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Preparation of highly dispersed molybdenum on alumina by thermal decomposition of $Mo(CO)_6$

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Abstract

Supported molybdenum catalysts are uniquely suitable for a number of reactions, notably the metathesis reaction between hydrocarbons with terminal double bonds. Heterogeneous catalysis offers advantages over homogenous routes with respect to catalyst recycling and separation. A way to produce extremely highly dispersed Mo-metal particles on completely dehydroxylated surfaces from $Mo(CO)_6$ is described. The metal dispersion is found to depend on: metal loading – higher loading leads to lower dispersion and larger particles; initial dispersion of the precursor – a dry process by subliming the $Mo(CO)_6$ onto the support was found to give a lower metal dispersion than a wet impregnation process, starting from a pentane solution of $Mo(CO)_6$. A method for the determination of Mo-dispersion on highly activated alumina surfaces by CO chemisorption has been established. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Molybdenum; Metal dispersion measurement; CO chemisorption

1. Introduction

Molybdenum-based catalysts have found many applications, both in homogeneous and heterogeneous catalysis [1]. Brenner and Burwell [2–7] did an extensive study of supported Mo-catalysts, derived from $Mo(CO)_6$. It was found that the surface assisted decomposition of the metal carbonyl on γ-alumina takes place via an intermediate surface-bound tricarbonyl species, which is stable enough for IR-spectroscopic examination. Further decomposition of this subcarbonyl species is accompanied by the evolution not only of CO, but also of hydrogen, indicating that the molybdenum undergoes oxidation as a result of a reaction with surface OH (σ-OH)-groups. It had been claimed at some time that whereas bulk MoO_3 was easily reduced by hydrogen, the surface-adsorbed molybdenum oxide could not be reduced to the metal, but Nakamura et al. [4] showed that metallic molybdenum could be obtained by the decomposition of $Mo(CO)_6$ over completely dehydroxylated alumina. The work of Hall and his group [8] proved that at sufficiently high temperature (>1100 K), supported MoO_3 can be reduced by hydrogen to give an essentially identical catalyst. However, the metal lost some of its high dispersion when treated to such high temperatures, and the support too lost surface area.

Since surface hydroxyl groups are responsible for the oxidation of molybdenum during the decomposition of complexes which contain the metal in its zero oxidation state, it was reasoned that complete removal of surface OH-groups should allow one to obtain metallic particles directly by decomposition of

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$Mo(CO)_6$. This has been proven in the earlier work by Brenner's and Burwell's groups. We followed this idea and investigated the structure of the adsorbed species at the surface with temperature programmed decomposition, monitoring the CO and hydrogen signal with a mass spectrometer. We were able to confirm the earlier reports that the decomposition spectrum changes with the chemical nature of the support [9] and with the degree of dehydroxylation of the surface [10]. Furthermore, we observed that the desorption spectrum depends also on the loading with $Mo(CO)_6$. This can be explained if one assumes that the adsorbed $Mo(CO)_6$ has high mobility at the surface; at low concentration, it becomes preferentially adsorbed at certain "deep trap" sites, e.g., kinks or missing atoms within terraces. The energetics of the decomposition reaction over these sites as revealed by temperature programmed decomposition (TPDE) are different from the situation at the more abundant step or terrace sites. Thus, by measuring TPDE spectra at various $Mo(CO)_6$ loadings, it is possible to "titrate" certain types of surface sites.

2. Experimental

2.1. Materials

$Mo(CO)_6$ (Alpha Chemicals) was used as received. Alumina (Degussa Aluminum Oxide C) was dehydroxylated by evacuating and heating to 1000°C. At this temperature, almost complete dehydroxylation is achieved. The resulting material had a surface area of 93.4 m^2/g, slightly lower than the 98 m^2/g of the original material, after drying at 300°C. Gases for adsorption measurements (hydrogen, nitrogen and CO) were of the highest commercial purity, and were dried by passing them over traps with molecular sieve 4 Å. In order to remove small quantities of $Fe(CO)_5$ which had formed during storage, the CO was in addition passed through a trap with activated carbon.

2.2. Techniques

For the dispersion measurements, the alumina was dehydroxylated in a quartz sample cell connected to the vacuum line of a home-built volumetric adsorption apparatus. The material in the cell was slowly heated to 1000°C, and great care was taken that the light material was not carried out of the cell by the evolving gases. The cell was then cooled under vacuum and filled with helium. $Mo(CO)_6$ was added either in bulk (dry preparation) or as a solution in pentane. The dry-mixed preparations were treated as follows: the alumina/$Mo(CO)_6$-mixture was cooled in an ice bath and evacuated for 10 min. The valve connecting the calibrated volume to the pump was then closed, and the sample was heated slowly to 300°C, and kept at this temperature for 1 h to achieve complete decomposition of the molybdenum carbonyl. Previous studies of the thermal decomposition of the carbonyl complex had shown that below 350°C, no hydrogen was evolved, indicating that the metal remained in the zero oxidation state. The amount of CO evolved could be determined from the pressure rise in the calibrated volume. In the alternative solution method, between 2 and 20 mg $Mo(CO)_6$ was dissolved in 5 ml freshly distilled pentane, and 4 ml of this solution was injected into the support with a gas tight syringe. The solution was allowed to remain in contact with the support for about 10 min. Thereafter, the pentane was removed by pumping; the reaction mixture was kept at 0°C during the entire preparation. After all solvent had been removed, the temperature was increased to 300°C as with the dry samples. However, since substantial amounts of solvent were still desorbing, the pressure rise could not be used as an indicator of the amount of $Mo(CO)_6$ decomposed.

The entire adsorption apparatus is constructed from stainless steel with the exception of the sample cell, which is made from quartz. All valves were Nupro bellows valves. The pressure was measured by a two-sensor capacitance manometer system (MKS Baratron 122A). Samples were kept for 1 h at the decomposition temperature and subsequently evacuated to $<10^{-6}$ mbar. Complete CO adsorption isotherms from 1 to 1000 mbar were recorded to determine the metal dispersion. Initially, the adsorption isotherms were recorded at -78°C. It was found that the amount of CO adsorbed under these conditions was very high. Obviously, the coordinatively unsaturated sites which have been created at the surface during dehydroxylation of the alumina also bind CO strongly [11,12]. It was attempted to separate adsorption on the alumina from that on the Mo by the two-isotherm method [13]: after recording the first isotherm, the sample was pumped down again to remove physisorbed CO, and a second adsorption isotherm was recorded which then gives the reversibly physisorbed amount only. The difference between these two isotherms should correspond to the chemisorbed CO. However, the amount determined by this method seemed too high, and the results varied with the pumping time, indicating that there is not sufficient difference between the sorption strength to the Mo-metal, and to the support. Measurements of the CO sorption capacity of the support alone proved to be very reproducible, and an attempt was made to measure the Mo-dispersion from the difference between the adsorption isotherm of the pure support, and the isotherm of the impregnated material after decomposition of $Mo(CO)_6$ at 300°C. The amount of CO adsorbed on the metal-loaded catalyst was lower than that on the clean support. We assume that the molybdenum binds to coordinatively unsaturated (cus) sites on the alumina surface, which are then no longer available to adsorb CO. One Mo-atom removes several cus–Al sites, and therefore a lower CO sorption capacity is observed for the metal-loaded samples. Finally, the following modification of the method was found to give satisfactory results: the adsorption capacity was measured at room temperature, first for the pure support, and then for the material after impregnation and decomposition. The total amount of CO adsorbed was much smaller at the higher temperature, and the adsorption capacity of the Mo-loaded material was consistently higher than that of the support (Fig. 1). The two isotherms are almost parallel and become linear at higher pressure. To obtain the amount of CO bound to Mo, the linear part of the upper curve (adsorption at the Mo plus the support) and the lower curve (adsorption on the support only) were extrapolated to zero pressure, and the difference was taken as the volume of CO chemisorbed at the metal.

An attempt was also made to use hydrogen chemisorption as a selective method to determine metal dispersion. It was found that even after activation at 1000°C, the γ-alumina support by itself did not adsorb any hydrogen at room temperature. However, the Mo-containing material after activation did also not adsorb any measurable amount of hydrogen. Only after the sample was reduced in hydrogen at 800°C did hydrogen uptake occur. However, the isotherm (Fig. 2) is very unusual: the amount adsorbed is essentially zero up to a pressure of 300 mbar; thereafter, it increases almost linearly with pressure. Since the isotherm did not reach any saturation value, it did not allow for any meaningful determination of the number of adsorption sites. All further work was restricted to CO adsorption isotherms at room temperature.

For TPDE at different loading, a flow microreactor connected to a small mass spectrometer for evolved gas analysis was used [9]. The support (~0.5 g) was dehydroxylated in flowing helium and allowed to cool down. A solution of $Mo(CO)_6$ in freshly distilled pentane was added, and the pentane was completely evaporated at 0°C. A temperature ramp was then applied, and the signals for CO and H_2 in the He-carrier were monitored as a function of temperature. After every measurement, the instrument was cali-

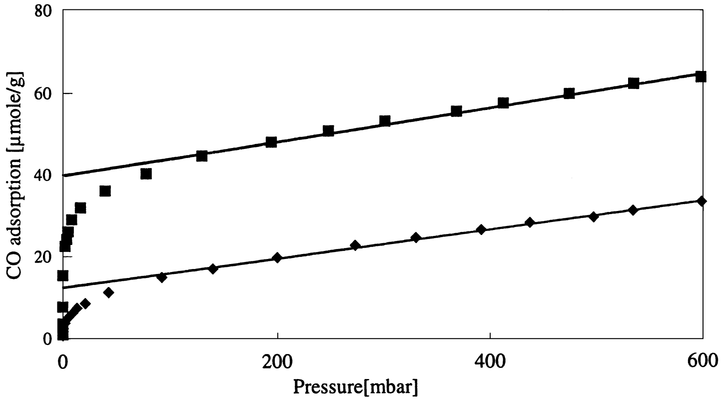


Fig. 1. CO adsorption isotherms at room temperature on dehydroxylated alumina (lower trace) and molybdenum/alumina (upper trace).

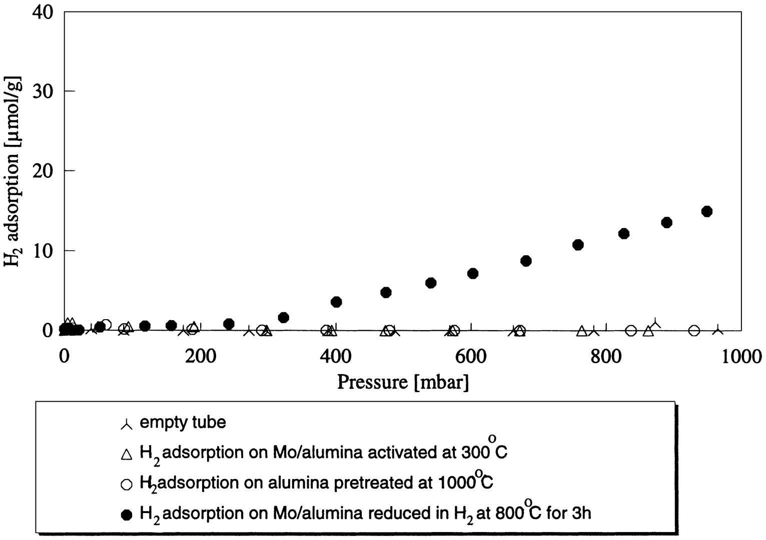


Fig. 2. Hydrogen adsorption isotherm at room temperature.

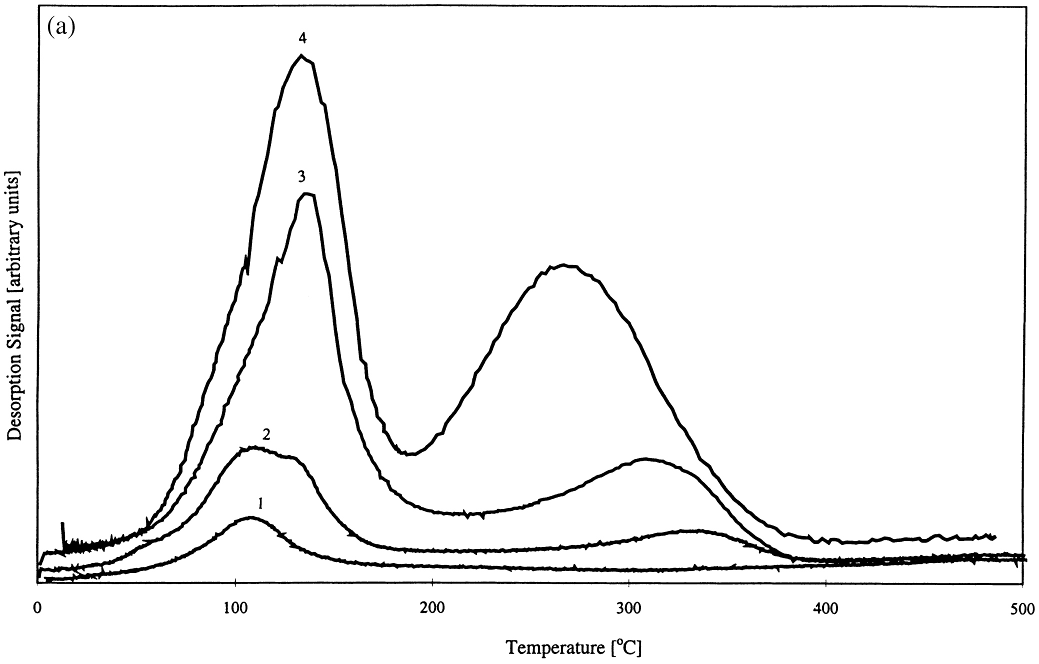
brated with an injection of a known amount of the gases.

3. Results

Two preparations of supported Mo were made by the dry-mixing method with different initial $Mo(CO)_6$ loading. The dispersion as determined by CO adsorption is rather low: 0.09 and 0.17, respectively, for samples which differed in Mo-loading by a factor of 2. Both samples adsorbed almost equal amounts of CO, even though sample 2 had only 1/2 the $Mo(CO)_6$-loading. The results are shown in Table 1 and compared with the samples which were prepared by the solution impregnation method. The trend observed in the dry-mixed series becomes even more pronounced within the solvent series: the dispersion increases considerably with decreasing loading. However, the solution-derived samples show much higher dispersion: at a loading comparable to that of the dry-mixed samples, the dispersion was 0.40 for the more concentrated sample, and 0.71 for a sample with a loading of 0.28 Mo/nm^2. If the surface concentration was reduced even further, a dispersion of 1 was achieved. For the determination of the dispersion, a 1:1 relationship between surface exposed Mo-atoms and CO molecules has been assumed. The dispersion is defined as (number of atoms in the surface)/(number of atoms in the sample). We assume that one metallic molybdenum site can bind one CO molecule. A dispersion of $D=1$ could indicate a mono-atomic layer of Mo-metal on the surface. However, the Mo-loading is too much low to form a continuous mono-layer.

Table 1
Mo dispersion and particle size determined from the CO adsorption at room temperature

Sample	Mo (wt%)	Total Mo atoms (nm^{-2})	CO ads. (µmol/g)	Adsorption sites (nm^{-2})	Dispersion, D	Particle size (nm)
Dry mix 1	1.25	0.84	12.0	0.077	0.092	12
Dry mix 2	0.67	0.45	11.8	0.076	0.17	6.6
Solv 1	0.89	0.60	37.0	0.24	0.40	2.8
Solv 2	0.42	0.28	30.7	0.20	0.71	1.6
Solv 3	0.25	0.17	26.5	0.17	1.0	1.1
Solv 4	0.13	0.087	13.6	0.088	1.0	1.1



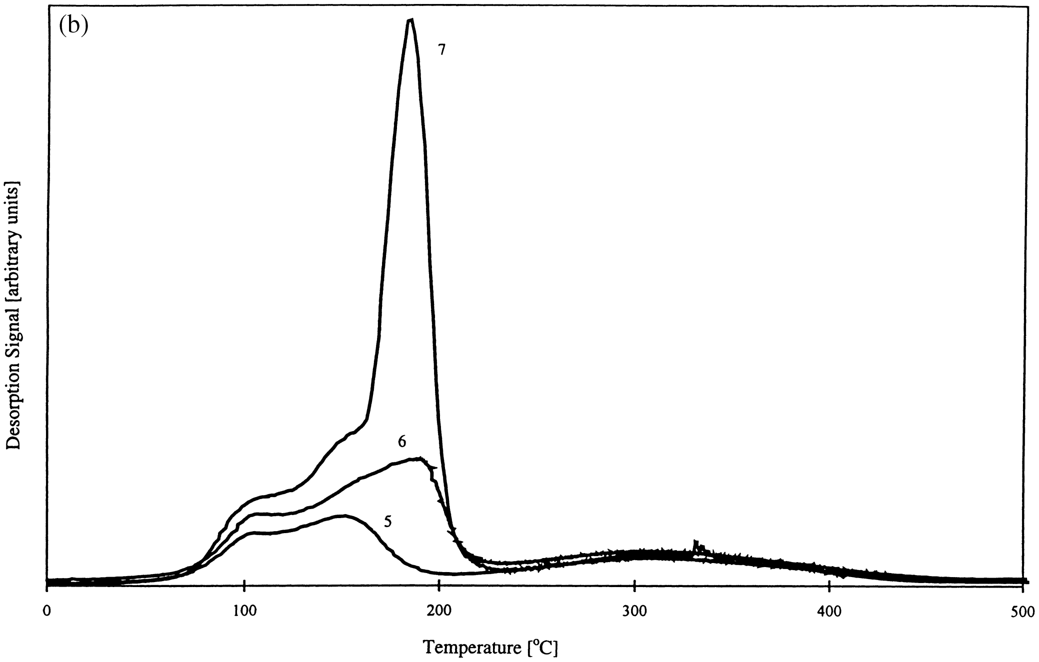


Fig. 3. (a) CO evolution spectra during TPDE of samples with low Mo-loading. Loading [Mo/nm^2]: (1) 0.004; (2) 0.013; (3) 0.034; (4) 0.140. (b) CO evolution spectra during TPDE of samples with high Mo-loading. Loading [Mo/nm^2]: (5) 0.26; (6) 0.32; (7) 0.55.

Another model which can explain the high dispersion is that of a mono-layer raft structure [14]. Such structures may be stabilized by the adsorption of CO. We assume that the Mo-metal exists in the form of small crystallites on the surface, which are too small to be detected by powder X-ray spectroscopy. The average particle diameter can be calculated from the dispersion using the relation d (nm)$=1.11/D$ as derived in Section 4. The values are also included in Table 1.

Our values for the particle size have to be compared with the value of 3 nm cited by Burwell [5] from an analysis of TEM micrographs for a material with a dispersion of 0.30. Finally, we cannot exclude the possibility that the decomposition product at 300°C is not entirely metallic, but contains carbidic carbon, which can stabilize a metal cluster. Lee and Boudard [15] determined the structure of a supported Mo-catalyst, using EXAFS. Their material was obtained by heating $Mo(CO)_6$ on dehydroxylated alumina in flowing hydrogen. Initially, a highly C-deficient Mo_2C was formed, which transformed into metallic molybdenum only at a temperature of 700°C.

To obtain more information on the reaction path which leads from adsorbed carbonyl complexes to metallic deposits, the TPDE of γ-alumina with different $Mo(CO)_6$-loading was studied over a wide concentration range. The support had been pretreated at 500°C. These conditions led to a partially dehydroxylated surface. The most dilute samples contained only 0.004 Mo/nm^2, whereas the highest concentration of 0.55 Mo/nm^2 was close to mono-layer coverage of the precursor, $Mo(CO)_6$. Burwell [5] reported that the number of σ-OH on a hydroxylated surface is about 15 OH/nm^2 and drops to 0.12 OH/nm^2 on material that has been dehydroxylated at 900°C. The samples thus cover the range from Mo<σ-OH to Mo>σ-OH. A series of TPDE spectra is shown in Fig. 3.

4. Discussion

The adsorption of a mono-nuclear metal carbonyl leads initially to physisorption of the molecular complex. From this state, the carbonyl may either desorb again, or it loses one (or more) CO-groups and becomes chemisorbed to the surface. On a partially dehydroxylated γ-alumina surface, Lewis acid (coordinatively unsaturated aluminum ions) and Bronsted acid sites as well as base sites are present. Several mechanisms can be perceived for the initiation of the CO loss: at a strong Lewis acid site, the CO ligand will donate electrons to the acid center, resulting in *trans*-labilization of the complex. This labilized CO molecule will thus dissociate from the complex at lower temperature. The stronger the acid site, the larger is the *trans*-labilizing effect. Strongly acidic surface sites will therefore result in a CO signal at low temperature. Alternatively, reaction with a basic, electron-donating σ-OH group can transform a carbonyl group into the acyl group –C(=O)–O–, resulting in *cis*-labilization of the complex. Furthermore, σ-OH can react in a nucleophilic ligand substitution reaction with the complex. Molybdenum hexacarbonyl is a highly symmetric, spherical molecule, and it is easy to perceive that it has considerable mobility on the surface. Thus, it will move until it finds a binding site which holds it more strongly. Steps and kinks have been identified as such sites, as well as clusters of σ-OH groups. At the lowest Mo-concentration, the reaction pathway is dominated by the most strongly binding sites. These sites catalyze the direct decomposition of the mono-nuclear carbonyl complex in a single step; the decarbonylation sets in already below 100°C, and the desorption signal consists of a single sharp peak (curve 1 in Fig. 3). At a loading between 0.013 and 0.034 Mo/nm^2, a second desorption signal, well separated from the first peak, appears at >300°C. The absence of any CO desorption at intermediate temperatures indicates the presence of a stable surface-adsorbed subcarbonyl species, the stoichiometry of which can be obtained from the area of the CO desorption signals. At low concentration, the area of the two peaks is in the ratio of 2:1, indicating that a species of the composition $Mo(CO)_2$ is stabilized at the surface. We assume that this species, which has lost four CO-groups out of the complex, is located at the step sites of the six support where four bonds can form with σ-OH. At a yet higher loading of 0.14 Mo/nm^2, the number of step sites is not sufficient, and the decomposition reaction takes place on the terraces. Here only bonding to three σ-OH groups is possible if the central Mo-atom is to maintain its octahedral coordination. This results in the typical spectra with two broad desorption peaks with a ratio of 1:1 as first reported by Brenner [2]. As the loading is further increased, both the low temperature and the high temperature bands show additional changes: the high temperature band moves to a higher temperature, but remains virtually unchanged for even higher concentrations. We have shown earlier [10] that the desorption band can be deconvoluted into signals for the individual CO molecules which are eliminated from the complex in a step-wise fashion. A careful analysis of the desorption signals thus indicated that multinuclear molybdenum carbonyl clusters form at the surface as a step on the way which leads to metallic particles. We assign the high temperature band to the loss of CO from the surface of extended clusters or essentially metallic particles, and to the decomposition of the carbidic material which has been observed by Lee and Boudard [15]. The carbidic carbon is converted to CO, probably by reaction with the oxidic support which provides the necessary oxygen. The low temperature peak too changes in appearance: a shoulder appears at 100 °C, and the center of gravity of the signal shifts to higher temperature. This indicates that surface sites of increasingly weaker acidity are used to bind the carbonyl complex to the surface.

The TPDE obtained on completely dehydroxylated surfaces is similar to that obtained on a partially dehydroxylated surface at high metal carbonyl loading. That indicates that the ratio σ-OH:metal controls the decomposition pathway; a low value for this ratio is obtained either by decreasing the amount of σ-OH by the high temperature pretreatment of the support, or by increasing the amount of molybdenum carbonyl adsorbed at the surface. The subcarbonyl species are much more mobile in the absence of surface hydroxyl groups, which provide for anchoring places. Thus, clustering and finally nucleation of small metal particles can take place. Brenner [2] had shown that the early precursor, e.g., the mono-nuclear subcarbonyls with three or more CO ligands, can be reversibly carbonylated to form $Mo(CO)_6$. However, the loss of additional CO is irreversible.

We use the selective chemisorption of CO to the metal surface as a method to determine the metal dispersion. In order to apply this method successfully, it is necessary to know the stoichiometry of the adsorption process. This is especially problematic for very small particles where the number of steps and kinks is large. Atoms in such sites are more accessible, and may bind more than one CO molecule [14]. We use here the concept that one CO binds to one site; a site corresponds to the cross-sectional area of a metal atom. From the dispersion, the average size of the metallic particles can be derived. We use a simple geometrical argument to obtain an estimate of the particle size. It is assumed that all metal particles can be visualized as half-spheres which sit on the surface of the alumina. The average radius of the particles is R. The volume of a half-sphere is $2/3\pi R^3$, and the surface area $2\pi R^2$. The number of atoms in the crystallite is found by dividing the volume of the crystallite by the volume of an individual molybdenum atom, and the number of potential adsorption sites is the surface area of the crystallite divided by the cross-sectional area of an atom, given as πr^2. The atomic radius of Mo is taken as 0.139 nm. According to this model, the particle diameter d is connected with the dispersion D by the relation $d{=}2R{=}1.11/D$. The diameter of the deposited molybdenum particles as calculated with this formula is found to vary from 12 nm for the dry-impregnated sample at high $Mo(CO)_6$ concentration to as little as 1.1 nm for the most highly dispersed samples at low loading. Obviously, a low concentration favors the formation of very small metal particles. At a low concentration, most $Mo(CO)_6$ become localized at "deep trap" sites, and decomposition takes place in a single step. In contrast, at a higher concentration, subcarbonyls with considerable surface mobility [16] are much more abundant, and grain growth to larger crystallites can take place. The dry impregnation method does not lead to very uniform distribution of the carbonyl in the starting material [17]. Thus, most of the $Mo(CO)_6$ is deposited in patches with relatively high concentration, and consequently, bigger metal particles are formed.

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