

LOW TEMPERATURE OXIDATION OF CO OVER SUPPORTED PdCl₂-CuCl₂ CATALYSTS

Dong Jun Koh, Jae Hwal Song, Sung-Won Ham*, In-Sik Nam[†],
Rae-Woong Chang, Eun Duck Park, Jae Sung Lee and Young Gul Kim

Environmental Catalysis Research Team, Research Institute of Industrial Science & Technology (RIST)/
Department of Chemical Engineering, School of Environmental Engineering,
Pohang University of Science and Technology (POSTECH), San 32 Hyoja Dong, Pohang 790-330, Korea
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Abstract – PdCl₂-CuCl₂ catalyst supported on activated carbon was examined for the low temperature oxidation of CO. The catalyst developed in the present study was active and stable at ambient conditions if water were existing in the feed gas stream. The addition of Cu(NO₃)₂ into the PdCl₂-CuCl₂ catalyst significantly enhanced the CO oxidation activity. X-ray diffraction study revealed that the role of Cu(NO₃)₂ was to stabilize active Cu(II) species, Cu₂Cl(OH)₃, on the catalyst surface which maintains the redox property of palladium. When HCl and SO₂ were also existing in the feed, they easily inactivated the catalyst. It was found that HCl and SO₂ inhibited the formation of active Cu(II) species on the catalyst surface.

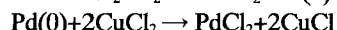
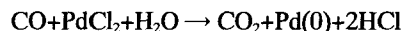
Key words: Carbon Monoxide Oxidation, Low Temperature Oxidation, Supported PdCl₂-CuCl₂, Wacker-type Catalysts

INTRODUCTION

CO emitted from high temperature heating apparatus such as utility and industrial boilers and transportation vehicles as well as NO_x and SO_x as an air pollutant. From the economic view point, the catalytic oxidation of CO is regarded as the most attractive method to remove CO, unless CO₂ is not regarded as a cause of the global warming of the earth. Supported noble metal catalysts [Yao, 1984; Oh and Eickel, 1991; Imamura et al., 1995] often require reaction temperature higher than 200 °C. Metal oxide catalysts such as hopcalite [Brittan et al., 1970] and SnO₂-CuO [Fuller and Warwick, 1973] need much lower temperatures than 200 °C, but they are easily poisoned by water vapor contained in the flue gas. Recently, several new catalytic systems such as Au/metal oxide [Tanielyan and Augustine, 1992; Haruta et al., 1993] and Pt/SnO₂ [Boulahouache et al., 1992] have been reported to be highly effective for low temperature CO oxidation even in the presence of water.

The supported Wacker catalyst, in which an aqueous solution of PdCl₂-CuCl₂ is loaded onto the pores of the high surface area supports, is known to accelerate the oxidation of CO at low reaction temperature [Lloyd and Rowe, 1974; Kim et al., 1994; Lee et al., 1995; Desai et al., 1983]. The catalyst exhibits high CO conversion at near room temperature and is stable even in the presence of water in the feed. The overall chemistry of CO oxidation in this catalytic system is similar to that of the Wacker process as follows [Desai et al., 1983;

Lloyd and Rowe, 1971]:



Initially, PdCl₂ is reduced to Pd(0) by CO, and then Pd(0) is reoxidized to PdCl₂ by CuCl₂. CuCl formed during the oxidation procedure is reoxidized to CuCl₂ by molecular O₂ also included in the feed gas stream. The presence of water is essential for the chemistry of this reaction as shown above.

In the supported PdCl₂-CuCl₂ catalyst system, the characteristic of the supports is also a critical parameter for its catalytic performance. Alumina and carbon supports were both effective and the silica support was totally inactive for this reaction system [Kim et al., 1994]. Choi and Vannice [1991] investigated the mechanism of CO oxidation by the kinetic and IR studies. They suggested that the active species on the catalyst surface were PdClCO, CuClCO and possibly Pd-Cu complex. From the X-ray absorption fine structure (XAFS) study, Lee et al. [1996] observed that the active phase of palladium was Pd(II) species containing Cl and carbonyl ligands. Any direct interaction of Pd-Pd or Pd-Cu was not observed on the catalyst surface. The active phase of copper, however, was suggested to be solid Cu₂Cl(OH)₃ particles.

In this work, CO oxidation over the activated carbon supported PdCl₂-CuCl₂ catalytic system has been extensively examined at ambient conditions. The role of Cu(NO₃)₂ as a promoter and the effect of reaction conditions were also investigated.

EXPERIMENTAL

1. Catalyst Preparation

The catalyst was prepared by using the incipient wetness

[†]To whom all correspondence should be addressed.

E-mail: isnam@vision.postech.ac.kr

*Present Address: Chemical Engineering Department, Kyung-il University

method to impregnate palladium and copper on activated carbon support. The support (Aldrich, 100 mesh) was dried at 200 °C for 3 hr in atmospheric condition before impregnation. The metal precursors were PdCl_2 (Aldrich), $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (Aldrich) and $\text{Cu}(\text{NO}_3)_2$ (Aldrich). A typical composition was 1.7 wt% Pd and mole ratio of Cu/Pd was 5.5. After impregnation, the catalyst was dried in ambient condition for a day.

2. Reaction Condition

The catalytic oxidation of CO was examined in a fixed-bed flow reactor system under atmospheric pressure. The reactor was a 3/8-inch Pyrex tube with the sintered glass disc to hold the catalyst in the reactor. Reaction temperature was controlled by the thermocouple inserted into the center of the catalyst bed. Feed gas of 1.0% CO in air was supplied through mass flow controller into the reactor. The CO/air stream was saturated with water through an H_2O vapor saturator enclosed in a constant temperature bath and fed to the reactor. The constant reaction temperature throughout the reactor was achieved by the cooling and/or heating bath with a temperature controller. Reactants and products were analyzed by an on-line gas chromatograph (HP 5890A) and CO infrared analyzer (Model 48H, Thermo Environmental Instruments Inc.).

RESULTS AND DISCUSSION

1. Effect of Water

The activated carbon-supported $\text{PdCl}_2\text{-CuCl}_2$ catalyst was active and stable in the CO oxidation at low temperature if water were supplied into the feed gas stream, as shown in Fig. 1. However, when the water feed was terminated, CO conversion was rapidly decreased to near zero. It reveals that the catalytic activity of CO oxidation is reversible depending upon the existence of water in the feed.

Fig. 2 also shows the change of CO oxidation activity over the water contents in the feed gas stream. The $\text{PdCl}_2\text{-CuCl}_2$ catalyst supported on activated carbon exhibited a stable CO oxidation activity regardless of the water contents un-

like the alumina-supported catalyst [Kim et al., 1994] which showed maximum activity at a certain content of water in the feed gas stream. The distinction is primarily due to the different surface properties of the two supports with respect to water. Alumina is a hydrophilic support but carbon is a hydrophobic one. Hence, the decrease in the activity of the alumina-supported catalyst at high water contents is mainly attributed to the capillary condensation of water in the catalyst pores [Kim et al., 1994; Desai et al., 1983; Yaparpalvi and Chuang, 1991]. Water-filled pores cause the decreased gas-liquid interfacial surface area of the support. It leads to the decrease of the CO oxidation activity. However, the capillary condensation in the carbon support is not significant because of its hydrophobicity.

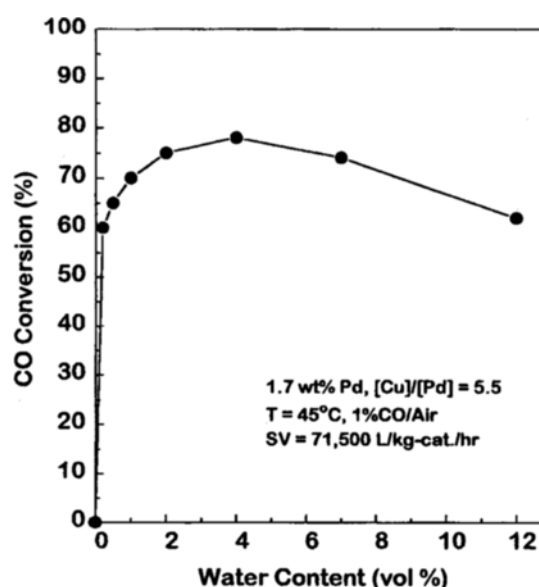


Fig. 2. Effect of water contents on CO conversion over $\text{PdCl}_2\text{-CuCl}_2$ /activated carbon catalyst.

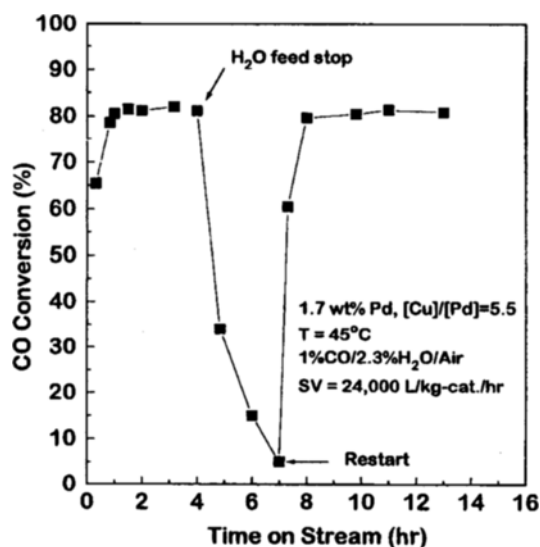


Fig. 1. Effect of water on CO conversion over $\text{PdCl}_2\text{-CuCl}_2$ /activated carbon catalyst.

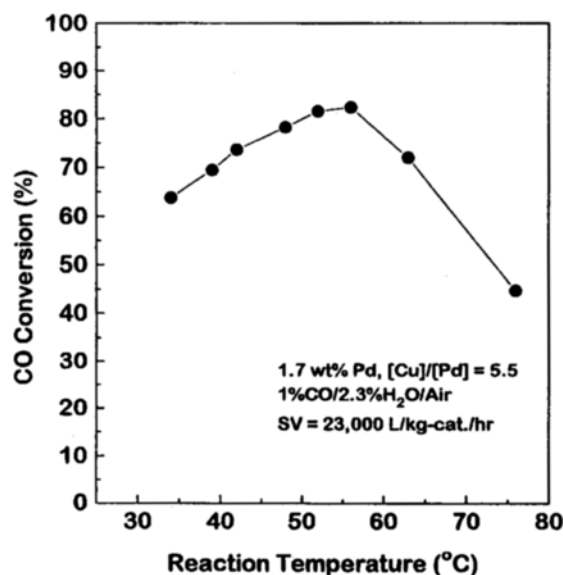


Fig. 3. Temperature dependence of the $\text{PdCl}_2\text{-CuCl}_2$ /activated carbon catalyst on CO conversion.

The effect of the reaction temperature on the activity is shown in Fig. 3. When the reaction temperature increased, the activity increased and showed a maximum at around 55 °C. When the temperature was further increased, the activity gradually decreased. The activity increase below 55 °C is due to the increase of reaction rate by the temperature increase. The decrease in the activity at higher reaction temperature seems to be due to the alteration of the adsorption behavior of water on the carbon support. The presence of water in this catalytic system is essential for the maintenance of the activity. The lower coverages of water on the catalyst surface at higher temperature might be the cause of the decrease of the CO oxidation activity. Furthermore, the decrease in the solubility of reactants at high temperature may also decrease the activity. Therefore, the unusual activity decrease is believed to be the result of the fact that the alteration of the adsorption of water and CO on the catalyst surface might be dominant to the usual kinetic acceleration of the reaction rate at high temperatures.

2. Role of $\text{Cu}(\text{NO}_3)_2$ as a Promoter

Fig. 4 shows the role of the various additives onto the $\text{PdCl}_2\text{-CuCl}_2$ catalyst for CO oxidation activity. $\text{Cu}(\text{NO}_3)_2$ might be one of the best choices among the additives examined in the present study.

In the $\text{PdCl}_2\text{-CuCl}_2$ catalytic system, the role of $\text{Cu}(\text{NO}_3)_2$ as a promoter is not clear yet. Lloyd and Rowe [1974] claimed that the role of $\text{Cu}(\text{NO}_3)_2$ was simply a promoter to the catalyst system. Desai et al. [1983], however, could not observe any promotional effect of $\text{Cu}(\text{NO}_3)_2$ in the $\text{PdCl}_2\text{-CuCl}_2/\text{Al}_2\text{O}_3$ catalyst. It is probably due to the prechlorination of the catalyst before the reaction. Fig. 5 shows the effect of the addition of $\text{Cu}(\text{NO}_3)_2$ to the catalyst on the activity with its contents. CO oxidation activity of the $\text{PdCl}_2\text{-Cu}(\text{NO}_3)_2$ catalyst was lower than that of the $\text{PdCl}_2\text{-CuCl}_2$ catalyst. However, when $\text{Cu}(\text{NO}_3)_2$ was added to the $\text{PdCl}_2\text{-CuCl}_2$ catalyst, the activity significantly increased.

From the studies of X-ray diffraction (XRD) and X-ray

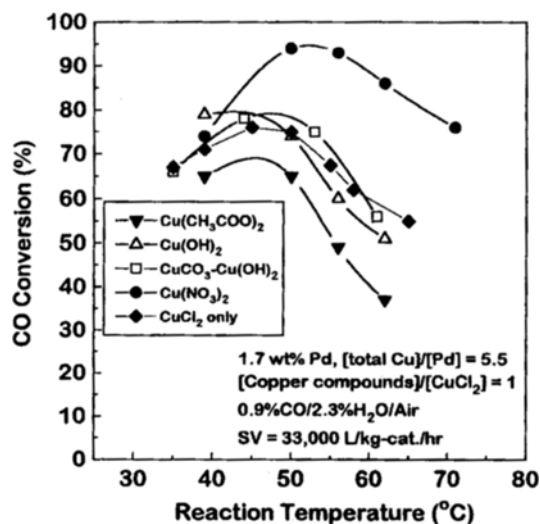


Fig. 4. Effect of the additives on the CO conversion over $\text{PdCl}_2\text{-CuCl}_2$ /activated carbon catalysts.

absorption fine structure (XAFS), Kim et al. [1994] and Lee et al. [1996] reported that the active phase of copper was solid $\text{Cu}_2\text{Cl}(\text{OH})_3$ particles, formed by an interaction between CuCl_2 and the surface of the support. The existence of $\text{Cu}_2\text{Cl}(\text{OH})_3$ on the catalyst surface was also observed by XRD in the present study. Fig. 6 shows XRD patterns of supported $\text{PdCl}_2\text{-CuCl}_2$ and $\text{PdCl}_2\text{-CuCl}_2\text{-Cu}(\text{NO}_3)_2$ catalysts before and after reaction. In XRD patterns, fresh catalysts exhibited peaks due to only $\text{Cu}_2\text{Cl}(\text{OH})_3$. The peaks of $\text{CuCl}_2\cdot 2\text{H}_2\text{O}$ and $\text{Cu}(\text{NO}_3)_2$, the initial forms of copper salts employed in the preparation of the catalyst, were not observed even in the fresh

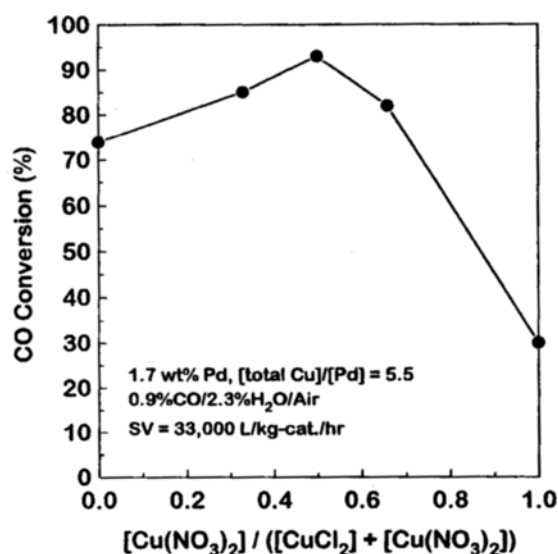


Fig. 5. Effect of the contents of $\text{Cu}(\text{NO}_3)_2$ over $\text{PdCl}_2\text{-CuCl}_2$ /activated carbon catalyst on CO conversion.

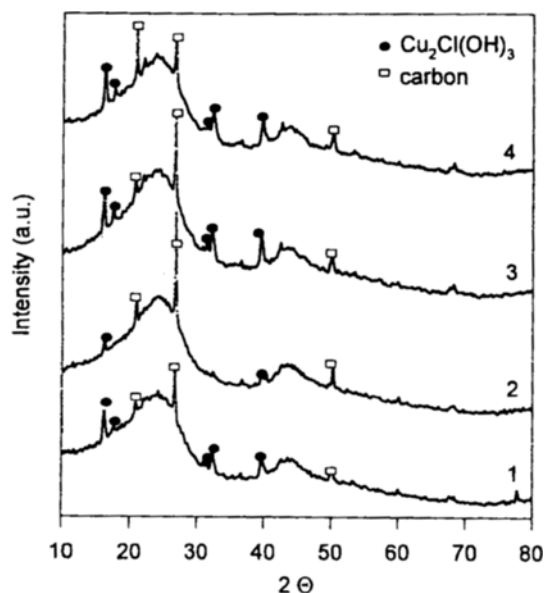


Fig. 6. X-ray diffraction patterns of the activated carbon supported Wacker-type catalysts.

(1) $\text{PdCl}_2\text{-CuCl}_2$ /activated carbon before reaction, (2) $\text{PdCl}_2\text{-CuCl}_2$ /activated carbon after reaction at 40 °C, (3) $\text{PdCl}_2\text{-CuCl}_2\text{-Cu}(\text{NO}_3)_2$ /activated carbon before reaction, (4) $\text{PdCl}_2\text{-CuCl}_2\text{-Cu}(\text{NO}_3)_2$ /activated carbon after reaction at 40 °C.

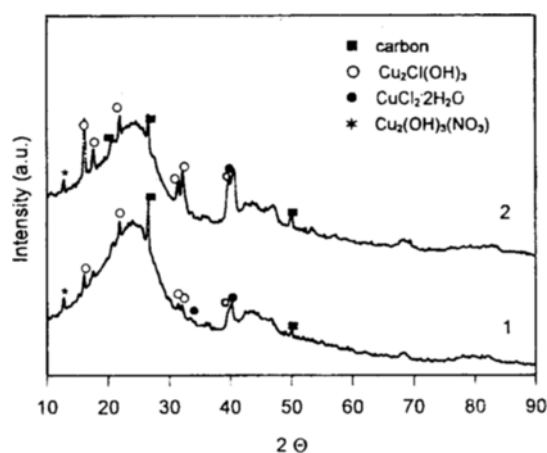


Fig. 7. X-ray diffraction patterns of the PdCl₂-Cu(NO₃)₂/activated carbon catalyst.

(1) before reaction, (2) after reaction at 40 °C.

catalyst before the reaction. After impregnation, the catalyst was simply dried in the ambient condition. Therefore, most of the copper salts in the catalyst surface changed into Cu₂Cl(OH)₃ forms when they were added to the support by incipient wetness method. The new copper phase, Cu₂Cl(OH)₃, is believed to be formed by the interaction between CuCl₂·2H₂O and the surface of the support during the impregnation.

The XRD pattern for the fresh PdCl₂-Cu(NO₃)₂ catalyst revealed that the copper species on the catalyst surface were existing in the forms of Cu₂(OH)₃(NO₃), Cu₂Cl(OH)₃ and CuCl₂·2H₂O as shown in Fig. 7. The copper species containing chlorine were probably formed by the transfer of Cl⁻ ions of the PdCl₂ into the Cu²⁺ ions during the preparation of catalyst. The CO oxidation activity of the PdCl₂-Cu(NO₃)₂ catalyst might be attributed to the Cu₂Cl(OH)₃ which was formed on the catalyst surface by the interaction of PdCl₂ and Cu(NO₃)₂.

In PdCl₂-CuCl₂ catalyst, the intensity of Cu₂Cl(OH)₃ peaks slightly decreased after the reaction at 40 °C. However, the Cu₂Cl(OH)₃ peaks in the Cu(NO₃)₂-promoted catalyst were stabilized even after reaction. Furthermore, the addition of Cu(NO₃)₂ significantly enhanced the CO oxidation activity. Therefore, it is believed that the role of Cu(NO₃)₂ is to stabilize the active Cu(II) species, Cu₂Cl(OH)₃, on the catalyst surface which maintains the redox property of palladium.

3. Effect of HCl and SO₂ on the Catalyst Deactivation

The presence of chlorine is essential to carry out the catalytic cycle of CO oxidation in the Wacker catalytic system. Desai et al. [1983] reported that the CO conversion over the PdCl₂-CuCl₂-Cu(NO₃)₂/Al₂O₃ catalyst decreased from 90 % to 26 % over the period of 35 hr of on-stream time at 60 °C. They suggested that the prechlorination of the catalyst before the reaction significantly improved the catalyst durability. Kim et al. [1994] also observed the loss of HCl from the liquid phase on the catalyst during the reaction by mass spectroscopy. Therefore, the addition of HCl into the feed gas stream might be expected to have a positive effect for the oxidation activity. However, the addition of HCl decreased the CO conversion as shown in Fig. 8. The increase in the concentra-

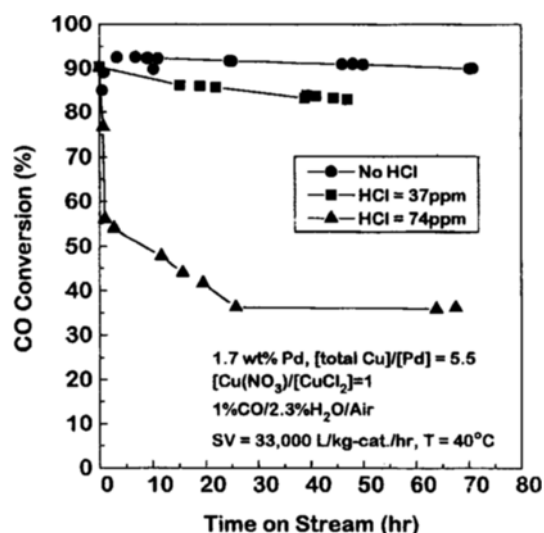


Fig. 8. Effect of HCl on CO conversion over PdCl₂-CuCl₂-Cu(NO₃)₂/activated carbon catalysts.

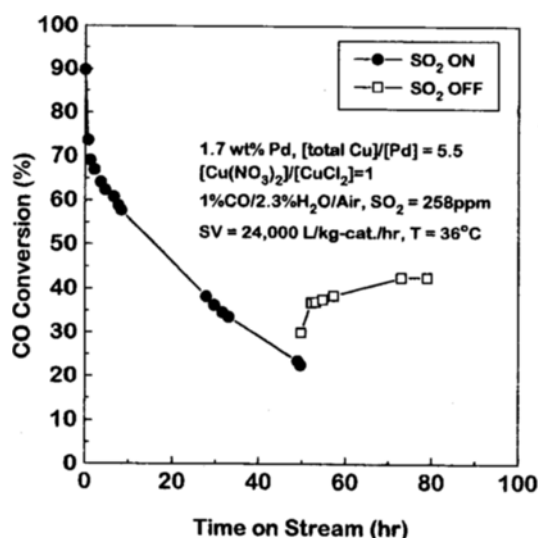


Fig. 9. Effect of SO₂ on CO conversion over PdCl₂-CuCl₂-Cu(NO₃)₂/activated carbon catalysts.

tion of HCl into the reactor further reduced the activity. Desai et al. [1983] reported that the excessive prechlorination in excess of HCl resulted in the depression of the activity. The addition of HCl which exceeds the amount released from the catalyst during the course of the reaction seems to be the cause of the decrease of the oxidation activity.

Fig. 9 shows the effect of SO₂ on the CO oxidation activity. The addition of SO₂ severely deactivated the catalyst and the activity was not restored even if the feed of SO₂ was terminated. From the XRD data as observed in Fig. 10, the peaks of Cu₂Cl(OH)₃ disappeared after the reaction with HCl and SO₂. The disappearance of Cu₂Cl(OH)₃ will decrease the redox activity of palladium. It is believed that the addition of HCl and SO₂ into the feed gas stream inhibits the formation of active and stable Cu(II) species on the catalyst surface, although the effect of HCl and SO₂ on the catalyst activity was not systematically examined in the present study.

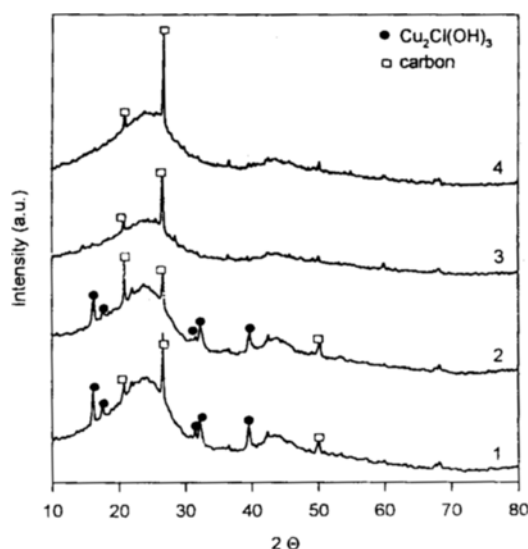


Fig. 10. X-ray diffraction patterns of the $\text{PdCl}_2\text{-CuCl}_2\text{-Cu(NO}_3)_2$ /activated carbon catalyst.

(1) before reaction, (2) after reaction at 40°C , (3) after reaction at 40°C with HCl , (4) after reaction at 40°C with SO_2 .

CONCLUSIONS

CO oxidation over the $\text{PdCl}_2\text{-CuCl}_2$ catalyst supported on activated carbon was investigated. The catalyst was active and stable at near room temperature if water were supplied into the feed gas stream. The catalytic activity with respect to reaction temperature showed a maximum at around 55°C of the reaction temperature. The addition of $\text{Cu(NO}_3)_2$ onto the $\text{PdCl}_2\text{-CuCl}_2$ catalyst significantly enhanced the CO oxidation activity. The role of $\text{Cu(NO}_3)_2$ is believed to stabilize active Cu(II) species on the catalyst surface. When HCl and SO_2 were present in the feed, the CO oxidation activity was significantly altered by the inhibition of the formation of active Cu(II) species on the catalyst surface.

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