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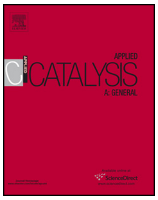

Effect of the size and distribution of supported Ru nanoparticles on their activity in ammonia synthesis under mild reaction conditions

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ABSTRACT

$Ru/\gamma\text{-}Al_2O_3$ catalysts were prepared using three different methods: wet impregnation, colloidal method and microemulsion. Ru-supported nanoparticles with different average sizes and distribution of sizes were obtained. The catalysts were tested in ammonia synthesis under mild reaction conditions, namely low temperature (100 °C) and low pressure (4 bar), and characterized by N_2 adsorption, XRD, XPS, TEM and TPR techniques. The results indicate that a good catalytic performance can be achieved by Ru supported nanoparticles fulfilling two requirements: (i) a relatively high average size (despite the usual assertion that only small particles are required) and (ii) a broad distribution of sizes that ensures the presence of both small particles, containing highly active sites, and large nanoparticles, which are shown to promote the reaction on small particles. This promotion results from a cooperative effect between small and large nanoparticles in good contact, which also allows keeping a highly reduced surface of ruthenium.

It is proposed that, under mild reaction conditions, large Ru nanoparticles promote the ammonia synthesis reaction by allowing a more effective activation and transfer of hydrogen atoms, able to hydrogenate strongly adsorbed nitrogen atoms, and thus to release active sites for the activation of N_2.

1. Introduction

Ammonia synthesis is one of the highest energy consumer processes in the chemical industry. This exothermic reversible reaction is strongly limited by the thermodynamic equilibrium, so the industrial operating conditions have been set to high temperatures (300–500 °C) and high pressures (100–200 bar). The synthesis of highly active catalysts and the development of new concepts in ammonia synthesis at low temperature open interesting possibilities for improving existing technologies and for designing new processes of low energy consumption [1,2]. The use of Ru-based nanocatalysts has been shown to be a key factor to perform this reaction under mild conditions [3–8]. It has been claimed that metal-supported nanoparticles present high catalytic performances, not exclusively due to the high surface area, but also because of the special properties arising from the nano-size dimension, which are expected to change the electronic structure of the metal, thus leading to unusual catalytic activities [9,10].

The N_2 dissociative adsorption is the rate-determining step in ammonia synthesis. Density functional calculations (DFT) have shown that there is a linear relationship (Brønsted–Evans–Polanyi type) between the activation barrier of N_2 dissociation and the energy of N_2 dissociative chemisorption [11,12]. According to this relationship, a reduction in the activation barrier of N_2 dissociation may lead to a surface blocking by adsorbed nitrogen atoms. DFT calculations [13–15] indicate that the most active sites for N_2 dissociative adsorption are the B_5-type sites, exposing a three-fold hollow site close together with a bridge site. These sites ensure that the two nitrogen atoms are not bonded to the same Ru atom during the dissociation, thus leading to a significant decrease in activation energy without a similar increase in the adsorption energy of nitrogen atoms. Dahl et al. [13,14] proposed that the N_2 dissociation on the Ru(0 0 0 1) single-crystal plane only occurs at mono atomic steps, whose reactivity is significantly higher than the activity of atoms on terraces. It has been suggested that the catalytic performance of Ru surfaces can be determined by the concentration of B_5-type sites. Jacobsen et al. [15] have shown that the probability of forming B_5 sites is maximum for sizes of 1.8–2.5 nm, and it decreases for larger particles. They obtained very low TOFs (at 475 °C and 50 bar in 3:1 H_2/N_2) for the $Ru/MgAl_2O_4$ catalyst having Ru crystals smaller than 1 nm, which are expected to contain a low number of B_5 sites. Recently, Lin et al. [16] showed that

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Sm-promoted Ru nanoparticles supported on γ-Al_2O_3 with an average size of 2.1 nm are the most active under conditions of high temperature (200–500 °C) and pressure (100 bar). Additionally to the size effect of the Ru nanoparticles, changes in the active sites properties were proposed to explain catalytic results.

The effect of the Ru particle size on the catalytic performance has been also studied in the presence of alkali promoters, which are known to affect the electronic properties of the active sites and even modify the specific surface. The results reported show that the catalytic activity increases with the size of Ru crystallites. For Ba-promoted Ru/C catalysts, Kowalczyk et al. [17] found that the TOF value (at 400 °C and 60 bar in 3:1 H_2/N_2, 8% NH_3) increases with the Ru particle size, reaching a constant value for particles larger than 3 nm. Rarog-Pilecka et al. [18] obtained the same trend for Cs-promoted catalysts, at similar conditions (400 °C and 63 bar, in 3:1 H_2/N_2, 8.5% NH_3). According to Liang et al. [19], the TOF value (at 400 °C and 30 bar in 3:1 H_2/N_2) increases with the Ru particle size ranging from 2 to 10 nm, for K and Ba-promoted Ru/C catalysts.

However, all these results have been obtained for the reaction at high temperatures (>400 °C) and pressures (>30 bar). Under mild reaction conditions, it is expected that other features in the surface configuration of Ru nanocatalyst will affect its catalytic activity.

The aim of this work is to study the catalytic performance of Ru-supported nanocatalysts in ammonia synthesis under mild reaction conditions, and to determine the effect of the catalyst surface configuration (distribution of particles on the support, particle sizes and distribution of sizes) on the activity. Until now the literature is poor in studies addressing these issues for the ammonia synthesis reaction performed at truly mild conditions (<200 °C).

For this purpose we have synthesized catalytic Ru-supported nanoparticles with different tailored-size distributions, by (i) the traditional wet impregnation of the support with the Ru precursor and (ii) the deposition on the support of a suspension containing RuO_2 nanoparticles already formed by a colloidal method [20] or microemulsion [21], which is known to allow the synthesis of small particles with a narrow size distribution [22,23]. The catalysts were used to produce ammonia from nitrogen and hydrogen, at low temperature (100 °C) and low pressure (4 bar). In order to study the activity of the Ru nanoparticles as a function of their size, distribution of sizes and Ru oxidation state, the catalysts were analyzed by X-ray diffraction, X-ray photoelectron spectroscopy and transmission electronic microscopy. The results obtained in this work not only allow a better understanding of the catalytic performance of Ru-supported nanoparticles in ammonia synthesis, but could also provide insights into the catalytic performance of other noble metal in reactions operating at mild conditions.

2. Experimental

2.1. Synthesis of catalysts

Samples denoted as 'calcined' correspond to 450 °C calcined fresh catalysts, while samples denoted as 'tested' correspond to catalysts obtained after the catalytic test, which includes the reduction pretreatment and the subsequent ammonia synthesis reaction.

2.1.1. Wet impregnation (WI)

Catalysts were prepared by wet impregnation of γ-Al_2O_3 (Alfa Aesar, $S_{BET} = 73\ m^2/g$). The powdered support was dipped into an aqueous solution of ruthenium (III) chloride hydrate (Alfa Aesar, 99.99%), in the amount required to obtain a theoretically 2, 3 and 7 wt.% of Ru. After stirring for 2 h at room temperature, the solvent was evaporated under reduced pressure, in a rotavapor at 35 °C. The resulting solid was dried at 110 °C overnight and later calcined in air at 450 °C for 4 h. The catalysts are denoted as Ru*X*/Al-WI (*X*: 2, 3 or 7 wt.%).

2.1.2. Colloidal method (COLL)

Catalysts were prepared by depositing on γ-Al_2O_3 a colloidal suspension of RuO_2 nanoparticles. The colloidal suspension was synthesized via hydrolysis, by using H_2O_2 as oxidizing agent and surface etchant to achieve the particle size control [20]. An aqueous solution of H_2O_2 (Acros Organics, 35 wt.%) was slowly added into a solution of $RuCl_3{\cdot}3H_2O$ (Alfa Aesar, 99.99%), under magnetic stirring. The suspension was placed in an oven at 95 °C for 2 hours and after cooling down to room temperature, the powdered support was added under vigorous agitation. The catalyst was recovered via evaporation of the solvent in rotavapor under reduced pressure at 50 °C, and then it was calcined in air at 450 °C for 16 h. The catalysts are denoted as Ru*X*/Al-COLL (*X*: 3 or 7 wt.%).

2.1.3. Microemulsion method (MIC)

Catalysts were synthesized via the water in oil microemulsion method [21–23]. Oil phases containing different surfactants, tetraethylene glycol dodecyl ether (Brij30, Sigma–Aldrich, 99.9%), sodium bis(2-ethylhexyl)sulfosuccinate (AOT, Sigma–Aldrich, 99.9%) or hexadecyltrimethylammonium bromide (CTAB, Alfa Aesar, 99.9%) and organic solvents (n-heptane, 1-butanol or cyclohexane, Fluka, 99.9%) were used. Hydrazine hydrate (Fluka, 80%) was used as the reducing agent. The molar ratios of surfactant-to-Ru and water-to-surfactant were maintained at 40:1 and 9:1, respectively. A solution of $RuCl_3{\cdot}3H_2O$ in distilled water was added, under magnetic stirring, into an oil phase containing the appropriate amount of surfactant in 50 ml of organic solvent. Always under stirring, the microemulsion was heated up to 60 °C in a thermostated oil bath and then the γ-Al_2O_3 support was added. After 30 min, hydrazine was injected in an amount corresponding to a hydrazine-to-Ru molar ratio of 9:1. After 30 min of reduction, the solution was washed with acetone (99%, VWR) and distilled water. The resulting solid was dried at 110 °C overnight and calcined in air at 450 °C for 4 h. The catalysts are denoted as Ru3/Al-MIC X/Y, where X corresponds to the surfactant and Y to the organic solvent.

2.1.4. Mechanical mixtures

Mechanical mixtures of Ru3/Al-WI and Ru7/Al-WI, in different percentages (25, 50 and 75 wt.%), were obtained by dispersing both catalysts in n-pentane (Merck, >98%) under vigorous agitation assisted by ultrasonic dispersion. The n-pentane was evaporated under agitation at 25 °C and the recovered solid was dried at 110 °C overnight. After drying, the mixtures were not calcined. The single Ru3/Al-WI and Ru7/Al-WI catalysts were subjected to exactly the same treatment as the mixtures. Mixtures are denoted as 75Ru3/Al-WI + 25Ru7/Al-WI, 50Ru3/Al-WI + 50Ru7/Al-WI, 25Ru3/Al-WI + 75Ru7/Al-WI, where the numbers preceding each catalytic component (Ru3/Al-WI and Ru7/Al-WI) indicate the respective weight percentages in the mixture.

2.2. Catalytic activity measurements

Catalytic tests were carried out in a metallic fixed-bed tubular (i.d. 8 mm) reactor equipped with a frit to hold the catalyst and a K-type thermocouple to measure and control the temperature of the catalytic bed. The catalyst (400 mg) previously sieved to a particle size range of 100–315 μm was reduced in pure H_2 (Praxair, 4.8) at 200 °C during 2 h (heating rate of 10 °C/min). Isothermal experiments were performed in a flowing mixture (40 ml/min) of N_2/H_2 (1/3 vol.%), at 100 °C, 4 bar and a space velocity of 6000 ml/h/gcat. The effluents were analyzed online by using a gas chromatograph equipped with two thermal conductivity detectors. The sequence