



Review

‘Vibrational frequencies of CO adsorbed on silica-supported Mo atoms from density functional calculations’: a re-interpretation of results reported by N. López, F. Illas, G. Pacchioni

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In a recent work, López et al. [1] studied the interaction of CO with silica-supported molybdenum atoms by means of density functional theory calculations. They considered different reactive sites, with Mo atoms in various formal oxidation states (O-S), ranging from +II to +VI, and using both molecular and cluster models of the Mo/SiO₂ surface sites. According to their calculations, models with neutral Mo atoms in any O-S from +II to +V result in negative (“red”) shifts of $\nu(\text{CO})$, the frequency of the adsorbed CO molecule, with respect to that of gas phase CO. Thus, these models can not account for the IR peak at 2170 cm⁻¹ (“blue” shifted by 27 cm⁻¹) which had been observed experimentally [2] for allyl-derived Mo/SiO₂ catalysts reduced in hydrogen at 823 K. This peak had been assigned [2] to Mo(II) (or Mo²⁺, see below) species, which were detected by XPS in >90% concentration with respect to total Mo in the surface of the catalyst reduced at 823 K [3]. On the other hand, calculations by López et al. [1] for CO interaction with Mo(VI) neutral atoms or with selected “Mo cations carrying a real positive charge” result in positive shifts of the CO frequency. Thus, they state that it is not possible to support a neutral Mo(II) species as responsible for the band at 2170 cm⁻¹; instead, calculations of CO adsorption on a doubly charged Mo(IV) species showed the best agreement with this frequency. We think that most of the models of CO bonded to Mo atoms (both neutral and charged species) employed by López et al. could not agree with our experimental results for CO physisorbed onto the surface of our samples because those calculations reflect the thermodynamic equilibrium situation obtained after activated adsorption (chemisorption), as shown by the considerable extent of back donation

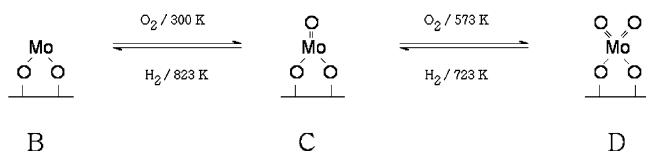
of electron density from the metallic center towards CO. Thus, we maintain our conclusion [2] that the blue shifted 2170 cm⁻¹ band is diagnostic of the presence of Mo(II) surface sites in the catalyst, as we shall discuss below.

In their paper, López et al. [1] emphasize that they adopt the notation Mo(R), where R is a roman numeral, to indicate the formal +R O-S of a neutral system, while Mo(R)ⁿ⁺ designates a real cation of O-S +R and positive charge *n*. The latter situation occurs in those model species where the charge of the metallic center is not fully compensated neither by the ligands around it nor by an appropriate change of the formal O-S of the metal. On the other hand, in our previous work [2,3] the notation Moⁿ⁺ designated the +*n* O-S of a real species (as probed by XPS). It was assumed that such species are of the type described by López et al. as neutral, because they should be more stable than the charged ones. Note that, due to the versatility of Mo, the metallic center could easily change its O-S to compensate changes in the number and nature of ligands. Although in most related work, e.g. [3–9], the Moⁿ⁺ notation is generally employed to designate the O-S of the postulated surface species, to facilitate the comparison we will adhere in this letter to the use of the Mo(R) notation to indicate the formal O-S of a given species.

Model supported catalysts synthesized by grafting of molecular allylic molybdenum compounds, such as Mo($\eta^3\text{-C}_3\text{H}_5$)₄, and Mo₂($\eta^3\text{-C}_3\text{H}_5$)₄, on the surface of silica or alumina, have been shown to lead to active species with narrow distributions of Mo O-S; thus, a single, well defined species in a chosen O-S would be prepared with the correct reductive pretreatment [3–5]. On the other hand, conventional catalysts prepared by impregnation techniques generally show broader distributions of Mo O-S, with several species simultaneously present at any reduced state of the catalyst [6,7]. An example of a set of catalysts derived

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Scheme 1.

from the reaction of $\text{Mo}(\eta^3\text{-C}_3\text{H}_5)_4$ with the OH groups of silica and submitted to red–ox pretreatments, is depicted in Scheme 1. In this particular case, stoichiometry red–ox cycles (volumetric measurements of gas consumption performed after heating under H_2 or O_2) suggested [3,4] the exclusive presence of Mo(IV) in state C, and Mo(II) in B; Mo(VI) is assumed to be the only possible species in D, the fully oxidic catalyst. By means of XPS it was confirmed [3] that a single Mo(VI) species was present in D, as expected. In B there was more than 90% of Mo(II) and a much lower amount of higher O–S Mo species, most likely Mo(IV). On the other hand, in the solids and conditions reported in [3], state C was not a single species but a mixture of several Mo O–S, ranging between III and VI.

FTIR was employed to measure the vibrational frequencies of CO adsorbed on catalysts in the states represented by B, C, and D [2], with the aim of finding correlations between the O–S of well defined surface species and the vibrational frequency of CO adsorbed on such species. No peaks due to adsorption of CO on states C and D were detected by FTIR; in the case of B, the band at 2170 cm^{-1} was observed. Note that this peak disappeared completely and readily upon evacuation at room temperature of the gas adsorption cell and was fully restored after re-admission of CO [2]. After 24 h of exposure to CO under either natural or artificial light illumination, a peak at 1990 cm^{-1} and several other minor ones between 2125 and 2035 cm^{-1} developed at the expense of the initial 2170 cm^{-1} signal. The peak at 2170 cm^{-1} was assigned [2] to CO adsorbed on the dominant (>90%) Mo(II) species measured by XPS in state B [3]. It was further suggested, on account of the positive shift in $\nu(\text{CO})$, that bonding to the surface sites should be of a σ character and rather weak, with no reinforcement by back donation (π bonding).

The characteristics of the signal at 2170 cm^{-1} (blue shifted and showing fast and completely reversible appearance/disappearance upon exposure to gas phase CO) strongly suggest that it corresponds to physisorbed CO rather than to chemisorbed CO or coordinated surface carbonyl groups. On the other hand, those of the peak at 1990 and of the small related bands, all red shifted with respect to gas phase CO, requiring much longer times of exposition and where an activation energy barrier is hinted by the need of irradiation with light, suggest that they are due to chemisorbed CO (or carbonyl groups) on the surface Mo sites in the catalyst. For species originating these latter peaks, it could be expected, indeed, that back donation of electron density occurs, due to the presence of partially filled d levels in the metal center that effectively overlap the anti-bonding CO electron orbitals. This is the reason

why the models and calculations of López et al. for neutral Mo atoms with d^n ($n \neq 0$) electronic configurations, where electron back donation always occurs, could not reflect the presence of species rendering a positive shift, but showed instead a considerable red shift for CO adsorption on these reduced Mo sites. Those models correspond to the thermodynamically stable situation obtained after activated chemisorption of CO upon reduced Mo sites. The kinetically controlled physisorption can be modeled by assuming electrostatic interaction between charged surface sites and the CO probe molecule, not allowing additional electronic interaction. Conspicuously, species with d^0 electronic configuration showed blue-shifted frequencies in López et al. [1] calculations, in particular the fully oxidic Mo(VI) neutral species. However, CO adsorption has never been observed in the case of oxidic Mo-based catalysts [2,8,9]. Clearly, physical shielding of the metal center by the oxygen groups makes CO adsorption on Mo(VI) sites very unlikely. The success of that model in reflecting the positive shift of $\nu(\text{CO})$ is probably due to the absence of d electrons.

If (following the suggestion by López et al.) the peak at 2170 cm^{-1} in state B were assigned to adsorption of CO on the low fraction (<10%) of Mo species in a higher O–S than Mo(II), it could be expected that a similar signal would be observed in state C, where species ranging from Mo(III) to Mo(VI) co-existed, according to XPS measurements [3]. This is not the case, as no peaks were observed upon CO exposure of either type of species in state C, reduced from the fully oxidic D state or oxidized from B [2].

Much controversy exists in previous works [8,9], and references therein] which attempted to correlate the observed vibrational frequencies of adsorbed CO with the O–S of Mo surface species, mainly because the catalysts studied were generally those of conventional type, prepared by impregnation. After reductive pretreatments, such catalysts have been demonstrated to consist of several Mo species simultaneously present, with varying O–S and nuclearities (i.e. cluster versus monometallic species) [6,7]. Thus, assignation of the observed IR signals was not straightforward. In addition, no previous work employed an independent technique such as XPS, capable to proof the O–S of surface sites, to analyze the same set of catalysts object of the IR study. Nevertheless, most if not all of the former authors assign the blue shifted signals between 2190 and 2170 cm^{-1} to CO physisorbed to or electrostatically interacting with the reduced sites. Lower frequency signals, specially that around 1990 cm^{-1} , have been assigned to stronger Mo–CO interaction involving π bonding, e.g. to chemisorbed molecular $\text{Mo}(\text{CO})_6$ [9]. López et al. have employed models where a strong interaction reinforced by π back donation occurs, a situation obviously in conflict with all that is known of the blue shifted signals, but that could explain the lower frequency peaks. On the other hand, purely electrostatic models as that used by Knözinger and coworkers [8], have been employed to model the interaction of CO with A^{n+} charged surface sites, showing better agreement with the positively shifted peaks.

Interestingly, in the calculations of López et al., the species that more successfully models the experimentally observed frequency of the blue shifted signal was a charged complex of formula $[(\text{HO})_4\text{OSi}_2\text{O}_2\text{-Mo}]^{2+}$. As the authors present results for both singlet and triplet states of this species, one infers that it has a d^2 metallic center of O-S (IV) (formally, loss of the 4s electrons upon ionization of the metal). The uncharged equivalent species would have a d^2 metallic center with O-S (II), similar to B in Scheme 1. We suppose that the real Mo(II) surface species could be in dynamic equilibrium with similarly equivalent structures showing (partial) positive charge due to the presence of the support, that would behave as a giant electron density drawing ligand. Gas phase CO could approach the more positive species, resulting in weak physisorption and possibly reinforcing the positive character of the surface site. Thus, the positive charge on the resulting interaction species would be a consequence of CO physisorption, and not a prerequisite for it. After prolonged exposure, surface changes could be induced thermally or by light, resulting in chemisorption and/or formation of carbonyl and carbonate groups [2]. In this sense it must be noted that the appearance of the low frequency signals occurs at the expense of the initial 2170 cm^{-1} one.

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