Ammonia Synthesis from Methane, Water, and Nitrogen over Silica-supported Ruthenium

By Shuichi Naito* and Kenzi Tamaru

(*Department of Chemistry, Faculty of Science, the University of Tokyo, Hongo, Bunkyo-ku, Tokyo,* 113 *Japan*)

Summary It is demonstrated for the first time that supported ruthenium catalyst is active for ammonia synthesis from methane (or carbon monoxide) water and nitrogen molecule.

It is well known that ruthenium is a highly active catalyst for ammonia synthesis,[1] methanation, and Fischer–Tropsch synthesis.[2] However there have been no reports on attempts to combine these reactions on ruthenium and to investigate the influences of any one reactant on the others. We now report that ammonia can be synthesized from methane (or carbon monoxide), water, and nitrogen, and also in the presence of water and carbon monoxide, on a silica supported ruthenium catalyst prepared from $RuCl_3$ or $Ru_3(CO)_{12}$.

When water vapour was introduced on to the ruthenium catalyst which had been reduced at 400 °C, hydrogen was evolved and oxygen remained on the surface. After evacuation of hydrogen and water vapour the surface oxygen was easily reduced by introduction of methane, forming hydrogen and carbon monoxide in the gas phase as shown in Figure 1 (steam reforming reaction). Nitrogen and excess of water were then introduced to the system after 2 h, and after circulation of the mixture for 14 h in a closed system, ammonia was detected by i.r. spectroscopy and analysed colorimetrically in the excess of water using Nessler's reagent. The gas-phase composition, which was determined by gas chromatography, was almost constant during the reaction, but when H_2O was removed from the gas phase in a solid CO_2–MeOH trap, the amount of H_2, CO, and CO_2 immediately decreased and the amount of methane increased. These results suggest that the gas-phase equilibrium between CH_4 and H_2O is achieved quickly by the reverse of methanation and the water gas shift reaction, and the hydrogen produced reacts with nitrogen to form ammonia.

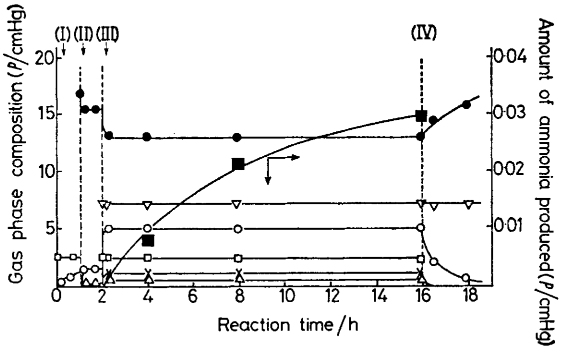

Figure 1. Ammonia synthesis from CH_4, H_2O, and N_2 over silica-supported Ru at 400 °C (0·4 wt. % Ru–silica; 15 g) ○, H_2; ●, CH_4; ▽, N_2; △, CO; ×, CO_2; □, H_2O (vapour pressure); ■, NH_3 (amount of ammonia formed); (I) introduction of H_2O vapour; (II) CH_4 added after evacuation of H_2O; (III) H_2O and N_2 added; (IV) solid CO_2–MeOH trap.

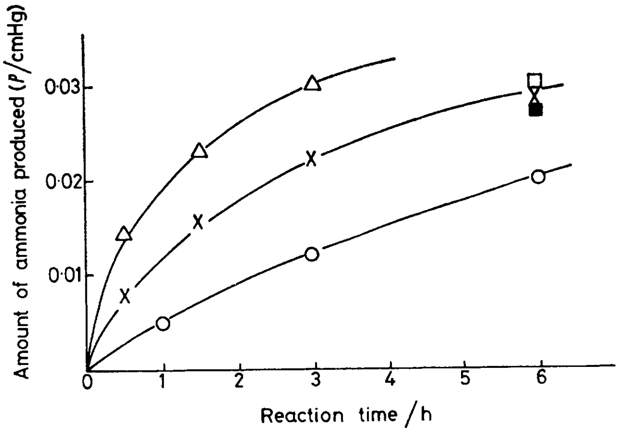

Figure 2. Rate of ammonia formation under various conditions over silica supported Ru and Ru cluster catalysts at 400 °C [0·4 wt. % Ru–silica; 15 g; $P(H_2)$ 5, $P(N_2)$ 9, $P(CH_4)$ 9 cmHg]; ○, $CH_4 + H_2O + N_2$ (Ru–silica); ×, $H_2 + N_2$ (Ru–silica); □, $H_2 + N_2 + CH_4$ (Ru–silica); ■, $H_2 + N_2 + H_2O$ (Ru–silica); △, $CH_4 + H_2O + N_2$ (Ru cluster–silica).

Figure 2 shows the rate of ammonia synthesis under various conditions. The rate of the H_2–N_2 reaction was not affected by the presence of CH_4 or H_2O. However, when methane and water were used as hydrogen source, the rate of reaction decreased by one half or one third, probably because of the presence of strongly adsorbed carbon monoxide formed during the reaction. When CO, N_2 and excess of H_2 were introduced on to the catalyst, ammonia was formed after the rapid equilibration of the methanation reaction, but ammonia was not detectable under conditions involving H_2, N_2, and excess of CO. The rate of ammonia formation in the reaction of CH_4, H_2O, and N_2 over a silica-supported ruthenium cluster catalyst which had been prepared from $Ru_3(CO)_{12}$ was faster than that over the catalyst which had been prepared from $RuCl_3$, as shown in Figure 2. From the amount of chemisorbed hydrogen at room temperature, the degree of dispersion was higher in the cluster catalyst than the catalyst, prepared from $RuCl_3$, which may be the main reason for its higher activity. Ammonia was also synthesized at a similar rate when carbon monoxide was used as a reactant instead of methane.

It is known that an iron catalyst is easily oxidized by water, and higher temperatures are required to reduce it by hydrogen. Accordingly ammonia synthesis over an iron catalyst is inhibited by water.[3] However, in the case of ruthenium, the oxidized surface can easily be reduced by methane (Figure 1). Consequently, the ruthenium surface may be kept in the reductive atmosphere even during the methanation or water gas shift reaction, and there may always exist vacant sites available for nitrogen activation.

(*Received, 5th September* 1978; *Com.* 970.)

---

[1] A. Mittasch, *Adv. Catalysis*, 1949, **2**, 83.

[2] F. Fischer, H. Tropsch, and P. Dilthey, *Brenstoff-Chem.*, 1925, **6**, 265.

[3] von R. Brill, J. Hensel, and H. Schaefer, *Ber. Bunsengesellschaft Phys. Chem.*, 1969, **73**, 1003.