CHEMISTRY LETTERS, pp. 1355-1358, 1978. Published by the Chemical Society of Japan

DETERMINATION OF THE NUMBER OF $V^{5+}=O$ SPECIES ON THE SURFACE OF VANADIUM OXIDE CATALYST

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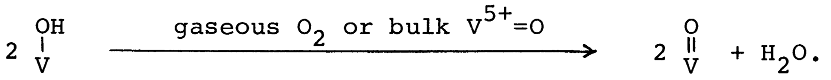
The number of $V^{5+}=O$ species on the surface of V_2O_5 was determined by detecting the concentration profile of N_2 produced by the NO-NH_3 reaction on V_2O_5 using the rectangular pulse technique. The quantity of $V^{5+}=O$ species on the surface obtained agreed with the BET surface area of the catalyst.

Vanadium oxide has been used as a main catalyst in the oxidation of hydrocarbons and SO_2. Recently, this catalyst has received attention as one of the best catalysts for the reduction of nitric oxide with ammonia from the environmental point of view. Concerning the mechanism of the catalytic reactions on vanadium oxide, $V^{5+}=O$ species have been shown, in many studies, to play a significant role as the active site for the reactions.[1-3] Therefore, it is highly desirable to know the quantity of $V^{5+}=O$ species on the surface of a catalyst in order to evaluate the specific activity of the catalyst and to elucidate the role of the additive or the support of the vanadium oxide catalyst. However, a method to determine the number of $V^{5+}=O$ species on the surface of the catalyst has not been established. Although the infrared absorption peak near 1020 cm^{-1} gives an important information on the number of $V^{5+}=O$ species,[1,2,4] the peak can hardly distinguish between surface and bulk $V^{5+}=O$ species. In the previous studies, the authors obtained data that, on V_2O_5 catalyst, $V^{5+}=O$ species plays the active site for the NO-NH_3 reaction.[5,6] Namely, the following reactions can be proposed:

$$NO + NH_3 + \overset{O}{\overset{\|}{V}} \longrightarrow N_2 + H_2O + \overset{OH}{\overset{|}{V}}, \qquad (1)$$



$$2\,\overset{OH}{\overset{|}{V}} \xrightarrow{\text{gaseous } O_2 \text{ or bulk } V^{5+}=O} 2\,\overset{O}{\overset{\|}{V}} + H_2O. \qquad (2)$$

Consider the process of the reactions when the mixtures of NO and NH_3 is introduced onto the vanadium oxide catalyst in the absence of gaseous oxygen. In the initial stage of the reaction, N_2 due to the surface $V^{5+}=O$ will be produced according to Eq. (1). Then, N_2 formation due to the $V^{5+}=O$ reproduced by the diffusion of bulk oxygen to the surface(Reaction (2)) should follow. Consequently, if we can separate the initial reaction due to the surface $V^{5+}=O$ from the secondary process due to the reoxidation of the surface, we can expect to determine the number of the $V^{5+}=O$ species on the surface of vanadium oxide catalyst.

Experiments were carried out with the rectangular pulse apparatus described previously[5)]; however the separation columns were removed in order to introduce the product gas directly to the thermal conductivity detector(TCD) where the shape of the peak of N_2 was detected. Components other than N_2, i.e. unreacted NO and NH_3 and produced H_2O, were completely removed by the liquid nitrogen cooled trap installed between the reactor and the detector. Carrier gas(He) flow rate was 90 cm^3/min. V_2O_5 catalyst was prepared by the thermal decomposition of ammonium metavanadate at 500 °C in the stream of oxygen. BET surface area of V_2O_5 was 5.4 m^2/g. V_2O_5/TiO_2 catalyst treated with an ammoniacal solution was prepared in a similar manner as that by Yoshida et al.[7)] The weights of the samples were 0.1 g for V_2O_5 and 0.02 g for V_2O_5/TiO_2. Between the pulses of reactants(mixture of NO and NH_3), the catalyst was treated with O_2 gas stream at 500 °C in order to hold it before the pulse in the defined state, i.e. V_2O_5, and to remove any adsorbates on it.

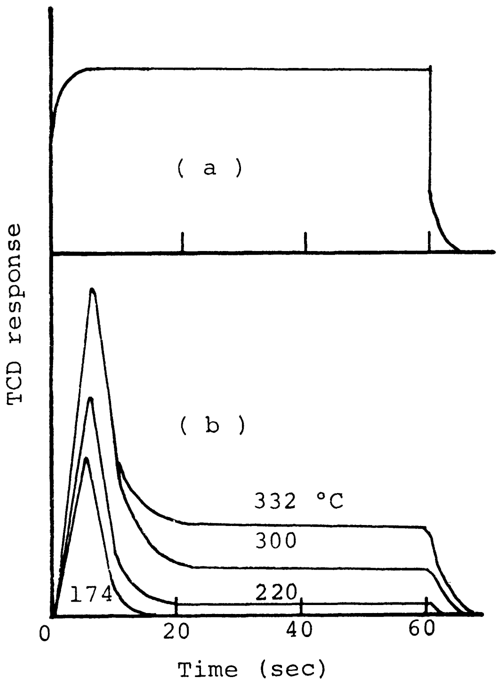


Fig. 1 Concentration profile of the mixture of NO and NH_3 at the inlet (a) and that of N_2 at the outlet of the reactor(b)

In Fig. 1, TCD responses at the inlet (a) and the outlet(b) of the reactor are shown. The inlet response(a) represents the concentration of the mixture of NO and NH_3 at the inlet of the reactor(a rectangular pulse with the pulse width of 60 sec.), while the outlet response(b) represents the concentration profile of N_2 produced on V_2O_5 at various temperatures. As shown in Fig. 1 (b), at 174 °C, only the initial part was observed, whereas at higher temperatures such as 220, 300 and 332 °C, the tailing of the N_2 peak occurred. The concentration of N_2 at the tailing part becomes higher as the temperature becomes higher. In conformity with the pulse width, the concentration of N_2 at the tailing part decreased abruptly at the end of the rectangular pulse. Separating the initial part of the N_2 peak(A) from the tailing part(B) after the manner shown in Fig. 2, we obtain Fig. 3, where the amount of N_2 of the initial part(A) and the total amount of produced N_2(A + B) are indicated. As shown in Fig. 3, total amount of N_2(A + B)

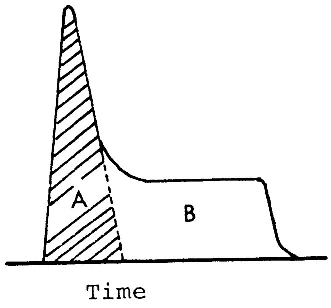


Fig. 2 The way of separation of N_2 peak into the initial part(A) and the tailing part(B)

increases monotonously with temperature, whereas the quantity of N_2 corresponding to the initial part(A) is approximately constant at the temperatures higher than 280 °C. Since the quantity of V^{5+}=O species on the surface ought not to vary with temperature, the constancy of the amount of the initial peak above 280 °C supports the validity of assigning the initial part of the peak(A) to V^{5+}=O species on the surface. Furthermore, it should be noted that the quantity of the initial N_2, i.e. (2.2 ± 0.1)×10^{-5} mol/g-V_2O_5, was confirmed to be constant irrespective of the change in the experimental variables such as the weight of V_2O_5, the carrier gas flow rate, the concentrations of NO and NH_3 in pulse and inlet pulse width. The decrease in the quantity of the initial part(A) below 280 °C may be due to remaining unreacted V^{5+}=O species on the surface because of the slower reaction rate at the lower temperatures. Since, according to Eq. (1), the amount of produced N_2 is equal to the amount of reacted V^{5+}=O species, we can note that the quantity of V^{5+}=O species on the surface of V_2O_5 is (2.2 ± 0.1)×10^{-5} mol/g-V_2O_5.

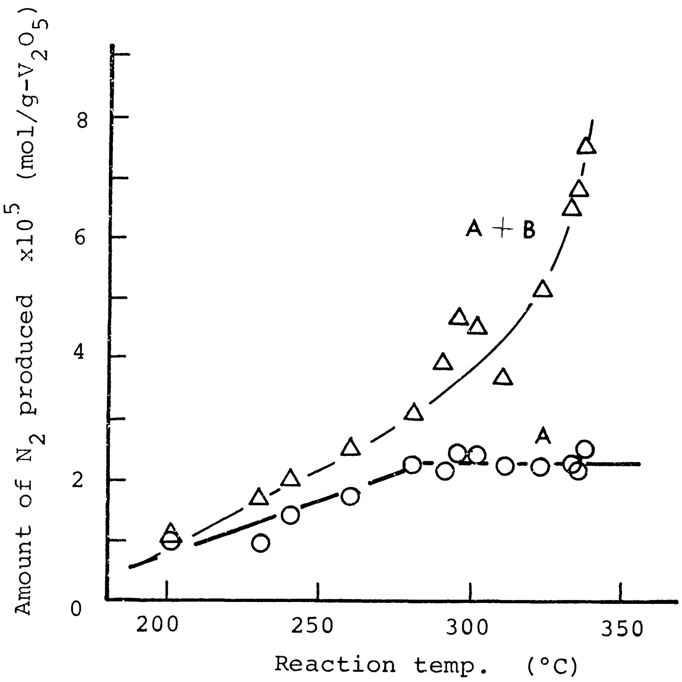


Fig. 3 The amount of the initial peak(A) and the total amount of N_2 peak(A + B) against reaction temperature

According to Bystrom et al.,[8] V^{5+}=O species is located on the (010) face of V_2O_5 crystal. Thus, if we tentatively assume that (010) face is selectively exposed to the surface of V_2O_5, the amount of V^{5+}=O species on the surface obtained above and the lattice parameters of V_2O_5 give the value of 2.7 m^2/g-V_2O_5 as the specific surface area of V_2O_5, which is one half of the BET surface area of V_2O_5, i.e. 5.4 m^2/g-V_2O_5. Since the powder of V_2O_5 may actually expose various crystal faces in addition to (010) face, we can say that the coincidence between both data is satisfactory. This also supports the validity of assigning the initial peak(A) to V^{5+}=O species on the surface.

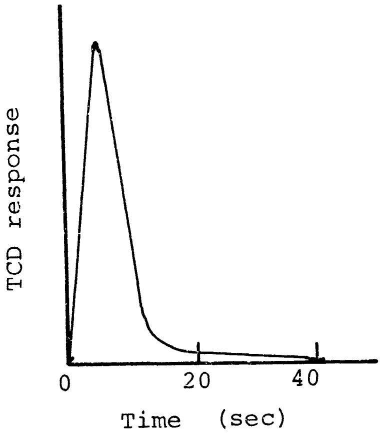


Fig. 4 Concentration profile of N_2 produced by the reaction at 335 °C on V_2O_5/TiO_2 treated with an ammoniacal solution

In addition to the above data, we present another evidence for the validity of assigning the initial peak(A) to $V^{5+}=O$ species on the surface. According to Yoshida et al.[7)] the treatment of supported vanadium oxide catalyst with an ammoniacal solution dissolves the isolated, massive vanadium oxide into the solution, while the residual vanadium oxide is regarded to be chemically interacting with the carrier. Thus, if the assignment of the peak described in Fig. 2 is valid, the tailing part (B) due to the reoxidation of the surface by the bulk oxygen should disappear when the sample is treated with an ammoniacal solution. In fact, as shown in Fig. 4, the result for V_2O_5/TiO_2 treated with the ammoniacal solution is in accord with the prediction. Namely, only the initial part(A) was observed even at temperatures as high as 335 °C and the quantity of the tailing part(B) was negligibly small. Moreover, we should mention that the way of separation between A and B peaks shown in Fig. 2 was also proved to be valid by the simulation of both surface reaction and diffusion processes in V_2O_5.

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(Received September 14, 1978)