

Summary Abstract: The reaction of saturated and unsaturated hydrocarbons with single crystalline surfaces of iridium^{a)}

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When studying the reactions of hydrocarbon molecules on transition metal surfaces, it is valuable to find similarities in the reaction chemistry of molecules which vary widely in structure. Such similarities are then characteristic of the surface and of the resulting surface species. Here, the reactions of several hydrocarbon molecules on the reconstructed Ir(110)-(1×2) surface and on the close-packed Ir(111) surface are considered. The Ir(110)-(1×2) surface has been shown to reconstruct by a missing row model in which every other row of surface atoms in the [001] crystallographic direction are absent.¹ The surface can be pictured as a series of two-layer deep troughs, the sides of which are (111) microfacets.

The adsorption and dehydrogenation of cyclopropane^{2,3} and of propane⁴ on the Ir(110)-(1×2) surface have been studied previously in this laboratory by techniques including thermal desorption mass spectrometry and low-energy electron diffraction (LEED). These studies have been extended recently to include three other hydrocarbon molecules which also contain three carbon atoms, namely propylene, propyne, and allene. Despite the diverse nature of the electronic and the geometric structure of these molecules, their surface chemistry is dominated by the presence of reactive β'_2 adsites on this surface. These adsites are believed to be the asymmetric fourfold sites in the troughs between the (111) microfacets. That such an adsite is critical to this particular dehydrogenation pathway is confirmed further by studies of propane, cyclopropane, and propylene on the close-packed Ir(111) surface.

On the Ir(110)-(1×2) surface, the most striking similarity between the five hydrocarbon molecules under consideration is their irreversible adsorption at temperatures on the order of 130 K or below, and their further dehydrogenation upon heating. Even for propane, the initial probability for irreversible chemisorption is unity at temperatures as low as 130 K. Saturation coverages, in molecules cm^{-2} , of the irreversibly absorbed molecules are $(1.1 \pm 0.3) \times 10^{14}$ for propane, $(2.1 \pm 0.2) \times 10^{14}$ for cyclopropane, and 2.5×10^{14} or greater for propylene, propyne, and allene. Thermal desorption spectra of hydrogen subsequent to the adsorption of these hydrocarbons always exhibit two features at low coverages, a β'_2 adstate at 400 K, and a γ adstate at 550 K. The β'_2 adstate is similar in temperature maximum and intensity to the β_2 adstate of hydrogen on the clean surface,⁵ indicating that it originates from hydrogen bound to the metal surface. The γ adstate has been shown by annealing and attempted repopulation experiments to originate from hydrogen de-

sorbing in a reaction-limited manner from hydrocarbon fragments. The γ fragments are stable with respect to dehydrogenation by the vacant β'_2 adsites when the surface is annealed to 400 K. However, postadsorption of these hydrocarbons on small precoverages of deuterium in the β_2 adstate shows exchange into the γ adstate in thermal desorption, proving that the (stable) fragments undergo exchange on the surface. LEED studies have shown that the presence of the hydrocarbon fragments or of the surface carbon resulting from complete dehydrogenation does not affect the stability of the surface reconstruction.

The stoichiometry of the hydrocarbon fragments can be calculated from the thermal desorption of hydrogen. In each case, the value is C_3H_2 at low coverages. In a previous study in this laboratory of ethane, propane, isobutane, and neopentane,⁴ similar thermal desorption spectra of hydrogen were observed. The stoichiometry of the stable fragment generally could be explained by considering that alternate carbon atoms of a chain were dehydrogenated below 400 K by β'_2 adsites, forming a metallocycle. The bridging carbon atom, along with its substituents, remained to form the γ fragment. (Ethane, with only adjacent carbon atoms, exhibited no γ adstate.) Such an argument can be applied to cyclopropane as well to explain the stoichiometry of its γ fragment. The other species containing π bonds do not have two hydrogen atoms bonded to the central carbon atom. However, if 1, 2 hydrogen shifts to the central carbon atoms are assumed to occur, as is suggested by the exchange experiments, then the stoichiometry of these adsorbed hydrocarbons is also explained by this model. It must be emphasized that there is yet no spectroscopic proof for such structures, however. It is the regularity in the stoichiometry of the hydrocarbon fragments from widely varying adsorbates which strongly suggests a common structure for hydrocarbon fragments. The metallocycle structure is a consistent model of what such a structure may be, and has been inferred previously in classical studies.⁶

At higher coverages, all five hydrocarbons adsorbed reversibly on the irreversibly adsorbed overlayers. In addition, propylene, propyne, and allene exhibit irreversibly absorbed adstates which appear to be formed through reaction with the π bond electrons, as opposed to being formed through dehydrogenation by β'_2 adsites. At high surface coverages, the β'_2 adsites are saturated, and the chemistry is then particular to each hydrocarbon. Similarly, when the β'_2 adsites are poisoned by surface carbon or by sufficient precoverages of CO, no irreversible absorption occurs.

The importance of the β'_2 adstate, and that its presence is due to the "stepped" nature of the reconstructed surface, has been confirmed further by studies of propane, cyclopropane, and propylene on the Ir(111) surface. For the species which do not contain π bonds, very little reactivity is observed. An approximate estimate (assuming that the saturation coverage for hydrogen corresponds to one hydrogen atom per iridium surface atom) suggests that less than 2×10^{13} molecules cm^{-2} adsorb irreversibly. This would imply that the number of hydrogen adsorption sites involved is approximately $1.5 \times 10^{14} \text{ cm}^{-2}$, which could be accounted for as sites occurring on the crystal edge and at surface defects. Propylene, however, has been found to be approximately as reactive on this surface as on the Ir(110)-(1 \times 2) surface, with a saturation coverage of the irreversibly absorbed overlayer of $(2 \pm 0.5) \times 10^{14}$ molecules cm^{-2} . Apparently, no particular adsite dominates the Ir(111) surface chemistry, in con-

trast to the importance of the β'_2 adsite on the Ir(110)-(1 \times 2) surface (especially insofar as the adsorption of paraffins is concerned).

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Summary Abstract: The adsorption and decomposition of N₂O on Ru(001)^{a)}

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Several studies of the linear triatomic N₂O as a ligand in the inorganic chemistry of Ru have appeared in the literature.¹ One question addressed in these studies concerns the mode of bonding: Ru-N-N-O or Ru-O-N-N? In the present work, we have used high resolution electron energy loss spectroscopy (EELS) and thermal desorption mass spectroscopy (TDMS) to investigate the adsorption of N₂O on the Ru(001) surface; the results are compared with the inorganic chemistry of Ru-N₂O complexes. We find evidence that N₂O binds to Ru(001) at 75 K via the N atom in both vertical and inclined configurations, and that chemisorbed N₂O both desorbs molecularly and decomposes to N₂(g) and O(ads) when the surface is heated.

Figure 1 shows a series of EEL spectra recorded for the adsorption of N₂O on Ru(001) at 75 K. For low exposures [~ 0.8 langmuir (L)], the spectra are dominated by dipolar features at 2290 cm^{-1} (N-N stretch), 1290 cm^{-1} (N-O stretch) and 230 cm^{-1} (Ru-N₂O vibration). The additional feature at 470 cm^{-1} is assigned to the N-N-O bending mode of the adsorbed species, and its weak intensity indicates, via the surface dipole selection rule, that N₂O is terminally bonded in a nearly vertical configuration. The absence of features at 280 and 2200 cm^{-1} due to adsorbed N₂² and at 500–550 cm^{-1} due to adsorbed oxygen³ indicates that decomposition is not detectable for adsorption at 75 K. For N₂O exposures > 2 L, the NNO bending mode appears at

540 to 560 cm^{-1} , and its intensity grows more rapidly with increasing exposure than the intensities of the modes at 1290 and 2290 cm^{-1} . This suggests that an inclined linear configuration is dominant at high surface coverages, as has been observed at all coverages for N₂O on Pt(111).⁴ Also visible in the spectra for exposures > 2 L is a band at 2570 cm^{-1} . This feature is assigned to the first overtone of the NO stretch, appearing with enhanced intensity due to Fermi resonance with the fundamental band at 2290 cm^{-1} .⁵ The N₂O monolayer in contact with the substrate is filled at an exposure of 10 L, and the coverage is approximately twice that at 3 L.

The EELS bands at 2290, 1290, and 540–560 cm^{-1} can be compared with the corresponding gas phase vibrations at 2224, 1286, and 588 cm^{-1} , respectively.⁵ The appearance of a "blue shift" of the N-N stretch from 2224 to 2290 cm^{-1} upon adsorption, while the NO stretch is unchanged, suggests that N₂O bonds via the N end of the molecule. A similar conclusion was reached by Umbach and Menzel⁶ who deduced from ultraviolet photoemission spectroscopy that bonding to Ru(001) at low coverages occurs via the 7 σ orbital, localized on the N end of N₂O. This assignment is also consistent with the most probable bonding of N₂O in Ru complexes,¹ and of N₂O on Pt(111).⁴

When the surface is heated to 115 K following a low exposure (0.8 L N₂O at 75 K), a new EELS feature grows at 490–500 cm^{-1} as the other peaks decrease in intensity. This fea-