Infrared spectroscopy of CO adsorbed on hydrocarbon-covered Mo(100)

M. Kaltchev and W.T. Tysoe *

Department of Chemistry and Laboratory for Surface Studies, University of Wisconsin-Milwaukee, Milwaukee, WI 53201, USA
E-mail: wtt@csd.uwm.edu

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The adsorption of CO at high pressures (up to 120 Torr) on a hydrocarbon-precovered Mo(100) surface is studied by reflection–absorption infrared spectroscopy (RAIRS). It is shown that CO adsorbs reversibly on the Mo(100) surface even in the presence of a thick ($\sim C_8$) carbonaceous layer and forms a saturation coverage of about 20% of that on clean Mo(100). Although CO is used as a probe molecule, this result confirms that, under high pressure, the reactants still can adsorb on the catalyst in spite of the presence of a thick carbonaceous layer formed under the reaction conditions.

Keywords: molybdenum, low-index single-crystal surfaces, propylene, carbon monoxide, chemisorption, catalysis

1. Introduction

One of the central conundrums in relating surface chemistry scrutinized under ultrahigh vacuum and the corresponding reactions carried out under catalytic conditions at higher pressures is the difference in the range of pressure over which reactants adsorb on the surface in each régime. Thus, saturation of most catalytic reactants is attained in ultrahigh vacuum after exposure to pressures of $\sim 1 \times 10^{-6}$ Torr for a few seconds (langmuirs exposure), whereas reaction rates during catalysis, and presumably the corresponding surface coverages, vary over much larger pressures ranges (Torr to atmospheres). Consequently, there exist fundamentally difference pressure ranges for each régime. Part of the resolution of this problem lies in the fact that the catalyst's surface often rapidly becomes modified by the reactant so that, for example during reaction involving hydrocarbons, the surface becomes covered by a strongly bound carbonaceous layer, where the nature of this layer depends on the surface, the reactant and reaction conditions. This was first discovered on Pt(111) following ethylene hydrogenation [1], where an ethylidyne layer was identified. This layer was found to react sufficiently slowly with hydrogen that it could not itself be responsible for the formation of the reaction product, ethane [2,3]. It was further discovered that ethylene could not adsorb onto the ethylidyne-covered platinum surface under ultrahigh vacuum conditions, so that it was suggested that the role of the ethylidyne species in the catalytic reaction might be to act as an agent for the transfer of hydrogen, which had dissociated on the metal surface, to an ethylene relatively weakly adsorbed on the hydrocarbon (ethylidyne) layer [1]. More recently, it has been demonstrated using sum-frequency generation spectroscopy that π-bonded ethylene *can* adsorb onto an ethylidyne-covered Pt(111) surface where approximately 4% of saturation could adsorb on a surface pre-covered by ethylidyne [4–7] excluding the reaction mechanism cited above. This implies that, under high pressure conditions, reactants can adsorb onto the catalyst in spite of the presence of a strongly bound carbonaceous layer that successfully blocks access in ultrahigh vacuum.

Analogous, but much thicker, layers have also been found during hydrocarbon reactions catalyzed by molybdenum [8–10]. For example, Mo(100)-catalyzed ethylene hydrogenation proceeds in the presence of a layer which is equivalent to an adsorbed C_3 to C_6 hydrocarbon [8]. Propylene metathesis catalyzed by metallic molybdenum similarly proceeds in the presence of a layer which is equivalent to a C_8 to C_{10} hydrocarbon anchored to the surface [9]. Restart reactions, where the hydrocarbon-covered sample is moved into ultrahigh vacuum and reinserted into the catalytic reactor, show identical reaction rates as the initially clean sample, implying that reactants can indeed access the surface in spite of the presence of a rather thick layer [8,9]. This notion is tested in the following by measuring the adsorption of CO on Mo(100) which has been reacted in propylene to form a thick hydrocarbon layer ($\sim C_8$) anchored to the surface [10]. The amount of CO adsorbed onto the surface is monitored using infrared spectroscopy, where it is found that, while no CO adsorbs onto the hydrocarbon-covered surface in ultrahigh vacuum (with pressures $\sim 10^{-6}$ Torr), higher CO pressures lead to significant CO adsorption. Also, in contrast to the behavior found for ethylene adsorbed on ethylidyne-covered Pt(111) [4–7], the amount of CO accommodated onto the surface varies reversibly with the external CO pressure. CO is used as a probe molecule in this case, in spite of not being a reactant in any of the chemistry referred to above, since it has

* To whom correspondence should be addressed.

a large infrared absorption cross section and is, therefore, easy to detect [11].

2. Experimental

The infrared spectrometer has been described in detail elsewhere [12]. The sample cell used for these experiments is constructed from a 2 3/4″ flange, six-way cross which was modified by moving one flange by ∼20° to allow infrared radiation to impinge on the sample with the optimal 80° infrared incidence angle. The cell is attached to the main chamber via a gate valve which, when closed, completely isolates the infrared cell from the ultrahigh vacuum chamber and, when open, allows sample transfer into it.

The infrared optical train is mounted onto a 3″-thick optical table, that is, mounted to the same frame as the ultrahigh vacuum chamber. Light from a Midac M2000 Fourier transform infrared spectrometer is steered onto the sample via a Harrick polarizer, made by placing chevrons of germanium at the Brewster angle, and detected using a liquid-nitrogen-cooled mercury cadmium telluride (MCT) infrared detector (Grazeby Detectors, Inc.).

The infrared spectrometer is controlled using SpectraCalc software running on a microcomputer. This collected and transformed the signal and has capabilities for smoothing and plotting the data. The background and adsorbate-covered spectra were collected for ∼1000 scans depending of the desired level of signal-to-noise ratio with a spectral resolution of 4 cm^{-1}. The infrared radiation is furnished by an air-cooled Globar source incorporated into the Midac spectrometer.

The Mo(100) single crystal was cleaned using a standard protocol [13] and its cleanliness monitored using Auger spectroscopy. The thick carbonaceous layer was formed by heating the initially clean Mo(100) sample in 450 Torr of propylene at 880 K [10]. This procedure has been previously shown to form a carbonaceous layer with a thickness equivalent to approximately a C_8 hydrocarbon. The presence of carbon was confirmed in this case using Auger spectroscopy.

3. Results

Figure 1(a) displays the RAIRS spectrum collected from a clean Mo(100) surface saturated with CO at 80 K, displaying an intense peak at 2091 cm^{-1} with a shoulder at 1974 cm^{-1}, this line shape being due to coupling between adsorbed CO dipoles. This has been detected previously in electron energy loss spectroscopy [14] and assigned to the presence of CO at an atop site on Mo(100). Another lower frequency mode was detected at 1130 cm^{-1} and is assigned to the presence of CO adsorbed in the four-fold hollow site on the Mo(100) surface [14]. This feature is not shown since the spectrum of the clean surface is primarily used for calibration and since no features were detected in this

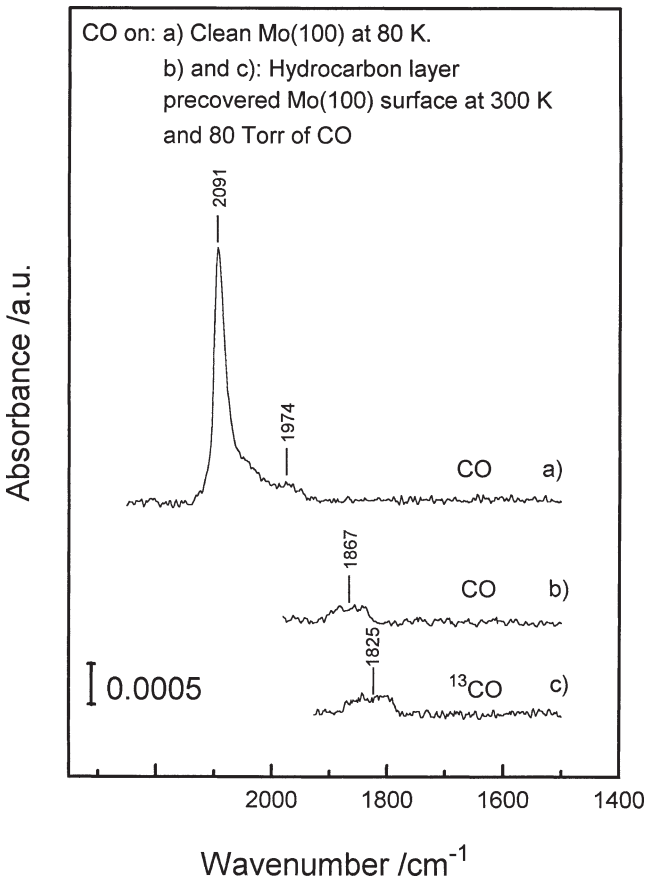

Figure 1. Infrared spectra displaying the CO stretching mode for adsorption of (a) ^{12}CO on clean Mo(100) at 80 K, (b) ^{12}CO (80 Torr) at 300 K on Mo(100) covered by hydrocarbon, and (c) ^{13}CO (80 Torr) at 300 K on Mo(100) covered by hydrocarbon.

region due to CO adsorbed on a hydrocarbon-covered surface. Exposure of the hydrocarbon-covered Mo(100) sample to several langmuirs (1 langmuir (L) $= 1 \times 10^{-6}$ Torr s) of CO results in no CO adsorption. However, pressurizing the cell to 80 Torr led to the detection of a signal due to CO on the surface (at 1867 cm^{-1}; figure 1(b)), where the signal intensity varied reversibly with CO pressure. In order to verify the signal was due to CO adsorption, the experiment was repeated using ^{13}CO and the resulting signal displayed in figure 1(c). This yields a feature at 1825 cm^{-1}, a shift of 42 cm^{-1} from the mode due to ^{12}CO, in extremely good agreement with the calculated value (41.5 cm^{-1}) confirming that CO does indeed adsorb onto the surface.

Figure 2 displays the CO coverage estimated by assuming unity coverage for the 2091 cm^{-1} signal in figure 1(a) [14] (where coverages are normalized to the density of unit cells on the (100) surface). This reveals that ∼20% of the amount that can be accommodated on the clean surface adsorbs reversibly on the hydrocarbon-covered surface. The line shown in these data represents a simple Langmuir isotherm fit to the data, although the accuracy is not sufficiently good to unequivocally confirm that this accurately describes CO adsorption.

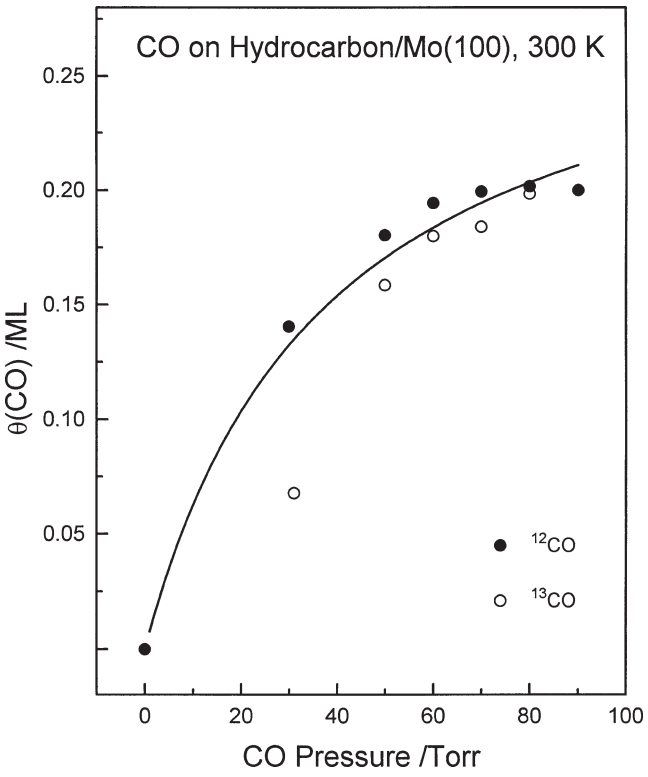

Figure 2. Plot of integrated infrared intensity, normalized to the signal for CO adsorbed on Mo(100) (at a frequency of 2091 cm^{-1}), of ^{12}CO and ^{13}CO adsorbed on a hydrocarbon-covered surface versus pressure, where the hydrocarbon layer was prepared by heating a clean Mo(100) crystal in 450 Torr of propylene at 880 K.

4. Discussion

The presence of a thick carbonaceous layer on Mo(100) completely alters the chemistry of CO on molybdenum so that, rather than saturating after an exposure of a few langmuirs on the clean metal [14], it adsorbs reversibly reaching a saturation coverage with an external pressure of 80 Torr with a behavior that closely mimics that encountered during catalysis, where coverages vary over pressures of Torr or even atmospheres. Since the surface covered by the carbonaceous layer mimics the working catalysts more closely than does a clean metal, this behavior helps rationalize differences between the pressure scales encountered in ultrahigh vacuum and under catalytic conditions since, in the latter case, the surface is substantially modified. Importantly, these data further confirm that reactants can adsorb onto the metal surface in spite of the presence of a thick, densely packed carbonaceous layer and still access the metal. In this case, reversible adsorption of CO is reasonably well described by a conventional Langmuir isotherm.

The CO stretching frequency at 1867 cm^{-1} is substantially lower than that for CO adsorbed on an atop site on Mo(100) (2091 cm^{-1}) and indicates that CO adsorbs onto a higher coordination site, possibly a bridge site. However, clearly the environment around an adsorbed CO is substantially modified, either by perturbing the carbonaceous layer or the metal underneath or both, so that it is difficult to assign an adsorption site based on previous studies of CO on clean surface. Note also that the low CO saturation coverage (∼20% of that accommodated on the clean surface) limits dipole–dipole coupling between CO molecules on the surface so that the frequency likely reflects the local geometry. In addition, the width of both the ^{12}CO and ^{13}CO features (figure 1 (b) and (c)) compared to that on clean Mo(100) (figure 1(a)) indicates that the CO adsorption environment on the carbonaceous-layer-covered surface is rather heterogeneous. Note that any surface features above ∼2000 cm^{-1} are obscured by intense gas-phase peaks so that coverages displayed in figure 2 represent a lower limit.

5. Conclusions

CO adsorbs reversibly on a Mo(100) surface, covered by a thick carbonaceous layer formed by reacting it in propylene at high temperatures (880 K) and pressure (450 Torr). It has a characteristic frequency of 1867 cm^{-1}, and ∼20% of a monolayer (referenced to a clean surface) can adsorb on the hydrocarbon-covered surface. Since the hydrocarbon-covered surface likely more closely mimics a working catalyst than does an clean Mo(100) sample, adsorption in the presence of the carbonaceous layer probably more accurately reproduces the adsorption behavior of a real catalysts than does a single-crystal sample.

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