In-situ $H_2$ production via low temperature decomposition of ammonia: Insights into the role of cesium as a promoter

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Abstract
Cesium-promoted ruthenium nanoparticles supported on multi-walled carbon nanotubes catalysts are shown to be highly active for hydrogen production by ammonia decomposition. Its low temperature activity is significantly improved as the cesium loading increases, reducing the activation energy from 96.7 kJ/mol in the absence of cesium to 59.3 kJ/mol with a cesium/ruthenium molar ratio of 3. Hydrogen production was observed to proceed below 590 K which represents a breakthrough towards the use of ammonia as chemical storage for in-situ hydrogen production on fuel cells. The catalytic enhancement is shown to be due to the electronic modification of ruthenium by the electron donating cesium promoter located on the ruthenium surface and in close proximity on the CNT surface. However, higher promoter loadings above a cesium/ruthenium ratio of 3 leads to ammonia inaccessibility to the catalytic active sites.

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Introduction

Hydrogen is widely recognized as an alternative portable energy medium to fossil fuels. It can be utilized for road transport applications presenting high energy efficiencies in combination with a proton exchange membrane fuel cell (PEM-FC) with zero emissions at the point of use [1]. Despite the vast potential of the use of hydrogen as an energy vector in the so-called hydrogen economy, its widespread implementation is currently limited by the capacity limitations of current hydrogen storage technologies and by the safety issues associated with its storage and transportation [1,2]. Hydrogen is a highly flammable gas in the presence of oxygen and, therefore, its storage in cylinders at high pressure makes public acceptance difficult due to safety reasons. During the last two decades, great scientific effort has been made to discover a suitable way of storing hydrogen. Adsorption into a variety of solid porous materials including metal organic frameworks is the most promising approaches [2,3]. Despite this, none of these materials have, to date, successfully fulfilled the 5.5 wt.% hydrogen content target established by the US Department of Energy for a complete storage system [4].

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The use of hydrogen enriched compounds such as hydrates as storage molecules is a viable chemical alternative to the above mentioned physical methods. Amongst such compounds, ammonia is one of the most promising due to its availability and narrow flammability limits. Liquid ammonia has a high hydrogen content of 17.3 wt.%, higher than liquid hydrogen [5] and can be easily stored as a liquid or incorporated within solid salts [6]. In addition, ammonia synthesis is amongst the most energy efficient commercial processes with an overall energy conversion efficiency of 75% [7].

The decomposition of ammonia reaction for hydrogen production has been extensively studied in the literature with most of the efforts focused on the development of active catalytic systems. Despite the reversibility of the reaction, the optimum catalytic system for the synthesis of ammonia from molecular hydrogen and nitrogen differs from the optimum catalyst for ammonia decomposition. Low temperature ammonia decomposition requires a catalyst that is active for the recombinative desorption of nitrogen adatoms [8], which has been shown to be the rate determining step [9]. Iron based ammonia synthesis catalysts tend to bind nitrogen adatoms too strongly and the surface becomes saturated and consequently poisoned at low temperature [10]. Ruthenium-based catalysts present the highest rate of hydrogen production from ammonia to date [11,12]. Highly conductive and basic supports promote nitrogen recombinative desorption while high surface areas lead to high metal dispersion. Consequently, carbon nanotubes and super-basic supports such as potassium-zirconia have the highest reported catalytic performance [7,13]. The ruthenium activity is commonly enhanced by the presence of promoters as electron donors [14–16]. The effectiveness of the promoter is partially related to its basic character and its interaction with both the active species and the support [15,16]. Of all promoters considered to date, cesium is the best performing ahead of barium and potassium which are also highly effective [13,17]. Despite this, the role of the promoter is still debated in the literature with most authors suggesting an electronic modification of the metal particle properties although some have proposed a structural effect upon the metal particle [17].

Despite the extensive investigation and progress in this area, most studies are carried out at high reaction temperatures in excess of 670 K where the equilibrium conversion towards hydrogen formation is above 99%. However, the application of ammonia as a hydrogen vector for a low carbon energy delivery system requires in-situ hydrogen production at temperatures suitable for the PEM fuel cell technology (below 470 K). The thermodynamic equilibrium at these conditions can be overcome using engineering approaches such as membrane reactors for in-situ removal of hydrogen [18]. This leaves the development of a catalytic system sufficiently active at low temperature as the foremost challenge.

To date, only a few scattered studies have investigated the decomposition of ammonia at temperatures below 670 K. Klerke et al. [19] found that ruthenium nanoparticles supported on cesium-titanate nanowires become active at 593 K due to the high electron donating character of the super-basic support. Even lower temperature reactivity was observed by Sorensen et al. [20] in a microreactor using ruthenium nanoparticles supported on graphitic carbon with a high loading of cesium promoter. No apparent change in the reaction mechanism at low temperature was observed by either study. Following these preliminary results, this paper demonstrates the reduction of the ammonia decomposition activation energy at low temperature when the Cs/Ru ratio reaches an optimum value (~3 when carbon nanotubes are used as support). Investigations into the interaction between the cesium promoter and the ruthenium species reveal the electronic modification of the ruthenium active sites by partially reduced cesium located on the metal surface or its close surroundings.

**Experimental**

**Synthesis and characterization of catalysts**

All catalysts were prepared by incipient wetness impregnation of multi-walled carbon nanotubes (Sigma Aldrich, OD 6–9 nm, length 5 μm, S_{BET} 253.0 m² g⁻¹). Ru(NO)(NO₃)₃ (Alfa Aesar) and CsOH.xH₂O (Sigma Aldrich, x = 0.17) were used as ruthenium and cesium precursors respectively. On a typical catalyst synthesis, an aqueous solution with a final volume
corresponding to the pore volume of the carbon nanotubes support was prepared containing the desired amount of ruthenium and cesium. This solution was then slowly drop-ped into the solid support, wetting it homogeneously. After synthesis, the catalysts were dried to remove the water solvent under vacuum at 350 K for 3 h and reduced under hydrogen at 500 K for 1.5 h.

N₂ adsorption analyses at 77 K were carried out using a Micromeritics ASAP 2020 and the surface area was calculated using the Brunauer, Emmett and Teller (BET) method. Powder X-ray diffraction was undertaken using a Bruker AXS D8 Advance with monochromatised Cu-Kα radiation (λ = 0.15406 nm), 40 kV and 40 mA. Ruthenium nanoparticle size distribution was determined with a JEOL TEM-2100 200 kV ultra-high resolution transmission electron microscope. Samples were prepared by depositing a drop of ~0.5 mg/mL of the material suspended in ethanol onto a Lacey carbon coated copper mesh grid and dried under vacuum. CO pulse chemisorption analyses at 308 K were carried out using a Micromeritics Autochem II equipment equipped with a thermal conductivity detector (TCD). Samples were pre-treated at 523 K under helium flow for 1 h to ensure the desorption of water or any other impurity from the catalyst surface. The same equipment was used for the temperature programmed reduction experiments. In this case, catalysts were pre-treated at 773 K under flowing argon for 20 min prior to temperature programmed reduction using 30 mL/min of 5% H₂/Ar from 333 to 1273 K with a ramp rate of 10 K/min.

**Ammonia decomposition**

In a typical reaction, 25.0 mg of catalyst were evenly dispersed in a packed bed with 450 mg of inert silicon carbide acting as a diluent inside a U-shape 1/4" O.D. quartz reactor. The temperature of the packed bed was regulated by an external tubular furnace (Carbolite) and a type K thermocouple situated at the exit of the catalyst bed. A mixture of NH₃ and He was continuously fed into the reactor giving a gas hourly space velocity of 5200 mLNH₃ g⁻¹ cat⁻¹ h⁻¹. Gas analyses were performed using on-line gas chromatography equipped with a HayeSep Q column and thermal conductivity detector and the mass balance was closed to within a ±10% error. A blank test was conducted in a reactor with SiC only showing no conversion within the experimental temperature range.

**Results and discussion**

A series of promoted ruthenium-based catalysts supported on multi-walled carbon nanotubes (CNT) were used for the production of hydrogen via decomposition of ammonia at low temperatures (below 650 K). In order to study the effect of ruthenium and cesium loadings, two sets of catalysts were prepared. Firstly, the effect of the ruthenium content on the ammonia decomposition activity was studied by varying the ruthenium loading in the range from 3 to 13.2 wt.%, keeping...
the promoter loading constant at 4.2 wt.% of cesium. Secondly, the role of cesium as a promoter was investigated by preparing a set of catalysts with a constant ruthenium loading (7 wt.%) while varying the cesium content by up to 50 wt.%. All catalysts were prepared by simultaneous incipient wetness impregnation of ruthenium and cesium precursors on multi-walled carbon nanotubes as support. The catalytic activity of both sets of catalysts towards ammonia decomposition as a function of temperature is shown in Figs. 1 and 2 respectively. Increasing the ruthenium loading on the Ru/CNT catalysts while maintaining the cesium loading (4.2 wt.%) constant increases the ammonia conversion for a given reaction temperature (Fig. 1(a)). Similar turnover frequency activity (TOF, calculated per mole of Ru) is observed in all cases, suggesting not only the presence of the same active sites, but also the same concentration of active sites per mass of ruthenium (Table 1).

The effect of the cesium content has a more remarkable function in determining the Ru/CNT activity, especially at low temperatures. The role of cesium is purely as a promoter, with cesium supported on CNT (20 wt.% Cs/CNT) not showing any ammonia decomposition activity in the range of temperatures studied. The presence of cesium enhances the Ru/CNT ammonia decomposition activity by reducing its activation energy and its incremental effect remains significant even at high Cs to Ru ratios, as shown in Table 2. In these cases, the Cs−Ru/CNT catalysts show activity towards ammonia decompositions at temperatures as low as 500 K (Fig. 2(a)).

Fig. 3 shows the volcano-type effect of cesium loading on the rate of reaction measured at 600 K. As the Cs/Ru ratio in the catalyst increases, the ammonia decomposition rate increases linearly reaching a maximum at Cs/Ru molar ratio of around 3. When the cesium loading is further increased (Cs/Ru >> 3), the rate of reaction decreases; however, the beneficial effect of cesium at low Cs/Ru ratio is greater than its detrimental effect at high Cs/Ru ratios, with similar rates of reaction obtained at Cs/Ru ratios of 1.4 and 7.1. This finding is in agreement with previous observations on the detrimental effect of cesium on the catalytic activity at very high promoter loadings [21]. The presence of an excess of cesium seems to partially block the access to the active ruthenium sites, reducing the hydrogen production rate [22]. This steric effect suggests that cesium decarates not only the CNT support but also the ruthenium surface, at least at high Cs/Ru ratios. The promotional effect of cesium would only be observed if it directly interacts with the ruthenium to ensure the electron donation [16], which not only increases its catalytic activity but consequently also modifies the nature of the ruthenium active species. This catalytic enhancement is observed at all Cs/Ru ratios and it significantly reduces the activation energy of the system from 97 kJ/mol in the absence of cesium to a minimum value of 60 kJ/mol when the Cs/Ru ratio has a value of 3, as shown in Table 2. These findings would suggest that cesium is present upon the surface of the ruthenium nanoparticle for all catalysts investigated.

The disparity of the promotional effect of cesium at different Cs/Ru ratios is explained by the effect of the cesium loading on its location across the catalyst. The distribution of cesium over the ruthenium surface and the CNT support respectively depends on the relative heat of adsorption [23]. At low promoter loadings, cesium strongly adsorbs on the surface of the CNT, although a small proportion is located on the ruthenium surface and its proximity, with a significant promotional effect. As the heat of adsorption on the carbon support decreases dramatically as the adsorbed cesium content increases [24], the relative amount of cesium adsorbed on the ruthenium surface increases at high cesium loadings. An optimum ruthenium coverage is observed when the Cs/Ru ratio is

![Fig. 3 — Rate of reaction of ammonia decomposition (at 600 K) as a function of the Cs loading using 7 wt.% Ru/CNT as catalyst.]

| Cesium loading/wt.% | Cs/Ru ratio | Ru average particle size/µm | Metallic Ru surface area/m² g⁻¹ | TOF @ 600 K molNH₃⁻¹ mol₉Ru⁻¹ h⁻¹ | Rate of reaction @ 600 K molNH₃ m⁻² mol₉Ru⁻¹ h⁻¹ (x10⁻²) | Activation energy/kJ mol⁻¹ |
|---------------------|-------------|-----------------------------|-------------------------------|----------------------------------|------------------------------------------------------|--------------------------|
| 0.0                 | —           | 1.6                         | 154                           | 0.0018                           | 1.2                                                  | 96.7                     |
| 4.2                 | 0.6         | 1.6                         | 160                           | 0.0151                           | 7.1                                                  | 78.6                     |
| 10                  | 1.4         | 2.4                         | 125                           | 0.0256                           | 20.0                                                 | 71.48                    |
| 20                  | 2.8         | 2.0                         | 167                           | 0.0426                           | 25.2                                                 | 59.33                    |
| 30                  | 4.3         | 2.4                         | 110                           | 0.0371                           | 33.4                                                 | 64.5                     |
| 50                  | 7.1         | 2.2                         | 56                            | 0.0242                           | 42.7                                                 | 66.1                     |

* Average metal particle size determined by TEM.

* Determined by CO pulse chemisorption.
~3 above which, blockage of the active sites occurs having a detrimental effect on the catalytic activity. This optimum ratio is dependent on the support and the promoter used [22].

In addition to the promoting electronic effect of cesium, transmission electron microscopy (TEM) was used to determine its effect on the size and morphology of ruthenium nanoparticles. Fig. 4 shows representative TEM images of 7 wt.% Ru/CNT with different cesium loadings. The presence of cesium does not seem to have an effect on the distribution of the ruthenium nanoparticles. Similar particle size distributions (histograms in Fig. 4) are observed independently of the cesium content with the majority of ruthenium nanoparticles in sizes between 1 and 4 nm and mostly between 1.5 and 2.5 nm. The observed variance between TEM nanoparticle

![Fig. 4 - TEM images and particle size histograms of 7 wt.% Ru/CNT catalysts. (a) 0 wt.% Cs, (b) 4.2 wt.% Cs and (c) 10.0 wt.% Cs, (d) 20 wt.% Cs, (e) 30 wt.% Cs and (f) 50 wt.% Cs.](image)
size results can be attributed to the limitations of measuring the metal particle sizes by TEM. Cesium is not detectable by TEM even at the higher loading contents studied, its presence on the catalyst was confirmed through EDS experiments.

It is well-accepted in the literature, that the ruthenium B5-type sites [11], a specific arrangement of five ruthenium atoms, are the active sites for the structured sensitive ammonia decomposition reaction [25]. The increase of catalytic activity per mole of ruthenium as the cesium loading increases up to Cs/Ru ratios \( \approx 3 \) (Table 2, TOF values) could lead to the misinterpretation of an increase of ruthenium B5 active site concentration as the cesium loading increases. However, this explanation does not successfully explain the changes on the activation energy suggesting that the main role of cesium is electronic rather than structural [14,16].

A similar study of the effect of ruthenium loading on its particle size was carried out using TEM images (Fig. 5). Up to 13.2 wt.% of ruthenium was loaded on the high surface area carbon nanotubes by incipient wetness impregnation with no apparent effect on the ruthenium particle size distribution as shown in the histograms. The average sizes range from 1.5 to 2.3 nm (Table 1) as the ruthenium content varies from 3.0 to 13.2 wt.%. At higher metal loadings, elongation of some of the metal particles inside the CNT support is observed. Visible

Fig. 5 – TEM images and particle size histograms of 4.2 wt.% Cs promoted Ru/CNT catalysts. (a) 3.0 wt.% Ru, (b) 7.0 wt.% Ru and (c) 13.2 wt.% Ru.

Fig. 6 – Effect of (A) ruthenium loading on 7 wt.% Cs promoted Ru/CNT catalysts and (B) cesium loading on 7 wt.% Ru/CNT catalysts on average ruthenium particle size measured by (◊) CO pulse chemisorption and (■) TEM.
elongation of nanoparticles suggests that they are generally located inside the carbon nanotubes with a small proportion decorating the external surface. However, in all cases, a similar activity per mole of ruthenium and activation energy is calculated for the ammonia decomposition reaction. Thus, similar active species and concentration per amount of ruthenium is present in all the catalysts independently of the observed particle elongation.

CO pulse chemisorption at 308 K was also used to estimate the ruthenium particle size and metal surface area by quantifying the amount of CO chemisorbed on the metal surface assuming a CO/Ru stoichiometry ratio of 2 and a ruthenium density of 12.45 g/cm³ [26]. In this case, it is observed that CO pulse chemisorption overestimates the ruthenium particle size compared to the data obtained by TEM. At low ruthenium and cesium loadings, the small differences between techniques could be caused by the assumption of hemispherical metal particles (support – metal contact angle of 90°) by the CO chemisorption method. However, the disparity of average ruthenium sizes estimated by both techniques further increases as the ruthenium and cesium loadings increase, as shown in Fig. 6. As observed by TEM, at high ruthenium loadings, partial encapsulation inside the carbon nanotubes support and consequent elongation of the particle takes place which partially blocks the access of CO to the ruthenium surface, consequently overestimating its average particle size (Fig. 6(a)) by decreasing the measured metal surface area (Table 1). Additionally, the difference between average particle sizes estimated by TEM and CO pulse chemisorption as a function of the cesium promoter content (Fig. 6(b)) further supports the previous observations related to the location of cesium within the catalytic system. As stated above, at low cesium content (Cs/Ru ratio below 3), although cesium is present on the ruthenium surface and proximity having a significant promotion effect, it preferentially adsorbs on the CNT support, leaving the ruthenium surface easily accessible to CO during the pulse chemisorption analyses. Thus, similar ruthenium particle sizes are estimated by both TEM and CO chemisorption methods. However, as the cesium loading increases, it selectively covers the ruthenium surface and consequently makes it inaccessible to CO. In this way, the latter method overestimates the ruthenium size, aligned with the decrease of ruthenium surface area when the Cs/Ru ratio is higher than 3 (Table 1). This observation is also in agreement with the
decrease of catalytic activity observed at high promoter loadings (Fig. 3) due to the ammonia inaccessibility to the active sites and supports previous observations of cesium increasingly decorating the ruthenium surface as the Cs/Ru ratio increases [15].

Fig. 7 shows the XRD spectra of (4.2 wt.%) cesium promoted Ru/CNT catalysts with different ruthenium loadings. The spectra of the carbon nanotubes support is shown for reference showing broad diffraction peaks at 25.8 and 43.2 2θ values. No diffraction peaks corresponding to ruthenium are shown independently of its loading which is in agreement with the TEM observation of its low particle size (<3 nm) [13]. No diffraction peaks corresponding to reduced cesium at 19.9°, 28.3°, 34.8°, 40.5°, 45.4° and 50° or any of its proposed chemical forms such as CsOH are observed. It is likely that cesium is present in a disordered form as observed in the literature by HR-TEM studies [15].

Temperature programme reduction of the different catalysts under hydrogen flow was carried out to further understand the interaction between the ruthenium, the cesium promoter and the CNT support and its effect on the final catalytic activity towards ammonia decomposition. Temperature programme reduction of the carbon nanotubes shows a considerable hydrogen uptake from 650 K with a maximum at 778 K (Fig. 8). The presence of cesium only on the CNT surface (20 wt.% Cs/CNT) shows a higher hydrogen intake with respect to the CNT support without a temperature shift of the peak, probably due to the reduction of the cesium hydroxide precursor (CsOH) to substoichiometric Cs2O in which cesium is partially reduced [23]. Additionally, the presence of cesium also shows a negative peak at ~950 K when compared to the results for the unmodified carbon nanotubes (Fig. 9).

TPR of ruthenium supported on un-promoted CNT catalysts (7 wt.% Ru/CNT) shows two additional peaks with respect to the CNT support. The first negative peak at ~300 K is caused by the decomposition of the ruthenium nitrosyl nitrate precursor with an associated release of nitrate species and water [23]. The second hydrogen uptake peak at ~430 K is associated with the reduction of ruthenium in line with reported values in the literature between 400 and 450 K [13]. The combined presence of ruthenium and cesium in the catalysts (Ru–Cs/CNT) markedly modifies the reduction temperature of both components. The peak temperature and the integration area for the ruthenium reduction peak increase from 430 K to 570 K as the cesium loading increases. The hydrogen consumption during the reduction calculated by integration of this peak suggests a degree of ruthenium reduction increasing from 14% for 0 wt.% Cs, to 88% for 10 wt.% Cs and 120% for 20 wt.% Cs catalysts respectively (all catalysts containing 7 wt.% Ru). This ‘over-reduction’ of ruthenium is explained by the partial reduction of cesium occurring on the surface of the ruthenium nanoparticle accounting for the additional hydrogen uptake. This finding is in accordance with the results previously published by Rarog-Pilecka et al. [23] who found by in-situ XRD that CsNO3 is converted to CsOH at 373–393 K and then reduced to a partially reduced substoichiometric oxide of Cs2O in which the degree of cesium reduction varied from 0.25 to 0.45 at around 430 K. Based on our current results, we can now confirm that cesium reduces only on the surface of the ruthenium nanoparticle as no cesium reduction is observed to occur at this temperature for the samples with no ruthenium. The reduction of cesium on the surface of ruthenium at temperatures between 470 and 570 K can be explained by the capability of ruthenium of dissociating hydrogen [27] which consequently spills over reducing the cesium in either direct contact to ruthenium or in the close surroundings. Reduced cesium on the surface of ruthenium would act as a strong electron donor and this explains the powerful effect that the addition of CsOH has upon the ruthenium catalyst for activity towards ammonia decomposition.

Conclusions

Hydrogen production from ammonia decomposition is shown at temperatures below 500 K using ruthenium supported on carbon nanotubes catalysts promoted with cesium which has a strong effect in reducing the activation energy of the reaction. A combination of characterisation methods
reveal the strong interaction of the cesium promoter with both the ruthenium and the carbon nanotubes support; cesium is partially located on the surface of the ruthenium where it undergoes partial reduction between 450 and 570 K in parallel with the ruthenium reduction, acting as a powerful electron donor. However, an excess of cesium can have a detrimental steric effect, making the ruthenium active sites inaccessible.

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