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Insights in the mechanism of deposition and growth of RuO_2 colloidal nanoparticles over alumina. Implications on the activity for ammonia synthesis

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ABSTRACT

Choosing and controlling the size distribution of Ru-supported nanoparticles are crucial steps to reach a high activity in ammonia synthesis under low temperature and pressure. A promoted reaction is expected on surfaces exhibiting polydispersed Ru nanoparticles, where small and larger particles give rise to a catalytic cooperation process. In this work we implement new strategies for the synthesis of supported RuO_2 nanoparticles with broad size distributions. Catalysts with high heterogeneity of Ru sizes were successfully prepared and they shown enhanced activity in ammonia synthesis, as long as a sufficient concentration of small particles was reached. Indeed, catalytic activity drastically decreased for low concentrations of 2–3 nm Ru particles. A model is proposed for the deposition and growth of RuO_2 colloidal nanoparticles on alumina, providing insights in processes associated to other synthesis methods. According to this model, firstly attached RuO_2 particles behave as nucleation points for further deposition of hydrated RuO_2, while remaining RuO_2 nanoparticles in suspension are successively deposited in a constantly changing surface, triggering growth of supported clusters.

1. Introduction

Ammonia synthesis constitutes one of the biggest energy consumer processes in the chemical industry. In order to catalyze ammonia synthesis reaction at mild ambient conditions (i.e. low temperature and low pressure), the development of highly active materials is mandatory. High catalytic performances can be reached when the active phase presents nanoscale properties. Therefore, the synthesis of metal nanocatalysts is a priority for improving existing technologies and designing new processes of low energy consumption [1,2].

Ru-supported nanoparticles exhibit a high catalytic activity for ammonia synthesis under mild ambient conditions [3–8]. The properties arising from the nano-size dimension are expected to change the electronic structure of the metal, leading to unusual catalytic activities [9,10].

We have shown [11,12] that the surface configuration (average particle size and distribution of sizes) of Ru-supported nanoparticles has a significant effect on the catalytic activity for ammonia synthesis. The process is better conducted on surfaces having a broad size distribution (2–12 nm) of Ru nanoparticles, where small and larger particles give rise to a catalytic cooperation process. Small particles contain the most active sites for the activation of nitrogen [13,14]. However, hydrogen is slowly activated and strongly attached to these particles at low temperatures, which affects the hydrogenation of NH_x intermediate species and the release of active sites for N_2 adsorption. Indeed, according to the kinetic study previously reported [12], the release of active sites

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becomes the limiting step for the reaction over small Ru particles. On the contrary, larger Ru nanoparticles decrease the energetic barrier for H_2 activation and allow a higher mobility of hydrogen atoms. It was suggested that the catalytic cooperation mechanism involves the migration of H atoms from large to small Ru nanoparticles, promoting the hydrogenation of adsorbed NH_x species on small metal particles and the release of blocked active sites [12].

In consequence, choosing and controlling the size distribution of supported Ru nanoparticles are crucial steps to reach a high activity in ammonia synthesis under mild ambient conditions. Moreover, the quantification of the size distribution is essential for a correct interpretation of the catalytic performance. Chemisorption methods or, eventually, XPS analysis are often used to determine mean sizes of supported metal particles. However, these values are rarely considered as average sizes, even though particles in real catalyst present most likely a certain size distribution, and not a uniform size. Only selected studies include a detailed TEM analysis to consider these aspects.

Traditional synthesis methods (precipitation, impregnation, etc.) do not allow efficiently controlling, at nanoscale, the surface configuration and size distribution of catalytic supported crystallites. Sol–gel, citric and microemulsion methods allow a more accurate control of the particle size, but not the distribution of sizes. In this work, active Ru-supported nanoparticles were obtained via impregnation of a colloidal suspension of RuO_2 nanoparticles on alumina [11]. This 'colloidal method' allows a fine-tuning of the size and a narrow distribution of Ru particles [15–17]. However, the possibilities of increasing the particle size and to obtain a broad size distribution are limited with the colloidal technique, as also are the possibilities for improving the catalytic activity.

Our goal is to implement new strategies for the synthesis of supported Ru nanoparticles with a relatively high average size and a broad distribution of sizes. The strategies consist on the sequential impregnation of two colloidal suspensions (having different Ru mass contents) on alumina, and the mixture of the two colloids before impregnation on the support. A significant enhancement of the catalytic activity is achieved and a model is proposed for the deposition and growth of RuO_2 nanoparticles on alumina, which can provide insights in the processes occurring for other synthesis methods.

2. Experimental

2.1. Preparation of catalytic materials

2.1.1. Synthesis of RuO_2 colloids

Colloidal suspensions of RuO_2 nanoparticles (~2 nm) were synthesized via hydrolysis/condensation, by using H_2O_2 as oxidizing agent [15]. An aqueous solution of 13.513 vol.% H_2O_2 (Acros Organics, 35 wt.% stabilized) is slowly added into a 0.11 M $RuCl_3{\cdot}3H_2O$ (Alfa Aesar, 99.99%) solution, under magnetic stirring. In order to get a stable colloid, the final solution is placed in an oven in air at 95 °C for 2 h and then it is cooled down to room temperature. All colloidal suspensions were prepared with the same concentration of ruthenium (0.0072 M). However, the volume of suspension was changed to obtain different contents of ruthenium in the final catalysts. The following RuO_2 colloids were then prepared:

(i) Colloid 1, containing the Ru mass required for a 3 wt.% Ru catalyst, which corresponds to 25% of a theoretical monolayer of RuO_2 on the support.
(ii) Colloid 2, containing the Ru mass required for a 5 wt.% Ru catalyst, which corresponds to 42% of a theoretical monolayer of RuO_2 on the support.
(iii) Colloid 3, containing the Ru mass required for a 7 wt.% Ru catalyst, which corresponds to 60% of a theoretical monolayer of RuO_2 on the support.

2.1.2. Single impregnation of colloids on alumina (standard method)

Samples were prepared via wet impregnation of alumina with RuO_2 colloids. The powdered γ-Al_2O_3 (Alfa Aesar, SBET = 73 $m^2\,g^{-1}$) was added into each colloid (Colloids 1–3), under vigorous agitation. The sample was recovered via evaporation of the solvent in rotavapor, under reduced pressure at 50 °C, and then it was dried overnight at 110 °C in air. The samples are denoted as RuX/Al-COLL (dried), where X corresponds to the Ru loading percentage (X: 3, 5 or 7 wt.%).

2.1.3. Synthesis of Ru/γ-Al_2O_3 standard catalysts

Ru3/Al-COLL (dried), Ru5/Al-COLL (dried) and Ru7/Al-COLL (dried) samples were calcined in air (at 450 °C for 4 h), in order to obtain the final catalysts with 3, 5 and 7 wt.% of Ru. These catalysts are denoted as Ru3/Al-COLL, Ru5/Al-COLL and Ru7/Al-COLL, respectively, to which we will refer in general as 'standard catalysts'.

2.1.4. Synthesis of Ru/γ-Al_2O_3 catalysts via modified colloidal methods

Two different strategies were followed to synthesize Ru(10 wt.%)/γ-Al_2O_3 catalysts (Fig. 1):

(i) Sequential impregnation of colloids (Fig. 1b): Ru7/Al-COLL (dried) and Ru3/Al-COLL (dried) samples were respectively used as supports for the impregnation of another RuO_2 colloid. Precisely, Ru7/Al-COLL (dried) was added under vigorous agitation into Colloid 1 (3% Ru), while Ru3/Al-COLL (dried) was added into Colloid 3 (7% Ru). In each case, the resulting solid was recovered via evaporation of the solvent in rotavapor, under reduced pressure at 50 °C, then it was dried overnight at 110 °C in air. The resulting samples are denoted as Ru3/(Ru7/Al-COLL) (dried) and Ru7/(Ru3/Al-COLL) (dried), both containing 10 wt.% of Ru. After 4 h at 450 °C calcination, the final catalysts are obtained and simply denoted as Ru3/(Ru7/Al-COLL) and Ru7/(Ru3/Al-COLL).
(ii) Impregnation of a mixture of colloidal suspensions (Fig. 1a′): Colloids 1 and 3 were mixed and gently agitated to form a new colloidal suspension. Alumina was then impregnated with the resulting colloid, following the procedure described above. The catalyst prepared in this way is denoted as Ru(7+3)/Al-COLL and it also contains 10 wt.% of Ru.

It is noteworthy that when the dried catalysts (heated at 110 °C) are dipped in water and stirred for 30 min, the solution remains clear, meaning that RuO_2 particles are strongly attached to the support.

2.1.5. Denotation of samples

In the following sections we will refer as 'calcined' samples to the fresh calcined catalysts, and as 'tested' samples to the catalysts obtained after the catalytic test, including the reduction pretreatment and the subsequent ammonia synthesis reaction.

2.2. Catalytic activity measurements

Catalytic tests were carried out in a metallic fixed-bed tubular (8 mm I.D.) 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