

ENHANCED CATALYTIC PERFORMANCE OF Cu/Ag/CeO₂ CATALYST FOR THE SCR OF NO BY PROPYLENE

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ABSTRACT

The modification of the Cu(4)/CeO₂ catalyst with 1 wt% of Ag resulted in a significant increase in the NO reduction activity compared to 2 and 3 wt% Ag. The Cu(4)/Ag(1)/CeO₂ catalyst consisted of isolated Cu²⁺ species and Ag_n^{δ+} clusters, while the Cu(4)/Ag(3)/CeO₂ catalyst contained mostly octahedral Cu²⁺ species as indicated by the results from the UV-Vis DRS characterization. Therefore, it is presumed that isolated Cu²⁺ species on the Cu(4)/Ag(1)/CeO₂ catalyst and Ag_n^{δ+} clusters formed active-sites responsible towards a higher catalytic activity for NO reduction by propylene compared to octahedral Cu²⁺ species. The competitiveness factor (S_{SCR-HC}) for Cu(4)/Ag(3)/CeO₂ catalyst was much lower than Cu(4)/Ag(1)/CeO₂ catalyst in the whole temperature range, indicating that the high loading of Ag enhanced the oxidation of C₃H₆ by O₂. As a result, less amount of C₃H₆ reacted selectively with NO. In addition, the selectivity of CO for NO + C₃H₆ + O₂ reactions was higher than those for C₃H₆ + O₂ reactions on all the Cu(4)/Ag/CeO₂ catalysts indicating the generation of organic intermediates by partial oxidation of hydrocarbon which would lead to the production of significant amount of CO related to NO reduction.

Keywords: Enhanced Catalytic Performance, SCR, Cu/Ag/CeO₂, Propylene.

1 INTRODUCTION

Ceria-based catalysts have been studied extensively for selective catalytic reduction (SCR) of NO (Liese et al., 2001). Recently, the reduction of NO in the presence of CO over Cu/CeO₂ catalyst has been demonstrated by Hu et al. (2001). They reported that the catalytic activities of the Cu/CeO₂ catalyst increased compared to that of CeO₂ alone, probably due to the presence of surface dispersed copper oxide species. In addition, Ag supported catalysts have been found to promote NO_x removal (Bethke and Kung, 1997). They proposed that 1⁺ oxidation state of Ag showed high NO conversion activity over Al₂O₃ catalyst. It could also be established that the Ag site is very important for generating isocyanate (-NCO), which is an important intermediate for lean NO_x reduction (Sato et al., 2003).

The formulation of bimetal catalyst has been reported to increase the interaction of hydrocarbons and NO_x stimulated by the different active catalytic sites (Ansell et al., 1993). For example, the addition of small amount of Ag has been demonstrated to improve the catalytic performance of the Rh/Al₂O₃ for NO reduction by propylene (Kotsifa et al., 2002). Besides, the activity of NO reduction was also enhanced by the addition of Cs to Ag/Al₂O₃ catalyst in the presence of SO₂ (Son et al., 2001).

In previous studies, the reduction of NO under lean condition at 400°C was reported to be greatly enhanced by the addition of Cr (Amin et al., 2003) and Ag (Amin et al., 2004) to Cu/CeO₂ catalyst. However, the catalytic performance of the Cu/Ag/CeO₂ catalyst was not comprehensively described over a wide temperature range in the previous papers. Therefore, the present work attempts to investigate the SCR of NO by propylene in the presence of excess oxygen over the bimetallic Cu-Ag catalysts supported on CeO₂ from 250 - 550°C. The influences of Ag loading on the catalytic activity of Cu/CeO₂ catalyst in the SCR-HC are also discussed in this paper.

2 EXPERIMENTAL

2.1 CATALYST PREPARATION

Cu/CeO₂ catalyst with copper content of 4 wt% and Ag/CeO₂ catalyst with silver content of 1 wt% were prepared by impregnation method. The desired amount of Cu(NO₃)₂·3H₂O aqueous solution or AgNO₃ aqueous solution was added to a certain amount of CeO₂, respectively. The resulting solution was first stirred at room temperature for 17 h and then dried in an oven at 110°C overnight, followed by calcinations at 550°C for 5 h to decompose the nitrate species present in the catalysts.

The co-impregnation method was employed to synthesize the Cu/Ag/CeO₂ catalysts. In this case, the required amounts of copper nitrate aqueous and silver nitrate aqueous solution were simultaneously impregnated with the CeO₂ catalyst support. Subsequently, the resulting solution was stirred for 17 h at room temperature. All the procedures in the drying and calcinations of Cu/CeO₂ catalyst were repeated to completely produce Ag promoted Cu/CeO₂ catalyst. The amount of Cu in these bimetal catalysts was fixed at 4 wt%, while that of Ag additive varied from 1 to 3 wt%. The catalysts are denoted as Cu(x)/Ag(y)/CeO₂, where (x) represents the weight percent of Cu and (y) denotes the weight percent of Ag in the catalysts.

2.2 CATALYST CHARACTERIZATION

UV-Vis spectra were recorded by using a UV-Vis spectrometer (Perkin Elmer Lambda-900 spectrometer) in a diffuse reflectance mode in the range between 190 and 800 nm at a step of 0.5 nm with a band width of 2 nm. BaSO₄ was used as a reflectance sample to measure the baseline spectrum.

2.3 CATALYTIC ACTIVITY MEASUREMENTS

Catalytic activity measurements were carried out in a flow apparatus by using a lab-scale fixed bed reactor (Stainless steel 316) with inner diameter 10 mm and length 300 mm. Prior to the reaction, one gram of the synthesized catalyst, supported on ceramic wool, was loaded into the reactor. The catalyst was pretreated using helium gas at 500°C for 1 h. After the preheating period, the reactant gas mixtures comprising of 2000 ppm NO, 2000 ppm C₃H₆, 10% O₂ and balance He were fed into the reactor. The total gas flow rate was 500 ml/min. The total gas flow rate employed in this research work was confirmed to be in the reaction-limited regime by measuring the NO conversion versus F/W curve. The reaction temperature controlled by a temperature programmed reactor furnace (Carbolite® VST 12/30/200) was increased from 250 to 550°C in steps of 50°C. The concentration of NO was analyzed with a NO_x emission analyzer (Bacharach NONOXOR® II). The compositions of other products were analyzed by using a gas chromatograph (Agilent 6890 Series) equipped with a TCD detector. The concentrations of CO₂ and C₃H₆ were analyzed by a Porapak N column, while a Molecular Sieve 5A column was used for the analysis of N₂ and CO.

3 RESULTS AND DISCUSSIONS

3.1 CATALYTIC ACTIVITY

As shown in Fig. 1, Cu(4)/CeO₂ and Ag(1)/CeO₂ catalyst showed lower catalytic activities in the whole temperature region (250–550°C), giving a maximum NO conversion of 40% at 400°C and 32% at 450°C, respectively. By co-impregnating the Cu(4)/CeO₂ catalyst with 1 wt% Ag, the NO conversion improved significantly up to 86% at T_{max} = 450°C. Meanwhile, it can be seen from Figs. 1(a) and (b) that although the conversions of C₃H₆ over the Cu(4)/CeO₂ catalyst were higher than those achieved over the Cu(4)/Ag(1)/CeO₂ catalyst, the NO conversions of the latter were much more higher. This phenomenon is attributed to the dominant non-selective oxidation of C₃H₆ by O₂ and the diminished reduction of NO by C₃H₆ over the Cu(4)/CeO₂ catalyst. In addition, the low NO reduction activity over the Ag(1)/CeO₂ catalyst could be attributed to its low C₃H₆ activation activity where the C₃H₆ conversions in the whole temperature range were rather low as can be seen

seen in Fig. 1(b). Thus, only a little amount of organic intermediates formed by the partial oxidation of C_3H_6 were available to selectively reduce NO over this catalyst.

The maximum NO conversion ranged from 66 to 86% in the following sequence: $Cu(4)/Ag(1)/CeO_2 > Cu(4)/Ag(2)/CeO_2 > Cu(4)/Ag(3)/CeO_2$. These results show that further increment of Ag content in the $Cu(4)/Ag/CeO_2$ catalysts above 3 wt% will definitely decrease the NO conversion for SCR-HC reaction. As shown in Figs. 1(a) and (b), the temperature required to achieve the maximum NO conversion corresponded to that of total C_3H_6 oxidation for the $Cu(4)/Ag(1)/CeO_2$ catalysts. In contrast, the $Cu(4)/Ag(2)/CeO_2$ and $Cu(4)/Ag(3)/CeO_2$ catalysts showed maximum NO conversion at temperature lower than that corresponding to total combustion of C_3H_6 . These results indicate that C_3H_6 did not selectively reduce NO at temperature higher than 400°C over the catalysts with higher Ag loading.

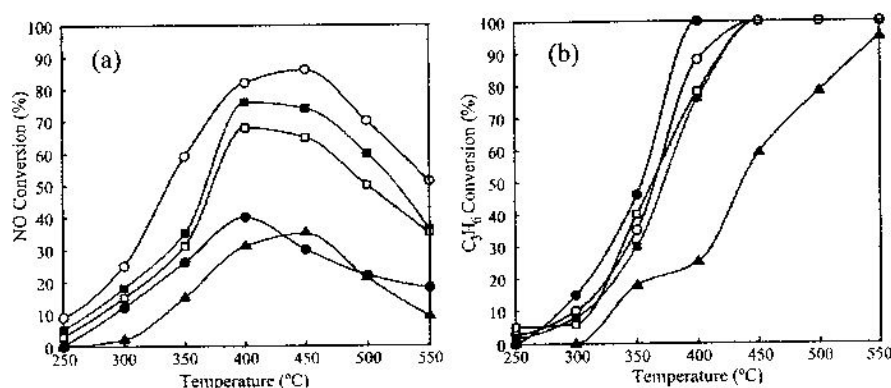


FIGURE 1. Conversion of (a) NO and (b) C_3H_6 vs. temperature over (●) $Cu(4)/CeO_2$; (▲) $Ag(1)/CeO_2$; (○) $Cu(4)/Ag(1)/CeO_2$; (■) $Cu(4)/Ag(2)/CeO_2$; (□) $Cu(4)/Ag(3)/CeO_2$. Reaction condition: 2000 ppm NO, 2000 ppm C_3H_6 , 10% O_2 with balance of He, F/W = 30,000 ml/g-cat.hr

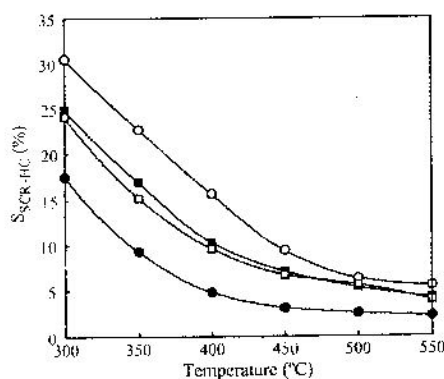


FIGURE 2. S_{SCR-HC} vs. temperature over (●) $Cu(4)/CeO_2$; (▲) $Ag(1)/CeO_2$; (○) $Cu(4)/Ag(1)/CeO_2$; (■) $Cu(4)/Ag(2)/CeO_2$; (□) $Cu(4)/Ag(3)/CeO_2$. Reaction condition: 2000 ppm NO, 2000 ppm C_3H_6 , 10% O_2 with balance of He, F/W = 30,000 ml/g-cat.hr

Fig. 2 depicts the trends of the S_{SCR-HC} values as a function of reaction temperature, for $Cu(4)/CeO_2$ and $Cu(4)/Ag/CeO_2$ catalysts. In spite of their high S_{SCR-HC} values, the NO conversions obtained over all the catalysts were very low in the temperature range between 300 and 350°C indicating the low activation of C_3H_6 to form the organic intermediates that are important for NO reduction activity at temperatures lower than 400°C. As the reaction temperature increased, the S_{SCR-HC} values for all the catalysts decreased due to the concomitant oxidation of C_3H_6 by O_2 which was more favored than the reduction of NO by C_3H_6 . As shown in Figs. 1(b) and 2, the C_3H_6 conversions achieved over the $Cu(4)/CeO_2$ catalyst were the highest among all the catalysts tested but its S_{SCR-HC} values were the lowest in the whole temperature range. These results continued that the combustion of C_3H_6 by O_2 prevailed over C_3H_6 oxidation by NO on the $Cu(4)/CeO_2$ catalyst. At the same time, the S_{SCR-HC} values obtained over all the Ag-

promoted Cu(4)/CeO₂ catalysts were much higher than those of Cu(4)/CeO₂ catalyst, reinstating that the presence of Ag species can promote the reduction of NO by C₃H₆. In addition, further increase of Ag loading (2 wt% and above) resulted in a smaller S_{SCR-HC} values in the whole temperature range (300-550°C). Consequently, Cu(4)/Ag(2)/CeO₂ and Cu(4)/Ag(3)/CeO₂ catalysts exhibited lower NO conversion than Cu(4)/Ag(1)/CeO₂ catalyst, as shown in Fig. 1. The study on the catalytic performance unequivocally indicates conclusively pointed out that high loading of Ag would enhance oxidation of C₃H₆ by O₂ and thus reduce the amount of C₃H₆ to selectively react with NO.

TABLE 1. Catalytic activity of Cu(4)/Ag(1)/CeO₂, Cu(4)/Ag(2)/CeO₂ and Cu(4)/Ag(3)/CeO₂ for propylene oxidation in the presence and absence of NO at 400°C

Catalyst	C ₃ H ₆ Conversion (%)	CO Selectivity (%)	CO ₂ Selectivity (%)
NO + C ₃ H ₆ + O ₂			
Cu(4)/Ag(1)/CeO ₂	88	11	89
Cu(4)/Ag(2)/CeO ₂	76	8	92
Cu(4)/Ag(3)/CeO ₂	78	6	94
C ₃ H ₆ + O ₂			
Cu(4)/Ag(1)/CeO ₂	45	1.2	98.8
Cu(4)/Ag(2)/CeO ₂	53	0.6	99.4
Cu(4)/Ag(3)/CeO ₂	57	0.5	99.5

Reaction condition: 2000 ppm NO, 2000 ppm C₃H₆, 10% O₂ with balance of He, F/W = 30,000 ml/g-cat.hr

As shown in Table 1, it was found that the selectivity of CO for the NO + C₃H₆ + O₂ reaction was higher than those for the C₃H₆ + O₂ reaction on all the Cu(4)/Ag/CeO₂ catalysts. Cu(4)/Ag(1)/CeO₂ catalyst gave the highest CO selectivity possibly due to the generation of CO from the partial oxidation of hydrocarbon to form organic intermediates. Shimizu et al. (2001) reported that the presence of these organic intermediates would result in a significant improvement in SCR-HC activity, and the partial oxidation of hydrocarbon is always accompanied by high rate of CO formation. Therefore, it can be concluded that partial oxidation of hydrocarbon is an important reaction step for SCR-HC over Cu(4)/Ag(1)/CeO₂ catalyst. In contrast, Cu(4)/Ag(3)/CeO₂ and Cu(4)/Ag(2)/CeO₂ catalysts exhibited lower CO selectivity compared to Cu(4)/Ag(1)/CeO₂ catalyst implying that complete oxidation of C₃H₆ to CO₂ prevailed over both catalysts with higher Ag content.

3.2 UV-VIS DIFFUSE REFLECTANCE SPECTROSCOPY (UV-VIS DRS)

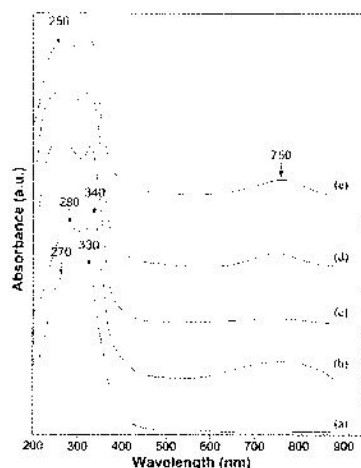


FIGURE 3. Diffuse reflectance UV-Vis spectra of (a) CeO₂; (b) Cu(4)/CeO₂; (c) Cu(4)Ag(1)/CeO₂; (d) Cu(4)Ag(2)/CeO₂; (e) Cu(4)Ag(3)/CeO₂

As shown in Figs. 3(a) and (b), the charge transfer band at 270 and 330 nm over the CeO₂ support were shifted toward higher wavelength at 280 nm and 340 nm, respectively over the Cu(4)/CeO₂ catalyst. The red shift of the Ce⁴⁺←O²⁻ band is attributed to the presence of Cu species on the CeO₂ support, which is in agreement with that reported by Ratnasamy et al. (2004). Furthermore, the spectra of Cu/CeO₂ catalyst also showed an absorption band around 700-800 nm, coincides with the band observed for Cu/Al₂O₃ catalyst (Chen et al., 1999). Since no other absorption band for Cu species was observed, it is presumed that the majority of the Cu species on the Cu(4)/CeO₂ catalyst formed the Cu²⁺ species in a distorted octahedral symmetry.

With the presence of 1 wt% Ag on the Cu(4)/CeO₂ catalyst, the intensity of the band around 700-800 nm was significantly decreased, while a strong band at ~250 nm, assignable to Cu²⁺←O²⁻ charge transfer (Praliaud et al., 1998), was observed. The result implies that the concentration of octahedral Cu²⁺ species in this catalyst is lower compared to Cu(4)/CeO₂ catalyst, and the isolated Cu²⁺ species became predominant. In addition, it has been reported that an absorption band around 258 nm can be attributed to the formation of Ag_n^{δ+} clusters (Li and Stephanopoulos, 1999). In view of that, it can be estimated that the band at ~250 nm is due to Ag_n^{δ+} clusters. With increasing Ag content, the intensity of the band at 700-800 nm was slightly increased and the band at ~250 nm became weak, indicating that a significant amount of octahedrally coordinated Cu²⁺ is present in the Cu(4)/Ag/CeO₂ catalyst with higher Ag loading. Consequently, we assumed that high Ag loading would inhibit the formation of isolated Cu²⁺ over the Cu/Ag/CeO₂ catalyst. Besides, we also attributed the decrease in the intensity of the band at ~250 nm to a decrease of Ag_n^{δ+} clusters formation.

The profile of NO conversion with temperature in Fig. 1 shows that the catalytic activity order of the Cu/CeO₂ and Cu/Ag/CeO₂ catalysts is in the following order: Cu(4)/Ag(1)/CeO₂ > Cu(4)/Ag(2)/CeO₂ > Cu(4)/Ag(3)/CeO₂ > Cu(4)/CeO₂. Since Cu(4)/Ag(1)/CeO₂ catalyst showed very high SCR-HC activity, it is presumed that isolated Cu²⁺ species is more active towards NO reduction by propylene compared to octahedral Cu²⁺ species. Moreover, the presence of oxidized Ag on the Cu/Ag(1)/CeO₂ catalyst would enhance the NO reduction by propylene as reported by Bethke and Kung (1997) and Sato et al. (2003). In contrast, the NO reduction activities of Cu(4)/Ag(2)/CeO₂ and Cu(4)/Ag(3)/CeO₂ catalysts are low, which can be attributed to the lack of hydrocarbon available due to higher non-selective C₃H₆ oxidation activity over the two catalysts. Hoost et al. (1997) and Son et al. (2001) reported that low NO reduction activity over Ag/Al₂O₃ catalysts was due to the high Ag loading which promoted the formation of metallic Ag.

4 CONCLUSION

Bimetallic Cu/Ag/CeO₂ catalyst exhibits high catalytic performance for selective reduction of NO by propylene in the presence of excess O₂. The activity of Cu(4)/CeO₂ catalyst is improved by doping Ag and the optimum doping level is 1 wt%. Catalyst characterizations by UV-Vis DRS confirmed the presence of isolated Cu²⁺ ions and Ag_n^{δ+} clusters in the Cu(4)/Ag(1)/CeO₂ catalyst. We assume that these two species played a vital role in generating the intermediates like isocyanate and subsequently enhanced the NO conversion in the presence of excess oxygen. On the other hand, the low NO reduction activities exhibited by the catalysts with higher Ag loading can be attributed to the lack of isolated Cu²⁺ species in the catalysts and the presence of metallic Ag clusters which are active for non-selective oxidation of hydrocarbons.

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