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Nb_2O_5 Supported on TiO_2. Catalytic Activity for Reduction of NO with NH_3

Susumu Okazaki* and Tetsuhiro Okuyama
Department of Industrial Chemistry, Faculty of Engineering, Ibaraki University, Nakanarusawa-cho Hitachi 316

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Synopsis. Niobium(V) oxide supported on TiO_2 showed a high catalytic activity for the reduction of NO with NH_3 at temperatures higher than 450 °C. The presence of SO_4^{2-} in Nb_2O_5 or in Nb_2O_5 supported on TiO_2 brought about an increase in the catalytic activity.

Vanadium(V) oxide[1)] supported on TiO_2 is commonly used for the reduction of NO with NH_3. Other metal oxides such as MoO_x[2)] and FeO_x[3)] supported on TiO_2 also show considerable catalytic activity for this reaction. Although Nb is a neighbor of Mo or V in the periodic table, the catalytic activity of Nb_2O_5 for denitration has not been well-studied; this topic is presented here. In particular, the effect of SO_4^{2-} on the catalytic activity was carefully studied, since in industrial denitration processes small amounts of SO_2 included in the reacting gas combine with O_2 to form SO_4^{2-}, which may be adsorbed and further combined with the catalysts.

Most catalyst samples were prepared by a coprecipitation method in which a mixture of niobium(V) oxide hydrate and titanium tetraisopropoxide was neutralized with 28% aqueous ammonia, followed by washing and drying. The niobium(V) oxide hydrate, supplied by the CBMM Company, contained about 55 wt% of Nb and no detectable amounts of alkali components such as Na and K, which would decrease the catalytic activity for denitration. For comparison of the activities as catalyst carriers, Al_2O_3, ZrO_2, and SiO_2 were prepared from $Al(NO_3)_3$, $Zr(OH)_4$, and colloidal silica respectively.

To elucidate the effect of the preparation method on the catalytic activity, some catalyst samples were prepared by impregnating TiO_2 with niobium(V) oxide hydrate dissolved in a 20 wt% aqueous solution of oxalic acid. Other niobium(V) oxide catalysts supported on Al_2O_3, ZrO_2, and SiO_2 were prepared by impregnation similarly to the TiO_2 supported niobium(V) oxide.

The samples containing definite amounts of SO_4^{2-} were prepared by adding ammonium sulfate to a solution containing the catalyst components.

All the catalyst samples were heat-treated at 500 °C for 3 h immediately before use as catalysts in the same reactor used for the denitration.

The specific surface area was determined by applying the BET equation to the adsorption of N_2 at −196 °C. The solid acidity was measured by NH_3 adsorptions at 250 and 450 °C. The acidity was further examined by the catalytic activity for isomerization of cyclopropane to propene which is promoted only by Brönsted acid sites.[4)]

The reaction of NO with NH_3 was carried out at 200—500 °C by using a conventional flow reactor. The mixture of NO and NH_3, which was diluted with air so that the concentrations of both gases were 500 ppm, was passed through 2 g of catalyst, the flow rate and space velocity being 35 ml min^{-1} and 50000 h^{-1}, respectively. After the reaction, the amount of unreacted NO was measured by a NO_x meter(Kyoto Denki Kogyo, NX 22 or Takeda Kikai, KN 400 type).

The catalytic activity of Nb_2O_5 supported on TiO_2 for the reduction of NO with NH_3 in the presence of air was much higher than those of Nb_2O_5 supported on other oxides(Fig. 1). As is shown in Fig. 2, the activities of Nb_2O_5–TiO_2 were also higher than those of the component oxides. The catalytic activity for the mixed oxides prepared by coprecipitation had a maximum at the atomic ratio(Nb/Ti) of 1/1.

Figure 3 shows that the specific surface area of the mixed oxide is maximum at the atomic ratio of, not 1/1, but 1/9. Further, the specific activity(conversion/surface area) is especially high at the ratio(1/1). So, the higher activity is not merely due to the high dispersibility of the Nb component on TiO_2. It has been observed that the solid acidity is closely related to

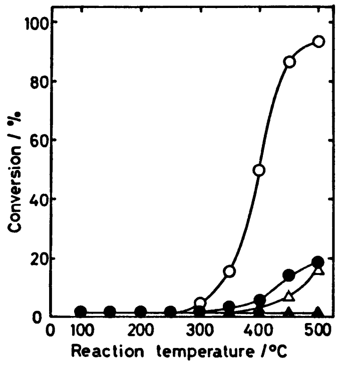

Fig. 1. Catalytic activities of Nb_2O_5 supported on various oxides at different temperatures.
○: Nb_2O_5-TiO_2(Nb/Ti=1/9), △: Nb_2O_5-Al_2O_3 (Nb/Al=1/9), ●: Nb_2O_5-ZrO_2(Nb/Zr=1/9), ▲: Nb_2O_5-SiO_2(Nb/Si=1/9).

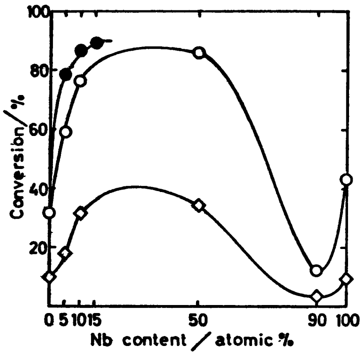

Fig. 2. Effect on catalytic activity of Nb_2O_5 content in Nb_2O_5-TiO_2 prepared by coprecipitation and impregnation.
○: Coprecipitation(reaction temperature: 450 °C), ◇: coprecipitation(350 °C), ●: impregnation(450 °C).

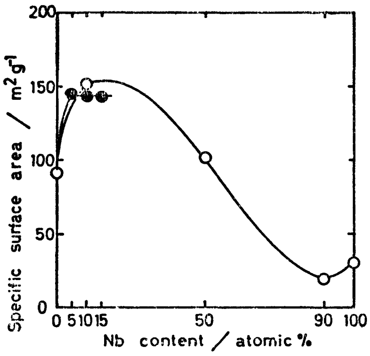

Fig. 3. Effect on specific surface area of Nb_2O_5 content on Nd_2O_5-TiO_2 prepared by coprecipitation and impregnation. ○: Coprecipitation, ●: impregnation. All the samples were heat-treated at 500 °C for 3 h immediately before determinations.

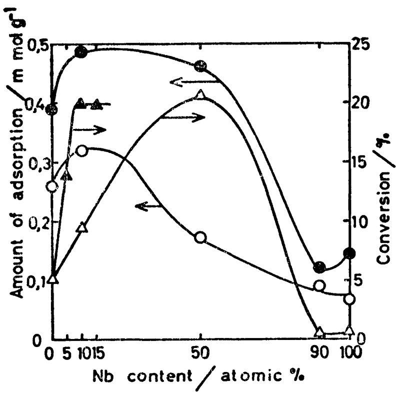

Fig. 4. Effects on adsorptive activity for NH_3 and catalytic activity for cyclopropane isomerization of Nb_2O_5 content.
○: NH_3 adsorption at 450 °C, ●: NH_3 adsorption at 250 °C, △: cyclopropane isomerization over mixed oxides prepared by coprecipitation, ▲: cyclopropane isomerization over mixed oxides prepared by impregnation. The condition of cyclopropane isomerization are as following; pulse method; pulse size: 1.09 ml, catalyst weight: 50 mg, reaction temperature: 250 °C, carrier gas: He, 40 ml/min.

the catalytic activity for the denitration of MoO_x-TiO_2.⁵⁾ However, as Fig. 4 shows, the total acidity measured by NH_3 adsorptions at 250 and 450 °C, was maximum at the atomic ratio of 1/9; thus this observation is unable to explain the catalytic activity of Nb_2O_5-TiO_2 prepared by coprecipitation. The catalytic activity is more adequately explicable by the Brönsted acidity determined by the catalytic activity for the isomerization of cyclopropane. Also, the fact that the activity of the mixed oxide of low Nb/Ti atomic ratio prepared by impregnation is higher than that prepared by coprecipitation may be due to the high Brönsted acidity of the sample prepared by impregnation. In the reduction of NO with NH_3, the NH_3 molecules are considered to be adsorbed on Brönsted acid sites as NH_4^+.⁶⁾ Thus, the Brönsted acid sites formed on the mixed oxides may contribute to activation of NH_3.

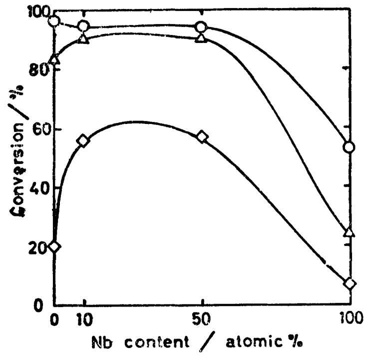

Fig. 5. Effect on catalytic activity of Nb_2O_5 content in Nb_2O_5-TiO_2 containing SO_4^{2-}.
Reaction temperature; ○: 450 °C, △: 400 °C, ◇: 350 °C. Mixed oxides were prepared by coprecipitation. The atomic ratio of S to the sum of Nb and Ti, S/(Nb+Ti) was kept constant at 5/95.

The catalytic activities of the oxides containing SO_4^{2-} shown in Figure 5 are considerably higher than those of oxides free from SO_4^{2-} (shown in Fig. 2). The effect of SO_4^{2-} addition is especially remarkable for the activities of TiO_2 and mixed oxides of high Ti content. Since it is already known that an addition of small amount of SO_4^{2-} greatly increases the solid acidity of TiO_2,⁷⁾ the enhancement in catalytic activity may also be due to the increase in Brönsted acidity. The addition of SO_4^{2-} to an extent that an atomic ratio of S to the sum of Nb and Ti, (S/(Nb+Ti)) equaled 5/95 appeared to be enough for the enhancement of the catalytic activity of Nb_2O_5-TiO_2 prepared by coprecipitation.

Compared to the catalytic activities of V_2O_5-TiO_2 and MoO_3-TiO_2,⁵⁾ that of Nb_2O_5-TiO_2 was still lower, especially at temperatures lower than 300 °C. Unlike V_2O_5 and MoO_3, Nb_2O_5 is not readily reduced, as is shown by the fact that NbO_2 is formed with difficulty by treating Nb_2O_5 with H_2 at temperatures as high as 1000—1200 °C.⁸⁾ Hence, the redox activity of Nb component may be not so large as V and Mo components. This seems to be the reason why Nb_2O_5-TiO_2 shows only relatively low catalytic activity, even though it has a considerable amount of Brönsted acid sites.

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