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Reply to the Letter of In-Sik Nam Concerning the Paper "Preparation and Performance of a Silica-Supported V_2O_5 on TiO_2 Catalyst for the Selective Reduction of NO with NH_3"

Since our paper [E. T. C. Vogt, A. Boot, A. J. van Dillen, J. W. Geus, F. J. J. G. Janssen, and F. van den Kerkhof, *J. Catal.* **114,** 313 (1988)] is concerned mainly with the effects of the structure of catalysts containing vanadium oxide and titanium oxide supported on silica, we did not deal extensively with the reaction between ammonia and nitrogen oxide. In-Sik Nam's remark is addressed to the involvement of molecular oxygen in the reaction of nitrogen oxide and ammonia. The two reactions considered are

$$6NO + 4NH_3 = 5N_2 + 6H_2O \text{ and}$$
$$4NO + 4NH_3 + O_2 = 4N_2 + 6H_2O.$$

Nam advocates the first reaction and compares the activities represented in Fig. 2 of our paper with the selectivities mentioned in Table 3. Since the results of Fig. 2 and the data of Table 3 were measured with different catalyst beds, the conversions were different. The selectivities of the isotopic studies mentioned in Table 3 are therefore not relevant for the data represented in Fig. 2. Whereas the activities represented in Figs. 2 and 3 were measured on a catalyst bed of 50 mg in a reactor of a diameter of 3 mm, the experiments with nitrogen isotopes were performed with a catalyst bed of 100 mg in a reactor of a diameter of 8 mm. In both cases the space velocity was 60,000 h^{-1}. Because the linear velocity of the gas flow is higher by a factor of 7 in the experiments with the catalyst bed of 50 mg, the rate of transport to the surface of the catalyst particles was much higher. This led to a higher conversion in the experiments of Figs. 2 and 3, which was about 100%. In the experiments of Table 3, the conversion was lower, viz., 85%. Also the fraction of ammonia which was oxidized to molecular nitrogen was higher in the experiments with the larger catalyst bed. In view of the composition of the gas flow, oxygen 2%, NO 500 ppm, and ammonia 500 ppm, a slower transport to the surface of the catalyst particles will lead to a suppression of the reaction of nitrogen oxide and ammonia. The oxidation of ammonia by molecular oxygen was therefore promoted.

The results of the experimental stoichiometry of the reaction, as evident in Figs. 2 and 3, indicate that in our experiments molecular oxygen participates in the reaction of nitrogen oxide and ammonia. The data of Fig. 2 show that the consumptions of NO and NH_3 are equal and that the growth in the concentration of molecular nitrogen is equal to the drop in the ammonia and nitrogen oxide concentrations. Catalyst D, the activity of which is represented in Fig. 3, brought about the oxidation of NH_3 to N_2 at higher temperatures. At temperatures up to about 250°C, the oxidation of ammonia to molecular nitrogen did not proceed significantly. It can be seen that below about 250°C this catalyst also displayed an equal consumption of NH_3 and NO and a growth in the concentration of N_2 which was equal to the decrease in the concentration of NO and NH_3. The reaction proposed by Nam would ask for a ratio of the rates of consumption of NO and NH_3 of 1.5, and a ratio of the rates of consumption of NO and of production of N_2 of 1.2.

The above conclusion from the experimental stoichiometry of the reaction can be corroborated by results from isotopic ex-

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periments. In isotopic experiments using ^{15}NO and $^{14}NH_3$, only $^{14}N^{15}N$ was observed as dinitrogen species. Heavy dinitrogen $^{15}N_2$ formed due to the oxidation of $^{15}NH_3$ cannot be distinguished from ^{14}NO. However, the reaction proposed by Nam would lead to $^{14}N_2$, which was never observed. Using $^{14}NH_3$ and ^{15}NO, on the other hand, oxidation of ammonia with molecular oxygen leads to formation of $^{14}N_2$. As an example we give the results of an experiment with ^{15}NO and $^{14}NH_3$ at 400°C in which a significant oxidation of ammonia by molecular oxygen proceeded. The reaction products were

^{15}NO	73 ppm
$^{14}NH_3$	15 ppm
$^{14}N^{15}N$	385 ppm
$^{14}N^{15}NO$	3 ppm
^{14}NO	0 ppm
$^{14}N_2O$	3 ppm
$^{14}N_2$	69 ppm.

The error in the above figures is about 10%. It can be calculated that the relative amount of nitrogen atoms from ammonia ending up in $^{14}N_2$ is 0.26. It is also evident that neither ^{14}NO nor $^{15}N_2$ is formed. The dinitrogen species formed were either from the reaction between NO, NH_3, and O_2 or from the reaction between NH_3 and O_2. The last reaction leads to $^{14}N_2$. The amount of $^{14}N^{15}N$ agrees within the limits of error with the conversion of ^{15}NO, viz., 385 and 427 pm, respectively.

It has been observed that the reaction of ammonia with the catalyst leads to the presence of nitrogen on the surface of the catalyst that is rather tenaciously adsorbed. Reaction of nitrogen oxide with the adsorbed nitrogen atoms results in desorption of dinitrogen and adsorption of oxygen. The hydrogen atoms of the ammonia react with oxygen atoms of the surface of the catalyst to hydroxyl groups. Desorption of water from neighboring hydroxyl groups leads to surface oxygen vacancies that are subsequently filled by molecular oxygen. Consequently molecular oxygen participates in the reaction by filling oxygen vacancies generated on the surface of the catalyst by reaction with the hydrogen atoms from the ammonia. Only if no molecular oxygen is present are the surface vacancies filled by oxygen from NO and the reaction proposed by Nam proceeds. With the excess of oxygen usually present during selective catalytic reduction of NO, however, the reaction presented in our paper proceeds exclusively.

E. T. C. VOGT
A. J. VAN DILLEN
J. W. GEUS

Department of Inorganic Chemistry
University of Utrecht
Croesestraat 77[a]
3522 AD Utrecht, The Netherlands

F. J. J. G. JANSSEN
F. VAN DEN KERKHOF

Arnhem Institutions of the Dutch
Electricity Utilities N.V.
KEMA, R4D Division
Department of Chemical Research
P.O. Box 9035
6800 ET Arnhem, The Netherlands

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