catalysis, and equally in homogeneous and heterogeneous catalysis (Hill and Prosser-McCartha, 1995; Kozhevnikov, 1998; Bäckvall, 2004; Hill, 2007; Mizuno *et al.*, 2011; Streb, 2012). In recent years, tungsten-based POMs have received increasing interest in selective oxidation of organic compounds with hydrogen peroxide (Reinoso *et al.*, 2007; Liu *et al.*, 2008).

In addition to the above catalytic properties of POMs, their scope as carriers for nanoparticles (NPs) has also been discussed (Maayan and Neumann, 2005). The high anionic charge helps to increase the stability of the catalyst and prevents sintering of the NPs (Troupis *et al.*, 2002; Sharet *et al.*, 2012). The role of POMs in the preparation and stabilization of nanoscale materials such as nano gold is a new development in this field (Jameel *et al.*, 2016). Supported nano gold catalysts have also been successfully used for epoxidation of cyclic olefins including cyclooctene (Hughes *et al.*, 2005; Álvaro *et al.*, 2007; Bawaked *et al.*, 2009; 2011a; 2011b). One such catalyst has been reported using molecular oxygen as a green oxidant (Cai *et al.*, 2010). Oxidation by nano gold catalysts is important in supporting green processes using stable, selective, and non-toxic heterogeneous catalysts, also using ecofriendly oxidants such as pure O_2 (Pina *et al.*, 2012).

Earlier our group used Au/Al_2O_3 catalyst for the oxidation of cyclohexane using oxygen in the absence of any solvent and initiator. The Al_2O_3 support stabilized Au NPs after calcination at 500 °C for 3 h (Xu *et al.*, 2007). Hereijgers and Weckhuysen (2010) compared the aerobic oxidation of cyclohexane to cyclohexanone and cyclohexanol over Au catalysts (Au/Al_2O_3 , Au/TiO_2 , and $Au/SBA-15$) with the

industrial autoxidation process. No conversion was observed in the absence of nano gold and a small amount of t-butyl hydroperoxide (TBHP) was substantive to initiate the reaction, suggesting a complex radical chain mechanism. Supported metal nanoparticles and gold catalysts in particular have been found effective in catalyzing the epoxidation of cycloalkenes (Dimitratos *et al.*, 2012). Therefore, the characteristics of POMs urge the researchers to employ them in the synthesis of metal NPs using simple, efficient, and ambient temperature techniques (Triantis *et al.*, 2009).

Thirdly, organic solvents are used for olefin epoxidation (Tolstikov, 1976; Timofeeva *et al.*, 2003). They improve the conversion and selectivity of the reaction by playing a complex role according to the polarity and solubility of the reactants as well as the products. A solvent imparts diffusion and counter-diffusion effects interacting with the active center of the catalyst.

In this study, to gain the advantage of the catalytic properties of POMs and nano gold together in search of an active catalyst towards molecular oxygen and cyclooctene activation, we present a new nano gold-POM catalyst supported on the surface of γ -Al₂O₃ (Au/BW₁₁/Al₂O₃). To our knowledge, no study has been reported on a supported Keggin-type tungstoborate K₈[BW₁₁O₃₉H]·nH₂O (BW₁₁). There is one report regarding unsupported BW₁₁ for the oxidation of alcohols (Zhao *et al.*, 2010) and another for cyclohexene epoxidation by our research group (Hu *et al.*, 2015). We extend our research and use this POM-gold hybrid catalyst for solvent-free epoxidation of cyclooctene using molecular oxygen as an oxidant and TBHP as an initiator. The effect of various reaction parameters, such as reaction time, temperature, amount of catalyst, and recyclability of the catalyst on the conversion and products selectivity, is investigated. The possible mechanism of molecular oxygen activation on the surface of catalyst is also discussed.

2 Experimental

2.1 Catalyst preparation

2.1.1 Reagents

All reagents were commercially available analytical grade and were used without further purification.

2.1.2 Synthesis of BW₁₁

BW₁₁ was prepared according to the procedure in the literature (Tézé *et al.*, 1997; Maksimovskaya and Maksimov, 2011). Sodium tungstate (100 g) and boric acid (6.66 g) were dissolved in boiling water (170 ml). To this solution, a 6 mol/L hydrochloric acid solution (approx. 64 ml) was added drop-wise with vigorous stirring in order to dissolve the local precipitate of tungstic acid until the pH was 6. Afterwards the solution was boiled for 1 h and kept at 4 °C for 24 h. The resulting precipitate was separated by suction filtration. To the clear solution separated, KCl (approx. 33 g) was added. The desired BW₁₁ salt was precipitated and removed from the solution by suction filtration. It was dissolved in 335 ml of lukewarm water. After eliminating the insoluble part, the BW₁₁ salt was again precipitated by the addition of KCl (approx. 33 g). The BW₁₁ salt was filtered and dried in an oven at 120 °C for 5 h prior to use in the catalyst synthesis procedure.

2.1.3 Synthesis of Au/Al₂O₃

Au/Al₂O₃ was synthesized using the following standard deposition precipitation method. A solution of HAuCl₄·3H₂O (5 ml, 1 g in 100 ml distilled water) was diluted in water. The solution was added, with continuous stirring, to a slurry of γ -Al₂O₃ support in water (5 g in 50 ml water). The mixture was stirred for 1 h at 30 °C, maintaining the pH at 10. The mixture was heated to 70 °C and formaldehyde was added as a reducing agent. The solid formed was separated by filtration and washed with water many times to make it chloride free, then dried at 110 °C for 16 h. It was denoted as Au/Al₂O₃.

2.1.4 Synthesis of Au/BW₁₁/Al₂O₃

The wet impregnation method was used to prepare the catalyst Au/BW₁₁/Al₂O₃ by adding Au/Al₂O₃ (1 g) and BW₁₁ (0.2 g) into 30 ml of conductivity water and stirring for 36 h at 30 °C. The resulting solid was dried at 100 °C for 10 h. The final product obtained was named as Au/BW₁₁/Al₂O₃ catalyst containing 1% Au by weight. The catalyst was calcinated at 500 °C for 3 h prior to the catalytic reaction.

2.2 Catalyst characterization

The Fourier transform infrared spectroscopy (FT-IR) spectrum of the catalyst was acquired using

the KBr wafer on a Tensor 27 Bruker instrument (Germany). The scanning electron micrographs were taken on a Zeiss ULTRA 55 Gemini field emission scanning microscope (Germany) with a Schottky emitter at an accelerating voltage of 3 kV. The structure of the catalyst was studied by X-ray diffraction (XRD). A D/max-RA instrument with $\text{CuK}\alpha$ radiation with a beam voltage of 40 kV and a beam current of 40 mA was used to collect the X-ray data. The chemical composition of the synthesized catalysts was determined by an energy dispersive X-ray analysis (EDX) on a Philips Oxford 7426 EDX spectrometer (the Netherlands) and by induced coupled plasma optical emission spectrometry (ICP-OES) on a Leeman Prodigy instrument (USA). The adsorption-desorption isotherm was obtained by the Brunauer-Emmett-Teller (BET) method using an Autosorb-1-C instrument.

2.3 Catalytic testing

In a typical oxidation reaction, 5 ml cyclooctene and 0.15 g of the catalyst were placed into a polytetrafluoroethylene (PTFE)-lined autoclave (the capacity is 20 ml) with TBHP as a reaction initiator. The reactor was heated to the desired reaction temperature in an oil bath under oxygen pressure using a magnetic stirrer. The reactor was allowed to cool to room temperature after the reaction, and the product obtained was subjected to centrifugation in order to separate catalyst from the liquid phase. The solid catalyst was washed by acetone and dried at 120 °C for 5 h. The liquid samples were subjected to analysis by gas chromatography (GC) with an SE-54 capillary column (30 m×0.32 mm×0.5 μm) and a flame ionization detector (FID). N-hexane was used as an internal standard for product analysis.

3 Results and discussion

3.1 Catalytic properties

The polyhedral model of BW_{11} is shown in Fig. 1. The energy dispersive spectroscopy (EDS) analysis and ICP-OES were performed to determine the elemental composition of BW_{11} . The results are close to the theoretical values: theoretical values are 9.6 for K, 63 for W, and 0.34 for B; practical values are 9.15 for K, 66.6 for W, and 0.26 for B. The scan-

ning electron microscopy (SEM) images of $\text{Au}/\text{BW}_{11}/\text{Al}_2\text{O}_3$ and BW_{11} are shown in Fig. 2. Fig. 2a shows the spherical morphology of the support after dispersion of BW_{11} and gold nanoparticles and different particle sizes can be observed ranging in nanometers. Fig. 2b reveals the crystalline nature of BW_{11} showing a smooth surface. The smooth surface implies that the growth of crystal takes place by either birth and spread, or spiral growth. At a low supersaturation, the interface is smooth, and spiral growth is observed. After reaching a critical supersaturation for 2D nucleation, birth and spread dominate the growth. In these two domains, crystals are bound by crystallographically flat faces with polyhedral morphologies.

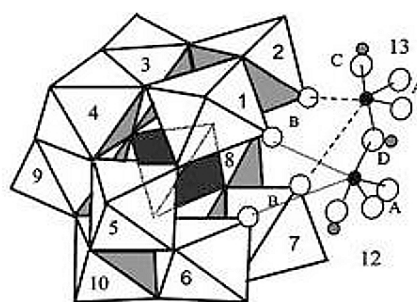


Fig. 1 Polyhedral model of $[\text{BW}_{11}\text{O}_{39}\text{H}]^{8-}$

B atom in center with W atoms around with attached $\{\text{W}_2\text{O}_7\text{H}_3\}$ fragment (in the ball-and-stick model: white circles, oxygen; black circles, tungsten; gray circles, protons). Reprinted from (Maksimovskaya and Maksimov, 2011), Copyright 2011, with permission from American Chemical Society

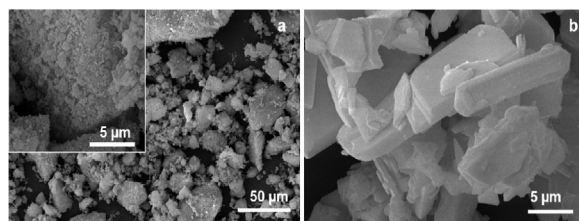


Fig. 2 SEM images of $\text{Au}/\text{BW}_{11}/\text{Al}_2\text{O}_3$ (a) and BW_{11} (b)

The FT-IR spectrum of $\text{Au}/\text{BW}_{11}/\text{Al}_2\text{O}_3$ (Fig. 3) exhibits a characteristic peak at 706 cm^{-1} which can be attributed to stretching vibrational bands of W–O–W. The peak at 892 cm^{-1} belongs to W=O stretching, the 3400 cm^{-1} peak corresponds to symmetric aquo stretching, and two bending vibrations at 1086 and 1633 cm^{-1} belong to asymmetric stretching of B–O bonds as cited from Selvaraju and Marimuthu

(2013). The bending vibration at 616 cm^{-1} is attributed to Al–O–H vibration. FT-IR analysis reveals that the crystal structure of Keggin type BW_{11} is retained after distribution on an Al_2O_3 surface. Fig. 4 describes the FT-IR spectra of BW_{11} before and after calcination, and it is apparent that BW_{11} is able to maintain its structure even after calcination at $500\text{ }^\circ\text{C}$, which supports the fact that POMs are thermally stable compounds, as mentioned by Pope and Müller (2001).

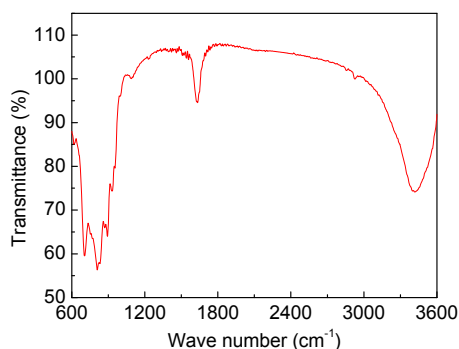


Fig. 3 FT-IR spectrum of $\text{Au}/\text{BW}_{11}/\text{Al}_2\text{O}_3$ dried at $100\text{ }^\circ\text{C}$

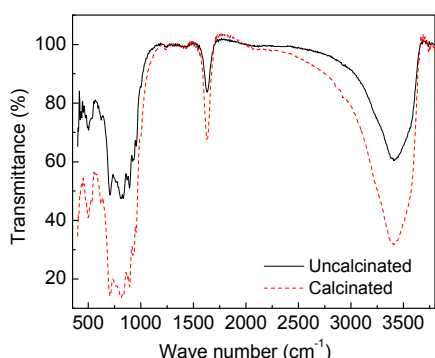


Fig. 4 FT-IR spectra of BW_{11} uncalcinated and calcinated at $500\text{ }^\circ\text{C}$ for 3 h

The XRD pattern of BW_{11} presented in Fig. 5a shows its crystalline nature (Moghadam *et al.*, 2010). Figs. 5b and 5c compare the XRD patterns of bare Al_2O_3 and $\text{Au}/\text{Al}_2\text{O}_3$. In the XRD pattern of $\text{Au}/\text{Al}_2\text{O}_3$, the characteristic diffraction peaks can be readily indexed as the (1 1 1), (2 2 0), and (3 1 1) planes of Au (Han *et al.*, 2013) indicating a successful impregnation of gold nanoparticles on the surface of the support. The XRD for both POM and gold supported on the alumina surface is given in Fig. 5d where the characteristic peak for POM is too weak to be observed, which is due to the small quantity of POM in

the composite. Other evidence like that of FT-IR confirms the formation of composite $\text{Au}/\text{BW}_{11}/\text{Al}_2\text{O}_3$.

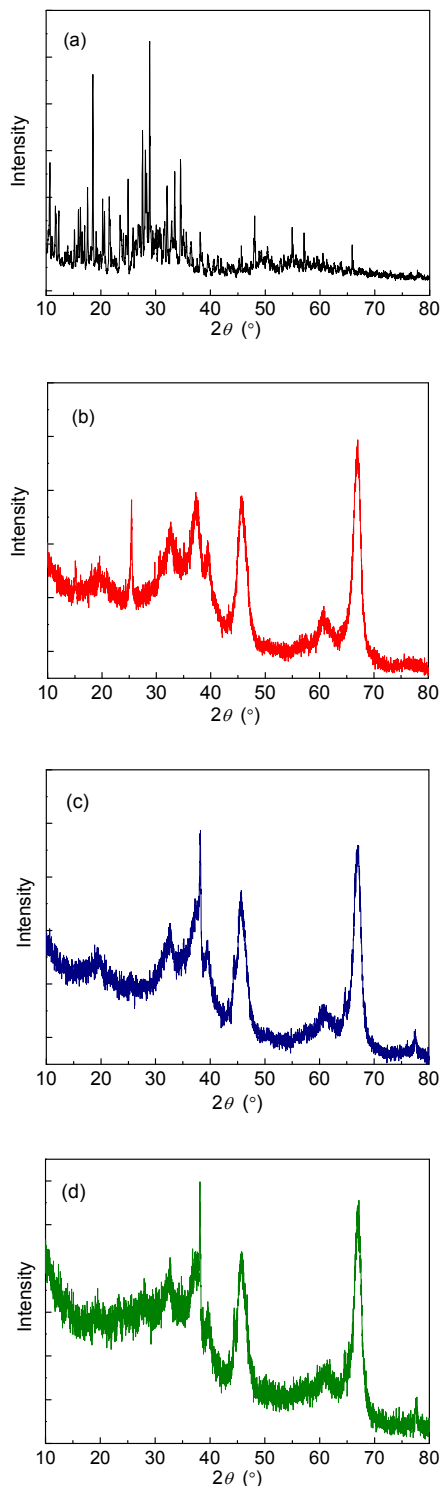
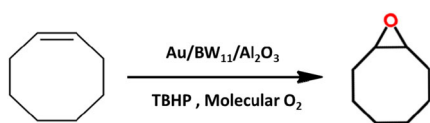


Fig. 5 XRD patterns of Keggin type BW_{11} (a), bare Al_2O_3 support (b), $\text{Au}/\text{Al}_2\text{O}_3$ (c), and $\text{Au}/\text{BW}_{11}/\text{Al}_2\text{O}_3$ (d) (2θ represents the detector position)

The adsorption-desorption isotherms of the catalyst Au/BW₁₁/Al₂O₃ and bare Al₂O₃ support are shown in Fig. 6 along with the respective Horváth-Kawazoe (HK) pore distribution curves. It shows a Type-II isotherm which is achieved when adsorption occurs on non-porous powders or powders with pore diameters larger than micro-pores. This sort of isotherm suggests an indefinite multi-layer establishment after completion of the monolayer. The inflection point or knee of the isotherm normally occurs close to the completion of the first adsorbed monolayer. Then the second and higher layers are accomplished with increasing relative pressure until the number of adsorbed layers becomes infinite at saturation. At high pressure, the catalyst has shown better adsorption capacity around 650 cm³/g as compared with bare Al₂O₃ support whose adsorption capacity is less than 500 cm³/g. The surface areas of the catalyst and bare Al₂O₃ support were found to be 109.78 m²/g and 106.06 m²/g, respectively. The enhanced pore volume in the case of the catalyst compared with the support provides more surface area for adsorption of the substrate facilitating the catalytic process.

3.2 Pseudo-catalytic mechanism

Cyclooctene oxidation over the catalyst Au/BW₁₁/Al₂O₃ is shown in Scheme 1. The lacunary BW₁₁ and nano gold act as an active metal centre towards the epoxidation of the cyclooctene. A possible mechanism for the activation of oxygen at the surface of the POM-gold hybrid catalyst surface might be the existence of an equilibrium state in the supported hybrid material. Molecular oxygen might be activated by interaction with an active W centre forming a hydroxo species, which could eliminate a water molecule to give peroxy species. This peroxy species can then react with cyclooctene adsorbed on the surface of Au to give epoxide. From the possible oxygen activation mechanism above, the catalytic oxidation ability of the present catalyst might be explained.



Scheme 1 Cyclooctene oxidation using TBHP as radical initiator over supported POM-gold catalyst

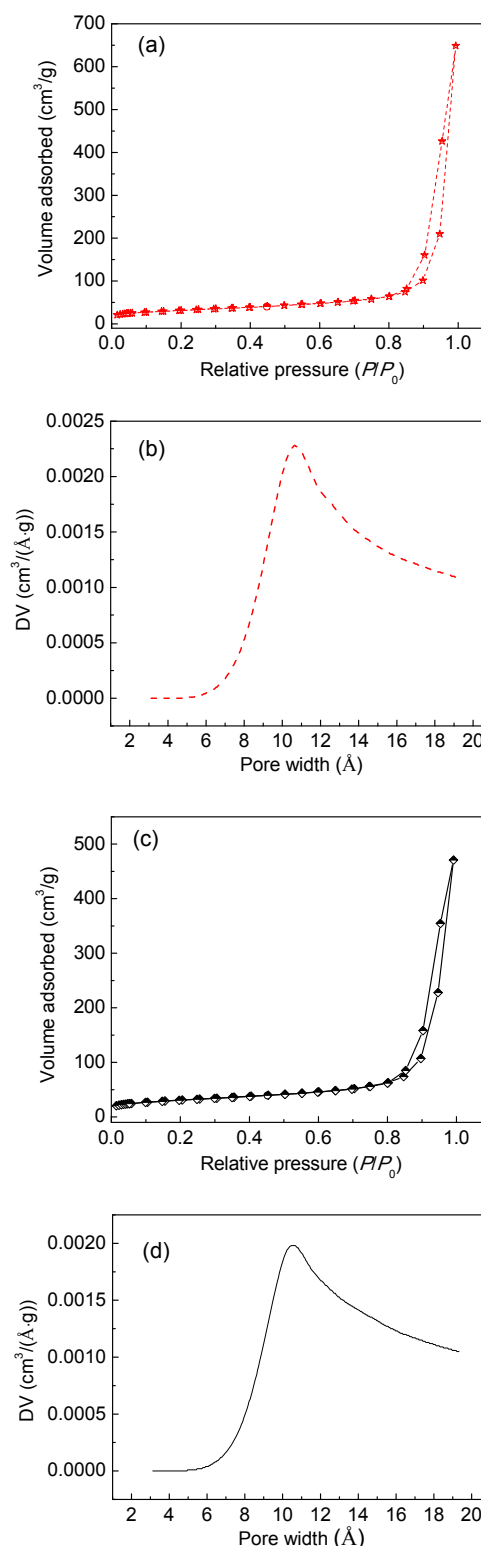


Fig. 6 BET adsorption-desorption isotherms of Au/BW₁₁/Al₂O₃ calcinated at 500 °C (a) and bare Al₂O₃ support (c), and HK pore distribution curves of Au/BW₁₁/Al₂O₃ calcinated at 500 °C (b) and bare Al₂O₃ support (d) (DV is the differential pore volume)

3.3 Catalytic performance

Epoxidation of cyclooctene was carried out in order to evaluate the activity of the catalyst by changing reaction conditions such as calcination temperature, reaction temperature, catalyst dosage, reaction time, recyclability, and use of different solvents and oxidants. High selectivity was obtained using TBHP as the initiator. It is emphasized that sub-stoichiometric quantities of the initiator were necessary, while molecular oxygen from an oxygen cylinder was the stoichiometric oxidant source (Hughes *et al.*, 2005). No conversion was observed in the absence of a radical initiator as cited in the literature many times (Turner *et al.*, 2008; Dhakshinamoorthy *et al.*, 2012; Habibi *et al.*, 2013; Skobelev *et al.*, 2013). This accorded with literature where nano gold catalysts were prepared on supports including carbon, alumina, iron oxide, and titania, and the influence of the nature of the radical initiator on the reaction selectivity had been found critical (Lignier *et al.*, 2008). Certainly, the choice of support leads to enhanced wetting of gold particles in the TBHP-initiated epoxidation (Mendez *et al.*, 2010).

3.3.1 Effect of calcination temperature

The reaction was investigated at five different calcination temperatures (200–600 °C) to optimize the catalyst preparation conditions (Fig. 7). The results show that increasing calcination temperature improves both the conversion and selectivity. At first, both the conversion and selectivity increase fairly well, but then the change becomes slightly moderate by further increase of calcination temperature. Hence, the optimal calcination temperature was 500 °C. According to a recent study (Tebandeke *et al.*, 2014), the gold in the sample calcinated at low temperature is mainly present in an oxidized state, while the clusters in the sample calcinated at high temperature are reduced to the metallic state which might be the reason for altered activity.

3.3.2 Effect of catalyst dosage

As is shown in Fig. 8, the conversion increases reasonably when the dosage of the catalyst is increased up to 0.2 g. With the increase in the amount of the catalyst, the concentration of the tungsten and gold species in the system also increases. This sug-

gests that the tungsten and gold species function as active sites for oxidation. After 0.2 g of the catalyst dosage, the conversion remains almost constant. A possible reason for this could be the fact (Shanmugam *et al.*, 2004) that the reaction undergoes an adsorption behavior rather than the pseudoliquid phenomenon in catalysis using heteropolyacids. The nonpolar molecules might be adsorbed on the surface covering active sites without entering the bulk and therefore addition of more catalyst makes no difference.

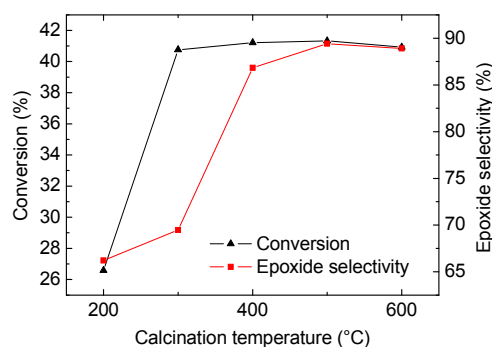


Fig. 7 Effect of calcination temperature on catalytic performance

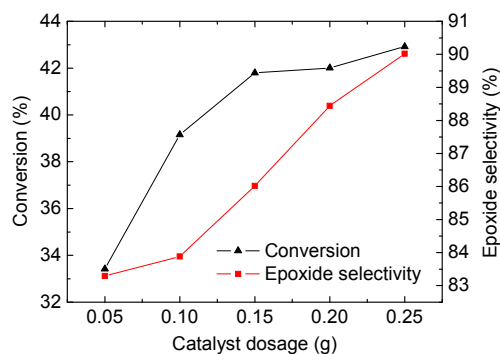


Fig. 8 Effect of catalyst dosage on catalytic performance

3.3.3 Effect of reaction temperature

Four different reaction temperatures were used to optimize the reaction temperature, the results for which are shown in Table 1. Initial increase of temperature proved good for conversion but the trend then became a little slower. Observation of the outcomes makes 80 °C the optimum reaction temperature as only a negligible improvement in conversion was observed after 80 °C.

The product ratio between epoxide and other oxygenated products might be due to parallel

pathways but also could be due to partitioning of an intermediate species on the gold surface as quoted in (Bawaked *et al.*, 2009). This partitioning is between attacking cyclooctene at its double bond or two allylic positions. Withdrawal of H from the allylic positions would lead to allylic hydroperoxide formation, by incorporating O₂, which could either remove water to produce cyclooctenone or get involved in the catalytic cycle, likely as TBHP, to produce more of the O-transfer species. After O-transfer to the olefin, the surface species would have to be restructured either from gaseous O₂ or indirectly by formation of the intermediate allylic hydroperoxide (Bawaked *et al.*, 2009).

Table 1 Effect of different reaction temperatures on catalytic performance in cyclooctene epoxidation

Entry	Reaction temperature (°C)	Conversion (%)	Epoxide selectivity (%)
1	40	29.54±0.73	89.25±0.86
2	60	34.97±1.20	88.98±0.90
3	80	40.34±0.91	86.87±0.54
4	100	42.67±0.78	86.04±0.61

All reactions were performed with 0.15 g Au/BW₁₁/Al₂O₃ catalyst, calcinated at 500 °C, 5 g cyclooctene, 0.01 g TBHP, reaction time of 24 h, and oxygen pressure of 0.4 MPa

3.3.4 Effect of reaction time

It is shown in Fig. 9 that the initial increase in reaction time increases the conversion slowly. There was a gradual increase in the conversion with almost 87% selectivity for epoxide up to 24 h. It is interesting that when the reaction time was increased to 48 h, the selectivity towards epoxide decreased from 87% to 85%. The distribution of the product alters with increase in the reaction time. As in cyclic olefins, an allylic attack is preferred, which gives rise to epoxide. It might be possible that prolonging the reaction time caused the epoxide to rearrange by reductive elimination of the catalyst leading to further oxygenated products. With increase in the reaction time, in the presence of a constant supply of oxidant and high temperature, the epoxide might be converted to the more stable products by a bond cleavage mechanism. Hence, 24 h is considered as the optimal reaction time.

3.3.5 Use of different oxidants

The effect of different oxidants on cyclooctene epoxidation, such as H₂O₂, NaIO₄, tert-BuOOH, and molecular oxygen, was investigated to check the versatility of the catalyst. The results (Table 2) demonstrated that TBHP is the best and NaIO₄ the most undesirable oxidant in terms of high conversion and selectivity in the present case. Bujak *et al.* (2012) discussed TBHP as an effective oxidant in making the catalyst accessible for the oxidation as it results in increase of the surface wettability of the catalyst. So TBHP increases the surface wettability of the catalyst making it more effective given the conditions. Undoubtedly, H₂O₂ is a desired oxidant because of its low price, availability, and generation of water as the by-product. TBHP, on the other hand, is expensive and generates tert-butyl alcohol as the by-product. Likewise, H₂O₂ showed high selectivity towards epoxide. Molecular oxygen proved to be a reasonable oxidant from a green chemistry perspective with significant conversion and selectivity near to that of

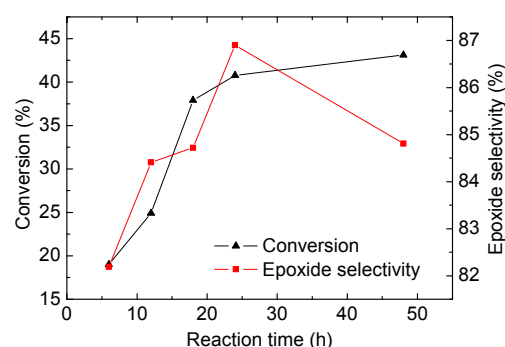


Fig. 9 Effect of reaction time on catalytic performance

Table 2 Effect of different oxidants on catalytic performance in cyclooctene epoxidation

Entry	Oxidant	Conversion (%)	Epoxide selectivity (%)
1	H ₂ O ₂	32.49±1.19	92.38±1.12
2	NaIO ₄	10.30±1.80	42.41±1.03
3	tert-BuOOH	52.80±1.63	97.04±2.20
4	Molecular oxygen	40.57±0.76	87.32±0.87

All reactions were performed with 0.15 g Au/BW₁₁/Al₂O₃ catalyst, calcinated at 500 °C, 5 g cyclooctene, at temperature of 80 °C, and reaction time of 24 h; Entries 1, 2 or 3: 2 g oxidant dosage; Entry 4: oxygen pressure of 0.4 MPa

using TBHP as the oxidant. Therefore, molecular oxygen is an appropriate oxidant for this catalytic epoxidation reaction.

3.3.6 Use of different solvents

The nature of the solvent has a substantial effect on the distribution of the catalyst between the organic and aqueous phases. It is mentioned in the literature that low boiling chlorine containing hydrocarbons like 1,2-dichloroethane are the most appropriate solvents for such reactions (Timofeeva *et al.*, 2003). Their application heightens the yield and selectivity of the process, which accords with published data (Tolstikov, 1976). Lignier *et al.* (2007) discovered that nano gold catalysts can promote the liquid phase epoxidation of trans-stilbene in methylcyclohexane by taking part in a chain reaction which involves a radical formed from the solvent. For further optimization of the reaction conditions, the reaction was performed under different solvents while keeping all other parameters fixed. Results (Table 3) show that some of the solvents, like 1,2-dichloroethane, acetone, acetonitrile, and a mixture of 1,2-dichloroethane:acetonitrile, gave promising results towards high selectivity. The conversion and selectivity profile is substantial when observed in the absence of any solvent.

3.3.7 Reusability of the catalyst

An intriguing goal of liquid phase oxidation catalysis is to design novel heterogeneous catalysts which are easily recyclable without the loss of activity and selectivity. At the end of a reaction, the catalyst was retrieved by centrifugation and washed with

acetone. Later it was dried at 100 °C for 1 h before reuse. After the first run (Table 4) no obvious change in selectivity was observed while the conversion decreased a bit with each run. This might be due to loss of catalyst every time after the run in the washing process as selectivity remained almost consistent.

4 Conclusions

We have shown that the solid catalytic system Au/BW₁₁/Al₂O₃ combining gold nanoparticles and the Keggin type POM over γ -Al₂O₃ support for aerobic epoxidation of olefins is highly active under mild conditions without using any organic solvent. The superiority of the catalyst lies in an efficient activation of molecular oxygen and cyclooctene. Furthermore, the catalyst can be regenerated and used successfully without any significant loss in catalytic activity for up to three cycles. However, the nature of the above interaction and its mechanism in molecular oxygen activation is still not clear. On the other hand, this catalyst is not active for some other olefin

Table 4 Cyclooctene epoxidation with recycled catalyst

Catalytic run	Catalyst	Conversion (%)	Epoxide selectivity (%)
1st	Au/BW ₁₁ /Al ₂ O ₃	40.39±0.56	85.50±0.48
2nd	Au/BW ₁₁ /Al ₂ O ₃	39.20±0.77	85.32±0.31
3rd	Au/BW ₁₁ /Al ₂ O ₃	38.65±0.26	85.20±0.68
4th	Au/BW ₁₁ /Al ₂ O ₃	36.59±0.34	85.29±0.89

All reactions were performed with 0.15 g Au/BW₁₁/Al₂O₃ catalyst, calcinated at 500 °C, 5 g cyclooctene, 0.01 g TBHP, at temperature of 80 °C, reaction time of 24 h, and oxygen pressure of 0.4 MPa

Table 3 Effect of different organic solvents on catalytic performance in cyclooctene epoxidation

Entry	Solvent	Polarity	Conversion (%)	Epoxide selectivity (%)
1	No solvent		41.36±0.87	87.02±0.73
2	1,2-dichloroethane	3.7	45.79±1.62	93.65±1.38
3	Acetonitrile	5.8	39.50±0.82	95.88±0.55
4	Toluene	2.4	26.15±1.47	70.63±1.34
5	Dichloromethane	3.1	29.40±1.63	83.91±1.80
6	Carbon tetrachloride	1.7	22.47±0.94	75.80±1.02
7	Chloroform	4.1	39.65±1.32	85.01±1.50
8	Acetone	5.4	44.23±2.10	94.11±1.43
9	1,2-dichloroethane:acetonitrile	–	46.64±0.75	97.31±1.01

All reactions were performed with 0.15 g Au/BW₁₁/Al₂O₃ catalyst, calcinated at 500 °C, 5 g cyclooctene, 10 g solvent, 0.01 g TBHP, at temperature of 80 °C, reaction time of 24 h, and oxygen pressure of 0.4 MPa

epoxidation such as cyclohexene. Therefore, further studies are required to investigate the role of POM and gold (or other elements) in olefin epoxidation.

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中文概要

题目: 环境友好非均相多金属氧酸盐-金催化剂 Au/BW₁₁/Al₂O₃上环辛烯分子氧绿色环氧化研究

目的: 环氧化物是多种有机合成反应的重要中间体,也可作为环氧树脂、染料和表面活性剂的原料。传

统的环氧化存在催化剂分离难、氧化剂成本高和过程含有溶剂等缺点。本文旨在探讨纳米金和多金属氧酸盐负载非均相催化剂用于无溶剂条件下环辛烯环氧化的反应条件对催化性能的影响。

创新点: 1. 把纳米金颗粒和多金属氧酸盐(即 BW₁₁)结合并负载在固体载体上制备出了一种新型复合催化剂材料; 2. 采用分子氧作为氧化剂而不是传统的有机酸或者过氧酸; 3. 在温和条件下可获得良好的转化率和较高的环氧化物选择性; 4. 催化反应体系未使用有机溶剂; 5. 催化剂稳定并可循环使用。

方法: 1. 根据文献中所述方法制备 BW₁₁; 2. 采用标准沉积沉淀法合成 Au/Al₂O₃; 3. 采用湿式浸渍法制备催化剂 Au/BW₁₁/Al₂O₃; 4. 环辛烯环氧化使用叔丁基过氧化氢(TBHP)作为引发剂,氧气作为氧化剂,在高压反应釜中进行反应; 5. 采用扫描电镜和X射线衍射等对催化剂进行表征。

结论: 1. 提高焙烧温度可改善催化反应性能; 2. 随着催化剂量增加到0.2 g,转化率也随之增加(图8); 3. 反应的最佳温度为80 °C(表1); 4. 随着反应时间的增加直到24 h,转化率逐渐增加,环氧化物选择性也增加到约87%(图9); 5. 催化剂可适用于多种氧化剂(表2); 6. 无溶剂下转化率和选择性相对较大(表3); 7. 催化剂可以有效活化分子氧和环辛烯; 8. 催化剂可以再生,在使用三次后,其活性损失不大。

关键词: 纳米金; 多金属氧酸盐; 环辛烯; 环氧化; 分子氧