Communication

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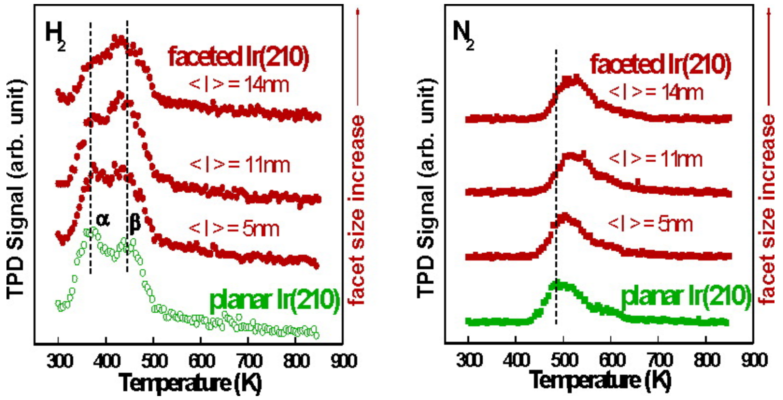
J. Am. Chem. Soc., **2005**, 127 (14), 5014-5015• DOI: 10.1021/ja042617c • Publication Date (Web): 19 March 2005



Journal of the American Chemical Society is published by the American Chemical Society. 1155 Sixteenth Street N.W., Washington, DC 20036

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Decomposition of Ammonia and Hydrogen on Ir Surfaces: Structure Sensitivity and Nanometer-Scale Size Effects

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We report measurements of structure-sensitive reactions on Ir surfaces that can be prepared reversibly in situ with different surface morphologies, from planar to nanometer-scale facets. Nanoscale facets of specific crystal orientations and various sizes are formed on the planar oxygen-covered Ir(210) surface upon annealing at $T \geq 600$ K, and a clean faceted surface can routinely be prepared in situ by heating in hydrogen at 400 K.[1] Recent studies indicating structure sensitivity of NH_3 decomposition on Ir(100)[2] with respect to Ir(111)[3] as well as C_2H_2 decomposition on planar Ir(210) versus faceted Ir(210)[4] suggest that nanoscale-faceted Ir(210) is a promising candidate substrate for investigating structure sensitivity and size effects in important catalytic reactions. The decomposition of ammonia is a potential source for on-site generation of hydrogen for fuel cell applications.[5] NH_3 decomposes on many metallic substrates, but N_2 desorbs from Ir at a temperature lower than that of other transition metals,[2,6−8] thus reducing potential N self-poisoning problems.

Temperature-programmed desorption (TPD) spectra are acquired in an ultrahigh vacuum (UHV) chamber described previously.[4] Scanning tunneling microscope (STM) images are obtained in a separate UHV chamber.[9] Research purity NH_3, H_2, and O_2 are used without further purification, and the gases are dosed from the background. The Ir(210) sample is heated resistively and by electron bombardment as described previously.[4] Clean planar Ir(210) is obtained by heating to 1700 K in O_2 (5×10^{-8} Torr) followed by flashing to 1700 K in UHV. The surface cleanliness is confirmed by Auger electron spectroscopy (AES) and TPD, while the surface structure is monitored by low-energy electron diffraction (LEED) and STM. The three clean faceted Ir(210) surfaces used in this study are generated in two steps. In the first step, oxygen-covered faceted Ir(210) is obtained by annealing clean planar Ir(210) in O_2 (5×10^{-8} Torr) at 600 (2 min), 950 (2 min), and 1700 K (flash), respectively, and subsequent cooling in O_2 to 300 K. A representative STM image of faceted Ir(210) is shown in Figure 1. In the second step, clean faceted Ir(210) is prepared by removing surface oxygen from oxygen-covered faceted Ir(210) via reaction with H_2 (5×10^{-9} Torr) at 400 K. Atomically clean facets prepared in this way retain their original size and structure.[1] Faceted Ir(210) is covered by three-sided nanometer-size pyramids exposing two different kinds of facets (one (110) face and two {311} faces on each pyramid).[1] The average facet size $\langle l \rangle$ increases in the order: 600 K-faceted (5 nm) < 950 K-faceted (11 nm) < 1700 K-faceted (14 nm),[1,9] where $\langle l \rangle$ is calculated from the average facet number density $\langle n \rangle$ as $\langle l \rangle = \langle n \rangle^{-1/2}$. The LEED beam sizes change with the facet size; the bigger the facet size, the sharper the LEED beams.[1,9]

Figure 2 displays H_2 TPD spectra following adsorption on clean planar and clean faceted Ir(210) at 300 K. There are two peaks from faceted Ir(210) at saturation coverage, while only one broad peak is seen from planar Ir(210), indicating structure sensitivity in recombination and desorption of H_2. The 360 K peak (A) can be tentatively ascribed to H_2 desorption from the (110) faces, and the 440 K peak (B) to the {311} faces, a conclusion based on several observations. The ratio of integrated peak areas is in qualitative agreement with the surface area ratio of the (110) and {311} faces; only one H_2 desorption peak from other Ir surfaces is seen following adsorption at room temperature.[10−12] The peak desorption temperature for H/Ir(110) is 380 K,[12] which agrees well with peak A. In addition, Payne et al. have found a 50 K increase in H_2 desorption peak temperature between fcc Rh(110) and Rh(311).[13] Therefore, peak B at a temperature higher than that of peak A is not unexpected since Ir has identical fcc structure and similar H_2 chemistry as that of Rh.[14] As expected, for fractional monolayer coverage, only the high binding state (B) is populated because of rapid diffusion of H adatoms from the (110) faces to the {311} faces. The breadth of the spectra from planar Ir(210) may be attributed to the existence of multiple inequivalent high coordination adsorption sites (e.g., 4-fold sites) since H atoms generally prefer sites of high coordination.[15]

When clean Ir(210) is dosed with NH_3 at 300 K and then heated, the dominant desorption products (>97%) are H_2 and N_2 with traces of NH_3 desorption (<3%), indicating that Ir(210) is highly active in NH_3 decomposition. Figure 3 shows TPD spectra for recombi-

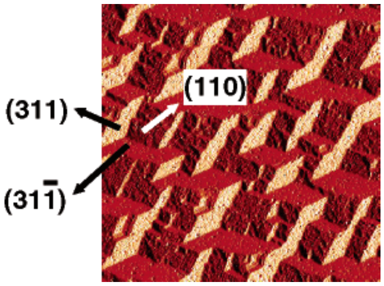

Figure 1. STM derivative image (100 nm × 100 nm) from an oxygen-covered faceted Ir(210) prepared by flashing Ir(210) in O_2 (5×10^{-8} Torr) to $T > 1700$ K and subsequent cooling in O_2 to 300 K. Following a flash anneal in O_2, facets form as the crystal cools below ∼1150 K.

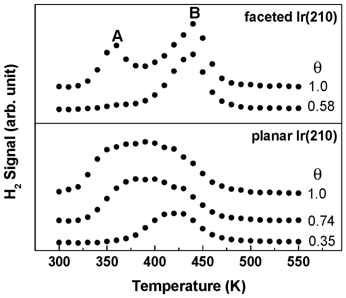

Figure 2. TPD spectra of H_2 from clean planar Ir(210) and clean faceted Ir(210) ($\langle l \rangle = 14$ nm) following adsorption at 300 K. The sample heating rate is ∼5 K/s. Coverages are expressed as a fraction of saturation coverage at 300 K.

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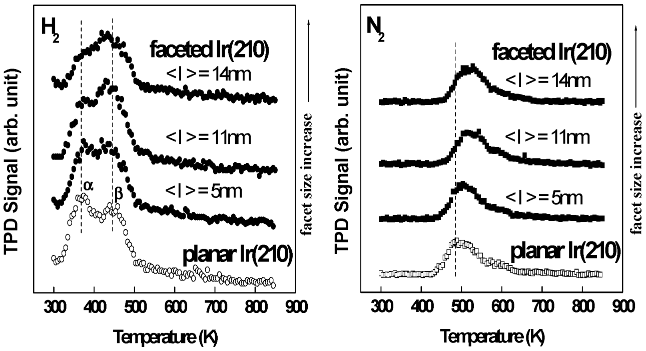

Figure 3. TPD spectra of H_2 (a) and N_2 (b) from clean planar Ir(210) and clean faceted Ir(210) with different facet sizes following adsorption of 5.0 L of NH_3 at 300 K. The sample heating rate is ∼2.5 K/s.

native desorption of H_2 and N_2 from NH_3 on clean planar and faceted Ir(210) with different facet sizes. These spectra show a pronounced evolution as the facet size varies and exhibit structure sensitivity in thermal decomposition of NH_3 on planar versus faceted Ir(210). On planar Ir(210), there are two H_2 peaks labeled α and β with the intensity higher for α than for β. On faceted Ir(210), as facet size increases, the relative α and β intensities change; the ratio of α to β decreases as facet size increases. In the case of N_2, both planar and faceted Ir(210) display broad peaks, and the peak temperature for faceted Ir(210) is higher than that for planar Ir(210). Furthermore, the N_2 peak temperature increases with facet size. Such size effects on pure elemental metal surfaces have not been reported previously. This demonstrates that faceted Ir(210) is an excellent model nanocatalyst for studying size effects in surface chemistry in the absence of any support material or any other adsorbate, both of which are known to considerably influence catalytic activity. Notably, size effects in acetylene reactions have been observed on bimetallic nanofaceted Pd/W.[16,17]

Significantly, the N_2 desorption peak temperature from NH_3 on Ir(210) (∼500 K) is much lower than that on W (≥1000 K),[6] Fe (∼900 K),[7] and Mo (∼1350 K),[8] which are also very active for NH_3 decomposition. This suggests that self-poisoning by N is less of a problem on Ir than on other metal catalysts. Reactor studies (0.01−1 Torr) show that the NH_3 decomposition rate is faster on Ir by several orders of magnitude than that on other metals (Pd, Pt, and Rh).[18] Iridium's high reactivity for breaking N−H bonds and low temperature for N_2 desorption imply that Ir may be a promising catalyst component to produce CO_x-free H_2 for fuel cell applications. The lower N_2 desorption temperature from Ir is attributed to the lower bond energy of Ir−N than that of X−N (X = W, Mo, or Fe).[19] Moreover, W, Mo, and Fe form nitrides, while Ir does not.[20]

The high reactivity of Ir(210) in breaking N−H bonds might be associated with the presence of low-coordination C_6 sites [six nearest-neighbors (nn)] on the surface.[4] The size effects in NH_3 decomposition on faceted Ir(210) can be attributed to the finite areas of facet planes and to the effects of edges, corners, and defects introduced by formation of faceted surfaces. Although (110) and {311} facets do not contain the C_6 sites present on planar Ir(210), both contain C_7 sites.[21] The fact that faceted Ir(210) is also very reactive in breaking N−H bonds indicates that low coordination Ir edge and corner atoms (nn = 6) at the boundaries of the facet planes may be active toward N−H bond scission. Although faceted Ir(210) with smaller facet sizes has a relatively high density of Ir edge and corner atoms, the concentration of these atoms is much lower than that of C_6 sites on planar Ir(210). This suggests that the edge and corner atoms alone cannot account for the high reactivity of faceted Ir(210) in NH_3 decomposition; C_7 sites on the facet planes may also favor N−H bond scission, although they are less active than C_6 sites on planar Ir(210). The strong dependence of NH_3 reaction kinetics on facet size, as evidenced by the change in H_2 spectra profiles and N_2 desorption peak temperatures, clearly illustrates that controlling facet size on the nanoscale can substantially change the catalytic reactivity of Ir toward NH_3 decomposition. A detailed study of decomposition mechanisms for NH_3 on planar and faceted Ir(210) will be reported elsewhere.[22]

In summary, we find clear evidence for structure sensitivity in recombination and desorption of H_2 and in thermal decomposition of NH_3 on clean planar versus clean faceted Ir(210). In addition, we show evidence for size effects in NH_3 decomposition over faceted Ir(210) on the nanometer scale; this experiment allows the study of size effects in surface chemistry on an unsupported monometallic catalyst with well-defined crystal structure and controlled size, without switching from sample to sample.

Acknowledgment. This work is supported in part by the U.S. Department of Energy (DOE), Office of Basic Energy Sciences.

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JA042617C