CHEMISTRY LETTERS, pp. 897-900, 1976. Published by the Chemical Society of Japan

NEW METAL HALIDE CATALYSTS FOR REDUCTION OF NITRIC OXIDE WITH AMMONIA

Naoyuki TODO, Akio NISHIJIMA, Akifumi UENO, Minoru KURITA,
Hiroyuki HAGIWARA, Toshio SATO, and Yoshimichi KIYOZUMI
National Chemical Laboratory for Industry, 2-19-19, Mita,
Meguro-ku, Tokyo 153

The effect of counter anions on the catalytic activities of cupric and ferric ions, when salts of them are used as catalysts for the reduction of nitric oxide with ammonia, was investigated. The order of the co-catalyst activity of the counter anions investigated is Br^-, Cl^-, $SO_4{}^{2-}$, and O^{2-}.

The removal of nitrogen oxides from flue gas involves important and complex problems.[1~3] Among various techniqes proposed for reducing nitrogen oxides emissions, catalytic reduction of nitric oxide with ammonia has been considered to be one of the most favorable methods in the reduction of NO emissions from stationary combustion equipments.[4~7] In this ammonia method, metal oxide supported catalysts such as CuO (or Fe_2O_3, or V_2O_5) on gamma-alumina are now practically applied. These catalysts are currently used at reaction temperatures above 300 °C. From economical point of view, however, catalysts which are active at lower temperatures are desirable. The present authors have been trying to find new type of catalysts having higher activity at temperatures as low as possible. The activity of metal sulfate catalysts in the lower temperature region has been shown higher than that of metal oxide catalysts.[8] This fact seems to indicate that the anions of those metal compounds affect the catalytic activity of NO reduction to some extent. Upon this idea, the counter anions were varied, from oxides and sulfates, to chlorides and bromides. The halide catalysts showed higher activities than those of the oxide and sulfate catalysts.

The catalysts employed in this work were prepared by impregnating preformed gamma-alumina spheres (1.5 mm in diameter, surface area 250 m^2/g, average pore radius 58 Å, alkali content less than 0.01 wt%) with aqueous solutions of metal halides or metal sulfates. After the impregnation, the catalysts were dried for 3 hr at 120 °C, and then calcined in air at 200 °C for 3 hr. Metal oxide catalysts were prepared by calcining in air at 500 °C. The cation content in these catalysts was kept constant so as to be able to examine definite effect of anions. Activity measurements were carried out using a conventional flow reactor (25 mm in diameter) under space velocity of 15,000 hr^{-1}. As a standard feedstream, the gas mixture consisting of NO 300 ppm, NH_3 450 ppm, O_2 5 vol%, water vapor 9.2 vol%, SO_2 200 ppm, and N_2 balance gas was used. Analysis of NO and NH_3 were made by means of chemiluminescence type NOx analyzer and chemical method indicated in JIS-K-0091, respectively.

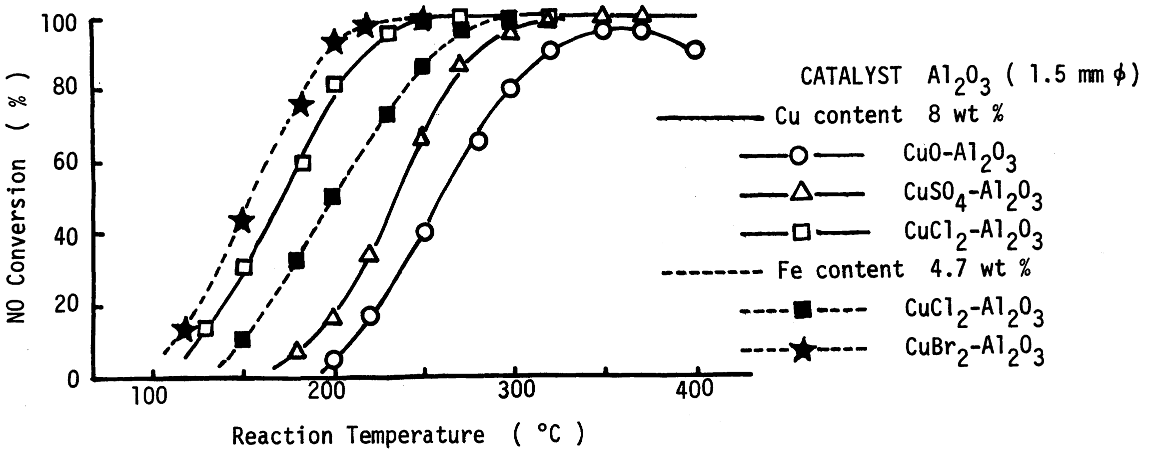

FIG. 1. EFFECT OF ANIONS ON CATALYTIC ACTIVITY OVER COPPER SALT SUPPORTED CATALYSTS.

Gas Composition : NO 300 ppm, NH_3 450 ppm, O_2 5 vol %, H_2O 9.2 vol %, SO_2 200 ppm, N_2 balance.

Space Velocity : 15,000 hr^{-1}.

In the reaction of NO removal, it was observed that the activities of the catalysts increased with the increase of cation content and were saturated over a certain cation content.

The copper content in $CuO-Al_2O_3$, $CuSO_4-Al_2O_3$, and $CuCl_2-Al_2O_3$ were 8 wt%. In the case of $CuBr_2-Al_2O_3$, the activity curve has already reached the saturation region at 8 wt%. Accordingly the cupric ion content of 4.7 wt% was used when comparing the difference between the anion effects of Br^- and Cl^- on the catalytic activities of $CuBr_2$ and $CuCl_2$ catalysts. The effect of anions on the catalytic activity is shown in Fig. 1. In the lower temperature region, the activity of $CuCl_2-Al_2O_3$ catalyst was higher than those of $CuSO_4-Al_2O_3$ and $CuO-Al_2O_3$ catalysts. The activity of $CuBr_2-Al_2O_3$ catalyst was the highest. Therefore, the activity order of the catalysts used was, $CuBr_2 > CuCl_2 > CuSO_4 > CuO$. Similar experiments were made using iron catalysts. Figure 2 shows the results obtained by ferric salts supported on gamma-alumina. The order of the activity of ferric salts was found to be $FeBr_3 > FeCl_3 > Fe_2(SO_4)_3 > Fe_2O_3$. This order agrees with that obtained with cupric salts. From the above results, it is considered that the order of co-catalytic activities is, Br^-, Cl^-, SO_4^{2-}, and O^{2-}.

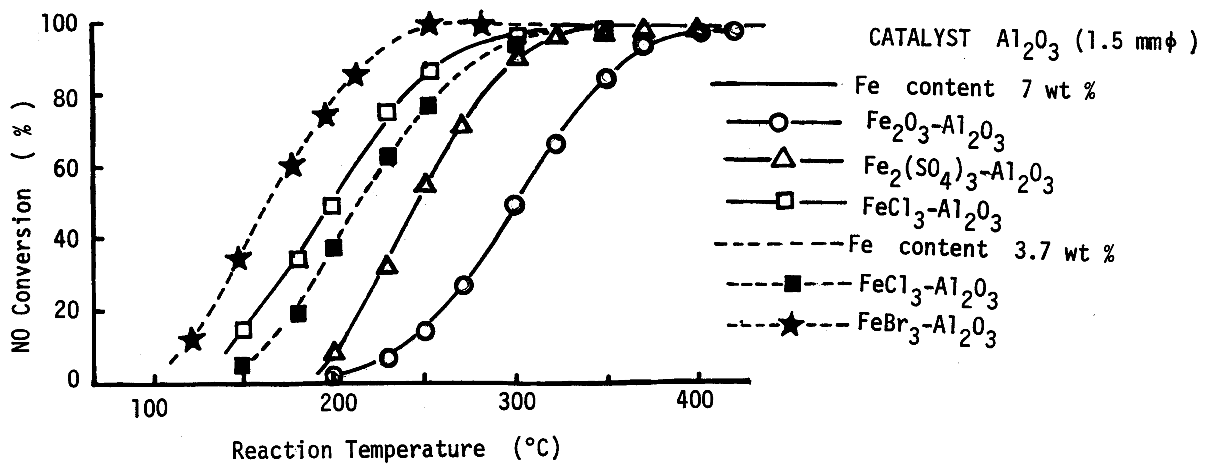

FIG. 2. EFFECT OF ANIONS ON CATALYTIC ACTIVITY OVER IRON SALT SUPPORTED CATALYSTS.

Gas Composition : NO 300 ppm, NH_3 450 ppm, O_2 5 vol %, H_2O 9.2 vol %, N_2 balance.

Space Velocity : 15,000 hr^{-1}.

As for other transition metal compounds, effects of anions on the catalytic activity could not be confirmed because of instabilities of metal halides at reaction temperatures. Although the above conclusion has been obtained with only cupric and ferric salts, it may be possible to say that the weaker the electronegativity of the element which forms the counter anion is, the higher is the co-catalyst activity.

REFERENCES

1) W.Bartok, A.R.Crawford, and A.Skopp, Chem. Eng. Prog.,67, 64, (1971).
2) T.H.Maugh, Science, 177, 685, 1090, (1972).
3) O.J.Adlhart, S.G.Hindin, and R.E.Kenson, Chem. Eng. Prog., 67, 73, (1971).
4) G.Chakrabarti and C.Chu, Atomospheric Enviroment, Pergamon Press, 6, 297, (1972).
5) S.Jarros and J.Krizek, International Chemical Engineering, 8, 261. (1968).
6) K.Otto and M.Shelef, J.Phys. Chem., 76, 37, (1972).
7) P.L.Klimisch and K.C.Taylor, Env. Sci. & Technol., 7, 127, (1973).
8) N.Todo, M.Kurita, H.Hagiwara, A.Ueno, and T.Sato, The Japan-U.S.A. Seminar on Catalytic NOx Reactions, Susono, Japan, (1975).

(Received June 30, 1976)