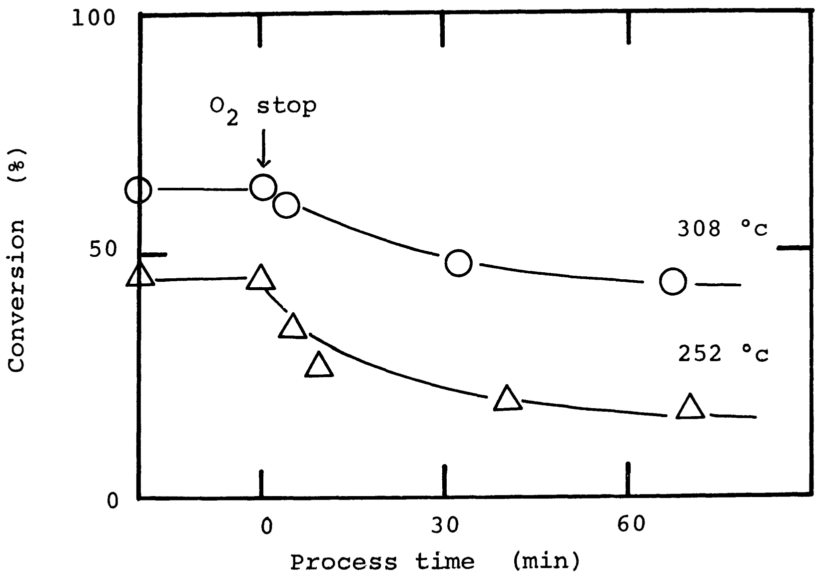
CHEMISTRY LETTERS, pp. 799-802, 1978. Published by the Chemical Society of Japan

THE (V^{5+}=O) BOND RESPONSIBLE FOR THE ACCELERATION OF THE NO-NH_3 REACTION ON VANADIUM OXIDE IN DILUTE GAS CONDITION

Makoto INOMATA*, Akira MIYAMOTO, and Yuichi MURAKAMI
Department of Synthetic Chemistry, Faculty of Engineering,
Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464
* Kinuura Kenkyu-sho, Nikki K.K., Sunosaki, Handa 475

The NO-NH_3 reaction was markedly accelerated by the addition of O_2 up to 1%. It was found that the (V^{5+}=O) bond on the surface of vanadium oxide plays as active site for the reduction of NO by NH_3 and the reaction is accelerated in proportion to the amount of the (V^{5+}=O) bond.

It is generally accepted that the NO-NH_3 reaction on vanadium oxide is markedly accelerated in the presence of oxygen.1)2) Several mechanisms of this reaction on vanadium oxide have already been reported.3)4) Tamaru et al. studied the mechanism of the NO-NH_3 reaction in the presence of O_2 by means of IR, XPS, mass spectrometer and volumetric techniques and indicated that NO_2(ad) produced by the reaction; $NO+1/2O_2 \rightarrow NO_2$(ad), reacts readily with NH_4^+(ad) to form N_2 molecule.3) The authors et al. studied a role of the (V^{5+}=O) bond on vanadium oxide with various oxidation states (V_2O_4-V_2O_5) by means of IR, ESR and pulse techniques and indicated that the (V^{5+}=O) bond on the surface of vanadium oxide plays as the active site for the reduction of NO by NH_3 and accelerates the reaction.4) As mentioned above, oxygen species responsible for the reaction differ evidently according to the experimental conditions. Furthermore, the experimental conditions in these works differ considerably from dilute gas condition employed in the industrial process. Therefore, the mechanism of acceleration of the NO-NH_3 reaction on V_2O_5 by O_2 under dilute gas condition



NO ;1000ppm
NH_3;1000ppm
O_2 ;1.3 - 0.0%
He ;balance

W/F;0.33g-cat·hr/mol

Fig.1 The change of the catalytic activity after a stop of O_2 gas supply

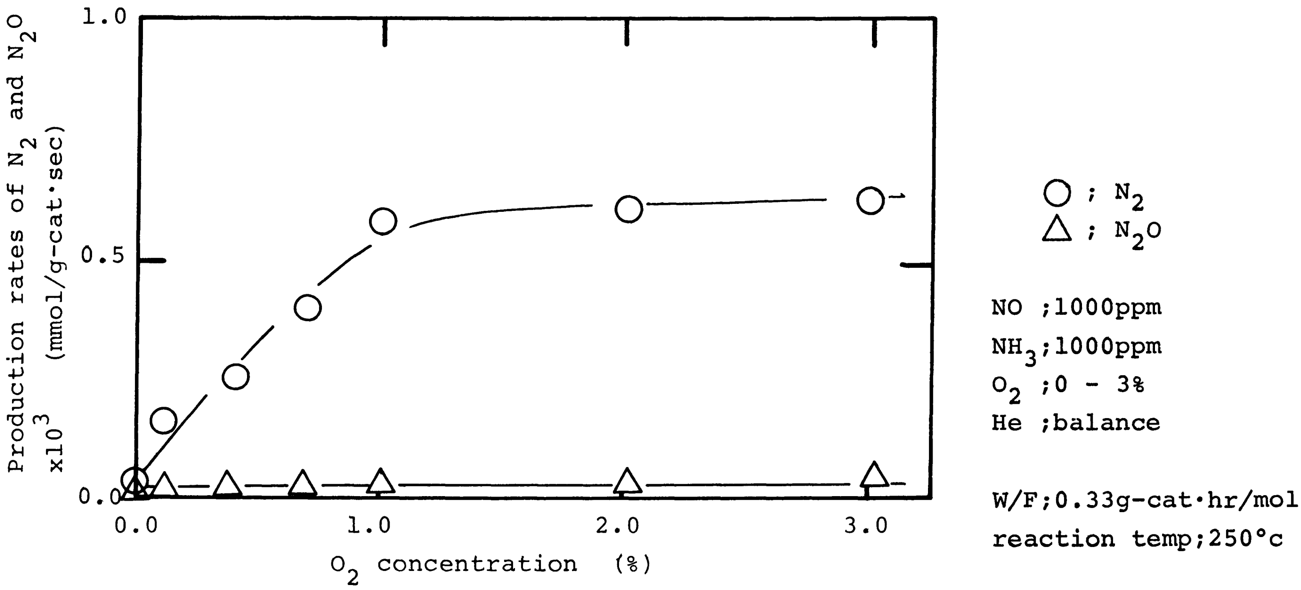


Fig.2 Effect of O_2 concentration on the production rates of N_2 and N_2O

has not been established unequivocally. In this work, we will elucidate oxygen species responsible for O_2 enhancement of NO reduction under dilute gas condition.

Kinetic studies were carried out by a conventional flow method under a dilute gas composition. The gas mixture consisting of NO 1000ppm, NH_3 1000ppm and O_2 0-3% with He balance gas was used. The quantity of O_2 as an impurity in NO, NH_3 or He gas was negligible. W/F was 0.33g-cat·hr/mol, reaction temperature was 250°c-310°c at which the oxidation of NH_3 was negligible. Products, N_2 and N_2O, were analyzed by gas chromatography. Steady states of the activities and the structures of catalysts were attained after the reaction of the 60-80 hrs′ duration. The samples thus obtained were used for the measurements of the activities, IR and ESR. IR spectra and ESR spectra were obtained by KBr disk technique on a JASCO IR-G spectrometer and at room temperature on a JEOL ME1X spectrometer, respectively. V_2O_5(BET surface area; 4.61m^2/g) was prepared by thermal decomposition of extra-pure NH_4VO_3 in the stream of dry oxygen at 500°c for 3hr.

Fig.1 shows the change of the catalytic activity after a stop of O_2 gas

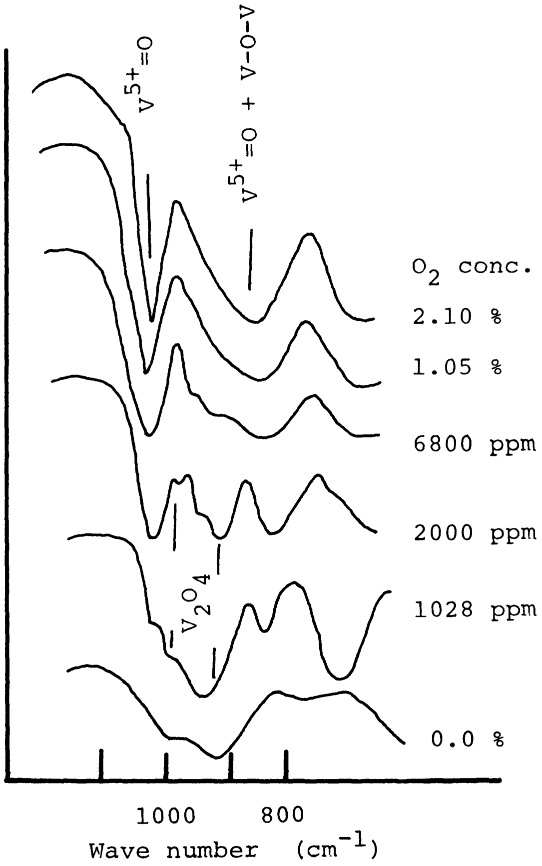


Fig.3 IR spectra of the vanadium oxides with various O_2 concentrations

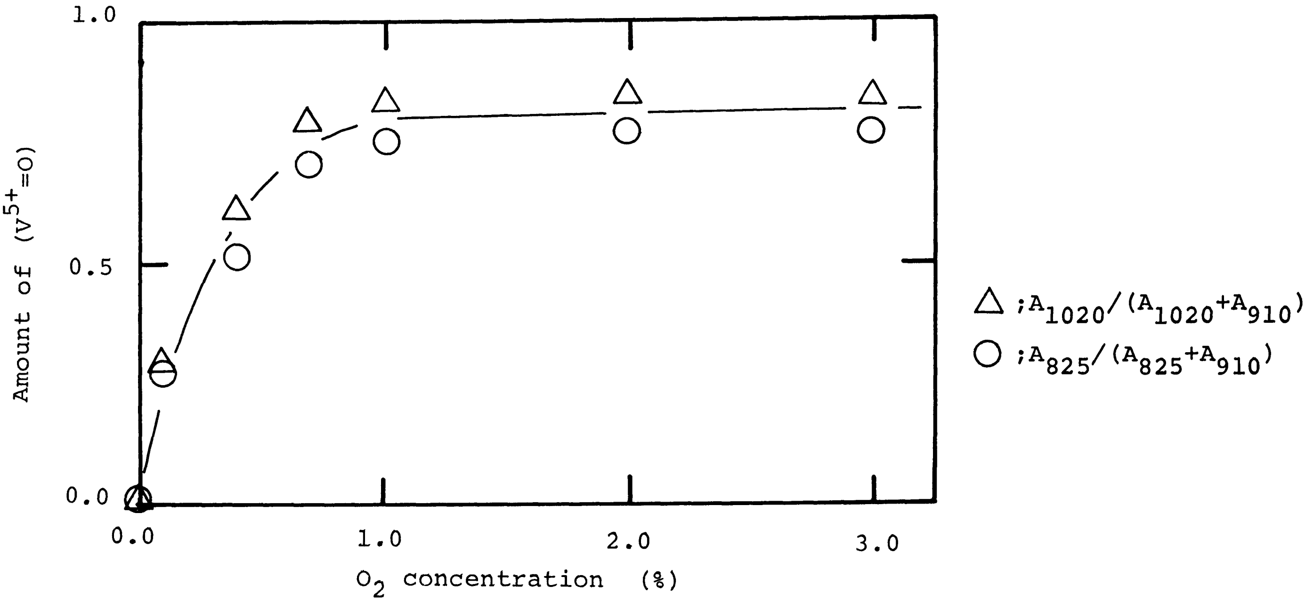


Fig.4 Effect of O_2 concentration on the relative intensities of IR peaks

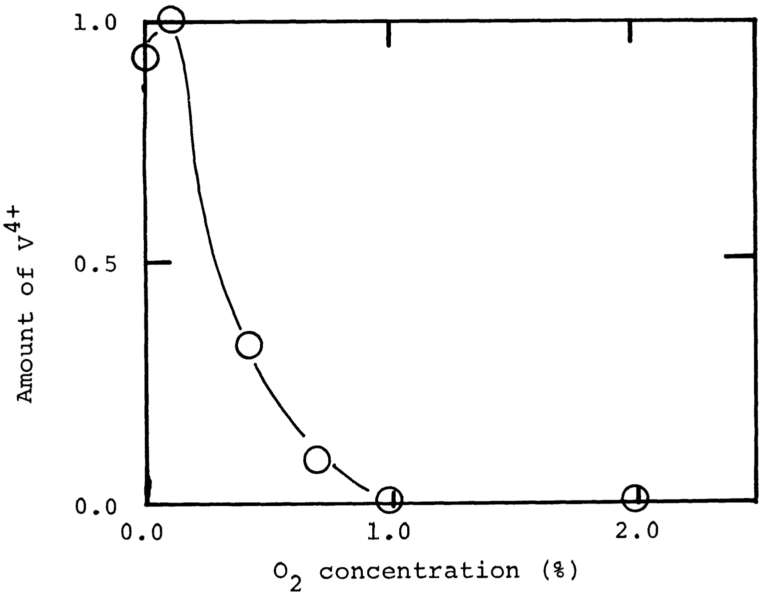


Fig.5 Effect of O_2 concentration on the relative intensity of ESR signal at g=1.96

supply (O_2 in a reactor is entirely removed within 10 seconds after a stop of O_2 gas supply). The catalytic activity did not decrease rapidly. If NO is oxidized by O_2 and is adsorbed as NO_2(ad), the activity should decrease rapidly after a stop of O_2 gas supply. However, the activities at 308°c and at 252°c decrease gradually. Thus, it seems that the mechanism; $NO+1/2O_2 \rightarrow NO_2$(ad), can not apply to the reaction under dilute gas condition. No adsorbed oxygen species, such as O_2^- and O^-, were detected by ESR and temperature-programed desorption techniques. We may therefore regard the lattice oxygen as the active site for the NO-NH_3 reaction. Fig.2 shows the effect of O_2 concentration on the production rates of N_2 and N_2O. The rate of N_2 increases almost linearly with O_2 concentration up to 1% and increases only slightly above 1%. In Fig.3, the changes in ir spectra of vanadium oxides after the reaction under various O_2 concentrations are shown. The vanadium oxides after the reaction above 1000ppm O_2 gave the absorption bands at about 1020cm^{-1} and 825cm^{-1} which are assigned to the stretching vibration of (V^{5+}=O) and the coupled vibration between (V^{5+}=O) and (V-O-V), respectively. In the vanadium oxides below 1% O_2, new absorption bands at 990cm^{-1} and 910cm^{-1} appeared. These bands are assigned to the absorption bands of

V_2O_4.[5)] Thus, calculated values of $A_{1020}/(A_{1020}+A_{910})$ and $A_{825}/(A_{825}+A_{910})$ were used for measures of the quantitative change of the amount of (V^{5+}=O) in vanadium oxide (A;absorbance). Fig.4 shows the relation between the amount of (V^{5+}=O) and O_2 concentration. The amount of (V^{5+}=O) increases almost linearly with O_2 concentration up to 1%. From both Fig.2 and Fig.4, a good correlation between the catalytic activity and the amount of (V^{5+}=O) is obtained. In all vanadium oxides below 1% O_2, ESR signal of V^{4+}(g=1.96) was observed as shown in Fig.5 and the amount of V^{4+} varies in inverse proportion to the catalytic activity.

These results indicate that the (V^{5+}=O) bond on the surface of vanadium oxide which is regenerated by the oxidation of V^{4+} with O_2 plays an important role as the active site for the NO-NH_3 reaction and the reaction is accelerated in proportion to the amount of (V^{5+}=O). The relation between the amount of (V^{5+}=O) and the catalytic activity agrees well with the experimental results of the reduction of NO by NH_3 on vanadium oxide by a pulse technique.[4)]

REFERENCE

(1) N.Todo, M.Kurita, H.Hagiwara, H.Ueno and T.Sato, Preprints of Papers of the Japan-USA Seminar on Catalytic NO_x Reactions, 3-1(1975)

(2) G.L.Bauerle, S.C.Wu and K.Nobe, Ind. Eng. Chem. Prod. Res. Dev., 14, 268(1975)

(3) M.Takagi, T.Kawai, M.Soma, T.Onishi and K.Tamaru, J. Catal., 50, 441(1977)

(4) A.Miyamoto, Y.Yamazaki and Y.Murakami, Nippon Kagaku Kaishi., 1977,619

(5) L.D.Frederickson and D.M.Hansen, Anal. Chem., 35, 818(1963)

(Received April 17, 1978)