

Minimization of the metal-support interaction by using Ru nanoparticles for ammonia synthesis

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Uniform ruthenium nanoparticles with an average diameter of 5 nm were prepared by polyol method and then deposited on acidic (Al_2O_3) and basic (MgO) type of supports. After conditioning, the catalytic activity of the supported Ru nanoparticles was tested for ammonia synthesis. The present study revealed some very interesting features of the nano-sized Ru nanoparticles (i. e. Ru-nano/ Al_2O_3) as compared with the conventional catalysts (Ru-conv/ Al_2O_3). In contrast to the conventionally prepared catalysts (by impregnation), the morphology of the well-defined Ru nanoparticles on the support was independent of metal loading. Thus, the TOF values in the kinetic region were not affected by metal loading. It was observed also that, the catalytic activity of the Ru nanoparticles was little affected by the nature of the support. Due to the minimization of the metal-support interaction, the Ru-nano/ Al_2O_3 catalyst exhibited high activity for ammonia synthesis. The maximum reaction rate over Ru-nano/ Al_2O_3 was at least one order of magnitude higher (around $925 \mu\text{mol g}^{-1} \text{h}^{-1}$) than the rate observed over conventional Ru/ Al_2O_3 catalysts. The activation energies for ammonia formation over alumina and magnesia supported Ru nanoparticles were 107 and 77 kJ mol^{-1} .

Key words: Ru nanoparticles, metal-support interaction, ammonia synthesis

1. INTRODUCTION

Ruthenium is known to have one of the highest catalytic activity for ammonia synthesis. Typically, the conventional Ru catalysts are prepared by impregnation of the oxide support with the solution of a ruthenium precursor. In most of the cases the resulted metal particles are not uniform in size and shape. On the other hand, it is well known that catalytic activity of the conventional catalyst for ammonia synthesis is strongly related to the morphology of the supported metal as well as to the nature of the oxidic support [1]. Alumina is frequently used as a support for metal catalysts due to its high surface area and good thermal stability. The disadvantage for ammonia synthesis is that the support acidity have a strong inhibiting effect on the catalytic activity of Ru particles [2]. The addition of alkali and lanthanide promoters lead only to a limited enhancement in the catalytic activity [3]. In order to overcome the inconveniences related to the conventional catalysts, it is effective to prepare well-defined Ru nanoparticles having an adequate morphology and eventually to minimize metal-support interaction. The polyol method is a convenient way to prepare well-defined Ru nanoparticles of around 5 nm [4].

The aim of this work is to observe the intrinsic catalytic behavior of the well-defined metal Ru nanoparticles in a structure sensitive reaction such as ammonia synthesis. This is possible because support has only a limited influence on the catalytic activity of Ru nanoparticles of around 5 nm. Thus, the TOF (turnover frequencies) associated to a particular average dimension of the metal Ru nanoparticles as well as the apparent activation energies can be obtained without a significant interference from the support.

2. EXPERIMENTAL

The detailed preparation method for the well-defined Ru nanoparticles of around 5nm by polyol method as well as the deposition procedure on the oxidic support was already reported [4]. Briefly, either Al_2O_3 (Aerosil, $96 \text{ m}^2 \text{ g}^{-1}$) or high surface area MgO (Soekawa, $129 \text{ m}^2 \text{ g}^{-1}$) was suspended into ethylene glycol solution of $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$ (Wako Chemicals, purity > 99%). The temperature of the resulted slurry was then raised to 180 °C by using an oil bath. The solid was collected by filtration, washed several times by ethanol and dried in an oven at 100 °C for 8 h. The final Ru loading on Al_2O_3 and MgO was 6 wt%. Additionally, a 12% Ru/ Al_2O_3 material was prepared in

order to observe the effect of metal loading on the final morphology of Ru nanoparticles (shape, average size) as well as on the catalytic behavior for ammonia synthesis.

The catalytic tests for ammonia synthesis were performed at atmospheric pressure in a stainless steel reactor containing 0.4 g of catalyst. Prior to the catalytic test, the material was pelletized, crushed and sieved. The fraction, from 335 to 1000 μm , was used for catalytic tests. Prior to the test, the catalyst was conditioned *in situ* in H_2 flow at 550 $^\circ\text{C}$ for 2 h. The catalytic tests were carried out at a flow rate of the reaction mixture of 60 $\text{cm}^3 \text{mon}^{-1} \text{STP}$ (45 $\text{cm}^3 \text{min}^{-1} \text{H}_2$ and 15 $\text{cm}^3 \text{min}^{-1} \text{N}_2$). The produced ammonia was trapped by a 0.002 N solution of H_2SO_4 , and the rate of ammonia formation was determined from the decrease in the conductivity of the solution.

The samples were characterized by XRD (X-ray diffraction, Rigaku Geiger Flex) and TEM (Transmission Electron Microscopy (Hitachi H8100)). The physical surface area (BET) and the exposed metal surface area were measured by N_2 adsorption and H_2 chemisorption, respectively, by using a Chembet 3000 Quantacrome apparatus.

3. RESULTS AND DISCUSSION

The typical TEM images of the colloidal and of the alumina supported Ru nanoparticles are presented in Fig. 1A and B, respectively. The size of the ellipsoidal-shaped colloidal Ru nanoparticles, obtained by the reduction of ruthenium precursor in ethylene glycol in the absence of the support, was around 5 nm (Fig. 1A). The reduction of the ruthenium precursor by ethylene glycol in the presence of Al_2O_3 or MgO gave also, regardless the presence of the supports, uniform Ru nanoparticles of ≈ 5 nm (see Fig. 1B).

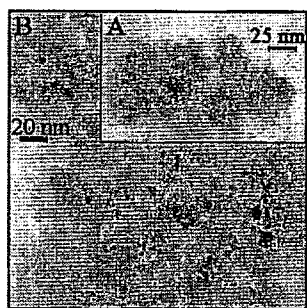


Fig. 1 TEM images of the colloidal (A) and alumina supported Ru nanoparticles (6%Ru/ Al_2O_3) (B).

Figure 2 shows that the size of the supported Ru nanoparticles on Al_2O_3 as well as on MgO have a Gaussian type distribution. The average size (≈ 5 nm) of the supported Ru nanoparticles was relatively little affected by the nature of the support as well as by the metal loading. The average sizes of the Ru nanoparticles for 6%Ru/ Al_2O_3 , 6%Ru/ MgO and 12%Ru/ Al_2O_3 catalysts were centered at 4.8, 4.6 and 5.6, respectively.

The supported Ru nanoparticles were characterized also by H_2 chemisorption. The exposed metal surface and the average size (d_{H_2}) of Ru nanoparticles are presented in Table I. The average particle size was calculated by assuming a spherical geometry and $a(\text{H}_{\text{ads}}/\text{Ru atom}) = 1$ stoichiometry. The physical surface areas of the catalysts

(BET) are also presented in Table I. The chemisorption data are in good agreement with TEM data. Slightly higher d values were obtained from chemisorption data as compared to TEM data. One possible reason for the size overestimation of chemisorption measurements is that the real stoichiometry $\text{H}_{\text{ads}}/\text{Ru}$ is lower than unity for the bulky (≈ 5 nm) Ru nanoparticles. However, the chemisorption measurements are essential to determine the molar number of exposed Ru atoms (N). From here the TOF (s^{-1}) values for the supported Ru nanoparticles could be calculated by dividing the reaction rate of ammonia formation (mol s^{-1}) into N .

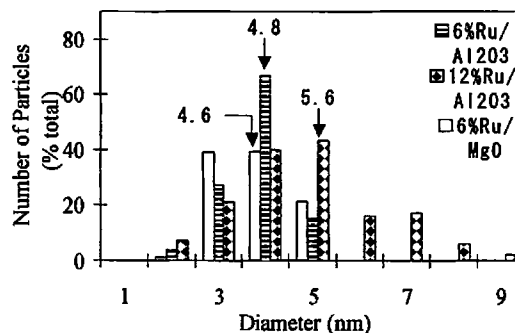


Fig. 2 Size distribution for the Ru nanoparticles supported on Al_2O_3 and MgO .

Table I Characterization data for the supported Ru nanoparticles and TOF values for ammonia synthesis as a function of temperature.

Catalyst	6%Ru/ Al_2O_3	12%Ru/ Al_2O_3	6%Ru/ MgO
$S_{\text{BET}} / \text{m}^2 \text{g}^{-1}$	87	74	115
$d_{\text{TEM}} / \text{nm}$	4.8	5.6	4.6
$S_{\text{Ru}} / \text{m}^2 \text{g}^{-1}$	4.3	7.3	4.6
$d_{\text{H}_2} / \text{nm}$	6.6	8.0	6.2
TOF $\cdot 10^{-4} / \text{s}^{-1}$	365 $^\circ\text{C}$	3.8	4.1
	385	7.5	7.7
	400 $^\circ\text{C}$	11.5	10.8
	450 $^\circ\text{C}$	21.3	12.6
	500 $^\circ\text{C}$	13.7	-

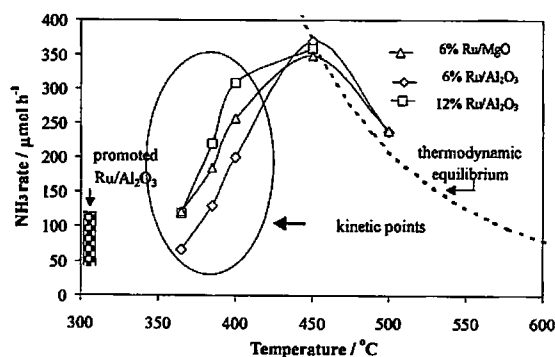


Fig. 3 Temperature dependence of the rate of ammonia synthesis over alumina- and magnesia-supported Ru nanoparticles. The rates over conventional (simple and promoted) Ru/ Al_2O_3 catalysts are also shown for comparison.

The catalytic activity (expressed as $\mu\text{mol h}^{-1}$) for ammonia synthesis of the supported Ru nanoparticles is presented in Fig. 3. The thermodynamic equilibrium curve vs. temperature and the catalytic activity domains of the promoted and simple conventional Ru/Al₂O₃ catalysts [2, 3] are represented also for comparison in the same figure.

From the comparison with the conventional catalyst [2, 3] some specific features of the supported Ru nanoparticles can be observed. One is that the catalytic activity for ammonia synthesis is shifted to higher temperatures. The explanation is that the activation of N₂, which is the rate determining step, on the large Ru nanoparticles of ≈ 5 nm takes place at higher temperatures as compared to the smaller Ru particles of the conventional catalysts having typically ≈ 1 -2 nm in size. The second important observation is that the alumina supported Ru nanoparticles exhibited high catalytic activity for ammonia synthesis, although they were not promoted with alkali elements. The highest reaction rate over supported Ru nanoparticles of $\approx 360 \mu\text{mol h}^{-1}$ ($900 \mu\text{mol g}^{-1} \text{h}^{-1}$) was observed at 450 °C. Over this temperature the ammonia production was limited by the thermodynamic equilibrium (see Fig. 3). Therefore, from practical point of view it is preferable to have a catalyst that is more active in the lower temperature domain so to be not limited by thermodynamic equilibrium. The encircled points in Fig. 3 are located in kinetic region, below the equilibrium temperature ($T < 450$ °C).

It is worthwhile to note that the support has only a limited effect on the catalytic activity of the supported Ru nanoparticles. From Fig. 3 it can be seen that the reaction rate over unpromoted conventional Ru catalyst is very small ($< 25 \mu\text{mol h}^{-1}$). It is well known that the acidity of alumina strongly depresses the catalytic activity of the conventional Ru/Al₂O₃ catalysts as a result of strong metal-support interaction. As it is shown in Fig. 3, the addition of alkaline (Cs, Rb, K) or rare earth (La, Ce, Sm) elements to the conventional Ru/Al₂O₃ catalysts improved to some extent their catalytic activity [5]. In the case of the conventional catalysts, slight changes in the preparation variables result in significant changes in catalytic activity which are often difficult to be explained and therefore controlled. In contrast, the catalytic behavior of the Ru nanoparticles supported on the acidic alumina resembled to that Ru nanoparticles supported on magnesia having basic character (see Fig. 3). In our view, this is a clear proof that the support effect is minimized when larger, well-defined Ru nanoparticles are deposited on oxide support. However, some support effect can be evidenced if TOF values vs. temperature are represented instead of reaction rates.

The TOF values as a function of reaction temperature are represented in Fig. 4. It can be seen that the TOF values are not affected by metal loading. The same TOF dependence on temperature was obtained for 6 and 12% Ru/Al₂O₃ in the kinetic region (375 – 400 °C). On the other hand, the kinetic TOF values for Ru nanoparticles supported on MgO are shifted slightly to higher values as compared to Ru nanoparticles supported on Al₂O₃. This shift is clearly attributable to the support effect (basicity of MgO) on the catalytic activity of Ru nanoparticles. The morphological effects to explain the variation in catalytic activity can be excluded because the size as well as the shape of Ru nanoparticles was preserved regardless the

metal loading or the nature of the used support. However, the support effect on the catalytic activity of Ru nanoparticles was small. Therefore, it can be assumed that the Ru nanoparticles of 5 nm showed their intrinsic catalytic properties without a significant interference from the support.

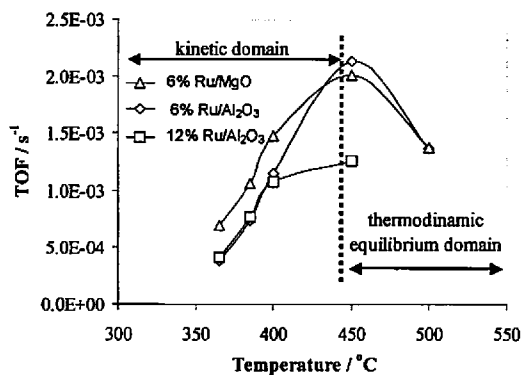


Fig. 4 Temperature dependence of the TOF for ammonia formation over alumina and magnesia supported Ru nanoparticles.

From the plot represented in Fig. 4 it is obvious that the morphology of the Ru nanoparticles is not affected by metal loading. Any change in the morphology of the Ru nanoparticles would have a visible effect on the TOF values because ammonia formation is a structure-sensitive reaction. As a consequence, these catalysts are ideal materials to measure a reliable reaction kinetic as this will be shown in what comes.

One of the most definitive methods for the evaluation of transport limitations are the Madon-Boudart criterion [6]. The concept of the Madon-Boudart is that, in the absence of all transport limitations, the rate of reaction is proportional to the number of active sites or the TOF. For reactions performed on supported metal catalysts, this test requires the preparation of at least two catalysts with widely varying concentration of surface metal atoms. If the reaction is structure sensitive the metal dispersion (particle morphology) must be kept constant among catalysts. It is well known that ammonia synthesis is structure sensitive, slight changes in the morphology lead to significant changes in the catalytic activity. To prepare catalysts with different metal loadings but keeping the dispersion constant is not an easy task. Typically, the dispersion of the impregnated materials decreases with increasing the metal loading. In addition, the effect of metal-support interaction is little understood and difficult to be quantified. In contrast to the impregnated catalytic materials, the morphology (size and shape) of Ru nanoparticles is preserved regardless the metal loading (see Table I). Thus, the Madon-Boudart criteria can be applied to calculate the reaction activation energy by using the TOF or the reaction rate data which are unaffected by transport phenomena (kinetic data).

In the absence of transport limitations, a \ln - \ln plot of the activity vs. the number of surface atoms will exhibit a linear correlation with a slope of unity. Control by internal pore diffusion gives a slope of 0.5 while external diffusion control gives a slope of zero. When the test is

performed at two or more reaction temperatures, it can verify that both heat and mass transfer effects are absent. The slopes of the representations \ln of rate of ammonia formation vs. \ln of number of exposed Ru atoms in 365–400 °C temperature range between 1.1 and 0.9 (see Fig. 5). The slope values close to unity confirm one more time that the distortions induced by transport effects on the selected points are insignificant. Thus, the kinetic points can be further used for the determination of the activation energies for ammonia formation.

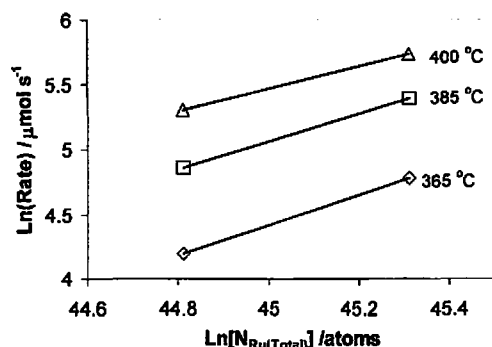


Fig. 5 The logarithms of ammonia formation rate over 6 and 12% Ru/Al₂O₃ catalysts vs. logarithm of $N_{\text{Ru(Total)}}$ plots at 365, 385 and 400 °C.

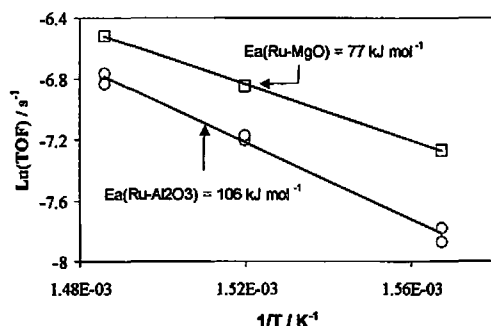


Fig. 6 The Arrhenius plot for ammonia formation over 6, 12% Ru/Al₂O₃ and 6% Ru/MgO catalysts.

The apparent activation energies for alumina and magnesia supported Ru nanoparticles, determined from the Arrhenius plots in Fig. 6, were 105.8 and 76.7 kJ mol⁻¹, respectively. The reported apparent activation energies for promoted and Ru/MgO and Ru/Al₂O₃ range between 44 and 101 kJ mol⁻¹ [2]. One of reasons for such a broad range of the activation energies for the conventionally prepared materials can be explained by the fact that each preparation method gives Ru particles with variable morphology having a specific metal-support interaction. Thus, the catalytic activity and the related kinetic parameters are also very different from one catalyst to the other. Another possible reason for the differences observed in the activation energies is the absence of a careful analysis of the experimental data used for calculations. In most of the published studies it is not clearly proved that data used for calculations are located in the kinetic region.

Our data show that the supporting the Ru nanoparticles on MgO have a slight beneficial effect on their catalytic

activity by decreasing the apparent activation energy for ammonia formation from ≈ 106 to ≈ 77 kJ mol⁻¹. This phenomenon can be attributed to the positive effect of the support basicity on the catalytic activity of Ru the nanoparticles.

CONCLUSIONS

Interesting features and important advantages of using well-defined metal nanoparticles as catalysts in structure sensitive reactions such as ammonia synthesis were revealed for the first time in the present work. Significant higher catalytic activity for ammonia synthesis was observed over supported Ru nanoparticles as compared to the conventional Ru-based catalysts. In contrast to the conventionally prepared catalyst, the influence of the support acidity on the catalytic activity of the well-defined Ru nanoparticles was very limited. Thus, beside the high catalytic activity, it was possible to evidence the intrinsic catalytic activity of the Ru nanoparticles of around ≈ 5 nm. An important advantage over the conventional materials is that the morphology of the well-defined Ru nanoparticles is preserved regardless of the metal loading. This enabled us to identify data free of transport effects (kinetic data) by using the Maddon-Boudart criteria and calculate TOF values as well as of the activation energies for ammonia formation.

The reduction of the average size of the Ru nanoparticles may bring in the future further improvements in catalytic activity by decreasing the reaction temperature without affecting the advantages shown by the large Ru nanoparticles. It is expected also that catalytic tests performed at high pressure will reveal new interesting features of the supported Ru nanoparticles.

REFERENCES

- [1] B. C. Gates, *Chem. Rev.*, **95**, 511 (1995).
- [2] S. Murata and K. Aika, *J. Catal.*, **136**, 110 (1992).
- [3] S. Murata and K. Aika, *J. Catal.*, **136**, 118 (1992).
- [4] A. Miyazaki, I. Balint, K. Aika, Y. Nakano, *J. Catal.*, **204**, 364 (2001).
- [5] P. Moggi, G. Albanesi and G. Spato, *Appl. Catal. A*, **123**, 145 (1995).
- [6] R. J. Madon and M. Boudart, *Ind. Eng. Chem. Fundam.*, **21**, 438 (1982).

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