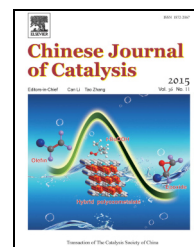


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Article

Effects of structures of molybdenum catalysts on selectivity in gas-phase propylene oxidation



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ABSTRACT

Molybdenum-based catalysts for the gas-phase oxidation of propylene with air were investigated. Various types of silica-supported molybdenum oxide and molybdenum-bismuth mixed oxide catalysts were prepared from inorganic and organometallic molybdenum precursors using wet impregnation and physical vapor deposition methods. The epoxidation activities of the prepared catalysts showed direct correlations with their nanostructures, which were identified using transmission electron microscopy. The appearance of a partly or fully crystalline molybdenum oxide phase, which interacted poorly with the silica support, decreased the selectivity for propylene oxide formation to below 10%; non-crystalline octahedrally coordinated molybdenum species anchored on the support gave propylene oxide formations greater than 55%, with 11% propylene conversion. Electrochemical characterization of molybdenum oxides with various morphologies showed the importance of structural defects. Direct promotion by bismuth of the epoxidation reactivities over molybdenum oxides is disputed.

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1. Introduction

The selective oxidation of C–H and C=C bonds is one of the most widely used processes in the chemical industry for preparing value-added products. Propylene, which contains both C–H and C=C bonds, is used for the formation of various oxidation products such as acrolein, acrylic acid, and propylene oxide (PO), all of which are industrially important intermediates. However, the allylic hydrogen in the propylene molecule is more prone to attack by nucleophilic oxygen than the C=C bond is. Allylic oxidation therefore usually competes strongly with epoxidation [1].

Acrolein is typically manufactured using a bismuth molybdate catalyst and air as the oxidizing agent; 90% propylene conversion and 85% selectivity for acrolein are achieved. Bis-

muth-molybdenum catalysts for epoxidation reactivities have rarely been reported [2]. PO is usually produced industrially using either the chlorohydrin or Halcon process. These multi-step liquid-phase routes involve the formation of stoichiometric amounts of by-products. Novel industrial routes using cumene hydroperoxide or hydrogen peroxide as the oxidant in the liquid phase have been reported [3]. In recent years, several alternative processes for propylene epoxidation have been developed, but the direct gas-phase epoxidation of propylene remains a challenge [4]. Unlike ethylene epoxidation, for which silver-based catalysts have been successfully used commercially for decades, the gas-phase epoxidation of propylene with air is impeded by the presence of a reactive allylic hydrogen atom in the propylene molecule. Propylene therefore tends to give acrolein as the oxidation product instead of PO [5]. Heavily

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modified silver-based catalysts give moderate propylene epoxidation, but the PO selectivity barely exceeds 50% even at low propylene conversions [6]. A continuous supply of chlorinated compounds can increase the selectivity for PO, probably by poisoning non-selective active sites on silver, but the use of chlorinated hydrocarbons causes complications and is not feasible in practical application [5].

A halogen-free, gas-phase reaction system with a copper-doped SBA-15 catalyst and air as the oxidant was reported to give up to 50% PO selectivity at propylene conversions below 5% [7]. Gold was reported to catalyze the epoxidation of propylene by molecular oxygen at atmospheric pressure with selectivity up to 50% at conversion not exceeding 1%; an increase in conversion, and an increase in the gold particle size, led to a drop in selectivity [8].

Titanosilicates are often used as catalysts for liquid-phase propylene epoxidation by hydrogen peroxide [9]. Other titanosilicate-based catalytic systems use a potentially hazardous mixture of H_2/O_2 instead of hydrogen peroxide as the oxidant [10]. Aluminum-containing titanosilicates were reported to catalyze the epoxidation of propylene with molecular oxygen, even without hydrogen as a coreactant, with PO yields up to 11.3%, but with moderate PO selectivity (up to 12.5%) [11].

Molybdenum oxides, which have diverse morphologies, depending on the preparation technique, are widely used because of their chemical, electrical, and optical properties [12]. Molybdenum oxides are used industrially as a component of the catalytic system for allylic oxidation of propylene to acrolein, and have also been used for propylene epoxidation. MoO_2 , which has an unusually high electrical conductivity for a metal oxide, was reported to epoxidize propylene with 42% PO selectivity, using N_2O as the oxidizing agent. However, MoO_2 is unstable under the reaction conditions used for propylene epoxidation with molecular oxygen. Its oxidation and morphological transformation to MoO_3 in the presence of molecular oxygen results in catalyst deactivation [13,14].

Silica-supported molybdenum oxide is the most active among Li, Mg, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, Zr, Nb, Mo, In, W, Bi, Ce, and Sm oxides for gas-phase epoxidation of propylene with molecular oxygen. The most suitable molybdenum precursor is molybdic acid. PO selectivities up to 35% at propylene conversions up to 15% at 0.45 MPa have been reported. The conversion was proportional to the oxygen partial pressure. Crystalline MoO_3 particles were deemed to be responsible for the epoxidation reactivity [15]. Bismuth molybdate is a well-known component of catalysts for propylene oxidation to acrolein [16]. However, its presence in crystalline form does not guarantee a good catalytic performance. Electron-donating interactions between the components of the catalyst are considered to be essential in the oxidation of propylene to acrolein. Enhanced activity in acrolein formation is attributed to electronic interactions between the (0 1 1) faces of $\alpha-Bi_2(MoO_4)_3$ and the surface of the MoO_3 support [15,17]. Supported bismuth-molybdenum mixed oxides showed high selectivity in propylene epoxidation, above 50%, using molecular oxygen as the oxidizing agent. The epoxidation reactivity over such catalysts is explained by the promoting effect of bismuth oxides on

molybdenum oxide nanoparticles [2].

Various molybdenum precursors such as metallic molybdenum deposited using physical vapor deposition (PVD) [16], ammonium heptamolybdate (AHM) [16], oxoperoxy molybdenum species [18], α - and β -silicomolybdic acids [19], and organometallic precursors have been used to prepare various types of supported molybdenum oxide species.

Molybdenum uptake by silica from aqueous molybdate or molybdenum polyoxo solutions is generally low, except at low pH, at which silicomolybdates are formed. However, the silicomolybdates are not anchored to the silica surface, but are released into solution [18]. Subsequently, on calcination, the molybdates and silicomolybdates decompose on the catalyst surface, resulting in the formation of different molybdenum oxide agglomerates [20,21]. Metastable monoclinic $\beta-MoO_3$ or a more stable orthorhombic $\alpha-MoO_3$ phase is formed, depending on the severity of the calcination conditions [22]. In the oxidation of propylene to acrolein, two partial reactions, i.e., abstraction of the allylic hydrogen and oxygen insertion into the hydrocarbon, occur on different crystal faces of $\alpha-MoO_3$, the former reportedly taking place on the (0 0 1) and (1 0 0) faces, and the latter on the (0 1 0) face [23]. The (0 1 0) face was proposed to be the only active one in the formation of CO_2 [24]. In addition, the crystal structure of $\alpha-MoO_3$ comprises distinct forms of oxygen in terms of formal negative charges (influencing the nucleophilicity) and vacancy formation energy, the symmetric bridging oxygen atom being the most nucleophilic and most prone to vacancy formation [23]. These parameters, combined with the effects of crystallinity, and potentially of other doping metals, result in the presence of a large number of different active species on MoO_x/SiO_2 catalysts prepared from AHM, leading to different catalytic activity in propylene oxidation.

It has been suggested that to achieve higher dispersion of molybdenum oxide species on the silica surface, a molybdenyl acetylacetonate precursor is more suitable than AHM, because it gives better grafting of molybdenum via Si–O–Mo linkages [25]. Use of an SBA-15 support and $MoO_2(acac)_2$ leads to the formation of oligomolybdate and/or polymolybdate species at molybdenum contents <12 wt%; above this value, segregated polycrystalline MoO_3 is formed [26].

Molybdyl chloride can serve as a catalyst for various Lewis-acid-catalyzed reactions, e.g., acylations or redox processes (such as oxidation of alcohols), in the liquid phase or as a heterogenized homogeneous complex. In these liquid-phase application, molybdenyl chloride tends to form octahedral complexes $MoO_2Cl_2L_2$ (L is a solvent molecule or ligand) almost exclusively [18]. Along with its Lewis acidity, MoO_2Cl_2 exhibits another promising property, which helps to anchor it on the support: in the solid state, its structure consists of a two-dimensional network of –O–Mo–O– chains, with hexacoordinated molybdenum atoms [27]. In comparison with the traditional AHM precursor, MoO_2Cl_2 is therefore a promising molybdenum source for depositing less-aggregated, better-anchored molybdenum species.

Molybdyl chloride is typically prepared with difficulty by the reaction of molybdenum oxide or sulfide using a dry oxygen-chlorine mixture at elevated temperatures, because

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