Effect of Ammonia Pre-treatment on Catalytic Activity of Metal Halide Catalyst for Reduction of Nitrogen Monoxide

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Synopsis. Effects of ammonia pre-treatment on catalytic activities of metal halides for the reduction of nitrogen monoxide are investigated in order to obtain highly active catalysts at lower temperatures. By the pre-treatment with NH_3, some supported metal halide catalysts such as $CeCl_2$, $MnCl_2$, $TiCl_4$, $FeBr_3$, and $CuCl_2$, showed higher activities than untreated ones.

Among the various techniques proposed for reducing nitrogen oxides (NO_x) emitted from stationary combustion equipments, the catalytic reduction of nitrogen monoxide (NO) with ammonia (NH_3) has been considered to be one of the most favorable methods.[1-3] In this process, metal oxide supported catalysts such as V_2O_5, CuO, Fe_2O_3, and MoO_3 on γ-Al_2O_3 or TiO_2 have been applied for practical use. They are used at reaction temperatures over 300 °C in order to obtain effective reduction of NO_x. From economical point of view, 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. The present authors have been trying to develope new type of catalysts having higher activities at temperatures as low as possible. Metal halide catalysts were found to show high activities at temperatures under 200 °C.[4] Another investigation showed that the most favorable electronic state of cations in the catalysts can be obtained by a proper combination of the cation with a counter anion and carrier for high activity.[5] In this work, it was found that supported metal halide catalysts pre-treated with NH_3 show higher activities than those of untreated ones.

Experimental

The catalyst used in this study were prepared by impregnating γ-Al_2O_3 spheres (diam. 1.5 mm, surface area 250 m^2/g, average pore radius 58 Å, alkali content 0.01 wt%) with aqueous solution of metal halides. After the impregnation, the catalysts were dried for 3 h at 120 °C and then for 2 h at 180 °C in air stream. The catalysts were then placed in a glass vessel containing gaseous ammonia for 10 h at room temperature. Activity measurements were carried out using a conventional flow reactor (stainless steel, length 200 mm, diam. 15 mm) under the space velocity of 15000 h^{-1}. As a standard feedstream, the gas mixture consisting of NO 300 ppm, NH_3 400 ppm, O_2 5 vol%, H_2O 9.2 vol%, SO_2 200 ppm, and N_2 balance was used. Analysis of NO and NH_3 were made by means of a chemiluminescence type NO_x analyzer and the chemical method (JIS-K-0099), respectively.

Results and Discussion

The effect of NH_3 pre-treatment on the activity of $CeCl_2$–Al_2O_3 catalyst for the reduction of NO is shown in Fig. 1. In the temperature region lower than 200 °C, $CeCl_2$–Al_2O_3 catalyst treated with ammonia showed higher activity than untreated ones. Figures 2 and 3 show results obtained on $MnCl_2$–Al_2O_3 and $TiCl_4$–Al_2O_3 catalyst, respectively. Though almost no activity was observed on untreated one on $TiCl_4$–Al_2O_3 catalyst, much higher activity was obtained after NH_3 pre-treatment. Similar effects were observed on some supported metal halide catalysts such as $FeBr_3$, and $CuCl_2$ on γ-Al_2O_3. These activities enhanced by NH_3 pre-treatment continued longer

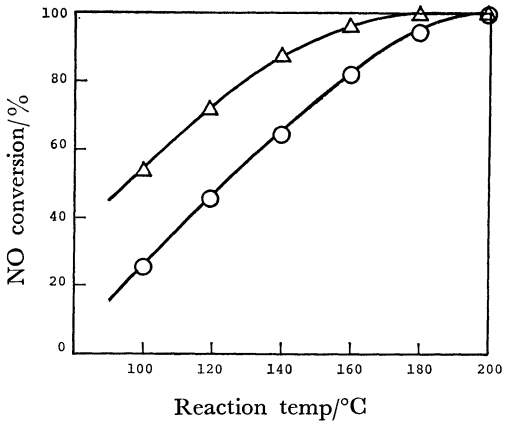

Fig. 1. Effect of NH_3 pre-treatment on activity of $CeCl_2$–Al_2O_3 catalyst.
△: Treated with NH_3, ○: untreated.
Reaction conditions; SV: 15000 h^{-1}, NO: 300 ppm, NH_3: 400 ppm, O_2: 5 vol%, H_2O: 9.2 vol%, SO_2: 200 ppm, N_2: balance.

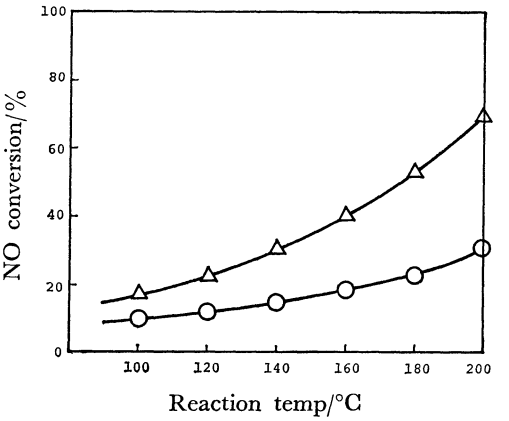

Fig. 2. Effect of NH_3 pre-treatment on activity of $MnCl_2$–Al_2O_3 catalyst.
△: Treated with NH_3, ○: untreated.
Reaction conditions; SV: 15000 h^{-1}, NO: 300 ppm, NH_3: 400 ppm, O_2: 5 vol%, H_2O: 9.2 vol%, SO_2: 200 ppm, N_2: balance.

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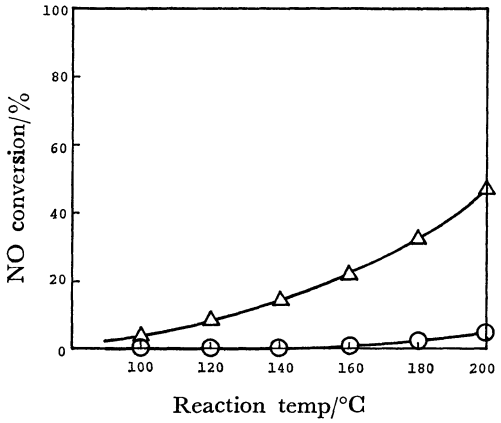

Fig. 3. Effect of NH_3 pre-treatment on activity of $TiCl_4$–Al_2O_3 catalyst.
△: Treated with NH_3, ○: untreated.
Reaction conditions; SV: 15000 $h,^{-1}$ NO: 300 ppm, NH_3: 400 ppm, O_2: 5 vol%, H_2O: 9.2 vol%, SO_2: 200 ppm, N_2: balance.

than 3 h.

Metal halides are well known to form metal halide ammonium complexes. The color of each catalyst changed to that of metal halide ammonium complex by NH_3 pre-treatment, indicating that metal halide ammonium complexes were formed on the catalysts. It is also known, however, that ammonium complexes are unstable at temperatures over 100 °C. The activities of the present catalysts pre-treated with NH_3 disappeared when they were heated over 300 °C. A thermogravimetric analysis showed that although the amount of NH_3 in these complexes decreased with the temperature elevated, NH_3 were still remained at temperatures over than 200 °C. These results show that NH_3 coordinates to metal ions in metal halides at lower temperatures, indicating the increase of the concentration of NH_3 available for the reduction of NO on active sites. On the other hand, previous study showed that proper amount of NO adsorption on catalyst is also essential as well as that of NH_3 adsorption for producing highly active state, and that the most favorable electronic state of the cation in the catalyst is required for this purpose.[5] NH_3 coordination is considered to affect on the electronic state of the cation. In fact, the binding energy of Fe $2p_{3/2}$ photoelectron peak on $FeBr_3$–Al_2O_3 catalyst measured by a photoelectron spectrometer(XPS) changed from 711.6 to 711.1 eV after NH_3 pre-treatment. These results will indicate that the enhancement of the activity by NH_3 pre-treatment is mainly due to the improvement of the electronic state of the cation. More research is now needed on such metal halide ammonium complex catalysts to fully understand the mechanism of the enhancement of the catalysts.

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