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Probing silica-supported Mo^{2+} by means of FT-IR of adsorbed CO

Joaquín L. Brito* and Beulah Griffe

Laboratorio de Fisicoquímica de Superfícies, Centro de Química, Instituto Venezolano de Investigaciones Científicas (I.V.I.C.),
Apartado 21827, Caracas 1020-A, Venezuela
E-mail: joabrito@ivic.ivic.ve

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Well defined Mo^{2+} surface sites of silica-supported catalyst, produced by H_2 reduction of the fixed molybdenum tetraallyl precursor, show a characteristic IR signal at 2170 cm^{-1} due to adsorbed carbon monoxide. Higher oxidation states of Mo in the same catalyst do not show any signal related to this probe molecule.

Keywords: CO adsorption, IR spectroscopy, Mo–allyl precursor, Mo/SiO_2 catalysts

Molybdenum based catalysts play a significant role in a variety of different reactions, ranging from partial oxidation processes to deep reductive transformations [1]. This versatility is in part the result of the ample range of stable oxidation states (O.S.) that this metal can adopt, depending on the operating reaction conditions, pretreatments, type of support, metal loading, etc. In particular, the industrial-like Mo catalysts are quite complicated materials that may include a variety of surface structures: In the case of Mo/SiO_2, e.g., molybdate-like monomers with tetrahedral symmetry, octahedrally coordinated polyanions, heteropolymolybdate structures (silicomolybdic anions), and microcrystalline MoO_3 have all been reported [2]. Activation of the catalysts, carried out by means of reductive processes (thermal or photo reduction, sulfiding, etc.), results in extremely complex distributions of species in several valence states [3,4]. On the other hand, the Mo/SiO_2 and Mo/Al_2O_3 catalysts obtained by reaction between $Mo(\eta^3\text{-}C_3H_5)_4$ and the OH groups of the supports have been proposed to show uniform surface sites that could be reversibly shifted between discrete Mo^{2+}, Mo^{4+} and Mo^{6+} O.S., as can be seen in scheme 1 [5,6]. The proposed uniqueness of these "model" catalysts, reflected in the transformations shown in the scheme, has been challenged by Kaliaguine et al. [7] and Ekerdt et al. [8], who found no significant differences between Mo/SiO_2 catalysts prepared by impregnation with ammonium heptamolybdate solutions and those synthesized by immobilization of the allyl precursor. It must be noted, however, that these workers did not follow the preparation/pretreatment protocol shown in scheme 1, which according to Yermakov [5] and Iwasawa [6] renders reversibility in the indicated transformations. More recently, in the course of an X-ray photoelectron spectroscopy (XPS) study [9], it was confirmed that the Mo^{2+} and Mo^{6+} O.S. of Mo–allyl derived catalysts, submitted strictly to the red-ox treatments employed by the Yermakov and Iwasawa groups, consist almost exclusively of uniform species in the corresponding valence states. On the other hand, it was shown that the Mo^{4+} "O.S." is actually a mixture of several species ranging from Mo^{3+} to Mo^{6+} [9].

Infrared spectroscopy of adsorbed carbon monoxide has been employed as a convenient characterization technique to probe the characteristics, especially oxidation state, of supported transition metal ions [10]. Mo-based catalysts prepared by conventional impregnation from aqueous solutions (industrial-like catalysts) have received some attention in this regard [11]. However, the complexity of these systems as well as the lack of direct means of checking the O.S. of surface species to correlate with the previous IR studies has resulted in disagreement in the assignations of the observed CO absorption bands [11,12]. Other preparation methods, such as grafting of $MoCl_5$ [12] or of allyl complexes have been comparatively much less used, although such methods should render more convenient solids to probe the nature of the surface sites, due to the higher homogeneity of the resulting surfaces.

It is clear that well defined catalysts with uniform surface species in a single known valence state would be desirable "standards" to properly correlate the IR frequency observed to the O.S. of the probed Mo^{n+} site. In this communication we report the use of $Mo(\eta^3\text{-}C_3H_5)_4$ derived catalysts supported on SiO_2 to establish a relationship between the IR frequency of adsorbed CO and the O.S. of supported Mo^{2+} species. It is shown that higher O.S. of these presumably isolated Mo sites do not adsorb CO.

The preparation of Mo/SiO_2 samples was carried out in situ in the IR cell by sublimation of $Mo(\eta^3\text{-}C_3H_5)_4$ onto wafers of silica, which were pressed beforehand and calcined at 550°C in flowing O_2 for 2 h followed by eva-

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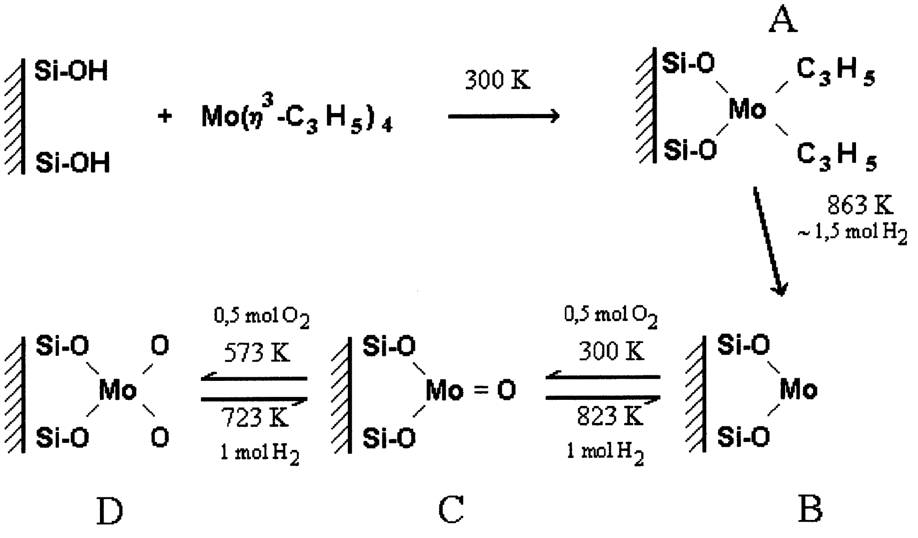
* To whom correspondence should be addressed.



Scheme 1. Scheme for the synthesis and reversible red-ox transformations of Mo/SiO_2 derived from $Mo(\eta^3\text{-}C_3H_5)_4$. The experimental conditions and stoichiometries of the synthesis and red-ox transformations are indicated.

cuation at the same temperature for 2 h. Sublimation of the complex from an attached cold finger was done under a reduced pressure of purified N_2. Prolonged evacuation at room temperature ensured removal of any physisorbed complex. The Mo loading was verified by atomic absorption spectroscopy. Subsequent red-ox treatments, under the conditions shown in scheme 1, were performed in the cell to obtain the desired state of the catalyst before admission of CO. For the FT-IR analyses, an IR glass cell with magnetic driving was employed which allowed in situ pretreatment of samples in an upper quartz zone, and loading of the complex and IR measurements in the Pyrex bottom part. Calcium fluoride optics were employed. The cell was connected to an all-glass line for gas admission or evacuation. Heating was carried out with a built-in furnace in the quartz region of the cell. Spectra were recorded in absorbance mode with a Nicolet 5DXC instrument at a resolution of 2 cm^{-1}; 100 interferograms, recorded at beam temperature, were accumulated per spectra. All measurements were corrected by subtraction of the gas phase background, taken by raising the sample from the beam path.

X-ray photoelectron spectroscopic results [9] of the catalysts submitted to the first two red-ox cycles had shown for species B (scheme 1) a main contribution due to a single oxidation state of Mo, which was assigned to Mo^{2+} on the basis of both stoichiometric measurements of H_2/O_2 consumption during reduction/oxidation and binding energies of the Mo 3d doublet [9]. A minor contribution (less than 10%) due to a Mo^{4+} species was also detected in this state of the catalyst. For the proposed species C, which according to the stoichiometric measurements presents an average O.S. Mo^{4+}, a broad Mo 3d XPS envelope was observed which could only be curve-fitted with contributions from several oxidation states, ranging from Mo^{3+} to Mo^{6+} [9]. This showed that a single species such as C is not *exclusively* present in this state of the catalyst, contrary to the original claims [5,6]. Oxidation at 573 K produced Mo^{6+}, most probably as a single isolated species tetrahedrally bound, according to a thorough characterization study of this state of the catalyst by Iwasawa [13]. However, Williams et al. have discussed that an octahedral coordination of Mo in such catalysts cannot be completely ruled out [8]. After oxidation and a second reduction at 823 K, the dominating Mo^{2+} species is once again observed. The reversibility in the XPS measurements of these first two cycles of red-ox transformations supports the assignation of species A, B and D as single isolated Mo sites well dispersed onto the silica support (see below).

After the first reduction in H_2 at 823 K and evacuation at the same temperature (species B), the fixed Mo/SiO_2 catalyst presents a single and relatively sharp peak at $\sim$ 2170 cm^{-1} in the presence of 20–150 Torr of CO at room temperature (figures 1a, 1b). The intensity of this signal is independent of the CO pressure within the range studied, but it increases with the amount of complex loaded onto the catalyst (compare figures 1a and 1b). If the sample reduced at 823 K is not evacuated at high temperature, but instead it is cooled in H_2 to room temperature before evacuation and admission of CO, the peak at 2170 cm^{-1} is strongly decreased in intensity. This suggests that adsorbed hydrogen can block the adsorption sites for CO. Whenever it is present, this signal disappears readily after evacuation at room temperature, and is fully restored upon re-admission of CO. However, if the sample is exposed to O_2 at room temperature (forming the mixture of Mo^{n+} species described above), no peaks due to adsorbed CO are detected, even after prolonged evacuation at 823 K. No further carbonyl bands were observed neither in the fully oxidic samples

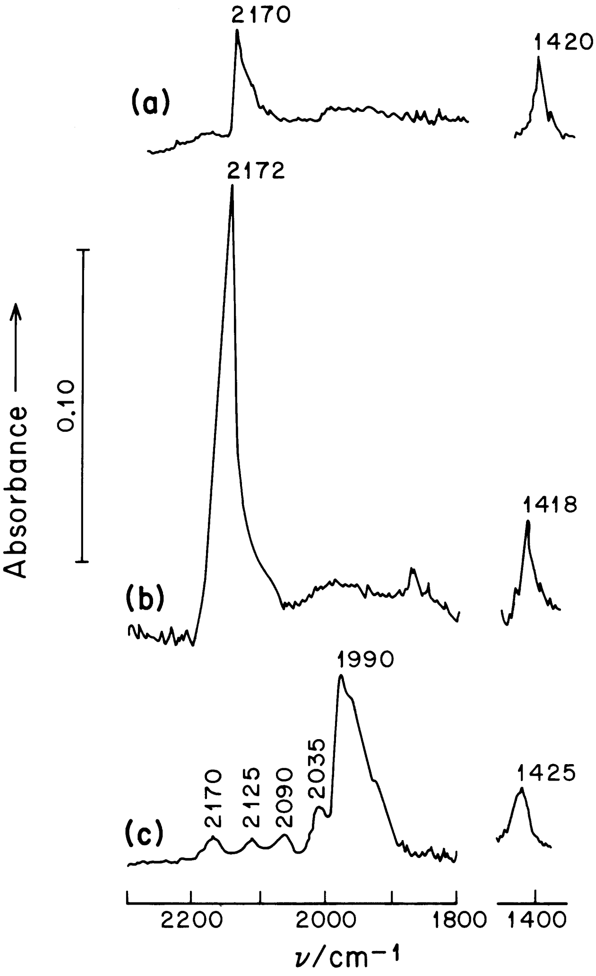


Figure 1. FT-IR spectra of CO adsorbed on Mo/SiO_2 reduced at 823 K in 200 Torr H_2 for 2 h. (a) 0.5 wt% Mo, after 2 h in contact with 40 Torr CO; (b) 1.6 wt% Mo, after 2 h in contact with 40 Torr CO; (c) 1.6 wt% Mo, after 24 h in contact with 60 Torr CO.

(species D) nor in that reduced at 723 K in 100 Torr of H_2 for 2 h (mixture of several species, mean O.S. Mo^{4+}). After a second reduction at 823 K, the 2170 cm^{-1} band is again present upon exposure to CO, with an intensity similar to that obtained in the first red-ox cycle. If the samples that show the 2170 cm^{-1} peak are left in contact with gaseous CO, a peak at ~ 1420 cm^{-1} develops slowly, its intensity stabilizing after ca. 2 h, and being independent of the amount of Mo in the catalyst (compare figures 1a and 1b). Upon increasing periods of time (up to 24 h), a peak at 1990 cm^{-1} appears and increases in size slowly with time in contact with CO, at the expense of the 2170 cm^{-1} band which decreases sharply (figure 1c). Smaller bands also become apparent at ~2120, ~2090 and ~2030 cm^{-1}. It is interesting that this evolution of the IR bands seems to require the presence of light; if the sample is kept in the dark, the intensity variations of the main peaks (2170 and 1990 cm^{-1}) are strongly slowed down.

These results allow one to assign the signal at 2170 cm^{-1} to isolated Mo^{2+} sites in the catalysts, as confirmed by XPS, and show that higher O.S. of Mo in this type of catalyst are unable to adsorb the carbon monoxide probe molecule. Peaks of adsorbed CO at around 2170 cm^{-1} have been assigned previously to Mo^{3+} sites supported on silica [11,12]. However, as indicated by Louis et al [12], "these assignments were based on previous attributions which were themselves empirically made".

To the best of our knowledge, this is the first report on the characterization of the adsorption of CO by IR spectroscopy carried out on a Mo-based heterogeneous catalyst showing an uniform type of species in a single O.S., which has been independently verified by stoichiometric red-ox measurements *and* XPS. Louis et al. attempted the preparation of similar catalysts by grafting $MoCl_5$ to the surface OH groups of silica [12]. However, the proposed O.S. of the surface species was not verified by an independent technique, such as XPS, which could not be performed with the same pretreatment conditions as the IR measurements [12]. In addition to this, the treatment of the catalysts after loading the Mo compound included oxidation at 873 K before reduction. It must be noted that the conditions reflected in scheme 1 (for the case of the allylic precursor) require reduction of the supported species before any oxidative step and impose an upper temperature limit of 673 K for oxidation of the samples. It has been verified that molybdenum tetraallyl-derived samples calcined at higher temperatures do not perform reversibly in the red-ox cycles indicated in scheme 1, and that their XPS spectra upon reduction at 823 K show the presence of metallic Mo [14]. These results, as well as the previous reports by Kaliaguine et al. [7] and Ekerdt et al. [8], showing no important differences between conventionally synthesized Mo/SiO_2 catalysts and supported Mo–allyl samples calcined before reduction of the allyl species, can be explained by the assumption that the isolated species originally present in allyl-derived samples become aggregated into Mo oxo-clusters, when calcined either before reduction or at high temperatures. Thus, reversibility in both XPS and FT-IR of CO adsorption should indicate that changes in the structure of the isolated Mo species have not taken place.

The peaks observed at 1990, 2030 and 2120 cm^{-1} indicate that $Mo(CO)_6$ is present in the catalysts after long time exposure to gaseous CO [15]. The observation that this reaction is inhibited by the absence of light suggests a photoreductive process induced probably by ambient UV radiation. The signal observed at ~1420 cm^{-1} is located in the region corresponding to carbonate groups [10].

The relatively high frequency observed for the band due to Mo^{2+} sites suggests that the bonding of CO to the surface is of a σ character and rather weak, consistent with the easy and complete desorption observed upon evacuation: No reinforcement by back donation (π bonding) seems to be taking place. In previous literature

[11,12], some bands at frequencies below that of free CO (2143 cm^{-1}) were assigned to Mo^{2+} sites – again, without direct evidence as to the state of the sites – assuming that back donation would be characteristic of such a low O.S. of these sites. It should be noted, however, that the (presumably) isolated sites in the present catalysts need not be typical of the real catalysts, where polymeric oxo-molybdic species are the most probable ones, due to the type of chemistry involved in the synthesis of catalysts. It could be speculated that Mo^{n+} sites on top of a cluster of molybdenum oxo-species should behave differently to the type of Mo species present in the catalysts studied in this work.

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