
V.D.24 An Integrated Approach toward Rational Nanocatalyst Design for Hydrogen Production

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Objectives

The overall objective of the proposed work is to develop a rational framework for the discovery of low cost, robust, and active nano-catalysts that will enable efficient hydrogen production. Our approach will be the first demonstration of integrated multiscale model, nano-catalyst synthesis, and nanoscale characterization assisted high throughput experimentation (HTE). We will initially demonstrate our approach with ammonia decomposition on noble metal catalysts. Within the scope of this work, we first plan to focus on mono- and then on bi-metallic catalysts.

Technical Barriers

We need to develop a computational framework that capitalizes on the massive information content derived from HTE and the fundamental understanding created by powerful quantum mechanical density function theory (DFT) techniques to carry out model-based design of experiments and catalysts. Furthermore, we need to link state-of-the art characterization of nanostructured catalysts with nanoparticle catalyst synthesis and measured chemical activity. These structure-performance-synthesis relations need to be incorporated into the aforementioned theoretical framework to drive experiments toward synthesis of nanomaterials for improved ammonia decomposition catalysts.

Abstract

We have carried out screening HTE for single metals and bimetallic catalysts. We have found that Ru is the best single metal catalyst. Furthermore, we have investigated promoting effects (i.e., K, Cs, and Ba) on

the Ru catalyst. We have found that K is the dominant promoter of increased Ru activity. Response surface experimental design has led to substantial improvements of the Ru catalyst with promotion. It has been found that the promoting effect is not limited to K but extendible to some other alkaline metals. In addition, it has been found that solvent has an interesting effect on activity. Advanced characterization of the Ru/K promoted catalyst has been carried via SEM, TEM, selected-area electron diffraction, and energy dispersive x-ray spectroscopy. It has been found that the Ru catalyst is composed of agglomerates, whereas the K-promoted catalyst of “nanowiskers” with a KRu_4O_8 hollandite structure (an important result). A number of microkinetic models for single metals have been developed and a methodology for linking models for bimetallic catalysts in a thermodynamically consistent manner has been implemented.

Progress Report

High Throughput Experimental Results. We have explored the activity of various single metals and some bimetallic metals on ammonia decomposition HTE. Some of these data have been used to develop microkinetic models, as elaborated below. In parallel, we investigated the effect of adding different promoters (i.e., K, Cs, and Ba) to Ru based catalysts. The catalysts were synthesized via incipient wetness on $\gamma-Al_2O_3$ support and ruthenium chloride, potassium nitrate, cesium chloride, and barium nitrate (Strem Chemicals) as precursors. Ba is believed to act as a surface promoter that disperses the metal over the support, whereas K and Cs are believed to be electrical promoters, which allow for electrons to be transferred to the support and aid in the N_2 desorption off the surface. The gas mixture used for catalyst testing was 10% NH_3 in He. The catalysts were tested by heating this mixture from 200°C to 500°C and by measuring the NH_3 conversion every 50°C.

In order to effectively determine the impact of each promoter, a response surface study was conducted for the Cs/Ba/K promoted system at a constant weight percent of Ru (4%). The design for the metal composition is shown in Figure 1. A response surface model was developed for the % NH_3 conversion at 350°C as a function of metal composition. It was found that addition of 12% K improves the NH_3 conversion efficiency at 350°C by ~35%. Figure 1b compares model predictions and the experimental data and Figure 1c lists the normalized model coefficients.

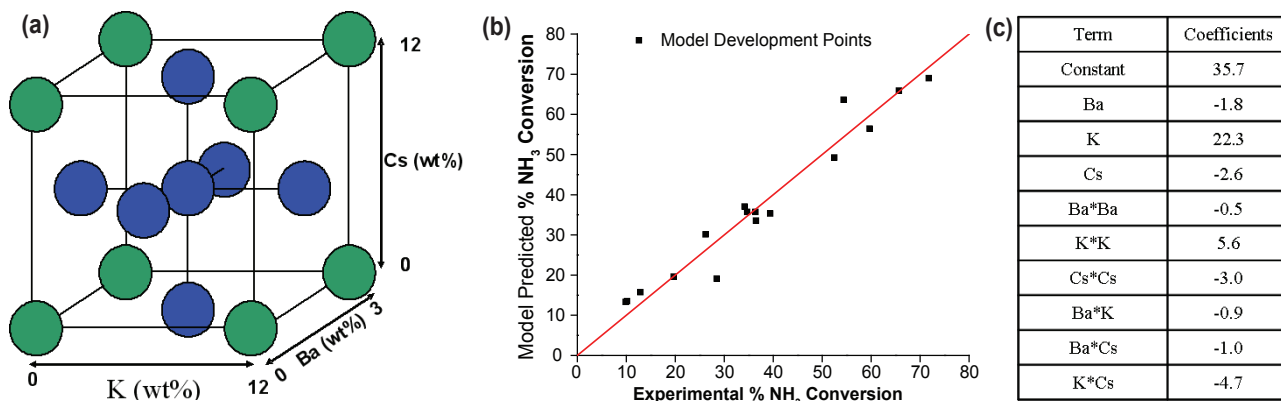


FIGURE 1. a) Response Surface Model for Ba/Cs/K system with 4% Ru on Alumina Support. b) Model prediction compared to experimental data. c) List of the normalized model coefficients.

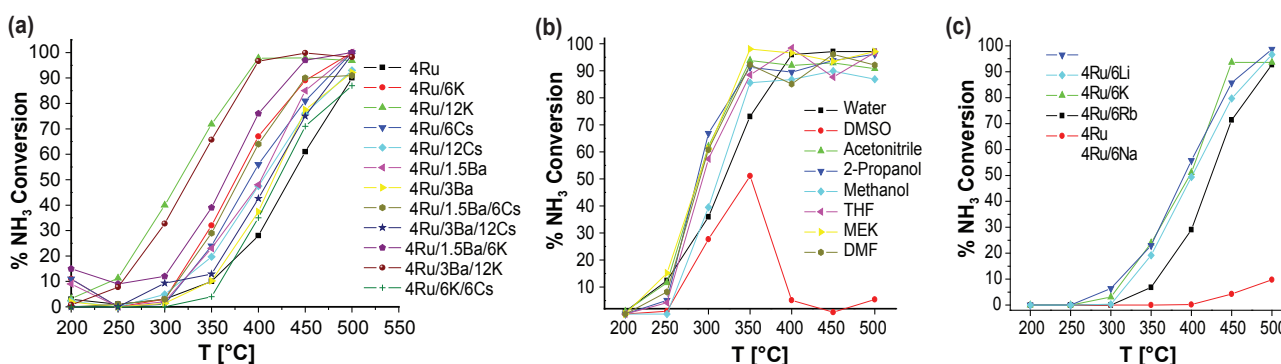


FIGURE 2. a) Performance of variety of Ru/K/Ba/Cs catalysts. b) Performance of 4Ru/12K catalyst synthesized using different solvents. c) Effect of adding other alkali metals as promoters to Ru catalyst.

The model indicates that the Ru promotion is governed mainly by K. Motivated from this result, we also studied the addition of other alkaline metals (Rb, Li, Na) and the use of different solvents (i.e., ACN, THF, MEK, DMF) for the synthesis of 4Ru/12K catalyst. Figure 2 shows the effect of different solvents (2b) and other alkali metals (2c). It was found that other solvents were able to further improve the performance of the 4Ru/12K catalyst compared to water, especially at low temperatures. Figure 2c shows that both Li and Rb cause a similar promotional effect as K, but Na was not effective.

Advanced Characterization. Advanced characterization was focused on the K promoted catalysts synthesized using H₂O since the 4Ru/12K showed enhanced performance over the Ru monometallic catalyst. Characterization was aimed at identifying the differences between the active vs. less active catalyst. Figure 3a and 3b show representative post-calcination TEM and SEM images for the Ru catalyst and Figure 3c and 3d show images for the 4Ru/12K catalyst. The Ru catalyst is composed of agglomerates that range in size from 30 nm up to a micron in size. Ru agglomerates are well-distributed on

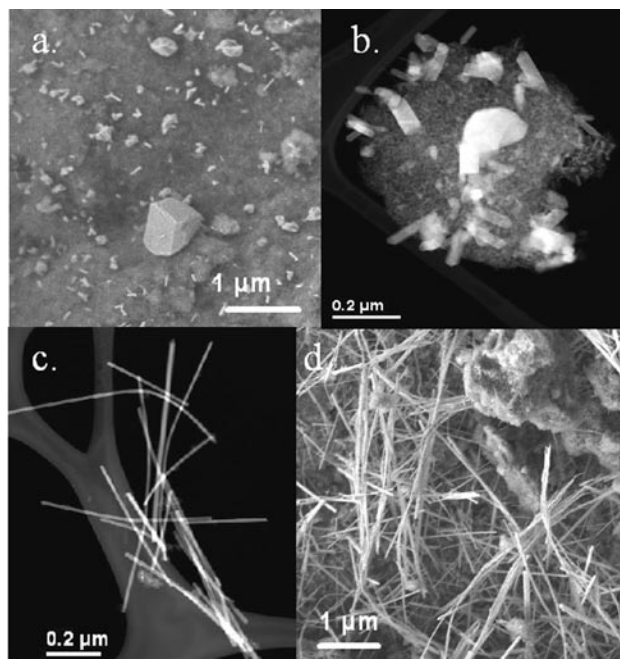


FIGURE 3. Representative TEM (b & c) and SEM (a & d) images showing the pure Ru/Al₂O₃ catalyst (a & b) and the K-promoted Ru/Al₂O₃ (c & d).

the support, but the surface area is low due to the large particle size. In contrast, the K-promoted catalyst is composed of a complex network of “nanowhiskers” that cover the surface of the γ - Al_2O_3 support. The whiskers have a rectangular base that exhibits edge lengths of 10-50 nm and lengths that can extend from a few nm to several microns.

Further TEM characterization revealed that the whiskers are crystalline as evidenced by the high-resolution image showing the well-ordered atomic level structure. The whiskers have a KRu_4O_8 hollandite structure that was confirmed using individual “whiskers” and selected-area electron diffraction (SAED). Figure 4b shows the experimentally measured interplanar d-spacings compared to the known hollandite structure (JCPDS card 70-0724). Assuming the whiskers are the active phase, the possibility of an active hollandite structure is significant since this is one member of a large class of materials. Members of the hollandite class have the general formula $\text{A}_x\text{B}_4\text{O}_{16}$, where A is typically a large cation (Ba, K, Na, Sr, Rb), B a cation that can form oxygen octahedra (Mn, Ti, Al, Ru), and x is typically near one and controls the mix of +3 and +4 valence on the B-site. The identity of A and B can be mixed to form a large variety of materials. Characterization after reaction is shown in Figure 5. SEM shows four distinct structures. The first two have already been discussed and are the Al_2O_3 support material and the

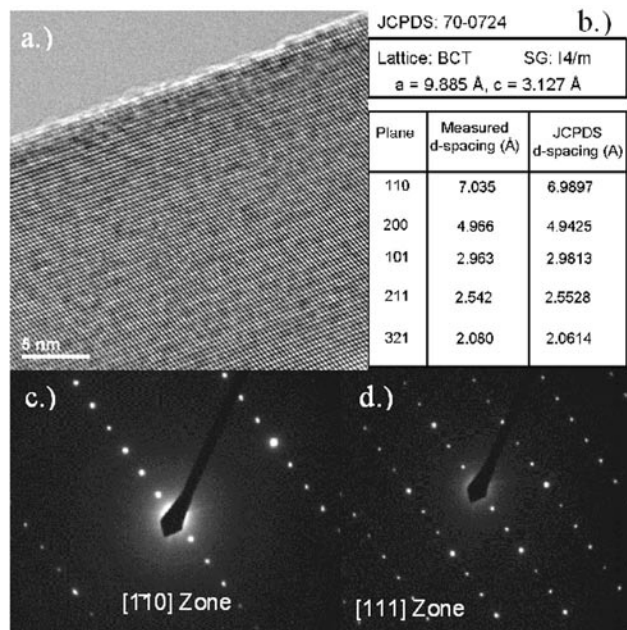


FIGURE 4. Post-calcination characterization of the “nanowhiskers” using (a) high resolution imaging, (c & d) selected-area electron diffraction. Table in (b) compares the experimental d-spacings to a known potassium Ru oxide.

hollandite “nanowhiskers”. The third structure in Figure 5a (boxed) appears to be nanoparticles and nanowires with an irregular morphology (also shown in the TEM in 5b). These nanowires were probed further using energy dispersive x-ray spectroscopy (EDS) in Figure 5d (blue line). The assignment of the peaks indicates that these nanowires are Ru metal. The large C peak is due to the supportive film of the Cu grids used for the TEM analysis. Ru wires were only observed in the post-reacted sample and were assumed to form during the reaction. The fourth structure shown in 5c is glassy-like in appearance. EDS (black line) shows the elements K, Cl, Al, and O. The Al and O can be attributed to the support and the K and Cl appear to form a KCl structure.

Modeling. Using HTE data, we developed microkinetic models for various catalysts. An example is shown in Figure 6. Significant difference on dominant adsorbates and the effect of lateral interactions on the chemistry among various catalysts has been found. This approach is being extended to a library of catalysts. In addition, a framework for linking models for different catalysts in a thermodynamically consistent manner has been developed. One application of this framework is to predict the activity of heterogeneous catalysts consisting of multiple types of sites, such as various Ru sites in nanoparticles.

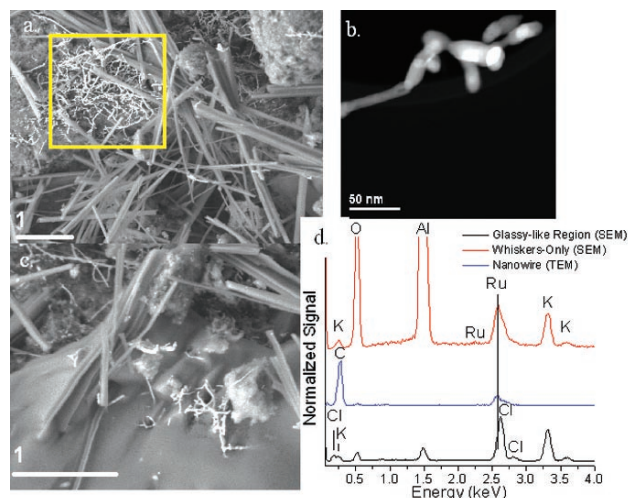


FIGURE 5. Representative SEM (a & c) and TEM (b) images of the K-promoted $\text{Ru}/\text{Al}_2\text{O}_3$ after NH_3 decomposition. Elemental analysis using energy dispersive x-ray spectroscopy is shown in (d).

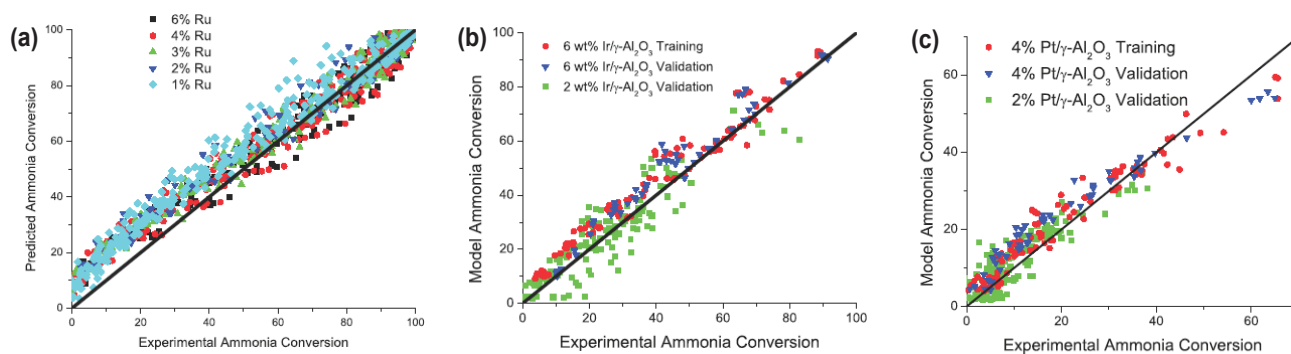


FIGURE 6. Parity graphs of HTE and model prediction for NH_3 conversion for Ru (left), Ir (middle), and Pt (right). For the Ru catalyst, more than 1000 experimental points have been collected and simulated.

Future studies

The following studies are planned:

1. Identify the effect of N_2 and H_2 on the activity of Ru/K catalyst. This will aid us in probing the reaction mechanism.
2. Further characterize the different catalyst with different promoters and identify the mechanism of promotion and the effect of solvents during synthesis.
3. Optimize the composition using a response surface design.
4. Identify optimal conditions that lead to the formation of hollandite structures and would further aid in enhancing the performance of the existing catalysts.
5. Complete a fairly rich library of microkinetic models on single metals for rational selection of bimetallic catalysts.