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Role of promoters on highly active nano-Ru catalyst supported on Mg–Al hydrotalcite precursor for the synthesis of ammonia

P. Seetharamulu [a], K. Hari Prasad Reddy [a], A.H. Padmasri [b], K.S. Rama Rao [a,*], B. David Raju [a,*]

[a] Inorganic & Physical Chemistry Division, Indian Institute of Chemical Technology, Hyderabad 500 007, India
[b] Department of Chemistry, University College for Women, Osmania University, Koti, Hyderabad 500 001, India

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ABSTRACT

Single (Ba) and double promoted (Ba and Cs) Ru catalysts supported on calcined Mg–Al hydrotalcite were prepared by polyol reduction method to investigate the role of promoters on catalytic activity for NH_3 synthesis at atmospheric pressure. The activities of these catalysts were compared with those of their corresponding impregnated catalysts. All the catalysts were characterized by X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption (TPD) of CO_2 to determine basicities of the catalyst, BET surface area and CO chemisorption studies to find out particle size and active metal area of Ru. The reaction rate on the double promoted Ru catalysts was found to be higher than single promoted one. The double promoted catalyst prepared by polyol method exhibited exceptionally high activity (0.76%, v/v) at 598 K among all the other catalysts studied. The higher activity was attributed to the availability of more number of basic sites due to the presence of both Cs and Ba promoters as observed from CO_2 TPD and to the easily reducible Ru species, which was confirmed by TPR analysis.

1. Introduction

Alkali metal precursors are widely used as promoters to improve the catalytic performance in many commercially important processes. The addition of alkali metal precursors improves the efficiency of catalyst activity and prolongs the catalyst lifetime [1]. Haber and Bosch first performed NH_3 synthesis over double promoted (K, Al) and over triple promoted (K, Al, Ca) iron catalysts to increase NH_3 yields. However, the ruthenium catalyst supported on carbon with alkali metal precursors as promoter seems to be one of the most promising second-generation ammonia synthesis catalyst [2]. The promoting effect is found to be inversely proportional to the electronegativity of the alkali metal and the activity results of the catalysts with alkali promoter are in the order, $Cs > K > Na$. The chemical state of the alkali promoters and their role in ammonia synthesis has been the subject of numerous investigations [3]. The effectiveness of promoter seems to arise from its electron-donating effect, which has been explained by the formation of a complex with Ru, which is essential in order to increase the rate of the slowest step of the reaction, i.e. dissociative adsorption of nitrogen [4]. Moreover, alkali metal promoters seem to interact with the support, which was confirmed by XPS and UPS results of intercalation compounds of Cs and K with graphitised carbon [5]. The same correlation between promoting effect and electronegativity is found also with alkaline-earth metals, whose activity order is $Ba > Sr > Ca$ [6]. It has been shown previously that cesium is effective promoter on MgO and carbon covered alumina supported Ru system [6,7–9]. Later studies demonstrated that barium might also be used as an activator of ruthenium [10,11]. Temperature programmed N_2 adsorption and desorption experiments indicate that the promotion by cesium enhances both the rates of dissociative adsorption and associative desorption [12]. The studies on ammonia synthesis catalyzed by ruthenium supported on basic zeolites concluded that the promotional effect of barium might be due to the creation of highly active sites at the promoter metal interface [13]. Our recent work on the Mg–Al hydrotalcite precursor supported Ru catalyst promoted with cesium showed competent activity for ammonia synthesis at atmospheric pressure [14]. The aim of the present work is concerned with the study of activity for ammonia synthesis under atmospheric pressure on individual and combined effect of the most effective promoters (Cs, Ba) over Mg–Al hydrotalcite supported Ru catalysts prepared from impregnation and polyol reduction method. To get a closer insight into the role of the promoters and for better understanding of the effect of the double

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* Corresponding authors. Tel.: +91 40 27193510; fax: +91 40 27160921.
E-mail addresses: ksramarao@iict.res.in (K.S. Rama Rao), david@iict.res.in (B. David Raju).

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promoter CO_2-TPD of individual and double promoted catalysts have been investigated. CO chemisorption technique is used for particle size determination and measuring active metal area.

2. Experimental

2.1. Preparation of catalysts

The Mg–Al hydrotalcite (HT) (Mg/Al = 2) was prepared by Reichle's method of co-precipitation under super saturation conditions and calcined at 723 K for 18 h [15]. The cesium promoted catalysts by impregnation method and by polyol reduction method were prepared as per our recent report [14]. These catalysts were designated as Cs–Ru/HT and Cs–Ru/HT (ED), respectively. The barium promoted catalyst was prepared by impregnating the support with aqueous $Ba(NO_3)_2$ solution. After drying in air (373 K, 12 h), the sample was calcined at 723 K for 4 h. The calcined sample was then impregnated with 10 wt.% aqueous solution of $RuCl_3{\cdot}3H_2O$ (M/S. Loba Chemie) followed by drying at 393 K for 12 h. The catalyst was designated as Ba–Ru/HT. The double promoted catalyst was prepared by reducing the barium promoted catalyst (Ba–Ru/HT) at 723 K for 4 h and impregnated with aqueous $CsNO_3$ solution. It was designated as Ba-Cs-Ru/HT. Barium and double promoted catalysts by polyol reduction method were prepared as those of impregnated catalysts except that deposition of Ru was done under refluxing conditions with $RuCl_3{\cdot}3H_2O$ in presence of ethylene glycol, a detailed procedure of which was described in elsewhere [16]. The catalysts were designated as Ba–Ru/HT (ED) and BaCs–Ru/HT (ED), respectively. In all single promoted catalysts the Ru:Cs/Ba:support weight ratio was kept 10:51:100 and in double promoted catalyst the Ru:Cs:Ba:support was kept as 10:25.5:25.5:100.

2.2. Characterization techniques

B.E.T surface areas of the reduced catalysts of both single and double promoted catalysts were obtained on Autosorb Automated Gas Sorption System (M/S. Quantachrome, USA) with N_2 as adsorbate at liquid nitrogen temperature. X-ray powder diffraction (XRD) patterns of both single and double promoted reduced catalysts were recorded on a Rigaku Miniflex (M/S. Rigaku Corporation, Japan) instrument using Ni filtered Cu Kα radiation, with a 2°/min scan speed in the 2θ range of 2–80° at 30 kV and 15 mA. Temperature programmed reduction (TPR) profiles of the single and double promoted catalysts were generated on a home made on-line quartz microreactor interfaced to a thermal conductivity detector (TCD) equipped with a gas chromatograph (M/S. Shimadzu, model: GC-17A, Japan) and the profiles were recorded using a GC software Class-GC10. H_2/Ar (10 vol.% of H_2 and balance Ar) mixture was used as the reducing gas while the catalyst was heated at a linear heating ramp of 10 K min^{-1} from 303 K to 973 K. Pulse chemisorption followed by temperature programmed desorption (TPD) of CO_2 was employed to evaluate basic site distribution of the catalysts using 10% CO_2 in He through a six-port valve followed by TPD of CO_2 as described in literature [17]. The CO chemisorption was carried out at 303 K on a homemade pulse reactor to evaluate the metal particle size and active metal area. Assuming CO:Ru stoichiometry of 1:1, particle size and metal area of Ru were calculated using Ru metal cross-sectional area as 0.0821 nm^2 as described elsewhere [14].

2.3. Activity studies

Activity tests over Cs and Ba promoted catalysts were carried out in a fixed bed glass reactor with 30 mm outer diameter and 40 cm length under atmospheric pressure. The stoichiometric ratio of N_2–H_2 mixture was 1:3 and the total flow rate was 10 l/h. The NG 2081 (M/S. Claind, Italy) nitrogen generator, HOGEN GC300 (M/S. Proton Energy Systems, USA) Laboratory hydrogen generators were used for N_2 and H_2 gases respectively with 99.9999% purity each. Prior to the activity measurements the catalysts were reduced at 723 K for 4 h. The complete reduction of the catalyst was confirmed by testing the vent gas with silver nitrate solution for hydrochloric acid coming from Cl^- ion and Nessler's reagent for ammonia coming from NO_3^- ion. The ammonia concentration in the gas flow was determined by neutralizing with a definite amount of an aqueous H_2SO_4 solution of known concentration.

3. Results and discussion

The BET surface areas of reduced catalysts are summarized in Table 1. The surface area of the support is 172 m^2 g^{-1} and it was decreased after incorporation of Cs [14] which indicate that barium promoted catalysts show higher surface area compared to cesium promoted and double (Ba and Cs) promoted catalysts. Exceptionally barium promoted catalyst prepared by polyol reduction method shows highest surface area among all catalysts. Addition of promoter and sintering of ruthenium particles during the reduction leads to significant loss in the surface area of catalysts. Cs prevents sintering of Ru particles on this support and Ba effectively stabilizes the size of ruthenium particles in the catalyst [18,19]. Ba promoted Ru catalyst prepared by polyol reduction method possesses nearly same surface area as the catalyst without promoter. This suggests that barium is well dispersed on the ruthenium surface and it acts as a structural promoter [20]. Table 1 presents the results of CO chemisorption studies for both the single and double promoted ruthenium catalysts. It is noticed that the double promoted catalysts contain larger particles of Ru and though the total loading of double promoters is same as that of single promoter, the surface area and particle size are very low. The synergistic effect observed for Ba and Cs might be explained either by different mode of action of the promoters or by different location of the promoters, even if they act in the same mode.

Fig. 1 presents X-ray diffraction patterns of reduced Ru catalysts. Both single and double promoted catalysts showed reflections corresponding to Ru^0 phase [ICDD No. 06-0663]. The XRD patterns indicate that the Ru signals are more intense in Cs–Ru/HT (ED) catalyst [14], than those in Ba promoted catalysts. XRD patterns of Cs–Ru/HT and Cs–Ru/HT (ED) were shown in our previous article [14]. The X-ray diffraction analysis of reduced

Table 1
Surface area, CO uptake, active metal area and particle size of Ru in single and double promoted Ru catalysts

Catalyst	Surface area (m^2/g)	CO uptake (μmol/g)	Metal area[a] (m^2/g)	Particle size[b] (nm)
Ba–Ru/HT	36.7	247.2	1.95	15.3
Ba–Ru/HT (ED)	146	366.1	4.37	6.8
BaCs–Ru/HT	29.1	42.9	0.33	90.9
BaCs–Ru/HT (ED)	38.48	63.18	0.503	59.6

[a] Metal area is calculated as metal cross-sectional area × no. of Ru atoms on surface. Metal cross-sectional area of Ru is 0.0821 nm^2.

[b] Particle size (nm) is calculated as 6000/[metal area (m^2 g Ru^{-1}) × ρ] [Ru density (ρ) = 12.4 g cm^{-3}].

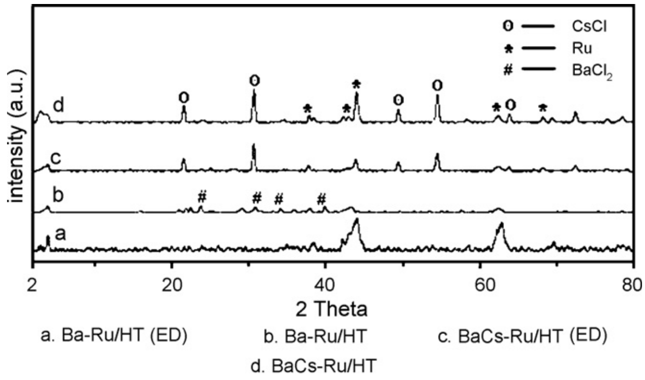

Fig. 1. XRD patterns of single and double promoted reduced Ru catalysts on hydrotalcite support.

single promoted samples gave signals due to $BaCl_2$ [ICDD No. 24-0094]. Similarly CsCl signals were observed in case of Cs–Ru/HT and Cs–Ru/HT (ED) catalysts [14]. These are due to anion exchange between metal precursor and promoter precursor. In double promoted catalysts only CsCl reflections are observed and no $BaCl_2$ reflections are detected. A closer inspection of the XRD pattern reveals that there are no $BaCl_2$ reflection observed in Ba promoted catalyst prepared by polyol method, but in double promoted catalyst prepared by polyol method CsCl reflections are observed even though $CsNO_3$ is added at the end of the catalyst preparation. This information confirms that some amount of Cl^- is still present in barium promoted catalyst prepared by polyol method. However this Cl^- is not exchanged between metal and Ba promoter but is weakly bound with Ru. This also is confirmed from the presence of $RuCl_3$ reduction peak in the TPR pattern of Ba–Ru/HT (ED) catalyst.

The reducibility of the ruthenium catalysts is studied by TPR. The TPR profiles of single (Ba) promoted and double (Cs and Ba) promoted Ru catalysts are displayed in Fig. 2. The profiles of all the catalysts show a two-stage reduction of ruthenium species in the temperature range of 473–773 K. The patterns reveal that the catalysts prepared by polyol method get reduced at lower temperatures compared to the catalysts prepared by conventional impregnation method. Also it is quite worthy to observe that the ease of reducibility of ruthenium species is enhanced with Cs addition as the intensity of the low temperature peak increased accompanied by the lowering of the intensity of high temperature peak. TPR patterns of Cs–Ru/HT and Cs–Ru/HT (ED) were shown in our earlier article [14]. This clearly shows that incorporation of Cs enhances the ease of reducibility and indeed in Cs–Ru/HT (ED) and Ba-Cs-Ru/HT (ED) catalysts most of the species get reduced at 473–523 K itself. The catalysts prepared by polyol method though reduce at lower temperature, i.e. $T_{\max}$ peaks shifted to low temperature compared to the conventionally prepared catalysts in which a two-stage reduction of the ruthenium species is seen. In the conventionally prepared catalyst addition of Ba shifted the reduction temperature to higher side as compared to Cs–Ru/HT. However by the polyol method the temperature brings down to lower side of the temperature scale.

It is found that catalytic activity for ammonia synthesis is related to the basicity of the support: the more basic is the support, the higher is the activity of the catalyst towards ammonia synthesis [21,22]. It is also well known that the activity of ruthenium catalysts for ammonia synthesis depends strongly on the basicity of the promoter [23,24]. Fig. 3 shows the TPD profiles of CO_2. All the TPD results show two-peak profile, a low temperature peak at 473–573 K and a high temperature peak at 673–873 K. These peaks correspond to weak and strong basic sites. It is apparently observed from Fig. 3 that pure support and Ba promoted catalysts show higher strong basic site densities compared to weak basic site densities. On the contrary Cs promoted catalysts show higher weak basic site densities than strong basic site densities. In double promoted catalyst both (weak and strong) basic site densities are nearly same. All catalysts prepared from polyol method show higher number of weak basic sites. Basicity of the support plays a key role in determining the activity of the catalyst. Activity of the Ru catalysts is explained by electron donation theory that a donation of electrons through its d-orbital to the anti-bonding orbital of N_2 makes the N_2 dissociation easier by weakening the N≡N triple bond [1]. Thus the promoting effect of support is in terms of its electron donating nature. MgO is known to have the electron donating ability, which can make ruthenium more electron rich and thus enhance the rate of dissociation of N_2, which is the rate determining step of the NH_3 synthesis process. However, MgO possess high temperature basicity ($O_2{}^-$), i.e. above 673 K, which may be the reason for the Ru/MgO catalysts showing a high temperature activity [13]. But ammonia synthesis being an equilibrium-constrained reaction operation at higher temperatures reduces the equilibrium yields of NH_3 formation. It can be clearly seen from TPD results that Ba promotion enhances the stronger basicity and hence shows a high temperature activity. On the contrary Cs promotion leads to enhance weak basicity showing a higher activity, rate and TOF values at lower temperatures. The structure sensitivity of

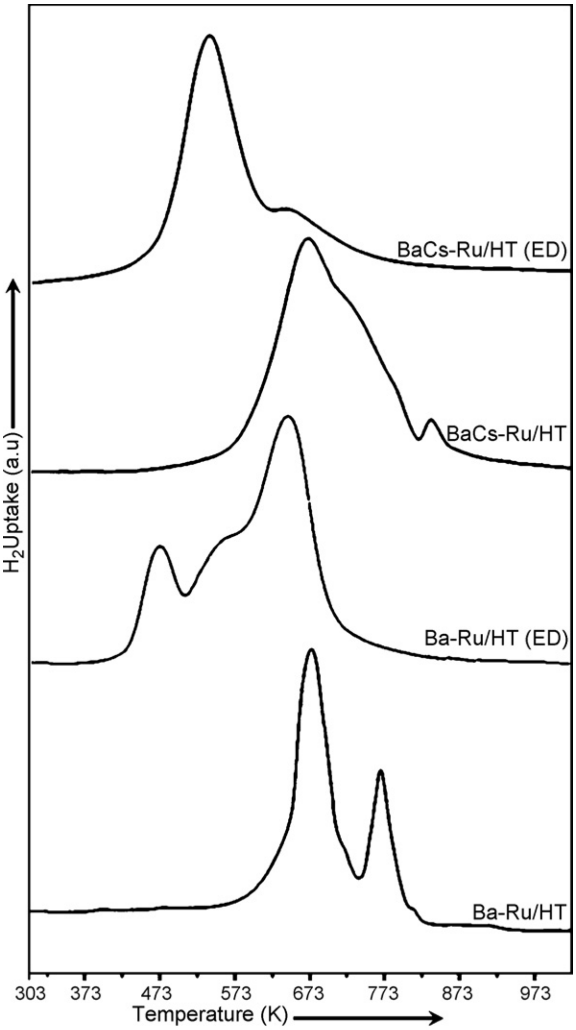

Fig. 2. TPR patterns of single and double promoted Ru catalysts on hydrotalcite support.

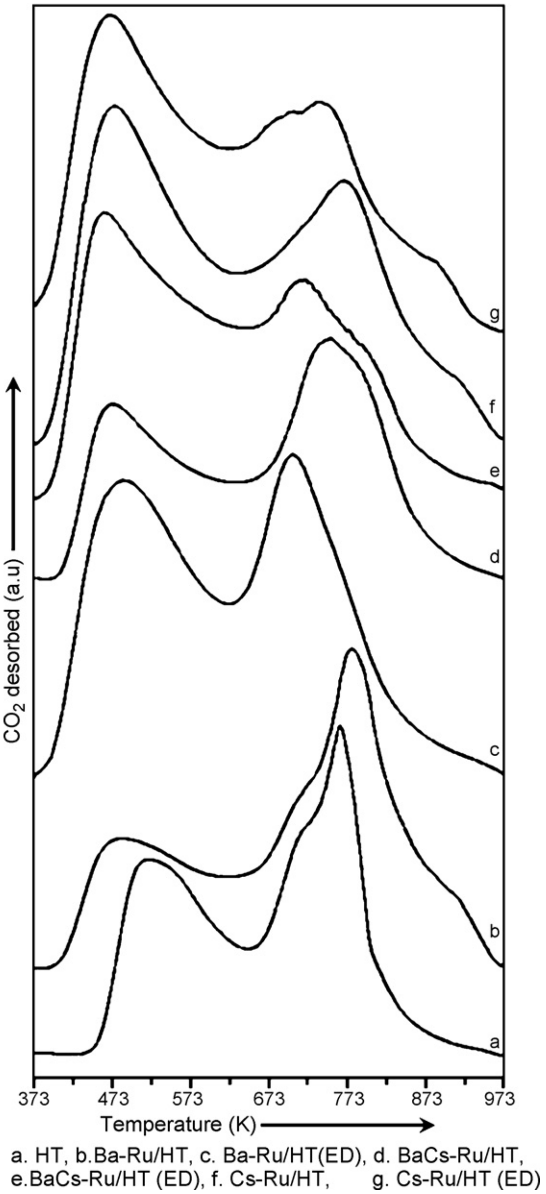

Fig. 3. TPD of CO_2 patterns of single and double promoted Ru catalysts on hydrotalcite support.

ammonia synthesis on ruthenium is ascribed to the presence of the so-called B_5 sites, which are believed to be extremely active to dominate the reaction rate [25]. The B_5-type sites may exist on the surfaces of various metals, such as platinum, palladium, nickel, or ruthenium, and they were early recognized to be responsible for strong physical adsorption of nitrogen [26]. It has been postulated that barium acts as a structural promoter that modifies the local arrangement of surface Ru atoms, thus creating the sites of highly active B_5 sites [10]. However Ba being a structural promoter of Ru creates more B_5 sites that are required for the synthesis of NH_3, but single Ba promoted on Ru/HT does not show significant activity for NH_3 synthesis.

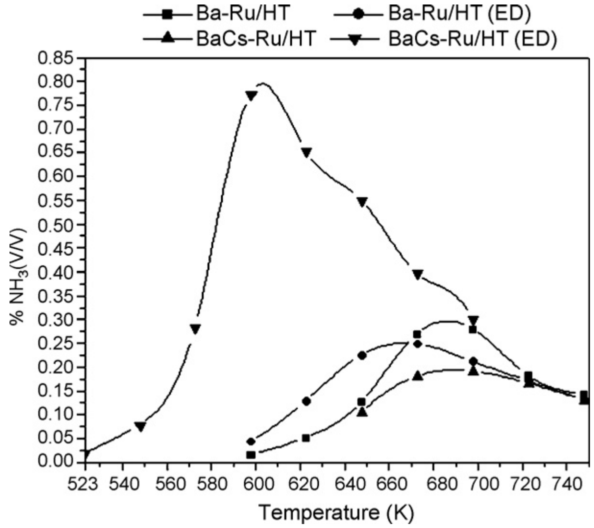

Fig. 4. Effect of reaction temperature on the steady-state concentrations of ammonia over single and double promoted Ru catalysts on hydrotalcite support.

Fig. 4 shows the effect of reaction temperature on ammonia synthesis activities expressed as steady-state rates over single promoted (Ba/Cs) and double (Ba and Cs) promoted catalysts. The highest activity is observed on Ba-Cs-Ru/HT (ED) catalyst. Cs promoted catalysts are found to show activity at lower temperatures as compared to the reaction temperatures of Ba promoted catalysts. Double promoted Ru catalyst prepared by polyol reduction method show maximum activity (0.76%, v/v) at a temperature of 598 K which is better than the previously reported Cs promoted catalyst prepared by polyol method (0.70%, v/v) [14]. This can be explained from TPD results that double promoted catalyst from polyol method contains more number of weak basic sites similar to that of Cs promoted catalyst from polyol method. Fig. 5 illustrates a correlation between rate, TOF, number of Ru sites and basicity. It is clearly observed from Fig. 5 that CO_2 uptakes are high in those catalysts prepared by polyol method as compared to impregnated catalysts. In impregnated catalysts, the basicity of double promoted catalysts is almost average of single promoted catalysts, but in the case of catalysts prepared by polyol method the basicity of double promoted catalysts is equal to sum of the single promoted catalysts. The number of active Ru sites in double

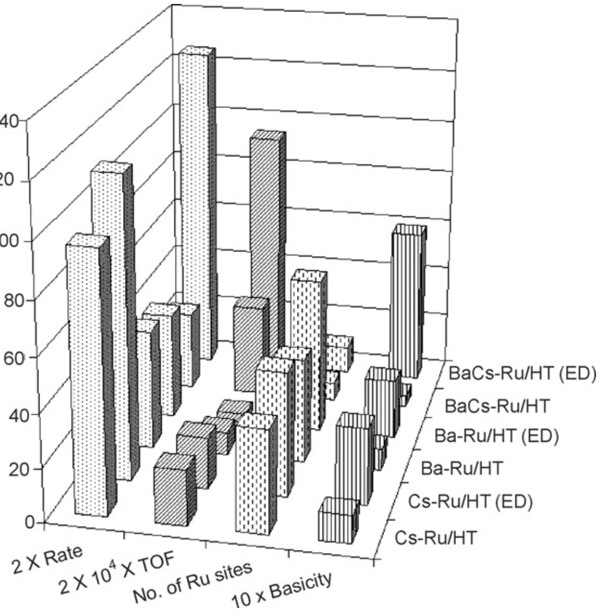

Fig. 5. Three-dimensional correlation diagram between basicity and no. of Ru sites, TOF and rate Units on Y-axis in Fig. 5. Rate: NH_3 cm^3 g Ru^{-1} h^{-1}; TOF: no. of NH_3 molecules formed Ru $site^{-1}$ s^{-1}; no. of Ru sites: μmol of Ru g $cat.^{-1}$); basicity: μmol NH_3 g $cat.^{-1}$.

promoted catalysts is very less compared to single promoted catalyst, may be due to low metal area. Even though having less number of Ru sites double promoted catalyst prepared by polyol method shows highest rate of ammonia formation and TOF values among all catalysts. But double promoted catalyst prepared by impregnation method showed lower rate of ammonia formation and TOF values than cesium promoted catalyst. Fig. 5 reveals that the TOF values for single promoted catalyst are very less, but in double promoted catalysts TOF values increased tremendously. This can be explained from the fact that Cs acts as an electronic promoter and transfer electrons to the active metal surface, thus leading to the lowering of the N_2 dissociating barrier resulting in the remarkably increase in the effective sticking coefficient for dissociative nitrogen adsorption [27–29]. On the other hand Ba acts as structural promoter that modifies the local arrangement of surface Ru atoms, creating highly active B_5 sites [10,30–32]. To increase the rate and TOF for ammonia formation double promoted catalyst has been prepared by polyol method. This catalyst showed almost a fourfold increase in rate of formation of ammonia and nearly threefold increase in TOF values over the impregnated catalyst. The effect of double promoters in both impregnation and polyol methods can be seen in the enhancement of activity per site (higher TOF values) even though increase in particle size and decrease in number of Ru sites. Acidic supports are inferior to basic supports in yielding good NH_3 synthesis activity over Ru catalysts [7]. That is the reason why the acidity of γ-Al_2O_3 has been greatly destroyed by incorporation of carbon layer on it in order to get good ammonia synthesis activity over Cs and Cs–Ba promoted Ru catalyst supported on carbon covered alumina (CCA) [9,11]. The maximum activity reported on BaCs–Ru/CCA [11] at 648 K is 0.76% (v/v) of NH_3. The advantage of Cs–Ba-double promoted Ru/HT catalyst of the present study is to bring down the reaction temperature to 598 K without compromising the maximum NH_3 synthesis yield of 0.76% (v/v). This is possible because of the higher basicity and easily reducible Ru precursors, which in turn are due to the application of polyol reduction method. It is interesting to observe that the catalysts, which show higher rates of NH_3 synthesis activities at 598 K, get reduced at low temperatures as evidenced from TPR. Thus one can speculate that the ammonia synthesis activity of a catalyst depends on the following factors: (a) basicity; (b) easy reducibility of Ru precursors. It seems that both the factors either independently or combinedly determine the activity.

4. Conclusions

It is confirmed that double promoted Ru catalyst on hydrotalcite support is a promising catalyst for ammonia synthesis. Because of presence of barium and cesium promoters the number of basic sites increased drastically with a consequent increase in the TOF values. The double promoted Ru catalyst on Mg–Al hydrotalcite prepared by polyol reduction method is showing almost three times increase in TOF values as compared to similar catalyst with double promoters prepared by conventional impregnation method. Another advantage of this catalyst is that it showed highest activity at lower temperature, i.e., at 598 K. This catalyst showed highest yield of NH_3 and highest TOF values over the other catalysts. This may be attributed to the higher ease of reducibility of Ru species with the addition of promoters and method of preparation of the catalyst as observed from TPR analysis and availability of higher number of basic sites. It thus shows that the double promoted Ru/HT catalyst of the present by polyol method is an efficient catalyst for ammonia synthesis.

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