

Hydrogen-Induced Transition from Dissociative to Molecular Chemisorption of CO on Vanadium Clusters

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Abstract: We report on the size-dependent interaction of carbon monoxide molecules with hydrogen covered vanadium clusters containing between 5 and 20 atoms. Structural information on these hydrogen covered vanadium clusters and their complexes with CO is obtained from infrared multiple photon dissociation spectroscopy, complemented with density functional theory calculations for the V_5 to V_9 cluster sizes. The non-dissociative or dissociative binding of CO on the metal clusters is detected by the presence or absence of the $\nu(\text{CO})$ stretching band in the infrared spectra. It is found that the CO molecule dissociates on bare vanadium clusters, while it adsorbs intact on all saturated hydrogen covered V_{5-20}^+ clusters, with the distinctive exceptions of V_5^+ , V_9^+ , V_{11}^+ , and V_{19}^+ . We show that dissociative chemisorption is prevented when the potential binding sites of atomic C and O atoms are blocked by H atoms.

Introduction

Metal nanoparticles play, or promise to play, an important role in a wide range of systems, including heterogeneous catalysts, fuel cells, hydrogen storage materials, and magnetic devices including high-density recording media. The presence of adsorbates on the nanoparticles strongly affects the nanoparticle properties with respect to these applications. Indeed, the interaction of an adsorbate with a nanoparticle is one of the crucial issues in nanoscience. The chemical nature of the nanoparticle-adsorbate interaction is of fundamental chemical interest, especially for catalysis.¹ The interaction bears resemblance to both the metal-ligand interactions in coordination chemistry and to the surface-adsorbate interactions studied in the field of surface science. With the nanoparticles getting smaller, free clusters are an important testing ground for basic adsorption phenomena.

In this Article, we study gas-phase transition metal clusters and their interaction with hydrogen and carbon monoxide. The determination of the bonding sites and ground-state geometries of metal hydrides yields important information for the study of hydrogen storage in nanoparticle systems.² In addition, the interaction of free clusters with CO and H_2 provides detailed model systems for Fischer-Tropsch synthesis, which is a catalytic process to transform supported metal nanoparticles that transform mixtures of CO and H_2 into long-chain hydrocarbons.^{3,4} Using the interaction of a surface with an adsorbate as

a starting point, one finds that, at room temperature, all metals to the left of the diagonal Co-Ru-Re in the periodic table dissociate CO.⁵ At elevated temperatures, Co, Ru, and Ni also dissociate CO, and, for example, supported Ru, Co, and Fe nanoparticles are used in the Fischer-Tropsch process.

The reaction of gas-phase clusters of the late transition metals Co, Ni, Rh, and Au with CO has been studied using IR spectroscopy at room temperature, and, in analogy with supported nanoparticles and metal surfaces, non-dissociative chemisorption has been observed.^{6,7} In contrast, it has been shown by a combined spectroscopy/DFT study that CO is dissociatively chemisorbed on small clusters of the early transition metal Nb.⁸ Previous studies on the reaction of H_2 with transition metal clusters have been discussed in two reviews.^{9,10} The reactivity of H_2 toward transition metal clusters strongly depends on the size of the cluster and correlates with the energy required to promote an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO) of the cluster.¹¹ Vibrational spectra of Fe_nH_m complexes have been measured using a tunable CO_2 laser covering the spectral range from 885 to 1090 cm^{-1} . Several absorption features were observed in this spectral range that were ascribed to Fe-H

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modes.¹² On neutral and charged vanadium clusters, the adsorption of H₂, D₂, and CO has been studied using flow tube and ion trap techniques.^{13–20} By studying the collision-induced dissociation of cationic vanadium hydride complexes, the binding energy of H₂ to V₅⁺ has been determined to be 2.4 ± 0.3 eV, implying dissociative chemisorption.¹⁴ Reaction rates for the adsorption of D₂, H₂, and CO toward neutral and charged vanadium clusters have been measured.^{13,16–18,20} From these and other studies, it has been found that individual H₂ and CO molecules chemisorb dissociatively on clusters of the early transition metals V and Nb.^{8,13–16,19,21}

We report here on saturated hydrogen complexes of gas-phase cationic vanadium clusters and on the effects of coadsorption of H₂ and CO. A saturation behavior in the reaction with hydrogen has been observed before for niobium, iron, and cobalt clusters.^{22,23} However, so far there are no conclusive explanations for the saturation stoichiometries, for example, in terms of cluster structure or H adsorption geometries. We apply infrared multiple photon dissociation (IR-MPD) spectroscopy to measure vibrational spectra of the hydrogen saturated cationic vanadium clusters (V_nH_m⁺) and their complexes with CO (V_nH_m-CO⁺) containing up to 20 vanadium atoms in the 500–2200 cm⁻¹ range. The spectral range covered in the experiment includes the range of the C–O stretch vibration (1600–2200 cm⁻¹) and of the V–H stretch and deformation modes (700–1500 cm⁻¹). The experimental work is complemented with density functional theory (DFT) calculations to obtain information on the geometry and chemical bonding in the saturated vanadium hydrides and the monocarbonyl vanadium hydride complexes. It is shown that it is possible to induce a transition from dissociative to molecular chemisorption of CO by coadsorbing hydrogen on the metal cluster.

Experimental Section

The experiments have been performed using a molecular beam apparatus coupled to a beamline of the free electron laser for infrared experiments (FELIX)²⁴ at the FOM Institute for Plasma Physics in Nieuwegein, The Netherlands. This FEL can produce continuously tunable IR radiation (40–2200 cm⁻¹) in a train of macropulses, 5–10 μs in length, at a repetition rate of up to 10 Hz. Each macropulse consists of a train of micropulses with a length of a few picoseconds that are typically separated by 1 ns. The experimental setup and measurement procedure has been described in detail before.^{7,25,26} Vanadium clusters are produced by pulsed laser ablation using the second harmonic of a Nd:YAG laser and entrained in a flow of He.

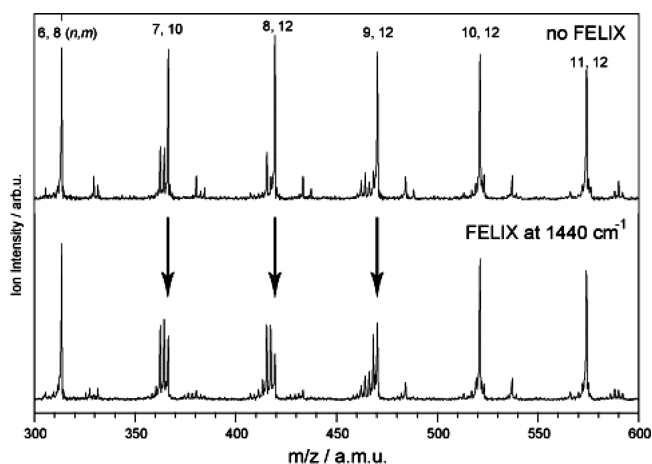


Figure 1. Mass spectra of fully hydrogen saturated V_nH_m⁺ complexes with mass/charge ratios between 300 and 600. The top spectrum shows part of the mass distribution of cluster complexes in the molecular beam where 7,10 indicates the V₇H₁₀⁺ complex, etc. The lower mass spectrum shows the changed mass distribution upon overlap of the molecular beam with a beam of IR radiation resonant with an infrared active mode of the cluster complexes. The arrows indicate photoinduced fragmentation.

Neutral, anionic, and cationic clusters are produced in this process. Reactions with H₂ and CO are initiated by adding either pure H₂ or CO or a mixture of 0.1% CO in H₂ via a pulsed valve into a small flow reactor channel downstream of the cluster source. The extent of complex formation is controlled by adjusting the gas flow through the valve. After passing the reactor channel, the molecular beam is expanded into vacuum and shaped by a skimmer and an aperture before entering the extraction region of a time-of-flight mass spectrometer. A counter-propagating pulsed IR beam delivered by FELIX is focused to fill the aperture to ensure that the full cross-section of the molecular beam is exposed to the IR radiation. When the IR radiation is resonant with an IR-allowed transition of the cluster complex, sequential absorption of single photons can take place. This process is facilitated by the high density of vibrational states and the fast internal vibrational redistribution of energy. The photon energy is quickly transferred to a heat bath of other modes such that subsequent absorption of other photons is possible on the same transition. In principle, relaxation can occur by emitting photons or electrons or by fragmentation. Both electron emission and fragmentation lead to changes in the cluster distribution that can be probed using mass spectrometry. The dissociation energy of metal hydride and deuteride clusters is typically on the order of several electronvolts,^{17,27–31} and hence many photons have to be absorbed to overcome the barrier to fragmentation. For example, the binding energy of H₂ on V₅⁺ is 2.4 ± 0.3 eV,¹³ so at a minimum 14 photons at 1400 cm⁻¹ have to be absorbed to induce fragmentation. For the vanadium hydride complexes, fragmentation is observed to be the dominant cooling process. Irradiation of vanadium hydride complexes with IR radiation of a frequency of 1440 cm⁻¹ leads to fragmentation of the saturated complexes under loss of H₂ molecules. This can be seen in Figure 1 where significant fragmentation is observed for the V₇H₁₀⁺, V₈H₁₂⁺, and V₉H₁₂⁺ complexes upon irradiation with IR photons with a frequency of 1440 cm⁻¹ and complementing growth of the V₇H₈⁺, V₈H₁₀⁺, and V₉H₁₀⁺ complexes. The arrows in Figure 1 illustrate this process.

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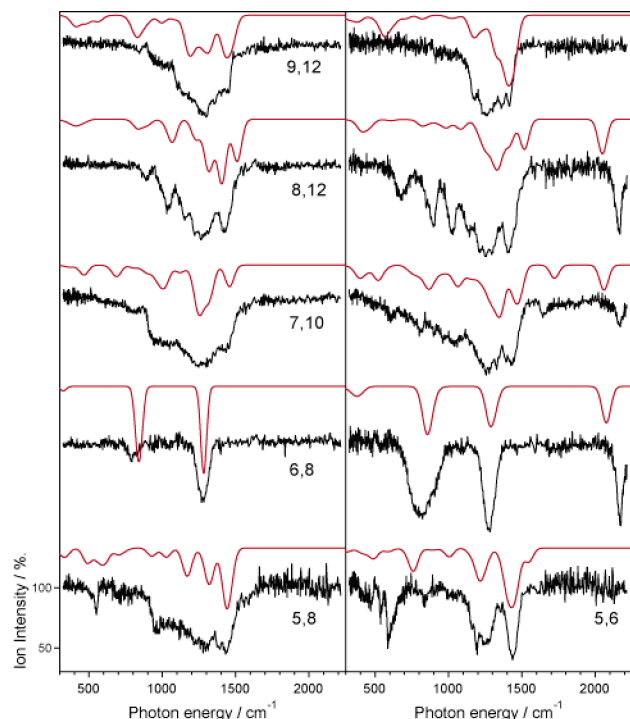


Figure 2. IR-MPD spectra (black) of fully saturated $V_nH_m^+$ (left panel) and the corresponding $V_nH_mCO^+$ complexes for $n = 5-9$ (right panel, bottom to top). Values of n and m for the fully saturated clusters are denoted as n,m in the graph. The spectra depicted in red are calculated IR spectra for the structures shown in Figure 3. The calculated spectrum of $V_7H_{10}CO^+$ is a linear combination of the two isomers depicted.

The mass spectrometer extraction pulse is timed such that spectra are recorded of a part of the cluster distribution that is exposed to a macropulse of IR radiation (lower trace in Figure 1). Mass spectra of a reference distribution that is not exposed to IR radiation are recorded on alternate shots to compensate for shot to shot variations in the cluster intensities (upper trace in Figure 1). Tracking the intensity of complexes in the mass spectrum as a function of the IR frequency allows the construction of the IR-MPD spectra. The spectral range covered in the experiment includes the range of the C–O stretch vibration (1600–2200 cm^{-1}) and of the V–H stretch and deformation modes (700–1500 cm^{-1}).

Results and Discussion

Reactions of the vanadium clusters with molecular hydrogen lead to successive addition of H_2 molecules to the cluster until a cluster size-specific coverage is reached. For example, V_6^+ can be saturated with 8 hydrogen atoms; V_7^+ and V_8^+ bind maximally 10 and 12 hydrogen atoms, respectively. A typical mass spectrum of vanadium cluster cations saturated with hydrogen is shown in the upper trace of Figure 1 along with the saturation stoichiometries of $V_nH_m^+$ ($n = 6-11$). Irradiation of this complex distribution with IR light of a frequency of 1440 cm^{-1} leads to fragmentation of the saturated complexes under loss of H_2 molecules (lower trace in Figure 1).

The IR-MPD spectra of the $V_nH_m^+$ and $V_nH_mCO^+$ complexes are constructed from the changes of their initial intensity when scanning the IR frequency and are shown in Figure 2 for the size range of $n = 5-9$. The spectra of the larger $V_nH_m^+$ and $V_nH_mCO^+$ complexes ($n = 10-20$) are shown in Figure S1 in the Supporting Information. Several absorption bands are identified between 700 and 1500 cm^{-1} . For the vanadium hydride complexes, no bands are observed at higher frequencies. The observed absorption bands are not in all cases fully resolved.

$V_6H_8^+$ is the only complex in the size range ($n = 5-20$) studied that shows two well-resolved bands, implying a highly symmetric structure. Other clusters seem to have a less symmetric structure. IR-MPD spectra of bare vanadium clusters show exclusively modes below 450 cm^{-1} , and we therefore assign the absorption bands in the 700–1500 cm^{-1} range to V–H stretch and deformation vibrations.^{32,33}

The far-infrared spectra of bare V_n^+ clusters as compared to calculated IR spectra led to the determination of the structures for small vanadium clusters.³³ For many of these clusters, there is a direct relation between the number of triangular facets on the bare clusters and the observed hydrogen saturation number. This strongly suggests that the hydrogen atoms mainly occupy three-fold hollow sites (μ^3 coordination) on the cluster surface. The only exception is the V_5^+ cluster, which has a hydrogen saturation stoichiometry of 8, but the metal cluster has 6 triangular facets. Therefore, at least some hydrogen has to be two-fold (μ^2) coordinated to the metal cluster. Comparison of IR-MPD spectra and calculated vibrational spectra supports this assignment and will be discussed below.

The reaction of vanadium clusters with hydrogen in the presence of a small amount of CO (0.1%) yields mainly saturated vanadium cluster hydrides and, to a small fraction, their complexes with single CO molecules. Although H_2 and CO may compete in the reaction with the clusters, the high excess of H_2 relative to CO leads in most cases to the initial formation of the hydrogen saturated complexes like in the absence of CO. This indicates that the CO reacts mainly with preformed hydrogen covered clusters. The IR-MPD spectra of the complexes of cationic vanadium cluster hydrides with CO ($V_nH_mCO^+$) are shown in the right panel of Figure 2 for $n = 5-9$. The spectra of the $V_nH_mCO^+$ complexes closely resemble the spectra of the corresponding hydride complexes in the 700–1700 cm^{-1} range for most $V_nH_mCO^+$ complexes. Significant changes in this range are only found in the spectra of $V_5H_6CO^+$ and $V_7H_{10}CO^+$. The hydrogen saturation stoichiometry of a V_5^+ cluster decreased from 8 to 6 in the presence of CO, indicating competitive adsorption of CO and H_2 .

The spectra of CO adsorbed on vanadium clusters without hydrogen adsorption show no detectable absorption features in the range of the $\nu(CO)$ stretching vibration (1650–2200 cm^{-1}), indicating that CO is dissociatively chemisorbed on all bare vanadium clusters. In contrast, for most of the CO complexes of the hydrides a band corresponding to the C–O stretching vibration of atop (μ^1) bonded CO between 2120 and 2170 cm^{-1} is observed. The presence of a $\nu(CO)$ band implies that it is possible to molecularly chemisorb CO on cationic vanadium clusters by coadsorbing hydrogen molecules. On hydrogen covered cationic vanadium clusters containing 5, 9, 11, and 19 V atoms, no $\nu(CO)$ stretching band was observed, indicating dissociative chemisorption of CO on these cluster sizes.

To probe the origin of the size-dependent stabilization of CO on hydrogen covered vanadium clusters with respect to the behavior on the bare metal clusters and to obtain information on the binding geometries of the adsorbed species, we performed density functional theory (DFT) calculations using the TURBOMOLE quantum chemistry package.^{34–36} All calculations

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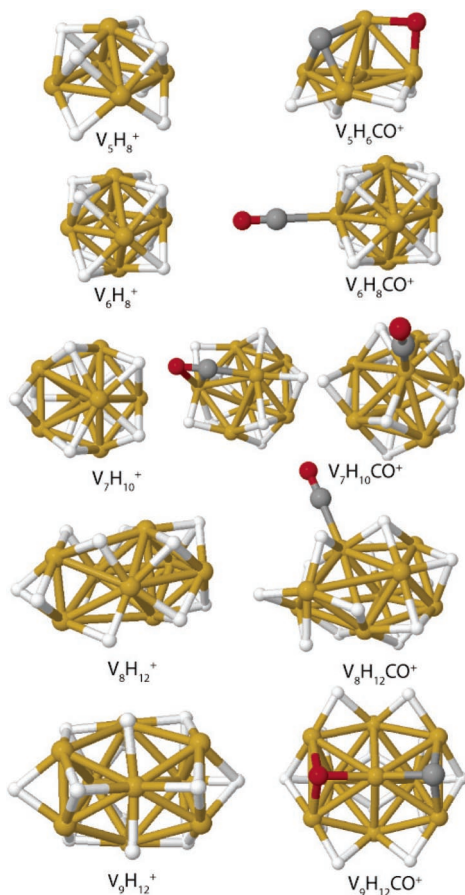


Figure 3. Geometric structures of isomers of saturated $V_nH_m^+$ (left) and $V_nH_mCO^+$ complexes (right) for $n = 5-9$ selected on the basis of the comparison of experimental and calculated IR spectra.

were performed using the BP86 parametrization of the exchange-correlation functional and a triple- ζ valence plus polarization (TZVP) basis set.³⁷ As a starting point for the calculations, we used the geometries of the bare vanadium clusters as identified by a combined theoretical/IR-MPD study³³ and placed hydrogen atoms in three-fold hollow (μ^3) sites. For V_9 complexes, an additional similar metal cluster geometry was used that was found to be degenerate in energy.³³ The ground-state structures of several geometric isomers in different spin states have been optimized for every cluster complex. We note that in this process only a small portion of the configurational space is probed, and it is possible that the actual structures are different from the structures shown in Figure 3. In many cases, several different structures are close in energy, and theory might not be accurate enough to correctly predict the most stable complex. Moreover, for kinetic reasons, the experiment may favor metastable species. The IR spectra are sensitive to the geometry and the electronic state of the cluster complex, and the energy differences between low energy isomers are typically on the order of 0.1–1 eV. In case a structure could not be assigned on the basis of energetic considerations alone, a structure was assigned on the basis of the comparison of the calculated and experimental spectra. These selected structures correspond, in most cases, with the lowest energy isomers found in the calculations. (The exceptions are

$V_5H_6CO^+$ and $V_7H_{10}^+$, for which the calculations indicate that the lowest energy isomers have a triplet spin state. However, the experimental spectra are in better agreement with isomers with a singlet spin state that are only 0.12 and 0.20 eV higher in energy, respectively. This is close to the expected accuracy of the calculations.) Typically the energy difference between spin states is small, less than 0.2 eV, and it is therefore not possible to assign a particular spin state to a cluster on the basis of energetic considerations alone. The calculated cross-sections were converted to transmission scale to allow for a direct comparison with the experimental spectra. The calculated spectra, folded with a Gaussian peak shape of 30 cm^{-1} width, that are in best agreement with the experimental data are shown in Figure 2 directly above the experimental IR-MPD spectra. No frequency scaling is applied. The intensity of the calculated CO stretching peak in Figure 2 has been scaled to 20% of the calculated value for ease of comparison. This intensity scaling accounts for the considerable lower IR laser intensity used in the dissociation experiments in the range of the $\nu(CO)$ vibration (15 mJ/pulse at 2200 cm^{-1} vs typically 60 mJ/pulse in the range from 600 to 1500 cm^{-1}). The intensity ratios between different peaks may be different in the calculated and experimental spectra due to the fact that the calculations give single photon cross-sections, while IR-MPD is a multiple photon process.

The optimized cluster geometries as found from the calculations are shown in Figure 3. For $V_6H_8^+$, the lowest energy structure has octahedral symmetry and therefore a relatively simple IR spectrum, in agreement with experiment. The hydrogen atoms bind on top of the facets of the octahedron formed by the V atoms. The band centered at 1275 cm^{-1} can be assigned to a collective antisymmetric stretch mode of three-fold coordinated (μ^3) H atoms. The band observed experimentally at 800 cm^{-1} corresponds to a collective bending mode of three-fold coordinated (μ^3) H atoms. The calculated structures of the other complexes are less symmetric. The vibrations in the 700–1400 cm^{-1} regime involve collective motion of many different atoms; that is, the vibrations are not localized, and it is not straightforward to assign modes to absorption bands. Experimentally, many of the cluster complexes (see Figure 2 for the experimental spectra of $V_5H_8^+$, $V_7H_{10}^+$, $V_8H_{12}^+$, $V_9H_{12}^+$, and their complexes with CO) show an absorption band around 1450 cm^{-1} . This absorption feature can only be reproduced in the calculations by assuming that some of the hydrogen atoms bind in bridging (μ^2) sites. The structures of $V_5H_8^+$, $V_7H_{10}^+$, $V_8H_{12}^+$, and $V_9H_{12}^+$ shown in Figure 3 contain at least one hydrogen atom in a bridging site. We therefore conclude that hydrogen predominantly binds in three-fold hollow sites, but a minor number of two-fold coordinated hydrogen atoms can be present.

The calculations find that CO is dissociatively chemisorbed in $V_5H_6CO^+$, in agreement with the competitive adsorption of CO and H₂ and the absence of detectable absorption features in the range of the $\nu(CO)$ stretching vibration (1650–2200 cm^{-1}). For $V_6H_8CO^+$, all three-fold hollow sites are occupied with hydrogen atoms and CO is molecularly chemisorbed to one metal atom. Its experimental IR spectrum is relatively simple, due to the high symmetry of the complex, and well reproduced by the calculations. $V_7H_{10}CO^+$ is the only cluster complex in this size range for which we were not able to fully deplete the ion intensity by exciting the CO stretch mode at ~ 2163 cm^{-1} , which is an indication for the presence of isomers. Moreover, it is the only cluster complex whose IR-MPD

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spectrum exhibits a weak absorption at 1650 cm^{-1} . For all other cluster complexes, the highest observed V–H absorption band is around 1450 cm^{-1} . In the calculations, this feature can be accounted for by a CO molecule that is bridge bonded to this cluster in a tilted configuration (η^2 coordinated). The energy difference between configurations with atop and η^2 bridging CO is only $\sim 0.2\text{ eV}$, and it is likely that both isomers coexist in the molecular beam. Together with the experimental evidence, we conclude that the spectrum in Figure 2 has contributions from at least two different isomers of $\text{V}_7\text{H}_{10}\text{CO}^+$. Structures with three-fold coordinated CO were found to be unstable and can therefore not be the origin of the band observed experimentally at 1650 cm^{-1} .

The geometry with the tilted bridge (η^2) bonded CO molecule could resemble a precursor state to dissociation that is stabilized by the coadsorbed hydrogen atoms. In fact, structures very similar to the complex with the tilted bridge (η^2) bonded CO molecule have been observed experimentally for CO adsorbed on Fe(100), Fe(001), and Cr(110).^{38–41} At the low temperatures employed in these experiments, the precursor state for dissociation is stabilized. Tilted bridge (η^2) bonded CO molecules have also been predicted to play an important role in the dissociation of CO on transition metals.^{42,43}

For $\text{V}_8\text{H}_{12}\text{CO}^+$, good agreement between the calculated and the experimental IR spectrum is obtained for a structure where 10 hydrogen atoms bind in three-fold hollow sites while two hydrogen atoms are bridge bonded. The band pattern that is observed experimentally is also reproduced by the calculations. CO is molecularly chemisorbed to one of the V atoms. For $\text{V}_9\text{H}_{12}\text{CO}^+$, we did not observe an absorption band in the range of the CO stretch vibration, indicating dissociative chemisorption of CO. Bare V_9^+ has 14 three-fold hollow sites,³³ while the highest hydrogen saturation number that could be achieved under our experimental conditions was 12. As can be seen from the calculated geometry of $\text{V}_9\text{H}_{12}^+$ (Figure 3), 2 hydrogen atoms are coordinated in a convex site spanned by 4 V atoms, effectively blocking 2 three-fold hollow sites. The adsorption energy of an additional hydrogen molecule is not enough to cause a rearrangement of the $\text{V}_9\text{H}_{12}^+$ cluster that could be followed by adsorption of the additional hydrogen molecule. Upon adsorption of CO, the hydrogen ligands can undergo a rearrangement, as is indicated by the calculated cluster geometries, and CO adsorbs dissociatively. Complexes with dissociated CO will always be lower in energy due to the formation of stable oxide and carbide bonds. In the case of $\text{V}_9\text{H}_{12}\text{CO}^+$, our calculations indicate that geometries with molecular chemisorbed CO are more than 1.75 eV (170 kJ/mol) higher in energy than geometries with dissociatively chemisorbed CO. This implies that, in the absence of energetic barriers, CO will be dissociatively chemisorbed in $\text{V}_9\text{H}_{12}\text{CO}^+$.

The mechanism of CO dissociation is thought to involve tilted precursor states.⁴³ If the surface is completely covered with

hydrogen, these tilted precursor states cannot form, nor are there sites available for the C and O atom, leading to molecular instead of to dissociative chemisorption. Only for vanadium clusters where the hydrogen saturation stoichiometry matches the number of triangular facets (clusters with 6, 7, and 8 vanadium atoms) a $\nu(\text{CO})$ vibration is observed.

Clusters with 5, 9, 11, and 19 vanadium atoms do not show a band in the range of the $\nu(\text{CO})$ vibration. For V_5H_m^+ , the saturation stoichiometry (m) is 8. However, in the presence of CO, the maximum number of hydrogen atoms that can bind to the cluster is only 6, indicating competitive adsorption of CO and H_2 . For $\text{V}_9\text{H}_{12}\text{CO}^+$, we have seen that CO does dissociate because the surface is not completely covered with hydrogen (14 sites available and only 12 are occupied by hydrogen atoms). For $\text{V}_{11}\text{H}_m^+$, the saturation stoichiometry (m) is 14, and the bare vanadium cluster has 17 triangular facets.³³ The exact structure of the bare V_{19}^+ cluster is not known, and it is therefore not possible to relate the number of triangular facets with the hydrogen saturation stoichiometry. For these cluster sizes, on which CO is dissociatively chemisorbed, not all available sites are blocked with hydrogen.

Conclusion

The saturation behavior in the reaction of vanadium cluster cations with hydrogen has been explained by a covering of the cluster surface with H atoms, which are predominantly bound in μ^3 configuration on triangular facets of the metal cluster. Completely H covered vanadium cluster cations bind coadsorbed CO molecules non-dissociatively, whereas in cases that the number of bound H atoms is smaller than the number of triangular facets the absence of the characteristic $\nu(\text{CO})$ band indicates dissociation of coadsorbed CO molecules.

We therefore conclude that blocking of available adsorption sites by hydrogen causes the transition from dissociative to molecular chemisorption of CO on vanadium clusters and leads to the stabilization of the CO complex against thermodynamically favorable dissociative chemisorption. There have to be at least two vacant three-fold hollow sites on the cluster to accommodate the C and O atoms to enable dissociation of CO.

These results show that the interaction of CO molecules with vanadium clusters can be controlled by coadsorption of hydrogen molecules without changing the fundamental electronic structure of the nanoparticle. This is probably a more general effect, and we are currently studying the H/CO coadsorption on other transition metal clusters. Our findings show how the reactivity of metal nanoparticles is affected by their H coverage. This aids the atomistic understanding of the influence of H coadsorption on the reactivity.

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Supporting Information Available: IR-MPD spectra of V_nH_m^+ and $\text{V}_n\text{H}_m\text{CO}^+$ complexes with $n = 10–20$. Additional details of the DFT calculations. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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