DOI: 10.1002/anie.200605165

Cluster Surface Chemistry

Controlling the Bonding of CO on Cobalt Clusters by Coadsorption 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 iron and cobalt nanoparticles has been widely studied owing to its 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.

Herein, we report on the coadsorption of H_2 and CO on small cationic Co clusters ($[Co_n]^+$, $n = 4$–20) in the gas phase, and we specifically address the effect on the C–O bond. We discuss how H_2 adsorption modifies 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.

Vibrational spectroscopy was used to monitor the C–O bond strength, where infrared multiple photon dissociation (IR-MPD) spectroscopy was relied on to measure the IR spectra of (hydrogenated) monocarbonyl complexes in the range of the C–O stretching vibration (1600–2200 cm^{-1}). A molecular beam of cluster complexes is overlapped with a counterpropagating 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 photoinduced fragmentation. IR spectra are generated by measuring the photoinduced 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 $[Co_{11}H_mCO]^+$ ($m = 0, 2, 4, 10$, and 12) are shown in Figure 1a. No absorption bands were detected in the 1600–1950 cm^{-1} region, which indicates that CO is exclusively terminally (μ^1) bound to hydrogen-covered $[Co_n]^+$ clusters. This situation has also been found for CO adsorption on bare $[Co_n]^+$ clusters.[9] H_2 adsorbs dissociatively on cationic Co clusters.[10] In Figure 1b, the value of $\tilde{\nu}$(CO) is plotted as a function of the number of coadsorbed hydrogen atoms for complexes containing 4, 5, 7, 9, and 11 Co atoms. Upon increasing H-atom coverage, the C–O stretching frequency $\tilde{\nu}$(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 $\tilde{\nu}$(CO) upon adsorption of the first H_2 molecule. The C–O stretching vibration of the corresponding H-saturated complexes ($[Co_7H_8CO]^+$, $[Co_8H_8CO]^+$, and $[Co_9H_8CO]^+$) was again higher than the value for the corresponding monocarbonyl complex $[Co_nCO]^+$. The initial decrease of $\tilde{\nu}$(CO) correlates with a particularly low reactivity of these clusters towards hydrogen.[11] For the small clusters, the shift of $\tilde{\nu}$(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 not possible experimentally to measure $\tilde{\nu}$(CO) at intermediate hydrogen coverage for these clusters. Values of $\tilde{\nu}$(CO) for the monocarbonyl complexes and the hydrogen-saturated monocarbonyl complexes are given in the Supporting Information.

In organometallic 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 antibonding 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

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[**] We gratefully acknowledge the support of the Stichting voor Fundamenteel Onderzoek der Materie (FOM) in providing beam time on FELIX. We would like to thank the FELIX staff for their skillful assistance, in particular Dr. A. F. G. van der Meer and Dr. B. Redlich. NWO-CW and NRSCC are gratefully acknowledged for financial support.

Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

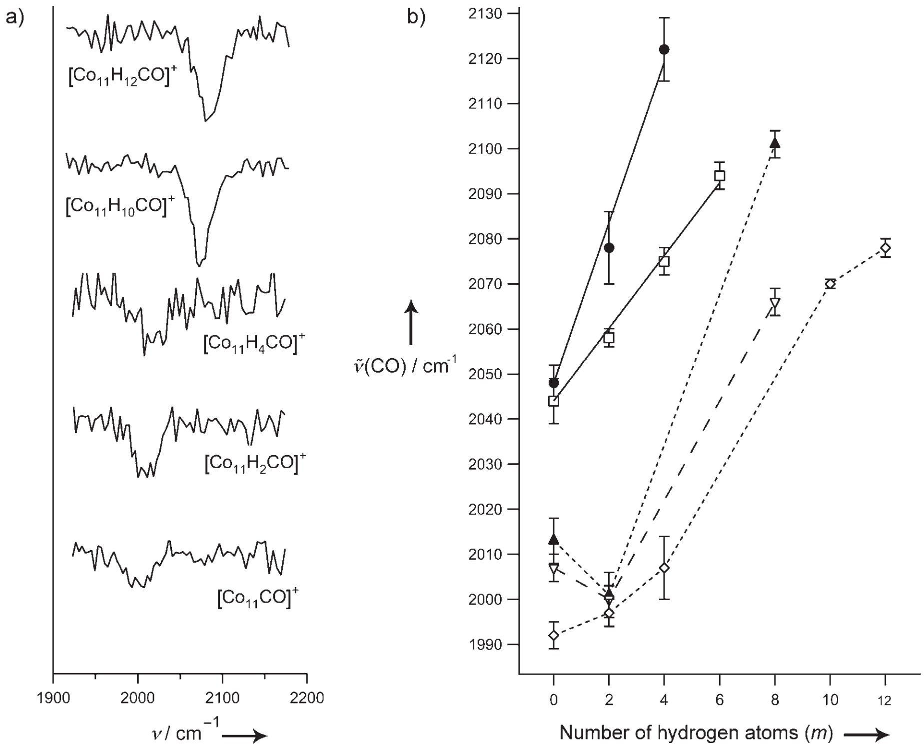

Figure 1. a) IR-MPD spectra of $[Co_{11}H_mCO]^+$ complexes with 0, 2, 4, 10, and 12 coadsorbed hydrogen atoms in the range of the C–O stretching vibration. b) Frequency of the C–O stretching vibration of monocarbonyl complexes as a function of the number of coadsorbed H atoms for complexes containing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

CO on a bare transition metal, the C–O bond usually becomes weaker because of the increased population of the antibonding $2\pi^*$ orbital, which is reflected in a shift of $\tilde{\nu}$(CO) to lower frequencies compared to its gas-phase value. As can be seen in Figure 1 b, the coadsorption of H_2 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 $2\pi^*$ orbital of CO.[15,16] Upon coadsorption of H_2, the population of the $2\pi^*$ 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 $\tilde{\nu}$(CO) for CO bound to hydrogen-covered nickel and cobalt particles on surfaces.[17,18]

We can use the recently measured charge dependence of $\tilde{\nu}$(CO) in cobalt cluster monocarbonyl complexes[9] to estimate the amount of charge transferred into the Co–H bonds. For example, for $[Co_{11}CO]^{+/0/-}$, values for $\tilde{\nu}$(CO) of 1992, 1943, and 1868 cm^{-1}, respectively, are found, resulting in a shift of about 62 cm$^{-1}/z$ where $z\,e$ is the charge on the cluster (e the elementary charge). This result can be compared to the dependence of $\tilde{\nu}$(CO) on the number of coadsorbed H atoms (m), as shown in Figure 1 b, which gives for $[Co_{11}H_mCO]^+$ an average shift of about 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 $\tilde{\nu}$(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 as well as the effect of donation of electron density from the metal to the $2\pi^*$ orbital of CO. The cluster size plays a role because of delocalization of charge over the cluster surface. The validity of this assumption has been shown before.[9,19]

The effect of coadsorption of H_2 can be incorporated into the model by introduction of an additional term in the expression that describes the population of the $2\pi^*$ orbital, $P(2\pi)$, of the CO molecule [Eq. (1)].

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

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 because of the charge ($z\,e$) 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 ith 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. Proceeding as described in reference [9], the following expression for $\tilde{\nu}$(CO) is then obtained [Eq. (2)]:

$$\tilde{\nu}(CO) = \tilde{\nu}(CO)_0 + \frac{\gamma^* \sum_{i}^{n_H} \delta_i}{n_S} \qquad (2)$$

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

If the effect of each of the subsequently added H ligands on $P(2\pi)$ is identical, δ_i will have the same value for each coadsorbed H atom. This situation appears to be the case for small clusters with $n \leq 6$, where $\tilde{\nu}$(CO) shifts linearly with the number of coadsorbed H atoms. In this case, Equation (2) can be simplified to Equation (3).

$$\tilde{\nu}(\mathrm{CO}) = \tilde{\nu}(\mathrm{CO})_0 + \frac{\gamma^* n_\mathrm{H}\, \delta}{n_\mathrm{S}} \qquad (3)$$

In this case, $\gamma^*\delta/n_\mathrm{S}$ is the shift induced per adsorbed H atom and can be evaluated from the slope of the plot of $\tilde{\nu}(\mathrm{CO})$ against n_H. The solid lines in Figure 1 b 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 we use the shift measured for the saturated complexes to evaluate an average δ value directly from Equation (3) using the values of $\tilde{\nu}(\mathrm{CO})_0$ and γ^*/n_S as reported in the literature.[9] With our measurements, the amount of electron transfer to coadsorbed H ligands can be quantified. The values of δ for clusters with 4–20 metal atoms range from 0.09 to 0.25 electrons per H atom, depending on cluster size (Figure 2). 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 $\tilde{\nu}(\mathrm{CO})$ with hydrogen-atom coverage demonstrates that CO is not influencing charge transfer between the cluster and the H ligands to any appreciable extent. Therefore, CO can be used as a probe for the electron density within the $[\mathrm{Co}_n(\mathrm{CO})\mathrm{H}_2]^+$ cluster complexes.

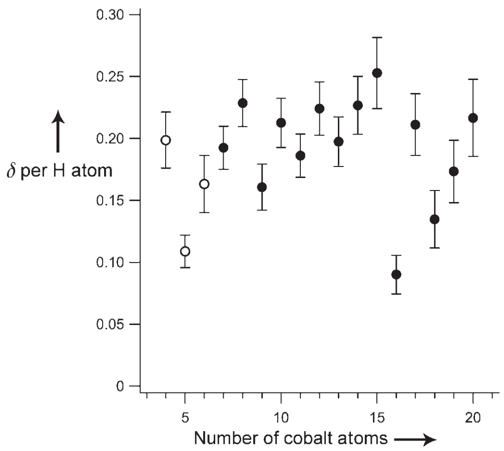

Figure 2. Average δ values for $[\mathrm{Co}_n]^+$ clusters ($n=4$–20). Open symbols indicate values obtained from a fit of the data to Equation (3); solid symbols indicate that only values of the monocarbonyl and hydrogen saturated complexes have been used.

Equation (3) predicts that as long as the ratio $n_\mathrm{H}/n_\mathrm{S}$ is significant, a shift in $\tilde{\nu}(\mathrm{CO})$ will be detected. This relationship implies that a shift in $\tilde{\nu}(\mathrm{CO})$ should be detected even for CO adsorbed on bigger particles if they are sufficiently covered with hydrogen. In fact, a shift of $\tilde{\nu}(\mathrm{CO})$ to higher frequency was detected for coadsorption of CO and H_2 on $\mathrm{Ru/Al_2O_3}$, $\mathrm{Co/SiO_2}$, and on Ni surfaces;[18,20–25] for nickel, this effect has also been found from DFT calculations.[26]

This treatment ignores the fact that for $[\mathrm{Co}_7(\mathrm{CO})\mathrm{H}_2]^+$, $[\mathrm{Co}_8(\mathrm{CO})\mathrm{H}_2]^+$, and $[\mathrm{Co}_9(\mathrm{CO})\mathrm{H}_2]^+$, we detect an initial red shift in $\tilde{\nu}(\mathrm{CO})$. According to the charge localization arguments outlined above, for these complexes, more electron density should be available on the metal center for donation into the $2\pi^*$ orbital of the CO ligand than in the monocarbonyl complexes. The behavior exhibited by most of the complexes establishes that H atoms bound as hydrides increase $\tilde{\nu}(\mathrm{CO})$, which leads 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 $[\mathrm{Co}_7(\mathrm{CO})\mathrm{H}_2]^+$, $[\mathrm{Co}_8(\mathrm{CO})\mathrm{H}_2]^+$, and $[\mathrm{Co}_9(\mathrm{CO})\mathrm{H}_2]^+$. So-called nonclassical hydrides in which H_2 binds molecularly are known in organometallic chemistry.[27] The bonding is characterized as a three-center, two-electron σ interaction involving donation of charge from the H_2 molecule to the metal center. Molecular H_2 binding in $[\mathrm{Co}_7(\mathrm{CO})\mathrm{H}_2]^+$, $[\mathrm{Co}_8(\mathrm{CO})\mathrm{H}_2]^+$, and $[\mathrm{Co}_9(\mathrm{CO})\mathrm{H}_2]^+$ can therefore be expected to lower $\tilde{\nu}(\mathrm{CO})$, 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 average δ values for $[\mathrm{Co}_7]^+$, $[\mathrm{Co}_8]^+$, and $[\mathrm{Co}_9]^+$ obtained from the H-saturated complexes are very similar to the values from clusters of 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 coadsorption of H_2. Each coadsorbed H atom reduces the amount of electron density available for back-donation by on average 0.09–0.25 electrons, depending on cluster size. Indications were found that H_2 could be molecularly bound in the special cases of $[\mathrm{Co}_7(\mathrm{CO})\mathrm{H}_2]^+$, $[\mathrm{Co}_8(\mathrm{CO})\mathrm{H}_2]^+$, and $[\mathrm{Co}_9(\mathrm{CO})\mathrm{H}_2]^+$. From a catalysis point of view, the coadsorption 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 clusters with low H coverage will show the highest reactivity. The observed relationship between $\tilde{\nu}(\mathrm{CO})$ and hydrogen-atom coverage demonstrates that, at least for $[\mathrm{Co}_n(\mathrm{CO})\mathrm{H}_2]^+$ complexes, CO is a suitable probe for the electron density. These results demonstrate how the concepts of donation and back-donation developed in organometallic chemistry extrapolate to larger systems such as clusters or even extended surfaces. We hope that the availability of this quantitative data stimulates further theoretical investigations.

Received: December 21, 2006
Revised: March 20, 2007

Keywords: carbon monoxide · cluster compounds · coadsorption · cobalt · IR spectroscopy

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