Catalytic Performance and Reaction Pathways of Cu/SiO₂ and ZnO/SiO₂ for Dehydrogenation of Ethanol to Acetaldehyde

Masahiro OHIRA 1, Huimin LIU 2, Dehua HE 3, Yoshiya HIRATA 1, Makoto SANO 1, Toshimitsu SUZUKI 1, and Takanori MIYAKE 1, 2

1) Dept. of Chemical, Energy and Environmental Engineering, Graduate School of Science and Engineering, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, JAPAN
2) Organization for Research and Development of Innovative Science and Technology, Kansai University, 3-3-35 Yamate-cho, Suita, Osaka 564-8680, JAPAN
3) Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Dept. of Chemistry, Tsinghua University, Beijing 100084, P. R. CHINA

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Vapor-phase dehydrogenation of ethanol to acetaldehyde was studied using Cu/SiO₂ and ZnO/SiO₂ catalysts prepared by the conventional impregnation method. Catalysts were characterized by XRD, nitrogen adsorption-desorption analysis, XPS, N₂O-pulse method, CO₂-TPD and C₂H₅OH-TPD. Use of copper ammonium complex for the preparation of Cu/SiO₂ catalysts formed Cu particles on SiO₂ too small for detection by XRD. The prepared Cu/SiO₂ catalyst had high and selective dehydrogenation activity of ethanol to acetaldehyde. However, Cu/SiO₂ catalyst was less stable at 350 °C due to sintering of Cu. Interestingly, a metal oxide catalyst, ZnO/SiO₂, had fairly high and fully selective activity for dehydrogenation of ethanol to acetaldehyde. Furthermore, no changes in the activity and selectivity were observed for at least 6 h at 350 °C. The reaction pathways on the metal catalyst, Cu/SiO₂, and the oxide catalyst, ZnO/SiO₂, were studied by C₂H₅OH-TPD. Evolution of H₂ was observed from ethanol contacted with Cu/SiO₂ catalyst at 50 °C, suggesting dehydrogenation at this temperature. Desorption of acetaldehyde was observed above 200 °C. On the other hand, simultaneous desorption of H₂ and acetaldehyde occurred on ZnO/SiO₂ catalyst above 240 °C, suggesting that the rate determining step is the dissociative adsorption of ethanol at this temperature. Thus, the reaction pathways were very different for the metal catalyst and the oxide catalyst.

Keywords
Dehydrogenation, Ethanol, Acetaldehyde, Zinc oxide catalyst, Reaction pathway

1. Introduction

Ethanol production has significantly increased in the last decade, mainly based on the fermentation of glucose, and a large amount of the so-called bio-ethanol is used for a transportation fuel or fuel additive. From a viewpoint of CO₂ fixation, other uses of ethanol must be developed.

Acetaldehyde is an important bulk chemical used as a raw material for the production of ethyl acetate. Acetaldehyde is produced by the Wacker process from ethylene as the raw material using PdCl₂-CuCl₂ catalyst. However, this process has the disadvantages of corrosion of the reactor, chlorinated by-products and deposition of metallic Pd. Therefore, other routes to produce acetaldehyde are desirable.

Acetaldehyde can be synthesized by dehydrogenation or oxidative-dehydrogenation of ethanol. Lower cost ethanol production will promote the ethanol-based production of acetaldehyde, and the hydrogen by-product has various uses which will further improve the competitiveness of the acetaldehyde production.

Oxidative dehydrogenation of ethanol to acetaldehyde has been studied using metal catalysts or oxide catalysts. Au-CuO/SiO₂ catalyst at 200 °C achieved 90% conversion of ethanol with 80-90% selectivity for acetaldehyde. Sobolev et al. studied low temperature gas-phase oxidation of ethanol on Au/TiO₂. Idriss and Seebauer used oxide catalyst such as Fe₂O₃, CaO and TiO₂. Acetaldehyde selectivity was high on CaO catalyst, but the conversion was lower than 15%. Therefore, acetaldehyde selectivity is not sufficient for oxidative dehydrogenation of ethanol.
Many studies have examined dehydrogenation of ethanol to acetaldehyde and hydrogen \(^n\)\(^{20-23}\). Metal catalysts using \(\text{Cu}^{+}\)\(^{14}\), \(\text{Ni-Cr}^{+}\)\(^{15}\), \(\text{Ag}^{+}\)\(^{16}\) and \(\text{Pd}^{+}\)\(^{17}\) were mainly studied. In particular, Cu catalysts have been most commonly studied and the reaction kinetics\(^{9,12}\) and reaction mechanisms\(^{14,16}\) are reported. Many papers have estimated that once ethoxy species formed and followed by dehydrogenation. Density functional theory (DFT) simulation of ethanol dehydrogenation has also been reported for \(\text{Cu}^{14}\), \(\text{Pd}^{18}\) and \(\text{Pt}^{19}\) catalysts. DFT study on ethanol adsorption and dehydrogenation on \(\text{Cu}/\text{Cr}_2\text{O}_3\) indicated that ethanol adsorbed dissociatively on \(\text{Cr}^{3+}\) as the ethoxy species, and the interface of \(\text{Cu}\) and \(\text{Cr}_2\text{O}_3\) was important for adsorption and dehydrogenation\(^{14}\). DFT simulation on Pt concluded that the rate determining step was dissociation of \(-\text{H}\) bond of adsorbed ethoxy species\(^{19}\). Oxide catalysts were also occasionally studied for the dehydrogenation of ethanol\(^{20,21}\), but metal catalysts are generally recognized as more active for hydrogenation and dehydrogenation reactions.

\(\text{ZnO}\) is rare as a main catalyst element but is often reported as a catalyst component\(^{9}\) or catalyst support\(^{15,17}\). \(\text{ZnO}\) without metal catalyst, \(\text{Ni-Co}\), showed dehydrogenation activity at 350 K\(^{15}\). Dehydrogenation occurred on \(\text{ZnO}\) at 523 K as the conversion of ethanol was one order lower than that on \(\text{Pd}\) catalysts supported on various metal oxides\(^{17}\). Comparison of dehydrogenation of ethanol on \(\text{Cu}\) and \(\text{ZnO}\) concluded that \(-\text{H}\) bonded to the \(\text{α}\)-carbon of adsorbed ethoxy species dissociated on \(\text{Cu}\) catalyst but \(-\text{H}\) bonded to the \(\beta\)-carbon of adsorbed ethoxy species dissociated on \(\text{ZnO}\) catalyst, both processes giving acetaldehyde\(^{22}\). However, the reaction pathway on \(\text{ZnO}\) catalyst remains unclear and understanding of the reaction pathway is necessary to improve the catalytic performance.

In this study, the dehydrogenation performance of \(\text{Cu}/\text{SiO}_2\) and \(\text{ZnO}/\text{SiO}_2\) catalysts was compared firstly and then the reaction pathway was investigated in detail.

2. Experimental

2.1. Preparation of Catalysts

Catalysts were prepared by the conventional impregnation method. Copper salt 1.57 mmol, \(\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}\), \(\text{Cu}^{2+}\) in an Ar stream was dissolved in 30 mL of distilled water and \(\text{SiO}_2\) (270 m\(^2\) g\(^{-1}\)) was added. After drying at 80 °C and 200 hPa, the obtained powder was further dried overnight at 80 °C. Finally, the catalyst precursor was reduced at 250 °C in \(\text{H}_2\) stream of 250 mL min\(^{-1}\) to obtain 10 wt% \(\text{Cu}/\text{SiO}_2\) catalysts. The catalyst prepared with \(\text{CuCl}_2\cdot2\text{H}_2\text{O}\) was reduced at 400 °C. To improve the dispersion of \(\text{Cu}\), aqueous \(\text{NH}_3\) (10 %) was added to the impregnation solution of \(\text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O}\) until the pH reached 11.0 and drying was carried out at 80 °C and 350 hPa. Thus, the \(\text{Cu}\) catalyst \([\text{Cu}^{+}\text{NH}_3\text{]}_2\text{Cl}_2\) was obtained. The 10 wt% \(\text{ZnO}/\text{SiO}_2\) catalyst was prepared by dissolving 0.61 mmol of \(\text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O}\) in 30 mL of distilled water and increasing the pH to 11.0 with aqueous \(\text{NH}_3\) (10 %). Then, 0.450 g of \(\text{SiO}_2\) with various BET surface areas (Fuji Silysia Chemical Ltd., CARiACT Q; 60, 120, 270 or 700 m\(^2\) g\(^{-1}\)) was added. The mixture was stirred for 2 h and then dried under reduced pressure of 350 hPa at 80 °C. After further drying at 80 °C overnight, the precursor powder was calcined at 250 °C for 2 h to give 10 wt% \(\text{ZnO}/\text{SiO}_2\) catalyst. Binary catalyst \(\text{Cu-ZnO}/\text{SiO}_2\) was prepared by the co-impregnation method using nitrate as raw materials and controlling pH using aqueous ammonia. \(\text{CuMgO}/\text{SiO}_2\) was prepared by a consecutive impregnation; namely, \(\text{Cu}\) was loaded on \(\text{MgO}/\text{SiO}_2\).

2.2. Characterization of Catalysts

The crystalline structure of the catalysts was analyzed by X-ray diffraction (XRD; Rigaku Corp., RINT TTR III) using \(\text{Cu Kα}\) radiation (\(λ = 1.5418 \text{ Å}\)) at 40 kV and 20 mA.

The BET specific surface area of supports and catalysts was calculated based on the \(\text{N}_2\) adsorption-desorption isotherm measured with a Belsorp BELmini (Bel Japan Inc., Japan). Pre-treatment for the measurement was at 200 °C for 1 h in \(\text{N}_2\) stream.

X-ray photoelectron spectra (XPS) were measured with a JPS-9000 MX (JEOL Ltd., Japan) using \(\text{Mg Kα}\) radiation at 10 kV and 10 mA. Peak position was calibrated for C1 s at 284.2 eV.

The surface area of \(\text{Cu}\) was measured by the \(\text{N}_2\) titration method\(^{20}\). A 100 mg portion of a \(\text{Cu}/\text{SiO}_2\) catalyst was pre-treated in-situ at 250 °C in an \(\text{Ar}\) stream. Then, the temperature was decreased to 50 °C. First, the catalyst was reduced from 50 to 250 °C at 2 °C min\(^{-1}\) in 5.0 % \(\text{H}_2/\text{Ar}\) and held at this temperature for 1 h. The temperature was reduced to 50 °C and the gas phase was flushed in an Ar stream for 30 min. The catalyst was oxidized in an 8.06 % \(\text{N}_2\text{O}/\text{Ar}\) gas flow for 30 min. After flushing the remaining \(\text{N}_2\text{O}\) with an \(\text{Ar}\) flow at 50 °C for 30 min, the catalyst was reduced in a 5.0 % \(\text{H}_2/\text{Ar}\) flow up to 700 °C at 15 °C min\(^{-1}\). The concentration of \(\text{H}_2\) in the effluent stream was analyzed with a gas chromatograph equipped with a thermal conductivity detector (TCD). The surface area of \(\text{Cu}\) was calculated according to the following stoichiometry in Eq. (1).

\[
\text{H}_2 + \text{Cu}_x\text{O}_{\text{surface}} \rightarrow 2\text{Cu}_{\text{surface}} + \text{H}_2\text{O}
\] (1)

Temperature-programmed desorption (TPD) of \(\text{CO}_2\) and \(\text{C}_2\text{H}_5\text{OH}\) (\(\text{CO}_2\)- and \(\text{C}_2\text{H}_5\text{OH}-\text{TPD}\), respectively) was carried out using a TPD-a-AT-w (Bel Japan Inc., Japan). A 50 mg portion of the catalyst was placed in a quartz cell and pre-treated in-situ at 250 °C for 1 h under \(\text{He}\) flow. Then, the catalyst was cooled to 100 °C and contacted with \(\text{CO}_2\) at 13.3 kPa. After removing
CO₂ in the gas phase for 5 min, temperature was increased at 10 °C min⁻¹ to 850 °C in He flow. The product from the catalyst was analyzed using Q-mass. For C₅H₁₀OH-TPD, Cu/SiO₂ catalysts or ZnO/SiO₂ catalysts were pre-treated in-situ at 120 °C in He flow. After cooling to 50 °C, ethanol vapor at room temperature was contacted with the catalyst for 5 min. Without sweeping the vapor phase, the temperature was increased from 50 to 400 °C at 10 °C min⁻¹ in He flow. The effluent gas was analyzed with Q-mass at m/z 31, 44 and 2 for ethanol, acetaldehyde and hydrogen, respectively.

2.3. Dehydrogenation of Ethanol and Analysis of Products

The dehydrogenation reaction was carried out with a fixed-bed, continuous flow-type reactor. Typically, a 0.050 g portion of the catalyst was placed in a tubular glass reactor. Both ends of the catalyst was plugged with quartz wool. Cu/SiO₂ catalyst was pre-treated in-situ at 250 °C for 1 h in a gas stream consisting of H₂ 5 mL min⁻¹ and N₂ 45 mL min⁻¹. ZnO/SiO₂ catalyst was pre-treated at 120 °C for 1 h in N₂ flow at 40 mL min⁻¹. After the pre-treatment, the catalyst was cooled to room temperature. Then, N₂ flow at 40 mL min⁻¹ (STP) was fed using a mass-flow controller and ethanol was fed using a syringe pump. The flow rate of ethanol was 10 mL min⁻¹ (STP). The temperature was increased to the desired value between 150 °C and 350 °C and held at each temperature for 30 min. The effluent gas was introduced into a cold trap of water held at ca. 0 °C.

The products in the cold trap were analyzed by the internal standard method with a gas chromatograph equipped with a flame-ionization detector using 2-propanol as the internal standard. The gas after the cold trap was also analyzed with a gas chromatograph equipped with a TCD. The column used for the trap was CP-PoraPLOT Q (length 27.5 m, internal diameter 0.32 mm, film thickness 10 μm, liquid phase styrene-divinylbenzene polymer; Varian, Inc.) and columns (internal diameter 3.2 mm and length 2.0 m) used for gas were Sunpak-A (Shinwa Chem. Ind. Ltd.) and Molecular Sieve 5A (GL Sciences Inc.).

3. Results and Discussion

3.1. Dehydrogenation on Cu/SiO₂ Catalysts

Preliminary experiments evaluated the loading of Cu and the relationship to catalytic activity. Yields of acetaldehyde using 1 wt%Cu/SiO₂ and 5-15 wt%Cu/SiO₂ were ca. 5 % and 40 % at 250 °C, and ca. 14 % and ca. 70 % at 300 °C, respectively. Therefore, the loading was fixed at 10 wt%Cu on SiO₂. The selectivity for acetaldehyde was 100 % and no other products were observed under the conditions studied. The oxidation state of Cu was checked by XPS and the presence of metallic Cu was confirmed.

Firstly, the effect of the copper source was investigated using copper chloride, nitrate and acetate. Ammine complex was also generated in-situ and supported on SiO₂ by the same conventional impregnation method. Figure 1 shows the XRD patterns of various Cu/SiO₂ catalysts. Copper particle size estimated from the diffraction peak at about 43° was chloride (34 nm) > nitrate (22 nm) > acetate (15 nm) > ammine complex. In particular, the catalyst prepared from ammine complex had no distinct XRD pattern, suggesting high dispersion of Cu on SiO₂. The temperature dependence of dehydrogenation activity on various catalysts is shown in Fig. 2. The order of activity at 350 °C agreed with the inverse order of estimated Cu particle size, so that higher catalytic activities were associated with smaller particles. Figure 3 shows the relationship between Cu surface area measured by the N₂O titration method and the yield of acetaldehyde. The yield of acetaldehyde was linearly correlated with the Cu surface area. However, increase in Cu surface area, for example from 4 to 12, did not increase acetaldehyde yield by three times, possibly because not all
the sites measured by N₂O titration were active for the reaction.

The dependences of acetaldehyde yield on the reaction temperature between 150°C and 300°C or 350°C are shown in Fig. 4. Here, Cu/SiO₂ catalyst prepared with copper nitrate was used. This experiment was carried out using one catalyst and changing the temperature stepwise. The reaction temperature was raised from 150°C up to 350°C in the first run, and then decreased to 150°C, resulting in significantly lower activity at the same reaction temperatures during the second run (Fig. 4(a)). A similar procedure carried out at the final temperature of 300°C (Fig. 4(b)) resulted in similar or slightly higher yield of acetaldehyde at the same temperatures during the second run, so no activity loss was observed. Thus, Cu/SiO₂ catalyst was deactivated at 350°C. Figure 5 shows the XRD patterns of Cu/SiO₂ prepared using copper nitrate before and after the reaction. The intensity of main peak for Cu at about 43° increased, suggesting sintering of Cu on the SiO₂ support.

3.2. Dehydrogenation on ZnO/SiO₂ Catalysts

The effect of additives was studied to improve the stability of Cu/SiO₂ catalysts without sintering. Cu–ZnO/SiO₂ and Cu/MgO/SiO₂ catalysts with various loadings were prepared and tested for the dehydrogenation of ethanol. These combinations have been used for hydrogenation²⁵ and so we expected that these elements would have favorable effects on the reverse dehydrogenation reaction. Preliminary study revealed that the combination of ZnO or MgO with Cu greatly improved the catalytic activity. For example, 10 wt%Cu/SiO₂ gave acetaldehyde yield of ca. 50% and 5 wt%Cu–5 wt%ZnO/SiO₂ gave ca. 80% yield at the time-on-stream of 3 h. Furthermore, 5 wt%Cu/5 wt%MgO/SiO₂ prepared from MgO/SiO₂ gave ca. 70% acetaldehyde yield. However, the expected improvement in stability was not observed.

The stability of Cu–ZnO/SiO₂ was better than that of Cu/MgO/SiO₂, so ZnO/SiO₂ was investigated and a very interesting behavior was observed. Figures 6 and 7 show the XRD patterns and yields of acetaldehyde on ZnO/SiO₂ with various ZnO loadings, respectively. XRD diffraction peaks ascribed to ZnO were observed only with high loading of ZnO at 30 wt%, suggesting high dispersion of ZnO up to 20 wt% loading (Fig. 6). The loading of ZnO influenced the yield of acetaldehyde at 350°C (Fig. 7); as ZnO loading of 5 wt% and 10 wt% showed similar yields and 20 wt% and 30 wt% loading gave higher but similar yields. Thus, the yield of acetaldehyde seems to depend on other factors as well as the dispersion of ZnO.

The effect of the surface area of SiO₂ support was investigated (Fig. 8). The yield of acetaldehyde was influenced by the surface area of SiO₂, and the highest yield was achieved with SiO₂ of 120 m² g⁻¹. Catalysts
prepared with SiO₂ having higher or lower surface area than 120 m² g⁻¹ gave inferior performance. We should emphasize the stability of catalytic activity; the yield of acetaldehyde was stable for at least 6 h at 350 °C, the temperature at which Cu/SiO₂ gradually deactivated. Furthermore, bio-ethanol usually contains small amounts of N- or S-containing impurities²⁶), and these compounds deactivate metal catalysts²⁷)₂⁹). However, oxide catalysts, such as ZnO/SiO₂ catalyst, should have more tolerance against these impurities²⁹).

To further evaluate the factors influencing the activity, the amount of basic sites on ZnO/SiO₂ catalysts was evaluated by CO₂-TPD. Figure 9 shows that the yield of acetaldehyde seemed to correlate with the amount of CO₂ desorbed from ZnO/SiO₂ catalysts. Yield of acetaldehyde for 10 wt%ZnO/SiO₂ (700 m² g⁻¹) deviated from the trend, possibly because the pore size was too small to allow rapid diffusion of the reactant and products. The relationships among the catalytic activity, dispersion of ZnO on SiO₂ and the amount of basic sites are not yet completely understood and further study is needed.

### 3.3 Reaction Pathway

Both the metal catalyst, Cu/SiO₂, and the oxide catalyst, ZnO/SiO₂, catalyzed the dehydrogenation of ethanol. Generally, catalysis of metals and oxides has been recognized to be very different³⁰) and so C₂H₅OH-TPD was investigated. Evolution of hydrogen was confirmed whereas no acetaldehyde desorption was detected over Cu/SiO₂ catalyst contacted with C₂H₅OH at 50 °C (Fig. 10). Therefore, ethanol was dehydrogenated easily even at 50 °C and hydrogen desorbed from the Cu surface.
However, acetaldehyde did not desorb and remained on Cu. Desorption of acetaldehyde was observed at about 200 °C without accompanying additional desorption of hydrogen. Recently, similar phenomena were reported using Pt–Cu alloy and Cu31). Desorption of hydrogen and acetaldehyde were observed up to 400 K, suggesting dissociation of C–H and O–H bonds at low temperatures. On the other hand, neither hydrogen evolution nor desorption of acetaldehyde was observed over ZnO/SiO2 catalyst at 50 °C (Fig. 11). However, simultaneous desorption of hydrogen and acetaldehyde was observed at about 240 °C, suggesting that adsorbed ethanol stayed on the catalyst surface without dissociation of bonds. Once dissociation of bonds started, both hydrogen and acetaldehyde desorbed from the catalyst surface at the same time. However, desorption peaks of hydrogen and acetaldehyde were different; about 280 °C for hydrogen and around 400 °C for acetaldehyde, suggesting stronger interaction between acetaldehyde and the catalyst surface. The amounts of desorbed hydrogen and acetaldehyde were calculated by the absolute calibration method. Figures 10 and 11 show that the ratios of acetaldehyde to hydrogen were 1.1 and 1.3 for 10 wt% Cu/SiO2 and 10 wt% ZnO/SiO2, respectively. Low temperature dissociation of ethanol and retention of hydrogen and acetaldehyde on ZnO/SiO2 might be possible at the reaction temperature adopted in this study. However, the conversion was quite low at 250 °C, unreacted ethanol was recovered and the material balance was substantially 100%, which suggests that dissociation occurred at or above 250 °C. These results explain why Cu/SiO2 catalyst had higher catalytic activity than ZnO/SiO2 at lower temperatures. In addition, the rate determining steps for the two catalysts, Cu/SiO2 and ZnO/SiO2, were apparently completely different; desorption of acetaldehyde for Cu/SiO2 and simultaneous dissociation of O–H and C–H bonds for ZnO/SiO2.

Assuming ethanol dehydrogenation to be first order, the reaction rate constant was calculated and the Arrhenius plot is given in Fig. 12. The activation energies for Cu/SiO2 and ZnO/SiO2 were calculated as 20.0 kJ mol⁻¹ and ca. 70 kJ mol⁻¹, respectively. The difference in these activation energies can be ascribed to differences in the rate determining step: lower activation energy for desorption of acetaldehyde and higher activation energy for the dissociation of covalent bonds. Our proposed reaction pathway is described in Fig. 13.

Most studies of ethanol dehydrogenation have reported that ethanol adsorbs on Cu and forms ethoxy species.

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![Fig. 11 - C₂H₅OH-TPD Spectra of 10 wt% ZnO/SiO₂ Catalyst](image)

![Fig. 12 - Arrhenius Plots for the Dehydrogenation of Ethanol on 10 wt% Cu/SiO₂ and 10 wt% ZnO/SiO₂ Catalysts](image)

![Fig. 13 - Proposed Reaction Pathways for Cu/SiO₂ and ZnO/SiO₂ Catalysts](image)
and hydrogen atoms combine and desorb as hydrogen molecules. If this is true, acetaldehyde desorption after C–H bond scission should be associated with desorption of another hydrogen molecule. However, our results in Figs. 10 and 11 exclude this generally accepted reaction mechanism. Thus, our results suggest re-investigation of the reaction pathway of ethanol to acetaldehyde and hydrogen.

4. Conclusions

Dehydrogenation of ethanol to acetaldehyde and hydrogen was studied with a metal catalyst, Cu/SiO₂, and an oxide catalyst, ZnO/SiO₂. Cu/SiO₂ catalyst prepared using copper ammine complex and SiO₂ with adequate surface area had high catalytic performances. Activity was correlated with copper surface area measured by the N₂O titration method. Deactivation by sintering was observed using Cu/SiO₂ at 350 °C, but this catalyst was promising when used at or lower than 300 °C. Unexpectedly, ZnO/SiO₂ catalyst showed moderate activity and excellent stability and selectivity at 350 °C. Activity was correlated with the amount of basic sites as evaluated by CO₂-TPD. Activation energies calculated by Arrhenius plot were 20.0 kJ mol⁻¹ and ca. 70 kJ mol⁻¹ for Cu/SiO₂ and ZnO/SiO₂ respectively, which suggested different rate-determining steps for the two catalysts. C₃H₇OH-TPD revealed that hydrogen was evolved even at 50 °C on Cu/SiO₂ and desorption of acetaldehyde was observed from 200 °C. On the other hand, simultaneous desorption of acetaldehyde and hydrogen was observed from ca. 240 °C on ZnO/SiO₂. Thus, the rate determining step for Cu/SiO₂ was desorption of adsorbed acetaldehyde and that for ZnO/SiO₂ was simultaneous dissociation of O–H and C–H bonds.

References

要 旨

エタノールのアセットアルデヒドへの脱水素反応に対する Cu/SiO_{2} および ZnO/SiO_{2} の触媒性能と反応経路

大平 将寛†1, 刘 会敏†2,†4, 賀 徳華†3, 平田 佳也†1, 佐野 直也†1,†2, 鈴木 俊助†1, 三宅 孝典†1,†2

†1 関西大学大学院理工学研究科エネルギー・環境工学分野, 564-8680 大阪府吹田市山手町3-3-35
†2 関西大学先端科学研究機構, 564-8680 大阪府吹田市山手町3-3-35
†3 Innovative Catalysis Program, Key Laboratory of Organic Optoelectronics and Molecular Engineering of Ministry of Education, Dept. of Chemistry, Tsinghua University, Beijing 100084, P. R. CHINA
†4 (現在) Laboratory for Catalysis Eng., School of Chemical & Biomolecular Eng., The University of Sydney, NSW 2006, AUSTRALIA

含浸法により調製した Cu/SiO_{2}, ZnO/SiO_{2} を触媒とし、気相でのエタノールの脱水素によるアセットアルデヒド合成を検討した。触媒は、XRD、窒素吸着脱着解析、N_{2}O バルス法、CO_{2} と C_{2}H_{5}OH-TPD により解析した。Cu/SiO_{2}触媒の調製にあたり、銅アンモニウム塩を使用することで、SiO_{2} 上の Cu 粒子径は XRD
で検出されないくらい小さくなった。このことにより調製した
Cu/SiO_{2}触媒は、エタノールの脱水素によるアセットアルデヒド
合成において高い活性、選択性を示した。しかしながら、Cu/
SiO_{2}触媒は、350 ℃ では Cu のシンタリングのため活性低下が
見られた。興味深いことに、金属酸化物触媒である ZnO/SiO_{2}
は、本反応に対し中程度の活性と 100 % の選択性を示した。さ
らに、350 ℃ において少なくとも 6 h、活性、選択性変化は見
られなかった。金属触媒 Cu/SiO_{2} 上と酸化物触媒 ZnO/SiO_{2} 上
での反応経路を C_{2}H_{5}OH-TPD で調べた。50 ℃ で Cu/SiO_{2} に
C_{2}H_{5}OH を接触させると水素の発生が観られ、このことは既に
この温度で脱水素反応が進行することを示唆した。アセットアル
デヒドの脱離は 200 ℃ 以上で見られた。一方、ZnO/SiO_{2} では
240 ℃ 以上で水素とアセットアルデヒドの同時脱離が認められ、
これはこの温度でのエタノールの解離吸着が律速段階であるこ
とを示唆した。このように、金属触媒と酸化物触媒では反応経
路が大きく異なっていることが明らかとなった。

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