

# Performance of Mo-Bi-Co-Fe-K-O catalysts prepared from a sol–gel solution containing a drying control chemical additive in the partial oxidation of propylene

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## Abstract

The performance of  $\text{Mo}_{12}\text{Bi}_{1.0}\text{Co}_{4.4}\text{Fe}_{1.0}\text{K}_{0.07}\text{O}_x$  mixed-metal oxide catalysts in the partial oxidation of propylene was investigated. Such catalysts were prepared by precipitating catalyst components from a sol–gel solution that contained a drying control chemical additive (DCCA). The addition of DCCA, selected from among glycerol, formamide and propionic acid, to a sol–gel solution did not change the crystallite phases of the prepared catalysts, which included  $\text{MoO}_3$ ,  $\text{Bi}_2\text{Mo}_3\text{O}_{12}$ ,  $\text{Bi}_2\text{MoO}_6$ ,  $\text{CoMoO}_4$ ,  $\text{Fe}_2\text{O}_3$ , and  $\alpha\text{-FeMoO}_4$ , but did decrease the crystallite sizes, thereby increasing the catalytic activity. The DCCA-modified catalysts also exhibited selectivity values for the production of acrolein and acrylic acid that were higher than that of the catalyst prepared without using the additive. Among three DCCAs tested in this study, propionic acid added in a proper amount increased the selectivity to the greatest extent because propionic acid decreased the amounts of Brønsted-type acidic sites on the catalyst, which are detrimental to the selectivity.

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## 1. Introduction

Acrylic acid, a raw material for synthesizing acrylate polymers [1,2], is commonly produced by a two-step process starting from propylene using multi-component metal oxides based on Mo and Bi and subsequently Mo and V mixed-oxides as catalysts for individual steps [1,3–9]. The properties of the catalysts for the first step, i.e. propylene oxidation to acrolein, are determined by several factors, including their composition, surface area, crystallinity, and surface acidity [1,3,6,7,10–19]. The catalyst surface area is important because it determines not only the mass activity of the catalyst but also its selectivity for desired products [20].

According to the reaction mechanism proposed in previous studies [3,15,19–21], propylene is subject to oxidation via three major routes. One consists of reactions with lattice oxygen proceeding on the catalyst surface, leading to the production of

desired products such as acrolein and acrylic acid. The second involves gas-phase reactions, which contribute to the production of propylene oxide and therefore decrease the catalyst selectivity for desired products. The third route, which is promoted by strong acidic sites of the catalysts, also decreases the catalyst selectivity by producing undesired compounds such as acetone, acetic acid and carbon oxides.

Consequently, one of the strategies for preparing a catalyst with improved performance in this process can be to increase its surface area such that the mass activity is increased and the reactions proceeding on the catalyst surface are promoted to a greater extent than those proceeding in the gas phase. According to previous studies, the surface areas of catalysts prepared by a co-precipitation method were about 8–10  $\text{m}^2/\text{g}$  [1,22] and those prepared by a sol–gel method were in the range of 10–12  $\text{m}^2/\text{g}$  [19,23,24]. The other factor for consideration in catalyst design is the acidity of the catalysts, which can be controlled by adding compounds of different acidity to the sol–gel solution.

In this study, we attempted to increase the surface area of catalysts prepared by a sol–gel method using a solution that

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contained a “drying control chemical additive (DCCA),” which lowered the surface tension of the solution [25–27]. Because catalysts of relatively low surface area were obtained due to a large difference in the interfacial tension between the sol and gel phases in the drying step, the addition of the DCCA to the solution was expected to reduce the difference in the interfacial tension and eventually to increase the catalyst surface area. Glycerol, formamide, and propionic acid, which exhibit different acidity in an aqueous solution, were used as the DCCAs in this study.

## 2. Experimental

### 2.1. Catalyst preparation

The precursors of metal oxides used in the catalyst preparation were ammonium molybdate tetrahydrate ( $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ ), bismuth(III) nitrate pentahydrate ( $\text{Bi}(\text{NO}_3)_3\cdot 5\text{H}_2\text{O}$ ), cobalt(II) nitrate hexahydrate ( $\text{Co}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ ), iron(III) nitrate nonahydrate ( $\text{Fe}(\text{NO}_3)_3\cdot 9\text{H}_2\text{O}$ ), and potassium nitrate ( $\text{KNO}_3$ ). The metal precursors were added to the preparation solution at the atomic/molar ratios of Mo:Bi:Fe:Co:K: citric acid = 12:1:1:4.4:0.07:6.3 [24], as described in Fig. 1. The Mo precursor in an amount of 200 g was dissolved in 450 ml of distilled water maintained at 75 °C. This was followed by the addition of 115 ml citric acid, an amount determined according to the above ratio. Then, 120.9 g of the Co precursor and 38.1 g of the Fe precursor were dissolved in distilled water and the resulting solutions were slowly added to the Mo solution in sequence. For this discussion, the resulting Mo–Co–Fe solution will be designated as Solution I. Next, 45.8 g of the Bi precursor was added to 15 ml of 70% nitric acid, which initially formed a slurry phase but was transformed to a homogeneous one after the addition of water. Then 0.67 g of K precursor was added to the above solution. The resulting Bi–K solution will be designated as Solution II. One of the DCCAs, i.e. glycerol, formamide or propionic acid, was added to Solution II before the resulting Solution II was finally mixed with Solution I. The amounts of the DCCA in the final solution were 5 ~ 60 mol% of the amounts of citric acid.

The final solution, which had changed to a gel by aging at 75 °C, was dried at 110 °C. Different sample catalysts were

prepared by changing the periods of aging and drying. Dried catalysts were ground in a porcelain bowl, heated in air at a ramping rate of 1 °C/min to 450 °C, and finally calcined at 450 °C for 5 h.

### 2.2. Reaction

Molar ratios of reactants in a stream used for propylene oxidation were propylene:oxygen:nitrogen:water = 0.07:0.13:0.73:0.08. The amounts of the catalysts were 0.6 g and the space time was 940 h<sup>-1</sup>. Reaction tests were conducted at temperatures between 300 and 340 °C using a Pyrex reactor (ID1 = 6 mm). The lines connecting the reactor to the detector were maintained at 220 °C to prevent the condensation or polymerization of products. A gas chromatograph equipped with a flame ionization detector (FID) was used for analyzing propylene, acrolein, and acrylic acid. A thermal conductivity detector (TCD) was used for analyzing nitrogen, oxygen, and carbon mono- and di-oxides. The GC was equipped with a capillary Alltech AT-1000 column for the separation of hydrocarbons and a Supelco carboxen 1000 column for the separation of other chemicals. The conversion of propylene was calculated based on carbon balance and the selectivity of oxidation from the ratio of the summed amounts of acrolein and acrylic acid to the amounts of converted propylene.

### 2.3. BET and XRD

The surface area and pore size distribution of prepared catalysts were measured by N<sub>2</sub> adsorption using ASAP 2010 (Micrometics). The samples were pretreated in a vacuum at 200 °C for 1 h before the adsorption experiments. The catalysts were also analyzed by X-ray diffraction (XRD: MAC Science Co., M18XHF-SRA). The phases of the catalyst components were identified by comparing the observed results with the database of the Joint Committee on Powder Diffraction Standards (JCPDS); the crystallite sizes were estimated based on Scherrer's equation.

### 2.4. NH<sub>3</sub> TPD and pyridine-IR

The types and the amounts of acidic sites on the catalyst surface were analyzed based on the temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) and the infrared spectra of pyridine adsorbed on the catalysts (pyridine-IR). For the NH<sub>3</sub>-TPD, the catalysts were pre-treated in helium at 110 °C for 1 h, then cooled to room temperature, and finally NH<sub>3</sub> was adsorbed on them at atmospheric pressure. After physically adsorbed NH<sub>3</sub> was removed from the catalyst by purging the reactor in He for 1 h, NH<sub>3</sub> TPD peaks were recorded while the temperature was raised from 20 to 600 °C at a rate of 10 °C/min. The effluent gas was analyzed for NH<sub>3</sub> with a mass spectrometer.

Pyridine-IR measurements were made in an IR cell using a self-supporting catalyst wafer [28]. All samples were pre-treated in nitrogen at 110 °C for 1 h before 20 Torr of pyridine was dosed into an IR cell evacuated to a base pressure of  $5.41 \times 10^{-4}$  Torr. After physically adsorbed pyridine was

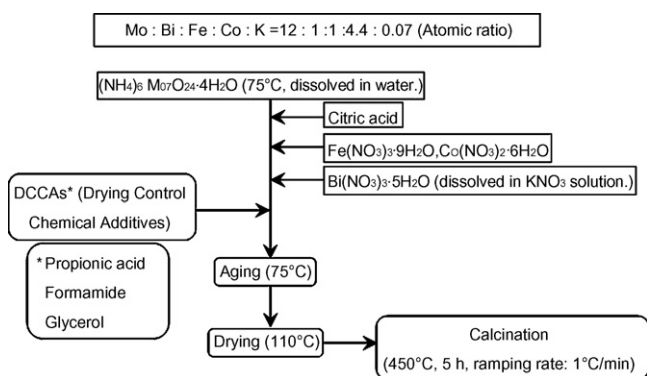


Fig. 1. Catalyst preparation by a modified sol–gel method using DCCAs.

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