Journal of Catalysis **185,** 106–113 (1999)
Article ID jcat.1999.2470, available online at http://www.idealibrary.com on IDEAL®

Kinetics of the Selective Reduction of NO with NH_3 over a $V_2O_5(WO_3)/TiO_2$ Commercial SCR Catalyst

Hiroyuki Kamata,* Katsumi Takahashi,* and C. U. Ingemar Odenbrand†

*Research Institute, Ishikawajima-harima Heavy Industries Co., Ltd., 1 Shin-nakahara-cho, Isogo-ku, Yokohama, 235-8501 Japan; and †Department of Chemical Engineering II, Chemical Center, Lund University, Institute of Technology, P.O. Box 124, S-221 00 Lund, Sweden

Received October 9, 1998; revised February 18, 1999; accepted March 4, 1999

In order to clarify the mechanism of the selective catalytic reduction of nitric oxide with ammonia over a $V_2O_5(WO_3)/TiO_2$ commercial SCR catalyst, measurements were made on the reaction rate, r_{NO}, as a function of partial pressure of nitric oxide, P_{NO}, partial pressure of ammonia, P_{NH_3}, and partial pressure of oxygen, P_{O_2}, from 513 to 553 K under steady-state conditions. The adsorption of NO and NH_3 on the catalyst was also observed by infrared spectroscopy (DRIFT). The apparent reaction orders with respect to NO were observed to be less than unity, 0.6–0.8. The reaction rate was nearly independent on P_{NH_3} at lower temperatures. As temperature increased, r_{NO} became slightly increased with increasing P_{NH_3} at lower partial pressures of ammonia and tended to be saturated with further increases of P_{NH_3}. The dependence of r_{NO} on P_{O_2} was similar to that of P_{NH_3}: r_{NO} increased with increasing P_{O_2} at lower partial pressures of oxygen and was saturated with further increase of P_{O_2}. The spectroscopic study showed that NO does not adsorb significantly on the oxidized nor on the NH_3 preadsorbed surface of catalysts above at least 473 K. The SCR reaction was considered to proceed as follows. NH_3 adsorbed on the Brønsted acid sites as ammonium ions. Ammonium ions were activated with the terminal oxygen groups, $V^{5+}{=}O$, prior to the reaction with gaseous NO. Subsequent reaction with NO produced N_2, H_2O, and the hydroxyl groups bonded to the reduced vanadium, V^{4+}–OH, which would be reoxidized by oxygen to the $V^{5+}{=}O$ species. The Brønsted acid sites where NH_3 adsorbed were then recreated. The results obtained in this study suggested that the Brønsted acid sites and/or the $V^{5+}{=}O$ species were equilibrated with the other species on the surface, implying that the number of each site changed with the experimental conditions such as P_{O_2}. The relative amount of the $V^{5+}{=}O$ species would vary from ∼0.1 to ∼0.4 with increasing P_{O_2}.

1. INTRODUCTION

The selective catalytic reduction (SCR) of nitric oxide (NO) with ammonia (NH_3) as reductant is the most successful method for eliminating NO from waste gases of stationary sources (1). It is generally accepted that the SCR reaction occurs according to the following stoichiometry:

$$NO + NH_3 + 1/4\,O_2 \rightarrow N_2 + 3/2\,H_2O. \qquad [1]$$

As commercial SCR catalysts, mixed oxides of V_2O_5 and WO_3 or MoO_3 supported on TiO_2 are commonly used because of their high catalytic activity. The addition of WO_3 and MoO_3 is expected to improve the thermal stability and retard the oxidation of SO_2 to SO_3 (2, 3).

The SCR reaction is generally considered to occur between strongly adsorbed NH_3 and gaseous or weakly adsorbed NO over the V_2O_5-based catalysts (4–8). The reaction mechanisms proposed often involve two adjacent vanadium species, namely the terminal oxygen species, V=O, and the hydroxyl groups, V–OH (4, 9–11). Inomata *et al.* (4) suggested that NO reacts with NH_3 adsorbed on a site composed of V–OH and an adjacent V=O species. They also found that the reaction rate is proportional to the number of V=O sites on the surface. Topsøe *et al.* (9–11) have put forward a mechanism, which also takes into account both V=O and V–OH species, based on their spectroscopic study. They suggested that the activation of NH_3 adsorbed on the Brønsted acid sites with the V=O species is needed prior to the reaction with gaseous NO. On the other hand, Ramis *et al.* (12) proposed a mechanism involving a nitrosamidic intermediate on Lewis acid sites. In line with this mechanism, Tufano and Turco (13) derived the kinetic equation and suggested the formation of relatively stable nitrosamidic intermediates at lower temperatures. Koebel and Elsener (14) also suggested that the reaction proceeds by the Langmuir-Hinshelwood-type or the nitrosamidic intermediate-type mechanism. The mechanistic aspects based on the literature published so far are summarized and discussed in the recently published reviews (15, 16).

The purpose of the present study is to obtain further understanding of the nature of commercial $V_2O_5(WO_3)/TiO_2$ catalysts under the SCR reaction conditions. Along with this, we measured the reaction rate as a function of partial pressure of nitric oxide and ammonia under different

0021-9517/99 $30.00

oxygen partial pressures. The change of the reaction mechanism with the reaction conditions is also discussed.

2. EXPERIMENTS

Catalyst

The catalyst used in this study was obtained by gently crushing and sieving a commercial BASF honeycomb monolith into particles of 100–180 μm in diameter. The specific surface area measured by the BET method was 64.4 m^2/g. The chemical composition of the catalyst was determined by a Perkin-Elmer Plasma 2000 ICP-AES according to the ASTM D3682 method; 1 wt% V_2O_5 and 8 wt% WO_3 supported on TiO_2 with silica-alumina-based material as a fiber, which is approximately 10 wt% of total. The catalyst also contains small amounts of alkali metals and sulfur species. From X-ray diffraction analysis, only the anatase structure of TiO_2 was confirmed. The peaks of crystalline V_2O_5 and WO_3 were not observed.

Infrared Spectroscopy

The infrared spectra (DRIFT) were collected using a Mattson Polaris spectrometer with a heatable reaction cell, with a resolution of 4 cm^{-1}. The catalyst powder was preheated in the reaction cell at 573 K for 1 h under a stream of oxygen before adsorption of NO was carried out. After being cooled down to the reported temperature which was in the range RT to 473 K, the reaction cell was purged with helium for 15 min. Then the catalyst was exposed to a gas mixture of 1000 ppm NO and helium at each temperature. The spectra were recorded as a function of the contact time with NO-containing gas.

The infrared spectra of adsorption of NO on the NH_3 preadsorbed surface were collected as follows. After being heated at 573 K for 1 h under a stream of oxygen, the catalyst powder was cooled down to 473 K in oxygen. Then the reaction cell was purged with helium for 30 min. The catalyst was exposed to a gas mixture of 1.5% NH_3 and nitrogen for 30 min before being purged with helium for another 1 h. It was confirmed that the intensity of the bands due to NH_3 adsorbed on the catalyst surface does not change much with the time of the purge with helium. A gas mixture of 1000 ppm NO and helium was then introduced to the reaction cell at the same temperature. The change of the bands of adsorbed species was observed as a function of contact time of gaseous NO with a NH_3 preadsorbed surface.

Measurements of Reaction Rate

Measurements of the reaction rate were carried out under steady-state conditions in a plug-flow micro-reactor (5 mm in diameter). The concentration of reactants and products was determined by a mass spectrometer (Balzers, Type QMG 311). The flow contained ~3000 ppm of Ar as an internal standard for the analysis. The apparatus was essentially the same as that described in the literature (17). To avoid a homogeneous reaction, the flows of NH_3 and $O_2 + NO$ were separately preheated in an electric oven and were then mixed at the reaction temperature before reaching the reactor. The operating conditions were total flow rate (STP), 900 ml/min; total pressure, approximately 0.12 MPa; and reaction temperature, 513–553 K. The reaction rate, r_{NO}, was measured as a function of the partial pressure of nitric oxide, P_{NO}, and ammonia, P_{NH_3}, under different partial pressures of oxygen. In the measurements of the dependence on P_{NO} ($P_{NO} = \sim 10\text{–}\sim 130$ Pa), P_{NH_3} was fixed to be approximately 74 Pa. To measure the influence of P_{NH_3} ($P_{NH_3} = \sim 3 - \sim 130$ Pa), similarly P_{NO} was fixed to be approximately 78 Pa. The measurements were performed under different oxygen partial pressures from ~60 to ~6000 Pa. The catalyst was diluted with a proper amount of inactive TiO_2 particles of the same diameter as the catalyst used.

Preliminary experiments, with catalyst particles of several sizes, showed that the effects of diffusion limitation in the pore of the particles were negligible under the experimental conditions mentioned above. Our calculations also showed that the external diffusion limitation was absent. Because we have not observed any side reactions, we only considered the main reaction of SCR, which is represented by Eq. [1]. The reaction rate, r_{NO}, was calculated by the rate expression for a differential reactor,

$$r_{NO} = F^0_{NO}\, \Delta X_{NO}/W, \qquad [2]$$

where F^0_{NO}, ΔX_{NO}, and W are the molar flow of NO in inlet, the conversion of NO, and the catalyst weight, respectively. The conversion of NO, ΔX_{NO}, is less than 0.15 throughout the experiments.

3. RESULTS AND DISCUSSION

P_{NO} Dependence of r_{NO}

Figures 1a and 1b show the dependence of r_{NO} on the partial pressure of nitric oxide, P_{NO}, under different partial pressures of oxygen at 513 and 553 K, respectively. The reaction rate, r_{NO}, increases with increasing both temperature and P_{NO}. With increasing P_{O_2}, r_{NO} increases and then tends to saturate with further increase of P_{O_2}. At all temperatures, the apparent reaction orders with respect to NO are less than unity, 0.6–0.8. This observation is consistent with those by other researchers (13, 14, 17, 18). Odenbrand *et al.* (17) reported that the apparent reaction orders are 0.74–0.79 at 493–583 K for the V_2O_5/TiO_2 catalyst. Lintz and Turek (18) and Tufano and Turco (13) also reported that the order of NO is less than unity, which depends on the reaction temperature.

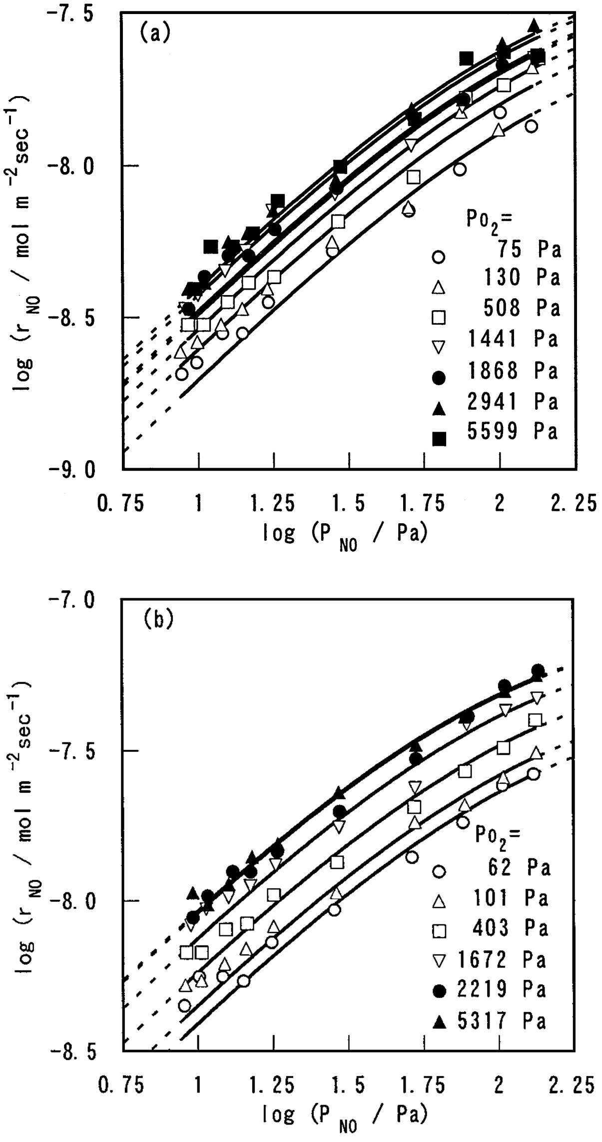

FIG. 1. The dependence of the reaction rate, r_{NO}, on the partial pressure of NO, P_{NO}, under different partial pressures of oxygen at (a) 513 K and (b) 553 K, respectively. Curves were calculated by Eq. [18].

Concerning the dependence of the observed reaction order with respect to NO on P_{O_2}, the order of NO was observed to decrease somewhat with increasing P_{O_2}. This suggests that the apparent reaction order may depend on the oxidation state of the catalyst surface caused by reaction conditions such as P_{O_2}.

P_{NH_3} Dependence of r_{NO}

Figures 2a and 2b show the dependence of r_{NO} on the partial pressure of ammonia, P_{NH_3}, under different partial pressures of oxygen at 513 and 553 K, respectively. The reaction rate was nearly independent on P_{NH_3} at lower temperatures. As temperature increased, r_{NO} slightly increased with increasing P_{NH_3} at lower partial pressures of ammonia and tended to be saturated with further increase of P_{NH_3}. Similar to the dependence of r_{NO} on P_{NO} under different partial pressures of oxygen, r_{NO} increases with increasing P_{O_2} and then tends to saturate with further increase of P_{O_2}.

Infrared Spectroscopic Study

The adsorption of NO on the V_2O_5/TiO_2 catalyst has been studied by means of infrared spectroscopy (7, 12, 19, 20) and other techniques (21, 22). The observations reported so far concerning the adsorption of NO together with that of NH_3 on the catalysts were reviewed by Busca *et al.* (15). Most of the experimental results show that the interaction of NO

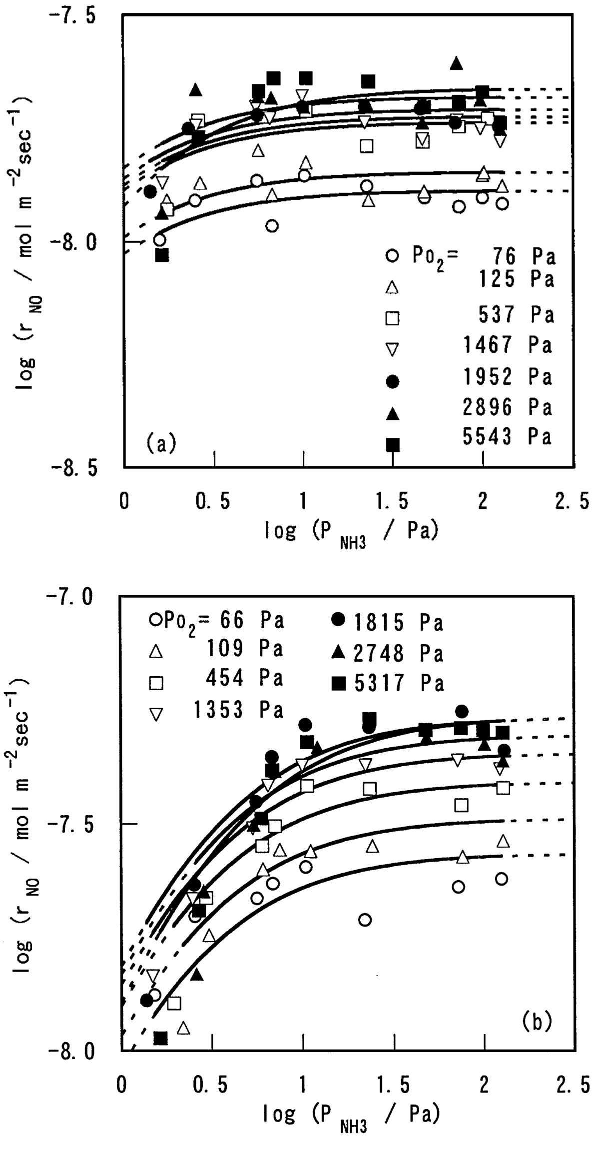

FIG. 2. The dependence of the reaction rate, r_{NO}, on the partial pressure of NH_3, P_{NH_3}, under different partial pressures of oxygen at (a) 513 K and (b) 553 K, respectively. Curves were calculated by Eq. [18].

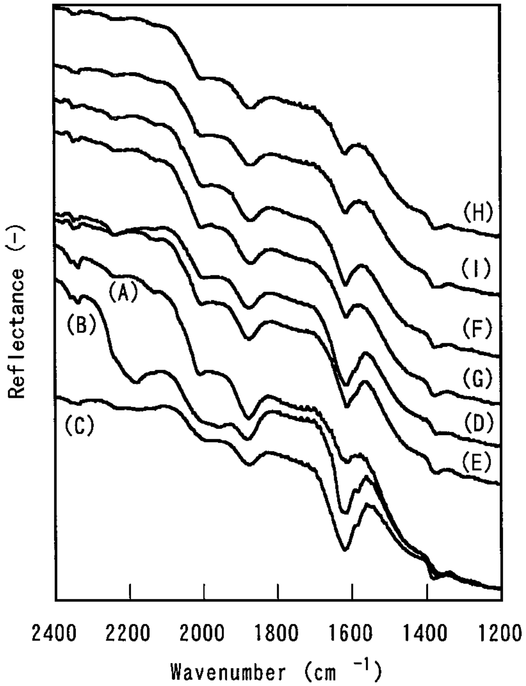

FIG. 3. Infrared spectra of the adsorption of NO on the $V_2O_5(WO_3)/TiO_2$ catalyst at (A–C) RT, (D, E) 373, (F, G) 473, and (H, I) 523 K. After being exposed to gaseous NO (1000 ppm) for (B) 20 and (C) 180 min at RT, (E) 240 min at 373 K, (G) 120 min at 473 K, and (I) 180 min at 523 K. (A, D, F, and H): Backgrounds (after being heated in a stream of oxygen and subsequently purged with helium at each temperature).

with the surface of the V_2O_5/TiO_2 catalyst is very weak. Especially on the oxidized surface of the V_2O_5/TiO_2 catalyst, NO probably does not adsorb. However, because of the variety of experimental conditions as well as the catalyst itself used for the measurements, it is still not clear whether NO adsorbed on the catalyst participates in the SCR reaction or not especially at lower temperatures.

Figure 3 shows typical infrared spectra of the catalyst after contact with gaseous NO at room temperature to 523 K. At room temperature, several bands due to the adsorbed NO species were observed. They increase in intensity with increasing contact time and then become constant. The NO adsorption seems to become weak with increasing temperature because the intensity of the NO band decreases greatly by increasing adsorption temperatures up to 373 K. According to Ramis *et al.* (12) and Dines *et al.* (23), for example, the bands at 1620 and 1582 cm^{-1} are assigned to different types of surface nitrate species. However, above 473 K, no NO adsorption was observed over the oxidized catalyst surface. Because we used a commercial SCR catalyst which contains several metal compounds such as silica-based material as well as active components, it is more difficult to assign the observed bands to the exact adsorption species.

As shown in Fig. 4, ammonia adsorption on both the Brønsted and the Lewis acid sites is observed after contact with gaseous NH_3 at 473 K. The band at 1423 cm^{-1} and broad extension around 2800–3000 cm^{-1} are assigned to ammonium ions, NH_4^+ (7, 24). As to NH_3 adsorbed on the Lewis sites, the bands at 1607 and 3258 cm^{-1} are confirmed (7, 24). After being exposed to gaseous NO (a mixture of 1000 ppm NO and He) at the same temperature, the bands due to both NH_4^+ ions and coordinatively adsorbed NH_3 decrease in intensity with increasing contact time probably due to the reaction with gaseous NO. The formation of adsorbed water is observed (band at 1613 cm^{-1}). Even after all bands of adsorbed ammonia disappear, no band due to the NO adsorption is observed at 473 K.

Because significant NO adsorption is neither observed on the oxidized nor the NH_3 preadsorbed surface above 473 K, the adsorbed NO species probably do not participate in the SCR reaction. The reaction might occur between adsorbed NH_3 species and gaseous NO at least above certain temperatures.

Attempt to Apply Previously Reported Reaction Mechanisms

Because no significant amount of NO adsorbed was observed above 473 K although the observed reaction order with respect to NO has been confirmed to be less than unity, the reaction mechanisms, which involve the adsorption of NO (14, 19), were not concerned in this study. Instead we first tried to fit Eq. [3] to the observed relationship between r_{NO} and P_{NO} to examine how the kinetic parameters change

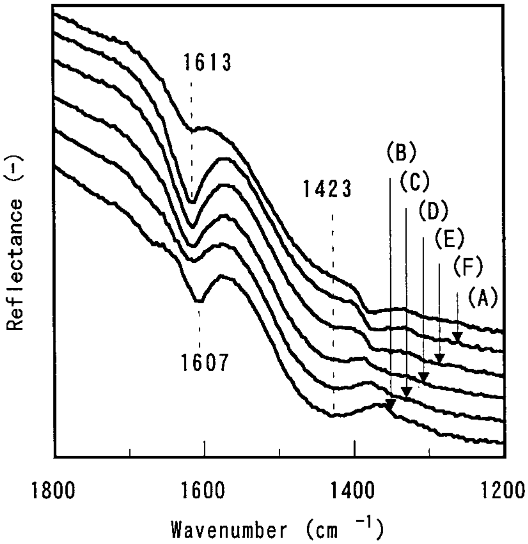

FIG. 4. Infrared spectra of the adsorption of NO on the NH_3 preadsorbed $V_2O_5(WO_3)/TiO_2$ catalyst at 473 K. (A) after being heated in a stream of oxygen at 593 K, (B) after being exposed to gaseous NH_3 and subsequently purged with helium at 473 K, (C–F) after being exposed to gaseous NO (1000 ppm) for (C) 60, (D) 90, (E) 120, and (F) 180 min at 473 K.

with P_{O_2}.

$$r_{NO} = \frac{P_{NO}}{g_1 + g_2 P_{NO}}, \qquad [3]$$

where g_1 and g_2 are expected to be functions of P_{O_2}. For the dependence of r_{NO} on P_{NH_3} under different partial pressures of oxygen, similarly we tried to fit Eq. [4] to the observed results.

$$r_{NO} = \frac{P_{NH_3}}{g_3 + g_4 P_{NH_3}}, \qquad [4]$$

where g_3 and g_4 are also functions of P_{O_2}. From the results of this preliminary curve fitting, we found that g_1 is nearly proportional to $P_{O_2}^{-1/4}$ and g_2 is almost independent on P_{O_2}. It was also found that the dependence of g_3 on P_{O_2} is weak and g_4 is nearly proportional to $P_{O_2}^{-1/4}$. It suggests that the apparent kinetic parameters involved in the SCR reaction change with P_{O_2}. This behavior can be explained neither by the simple Eley-Rideal type equation (4, 25) nor by the rate equation proposed by Dumesic *et al.* (26), which involves the activation process of adsorbed NH_3 with the V=O species. Thus we tried to derive a kinetic equation based on the reaction scheme proposed by Inomata *et al.* (4) and Topsøe *et al.* (9–11) so as to explain this apparent kinetic behavior.

Derivation of the Kinetic Equation

Physicochemical properties of the ternary V_2O_5-WO_3/TiO_2 system have been intensively investigated for a homemade catalyst (27) and a commercial one (28). The interaction of V_2O_5 and WO_3 and the TiO_2 support has been suggested to explain their higher catalytic activity compared to the corresponding binary catalyst (28). However the catalytic activity of WO_3/TiO_2 itself is relatively low compared with that of V_2O_5/TiO_2 especially at lower temperatures. Thus in this study, as our first trial, we assumed that only vanadium is a major active component on the surface for the SCR reaction.

According to the mechanism proposed by Inomata *et al.* (4) and recently by Topsøe *et al.* (9–11), the SCR reaction requires two different functionalities, namely the Brønsted acidity and the redox sites. Concerning the NH_3 adsorption sites, it has been suggested by some researchers that NH_3 takes part in the reaction in form of ammonium ions on the Brønsted acid sites (4, 6, 7, 29, 30). Our previous studies also show that NH_3 adsorbed on the Brønsted acid sites is one of major intermediates of the SCR reaction (31). For the $V_2O_5(WO_3)/TiO_2$ catalyst poisoned by different amounts of potassium oxide, the SCR activity decreases in a similar way with the decrease of the amount of NH_3 adsorbed on the catalyst surface. The spectroscopic study shows that large the decrease of the amount of NH_3 adsorbed may be due to the decrease of the Brønsted acid sites by potassium poisoning (31). The loss of Brønsted acid sites by poisoning has been also found by Chen and Yang (30), suggesting the participation of NH_4^+ ions in the SCR reaction. The equilibrium of NH_3 adsorption on the Brønsted acid sites can be expressed by

$$V^{5+}\text{–}OH + NH_3 \leftrightarrow V^{5+}\text{–}ONH_4$$
$$K_{NH_3} = \frac{\theta_{NH_3}}{s_{V^{5+}-OH} P_{NH_3}}, \qquad [5]$$

where K_{NH_3} and θ_{NH_3} are the equilibrium constant for NH_3 adsorption and the surface coverage of NH_3 adsorbed as ammonium ions to the total number of the sites, respectively. The term $s_{V^{5+}-OH}$ represents the ratio of the Brønsted acid sites, which are not occupied by adsorbed NH_3, to the total number of the sites on the surface. Hereafter a suffix of θ, s, and S indicates the type of the adsorptive and/or the surface species such as $V^{5+}{=}O$ and $V^{5+}\text{–}OH$. Prior to the reaction with gaseous NO, NH_3 adsorbed on the Brønsted acid sites is activated with the $V^{5+}{=}O$ species. The formation of the active intermediate which comprises both NH_3 adsorbed on the $V^{5+}\text{–}OH$ sites and the $V^{5+}{=}O$ sites leads to the reduction of the $V^{5+}{=}O$ sites.

$$V^{5+}\text{–}ONH_4 + V^{5+}{=}O \rightarrow V^{5+}\text{–}ONH_4^+\text{–}OV^{4+}. \qquad [6]$$

Subsequent reaction with NO produces N_2, H_2O, and the hydroxyl groups bonded to the reduced vanadium, $V^{4+}\text{–}OH$. The Brønsted acid sites, $V^{5+}\text{–}OH$, which originally exist on the surface, are then recreated.

$$\begin{aligned} &V^{5+}\text{–}ONH_4^+\text{–}OV^{4+} + NO \\ &\quad \rightarrow N_2 + H_2O + V^{5+}\text{–}OH + V^{4+}\text{–}OH. \qquad [7] \end{aligned}$$

The production of the reduced $V^{4+}\text{–}OH$ groups during the SCR reaction has been confirmed by means of infrared spectroscopy (9, 10). Assuming that the reactions [6] and [7] are under steady state, the time derivatives of the species are zero. Thus, the following relationship can be obtained.

$$\begin{aligned} &\frac{ds_{V^{5+}-ONH_4^+-OV^{4+}}}{dt} \\ &\quad = 0 = k_1 \theta_{NH_3} s_{V^{5+}=O} - k_2 s_{V^{5+}-ONH_4^+-OV^{4+}} P_{NO}, \qquad [8] \end{aligned}$$

where k_1 and k_2 are the rate constants for reactions [6] and [7], respectively. According to Topsøe *et al.* (10), the regeneration of the $V^{5+}{=}O$ species occurs through two steps, which involve the production of V^{3+} and the oxidation of this reduced species by gaseous O_2. However, to make the discussion simple, we assumed here that the newly produced $V^{4+}\text{–}OH$ groups are simply oxidized by gaseous O_2 according to the following equilibrium.

$$V^{4+}\text{–}OH + 1/4\ O_2 \leftrightarrow V^{5+}{=}O + 1/2\ H_2O$$
$$K_{OX} = \frac{s_{V^{5+}=O} P_{H_2O}^{1/2}}{s_{V^{4+}-OH} P_{O_2}^{1/4}}, \qquad [9]$$

where K_{OX} is the equilibrium constant for the reoxidation of the V^{4+}–OH groups to the V^{5+}=O species.

As mentioned above, the result of the preliminary parameter fitting (using Eqs. [3] and [4]) shows that the kinetic parameters involved in the SCR reaction apparently change with P_{O_2}. Therefore we tried to estimate how the number of the active sites changes with the reaction condition. As a first approximation, we assumed that only two kinds of species, V^{5+}=O and V^{5+}–OH, originally exist on the surface before the SCR reaction occurs. The total number of these sites can be expected to be constant.

$$S_{\mathrm{V^{5+}=O}} + S_{\mathrm{V^{5+}-OH}} = 1, \qquad [10]$$

where $S_{\mathrm{V^{5+}=O}}$ and $S_{\mathrm{V^{5+}-OH}}$ are the ratio of the number of the V^{5+}=O and the V^{5+}–OH species to the total, respectively. Here we introduce the ratio of $S_{\mathrm{V^{5+}=O}}$ to $S_{\mathrm{V^{5+}-OH}}$, m, into Eq. [10]. Thus $S_{\mathrm{V^{5+}=O}}$ and $S_{\mathrm{V^{5+}-OH}}$ are given by

$$S_{\mathrm{V^{5+}=O}} = \frac{m}{1+m} \qquad [11]$$

and

$$S_{\mathrm{V^{5+}-OH}} = \frac{1}{1+m}, \qquad [12]$$

respectively. The ratio, m, is considered to be a function of P_{O_2} and P_{H_2O}. Under the reaction conditions, the site balances for each original site, V^{5+}–OH and V^{5+}=O, are preserved according to

$$S_{\mathrm{V^{5+}=O}} = s_{\mathrm{V^{5+}=O}} + s_{\mathrm{V^{4+}-OH}} + s_{\mathrm{V^{5+}-ONH_4^+-OV^{4+}}} \qquad [13]$$

and

$$S_{\mathrm{V^{5+}-OH}} = s_{\mathrm{V^{5+}-OH}} + \theta_{\mathrm{NH_3}} + s_{\mathrm{V^{5+}-ONH_4^+-OV^{4+}}}. \qquad [14]$$

Because NH_3 may preferentially adsorb on the Brønsted acid sites, the ratio of the active intermediate, $s_{\mathrm{V^{5+}-ONH_4^+-OV^{4+}}}$, would be sufficiently small ($s_{\mathrm{V^{5+}-ONH_4^+-OV^{4+}}} < \theta_{\mathrm{NH_3}}$). Therefore Eq. [14] can be simplified to Eq. [15].

$$S_{\mathrm{V^{5+}-OH}} = s_{\mathrm{V^{5+}-OH}} + \theta_{\mathrm{NH_3}}. \qquad [15]$$

From Eqs. [5] and [15], the coverage of NH_3 adsorbed on the Brønsted acid sites is given by

$$\theta_{\mathrm{NH_3}} = S_{\mathrm{V^{5+}-OH}} \frac{K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}}{1 + K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}}. \qquad [16]$$

Similarly, from Eqs. [8], [9], and [13], the ratio of the V^{5+}=O species to the total during the SCR reaction is given by

$$s_{\mathrm{V^{5+}=O}} = \frac{S_{\mathrm{V^{5+}=O}}}{1 + \frac{P_{\mathrm{H_2O}}^{1/2}}{K_{\mathrm{OX}} P_{\mathrm{O_2}}^{1/4}} + \frac{k_1 \theta_{\mathrm{NH_3}}}{k_2 P_{\mathrm{NO}}}}. \qquad [17]$$

Under steady-state conditions, the reaction rates represented by Eqs. [6] and [7] are the same. Therefore, using Eqs. [11], [12], [16], and [17], the total reaction rate, r_{NO}, is given by

$$r_{\mathrm{NO}} = k_1 s_{\mathrm{V^{5+}=O}} \theta_{\mathrm{NH_3}}$$
$$= \frac{m}{(1+m)^2} \frac{K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}}{1+K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}} \frac{k_1}{1+\frac{P_{\mathrm{H_2O}}^{1/2}}{K_{\mathrm{OX}} P_{\mathrm{O_2}}^{1/4}} + \frac{k_1}{(1+m) k_2 P_{\mathrm{NO}}} \frac{K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}}{1+K_{\mathrm{NH_3}} P_{\mathrm{NH_3}}}}. \qquad [18]$$

Determination of Kinetic Parameters

In Eq. [18], four parameters, $K_{\mathrm{NH_3}}$, k_1, k_2, K_{OX}, are expected to be constant at each temperature. However the ratio of $S_{\mathrm{V^{5+}=O}}$ to $S_{\mathrm{V^{5+}-OH}}$, m, may depend on the reaction condition such as P_{O_2} because the V^{5+}=O sites and/or the hydroxyl groups are expected to be equilibrated with oxygen and water in the gas phase. We tried to fit Eq. [18] to the observed kinetic data shown in Figs. 1 and 2 with $K_{\mathrm{NH_3}}$, k_1, k_2, K_{OX}, and m as parameters. Because it is difficult to determine these parameters accurately at a time, first we estimated the parameters by the trial-and-error method and then determined them more accurately by the least-squares method. This preliminary calculation shows that K_{OX} does not much affect the behavior of r_{NO}, suggesting that the equilibrium of Eq. [9] is far from the left. Thus we continued to fit Eq. [18] to the data without the parameter K_{OX} by the least-squares method.

Figures 1 and 2 show the fitted curves together with observed data points. Figure 5 shows the dependence of determined $K_{\mathrm{NH_3}}$, k_1, and k_2 on temperature. The ratio of $S_{\mathrm{V^{5+}=O}}$

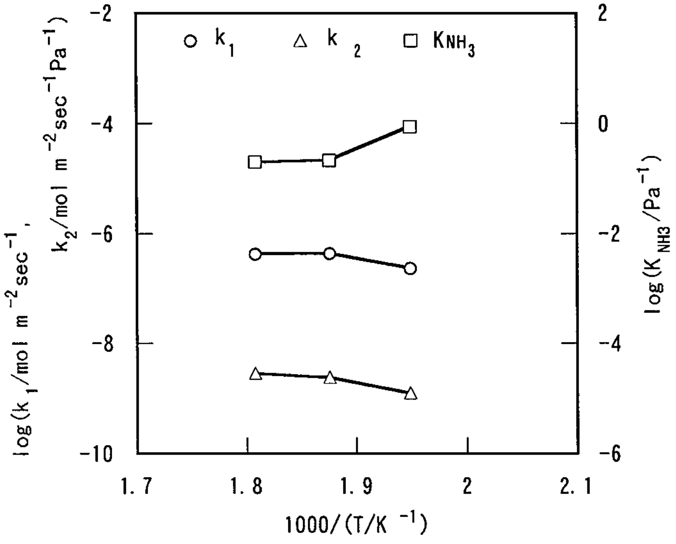

FIG. 5. The dependence of the calculated kinetic parameters, k_1 and k_2, and equilibrium constant for NH_3 adsorption, $K_{\mathrm{NH_3}}$, on temperature.

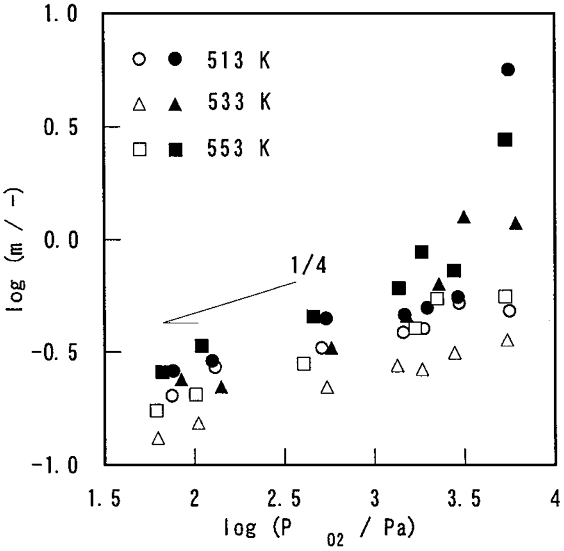

FIG. 6. The dependence of the ratio of number of the $V^{5+}{=}O$ species to the $V^{5+}{-}OH$ groups, m, on the partial pressure of oxygen, P_{O_2}. Open and closed symbols were obtained from the dependence of r_{NO} on P_{NO} and P_{NH_3}, respectively.

to $S_{V^{5+}-OH}$, m, is shown in Fig. 6 as a function of P_{O_2}. We discuss the nature of the surface species using determined kinetic parameters in following paragraph.

Nature of Surface Species

As shown in Fig. 6, the ratio of $S_{V^{5+}=O}$ to $S_{V^{5+}-OH}$, m, is essentially proportional to $P_{O_2}^{1/4}$ at all temperatures. The values, especially determined from the dependence of r_{NO} on P_{NH_3}, scatter greatly at higher partial pressures of oxygen. Using the determined m, $S_{V^{5+}=O}$ and $S_{V^{5+}-OH}$ can be calculated by Eqs. [11] and [12], respectively. The relative amount of the $V^{5+}{=}O$ species varies from ~0.1 to ~0.4 with increasing P_{O_2}. It suggests that the importance of the $V^{5+}{=}O$ and $V^{5+}{-}OH$ species for the SCR reaction could change with P_{O_2} as suggested by Topsøe *et al.* (9, 10) from their *in situ* spectroscopic study.

A close relationship between the existence of the surface species, such as the V=O species and the hydroxyl groups, and the crystalline plane of bulk V_2O_5 has been suggested (6, 32). Gasior *et al.* (6) found that the hydroxyl groups are mainly located on the (100) plane of V_2O_5 explaining that the SCR reaction proceeds with participation of NH_3 adsorbed on the Brønsted acid sites. Andersson (32) also suggested that the V=O sites are mainly located on the (010) plane whereas the hydroxyl groups on the (100) and (001) planes of V_2O_5. As to V_2O_5 supported on TiO_2, it has been suggested that the (010) plane where the V=O sites are located is preferentially exposed to the surface (33). Regarding a commercial SCR catalyst which has low vanadium contents, normally ~1 wt%, the surface vanadium species are expected to be isolated. Because the ratio of the number of $V^{5+}{=}O$ to $V^{5+}{-}OH$ sites apparently changes with P_{O_2} as shown in Fig. 6, the number of the surface hydroxyl groups and/or the terminal V=O sites may be easily changed. The nature of such well-dispersed species is probably different from that expected for the surface of the bulk compounds. There are several kinds of equilibrium which could explain the observed dependence of m on P_{O_2}. Concerning the V=O species, one possible equilibrium is

$$V{=}O + 1/2\ H_2O \leftrightarrow V{-}OH + 1/4\ O_2. \qquad [19]$$

The V=O species are equilibrated with the hydroxyl groups bonded to the reduced vanadium sites. If we assume the participation of the unsaturated vanadium atoms in this equilibrium, the relationship between the V=O and the other species would be more complex.

$$\begin{aligned} V{=}O &\leftrightarrow V + 1/2\ O_2 \\ V{=}O + V + H_2O &\leftrightarrow 2\ V{-}OH. \end{aligned} \qquad [20]$$

Further study concerning the chemistry of such surface species is still required to verify their nature in detail.

The activation energies of the rate constants, k_1 and k_2, are 36 and 49 kJ/mol, respectively. The heat of NH_3 adsorption is 88 kJ/mol. The equilibrium constant for NH_3 adsorption is approximately 0.2 Pa^{-1} at 533 K which is comparable to that determined by the NH_3 chemisorption measurements, ~0.3 Pa^{-1} (31).

As mentioned above, the equilibrium constant for the reoxidation step of $V^{4+}{-}OH$ to the $V^{5+}{=}O$ species, K_{OX}, is found to be large in this study. It suggests that the $V^{4+}{-}OH$ groups formed by the SCR reaction are readily oxidized to the $V^{5+}{=}O$ species. Under typical industrial conditions, however, the water concentration is much higher compared with that in this study (probably $P_{H_2O} < {\sim}10$ Pa). The reoxidation of the $V^{4+}{-}OH$ groups produced by the SCR reaction is reasonably considered to be slower under such conditions. The effect of water on the kinetics would be very important under industrial SCR conditions.

4. CONCLUSIONS

The kinetics of the selective reduction of NO with NH_3 over a commercial $V_2O_5(WO_3)/TiO_2$ catalyst was studied. The observed kinetic behavior was well explained by a reaction mechanism based on the ones proposed by Inomata *et al.* (4) and Topsøe *et al.* (9, 10). The SCR reaction proceeds via two functionalities of the catalyst, namely the Brønsted acid sites and the redox sites. Ammonia takes part in the reaction in the form of ammonium ions on the Brønsted acid sites. The activation step of adsorbed NH_3 with the $V^{5+}{=}O$ sites might be needed prior to the reaction with gaseous NO. The reduced $V^{5+}{=}O$ sites, newly formed hydroxyl groups $V^{4+}{-}OH$, are reoxidized by gaseous oxygen under the reaction conditions examined. Under industrial SCR conditions, the effect of this reoxidation step would become more important because of the higher water concentrations. The ratio of the number of the $V^{5+}{=}O$ species to the Brønsted acid sites, $V^{5+}{-}OH$, is apparently changed with P_{O_2}. The relative amount of the $V^{5+}{=}O$ sites varies from ∼0.1 to ∼0.4 with increasing P_{O_2} in this study. From this study, it was suggested that the nature of well-dispersed vanadium species on such commercial catalyst is different from that expected for the surface of the bulk V_2O_5. The fiber materials, alkali metals, and sulfur species on the surface also might make a difference to the acidic nature of the commercial catalyst from one expected for the V_2O_5/TiO_2 catalyst.

ACKNOWLEDGMENTS

We are grateful to Mrs. Birgitta Svensson for the BET measurement. We gratefully acknowledge Dr. Arne Andersson for stimulating discussions. The financial support from the Japan Cooperation Center Petroleum (JCCP) is also acknowledged.

REFERENCES

1. Bosch, H., and Janssen, F. J. J. G., *Catal. Today* **2**, 369 (1989).
2. Morikawa, S., Takahashi, K., Mogi, J., and Kurita, S., *Bull. Chem. Soc. Japan* **55**, 2254 (1982).
3. Svachula, J., Alemany, L. J., Ferlazzo, N., Forzatti, P., Tronconi, E., and Bregani, F., *Ind. Eng. Chem. Res.* **32**, 826 (1993).
4. Inomata, M., Miyamoto, A., and Murakami, Y., *J. Catal.* **62**, 140 (1980).
5. Bosch, H., Janssen, F. J. J. G., Oldenziel, J., van den Kerkhof, F. M. G., van Ommen, J. G., and Ross, J. R. H., *Appl. Catal.* **25**, 239 (1986).
6. Gasior, M., Haber, J., Machej, T., and Gzeppe, T., *J. Mol. Catal.* **43**, 359 (1988).
7. Topsøe, N., *J. Catal.* **128**, 499 (1991).
8. Odenbrand, C. U. I., Bahamonde, A., Avila, P., and Blanco, J., *Appl. Catal. B* **5**, 117 (1994).
9. Topsøe, N.-Y., Topsøe, H., and Dumesic, J. A., *J. Catal.* **151**, 226 (1995).
10. Topsøe, N.-Y., Dumesic, J. A., and Topsøe, H., *J. Catal.* **151**, 241 (1995).
11. Dumesic, J. A., Topsøe, N.-Y., Topsøe, H., Chen, Y., and Slabiak, T., *J. Catal.* **163**, 409 (1996).
12. Ramis, G., Busca, G., Lorenzelli, V., and Forzatti, P., *Appl. Catal.* **64**, 259 (1990).
13. Tufano, V., and Turco, M., *Appl. Catal. B* **2**, 9 (1993).
14. Koebel, M., and Elsener, M., *Chem. Eng. Sci.* **53**, 657 (1998).
15. Busca, G., Lietti, L., Ramis, G., and Berti, F., *Appl. Catal. B* **18**, 1 (1998).
16. Pârvulescu, V. I., Grange, P., and Delmon, B., *Catal. Today* **46**, 233 (1998).
17. Odenbrand, C. U. I., Lundin, S. T., and Andersson, L. A. H., *Appl. Catal.* **18**, 335 (1985).
18. Lintz, H.-G., and Turek, T., *Appl. Catal.* **85**, 13 (1992).
19. Takagi, M., Kawai, T., Soma, M., Onishi, T., and Tamaru, K., *J. Catal.* **50**, 441 (1977).
20. Dines, T. J., Rochester, C. H., and Ward, A. M., *J. Chem. Soc. Faraday Trans.* **87**, 1617 (1991).
21. Srnak, T. Z., Dumesic, J. A., Clausen, B. S., Törnqvist, E., and Topsøe, N.-Y., *J. Catal.* **135**, 246 (1992).
22. Lietti, L., Nova, I., Camurri, S., Tronconi, E., and Forzatti, P., *AIChE J.* **43**, 2559 (1997).
23. Dines, T. J., Rochester, C. H., and Ward, A. M., *J. Chem. Soc. Faraday Trans.* **87**, 643 (1991).
24. Busca, G., *Langmuir* **2**, 577 (1986).
25. Wang, W. C., and Nobe, K., *Ind. Eng. Chem. Prod. Res. Dev.* **23**, 564 (1984).
26. Dumesic, J. A., Topsøe, T.-Y., Slabiak, T., Morsing, P., Clausen, B. S., Törnqvis, E., and Topsøe, H., New Frontiers in Catalysis, *in* “Proceedings, 10th International Congress on Catalysis” (L. Guczi, F. Solymosi, and P. Tetenyi, Eds.), p. 1325. Akademiai Kiado, Budapest, 1993.
27. Alemany, L. J., Lietti, L., Ferlazzo, N., Forzatti, P., Busca, G., Giamello, E., and Bregani, F., *J. Catal.* **155**, 117 (1995).
28. Alemany, L. J., Berti, F., Busca, G., Ramis, G., Robba, D., Toledo, G. P., and Trombetta, M., *Appl. Catal. B* **10**, 299 (1996).
29. Rajadhyaksha, R. A., and Knözinger, H., *Appl. Catal.* **51**, 81 (1989).
30. Chen, J. P., and Yang, R. T., *J. Catal.* **125**, 411 (1990).
31. Kamata, H., Takahashi, K., and Odenbrand, C. U. I., in press.
32. Andersson, A., *J. Solid State Chem.* **42**, 263 (1982).
33. Inomata, M., Mori, K., Miyamoto, A., Ui, T., and Murakami, Y., *J. Phys. Chem.* **87**, 754 (1983).