



Direct catalytic epoxidation of ethene over copper and alumina-supported copper

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ABSTRACT

Silver is credited with being a unique catalyst for direct epoxidation of ethene. Copper(II) oxide is known for its combustion catalytic properties in such reactions. In this paper it is reported for the first time that copper oxides under certain conditions can catalyze direct epoxidation of ethene. Reduced copper oxide, ethene, and molecular oxygen are the minimum necessary and sufficient conditions for olefin epoxidation. There is an induction period for the onset of epoxidation. On continual use of this mixed oxide, the selectivity diminishes progressively to about 1%. Reduction of the used mixed oxide restores selectivity, at least in part. A two-stage pulsed reaction (alternating pulses of hydrogen and oxygen in flowing ethene) maintains the selectivity, suggesting that the active species in epoxidation reaction is close to the Cu(I) state. It is also possible to maintain this active species for the sustained reaction by adjusting the oxygen partial pressure to be close to 0.07.

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1. Introduction

Ethene oxide (EO) is a major chemical intermediate with an annual production of about 19×10^6 metric tons in 2009, with an average growth forecast between 3% and 5% until 2019 [1]. Silver is unique in its ability to catalyze the direct epoxidation of ethene to EO with high selectivity. The industrial process involves silver metal supported on α -alumina as catalyst and promoted by alkali metals and chlorides. The uniqueness and industrial importance of the direct catalytic epoxidation of ethene over silver have provoked diverse studies on both dispersed catalysts and single crystals [2,3]. Oxygen adatoms rather than adsorbed dioxygen are the deoxidizing species [4], which is inserted into a minimally rehybridized ethene π -bond [5]. Oxygen adatoms have been generated on copper [6] and proposed on gold [7]; π -bonded olefins have been observed on copper [8,9] and inferred on gold [10–13].

Gas-phase epoxidation of propene using hydrogen and oxygen (hydrooxidation) over nanosize gold particles dispersed on titanium has been extensively reported by Haruta [14]. Highly selective epoxidation of propene by molecular oxygen over reduced mixed copper oxides was achieved with alternating pulses of oxidizing and reducing conditions [15]. Direct catalytic epoxidation

of styrene and cyclohexene over copper phosphates also proceeded with moderate selectivities [16]. The tentative mention of adsorbed hydroxyl radicals as possible active species echoes their role in an analogous reaction in solution chemistry [17].

Ultrasensitive epoxidation of butadiene and styrene by reaction under temperature-programmed reaction (TPR) conditions with oxygen preadsorbed on copper single crystals (Cu{111}) established that provision of oxygen adatoms and olefin molecules co-adsorbed at Cu metal sites are the minimum necessary and sufficient condition for this reaction [5,18]. Cu{111} is also effective in the selective epoxidation of *trans*-methylstyrene. Oxygen is adsorbed as oxygen adatoms and oxidic oxide. The former leads to epoxidation whereas the latter induces combustion [19]. Torres et al. have predicted by theoretical methods that copper is more selective in epoxidizing alkenes, especially at low oxygen coverage [20].

Hydrogen contamination in the ethene feed will help the epoxidation reaction over copper catalysts by slowing down catalyst oxidation, whereas any hydrogen gets burned over silver, causing front-end hot spots leading to catalyst decay [21]. The reaction mechanism on the silver catalyst is thought to involve a common oxametallocycle intermediate reacting along dichotomous pathways to form EO and CO₂. There is a consensus that oxygen adatoms (O_a) on silver are responsible for epoxidation [22]. It is believed that the minimum necessary and sufficient conditions for olefin epoxidation to occur on catalytic surfaces are (a) π -adsorbed olefin and (b) oxygen adatoms [23]. Both conditions are met by copper [24]. As a simple extension of this concept, copper should, in principle, epoxidize ethene.

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There is, however, no report on epoxidation of ethene over pure or supported copper, though copper is used with silver as a bimetallic catalyst or as a promoter with silver [25,26]. The present study reports the direct epoxidation of ethene on pure and supported copper in single- and two-stage (pulsed) procedures. Copper catalysts prepared by a sol-gel route achieved an initial EO selectivity of 28%, which falls progressively with time. Both supported and pure copper catalysts showed an induction time before achieving epoxidation. The selectivity for EO could be maintained in a two-stage pulse reaction with alternating reduction and reactant pulses or by maintaining a very narrow range of oxygen partial pressure. Copper(II) oxide, on the other hand, favors combustion, significantly reducing the selectivity of EO. It is suggested that there is an active Cu state, probably close to Cu(I), for EO conversion and for higher EO selectivity, which needs to be stabilized.

2. Experimental

2.1. Catalyst preparation

Unsupported copper and 5%Cu/Al₂O₃ catalysts were prepared by a sol-gel route. Equimolar aqueous solutions of Cu(NO₃)₂·3H₂O (Fison) and citric acid (Aldrich) were mixed and gelled by heating with continuous stirring. The required amount of alumina powder (SA5562, 100–200 μm) to get 5% Cu on alumina was also added for the alumina-supported catalyst. The resultant gel was dried at 393 K for 15–20 h and calcined at 773 K for 4 h. The ground and sieved catalysts were loaded onto the testing rig and reduced in situ using 5% H₂ in argon (10 mL/min) at 573 K for 3 h before testing. The epoxidation experiments were carried out in a microreactor system (Fig. 1) under atmospheric pressure. Research grade ethene, oxygen, hydrogen, and argon (all supplied by BOC) were used without further purification. The flow of gases was regulated by mass flow controllers (Brooks 5850E). The reaction products were analyzed using an online GC system (HP5890) and by a HAL200 quadrupole MS system (Hiden). The reaction products were separated by a Poraplot Q capillary column and detected by TCD. In a typical experiment, about 200–300 mg of the catalyst (200–400 μm) was packed between quartz wool in a glass-lined tube. The reactor tube was heated in an electric furnace that can be controlled to ±1 K. The typical reaction gas mixture (10% O₂, 70% C₂H₄, and balance Ar) was continuously fed at a GHSV of 800–1000/h in a single-stage reaction condition. In the two-stage

operation, ethene was fed to the reactor continuously with alternating pulses of H₂ (5 min, for reduction of catalyst) and O₂ (4 min, for the reaction) being introduced with a 2-min pause between the pulses to flush out any H₂ or O₂ from the reactor to eliminate any co-feeding of O₂ and H₂.

2.2. Catalyst characterization

X-ray diffraction patterns for the calcined catalysts (supported and unsupported) are shown in Fig. 2a and 2b is the SEM micrograph of calcined unsupported catalyst. The XRD patterns show the presence of a CuO (tenorite) phase in both supported and unsupported catalysts, along with small quantities of cuprite and metallic copper. The XRD peaks marked with asterisks are for the commercial alumina SA5562 used as support. The SEM micrograph shows a porous structure as a result of escaping gas during calcination. The TEM (Fig. 2c) of the unsupported oxide catalyst shows nanocrystalline particles with an average size of 10 nm.

3. Results and discussion

The EO yield and selectivity as functions of reaction time over pure copper prepared by a sol-gel method in a single-stage continuous operation at 523 K are presented in Fig. 3. The catalyst was reduced in situ by 5% hydrogen in argon before the reaction was started by feeding a mixture of ethene and oxygen. The only other product formed in this reaction was carbon dioxide. Initially, at the start of the reaction, virtually no EO was formed. The EO production rate picked up with time and the selectivity reached a maximum of 28% in 10 min with a maximum EO production rate of 0.48 mol/kg_{cat}/h. The selectivity and the activity showed a progressive decline after 10 min and reached 1% and 0.02 mol/kg_{cat}/h after 60 min. Following a second reduction treatment and a similar experiment, the second ethylene oxidation curve retraced the course of the first, except with a slightly higher selectivity.

Fig. 4 shows the mass spectral fragments for oxygen (*m/e* 32) and carbon dioxide (*m/e* 44 after EO contributions are subtracted) for a few minutes before and after oxygen was switched on. Initially the oxygen was completely consumed. During this time, EO production was negligible, with the production of only a small but significant amount of carbon dioxide. Most of the consumed oxygen was used in the oxidation of Cu metal, with a small portion forming CO₂. A conservative estimate of the copper oxidation state when oxygen broke through into the product gas shows that

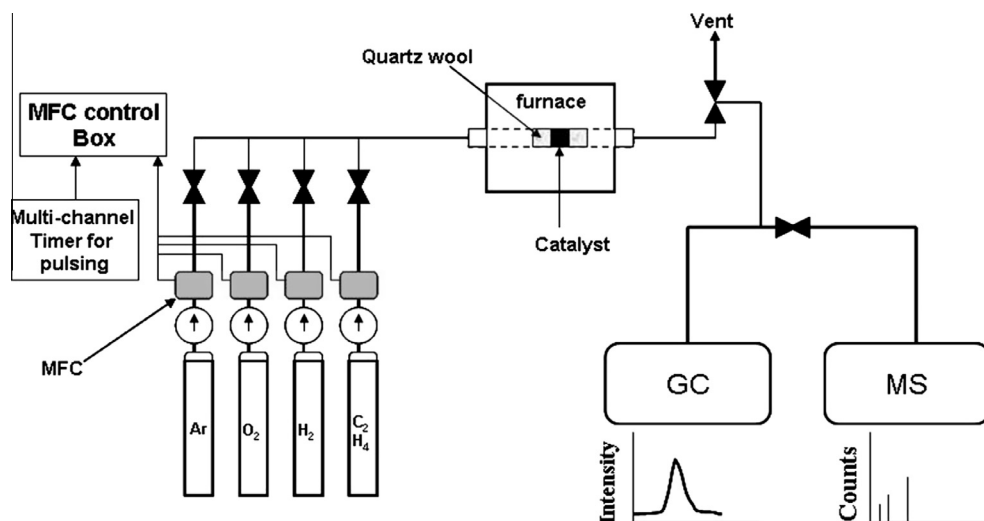


Fig. 1. Schematic of reactor and the experimental setup.

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