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Hydrogenation of CO at 100 K on the Ru(001) Surface: Spectroscopic Identification of Formyl Intermediates

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An improved understanding of Fischer–Tropsch synthesis and the methanation reaction involving the catalytic reaction of CO and H_2 on transition metals to form hydrocarbons (CO bond scission) and alcohols (CO bond preserved) is of obvious industrial importance. As a result, this reaction has been studied intensely over numerous transition metals and over a wide range of temperatures and pressures. Under ultrahigh-vacuum (UHV) conditions (base pressure below 10^{-10} Torr and working pressure below 10^{-7} Torr), no reaction between CO and H_2 has been observed on single-crystalline metal surfaces. Consequently, UHV studies have been restricted to analyzing coadsorption phenomena where it is found that the CO–H interaction is repulsive, with this repulsion decreasing as one proceeds from the close-packed [fcc(111), hcp(001)] to the more open [fcc(110), bcc(100)] crystallographic orientations.[1] High-pressure studies (order of 10–100 Torr), however, have revealed a steady-state reaction between coadsorbed CO and hydrogen to produce methane (and some higher alkanes) on Ru, Ni, Pt, Pd, Ir, and Fe.[2–4] These studies show the reaction rate to be structure insensitive (i.e., independent of crystallographic orientation), and of the metals investigated, Ru was found to exhibit the highest activity. Using *ex situ* characterization of the surface, a mechanism was proposed that is based on the initial dissociation of CO, followed by hydrogenation of the surface carbon to CH_4.[2,5] However, CO chemisorbs *molecularly* on Ru, Pt, Pd, and Ir, and it is difficult to activate on these as well as on all other late transition metals. Thus, it is feasible that insertion of hydrogen into the Ru–CO bond, or vice versa, to form a H_xCO intermediate may occur,[4] a possibility supported in the organometallic literature (ref 6 and references therein). This intermediate can then dehydrate under reaction conditions to give hydrocarbons, or it can hydrogenate further to give alcohols. The initial steps involved in the hydrogenation reaction have not yet been identified, and *in situ* spectroscopy on this *reaction* system must be carried out.

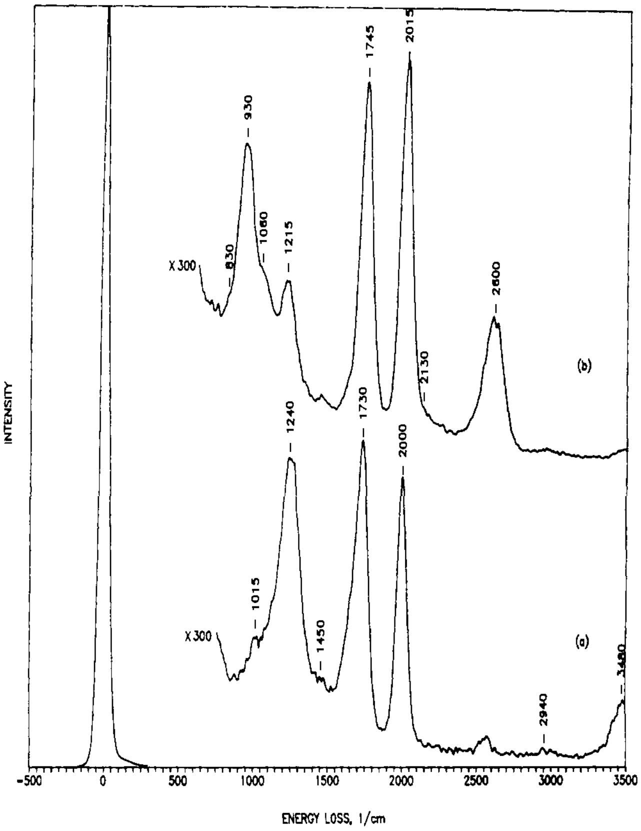
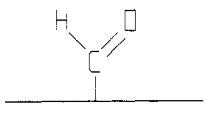


Figure 1. High-resolution electron energy loss spectra recorded after exposure of a saturated overlayer of CO on Ru(001) to "110 L" of atomic hydrogen (a), or deuterium (b), at 100 K and after annealing to 150 K. The peaks near 1200, 1700 and 2000 cm^{-1} identify η^2-HCO, η'-HCO, and chemisorbed CO respectively.

We have hydrogenated CO on a single-crystalline surface, under UHV conditions, which has allowed us to perform high-resolution electron energy loss spectroscopy (HREELS) to determine unambiguously the initial surface reaction intermediates. The preliminary spectroscopic study presented here clearly identifies η^1(C)-HCO (**1**) and η^2(C,O)-HCO (**2**) as these intermediates on the Ru(001) surface. We were able to effect reaction, under UHV conditions, by exposing gas-phase atomic hydrogen,[7] rather than molecular hydrogen, to a Ru(001) surface that is saturated with CO. By virtue of the bond dissociation energy, atomic hydrogen corresponds to a state of *much* higher chemical potential and, consequently, to a state of higher reactivity.[8] The UHV chamber in which the HREELS experiments were performed has been described previously,[11] as have the properties and method of preparation of the saturated CO overlayer, the fractional coverage of which is 0.65.[12]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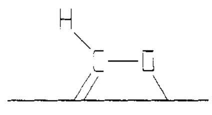
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Shown in Figure 1 are HREEL spectra recorded after exposure of the saturated CO overlayer on the Ru(001) surface to "110 langmuirs" of atomic hydrogen (Figure 1a) and atomic deuterium (Figure 1b)[13] at 100 K, followed by annealing to 150 K (to desorb

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(7) The atomic hydrogen is generated by a hot (~1800 K) tungsten filament.

(8) This reactivity is verified by the observation that the saturation fractional coverage of hydrogen on Ru(001), θ_H, is 1.5 by dosing atomic hydrogen;[9] the saturation coverage of dissociatively chemisorbed molecular hydrogen is unity.[10]

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(13) The atomic hydrogen exposure is calculated in terms of the background molecular hydrogen pressure, since the dissociation efficiency of the hot filament is unknown. Note that 1 langmuir = 10^{-6} Torr·s.

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Table I. Mode Assignments for η^1-HCO Produced by CO Hydrogenation on Ru(001), with Corresponding Assignments for the Model Compounds $CH_3O(HCO)$[a] and RhOEP(HCO) [OEP = octaethylporphyrin][b,c]

mode	η^1-HCO	CH_3O-(HCO)	RhOEP-(HCO)	η^1-DCO	CH_3O-(DCO)
ν(CO)	1730	1754	1700	1745	1739
ν(CH)	2940	2943	-	2130	2216
δ(CH)	1450	1371	-	1060	1048
π(CH)	1015	1032	-	830	870

[a] Reference 14. [b] Reference 15. [c] All frequencies are in cm^{-1}.

multilayer water that adsorbs from the background). Comparison of these spectra allows immediate identification of the peaks at 1240 and 1215 cm^{-1}, 1730 and 1745 cm^{-1}, and 2000 and 2015 cm^{-1} as being due to carbon–oxygen stretching vibrations, since there is no significant isotopic shift. We assign the 2000-cm^{-1} modes to unreacted CO; the 1700-cm^{-1} modes to a double bond between carbon and oxygen (i.e., the carbon atom has rehybridized from sp in CO to sp^2), which suggests η^1-HCO; and the 1200-cm^{-1} modes to a carbon–oxygen bond with a bond order that has nearly decreased to 1, suggesting η^2 coordination and, hence, η^2-HCO. The remaining vibrational modes of the surface formyls, which confirm their presence, are assigned as follows: δ(CH) [δ(CD)], the in-plane bend at 1450 (1060) cm^{-1}; and ν(CH) [ν(CD)], the carbon–hydrogen stretch at 2940 (2130) cm^{-1} (resolved clearly in off-specular spectra). The peaks at 1015 (830) and 1240 (930) cm^{-1} are assigned to π(CH) [π(CD)], the out-of-plane bend, of η^1-formyl and η^2-formyl, respectively. Justification for these mode assignments can be obtained by comparison with vibrational data for the model compounds $CH_3O(HCO)$ and $CH_3O(DCO)$,[14] as well as organometallic analogues,[15] for the η^1-formyl, and HREELS data describing formaldehyde decomposition on Ru(001)[16] for the η^2-formyl. The correspondence is shown in Tables I and II. The peak at 3480 (2600) cm^{-1} is assigned to the stretching mode of a small amount of adsorbed H_2O (D_2O),[17] introduced as a result of the atomic dosing procedure.

Since the hydrogenation reaction occurs with high probability at an astonishingly low surface temperature (100 K), the reaction appears to obey pseudo-Eley–Rideal (ER) kinetics, as alluded to by Harris and Kasemo,[18] where the incident hydrogen atom traps (i.e., loses the normal component of its gas-phase momentum) but does not accommodate (i.e., maintains its parallel momentum) to the surface temperature.[19] Subsequently, this atom, by virtue of the momentum retained in the parallel direction, collides and reacts with a chemisorbed CO molecule to form η^1-HCO. Herein lies the chemical advantage of the atomic hydrogen: at no point do we need to break the strong Ru–H bond, this being the major reason why the Langmuir–Hinshelwood (LH) reaction[20] is thermodynamically and kinetically unfavorable. Overlap of the nonbonding orbital of HCO with the empty metal d_σ-orbitals, along with backdonation from the filled metal d_π-orbitals into the π^*-orbital of the HCO, can then result in the more stable η^2-HCO bonding configuration. The concentration ratio of η^1- to η^2-formyls would be expected to be dictated by the electron density of the Ru surface at the Fermi level which is available for backdonation. On Ru(001), this density seems insufficient to form a uniform overlayer of the favored η^2-HCO.

Table II. Mode Assignments for η^2-HCO Produced by CO Hydrogenation on Ru(001), with Corresponding Assignments for η^2-HCO Produced by Formaldehyde Decomposition on Ru(001)[a,b]

mode	η^2-HCO		η^2-DCO	
	this study	ref 16	this study	ref 16
ν(CO)	1240	1180	1215	1160
ν(CH)	2940	2900	2130	-
δ(CH)	1450	1400	1060	980
π(CH)	1240	1065	930	825

[a] Reference 16. [b] All frequencies are in cm^{-1}.

In conclusion, we can confidently assert that we have observed the hydrogenation of CO (to formyl intermediates) on a well-characterized metal surface, under UHV conditions. A more complete discussion on this work will be presented elsewhere.[22]

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(19) We do not expect the direct ER mechanism (where the incident H atom neither traps nor accommodates to the surface before reaction) to contribute to the production of HCO because the orientation of the adsorbed CO molecule, with the oxygen (or nonreactive) end protruding from the surface, will result in a vanishingly small direct reaction cross section.

(20) Most surface reactions exhibit LH kinetics, where both reactants have trapped and accommodated to the surface before reaction.[21]

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