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ScienceDirect

Journal of Catalysis 245 (2007) 55–64

JOURNAL OF CATALYSIS

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Molybdenum-doped epoxy resins as catalysts for the epoxidation of alkenes

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Received 4 August 2006; revised 15 September 2006; accepted 15 September 2006

Abstract

Epoxy resins were polymerised using molybdenum ethoxide and 2-ethylhexanoate as polymerisation initiators. The thermosets thus obtained are useful epoxidation catalysts for a variety of alkenes, including propene with *tert*-butyl hydroperoxide as an oxidant. To investigate the long-term performance of these resins, they were used repeatedly in up to 120 reactions without any reconditioning. Compared with other catalyst systems based on organic polymers, they reveal unprecedented long-term activities over periods of months so that catalyst lifetimes of years can be expected. Di-, tri-, tetra- and oligofunctional epoxy resin monomers were used and compared. The catalytic performance of the thermosets strongly depends on the resin type and the polymerisation initiator. Promising results were obtained with monomers bearing 3 or 4 glycidyl groups in combination with $Mo(OEt)_5$ as an initiator. Metal leaching, determined by sensitive atomic spectroscopic techniques, is extremely low. Inorganic–organic hybrid catalysts can be easily prepared by adding inorganic components such as silicagel to the liquid resins, followed by polymerisation.

Keywords: Epoxidation; Molybdenum; Epoxy resins; Polymer-supported catalysts; Catalyst recycling

1. Introduction

Intensive research into the immobilisation of catalytically active metal species on organic polymers has been carried out over the last several decades [1–4]. In this context, the recent work of Kobayashi et al., who focused on polymer-supported microencapsulated catalysts [5,6], has sparked new interest in this well-established research area. High long-term stabilities of polymer-based catalysts are as desirable as high activities and selectivities and serve as a basic prerequisite for applications in continuously operating processes. A catalyst system that exhibits an excellent initial performance is, from a technological standpoint, worthless if it deactivates after some reaction cycles by either catalyst poisoning or decomposition. Numerous polymer-based catalysts were shown to be recyclable. However, no data on their long-term performance over periods of weeks or months are available, and in most cases mechanistic considerations, such as the distinction between heterogeneous and homogeneous catalysis, came to the fore rather than the evaluation of their long-term applicability.

Since the emergence of the Halcon–Arco process [7,8] for the homogeneously catalysed epoxidation of propene, numerous attempts were made to immobilise molybdenum on various supports to gain heterogeneous epoxidation catalysts. Inorganic supports such as silica [9–14], modified MCM-41 [15–22], SBA-15 [23], zeolites [24], or layered double hydroxides [25] have been used. Sol–gel-derived hybrid organic–inorganic materials were also synthesised [26]. With respect to organic polymers, modified polystyrenes [27–30], modified Merrifield resins [31,32], benzimidazole-functionalised dendrons [33], polyaniline [34], ion-exchange resins [35], poly(thioether-amido-acid) cross-linked resins [36], polymethacrylate-based systems [37], ethylene–propylene rubber, and modified poly-(ethylene oxide) [38], as well as modified polyethylene and polypropylene [39], were investigated as supports. Catalyst systems based on polybenzimidazole [40–43] and polyimides [44, 45] reported by Sherrington et al. yielded outstanding results in the liquid-phase epoxidation of alkenes. However, data on their

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doi:10.1016/j.jcat.2006.09.017

long-term performance exceeding periods of some days are not available.

We recently reported on the use of metal-doped epoxy resins as highly stable catalysts for the epoxidation of cyclohexene with *tert*-butyl hydroperoxide (TBHP) as oxidant [46]. The catalysts were obtained in a convenient one-step procedure in which metal complexes act as both initiators for anionic epoxy resin polymerisation and precursors for the catalytically active species in the resulting polymer. The catalysts were characterized, and mechanistic studies revealed a superposition of heterogeneous and homogeneous catalysis. To demonstrate the versatility and applicability of this new type of catalysts, here we report on an extension of this initial study. Several molybdenum-doped epoxy resins built up by different resins and molybdenum compounds are compared. They were tested in the epoxidation of a series of alkenes including propene, focusing on their long-term activities and stabilities for periods up to months.

2. Experimental

2.1. General

The epoxy resins 4,4′-methylene-bis-(N,N-diglycidylaniline) (TGMDA) and N,N-diglycidyl-4-glycidyloxyaniline (TGAP) were purchased from Aldrich, and the diglycidylether of bisphenol A (DGEBA, Bakelite EPR 164) and the epoxy novolac (Bakelite EPR 600) were obtained from Bakelite AG. $Mo(OEt)_5$ and molybdenum 2-ethylhexanoate ($(Mo(EH)_n$, a mixture of compounds $Mo[OOCCH(C_2H_5)C_4H_9]_n$ containing 15 wt% molybdenum), were obtained from Gelest and Strem, respectively. Silicagel type 62 with particle sizes of 75–250 µm (Aldrich) was used for the preparation of silicagel-epoxy hybrid catalysts. Anhydrous TBHP in toluene was prepared by azeotropic drying of TBHP (T-HYDRO solution, Aldrich, 70 wt% TBHP in water) [47]. TBHP concentrations were determined by iodometric titration [48]. Rotilabo syringe filters (PTFE, 0.45 µm pore width) were used for catalyst separation. SEM images were recorded on a Leo 982 digital scanning microscope combined with an Oxford Instruments ISIS 300 EDX unit. DSC data were obtained with a heating rate of 10 °C/min using a Mettler Toledo DSC822^e device. ICP-AES and AAS analyses were carried out on Varian Liberty 150 and Varian SpectrAA 800 instruments, respectively. Reaction mixtures were analysed by GC-FID using an Agilent 6890N gas chromatograph equipped with a PHENOMENEX ZB-1 column (60 m × 0.32 mm; 1 µm film thickness). Products were quantified using calibration curves obtained with standard solutions and dodecane as an external standard. Unknown products were identified by GC-MS using an Agilent 6890N instrument (J&W Scientific, DB5 column; 30 m × 0.25 mm; 0.25 µm film thickness) coupled with an Agilent 5973 mass selective detector. In the epoxidation of propene, dodecane was added to the reaction mixtures as an internal standard. Propene oxide yields are based on TBHP consumption. The yields were determined by TBHP titration and by GC-FID.

2.2. Preparation of the catalysts

2.2.1. Typical preparation procedure for catalysts of the type resin–$Mo(OEt)_5^{0.75\%Mo}$

The resin (10 g) was heated to 50 °C (100 °C in the case of the epoxy novolac Bakelite EPR 600), and $Mo(OEt)_5$ (0.258 g) was added. The mixture was stirred vigorously for 30 min and transferred to an aluminium mold. A thin (ca. 1 mm) layer was cured in an oven at the following temperatures: 120 °C for 1 h, 180 °C for 3 h, 200 °C for 2 h, and 230 °C for 1 h. The resulting resin plate was cut and ground with an analytical mill, yielding a fine-grained material with particle diameters <800 µm. Subsequently, the polymer was annealed at 230 °C for 4 h and sieved. The catalytic reactions were run using the fractions with particle diameters of 150–300 µm.

2.2.2. Preparation of TGMDA–$Mo(OEt)_5^{1.5\%Mo}$

$Mo(OEt)_5$ (0.534 g, 1.7 mmol) was added to TGMDA (10 g, 23.7 mmol), and the mixture was processed as described above for systems of the type resin–$Mo(OEt)_5^{0.75\%Mo}$.

2.2.3. Typical preparation procedure for catalysts of the type resin–$Mo(EH)_n^{1.5\%Mo}$

Molybdenum 2-ethylhexanoate ($Mo(EH)_n$, 1.111 g) was added to the respective resin (10 g), and the mixture was stirred vigorously at 100 °C for 30 min. The formulation was transferred to an aluminium mold and a thin (ca. 1 mm) layer was cured in an oven by raising the temperature successively from 120 to 230 °C (120 °C for 1 h, 180 °C for 1 h, 200 °C for 1 h, and 230 °C for 4 h). The resin plate thus obtained is cut and milled, yielding a fine-grained polymer with particle diameters <800 µm. The material was annealed for 6 h at 230 °C and sieved. Unless stated otherwise, the catalytic reactions were run using the fractions with particle diameters of 300–500 µm.

2.2.4. Preparation of silicagel/TGMDA–$Mo(OEt)_5^{0.5\%Mo}$

A mixture of silicagel (8.230 g), TGMDA (13.355 g), $Mo(OEt)_5$ (0.343 g), and Et_2O (5 ml) was homogenised and cured in an oven at the following temperatures: 120 °C for 1 h, 180 °C for 3 h, 200 °C for 2 h, and 230 °C for 1 h. The brittle material thus obtained was pulverised and annealed at 230 °C for 8 h.

2.3. Epoxidation procedures

2.3.1. Typical procedure for the epoxidation of liquid alkenes

All reactions were carried out without precautions against moisture and air. In a typical experiment, a mixture of the alkene (10 mmol), a 3.2 M solution of TBHP in toluene (12 or 16 mmol) and 500 mg of catalyst was magnetically stirred at 90 °C for 24 h. The catalyst was separated by filtration (PTFE filters, 0.45 µm pore width) and subjected to the next catalytic run without any reconditioning. The filtrate was analysed by GC, and liquid components were distilled off. The reaction residue was dissolved in 2 g of concentrated HNO_3, and the solution was diluted with an appropriate volume of water, de-