

(lit.,¹¹ 38-39 °C); MS (m/z); 226 (M⁺). 4,4'-Dichloroazoxybenzene: mp 155 °C (lit.,⁹ 156-157 °C); MS (m/z); 266 (M⁺). 4,4'-Dichloroazobenzene: mp 182-184 °C (lit.,⁹ 186-187 °C); MS (m/z); 250 (M⁺). 4,4'-Dimethoxyazobenzene: mp 158-160 °C (lit.,¹⁴ 160 °C); MS (m/z); 242 (M⁺). 4,4'-Dimethoxyazoxybenzene: mp 116-119 °C (lit.,¹⁴ 119-120 °C); MS (m/z); 258 (M⁺).

Acknowledgment. This paper was supported (in part) by Non Directed Research Fund, Korea Research Foundation, 1993.

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Comparative Oxidation of Carbon Monoxide over Supported Catalysts

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Received September 8, 1994

Carbon monoxide becomes one of the hazardous pollutants in air, which is produced during high temperature combustion in industrial boilers and motor vehicles.

The most popular method for CO removal or lowering its concentration is the catalytic oxidation to CO₂. The activity of transition metal oxides and noble metals for CO oxidation has been described in numerous literatures.¹⁻³ Typical catalysts used for this purpose contain noble metals such as Pd, Pt, or Rh dispersed on various oxides. Although transition metals alone show insufficient activity for low temperature CO oxidation, catalysts with mixed bimetallic composition (transition metal+noble metal) have higher activity than noble metals alone. There are several factors affecting the catalytic activity such as composition of metals, types of supports, pretreatment of catalysts and methods for metal loading.

In this work the influence of metal loadings as well as the metallic compositions on the activity of the catalysts has been investigated.

Experimental

γ -Al₂O₃ (Janssen, 50-200 μ , 210 m²/g) and HZSM-5 (PQ Co., 430 m²/g) were purchased commercially.

Typical procedures for the preparation of metal-containing catalysts are as follows.

Impregnation. In order to prepare γ -Al₂O₃ supported catalysts containing 4.0 wt% Cu, simply expressed as 4.0% Cu/ γ -Al₂O₃ hereinafter, 1.52 g of Cu(NO₃)₂·3H₂O was dissolved in 100 mL distilled water, to which 9.6 g of γ -Al₂O₃ was added. The mixture was stirred at 60-70 °C for 8-10 h until the water is completely evaporated. The resulting product was dried at 100 °C overnight.

Ion-exchange+impregnation. In order to prepare ZSM-5 supported catalysts containing 2.0 wt% Cu, simply being termed hereinafter as 2.0% Cu/ZSM-5i, 0.76 g of Cu(NO₃)₂·3H₂O was dissolved in 250 mL H₂O into which 9.8 g of ZSM-5 was dispersed. The resulting suspension was stirred for 50 h at 30-40 °C. After 50 h, temperature was increased to 50-60 °C and complete removal of water was attempted. Finally the residue was dried at 100 °C overnight.

For the preparation of bimetal-containing zeolite catalysts such as Pt-Cu/ZSM-5i and Pt-Co/ZSM-5i, Pt was introduced into HZSM-5 first by ion-exchange, which was calcined in air at 520 °C for 3 h. Pt-ZSM-5 was then impregnated with aqueous solution of copper and cobalt nitrate, respectively. The zeolite-supported catalysts were dried at 100 °C over-

night.

Solid state reaction. $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and ZSM-5 were used to prepare a catalyst, simply being expressed as 1.0% Pt-2.0% Co/ZSM-5s: 0.0733 g of $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ and 0.444 g of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ were first ground to a fine powder, which were then mixed with 1.0 g of ZSM-5 in a mortar and pestle for about 20 min. Then the powder mixture was pressed in a steel die to make a tablet. The shaped catalyst was placed in an alumina boat and heated in a muffle furnace at 570 °C in air for 6 h.

All the resulting samples were pretreated before catalytic activity test. (1) calcination in air at 520 °C for 3 h was performed at a heating rate of 2 °C/min, except for the solid-state ion-exchanged product and (2) reduction in H_2 at 540 °C for 3 h was carried out at a heating rate of 3 °C/min and at a flow rate of 40 cc/min.

Measurements

The catalytic activity was measured under an atmospheric pressure, employing an apparatus consisting of a flow reactor on-line connected to gas chromatograph (Hitachi 063) having thermal conductivity detector (TCD) *via* six-loop-valve. The fixed-bed flow reactor was made of pyrex tubings of 20 mm inner diameter externally heated. 0.5 g of each catalyst was placed in a sintered glass disc inside the reactor. A thermocouple was inserted into the center of the disc for the temperature measurement. The gas mixture was made up with 4.0% CO, 20% O_2 and 76% N_2 . The total flow rate of the reactant mixture was adjusted to be 40 cc/min. A chromatographic column containing molecular sieve 13X with dimension of 3.1 mm o.d. \times 1.5 m long was used to analyze the sample gases at 25 °C. The catalytic activity was expressed in terms of % conversion as derived from CO chromatographic responses of reactor input and output samples. Chromatographic data were recorded by Spectra-Physics 4290 integrator.

Results and Discussion

The XRD patterns of all metal-containing supports such as $\gamma\text{-Al}_2\text{O}_3$ and ZSM-5 were identical to those of parent supports, indicating that metal/supports have the same structure as supports and no metal oxide pattern was detected probably due to the low metal loadings provided.

The BET surface areas (measured 410 m^2/g) of ZSM-5 loaded with metal ions from ion-exchange + impregnation were almost identical to those of metal/ZSM-5 from solid-state reaction method within $\pm 4\%$.

CO oxidation can be expressed in a simple equation, $\text{CO} + 1/2 \text{O}_2 = \text{CO}_2$, but is still an intriguing subject of disputation.

Figure 1 shows CO conversion as a function of temperature over $\gamma\text{-Al}_2\text{O}_3$ supported catalysts containing equal amount of different transition metals (Co, Cu, Cr). Catalytic activity of transition metals dispersed on the $\gamma\text{-Al}_2\text{O}_3$ decreases in the following sequences: $\text{Co} > \text{Cu} > \text{Cr}$. The activities of the Co and Cu containing catalysts for CO oxidation were similar, while the Cr loaded catalyst is much less active. With 4.0% Co/ $\gamma\text{-Al}_2\text{O}_3$ and 4.0% Cu/ $\gamma\text{-Al}_2\text{O}_3$, 100% conversion of CO was achieved at 200 °C and 215 °C, respectively. For 4.0% Cr/ $\gamma\text{-Al}_2\text{O}_3$ complete conversion was observed only be-

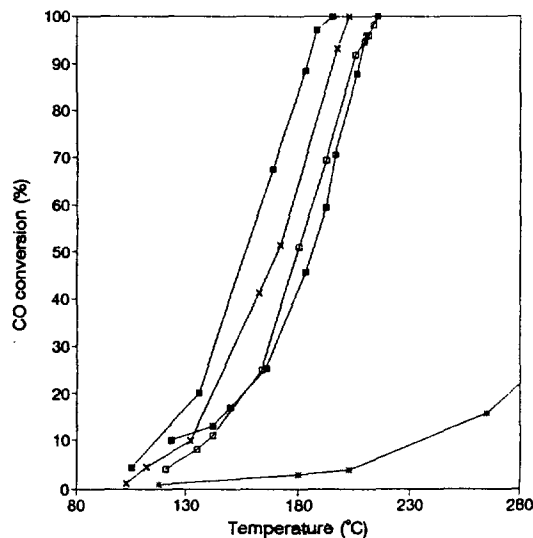


Figure 1. Comparison of CO conversion of Co, Cu and Cr loaded $\gamma\text{-Al}_2\text{O}_3$ and ZSM-5 as a function of temperature. (■) 4.0% Co/ $\gamma\text{-Al}_2\text{O}_3$, (□) 4.0% Cu/ $\gamma\text{-Al}_2\text{O}_3$, (*) 4.0% Cr/ $\gamma\text{-Al}_2\text{O}_3$, (⊗) 2.0% Cu/ZSM-5i, (×) 2.0% Co/ZSM-5i.

yond 400 °C. Moreover for both Co and Cu containing catalysts the reaction of CO oxidation started at 95-100 °C, while 4.0% Cr/ $\gamma\text{-Al}_2\text{O}_3$ started only at 190-200 °C. The catalytic activity of Cu containing samples increased appreciably with increasing loadings within the narrow region between 4.0 to 6.0 wt%. The higher activity for 6.0% Cu/ $\gamma\text{-Al}_2\text{O}_3$ is probably due to the increased number of active Cu species on the supported surface than those of 4.0% Cu/ $\gamma\text{-Al}_2\text{O}_3$. Different concentration of Cu can be related to the numbers of active centers and the different Cu structures formed on the surface during pretreatment and reaction process.^{4,5} Usually at higher metal loadings the nature of active species on catalyst surface is complicated and remains as the subject of further elucidation.⁶⁻⁸ At lower metal loadings (<5.0% Cu/ $\gamma\text{-Al}_2\text{O}_3$), for example, 'surface spinel' such as CuAl_2O_4 is known as an active species, while at higher metal loadings, CuO also contributes to the activity of catalysts.^{4,9} In this study the catalytic activity of CO oxidation has been compared with lower metal loadings on supports.

The higher activities of Co and Cu loadings are probably due to their higher (easier) reducibility. The reducibility of transition metals is important for their catalytic behavior in oxidation reaction.¹⁰⁻¹²

Under the reduction condition, the large number of oxygen vacancies can be created on the surface of transition metal oxides. The nature and local structure of the oxygen vacancies in the catalytic systems containing transition metals are important, since the process of their formation is closely related to the electronic state change of the transition metal cations during pre-reduction and subsequent reaction stages. Oxygen vacancies can be the active centers created by the absorption of gaseous oxygen, which is an active reactant in the CO oxidation. The adsorption of gaseous oxygen is an important step for CO oxidation, since the mechanism of CO oxidation over transition metal oxides may involve the adsorption of CO and O_2 with subsequent reaction of the adsorbed species. Thus, the pretreatment conditions are

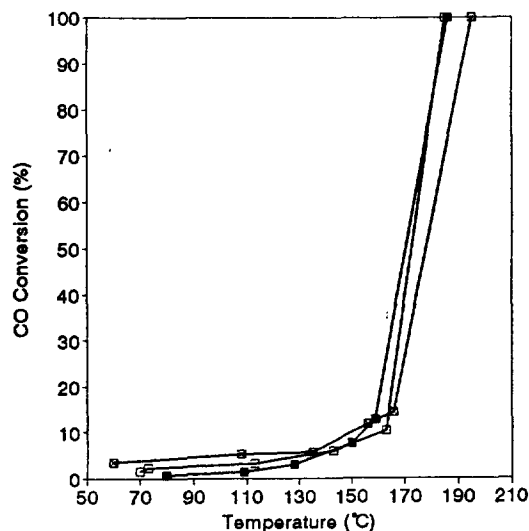


Figure 2. Influence of CO conversion over 1.0% Pt/ZSM-5s with variation of $\text{SiO}_2/\text{Al}_2\text{O}_3=30$ (■), 50 (□), and 80 (⊗), respectively.

Table 1. Comparative catalytic activity of catalysts with various promoters and supports for CO oxidation on $\gamma\text{-Al}_2\text{O}_3$ and ZSM-5

No	Catalysts	T_{conv}^{100} (°C) ^a	Preparation ^b	Ref.
1	4.0 Cu/ $\gamma\text{-Al}_2\text{O}_3$	215	imp	d
2	4.0 Co/ $\gamma\text{-Al}_2\text{O}_3$	200	∕	d
3	4.0 Cr/ $\gamma\text{-Al}_2\text{O}_3$	415	∕	d
4	6.0 Cu/ $\gamma\text{-Al}_2\text{O}_3$	195	∕	d
5	1.0 Cu/ $\gamma\text{-Al}_2\text{O}_3$	~235	∕	e
6	HZSM-5	395	syn	d
7	2.0 Cu/ZSM-5	215	i	d
8	2.0 Co/ZSM-5	200	∕	d
9	1.5 Ga/ZSM-5	280	∕	d
10	1.0 Mo/ZSM-5	305	∕	d
11	2.0 Fe/ZSM-5	290	∕	d
12	1.0 Pt/ZSM-5	180	∕	d
13	1.0 Pt/ $\gamma\text{-Al}_2\text{O}_3$	~160	imp	e
14	1.0 Pt-2.0 Co/ZSM-5	180	i	d
15	1.0 Pt-2.0 Cu/ZSM-5	190	∕	d
16	0.25 Pt-0.75 Cu/ $\gamma\text{-Al}_2\text{O}_3$	~170	coimp	e
17	2.0 Co-2.0 Cu/ZSM-5	200	i	d
18	1.0 Pt-2.0 Co/ZSM-5	140	s	d
19	1.0 Pt-2.0 Cu/ZSM-5	190	∕	d
20	3.75 Pt/95Al ₂ O ₃ -5SiO ₂	215 ^c	imp	f

^aTemperature of 100% CO conversion. ^bimp means impregnation, syn means synthesized, i means ion-exchange followed by impregnation, coimp means co-impregnation, and s means loading of transition metals by a solid-state reaction at high temperature. ^cTemperature of 50% CO conversion. ^dThis work. ^eref. 16. ^fref. 19.

very important for transition-metal-containing catalysts to form the active catalytic surface.

Both metal loading and pretreatment conditions are important factors to form the most effective catalysts.^{13,14}

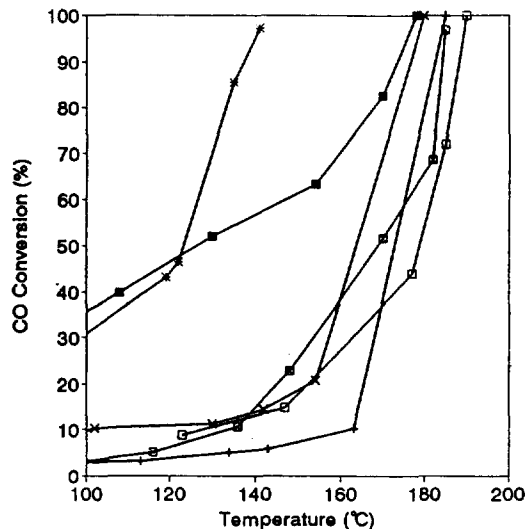


Figure 3. Comparison of CO oxidation activities for mono- (1.0% Pt) and bi-metallic (1.0% Pt+2.0% Cu and 1.0% Pt+2.0% Co) loaded ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3=30$) with two different preparative methods, ion-exchange followed by impregnation, and high temperature solid-state reaction. (■) 1.0% Pt-2.0% Co/ZSM-5i, (*) 1.0% Pt-2.0% Co/ZSM-5s, (□) 1.0% Pt-2.0% Cu/ZSM-5i, (⊗) 1.0% Pt-2.0% Cu/ZSM-5s, (X) 1.0% Pt/ZSM-5i, (+) 1.0% Pt/ZSM-5s.

Figures 1, 2 and Table 1 demonstrate the comparative catalytic activities of various metal-containing ZSM-5 for CO oxidation.

It is expected that the transition metal ions may well be stabilized in zeolite structure, being more active for CO oxidation in comparison with the same cations dispersed on the Al_2O_3 surface. Because zeolites such as mordenite, Y, ZSM-5 are prospective supports due to their well defined cation exchanged sites, higher internal surface area, high thermal stability and relatively low contents of Al in zeolite lattice. It is also known that Al_2O_3 is improper support material for practical use, since SO_x in the exhaust gas can react with Al_2O_3 to form aluminum sulfate, which causes a deactivation of catalytic properties.

In Figure 1, relative CO oxidation activities have been compared for 4.0% Co-, 4.0% Cu- and 4.0% Cr-impregnated $\gamma\text{-Al}_2\text{O}_3$, and 2.0% Cu/ZSM-5 and 2.0% Co/ZSM-5. It seems that the activity does not seriously depend on the supports, but on the type and the amount of transition metals.

Figure 2 shows the relative CO conversions for 1.0% Pt/ZSM-5s with the ratios of $\text{SiO}_2/\text{Al}_2\text{O}_3=30, 50,$ and 80, respectively. While all the CO oxidation activities appear to be similar in the range of 20-160 °C, 1.0% Pt/ZSM-5s with $\text{SiO}_2/\text{Al}_2\text{O}_3=30$ and 50 shows a slightly higher activity than that with $\text{SiO}_2/\text{Al}_2\text{O}_3=80$ beyond 160 °C. The smaller ratio of $\text{SiO}_2/\text{Al}_2\text{O}_3$, the higher numbers of H^+ in ZSM-5 framework, generating cation-exchangeable site available. The protonic sites can be exchanged by active cations and play an important role in determining the surface activity. Hence in this work ZSM-5 only with $\text{SiO}_2/\text{Al}_2\text{O}_3=30$ was used.

Figure 3 shows brief answers to the following questions, (i) when Cu and Co are loaded respectively with Pt on ZSM-5, is there any effect on the catalytic activity? (ii) when

the metal loadings are carried out with different methods, is there any difference in the activity ?

Obviously the catalyst of 1.0% Pt-2.0% Co/ZSM-5 shows higher activity in higher CO conversion than that of 1.0% Pt-2.0% Cu/ZSM-5 and 1.0% Pt/ZSM-5. With 1.0% Pt-2.0% Co/ZSM-5i, 100% CO oxidation was obtained at 180 °C, while for 1.0% Pt/ZSM-5i and 1.0% Pt-2.0% Cu/ZSM-5i complete conversion was observed at 180 °C and 190 °C, respectively.

It is interesting to note that the activity depends on the loading method of metals into supports. High temperature solid-state reaction is an alternative mean of transition metal ion introduced into zeolites or molecular sieves.¹⁵ The catalyst of 1.0% Pt-2.0% Co/ZSM-5s shows much higher activity than 1.0% Pt/ZSM-5i&s by 20-25, 30-35 and 90% at 100, 120, and 140 °C, respectively. On the other hand the activity of 1.0% Pt-2.0% Cu/ZSM-5s catalyst shows higher than 1.0% Pt-2.0% Cu/ZSM-5i by about 10% beyond 140 °C. However the activity of 1.0% Pt/ZSM-5s is lower than 1.0% Pt/ZSM-5i. There is no evidence that 1.0% Pt-2.0% Cu/ZSM-5 reveals higher activity than 1.0% Pt/ZSM-5.

Liao *et al.*¹⁶ also has reported that there was no improvement of catalytic activity on CO oxidation for Pt-Cu/ γ -Al₂O₃, where Pt and Cu were loaded by co-impregnation of γ -Al₂O₃ with salt solutions of Pt and Cu.

The relative catalytic activity of various catalysts for CO oxidation is summarized and compared in Table 1. Pure HZSM-5 without promoters shows very low activity for CO oxidation. Other promoters such as Ga, Mo, Fe and Cu+Co do not show higher activities than Co, Cu and Pt.

In order to understand the behavior of bimetallic catalysts, Pt-Co/ZSM-5 with different metallic concentrations have been investigated by X-ray diffraction. However ZSM-5 supported catalysts could not be examined due to the interference between the metal and the support.

Dees and Ponec¹⁷ observed partial alloy formation of Pt/Co on silica-supported catalysts with XRD evidence. This alloy formation seems to improve the CO oxidation performance than any other active metals studied in this work.

There is only a few reports on the CO oxidation with Pt-Cu and Pt-Co dispersed on the support.^{16,18} Similar work is currently under study by the authors.

Generally it's desirable for catalysts to maintain high activity without significant decay in performance. In order to measure water vapor effect, water vapor was supplied *via* by-pass route to feed gases as necessary, prior to their reach of the reactor. From our limited study for CO oxidation, Pt-Co catalyst showed higher activity than others. For 1.0% Pt-2.0% Co/ZSM-5, it was observed that CO oxidation activity in the presence of water vapor were almost identical to that in the absence of water vapor within $\pm 6\%$, while 100% conversion temperature was the same each other, and the overall activity was retained at least 300 min even in the presence of water vapor.

Conclusively the catalyst of 1.0% Pt-2.0% Co/ZSM-5s is the most active catalyst for CO oxidation examined thus far in this work. The selection of the most active transition metals as well as the addition of the noble metals are efficient in improving the active catalytic activity for CO oxidation. It is also found that for the loading of metal ions high temperature solid-state reaction method is more effective than

the ion-exchange followed by impregnation method.

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Monoalkylation of Calix[4]arene

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Received October 20, 1994

Selective functionalization of calixarene has greatly widened the use of calixarenes in Host-Guest chemistry. Several synthetic procedures have been reported that alkylated the calix[4]arene selectively such as the 1,3-dialkylation,^{1,2} 1,2-dialkylation,³ and trialkylation⁴ at the lower rim of calix[4]arene. Utilizing the selective functionalization at the lower rim of calix[4]arene, the monoalkylated calix[4]arenes