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AMMONIA SYNTHESIS FROM CARBON MONOXIDE, WATER, AND DINITROGEN OVER Ru-MgO-Cs_2O

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NH_3 is formed from CO, H_2O, and N_2 at a steady rate over Ru-MgO-Cs_2O without forming any hydrocarbons at 370° to 430°C under 1 atm. The rate is proportional to N_2 pressure, increases with H_2O pressure, but has a maximum at about 5 Torr of CO pressure at 405°C. Normal hydrogen isotope effect was observed both in the title reaction and in the water gas shift reaction.

The energy cost to make pure hydrogen for the ammonia synthesis may be saved greatly by utilizing water as the hydrogen source in the following consecutive reaction:

$$H_2O + CO \longrightarrow H_2 + CO_2 \quad (1)$$

$$N_2 + 3H_2 \longrightarrow 2NH_3 \quad (2)$$

In order to carry out the reactions in a single process, it is neccessary to develop a catalyst which can activate N_2 even in the presence of CO and H_2O, both of which are known to be poisonous to the iron catalyst. Ruthenium is likely more tolerant than iron to CO or H_2O and the possibility has been pointed out by using Ru-Al_2O_3-K_2O¹⁾.

MgO (BET area of 126 m^2/g) was impregnated with $RuCl_3\cdot 3H_2O$ - acetone solution, and with $CsNO_3$ - aqueous solution. The dryed and reduced catalyst contains 2 wt% of Ru and 10 times more Cs_2O in Cs/Ru molar ratio. The catalyst weight used was 2.00 g before $CsNO_3$ addition. The reaction apparatus is a conventional flow system equipped with a H_2O bubbler and a cold trap for the purpose of H_2O pressure control. Produced ammonia was fixed in H_2SO_4 solution at the outlet of the flow system and the concentration was determined by electroconductivity change. Other products were analyzed by gas chromatography or mass spectrometry. Ammonia was found to be produced from CO,H_2O and N_2 with a steady rate even in the presence of gaseous CO through the reactor at about 400°C. The rate is shown as a function of temperature in Fig. 1, where CO pressure at the outlet is also shown.

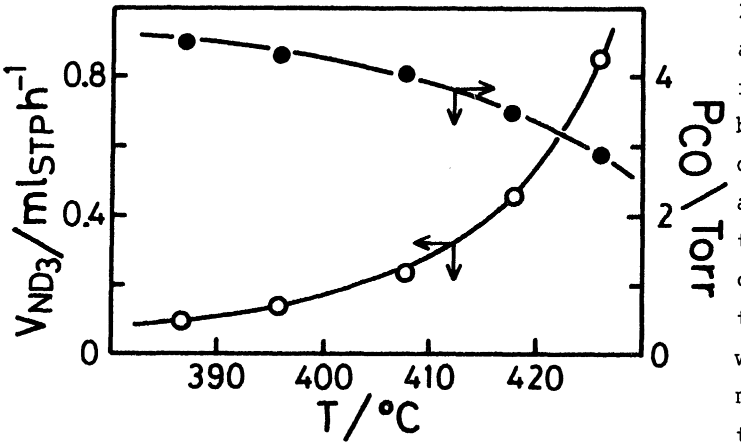

Fig. 1. ND_3 synthesis rate and outlet CO pressure as a function of temperature at a flow rate of 7.1 l_{STP}/h and under the inlet pressures of $P_{CO}=10$, $P_{D_2O}=18$, and $P_{N_2}=732$ Torr.

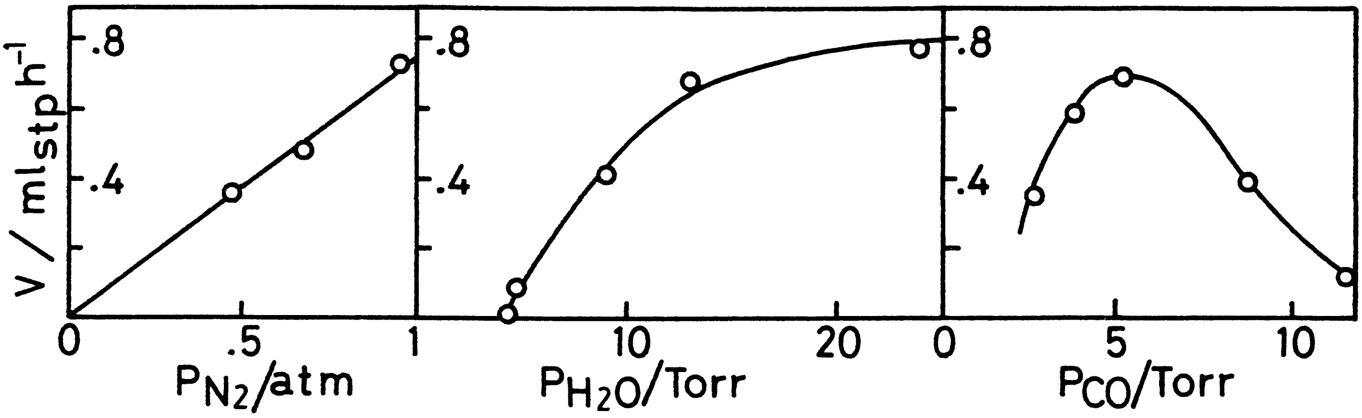

Fig. 2. NH_3 synthesis rate as a function of partial pressures at 405°C and at a flow rate of 7.1 l_{STP}/h. The fixed inlet pressures are; P_{CO}=10, P_{H_2O}=18, or P_{N2}=732 Torr. The average values between inlet and outlet pressure of H_2O or CO are plotted.

No hydrocarbon such as CH_4 was observed except for the initial period after a catalyst charging. The products other than NH_3 were H_2 (D_2) and CO_2 under a steady condition with a carbon balance of 100±5%. This means reactions (1) and (2) occur exclusively, where reaction (1) is much faster.

The partial pressure dependences of NH_3 synthesis rate are shown in Fig. 2. The linear relations to N_2 pressure observed here is well known for the NH_3 synthesis reaction from N_2 and H_2, where dissociative adsorption is believed to be the rate-determining step. The rate increases with H_2O pressure, but has a maximum at about 5 Torr of CO pressure under these conditions. Normal isotope effect on the title reaction was observed as is shown in Fig. 3. This effect is contrary to the case in the ammonia synthesis from N_2 and H_2 (D_2). The water gas shift reaction (1) was studied kinetically in connection with the title reaction at lower temperatures. It was found that the reaction order in CO was -0.3 and the order in H_2O was +0.5 at 256°C where CO conversion is lower than 10%. Apparent activation energies are obtained to be 22.4 kcal/mol for H_2O system and 24.9 kcal/mol for D_2O system. Normal isotope effect (2.0 ± 0.1) was also observed for this reaction at 200 to 300°C, which is probably related with the isotope effect in the title reaction.

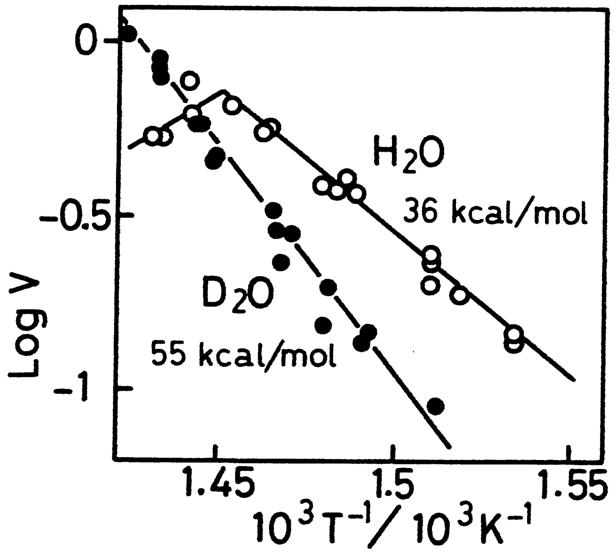

Fig. 3. Arrhenius plots of the ammonia synthesis rate, V ($ml_{STP}NH_3$/h), for H_2O and D_2O system. Flow rate; 7.1 l_{STP}/h, Inlet pressure; P_{N_2}=732, P_{CO}=10, $P_{H_2O(D_2O)}$ = 18 Torr.

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Reference

1) K. Shimazaki, K. Urabe, K. Aika, and A. Ozaki, Proc. 37th Annual Meeting Chem. Soc. Japan Tokyo, 1978, Vol. 1, p 464(1Q34)