A Study of NO+CO Reaction over Various Supported Catalysts in the Presence of O_2 and H_2O

K. Shanmugapriya, Hyun-Seok You,[†] Hyun-Chan Lee,[‡] Dal Ryung Park,[‡] Jung-Seong Lee,[†] and Chul Wee Lee[*]

Advanced Chemical Technology Division, KRICT, Daejeon 305-600, Korea. [*]E-mail: chulwee@krict.re.kr
[†]Center for Gas Utilization, R&D Center, Korea Gas Co., Kyunggi, Ansan 425-790, Korea
Received November 4, 2006

NO and CO are the main gases emitted into the atmosphere from both stationary and mobile combustion systems. These toxic gases represent major form of pollutants and contribute mainly to the formation of smog. acid rain and ozone depletion in the stratosphere. The simultaneous elimination of these two toxic gases leading to non-toxic compounds such as N_2 and CO_2 is considered an efficient process. Although the studied reaction is spontaneous, it is well known that the presence of a catalyst is necessary. For the catalytic reduction of NO_x. reducing agents such as carbon monoxide (CO). hydrogen (H_2). ammonia (NH_3). urea ((NH_2)$_2$CO) and different hydrocarbons are usually being employed.[1,2] Many supports such as alumina, titania. zirconia. ceria were usually used for dispersing the active phase for the elimination of nitrogen oxide. It is well known that supports play an important role in determining the nature and number of active sites. and consequently in the activity of the catalysts. The metal oxides are advantageous for the stability of the catalyst support and/or for enhancement of the catalyst activity under dynamic operations.[3] Among the transition metals studied, copper show a potential activity in the NO+CO reaction and have been extensively studied.[4-6] Sakurai *et al.* tested catalytic activities of cupric oxide and alumina-supported copper oxides in NO reduction by CO.[7] Metal oxides such as Ce and Ni are commonly employed O_2 storage component, which are frequently added to the catalyst to enhance the catalytic active sites. These oxides improve the performance of the catalyst. further making it less sensitive to temporary variations in the air-fuel ratio by getting reversibly oxidized or reduced at typical operating temperatures. Loof *et al.* stated that at higher temperatures, the O_2 storage capacity in catalysts containing Pt, Rh. Ni and Ce supported on Al_2O_3. Ni is found to be the dominant storage metal and Ce predominates over Pt and Rh.[8] The reduced surface of Ce in contact with reduced noble metals is the most effective state of the catalyst and greater activity is detected with decreasing CeO_2 crystallite size.[9] Addition of cerium oxide play an important role in providing oxygen storage by transforming between Ce_2O_3 under reducing conditions and CeO_2 under oxidizing conditions.[10] It is further believed that doped ceria inhibits the deactivation of active components in the reaction due to the sintering of the metals and surface deterioration of the support. Garcia *et al.* pointed out that the Cu-Ce

interaction affected the reactivity of the catalysts towards NO thereby increasing the amount of adsorbed species which in turn lead to high NO adsorption at low temperature.[11] The NO dissociation peaks were shifted towards low temperature upon addition of ZrO_2 onto CuO/TiO_2. indicating NO decomposition activity was higher in $CuO-ZrO_2/TiO_2$ than by CuO/TiO_2.[12] Hernandez *et al.* suggested that the presence of acid-base sites on Pt/ZrO_2-CeO_2 seemed to be important for the NO+CO reaction.[13] The Cu-Ce synergism for NO reduction with CO in the presence of O_2, H_2O and SO_2 has been investigated by Wen and He.[14] The results suggested that the synergistic effect between Cu and Ce ions could enhance the performance of catalyst both in activity and resistance to H_2O and SO_2. Redox Mechanism involving lattice oxygen/oxygen vacancy participation was proposed for CO oxidation on CeO_2.[15] Sayle *et al.* conducted atomic simulation of a CO oxidation mechanism on CeO_2 and suggested that the surface oxygen of CeO_2 is more active than the bulk oxygen.[16] In the present study the importance of (i) method involved in preparation of catalyst, (ii) metal support interaction of catalyst and (iii) Cu-Ce synergistic effect in the NO reduction by CO are discussed.

Experimental Section

The supports used were CeO_2 (Acros Organics), γ-Al_2O_3 (New Acros, ball mill for 17 h). ZrO_2 (Kanto chemical Co., Inc.). TiO_2 (Junsei Chemical Co.. Ltd.). Catapal Alumina (Condea Vista Co.. Ltd.), and Co_3O_4. Co_3O_4 was obtained by thermal decomposition of $Co(NO_3)_2 \cdot 6H_2O$ (Yakuri pure chemicals Co.. Ltd.) in air at 550 °C for 5 h. 5% Cu-Ce modified supports were prepared by incipient wetness impregnation of supports mentioned above with an aqueous solution containing requiste amount of metals. The catalysts were dried in air at 100 °C for 12 h. followed by calcination in an air stream at 500 °C for 2 h.

In the sol-gel method. precursor of alumina *i.e.*. Aluminum iso-propoxide (AIP) was dispersed in water (AIP:H_2O = 1:2) ultrasonically (Power Sonic 410) till a clear translucent stable gel like dispersant is formed. Then it is kept for stirring at 65 °C for about 2 h. Then the slurry is peptised with acetic acid (AIP:AA = 1:1). The aluminium monohydroxide sol thus obtained was refluxed over night by fixing a condenser to it. Then 5% Cu, Ce solution was added

drop by drop into the sol. Again it was stirred vigorously till a uniform gel is obtained. Then the sample is dried at 100 °C for 5 h and calcined at 500 °C for 2 h.

The catalytic reaction was carried out in a quartz glass tubular reactor in a steady-state plug-flow mode. Prior to the catalytic tests, the samples were pretreated at 300 °C in He atmosphere. The catalytic activity was determined under steady state, involving a feed steam with a fixed composition, NO 0.02%, CO 0.08%, CO_2 6% and He 83.9% by volume as a diluent in the presence of 10% O_2. The water content was varied as 3% and 10%. The catalysts were crushed into 20/40 mesh size before packing into the quartz glass tube.

The total gas flow rate and gas hourly space velocity (GHSV) were maintained as 200 cc/min and 20000 h^{-1}, respectively. A chemiluminescence NO_x analyse (KIMOTO model 272), equipped with a catalytic converter for conversion of NO were used for analysis of the effluent gases. The temperature was increased from 300 to 600 °C and the increase in ramping temperature was set as 1 °C/min. The maximum hold temperature at which high NO conversion attained was found after ramping and the effect of water content (3% and 10%) was studied at that particular temperature.

The catalytic activity was calculated using the following formula:

$$[NO]_{conv.} = \{ [NO]_{in} - [NO]_{out} \} / [NO]_{in}$$

Results and Discussion

Table 1 represents the conversion of NO by CO (i) in 10% O_2 atmosphere, (ii) in presence of 3% and 10% H_2O and (iii) maximum hold temperature. Both copper and cerium are found to be focused by several researchers in NO+CO reaction and the following conclusions were thus attained:

(i) Cu^+ ions are found to be active for CO adsorption[14]

(ii) Partially reduced Cu^+ species play a significant role as active species in the catalytic decomposition of NO[17]

(iii) Cu^{2-} ions are active for NO adsorption[18]

Several infrared studies have shown that isocyanate species NCO is formed as an intermediate during the reduction

reaction of NO by CO.[19] NO molecule is kinetically stable[20] and its homolytic dissociation into N and O atoms need a higher energy (153.3 kcal/mol). NO is in a metastable equilibrium state. As a first step CO gets adsorbed on the active copper sites leading to CuCO linear molecule. In the second step, NO reacts with CuCO molecule and leads to CuO and NCO. The formation of NCO is an important process in dissociating the NO molecule. The isocyanate molecule then reacts with the copper oxide which rapidly leads to the formation of elemental N_2 and CO_2.

The monovalent copper atom links to both CO and NO molecule which leads to the isocyanate molecule formation. This is accomplished by the electro positive character of copper which balances with negative charges on N and O atoms. Even the high dispersion and interaction of active copper species on the support contributes to this behaviour. A similar possible reaction intermediate (*cis*-type coordinated species of NO and CO to one iridium atom) leading to N_2 formation has been proposed by Haneda *et al.*[21]

As shown in Table 1, among the catalyst studied 5% Cu-Ce/Co_3O_4 (unsupported) was found to be more active even in the presence of O_2 and water vapour. The strong interaction of copper and cerium leads to replacement of Ce^{4-} ions in the lattice by copper ions, resulting in Cu^- ions and oxygen vacancies, providing extra sites for NO and CO adsorption.[14] The results indicate that the activity of surface-dispersed copper oxide species towards reduction of NO is greatly enhanced by the presence of ceria which stores and releases O_2. The synergistic effect of Cu and Ce has also been well documented in literature.[4,5] The surface layer of unsupported $CuCo_2O_4$ shifts to the reduced state when exposed to NO+CO gas mixture. The specific surface area of the support along with strong metal interaction (in presence of Cu and Ce) plays an important role in attaining the high catalytic activity in NO+CO reaction.

The NO+CO reaction was carried out in presence of 10% O_2 and this obviously oxidizes some of the Cu^- ions into its higher oxidation state (Cu^{2+}) which in turn favours NO adsorption. N_2 is obtained as the main product at higher temperature. The reduction reaction takes place on Cu^{2+} site which promotes NO adsorption, further on reduced copper site which receives O^{2-} ions evolved during NO decomposition. At much higher temperature the well dispersed surface oxide species which are actively engaged in NO conversion are covered by their homologous bulk crystalline metal oxides. The results indicate that the catalytic activity of surface dispersed metal species is greatly influenced by the nature and acidic properties of the support. The performance of catalytic systems involving various transient techniques for NO-CO, N_2O-CO and O_2-CO reactions have been carried out.[22,23] It has been found that under the conditions of O_2+NO+CO gas mixture (with 40% excess of oxidants) the unsupported catalysts are capable to some extent in preserving their activity in NO reduction.[24] Wen *et al.*[14] demonstrated the enhanced performance of Cu-Ce catalyst in NO+CO reaction. The XRD and XPS spectra in the above study well documented the facts that (i) presence of cerium

Table 1. Conversion of NO by CO over various supported catalysts

No	Catalyst	NO Conversion (%)			Maximum hold of temperature (°C)
		Concentration (%)			
		O_2	H_2O		
		10%	3%	10%	
1	5% CuO-CeO₂/Al₂O₃[a]	52	31	32	330
2	5% CuO-CeO₂/ZrO₂	80	46	43	325
3	5% CuO-CeO₂/Co₃O₄	86	74	71	300
4	5% CuO-CeO₂/TiO₂	24	25	25	440
5	5% CuO-CeO₂/ Al₂O₃[b]	63	49	49	350
6	5% CuO-CeO₂/ Al₂O₃[c]	62	44	42	400

[a]Al₂O₃ (New Acros). [b]Catapal Alumina. [c]Al₂O₃ prepared by sol-gel method in this work.

Notes

Bull. Korean Chem. Soc. **2007**, Vol. 28, No. 6   1041

strongly hindered agglomeration of CuO and (ii) low-valent copper is present as Cu⁻. The IR study [25] reveal that Cu⁺ is active for CO adsorption and oxygen vacancy provides the site for NO adsorption. TPR-TPO studies of CuO phase reveals the extent of CuO reduction and Cu(O) re-oxidation and the results indicate that the oxidation of Cu to CuO proceeded in two steps: at first, an oxidation of dispersed copper species and at high temperature, the occurrence of bulk oxidation takes place.[26]

NO conversion over the catalyst prepared by sol-gel technique showed a maximum hold temperature of about 400 °C. The result reveals the fact that there is a high dispersion of metal oxides in small aggregates or domains in the support material which is highly impossible to attain by the conventional methods such as impregnation or ion-exchange. The sol-gel prepared mixed oxides exhibit homogeneity throughout the bulk at the molecular scale and show enhanced acidic properties, high surface area and thermal stability which are the essential criteria for high catalytic activity in NOx reduction process.[27]

In the sol-gel catalyst prepared it is a well known fact that the metal particles were directly incorporated into the framework of the support[28] or partially buried at the surface of the support.[29] Due to this, the metal particles are less exposed to deterioration and prolonged activity is noticed. It is well evident from the result that there prevails a strong metal support interaction in the catalyst which consequently leads to high sintering resistance capability. Since the sol-gel catalysts are prepared from a homogeneous solution containing metal particles as well as support precursors, the metal particles strongly adhere to the support by metal-support oxygen bonding.

From this study, it can be suggested that (1) among the catalyst studied Cu-Ce modified catalyst over Co_3O_4 support shows an excellent conversion even in the presence of O_2 atmosphere and had a high resistance property towards water vapor. The decrease in conversion at higher temperature may be due to surface reduced active species on the support which are considered active sites in NO+CO reaction, and (2) the sol-gel catalyst shows higher hold temperature, since partially buried metal particles are less exposed to deterioration under the reaction conditions.

References

1. Joubert, E.; Courtois, X.; Marecot, P.; Duprez, D. *Appl. Catal. B* **2006**, *64*, 103.
2. Kim, J. W.; You, H.-S.; Lee, H.-C.; Lee, J.-S.; Lee, C. W. *Bull. Korean Chem. Soc.* **2006**, *27*, 1287.
3. Taylor, K. C. *Catal. Rev. Sci. Eng.* **1993**, *35*, 457.
4. Hu, Y.; Dong, L.; Wang, J.; Ding, W.; Chen, Y. *J. Mol. Catal.* **2000**, *162*, 307.
5. Xiaoyuan, J.; Liping, L.; Yingxu, C.; Xiaoming, Z. *J. Mol. Catal. A: Chem.* **2003**, *197*, 193.
6. Zhu, H.; Shen, M.; Gao, F.; Kong, Y.; Dong, L.; Chen, Y.; Jian, C.; Liu, Z. *Catal. Commun.* **2004**, *5*, 453.
7. Sakurai, K.; Okamoto, Y.; Imanaka, T.; Teranishi, S. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 1732.
8. Loof, P.; Kasemo, B.; Heck, K. H. *J. Catal.* **1989**, *118*, 339.
9. Nunan, J. G.; Robota, H. J.; Cohn, M. J.; Bradley, S. A. *J. Catal.* **1992**, *133*, 309.
10. Gonzalezvelasco, J. R.; Entrena, J.; Gonzalezmacros, J. A.; Gutierrezortiz, J. I.; Gutierrezortiz, M. A. *Appl. Catal. B* **1994**, *3*, 191.
11. Garcia, M. F.; Rebello, E. G.; Ruiz, A. G.; Conesa, J. C.; Soria, J. *J. Catal.* **1997**, *172*, 146.
12. Jiang, X.; Ding, G.; Lou, L.; Chen, Y.; Zheng, X. *Catal. Today* **2004**, *93-95*, 811.
13. Hernandez, R. P.; Aguilar, F.; Gomez-Cortes, A.; Diaz, G. *Catal. Today* **2005**, *107-108*, 175.
14. Wen, B.; He, M. *Appl. Catal. B: Envir.* **2002**, *37*, 75.
15. Breysse, M.; Guenin, M.; Claudel, B.; Latreille, H.; Veron, J. *J. Catal.* **1972**, *28*, 54.
16. Sayle, T. X. T.; Parker, S. C.; Catlow, C. R. A. *J. Chem. Soc. Chem. Commun.* **1992**, 977.
17. Anpo, M.; Matsuko, M.; Shioya, Y.; Yamashita, H.; Giamello, E.; Morterra, C.; Che, M.; Patterson, H. H.; Webber, S.; Ouellette, S.; Fox, M. *J. Phys. Chem.* **1994**, *98*, 5744.
18. Fu, Y.; Tian, Y.; Lin, P. *J. Catal.* **1991**, *132*, 85.
19. Miquel, F. M.; Hung, C. H.; Katz, J. L. *J. Mater. Res.* **1993**, *8*, 2404.
20. Pratsinis, S. E. *Prog. Energy Combust. Sci.* **1998**, *24*, 197.
21. Haneda, M.; Yoshinari, T.; Sato, K.; Kintaichi, Y.; Hamada, H. *Chem. Commun.* **2003**, 2814.
22. Kaspar, J.; Leitenburg, C. de; Fornasiero, P.; Trovareli, A.; Graziani, M. *J. Catal.* **1994**, *146*, 136.
23. Sadhankar, R. R.; Lynch, D. T. *J. Catal.* **1994**, *149*, 278.
24. Panayotov, D.; Khristova, M.; Mehandjiev, D. *J. Catal.* **1995**, *156*, 219.
25. Huang, S. J.; Walters, A. B.; Vannice, M. A. *J. Catal.* **1998**, *173*, 229.
26. Bennici, S.; Carniti, P.; Gervasini, A. *Catal. Lett.* **2004**, *98*, 187.
27. Enache, D.; Auberger, R.; Esterle, K.; Revel, R. *Colloids Surf. A: Physicochem. Eng. Aspects* **2003**, *220*, 223.
28. Lopez, T.; Gomez, R.; Novaro, O.; Rmirez-Solis, A.; Sanchez-Mora, E.; Castillo, S.; Poulain, E.; Martinez-Magadan, J. M. *J. Catal.* **1993**, *141*, 114.
29. Bosch, P.; Lopez, T.; Lara, V. H.; Gomez, R. *J. Mol. Catal.* **1993**, *80*, 299.