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Kinetic hydrogen isotope effects in ethylene oxidation on silver catalysts

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Abstract

Kinetic hydrogen isotope effects (KHIEs), $(k)_D/(k)_H$, for ethylene oxide formation, ethylene oxide combustion, and carbon dioxide formation in ethylene oxidation on silver catalysts were determined using rate constants of empirical reaction rate equations. These rate constants were obtained on pure Ag and K_2SO_4-Ag catalysts at 413–473 K and NaCl-Ag catalyst at 518–576 K keeping steady active states in the fixed bed flow reactions. On the Ag and K_2SO_4-Ag catalysts resulting in ethylene oxide selectivity values of 30.9–63.3%, KHIEs for total formation of carbon dioxide (0.43–0.61) were in disagreement with theoretical values of 0.25–0.30 for C–H bond breaking reaction and also with the value of 0.73 for intramolecular hydrogen transfer reaction, while KHIE for ethylene oxide combustion coincided with the theoretical value 0.73. Consequently, the KHIE for total formation of carbon dioxide was considered to be fixed by the constructive ratio of the direct ethylene combustion route and the ethylene oxide combustion route, which have the C–H bond breaking step and the intramolecular hydrogen transfer step as a rate-determining step, respectively. On the NaCl-Ag catalyst indicating ethylene oxide selectivity of 80.0–88.8%, KHIEs for carbon dioxide formation were 0.67–0.80, but no ethylene oxide combustion occurred; these results suggested that the rate-determining step of the direct ethylene combustion route was the intramolecular hydrogen transfer step. KHIEs for ethylene oxide formation on the Ag and K_2SO_4-Ag catalysts decreased from 1.99 to 1.19 with increase in ethylene oxide selectivity, while those on the NaCl-Ag catalyst were 0.86–1.14, of which the average value was almost 1.0. The KHIEs larger than 1.0 for ethylene oxide formation were explained as mainly due to an ensemble isotope effect caused by remarkable reduction in decomposition rates of combustion intermediates of ethylene and ethylene oxide on replacing of H by D. Additionally, three cycle mechanisms for the ethylene oxidation on silver catalysts were discussed.

Keywords: Ethylene oxidation; Rate equation; Kinetic hydrogen isotope effect; Silver catalyst; Rate-determining step; Mechanism

1. Introduction

Oxidation of ethylene is one of the simplest complex reactions; it consists of epoxidation of ethylene, secondary oxidation of ethylene oxide, and direct complete oxidation of ethylene. The mechanism of the oxidation has already been studied by many investigators. Twigg reported in 1934 that ethylene oxide was formed from gaseous ethylene and one oxygen atom adsorbed on silver catalyst and that carbon dioxide was produced through the interaction between ethylene and two oxygen adatoms [1]. After that, the characteristics of oxygen species adsorbed on silver surfaces have been revealed by static oxygen adsorption methods [2–5,7] and spectroscopic studies using IR [6,7], ED [8,9], EPR [10–12], and SERS [14–17]. Gerei et al. [6], Kilty et al. [7], and Kagawa et al. [9] indicated the presence of adsorbed oxygen molecules, i.e., superoxide O_2^-, using IR spectroscopy and they suggested the scheme in which ethylene oxide was formed from the superoxide and ethylene. Clarkson and Cirillo [10,11], and Shimizu et al. [12] have observed ESR spectra due to superoxide O_2^- on silver. Tanaka and Yamashina indicated that the ESR spectrum intensity was reduced vigorously after the silver surface having superoxide was exposed to ethylene [13]. In the researches with surface-enhanced Raman spectroscopy (SERS), the ν(O–O) spectrum for adsorbed oxygen molecule ion which was perpendicular to silver surface was observed at $815\ \mathrm{cm}^{-1}$ [14–16]. The intensity depended

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sensitively on partial pressure ratio of oxygen/ethylene [17]. The studies using XPS and UPS [18,19], XPS [20], HREELS and XPS [21], and AES, XPS and TPD [22] also showed the existence of oxygen admolecules on silver. These results support strongly the concept that ethylene oxide was formed by the reaction of superoxide and ethylene.

On the other hand, from the results obtained by such surface-scientific analyses as LEED, AES, and TPD, the concept has been proposed that ethylene oxide was produced by the reaction between oxygen adatom and adsorbed ethylene [23–25]. Grant and Lambert stated that ethylene oxide was formed by the interaction between the double bond of ethylene and acidic oxygen adatom, while the formation of carbon dioxide was initiated with the reaction between the weakly acidic hydrogen of ethylene and basic oxygen adatom [24]. Bukhtiyarov et al. recently showed using a combination technique of XPS and PTRMS that electrophilic oxygen was active for ethylene oxide formation and that nucleophilic oxygen was active for carbon dioxide formation [26]. For the combustion of ethylene, Force and Bell showed the presences of sequential intermediates of $Ag–O–CH_2–{}^{\bullet}CH_2$, $Ag–O–CHCH_3–O–Ag$, and Ag–O–CO–O–Ag for carbon dioxide formation, based on the dynamic IR observations of long-living chemical species adsorbed on Ag/Cab–O–Sil catalyst surface during the course of ethylene oxidation [27,28]. In addition, it was apparent that the combustion of ethylene oxide occurs simultaneously and consecutively on the same silver surface during the ethylene oxidation [29–31].

Recently, studying on oxygen adsorption during ethylene oxidation, Ayame et al. indicated the possibility that the active site was an adsorbed oxygen atom $Ag–O^{-}$ [32]. Stegelmann et al. proposed the surface oxide formation by two silver atoms and an oxygen atom as an active site [33–35]. They anticipate $Ag_2O–O–CH_2–{}^{\bullet}CH_2$ as an intermediate in ethylene oxide formation route. Linic et al. [36] and Jankowiak and Barteau [37,38] described that the active sites were Ag_2O on Ag catalyst and Cu–O–Ag on Cu-Ag bimetallic catalyst [34]. These authors consider that the ethylene oxide formation intermediate is $Ag_2O–CH_2–{}^{\bullet}CH_2$. Additionally, Lambert et al. stated that at least sufficient conditions for epoxidation were the presence of π–adsorbed ethylene and oxygen adatom [39]. As having stated above, since there are many differences in understanding of experimental results for the reactions between oxygen species on silver and ethylene, the overall reaction mechanism including ethylene and ethylene oxide combustion routes is not yet clear.

The present work aims to elucidate the rate-determining steps in partial oxidation of ethylene, especially the carbon dioxide formation routes, and then to clarify the overall mechanism from kinetic hydrogen isotope effects (KHIEs) for ethylene oxide formation, ethylene oxide combustion, and carbon dioxide formation; these effects are determined on several silver catalysts, resulting in different selectivities. For the KHIEs, Cant and Hall [31], van Santen et al. [23,40], Grant and Lambert [24], and Kung [41] have reported the results obtained in their valuable works. Cant and Hall have explained the KHIE by the consideration that ethylene oxide and carbon dioxide were formed in parallel reactions from perepoxy-intermediate consisting of superoxide and ethylene [31]. Stegelmann et al. reconfirmed experimentally the results reported by Cant and Hall [35]. Van Santen et al. [23,40] and Grant and Lambert [24] interpreted the KHIEs using the reaction model consisting of two different intermediates to produce ethylene oxide and carbon dioxide. However, since, in each work described above, only one kind of silver catalyst was used, the relations between the KHIEs and silver catalysts that indicate different performances remain unknown. As far as we know, no explanation for the KHIEs using theoretically estimated values has been performed so far.

In the present work, kinetic data for the ethylene oxidation were measured on pure Ag, K_2SO_4-promoted Ag, and NaCl-promoted Ag catalysts using an integral fixed bed flow reactor. These catalysts resulted in different ethylene oxide selectivities. Activity states of the Ag and K_2SO_4-Ag catalysts varied frequently for 10 h or longer and then reached a new different steady state, when the partial pressure ratio of ethylene to oxygen in feed gases was changed, even if sufficient conditionings of the catalysts were preliminarily performed [42]. So, the measurements of kinetic data were carried out on the steady state catalyst surfaces, which were attained under two kinds of feed gases with ethylene-rich and oxygen-rich compositions [42–44]. Subsequently, KHIEs for the ethylene oxide formation, ethylene oxide combustion, and total formation of carbon dioxide were evaluated from the rate constants of the integral reaction rate equations obtained. In addition, to explain more precise meanings of the KHIEs or mechanisms, the oxidation and isomerization of ethylene oxide were attempted on the hydrogen-reduced catalyst surfaces, using a conventional pulse reaction technique. The ethylene oxidations on Cs and Re-copromoted Ag catalysts, yielding ethylene oxide selectivity higher than 80%, and also on Pt-supported α-alumina and silica catalysts were carried out by the pulse reaction technique.

2. Experimental

2.1. Chemicals

Chemicals of $AgNO_3$ (99.9% up), KOH (99.7% up), K_2SO_4 (98%), NaCl (99.9% up), and oxalic acid (super pure) were materials supplied by Kanto Chem. Co. $CsNO_3$ (99%) and ethylenediamine (99%) were supplied from Kishida Chem. Co. and also Re_2O_7 (99.99%) from Mitsuwa Chem. Co. Highly pure C_2H_4 (99.5% up) and C_2D_4 (D-content 99.5%) were purchased from Seitetsu Kagaku KK and Merck Dohme Canada Ltd., respectively. Also, commercial gases of super-pure O_2 (99.8% up) and He (99.9999%) were used without further purifications. C_2H_4O was prepared from the dehydrochlorination of ethylenechlorohydrine (Kanto Chem. Co.) by KOH. C_2D_4O was provided from C_2D_4 using the method reported by Cox and Warne [45]. QM-spectroscopic purities of the dried C_2H_4O and C_2D_4O were above 98 and 96%, respectively; the impurities were O_2, N_2, and He.

Three kinds of α-aluminas and silica were also used as catalyst carriers: Norton Standard Catalyst Carrier No.