Characterization of K-Promoted Ru Catalysts for Ammonia Decomposition Discovered Using High-Throughput Experimentation

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Introduction

Due to ever-increasing fuel prices, stringent emission regulations, and depleting fuel resources, there has been an increasing interest in alternative energy sources. The most attractive option is H_2, as it has high-energy efficiency and H_2O is the only byproduct of its combustion. However, current sources of hydrogen generation involve the use of carbonaceous substances such as methanol and methane, which give off undesired CO_x (x = 1,2) emissions. Thus, there is a need to find an alternative source for hydrogen production.

Ammonia has emerged as the leading alternative because of its high hydrogen storage capacity (17.7 %) and energy density (3000 Wh/kg) & the catalytic decomposition of NH_3 has been proposed as a potential source of CO_x free hydrogen [1]. From an environmental standpoint, N_2 is the only byproduct of the decomposition. In addition, NH_3 is easy to transport and store for applications as automotive fuel cells. The reaction is endothermic (ΔH = +46 kJ/mol) and the reaction temperature is based on the catalyst used [1]. Many of the catalysts that have been studied have included supported Ni, Fe, Ru, Rh and, to a more limited extent, the classic noble metals (Pt, Ir, Pd) [2] and alkali metals (K, Cs, Ba) [3,4]. In the current work, we have investigated the effect of adding different promoters like K, Cs, and Ba on Ru based NH_3 decomposition catalyst using different solvents and different support materials.

Experimental

The catalysts were synthesized via incipient wetness on γ-Al_2O_3. Ruthenium chloride, potassium nitrate, cesium chloride and barium nitrate (Strem Chemicals) were dissolved in distilled water prior to impregnation. Details concerning the catalyst preparation procedure can be found elsewhere [5].

All catalytic tests were performed using a 16-channel parallel reactor and the products gases were analyzed using Fourier transform infra red spectroscopic imaging technique. The optical setup consists of a Bruker Equinox 55 FTIR spectrometer interfaced with a 64x64 pixel mercury cadmium telluride FPA detector (Santa Barbara Focalplane, Goleta, CA, USA) capable of collecting IR spectra of the effluents from all 16 reactors in less than 2 seconds. Details of the reactor setup, optical setup, and analytical methods have been described in previous publication [6]. Catalyst characterization was completed using the JEOL 2010F transmission electron microscope and the JEOL 7400F scanning electron microscope.

Results and Discussion

Using statistical design of experiments, Figure 1 shows the initial results for NH_3 decomposition efficiency using various temperatures and metal promoters by flowing 10% NH_3 in helium gas mixture. It was found that addition of K to 4 wt% Ru improves the NH_3 conversion efficiency at T=350ºC by ~35%, whereas Cs and Ba had a minimal effect on performance. Characterization using TEM and SEM in Figure 1 shows comparison between the 4 wt% Ru catalyst and the 4 wt% Ru / 12 wt% K catalyst. The addition of K (greater than 6 wt%) promotes the growth of nano-whiskers rather than the Ru clusters observed in the monometallic catalyst. The widths of these whiskers are 10-25 nm and have lengths extending from a few nanometers to several microns. X-ray analysis using the TEM shows that the whiskers contain K, Ru, and O forming a $K_xRu_yO_z$ type material. Diffraction and high resolution imaging studies are currently underway to identify the structure of these whiskers.

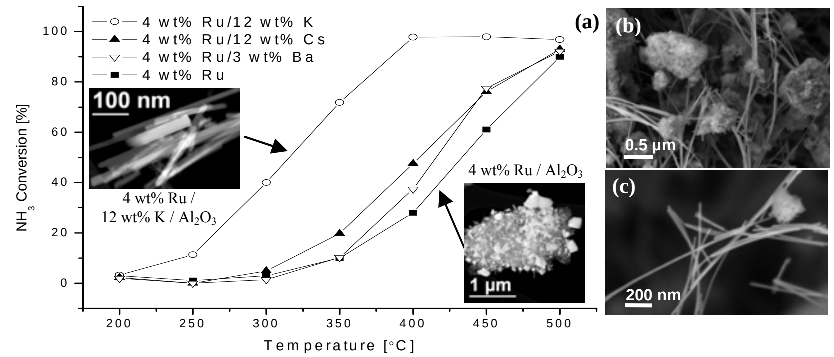

Figure 1. (a) Effect of addition of K, Ba, and Cs on NH_3 decomposition efficiency of 4% Ru catalyst on Al_2O_3 with representative high-angle annular dark field images of selected catalysts (b & c) SEM images of the 4 wt% Ru / 12 wt% K catalyst showing complex whisker network.

Overall, we have studied the effect of using different supports, solvents, promoter loadings, and catalyst preparation procedures for NH_3 decomposition efficiency. The results showed optimal performance was achieved using 4 wt% Ru catalyst promoted with 12 wt% K supported on Al_2O_3 using incipient wetness with a water solvent.

Significance

Initial results suggest that adding K to Ru based catalysts promote the formation of $K_xRu_yO_z$ nano-whiskers in the fresh catalyst that lead to efficiency increases up to 35% in NH_3 decomposition compared to pure Ru catalyst. Finding a suitable catalyst for NH_3 decomposition would have a significant impact in terms of finding an alternative fuel source. This would further reduce the load on natural fuel resources and decrease the environmental pollution. The work presented here is a step towards achieving this task.

References

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