Available online at www.sciencedirect.com

SCIENCE DIRECT®

Chemical Physics Letters 392 (2004) 127–131

CHEMICAL PHYSICS LETTERS

www.elsevier.com/locate/cplett

CO Adsorption study of V/SiO_2: the low vanadium coverage regime

B. Immaraporn, N. Magg, S. Kaya, J. Wang, M. Bäumer, H.-J. Freund *

Department of Chemical Physics, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, Berlin D-14195, Germany

Received 7 April 2004; in final form 10 May 2004
Available online 8 June 2004

Abstract

Adsorption of CO and its isotopic mixtures on vanadium particles in the very low coverage growth regime (0.02–0.05 MLV) on an ultra-thin ordered silica film is monitored by IRAS at 60 K. At different CO exposures, development of different vibrational peaks was observed. These peaks are assigned to either mono- or tri-carbonyl species [$V(CO)_x$; $x = 1, 3$] via isotopic mixture experiments. Comparing vanadium growth both on the alumina and silica films, it can be inferred from CO adsorption experiments that the metal–support interaction is weaker for vanadium growth on the silica film. The charge transfer between the vanadium metal center and the silica film is estimated based on a charge–frequency relationship to be +0.4e.

1. Introduction

Heterogeneous catalysts are widely used in many industrial processes. In general, selectivities of heterogeneous catalysts are poor as compared to those of homogeneous catalyst counterparts. The ultimate goal in heterogeneous catalysis is then to make catalysts that can produce selectivities and reactivities approaching 100%. An emergence of the so-called ‘single-site’ heterogeneous catalysts is for instance a result of the determination to fulfill that goal. Single-site heterogeneous catalysis is a novel field and has been receiving a lot of attention recently [1–4]. One possibility, for example, to realize this idea is to transfer homogeneous catalysts uniformly onto solid supports. By anchoring these catalysts on the supports, one hopes to not only retain the desired advantages provided by a homogeneous catalyst but also gain the necessary characteristics of a heterogeneous catalyst. In order to prepare these catalysts successfully, the choice of the support plays a very critical role because it should not alter the desired reactivity of the catalytic center and simultaneously guarantee uniform distribution of the anchored sites on the surface of the support. Furthermore, pretreating conditions of the support as shown in the literature [1] can dictate the final properties of these catalysts. In analogy to the example given above, isolated metal atoms can be produced on a solid support under ultrahigh vacuum condition where systematic, well-defined characterizations are possible. These single metal atoms can potentially serve as a precursor for a single-site heterogeneous catalyst.

The development of thin ordered oxide films (Al_2O_3/NiAl(1 1 0) [5], SiO_2/Mo(1 1 2) [6], etc.) in our group has provided many possibilities to explore a number of model catalyst studies [7–10]. These well-defined oxide films have served as model supports upon which the active materials can grow, allowing also the study of the influence of the support. Previously, Pd [7–9] and vanadium particles [10] growth on both the alumina (Al_2O_3/NiAl(1 1 0)) and silica (SiO_2/Mo(1 1 2)) films exemplified how different supports can affect the morphologies and properties of these particles. Isolated single metal particles are obtained when deposition is carried out at very low metal coverages and/or at low substrate temperatures. These single-particle species can be probed indirectly by CO adsorption experiments. This was demonstrated in the cases of Pd, Rh, Ir and V deposited on Al_2O_3/NiAl(1 1 0) [7,8,10].

Recently, the study of vanadium particles deposited on the alumina film was performed via STM, XPS and

---

* Corresponding author. Fax: +493084134101.
E-mail address: freund@fhi-berlin.mpg.de (H.-J. Freund).

0009-2614/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cplett.2004.05.032

IRAS [10]. Single vanadium atoms were probed by CO adsorption in that study. Infrared results of CO adsorbed on V/SiO_2 where the deposition temperature was 90 K were also presented. However, the temperature was too high to obtain single vanadium metal atoms on the silica film because of the high mobility on this substrate.

In this study, we investigate V particle growth at low vanadium coverages (0.02–0.05 MLV) on the well-ordered crystalline silica film (SiO_2/Mo(1 1 0)) at 60 K. These particles are characterized by CO adsorption experiments. A comparison with the data formerly obtained from V/Al_2O_3 grown at 300 K is also presented in order to gain more insight into the role of support.

2. Experimental

All the experiments were performed in an ultra-high vacuum system with a base pressure of 2×10^{-10} Torr or below. The system is equipped with LEED, an XPS/UPS setup, an Omicron variable temperature STM, and a Bruker IFS 66v/S infrared spectrometer. The latter setup is used in a reflection absorption geometry, where the angle of reflection is set to 84°. X-ray photoemission spectroscopy (XPS) was performed using a twin-anode X-ray source and a Scienta SEC 200 concentric hemispherical electron energy analyzer.

The Mo(1 1 2) sample is cleaned by annealing the crystal in 2×10^{-6} Torr O_2 at 1600 K for 10 min, followed by flashing the sample to 2200 K to remove excessive oxide layer. The cleanliness is checked with LEED and XPS. The sample is cooled to 90 K with liquid N_2 and at 60 K with liquid He. The silica film preparation was carried out according to the previously described procedure [6]. Vanadium is evaporated from a vanadium rod (>99.9%), which is heated by electron bombardment. The deposition rate is calibrated with a microbalance to be approximately 0.009 ML/s. The substrate is also biased at the same potential as the V rod to avoid sputtering the film by V ions. Carbon monoxide is obtained from AGA with 99.997% purity. It is purified by a liquid nitrogen trap and dosed through a pinhole doser.

3. Results and discussions

3.1. V/SiO_2 at 300 and 90 K

The infrared spectra of CO at saturation adsorbed on the vanadium particles deposited on the silica film (V/SiO_2) at 300 and 90 K are displayed in Fig. 1. In the same figure a spectrum of CO adsorbed on the alumina supported vanadium particles (V/Al_2O_3) deposited at 300 K is also included. The spectrum of CO/V/SiO_2 (300 K) displays two infrared peaks at 2139 and 2178 cm^{-1}. These two peaks appear rather broad (FWHM ~ 50 cm^{-1}). The broad feature is typical for CO adsorption on large disordered aggregates. At 90 K, the spectrum of CO/V/SiO_2 shows a much narrower band (FWHM ~ 10 cm^{-1}) at 2075 cm^{-1}. In the spectrum also a broad feature appears between 1900 and 2200 cm^{-1}. It is shown below that this 2075 cm^{-1} feature belongs to tri-carbonyl species ($V(CO)_3$). The background is assigned to on-top site adsorption on larger aggregates [10]. When compared to the spectrum of CO on vanadia particles grown at 300 K on the alumina film, the difference is clearly visible [10]. There are numerous peaks at various positions for CO/V/Al_2O_3. These peaks also appear quite intense. No visible background is observed for CO/V/Al_2O_3. The most intense peak on the alumina supported particles at 2057 cm^{-1} has previously been assigned to tri-carbonyl species [10]. In the same study it was shown that CO adsorption on large vanadium aggregates is not visible until higher vanadium coverages are applied [10].

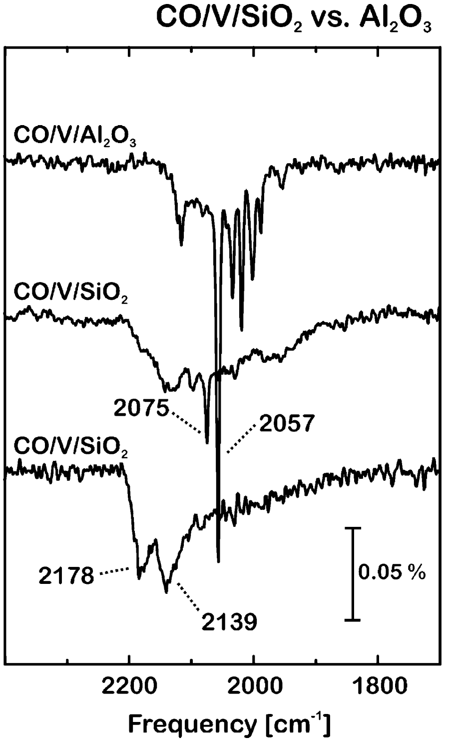

Fig. 1. Infrared spectra of CO saturated vanadium particles grown at 90 and 300 K on alumina and silica (see the right side of the figure).

From Fig. 1 the influence of the support on the growth of the particles can be inferred. The interaction between vanadium particles and the silica substrate is comparatively weaker than that of vanadium particles on the alumina film as evident from the appearance of larger aggregates even when deposition is performed at 90 K (see Fig. 1). The large aggregates are present even at a growth temperature of 60 K (see Fig. 2). The interpretation of the finding here is in line with another

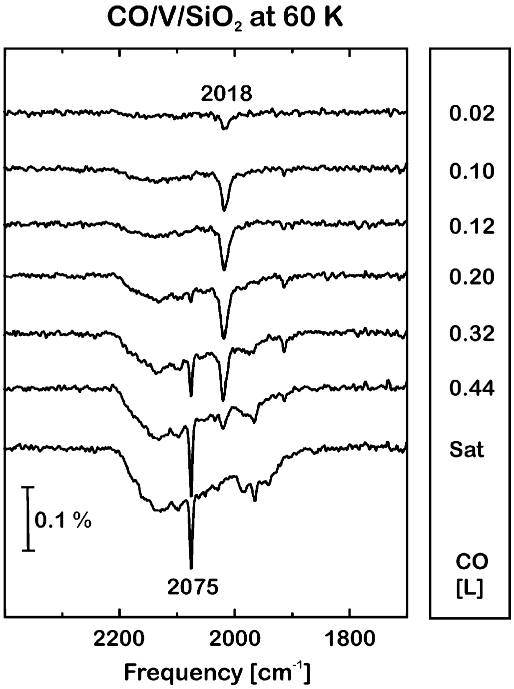

Fig. 2. Vibrational spectra of CO adsorbed on silica-supported vanadium (0.03 MLV) grown at 60 K with varying CO exposure.

study [11] examining the role of the support on the growth and properties of vanadium oxide particles. In that study [11], the vanadium oxide particles interact more strongly with the alumina film than the silica film as inferred from the phonon spectra of the supported particles. The defect densities on alumina and silica films appear not to be the determining parameter for the observed differences [12].

3.2. V/SiO_2 at 60 K

Because of the weak particle–substrate interaction of V/SiO_2, the deposition was performed at 60 and 90 K in order to increase the number of vanadium single atom species. The evolution of the CO infrared spectra for different CO exposures at 60 K is displayed in Fig. 2. For CO dosages between 0.02 and 0.20 L, a single peak at 2018 cm^{-1} dominates the spectra. Between 0.20 and 0.32 L CO exposures, a peak at 2075 cm^{-1} and a broad region (1900–2200 cm^{-1}) develop. The peak at 2075 cm^{-1} then gains intensity and reaches a maximum at the saturation coverage of CO while the peak at 2018 cm^{-1} looses intensity and eventually disappears. In parallel to the 2075 cm^{-1} peak, the broad feature also gains maximum intensity at CO saturation exposure. Identification of the 2018 and 2075 cm^{-1} peaks is shown below via an isotopic study.

As described previously elsewhere [7,8,10], $M_x(CO)_y$ on a solid support where M is a metal atom and x and y are stoichiometric ratios can be identified via adsorption studies using isotopic mixtures. Spectra of ^{12}CO, ^{13}CO, and an equimolar mixture of ^{12}CO and ^{13}CO are shown in Fig. 3a. At low-to-medium CO exposures, ^{12}CO adsorption results in a peak at 2018 cm^{-1} as discussed above and shown in the top of the figure. A peak after ^{13}CO adsorption appears at 1973 cm^{-1} at the equivalent CO exposure (see the bottom of the figure). The peak shift due to the isotope effect is approximately 45 cm^{-1}. Adsorption of the isotopic mixture ($^{12}CO + {}^{13}CO$) leads to two peaks appearing at 2013 and 1970 cm^{-1} and coinciding favorably with ^{12}CO and ^{13}CO bands. Furthermore, the intensity ratio of the doublet is approximately

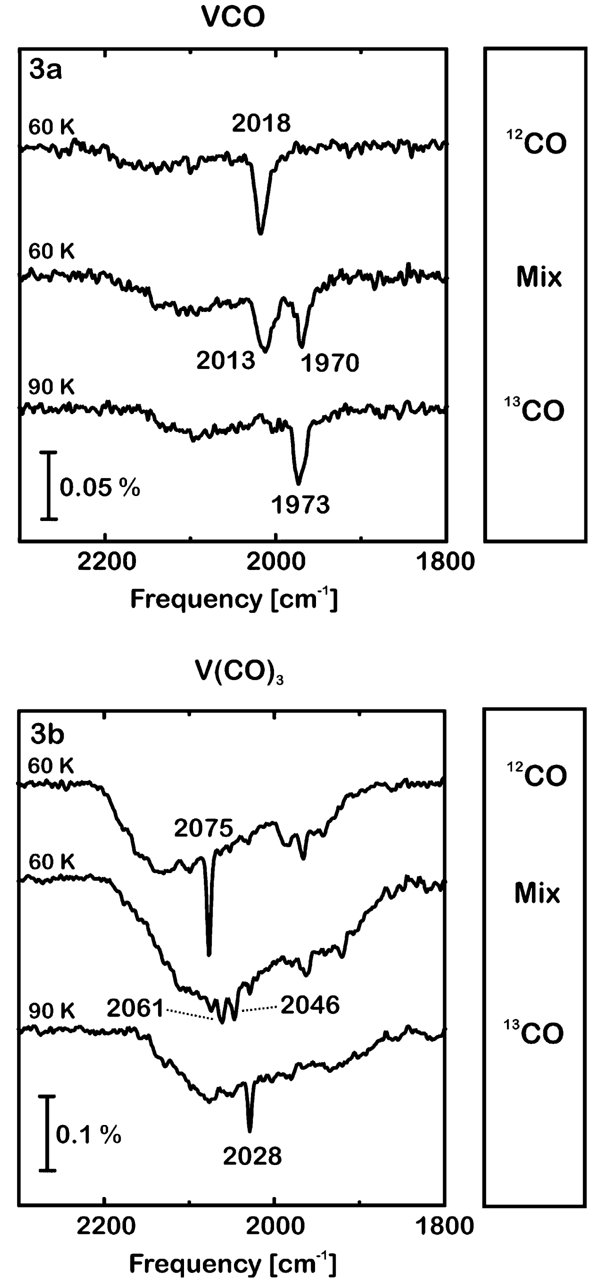

Fig. 3. (a) Infrared spectra of ^{12}CO, ^{13}CO and $^{12}CO + {}^{13}CO$ at low CO exposures adsorbed on V/SiO_2 with the deposition temperature indicated on the left side of each spectrum. (b) Infrared of $CO/V/SiO_2$ at saturation CO coverage.

1:1. Recalling results from Ne-matrix isolated vanadium monocarbonyls (VCO; $x, y = 1$) [12] and from VCO species grown on the alumina film [10], the ^{12}CO frequencies are 2034 cm^{-1} for the former and 1931 cm^{-1} for the latter. The ^{13}CO peaks of the Ne-matrix and the alumina supported studies are observed at 1990 and 1880 cm^{-1}, respectively. In both cases, the separation between the two different isotope peaks is ~44 cm^{-1}, agreeing well with the result seen on the silica film. Thus, the 2018 cm^{-1} species found in this study is assigned to vanadium monocarbonyl (VCO). It can be ruled out that the 2018 cm^{-1} peak emerges from V_xCO where $x \geqslant 2$ because the frequency should appear in a much lower region. The frequencies reported here and in the literature [10,12,13] are also listed in Table 1. It can be inferred from Table 1 that the frequencies of V^{12}CO growth on the alumina and the silica films are displaced by 103 and 87 cm^{-1} when compared to the value of the corresponding Ne-matrix isolated monocarbonyl species [12]. A relatively large shift in the frequency from the isolated matrix case is reasonably explained by the metal–support interaction via charge transfer as shown.

Fig. 3b displays the vibrational spectra of ^{12}CO, ^{13}CO and the isotope mixture adsorption at the CO saturation coverage. The ^{12}CO frequency is observed at 2075 cm^{-1} while the ^{13}CO peak shifts to 2028 cm^{-1}. Furthermore, the ^{12}CO + ^{13}CO mixture shows two additional peaks at 2061 and 2046 cm^{-1} beside the ^{12}CO and ^{13}CO peaks. The splitting of this 2075 cm^{-1} peak into a quartet for the isotope mixture suggests that this species is a tricarbonyl $V_x(CO)_3$ which is confirmed when compared to spectra of $V(CO)_3$ in a Ne-matrix studies [12] where the signal is detected at 1911 cm^{-1}.

Possible geometries of the $V(CO)_3$ species on the alumina film were also discussed in details in the previous publication [10] and a C_{3v} symmetry was suggested in comparison with an isotope study of $Sc(CO)_3$ [12]. On the alumina film, a peak separation of $V(CO)_3$ of −15, −14 and −17 cm^{-1} was observed. In this study, the displacements of the three isotope peaks from the ^{12}CO peak are −14, −15 and −18 cm^{-1}, agreeing well with the quantities found for $V(CO)_3$ on the alumina and the isolated matrix $Sc(CO)_3$. The ratio of the peak intensities is estimated to be approximately 1:3:3:1, which is consistent with the value predicted by statistical abundances. In summary, all indications point to a vanadium tricabonyl species.

Table 1
^{12}CO and ^{13}CO stretching frequencies (cm^{-1}) for monocarbonyl and tricarbonyl vanadium species in a Ne-matrix and deposited on a alumina film and a silica film [10,12,13]

Carbonyl	Ne-matrix [12,13]	V/Al$_2$O$_3$	V/SiO$_2$
VCO(^{12}C,^{13}C)	1931,1888	2034,1990	2018,1973
V(CO)$_3$(^{12}C,^{13}C)	1911,1869	2057,2011	2075,2028

Table 2
Charge state at the vanadium metal center in elementary unit (e) for neutral and singly charged vanadium monocarbonyl according to ab initio calculations [14–16]

Charged species	V charge state	Frequency (cm^{-1})
VCO$^+$	+0.87	2143[a]
VCO	+0.125	1931
VCO$^-$	−0.5[b]	1807

[a] The value is estimated assuming a similar blue-shift of the VCO$^+$ frequency from that of VCO in Ar-matrix [13].

[b] The charge state of VCO$^-$ is estimated based on the results of Ni and Pd monocarbonyls [17].

As discussed earlier, the large shift of the VCO frequency on the solid support cannot be solely explained by matrix effects. One has to account for the metal–support interaction, which can be quantified in the form of a charge state at the metal center. The frequencies of alumina supported VCO were previously used to quantify the amount of the charge transfer [10]. To obtain the quantity, first a correlation of the VCO frequencies obtained from the Ne-matrix study [12,13] and the charge states at the metal center calculated by an ab initio methods [14–16] were established. All the numbers are listed in Table 2. Then, assuming a linear relationship between these two quantities, the charge of vanadium centers on the alumina film was calculated to be +0.5e for a growth temperature of 300 K and +0.2e after deposition at 90 K. This difference was explained by different adsorption sites. At 300 K nucleation takes place at defect sites whereas nucleation occurs at ‘regular’ sites at 90 K since the metal–support charge transfer is governed by the charge state at the nucleation site [10]. The amount of charge transfer between metal centers and the support then modifies the extent of metal-to-CO π-back-donation, hence affecting the VCO frequency. Estimated in a similar manner, the amount of charge transfer on the vanadium metal center deposited on the silica film is approximately +0.4e. However, it should be pointed out here that there has not been any conclusive evidence to support whether the nucleation of the vanadium particles on the silica film occurs at defect or ‘regular’ sites. This remains an open issue and should be investigated further in the future.

4. Conclusion

Vanadium single atoms were prepared successfully at 60 K on a well-ordered silica thin film and characterized by a combined IRAS and CO adsorption. CO adsorption of this system gives rise to a monocarbonyl species at low CO exposure and a vanadium tricarbonyl at saturation coverage, similar to the results obtained on alumina-supported vanadium particles grown at 300 K. Nevertheless, the metal–support interaction is weaker on the silica than on the alumina as inferred from the CO adsorption experiments. The amount of the charge transfer between vanadium metal atoms and the silica support is estimated to be +0.4e.

Acknowledgements

The authors thank the Max Planck Society and the Deutsche Forschungsgemeinschaft (DFG) through the Sonderforschungsbereich 546 for financial support throughout the course of this work. Norbert Magg thank in particular the Studienstiftung des Deutschen Volkes for a fellowship.

References

[1] C. Copéret, M. Chabanas, R.P. Saint-Arroman, J.M. Basset, Angew. Chem. Int. Ed. Engl. 42 (2003) 156.
[2] M.A. Barteau, J.E. Lyons, I.K. Song, J. Catal. 216 (2003).
[3] M.D. Jones, R. Raja, J.M. Thomas, B.F.G. Johnson, Top. Catal. 25 (2003) 71.
[4] T.D. Tilley, J. Mol. Cat. A 182–183 (2002) 17.
[5] R.M. Jaegar, H. Kuhlenbeck, H.-J. Freund, M. Wuttig, W. Hoffmann, R. Franchy, H. Ibach, Surf. Sci. 259 (1991) 235.
[6] T. Schroeder, J.B. Giorgi, M. Bäumer, H.-J. Fruend, Phys. Rev. B 66 (2002) 165422.
[7] M. Frank, R. Kühnemuth, M. Bäumer, H.-J. Freund, Surf. Sci. 454–456 (2000) 968.
[8] M. Frank, M. Bäumer, H.-J. Freund, J. Phys. Chem. B 105 (2001) 8569.
[9] J.B. Giorgi, T. Schroeder, M. Bäumer, H.-J. Freund, Surf. Sci. 498 (2002) L71.
[10] N. Magg, J.B. Giorgi, M.M. Frank, B. Immaraporn, T. Schroeder, M. Bäumer, H.-J. Freund, J. Am. Chem. Soc. (in press).
[11] N. Magg, B. Immaraporn, J.B. Giorgi, T. Schroeder, M. Bäumer, J. Döbler, Z. Wu, E. Kondrarenko, M. Cherian, M. Baerns, P.C. Stair, J. Sauer, H.-J. Freund, J. Catal. (in press).
[12] N. Magg, Thesis, Humboldt Universität, 2003.
[13] M. Zhou, L. Andrews, J. Phys. Chem. A 103 (1999) 5259.
[14] M. Zhou, L. Andrews, C.W. Bauschlicher Jr., Chem. Rev. 101 (2001) 1931.
[15] C. Adamo, F. Lelj, J. Chem. Phys. 103 (1995) 10605.
[16] L.A. Barnes, C.W. Bauschlicher Jr., J. Chem. Phys. 91 (1989) 314.
[17] L.A. Barnes, M. Rosi, C.W. Bauschlicher Jr., J. Chem. Phys. 93 (1990) 609.