

Epoxidation of alkenes using inorganic polymer of silica zirconia molybdate as catalyst



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ABSTRACT

Silica zirconia sulfate was prepared by sol–gel copolymerization of the sulfated zirconium octanoxide and tetraethylorthosilicate (TEOS). Active polymer oxidation catalysts were obtained by introducing sodium molybdate into the polymer by a ligand exchange reaction. The prepared inorganic polymer designated as SZ-Mo was characterized by FT-IR, SEM, XRD, N₂ sorption isotherms, and ICP techniques. It was found that SZ-Mo successfully catalyzes the epoxidation of cyclooctene, cyclohexene, *trans*-stilbene, and norbornene with 22–95% conversion and 60–100% selectivity. The dependence of the SZ-Mo catalytic activity to the amount of adsorbed Mo within the polymer as well as the study of catalyst stability during the course of reactions will be described in this presentation.

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1. Introduction

Epoxidation of alkenes catalyzed by metal complexes is one of the important oxidation reactions in industrial chemistry. Epoxides are important synthetic intermediates for the synthesis of oxygen containing natural or synthetic compounds [1,2]. Many transition metal complexes such as Co, Ti, Mn, V, and Mo have been used as catalyst for epoxidation of cyclic olefins with high selectivity [2]. Molybdenum complexes as the efficient oxyfunctionalization catalysts of alkenes have been the subject of intense research over the last three decades. Different types of molybdenum complexes such as Mo carbonyl derivatives [3,4], molybdenum (VI) aminopyridinium [5], Mo₂O₆ (4,4'-ditertbutyl 2,2'-bipyridine)₂ [6], and dioxomolybdenum (VI) complexes of Schiff-bases derivatives [7–10] have been used as catalyst in epoxidation type reactions.

Liquid phase epoxidation is usually performed either in homogeneous or in heterogeneous systems. Due to easier recovery and recycling of the reaction catalysts, many research and developments have been directed on the heterogeneous processes. Different solid supports such as polymers [11,12], silica and silicate layers [13], microporous, mesoporous, and functionalized

mesoporous have been used for immobilization, encapsulation, or incorporation of Mo compounds [14–18].

Recent utilization of inorganic polymer supports such as sulfated silica zirconia materials has attracted much attention in the last years due to their high acidity induced by silica sulfation. These materials are known with the extensive catalytic activities in processes such as isomerization [19], alkylation [20], esterification [21], and those involving oxygenation of hydrocarbons [22].

In this work, inorganic polymer of silica zirconia molybdate was prepared using tetraethylorthosilicate, sulfated zirconia octanoxide, and sodium molybdate. Exploration of factors such as SO₄²⁻/Zr or Si/Zr and catalytic epoxidation behavior of SZ-Mo with TBHP and H₂O₂ will be discussed.

2. Experimental

2.1. Preparation of the catalysts

2.1.1. Preparation of sulfated silica–zirconia inorganic polymer

The preparation method of silica–zirconia sulphate is almost similar to that of our previously reported for the synthesis of Si–Zr–Mo nanocomposite [23] with minor modification. In a typical procedure, zirconium octanoxide was prepared from zirconium tetra-*n*-butoxide and 1-octanol by alcohol interchange method. Zr(Oct)₂ SO₄ was then prepared by addition of sulfuric acid to different amounts of Zr(Oct)₄ solution in order to adjust the SO₄²⁻/Zr

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Scheme 1. Preparation of SZ1-Mo and SZ2-Mo.

ration as 0.6/1 or 1:1. Zr–Si inorganic polymer designated as SZ1 and SZ2 were prepared with two different molar ratios as follows:

For SZ1: $\text{Zr}(\text{Oct})_2\text{SO}_4$ (4 mmol, 1.80 g), TEOS (40 mmol, 8.87 ml), EtOH (308 mmol, 17.96 ml), H_2O (440 mmol, 7.92 ml), and AcOH (88 mmol, 5.03 ml) and for SZ2: $\text{Zr}(\text{Oct})_2\text{SO}_4$ (4 mmol, 1.80 g), TEOS (4 mmol, 0.89 ml), EtOH (56 mmol, 3.27 ml), H_2O (80 mmol, 1.44 ml), and AcOH (16 mmol, 0.92 ml). Therefore, in a typical procedure, TEOS, ethanol, H_2O , and AcOH were mixed by stirring and $\text{Zr}(\text{Oct})_2\text{SO}_4$ (0.1 M in 1-octanol) was then added under vigorous stirring. The resulting sol was stirred for 3 h. The produced gel was decanted by centrifugation using 3900 r/min for 15 min and then dried at 180 °C for several hours.

2.1.2. Immobilization of Mo on the surface of sulfated silica–zirconia inorganic polymer

MoO_3 (1.5 g, 7.7 mmol) dissolved in NaOH (10 ml, 5 M) was initially titrated with HCl (0.5 M) until pH was adjusted on 7. Sulfated silica–zirconia inorganic polymer (0.5 g) was then added and the mixture heated at reflux for 3 h. Subsequently, the solid product (SZ1-Mo or SZ2-Mo) was decanted by centrifugation, washed with deionized water, and dried at 100 °C.

2.2. Characterization

All chemicals were purchased from Merck chemical company and used without further purification. Infrared spectra were performed (KBr pellets) on a Bruker Tensor 27FT-IR spectrometer. X-ray diffraction (XRD) patterns were recorded on a Philips PW-1800 diffractometer with Cu $K\alpha$ radiation. Chemical analysis of samples was carried out with Varian 150AX inductively coupled plasma optical emission spectrometer (ICP-OES). Electron microscopy was performed on a Vega Tescan, scanning electron microscope (SEM). Surface areas, pore volume, and pore size distributions were obtained from the N_2 isotherms which determined at 77 K using Quantachrome Nova 2200, Version 7.11 Analyzer. The products were analyzed by GC and GC–MS using Agilent 6890 Series, with FID detector, HP-5, 5% phenylmethylsiloxane capillary and Agilent 5973 Network, mass selective detector, HP-5 MS 6989 Network GC system, respectively.

2.3. Catalytic epoxidation

The catalytic reactions were carried out in a round-bottom flask equipped with a magnetic stirrer and condenser. In a typical procedure, the alkene (20 mmol, *trans*-stilbene, 1 mmol), catalyst (50 mg), and CH_3CN (5 ml) were added into the flask. The reaction was started by adding H_2O_2 (20 mmol, 2.04 ml, 30% in H_2O) or TBHP (20 mmol, 2.74 ml, 70% in H_2O). The mixture was heated at reflux for 8 h. The catalyst was filtered and the filtrate was subjected to GC and GC–MS analyses. The Mo, Si, and Zr contents of the recycled catalyst were measured using ICP-OES techniques.

3. Results and discussion

3.1. Characterization of the catalysts

SZ1-Mo and SZ2-Mo were prepared according to the procedure presented in Scheme 1.

The sulfated zirconia was prepared using the reaction between sulfuric acid and $\text{Zr}(\text{Oct})_4$. Subsequent treatment with a mixture of TEOS, EtOH, AcOH, and distilled H_2O afforded the corresponding

Zr–Si inorganic polymer SZ1 and SZ2. Upon addition of Na_2MoO_4 , SZ1-Mo, and SZ2-Mo were generated presumably via reaction between Zr– SO_4 and MoO_4^{2-} . The weight percentages of Zr, Si, S, and Mo in SZ1, SZ2, SZ1-Mo, and SZ2-Mo were measured using ICP-OES technique in order to calculate the molar ratios of Zr/Si and S/Zr (Tables 1 and 2). The mole ratios of Zr/Si and S/Zr were found to be 0.06 and 1.16 in SZ1 (Table 2) and 0.30 and 1.78 in SZ2 (Table 2), respectively. ICP-OES analysis also showed that weight percents of Mo in SZ1-Mo and SZ2-Mo are 45.42 and 31.31, respectively (Tables 1 and 2). After Mo adsorption, no significant amount of sulfur was detected using ICP-OES technique (Tables 1 and 2). As seen in Table 1, the sulfur moles of SO_4^{2-} anions in SZ-1 and SZ-2 are 0.035 and 0.160, respectively. Moreover, the moles of Mo as MoO_4^{2-} are 0.473 and 0.326, respectively. Based on the results obtained from ICP, EDX, and FT-IR, the MoO_4^{2-} not only have been exchanged with SO_4^{2-} in both SZ-1 and SZ-2, but also some were partly adsorbed on the sample surfaces. Since the surface area of SZ-1 and SZ-2 are 141 and 83 m^2/g respectively, some MoO_4^{2-} may have been exchanged with other anionic species accordingly.

The FT-IR spectrum of $\text{Zr}(\text{Oct})_2\text{SO}_4$ (Fig. 1a) shows vibrations at 500, 610, and 725 cm^{-1} , corresponding to Zr–O bending and stretching vibrations. The bands appearing at 1000–1300, 1300–1400, and 2800–2900 cm^{-1} are attributed to the C–O, CH_3 or CH_2 , and C–H stretching of alkoxy groups, respectively. A broad band displaying at 3400 cm^{-1} is due to the OH stretching associated with alcohol residue present in zirconium alkoxide. Furthermore, the band due to SO_4^{2-} stretching vibrations observed in the range of 900–1200 cm^{-1} is attributed to the symmetric and asymmetric stretching vibrations of S–O bonds present in inorganic chelating bidentate sulfate [20]. The FT-IR spectrum of SZ1 in Fig. 1b displays the bands at 800, 1070, and 1225 cm^{-1} due to the stretching vibrations of Si–O and a band appearing at 520 cm^{-1} belongs to the Si–O bending vibration. The broad band appearing at 1000–1500 cm^{-1} is probably due to the vibrations of Zr–O–Si group present between ZrO_2 and SiO_2 fragments [21]. As seen in Fig. 1c, the bands displaying at 907 and 960 cm^{-1} corresponding to Mo–O vibration are due to the immobilized Mo on SZ1 polymer [17,24]. Comparison of the FT-IR spectra presented Fig. 1a, b with that shown in Fig. 1c reveals that the MoO_4^{2-} has been exchanged with SO_4^{2-} anions because no vibration due to this group is detected.

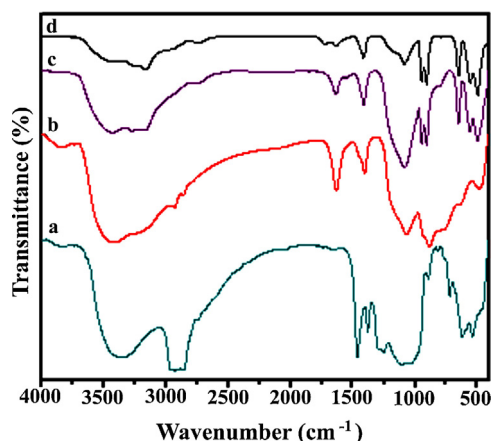


Fig. 1. FT-IR spectra of (a) $\text{Zr}(\text{Oct})_2\text{SO}_4$, (b) SZ1, (c) SZ1-Mo, and (d) SZ1-Mo after used as catalyst.

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