

Synthesis and Characterization of Ru/Al₂O₃ Nanocatalyst for Ammonia Synthesis

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ABSTRACT: Ru/Al₂O₃ catalysts were prepared by conventional incipient wetness impregnation as well as colloid deposition of RuCl₃ precursor via in situ reduction with ethylene glycol (polyol) method on alumina support. The samples were characterized by TEM, XRD and TPR techniques. The catalytic performance tests were carried out in a fixed-bed micro-reactor under different operating conditions. Ethylene glycol as the reducing agent in the polyol method produced well-dispersed and uniform ruthenium nanoparticles with an average diameter of 7 nm supported on Al₂O₃. In conventional method, however, reduction by hydrogen resulted in considerably larger particles with average size of 12 nm. The Ru/Al₂O₃ catalyst prepared by polyol method exhibited three-fold higher activity in ammonia synthesis compared to the catalyst prepared by conventional method. The turnover frequency ratio of ammonia synthesis of polyol to conventional catalyst was estimated to be 2.1 at 450°C implying the reaction is structure-sensitive over Ru-based catalysts.

KEY WORDS: Ammonia synthesis, Ruthenium, Nanoparticles, Structure-sensitivity, Alumina support.

INTRODUCTION

The catalytic synthesis of ammonia is one of the mankind largest synthetic chemical reactions. It is of strategic importance since ammonia is the ultimate source of nitrogen in nitrogen-containing chemicals. Ammonia is the second largest synthetic chemical product [1]. Ammonia synthesis reaction from N₂ and H₂ is composed of several steps, in which dissociation of N₂ is the rate determining step. The main role of ammonia synthesis catalyst is to dissociate the N₂ bond, because of its high bond energy [2]. The industrial synthesis of ammonia

is carried out under high pressures which results in remarkable energy consumption in the synthesis-gas (N₂+H₂) compression with the commercial fused iron catalysts [3]. Iron catalysts are prepared by fusion of iron oxides and promoters (e.g., aluminum, calcium and potassium oxides) in an electric furnace around 1500 °C, followed by cooling, crushing and sieving. Sulfur impurities and cooling rate affects catalyst performance [4]. In the meantime in 1996, a group of researchers reported and patented a new high-activity ammonia synthesis

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catalyst based on wustite (FeO) which increased the reaction rate by 30% compared to the traditional catalyst. However, this catalyst is less active than those based on magnetite and much less resistant to thermal deactivation.

In early 1970s, British Petroleum and M.W. Kellogg companies jointly developed a new type of catalyst, which was ruthenium over carbon support (Ru/C). The Kellogg Advanced Ammonia Process (KAAP), now licensed by Kellogg/Brown & Root, Inc., uses a new Ru-based catalyst supported on graphite-containing carbon and co-promoted with Cs (Rb) and Ba. It is capable to produce ammonia with a higher yield at lower pressure and lower temperature conditions than a conventional Fe-based catalyst. High ammonia yields of approximately 40-50% have been achieved over Ru/C catalyst at 370-400 °C and 50-100 atm [5].

Ruthenium is an active catalyst for a number of reactions including ammonia synthesis, Fischer-Tropsch synthesis, and methanol electro-oxidation. The coordination chemistry of ruthenium (II) and (III) has been well developed due to their ability to form stable complexes with a wide range of organic ligands. Ruthenium should be able to coordinate to either or nitrogen and the IR spectra indicate bonding to only the nitrile (end) nitrogen [6,7].

Ruthenium is a rather rare element. It is a precious metal and its resources are scarce and expensive, therefore, high contents in the catalysts results in high cost and this impedes its application [8]. Therefore, the development of active catalysts with lower Ru content is very important for the economic use of Ru-based catalysts for ammonia synthesis. Ruthenium is known to show significant activity for ammonia synthesis and it may be regarded as the second-generation of ammonia synthesis catalysts right alongside iron catalysts [9]. Ruthenium is remarkably promoted by addition of alkali (metallic or oxide) for the activation of dinitrogen, although it has the drawback of suffering from inhibition by hydrogen. The high activity thus attained makes it possible to reduce the reaction temperature so that the total pressure may be lowered to attain a desired conversion. Another advantage of Ru is that its lower susceptibility to poisons such as H₂O and CO than iron, when promoted with basic oxides instead of metallic alkali. In fact, it has been demonstrated that ammonia synthesis can be carried out in the presence of water and

carbon monoxide on ruthenium catalysts. Thus, the direct synthesis of ammonia from dinitrogen, carbon monoxide, and water is possible on ruthenium [10]. Ammonia synthesis over Ru-based catalysts is a structure-sensitive reaction [11]. The activity of the catalyst for structure-sensitive reactions is not only closely related to the number of active sites, but also to the crystal structure, inter-atomic spacing and crystallite size of the catalytic material. Consequently, the precise control of Ru particle size plays an important role in the performance of the resulting catalyst [12].

Nanocrystalline materials consist of nanometer-sized crystallites that have a high surface-to-volume ratio that distinguish them from conventional polycrystalline or amorphous materials [13]. The influence of Ru particle sizes on the ammonia synthesis rates had been studied based on theoretical calculations and experimental results. The dissociation and desorption of nitrogen exclusively take place at the step sites on the Ru(0001) surface. It seems that the most active sites for N₂ dissociation and ammonia synthesis are ensembles of five Ru atoms, which expose a three-fold hollow site and a bridge site close together where part of the atoms, are edge atoms [14]. This type of sites is known as B₅-type sites. Based on the statistics proposed by van Hardeveld and Hartog, the group of Jacobsen counted the relative number (in relation to the total number of atoms) of B₅ sites on hcp ruthenium crystallites of different sizes [15].

Among the various preparative techniques have been used, chemical routes offer the advantages of molecular or atomic level control and efficient scale-up for processing and production of nanoparticles. The polyol method is a simple, single-step process for preparing nanostructured powders and coatings. In this process, the metal precursor(s) are suspended or dissolved in a polyol such as ethylene glycol. The resultant glycol-metal precursor mixture is then heated to reflux and the metallic moieties precipitated out of solution. The preparation method and conditions strongly influence the catalyst performance. Ethylene glycol is an excellent reducing agent for the preparation of oxide-supported ruthenium catalysts [16].

Many materials such as carbon [17,18], MgO [19], Al₂O₃ [20,21] and zeolites [22] have been used as supports for ruthenium catalysts in ammonia synthesis. Metal oxides could be used to stabilize and anchor the nanoparticles to reduce the agglomeration of nanoparticles.

Among the well-developed ruthenium supports, alumina is a stable carrier under ammonia synthesis conditions. Great efforts have been paid to improve the catalytic activities of Ru/Al₂O₃ [23]. However, the previous works on Ru/Al₂O₃ catalysts synthesis by polyol method used alumina nanoparticles in powder form and atmospheric pressure for performance tests which is of little relevance to commercial practice.

In this work, the Ru/Al₂O₃ catalyst was prepared by RuCl₃ reduction and deposition on commercial spherical alumina support using ethylene glycol and it was compared with the conventional catalysts prepared by incipient impregnation with the same precursor. The catalysts were tested in representative industrial conditions for ammonia synthesis. In addition, the apparent activation energies determined for prepared samples.

EXPERIMENTAL SECTION

Catalyst preparation

Ruthenium (III) chloride hydrate (RuCl₃.xH₂O, 37 wt% Ru), sodium nitrate (NaNO₃) and ethylene glycol were of analytical grade and used as starting materials. Commercial γ -Al₂O₃ (1.8 mm in diameter and 200 m²/g surface area) supplied by Sasol Co, South Africa, was used as the support.

Ru catalysts were prepared by two methods with the nominal loading of Ru 2 Wt%. In the polyol method, RuCl₃.nH₂O was dissolved in 0.01 M ethylene glycol in a round flask and was stirred at room temperature for 60 min. Then the alumina support was added to the flask. A condenser was added to the flask and the assembly was put into a silicon oil bath with oil temperature at 180 °C for 30 min. The flask was then removed from the oil bath and immersed into an ice bath for about 30 min. After quenching, the ethylene glycol was removed by diluting the suspension with 0.3M NaNO₃ aqueous solution and the solid phase was collected by filtration, washed several times with distilled water, and dried at room temperature. The other Ru/ γ -Al₂O₃ catalyst was prepared by the incipient wetness impregnation method. The samples that are prepared by polyol and conventional methods are denoted Ru/Al₂O₃-P and Ru/Al₂O₃-IM, respectively.

Catalyst characterization

The TEM studies were performed with EM900 Zeiss instrument at 80 kV. Samples were prepared by ultrasonic

dispersion of the samples in ethanol. The resulting suspension was then placed onto carbon grids and pre dried before insertion.

The samples were analyzed for phase identification by powder X-ray diffraction using a Siemens X-ray diffractometer D5000 with Cu K α radiation (40 kV, 30 mA) at a scan rate of 12° per minute.

Temperature-programmed reduction (TPR) analysis of the samples was carried out by using a Belcat A instrument equipped with a thermal conductivity detector. Samples were heated up to 300 °C at 10 °C min⁻¹ in a gas stream of 7% hydrogen in argon.

Experimental set-up and catalytic tests

The catalyst activity for ammonia synthesis was measured in a stainless steel reactor (400-475 °C, 30 bar, gas hourly space velocity (GHSV) of 1325-5300 h⁻¹ and H₂/N₂ volume ratio of 3). Before testing, the catalyst prepared by impregnation method was activated in situ under the flow of H₂ from ambient temperature to 450 °C at a rate of 2.5 °C/min and holding at 450 °C for 6 hours. The ammonia content in the effluent was determined by an online gas chromatograph (Varian CP-3800).

Before performance test runs, a blank test was done to ensure that the reactor wall material could not exhibit catalytic activity in ammonia synthesis.

The mass reaction rate of ammonia synthesis was calculated by the following equation:

$$r'_m = \frac{V_0}{22.4W_c} \times \frac{\varphi_{\text{NH}_3}}{1 + \varphi_{\text{NH}_3}} \quad (1)$$

where r'_m is the reaction rate (mmol/(g_{cat}.h)), W_c catalyst weight (g), V_0 normal flow rate of feed gas (H₂+N₂) (Nml/h) and φ_{NH_3} is concentration of ammonia in reactor outlet (as volume fraction).

A schematic representation of the experimental set-up for ammonia synthesis and temperature-programmed reaction is shown in Fig. 1.

RESULTS AND DISCUSSION

The process of Ru reduction in ethylene glycol was accompanied with color changes. The color of the initial solution, i.e., glycolic solution of RuCl₃, was yellow. In the course of heating, the color changed to transparent (after 5 min), pink (after 8 min), brown (after 10 min) and finally to gray. It is generally agreed that the size of metal nanoparticles is determined by the rate of reduction of

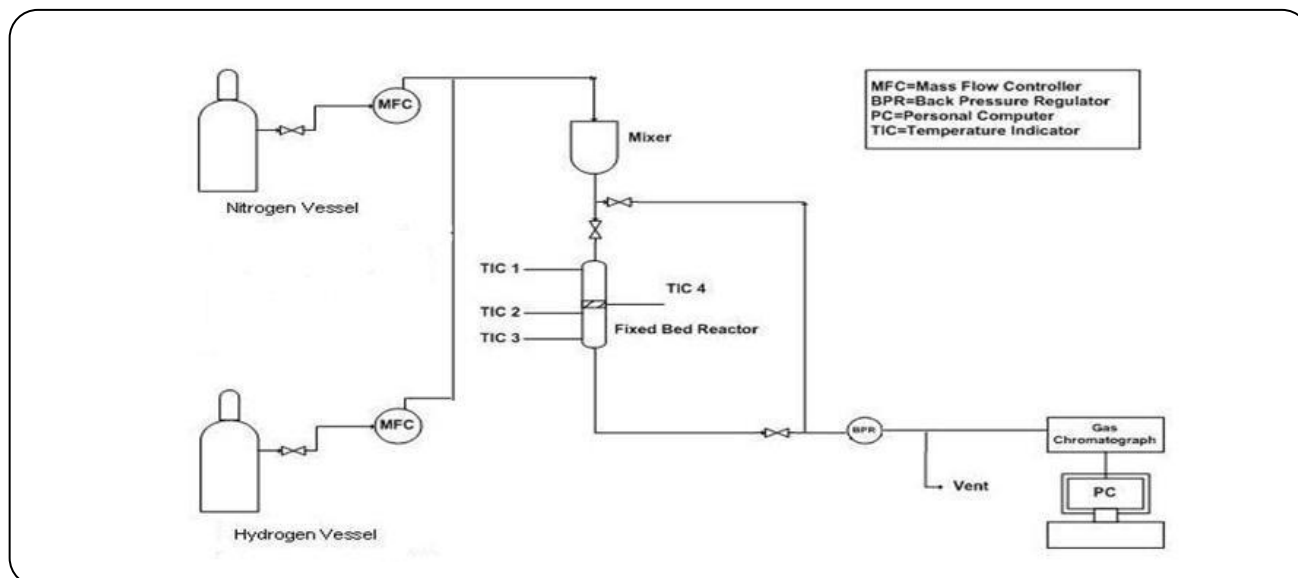
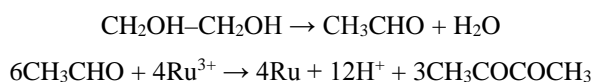


Fig. 1: A schematic representation of the experimental set-up.



Scheme 1: mechanism of ruthenium chloride reduction and deposition on the alumina support.

the metal precursor. At high temperatures, ethylene glycol is decomposed to yield the in situ reducing species CH_3CHO for the reduction of the metal ions to metallic particles. The reduction process of RuCl_3 in ethylene glycol can proceed in two steps: (i) ligand exchange around the Ru^{3+} ions and (ii) reduction of Ru^{3+} to Ru metal (Scheme 1).

The TEM micrograph of $\text{Ru}/\text{Al}_2\text{O}_3$ catalyst obtained by the polyol method showed the presence of many black and dispersed particles on the support (Fig. 2). It can be seen that the ruthenium particles were uniform in size and shape, and they were dispersed well over the surface of Al_2O_3 . The mean particle size of Ru nanoparticles supported on the alumina was estimated at 7.16 nm using the Gatan software.

The well dispersed feature is a result of the mild reduction conditions by ethylene glycol and also of the intermediate stabilization of Ru colloids by freshly produced alumina through the electrostatic forces.

Fig. 3 shows the TEM image of the sample prepared by the conventional method after reduction by exposure to H_2 at 450 °C for 6 h. The reduction process of samples with H_2 is essential stage in the conventional method

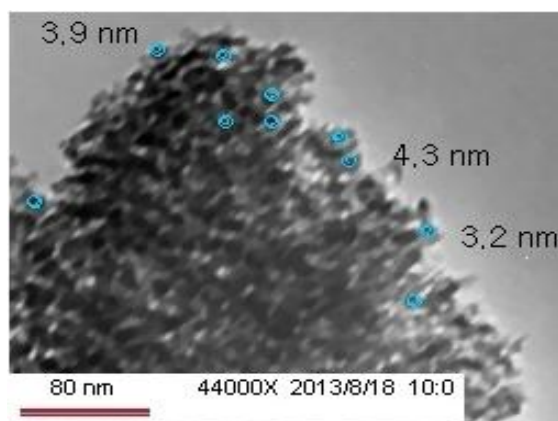
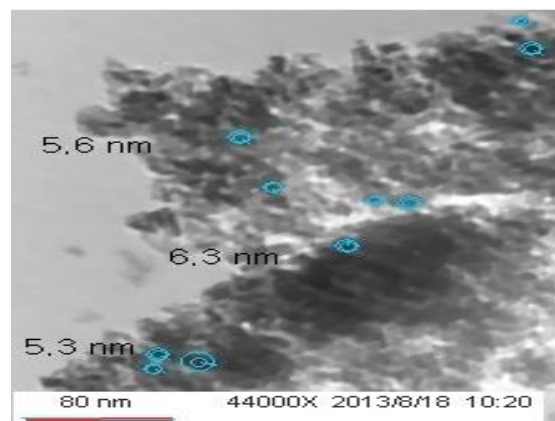
because of the ruthenium particles must be formed. This could cause thermal sintering of metallic particles. However, *Okal et al.* showed that Ru nanoparticles are stable at the surface of the alumina support up to 500 °C [24]. It can be observed that the Ru particles deposited on Al_2O_3 support were irregular and they were not well dispersed. The mean size of the particles was 12.1 nm.

The XRD patterns of $\text{Ru}/\text{Al}_2\text{O}_3\text{-P}$ and $\gamma\text{-Al}_2\text{O}_3$ support are shown in Fig. 4. According to the results of XRD analysis and comparison with the standard powder diffraction file (JPCDS No. 06-663), Ru should have the intense XRD peak at 43.7° that is related to (002) plane of Ru crystalline.

From the peak widths (full width at half max, FWHM) of the diffraction peak that was about 2° and measured with X'Pert High Score Plus software, the dimensions of the Ru particles were estimated based on Scherrer equation to one most intense peak. Due to overlapping Ru peaks with $\gamma\text{-Al}_2\text{O}_3$ and low concentration of Ru in the samples, the particle size of Ru of $\text{Ru}/\text{Al}_2\text{O}_3\text{-P}$ catalyst was approximately that listed in Table 1. It shows fair nearly agreement with the TEM results. It should be noted that XRD can only detect crystalline

Table 1: Particle size of Ru of Ru/Al₂O₃-P catalyst obtained by XRD and TEM.

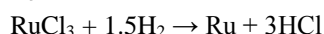
| Samples | Particle size (nm) | |
|--------------------------------------|--------------------|---------|
| | d (XRD) | d (TEM) |
| Ru/Al ₂ O ₃ -P | 4.5 | 7.16 |

**Fig. 2: TEM image of the polyol-based catalyst.****Fig. 3: TEM image of the conventional catalyst.**

materials having crystal domains larger than 3-5 nm, in concentrations exceeding 1-3 wt% [25].

The TPR profiles of samples are displayed in Fig. 5. TPR of bulk RuCl₃ indicates that RuCl₃ could be reduced at ~ 175 °C [26]. However, for the Ru/Al₂O₃-IM sample, the peak appears at 128 °C which is attributed to reduction of RuCl₃ deposited on support. Bulk RuCl₃ is reduced at higher temperatures than the RuCl₃ dispersed on support.

The hydrogen consumption could be estimated from RuCl₃ reduction reaction:



The amount of hydrogen consumed during the reduction of RuCl₃ was higher than the theoretical value and it could be probably due to spill over hydrogen from the metal to the support [27]. The data of H₂-TPR of Ru/Al₂O₃-IM and Ru/Al₂O₃-P samples is given in Table 2 (T_i: initial temperature, T_m: maximum temperature and T_f: final temperature for reduction).

In conventional methods for preparing Ru/Al₂O₃, some chloride ion remains on the surface of samples. These ions would promote the sintering of Ru particles, and thus decrease the dispersion of Ru in catalysts prepared with RuCl₃ precursor [28]. During the reduction process, hydrogen spills over from Ru to alumina surface to remove the chloride. Gas spillover includes three steps: adsorption and activation of a diatomic molecule

on a metal surface, the motion of the adsorbed species across the surface to the interface with the second surface and the diffusion of the spilling over species across the non-adsorbing surface. In the other words, H₂ molecules are dissociated on the sites of Ru surface, and then migrate to the sites at Ru-Al₂O₃ interface by surface diffusion or transport. Finally, the adsorbed hydrogen species move across the Ru-Al₂O₃ interface to alumina surface. Fig. 6 shows the scheme of hydrogen adsorption and the proposed location for chlorine on alumina-supported ruthenium catalyst. Chlorine can attach on alumina surface or be stabilized on Al₂O₃ matrix which is disadvantageous to hydrogen adsorption at Ru-alumina interface and the transfer of hydrogen from Ru metal to alumina [29].

In the case of Ru/Al₂O₃ catalyst prepared by in situ reduction with ethylene glycol, the peak observed at T_m = 103 °C is assigned to reduction of RuO₂ derived from the oxidation of some Ru metal to ruthenium oxide during drying treatment. It reduces at lower temperature, i.e. T_{max} peak shifted to a lower temperature compared to the conventionally prepared catalysts. *Seetharamulu et al.* investigated this phenomenon for Ru supported Mg-Al hydrotalcite [30]. The reducibility of Ru in Ru/Al₂O₃-P is attributed to high dispersion of ruthenium particles, formation of smaller particles and the lower interactions between Ru and aluminum support which induced lower reduction temperatures [31].

Table 2: H₂-TPR data of Ru/Al₂O₃-IM and Ru/Al₂O₃-P samples.

| Sample | Peak Position (°C) | | | H ₂ Consumption (mmol/g _{catalyst}) | |
|---------------------------------------|--------------------|----------------|----------------|--|-------------|
| | T _i | T _m | T _f | Actual | Theoretical |
| Ru/Al ₂ O ₃ -IM | 82 | 128 | 201 | 0.192 | 0.145 |
| Ru/Al ₂ O ₃ -P | 80 | 103 | 163 | 0.173 | - |

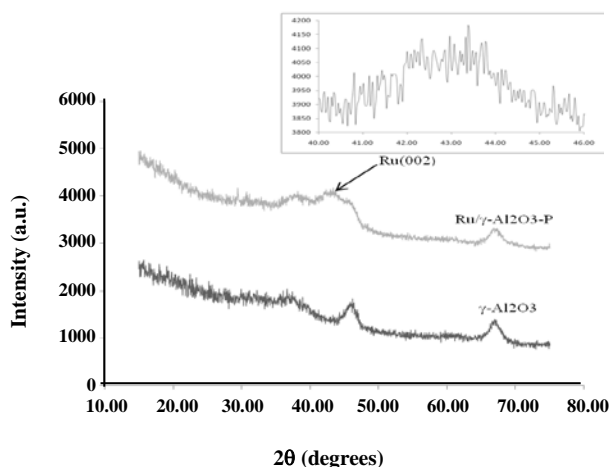
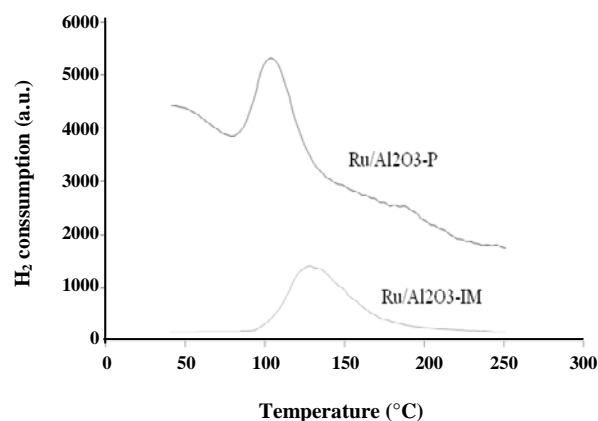
Fig. 4: XRD patterns of catalysts Ru/Al₂O₃-P and γ -Al₂O₃ support.

Fig. 7 shows the results of activity tests of the Ru/Al₂O₃-P and Ru/Al₂O₃-IM catalysts at different space velocities (5300, 2650 and 1325 h⁻¹) of the feed gas at 450 °C. In all runs, the catalyst prepared by polyol method, showed remarkably higher activities in NH₃ synthesis.

Table 3 shows the reaction rates expressed in millimole (mmol) ammonia per gram-hour over the catalysts at temperatures of 450 and 500 °C with GHSV 1325 h⁻¹. The polyol catalyst exhibits a nearly three-fold ammonia synthesis activity per catalyst weight compared to the conventional sample at 450 °C. Noting that for same loading and spherical particles the surface area of the metal is inversely proportional to particle diameter, one can show that the TurnOver Frequency (TOF) ratio of polyol to conventional catalyst was about 2.1 implying the reaction is structure sensitive over Ru-based catalysts. At 500 °C, the TOF ratio decreased to about 1.5. The observed decrease could be due to the higher approach to equilibriums at higher temperatures for the exothermic ammonia synthesis reaction, and partly, due to sintering which is favored at temperatures above 500 °C [24].

Performance of Ru/Al₂O₃-IM and Ru/Al₂O₃-P at various temperatures (425, 450, 475 and 500 °C) and

Fig. 5: H₂-TPR profiles of Ru/Al₂O₃-IM and Ru/Al₂O₃-P.

GHSV 1325 h⁻¹ are presented in Fig. 8. The reaction rate over both catalysts increased with temperature, with Ru/Al₂O₃-P sample exhibited higher ammonia synthesis activity.

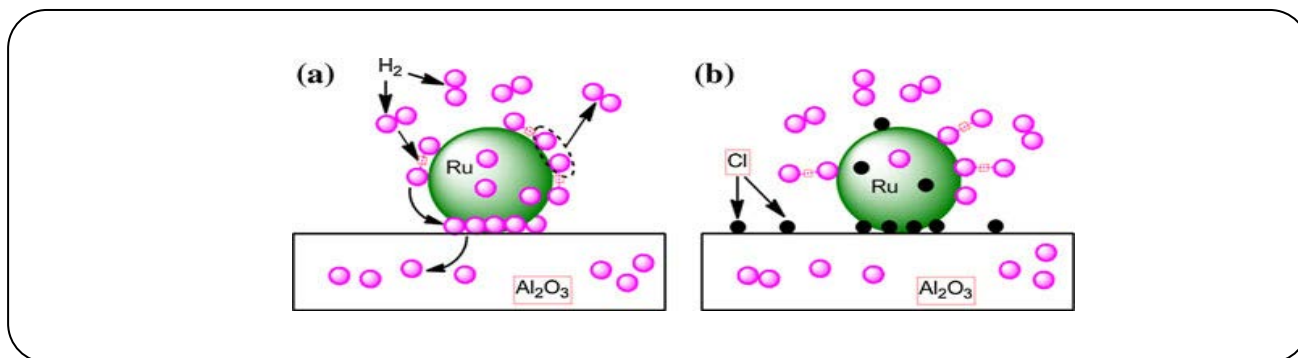
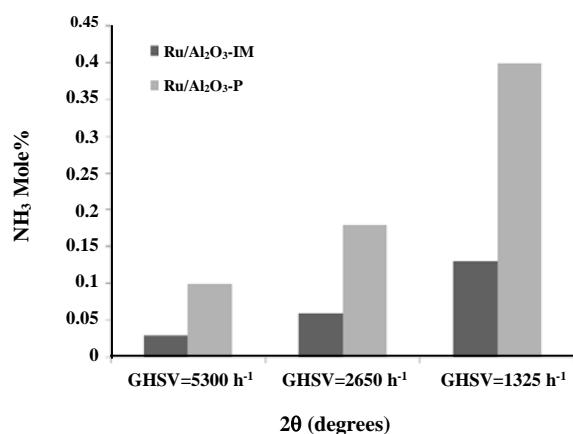
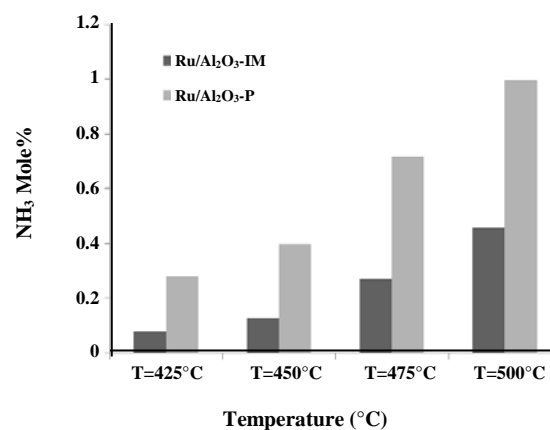
The activation energy of the reaction was estimated by changing the reaction temperature between 425 and 500 °C. The apparent activation energy (E_a) values were determined from the Arrhenius plots of the ammonia synthesis rate values. The Arrhenius-type plot given in Fig. 9 also shows the effect of preparation method on the activity of Ru/Al₂O₃ catalysts. The lower activation energy of the nanocatalyst prepared by polyol method is consistent with its superior activity in ammonia synthesis.

The apparent activation energies listed in Table 4 compare favorably with those of previous studies [28,32,33].

Factors other than particle size could influence the performance as well. The support, for example, plays an essential role in the formation of the active phase(s) when the catalysts were prepared by the impregnation method. The impregnation process can be regarded as complex sequences of chemical reactions taking place at the solid (the support) and liquid (impregnation solution) interface.

Table 3: Results of activity tests in terms of ammonia synthesis rate (mmol/g_{Cat}·h) (GHSV: 1325 h⁻¹).

| Sample Name | Ru/Al ₂ O ₃ -IM | Ru/Al ₂ O ₃ -P |
|----------------------------|---------------------------------------|--------------------------------------|
| Synthesis rate (T: 450 °C) | 0.42 | 1.47 |
| Synthesis rate (T: 500 °C) | 1.28 | 3.18 |

**Fig. 6: Scheme of hydrogen spillover and the proposed location for chlorine in (a) chlorine-free and (b) chlorine containing Ru/Al₂O₃ [29].****Fig. 7: Activity of the samples in different flows (T= 450 °C, P=30 bar).****Fig. 8: Activity of the samples in different temperatures (P=30 bar, GHSV=1325 h⁻¹).**

In conventional impregnation method, the acidity of the support and contamination of the Ru metal by aluminium could further decrease the activity. It is quite possible that part of the alumina support dissolved during impregnation participates with Ru in the formation of the active sites. In contrast, in the case of Ru/Al₂O₃ preparation by polyol method, Ru interacts with the support as metal particles rather than ions. The small amount of HCl resulted from the reduction of RuCl₃ with ethylene glycol seems to have little influence on the catalytic activity of Ru/Al₂O₃. Therefore, the interaction between the support and the Ru nanoparticles is minimized by this preparation method, and therefore

the active phase (Ru metal) is not contaminated by aluminum or chlorine ions derived from the support.

CONCLUSIONS

The preparation method has a strong influence on the performance of Ru/Al₂O₃ catalysts in ammonia synthesis. Ruthenium nanoparticles prepared by reducing RuCl₃ in ethylene glycol (polyol method) exhibit uniform shape and particle size about 7 nm. The higher activity and low activation energy of the samples prepared by polyol method compared to those prepared by conventional method is attributed to the smaller particle size and lower metal- support interactions and no contamination of metal

Table 4: Activation energy for ammonia synthesis in Ru/Al₂O₃-IM and Ru/Al₂O₃-P samples.

| Sample name | Activation energy (kJ/mol) |
|---------------------------------------|----------------------------|
| Ru/Al ₂ O ₃ -IM | 107.13 |
| Ru/Al ₂ O ₃ -P | 79.04 |

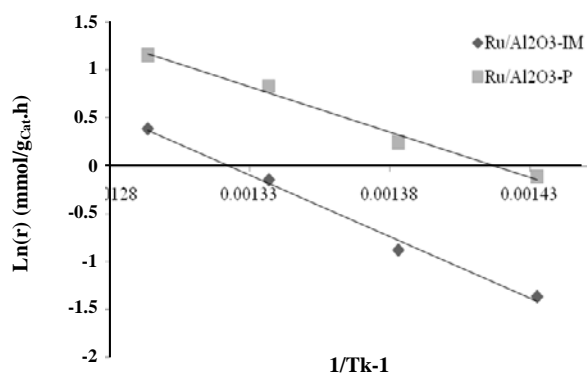


Fig. 9: Arrhenius plot for the ammonia synthesis rate over (◆) Ru/Al₂O₃-IM and (■) Ru/Al₂O₃-P (P= 30 bar, GHSV=1325 h⁻¹).

particles by support. The comparison TOF value on different catalyst implies that the reaction is structure-sensitive over Ru-based catalyst.

Acknowledgment

The authors wish to acknowledge the Petrochemical Research and Technology Company of National Petrochemical Company (NPC-RT) for the financial support of this work.

Received : Dec. 15, 2013 ; Accepted : Nov. 9, 2014

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