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Nano-faceting of the Ru $(1\,1\,\bar{2}\,0)$ surface

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ABSTRACT

Nano-faceting of Ru $(1\,1\,\bar{2}\,0)$ induced by NO_2 is studied by scanning tunneling microscopy (STM), low energy electron diffraction (LEED) and Auger electron spectroscopy (AES). The surface becomes fully faceted and covered with oxygen upon annealing the sample at $T \geqslant 650$ K in NO_2 (10^{-8} Torr) and the faceted surface is stable in ultra high vacuum (UHV) for sample temperatures <850 K. The kinematical LEED simulations and STM results show that the faceted surface consists of uniform long ridges running along [0 0 0 1] direction with four facets $(1\,0\,\bar{1}\,1)$, $(0\,1\,\bar{1}\,1)$, $(1\,0\,\bar{1}\,\bar{1})$, and $(0\,1\,\bar{1}\,\bar{1})$ on the ridges.

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Faceting as a form of self-assembly has been recognized for many years as a general phenomenon [1–3]. Faceting seldom occurs for a clean metal surface since the anisotropy of surface free energy is usually small, but a surface can become faceted when it is covered with adsorbates. There are many overlayer/substrate systems that exhibit faceting, including oxygen covered Pt(2 1 0) [4], oxygen and nitrogen covered Re surfaces [3,5], and gas covered vicinal Cu surfaces [2]. Faceted surfaces can be used as model catalysts to study structure sensitivity and size effects in catalytic reactions due to their well-defined structure and controlled facet sizes. For example, evidence for structure sensitivity and size effects has been found in acetylene reactions on planar and faceted Pd/W(1 1 1) [6] and in ammonia decomposition on planar and faceted Ir(2 1 0) [7], respectively. Faceted surfaces can also be used as nanotemplates for growth of catalytically active metal particles. The growth of Co nanoparticles with narrow size distribution has been achieved on faceted O/Re $(1\,2\,\bar{3}\,1)$ where Co particles nucleate preferentially along troughs [3,8].

Here we report a study of faceting of the Ru $(1\,1\,\bar{2}\,0)$ surface. Ru catalysts proved to be highly active for partial oxidation of methane [9]. Bulk Ru has a hexagonal close-packed (hcp) structure with unit cell parameters $a = 0.2706$ nm and $c = 0.4282$ nm [10]. The ideal structure of the Ru $(1\,1\,\bar{2}\,0)$ surface, as shown in Fig. 1a, is characterized by zig-zag chains along the [0 0 0 1] direction. As shown in the stereographic projection in Fig. 1b, the $(1\,1\,\bar{2}\,0)$ plane is near to several close-packed planes that can be potential facets, such as $\{1\,0\,\bar{1}\,1\}, \{1\,1\,\bar{2}\,2\}$, and $\{1\,0\,\bar{1}\,0\}$. Although the surface is rather smooth, with only two atomic layers exposed, the surface becomes faceted by annealing the sample in NO_2 at elevated temperatures.

All experiments were performed in two UHV chambers with base pressures better than 2×10^{-10} Torr. One chamber is equipped with Auger electron spectroscopy (AES), low energy electron diffraction (LEED), and quadrupole mass spectrometry (QMS). The other contains AES, LEED, and an Omicron scanning tunneling microscope (STM). In the first chamber, the sample temperatures were measured using a type-C thermocouple that was spot-welded to the back of the sample, while in the latter chamber a pyrometer was used. The Ru $(1\,1\,\bar{2}\,0)$ crystal is 10 mm in diameter and 1 mm thick. The sample was cleaned by cycles of *e*-beam heating in O_2 (1×10^{-7} Torr) followed by flashing in vacuum to 1600 K [11]. NO_2 and O_2 (both from Matheson Tri-gas) were used to dose the Ru surface by backfilling the chambers. All exposures shown here are in Langmuir (1 L = 10^{-6} Torr s = 1.3×10^{-4} Pa s) and are uncorrected for ion gauge sensitivity.

NO_2 was used to dose the Ru $(1\,1\,\bar{2}\,0)$ surface in this study as it is an effective source for atomic oxygen upon interaction with surfaces [12]. We first dosed the Ru $(1\,1\,\bar{2}\,0)$ surface with O_2 at room temperature and determined the saturation oxygen coverage, which is defined as 1 ML O. The relative oxygen coverage for a given NO_2 dose is determined by normalizing the measured O/Ru Auger peak height ratio to the saturation value. Shown in Fig. 2 is the oxygen uptake curve on the Ru $(1\,1\,\bar{2}\,0)$ surface by dosing NO_2 on the surface at 800 K. The relative oxygen coverage, 1.16 ML, is achieved at 20 L NO_2 dose. AES measurements show only oxygen; no nitrogen exists on the faceted surface after the sample was dosed with NO_2 at elevated temperatures ($\geqslant$400 K) (the inset of Fig. 2).

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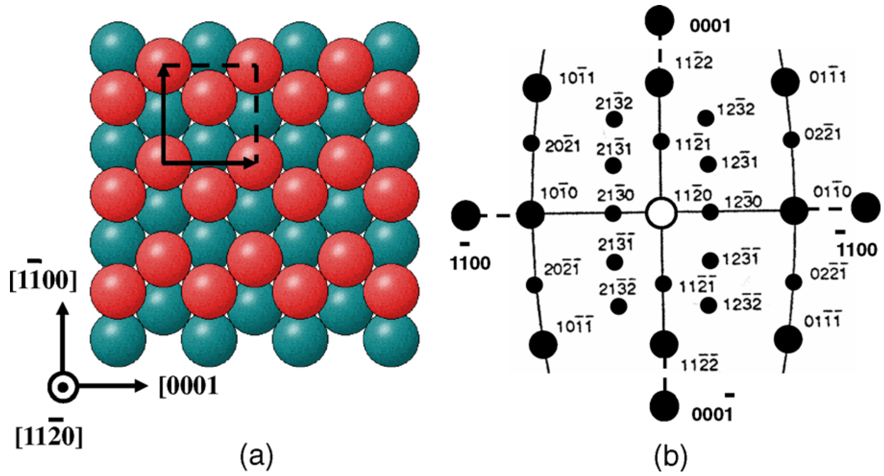

Fig. 1. (a) A hard-sphere model of the bulk-truncated Ru (1 1 $\bar{2}$ 0) surface with a unit cell marked. (b) The stereographic projection of the hcp structure on the (1 1 $\bar{2}$ 0) plane. The (1 1 $\bar{2}$ 0) plane is labeled by an open circle.

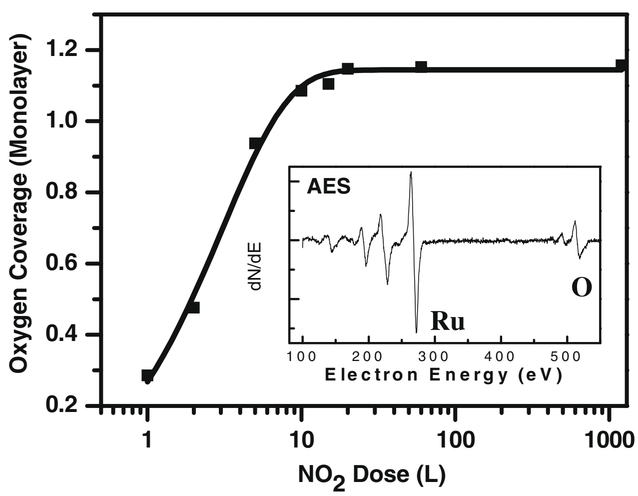

Fig. 2. Oxygen uptake curve on Ru (1 1 $\bar{2}$ 0) following exposing to NO_2 at 800 K. The oxygen coverage increases again at much higher NO_2 doses, which will be reported elsewhere. The inset to the figure is the AES spectrum of the faceted surface performed after dosing 20 L NO_2 at 800 K, indicating no nitrogen, only oxygen on the faceted surface. The nitrogen peak will appear at 379 eV if it adsorbs on the surface.

Fig. 3a shows a typical LEED pattern of the clean Ru (1 1 $\bar{2}$ 0) surface obtained with the incident electron energy (E_e) of 68 eV. All the spots are characteristic of a (1 × 1) structure. When E_e increases, all the diffraction spots move and converge to the center of the LEED screen. No new features appear in the LEED patterns when the surface is exposed to NO_2 up to 360 L at room temperature except for a decrease of the (1 × 1) spots and an increase in the background intensity.

Dosing NO_2 onto the sample at elevated temperatures causes new features in LEED patterns. Fig. 3b shows a typical LEED pattern at E_e = 70 eV from a faceted surface prepared by dosing 60 L NO_2 at 800 K and then cooling in vacuum to room temperature. The LEED pattern is different from that of the planar surface and all the spots are from the faceted structure. The diffraction spots of the faceted structures do not converge to the screen center, but move in four different directions towards their specular beams when E_e increases. The four specular beams lie out of the LEED screen and thus it is difficult to determine the facet orientations directly by comparing the specular beam positions of facets with the LEED spots from the planar surface [5]. However, following moving spots from the facets can provide a clue. Mark a_1 represents a spot from a facet and when E_e increases, a_1 moves symmetrically relative to [1 $\bar{1}$ 0 0] and [0 0 0 $\bar{1}$] towards its specular beam (as shown in Fig. 3b and c). Combined with the stereographic projection of hcp structure on (1 1 $\bar{2}$ 0) plane (Fig. 1b), (1 0 $\bar{1}$ 1) plane can be chosen as the potential facet. Similarly, the other three facet candidates are (1 0 $\bar{1}$ 1), (0 1 $\bar{1}$ $\bar{1}$), and (0 1 $\bar{1}$ 1) based on the directions of motion of a_2, a_3, and a_4. The four planes are spatially symmetric to (1 1 $\bar{2}$ 0) and have the same surface structure.

For surface faceting, the combination of facets must maintain the original macroscopic orientation of the planar surface. For Ru (1 1 $\bar{2}$ 0), the four planes above meet that requirement. Based on the two dimensional lattice of {1 0 $\bar{1}$ 1}, kinematical simulations of the LEED patterns were performed to verify the facet orientations [5]. Simulated LEED patterns of several incident electron energies were performed and the results are in good agreement with the LEED patterns observed experimentally. Simulated LEED pattern of Fig. 3b is shown in Fig. 3d. The spots are dense along the arcs on the LEED patterns (for example, see Fig. 3b), indicating that there are reconstructions on the facets. The simulation results confirm the presence of a reconstruction on the facets and suggest that all the facets have (1 × 3) reconstruction. The tilt angle between {1 0 $\bar{1}$ 1} and the (1 1 $\bar{2}$ 0) plane is 40.6°, which is a large value, and thus the angle between the specular beam of the facets and incident electron beam is 81.2°, larger than the half-maximum acceptance angle of the LEED screen (60°), which explains that the specular beams of the four facets all lie outside the screen.

The morphological phase transition of the surface occurs only in a narrow temperature window but within a wide NO_2 dose range. We studied faceting of the surface at various dosing temperatures from 300 K to 1000 K for NO_2 exposures of 20 L and 60 L. For both exposures, the surface becomes fully faceted at the temperature of 650 K. Below the threshold temperature of 600 K, the surface remains planar although it is still covered with oxygen. The faceted surface remains unchanged for NO_2 exposure from 20 L to 1200 L dosed at 800 K as revealed by LEED.

The oxygen-covered faceted surface transforms to a planar surface at a sample temperature of 850 K when annealing in UHV for three minutes. The transformation is attributed to the reduced oxygen coverage as revealed by AES. Thus the remaining oxygen