

Size Optimization of Ru Nanoparticles for the Generation of CO_x-free H₂ from Ammonia

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Introduction

The on-board generation of hydrogen for mobile fuel cell applications by the decomposition of ammonia boasts high H₂ storage density and zero CO_x emissions, rendering this option superior to many other proposed H₂ storage alternatives. Since NH₃ can in principle be synthesized using completely green processes, the environmental benefits are clear. However, in order to realize ammonia decomposition as an economically viable possibility for mobile hydrogen delivery, discovery of an inexpensive catalyst that is active at low temperatures is paramount.

Supported alkali-promoted ruthenium (Ru) is known to be the most active ammonia decomposition catalyst[1]. In addition, it has been proposed through modeling efforts that the formation of highly active Ru reaction sites is highly dependent upon particle size[2]. Toward this end, we have directed our efforts to optimizing a K-promoted Ru system that was found to form a single crystal morphology belonging to the Hollandite family of structures[3]. Recently, we have sought to systematically control Ru particle size using microemulsion synthesis.

Materials and Methods

Potassium (K)-promoted Ru catalysts were synthesized via wet co-impregnation on γ -Al₂O₃ support (Catalox® SBA-200, 200m²/g) as outlined in [3]. After drying at 120°C, the catalysts are calcined in air then reduced in situ. To form nanoparticle catalysts via microemulsion synthesis, two microemulsion systems were prepared, with reverse micelles containing either an aqueous solution of metal precursor or of hydrazine. The microemulsions were mixed to reduce the metal. An acetone wash was used to break the microemulsion and the reduced particles were allowed to settle onto γ -Al₂O₃ support. All catalysts were reacted in 10%NH₃/He, GHSV= 40,000 mL/(g_{cat}·hr) over a temperature range of 200 to 500°C at 1 atm.

Results and Discussion

The catalyst containing Hollandite improved catalyst performance at 350°C from 10% NH₃ conversion in the case of the unpromoted catalyst to over 65% in the Hollandite-containing catalyst. Formation of Hollandite was found to depend on promoter weight loading and for a 4 wt% Ru catalyst, the optimum K loading was 12 wt%. The apparent promotional mechanism is primarily structural, as Hollandite breaks down in reducing preparation conditions and Ru dispersion changed with K loading.

Through manipulation of the co-surfactant concentration in the microemulsion, we have achieved control of the size of the reverse micelles between approximately 25 and 2.5 nm to limit the particle size growth of Ru clusters. Our initial studies indicate that by using a Ru

catalyst synthesized using microemulsions, a reduction in the T₅₀ from a Ru catalyst synthesized using wet impregnation of 100°C is achievable (Fig. 1).

Significance

In this work we have demonstrated a unique method of dispersing Ru through the formation and degradation of Hollandite in order to achieve ammonia decomposition at lower temperatures. Microemulsion synthesis has been applied to this system, and initial results suggest control of reverse micelle size provides effective improvement over wet impregnation catalysts..

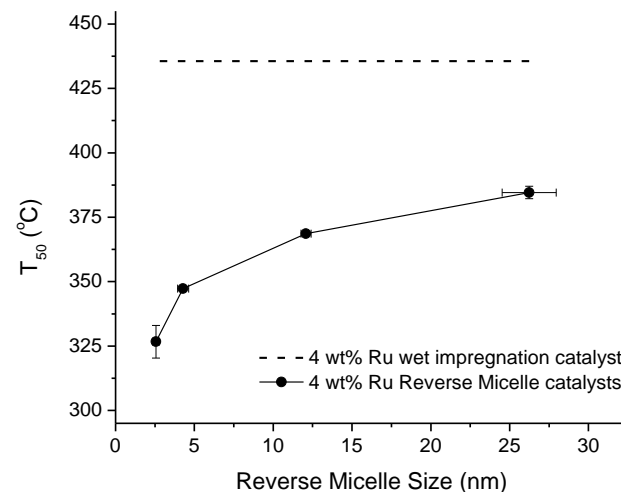


Figure 1. Catalysts prepared using microemulsion synthesis show improvement in T₅₀ compared to wet impregnation catalyst. Furthermore, T₅₀ decreases as reverse micelle size decreases, denoting improvement in catalytic activity

References

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