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# Preparation and characterization of Cu/Pt/BEA catalyst for low temperature CO oxidation

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The low temperature CO oxidation over Pt-based bimetallic catalysts was investigated. Various additives such as Ni, Cu, Pd, Ag and Au were added to the Pt/BEA catalyst by an ion-exchange method and the addition of Cu to the calcined Pt/BEA catalyst was found to remarkably improve the catalytic performance. A calcination step for the Pt/BEA before Cu ion-exchange was especially important in forming the active phases for CO oxidation. XRD results indicated that the metallic Pt was not considered to be related to the active site for CO oxidation. Moreover, interactions between Pt and Cu on the Cu/Pt*/BEA catalyst could be confirmed by CO-TPD. Pt was found to be an active component for CO oxidation, but is easily deactivated by the adsorption of CO molecules. It is thought that Cu, interacting with Pt, plays an important role in preventing the deactivation of Pt.

**KEY WORDS:** CO oxidation; low temperature; Cu/Pt/BEA catalyst; calcination effect.

## 1. Introduction

Low temperature CO oxidation has attracted considerable attention due to its potential in a variety of applications such as air purification devices, closed-cycle $CO_2$ lasers, automotive emission control and proton exchange membrane (FEM) fuel cells [1]. Preferential CO oxidation in $H_2$ has also been investigated for applications in PEM fuel cells to reduce CO concentration in the fuel gases produced down to 10 ppm, preventing the poisoning of the fuel cell electrodes [2]. Catalysts containing noble metals such as Pt, Rh and Au have proved to be very effective for low temperature CO oxidation [3–7]. Their reaction mechanisms have also been extensively investigated and a high activity for CO oxidation at higher reaction temperatures (150–250 °C) can be obtained on the Pt catalysts [7–10]. However, the competitive adsorption of CO and $O_2$ at low temperatures decreases the activity of the catalysts [5]. Moreover, the Pt metal surface is easily poisoned by trace amounts of CO [11].

Binary Pt-metal catalysts are considered promising catalysts in increasing the efficiency of CO oxidation at low temperature [12]. Recently, Pt–Ru and Pt–Sn binary catalysts have been investigated and their mechanisms proposed [13–17]. However, the role of Ru and Sn has not yet been completely clarified. Ru and Sn as an additive in fuel–cell catalysts are somewhat prohibitive due to its high price and limited availability. Cheaper and more abundant additives as alternatives to Ru and Sn are, therefore, greatly desired. Recent studies have suggested that Pt–Mo may be a better catalyst for CO oxidation than Pt–Ru [18,19].

Copper may be considered an interesting additive since it is inexpensive and widely available. Until now, Cu–Pt bimetallic systems had not been considered for low temperature CO oxidation, although characterization studies have been reported [20,21]. In this work, we have investigated and characterized Cu/Pt/BEA catalysts for their performance in low temperature CO oxidation.

## 2. Experimental

### 2.1. Catalyst preparation

The beta zeolite 'BEA' ($NH_4$-beta, ECP814E-22, Si/Al = 27.0, surface area = 680 $m^2/g$, Zeolite International) was used as a support. All of the samples were obtained by an ion-exchange method. Before ion-exchange, BEA was calcined in air at 973 K for 3 h to change $NH_4$-BEA to H-BEA. Pt (or Cu) ions were then exchanged on the H/BEA zeolite from an 0.0007 M aqueous solution of $Pt(NH_3)_4Cl_2$ (or 0.01 M aqueous solution of $Cu(CH_3COO)_2 \cdot H_2O$). Ion-exchange was carried out under vigorous stirring at room temperature for 24 h. The ion-exchanged zeolite was filtered and washed in distilled water and then dried at 373 K for 24 h in an oven. Two procedures were employed in the preparation of the bimetallic catalysts. First, the secondary ions (Pt or Cu) were exchanged at this point. For the second method, calcination was carried out in $O_2$ at 773 K for 2 h before the exchange of the secondary ions. After the exchange of the secondary ions, the samples

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were filtered, washed and dried under the above conditions. The asterisk ('*') indicates the calcined metal. Ion-exchange was repeated from 1 to 3 times in order to increase the loading of Pt or Cu on the BEA surface. All of the samples were analyzed using atomic absorption (AA-6400F, Shimadzu) to determine the loading of Pt and Cu.

### 2.2. *Catalytic activity measurements*

Catalyst samples of 100 mg were loaded in the fixed bed flow reactor. Before CO oxidation, the samples were pretreated *in situ* by the following temperature program: (1) The linear temperature was increased in $O_2$ from 298 to 773 K with a heating rate of 5 K/min and then kept for 1 h at this temperature under $O_2$ flow (50 $cm^3$/min); (2) Reduction was carried out in He (50 $cm^3$/min) at 773 K for 1 h; (3) The catalysts were cooled to room temperature in He. After pretreatment, CO and $O_2$ gases were introduced into the reactor at atmospheric pressure and room temperature. The flow rate of CO was 0.25 mL/min and the feed ratio of $CO/O_2$ was 0.5. The reaction products were analyzed by gas chromatography (Shimadzu GC-7A) with a Porapak-Q packed column.

### 2.3. *X-ray diffraction (XRD)*

X-ray diffraction (XRD) was used to detect the crystalline phases in the catalysts. The XRD patterns were recorded by X-Ray Diffractometer (Shimadzu, XRD-6100) with Cu–$K_\alpha$ radiation.

### 2.4. *CO-TPD*

After pretreatment, 30 mg of the catalyst was loaded in a TPD cell which was evacuated to 0.001 Torr. The catalyst was then heated to 473 K with a heating rate of 5 K/min and then kept for 1 h to remove water. After cooling to room temperature, the unit volume of CO (apx. 3.3 Torr) was introduced into the TPD cell. The TPD cell was again evacuated to 0.001 Torr and the catalyst was heated from 298 to 923 K at the rate of 5 K/min. The desorbed components were analyzed by Quadrupole Mass Spectrometer (ANELVA, M-QA100TS).

## 3. Results and discussion

In the first stage of this work, various additives such as Ni, Cu, Pd, Ag and Au were added to the Pt/BEA catalyst. The CO conversions for the bimetallic catalysts are shown in figure 1. No effect of the additives could be observed except for Cu and Pd while conversion for the Cu/Pt/BEA catalyst was the highest. Cu was, thus, chosen as the most promising additive for Pt/BEA and variations in the preparation method were examined to enhance its performance.

The CO conversions for the Pt, Cu and their bimetallic catalysts are shown in figure 2. All of the samples were deactivated as time progressed. The conversion rate for the monometallic catalysts was very low. However, the addition of a secondary metal was found to promote the catalytic activity although the effect was not initially remarkable. The conversion rate increased remarkably for the Cu/Pt*/BEA catalyst in which Cu was ion-exchanged to the calcined Pt*/BEA in $O_2$ at 773 K for 2 h. The initial CO conversion of Cu/Pt*/BEA was 66.9% with a rapid deactivation to approximately 14.8% after 2 h. In contrast, the conversion rate for the Pt/Cu*/BEA catalyst, in which Pt was ion-exchanged to the calcined Cu*/BEA in $O_2$ at 773 K for 2 h, was lower than that of Pt/Cu/BEA.

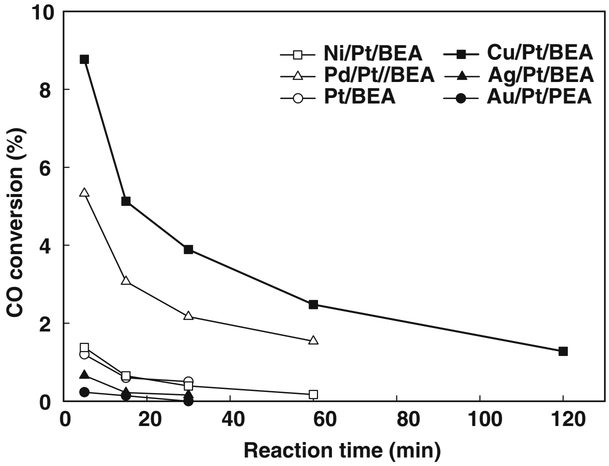

Figure 1. CO conversion for the bimetallic catalysts.

CO conversions with an increase in the Pt loading are shown in figure 3. Pt ion-exchange was repeated from 1 to 3 times in order to increase the loading of Pt on the BEA surface. As the Pt loading increased on the surface, the initial conversion also increased. However, all of the

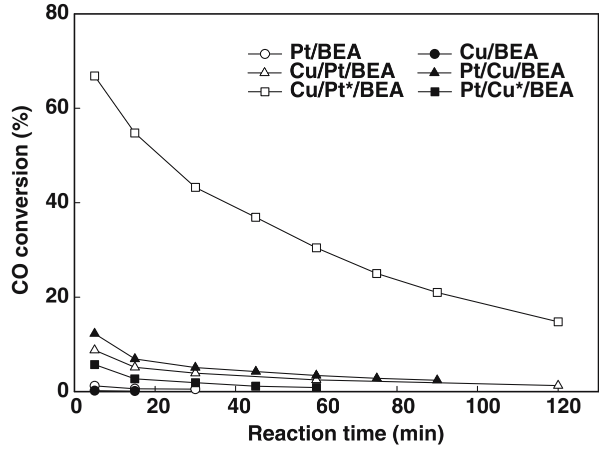

Figure 2. CO conversion for Pt, Cu and their bimetallic catalysts. The open symbols represent first the Pt and next, the Cu ion-exchanged catalysts. The black symbols represent first, the Cu and then the Pt ion-exchanged catalysts.

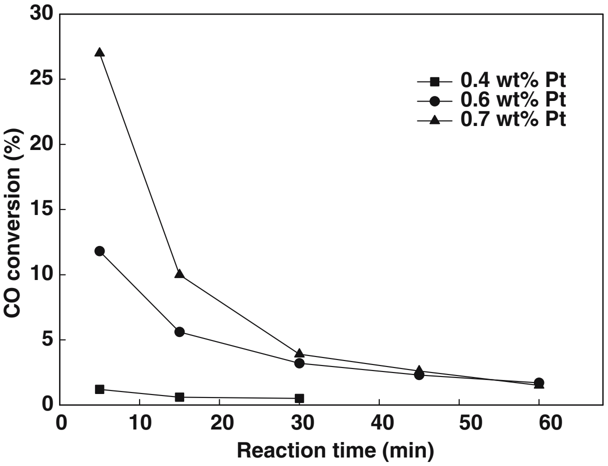

Figure 3. CO conversions with an increase in the Pt loading for the Pt/BEA catalysts.

samples became deactivated as time progressed. After 1 h, the conversions of all the samples decreased to less than 3%. Pt is considered to be the active component for CO oxidation, however, it is seen to be easily deactivated by the adsorption of CO molecules.

CO conversions with an increase in the Cu loading are shown in figure 4. Cu ion-exchange was repeated from 1 to 3 times to increase the loading of Cu on the calcined Pt*/BEA catalyst. As the Cu loading increased, the CO conversion decreased. An increase in the Pt loading promoted the CO conversion, however, an increase in the Cu loading showed the opposite results. In fact, a combination of Pt and Cu was observed to be more active than Pt or Cu alone. Cu is, therefore, considered to be a promoter, while Pt is the active component.

XRD experiments were carried out to study the evolution of the crystalline Pt phase on the BEA under calcination. The XRD patterns of Pt/BEA, Pt*/BEA, Cu/Pt/BEA and Cu/Pt*/BEA catalysts are shown in figure 5. Peaks appearing at 39.7 and 46.2°2 indicated the presence of metallic Pt while the peak at 43.5°2 represents the reflection of the BEA support. The XRD results indicated that after calcination, metallic Pt is formed and becomes more evoluted by the addition of Cu. However, metallic Pt is not considered to be related to the active site for CO oxidation due to the higher peak intensity of the Cu/Pt/BEA catalyst.

$H^+$ on the BEA catalyst was replaced by $[Pt(NH_3)_4]^{2+}$ during Pt ion-exchange [equation (1)]. The $H^+$ and $Cl^-$ ions were removed by filtration and subsequent washing. During calcination at 773 K, the Pt precursors ($[Pt(NH_3)_4]^{2+}$) were decomposed to $Pt^{2+}$ [equation (2)], and a minor fraction of $Pt^{2+}$ was reduced to the metallic Pt by the freed ammonia ligands [equations (3) or (4)] [22–25]. The presence of the reduced Pt was confirmed by XRD results while other reports have suggested that a significant amount of Pt still remains in an oxidized state [26,27]. However, reflections for the crystalline Pt oxides were absent in figure 5. The Pt oxides on the BEA may be either amorphous or too small to be detected by XRD.

$$[\mathrm{Pt(NH_3)_4}]^{2+}_{(aq)} + 2\mathrm{Cl}^-_{(aq)} + \mathrm{H^+BEA} \rightarrow \mathrm{H}^+_{(aq)} + 2\mathrm{Cl}^-_{(aq)} + [\mathrm{Pt(NH_3)_4}]^{2+}\mathrm{BEA} \quad (1)$$

$$[\mathrm{Pt(NH_3)_4}]^{2+}\mathrm{BEA} \rightarrow \mathrm{Pt^{2+}BEA} + 4\mathrm{NH_3} \quad (2)$$

$$\mathrm{Pt^{2+}} + 2\mathrm{NH_3} + \mathrm{O_2} \rightarrow \mathrm{N_2} + 2\mathrm{H_2O} + \mathrm{Pt} + 2\mathrm{H^+} \quad (3)$$

$$2\mathrm{Pt^{2+}} + 4\mathrm{NH_3} + 4\mathrm{O_2} \rightarrow 4\mathrm{NO} + 4\mathrm{H_2O} + 2\mathrm{Pt} + 4\mathrm{H^+} \quad (4)$$

The CO-TPD spectra are shown in figure 6. Before CO adsorption, all of the samples were oxidized using $O_2$ at 773 K for 1 h and reduction was then carried out in He at 773 K for 1 h. The CO-TPD spectrum for the Pt/BEA catalyst shows a wide peak between 373 and 873 K with four maxima at 423, 563, 671 and 784 K.

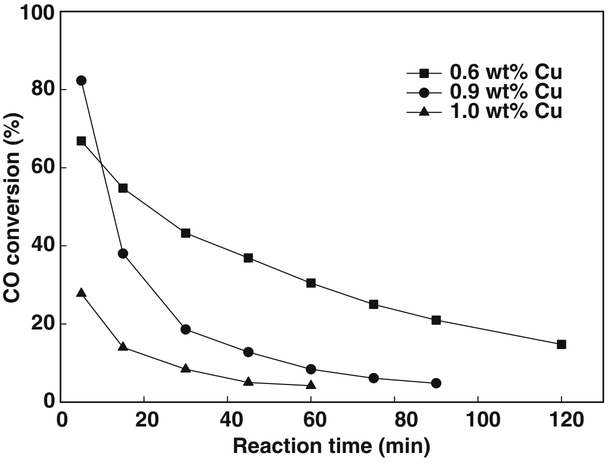

Figure 4. CO conversions with an increase in the Cu loading for the Cu/Pt*/BEA catalysts. Pt loading of all the samples was 0.4 wt%.

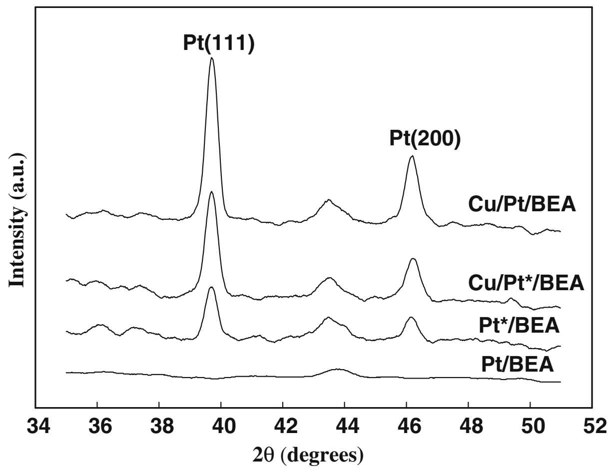

Figure 5. X-ray diffraction patterns for the catalysts.

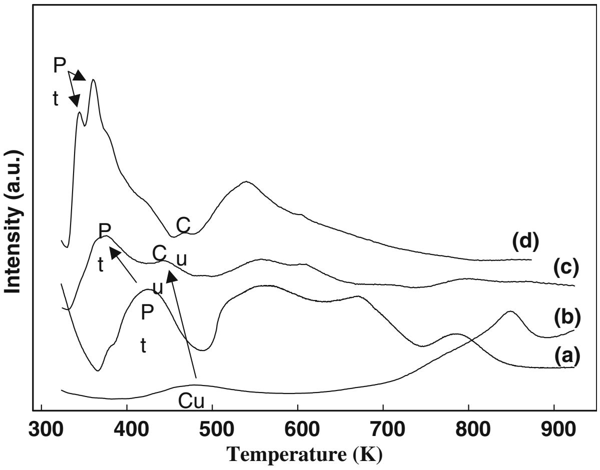

Figure 6. CO-TPD spectra for the catalysts. Before CO adsorption, the samples were oxidized using $O_2$ at 773 K for 1 h and reduction was carried out in He at 773 K for 1 h. After evacuation to 0.001 Torr, the unit volume of CO (about 3.3 Torr) was adsorbed on the catalyst at r.t. The heating rate was 5 K/min: (a) Pt/BEA (b) Cu/BEA (c) Cu/Pt*/BEA (d) Cu/Pt/BEA.

The Cu/BEA catalyst shows a small peak with its maximum at 478 K and a large peak at 849 K. The spectrum for the Cu/Pt*/BEA catalyst shows two peaks at 376 and 442 K corresponding to CO desorption from Pt and Cu, respectively. Moreover, the maxima for Cu/Pt*/BEA shifted to lower temperatures than for the Pt/BEA and Cu/BEA catalysts indicating that Pt and Cu may interact on the Cu/Pt*/BEA catalyst. The Cu/Pt/BEA catalyst shows a different spectrum than the Cu/Pt*/BEA catalyst. Two maxima corresponding to Pt were seen to shift to lower temperatures than for Pt/BEA. However, a maximum corresponding to Cu did not shift and, in fact, corresponded to the peak of the Cu/BEA catalyst. These results indicate that Pt and Cu do not interact on the Cu/Pt/BEA catalyst.

The Cu/Pt*/BEA catalyst was prepared by Cu ion-exchange on $Pt^{2+}$/BEA and Cu/Pt/BEA was prepared by Cu ion-exchange on$[Pt(NH_3)_4]^{2+}$BEA. The Pt in the Cu/Pt*/BEA catalyst may first be located on the BEA surface when the Pt/BEA catalyst was calcined while Cu may be located interacting with $Pt^{2+}$ on the BEA surface. On the other hand, the Pt in the Cu/Pt/BEA catalyst might be located at different sites than the Pt on the calcined Pt/BEA catalyst so that Cu did not interact with Pt.

## 4. Conclusions

The addition of Cu to the calcined Pt/BEA catalyst improved the catalytic performance for low temperature CO oxidation. The calcination of Pt/BEA before Cu ion-exchange was found to be an important factor in forming the active phases for CO oxidation. Moreover, Pt was found to be an active component for CO oxidation although it was easily deactivated by the adsorption of CO molecules. Our results indicate that Cu interacting with Pt may have played an important role in preventing the deactivation of Pt.

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