

## Novel preparation of nanocrystalline magnesia-supported caesium-promoted ruthenium catalyst with high activity for ammonia synthesis†

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**A caesium-promoted ruthenium catalyst supported on nanocrystalline magnesia with high activity for ammonia synthesis was conveniently prepared by using hydrated ruthenium trichloride and hexahydrate magnesium nitrate as precursors, whereas dechlorination post-treatment and ready-made magnesia were not necessary.**

Extensive and intensive researches on promoting magnesia-supported Ru catalysts for ammonia synthesis have been made by some pioneering groups, such as Aika's group,<sup>1–3</sup> Germanic group,<sup>4–9</sup> Kowalczyk's group,<sup>9</sup> Davis' group,<sup>10</sup> and so on. Recent investigations seem to show the promoting Ru/MgO catalyst as the most promising candidate of the so-called second-generation ammonia synthesis catalysts against the traditional iron ones.<sup>4,9</sup>

Yet the high preparative cost of the promoting Ru/MgO catalyst is now the main obstacle of its commercial application. So far, the common preparation method of Ru/MgO catalyst is wetness impregnation, that is, active Ru being impregnated on the ready-made magnesia support. Besides the troublesome and time-consuming preparation procedures and the very severe pretreatment conditions needed, the relatively expensive chlorine-free Ru precursor, usually Ru<sub>3</sub>(CO)<sub>12</sub>, must be used rather than the cheap and stable RuCl<sub>3</sub>·nH<sub>2</sub>O for enhancing catalytic performance, since the poisonous chlorine can not be effectively removed by hydrogenation post-treatment with hydrogen or ammonia synthesis gas. Additionally, magnesia must be a ready-made product. Magnesia supports used in literature<sup>4,8–10</sup> were usually less than 100 nm of crystal size and about 50 m<sup>2</sup> g<sup>-1</sup> of surface area. Ammonia synthesis over ruthenium has been found to be an even more structure sensitive reaction than over iron-based catalysts.<sup>11–13</sup> It was suggested that the so-called B<sub>5</sub>-type sites, which were primarily located at crystal edges and corners for a given Ru crystal morphology influenced by the support material, were primarily responsible for the activity of Ru catalysts and the optimum metal size was around 2 nm. Presently, the preparation of well-defined nanoparticulate magnesia with expectant surface area has been a hot field,<sup>14–17</sup> yet the challenges of scale-up synthesis in environmentally and conveniently benign ways still await further study. Furthermore, the metal particles obtained through conventional wetness impregnation are usually random or uneven, so it is difficult to control the final size and shape of the supported metal particles.

Herein we describe a novel convenient method for preparing highly active nanocrystalline magnesia-supported caesium-promoted Ru catalyst for ammonia synthesis. The catalyst was prepared by depositing beforehand well-defined Ru nanoparticles on nanocrystalline magnesia through a sol-gel process with ethylene glycol as solvent and reductant for the first time and, significantly, with the relatively cheap RuCl<sub>3</sub>·nH<sub>2</sub>O and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O as precursors and NaOH as a precipitant, whereas both the dechlorination post-treatment and ready-made

magnesia product were not necessary. Thus the preparative cost and the preparation procedures of Ru/MgO catalyst for ammonia synthesis were reduced and simplified greatly.

0.223 g of RuCl<sub>3</sub>·nH<sub>2</sub>O (*n* = 1–3, 37 wt% of Ru content) along with 12.8 g of Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was first dissolved in 50 ml of ethylene glycol solution under stirring at ambient temperature. The solution was heated to 383 K and maintained at 383 to 393 K for 1.5 h with an oil bath, then cooled down rapidly with an ice-water bath. The obtained solution was reported to be uniform atomic Ru colloid solution and part of the ethylene glycol had been oxidized into glyoxal in similar systems,<sup>18,19</sup> since the ethylene glycol acted as both the solvent and the reductant.

Subsequently, 25 ml of 4.0 mol L<sup>-1</sup> NaOH solution was added rapidly into the above solution containing dissolved Mg(NO<sub>3</sub>)<sub>2</sub> under vigorous stirring to give a suspension. The well-defined Ru metal colloidal particles were loaded or adsorbed on the freshly produced Mg(OH)<sub>2</sub> through electrostatic force. Because the Ru colloid was reported to be negatively charged in a solution with pH value above 4, and the p<sub>HZPC</sub> of Mg(OH)<sub>2</sub> is 12.4, in the system they were charged negatively and positively, respectively. As-prepared Mg(OH)<sub>2</sub> had a small average crystal size of 6.4 nm, determined from X-ray line broadening using the Scherrer equation (see Fig. S1 in the ESI†), and had high dispersity in the system. Thus the dispersion of Ru on the Mg(OH)<sub>2</sub> precipitate was also very high. After centrifugal separation, the precipitate was washed with distilled water to remove ethylene glycol and chlorine ions, and then dried at 383 K in an oven. The residual Ru in the solution could be economically reclaimed. Inductively coupled plasma (ICP) measurement showed that 80 wt% of the raw Ru had been loaded onto the dried solid.

The above solid was impregnated with aqueous solution of CsNO<sub>3</sub>, in the molar ratio of Cs to Ru = 2 : 1, for 12 h, and then dried in an oven. The dried material was finally calcined at 703 K for 1.5 h in a muffle to decompose the Mg(OH)<sub>2</sub> into MgO. The obtained sample was labeled as Cs-Ru/MgO, in which the Ru content was 2.37 wt%, and used as the catalyst for ammonia synthesis.

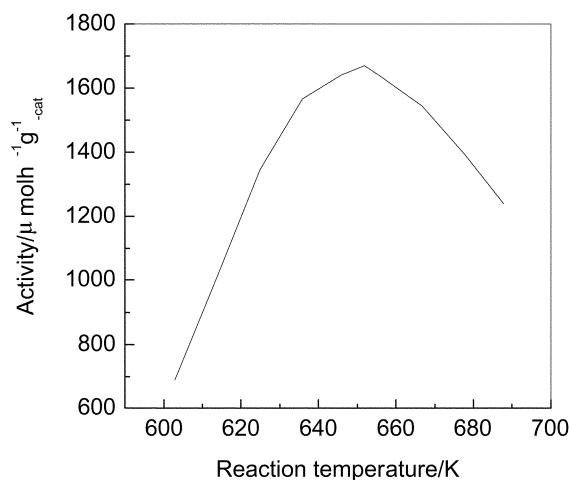
The Cs-Ru/MgO catalyst performance was tested in a fixed bed micro-reactor (id = 8 mm) made of stainless steel over 0.2 g of the catalyst powder under the flow of H<sub>2</sub> and N<sub>2</sub> mixture (H<sub>2</sub>/N<sub>2</sub> = 3 vol/vol, 30 to 60 ml min<sup>-1</sup>) at atmospheric pressure. The catalyst was activated in the stream of ammonia synthesis gas at 688 K for 3 h, and then cooled to the desired reaction temperature. After a stable ammonia production was reached in about 1 h, the catalytic activity, expressed as μ mol h<sup>-1</sup> g<sup>-1</sup><sub>cat</sub>, was determined by a chemical titration method using fixed amount of diluted sulfuric acid solution containing an indicator (methyl red) to absorb the produced ammonia.

The dependence of activity for ammonia synthesis on reaction temperature is illustrated in Fig. 1. It shows that the catalytic activity reached a maximum value of 1668 μ mol h<sup>-1</sup> g<sup>-1</sup><sub>cat</sub> under 30 ml min<sup>-1</sup> of gas flow rate at a reaction temperature of 652 K. However the highest activity values of two similar catalysts prepared *via* a conventional process using

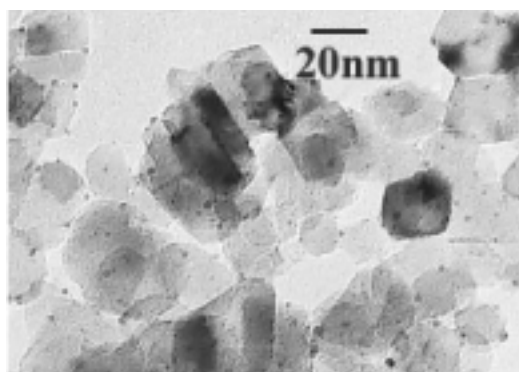
† Electronic supplementary information (ESI) available: Figs. S1–S4. See <http://www.rsc.org/suppdata/cc/b3/b307975a/>

$\text{Ru}_3(\text{CO})_{12}$  and  $\text{RuCl}_3$  as precursors, respectively, were reported to be about 820 and 400  $\mu\text{mol h}^{-1} \text{g}^{-1}_{\text{cat}}$  at optimum reaction temperatures of 588 and 673 K, respectively, and other similar conditions.<sup>2,3</sup> The activity of our catalyst could be further increased to 2660  $\mu\text{mol h}^{-1} \text{g}^{-1}_{\text{cat}}$  when the gas flow rate was raised to 60  $\text{ml min}^{-1}$  at a reaction temperature of 652 K (see Fig. S2 in ESI†). This activity is even higher than that of a barium promoted active carbon supported ruthenium catalyst, whose highest activity was about 2000  $\mu\text{mol h}^{-1} \text{g}^{-1}_{\text{cat}}$  at a reaction temperature of 588 K and other similar test conditions.<sup>20</sup>

The reason why this catalyst exhibits superior activity for ammonia synthesis to the catalysts prepared *via* conventional processes even at such low Ru content at least lies in the following three factors. First, the high dispersion of Ru and the appropriate Ru crystal size on the support. Fig. 2 shows the TEM image of the Cs-Ru/MgO after catalytic reaction revealing the presence of small and uniform Ru particles on the support. Almost no apparent lumpy Ru conglomerations can be found, meaning a high utilization ratio of Ru. Furthermore the average Ru particle size, about 1 to 2 nm, approximated the optimum crystal size possessing more  $\text{B}_5$ -type sites. Second, the moderate scale of nanocrystalline magnesia support. The sizes of magnesia in the catalyst before and after catalytic reaction were measured to be 7.1 and 24.1 nm, respectively, from the corresponding XRD patterns (see Fig. S3 in ESI†). It seems reasonable to conclude that the increase of magnesia crystal size



**Fig. 1** Dependence of ammonia synthesis activity on reaction temperature under 30  $\text{ml min}^{-1}$  of gas flow rate.



**Fig. 2** TEM image of Cs-Ru/MgO after catalytic reaction.

occurred and completed at the initial activation step of about 3 h, because stable catalytic activity could be maintained and no obvious variation of activity was observed at corresponding reaction temperature during the accumulative 120 h intermittent evaluation. This dimensional magnesia of a few 10s of nanometers may facilitate the formation of  $\text{B}_5$ -type sites. No distinctive Ru peaks appear in these patterns, since the average Ru size was less than the diffractometer detection limit of about 2 nm, in agreement with the TEM observation. Third, the satisfactory elimination of chlorine. Corresponding XPS spectra showed that most chlorine, originating from the raw material, a severe poison of ammonia synthesis, had been efficiently removed in the course of heating and washing procedures (see Fig. S4 in ESI†).

In conclusion, this method for preparing a Ru/MgO catalyst for ammonia synthesis is facile, economical and efficient. Though many factors, such as Ru loading content, calcination temperature, content and type of promoter, performance under high pressure, lifetime and so on, require further investigations, it shows a promising future for theoretical research and practical application.

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