Abstract

Core-shell or surface segregated bimetallic nanoparticles expose outstanding activity for many heterogeneously catalyzed reactions but the reasons remain elusive due to the difficulties in experimentally characterizing active sites. Using multiscale simulations for ammonia decomposition on various nickel loadings on Pt(111), we show that the very high activity of core-shell structures requires patches of the guest metal to create and sustain dual active sites: Ni terraces catalyze N–H bond breaking and Ni edges enable atomic nitrogen association. The structure sensitivity on these active catalysts depends profoundly on reaction conditions due to kinetically competing relevant elementary reaction steps. We expose considerable difference in active sites between transient and steady state conditions and provide insights into optimal material design.

Keywords

Bimetallic catalyst, Structure sensitivity, DFT, Kinetic Monte Carlo simulations, Ammonia, Materials design

Introduction

Over the past few years, considerable efforts have focused on finding and designing highly active, cheap and environmentally friendly catalysts. Recently, core-shell nanoparticles of transition metal alloys have shown remarkable advantage over traditional metal catalysts in applications of photo-electrocatalysis, biomass conversion, etc. This is mainly owing to the unique modification of structures and electronic properties by mixing two metals at the nanoscale. Due to the complex microstructures of the core-shell nanoparticles, materials’ design has remained elusive. Revealing the mechanisms of the enhanced activity and the active sites under working experimental conditions shall provide insights into the design and synthesis of novel catalytic materials (Guo et al., 2013).

Ammonia is mainly utilized for fertilizers. Ammonia can also serve as a feedstock for on-site CO₂ free hydrogen for fuel cells. In addition, ammonia decomposition is a prototypical reaction of structure sensitivity and is ideal for understanding the active site in materials’ design. Here, by performing the first multiscale calculations on patched bimetallic surfaces and apply them to the NH₃ decomposition on submonolayer Ni on Pt, we expose multifunctional catalysis of patched bimetallic surfaces. Specifically, Ni terrace sites on Pt catalyze ammonia decomposition and Ni step edges catalyze N–N association resulting from surface N spilling over from the terraces to the Ni step edges. The patched bimetallic surface offers not only better performance, but also ease of synthesis. Our findings open up the possibility for materials design
requiring multiple active sites: performance of materials may be boosted by purposely making use of the inevitable nonidealities in real materials to create multifunctionality.

Methods

We performed spin-polarized density functional theory calculations for the energetics of initial, final and transition states in NH$_x$ stepwise decomposition as well as H$_2$ and N$_2$ desorption. Then we employed kinetic Monte Carlo (KMC) simulations to obtain reaction turnover frequency (TOF) in a periodic lattice of 2016 sites.

Results

Ni/Pt serves as a bifunctional catalyst where the Ni terrace sites catalyze the N–H bond scission and the (110) edges of patches catalyze N$_2$ association (Guo and Vlachos, 2015). It is precisely this dual site behavior that is responsible for the two orders higher activity on patched Ni/Pt surfaces compared to ideal monolayer Ni-Pt-Pt and pure metal surfaces of Ni and Pt shown in Figure 1(a). We find that the NH$_x$ decomposition rate exposes a very weak structure sensitivity on Ni loading with a slightly higher rate at half monolayer of Ni loading as found in experiments (Rodriguez et al., 2014). We attribute this structure insensitivity to the presence of competing kinetically relevant elementary steps under certain conditions. In Figure 1(b) we show that only when the operating conditions are such that a single rate-determining step (RDS) prevails, the rate scales linearly with the number of the active sites that catalyze the RDS, as expected, resulting in strong structure (adlayer loading and shape) sensitivity. Under such conditions, small clusters show orders of magnitude higher activity than large clusters.

Conclusions

Our results provide insights into whether a single RDS prevails in experimental data and what the active site may be. Our patched bimetallic surfaces serve as a reasonable model for core-shell nanoparticles and provide insights into materials design in catalytic reactions requiring multiple active sites. Material synthesis efforts should be devoted to making and stabilizing sufficiently small clusters of the guest metal, which possess dual sites in close proximity, rather than large clusters or single atoms. These findings can impact the way we think, design and characterize core-shell bimetallic nanoparticles by purposely using ‘defects’ to tune the chemistry.

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References