Green NH_3 Synthesis via Hydroxyapatite-Supported Ru Catalysts for Sustainable H_2 Storage under mild conditions

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Significance and Relevance

This research demonstrates the potential of hydroxyapatite (HAp) as a novel support for ruthenium (Ru) nanoparticles, enabling efficient ammonia synthesis under milder conditions (1 bar). By optimizing the basicity of HAp, through controlled Ca/P ratios catalytic performance was enhanced, with the best results showing a 60% improvement in NH_3 turnover frequency (TOF) compared to a benchmark Ru/MgO catalyst. In particular, the study shows that the basicity of HAp plays a critical role in facilitating electronic transfer to Ru NPs, leading to improved nitrogen activation. Such advances are significant for achieving sustainable fertilizer production and clean energy solutions through more efficient ammonia synthesis.

Preferred and 2nd choice for the topic: (1) H_2 storage and transportation, green H_2 production, hydrogen vectors. (2) Sustainable and clean energy production and transport.

Preferred presentation: Oral preferred or Short Oral

Introduction and Motivations

Ammonia (NH_3) plays a dual role as a key fertilizer in global agriculture and as a promising hydrogen (H_2) carrier for renewable energy storage[1]. Traditionally, NH_3 synthesis via the Haber-Bosch process requires severe conditions, high temperatures (400-600 °C) and pressures exceeding 200 bar, accounting for nearly 2% of global energy consumption and producing substantial greenhouse gas emissions[2]. Improving this process to achieve efficient NH_3 production under milder conditions remains a significant challenge. Ru catalysts have been reported to be more active than conventional iron (Fe) and nickel (Ni) catalysts[3] and Ru/MgO has been considered as a benchmark catalyst for NH_3 synthesis[4]. It has been suggested that the basic nature of the support enhances the electron density of Ru, which facilitates the dissociation of the nitrogen triple bond N≡N that is claimed to be the rate-limiting step in NH_3 synthesis.

The present study investigates original hydroxyapatite-supported Ru catalysts for NH_3 synthesis. HAp is an environmentally friendly calcium phosphate known both for its high ability for metal dispersion[5] and for its basic properties that can be tuned by modifying its composition (Ca/P ratio) by adjusting the pH of the precipitation medium[6]. The influence of the synthesis conditions on the basic properties of the HAp supports, on the dispersion and electronic density of the Ru nanoparticles (NPs) are studied and discussed in line with the evolution of the TOF) for NH_3 synthesis.

Materials and Methods

HAp supports were synthesized by adding a phosphorus precursor solution ($NH_4H_2PO_4$) to a $Ca(NO_3)_2$ solution at 80 °C, at stationary pH ranging from 6.5 to 9.0 by controlled addition of NH_4OH and by using an Optimax 1001 workstation (Mettler Toledo). Subsequently, Ru (1-5 wt%) was deposited by wet impregnation of $Ru(NO)(NO_3)_3$ and the metallic nanoparticles were obtained by reduction under H_2 at 450 °C for 2 h. ICP-OES chemical analysis, N_2 sorption, XRD, SEM, TEM and N_2-FTIR were used to characterize Ru/HAps and the catalytic conversion of 2-methylbut-3-yn-2-ol was used as a model reaction to investigate the acid-base properties of HAps. Ammonia synthesis was performed in a fixed-bed flow reactor (FR-100, Micromeritics) with a 50 mL/min H_2:N_2 (3:1) flow at 1 bar using 100 mg of catalyst diluted with 4.8 g of SiC. The NH_3 concentration at the reactor outlet was recorded every 5 seconds using an on-line MKS 2030 infrared analyzer.

Results and Discussion

Properties of the Ru/HAp catalysts: Crystalline (XRD) rod-like (SEM) HAps with a global increase in Ca/P ratio with increasing precipitation pH were successfully prepared. All of them show very similar specific surface areas of about 35 m²/g. For all of the HAp_pH supports, well-dispersed Ru nanoparticles of 2.1 ± 0.2 nm (TEM) were obtained after reduction. This particle size was maintained with increasing Ru loading.

Catalytic performance: Ru/HAp catalysts were found to be active and stable with time on stream (at least 3 days) for NH_3 synthesis. The catalytic measurements showed that varying the Ru content on HAp had a limited effect on the TOF values for NH_3 production. In contrast, the Ca/P ratio of the HAp support, modulated by the precipitation pH, significantly affected the TOF, reaching an optimum of 0.41 min^{-1} at 400 °C for Ru (2 wt%)/HAp_7.6. This TOF was found to be about 60 % higher than that of a Ru/MgO benchmark catalyst (**Figure 1a**). This finding is consistent with the higher basicity of the corresponding support as measured by the 2-methylbut-3-yn-2-ol model conversion reaction. In addition, N_2 adsorption on Ru^0 NPs at 100 K followed by FTIR showed the most pronounced shift of the maximum of the N_2 absorption band toward lower wavenumbers (2191 cm^{-1}) for Ru (2 wt%)/HAp_7.6 (**Figure 1b**), which is consistent with an increased electron density of the Ru^0 NPs for such a sample.

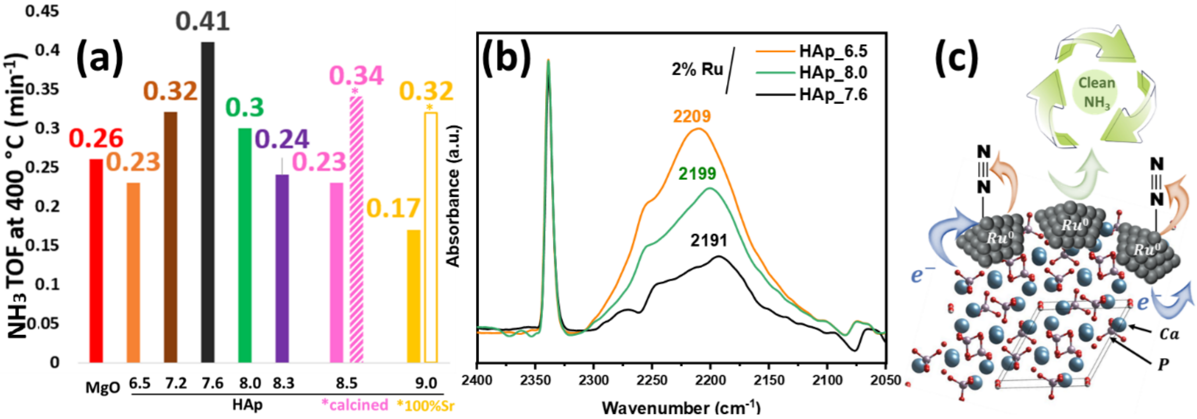

Figure 1. (a) NH_3 TOF at 400 °C and 1 bar over Ru/MgO and Ru/HAp_pH catalysts, (b) N_2-FTIR spectra at 100 K. (c) Schematic representation of the influence of HAp basicity on NH_3 synthesis.

Optimization paths: Better dispersion of the Ru NPs was achieved by performing a calcination step at 600 °C of the HAp support prior to Ru deposition. This reduced the size of the Ru NPs to 1.7 nm and resulted in an increase in TOF of about 50% for the calcined HAp_8.5 support compared to uncalcined HAp_8.5 (**Figure 1a, purple bars**).

Sr bulk-substituted HAp (Sr-HAp) was also prepared by coprecipitation, and the Sr-HAp support was found to be more basic than its Ca counterpart. This resulted in an increase in NH_3 TOF of about 90% for Ru/Sr-HAp_9.0 compared to Ru/HAp_9.0 (**Figure 1a, yellow bars**). These results not only highlight the potential of HAps and modified HAps as supports for Ru in NH_3 synthesis, but also provide a clear proof of concept of the critical role of the basic properties of the support on the electronic density of the Ru particles, and in turn on the activation of N_2 (**Figure 1c**).

References

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