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Publication Date
1985-09-01

Lawrence Berkeley Laboratory
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Materials & Molecular Research Division

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September 1985

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ABSTRACT

We find that the coadsorption of CO with ethylidyne, propylidyne, acetylene, fluorobenzene, benzene, and sodium on the Rh(111) surface induces ordering in the adsorbed overlayer. This phenomenon has been studied using HREELS, LEED, and TDS. HREELS indicates that the adsorbates maintain their molecular integrity when coadsorbed with CO though a change in adsorption site sometimes occurs. In all cases, the C-O stretching frequency of coadsorbed CO is substantially reduced from that of CO adsorbed on clean Rh(111) and ranges from 1410 cm^{-1} for CO coadsorbed with sodium to 1790 cm^{-1} for CO coadsorbed with ethylidyne.

INTRODUCTION

The initial discovery of CO-induced ordering of adsorbates on metal surfaces occurred during our study of the ordered structures of benzene on Rh(111) and Pt(111) surfaces (ref. 1). We found that many of the previously reported, ordered structures of benzene on these surfaces could only be reproduced by coadsorbing CO with benzene on these surfaces. Since that study, we have investigated the effect of coadsorbing CO with a large number of different adsorbates on the Rh(111) crystal surface. This paper summarizes the results of this recent study which a future publication will discuss in greater detail.

A wide variety of adsorbates on Rh(111) can be induced into ordered overlayers by coadsorption with CO. CO-induced ordering of adsorbates appears to be an excellent way to study the interactions between chemisorbed CO and other adsorbates, since the arrangement of the coadsorbates relative to each other can usually be determined once the unit cell is known. Further, the C-O stretching frequency provides insight into the chemical environment of the CO molecule within the ordered, coadsorbed structure.

The ordered, coadsorbed structures were studied using low-energy electron diffraction (LEED), high-resolution electron energy loss spectroscopy (HREELS), and thermal desorption spectroscopy (TDS). From the LEED patterns, the

periodicity and symmetry of the ordered structures were deduced. The integrity and orientation of the adsorbates within the ordered structures were determined from HREEL spectra. The relative coverages of the adsorbates within the various unit cells were determined by TDS.

EXPERIMENTAL

Our experiments were conducted in an ultra-high vacuum chamber which was equipped for LEED, Auger-electron spectroscopy, TDS, and HREELS. Our HREEL spectrometer is similar to other designs in use (ref. 2). The spectrometer was operated at an overall system resolution between 5 meV and 7.5 meV (40 cm^{-1} and 60 cm^{-1}) and with an incident beam energy of about 5 eV. The rhodium surface was cleaned by cycles of Ar^{+} sputtering, O_2 treatments, and annealing in vacuum at 1200 K. Surface cleanliness was monitored by Auger-electron spectroscopy and HREELS. The sample could be cooled to temperatures close to 77 K. During experiments, the background pressure in the chamber was typically 1×10^{-10} torr. Gases were checked for purity by mass spectrometry and used as obtained except for acetylene which was distilled from acetone using a dry ice - acetone bath. Gas dosing was performed with a capillary array doser having an enhancement factor of X 20. Sodium was dosed oxygen free using a thoroughly out-gassed SAES getter source.

RESULTS AND DISCUSSION

Table 1 lists the various LEED structures observed, the unit cell size, the types and number of adsorbates per unit cell, and the C-O stretching frequency(ies) of the adsorbed CO molecules. In several cases, M.A. Van Hove and coworkers have determined by a dynamical LEED analysis the adsorption sites of the CO molecules within the ordered structures (refs. 3,4,5); these sites are also indicated in Table 1.

As an example of CO-induced ordering, Fig. 1 shows the HREELS spectra and LEED patterns obtained when CO is coadsorbed with ethylidyne ($\equiv CCH_3$) on Rh(111). Below 270 K, ethylidyne orders, in the absence of CO, in a (2x2) lattice (ref. 6) but disorders above this temperature. Coadsorbing a quarter monolayer of CO with the disordered ethylidyne overlayer can reorder the ethylidyne into a c(4x2) lattice as shown by the uppermost LEED pattern in Fig. 1. The bottom HREEL spectrum is characteristic of the ethylidyne surface species (ref. 7); the ethylidyne vibrational spectrum does not change significantly when coadsorbed CO is present indicating that the structure of ethylidyne species does not change substantially when coadsorbed with CO. For the c(4x2) structure, the predominant C-O stretching frequency occurs at 1790 cm$_{-1}$; a recent dynamical LEED analysis of the c(4x2) CO-ethylidyne

2

structure by Van Hove et al (ref. 5) indicates that the CO is bonded at a
hollow site within the c(4x2) unit cell. (The losses at 1970 – 2010 cm^{-1}
are thought to be due to a small fraction of disordered CO adsorbed at top
sites.)

The vibrational spectra of the coadsorbates other than ethylidyne were
also obtained by HREELS both with and without the presence of coadsorbed CO;
as for ethylidyne, the vibrational frequencies of the coadsorbates do not
change significantly when coadsorbed with CO, indicating that the molecular
structure of the adsorbates does not change substantially when coadsorbed with
CO. However, a change in the adsorption site of benzene on Rh(111) may
occur when coadsorbed with CO, indicating that, for this molecule, the vibra-
tional spectra may not be very sensitive to the bonding site on the surface.

TABLE 1

CO-induced ordered structures on the Rh(111) surface.

Coadsorbate	LEED Structure*	Unit cell size (No. of Rh surface atoms)	No. of coadsorbates per unit cell	No. of CO's per unit cell	C-O stretching frequency(ies) (cm^{-1}) atoms)
--	$(\sqrt{3}x\sqrt{3})R30°$	3	0	1	2010 (top)
--	(2x2)	4	0	3	1855 (bridge)
					2060 (top)
ethylidyne ($\equiv CCH_3$)	c(4x2)	4	1	1	1790 (hollow)
propylidyne ($\equiv CCH_2CH_3$)	$(2\sqrt{3}x2\sqrt{3})R30°$	12	3	1	1750
Acetylene (C_2H_2)	c(4x2)	4	1	1	1725
Fluorobenzene (C_6H_5F)	(3x3)	9	1	2	1720
	c($2\sqrt{3}x4$)rect	8	1	1	1670
Benzene (C_6H_6)	(3x3)	9	1	2	1700 (hollow)
	c($2\sqrt{3}x4$)rect	8	1	1	1655 (hollow)
Na	$(\sqrt{3}x7)$rect	14	~3.5	7	1695
	c(4x2)	4	1	1	1410

* The notation (mxm) indicates a hexagonal unit cell with sides m times as long
as the (1x1) unit cell sides; R30° means the unit cell is rotated 30° with
respect to the (1x1) unit cell. The notation (m$\sqrt{3}$xn)rect indicates a
rectangular unit cell with sides m$\sqrt{3}$ and n times as long as the (1x1)
unit cell sides; the prefix "c" means the unit cell is a "centered" unit
cell rather than a "primitive" unit cell.
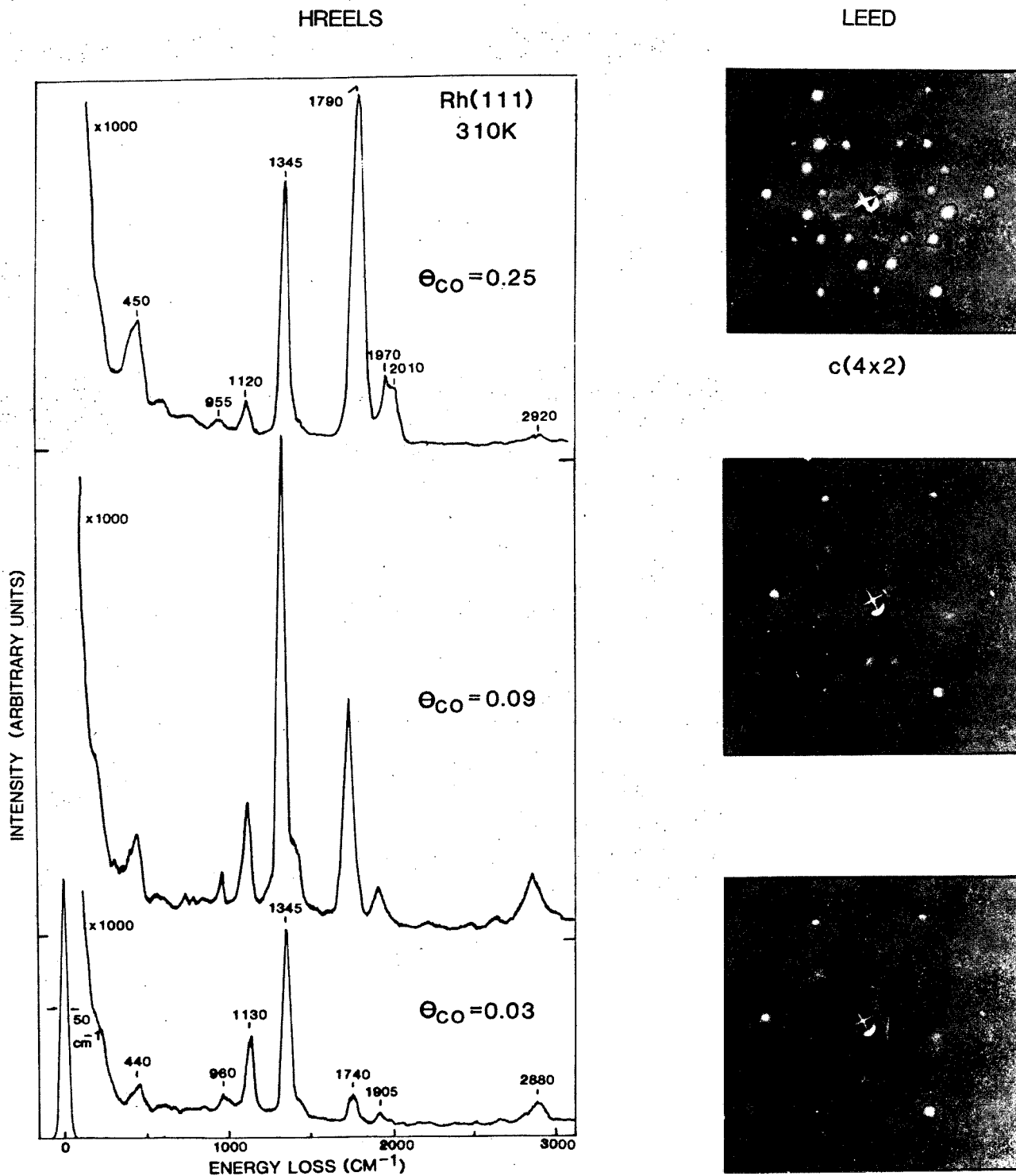
HREELS

LEED

c(4x2)

Fig. 1. HREELS and LEED patterns obtained for ethylidyne and ethylidyne plus CO adsorbed on Rh(111) at 310 K. CO coverages (θ_{CO}) are defined as the ratio of CO molecules to rhodium surface atoms.

[On the Rh(111) surface, chemisorbed benzene is thought to be centered over bridge sites in the absence of CO and over hollow sites in the presence of CO (ref. 1).]

For the few coadsorbed systems for which the structure has been determined by a dynamical LEED analysis, the CO molecule has been found to be bonded at a hollow site within the unit cell. Also, for all the coadsorbed structures studied on the Rh(111) surface, the C-O stretching frequencies are more characteristic of CO bonded to three metal atoms in metal carbonyl clusters than of bridge bonded or linearly bonded CO in these clusters (ref. 8). Therefore, CO is most likely bonded at hollow sites within all the coadsorbed structures listed in Table 1. This indicates that CO can shift adsorption sites when coadsorbed with other adsorbates, since, in the absence of other adsorbates, CO bonds only at bridge and top sites on the Rh(111) surface (ref. 3).

This shift in the CO adsorption site indicates that some interaction exists between the adsorbed CO molecules and the other coadsorbates; the C-O stretching frequency provides more insight into the nature of this interaction. The C-O stretching frequency is a sensitive probe of the chemical environment of the chemisorbed CO molecule, since, as shown in Table 1, the C-O stretching frequency changes substantially when coadsorbed with other adsorbates. On a clean Rh(111) surface, the C-O stretching frequency is ~2050 cm^{-1} for CO bonded at top sites and ~1850 cm^{-1} for bridge bonded CO; in both cases, the stretching frequency is reduced from the gas phase C-O stretching frequency of 2145 cm^{-1}. A further reduction in the C-O stretching frequency occurs for CO adsorbed in all the ordered, coadsorbed structures studied. The C-O stretching frequency ranges from 1790 cm^{-1} for CO in the c(4x2) CO-ethylidyne structure to 1410 cm^{-1} in the c(4x2) CO-Na structure.

Interactions that can cause shifts in the C-O stretching frequency of chemisorbed CO can be classified into one of two categories: Dynamical interactions, which result from the coupling between the dynamic dipole moments, and chemical interactions, which result from a weakening of the C-O bond. Dynamical interactions, however, can be ruled out as a cause of the reduced C-O stretching frequencies for coadsorbed CO, since these interactions result in an increase of the C-O stretching frequency (ref. 9). Therefore, one must resort to chemical interactions to explain the low C-O stretching frequencies observed.

The 1410 cm^{-1} C-O stretching frequency for CO in the c(4x2) structure with Na is an exceptionally low C-O stretching frequency, indicating that a strong interaction occurs between coadsorbed CO and Na. Similarly low C-O stretching frequencies (though usually not as low as with Na) have been reported for CO

5

coadsorbed with alkali atoms on other metal surfaces where the interaction between the coadsorbed CO and alkalis is thought to involve charge transfer from the adsorbed alkali atoms through the substrate into the antibonding $2\pi^*$ orbital of adsorbed CO (ref. 10). Since both Na and benzene are electron donors to metal surfaces as determined by workfunction measurements (refs. 10,11), charge transfer to the anti-bonding $2\pi^*$ of CO may be responsible for the very low CO stretching frequencies observed in the CO-Na and CO-benzene ordered structures. A similar effect may also be responsible for the broad range of C-O stretching frequencies observed when CO is coadsorbed with the other adsorbates listed in Table 1, and it may be possible to determine the relative electron donating ability of adsorbates to metal surfaces by the C-O stretching frequency of coadsorbed CO. However, other types of interactions between coadsorbates can not be ruled out.

A possible explanation of why CO induces order in an adsorbed overlayer is illustrated in Fig. 2 for CO-induced ordering of Na and ethylidyne on Rh(111). Both Na and ethylidyne form (2x2) ordered structures at low temperatures but, at higher temperatures (> 270 K), they shift away from the (2x2) lattice positions to form a disordered overlayer. Coadsorbing a quarter monolayer of CO with Na or ethylidyne blocks a large number of the Na or ethylidyne adsorption sites, thereby reducing the entropy increase associated with the order-disorder transition; consequently, an ordered overlayer becomes more energetically favorable. However, a CO molecule cannot fit into a (2x2) unit cell that already has one Na or ethylidyne, so the adsorbates must reorder into a c(4x2) lattice where the unit cell has the same area as the (2x2) unit cell, but now has room for a CO molecule to adsorb in the center due to the different shape of the c(4x2) unit cell.

CONCLUSIONS

CO-induced ordering has been observed for a large number of adsorbates on the Rh(111) surface. These adsorbates maintain their molecular structure when coadsorbed with CO. The C-O stretching frequency shifts 50 to 400 cm^{-1} lower in the coadsorbed structures studied than for CO adsorbed on clean Rh(111). Charge transfer from the adsorbates via the metal to the CO $2\pi^*$ orbital is thought to be a likely cause of the reduction of the C-O stretching frequency. Site blocking by CO is thought to be a possible cause of CO-induced ordering in the adsorbed overlayer.
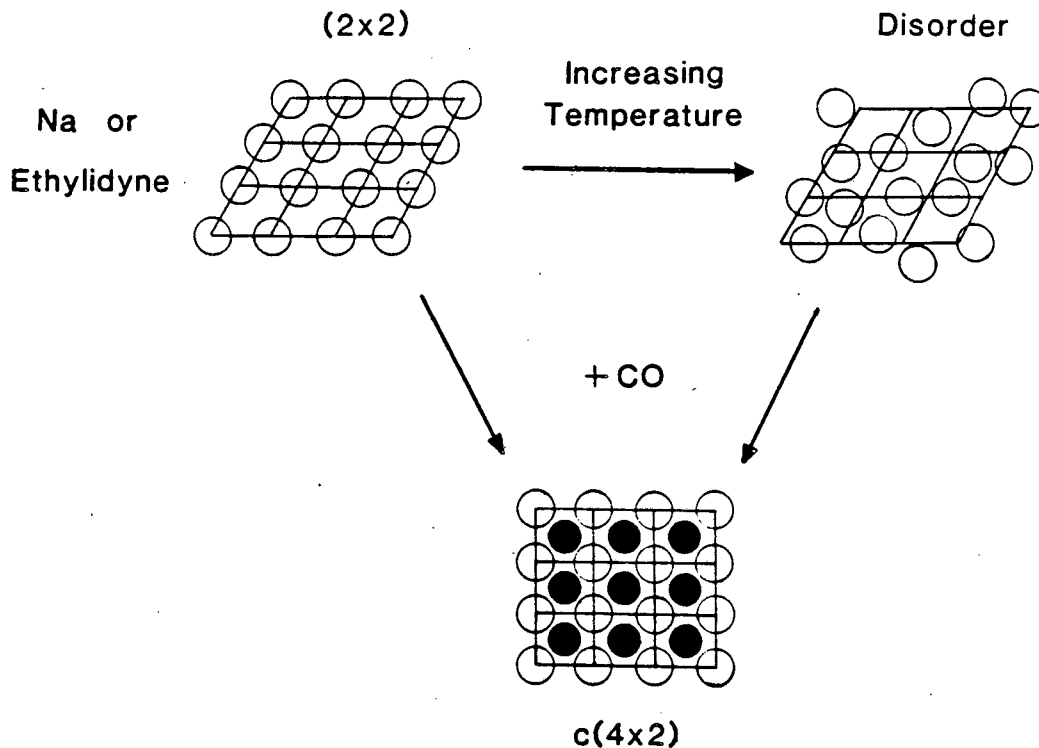
                                                           XBL 857-2938

Fig. 2. Schematic representation of the (2x2) to c(4x2) CO-induced transition
of Na and ethylidyne on the Rh(111) surface. The (○) circles represent
either Na or ethylidyne, and the (●) circles represent CO molecules.
The substrate atoms are not shown.

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