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Catalytic activity of hexagonal MoO_3 modified with silver, palladium and copper

Abstract: Catalytic activity of solvothermally-synthesized hexagonal molybdenum trioxide (*h*-MoO_3) in epoxidation of 1-octene by *tert*-butyl hydroperoxide and the effect of deposition of metal (Ag, Pd, Cu) nanoparticles on the properties of catalyst have been investigated. It has been shown that silver-modified MoO_3 demonstrates the highest catalytic activity and selectivity in the reaction of 1,2-epoxyoctane formation, whereas MoO_3 modified with Pd nanoparticles exhibits worse catalytic performance than bare MoO_3; by contrast, copper-modified MoO_3 does not catalyze the epoxidation reaction. The Ag/MoO_3 catalyst was also found to be active in the reaction of 1-octene oxidation by molecular oxygen at the initial stage of the oxidation process.

Keywords: epoxidation, molybdenum trioxide, metal nanoparticles

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1 Introduction

The epoxidation of unsaturated hydrocarbons is commonly used in the chemical industry and organic synthesis. Epoxy compounds are useful intermediates which can be transformed into a variety of chemical products [1-5]. Epoxides find applications in production of epoxy resins, polymers, surfactants, as well as some pharmaceutics and biologically active compounds. However, in many cases the direct epoxidation of olefins by chemical oxidants, *e.g.* hydrogen peroxide or organic hydroperoxides, appears to be ineffective and accompanied with the formation of unwanted by-products. The activity of oxidants to yield epoxides can be improved by using appropriate catalysts. Various catalysts have been investigated in the epoxidation reactions. Homogeneous catalysts for hydroperoxide epoxidation of olefins complexes of various transition metals have been successfully used [6-8]; however, the application of these catalysts for epoxidation reaction on a large scale is limited due to the problems arising with catalyst regeneration and its separation from the reaction products. Therefore, much attention was focused on the application of transition metal oxides as the heterogeneous catalysts for olefin epoxidation [9,10]; among transition metal oxides MoO_3 shows much promise due to pronounced catalytic activity [11-14] which can be enhanced by modification of the catalyst surface with fine metal particles [15].

Here, we report on catalytic activity of hexagonal MoO_3 and supported nanocatalysts Ag/MoO_3, Pd/MoO_3, Cu/MoO_3 in the epoxidation of 1-octene using *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant.

2 Experimental procedure

The MoO_3 particles used as the catalyst were synthesized via polycondensation of molybdic acid [16]. For this purpose, 75 mL of 0.5 M aqueous solution of molybdic acid (obtained by passing sodium molybdate solution through the column, 60cm×12mm, packed with Dowex HCR-W2(E) ion exchange resin) was incubated at 100°C for 4 h; the reaction volume during the treatment was maintained constant. The oxide particles were then separated by centrifugation, washed with distilled water to remove molybdate, rinsed with 1% (vol.) ethanol solution and dried at room temperature. The yield of solid product was

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of ca. 80%. The morphology of the resultant molybdenum trioxide particles was investigated by scanning electron microscopy (SEM) using LEO 1420 electron microscope.

Silver and palladium nanoparticles were deposited by a photocatalytic method [17,18]. For these purposes, 10 mg of MoO_3 was suspended in 10 mL of 10^{-5} M Ag_2SO_4 aqueous solution or in 10 mL of 10^{-5} M $PdCl_2$ solution acidified by HCl to pH 4 and then exposed to UV light for 2 min (in the case of Ag deposition) or 10 min (in the case of Pd deposition). Copper was deposited photochemically by UV light irradiation of 10 mg of MoO_3 suspended in 10 mL of 10^{-3} M $CuSO_4$ + 0.01 $H_2C_2O_4$ solution; the irradiation time was 3 min. In both cases, the high-pressure mercury lamp Philips HPK 125 W was used as the light source; the intensity of incident light was ~15 mW cm^{-2}. The formation of metal particles as the result of photodeposition was confirmed by X-ray photoelectron spectroscopy.

After metal deposition oxide particles were separated by centrifugation, thoroughly washed with distilled water and dried at room temperature. To view metal nanoparticles grown on the MoO_3 surface, the samples were embedded in poly(methylmethacrylate) and ultrathin sections (ca. 30 nm in thickness) were obtained using a Leica Ultracut UST ultramicrotome. This opens up the possibility of splitting MoO_3 crystallites into separate lamellae and makes metal nanophase deposites on their surface observable with the use of transmission electron microscopy (TEM). Carbon-covered copper grids were used to support thus obtained sections, and a Zeiss EM 912 Omega microscope was employed for analysis of the morphology of metal deposit.

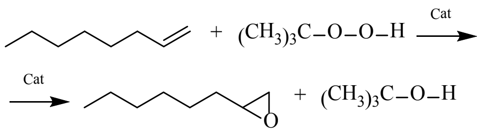
2.1 Epoxidation reaction

The epoxidation of 1-octene with TBHP as the oxidant was carried out under an argon atmosphere in a temperature-controlled glass reactor fitted with a magnetic stirrer and a reflux condenser. 1-Octene and chlorobenzene (solvent) obtained from Aldrich were additionally dried over anhydrous calcium chloride and then distilled. TBHP was synthesized from *tert*-butyl alcohol and hydrogen peroxide in the presence of sulfuric acid by the procedure given in [19]. In order to avoid hazards which can be connected with using hydroperoxide, we have worked with TBHP in safety conditions such as low amounts of hydroperoxide and low temperatures. Also, we have provided high purity of reagents which do not contain substances favoring the hydroperoxide decomposition.

In a typical run, 5.5 mL of chlorobenzene, 4 mL (25 mmol) of 1-octene and 0.5 mL (5 mmol) of TBHP were introduced into the reactor in this order. The solution was heated to 100°C and the reaction was started by adding 0.01 g of catalyst.

The hydroperoxide content was determined by iodometric titration [20,21]. Samples of reaction mixture were withdrawn at regular intervals and then analyzed using a Hewlett Packard HP 6890 N chromatograph with a capillary column DB-1 (60m×0.32mm×0.5μm) coated with dimethylsiloxane. The column temperature was increased from 50 up to 250°C with a rate of 10 deg min^{-1}.

The main product of the epoxidation reaction of 1-octene by TBHP was 1,2-epoxyoctane:



Tert-butanol is also formed in the reaction mixture as the product of TBHP decomposition in the presence of the catalyst:

$$2\,(CH_3)_3C\!-\!O\!-\!O\!-\!H \xrightarrow{Cat} 2\,(CH_3)_3C\!-\!O\!-\!H + O_2$$

The percentage-conversion of TBHP and the percentage-selectivity for 1,2-epoxyoctane (EP) formation in the epoxidation of 1-octene with TBHP were calculated as:

Conversion of TBHP = 100% · [TBHP reacted (moles)] / [TBHP initial (moles)]

Selectivity for EP production = 100% · [EP formed (moles)] / [TBHP reacted (moles)].

The EP yield was calculated by multiplying the conversion of TBHP and selectivity of EP production.

It was established in the blank experiments that TBHP does not decompose in the absence of the catalyst and EP is not formed under the reaction conditions.

2.2 Oxidation reaction

The oxidation of 1-octene by molecular oxygen was carried out in a glass reactor equipped with a magnetic stirrer and gasometrical unit [22] at a temperature of 80°C and $1{\times}10^5$ Pa of oxygen pressure. In the oxidation experiments, 1.4 mL (8.75 mmol) of 1-octene, 0.01 mL (0.10 mmol) of TBHP, 0.59 mL of chlorobenzene, and 0.0012 g of catalyst were introduced into the reaction. Gaseous oxygen used as an oxidant, prior to entering the reaction system, was dried by passing through a bed of soda lime and calcium chloride. The preliminary experiments have evidenced that the oxidation rate is not dependent on the oxygen pressure when the pressure is higher than $5{\times}10^4$ Pa. It was also found that under the reaction conditions the purified and distilled 1-octene is not oxidized with molecular oxygen by the catalysts in the absence of hydroperoxide. Therefore, the homogeneous initiator of radical processes, TBHP, was used in the oxidation reaction of 1-octene by molecular oxygen.

3 Results and discussion

It is seen from the SEM image given in Fig. 1a that the solvothermal method yields regular prism-like MoO_3 particles with an average length of ca. 2 μm. The XRD analysis has showed that the resultant oxide phase consists of a hexagonal MoO_3 with the admixture of monoclinic $MoO_3•2H_2O$. The concentration of the monoclinic phase was below 15% (the estimation was obtained from thermogravimetric data considering that the weight losses occurring in the temperature range of 110 – 150°C are consistent with dehydration of $MoO_3•2H_2O$). The TEM images given in Figs. 1b-1d provide evidence that the mean size of silver and palladium particles grown at the surface of MoO_3 microcrystals via photocatalytic deposition route was of ca. 10 nm, whereas copper deposit obtained *via* reduction of metal ions by radical species generated during photoconversion of oxalate [23,24] consists of the particles having ca. 5 nm in their size.

The catalytic performance of bare and metal-modified *h*-MoO_3 is evidenced from Figs. 2-4. These experiments have also shown that in the case of supported nanocatalyst Cu/MoO_3 no signs of TBHP decomposition were detected (Fig. 2) and EP was not formed in the reaction system. On the other hand, when one goes from bare MoO_3 to the supported nanocatalyst Ag/MoO_3, an increase in the efficiency of TBHP conversion from 55 to 73% was observed and the EP yield exhibits increase from 49 to 68%, while the selectivity of EP production increases from 89 to 93%. By contrast, the conversion of TBHP and selectivity of EP formation in the case of Pd/MoO_3 catalyst were lower compared to the bare MoO_3 and, consequently, the EP yield in the case of Pd/MoO_3 was lower than that shown by MoO_3. The similar effect of Pd particles on the rate of epoxidation reaction was observed in [25].

The catalytic performance demonstrated by tested catalysts in the epoxidation reaction of 1-octene thus varies in the following order: Pd/MoO_3 < MoO_3 < Ag/MoO_3, *i.e.*, Ag/MoO_3 has shown itself as the best catalyst for the epoxidation of 1-octene with TBHP; on the other hand, Pd/MoO_3 exhibits poor activity and selectivity in the epoxidation reaction, whereas Cu/MoO_3 does not catalyze this reaction.

High catalytic activity demonstrated by silver-modified MoO_3 towards an epoxidation reaction can be attributed to the fact that a charge transfer from Ag to MoO_3 occurs in Ag/MoO_3 catalyst [15] that creates favourable conditions for the attack of olefinic carbon by hydroperoxide-derived reactive oxygen species adsorbed

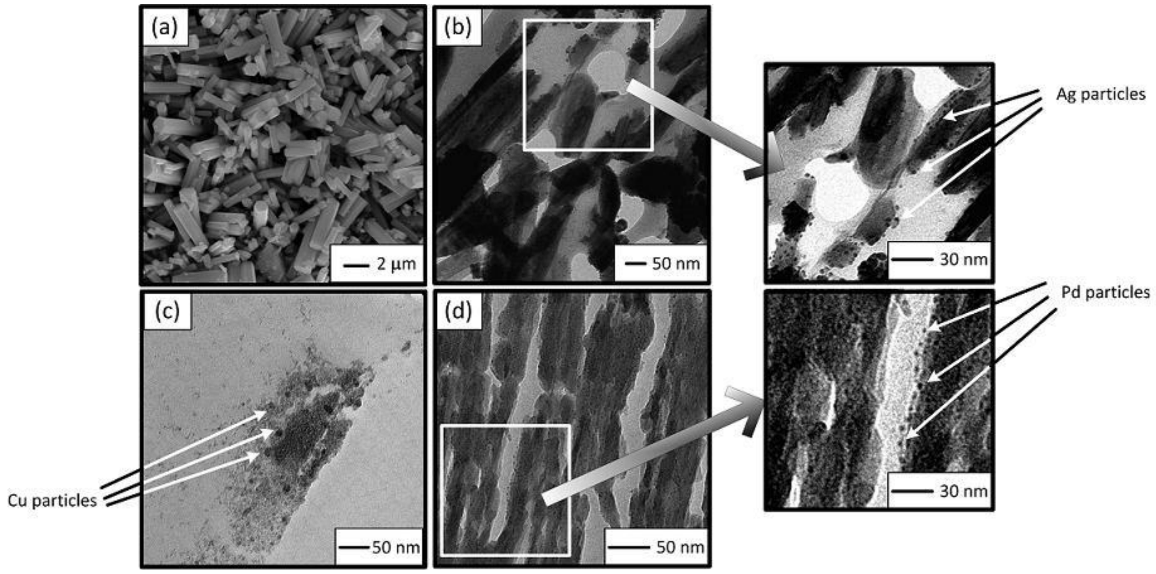


Figure 1: (a) SEM image of *h*-MoO_3 crystallites. TEM images of MoO_3 lamellae with (b) Ag particles, (c) Pd particles, (d) Cu particles. The insertions show the regions of metal-modified lamellae at the enhanced magnification.

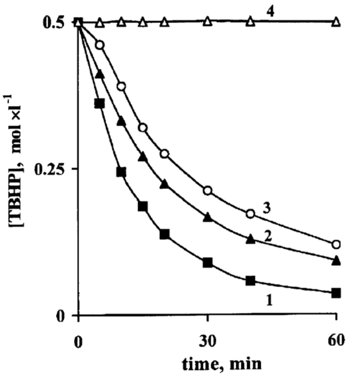


Figure 2: Kinetic curves for TBHP consumption in the epoxidation of 1-octene at 100°C in the presence of: (1) Ag/MoO_3, (2) MoO_3 (3), Pd/MoO_3 and (4) Cu/MoO_3. The amounts of reactants and catalysts: 4 mL (25 mmol) of 1-octene, 0.5 mL (5 mmol) of TBHP, 5.5 mL of chlorobenzene, 0.01 g of catalyst.

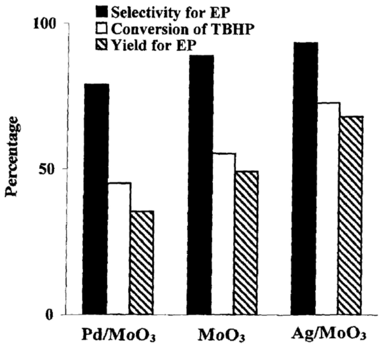


Figure 4: Catalytic performance of Ag/MoO_3, Pd/MoO_3 and MoO_3 in the epoxidation of 1-octene with TBHP at 100°C. The amounts of reactants and catalysts: 4 mL (25 mmol) of 1-octene, 0.5 mL (5 mmol) of TBHP, 5.5 mL of chlorobenzene, 0.01 g of catalyst.

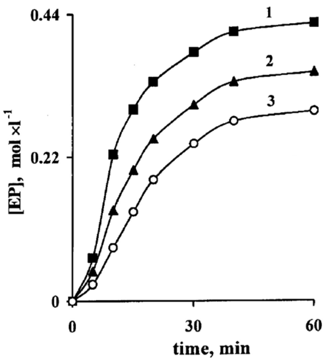


Figure 3: Kinetic curves for the EP accumulation during catalytic epoxidation of 1-octene with TBHP at 100°C in the presence of: (1) Ag/MoO_3, (2) MoO_3 and (3) Pd/MoO_3. The amounts of reactants and catalysts: 4 mL (25 mmol) of 1-octene, 0.5 mL (5 mmol) of TBHP, 5.5 mL of chlorobenzene, 0.01 g of catalyst.

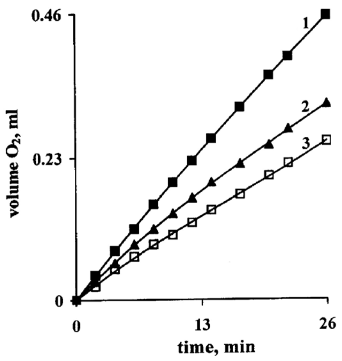


Figure 5: The kinetic curves for the oxygen consumption in the reaction of oxidation of 1-octene with molecular oxygen at 80°C in the presence of (1) Ag/MoO_3 and (2) MoO_3 as well as (3) in the absence of catalyst. The amounts of reactants and catalysts: 1.4 mL (8.75 mmol) of 1-octene, 0.01 mL (0.10 mmol) of TBHP, 0.59 mL of chlorobenzene, 0.0012 g of catalyst.

at the silver particles. The formation of electron-deficient Ag centers in the case of Ag/MoO_3 catalyst is also believed to be responsible for its activity towards epoxidation of propylene by molecular oxygen [26]. Contrastingly to the modification of MoO_3 with silver nanoparticles, the deposition of copper nanophase inhibits the MoO_3 catalyst. The most plausible explanation of the negative effect of copper deposition on the catalyst performance is given in [27]. The authors have pointed out that Cu^0 is not capable of operating as a true epoxidation catalyst because it may be readily oxidized under reaction conditions into Cu_2O or CuO [27]. Since photochemical deposition of copper involves adsorption of Cu^{2+} ions at the semiconductor surface followed by their reduction [24], the increase of copper particles concentrates at the sites at the surface of MoO_3 with the enhanced basic properties. One could expect that these sites are reponsible for activity of bare MoO_3 in the epoxidation reaction since their blocking by copper particles leads to the catalyst passivation (Fig. 2).

Taking into account the best catalytic performance of Ag/MoO_3 in the epoxidation of 1-octene with hydroperoxide, the catalytic activity of this supported nanocatalyst was also examined at the initial stage of oxidation of 1-octene by molecular oxygen in the presence of TBHP as the homogeneous initiator of radical processes. For comparison, bare MoO_3 was also investigated as a catalyst in that reaction. This reaction is of special practical interest because molecular oxygen is not only cheap but also an environmentally friendly oxidant. The obtained results are shown in Fig. 5, where the kinetic curves for the oxygen consumption during catalytic and non-catalytic oxidation processes are given. It is seen from Fig. 5 that in the presence of hydroperoxide the oxidation process of 1-octene occurs in the absence of catalyst. Fig. 5 also provides evidence that Ag/MoO_3 as well as MoO_3 show themselves as the favorable catalysts for oxidation of 1-octene with molecular oxygen, the most intense oxygen consumption at the initial stage of the oxidation process being observed in the presence of silver-modified MoO_3. The Ag nanoparticles thus play a role of promoter and improve the performance of the MoO_3 catalyst for the epoxidation and oxidation of 1-octene.

4 Conclusions

The hexagonal MoO_3 modified with silver, palladium and copper nanoparticles was investigated as the catalyst for epoxidation of 1-octene with hydroperoxide. It has been shown that deposition of palladium nanoparticles results in some decrease in the catalytic activity of MoO_3, whereas deposition of copper nanoparticles leads to complete inactivation of MoO_3. Silver-modified molybdenum trioxide was found to be the most active catalyst for the epoxidation reaction: the increase in the 1,2-epoxyoctane yield from 49 to 68% was observed when coming from MoO_3 to Ag/MoO_3, with the selectivity increasing up to 98%. Among the tested nanocatalysts, Ag/MoO_3 is the best choice for epoxidation of 1-octene with hydroperoxide as well as for its oxidation by molecular oxygen.

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