CHEMISTRY LETTERS, pp. 521-524, 1977. Published by the Chemical Society of Japan

LOW TEMPERATURE ACTIVITY OF THE COPPER OXIDE CATALYST SUPPORTED ON ACTIVATED CARBON FOR REDUCTION OF NITRIC OXIDE WITH AMMONIA

Fumio NOZAKI, Kenichiro YAMAZAKI, and Takashi INOMATA
Department of Industrial Chemistry, Faculty of Engineering,
Chiba University, Yayoi-cho, Chiba 280

The copper oxide catalyst supported on activated carbon showed a high activity even at the low temperature near 100 °C. The correlation between NO conversion and reaction temperature was really complicated, having both a maximum in the temperature range 120 - 150 °C and a minimum at the temperature near 300 °C. An appropriate amount of CuO supported on activated carbon was about 5 wt%.

The catalytic removal of nitrogen oxides from flue gas has recently been investigated very actively from a standpoint of air pollution controll.[1] Among various techniques, the reduction process of nitrogen oxides using NH_3 as a reducing agent is known to be an important and practical method.[2-3] Much useful imformations on the catalyst have already been presented ; various types of the catalysts such as noble metals,[4] metal oxides,[5] metal sulfates,[6] metal halides,[7] and transition metal ion-exchanged zeolites[8] were known to be active for the reaction. In particular, the metal halides and the metal ion-exchanged zeolites were known to be of interest to exhibit the low temperature activity.[7-8] The present paper describes briefly the low temperature activity of CuO catalyst supported on activated carbon.

Almost all the catalysts employed in this work were prepared by impregnating carrier pellets (1 - 2 mm in size) with aqueous solution of $Cu(NO_3)_2$. Activated carbon (Granular Charcoal, Wako), silica (prepared from Colloidal Silica Sol, Nissan Kagaku) and alumina (Neobead C-4, Mizusawa) were used as carriers of the catalysts. After impregnation, the catalysts were dried at 120 °C, and then calcined at 350 °C for 3 hr in air. The CuO catalyst without carrier was prepared from $Cu(NO_3)_2$ by precipitation with NH_4OH, and followed by calcination at 350 °C in air. Catalytic activity tests were carried out by using a conventional flow reactor (18 mm in diameter). The gas mixture consisting of NO 3 %, NH_3 2 % and He balance gas was passed through the catalyst bed of 0.5 g under the total gas flow rate of 60 ml/min (contact time, 0.5 g sec/ml). Analyses of the reaction products and reactor feed were made by means of gaschromatography using Porapak Q and Molecular Sieve 13 X columns.

Figure 1 shows conversion-temperature curves of various catalysts, where the NO conversion is the fraction of NO converted to N_2 and N_2O. The activity-temperature curves of CuO-activated carbon catalysts (curves 1 and 2) showed an unusual profile with a maximum at temperatures ranging from 120 to 150 °C, passed through a minimum at about 300 °C, and then increased again with an increase in temperature. This

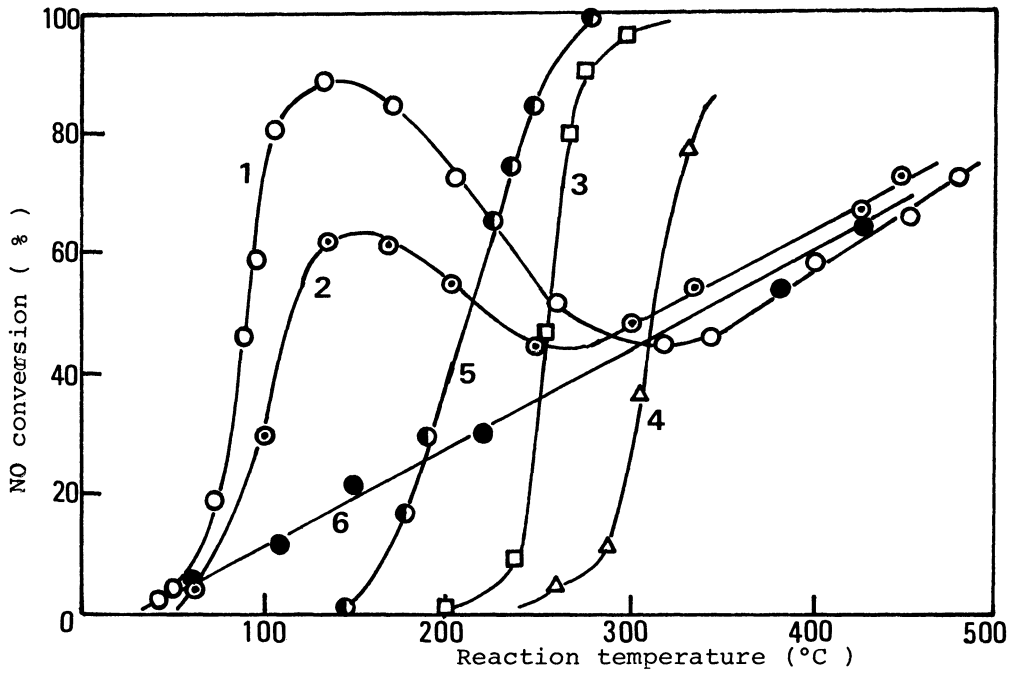

Fig.1. Temperature-conversion curves of various catalysts. NO:1.8 ml/min, NH_3:1.2 ml/min, He:57 ml/min,contact time:0.5 g sec/ml.
1. CuO(5 wt%)-Activated carbon, 2. CuO(3 wt%)-Activated carbon, 3. CuO(5 wt%)-Silica, 4. CuO(5 wt%)-Alumina, 5. CuO without carrier, 6. Activated carbon.

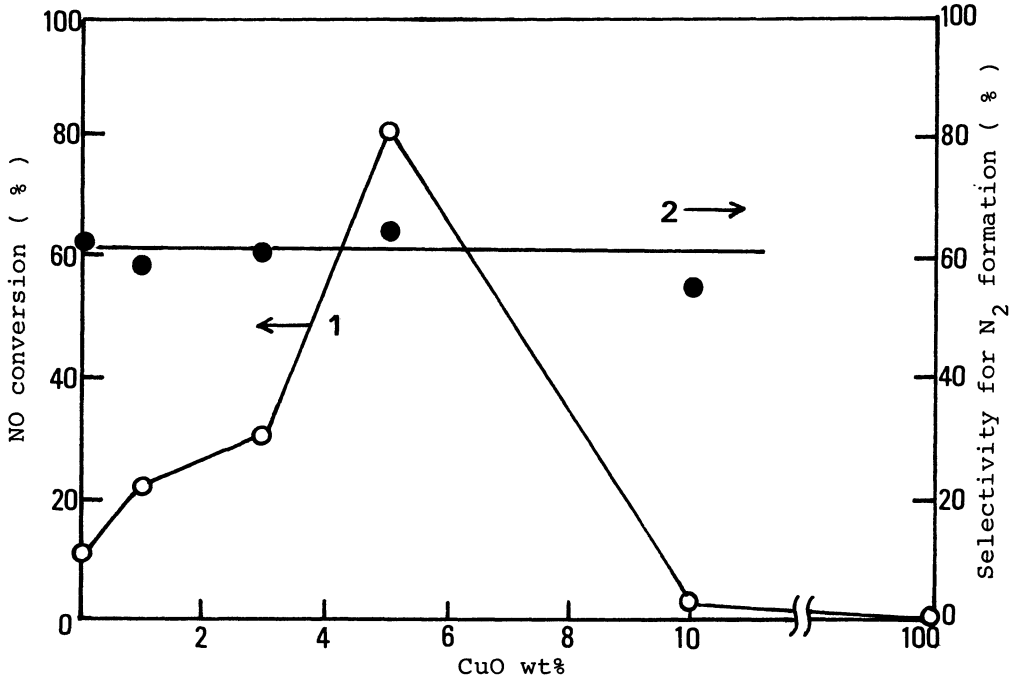

Fig.2. Influence of the supported amount of CuO upon the activity and selectivity. Catalyst: CuO-Activated carbon, Reaction temperature: 104 °C.
1. NO conversion, 2. Selectivity for N_2 formation.

complicated activity-temperature curve was approximately reproducible; the activity decrease in the temperature above 150 °C was not due to unrestorative change of the catalyst but an intrinsic phenomenon, because the activity-temperature curves could be retraced reversibly by changing temperature. In the cases of the catalysts of CuO-silica (curve 3), CuO-alumina (curve 4) and CuO without carrier (curve 5), there was no such low temperature activity as was observed in the CuO-activated carbon catalyst, and their activities indicated merely a monotonous increase with temperature. The catalytic activity expressed in units per gram of the catalyst was in order of CuO without carrier > CuO-silica > CuO-alumina.

Silica or alumina itself did not show any activity for the NO- NH_3 reaction. In contrast, activated carbon served as a week catalyst for the reaction. When NO or NH_3 was separately passed through the packed bed of activated carbon, there was absolutely no reaction over wide range of temperature. The characteristic activity-temperature curve of CuO-activated carbon catalyst (curves 1 and 2 in Fig.1) cannot be reproduced by simply overlapping the activity-temperature curves of CuO (curve 5) and that of activated carbon (curve 6). The low temperature activity of CuO-activated carbon catalyst observed in the temperature below 200 °C is speculated to be due to a cooperative action of the dispersed CuO and the activated carbon, on which NO and NH_3 were densely adsorbed. It is obvious from Fig.1 that the activity of CuO-activated carbon catalyst in the temperature above 300 °C is practically attributable to the catalytic action of activated carbon itself.

A quite similar activity-temperature curve to those of curves 1 and 2 in Fig.1 has already been reported by Seiyama et al.[8] investigated Cu(II)-Y-zeolite catalysts. In the case of CuO-activated carbon catalyst, the reason for appearance of the bell-type activity-temperature curve is still not elucidated. But, it may be attributed to the change in the valence of copper ion depending upon reaction temperature, by reference to the reaction mechanism on Cu(II)-Y-zeolite catalysts proposed by Seiyama et al.[8] It should be emphasized in this report, however, that the activity of CuO-activated carbon catalyst expressed in units per gram of the catalyst is significantly higher than those of Cu(II)-Y-zeolite catalysts.

Figure 2 shows the results obtained in the experiment in which influence of the supported amount of CuO upon the catalytic activity and selectivity was investigated with CuO-activated carbon catalyst at the low temperature of 104 °C. It can be seen that an appropriate amount of CuO is about 5 wt%. In general, the selectivity for N_2 formation varied in the range ca. 60 - 80 %, depending upon catalyst species and reaction temperature. As is clearly seen from Fig.2, the selectivity is about 60 % at the temperature of 104 °C and it is almost independent of a change in CuO wt%. At the low temperature, significant amount of N_2O was produced simultaneously with N_2 formation and it was unavoidable.

An additionnal information to be noted here is the following experimental results: the Fe_2O_3-activated carbon catalyst did not show such a low temperature activity as was obtained in the CuO-activated carbon catalyst. The CuO-titania catalyst showed a seemingly similar activity-temperature curve with both a maximum and a minimum to that of CuO-activated carbon catalyst, although it was inferior to the

activity of CuO-activated carbon catalyst. The activity of Cu(II) ion-exchanged carbon catalyst prepared separately was comparable to that of CuO-activated carbon catalyst prepared by the impregnation method: it was proved that there was no essential difference in their activity for the NO - NH_3 reaction. The Cu(II) ion-exchanged carbon catalyst was prepared by the conventional ion-exchange procedure, using a cation-exchanging carbon formed by oxidation of activated carbon with hot nitric acid.[9] Further studies on characterization of the catalysts are in progress.

This study was supported in part by the Grant in Aid for Scientific Research from the Ministry of Education.

REFERENCES

1) For example, O.J.Adlhart, S.G.Hindin, and R.E.Kenson, Chem. Eng. Prog., 67, 73 (1971); N.Todo, Shokubai, 15, 182(1973).
2) H.C.Anderson, W.J.Green, and D.R.Steele, Ind. Eng. Chem., 53, 199(1961).
3) N.Todo, M.Kurita, H.Hagiwara, A.Ueno, and T.Sato, The Japan- U.S.A. Seminar on Catalytic NO_x Reactions, Susono, Japan,(1975).
4) G.L.Bauerle , S.C.Wu, and K.Nobe, Ind. Eng. Chem. Prod. Res. Dev., 14, 123(1975).
5) H.Niiyama, T.Ookawa, and E.Echigoya, Nippon Kagaku Kaishi, 1975, 1871.
6) S.Kasaoka and H.Nagi, Nippon Kagaku Kaishi, 1976, 1797; H.Niiyama, M.Iwamoto, and E.Echigoya, ibid, 1976, 1947.
7) N.Todo, A.Nishijima, A.Ueno, M.Kurita, H.Hagiwara, T.Sato, and Y.Kiyozumi, Chem. Lett., 1976, 897.
8) T.Seiyama, T.Arakawa, T.Matsuda, N.Yamazoe, and Y.Takita, Chem. Lett., 1975,781; T.Arakawa, Y.Takita, N.Yamazoe, and T.Seiyama, Shokubai, 18, No.4(Abstract of the 39th Annual Meeting of Catalysis Soc. of Japan) p.124(1976).
9) M.Akiyoshi and T.Shirasaki, Nippon Kagaku Kaishi, 1976, 1181.

(Received February 28, 1977)