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Photoassisted NO reduction with NH_3 over TiO_2 photocatalyst

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Photoassisted selective catalytic reduction of NO with ammonia (photo-SCR) at low temperature over irradiated TiO_2 in a flow reactor was confirmed to proceed efficiently and the adsorbed ammonia reacted with NO under irradiation of TiO_2.

The NO in the exhaust gas from a stationary emission source is ordinarily removed by applying selective catalytic reduction with ammonia (ammonia SCR) over V–Ti based oxide catalysts.[1] The ammonia SCR can be operated at relatively high temperatures above 573 K. In the case of 'dirty gas' including variable amounts of halogens and SO*x*, the ammonia SCR process must be set downstream of de-halogen and de-SO*x* processes. Through these processes, the gas temperature drops to less than 473 K and re-heating the gas or heating catalyst bed is needed to activate the ammonia SCR system. Therefore, the development of an ammonia SCR system working at low temperature is now strongly desired.[2] In the present study, we attempted to realise low temperature SCR with the aid of light[3] and a photocatalyst.

TiO_2 photocatalyst, JRC-TIO-4, was kindly supplied by the Reference Catalyst Committee of the Catalysis Society of Japan. The reaction was carried out with a conventional fixed bed flow reactor at atmospheric pressure. The catalyst bed consists of two flat cells ($50 \times 15 \times 1$ mm^3) connected in series and TiO_2 with matched grain size in $25 - 50$ mesh was packed in the catalyst bed. The amount of the TiO_2 catalyst was 1.2 g and volume of the catalyst bed was 1.5 ml in total. Light was irradiated from a 300 W ultra-high pressure Xe lamp with reflection by a cold mirror. Prior to reaction, the catalyst was treated at 673 K by passing 5% O_2 diluted with Ar at a flow rate of 50 ml min^{-1}. The composition of the reaction gas was NO 1000 ppm, NH_3 1000 ppm, O_2 5%, and the balance Ar and the flow rate was 100 ml min^{-1} corresponding to the GHSV 4000 h^{-1}. The produced N_2O and N_2 were quantified by on-line gas chromatography. NO_2 was checked using a NO*x* meter and was not detected at all. The temperature of the catalyst bed was held to be 323 K. The origin of nitrogen atoms in the evolved N_2 and N_2O was investigated by the reaction with ^{15}NO and $^{14}NH_3$ and we found that all the nitrogen molecules were $^{15}N^{14}N$ and all the nitrous oxide was $^{15}N_2O$.

Fig. 1 shows the time course of the reaction. N_2O was produced only in trace amounts. The ammonia SCR is a down hill reaction and therefore it proceeds in the dark at low temperature at 20% conversion. Photoirradiation caused remarkable enhancement of activity. When the reaction gas was passed under irradiation, the evolution rate of N_2 gradually increased and attained a steady rate, *ca*. 80% conversion after 120 min irradiation. The induction period may be due to the time for saturation of the adsorption equilibrium of the reactant molecules. To examine this, in the first 90 min, the reaction gas was passed in the dark and after 90 min, irradiation was started. The result is shown in Fig. 2. In the dark, N_2 was evolved at 20% conversion as mentioned above, the conversion jumped remarkably to the level of the steady rate as soon as the irradiation was started. This clearly shows that the induction period is the time for equilibrium adsorption of reactant molecules. In order to find which reactant molecule is adsorbed first, we carried out a couple of experiments. In the first one NO and O_2 was passed in the first 90 min and then the feed gas was switched to NH_3. Neither N_2 or N_2O was detected in the outlet flow during the whole reaction time, and NO was not detected after switching the feed gas, suggesting that NO is very weakly adsorbed on TiO_2. In the second experiments NH_3 and O_2 was passed in the first 90 min in the dark and then the feed was changed to NO and O_2 at the same time as irradiation was started. The result is shown in Fig. 3. $N_2$was evolved at a steady rate the moment that the gas feed composition was changed and the irradiation was started. The evolution rate then gradually decreased. This shows that NH_3 was firstly adsorbed and consumed by the contact with NO. The total amount of formed N_2 was determined to be 0.23 mmol g-cat^{-1} by integrating the evolution rate of N_2, and the value was consistent with the amount of adsorbed ammonia over TiO_2 in equilibrium at 323 K, 0.24 mmol g-cat^{-1}. Evidently, NO reacts with adsorbed ammonia under irradiation. The kinetic experiment carried out under differential conditions in the pressure range $300 < p(\mathrm{NO}), p(\mathrm{NH_3}) < 2000$ ppm, and the presence of excess O_2 gave the result that the evolution rate of N_2 depends only on NO partial pressure; first order against NO, and zeroth order against O_2 and NH_3. This strongly suggests that the rate-determining step is the adsorption of NO

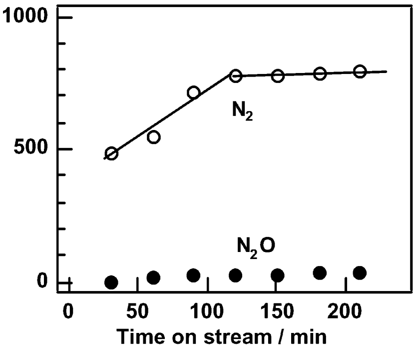

Fig. 1 Outlet concentration of N_2 and N_2O in the SCR of NO with ammonia at 323 K under irradiation.

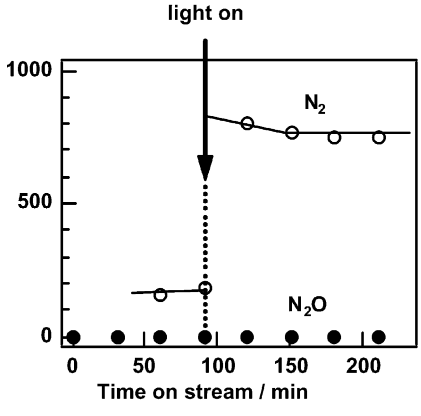

Fig. 2 Outlet concentration of N_2 and N_2O in the SCR of NO with ammonia at 323 K.

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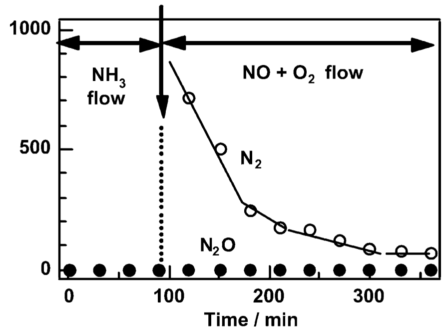

Fig. 3 Outlet concentration of N_2 and N_2O during varying experimental conditions. In the first 90 min, NH_3 was flowed in the dark and at 90 min, NH_3 flow was switched to NO and O_2 and the lamp was turned on.

to the irradiated TiO_2 adsorbing ammonia molecules. The Lewis acid site is very likely as an adsorption site of ammonia.[4] An adsorbed ammonia molecule is excited by irradiation of TiO_2 and reacts with an NO molecule to produce nitrogen.

We investigated the effect of water vapour by varying the humidity. The activity did not change with an increase in humidity until saturation was reached, when the activity abruptly declined due to the accumulation of liquid water.

From the results mentioned above, we conclude that an adsorbed ammonia molecule is excited by irradiation of TiO_2 and reacts with an NO molecule to produce nitrogen. Although we have not tried the reaction in the presence of SO*x*, the photo-SCR may be promising for the low temperature removal of nitrogen oxide.

Notes and references

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