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Controlling the Bonding of CO Adsorbed on Cobalt Clusters by Co-adsorption of H_2[**]

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Reactions of small molecules with transition metal nanoparticles have attracted considerable interest over the past decades since they can provide a conceptual framework for applications such as heterogeneous catalysis and hydrogen storage [1-4]. The reaction of H_2 and CO with Fe and Co nanoparticles has been widely studied due to the relevance to the Fischer-Tropsch process in which a mixture of H_2 and CO is converted into long chain hydrocarbons. An important step in this process is the breaking of the strong C-O bond. Upon adsorption of CO on a suitable catalyst (Fe, Ru or Co), the electron density in orbitals that are antibonding with respect to the C-O bond is increased by transfer of electron density from the metal, ultimately leading to the weakening, or activation, of the C-O bond. This activation and therefore the reactivity of CO towards hydrogenation can be influenced by controlling the electron density of the supported metal nanoparticle.

Here we report on the co-adsorption of H_2 and CO on small cationic Co clusters (Co_n^+, n=4-20) in the gas-phase, specifically addressing the effect on the C-O bond. We discuss how H_2 adsorption modifies the C-O bond strength by controlling the electron density available for back donation. We show that each adsorbed H atom formally withdraws 0.09 – 0.25 electrons, depending on the size of the cluster. This is of general interest as it gives quantitative insights into metal-ligand interactions.

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Vibrational spectroscopy is used to monitor the CO bond strength, relying on InfraRed Multiple Photon Dissociation (IR-MPD) spectroscopy to measure the IR spectra of (hydrogenated) mono-carbonyl complexes in the range of the C-O stretch vibration (1600 - 2200 cm^{-1}). A molecular beam of cluster complexes is overlapped with a counter-propagating beam of IR photons delivered by the Free Electron Laser for Infrared eXperiments, FELIX[5]. When the frequency of the IR photons is resonant with a vibrational transition, the complex absorbs photons. Sequential absorption of multiple photons leads to heating of the cluster complex and eventually to photo induced fragmentation. IR spectra are generated by measuring the photo-induced dissociation of complexes in the molecular beam as a function of laser frequency. Details on the experimental procedures have been given before[6-8].

The IR-MPD spectra of $Co_{11}H_mCO^+$, with m = 0, 2, 4, 10, and 12 (bottom to top) are shown in Figure 1a. No absorption bands were detected in the 1600 - 1950 cm^{-1} region, indicating that CO is exclusively atop (μ^1) bound to hydrogen covered Co_n^+ clusters. This has been found earlier for CO adsorption on bare Co_n^+ clusters[9]. H_2 adsorbs dissociatively on cationic Co clusters[10]. In Figure 1b the value of ν(CO) is plotted as a function of the number of co-adsorbed hydrogen atoms for complexes containing 4, 5, 7, 9, and 11 Co atoms. Upon increasing H_2 coverage, the C-O stretch frequency, ν(CO) shifts to higher energy. This behavior was observed for all cluster sizes studied, except for Co_7^+, Co_8^+ and Co_9^+ for which we observed a decrease of ν(CO) upon adsorption of the first H_2 molecule. The C-O stretch vibration of the H saturated complexes ($Co_7H_8CO^+$, $Co_8H_8CO^+$ and $Co_9H_8CO^+$) was again higher than the value of the corresponding mono-carbonyl complex. The initial decrease of ν(CO) correlates with a particular low reactivity of these clusters towards hydrogen[11]. For the small clusters the shift of ν(CO) is linear with hydrogen coverage and the slope decreases as the clusters become larger. Larger clusters readily react with H_2 and it was experimentally not possible to measure ν(CO) at intermediate H coverage for these clusters. Values of ν(CO) for the mono-carbonyl and the hydrogen saturated mono-carbonyl complexes are given in the supporting information.

In organo-metallic chemistry the classical picture of bonding between a transition metal atom and a CO molecule consists of donation of electron density from the 5σ orbital of CO to the metal and back-donation of electron density from the metal d-orbitals to the 2π* orbital of the CO molecule[12-14]. This 2π* orbital is anti-bonding with respect to the C-O bond. The frequency of the C-O stretching vibration is directly related to the strength of the C-O bond

and therefore also to the population of the 2π* orbital. Upon adsorption of CO on a bare transition metal, the C-O bond usually becomes weaker due to the increased population of the anti-bonding 2π* orbital, which is reflected in a shift of ν(CO) to lower frequencies compared to its gas-phase value. As can be seen in Figure 1b, the co-adsorption of H_2 molecules generally leads to an increase in C-O bond strength.

Qualitatively, upon adsorption of H_2 on Co_nCO^+ complexes some electrons of the metal cluster become localized in Co-H bonds, making them unavailable for back-donation to the 2π* orbital of CO [15, 16]. Upon co-adsorption of H_2, the population of the 2π* orbital will therefore be reduced which leads to a higher C-O stretching frequency. This assumption has been used earlier to explain the shift in ν(CO) for CO bound to hydrogen covered Ni and Co particles on surfaces[17, 18].

We can use the recently measured charge dependence of ν(CO) in cobalt cluster mono-carbonyl complexes[9] to estimate the amount of charge transferred into the Co-H bonds. For example one finds for $Co_{11}CO^{+/0/-}$ values for ν(CO) of 1992, 1943 and 1868 cm^{-1}, respectively, resulting in a shift of ~62 cm^{-1}/z where $z \cdot e$ is the charge on the cluster (e the elementary charge). This can be compared to the dependence of ν(CO) on the number of co-adsorbed H atoms (m), as shown in Figure 1b, which gives for $Co_{11}H_mCO^+$ an average shift of ~8 cm^{-1} per H atom. Binding of a single H atom therefore has, on average, the same effect as adding 8/62 = 0.13 of a single positive charge to the cluster.

More generally we can extend the quantitative model[9] for the charge dependence of ν(CO) in late transition metal carbonyl clusters to present a global picture of charge transfer in $Co_n(CO)H_m^+$ complexes. The model incorporates the electrostatic interaction between the charge of the cluster and the CO dipole and the effect of donation of electron density from the metal to the 2π* orbital of CO. The cluster size plays a role due to delocalization of charge over the cluster surface. The validity of this assumption has been shown before[9][19].

The effect of co-adsorption of H_2 can be incorporated in the model by introduction of an additional term in the expression that describes the population of the 2π* orbital, $P(2\pi)$ of the CO molecule. The extended equation reads:

$$P(2\pi) = P(2\pi)_\infty - \frac{\gamma z}{n_S} - \frac{\gamma \sum_i^{n_H} \delta_i}{n_S} \qquad (\mathbf{1})$$

The first term on the right hand side of equation (1), $P(2\pi)_\infty$ is the population of the $2\pi^*$ orbital of a CO molecule adsorbed on a cluster of infinite size. The second term describes the change in this number due to the charge ($z \cdot e$) of the cluster that is distributed over all surface atoms and is inversely proportional to the number of surface atoms, n_s with a proportionality constant γ. Localization of electron density in the i^{th} Co-H bond is postulated to have the same effect as increasing the charge of the Co_nCO^+ complex by $\delta_i.e$. We allow δ to depend on i to include possible variation in Co-H bonding with coverage. Following through as described in ref. 9 one then obtains the following expression for ν(CO):

$$\upsilon(CO) = \upsilon(CO)_0 + \frac{\gamma^* \sum_i^{n_H} \delta_i}{n_s} \qquad \textbf{(2)}$$

with $\nu(CO)_0 = \nu_\infty + \Delta\nu_{ES} + \gamma^* z/n_s$ the frequency for the specific cluster size in the absence of H, and $\gamma^* = \nu_\infty \beta\gamma/2F_\infty$. Here ν_∞ is the extrapolated value of ν(CO) for CO adsorbed on an infinite cluster (with C-O stretch force constant F_∞), $\Delta\nu_{ES}$ is the shift due to the electrostatic effect and β a proportionality constant relating the population of the $2\pi^*$ orbital to the C-O stretching force constant.

If the effects of the subsequently added H ligands on $P(2\pi)$ are identical, δ_i will have the same value for each co-adsorbed H atom. This appears to be the case for small clusters with n up to 6 where $\nu(CO)$ shifts linearly with the number of co-adsorbed H atoms. In this case equation 2 can be simplified to the form

$$\upsilon(CO) = \upsilon(CO)_0 + \frac{\gamma^* n_H \delta}{n_s} \qquad \textbf{(3)}$$

where $\gamma^* \delta/n_s$ is the shift induced per adsorbed H atom and can be evaluated from the slope of the plot of ν(CO) against n_H. The solid lines in Figure 1b indicate fits of the data to equation 3. For the larger clusters we have too few points to establish with certainty that the linear relationship continues to hold but proceed using the shift measured for the saturated complexes to evaluate an average δ directly from equation 3 using the values of $\nu(CO)_0$ and γ^*/n_s as reported in the literature[9]. With our measurements the amount of electron transfer to co-adsorbed H can be quantified. The values of δ for clusters with 4-20 metal atoms are

given in Figure 2. Values of δ range from 0.09 to 0.25 electron per H atom depending on cluster size. There is no obvious correlation of this size dependence with what is known about the geometric or electronic structure of Co clusters. The observed linear relationship of ν(CO) with hydrogen atom coverage demonstrates that CO is not influencing charge transfer between the cluster and H ligands to any appreciable extent. Therefore, CO can be used as a probe for the electron density within the cluster complex, at least for the $Co_n(CO)H_2^+$ complexes.

Equation (3) predicts that as long as the ratio n_H/n_s is significant, a shift in ν(CO) will be observed. This implies that a shift in ν(CO) should be observed even for CO adsorbed on bigger particles if they are sufficiently covered with hydrogen. In fact a shift of ν(CO) to higher frequency was observed for co-adsorption of CO and H_2 on Ru/Al_2O_3, Co/SiO_2 and on Ni surfaces [18, 20-25], for which it has also been found in DFT calculations [26].

This treatment ignores the observation that for $Co_7(CO)H_2^+$, $Co_8(CO)H_2^+$ and $Co_9(CO)H_2^+$ we observe an initial red shift in ν(CO). Following the charge localization arguments outlined above, this implies that for these complexes more electron density is available on the metal compared to the mono-carbonyl complexes for donation into the 2π* orbital of CO. The behaviour exhibited by most of the complexes establishes that H atoms bound as hydrides increase ν(CO), leading to the conclusion that hydrogen might be bound very differently in the three exceptional cases. A possible explanation is that H_2 is molecularly bound in $Co_7(CO)H_2^+$, $Co_8(CO)H_2^+$ and $Co_9(CO)H_2^+$. So called non-classical hydrides, where H_2 binds molecularly are known in organo-metallic chemistry[27]. The bonding is characterized as a 3-centre, 2 electron σ interaction involving donation of charge from the H_2 to the metal centre. H_2 binding molecularly in $Co_7(CO)H_2^+$, $Co_8(CO)H_2^+$ and $Co_9(CO)H_2^+$ can therefore be expected to lower ν(CO) as is observed. Given the prevailing consensus that H_2 binds dissociatively to transition metal clusters this proposal is somewhat remarkable and warrants further study. The averaged values of δ for Co_7^+, Co_8^+ and Co_9^+ obtained from the saturated complexes are very similar to the values of the other sizes, suggesting that at hydrogen saturation all hydrogen is present in the form of hydrides.

In summary it has been shown that the 3d electron density available for back-donation to an adsorbate can be controlled by co-adsorption of H_2 molecules. Each co-adsorbed H atom reduces the amount of electron density available for back-donation on average by 0.09 – 0.25 of an electron depending on cluster size. Indications were found that H_2 could be molecularly

bound in the special cases of $Co_7(CO)H_2^+$, $Co_8(CO)H_2^+$ and $Co_9(CO)H_2^+$. From a catalysis point of view, the co-adsorption of H_2 and CO on Co particles leads to a deactivation of CO towards dissociation. If there is to be a reaction of H_2 with CO on the cluster surface at higher temperatures, we predict that low H_2 coverage clusters will show the highest reactivity. The observed relationship between ν(CO) with hydrogen atom coverage demonstrates that, at least for $Co_n(CO)H_2^+$ complexes, CO is a suitable probe for the electron density. These results point to how the concepts of donation and back-donation developed in organic-metallic chemistry extrapolate to larger systems like clusters or even extended surfaces. We hope that the availability of this quantitative data stimulates further theoretical investigations.

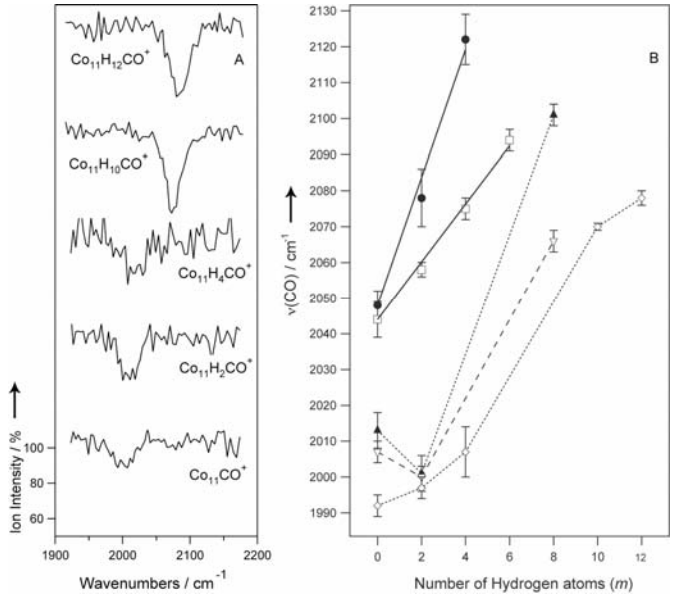

Figure 1. a) IR-MPD spectra of $Co_{11}H_mCO^+$ complexes with 0,2,4,10 and 12 co-adsorbed hydrogen atoms in the range of the C-O stretch vibration. b) Frequency of the C-O stretch vibration of mono-carbonyl complexes as a function of the number of co-adsorbed H atoms for complexes containing 4(●), 5(□), 7(▲), 9(▽), and 11(◇) cobalt atoms. The solid lines give fits of the data to equation 3. The dashed lines indicate trends.

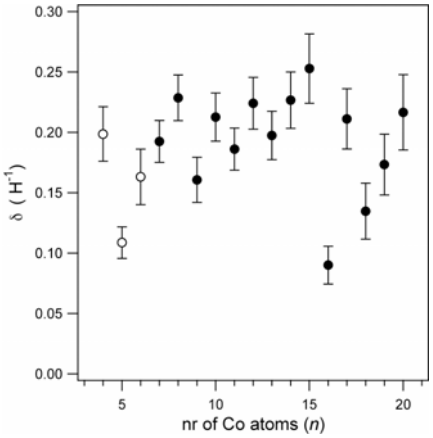

Figure 2. Averaged values of δ for Co_n^+ clusters (n = 4 – 20). Open symbols indicate values obtained from a fit of the data to equation 3, solid symbols indicate that only values of the mono-carbonyl and hydrogen saturated complexes have been used.

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