



Short communication

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



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### 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-SiO<sub>2</sub> 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 SiO<sub>2</sub> 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 H<sub>2</sub>O<sub>2</sub> [3–5], O<sub>2</sub>–H<sub>2</sub> gas mixture [6–9], and N<sub>2</sub>O [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/TiO<sub>2</sub> 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 Cu<sup>0</sup> species in highly dispersed atomic-like form are the active sites in epoxidation [28]. On the other hand, Zhu et al. claimed that Cu<sup>+</sup> is the active form [29]. Onal et al. suggested that isolated ionic Cu<sup>2+</sup> species were responsible for propylene epoxidation by O<sub>2</sub> [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 SiO<sub>2</sub>-supported trimetallic RuO<sub>2</sub>–CuO<sub>x</sub>–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 SiO<sub>2</sub> 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 SiO<sub>2</sub> support materials acquired commercially (*c*-SiO<sub>2</sub>, Alfa Aesar, surface area 97 m<sup>2</sup> g<sup>-1</sup>). The metal salts were loaded on SiO<sub>2</sub> by the incipient wetness impregnation method. During the preparation of metal containing catalyst, 2 g of SiO<sub>2</sub> 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 (RuCl<sub>3</sub>·xH<sub>2</sub>O), copper nitrate (Cu(NO<sub>3</sub>)<sub>2</sub>), silver nitrate (AgNO<sub>3</sub>), manganese nitrate (Mn(NO<sub>3</sub>)<sub>2</sub>), potassium nitrate (KNO<sub>3</sub>), sodium nitrate (NaNO<sub>3</sub>), 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*-SiO<sub>2</sub> 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<sup>-1</sup>, representing a differential reactor condition. Catalytic

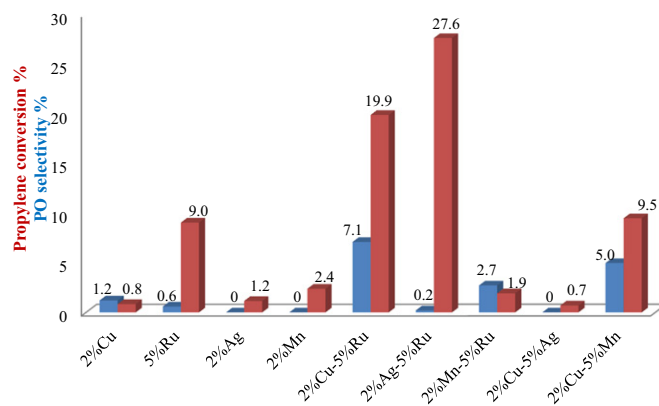


Fig. 1. Catalytic performance of mono- and bimetallic catalysts supported on *c*-SiO<sub>2</sub> (GHSV = 20,000 h<sup>-1</sup>, gas composition: C<sub>3</sub>H<sub>6</sub>:O<sub>2</sub> = 1:2, T = 300 °C).

screening experiments were performed at a propylene (C<sub>3</sub>H<sub>6</sub>)/oxygen (O<sub>2</sub>) molar ratio of 0.5 and at 300 °C. Helium (He) is used as a carrier gas. Reactant gas consists of 2.5 vol.% C<sub>3</sub>H<sub>6</sub>, 5 vol.% O<sub>2</sub> 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 C<sub>3</sub> products, such as acrolein (AC), acetone (AT) and acetaldehyde (AD) and the combustion reaction product of CO<sub>2</sub> 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 RuO<sub>2</sub>–CuO<sub>x</sub>–NaCl catalysts. Inspired by this work, the current study started with investigation of various *c*-SiO<sub>2</sub> supported bimetallic catalysts containing Cu–Ru binary systems and their binary combinations with other mostly investigated

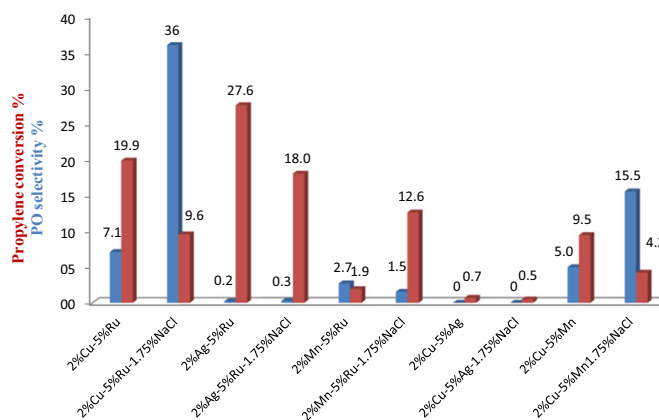


Fig. 2. Catalytic performance of NaCl-promoted and un-promoted bimetallic catalysts supported on *c*-SiO<sub>2</sub> (GHSV = 20,000 h<sup>-1</sup>, gas composition: C<sub>3</sub>H<sub>6</sub>:O<sub>2</sub> = 1:2, T = 300 °C).

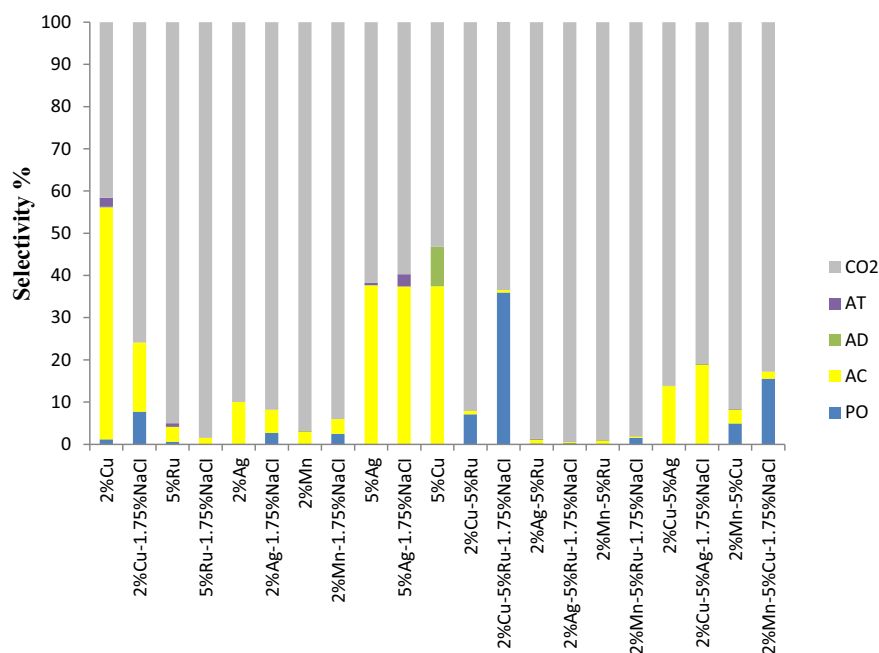


Fig. 3. Catalytic performance of NaCl-promoted and un-promoted mono- and bimetallic catalysts (GHSV = 20,000 h<sup>-1</sup>, gas composition: C<sub>3</sub>H<sub>6</sub>:O<sub>2</sub> = 1:2, T = 300 °C).

metals such as silver (Ag) and manganese (Mn). These bimetallic systems prepared with the same metallic weight ratio (2 wt.% X–5 wt.% Y). This ratio was determined in the preliminary study as an optimum metal–metal ratio for the bimetallic catalysts by screening a lot of catalysts by combinatorial approach [34]. So this ratio was held constant for different bimetallic systems to compare their performance in the production of PO by using high-throughput screening method.

Fig. 1 presents the propylene conversion and PO selectivity results of investigated monometallic and bimetallic systems. It is apparent that Cu–Ru bimetallic catalysts typically reveal higher propylene conversion and PO selectivity with respect to that of their monometallic counterparts indicating a synergistic interaction between Cu and Ru sites. It is also same for Ru–Mn/c-SiO<sub>2</sub> and Mn–Cu/c-SiO<sub>2</sub> bimetallic systems. When compared to monometallic counterparts, it was seen that Ru–Mn/c-SiO<sub>2</sub> and Mn–Cu/c-SiO<sub>2</sub> bimetallic systems increased PO formation (2.7% PO selectivity at 1.9% propylene conversion for Ru–Mn/c-SiO<sub>2</sub>; 5.0% PO selectivity at 9.5% propylene conversion for Mn–Cu/c-SiO<sub>2</sub>). When Ru–Ag/c-SiO<sub>2</sub> bimetallic system compared with monometallic Ag/c-SiO<sub>2</sub> and Ru/c-SiO<sub>2</sub> catalysts, it was seen that Ag–Ru/c-SiO<sub>2</sub> bimetallic system significantly enhanced propylene consumption. However, mainly combustion reaction took place and PO selectivity and

selectivity of other oxygenated products were obtained with a negligible amount. Fig. 1 also points out that Cu–Ag bimetallic system is inactive for PO formation. To summarize, among bimetallic catalytic systems containing Ag, Ru, Mn and Cu metals, c-SiO<sub>2</sub> supported Cu–Ru catalyst was determined as the most active catalytic system.

The study was continued with the investigation of NaCl effect on these bimetallic catalytic systems (2 wt.% X–5 wt.% Ru–1.75 wt.% Na) and the results were shown in Fig. 2. As seen in the figure, the addition of NaCl to the Ag–Ru/c-SiO<sub>2</sub> and Cu–Ag/c-SiO<sub>2</sub> bimetallic catalysts did not affect PO selectivity and complete combustion reaction again took place. Similarly, Mn–Ru/SiO<sub>2</sub> bimetallic system caused only a slight increase in PO selectivity after NaCl addition and caused combustion reaction. To summarize, desired improvement for PO production could not be obtained for Cu–Ag/c-SiO<sub>2</sub>, Ag–Ru/c-SiO<sub>2</sub> and Mn–Ru/c-SiO<sub>2</sub> bimetallic systems before and after NaCl modification. However, adding NaCl had a great curative effect on the performance of the Mn–Cu/c-SiO<sub>2</sub> system. While propylene conversion decreased from 9.5% to 4.2%, NaCl addition led to an improvement toward PO selectivity by a factor of ~3 times and 15.5% PO selectivity was obtained. More interestingly, the results shown in Figs. 2 and 3 proved the effectiveness of c-SiO<sub>2</sub> supported Ru–Cu–NaCl multimetallic system for direct epoxidation of

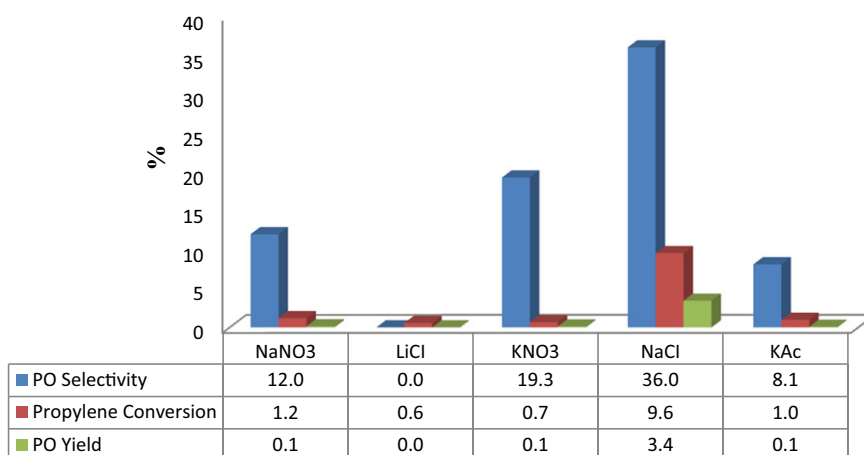


Fig. 4. Catalytic performance of 2%Cu/5%Ru catalysts modified by different alkaline metal salts (GHSV = 20,000 h<sup>-1</sup>, gas composition: C<sub>3</sub>H<sub>6</sub>:O<sub>2</sub> = 1:2, T = 300 °C).

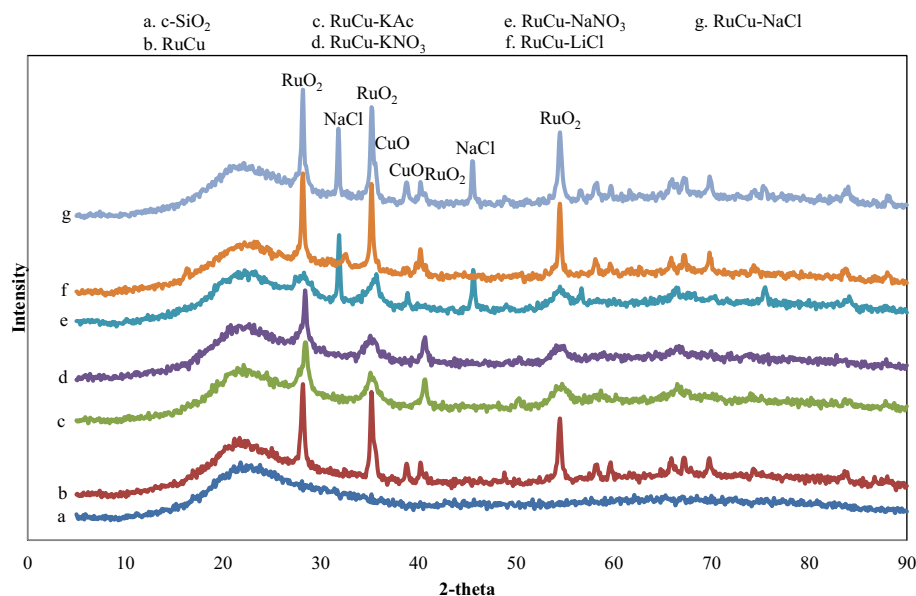


Fig. 5. XRD profiles of 2%Cu/5%Ru catalysts modified by different alkaline metal salts.

propylene. With the addition of NaCl to the Cu–Ru/SiO<sub>2</sub> bimetallic system, PO selectivity reached its maximum (36%), while propylene conversion decreased to 9.6%. In addition, there was no other oxygenated product with significant amount for promoted or un-promoted Cu–Ru/c-SiO<sub>2</sub> bimetallic systems as seen in Fig. 3.

After the observation of NaCl effect on Cu–Ru/c-SiO<sub>2</sub> catalyst, the effect of other commonly reported alkaline promoters (NaNO<sub>3</sub>, LiCl, KNO<sub>3</sub>, NaCl and KAc) on the performance of c-SiO<sub>2</sub> supported Cu–Ru catalyst was also investigated. As seen in Fig. 4, NaCl increased the PO yield of Ru–Cu catalyst more significantly than other promoters. The addition of KNO<sub>3</sub> also promoted PO selectivity but conversion remained at very low level (0.7%).

The effect of promoters on the morphology and crystallographic structure of Cu–Ru metals was investigated with X-ray diffractogram. XRD patterns of Cu–Ru/c-SiO<sub>2</sub> catalyst modified with various alkaline salts were shown in Fig. 5. Cu–Ru/c-SiO<sub>2</sub> catalyst revealed characteristic diffraction signals of RuO<sub>2</sub> ( $2\theta = 28.49, 35.59, 40.59, 55.65, 67.30^\circ$ ), and CuO ( $2\theta = 35.70, 38.95^\circ$ ) phases that show highly dispersed Cu and Ru system. The peak belongs to RuO<sub>2</sub> at 35.59° and CuO at 35.70° overlapped and made a small shoulder belongs to CuO. The addition of KAc and KNO<sub>3</sub> salts caused contraction and broadening of RuO<sub>2</sub> peaks while peaks belonging to CuO disappeared. The RuO<sub>2</sub> peaks remained the same with the addition of LiCl but CuO peak seen at 38.95° almost disappeared and the shoulder at the peak belonging to RuO<sub>2</sub>–CuO became smooth. The broadening and contraction of a peak show a decrease in the crystallite size of oxide and interaction between modified alkaline salts. He et al. investigated the 5 wt.% CuO<sub>x</sub>/SiO<sub>2</sub> catalyst modified by different alkali promoters at the molar ratio of 0.4 and observed that the crystallite size of CuO<sub>x</sub> getting smaller for all alkali metal ions. The crystallite size of CuO<sub>x</sub> decreased in the order Li<sup>+</sup> > Na<sup>+</sup> > K<sup>+</sup> > Rb<sup>+</sup> > Cs<sup>+</sup> [35].

However different precursors of Na showed different trends. According to the XRD analysis, NaCl salt formed after the addition of NaNO<sub>3</sub> into the Ru–Cu solution because of the reaction between Na ion and Cl ion coming from RuCl<sub>3</sub>·xH<sub>2</sub>O precursor. This alkaline addition caused again contraction and broadening of Ru peaks but CuO peaks were protected. However the addition of NaCl affected neither CuO nor RuO<sub>2</sub> peaks height and width. On the contrary there was a small increase in the peaks height belongs to oxides. Moreover the new NaCl peaks appeared at 31.81 and 45.54°. The particle sizes of CuO and RuO<sub>2</sub> remained almost constant (20 nm for RuO<sub>2</sub> and 28 nm for CuO) according to Scherrer equation after modification with NaCl. The

addition of NaNO<sub>3</sub>, LiCl, KNO<sub>3</sub> or KAc interacts with Ru and Cu oxide and changes their crystallite size but NaCl has no effect on the size and distribution of the oxide over support surface. Instead of the approximately same amount of modification (alkali/metal ratio of 0.4), different results were observed from He et al. study. As stated before there was no change in the CuO and RuO<sub>2</sub> particle size according to XRD results. As a summary, NaCl affected the catalytic performance more significantly than other promoters by functioning as an effective electronic promoter although there is no effect on the particle size.

#### 4. Conclusion

In this study, a combinatorial approach was used in order to investigate several bimetallic catalytic systems and the effects of promoters used on these catalysts for direct gas-phase epoxidation of propylene to PO by molecular oxygen. It was found that Mn–Cu/c-SiO<sub>2</sub> bimetallic system had a surprisingly higher PO selectivity and NaCl impressively increased the yield of the Mn–Cu/c-SiO<sub>2</sub> system. However, among bimetallic catalytic systems investigated in the study, the highest performance was obtained for 2%Cu/5%Ru/c-SiO<sub>2</sub> catalyst with a high propylene conversion and PO selectivity. Finally, the most effective catalyst and promoter in the epoxidation reaction was determined as NaCl promoted Cu–Ru catalyst supported over c-SiO<sub>2</sub> with 36% selectivity & 9.6% conversion (3.46% yield) at 300 °C and 0.5 feed gas ratio (C<sub>3</sub>H<sub>6</sub>/O<sub>2</sub>). NaCl acts only as an electronic promoter; however it has no effect on the particle size.

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