Effect of barium addition on the ammonia synthesis activity of a caesium promoted ruthenium catalyst supported on carbon-covered alumina (CCA)$^\alpha$

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INTRODUCTION

Synthesis of ammonia at atmospheric pressure on unpromoted and alkali metal/alkaline earth oxide promoted ruthenium catalysts has been the subject of several investigations especially by Aika and co-workers [1–5]. The promoting action of alkali metal and alkaline earth oxides has been explained in terms of electron donation to ruthenium [3]. The ammonia synthesis activity of the supported ruthenium catalyst is inversely correlated to the electronegativity of the principal support or promoter. Though activated carbon and alumina have been used frequently, it has been observed that the active carbon reduces the ammonia synthesis activity of unpromoted ruthenium, thus necessitating the addition of promoter [1]. The strong chemisorption of product ammonia on the acid centres of alumina makes it a less attractive support for ruthenium. In a recent study [6] it has been reported by the present authors that by covering the alumina surface with a carbon coating, the synthesis activity of the catalyst can be substantially improved. The carbon covered alumina (CCA) offers the advantages of the electron withdrawing capacity of carbon [6] and the stability of alumina and at the same time eliminates the disadvantages of the low strength of carbon and the acidity of alumina. Studying the effect of alkali and alkaline earth metal nitrates on the synthesis activity of active carbon supported ruthenium catalysts, Aika et al. [7] have shown that barium is more effective than caesium. There have been some patents [8–13] which also illustrate the importance of barium in improving the am-

monia synthesis activity. However, such information is not available for ruthenium catalysts supported on carbon covered alumina. In the present investigation, the influence of the addition of barium on the ammonia synthesis activity of caesium promoted ruthenium catalyst deposited on CCA has been reported.

EXPERIMENTAL

Commercial γ-alumina (Harshaw, Al-3996R) sieved to 18/25 mesh (BSS), was used to prepare the carbon covered alumina. The method followed was essentially that of Vissers et al. [14]. The alumina was first heated in a quartz tubular reactor of 30 mm diameter in flowing nitrogen (Iolar-1, India) to a temperature of 600°C and allowed to remain at the same temperature for 1 h. Then ethene (Matheson, USA) was introduced into the reactor. The flow-rates of ethene and nitrogen were 2 ml/min and 15 ml/min, respectively, per gram of alumina. The pyrolysis was continued at the same temperature in flowing nitrogen. Carbon analysis of the CCA was carried out on a CHN analyser (Model CHN-600: Leco Corporation, USA).

The catalysts were prepared by the stepwise impregnation method. Unpromoted Ru/CCA (Catalyst 1) was prepared by impregnating aqueous $RuCl_3$, $3H_2O$ (Aldrich Chemicals, UK) on CCA. This was dried at 110°C overnight. A portion of this catalyst was then reduced in hydrogen flow at 400°C, which was obtained with a gradual increase over a period of 4 h. An aqueous solution of $CsNO_3$ (Fluka Chemicals) was then deposited on this reduced sample followed by overnight drying at 110°C to obtain catalyst 2. Catalyst 3 was prepared by first impregnating the CCA support with aqueous $Ba(NO_3)_2$ (Reechem Pvt., India) solution followed by reduction at 400°C. Subsequent impregnation of $RuCl_3$, $3H_2O$ and $CsNO_3$ were then carried out according to the procedure described for catalyst 2. The weight ratio of the components was maintained at ruthenium–barium–caesium–CCA = 7.7 : 5 : 51 : 100 in catalyst 3.

BET surface areas were measured before and after reduction by nitrogen adsorption. The ruthenium dispersions on these catalysts were obtained from irreversible hydrogen uptakes measured at 25°C on reduced catalysts in a conventional high vacuum adsorption unit [15]. These properties are given in Table 1. The ammonia synthesis activities of these catalysts were determined in a glass microreactor under atmospheric pressure at different temperatures ranging from 250–400°C. Prior to the activity measurements the catalysts were reduced in hydrogen flow (10 l/h) at 400°C which was gradually obtained over a period of 4 h. The complete reduction of the catalyst was confirmed by testing the vent gas with silver nitrate for hydrochloric acid coming from Cl^- ion and with Nessler's reagent for ammonia coming from NO_3^- ion. The synthesis gas $(N_2 + 3H_2)$ was also maintained at a flow-rate of 10 l/h. The weight of the catalyst (about 4 g) in all the catalysts was fixed such that it gave a ruthenium

TABLE 1

Physical parameters of supported ruthenium catalysts

Catalyst	BET surface area $(m^2 g^{-1})$		Hydrogen uptake, $\mu mol\, g^{-1}$	Ruthenium dispersion $(\%)^a$
	Before reduction	After reduction		
Catalyst 1	98.2	135.1	22	6.9
Catalyst 2	57.6	71.4	85	41.2
Catalyst 3	68.3	82.1	101	50.7

^{a}Calculated as 200 (hydrogen uptake, $\mu mol\, g^{-1}$)/(total ruthenium, μg atom$\cdot g_{cat}{}^{-1}$).

TABLE 2

Turn-over frequencies of ammonia synthesis activity over ruthenium catalyst at various temperatures

Catalyst	$TOF \times 10^4$ at a reaction temperature of						
	250°C	275°C	300°C	325°C	350°C	375°C	400°C
Catalyst 1	0.07	0.12	0.22	0.57	1.05	1.83	2.61
Catalyst 2	1.71	6.77	9.56	6.49	4.65	3.22	2.27
Catalyst 3	6.28	8.98	7.09	4.96	3.46	2.44	1.71

content of 0.195 g. The turn-over frequencies (TOF) of ammonia synthesis over the three catalysts studied are given in Table 2.

RESULTS AND DISCUSSION

Pyrolysis of ethene on alumina is reported to give a uniform carbon coverage when compared to the other methods employed in the preparation of CCA [14]. The carbon content of the present support was estimated to be 17% by weight. The BET surface area, as obtained by nitrogen adsorption, was 154 m^2 g^{-1}. X-ray diffraction studies have revealed the amorphous nature of carbon. Reduction increased the surface area of all the catalysts (Table 1) presumably due to the decomposition of the precursor salts. It could also be observed that the incorporation of barium led to higher surface areas before and after reduction when compared to those of the catalysts without barium. Irreversible hydrogen uptake and hence ruthenium dispersion were increased by the addition of barium. It is known that caesium in the form of its hydroxide acts as a stable promoter against poisons such as water and carbon monoxide. As expressed by Aika et al. [2], the addition of barium might have helped in decreasing the coagulation of ruthenium atoms.

The effect of reaction temperature on the ammonia synthesis activities of

the catalysts, expressed as steady state rates of ammonia produced, is depicted in Fig. 1. The rate of ammonia synthesis over the unpromoted catalyst was almost negligible up to 300°C. There was a slight increase in the activity of the catalyst beyond this temperature. The promoted catalysts exhibited very high activities as can be observed from Fig. 1. Catalyst 2 exhibited maximum activity at 300°C while catalyst 3 showed the same at 275°C. Thus the addition of barium increased the activity of the catalyst in addition to increasing the ruthenium dispersion.

The TOF values (Table 2) compared very well with those of some of the catalysts studied by Aika et al. [2,5]. Whereas a low but gradual increase in the TOF value was observed for the unpromoted catalyst (catalyst 1) with increasing temperature, the promoted catalysts exhibited optima. The TOF values for catalyst 3 were much higher up to 275°C than the corresponding values for catalyst 2. The TOF values of both catalysts decreased beyond 300°C and catalyst 3 exhibited lower activity than catalyst 2 in the higher temperature region. The addition of alkaline earth metal, barium, might have increased the basicity of CCA. It was observed from a recent study on CCA by the temperature-programmed desorption of ammonia that as the carbon coverage in-
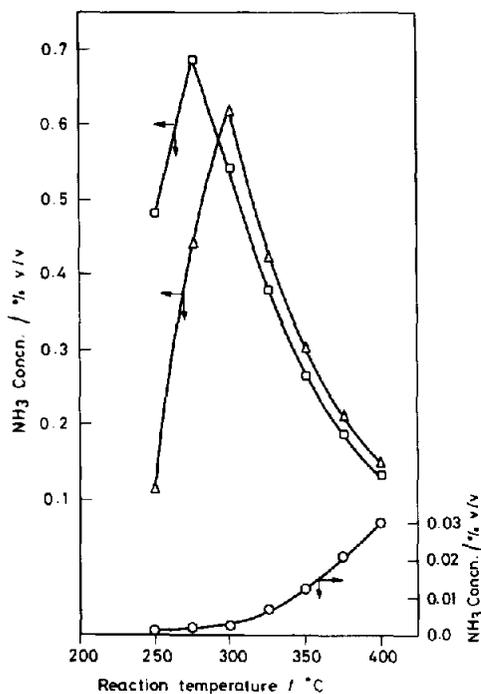

Fig. 1. Effect of reaction temperature on ammonia synthesis activity of supported ruthenium catalysts. (○) Catalyst 1 (Ru/CCA); (△) Catalyst 2 (Cs-Ru/CCA); and (□) Catalyst 3 (Cs–Ru–Ba/CCA).

creased the surface acidity of alumina drastically decreased [16]. The combined effect of decreased acidity and increased basicity could have enhanced the TOF of the barium added catalyst.

The distinct advantage of barium addition is the decrease in the temperature of the maximum rate of ammonia production, still maintaining a higher TOF value. Similar observations have also been reported by Aika et al. [1], in their work on potassium promoted ruthenium supported on active carbon and alumina where for a synthesis rate of 1 ml/h of ammonia the temperature decreased from 421°C for the unpromoted catalyst to 287°C for the promoted catalyst. The shift in the temperature of maximum activity to a lower region upon the addition of barium could be due to the increased dissociative chemisorption at lower temperatures when compared to that of the caesium promoted catalyst. The decrease in TOF with increased dispersion has been observed in the case of Fe/MgO by Dumesic et al. [17]. Aika et al. [5] are of the opinion that the influence of crystallite size is not that important when compared to the electronic effect. The decrease in TOF value (Table 2) beyond the optima for both the promoted catalysts may be due to the decrease in the amount of dissociative nitrogen chemisorption at higher temperatures.

Thus, the incorporation of barium into caesium promoted ruthenium on CCA support has been proved to give a better catalyst in terms of increased rate of ammonia synthesis in addition to the decrease in the temperature of maximum activity.

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