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EFFECT OF Nb_2O_5 ADDITION ON THE CATALYTIC ACTIVITY OF FeO_x FOR REDUCTION OF NO_x WITH NH_3 AND O_2

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Niobium oxide, Nb_2O_5, remarkably enhanced the catalytic activity of FeO_x for the reduction of NO_x with NH_3 and O_2. Thus, for the reduction catalyzed by FeO_x containing a small amount of Nb_2O_5, the conversion attained 90-100%, in contrast to less than 40% for the reduction catalyzed by FeO_x without Nb_2O_5. The catalytic activity of the mixed oxide was scarcely affected by addition of SO_2 to the reaction gas.

It is preferable to utilize iron oxide as a catalyst for the denitration of exhaust gases, since the oxide is extremely abundant, cheap, and innoxious. However, FeO_x is known to be catalytically less active for the reduction of NO with NH_3 and O_2 than other metal oxides such as MnO_x, CuO_x, VO_x, and MoO_x.[1] Thus, the activation of iron oxide as the denitration catalyst is worthy of a study, especially from the viewpoint of industry.

In a previous study, it was found that the catalytic activity of TiO_2 for the denitration was considerably enhanced by addition of Nb_2O_5.[2] Hence, the effect of Nb_2O_5 addition on the catalytic activity of iron oxide for the denitration was examined in this study.

Niobic acid(niobium(V) oxide hydrate)(AD 135) supplied by Companhia Brasileira de Metalurgia e Mineracao(CBMM) Ltd. was used as a raw material for Nb_2O_5. The raw material for FeO_x was a commercial reagent of guaranteed grade, $Fe(NO_3)_3 9H_2O$. Most catalyst samples were prepared by using a 28% aqueous ammonia from Nb_2O_5 dissolved in oxalic acid, and an aqueous solution of $Fe(NO_3)_3$. To know the effect of preparation method on the catalytic activity, some Nb_2O_5-FeO_x

catalysts were prepared by impregnation of the dissolved Nb_2O_5 on FeO_x which was obtained by hydrolysis of $Fe(NO_3)_3$. The catalyst samples were heat-treated in air at 500 °C for 3 h, and were fabricated to a size of 14 to 20 mesh. The structures and surface compositions of the catalyst samples were examined by using XRD and XPS, respectively.

The reactions of NO and O_2 with NH_3 were carried out at 100-500 °C using a conventional flow reactor. The mixture of NO and NH_3, which was diluted to 500 ppm in air was passed through 2 g of catalyst, the flow rate being 35 ml min^{-1}. In some cases, SO_2, which was diluted with air to be 1200 ppm, was added to the mixed gas to know its coexistent effect. After the reaction, the amount of unreacted NO was measured by a NO_x meter(Kyoto Denki Kogyo, NX 22).

Figure 1 shows the catalytic activities of several mixed oxides prepared at different Nb/Fe atomic ratio. As is shown in this figure, Nb_2O_5 alone had poor catalytic activity, barely promoting the reaction at and above 300 °C. When FeO_x was used without any addition, it promoted the reaction above 250 °C; however, the conversion was low, and it decreased at 300 °C or higher. If the Nb component is added to FeO_x in an amount as small as 5 atomic %, the activity of FeO_x rises in the low-temperature range, and the conversion reaches 90%. If the Nb component is further added to up an atomic ratio(Nb/Fe) 2/8, the catalyst gives a high conversion of 90-100% over a wide temperature range of 300 to 450 °C. With the increase in Nb content above this ratio, the activity gradually decreased in the low-temperature range, and came close to the activity of Nb_2O_5 alone.

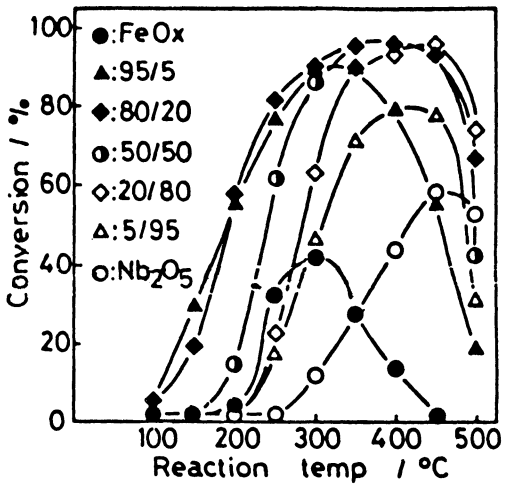

Fig.1. Catalytic activity of Nb_2O_5-FeO_x having various Nb/Fe atomic ratio. (prepared by coprecipitation)

Surface compositions of the mixed oxide prepared by coprecipitation(shown in Fig.2) indicate that the Nb component was somewhat accumulated in the surface layer. The content was nearly equal to that observed in the mixed oxide of the same atomic ratio, prepared by impregnation. X-Ray diffraction analyses revealed that the mixed oxides prepared by coprecipitation remained amorphous after the

heat-treatment at 500 °C. On the other hand, sharp peaks due to α-Fe_2O_3 were found on the XRD patterns of FeO_x alone, which was heat-treated under the same conditions as for the treatment of the mixed oxide. These informations obtained from XPS and XRD suggest that micro particles of Nb_2O_5 might be formed on FeO_x particles, and might prevent the aggregation and crystallization of iron oxide particles.

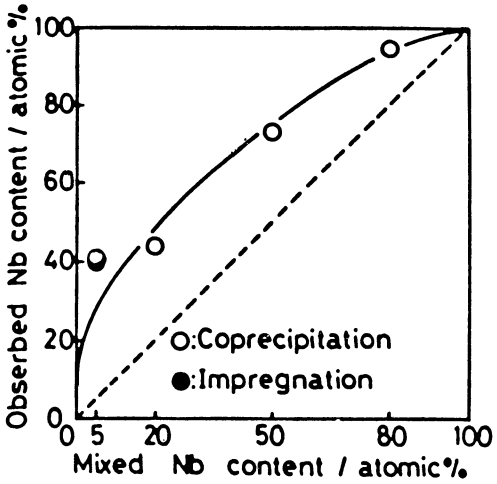

Fig.2. Mixed Nb content vs. observed Nb content.

As is shown in Fig.3, the mixed oxide prepared by impregnation had somewhat lower activity for the low-temperature range than that prepared by coprecipitation. However, the apparent conversion on the high-temperature side was appreciably higher. The fact may be due to that the Fe component promoting undesirable oxidation of NH_3 to NO_x, has been stabilized or coated by the Nb component, more effectively in the mixed oxide prepared by impregnation.

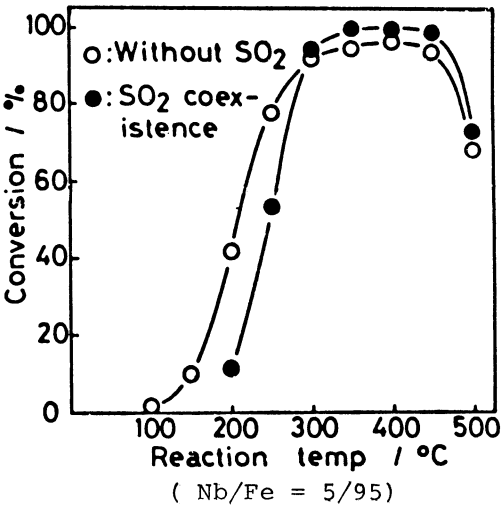

Fig.3. Catalytic activity of Nb_2O_5-FeO_x prepared by impregnation.

When SO_2 was allowed to coexist at a concentration more than twice as high as those of NO and NH_3, the conversion in the practical range of 300-400 °C reached almost 100%. Thus, the catalytic activity of the mixed oxide was scarcely affected by the coexistence of SO_2, even in the case of that the mixed oxide was prepared by the more simple method, impregnation method.

The fact that a high conversion close to 100% can be obtained continuously and stably in the presence of SO_2 at a low temperature of 300 °C, simply by impregnating less expensive iron oxide with a small amount of Nb_2O_5 and using the supported Nb_2O_5/FeO_x catalyst in the reaction seems quite interesting from a

practical point of view. The details of the catalytic activity at low reaction temperatures and the resistance to SO_x of the mixed oxide are to be investigated hereafter.

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References

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2) S. Okazaki and T. Okuyama, Bull.Chem.Soc.Jpn., 56, 2159(1983).

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