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ORGANOMETALLIC SURFACE CHEMISTRY: FINAL REPORT FOR PERIOD JULY 1, 1983-SEPTEMBER 14, 1986

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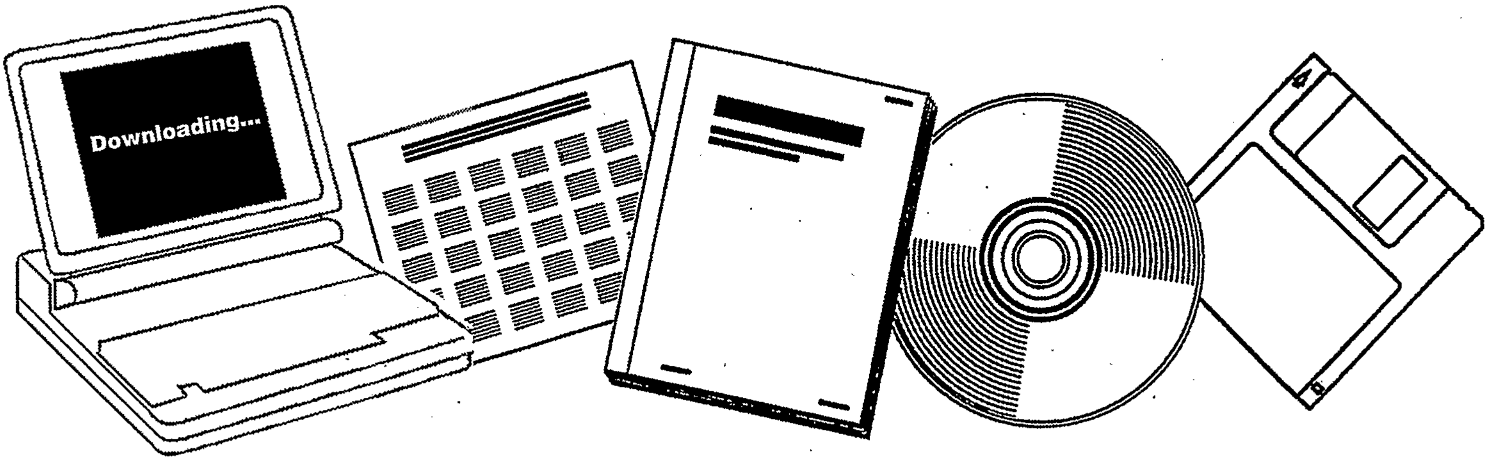

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ORGANOMETALLIC SURFACE CHEMISTRY

Final Report
for Period July 1, 1983 - September 14, 1986

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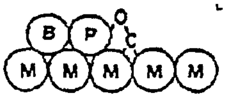
Abstract

Most of our research was directed toward the role of promoters in heterogeneous CO hydrogenation and in hydroformylation reactions. It was found that the addition of Zn to a Rh/SiO_2 hydroformylation catalyst influences the ratio of hydroformylation to ethylene hydrogenation. A maximum is selectivity toward the oxygenated products was observed at a mole ratio of 0.05 Zn/Rh. Some possible roles of zinc are site blocking and an increased rate of CO insertion by Zn(II)-OC interactions. The latter type of interaction is known to promote CO insertion in organometallic compounds. In a second area of research, CCO has been characterized by vibrational spectroscopy in $[Ru_3(CO)_9(CCO)]^{2-}$. Analogy with molecular cluster chemistry suggests that CCO is likely to form on carbided closest packed metal surfaces and vibrational spectroscopy is a promising tool for testing this postulate.

Results

Promoter Action in Fischer-Tropsch Catalysis (with Andrew Lang; William Hollenberg and W. M. Sachtler.)

We presented a model for these promoter effects based on the activation of CO by interaction of a promoter ion with the oxygen atom of a chemisorbed carbonyl. A schematic representation of this type of bonding is:



Precedence for carbon and oxygen-bonded carbon monoxide may be found in many structurally characterized organometallic compounds. In these compounds a formally positive metal ion may be bound to the carbonyl oxygen alone, or sometimes simultaneously bonded to both the carbon and oxygen of the carbonyl. It also has been found that carbon and oxygen bonding promotes a variety of organometallic reactions, including two which are important to the surface catalytic chemistry of carbon monoxide: CO cleavage and CO insertion into metal alkyl bonds. For example, rate enhancements of the order of 10^3 for the CO insertion reaction result in the presence of alkali metal ions which are known to bind to caarbonyl oxygen, and aluminum trihalides bring about enhancement factors of at least 10^8. Carbon and oxygen bonding also is strongly implicated in the cleavage of a CO ligand to produce carbidic cluster compounds.

Significantly, the Mn^{2+} promoted Rh catalyst that we have studied exhibits a band around 1530 cm^{-1}, suggesting that C- and O-bonded carbon monoxide is present. A CO stretching mode at this same frequency has been reported for C<u>O</u> on a stepped Ni surface Ni[5(111) x (110)](12) and on Fe(111). It is relevant that the 1530-cm^{-1} band on the stepped Ni surface virtually disappears upon increasing the temperature to only 310 K, and a concomitant appearance of bands at 470 and 700 cm^{-1} occurs. These observations indicate that the adsorbed C- and O-bonded CO dissociates to C_{ads} and O_{ads} with extraordinarily low activation energy. The binding of CO to these stepped surfaces is likely to be analogous to the C- and O-bonded CO in $[HFe_4(CO)^{13}]^-$, which has been induced to dissociate in homogeneous reactions. Based on these observations, it is likely that protruding atom of a stepped surface acts as an oxophilic promoter. According to the Smoluchowski theory this atom should indeed have a positive charge.

Selective Hydroformylation of Ethylene on Rh-Zn/SiO_2 (with M. Ichikawa, A. J. Lang and W. M. H. Sachtler).

As shown in Figure 1, the addition of Zn to Rh/SiO_2 increases the hydroformylation activity up to 50 times over that of the unpromoted catalyst.

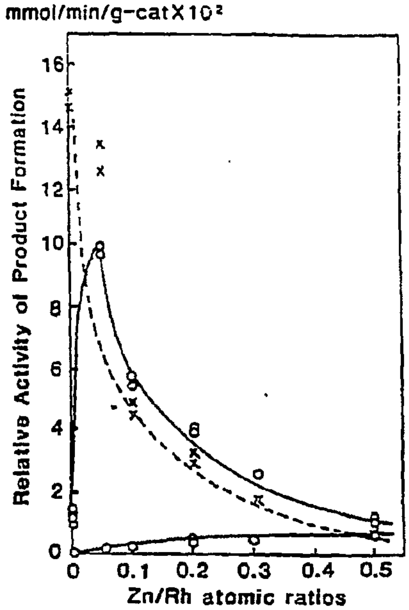
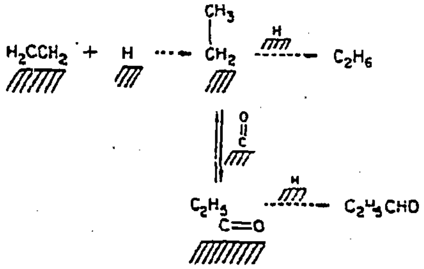


Figure 1. Rates of product formation (mmol/min/g of catalyst) C_2H_5-CHO (O), C_3H_7OH (O), and C_2H_6 (×), by changing Zn contents (Zn/Rh atomic ratios) in SiO_2-supported Rh-Zn catalysts. Catalyst; 4.0 wt % Rh loading, 0.4–0.5 g. Reaction conditions: C_2H_4:CO:H_2 = 10:10:10 mL/min, 180 ± 2 °C, 1 atm. SV = 1200 L/L/h.

Moreover, the selectivity toward hydroformylation, expressed by the ratio C_2H_5CHO/C_2H_6, is improved by a factor of 15 by the addition of Zn at Zn/Rh = 0.05-0.2. These measurements were performed in the temperature range 150-200°C. The addition of Zn also completely suppresses the formation of methane. The latter result suggests that Zn blocks sites for CO dissociation and increases selectivity toward hydroformylation. At the Zn/Rh ratio of 0.3 also CO insertion into surface ethyl groups is favored over the hydrogenation of surface ethyl groups to ethane:

Scheme II



The nature of the surface carbon monoxide was studied by infrared spectroscopy. Two strong bands at 2065 (HF band) and 1918 (LF band) cm^{-1} for CO on Rh/SiO are reasonably assigned to the linearly bonded (terminal) carbonyl and bridging carbonyl, respectively. In the absence of added Zn the two bands are of comparable intensity, but with increasing Zn content the LF band attributed to bridging CO decreases significantly and the HF band broadens and splits into a doublet (2041 and 1995 cm^{-1}) at high Zn content. In the presence of Zn, weak but distinct bands also are observed at 1620 and 1580 cm^{-1}. The dramatic change in the ratio of intensities of bridging and linear CO is similar to earlier observations with Fe-promoted Rh/SiO$_2$ and qualitatively different from the IR evidence obtained with oxophilic promoters on Rh. Clearly, a specific effect of the promoting cation is revealed. The observation is strikingly similar to that in our earlier work with Pd and PdAg alloys and strongly suggests that an analogous interpretation is valid: the multicenter or "Freundlich" sites on the Rh surface are blocked by the Zn ions, forcing the adsorbing CO molecules into the "on top" or "linear" positions. Electroneutrality requires, of course, that anions also occupy surface sites on Rh; but the striking difference between the two groups of cations would justify our interpretation that the blocking of Freundlich sites by zinc ions is dominantly responsible for the dramatic reversion of relative band intensities; i.e., CO is forced into the linear mode.

Weaker bands in the vicinity of 1600 cm-1 may arise from CO that is C coordinated to Rh and O coordinated to Zn similar to the case of the Mn-promoted Rh. These carbonyl groups may account for an apparent increase in CO insertion rate in the presence of Zn, because carbonyl interaction with electron acceptors is implicated in dramatic increases in the rate of CO insertion in organometallic compounds.

In summary, Zn atoms or ions on Rh apparently occupy Freundlich sites which block CO dissociation. The Zn also appears to increase the rate of CO insertion as indicated by an increase in selectivity for C_2H_5CHO formation.

Interaction between $HFe_4(CH)(CO)_{12}$ and Partially Dehydroxylated Alumina (with Mark A. Drezdzon, Claire Tessier-Youngs, Carrie Woodcock, Peter Miller Blonsky, Orlando Leal, Boon-Keng Teo, Robert L. Burwell, Jr.).

Judging from chemical and IR data, the initial reaction of $HFe_4(CH)(CO)_{12}$ with partially dehydroxylated alumina produces $[HFe_4(C)(CO)_{12}]^-$, which is bound to the surface. EXAFS and elution of the bound cluster indicates that evolution of CO occurs slowly by extensive loss of CO from a small number of cluster molecules. This process leads to the coexistence of intact $[HFe_4(C)(CO)_{12}]^-$ plus iron or iron carbide particles. In keeping with this interpretation, the supported material displays activities for the reduction of CO and the hydrogenation of benzene and product distributions that are typical of iron metal.

Vibrational Spectroscopic Characterization of the CCO Ligand and the Possible Occurrence of CCO on Surfaces (with Michael J. Sailor).

There is abundant evidence from metal cluster chemistry that a carbon atom capping a 3-metal array has a high affinity for CO, leading to the formation of a capping CCO group. Accordingly, we propose that CCO may exist on a carbided closest-packed metal surface in the presence of CO. For example, the surface carbide species on a Fischer Tropsch catalyst may be present as CCO. Vibrational spectroscopy represents one of the most promising methods for detecting CCO and therefore we undertook the vibrational characterization of CCO in the structurally characterized cluster $[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]^{2-}$, 1.

The cluster $[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}CCO)]^{2-}$, 1, was chosen for study by IR and Raman spectroscopy because its X-ray structure approaches C_{3v} symmetry and either or both of the CCO carbon atoms can be ^{13}C enriched. Three normal modes of A_1 symmetry in the idealized C_{3v} point group are predicted for the CCO group attached to three metals. As it turns out, these are fairly well seperated in frequency and can be described approximately as the M_3-C stretch, C-C stretch and C-O stretch.

A prominent Raman band at 319 cm^{-1} is assigned to the M_3C stretch on the basis of its polarization ($\rho = 0.12$ in CH_2Cl_2 solution). The shift in this band upon isotopic substitution (CCO vs $^{13}C^{13}CO$) is barely discernable (<u>ca</u>. 4 cm^{-1}). The predicted shift based on a simple valence force field model is 7 cm^{-1}. The C-C stretch was not evident in survey IR and Raman spectra, but it was eventually identified as a weak polarized Raman band at 1309 cm^{-1}, that shifts by 32 cm^{-1} in the spectrum of solid $[PPN]_2[Ru_3(CO)_9(^{13}CCO)]$, (Fig. 1). A shift of 25 cm^{-1} is calculated from a simple valence force field model for the Ru_3CCO moiety.

The CO stretch for the CCO ligand appears to be mixed with terminal CO stretches. For the combination of CCO and six terminal CO ligands there are three A_1 modes. Two of these can be identified at 2024 and 1980 cm^{-1} (Fig. 2) by Raman depolarization ratios and the lack of splitting in the spectra of the solid, where the E modes are split by the low site symmetry (C_1). Both the highest frequency band at 2024 cm^{-1} and the adjacent band at 1980 cm^{-1} shift in the $[Ru_3(CO)_6(\mu\text{-}CO)_3(\mu_3\text{-}{}^{13}C^{13}CO)]^{2-}$ isotopomer. Presumably a coupling between CCO and a metal-bound CO mode occurs through a dipole-dipole mechanism.

The vibrational frequencies determined for the CCO ligand on a triruthenium cluster framework should be similar to those of a CCO moiety in a threefold site on a closest packed metal surface, because the force field acting on the CCO is expected to be similar in either case. Because the vibrational modes reported here for 1 involve CCO motions normal to the face of the metal triangle, they will belong to a set of vibrations that are favored by the "surface selection rule" for adsorbates on metal surfaces.

Publications

"Promoter Action in Fischer-Tropsch Catalysis", W. M. H. Sachtler, D. F. Shriver, W. B. Hollenberg, and A. F. Lang, J. Catal., 92, 429-31 (1985).

"Selective Hydroformylation of Ethylene on Rh-Zn/SiO_2. An Apparent Example of Site Isolation of Rh and Lewis Acid Promoted CO Insertion", M. Ichikawa, A. J. Lang, D. F. Shriver and W. M. H. Sachtler, J. Am. Chem. soc., 107, 7216 (1985).

"A Chemical, FT-IR, and EXAFS Study of the Interaction Between $HFe_4(CH)(CO)_{12}$ and Partially Dehydroxylated Alumina", M. A. Drezdzon, C. Tessier-Youngs, C. Woodcock, P. M. Blonsky, O. Leal, B. K. Teo, R. L. Burwell and D. F. Shriver, Inorg. Chem., 24, 2349 (1985).

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