Theoretical and Experimental Studies of Ammonia Decomposition for Hydrogen Production

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Introduction

The ammonia decomposition reaction has recently received increased attention due to the possibility of ammonia being used as a hydrogen storage medium in a possible hydrogen economy. We have explored this decomposition reaction through multiscale microkinetic modeling for a number of transition metal catalysts, including Cu, Pt, Ir, Ru, Pd, Rh, Co, Ni, Fe, W, and Mo, to better understand the reaction mechanism. The mechanism consists of 12 elementary reaction steps and 5 surface species, namely N, H, NH, NH_2, and NH_3. For many of the metals, a large portion of the surface is covered by adsorbates. For these metals, repulsive adsorbate-adsorbate interactions are expected to change the binding energies of the surface species, thereby changing the elementary reaction activation barriers and modifying the catalytic activity [1]. An understanding of the reaction mechanism and electronic properties of the metals has given insight into how to tailor catalysts to improve catalytic activity for this reaction.

Density functional theory (DFT) calculations and the microkinetic models predicted the surface monolayer Ni/Pt bimetallic system to be a potentially active ammonia decomposition catalyst. To test the accuracy of these predictions, ammonia decomposition and nitrogen temperature programmed desorption (TPD) experiments were performed on the bimetallic Ni/Pt surface.

Materials and Methods

Coverage dependant atomic heats of chemisorption were calculated through DFT using the Vienna Ab-initio Simulation Package (VASP) for the various transition metal catalysts. Coverage dependant molecular binding energies were calculated using a method based on scaling relationships published by Abild-Pederson et al. [2]. Activation barriers were calculated through the bond-order conservation (BOC) method [3].

The Ni/Pt bimetallic surface was created by depositing Ni through physical vapor deposition on a Pt(111) crystal [4]. Ammonia was dosed at temperatures between 200 K and 425 K. The crystal temperature was then ramped at a linear heating rate of 3 K/s and the desorption products were recorded by a quadruple mass spectrometer.

Results and Discussion

Inclusion of the interaction parameters to the models resulted in reduced nitrogen coverages and a peak shift in the volcano curve. The conversions, sensitivity coefficients, and the most abundant reaction intermediate were plotted against the characteristic nitrogen heat of chemisorption for each metal, which was found to be an adequate descriptor for this reaction. The volcano curve of the conversions calculated through the microkinetic models are in good agreement with experimental data of single metal catalysts by Ganley and coworkers [5]. The maximum activity was found at a nitrogen heat of chemisorption of approximately 136 kcal/mol.

A DFT study of nitrogen binding energies on Pt-3d bimetallic surfaces showed a binding energy of 138 kcal/mol on the Ni/Pt surface, indicating that it could be a potentially active catalyst; therefore surface science experiments were performed to assess the microkinetic model and DFT results. Ammonia decomposition on this surface was shown to occur at temperatures below 400 K. Evidence of decomposition at 400 K can be seen from the presence of the nitrogen desorption peak in Figure 1. The peak temperature at 627 K did not change with coverage and seemed to be more representative of first order desorption than second order desorption, indicating possible surface reconstruction at higher nitrogen coverages.
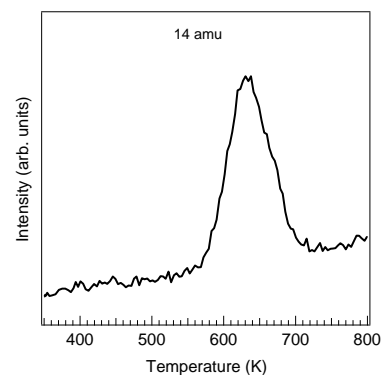
Figure 1. Nitrogen desorption from the Ni/Pt surface after a 3 Langmuir NH_3 exposure at 400K. The peak at 627 K is due to atomic nitrogen desorbing after being decomposed.

Significance

Through rational catalyst design, the Ni/Pt catalyst was predicted as a potentially active NH_3 decomposition catalyst. It was confirmed experimentally to be more active toward decomposing ammonia at low temperatures and desorbs nitrogen at lower temperatures than a Ru(0001) surface, [6] where Ru is currently the most active single metal catalyst.

References
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