Objectives

The goal of this work is to explore new aspects of nanoscale phenomena in surface chemistry and electrochemistry with the aim of characterizing the relationships between nanoscale surface features (facets and clusters) and catalytic reactivity/selectivity. A long-term goal is to improve reactivity and selectivity by controlling the shape and size distribution of nanoscale surface features. Our emphasis is on atomically rough and morphologically unstable surfaces that undergo nanoscale faceting when covered by adsorbate (gas or metal) and annealed to elevated temperatures. There are three parts of the project: faceting of model catalytic surfaces, growth of metallic nanoparticles on the faceted surfaces, and reactivity/selectivity of the nanoscale facets in catalytic reactions.

Technical Barriers

Recent work has demonstrated that reactivity and selectivity in catalysis can be tuned by controlling the nanoparticle size and shape. However, highly dispersed supported catalysts used in industry usually have a wide distribution of sizes and shapes of nanoparticles. Great progress has been recently made in controlling shape and size of nanoparticles. To elucidate the reaction mechanism, which is in turn beneficial to the design and development of new catalysts, macroscopic model catalysts (planar single crystals) and nanoscale model catalysts are usually used to catalyze the reactions. These structures can exhibit new phenomena in heterogeneous catalysis, as well as in electrochemical reactions.

Abstract

We have performed experimental and theoretical studies of planar and faceted transition metal surfaces in an effort to explore structure-reactivity relationships, as well as nanoscale size effects, in catalytic reactions for hydrogen generation and NO reduction. Adsorbate-induced faceting of the Ir(210) and Re(11-21) surfaces was studied using scanning tunneling microscopy (STM) and low energy electron diffraction (LEED). Oxygen-induced faceting of Ir(210) is sustained after the oxygen overlayer is removed by exposure to hydrogen. Then, the recombination of H$_2$ ads and desorption of H$_2$ was monitored by temperature programmed desorption. In a similar fashion, the role of co-adsorbed hydrocarbons on the NO reduction reaction was studied by pre-adsorption of C$_2$H$_2$ on the planar and faceted Ir(210) surfaces. In the latter case, no size effects were found, which is in contrast to the influence of pre-adsorbed CO on this reaction where the reaction was very sensitive to facet size. In an effort to extend this approach to electrochemical reactions we studied the hydrogen evolution reaction (HER) on carbon-induced faceted Re(11-21) surfaces that were covered with a monolayer of Pt. These surfaces exhibited a higher reactivity than pure Re(11-21) [not surprising] but also a higher reactivity than Pt(111) [very encouraging].

Progress Report

Structure sensitivity in adsorption and desorption of hydrogen on Ir.

We have performed a combined theoretical and experimental study of hydrogen adsorption and desorption on planar Ir surfaces and nanoscale Ir facets. As indicated in Figure 1, at saturation coverage, two TPD peaks of H$_2$ appear at 360K and 440K from faceted Ir(210) while one peak is observed from planar Ir(210), indicating strong structure sensitivity in recombination and desorption of H$_2$. At fractional coverage, only one peak is seen at 440K on faceted Ir(210). No evidence has been found for size effects in desorption of H$_2$ from faceted Ir(210). Density functional theory (DFT) in combination with the ab-initio atomistic
thermodynamics approach is used to study hydrogen on planar Ir(210) and faceted Ir(210), consisting of (311) and (110) facets. We find that H prefers to bind at the two-fold short-bridge sites on Ir surfaces. The calculations also suggest that the higher temperature peak is related to H$_2$ desorption from (311) faces. For hydrogen on planar Ir(210), $T_D$ is calculated to be 405 K, which lies between $T_D$ values for hydrogen on Ir(110) and Ir(311). The DFT results of desorption temperatures for hydrogen from (210), (311), and (110) of Ir are in good agreement with those observed by TPD.

**Reduction of nitric oxide by acetylene on Ir surfaces with different morphologies: Comparison with reduction of NO by CO.**

Reduction of nitric oxide (NO) by acetylene (C$_2$H$_2$) has been investigated by temperature-programmed desorption (TPD) on planar Ir(210) and faceted Ir(210) with tunable sizes of three-sided nanopyramids exposing (311), (311̅), and (110) facets. Upon adsorption, C$_2$H$_2$ dissociates to form acetylide (CCH) and H species on the Ir surfaces at low C$_2$H$_2$ precoverage. For adsorption of NO on C$_2$H$_2$-covered Ir, both planar and faceted Ir(210) exhibit high reactivity for reduction of NO with high selectivity to N$_2$ at low C$_2$H$_2$ precoverage, although the reaction is completely inhibited at high C$_2$H$_2$ precoverage. Coadsorbed C$_2$H$_2$ significantly influences dissociation of NO. The N-, H-, and C-containing TPD products are dominated by N$_2$, H$_2$, CO, and CO$_2$ together with small amounts of H$_2$O. For adsorption of NO on C-covered Ir(210) at fractional C precoverage, formation of CO$_2$ is promoted while production of CO is reduced. Reduction of NO by C$_2$H$_2$ is structure sensitive on faceted Ir(210) versus planar Ir(210), but no evidence is found for size effects in the reduction of NO by C$_2$H$_2$ on faceted Ir(210) for average facet sizes of 5 nm and 14 nm. The results are compared with reduction of NO by CO on the same Ir surfaces. As for NO+C$_2$H$_2$, the Ir surfaces are very active for reduction of NO by CO with high selectivity to N$_2$ and the reaction is structure sensitive, but clear evidence is found for size effects in the reduction of NO by CO on the nanometer scale. Furthermore, coadsorbed CO does not affect dissociation of NO at low CO precoverage whereas coadsorbed CO considerably influences dissociation of NO at high CO precoverage. The adsorption sites of CCH+H on Ir are characterized by density functional theory.

**Reduction of NO by C$_2$H$_2$ on planar and faceted Ir(210).**

Motivated by the possibility that faceted C/Re(11-21) may be a promising substrate for synthesizing nanoscale model (electro)catalyst, we deposited Pt ML (monolayer) onto nano-faceted C/Re(11-21) surface, denoted as Pt-ML/C/Re(11-21), as shown in Figure 3 and then tested its reactivity in electrochemistry. We have found that Pt-ML/C/Re(11-21) exhibits higher reactivity for hydrogen evolution reaction (HER) than pure Re(11-21) and Pt(111). This finding illustrates the potential for future studies of nanostructured bimetallic system relevant to electrocatalytic reactions. A detailed characterization of the Pt monolayer on faceted C/Re(11-21) surface as a function of carbon coverage will be the subject of future studies to elucidate the role of carbon in stabilizing the Pt ML on faceted C/Re(11-21). Note that our previous studies show that Pt is not able to induce faceting of the Re surface due to the fact that Pt does not "float" on the Re surface.

**Future Directions**

In the coming year, we will build on our current results and continue our work on faceting of metal surfaces, growth of metallic nanoclusters on the faceted metal surfaces, synthesis of nanoscale model (electro)catalysts of metal...
(Pt, Pd and Au) monolayer (ML) on clean and C-covered faceted metal surfaces, (electro)catalytic reactions on clean and metal-covered planar and faceted metal surfaces with focus on structure sensitivity and size effects in the reactions related to environmental applications and hydrogen production. It is important to note that the PI has long term collaboration with colleagues at the National Synchrotron Light Source (NSLS) to perform HRXPS studies, which allow us to identify the nature of surface oxygen on the oxygen-modified faceted metal surfaces.

**Publication list**