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Short communication

Direct epoxidation of propylene to propylene oxide over RuO_2-CuO-NaCl-TeO_2-MnO_x/SiO_2 catalysts

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ABSTRACT

Multi-metallic RuO_2-CuO-NaCl-TeO_2-MnO_x/SiO_2 catalysts were investigated for the epoxidation of propylene to propylene oxide (PO) using O_2 under atmospheric pressure. The metallic weight ratio and the total metal loading on SiO_2 support were optimized at Ru/Cu/Na/Te/Mn = 7.14/3.57/1.79/0.175/1.00 and 25.0 wt%, respectively. RuO_2 and CuO were determined to exhibit a critical bifunctional role for PO synthesis. These active sites were assisted by MnO_x and TeO_2 to increase PO formation rate and by NaCl to reduce CO_2 formation. With using the Box-Behnken design, a maximized PO formation rate of 1258 $g_{PO}\ h^{-1}\ kg_{cat}^{-1}$ was obtained by varying O_2/propylene feed ratio and reaction temperature.

1. Introduction

Propylene oxide (PO) is a valuable chemical intermediate for producing various commercial materials [1]. Currently, the chlorohydrin, hydroperoxide and co-product processes are the commonplace for the commercial-scale production of PO. However, these routes either elicit adverse environmental impacts or incur large capital costs [1,2]. Hence, the gas-phase epoxidation of propylene (C_3H_6) directly, by using molecular oxygen, offers a simpler, cleaner and potentially much more cost-effective alternative but hinges on the discovery of a viable heterogeneous catalyst.

In the past two decades, several interesting catalysts with and without a support material have been reported. However, all have failed to reach the commonly accepted standard for economic sustainability: 70% PO selectivity and 10% C_3H_6 conversion (i.e. 7% PO yield) [3]. Ag-based catalysts were initially studied because they were successfully used for ethylene epoxidation to ethylene oxide [4], but low PO selectivities (below 39%) with significant C_3H_6 conversions (1.4–46.3%) [3] in the C_3H_6 epoxidation due to the allylic hydrogen abstraction in intermediates resulting in complete combustion [5]. Au nanoparticles on TiO_2 support were first discovered by Haruta and coworkers in 1998 as giving nearly 100% PO selectivity but <1% propylene conversion [6]. Au-based catalysts have been developed and improved the C_3H_6 conversion to about 1.7–6.5% [6–14]. However, the catalysts require large amounts of co-fed H_2, interacting with gold and O_2 for the in situ generation of hydroperoxy intermediate, which consequently works as an oxidant to react with C_3H_6 to generate PO molecules. Later in 2005, Cu-based catalysts have become much attractive for the C_3H_6 epoxidation by eliminating the need for H_2 addition [15]. Nevertheless, PO selectivities reported hardly exceed 50% at a wide range of C_3H_6 conversion (0.24–20%, 0.08–8.00% PO yield) [16–25].

Among these Cu-based catalysts, RuO_2-CuO-NaCl/SiO_2 was the most active for PO production (~40–50% of PO selectivity and 10–20% of C_3H_6 conversion), 5–8% of PO yield or 153 $g_{PO}\ h^{-1}\ kg_{cat}^{-1}$ of PO formation rate. It has been suggested the vital role in the epoxidation route is provided by crystalline CuO_x. In this mechanism, O_2 favorably adsorbs onto the catalyst, specifically on a different component, which subsequently transfers O-atoms to the CuO_x surface for PO synthesis [26]. Moreover, the addition of combustion-inhibiting promoters (such as K^+ [27], Cs^+ [28], NaCl [29] and KAc [21]) has been shown to enhance the PO selectivity and/or PO formation rate by reducing acidity of active surfaces [28], possessing an electronic effect to the adsorbed oxygen species to become electrophilic, which is effective for C_3H_6 epoxidation [5], or lowering activation energy for PO formation [30].

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Herein, we investigate the most active Cu-based catalyst recently discovered, i.e. RuO_2-CuO-NaCl/SiO_2, for the direct gas-phase epoxidation of C_3H_6 at under atmospheric pressure by modifying it with tellurium and manganese, focusing on the optimization of the PO formation rate. This new multimetallic catalyst significantly improves the PO formation rate relative to earlier reports of Cu-based catalysts. The role of each metal species is identified and operating conditions with two parameters (reaction temperature and O_2/C_3H_6 feed gas ratio) are also investigated using the Box-Behnken design to obtain the maximized PO formation rate.

2. Experimental

2.1. Catalysts preparation

The catalytic materials were all prepared by co-impregnation on amorphous fumed silica powder (SiO_2, Alfa Aesar) with aqueous mixtures of Ru [$RuCl_3$, Alfa Aesar], Cu [$Cu(NO_3)_2$, Ajax], Na [NaCl, Carlo Erba], Te [$TeCl_4$, Aldrich], and/or Mn [$Mn(NO_3)_2{\cdot}4H_2O$, Alfa Aesar] at various metal ratios in a glass vial. Initially, different amounts of the aqueous Te solution were added into the mixture of Ru/Cu/Na at 7.14/3.57/1.79 by weight ratio. The mixtures were stirred at room temperature for 4 h, then stirred at 165 °C until dried, and calcined at 480 °C for 8 h in air. After the optimal weight ratio of Ru/Cu/Na/Te was achieved, a similar experiment with Mn was carried out (0.0–6.0 wt%). Subsequently, different total metal loadings of the optimal Ru/Cu/Na/Te/Mn ratio on SiO_2 were investigated from 5 to 33 wt%.

2.2. Catalytic performance evaluation

One-and-a-half milligrams of a prepared catalyst was packed in a quartz tube (0.5 cm in diameter) and sandwiched between two quartz wool plugs. As thin as possible a catalyst bed was used (~1 mm) in order to avoid complete combustion of the PO product. The reactant gases were O_2 (Praxair, 99.999%) and C_3H_6 (Linde, 99.5%) while He (Praxair, 99.999%) was used as an inert carrier. In the first step, the feed gas volume was $O_2/C_3H_6/He = 2/1/97$ at a total flow rate of 50 cm^3/min (GSHV = 848 h^{-1}) regulated by mass flow controllers (KOFLOC 3810 DSII). The reactor temperature was 250 °C under atmospheric pressure. In the second step, the Box–Behnken design was applied to determine optimal conditions in order to obtain the maximized PO product. Two variables were studied in this work, i.e. reaction temperature (190–310 °C), O_2 to C_3H_6 ratio (2–20 by fixing the C_3H_6 feed at 1 vol%). Data analysis was conducted by on-line gas chromatography (Varian CP-4900 Micro GC with thermal conductivity detector (TCD), Porapak U (10 m) and Molecular sieve 5 Å (10 m). The product selectivities and C_3H_6 conversions were calculated on the basis of carbon balances [25], and PO formation rates were calculated by grams of PO that produced from a kilogram of catalyst in 1 h. The repeatability of all experiments was within ±10%.

3. Results and discussion

Before presenting the results, it is important to note that PO formation rate is the criteria for choosing the best catalyst or condition in each set of experiments, and that only PO, CO_2, and trace amounts (<1.0% product selectivity) of acrolein (AC) and acetone (AT) (see Fig. S1) were detected. Hence, the CO_2 selectivity for an experiment is essentially 100% minus PO selectivity. Fig. 1A presents the catalyst performance of Te loaded on RuO_2-CuO-NaCl/SiO_2 catalysts. Increasing Te loading from 0.0 to 0.175 wt% resulted in increase of PO formation rate rapidly from 113 $g_{PO}\ h^{-1}\ kg_{cat}^{-1}$ to the optimum at 252 $g_{PO}\ h^{-1}\ kg_{cat}^{-1}$. Similarly, the PO selectivities increased from 25% to 34%, while C_3H_6 conversions were virtually unchanged at about 2.8%. This could be because the numbers of active TeO_2 (denoted as TeO_2 because of its final form, see Figs. S2–S3) close by the main active site (i.e. the proximity of RuO_2 and CuO [26]) become higher dispersed, thereby improving PO formation. Above 0.175 wt% of the Te loading, the PO formation rate and PO selectivity decreased from the optimum to 119 $g_{PO}\ h^{-1}\ kg_{cat}^{-1}$ and 17%, respectively, with a slight increase in C_3H_6 conversion from 2.8% to 3.6%. This is potentially because excessive amounts of TeO_2 block or cover the main active surface.

The catalyst exhibiting the optimal PO formation rate shown in Fig. 1A was selected to be doped with Mn from 0.0 to 6.0 wt%. The addition of Mn was deemed an attractive option because catalysts of Cu and Mn together increase PO yield compared to its unimetallic variants due to synergy between Cu and Mn [31–34]. The plots in Fig. 1B show the effect of Mn (denoted as MnO_x because of its final form, see Figs. S2–S3) loaded on RuO_2-CuO-NaCl-TeO_2/SiO_2 catalyst from 0.0 to 6.0 wt%. Increasing the Mn loading to 1.0% increased the PO selectivity and formation rate to 43% and 300 $g_{PO}\ h^{-1}\ kg_{cat}^{-1}$, respectively, whereas the C_3H_6 conversion remained relatively constant at 2.6%. At higher loadings (>1.0 wt% of Mn), the PO selectivity, C_3H_6 conversion, and PO formation rate started to decrease gradually. It is possible that excess MnO_x could obstruct the main active site and, in itself, become the dominant active material, consistent with the fact that Mn-based catalysts produce mostly CO_2 product [31].

To further optimize the performance of the multimetallic RuO_2-CuO-NaCl-TeO_2-MnO_x/SiO_2 catalysts, an investigation of the effects of total metal loading on the SiO_2 support was undertaken. The results are shown in Fig. 2. [FE-SEM images showing each metal distribution are presented in Figs. S4–S11]. Increasing the total metal loading from 5.0 to 25.0 wt% significantly increased the PO formation rate, from 41 to 641 $g_{PO}\ h^{-1}\ kg_{cat}^{-1}$. Similarly, the PO selectivity and the C_3H_6 conversion also gradually increased, from 28 to 32% and 0.6 to 5.2%, respectively.

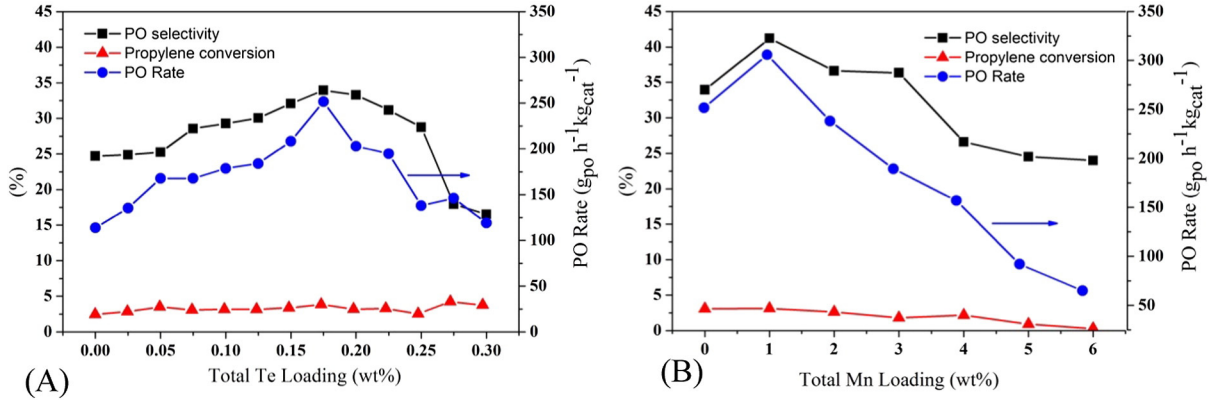

Fig. 1. (A) Te loading on Ru-Cu-Na/SiO_2 at 0.00–0.30 wt% (Ru/Cu/Na = 7.14/3.57/1.79 by wt%) (B) Mn loading on Ru-Cu-Na-Te/SiO_2 at 0.0–6.0 wt% (Ru/Cu/Na/Te = 7.14/3.57/1.79/0.175 by wt%).