



Short communication

Direct epoxidation of propylene to propylene oxide on various catalytic systems: A combinatorial micro-reactor study



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ARTICLE INFO

Article history:

Received 29 September 2014

Received in revised form 30 November 2014

Accepted 3 December 2014

Available online 4 December 2014

Keywords:

Propylene

Epoxidation

Ru

Cu

SiO₂

ABSTRACT

A combinatorial approach is used to investigate several bimetallic catalytic systems and the promoter effect on these catalysts to develop highly active and selective catalysts for direct epoxidation of propylene to propylene oxide (PO) using molecular oxygen. 2%Cu/5%Ru/c-SiO₂ catalyst yielded the highest performance with high propylene conversion and PO selectivity among the bimetallic catalytic systems including silver, ruthenium, manganese and copper metals. On the other hand, the most effective catalyst and promoter in the epoxidation reaction was determined to be sodium chloride promoted Cu–Ru catalyst supported over SiO₂ with 36% selectivity & 9.6% conversion (3.46% yield) at 300 °C and 0.5 feed gas ratio (propylene/oxygen).

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1. Introduction

Propylene oxide (PO) is a very important chemical feedstock for the production of a wide variety of commodity chemicals, such as polyether polyols and propylene glycol [1]. Currently, chlorohydrin and organic hydroperoxide processes are two of the commonly used industrial processes for PO synthesis in the chemical industry. These processes lead to the generation of a large amount of waste water and organic byproducts. Thus, they are not preferable due to their environmental and economical disadvantages [2]. Because of the deficiencies of the aforementioned PO production processes, novel methods of producing PO have been explored which included direct oxidation of propylene using various catalytic systems and proper oxidants, such as H₂O₂ [3–5], O₂–H₂ gas mixture [6–9], and N₂O [10,11]. However, high costs of these oxidants restrict the commercialization of these processes. Therefore, the direct gas-phase epoxidation of propylene to PO by molecular oxygen has been a focus of interest as an attractive alternative from both economical and environmental standpoints.

The recent discovery of the highly active Au/TiO₂ catalysts in various catalytic reactions led to the use of Au in conjunction with other reducible metal oxide support materials [7–9,12–15]. However, since highly selective Au catalysts typically exhibit low propylene conversion and require hydrogen co-feeding, such catalysts are industrially less promising for PO production [8]. Successful results obtained from modified Ag

catalysts in the gas phase epoxidation of ethylene by molecular oxygen led to many studies on propylene epoxidation over different support materials and modifiers [16–24]. However the conversion and the selectivity of Ag-based catalysts in PO production were lower than those for ethylene oxide production as a result of the existence of allylic hydrogen in propylene. Furthermore, surface chemistry studies on Ag and Cu single crystal surfaces suggested that Cu is more selective than Ag for the epoxidation of alkenes having allylic C–H bonds [25].

The reason behind the higher epoxidation activity of Cu with respect to that of Ag was explained by the lower basicity of oxygen adsorbed over Cu metal [26]. As a supporting study, the effect of the oxygen basicity on PO selectivity was investigated by Kizilkaya et al. [27]. In this theoretical DFT study over Cu and Cu–Ru catalytic systems, Kizilkaya et al. proposed that because of the higher basicity of atomic oxygen adsorbed over Cu–Ru, the scission of allylic hydrogen of propylene occurs with higher probability (much lower activation barrier) as compared to the formation of the PO intermediate. Several studies in the literature focused on the active oxidation state of Cu in epoxidation reactions. Vaughan et al. proposed that Cu⁰ species in highly dispersed atomic-like form are the active sites in epoxidation [28]. On the other hand, Zhu et al. claimed that Cu⁺ is the active form [29]. Onal et al. suggested that isolated ionic Cu²⁺ species were responsible for propylene epoxidation by O₂ [30].

The studies reported in the literature showed that bimetallic or multimetallic catalytic systems for the propylene epoxidation reaction often show superior catalytic properties in comparison to monometallic systems [30–32]. Onal et al. reported that PO yield is increased by several

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folds for Ag–Cu bimetallic catalysts because of a synergistic effect [30]. In addition to this, Kahn et al. reported that the PO formation rates of Cu–Mn bimetallic catalysts were about five times higher than the corresponding monometallic catalysts [31]. Although bimetallic catalysts have been commonly employed in propylene epoxidation, most of these catalytic systems suffered from low propylene conversion. Seubsai and co-workers have reported a new SiO₂-supported trimetallic RuO₂–CuO_x–NaCl catalyst with the highest PO yield (40–50% PO) selectivity at 10–20% conversion for the direct epoxidation of propylene by molecular oxygen under atmospheric pressures [32].

In this study, using a combinatorial approach, various catalytic systems were prepared on SiO₂ support in order to find an active and selective catalyst for the direct epoxidation of propylene to PO via molecular oxygen at atmospheric pressures. In order to achieve this goal, the study started with exploration of bimetallic systems followed by the exploration of the NaCl effect on these catalytic systems. Other electronic promoters on the most effective catalyst were also investigated in this study.

2. Experimental

2.1. Catalysts preparation

Incipient wetness method was employed in order to synthesize catalysts using SiO₂ support materials acquired commercially (c-SiO₂, Alfa Aesar, surface area 97 m² g⁻¹). The metal salts were loaded on SiO₂ by the incipient wetness impregnation method. During the preparation of metal containing catalyst, 2 g of SiO₂ support material was taken as a basis and the amount of chemicals added was determined on this basis. According to the method, first the water pore volume of calcined silica was measured by adding water drops to known amount of support materials. The volume was determined as the quantity of added water just before excess water appeared on the surface of the sample. Then desired amount of ruthenium chloride (RuCl₃·xH₂O), copper nitrate (Cu(NO₃)₂), silver nitrate (AgNO₃), manganese nitrate (Mn(NO₃)₂), potassium nitrate (KNO₃), sodium nitrate (NaNO₃), sodium chloride (NaCl), lithium chloride (LiCl) and potassium acetate (KAc) were dissolved in distilled water, and the solution was added to the support material. Metal amount was changed between 2 and 5 wt.% ratio and promoter was added with respect to 1.75 wt.% ratio. The mixture was heated while stirring (50 °C to 80 °C) until all the water was evaporated. The prepared sample was dried at 120 °C for 12 h and further calcined. c-SiO₂ supported catalysts were calcined at 550 °C for 5 h. In the synthesis of catalysts promoted with metal chloride (such as; LiCl, NaCl), catalysts were first prepared by the use of incipient wetness method described above without adding metal chloride salts and calcined at 550 °C for 5 h. Then desired amount of metal chloride was dissolved in distilled water and added to the calcined catalyst. The mixture was heated again while stirring (50 °C to 80 °C) until all the water was evaporated. Finally the prepared sample was dried at 120 °C for 12 h and calcined at 350 °C for 3 h.

2.2. Activity tests

Catalyst performance tests were carried out using a computer controlled array channel microreactor system which is described elsewhere [33]. In this microreactor system, up to 80 catalyst samples could be screened in a parallel fashion. In the current set of experiments, 20 catalyst candidates were tested in each screening experiment and a performance data point was obtained for each catalyst in about 3 min. In the array microreactors, reactant gases flow over the flat surfaces of the powder catalyst samples which are individually isolated within reactor channels where the flow regime is similar to that of a monolithic reactor. All experiments were performed using a 5 mg catalyst sample under atmospheric pressure and at a gas hourly space velocity (GHSV) of 20,000 h⁻¹, representing a differential reactor condition. Catalytic

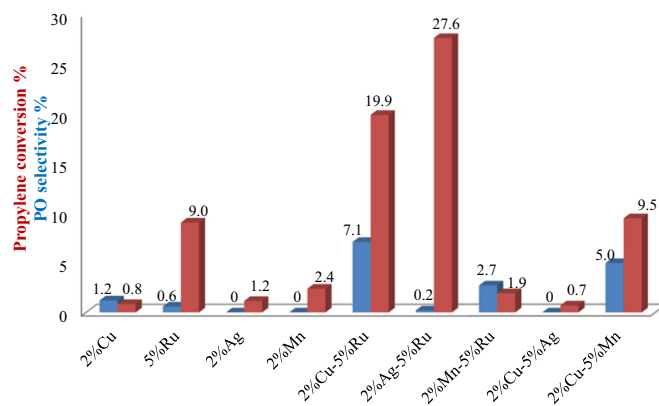


Fig. 1. Catalytic performance of mono- and bimetallic catalysts supported on c-SiO₂ (GHSV = 20,000 h⁻¹, gas composition: C₃H₆:O₂ = 1:2, T = 300 °C).

screening experiments were performed at a propylene (C₃H₆)/oxygen (O₂) molar ratio of 0.5 and at 300 °C. Helium (He) is used as a carrier gas. Reactant gas consists of 2.5 vol.% C₃H₆, 5 vol.% O₂ and balance with He. Products in the reactor effluent streams were sampled and analyzed using a heated capillary sampling probe and an on-line gas chromatograph (Varian CP-4900 Micro-GC with thermal conductivity detector, Porapak Q (10 m) and Molecular sieve 13 × (10 m) columns). The selectivity of PO is defined as the moles of carbon in PO divided by the moles of carbon in all of the carbon containing products. The selectivity of the other C₃ products, such as acrolein (AC), acetone (AT) and acetaldehyde (AD) and the combustion reaction product of CO₂ were also calculated in the same way.

3. Results and discussion

In our previous work [33], monometallic Cu catalysts promoted with various alkaline salt precursors were investigated; however, these catalyst candidates did not give a satisfactory catalytic performance (poor propylene conversion below 3%). On the other hand, some of the former reports in the literature, such as the one reported by Seubsai and co-workers [32], showed that bimetallic and trimetallic Cu containing catalytic systems can be promising catalysts for PO production from propylene and molecular oxygen at atmospheric pressure and without any co-reactant. In the study of Seubsai and coworkers, 40–50% PO selectivity at 10–20% propylene conversion was reached over a new class of silica-supported multimetallic RuO₂–CuO_x–NaCl catalysts. Inspired by this work, the current study started with investigation of various c-SiO₂ supported bimetallic catalysts containing Cu–Ru binary systems and their binary combinations with other mostly investigated

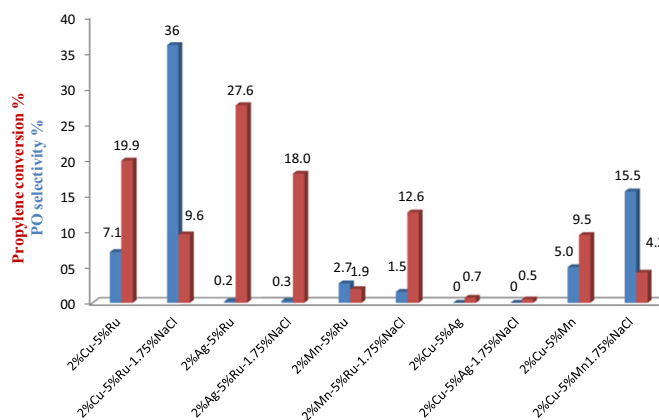


Fig. 2. Catalytic performance of NaCl-promoted and un-promoted bimetallic catalysts supported on c-SiO₂ (GHSV = 20,000 h⁻¹, gas composition: C₃H₆:O₂ = 1:2, T = 300 °C).

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