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Metal Halide Catalyst for Reduction of Nitric Oxide with Ammonia

Akio Nishijima,* Yoshimichi Kiyozumi, Akifumi Ueno, Minoru Kurita,
Hiroyuki Hagiwara, Toshio Sato, and Naoyuki Todo
National Chemical Laboratory for Industry, 2-19-19, Mita, Meguro-ku, Tokyo 153

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Counter anions of active components on catalysts were found to affect catalytic activities for NO reduction with NH_3. Halide ions promoted activity in copper and iron catalysts, but lowered it in chromium and manganese catalysts. The most favorable electronic state of a cation on catalysts was investigated by changing counter anions and/or carriers.

In the catalytic reduction of nitrogen oxides with ammonia the reduction rate is markedly accelerated by the presence of oxygen, no undesirable by-product being found by the reaction between reducing agents and components in flue gas. The method seems to be most advantageous for the reduction of nitrogen oxides (NO_x) emissions from stationary combustion equipments.[1-3] Metal oxide supported catalysts such as Fe_2O_3, V_2O_5, CuO, and MoO_3 on Al_2O_3 or TiO_2 are being employed. However, they are used at reaction temperatures above 300 °C in order to obtain effective reduction of NO_x. From an economical viewpoint, catalysts active at lower temperatures are desirable, since temperatures of flue gases emitted from a coke oven or sintering furnace are lower than 200 °C.

We have explored new catalysts having higher activity at low temperature and found that the activity of metal sulfate catalysts in the lower temperature region is higher than that of metal oxide catalysts.[4] This indicates that the anion of these metal compounds affects the catalytic activity for NO reduction. We have examined the effect of the counter anions and found that the halide catalysts are effective for producing activity at lower temperatures.[5]

In order to find the most favorable electronic state of cations of the catalysts, a study on metal halides has been made by changing anion species of the catalysts and carries.

Experimental

Catalyst. Metal halide and metal sulfate catalysts were prepared by impregnating preformed γ-Al_2O_3 (diam. 1.5 mm) with aqueous solutions of halides and sulfates, respectively. After being impregnated at 40 °C for 5 h, the catalysts were dried at 120 °C for 3 h, and then calcined at 200 °C for 3 h. In the case of metal oxide catalysts, the catalysts were prepared by calcining at 500 °C for 3 h, after being impregnated with metal nitrates, the cation contents being kept constant (8 wt % and 4.7 wt %) in order to examine the effect of counter anions. The copper catalysts used were $CuBr_2$–Al_2O_3, $CuSO_4$–Al_2O_3, $CuCl_2$–Al_2O_3, and CuO–Al_2O_3. In order to examine carrier effects on the catalytic activities, 15 wt % of $CuBr_2$ supported on SiO_2, active carbon and Al_2O_3 were used.

Activity Measurement. Figure 1 shows a flow diagram of the apparatus. The reactor is a stainless steel tube, length 200 mm, diam. 15 mm, set in a tubular furnace, length 250 mm. After introducing 10 ml of the catalyst into the reactor, activity measurements were carried out under space velocity of 15000 h^{-1}. As a standard feed stream, a gas mixture consisting of NO 300 ppm, NH_3 300 ppm, O_2 5 vol %, and N_2 balance gas was used. Analyses of NO, NO_2, and NH_3 were made by means of chemiluminescence type NO_x and NH_3 analyzer.

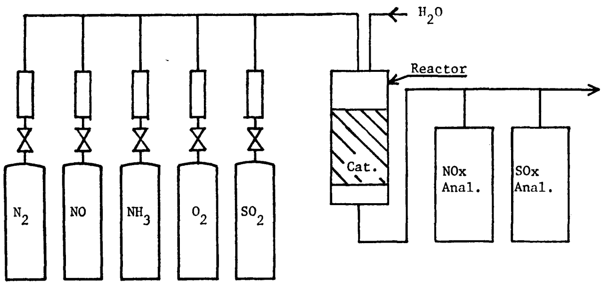

Fig. 1. Flow diagram of apparatus used.
□ : Rotor meter, |><| : variable valve.
Each cylinder contained 1 vol % of NO, NH_3, or SO_2.

Property of Catalyst. The amounts of NH_3 and NO adsorption on the catalysts were measured using a thermogravimeter (Shimadzu Co. DT 20) in N_2 feed stream (1 l/h) containing 5 vol % O_2. An X-ray photoelectron spectrometer (XPS) (Dupont Co. 650B) was used to measure the electronic states of the cations and anions in active components. Mg $K\alpha$ radiation was used to obtain XPS spectra. All binding energy values were refered to C 1s of contaminant carbon (285.0 eV).

Results

Copper Salt Catalyst. *Effect of Anion on Catalytic Activity*: In the reaction of NO removal, the activities of the catalysts increased with cation content, reaching a maximum at a certain cation content. Thus, for the measurement of relative activities the catalysts with lower cation content whose activity does not reach maximum were used. In the case of CuO–Al_2O_3, $CuSO_4$–Al_2O_3, and $CuCl_2$–Al_2O_3, Cu content was 8 wt%. In the case of $CuBr_2$–Al_2O_3 with 8 wt% of Cu, however, the activity attained saturation. The cupric ion content of 4.7 wt% was selected for a comparison of the anion effect of Br^- with that of Cl^- on the catalytic activities of $CuBr_2$ and $CuCl_2$ catalysts. The effect of anions on the catalytic activity is shown in Fig. 2. The activity order of the catalysts in lower temperature region was: $CuBr_2 > CuCl_2 > CuSO_4 > CuO$.

Effect of Carrier on Catalytic Activity: The effect of carriers on catalytic activity was investigated using γ-Al_2O_3, SiO_2, and active carbon (AC). The results are shown in Fig. 3. The activities decreased in the order: AC $>$ γ-Al_2O_3 $>$ SiO_2.

Amount of Adsorption of NO and NH_3: It was found

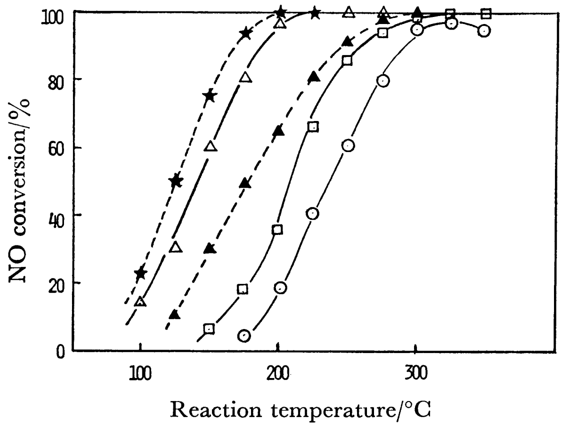

Fig. 2. Effect of anion on catalytic activity of copper salt supported catalyst.
Carrier: γ-Al_2O_3.
Active component:
—— Cu content; 8 wt %,
○: CuO, □: $CuSO_4$, △: $CuCl_2$.
---- Cu content; 4.7 wt %,
▲: $CuCl_2$, ★: $CuBr_2$.
Gas composition:
NO 300 ppm, NH_3 300 ppm, O_2 5 vol %, N_2 balance.
Space velocity: 15000 h^{-1}.

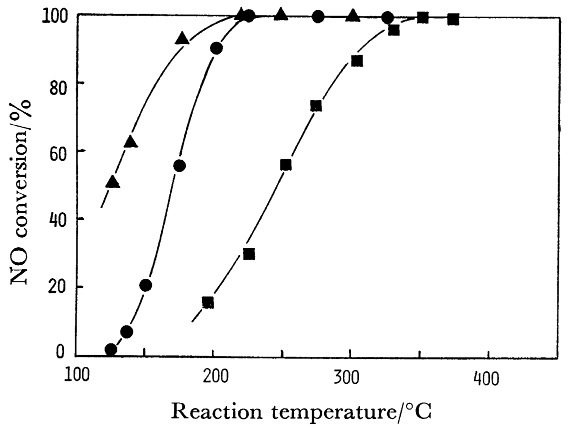

Fig. 3. Effect of carrier on catalytic activity of copper salt supported catalyst.
Carrier:
■: SiO_2, ●: γ-Al_2O_3, ▲: active carbon.
Active component: $CuBr_2$ (15 wt %).
Gas composition:
NO 300 ppm, NH_3 300 ppm, O_2 5 vol %, N_2 balance
Space velocity: 15000 h^{-1}.

Table 1. Amounts of NH_3 and NO adsorbed on the catalysts

	Amount of NH_3	Amount of NO
	mmol/l g of cat.	mmol/l g of cat.
$CuSO_4$-Al_2O_3	0.29	0.14
$CuBr_2$-Al_2O_3	0.21	0.20
CuO-Al_2O_3	0.16	0.25

Measurements were carried out with a thermogravimeter at 150 °C in N_2 feed stream containing 5 vol% of O_2. Cu content of each catalyst was 3.7 wt%.

Table 2. Electronic states of copper ions in the catalysts

	Cu $2p_{3/2}$ binding energy/eV
A) Effect of anions	
$CuSO_4$-Al_2O_3[a]	933.6
$CuBr_2$-Al_2O_3[a]	934.2
CuO-Al_2O_3[a]	934.9
B) Effect of carriers	
$CuBr_2$-Al_2O_3[b]	934.2
$CuBr_2$-Active carbon[b]	934.5
$CuBr_2$-SiO_2[b]	934.8

a) Cu content of each catalyst was 3.7 wt%. b) 15 wt% of $CuBr_2$ was supported on each carrier.

Table 3. Binding energies of N 1s for adsorbed NH_3 and NO on the copper catalysts

	N 1s binding energy/eV	Assignment
CuO-Al_2O_3+NH_3	402.1	NH_4^+
$CuSO_4$-Al_2O_3+NH_3	401.8	NH_4^+
$CuBr_2$-Al_2O_3+NH_3	402.0	NH_4^+
NH_4Br	401.9	
V_2O_5+NH_3	400.9[8]	NH_4^+ [8]
CuO-Al_2O_3+NO+O_2	407.5	NO_3^-
$CuSO_4$-Al_2O_3+NO+O_2	407.3	NO_3^-
$CuBr_2$-Al_2O_3+NO+O_2	407.4	NO_3^-
V_2O_5+NO+H_2O	406.2[8]	NO_3^- [8]
NH_4NO_3	401.8, 407.4	

that the amount of NH_3 adsorbed on $CuSO_4$-Al_2O_3 catalyst is 1.8 times that on CuO-Al_2O_3 catalyst (Table 1). The amount of NH_3 adsorbed on $CuBr_2$-Al_2O_3 catalyst, which showed the highest activity for NO reduction at lower temperature, is 1.3 times that on

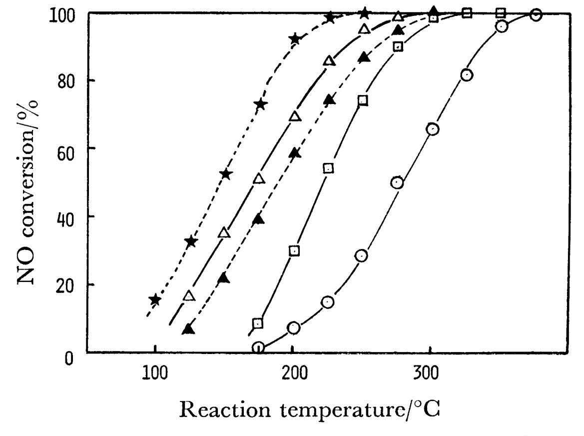

Fig. 4. Effect of anion on catalytic activity of iron salt supported catalyst.
Carrier: γ-Al_2O_3.
Active component:
——Fe content; 7 wt %,
○: Fe_2O_3, □: $Fe_2(SO_4)_3$, △: $FeCl_3$.
----Fe content; 3.7 wt %,
▲: $FeCl_3$, ★: $FeBr_3$.
Gas composition:
NO 300 ppm, NH_3 300 ppm, O_2 5 vol %, N_2 balance.
Space velocity: 15000 h^{-1}.

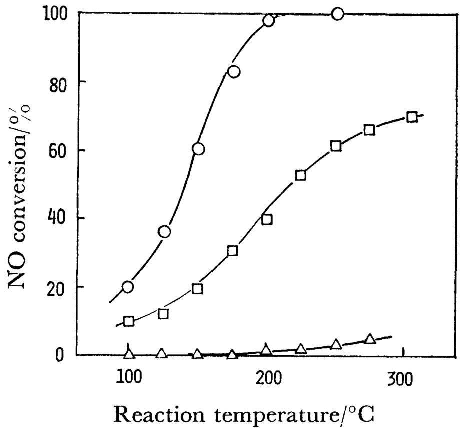

Fig. 5. Catalytic activity of chromium, cerium and manganese halide supported catalyst.
Carrier: γ-Al_2O_3.
Active component:
○: $CeCl_2$, □: $MnCl_2$, △: $CrBr_3$.
Cr, Ce and Mn content were 5 wt %.
Gas composition:
NO 300 ppm, NH_3 300 ppm, O_2 5 vol %, N_2 balance.
Space velocity: 15000 h^{-1}.

CuO-Al_2O_3 catalyst. The order of the amount of NH_3 adsorption is $CuSO_4$-Al_2O_3>$CuBr_2$-Al_2O_3>CuO-Al_2O_3, and that of NO adsorption on these three catalysts CuO-Al_2O_3>$CuBr_2$-Al_2O_3>$CuSO_4$-Al_2O_3.

Electronic State of Cation and Adsorbed NH_3 and NO: The effect of anions and carriers on electronic states of the cation in the catalysts obtained by using X-ray photoelectron spectrometer is given in Table 2. The electronic state of copper ions was found to depend on the kind of both anion and carrier. The electronic states of copper ions become electropositive in the order: $CuSO_4$>$CuBr_2$>CuO. On the other hand, when carriers were changed the electronic states of copper ions become Al_2O_3>AC>SiO_2. Binding energies of N 1s for adsorbed NH_3 and NO on the copper catalysts are given in Table 3. The binding energies of adsorbed NH_3 and NO agree with those of NH_4^+ and NO_3^-, respectively.

Iron Salt Catalyst. Similar experiments were carried out on iron salt catalysts. Figure 4 shows the result obtained for ferric salt supported catalysts. The effect of anions on activity was found to be in the same order as cupric salt catalysts: $FeBr_3$>$FeCl_3$>$Fe_2(SO_4)_3$>Fe_2O_3.

Other Metal Salt Catalyst. Effects of anions on catalytic activity were also investigated for transition metal compounds. Some metal halide catalysts such as $CeCl_2$ or $MnCl_2$ were found to show high activity at lower temperatures (Fig. 5). No activity was observed on $CrBr_3$, $ZnBr_2$, and $NiBr_2$ supported catalysts at lower temperatures. In the case of chromium salt catalysts, the activity order of the catalysts is: Cr_2O_3>$Cr_2(SO_4)_3$>$CrBr_3$.

Discussion

In the cases of Cu, Fe, and Ce, it was shown that the activity of metal halide supported catalysts is higher than that of oxide and sulfate supported catalysts. This indicates that among the anions we investigated, halide anions are the most effective for producing active states. However, catalytic activity and the activity order (Cu, Ce>Fe>Mn>Ti) obtained on metal halide suppored catalysts were found to differ from those of metal oxide suppored catalysts (Mn>Cr>Cu>Fe). In contrast, in the case of chromium metal, the activity of the halide supported catalyst was lower than that of oxide or sulfate supported catalyst. It seems that both cation and anion species of active components affect activity for NO reduction and that the selection of appropriate combination of a cation and an anion is essential for producing a highly active state.

Both copper oxide and halide supported catalysts show high activity at lower temperatures. Thus copper compound supported catalysts were studied in detail.

NO was predominantly reduced by NH_3 to N_2, no N_2O being detected. This is the most characteristic difference from the case in which CO or H_2 is used as a reduction agent. According to Otto and Shelef, in the reduction by CO or H_2, the participation of two molecules of NO is needed for the selective production of N_2; when NH_3 is used as a reduction agent, N-N bond is easily produced in the reaction of NO and NH_3.[6] In fact, Shelef found by using nitrogen isotope, that $^{15}N^{14}N$ is mainly produced by the reaction of ^{14}NO and $^{15}NH_3$.[7] This indicates that adsorption of both NH_3 and NO in the neighboring sites on the catalyst is necessary for reaction.

According to the results obtained by XPS, NH_3 and NO seem to undergo adsorption on the catalysts in the form NH_4^+ and NO_3^-, respectively.[8] It seems that the amount of NH_3 adsorbed on the catalysts decreases when the electronic state of the cation changes from an electropositive state to an electronegative one, and that the amount of NO adsorbed decreaes when the electronic state of the cation changes from an electronegative state to an electropositive one. Actually, the order of the amounts of NH_3 and NO adsorbed on the catalyst (Table 1) agreed with those of the electropositivity and the electronegativity of the cation (Table 2-A).

From the results we realize that the most favorable electronic state of the cation should be selected by changing counter anions in order to obtain proper amounts of both adsorbates of NH_3 and NO. In fact, the catalytic activity decreased when the electronic state of the cation changed to the electronegative ($CuSO_4$) or to the electropositive one (CuO) as compared with $CuBr_2$-Al_2O_3 catalyst (Fig. 2 and Table 2-A).

In these supported catalysts, Al_2O_3 or AC is usually employed as a carrier. The carriers are also considered to affect the electronic state of the cation of active components. When we change the carriers, the electronic state of the cation changes considerably (Table 2-B). The relation between the catalytic activity (Fig. 3) and the electronic states of the cation (Table 2-B) was the same as that obtained by changing counter anions. The result seems to support the above conclusion that the most favorable electronic state of the cation can be obtained by a proper combination of the cation with a counter anion and a carrier for high activity.

From a practical viewpoint, catalysts are required to be resistant against water vapor or SO_2 in a reaction gas, since they are usually contained in a flue gas emitted from stationary combustion equipments. The metal halide catalysts which show high activity at lower temperatures were not poisoned by water vapor, but their catalytic activity was found to decrease gradually when SO_2 was contained in the reaction gas. This is due to the change of the active component from $CuBr_2$ to $CuSO_4$. The electronic state of copper ions in deactivated $CuBr_2$–Al_2O_3 catalysts was found to be the same as that of $CuSO_4$–Al_2O_3 catalyst.

References

1) S. Jarros and J. Krizek, *Int. Chem. Eng.*, **8**, 261 (1968).

2) G. Chakrabarti and C. Chu, *Atmos. Environ.*, **6**, 297 (1972).

3) P. L. Klimisch and K. C. Taylor, *Env. Sci.* & *Technol.*, **7**, 127 (1973).

4) N. Todo, M. Kurita, H. Hagiwara, A. Ueno, and T. Sato, The Japan-U. S. A. Seminar on Catalytic NO_x Reactions, November 1975, Preprints 3-1.

5) N. Todo, A. Nishijima, A. Ueno, M. Kurita, H. Hagiwara, T. Sato and Y. Kiyozumi, *Chem. Lett.*, **1976**, 897.

6) K. Otto and M. Shelef, *J. Phys. Chem.*, **76**, 37 (1972).

7) M. Shelef, The Japan-U. S. A. seminar on Catalytic NO_x Reaction, November 1975, Preprints 1-1.

8) M. Takagi, T. Kawai, M. Soma, T. Onishi, and K. Tamaru, *Shokubai*, **18**, 4, 127 (1976).