Catalytic Synthesis of Ammonia by Graphite–Alkali Metal Complexes Containing Transition-metal Chloride

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Summary Graphite forms lamellar compounds with substances such as ferric chloride or potassium, some of which, *e.g.* the graphite–$FeCl_3$–K system, exhibit high catalytic activity for the synthesis of ammonia.

IT has already been shown that nitrogen fixation occurs and ammonia is formed during the reduction of certain transition-metal complexes in solution either electrically[1] or by alkali metals.[2] The catalytic formation of ammonia from nitrogen and hydrogen in the gas phase, however, has not been realized in these systems. It has also been reported that ammonia is catalytically produced from a mixture of nitrogen and hydrogen over the electron donor-acceptor (EDA) complexes of graphite or metal phthalocyanines with alkali metals.[3]

The golden or red-brown complex powders were prepared by heating pure graphite† and the transition-metal chloride (*ca.* 10:1 w/w) at 300—400 °C for 20 h under reduced pressure in a sealed tube by Croft's method.[4] An alkali metal such as K or Na was then added to the graphite–transition–metal chloride complex, and the mixture was heated at 350 °C *in vacuo*. The surface areas of the catalysts thus prepared were found by the BET method to be *ca* 20 $cm^2 g^{-1}$.

A large amount of nitrogen gas (*ca.* 40 cm^3, 2×10^{-3} mol) and hydrogen (*ca.* 400 cm^3, 2×10^{-2} mol) were rapidly absorbed by the graphite–$FeCl_3$–K powder (4·2 g, 4×10^{-2} mol) at 25—300 °C, and when a mixture of nitrogen (10—25 cmHg) and hydrogen (10—45 cm Hg) was circulated through the reaction vessel (45 cm^3 per min at 25 and 350 °C), ammonia was readily collected in a liquid nitrogen trap. The volume of the reaction system was *ca.* 300 cm^3; the ammonia was analysed quantitatively and qualitatively by g.l.c. and i.r. spectroscopy. The initial

TABLE

Catalyst (g) (G = graphite)	Stoicheiometric formulae	Partial pressure (cmHg) N_2	H_2	T/°C	Initial rate of NH_3 formation (cm^3/h)	% Conversion[a] in 10 h
G–$FeCl_3$–K	(2:0·2:2)	10	30	350	10·6	90
		10	30	300	5·1	55
		23	35	30	0·03	1·5
G–K[b]	(2:1)	8	24	306	0·008	0·1
G–$FeCl_3$	(2:0·2)	10	30	300	0	0
G–$RuCl_3$–K	(2:0·2:2)	15	40	300	2·9	30
G–$OsCl_3$–K	(2:0·2:2)	15	45	300	9·0	60
G–$MoCl_5$–K	(2:0·6:2)	15	45	300	0·15	1
G–$FeCl_5$–Na	(2:0·2:2)	15	45	300	2·4	22·5
G–$FeCl_3$–Rb	(2:0·2:2)	15	45	300	5·3	52
G–$FeCl_3$–K	(2:0·2:2)	8·4(air)	30	283	3·7	43
		10—10 (N_2–CO)	30	307	3·5	40

[a] Conversion of N_2 into NH_3 in 10 h. [b] Excess of potassium was removed from the system by the heating *in vacuo*.

† Contains < 5 p.p.m. of Fe and Al as ash.

rates of NH_3 formation and the amount of conversion of nitrogen into ammonia in 10 h from a mixture of nitrogen and hydrogen were investigated with various catalyst systems (see Table). The formation of ammonia is extremely slow at higher temperatures when an alkali metal, graphite, or transition metal compound is employed individually or in combination as a two component lamellar complex, but when a three-component lamellar complex is used, the rate of NH_3 formation is increased by a factor of several hundred, under similar reaction conditions. When a mixture of N_2, CO, and H_2 (1 : 1 : 3) was introduced over the graphite–$FeCl_3$–K and graphite–$OsCl_3$–K systems at 300 °C, a large amount of hydrocarbons (*e.g.* CH_4, C_2H_6) were obtained besides ammonia. It was also found that when CH_4 (40 cmHg) was used as the source of hydrogen with N_2 over the fresh graphite–$FeCl_3$–K catalyst at 300—400 °C, 4·3 cm^3 of ammonia was collected in the liquid-nitrogen trap in 20 h.

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