Effect of Carbon Modification on a Vanadium(110) Surface: Observation of Surface Reactivities Characteristic of Platinum-Group Metals

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Figure 1. HREELS spectra recorded after the adsorption of CO on (a) clean V(110) and (b) carbon-modified V(110) at 80 K. The CO exposure was 0.4 L (1 L = 10⁻⁶ Torr·s) for both surfaces. The C/V(110) surface was characterized by a C/V ratio of 1.0.

One of the most intriguing aspects of early transition-metal carbides is that they often show electronic, crystallographic, and catalytic properties similar to those of platinum-group metals (Ru, Os, Rh, Ir, Pd, Pt).[1] For example, it has been reported by Levy and Boudart that tungsten carbide (WC) has Pt-like catalytic properties.[2] A fundamental understanding of how carbide formation modifies the electronic and/or structural properties of early transition metals is, therefore, of practical importance in both catalysis and material science. We have used a vanadium-(110) single-crystal surface as a model system to investigate the effect of carbon modification. Using carbon monoxide and ethylene as probing molecules, we have found that the reactivities of vanadium are significantly modified by surface carbide formation. For example, CO adsorption changes from *dissociative* to *molecular* as carbide is formed on the surface. More interestingly, the decomposition of ethylene on clean and on carbon-modified vanadium produces different reaction intermediates. Ethylidyne species (CCH₃), which, on metals, *are produced exclusively on platinum-group surfaces*, are detected on carbon-modified vanadium surfaces.

The experiments reported here were carried out in an ultra-high-vacuum (UHV) chamber described previously.[3] The vibrational data were collected by using a high-resolution electron energy loss spectrometer (HREELS). The V(110) surface was cleaned by repeated cycles of Ne⁺ sputtering at 600 K (1.0 kV; 3 μA) and annealing at 1300 K. The impurity levels of residual C and S were less than 2% and 1%, respectively, based on Auger electron spectroscopy (AES); the residual O impurity on the surface was estimated by HREELS measurements to be less than 0.06 ML (monolayer).[4] Carbon-modified vanadium surfaces, with atomic ratios of carbon/vanadium in the range of 0.02–1.0, were produced by exposing the clean V(110) surface to ethylene or 1,3-butadiene at 600 K.[4] Although the intensity of the HREELS (0,0) beam depended strongly on the degree of carbide formation, we did not observe any well-characterized LEED pattern for the carbon-modified V(110) surfaces.[4] Finally, AES measurements of the C(KLL) Auger transition showed the characteristic line shape of carbides.

Figure 1 shows a comparison of HREELS spectra recorded after the adsorption of CO on clean an on carbon-modified V(110). As on other early transition-metal surfaces,[5] CO interacts very
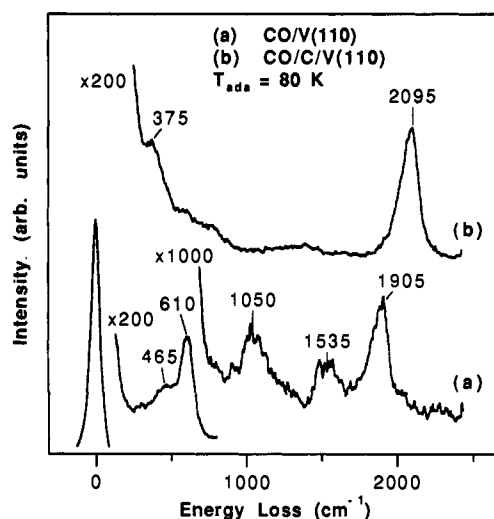
strongly with V(110), as indicated by the observation of an unusually low ν(CO) vibrational frequency at 1050 cm⁻¹ (Figure 1a). Off-specular HREELS results[6] allowed us to assign this 1050-cm⁻¹ feature to V–CO–V, i.e., both carbon and oxygen ends of CO bonded to the vanadium surface. By comparison with organometallic literature, such a low ν(CO) frequency corresponds to a CO bond order approximately 1,[7] representing a substantial reduction from the gas-phase CO bond order 3. Our combined HREELS, temperature-programed desorption (TPD), and AES results indicate that these V–CO–V species are the precursor states for the thermally-induced dissociation of CO bonds at temperatures above 150 K.[6] As discussed in detail elsewhere, vibrational features at 465 and 610 cm⁻¹ in Figure 1a are contributed mainly from residual oxygen impurities (<6%), whereas the 1535- and 1905-cm⁻¹ features are CO species bonded on defect and 2-fold bridging sites, respectively. These two types of CO species also dissociate via the V–CO–V precursor.[6]

The formation of carbide introduces significant changes in Figure 1b; CO molecules adsorb on the terminal sites in the conventional-bonding configuration (i.e., bonded via the carbon end only), as indicated by the characteristic ν(CO) and ν(V–CO) modes at 2095 and 375 cm⁻¹, respectively. HREELS and TPD results demonstrate that these terminal CO species desorb molecularly from the C/V(110) surface, i.e., no thermal decomposition.[6] The comparison in Figure 1 thus indicates that the thermal decomposition channel of CO is inhibited by the surface carbide formation, most likely by preventing the onset of V–CO–V species.

The relative amounts of molecular and dissociative adsorption of CO on transition-metal surfaces have often been used as an indication of the degree of electronic interaction between metal d-orbitals and 2π* antibonding orbitals of CO.[8] The propensity of adsorbed CO to dissociate on early transition-metal surfaces has been often related to the rather diffuse d-orbitals of these metals, which allow a greater degree of d–2π* overlap. In turn, this gives rise to the formation of M–CO–M species with substantially weakened CO bonds. On the other hand, the absence of thermal decomposition on low-index surfaces of group VIII (with the exception of Fe) and group IB metals[8] has been attributed to less d–2π* overlap. This favors the adsorption configuration with only the carbon end of CO bonded to the surface. The

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8876   *J. Am. Chem. Soc., Vol. 115, No. 19, 1993*

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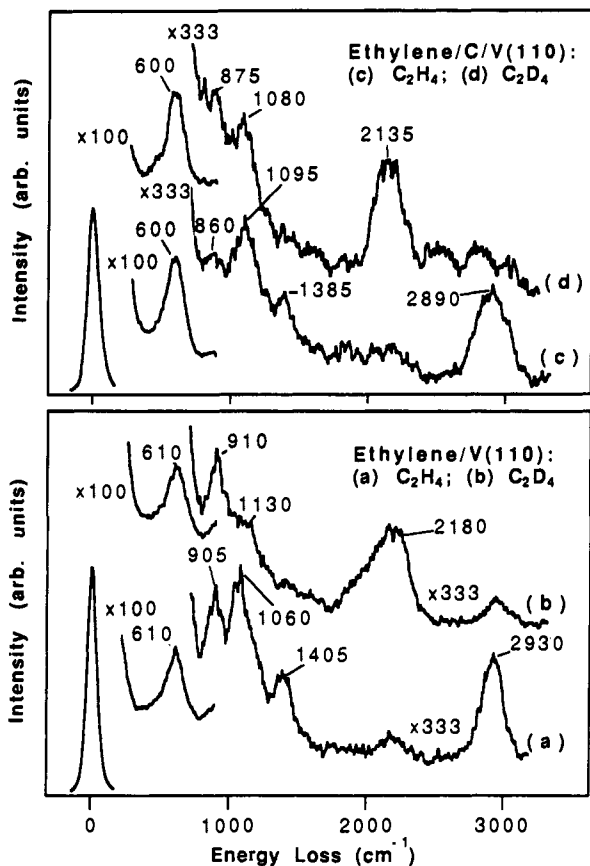
Figure 2. Comparison of HREELS spectra of ethylene on clean V(110) (spectra a and b, bottom) and on carbon-modified V(110) (spectra c and d, top). The adsorbed layers were prepared by exposing 1.0 L ethylene to all surfaces at 80 K followed by heating to 150 K. The C/V(110) layers were characterized by a C/V ratio of 0.33. The vibrational features at 600–610 cm^{-1} in Figure 2 are related mainly to ν(V–C) and ν(V–O) modes and will be discussed in detail elsewhere.[4]

Table I. Comparison of Vibrational Frequencies (cm^{-1}) of Ethylene on Clean V(110) and Those of Di-σ Ethylene Species[a]

mode	on V(110) (this work)	di-σ C_2H_4/Pt(111) (ref 9)	$C_2H_4Br_2$ (ref 10)
CH_2-stretch (s)	2930 (2180)	2920 (2150)	2953 (2174)
CH_2-scissor (s)	1405 (1130)	1430 (1150)	1420 (1141)
CH_2-wag (s)	1060	980 (740)	1278 (947)
ν-CC	905 (910)	1050 (910)	1019 (1014)

[a] The frequencies given in parentheses are those for deuterated compounds.

results shown in Figure 1, therefore, indicate that the formation of carbide on vanadium modifies the surface properties in a way consistent with changing the nature of d-orbitals of vanadium to mimic transition metals on the right side of the periodic table. More details concerning the electronic vs. structural modification on the adsorption of CO on carbon-modified V(110) will be discussed elsewhere.[4]

This interpretation is supported more clearly and is shown in Figure 2 by comparing the reaction of ethylene with clean and

Table II. Comparison of Vibrational Frequencies (cm^{-1}) of Ethylene on Carbon-Modified V(110) and Those of Ethylidyne Species[a]

mode	on C/V(110) (this work)	CH_3C/Pt(111) (ref 9)	$(CH_3C)Co_3(CO)_9$ (ref 11)
ν-CH_3 (s)	2890 (2135)	2890 (2080)	2888
δ-CH_3 (s)	1385 (?875)	1350 (990)	1356 (993)
ν-CC	1095 (1080)	1130 (1160)	1163 (1182)

[a] The frequencies given in parentheses are those for deuterated compounds.

carbon-modified vanadium surfaces. On the clean surface (Figure 2a and b), the characteristic vibrational frequencies are assigned to a strongly bonded di-σ species, V–CH_2–CH_2–V. The vibrational assignment is compared in Table I to the di-σ species observed on Pt(111)[9] and to $C_2H_4Br_2$.[10] The di-σ species decomposes at temperatures above 175 K on clean V(110),[4] due most likely to the strong interaction of metal d-orbitals with the $p\pi^*$ antibonding orbitals of adsorbed ethylene.

On the other hand, the reaction of ethylene on carbon-modified vanadium (Figure 2c and d) gives rise to the formation of an intermediate that can be described as ethylidyne, CCH_3 (CCD_3). A comparison of major vibrational modes of Figure 2c and d to those of ethylidyne on Pt(111)[9] and to ethylidyne in an organometallic compound[11] is given in Table II. The observation of ethylidyne on carbon-modified vanadium provides important information concerning the reactivities of these surfaces, since the formation of ethylidyne is generally *characteristic of platinum-group metal surfaces*.[12] Thus, as for CO, the formation of carbide changes the surface reactivities of vanadium to those typically observed on platinum-group metals for the reaction with ethylene.

Furthermore, formation of ethylidyne is almost exclusively reported on the close-packed planes of platinum-group metals with 3-fold symmetries, a requirement related to the bonding of ethylidyne to three surface atoms. On the carbon-modified V(110) surfaces, we found that the intensities of the three normal modes related to the formation of ethylidyne, $\nu_s(CH_3)$, $\delta_s(CH_3)$, and $\nu(CC)$, depend strongly on the carbon coverage and reach maxima near a C/V atomic ratio of 0.33. Assuming that carbon occupies the quasi-3-fold hollow sites on V(110), such a C/V atomic ratio would give rise to a uniform overlayer structure with each carbon modifying three vanadium surface atoms, i.e., consistent with the 3-fold symmetry requirement.

In summary, surface reactivities of clean vanadium are substantially modified by the formation of carbides. Especially, these results demonstrate the close relationship between the surface reactivities of carbon-modified vanadium and those of platinum-group metals. These results also suggest that single-crystal surfaces can be used as model systems to study carbon modification, thereby allowing one to apply modern surface science techniques to obtain fundamental information. Detailed XPS and NEXAFS experiments are in progress to investigate the electronic and structural properties of these model carbide surfaces.

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