

Effects of Alkaline-Earth Oxide Additives on Silica-Supported Copper Catalysts in Ethanol Dehydrogenation

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The dehydrogenation of ethanol has been studied over a series of Cu/SiO₂ catalysts modified with alkaline-earth oxide (Cu–MO/SiO₂, M = Mg, Ca, Sr, and Ba). The additive effects of alkaline-earth oxides on copper catalysts were examined by X-ray diffraction, scanning electron microscopy, temperature-programmed reduction, H₂–N₂O titration, temperature-programmed desorption of CO₂, and dehydrogenation of ethanol. The results indicated that the initial turnover frequencies can be improved by adding alkaline-earth oxides into the catalysts. MgO is an excellent promoter for increasing both the activity and stability of Cu/SiO₂ catalyst; however, the other alkaline-earth oxide modified catalysts are poor in stability. The increase in turnover frequencies of the modified catalysts is mainly due to the promotional effects of weakly basic sites on Cu metal. The strong basic sites can harm the stabilities of the catalysts.

Introduction

The catalysts for alcohol dehydrogenation can be mainly divided into two sorts: metal oxide and metal. Basic oxides such as ZnO, MgO, Cr₂O₃, and CuO are active for alcohol dehydrogenation (Tanabe et al., 1989). Of all the metal catalysts, copper is the most important one (Chhabra and Naidu, 1996; Chung et al., 1996; Han and Li, 1997; Li, 1995; Marchi et al., 1996). However, the activity of copper catalyst was found to decrease within a few hours. In recent years, attention has been focused on the copper catalysts combined with a small amount of metal oxide promoters on the catalytic properties of a dehydrogenation reaction (Benitez and Caro, 1996; Gil et al., 1996; Jung et al., 1995; Pepe and Polini, 1992; Prasad et al., 1985; Tu et al., 1994a,b; Tonner et al., 1994).

The dehydrogenation activity was found to be influenced by acid–base properties of additives combined with copper catalysts (Ai, 1984; Guerrero-Ruiz et al., 1991). The dehydrogenation activity of methanol to methyl formate was improved by the incorporation of a basic oxide of the catalysts (Ai, 1984). In the present work, a series of copper catalysts with various alkaline-earth oxides were investigated to elucidate the effects of additives on the activities and stabilities of Cu catalysts in an ethanol dehydrogenation reaction.

Experimental Section

Catalyst Preparation. The copper-based catalysts used in this study were prepared by incipient wetness co-impregnation of silica gel (G-57, Davison Chem. Co., surface area = 300 m²/g, pore volume = 1 mL/g) with aqueous nitrate solutions of Cu, Mg, Ca, and Sr. Since copper nitrate and barium nitrate cannot dissolve in water simultaneously, the Cu–BaO/SiO₂ catalyst was prepared by sequential impregnation. All the catalysts have a Cu to SiO₂ weight ratio of 14/86. For promoted catalysts, the molar ratio of alkaline-earth metal to Cu was kept at 1/10. The catalysts were dried at 100 °C

overnight, calcined at 450 °C for 3 h, and then reduced in a stream of 10% H₂ in Ar at 300 °C for 2 h.

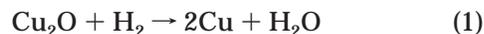
The MO/SiO₂ catalysts (M = Mg, Ca, Sr, Ba) with M to SiO₂ weight ratios of 1/100 were also prepared for the activity test.

XRD. X-ray diffraction patterns were obtained using a Siemens D-500 diffractometer employing nickel-filtered Cu K α radiation. The X-ray tube was operated at 40 kV and 25 mA. Catalysts were run as pellets mounted on a glass slide.

SEM. Scanning electron microscopy (SEM) was carried out for structure investigation using a Hitachi S-800 SEM (20-kV electron beam). All the catalysts, calcined, reduced, and used, were investigated.

TPR. The temperature-programmed reduction (TPR) experiment was carried out by using a quartz U-tube reactor. Details were described in a previous report (Tu et al., 1994b). Before starting the TPR experiments, 40 mg of catalyst was dried in flowing Ar at 100 °C for 1 h. A total of 10% H₂ in Ar was used as a reducing gas at a flow rate of 60 mL/min. The rate of temperature rise in the TPR experiment was 5 °C/min up to 800 °C.

H₂–N₂O Titration. The surface area of copper metal was determined by reaction of copper with nitrous oxide following the method of Bond and Namijo (1989) by two reduction processes. The number of surface copper atoms exposed by Cu particles in the calculation was taken as 1.47 × 10¹⁵ atoms/cm². Reduction of the catalyst was performed by heating the sample from ambient to 300 °C at 10 °C/min in 10% H₂/Ar flow (60 mL/min) and kept at 300 °C for 1 h at least. The temperature was then kept at 60 °C. The pure N₂O was allowed to flow over the sample for 1 h at 60 mL/min. It is believed that the surface metallic copper was oxidized to Cu₂O at this condition. The H₂–N₂O titration was carried out at a linear temperature program rise from room temperature to 800 °C.



The amount of H₂ used was detected with a thermal conductivity detector (TCD). The TCD signals were calibrated by injecting H₂ by using a Valco sampling

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valve of known volume. The copper surface area of catalyst can be determined from the amount of H₂ used.

TPD of CO₂. For characterization of surface basicity, in regard to both the amount and the strength of basic sites, temperature-programmed desorption (TPD) of preadsorbed CO₂ has become very popular. In a typical experiment, 2.00 g of sample was weighed and then placed in a U-shaped, quartz microreactor. At first, the catalyst was reduced in a stream of 10% H₂ in Ar at 300 °C for 2 h. The temperature was then dropped to 100 °C. CO₂ gas flowed at 60 mL/min for 1 h. The catalyst was then brought to room temperature slowly by cooling from 100 °C in CO₂ flow. The TPD experiment was carried out at a linear temperature program rise from room temperature to 800 °C in Ar (10 °C/min). Desorbed CO₂ was detected with a Shimadzu gas chromatograph (model GC-8A) equipped with a TCD. The TCD signal was calibrated by injecting CO₂ by using a Valco sampling valve of known volume.

Catalytic Activity. The dehydrogenation reactions were carried out in a continuous, U-shaped, quartz microreactor. About 40 mg of fresh catalyst was placed on a layer of quartz wool. The catalyst was first reduced with 10% H₂ in Ar at 300 °C for 2 h. A saturator containing ethanol was kept at a constant temperature of 22 °C. Nitrogen was used as a carrier gas at a constant flow rate of 60 mL/min. All experiments were performed at 300 °C. To prevent possible condensation, all gas-line connections and valves were wrapped with heating tape. The products were sampled by a six-port valve and analyzed by a Shimadzu gas chromatograph (GC-8A) with a TCD. The column was 3 m long and was loaded with Porapak QS which was maintained at 110 °C. Product gas concentrations were determined with a Shimadzu CR-6A integrator by comparing the peak areas to those for a standard mixture.

Results and Discussion

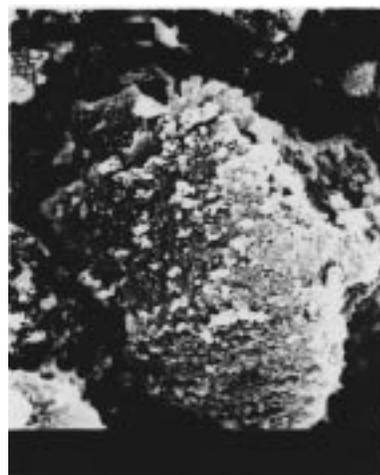
XRD. The calcined catalysts only exhibited a CuO phase, and the reduced catalysts only exhibited a metallic Cu phase. This shows that alkaline-earth oxide additives have no effect on the phase compositions of supported copper. In addition, copper oxide in the calcined samples is easily reduced to a metallic phase by flowing 10% H₂ in Ar at 300 °C. The XRD results did not show any characteristic peak of alkaline-earth oxide additives, indicating that it is too small to be detected or it is amorphous.

SEM. Scanning electron microscope images of the used catalysts are shown in Figure 1. The particle size of a MgO-modified catalyst is smaller than that of an unmodified one. Instead, the particle size of a BaO-modified catalyst is greater than that of an unmodified one. The sintering of a BaO-modified catalyst is serious, and the MgO additive can retard sintering in the reaction process.

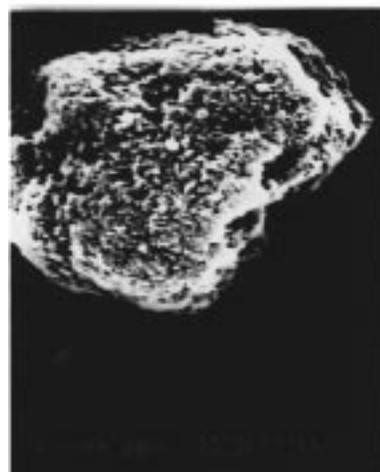
TPR. The TPR profiles for different catalysts are shown in Figure 2. The TPR of each catalyst exhibited only one peak. This peak is attributed to the reaction



The peak maximum of the Cu/SiO₂ catalyst is 265 °C, and the peak maximum of the modified ones is about 290 °C. This result indicated that the additives alleviate the reactivity of the copper oxide in the reduction process. The TPR results did not show any reduction



a



b



c

Figure 1. SEM images ($\times 20\text{K}$) of the used catalysts after reaction for 3 h: (a) Cu/SiO₂; (b) MgCu/SiO₂; (c) BaCu/SiO₂.

peak of alkaline-earth oxides, indicating that the alkaline-earth oxide additives were not reduced in the reduction process at temperatures below 800 °C.

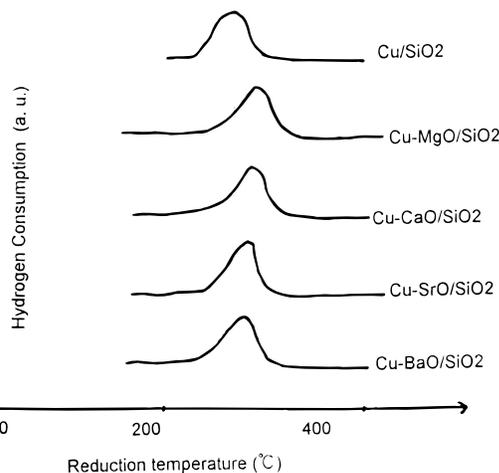


Figure 2. TPR profiles of catalysts.

Table 1. Copper Surface Areas of Catalysts^a

	Cu/ SiO ₂	Cu-MgO/ SiO ₂	Cu-CaO/ SiO ₂	Cu-SrO/ SiO ₂	Cu-BaO/ SiO ₂
S_0 (m ² /g of Cu)	51.4	48.6	47.5	49.2	47.2
$d_{Cu,0}$ (Å)	131	138	142	137	143
S_1 (m ² /g of Cu)	23.1	30.6	16.6	12.0	5.6
$d_{Cu,1}$	291	220	405	561	1201
S_1/S_0	0.45	0.63	0.35	0.24	0.15

^a S_0 : surface area of the fresh catalyst. $d_{Cu,0}$: diameter of copper metal of the fresh catalyst. S_1 : surface area of the used catalyst after reaction for 4 h. $d_{Cu,1}$: diameter of the copper metal of the used catalyst after reaction for 4 h.

Copper Surface Area. The copper surface areas of fresh (S_0) and used (S_1) catalysts determined by H₂-N₂O titration are listed in Table 1. The copper surface areas of the fresh alkaline-earth oxide-modified catalysts are slightly lower than that of an unmodified one. The lower metal area for spent than for fresh catalyst indicates that sintering occurs in the reaction process for all the catalysts. The MgO-modified catalyst has a better stability than the unmodified one; however, the addition of CaO, SrO, and BaO harmed the stability. Research in this laboratory (Tu et al., 1994a,b) has shown that the predominant decay of copper catalysts in ethanol dehydrogenation is sintering rather than coking. The average volume-surface diameter can be determined as

$$d = \frac{6 \times 10^{10}}{S\rho} (\text{Å}) \quad (3)$$

where S is the specific surface area (m²/g), and ρ is the density (g/cm³). For metallic copper, $\rho_{Cu} = 8.92 \times 10^6$ g/m³. Thus

$$d_{Cu} = 6.73 \times 10^3 / S_{Cu} (\text{Å}) \quad (4)$$

The d_{Cu} 's of catalysts are listed in Table 1.

TPD of CO₂. The TPD profiles of CO₂ on various catalysts are shown in Figure 3. The peak in the TPD profiles is considered to appear at higher temperature as the basic sites on the surface become stronger. Every catalyst has a lower temperature desorption peak (p_L) at nearly 200 °C, indicating that the "weak basic sites" exist on the catalyst surface. The CaO-, SrO-, and BaO-modified catalysts have a desorption peak at higher temperature (p_H), indicating that the "strong basic sites" are present on these catalysts. The desorption temper-

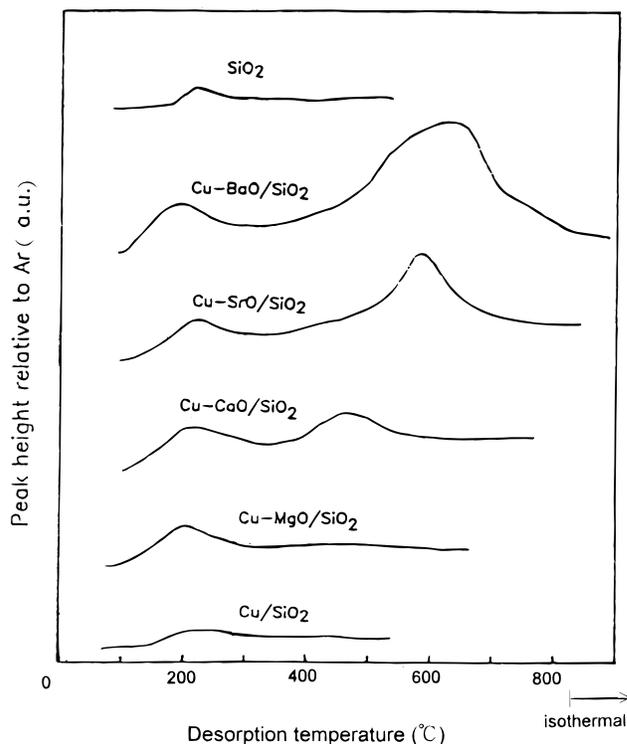


Figure 3. TPD profiles of CO₂ on catalysts.

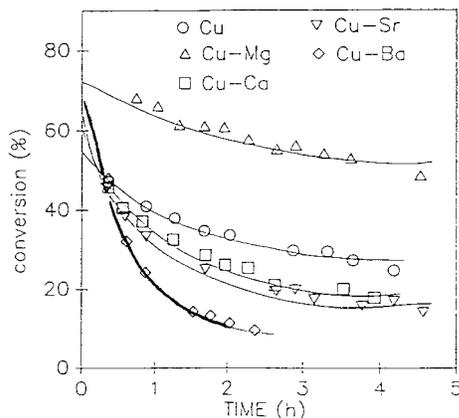
ature of p_H is in the following order: Cu-BaO/SiO₂ > Cu-SrO/SiO₂ > Cu-CaO/SiO₂. The basicity of alkaline-earth oxides can be influenced by the pretreatment procedures. Four types of active sites on alkaline-earth oxide were proposed by Hattori (1985, 1988). In this study, the CaO-, SrO-, and BaO-modified catalysts have two types of basic sites at least. The strength of basicity of the alkaline-earth oxide-modified catalyst is in the following order: Cu-BaO/SiO₂ > Cu-SrO/SiO₂ > Cu-CaO/SiO₂ > Cu-MgO/SiO₂.

It should be noted that weak basic sites appear on the Cu/SiO₂ catalyst. CO₂ adsorbed on copper only at lower temperature. Hass and Pritchard (1990) reported that CO₂ is not adsorbed on polycrystalline copper at 25 °C. If it is true, CO₂ should not adsorb on unmodified copper in this study. It has been reported that silica is a weak acid and base material (Tanabe et al., 1989), but the presence of impurities such as Na₂O and CaO may alter its behavior. The silica support was tested in this study to check its basicity. A desorption peak present at nearly 200 °C was observed as shown in Figure 3. One can conclude that the weak basic sites of the unmodified Cu/SiO₂ catalyst result from the basicity of the silica support, instead of copper metal.

The areas of p_L and p_H as shown in Figure 3, namely, A_L and A_H , can represent the amount of basic sites on the catalyst surface. The quantity of CO₂ adsorbed on catalyst is shown in Table 2. The A_L 's for silica support and Cu/SiO₂ catalyst are 20.9 and 18.4 μmol of CO₂/g, respectively. The A_L of Cu/SiO₂ catalyst roughly equals that of silica support based on the weight of silica. The A_L of alkaline-earth oxide-modified catalyst is about 3 times that of the unmodified one. Thus, the addition of alkaline-earth oxide can increase the concentration of the weak basic sites of the catalysts. The amounts of strong basic sites, i.e., A_H , of CaO-, SrO-, and BaO-modified catalysts increase with increasing the atomic number of the alkaline-earth metal.

Table 2. Amount of CO₂ Desorbed from Catalysts

	SiO ₂	Cu/SiO ₂	Cu-MgO/SiO ₂	Cu-CaO/SiO ₂	Cu-SrO/SiO ₂	Cu-BaO/SiO ₂
A _L (μmol of CO ₂ /g of catalyst)	20.9	18.4	50.0	59.9	55.1	62.0
A _H (μmol of CO ₂ /g of catalyst)	0	0	0	85.3	183.5	363.2

**Figure 4.** Dehydrogenation activities of catalysts. $T = 300\text{ }^{\circ}\text{C}$, GHSV = 90 mL/mg·h, concentration of ethanol in feed = 2.72 mmol/L.**Table 3. TOFs and Deactivation Rate Constants of Catalysts**

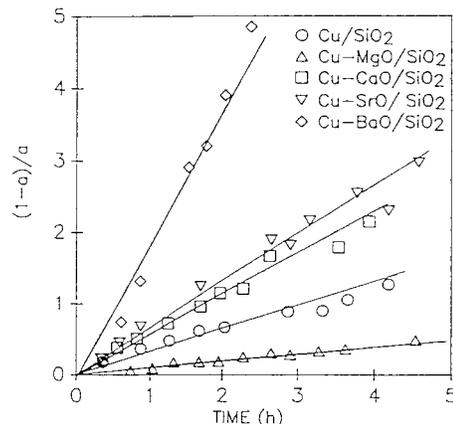
	Cu/SiO ₂	Cu-MgO/SiO ₂	Cu-CaO/SiO ₂	Cu-SrO/SiO ₂	Cu-BaO/SiO ₂
TOF ^a (s ⁻¹ site ⁻¹)	0.218	0.291	0.257	0.267	0.291
k _d (h ⁻¹) ^b	0.30	0.11	0.56	0.75	2.50

^a Calculated based on the initial activity and the metallic copper surface area of the fresh catalysts. ^b Deactivation rate constant.

Catalytic Activity. The dehydrogenation of ethanol to acetaldehyde and hydrogen is an endothermic reaction. The reaction selectivities of acetaldehyde on all catalysts were nearly 100% in this study. Thus, only the activity is discussed in this section.

The dehydrogenation activities of the catalysts are shown in Figure 4. The modified-copper catalysts display higher initial activities than the unmodified one. The turnover frequency is calculated based on the initial activity and the metallic copper surface area of the fresh catalyst. The turnover frequencies (TOFs) of the modified catalysts are higher than that of the unmodified one as exhibited in Table 3. The higher TOFs of the modified catalysts result from more of the weak basic sites on the catalysts. The MgCu/SiO₂ catalyst does not have any strong basic sites on the surface, but the TOF is not lower than that of the other modified catalysts. This indicates that the active sites of the catalysts are the weak basic sites alone or the structure promotional effects of weak basic sites on copper catalysts.

Both support and alkaline-earth oxide additive contain weak basic sites on the surface as discussed in the TPD of CO₂ section. The silica support and MO/SiO₂ catalyst (M = Mg, Ca, Sr, and Ba) in the absence of copper were tested for the dehydrogenation reaction at 300 °C. The conversions were less than 0.1% and 0.2%, respectively. The alkaline-earth oxide catalysts are active for alcohol dehydrogenation as reported by several authors (McCaffrey et al., 1972), but the activation energy (29.3 kcal/mol) is much higher than that of copper catalyst (12.8 kcal/mol) (Balandin, 1958). Therefore, the conversions on the silica-supported alkaline-earth metal oxides were low at 300 °C in this study. The results indicated that the weak basic sites play a

**Figure 5.** Test for the second-order deactivation.

role of promotion, instead of active sites. One can conclude that the high TOFs of the modified catalysts are mainly from the promotional effects of the weak basic sites on copper. The strong basic sites have no evidently promotional effect.

Catalyst Deactivation. The decay of copper catalyst in ethanol dehydrogenation is mainly caused by sintering (Tu et al., 1994a,b). Thus

$$-da/dt = k_d a^d \quad (5)$$

where a is the normalized activity, k_d is the rate constant for deactivation, and d is the order of deactivation. Integrating eq 5 yields

$$a = a_0 / (1 + a_0 k_d t), \text{ for second-order deactivation} \quad (6)$$

where a_0 is the initial normalized activity. Let $a_0 = 1$ and eq 6 becomes, on rearrangement,

$$(1 - a)/a = k_d t \quad (7)$$

Plots of $(1 - a)/a$ versus t for various catalysts are shown in Figure 5. Straight lines pass through the origin for all catalysts; thus, a second-order deactivation which is concentration-independent is applied in this study. The values of k_d for various catalysts are listed in Table 3. The MgO-modified catalyst is more stable than the unmodified one. In contrast, the CaO-, SrO-, and BaO-modified catalysts are poor in stabilities. The stability of the catalyst is in the order Cu-MgO/SiO₂ > Cu/SiO₂ > Cu-CaO/SiO₂ > Cu-SrO/SiO₂ > Cu-BaO/SiO₂.

Alkaline-earth oxides have higher melting points than copper metal (MgO = 2800 °C, CaO = 2570 °C, SrO = 2430 °C, BaO = 1923 °C, and Cu = 1083 °C). Prasad et al. (1985) reported that the better stability of Cr₂O₃-containing catalyst results from the higher melting point of Cr₂O₃ particles acting as spacers between crystallites of copper which help to prevent sintering of copper throughout the period of reaction. This can well explain the results of MgO-modified catalyst. However, this cannot explain the results of the other modified catalysts. At this stage, the authors cannot draw any

interpretation. However, the strong basic sites retard the stability of the catalyst.

Conclusions

The study of the additive effects of the alkaline-earth oxides on copper catalysts leads to the following conclusions:

1. The calcined catalysts only exhibited the CuO phase, and the reduced catalysts only exhibited the metallic copper phase. The XRD results did not show any peak of alkaline-earth oxide additives, indicating that it is too small to be detected or in the amorphous phase.

2. For TPD of CO₂, every catalyst has a low-temperature desorption peak (p_L) at around 200 °C. The p_L of Cu/SiO₂ catalyst results from the basicity of the silica support. The area of the low-temperature peak (A_L) of the alkaline-earth oxide-modified catalyst is about 3 times that of the Cu/SiO₂ catalyst. The CaO-, SrO-, and BaO-modified catalysts have a high-temperature desorption peak. The strength of the basic site of the modified catalyst is in the following order: Cu-BaO/SiO₂ > Cu-SrO/SiO₂ > Cu-CaO/SiO₂ > Cu-MgO/SiO₂.

3. The increase in TOFs of the modified catalysts is mainly due to the promotional effects of weakly basic sites on Cu metal. The strong basic sites have no promotional effect.

4. MgO-modified catalyst is more stable than the unmodified one in the dehydrogenation reaction process; however, the CaO-, SrO-, and BaO-modified catalysts are poor in stability. The strong basic sites can harm the stability of the catalyst.

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