

New Type of Carbon Coated Alumina Supports for the Preparation of Highly Active Ruthenium Catalysts for Ammonia Synthesis^a



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(Received 12 March 1990, revised manuscript received 24 April 1990)

Keywords: alumina, ruthenium/alumina, carbon coating, ammonia synthesis, catalyst preparation (impregnation, pyrolysis).

The conventional magnetite based catalyst is the economically most attractive catalyst for ammonia synthesis. Ruthenium was reported to be active for ammonia synthesis at atmospheric pressure when dispersed on suitable supports in the presence of promoters [1-3]. Aika et al. [1] and Aika and Ozaki [4,5] have found active carbon to be more efficient as support for ruthenium in the presence of alkali metal promoters than other classical supports like Al_2O_3 . The high activity of the active carbon promoted supported ruthenium catalysts was attributed to the electron deficient graphite lattice of active carbon [1]. Unpromoted ruthenium/active carbon catalysts were found to be inactive for ammonia synthesis, which may be due to the drift of Ru 'd' electrons into the graphite lattice. Addition of alkali metal promoter enables the graphite lattice to take electrons from it and transport them towards ruthenium.

A number of patents [6,7] have appeared in the literature on the methods of preparation of promoted and active carbon-supported ruthenium catalysts for ammonia synthesis. Though the alkali metal is a more efficient promoter than its cation, a catalyst with high activity sustained over a long period of time cannot be prepared with the metal promoter as it gets converted to its oxide or hydroxide [2]. In the present work advantage is taken of the beneficial

^aIICT Communication No. 2495

property of carbon, i.e. the electron transport capacity of the graphite lattice, the ionic alkali promoter and the stability of the classical support, Al_2O_3 , in the preparation of new ammonia synthesis catalysts based on ruthenium.

Two carbon-coated aluminas [SUMS No. 4 and ALX-IG/42 spheres (0.5 mm diameter)] and two granular active carbons (SKT and SYBUNIT) obtained from the Institute of Catalysis, Novosibirsk, U.S.S.R., were used as supports for the preparation of the catalysts. Carbon-coated aluminas are reported to have been prepared by pyrolysis of an alkene on $\gamma\text{-Al}_2\text{O}_3$ [8,9]. The supports were dried at 150°C under vacuum for 8 h. Ru/C- Al_2O_3 catalysts were prepared by impregnating the supports in aqueous $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ (Aldrich Chemicals) solution followed by evaporation of the excess water and drying at 110°C in an oven. The catalysts were then reduced in hydrogen flow for 12 h at 400°C which was attained gradually from room temperature over a period of 3 h. Cesium-promoted catalysts were prepared by impregnating the reduced catalysts with aqueous CsNO_3 (Fluka) solution and dried at 150°C for 6 h. In all the catalysts the Ru:Cs:Support weight ratio was kept at 10:51:100.

The activities of these catalysts for ammonia synthesis were evaluated in a twin-glass reactor (two catalysts can be loaded at a time) of 15 mm diameter provided with a coiled preheater. The reactor was heated in a tubular furnace of 4 in. diameter capable of attaining a maximum temperature of 800°C . For each experiment 4 g of catalyst were loaded into the reactor. Prior to the activity experiment, each catalyst sample was reduced in situ for 24 h at 400°C in a hydrogen flow of 10 l/h. The ammonia synthesis reaction was carried out at different temperatures varying from 250°C to 400°C under atmospheric pressure at a synthesis gas ($\text{N}_2 + 3\text{H}_2$) flow-rate of 10 l/h and a GHSV of 2200 h^{-1} . Ammonia concentration in the outlet gas mixture was continuously monitored by absorbing it in a known volume of 0.01 N H_2SO_4 solution till the methyl orange indicator changed its colour from red to yellow. It was observed that steady-state concentrations of ammonia were attained at a fast rate (within 10 min) on all the catalysts. The ammonia concentrations were constant over a period of study of 12 h.

The BET surface areas, pore volumes and mean pore radii of different supports used for catalyst preparation and the ammonia yields (at 350°C) of the catalysts are presented in Table 1. The effect of reaction temperature on the concentrations of ammonia for these catalysts each containing 0.25 g of ruthenium are shown in Fig. 1. It is clear from the figure that the ammonia synthesis activities of the catalysts, except that of catalyst 1, increase with rise in temperature and reach maximum values at 350°C , above which they decline and touch the equilibrium value at 400°C [0.44% (v/v)]. It is worthwhile to mention here that doubly promoted iron catalyst gave steady-state concentration of only 0.18% (v/v) of ammonia at 400°C at a flow-rate of 10 l/h of synthesis gas. Catalyst 1 has exhibited very low activity which may be due to the low dispersion of ruthenium in the microporous structure of the high-surface-area

TABLE 1

BET surface areas and pore volumes of supports and ammonia synthesis yields of cesium-promoted Ru catalysts

Catalyst ^a	Support	BET surface area (m ² g ⁻¹)	Pore volume (cm ³ g ⁻¹)	Mean pore radius (nm)	Steady-state NH ₃ Concr. at 350°C [% (v/v)]	NH ₃ Yield ^b [cm ³ h ⁻¹ g Ru ⁻¹]
1	Carbon (SKT)	1350	1.1	1.6	0.005	2
2	Carbon (Sybunit)	500	0.8	3.2	0.652	261
3	8% C-Al ₂ O ₃ (ALX-1G/42)	220	0.5	4.6	0.670	268
4	24% C-Al ₂ O ₃ (SUMS NO. 4)	230	0.5	4.4	0.763	305

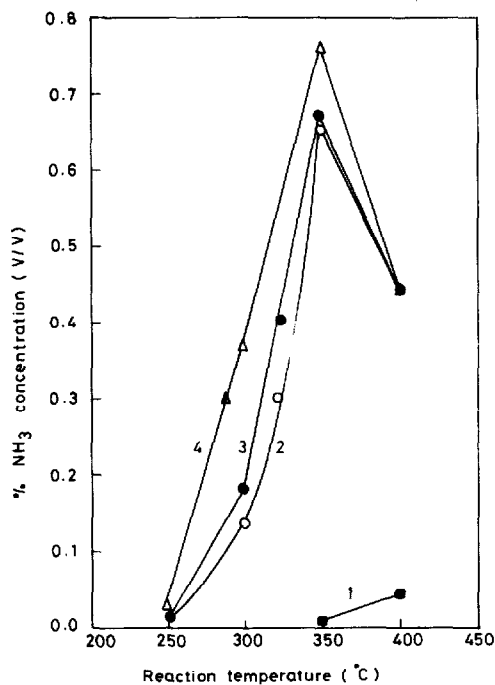
^aRatio by weight of Ru:Cs:Support = 10:51:100.^bCalculated from steady-state concentrations [% NH₃ (v/v)] at 350°C obtained by 4 g catalyst. Thermodynamic equilibrium NH₃ concentration at 350°C is 0.864% (v/v).

Fig. 1. Effect of reaction temperature on the steady-state concentrations of ammonia over cesium-promoted supported ruthenium catalysts. Flow-rate of synthesis gas (N₂ + 3 H₂): 10 l/h. Symbols: (■) catalyst 1: Cs-Ru/carbon (SKT), (○) catalyst 2: Cs-Ru/carbon (Sybunit), (●) catalyst 3: Cs-Ru/8% C-Al₂O₃ (ALX-1G/42), (△) catalyst 4: Cs-Ru/24% C-Al₂O₃ (Sums No. 4).

active carbon. The maximum concentrations of ammonia for the catalysts 2, 3 and 4 are 0.65%, 0.67% and 0.76% (v/v), respectively at 350°C. The difference in the activities of these catalysts can be attributed to the influence of the support. Catalyst 2 with 500 m²g⁻¹ surface area support has given a steady-state concentration of ammonia, very close to that of catalyst 3.

The high activities of the catalysts may be attributed to the better dispersion of ruthenium on the mesoporous supports brought about by the promoting effect of cesium and also the beneficial effect of the graphite lattice by accelerating the transfer of electrons from Cs to Ru crystallites. Another role of active carbon may be its capacity to hold alkali metal ion [1]. It is interesting to note that catalyst 4 with 24% carbon on Al₂O₃ has given an ammonia concentration of 0.76% at 350°C which is close to the thermodynamic equilibrium value (0.864%). The obvious reason for this appears to be its high carbon content dispersed on γ -Al₂O₃ surface. Charge transfer through alumina between two kinds of absorbates was also suggested as a reason for the high activity of supported Ru catalysts [10].

Thus it can be concluded that new types of promoted Ru catalysts can be suitably designed with very high activity for ammonia synthesis at atmospheric pressure using carbon-coated aluminas as supports.

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