Kinetics of hydrogen adsorption and mobility on Ru nanoparticles supported on alumina: Effects on the catalytic mechanism of ammonia synthesis

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ABSTRACT

Relevant findings on hydrogen adsorption and mobility are provided in this work to elucidate the mechanism of low-temperature ammonia synthesis, catalyzed by polydispersed Ru nanoparticles supported on alumina. H/D isotopic exchange technique, complemented by DRIFTS analysis, was applied to study the kinetics of hydrogen adsorption/desorption on metallic Ru and hydrogen diffusivity on alumina, for catalysts presenting different size distributions of Ru nanoparticles. H atoms adsorbed on large Ru nanoparticles present higher mobility and they migrate on alumina via exchange with OH groups. A broad size distribution of Ru nanoparticles leads to synergy in the rate of ammonia synthesis, and also in hydrogen mobility. The mechanism of catalytic cooperation involves transfer of H atoms from large to small nanoparticles, where the reaction rate is promoted. Considering dynamic catalytic processes in the formulation of kinetic models is crucial for a more accurate description of processes and the development of large-scale processes.

1. Introduction

Ru-based catalysts are considered the second-generation catalysts for production of ammonia from gaseous nitrogen and hydrogen, since they exhibit remarkably high activity compared to the conventional Fe-based catalysts [1–5]. Ru supported nanoparticles exposing stepped surfaces have shown to provide highly active sites for the dissociative adsorption of nitrogen, commonly accepted as the rate-determining step for ammonia synthesis [1,5–10]. Recent studies of the reaction on polydispersed Ru nanoparticles supported on alumina revealed important effects of hydrogen activation and mobility on the catalytic activity under mild conditions (temperature < 200 °C, pressure < 10 bar). Results showed, that ammonia synthesis is better conducted on alumina surfaces supporting Ru nanoparticles with broad distribution of sizes, where small and larger particles in close proximity give rise to a catalytic cooperation process [11]. Study of reaction orders, 'operando' DRIFTS analysis and preliminary experimental results of H/D isotopic exchange showed that hydrogen dissociative adsorption occurs at a low rate

on small Ru nanoparticles (2–3 nm), preventing the effective hydrogenation of NH_x reaction intermediates strongly adsorbed on the metal surface. On large Ru nanoparticles, meanwhile, hydrogen dissociation and hydrogenation of NH_x intermediates occur more rapidly. The catalytic cooperation mechanism between Ru nanoparticles of different sizes was suggested to involve migration of H atoms from large to small nanoparticles, thus promoting the hydrogenation of NH_x intermediates and the reaction rate on small metal particles [12]. This mechanism based on hydrogen transfer, which is proposed in this case for low-temperature ammonia synthesis, reveals the importance of taking into account the surface dynamic processes that may arise in a catalytic process, and their involvement in the reaction mechanism.

Given that hydrogen seems to play a relevant role in the reaction mechanism, it is essential to further study the adsorption and mobility of hydrogen on Ru particles supported on alumina, and the effect of Ru particle size on these processes. Adsorption energetics and kinetics of hydrogen molecules have been extensively studied on clean metal single crystal surfaces, following the traditional surface science model approach [13–15]. A non-activated 'spontaneous' dissociation is known to occur over clean transition metal surfaces, with the formation of stable H-metal bonds [16] and adsorption energies ranging from 80 to 120 kJ mol^{-1} [17]. The adsorption

energy is much lower on metals of Groups IB and IIB, which leads to an energy barrier preventing the 'spontaneous' dissociation of hydrogen (i.e. an activated dissociative adsorption) [18]. On supported metal crystallites, the adsorption of other atoms or molecules can strongly affect the strength of hydrogen adsorption, through direct electronic interference causing attractive or repulsive interactions with co-adsorbed hydrogen [16]. Therefore, the dissociative adsorption of hydrogen on transition metal particles could eventually become an activated process, in the presence of atoms or molecules that exhibit repulsive interactions with nearby H atoms, inducing a drastic decrease in hydrogen adsorption energy. The poisoning effect of electronegative atoms (such as sulfur and chlorine) on H_2 adsorption/desorption over Ru and other transition metal surfaces has been extensively studied [19–21]. The presence of impurities such as CO [22–24], oxygen [23,25,26] and carbon [23] has also shown to affect the hydrogen adsorption on Ru surfaces. Preliminary results have revealed an activated dissociative adsorption of hydrogen on Ru nanoparticles supported on alumina [12]. This might be related to the adsorption of other atoms or molecules, as mentioned above, and it is one of the aspects addressed in this study.

H/D isotopic exchange is a powerful tool to study the kinetics of hydrogen dissociative adsorption on Ru particles, via $H_2(g) + D_2(g) \leftrightarrows 2HD(g)$ equilibration reaction [27]. These 'homoexchange' experiments, performed at low temperatures, only involve H/D exchange at the metal surface, without participation of hydroxyl groups on alumina support. The diffusion of hydrogen on the support of Ru catalysts can be also studied by H/D isotopic exchange, in this case via 'heteroexchange' experiments, where deuterium atoms adsorbed on Ru particles are exchanged with OH groups exposed on alumina surface. In the present work, the kinetics of hydrogen adsorption-desorption on Ru-supported nanoparticles and the diffusivity of hydrogen on alumina support are studied by H/D isotopic exchange. The study addresses the effect of the size of Ru nanoparticles on rates of H/D equilibration and exchange, and the activated character of hydrogen dissociative adsorption. DRIFTS is used as complementary tool to analyze the oxidation state of Ru particles during ammonia synthesis and the formation and reactivity of NH_x reaction intermediates. Additionally, this technique is applied to confirm H/D isotopic exchange, since it leads to a significant shift of the OH stretching bands (formation of OD groups on alumina) in the IR spectrum [28,29].

The goal of the study was to elucidate the mechanism of catalytic cooperation between Ru particles of different sizes by analyzing catalysts containing (i) a narrow distribution of small Ru-supported nanoparticles, (ii) a narrow distribution of large Ru-supported nanoparticles, and (iii) a mixture of small and large Ru-supported nanoparticles, separately prepared. Experimental evidence is provided of the dynamic catalytic processes that occur during ammonia synthesis at low-temperature, in the presence of small and large Ru nanoparticles. A mechanism of catalytic cooperation between different-sized Ru nanoparticles is presented and discussed together with a kinetic model approach we have recently proposed for low-temperature ammonia synthesis and other hydrogenation reactions. This kinetic model approach emphasizes the importance of taking into account the dynamic phenomena and the metal particle size distribution to develop kinetic models that provide a more realistic representation of processes.

2. Material and methods

2.1. Synthesis of catalysts

2.1.1. Synthesis of colloidal suspensions of RuO_2 nanoparticles

Suspensions of RuO_2 nanoparticles were synthesized following the colloidal method [11,12,30]. An aqueous solution of ruthenium trichloride ($RuCl_3 * H_2O$ 99.99%, Alfa Aesar) and an aqueous solution of hydrogen peroxide (Acros Organics, 35 wt.% stabilized) were prepared. The H_2O_2 solution was slowly added into the ruthenium solution (0.11 M), under magnetic stirring (1500 rpm), allowing the oxidation of Ru(III) into Ru(IV). The final solution (0.0072 M in ruthenium) was placed in a static oven at 95 °C for 2 h, in a closed vessel. Then, it was cooled down to room temperature. A stable colloidal suspension was formed, containing RuO_2 nanoparticles of about 2 nm [31].

Two suspensions were prepared containing the Ru mass required for Ru loadings of 1 wt.% and 7 wt.% in the final catalysts.

2.1.2. Synthesis of RuO_2/γ-Al_2O_3 catalysts

Catalysts were then synthesized via impregnation of powdered γ-Al_2O_3 (Alfa Aesar, 99.97%, metals basis) with RuO_2 colloids. Alumina grains are present in different shapes (rectangular, square, diamond-shaped, rod-shaped), with a broad distribution of sizes (mean length of 51 ± 21 nm and mean width of 27 ± 16 nm, based on TEM analysis), and a specific surface area of 70 $m^2\,g^{-1}$. Alumina was added into each suspension, under vigorous stirring. Water was then evaporated, under reduced pressure at 50 °C, and the recovered sample was dried overnight in air at 110 °C. After a final calcination step, two catalysts were obtained:

(i) Ru1/Al-COLL450: sample with low content of Ru (1 wt.%), treated under moderate calcination conditions (450 °C) to favor the formation of very small Ru supported crystallites.

(ii) Ru7/Al-COLL650: sample with 7 wt.% of Ru, treated under high-temperature calcination conditions (650 °C) to promote further sintering and large size of supported Ru crystallites.

2.1.3. Synthesis of mechanical mixture

A mechanical mixture containing 50 wt.% of Ru1/Al-COLL450 and 50 wt.% Ru7/Al-COLL650 was prepared to have both small and larger Ru nanoparticles in close proximity. Both catalysts were dispersed in n-pentane (Merck, >98%) under vigorous stirring. The sample was recovered via slow evaporation of n-pentane, under stirring at 25 °C, and then it was dried overnight at 110 °C. The mixture was not further calcined and the final sample is denoted as MIX50-50.

2.2. Physicochemical characterization

N_2 (Praxair 5.0) adsorption and desorption isotherms of the samples were recorded at 77 K (temperature of liquid N_2) using a Micromeritics Tristar 3000 apparatus. Samples were previously degassed overnight at 150 °C and 0.15 mbar. The specific surface area was calculated according to the BET method.

Volumetric H_2-chemisorption analysis was performed in a Micromeritics ASAP 2010C apparatus. The catalyst (200 mg) was pelletized into about 4 mm diameter pellets and then placed in a U quartz tube. The reactor was purged in He (Praxair 4.6) at 300 °C for 30 min, and then it was cooled down to 50 °C and evacuated during 1 h. The catalyst was heated up to 200 °C at a rate of 10 °C min^{-1}, under pure H_2 (Praxair 5.0), to perform a reduction pretreatment at 200 °C during 2 h. A purge in He was performed as the sample was cooled down to 100 °C, which has been reported as the most suitable temperature for volumetric H_2 chemisorption on Ru/γ-Al_2O_3 [32]. The presence of surface impurities (e.g. chlorine, oxygen, carbon) has shown to cause slow kinetics of hydrogen chemisorption at low temperatures and, therefore, underestimation of the number of surface ruthenium atoms. A temperature of 100 °C was found to ensure the saturation of Ru surface with hydrogen atoms. After 1 h evacuation at 100 °C, the analysis was started. Isotherms were measured in the range 0.06–95 kPa. H_2 is