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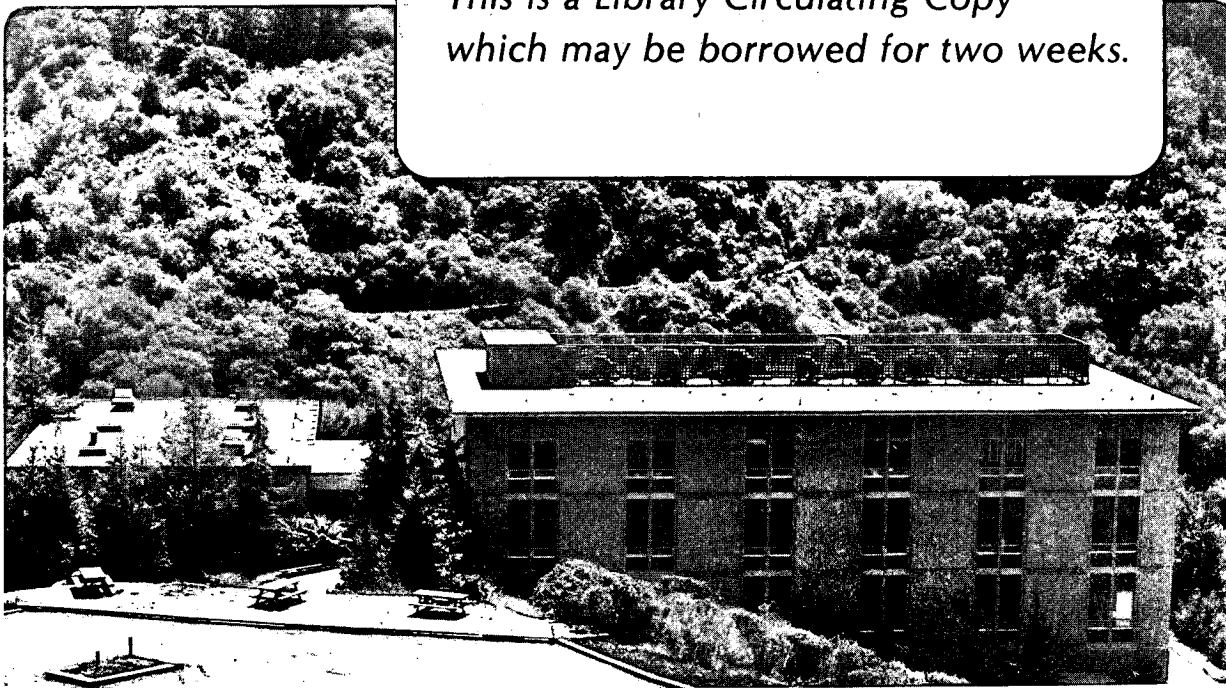
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C.-T. Kao, C.M. Mate, G.S. Blackman, B.E. Bent,
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Coadsorbate Induced Ordering on Rh(111) and Rh(100) Surfaces: Structural and Chemical Effects

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Summary Abstract

Carbon monoxide (CO) induced ordering of atomic and molecular coadsorbates on Rh(111) and Pt(111) surfaces was first observed in our laboratory^{1,2}. To further understand the interaction between coadsorbates in an ordered overlayer, the study has been extended to various pairwise combination of coadsorbates on Rh(111) and Rh(100) surfaces. The experiments were performed in three different ultra-high vacuum (UHV) chambers with a base pressure of 2×10^{-10} torr. These apparatus have been described previously³. Several experimental techniques including work function measurement, high-resolution electron energy loss spectroscopy (HREELS), and dynamical low-energy electron diffraction (LEED) structural analysis were utilized in these studies.

From the work function measurement results, a new coadsorbate induced ordering (CIO) model based on a dipole-dipole interaction is proposed to explain the mechanism of the ordering phenomenon observed on Rh(111). The appearance of a surface dipole moment upon adsorption is directly correlated with the change of the work function. The work function decreases for a positive surface dipole adsorbate and increases for an adsorbate with a negative surface dipole. We found that by coadsorbing a negative surface dipole molecule (such as CO or NO) with a positive surface dipole one (such as C_2H_3 - ethylidyne, benzene, or sodium), a new ordered structure is formed. Furthermore, a negative-negative (NO-CO) or a positive-positive ($Na-C_2H_2$, $Na-C_2H_3$, $Na-C_6H_6$) surface dipole combination either forms a disordered layer as judged by the LEED pattern, or two separate LEED patterns due to surface segregation. As the surface dipole of CO or NO is opposed in alignment to other positive surface dipole coadsorbates, this result suggests that the main driving force for the surface ordering is the attractive interaction between antiparallel dipole moments. Model calculations for ordered arrays of dipoles were done to compute the dipole-dipole interaction energies in a CO coadsorbed structure on Rh(111). In this model the surface dipole moment for each adsorbate was

extrapolated from the respective work function change, and the dipole moments of the coadsorbates were treated as point dipoles in the same plane. The interaction energies per coadsorbate pairs are calculated as the difference between the dipole-dipole interaction energy on the coadsorbed lattice, and the case where the dipoles are on two separate lattices. The energies of such a dipole-dipole interaction range from -0.09 eV for the $c(2\sqrt{3} \times 4)\text{rect-CO} + \text{C}_6\text{H}_6$ structure to -0.7 eV for the $c(4 \times 2)\text{-CO} + \text{Na}^4$. We attribute this attractive interaction energy between oppositely oriented dipoles to be the major stabilization factor for the CIO phenomena on Rh(111). A similar model may also be used to explain the induced ordering patterns on Pt(111)¹, Pd(111)⁵, and Rh(100)⁶ surfaces. [A recent study of acetylene chemisorption on Ni(111) reported a new ordered structure formed with 5 % CO coadsorption⁷. This might indicate the possibility of induced ordering on this nickel surface]. Table I summarizes the observed CO or NO LEED patterns with or without coadsorbates on different metal surfaces. The observed C-O or N-O stretching frequencies, bond lengths and adsorption sites from HREELS and LEED studies are also included in the table.

It can be seen from Table I that the C-O or N-O stretch shifts to lower frequencies by 100-600 cm^{-1} when it is coadsorbed with a positive surface dipole adsorbate. This could either be due to a shift in the adsorption site, or a weakening of the C-O or N-O bond strength. Indeed, LEED structural analyses for $c(4 \times 2)\text{-CO} + \text{C}_2\text{H}_3$ and $c(4 \times 2)\text{-NO} + \text{C}_2\text{H}_3$ prove that both CO and NO moved to hollow sites when coadsorbed with ethylidyne on Rh(111)¹¹ (without ethylidyne, CO prefers to adsorb on top site⁸, and NO prefers bridge site at 0.25 monolayer coverage²¹). A 0.02 Å bond elongation for both CO and NO also implies weakening of the C-O (N-O) bond in the presence of ethylidyne. On the Rh(100) surface, two new ordered LEED structures, $c(4\sqrt{2} \times 2\sqrt{2})\text{R}45^\circ$ and $c(4 \times 2)$, were seen by coadsorbing CO with benzene and ethylidyne respectively^{6,20}. In both cases the CO adsorption site changes from top to bridge based on HREELS results.

The chemical reactions of various organic adsorbates with or without the coadsorbed CO (or NO) was studied by HREELS as a function of temperature. The

change in the decomposition pathway of the organic overlayers were observed in both Rh(111)-CO+C₂H₂³ and Rh(100)-CO+C₂H₄⁶. In the first case, two different surface fragmentation channels were seen. Without CO, intra-molecular rearrangement from acetylene to CCH₂(vinylidene) was the major pathway. With 0.25 monolayer CO coadsorption, the disproportionation reaction from acetylene to CCH(acetylide) and ethylidyne becomes predominant. In the second case ethylene decomposes to acetylide and ethylidyne at room temperature on Rh(100). By preadsorbing a half monolayer of CO, the formation of acetylide can be selectively blocked, and ethylidyne was isolated to be the only species from the ethylene fragmentation. In both examples, the surface ethylidyne formation during the thermal fragmentation process was enhanced due to the coadsorption of CO.

Future work includes the LEED structural analysis of c(4x2)-CO+Na on a Rh(111) surface in order to understand the interaction between CO and sodium, which causes the C-O stretch to shift down to 1410 cm⁻¹ upon coadsorption². Another study extending the present work to the high step density Rh(331) surface is underway.

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Table 1: Coadsorbate Induced Ordering on Various Metal Surfaces.

Substrate	LEED Pattern	C-O (N-O) Stretch(cm^{-1})	C-O (N-O) Bond Length(\AA)	CO (NO)* Adsorption Site	Reference
Rh(111)	$(\sqrt{3} \times \sqrt{3})R30^\circ\text{-CO}$ $(2 \times 2)\text{-3CO}$	2010	1.07 ± 0.1	Top	8,9
		2060	1.15 ± 0.1	Top	8,10
	$c(4 \times 2)\text{-CO} + \text{C}_2\text{H}_3$ $(3 \times 3)\text{-2CO} + \text{C}_6\text{H}_6$ $c(2\sqrt{3} \times 4)\text{rect-CO} + \text{C}_6\text{H}_6$ $c(4 \times 2)\text{-CO} + \text{Na}$	1855	1.15 ± 0.1	Bridge	
		1790	1.17 ± 0.05	HCP Hollow	2,11
		1700	1.17 ± 0.1	HCP Hollow	1,12
		1655	1.21 ± 0.05	HCP Hollow	1,13
Pt(111)	$(2 \times 2)\text{-3NO}$	1410	—	—	2
		1840	1.15 ± 0.05	Top	14
	$c(4 \times 2)\text{-NO} + \text{C}_2\text{H}_3$ $c(4 \times 2)\text{-2CO}$	1515	1.15 ± 0.05	Bridge	
		1405	1.17 ± 0.05	FCC Hollow	11
		2100	1.15 ± 0.05	Top	15,16
		1850	1.15 ± 0.05	Bridge	
Pd(111)	$(2\sqrt{3} \times 4)\text{rect-4CO} + 2\text{C}_6\text{H}_6$ $(2\sqrt{3} \times 5)\text{rect-6CO} + 2\text{C}_6\text{H}_6$ $(\sqrt{3} \times \sqrt{3})R30^\circ\text{-CO}$ $(3 \times 3)\text{-2CO} + \text{C}_6\text{H}_6$	1800	1.15 ± 0.1	Bridge	2,17
		1815	—	—	2
		1840	1.15 ± 0.1	FCC Hollow	18,19
Rh(100)	$c(2 \times 2)\text{-CO}$ $c(4 \times 2)\text{-2CO} + \text{C}_2\text{H}_3$ $c(4\sqrt{2} \times 2\sqrt{2})R45^\circ\text{-2CO} + \text{C}_6\text{H}_6$	1735	1.17 ± 0.05	FCC Hollow	5
		2015	—	—	6
		1865	—	—	6
		1780	—	—	20

* The HCP hollow is defined as to have one second layer metal atom below the three fold site, while the FCC hollow does not have one.

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