

V.N.24 Nanoscale Surface Chemistry and Electrochemistry of Clean and Metal-Covered Faceted Substrates: Structure, Reactivity and Electronic Properties

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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, macroscale 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_{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_2H_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

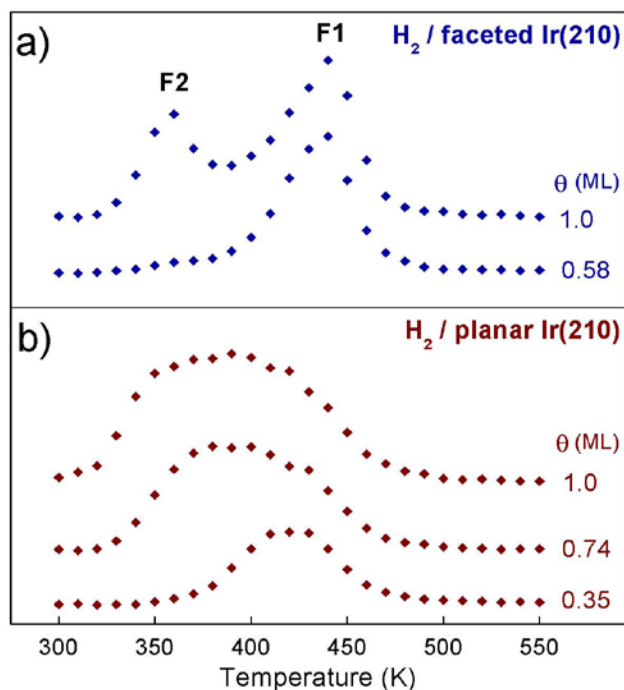


FIGURE 1. TPD spectra of H_2 from (a) planar and (b) faceted Ir(210), pre-exposed with H_2 at 300K.

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_2H_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), (311 \square), and (110) faces. Upon adsorption, C_2H_2 dissociates to form acetylide (CCH) and H species on the Ir surfaces at low C_2H_2 precoverage. For adsorption of NO on C_2H_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_2H_2 precoverage, although the reaction is completely inhibited at high C_2H_2 precoverage. Coadsorbed C_2H_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_2O . For adsorption of NO

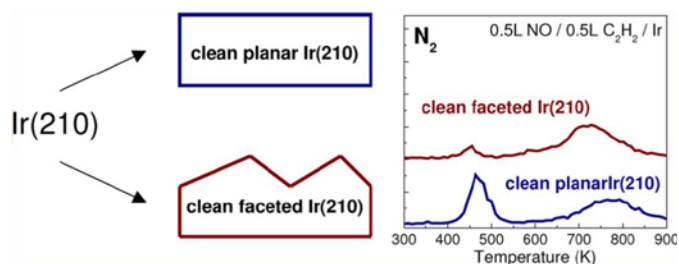


FIGURE 2. Schematic diagram of O-induced faceting of Ir(210) and a comparison of TPD spectra of N_2 from adsorption of 0.5L NO on planar and faceted Ir(210) pre-exposed to 0.5L C_2H_2 at 300K.

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_2H_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_2H_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 $NO+C_2H_2$, 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_2H_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

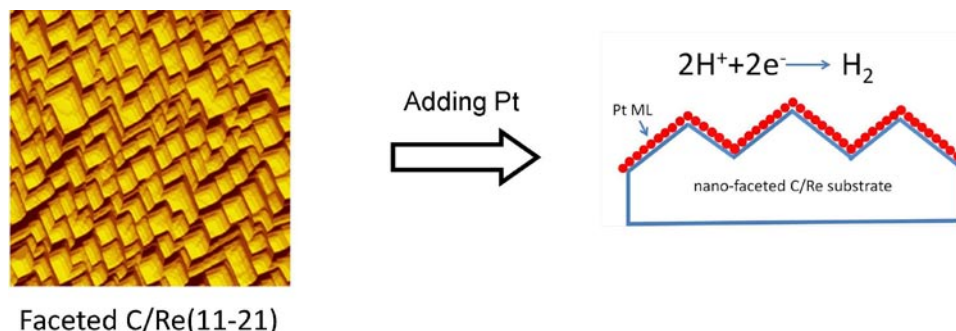


FIGURE 3. STM image of faceted C-covered Re(11-21) surface and a schematic diagram of synthesizing nanoscale model Pt electrocatalyst using nano-faceted C/Re metal substrate.

(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

1. Chen, W., Shen, Q., Bartynski, R.A., Kaghazchi, P., and Jacob, T., Reduction of Nitric Oxide by Acetylene on Ir Surfaces with Different Morphologies: Comparison with Reduction of NO by CO *Langmuir* **2013** 29 (4) 1113-1121..
2. Yang, X., Koel, B.E., Wang, H., Chen, W., and Bartynski, R.A., Nano-faceted C/Re(11-21): Fabrication, structure and template for synthesizing nanostructured model Pt Electrocatalyst for hydrogen evolution reaction, *ACS Nano* **2012** 6 (2) 1404-1409.
3. Chen, W., Bartynski, R.A., Kaghazchi, P., and Jacob, T., Oxidation of CO by NO on planar and faceted Ir(210) *J. Chem. Phys. C* **2012** 136 (22) 224701.
4. Kaghazchi, P., Jacob, T., Ermanoski, I., Chen, W., and Madey, T.E., New surfaces stabilized by adsorbate-induced faceting *J. Phys.: Condens. Matter* **2012** 24 (26) 265003.
5. Shen, Q., Chen, W., Wang, H., and Bartynski, R.A., Morphological Stability of Oxygen- and Nitrogen-covered Ru(11-21) *J. Phys.: Condens. Matter* to be submitted
6. Kaghazchi, P., Jacob, T., Chen, W., and Bartynski, R.A., TPD and DFT studies of adsorption and desorption of hydrogen on planar and faceted Ir(210) *J. Am. Chem. Soc.* To be submitted.
7. Kaghazchi, P., Jacob, T., Junno, G., Chen, W., and Bartynski, R.A., Morphological Stability of C-covered Re(11-21) *Phys. Rev. B.* to be submitted
8. Wang, H., and Madey, T.E., O-induced metastable facet formation on Re(11-21) *Phys. Rev. B.* to be submitted
9. Yang, X., Feng, T., Hsueh, C.-L., Wang, H., Chen, W., Koel, B.E., and Bartynski, R.A., Au-induced Nano-faceting of Re(11-21) in preparation.
10. Chen, W., and Bartynski, R.A., Applications of Nano-Faceted Metal Surfaces in preparation.
11. Shen, Q., Baier, R., Govind, Chen, W., Madey, T.E., Bartynski, R.A., Au-induced Faceting of Re(12-31), in preparation.