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## Effects of reaction temperature on the photocatalytic activity of photo-SCR of NO with NH<sub>3</sub> over a TiO<sub>2</sub> photocatalyst†

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Effects of reaction temperature on the activity of photo-assisted selective catalytic reduction (photo-SCR) of NO with NH<sub>3</sub> were investigated under very high GHSV conditions (100 000 h<sup>-1</sup>). The reaction temperature had a significant effect on the photo-SCR activity over a TiO<sub>2</sub> photocatalyst. Maximum NO conversion was achieved at 433 K (NO conversion = 84%, N<sub>2</sub> selectivity = 100%). The apparent activation energies in the low and high temperature range were evaluated to be 9.0 kJ mol<sup>-1</sup> (353–433 K) and –2.7 kJ mol<sup>-1</sup> (493–593 K), respectively. Kinetic analysis revealed that the rate-determining step in the photo-SCR was decomposition of NH<sub>2</sub>NO intermediates in all the ranges of the reaction temperature (353–593 K). The reaction temperature affects not only the rate constant of decomposition of NH<sub>2</sub>NO intermediates but also the total number of active sites ([S]<sub>0</sub>) and the equilibrium constant of NH<sub>3</sub> adsorption, resulting in the dynamic change in the reaction rate.

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### Introduction

The removal of NO<sub>x</sub> from the exhaust gas of diesel engines has become a major goal for the automotive industry in the last few years. Among the deNO<sub>x</sub> technologies, the selective catalytic reduction (SCR) is currently regarded as the most promising one for heavy-duty and light-duty diesel engines.<sup>1</sup> The SCR process is based on the reaction between NO<sub>x</sub> present in the flue gases and NH<sub>3</sub> (produced from urea) in the presence of O<sub>2</sub>. The V<sub>2</sub>O<sub>5</sub>–WO<sub>3</sub>/TiO<sub>2</sub> catalyst, which is commonly used for stationary SCR systems, shows a relatively high conversion at 623–723 K.<sup>2</sup> However, this type of catalyst exhibits insufficient performance for diesel engines because the exhaust gas from diesel engines has a wide temperature range (373–923 K) depending on the engine load.<sup>3</sup> Ion exchanged zeolites, which

are practically used in diesel cars, convert NO<sub>x</sub> to N<sub>2</sub> with high conversion and selectivity over 433 K.<sup>4–7</sup> However, the ion exchanged zeolites do not work efficiently below 433 K (conversion of NO is below 40% at 423 K in the case of Cu-ZSM-5 and Fe-ZSM-5, GHSV = 100 000 h<sup>-1</sup>).<sup>8</sup> On the other hand, non-supported MnO<sub>x</sub><sup>9,10</sup> and supported MnO<sub>x</sub> catalysts<sup>11</sup> show high activity for the NH<sub>3</sub>-SCR at low temperature, however, the selectivity to N<sub>2</sub> is low.

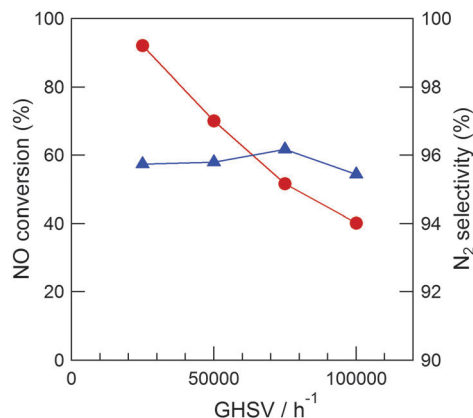
A photocatalyst, which works at ambient temperature, is one of the promising candidates for the de-NO<sub>x</sub> process at low temperature. Pichat and Courbon initially reported that NO produces N<sub>2</sub>O and N<sub>2</sub> over UV-irradiated TiO<sub>2</sub> at room temperature.<sup>12</sup> We have reported that photo-assisted selective catalytic reduction of NO with NH<sub>3</sub> (photo-SCR) in the presence of O<sub>2</sub> proceeds over a TiO<sub>2</sub> photocatalyst at room temperature.<sup>13–16</sup> More than 90% of NO conversion and approximately 100% of selectivity to N<sub>2</sub> were achieved in our systems (GHSV = 8000 h<sup>-1</sup>).<sup>16–18</sup> Approximately 10 000 h<sup>-1</sup> is a suitable GHSV for use with typical stationary sources such as power plants, blast furnaces, and incinerators. On the other hand, in the case of diesel engines, catalysts are required to work at a very high GHSV region because of a limited installation area of the process for the removal of NO<sub>x</sub> and a high flow rate of the exhaust gas. Ultimately, the catalyst volume must be of the order of the engine cylinder volume (typical GHSV in a three-way catalyst amounts to about 100 000 h<sup>-1</sup>).<sup>3</sup> This means that driving at much higher GHSV is absolutely imperative in the

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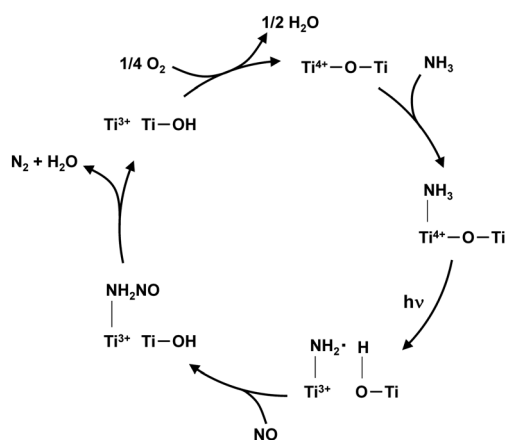
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**Fig. 1** Conversion of NO (●) and N<sub>2</sub> selectivity (▲) in the photo-SCR as a function of GHSV (catalyst amount: 110 mg, NO: 1000 ppm, NH<sub>3</sub>: 1000 ppm, O<sub>2</sub>: 2%).

case that the photo-SCR applies to the removal of NO<sub>x</sub> from the exhaust gas of diesel engines. Fig. 1 shows dependence of conversion of NO and selectivity to N<sub>2</sub> for the photo-SCR of NO with NH<sub>3</sub> over TiO<sub>2</sub> at room temperature on GHSV. Unfortunately, the conversion of NO decreased with increasing the GHSV, although the selectivity to N<sub>2</sub> (ca. 96%) did not change. The conversion of NO descended to 40% at 100 000 h<sup>-1</sup>. In order to use this photocatalytic system for the industrial SCR system, higher activity is required in the high GHSV region.

The mechanism of photo-SCR of NO with NH<sub>3</sub> over TiO<sub>2</sub> has already been reported by our group as shown in Scheme 1.<sup>19</sup> The process of decomposition of NH<sub>2</sub>NO intermediates is a rate-determining step at room temperature in the presence of excess O<sub>2</sub> gas.<sup>17</sup> This process will be promoted by increasing the reaction temperature because it proceeds without photoirradiation, indicating that the reaction rate can be dramatically accelerated by increasing the reaction temperature. Some researchers reported that increment of reaction temperature successfully improved activity for photocatalytic reactions.<sup>20–23</sup> However, the effects of the temperature on the rate of photocatalytic reactions in the gas phase have rarely been studied. In the present study, we



**Scheme 1** Proposed reaction mechanism of the photo-SCR over TiO<sub>2</sub>.

investigated effects of the reaction temperature on the photocatalytic activity of the photo-SCR.

## Experimental section

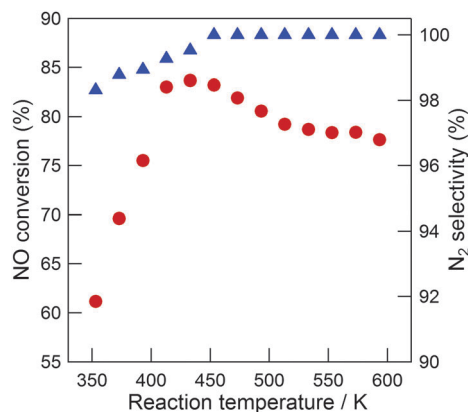
TiO<sub>2</sub> (ST-01, Ishihara Sangyo Kaisha, Ltd.), which has an anatase phase, was hydrated in distilled water for 2 h at 353 K and was dried at 353 K overnight, followed by calcination in dry air at 673 K for 3 h. The specific surface area of the prepared TiO<sub>2</sub> was evaluated to be 93 m<sup>2</sup> g<sup>-1</sup> by the Brunauer–Emmett–Teller (BET) method using a N<sub>2</sub> adsorption isotherm at 77 K.

The photo-SCR was carried out in a conventional fixed bed flow system at an atmospheric pressure at various temperatures. 110 mg of catalyst was fixed with quartz wool and filled up in a quartz reactor which has flat facets (12 mm × 10 mm × 1 mm). Before reactions, catalysts were pretreated at 673 K by flowing 10% O<sub>2</sub>/He gas at 50 mL min<sup>-1</sup> for 60 min. The reaction gas composition was as follows: NO 1000 ppm, NH<sub>3</sub> 1000 ppm, O<sub>2</sub> 2%, He balance gas. A 200 W Hg–Xe lamp equipped with fiber optics, collective lens, and a mirror (San-Ei Electric Co., Ltd., UVF-204S type B) was used as a light source and the sample was irradiated from one side of the flat facets of the reactor. The measured light irradiance was 360 mW cm<sup>-2</sup>. N<sub>2</sub> and N<sub>2</sub>O products were analyzed using a SHIMADSU GC-8A TCD gas chromatograph with MS-5A and Porapak Q columns, respectively.

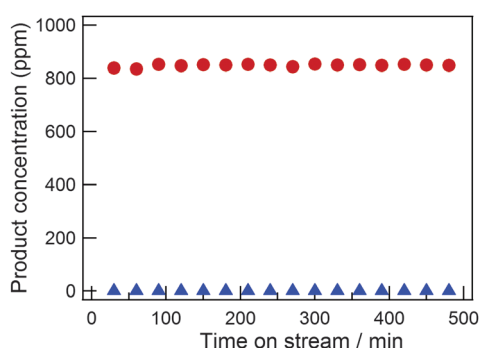
Adsorption isotherms of NH<sub>3</sub> were measured by a volumetric method using a closed vacuum system. 0.2 g of TiO<sub>2</sub> were evacuated at 673 K for 30 min and then pretreated by O<sub>2</sub> (80 Torr) at 673 K for 60 min. After evacuating at 673 K for 60 min, the catalyst was cooled down to a given temperature. Before adsorption measurements, the dead volume was measured using Ar gas at each temperature. In the first experiment, adsorption amounts of NH<sub>3</sub> were measured at various equilibrium pressures of NH<sub>3</sub> (physical adsorption and chemical adsorption). After evacuation for 90 min, the second adsorption experiment was carried out (physical adsorption). The chemical adsorption amount of NH<sub>3</sub> was calculated by subtracting the adsorption amount of the second experiment from the one of the first experiment.

## Results and discussion

Fig. 2 shows dependence of conversion of NO and selectivity to N<sub>2</sub> for the photo-SCR over TiO<sub>2</sub> on reaction temperature. The selectivity to N<sub>2</sub> slightly increased with increasing reaction temperature and then reached 100% above 453 K. The conversion of NO drastically increased with increasing the reaction temperature. The maximum conversion of NO (84%) was observed at 433 K. However, it decreased with further increment of the reaction temperature. Fig. 3 displays the time course for the photo-SCR over TiO<sub>2</sub> at 433 K. The conversion of NO reached 84% as soon as the TiO<sub>2</sub> photocatalyst was irradiated and was kept for at least 480 min, indicating that the TiO<sub>2</sub> photocatalyst used in this study was very stable under the reaction conditions.



**Fig. 2** Dependence of conversion of NO (●) and N<sub>2</sub> selectivity (▲) in the photo-SCR on the reaction temperature (catalyst amount: 110 mg, NO: 1000 ppm, NH<sub>3</sub>: 1000 ppm, O<sub>2</sub>: 2%, GHSV: 100 000 h<sup>-1</sup>).



**Fig. 3** Time course for the photo-SCR over TiO<sub>2</sub> at 433 K. ●: outlet concentration of N<sub>2</sub>, ▲: outlet concentration of N<sub>2</sub>O (catalyst amount: 110 mg, NO: 1000 ppm, NH<sub>3</sub>: 1000 ppm, O<sub>2</sub>: 2%, GHSV: 100 000 h<sup>-1</sup>).

The conversion in the photo-SCR system below 433 K is higher than those of Fe and Cu zeolite catalysts (the conversion of NO is below 40% in the case of Cu-ZSM-5 and Fe-ZSM-5 at 423 K at GHSV = 100 000 h<sup>-1</sup>).<sup>8</sup>

The conversion of NO increased with increasing the reaction temperature from 353 K to 433 K as shown in Fig. 2. The activation energy between 353 K and 433 K is estimated to be 9.0 kJ mol<sup>-1</sup> by the Arrhenius plot of the photo-SCR at lower contact time (Fig. S1 in ESI†). On the other hand, the NO conversion decreased as the reaction temperature increased from 433 K to 593 K. The apparent activation energy is estimated to be -2.7 kJ mol<sup>-1</sup>. The first increase of the photocatalytic activity will be due to the acceleration of the rate-determining step, which is the decomposition of NH<sub>2</sub>NO intermediates at room temperature.<sup>17</sup> To determine the rate-determining step in the temperature range between room temperature and 553 K, the kinetic study was carried out at various temperatures. The reaction rate of the photo-SCR is expressed using the following formula:

$$r = k P_{\text{NO}}^{\alpha} P_{\text{NH}_3}^{\beta} P_{\text{O}_2}^{\gamma} I^{\delta} \quad (1)$$

where  $P_x$  is the partial pressure of  $x$  ( $x = \text{NH}_3$ , NO, and O<sub>2</sub>) and  $I$  is the irradiance. To obtain the reaction order ( $\alpha$ ,  $\beta$ ,  $\gamma$  and  $\delta$ ) at

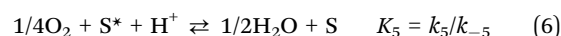
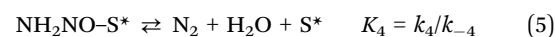
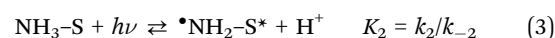
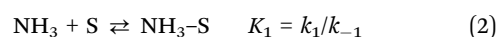
**Table 1** Reaction orders at each temperature

$T/\text{K}$	$\alpha^a$	$\beta^b$	$\delta^c$	$\delta^d$
323	0.17	0.49	0.29	0.58
373	0.12	0.46	0.29	0.60
433	0.09	0.48	0.19	0.71
553	0.01	0.58	0.33	0.75

<sup>a</sup> Reaction orders of NH<sub>3</sub>. <sup>b</sup> Reaction orders of NO. <sup>c</sup> Reaction orders of O<sub>2</sub>. <sup>d</sup> Reaction orders of irradiance.

various temperatures, the photo-SCR was carried out under the conditions of the various partial pressures of NO, NH<sub>3</sub> or O<sub>2</sub>, or different light intensities. The reaction orders at each temperature are listed in Table 1.

The rate constant and equilibrium constant of each elementary step are defined on the basis of the proposed reaction mechanism as follows:



We calculated the following rate equations by assuming that each step is a rate-determining step:

$$r = \frac{k_1 P_{\text{NH}_3} [S]_0}{1 + (1/K_5 P_{\text{O}_2}^{1/4})} \quad (7)$$

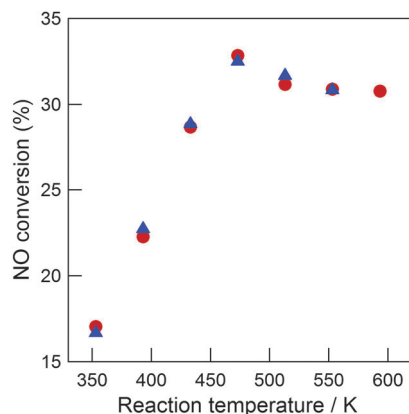
$$r = \frac{k_2 K_1 P_{\text{NH}_3} I [S]_0}{1 + K_1 P_{\text{NH}_3} + (1/K_5 P_{\text{O}_2}^{1/4})} \quad (8)$$

$$r = \frac{k_3 K_1 K_2 P_{\text{NH}_3} P_{\text{NO}} I [S]_0}{1 + K_1 P_{\text{NH}_3} + K_1 K_2 P_{\text{NH}_3} I + (1 + 1/K_5 P_{\text{O}_2}^{1/4})} \quad (9)$$

$$r = \frac{k_4 K_1 K_2 K_3 P_{\text{NH}_3} P_{\text{NO}} I [S]_0}{K_1 P_{\text{NH}_3} + K_1 K_2 P_{\text{NH}_3} I + K_1 K_2 K_3 P_{\text{NH}_3} P_{\text{NO}} I + (1/K_5 P_{\text{O}_2}^{1/4})} \quad (10)$$

$$r = k_5 P_{\text{O}_2}^{1/4} [S]_0 \quad (11)$$

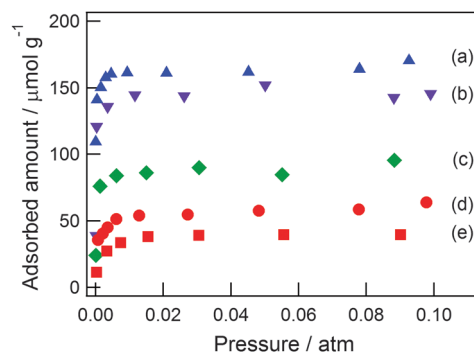
where  $[S]_0$  is the total number of active sites. The reaction orders of  $P_{\text{NO}}$  in eqn (7)–(9) and (11) do not satisfy the experimental reaction orders at all the temperatures listed in Table 1. Consequently, steps 2, 3, 4, and 6 are excluded from candidates for the rate-determining step. Eqn (10) satisfies the experimental reaction orders at all the temperatures, which indicates that the rate-determining step in the photo-SCR is the step of decomposition of NH<sub>2</sub>NO intermediates (step 5) in the temperature range studied. The conversion of NO increased with increasing the reaction temperature from 353 K to 433 K because the decomposition process of NH<sub>2</sub>NO intermediates was promoted by the thermal effect ( $k_4$  in eqn (10) increased as the reaction temperature increased).



**Fig. 4** Temperature cycle test in the heating procedure (●) and the cooling procedure (▲) (catalyst amount: 16 mg, NO: 1000 ppm, NH<sub>3</sub>: 1000 ppm, O<sub>2</sub> 2%, GHSV: 100 000 h<sup>-1</sup>).

The increase of  $k_4$  has only a positive effect on the activity. Accordingly, it is unaccountable for the reason why the NO conversion decreased as the reaction temperature increased from 433 K to 593 K. Two reasons have been proposed for the appearance of negative apparent activation energies. One is thermal deactivation of catalysts<sup>24</sup> and the other is the case that an exothermic and equilibrium reaction in elementary steps have an effect on the overall reaction rate.<sup>25</sup> To confirm whether thermal deactivation of the catalysts occurs or not, we elevated the reaction temperature in the photo-SCR to 593 K at first, and then lowered it to 353 K (Fig. 4). If the thermal deactivation occurs, NO conversion in the cooling procedure should be lower than that in the heating procedure. The hysteresis curve was not observed between the heating and cooling procedures. This result clearly indicated that the negative apparent activation energy was not due to the thermal deactivation of the catalysts.

In all the elementary steps (steps 2–6), adsorption of NH<sub>3</sub> (step 2) is an exothermic and equilibrium reaction. NH<sub>3</sub> adsorption isotherm experiments were carried out at various temperatures as shown in Fig. 5. The amount of NH<sub>3</sub> adsorption clearly decreased as the temperature increased. The Langmuir adsorption isotherm was used to describe the NH<sub>3</sub> adsorption as follows:



**Fig. 5** NH<sub>3</sub> adsorption isotherms on the TiO<sub>2</sub> catalyst at various temperatures: (a) 373 K, (b) 413 K, (c) 473 K, (d) 513 K, and (e) 553 K.

**Table 2** Langmuir isotherm parameters for the NH<sub>3</sub> adsorption on the TiO<sub>2</sub> at various temperatures

$T/K$	$q_m/\mu\text{mol g}^{-1}$	$K_1/\text{atm}^{-1}$
373	160.9	$1.65 \times 10^4$
413	146.5	$8.96 \times 10^3$
473	90.1	$3.13 \times 10^3$
513	57.8	$1.64 \times 10^3$
553	39.8	$9.45 \times 10^2$

$$P_a/q_e = P_a/q_m + 1/q_m K_1 \quad (12)$$

where  $q_e$  is the equilibrium adsorption amount ( $\mu\text{mol g}^{-1}$ ),  $P_a$  is the equilibrium partial pressure of NH<sub>3</sub> (atm),  $q_m$  is the maximum adsorption capacity ( $\mu\text{mol g}^{-1}$ ),  $K_1$  is the adsorption equilibrium constant ( $\text{atm}^{-1}$ ). The  $q_m$  and  $K_1$  at each temperature that are obtained using eqn (12) are listed in Table 2. The increase of the temperature decreased not only the equilibrium constant of NH<sub>3</sub> adsorption ( $K_1$ ) but also the maximum adsorption capacity ( $q_m$ ) of NH<sub>3</sub>. The  $q_m$  corresponds to the number of ammonia adsorption sites, which is assumed to be the total number of active sites ( $[S]_0$  in eqn (10)). From eqn (10), the decrease of  $[S]_0$  and  $K_1$  leads to the decline of the overall reaction rate. Thus, we concluded that the overall reaction rate decreased because both the total number of active sites ( $[S]_0$ ) and the value of  $K_1$  decreased with increasing the temperature from 433 K to 593 K.

In summary, three kinetic and thermodynamic parameters should be considered as a function of temperature to describe the reaction rate of the photo-SCR: (i) the rate constant of decomposition of NH<sub>2</sub>NO intermediates ( $k_4$ ), (ii) the total number of active sites ( $[S]_0$ ), and (iii) the equilibrium constant of NH<sub>3</sub> adsorption ( $K_1$ ). In the low temperature range (353–433 K),  $k_4$  dominates the overall reaction rate, which results in the straight and negative line in Arrhenius plots. In the middle temperature range (433–493 K),  $[S]_0$  and/or  $K_1$ , which decreases as the temperature increases, starts to contribute to the reaction rate, which results in the curved Arrhenius plots. In the high temperature range (493–593 K), contribution of  $[S]_0$  and/or  $K_1$  to the overall reaction rate becomes more dominant than that of  $k_4$ . As a result, the negative apparent activation energy appeared in the high temperature range.

## Conclusion

We found that the reaction temperature had a significant effect on the photo-SCR activity over a TiO<sub>2</sub> photocatalyst. The photocatalytic activity was increasing with an increase of the reaction temperature from 353 K to 433 K, however decreasing from 433 to 593 K. Maximum conversion was 84% at the high GHSV of 100 000 h<sup>-1</sup> at 433 K. The high efficiency of the NO removal indicates that the photo-SCR system has a potential for the practical de-NO<sub>x</sub> system in diesel engines. The kinetic analysis revealed that the rate-determining step in the photo-SCR is decomposition of NH<sub>2</sub>NO intermediates in all the temperature ranges studied. The calculated rate equation and the NH<sub>3</sub> adsorption experiment indicated that the absorption

amount of  $\text{NH}_3$  at high temperature affords the key to achieve the high NO conversion, because of a trade-off relationship between the absorption of  $\text{NH}_3$  and the decomposition of  $\text{NH}_2\text{NO}$  intermediates. We believe that thermodynamics and kinetics are becoming more important in the field of photocatalysis as well as catalysis.

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