

Short communication

# Immobilizing of oxo-molybdenum complex on cross-linked copolymer and its catalytic activity for epoxidation reactions



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## ABSTRACT

This work describes the immobilization of molybdenum acetylacetonate oxygen ( $\text{MoO}_2(\text{acac})_2$ ) on cross-linked porous copolymer support via covalent attachment under mild conditions. The obtained solid product DVB-AA-Mo was fully characterized by FT-IR, TG, CHN elemental analysis, nitrogen adsorption/desorption, and SEM, and was tested for the epoxidation of various alkenes with *tert*-butyl hydroperoxide (TBHP) as the oxidant. DVB-AA-Mo was proved to be a highly efficient catalyst for epoxidation reactions, it could easily be recovered by filtration and reused for five runs without significant loss in activity.

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## 1. Introduction

Epoxidation of alkenes is an important reaction in laboratory as well as in the chemical industry, because epoxides are widely used for manufacturing epoxy resins, surfactants, and intermediates, *etc.* in organic synthesis [1–4]. This reaction is catalyzed by a number of transition metal compounds, titanium silicalites, Cu oxide, W-containing compounds, and titanium-containing molecular sieves [5–9]. Among the most efficient catalysts suggested for alkene epoxidation are Mo-containing compounds [9–13].

As highly active oxidation species, organic metal molybdenum complexes are known to be good epoxidation catalysts due to their high activity and selectivity [14–16]. However, problems of catalyst separation and recyclability should be addressed for these homogeneous catalysts. To this end, several strategies involving immobilization of the active catalytic moiety, *viz.* to zeolites [17,18], polymer [19,20], silica [21], graphene nanosheets [22], layered double hydroxide [23], and amine modified multi-wall carbon nanotubes [24], have been reported. Though good activity was achieved in those cases, most of them still bear some drawbacks like need for excess metal complex, the slow reaction speed, leaching of active species, or limited accessibility to the reactants. To circumvent the limitations associated with the known methods, a new strategy for catalyst preparation to overcome the above problems is therefore highly desirable.

In this work, we demonstrate an efficient, high-yielding approach for the immobilization of molybdenum acetylacetonate oxygen

( $\text{MoO}_2(\text{acac})_2$ ) on cross-linked porous copolymer support via covalent attachment, and use it as the catalyst for epoxidation of alkenes with *tert*-butyl hydroperoxide (TBHP) as the oxidant. The catalytic activity of this newly prepared catalyst was higher than that of the homogeneous  $\text{MoO}_2(\text{acac})_2$ , and can be easily recovered and steadily reused.

## 2. Experimental

## 2.1. Reagents and analysis

Please see Supplementary material (SM).

## 2.2. Preparation of catalysts

## 2.2.1. Synthesis of copolymer support DVB-AA

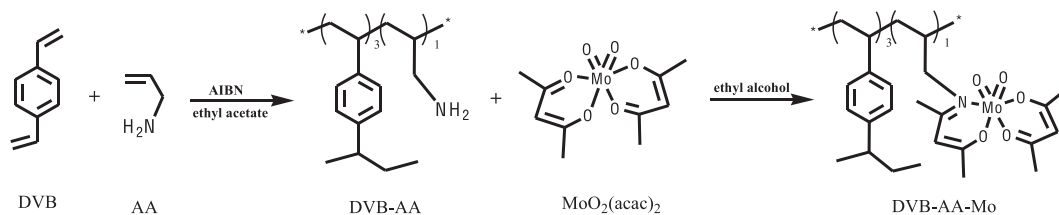
DVB-AA was prepared according the previous literature [25]. To prepare the cross-linked polymer DVB-AA, divinyl benzene (DVB) (3.9 g, 30 mmol), AIBN (0.1 g), and alyl amine (AA) (0.6 g, 5 mmol) were dissolved in ethyl acetate (100 ml) under nitrogen. The mixture was refluxed at 90 °C with stirring. After 24 h, a white solid formed was filtrated and was washed with ethanol for three times. The final product was dried in vacuum at 60 °C for 12 h. Element analysis: C, 86.4%; H, 8.13%; N, 3.02%. Theoretical value: C, 89.71%; H, 7.32%; N, 3.2%.

2.2.2. Synthesis of  $\text{MoO}_2(\text{acac})_2$ 

Molybdenyl acetylacetonate ( $\text{MoO}_2(\text{acac})_2$ ) was prepared according to the previous literature [26].

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**Scheme 1.** Synthesis of the immobilized  $\text{MoO}_2(\text{acac})_2$  catalyst DVB-AA-Mo.

### 2.2.3. Synthesis of DVB-AA-Mo

In detail, DVB-AA (2.68 g, 6 mmol) was dispersed in anhydrous ethanol (10 mL), the ethanol (10 mL) solution of  $\text{MoO}_2(\text{acac})_2$  (0.65 g, 2 mmol) was added into the above mixture with vigorous stirring, the resulting mixture was refluxed at 80 °C for 24 h under a nitrogen atmosphere. The formed light-blue solid precipitate was filtered off and washed thoroughly by  $\text{H}_2\text{O}$  and ethanol, and dried under vacuum. CHN elemental analysis for DVB-AA-Mo (by the mass percentage): C, 66.17%; N, 1.74%; H, 6.96%. Theoretical value: C, 69.16%; H, 6.4%; N, 1.87%.

### 2.3. Catalytic tests

Typically, cyclooctene (1 mmol),  $\text{CHCl}_3$  (5 mL), and catalyst DVB-AA-Mo (0.05 mmol) were added into a 25 mL round bottom flask. The reaction started after the addition of aqueous TBHP (3 mmol) at 70 °C under vigorous stirring. After the reaction, the catalyst was filtered off, washed with ethanol and dried for the next run. The product mixture was analyzed by gas chromatography (GC) (SP-6890A) equipped with a FID detector and a capillary column (SE-54 30 m  $\times$  0.32 mm  $\times$  0.3 m). The conversion and selectivity was calculated by calibration area normalization method, and each reaction mixture sample was detected at least three times to take the average. The epoxidation of other alkenes were carried out in the same way.

## 3. Results and discussion

### 3.1. Catalyst preparation and characterization

The copolymer support DVB-AA was prepared by free radical polymerization of divinyl benzene and allyl amine [25], and the required  $\text{MoO}_2(\text{acac})_2$  was prepared by the reaction of  $(\text{NH}_4)_6\text{MoO}_{24} \cdot 4\text{H}_2\text{O}$  with acetylacetone. Reaction of the obtained  $\text{MoO}_2(\text{acac})_2$  with support DVB-AA resulted in the covalently attached solid catalyst DVB-AA-Mo (Scheme 1), which is insoluble in common used solvents, such as

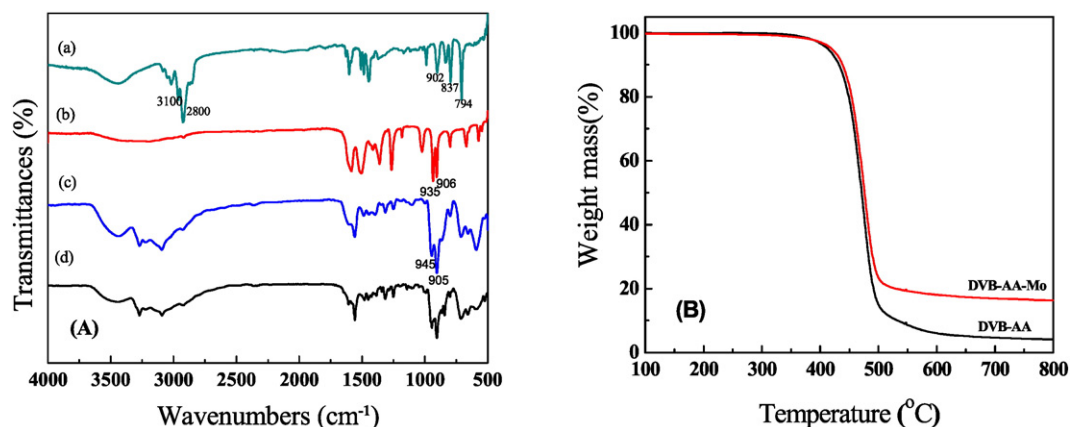
methanol, ethyl alcohol, chloroform, ethyl acetate, THF, DMF, DMSO, and  $\text{H}_2\text{O}$ .

DVB-AA-Mo was characterized by IR, CHN elemental analysis, TG, nitrogen adsorption/desorption, and SEM. As shown in Fig. 1(A), the IR spectrum of DVB-AA shows the bands at 2800–3100  $\text{cm}^{-1}$  assigned to symmetric and asymmetric vibration of  $-\text{C}-\text{H}$ , and the bands at 902, 837, and 794  $\text{cm}^{-1}$  assigned to vibration of substituted aromatic rings. The intense peaks appeared at 935 and 906  $\text{cm}^{-1}$  in the spectrum of  $\text{MoO}_2(\text{acac})_2$  is attributed to the symmetric and asymmetric stretching mode of the *cis*- $\text{MoO}_2$ . For DVB-AA-Mo, these peaks appeared distinctively with the slight shift of peak positions. Meanwhile, the intensity of the band at 906  $\text{cm}^{-1}$  corresponding to asymmetric stretching mode of the *cis*- $\text{MoO}_2$  increased, which reveals the covalent attachment of  $\text{MoO}_2(\text{acac})_2$  with DVB-AA support.

The TG spectra of DVB-AA-Mo in Fig. 1(B) illustrate a high thermal stability up to ca. 450 °C, and the weight loss in the temperature 450–500 °C is attributed to the decomposition of the organic groups. Sublimation of the left-over residue (18%) at 800 °C suggested the formation of  $\text{MoO}_3$  which revealed the percentage of Mo in the catalyst to be 12%. This result is in accordance with that of the elemental analysis. All these results suggest that DVB-AA-Mo has the structure illustrated in Scheme 1. The ICP-AES for the catalyst DVB-AA-Mo shows about 7.7 wt.% Mo in the catalyst, which is lower than the theoretical value 12.8% of Mo in DVB-AA-Mo. This is mostly due to that the catalyst could not completely dissolve in the solvents during the characterization.

The surface area and pore structure are examined by nitrogen sorption measurements (Figure S1, SM), the isotherm of DVB-AA is type IV with a clear H1-type hysteresis loop at partial pressure region of  $P/P_0 = 0.8$ –1.0, reflecting the existence of mesopores. DVB-AA has a high BET surface area of 866.4  $\text{cm}^2/\text{g}$ . After the combination of  $\text{MoO}_2(\text{acac})_2$ , DVB-AA-Mo also shows a IV type nitrogen sorption isotherm with high specific surface area of 801.2  $\text{cm}^2/\text{g}$ .

Fig. 2 shows the SEM images of DVB-AA and DVB-AA-Mo. The DVB-AA is collective spherical particles with size in micrometers (diameter: 1–3  $\mu\text{m}$ , Fig. 2A). After the attachment of  $\text{MoO}_2(\text{acac})_2$ , the smooth outer surface of DVB-AA changed to be rough with the appearance of small



**Fig. 1.** (A) FT-IR spectra of (a) DVB-AA, (b)  $\text{MoO}_2(\text{acac})_2$ , (c) DVB-AA-Mo, and (d) reused DVB-AA-Mo, and (B) TG curves of DVB-AA and DVB-AA-Mo.

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