

Selective catalytic reduction of NO by hydrocarbons over Cu/Al₂O₃ catalysts

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The reduction of NO by hydrocarbons was investigated over Cu/Al₂O₃ catalysts using a stainless steel flow reactor under highly oxidising diesel exhaust conditions (up to 15%). Three different Cu loadings (1, 5 and 10 wt.%) on an Al₂O₃ support were prepared and characterized using spectroscopic techniques. The catalytic activity tests show that different Cu loadings as well as temperature, oxygen, and hydrocarbon concentration levels significantly influence the NO reduction. Increasing Cu loadings up to 5 and 10 wt.% decreases the catalytic activities for NO reduction due to the formation of a bulk crystalline CuO phase, as observed from XRD and SEM images. In particular, the visualization of the copper dispersion on the surface using the SEM-BEI technique provides information on the extent of copper saturation, particle size, and the effects on NO reduction. However, the lower Cu loading (1 wt.%) increases the catalytic activity with a temperature window of 720-810K, thereby favoring the formation of well dispersed isolated Cu species, e.g. Cu²⁺ ions, which is related to selective NO reduction. The effects of other reaction parameters, such as oxygen, the hydrocarbon level and type, and byproduct emissions are further discussed.

Key words : diesel NO_x, SCR, catalytic reduction, hydrocarbon, Cu/Al₂O₃

1. Introduction

The reduction of NO_x emissions from lean-burn and diesel engines has recently developed into a key issue in environmental research and engineering societies as the use of these engines has sharply accelerated due to advantages such as fuel economy, high engine efficiency (~52%), and low emissions (CO and CO₂)¹⁾. Unfortunately, the typical three-way catalyst in a gasoline engine is not effective under such oxidizing conditions. Therefore, many studies and applications have been conducted to reduce diesel NO_x emissions using well-known, selective catalytic and noncatalytic reductions by NH₃/Urea (SCR and SNCR)²⁻⁴⁾ or recently by hydrocarbons^{5,6)}. Among these, the catalytic NO_x reduction by hydrocarbons (HC-SCR), first reported by Iwamoto⁷⁾, has received a lot of attention and been extensively studied over the last decade as a possible technology within practical exhaust temperatures (400-1000K). Various metals (Co, Cu, Fe, Pt, Ga, and Ag etc.) sup-

ported on zeolites and alumina have since been reported as effective for NO_x reduction under oxidizing conditions, yet most of these catalysts exhibited deactivation and ageing by moisture, sulfur, and oxygen^{1,8)}. In practice, the exhaust gases from lean-burn and diesel engines include a wide range of oxygen level (2~13%) and moisture (10~15%) and even a small amount of sulfur in some cases. Hence, suitable catalysts must be able to operate effectively under these severe conditions even with higher space velocities over 100,000h⁻¹.

In this paper, the selective catalytic reactions using simple gas mixtures (NO/Hydrocarbons/O₂) are investigated over Cu/Al₂O₃ catalysts for NO_x reduction in a stainless steel flow reactor, for practical reasons, in which the oxygen levels particularly range up to 15%, i.e. close to the levels in diesel exhaust. The catalytic activities are measured through parameter investigations, such as Cu loading, temperature, oxygen, and hydrocarbon levels. Furthermore, catalyst characterization using particularly XRD patterns and

SEM images is provided to determine the nature of the surface active species and their morphologies, and for analyzing the NO reduction.

2. Experimental

2.1. Catalyst Preparation

Copper oxide/alumina catalysts($\text{Cu}/\text{Al}_2\text{O}_3$) with different Cu loadings were prepared by incipient wetness impregnation using copper(II) nitrate as the precursor. The support was commercially available γ - Al_2O_3 (surface area of 162 m^2/g , BDH Co.) having a pore volume of 0.5~0.6 ml/g, and about 70% of the particles were sized less than 200 μm . The impregnated samples were dried in an oven at 110°C overnight, and calcined in air at 500°C for 4 hr. Three different Cu loadings(1, 5 and 10wt.%) of $\text{Cu}/\text{Al}_2\text{O}_3$ catalysts were made.

2.2. Characterisation

The catalyst characterisation in this study includes the measurement of the total surface area (BET) and analyses of XRD patterns and SEM images. The surface area of the catalysts was determined by N_2 adsorption, using a 3-point BET method(Quantasorb system). Approximately 0.07 g samples were outgassed in a N_2/He mixture at 350°C for 1 hr prior to adsorption. The measurements were conducted with relative pressures of N_2 to He of 0.1, 0.2, and 0.3 at 77K.

X-ray powder diffraction patterns were obtained using an APD 1700 powder diffractometer employing Cu K radiation($\lambda = 1.5406 \text{ \AA}$). The X-ray was operated at 40 kV and 25 mA. Samples were run as powders packed into a glass sample holder having a 20 x 16 x 2.5 mm cavity. Diffraction patterns were obtained using a scanning rate of 1.8°/min(in 2θ). The determination of the possible CuO crystalline size was based on X-ray diffraction line broadening. The mean crystalline sizes(\bar{d}) of the CuO particles were calculated using the Scherrer equation⁹⁾;

$$\bar{d} = \frac{K \lambda}{B_d \cdot \cos \theta} \quad (1)$$

where λ is the X-ray wavelength, K is the Scherrer constant(particle shape factor), taken as 0.9, and

B_d is the full width at half maximum(FWHM), in radians. The value of B_d is given by the equation ($B_d^2 = B_{\text{obs}}^2 - B_{\text{inst}}^2$) where the B_{obs} is the observed line width and B_{inst} the instrumental line width. This technique is known to be particularly applicable to metal crystallites of size 3–50 nm. Also, a quantitative analysis(wt.%) for crystalline CuO phases was obtained by comparing CuO ($\bar{1}11$)/ Al_2O_3 (400) intensity ratios.

The SEM analyses for the surfaces of alumina and three different Cu loading catalysts were performed using a Camscan Series 4. Samples in powder form were placed on an aluminium holder and coated with a thin layer of carbon. The purpose of the coating is to electrically ground the samples and reduce the effect of surface charging. For different views of the surface, both SEM techniques utilising a secondary electron imaging(SEI) and backscattered electron imaging(BEI) detector were adopted^{9,10)}. In particular, the SEM-BEI mode is expected to visualize the copper dispersion on the alumina surface at different atomic weights(Cu/Al) with higher copper loadings, which is quite important for a comparison of catalytic activities, while the SEM-SEI could produce higher resolution micrographs.

2.3. Activity Measurements

The catalytic measurements of NOx reduction by hydrocarbons under diesel oxidising conditions were performed in a simple downflow reactor system. For practical reasons, the reactor was made of a stainless steel tube, 20 mm ID and 600 mm long, rather than quartz or pyrex. The reactor temperatures were measured using two thermocouples(type K), where one was inserted into the inlet of the catalyst bed and the other on the surface of the reactor.

Approximately 1.0g of catalyst was put into the reactor for pretreatment by an air flow for 2 hr at 773 K and cooled back to room temperature. The reaction mixture(normally 500 ppm NO, 1000-3000 ppm C_2H_4 , and 11.2% O_2 in air) was then introduced at a total flow rate of 4 litre/min (STP). This flow rate per catalyst volume corresponded to a gas hourly space velocity (GHSV) of $\sim 200,000 \text{ hr}^{-1}$ for the catalyst(or $W/F = 0.015 \text{ g.sec/ml}$).

Gas analysis was performed for NO_x, N₂O, O₂, CO, and CO₂ simultaneously. The chemiluminescent NO_x(Rotork Model 440) and non-dispersive infrared N₂O analysers(NDIR, Hartman and Braun) were used for the NO/NO₂, and N₂O measurements. CO and CO₂ concentrations were measured by an analyser(NDIR, ADC type 370), while oxygen concentration was determined using a paramagnetic analyser(Servomex 570).

3. Results and Discussion

3.1. Catalyst Characterization

Amount of copper and surface area : The surface areas of the alumina-supported Cu catalysts as a function of Cu loading are given in Table 1. With increasing Cu loadings from 1 to 10 wt.%, the surface area is substantially diminished from 146 to 110 m²/g, and the catalyst color also changes from blue(1wt.% Cu) to gray(10wt.% Cu). These trends are qualitatively identical to those previously observed by other investigators¹¹⁻¹³. However, according to Radtke et al.¹⁴, the impregnation procedure had little influence on the surface area of the γ -Al₂O₃ support, and the surface area of the alumina support remains unchanged if a correction for the copper oxide content is given. Thus, a surface area reduction is expected if the pores in the support are partially filled with copper oxide.

XRD : Figure 1 shows XRD analysis for catalysts investigated in the present work. First, the characteristics of aluminas are observed at several 2θ values of 32°, 37°, 40°, 45°, and 67°, where the peak at 45° indicates γ -Al₂O₃¹². For lower Cu loadings(1 and 5wt.%), the XRD patterns show only reflections similar to γ -Al₂O₃ itself, which means that Cu element would be relatively well dispersed on the alumina surface. However, with an increased Cu loading up to 10 wt.%, crystalline CuO phase is detected, where two sharp peaks at $2\theta = 35.3^\circ$ and 38.3° are identified as CuO ($\bar{1}11$) and CuO(111). Thus, as Cu loading increases beyond the saturation content, large and three-dimensional cluster CuO phases start to develop, thereby reducing the surface area and potentially affecting the catalytic activity.

Table 1. Physical properties, and concentrations (wt.)/particle sizes(nm) of Crystalline CuO phase in various Cu/Al₂O₃ catalysts calculated from XRD analysis.

catalysts	Surface area(m ² /g) by BET	Crystalline phase(wt.%) measured by XRD	CuO particle size(nm) calculated by XRD
Al ₂ O ₃	162	-	-
1wt.%, Cu/Al ₂ O ₃	146	no detection	no detection
5wt.%, Cu/Al ₂ O ₃	125	no detection	no detection
10wt.%, Cu/Al ₂ O ₃	110	3.0	33.5
12wt.% ¹¹⁾	-	5.7	30
16wt.%, Cu/Al ₂ O ₃	-	10.8	30
20wt.%, Cu/Al ₂ O ₃	-	14.6	29
26wt.% ¹²⁾	-	-	32

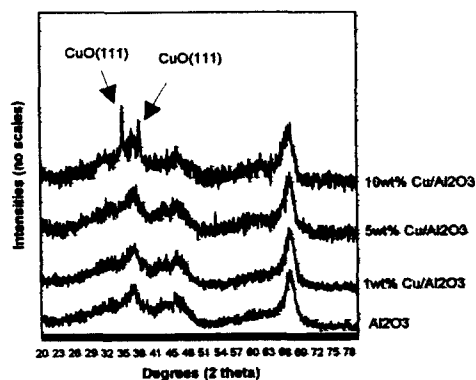


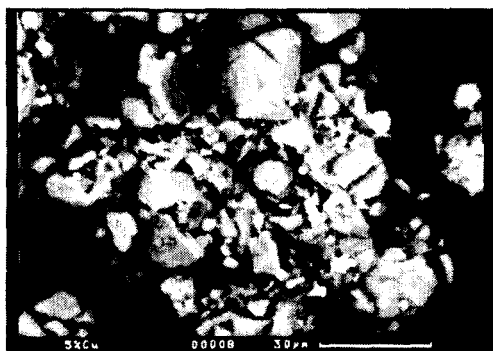
Fig. 1. XRD patterns measured for Al₂O₃ and three different Cu/Al₂O₃ catalysts.

Since the intensities of the CuO XRD peaks increase with increasing Cu content, it may be interesting to calculate the amount of CuO phase (wt.%) by comparing CuO($\bar{1}11$)/Al₂O₃(400) intensity ratios¹¹. Table 1 also shows the concentrations(wt.%) and particle sizes(nm) of crystalline CuO phases in various Cu/Al₂O₃ catalysts calculated from XRD analysis. The amount of crystalline CuO reaches about 3.0wt.% with our sample of 10wt.% Cu loading, which means that about 30% of Cu is present as CuO crystallites on the surface. Compared with literature values for higher Cu loadings(12, 16, 20, and 26 wt.% Cu), its value seems reasonable, and increased further with an increase in Cu loading. Next, the

particle size of CuO could be calculated from the XRD line broadening equation (1) where the only unknown value is the angular width B_d of the CuO (111) line (35.3° in 2θ). This was confirmed experimentally as 0.0043 radians, based on the equation ($B_d^2 = B_{obs}^2 - B_{inst}^2$), therefore, the mean CuO crystallite size reached 33.5 nm. This result seems to bear no relation to Cu loading based on a comparison with literature values ranging from 29–32 nm. Although there are still some uncertainties, as noted by Strohmaier¹²) and Anderson⁹), such as the consequences of particle size distribution and correction difficulties of instrumental broadening, this still provides a good relative comparison for crystalline CuO particle sizes.

SEM : The results of SEM analyses for Al₂O₃ and three different Cu loading catalysts (Cu/Al₂O₃) provided information on their surface morphology, particle size, and the extent of copper dispersion. All the samples (alumina and Cu-loaded catalysts) in this study had small sized particles (<40 μm) which eventually formed large aggregates by particle interaction (<200 μm)³).

To visualize the copper dispersion on the catalyst surface, a special technique (SEM-BEI) was adopted. Figure 2 shows the images of two samples (5, 10wt.% Cu) obtained by SEM-BEI which beamed exactly the same areas of the samples as in the SEM-SEI which however failed to visualise. Higher loadings (5 and, especially 10wt.% Cu) exhibit well-dispersed white spots, i.e. CuO particles, as similarly observed with Cu/ZSM-5 catalysts¹⁰), whereas with 1wt.% Cu loading, no copper particles are shown on the surface (not shown). The several white spots even with 5wt.%



a)



b)

Fig. 2. SEM-BEI micrographs of samples ; 5wt% Cu/Al₂O₃ (a), 10wt% Cu/Al₂O₃ (b). white spots show copper location.

Cu may indicate the saturation content capacity of alumina (e.g. 5wt.% Cu/162 m²/g Al₂O₃).

4. Catalytic Activity

4.1. Effect of Cu Loading

The NO conversion efficiencies by Cu/Al₂O₃ catalytic reactions for a mixture of NO/C₂H₄/O₂ were investigated over a temperature range of 473–873K and under highly oxidising conditions (up to 15% O₂). Figure 3 shows the influence of three different copper loadings and the stainless steel itself on NO reduction by C₂H₄ in the presence of 11.2% oxygen as a function of temperature. With increasing Cu loadings, the catalytic activities drastically decrease, yet the optimum NO reduction is observed over a similar temperature range from 720 to 850K. Among the catalysts investigated, 1wt.% Cu/Al₂O₃ shows the highest activity, and about 62% NO reduction is obtained at 810K. The catalytic activities tend to diminish in proportion to an increase in Cu loading. About a 46% NO reduction is achieved with 5wt.% Cu, and a 35% reduction with no maximum evident for 10wt.% Cu. The catalytic effect of the stainless steel reactor was tested with no catalyst in the reactor under the same conditions. The reactor (surface to volume ratio 0.2cm⁻¹) itself could produce up to a 15% NO reduction over a similar temperature range.

Based on previous studies^{11–16}), two facts can be pointed out for NO reduction by hydrocarbons. First, the catalytic activity is diminished with increasing Cu loadings where the saturation content

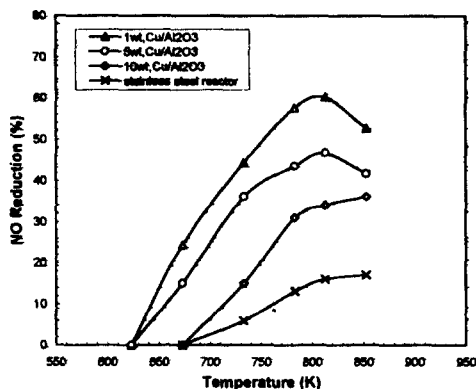


Fig. 3. Effects of different Cu loadings and stainless steel reactor as catalysts on NO reduction as a function of temperature in oxidizing conditions ; NO=500 ppm, C₂H₄/NO=6.0, O₂=11.2%, flow rate=4.0L/min(STP).

is about 5~6wt.% Cu/160 m²/g Al₂O₃. Second, the temperature window shifts to a lower temperature with an increased Cu loading. The present NO reduction data show similar low activities with increasing Cu loadings, but a shift in the temperature window is not evident, based on the optimum temperature. As observed by the XRD patterns, a higher Cu loading (especially 10wt.%) favors the formation of a bulk crystalline CuO phase on the surface of alumina, which decreases the surface area. In contrast, a lower Cu loading (1wt.%) favors the formation of an isolated Cu species, e.g. Cu²⁺ ions, and increases the catalytic activity for NO reduction. Furthermore, the catalytic activities (expressed by the moles of NO conversion per gram of copper per second) between 1, 5, and 10wt.% Cu loadings are approximately 9.22×10^{-5} , 1.49×10^{-5} , and 3.32×10^{-6} mole/g_{Cu}.sec at 810K, which implies that the lower Cu loading (1wt.%) is about 28 times more active than 10wt.%.

Thus, the selective reduction of NO in oxidising conditions must be related to the presence of these dispersed isolated Cu species, which is in line with Chajar et al.¹⁵⁾

4.2. Oxygen Effect

Figure 4 shows the effect of oxygen concentration (up to 15%) on NO reduction at a temperature of 770K. With 5 and 10wt.% Cu loadings, oxygen has negligible effect between 0~2%, increases the rate sharply between 2~7%,

and above 8%, the influence of oxygen increases steadily. For the lower Cu loading (1wt.% Cu), as expected the presence of O₂ enhances NO reduction significantly, compared with higher Cu loadings. The NO reduction and catalytic activity continue to increase sharply up to about 5% O₂ and then remain constant.

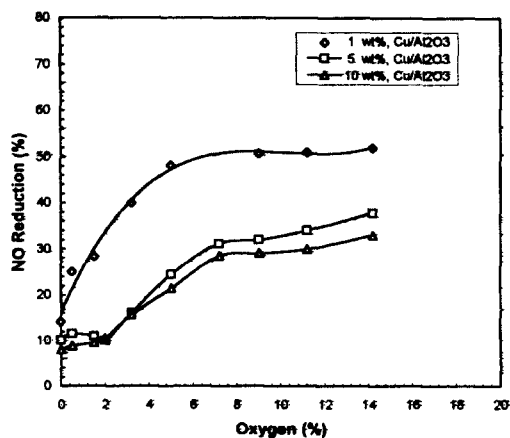


Fig. 4. Effect of oxygen levels on NO reduction with different Cu loadings ; NO=500 ppm, C₂H₄/NO=6.0, T_{cat}=770K.

Figure 5 shows another oxygen characteristics by comparing two gas mixtures, one with 11.2% O₂ (NO/C₂H₄/O₂) and one without O₂ (NO/C₂H₄) as a function of temperature with a 1wt.% Cu loading. This indicates that both reacting systems can reduce NO to N₂. The NO/C₂H₄ system shows a lower activity (maximum 30% reduction) below 850K, yet NO reduction is favored by higher temperatures. However, it is clear that, as far as Cu/Al₂O₃ catalysts and C₂H₄ as a reducing agent are concerned, the presence of oxygen in the NO/C₂H₄/O₂ can considerably enhance the NO conversion at temperatures above 620K. Increasing the temperature up to 810K causes a large increase in NO reduction, however, beyond that, any further increase in temperature results in a decrease in NO reduction.

This beneficial effect of oxygen can be explained in connection with C₂H₄ oxidation relative to temperature. Cho¹⁷⁾ asserted in his experiments with Cu/ZSM-5 catalysts that the C₂H₄ scavenging effect of oxygen, via oxidation, may facilitate NO adsorption toward catalytic active sites by clearing the diffusion paths. It proves that the interior of

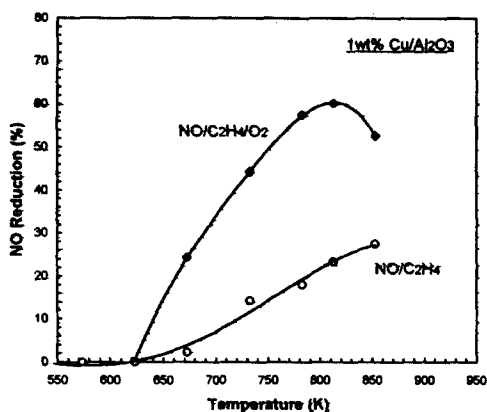


Fig. 5. Effect of oxygen on NO reduction as a function of temperature ; NO=500 ppm, $C_2H_4/NO=6.0$, 11.2% O_2 for $NO/C_2H_4/O_2$.

the catalyst is predominantly occupied by C_2H_4 , due to its strong adsorption affinity, especially below the optimum temperature. Then, as the complete oxidation of C_2H_4 is approached at higher temperatures, the inside of the catalyst is covered primarily with oxygen, therefore, the NO reduction starts to decrease.

As a consequence of both figures, the rate of NO reduction is dependent upon oxygen up to a level of around 6%, yet such kinetic behavior in all catalysts becomes less substantial at higher oxygen levels, approaching zero-order above 11%. This also means that the role of oxygen in HC-SCR reactions remains complex since it is influenced by various parameters simultaneously, such as the copper content, temperature, and type of hydrocarbon, i.e. paraffinic or olefinic.

4.3. Effect of hydrocarbon

Experiments were repeated this time with varying C_2H_4 concentrations at a constant oxygen concentration of 11.2%. Figure 6 shows the effect of C_2H_4 concentration on NO reduction with the three different Cu loadings at a temperature of 770K. The results show that the NO conversion increases markedly as the C_2H_4 concentration increases up to a molar ratio of ~ 6 , depending on Cu loading. The dependence of the NO reduction indicates that the NO is being reduced by C_2H_4 rather than other species like CO, especially in the presence of oxygen. With any further increase

in the C_2H_4 concentration, above a molar ratio of $(C_2H_4/NO) > 6$, this kinetic dependence becomes negligible. These experimental data are also in good agreement with previous work^{18,19}.

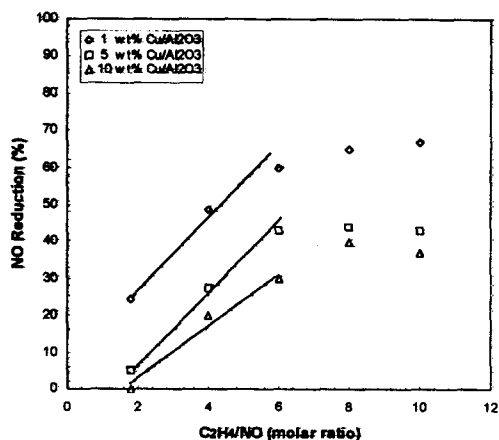


Fig. 6. NO conversion as a function of hydrocarbon concentration with three different Cu loadings ; NO=500 ppm, $O_2=11.2\%$, $T_{cat}=770K$.

In comparison to C_2H_4 (alkene), other alkane hydrocarbons, such as C_2H_6 and C_3H_8 over Cu/Al_2O_3 catalysts, gave very low NO_x reductions of 40 and 24%, respectively, in the absence of oxygen³. As soon as oxygen was introduced into the reacting mixture, the NO reduction decreased drastically and then approached zero at an 11.2% oxygen level. This observed behavior of C_2H_4 over Cu/Al_2O_3 with oxygen for NO reduction within the temperature range of interest supports the findings of Sumiya et al.¹⁹, concerning the individual ranking of hydrocarbons for NO_x reduction reactivity (i.e. alkynes diesel fuel > alkenes > alkanes). This ranking of hydrocarbons for NO_x reduction is similarly maintained for various other catalysts such as Cu, Co, $pt/ZSM-5$, Cu-Mordenite, and other zeolites.

4.4. CO_2 and Nitrogen-containing Byproducts

The injection of C_2H_4 for diesel NO_x reduction leads to concerns over the emissions of CO, CO_2 , and other nitrogenous byproducts. Figure 7 shows the conversion of C_2H_4 to CO_2 and N_2O formation with respect to three different Cu loadings at a molar ratio (C_2H_4/NO) of 6.0. The CO_2 conversion

increases steadily until 720K, and then sharply increases at and above the optimum temperature (810K), reaching about 95%, where little difference was found with different Cu loadings. If fuel addition is considered as a supplementary NO_x reductant, then this higher conversion of hydrocarbons is very important around the optimum temperature. Similar results¹⁰ were previously reported by adding C₂H₄ into the diesel exhaust stream, where the catalyst-out hydrocarbon concentration did not exceed the engine-out hydrocarbon concentration for an extended range of ethylene addition.

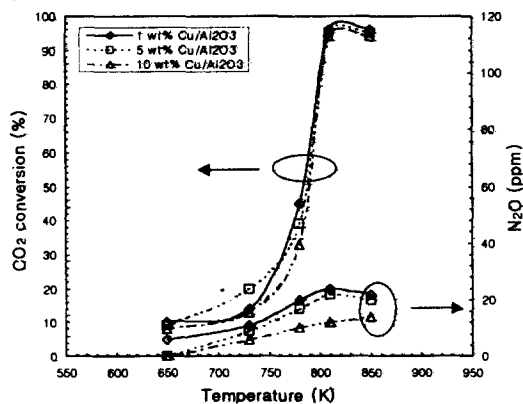


Fig. 7. Conversion of C₂H₄ to CO₂ and N₂O formation during NO reduction with different Cu loadings; NO=500 ppm, C₂H₄/NO=6.0, O₂=11.2%.

As Cu loading increases from 1, 5 to 10wt.%, the N₂O formation then decreases from 25 to 11 ppm at 810K. The temperature dependence of N₂O formation is consistent with that of NO reduction (see Figure 3), which also mirrors the N₂O formation in the SNCR process⁴). However, the results from Radtke et al.¹⁴) showed that with increasing Cu loadings from 0.46, 0.78 to 1.65wt.% on alumina, the N₂O formation was rather increased from 5 to 31 ppm at 740K. They insisted that its formation occurred at active sites involving Cu species since N₂O was not observed over alumina. From both investigations, the optimum Cu loading would appear to be around 1wt.% when NO reduction and N₂O formation reach maximum levels. In addition, a small amount of HCN was also observed

with a C₂H₄ additive, yet no NH₃ byproduct³).

Fortunately, there are commercially available oxidation catalysts that use noble metals (e.g. Pt), so the problem of CO and UHC emissions from HC-SCR processes can be avoided²⁰).

5. Conclusions

The present results show that different Cu loadings as well as reaction parameters, such as temperature, oxygen, hydrocarbon levels and types, significantly influence the NO reduction performance under oxidizing conditions. Temperature window ranges from 720~850K for catalytic NO reduction in which 60% NO reduction is obtained at an optimum temperature of 810K with a 1wt% Cu loading. A temperature shift downwards is not clear with increasing Cu loading. Higher Cu loadings (5 and 10wt.%) favor the formation of bulk crystalline CuO on the surface of alumina, as observed by XRD patterns and SEM images, which decreases the surface area. In contrast, the lower Cu loading (1 wt.%) favors the formation of isolated Cu species (e.g. Cu²⁺ ions), and increases catalytic activity. Thus, the selective reduction of NO in oxidising conditions must be related to the presence of these dispersed, isolated Cu species. As far as C₂H₄ and Cu/Al₂O₃ catalysts are concerned for NO reduction, the presence of oxygen is beneficial below optimum temperatures, yet at higher temperatures above 840K it could be detrimental for NO reduction because of the complete oxidation of C₂H₄. The type of hydrocarbon, e.g. alkene (C₂H₄) and alkanes (C₂H₆ and C₃H₈) affects the NO_x reduction over Cu/Al₂O₃ catalysts, amongst which C₂H₄ proves to be the most effective. In the NO/C₂H₄/O₂ reaction system, small amounts of nitrogenous byproducts, such as N₂O and HCN are observed.

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