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

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Abstract

Supported Ru catalysts using MgO, Al_2O_3 and calcined Mg–Al (2:1) hydrotalcite (HT) with alkali promoter (Cs) were prepared by two different methods viz., the conventional impregnation method and polyol reduction method using ethylene glycol as solvent for obtaining nano-Ru for ammonia synthesis under atmospheric pressure. The catalysts were characterized by XRD, BET surface area, TPR and evaluated for the synthesis of ammonia in the temperature range of 523–698 K at atmospheric pressure. CO chemisorption studies were performed to find out Ru dispersion, particle size and active metal area. The following sequence with respect to the $\%NH_3$ (v/v) formation was found: Cs–Ru/HT (ED) > Cs–Ru/HT > Cs–Ru/Al_2O_3 > Cs–Ru/MgO. The nano-Cs–Ru/HT (ED) catalyst prepared by polyol reduction method showed superior activity over the catalyst prepared from conventional impregnation method. The higher activity of the Cs–Ru/HT (ED) catalyst has been attributed to the presence of highly dispersed nano-particles of Ru as observed from CO chemisorption results and the presence of easily reducible Ru species as observed from TPR studies.
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1. Introduction

Ru-based catalysts are known to be active for NH_3 synthesis at atmospheric pressure [1–7]. The most stable and commercially available Ru precursor used for ammonia synthesis is $RuCl_3$ [2,5]. The main advantage of this metal precursor is its low cost in comparison to other metal precursors, but the main disadvantage of using $RuCl_3$ is the strong binding of chlorine atom with the metal surface even after reduction. Alkali metal nitrate used as a promoter is thought to have two effects: one is to remove chlorine ions from the catalyst and the other is to donate electrons to ruthenium. The promoting effect of alkali metal to Ru on NH_3 synthesis activity is found to be inversely proportional to the electro negativity of the alkali metal in the order of Cs > Ba > K > Na [8]. Many materials have been investigated as supports for ruthenium catalysts in ammonia synthesis, such as carbon [9,10], MgO [11–13], Al_2O_3 [14,15,2],

and zeolites [16,17]. It has been observed that the high activity of the active carbon supported promoted ruthenium catalysts are attributed to the electron deficient graphite lattice of active carbon [1]. However ruthenium can catalyze the methanation of carbon in the typical environment. The MgO support shows less activity because of strong interaction with chlorine in $RuCl_3$ [12]. The strong chemisorption of product ammonia on the acid centers of alumina makes it a less attractive support for ruthenium. The other supports show less activity compared to former. Hydrotalcite-like compounds are a class of precursors useful for the preparation of catalytically active oxides showing basic properties. The present work is related to the comparison of activity studies of ammonia synthesis over Ru supported on mixed oxide support obtained from Mg–Al HT precursor (with Mg/Al ratio of 2) with the Ru catalysts supported on simple oxides viz., MgO and Al_2O_3 under atmospheric pressure. To get a closer insight into the role of the supports and aiming at better understanding of the supported Cs–Ru systems the effect of Ru dispersion with and without Cs has also been investigated. CO chemisorption technique is used for particle size determination and dispersion.

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2. Experimental

2.1. Preparation of catalysts

The supports MgO and Al_2O_3 were prepared by precipitating 10 wt% aqueous solution of corresponding nitrate precursors with 10 wt% aqueous Na_2CO_3 solution up to pH 10–11. The precipitated mass was filtered and washed thoroughly with deionised water until excess of Na was completely removed. Then the filtered mass was kept for oven drying at 383 K for 10 h and then calcined at 773 K for 6 h. Mg–Al 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 [18]. The catalysts were prepared by impregnating the support with 10 wt% aqueous solution of $RuCl_3 \cdot 3H_2O$ (M/S. Loba Chemie) in a rotary evaporator. After drying in air (373 K, 12 h), samples were reduced in hydrogen at 723 K for 4 h. These reduced catalysts were named as Ru/MgO, Ru/Al_2O_3 and Ru/HT with Ru/support ratio (by weight) of 1:10. The reduced samples of supported Ru catalysts were impregnated with aqueous $CsNO_3$ solution and dried at 373 K for 12 h. In all these promoted catalysts the Ru:Cs:support weight ratio was kept at 10:51:100 and the catalysts after reduction were designated as Cs–Ru/MgO, $Cs–Ru/Al_2O_3$ and Cs–Ru/HT. An alternative method to obtain HT supported well-dispersed metal particles of Ru catalyst was prepared by polyol reduction method using ethylene glycol as solvent as described [19]. The catalysts were designated before and after the addition of Cs promoter as Ru/HT (ED) and Cs–Ru/HT (ED), respectively.

2.2. Characterization techniques

BET surface areas of the reduced catalysts of both promoted and unpromoted 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 reduced catalysts of both unpromoted and promoted were recorded on a Rigaku Miniflex (M/S. Rigaku Corporation, Japan) instrument using Ni filtered Cu Kα radiation, with a scan speed of $2°\,min^{-1}$ and a scan range of 2–80° at 30 kV and 15 mA. Temperature programmed reduction (TPR) profiles of the unpromoted and promoted Ru uncalcined samples were generated on a home made on-line quartz micro reactor 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 (11 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 $5\,K\,min^{-1}$ from 303 to 973 K. The CO chemisorption was carried out at 303 K on a homemade pulse reactor to evaluate the dispersion and metal particle size. In a typical experiment, about 150 mg of the catalyst sample was placed in a micro-reactor of 8 mm i.d., and 250 mm long quartz reactor and the catalyst sample was first reduced under a hydrogen flow at 723 K for 2 h, pre-treatment at 723 K for 1 h under He flow and finally was cooled in He flow up to 303 K. The outlet of the reactor was connected to a micro-thermal conductivity detector (TCD) equipped GC-17A (M/S. Shimadzu Instruments, Japan) through an automatic six-port valve (M/S. Valco Instruments, USA). After cooling, pulses of 10% CO balance He were injected at room temperature through a 1 ml loop connected to the six-port valve until no further change in the intensity of the outlet CO (from GC-software). Assuming CO:Ru stoichiometry of 1:1, dispersion, particle size and metal area of Ru were calculated using Ru metal cross-sectional area as $0.0821\,nm^2$ [20,21].

2.3. Activity studies

Activity tests over Cs promoted catalysts were carried out in a fixed bed glass reactor (i.d. 18 mm and 300 mm long) at temperatures ranging from 523 to 698 K with a successive rise of 25 K 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 generators, NG 2081 (M/S. Claind, Italy) and HOGEN GC300 (M/S. Proton Energy Systems, USA) were used for N_2 and H_2 gases, respectively, with >99.99% purity. 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 at the outlet mixture was determined by neutralizing with a known volume of 0.01N aqueous H_2SO_4 solution at regular intervals.

3. Results and discussion

The results of the BET surface area measurements are summarized in Table 1. It is observed that the surface area of Al_2O_3 is higher compared to HT and MgO supports. The addition of Ru to the support leads to decrease in the surface area and addition of Cs in succession leads to further decrease in the surface area of the catalyst. In case of MgO supported catalysts, the surface area decreased drastically by the addition of Ru and Cs in comparison to other supported catalysts. This is due to sintering of Cs in case of pure MgO supported catalyst [11]. The catalysts

Table 1
BET surface area of unpromoted and Cs promoted Ru catalysts on various supports

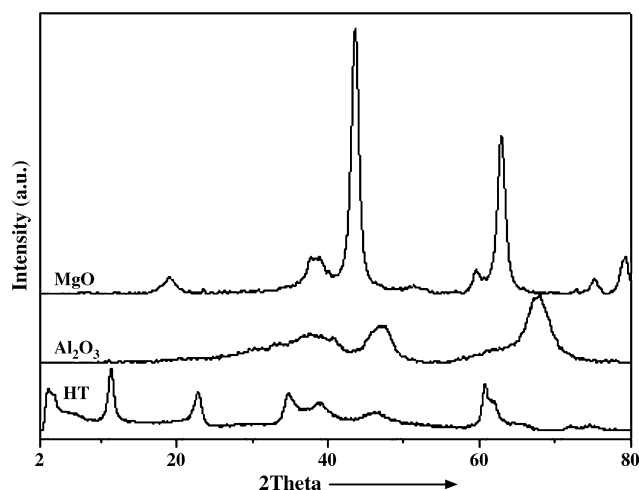| Catalyst	BET surface area (m^2/g)	Catalyst	BET surface area (m^2/g)	Catalyst	BET surface area (m^2/g)	Catalyst	BET surface area (m^2/g)
MgO	147	Al_2O_3	198	HT (Mg–Al)	172	–	–
Ru/MgO	17	Ru/Al_2O_3	170	Ru/HT	145	Ru/HT (ED)	158
Cs–Ru/MgO	9	$Cs–Ru/Al_2O_3$	63	Cs–Ru/HT	30	Cs–Ru/HT (ED)	68

Fig. 1. XRD patterns of MgO, Al$_2$O$_3$ and calcined Mg–Al HT.

Ru/HT (ED) and Cs–Ru/HT (ED) prepared by polyol reduction method show high surface areas in comparison to catalysts prepared by impregnation method.

The XRD pattern of calcined MgO, Al$_2$O$_3$ and HT supports are portrayed in Fig. 1. It is clearly observed from the figure that hydrotalcite structure [d = 7.84, 3.90, 2.57, ICDD no. 22-700] is regained by exposing to air after calcination [22]. The calcined samples of magnesia and alumina showed periclase [d = 2.11, 1.49, 1.20, ICDD no. 04-0829] and γ-Al$_2$O$_3$ phases [d = 1.4, 1.99, 2.46, ICDD no. 16-0394], respectively. Figs. 2 and 3 manifest the XRD patterns of reduced samples of both unpromoted and Cs promoted catalysts, respectively. Both unpromoted and promoted catalysts show the presence of Ru^0 phase [ICDD no. 06-0663] and the intensity of the peaks in unpromoted catalysts increases in the order of Ru/HT (ED) < Ru/HT < Ru/Al$_2$O$_3$ < Ru/MgO which indicates that MgO supported catalyst contains more crystalline Ru. The intensity of diffused peaks of Ru in the HT samples indicate the presence of highly dispersed/smaller particles of Ru which are further confirmed to be in nano-range from the CO-chemisorption results. The X-ray diffraction analysis of reduced promoted samples gave signals due to CsCl except in
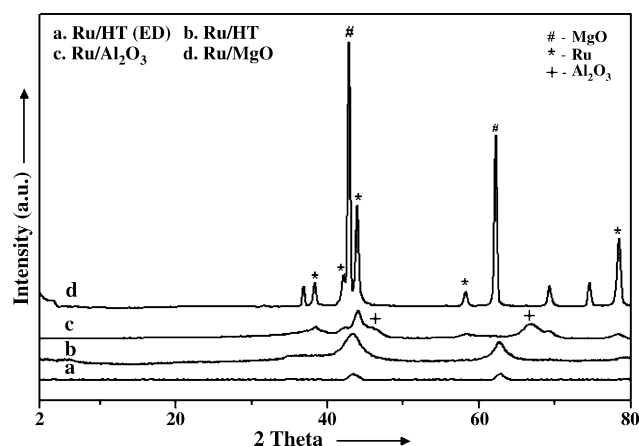
Cs–Ru/MgO catalyst. This means an anion exchange between RuCl$_3$ and CsNO$_3$ has occurred. In case of MgO supported catalyst no CsCl peak is observed but MgCl$_2$ is observed in unreduced unpromoted catalyst. After reduction, MgCl$_2$ can diffuse over the surface, although it is not volatile [17]. The intensity of CsCl peak is low in Cs–Ru/HT (ED) catalyst compared to other catalysts although it is prepared from polyol reduction method as some amount of RuCl$_3$ is left unreduced, and after addition of CsNO$_3$ the Cl$^-$ ion exchanged to NO$_3$$^-$ to form CsCl. Table 2 brings out the physical characteristics of Ru catalysts viz., dispersion, surface metal area and particle size. It is obvious from the data that the dispersion of Ru is high in the case of HT supported catalyst prepared from polyol method and low in the case of MgO supported catalyst. It is also clear that the Ru dispersion in Al$_2$O$_3$ supported catalysts decreased drastically by the addition of Cs promoter this is because of strong interaction between basic promoter and the acidic support. The presence of Cl$^-$ in case of MgO supported catalysts is known to catalyze brucite–periclase transformation [23,24]. As a result, Ru particles are decorated with MgO leading to lower values of Ru dispersion. In recent studies of Ru/graphite systems [25] demonstrate that at low metal surface concentration the particles have a

Fig. 3. XRD patterns of Cs promoted reduced Ru catalysts on various supports.

Fig. 2. XRD patterns of unpromoted reduced Ru catalysts on various supports.

Table 2
Dispersion, metal surface area and particle size of Ru in unpromoted and promoted Ru catalysts

Catalyst	CO uptake (μmol g^{-1})	Dispersion (%)[a]	Metal area (m^2/g)[b]	Particle size (nm)[c]
Ru/MgO	30.1	21	1.52	31.8
Ru/Al$_2$O$_3$	101	68	3.75	12.9
Ru/HT	76.0	52	5.0	9.7
Ru/HT (ED)	116.0	78	5.7	8.5
Cs–Ru/MgO	4.4	4	0.21	143
Cs–Ru/Al$_2$O$_3$	26.7	27	1.32	22.8
Cs–Ru/HT	38.5	39	1.90	15.8
Cs–Ru/HT (ED)	46.8	48	2.31	13.0

[a] Calculated as CO uptake (μmol g^{-1}) × 100/total Ru (μmol g^{-1}).
[b] 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.
[c] Particle size (nm) is calculated as 6000/[metal area (m^2 g Ru^{-1})ρ]. Ru density (ρ) = 12.4 g cm^{-3}.

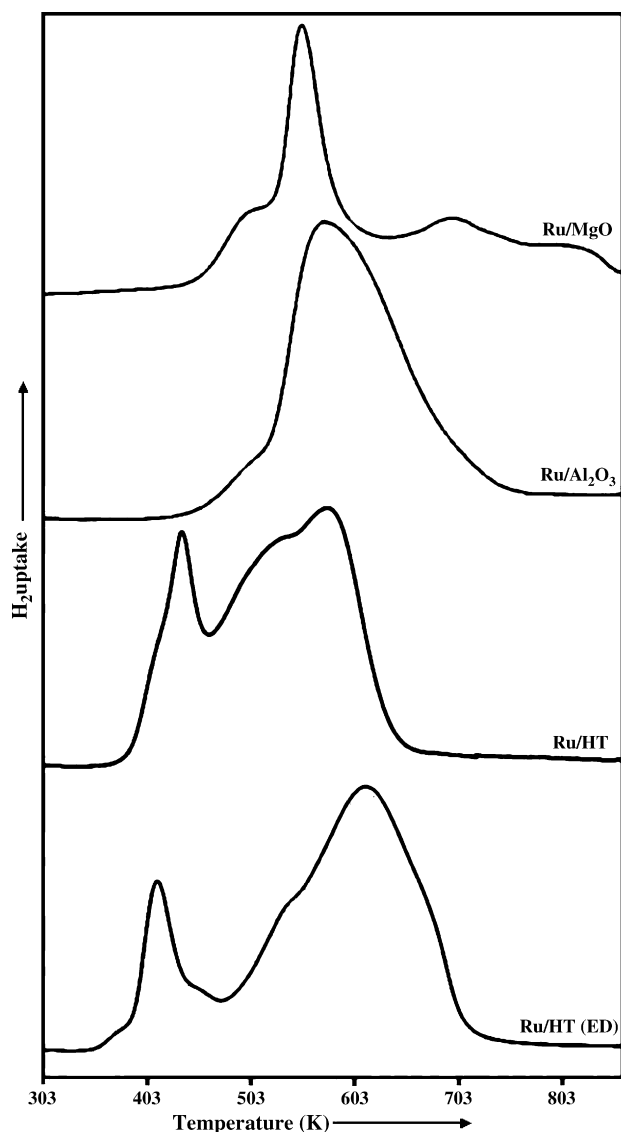Fig. 4. TPR patterns of unpromoted Ru catalysts on various supports.

Fig. 5. TPR patterns of Cs promoted Ru catalysts on various supports.

round shape and at high Ru surface concentration Ru forms flat particles and the latter one is more active in nitrogen desorption.

The TPR profiles of unpromoted and promoted Ru catalysts are displayed in Figs. 4 and 5, respectively. Fig. 4 indicates the presence of two major peaks with T_{max} varying in the range of 423–453 and 573 K. The HT supported samples showed the presence of low temperature peak at a T_{max} of 423 and 453 K over Ru/HT (ED) and Ru/HT, respectively. However, a very small shoulder at a $T_{max} > 473$ K is observed with Ru/MgO and Ru/Al$_2$O$_3$ catalysts and the high temperature is observed at a T_{max} of 573 K over all the unpromoted Ru catalysts. The presence of two different peaks clearly indicates the reduction of surface or more dispersed RuCl$_3$ and the bulk RuCl$_3$ over all the catalysts. The presence of low temperature peak in HT samples shows the ease of reducibility of these catalysts with Ru being in more dispersed form or in the form of smaller particles as compared to MgO and Al$_2$O$_3$ samples. From Fig. 5 it is clearly observed that the MgO supported Cs promoted Ru catalyst showed T_{max} at higher temperature and the Al$_2$O$_3$ supported
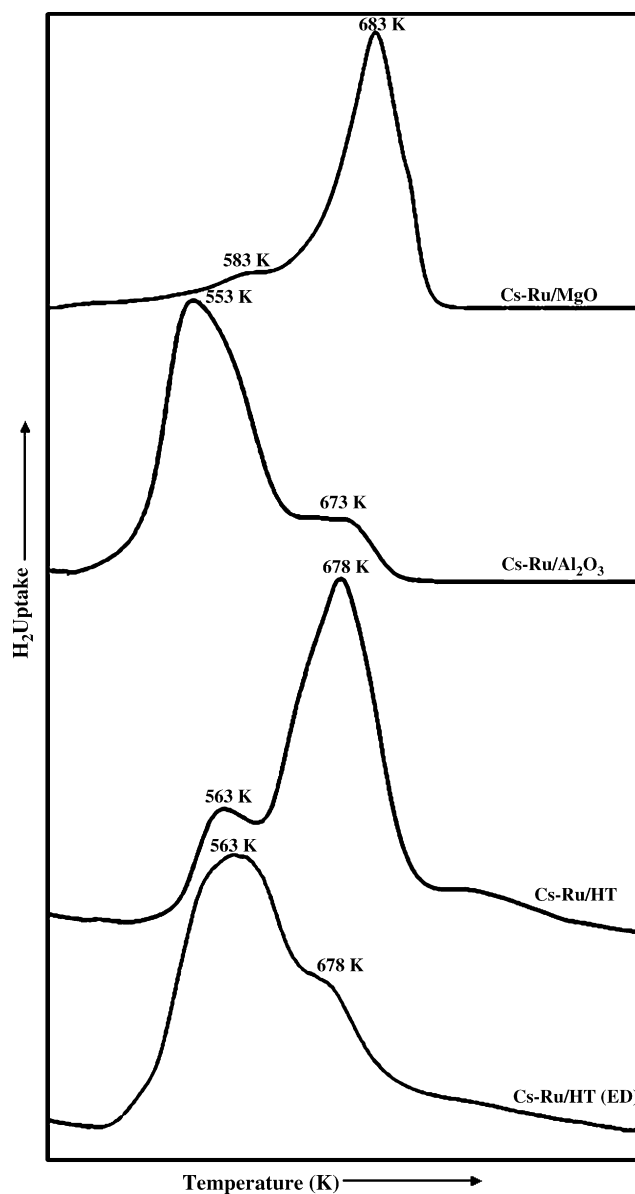
catalyst showed T_{max} at lower temperature compared to other catalysts. The higher reducibility of Ru precursor over Al$_2$O$_3$ and HT as compared to MgO can be attributed to the higher dispersion of Ru over high surface area supports of Al$_2$O$_3$ and HT. MgO possesses a very low surface area and hence the dispersion of Ru is also found to be much lower. This can be further supported from the formation of bigger particles of Ru as observed from CO-chemisorption results. In fact the particle size of Ru is the highest over MgO support. This is further complicated with the brucite–periclase transformation due to the presence of Cl$^-$ in MgO supported catalyst. The Ru precursors due to the coverage with MgO phase might not be accessible for the reduction. The T_{max} for unsupported RuCl$_3$ catalyst is reported at 433 K with another broad shoulder besides main peak, which has been attributed to the reduction of ruthenium oxide [26]. An interesting point observed in case of HT supported catalysts is that the catalyst prepared by conventional impregnation method showed
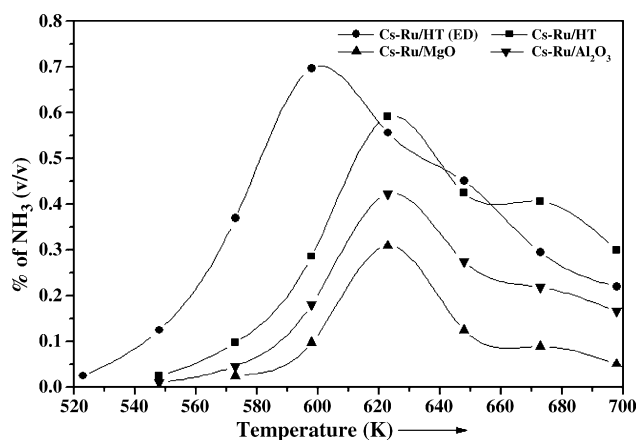
Fig. 6. Effect of reaction temperature on the steady-state concentrations of ammonia over Cs promoted supported Ru catalysts.

T_{max} at higher temperature which is nearer to T_{max} of MgO supported catalyst, but the catalyst prepared by polyol reduction method showed T_{max} at lower temperature which is closer to the T_{max} of Al_2O_3 supported one. This is due to high surface area and high dispersion of Cs–Ru/Al_2O_3 and Cs–Ru/HT (ED).

Fig. 6 shows the effect of reaction temperature on ammonia synthesis activities obtained under steady-state conditions over all the Cs promoted catalysts. Steady-state ammonia concentration and rate of formation of ammonia over all the catalysts at 598 K are shown in Table 3. The rate of NH_3 formation is much higher on Cs–Ru/HT (ED) catalyst. The higher Ru dispersion is responsible for the high activity. From Fig. 6, ammonia synthesis activities of the catalysts increase with rise in temperature and reach a maximum value at 623 K above that they decline. Among the three supported catalysts the HT supported catalysts shows highest activity. From Table 3, it is clear that the rate of formation of ammonia is more on HT supported catalysts compared to MgO and Al_2O_3 supported catalysts. The TOF value, as observed from Table 3, is higher for MgO supported catalyst compared to other catalysts, even though the number of Ru atoms on surface is very low. The higher TOF on MgO supported catalyst is indeed due to the basic character of MgO. However the presence of Cl^- and thereby the negative aspect of brucite–periclase transformation masks the beneficial role of MgO. The beneficial role of MgO is reported in the literature when organic precursor salts of Mg, Ru and Cs are employed [27]. In Al_2O_3 supported catalyst the TOF

value is much lower though it has considerable number of Ru on surface. The acidic character of Al_2O_3 may be the reason for lower TOF value towards NH_3 formation. Thus Mg–Al HT supported system can be considered as a better one, which shows a considerably good TOF value with higher number of Ru on the surface compared to the other two supported catalysts. The catalyst prepared by polyol reduction method using ethylene glycol as solvent, i.e. Ru–Cs/HT (ED) shows a two-fold increase in the TOF value compared to Ru–Cs/HT and higher rate of NH_3 formation at 598 K. At 623 K Ru–Cs/HT (ED) shows an equal rate of ammonia formation as on HT supported catalyst prepared by impregnation method. The structure sensitivity of ammonia synthesis on ruthenium is ascribed to the presence of the so-called B_5 sites, which are believed to be extremely active for ammonia synthesis and the number of active sites is correlated with the number of surface atoms. Larger particles are observed to have shown a discrepancy of active B_5 sites [28]. It is observed that on HT support the metal particle size is comparably lower hence availability of the number of active B_5 sites is higher. In the case of Cs–Ru/HT (ED) catalyst the dispersion is still high and particle size is comparably much lower over the other catalysts thus showing highest activity among all the catalysts studied. An additional advantage observed with Cs–Ru/HT (ED) is its higher activity at a lower temperature of 598 K as compared to other catalysts. It is observed that the major characteristics of a support for high catalytic activity is mainly related to the basicity [5], less interaction with Cl atom in $RuCl_3$ [2,11], and high surface area of the support. The more basic is the support; higher is the activity of the catalyst for ammonia synthesis, because basic supports donate electrons to Ru surface atoms, which promote the dissociation of dinitrogen. The lower activity for ammonia synthesis on MgO supported catalyst is due to low surface area and low dispersion before and after promoter addition and strong interaction with Cl atom. On other hand although Al_2O_3 supported catalysts have comparable surface area and dispersion before addition of promoter, an intense decrease of these is observed after addition of promoter. Due to acidic nature of Al_2O_3, which has strong interaction with ammonia probe, it shows less activity. The calcined hydrotalcite supported catalysts are having high basic nature, high surface area and high dispersion and also not having any strong interactions with Cl atom and hence the superior activity shown by HT supported catalysts.

Table 3
Ammonia synthesis yields and TOF of cesium promoted catalysts

Catalysts[a]	Temperature (K)	Steady-state NH_3 concentration [%, v/v]	NH_3 rate[b] [$cm^3\,h^{-1}\,g\,Ru^{-1}$]	TOF[c] $\times 10^4$ at a reaction temperature (K)
Cs–Ru/MgO	598	0.098	32	61.41
Cs–Ru/Al_2O_3	598	0.182	59	18.75
Cs–Ru/HT	598	0.287	93	20.50
Cs–Ru/HT (ED)	598	0.7	226	41.4

[a] Weight ratio of Ru:Cs:support = 10:51:100.
[b] Calculated from steady-state NH_3 concentrations [%, v/v] obtained by 5 g catalyst.
[c] TOF calculated as [NH_3 formed s^{-1}]/[Ru].

4. Conclusions

It is confirmed that calcined hydrotalcite precursor is the promising support for the ammonia synthesis. It is highly basic, thermally stable, and is resistant to Cl^- when compared to MgO support. HT supported catalyst is unveiling highest TOF values with paramount number of Ru surface atoms. Ru with Cs promoter over novel Mg–Al HT support is found to be very efficient for the synthesis of ammonia at atmospheric pressure compared to Cs–Ru catalysts on MgO and Al_2O_3 supports and the catalyst prepared by polyol reduction method is showing 10% more activity compared to impregnated catalyst at a lower temperature of 598 K. The higher activity of the Cs–Ru/HT (ED) catalyst has been attributed to the presence of easily reducible Ru species and nano-particles of Ru in highly dispersed form over calcined Mg–Al HT support.

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