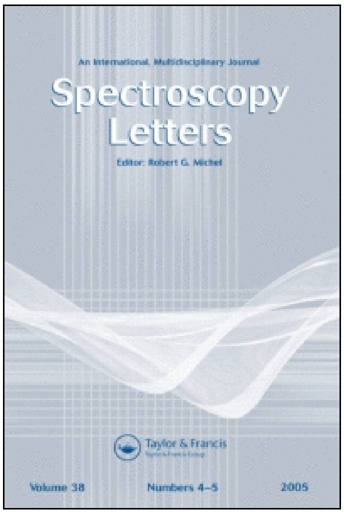

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Vibrational Spectroscopic Studies of Molybdena Dispersed on Ceria Support

Xuezhong Du[a]; Lin Dong[a]; Chun Li[a]; Yingqiu Liang[a]; Yi Chen[a]
[a] Department of Chemistry, Institute of Mesoscopic Solid State Chemistry, Nanjing University, Nanjing, China

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VIBRATIONAL SPECTROSCOPIC STUDIES OF MOLYBDENA DISPERSED ON CERIA SUPPORT

KEY WORDS: Vibrational spectroscopy, MoO_3, CeO_2, Dispersion

Xuezhong Du, Lin Dong, Chun Li, Yingqiu Liang and Yi Chen*

Department of Chemistry, Institute of Mesoscopic Solid State Chemistry,
Nanjing University, Nanjing 210093, China

ABSTRACT

Diffuse Reflectance Infrared Fourier Transform (DRIFT) and FT-Raman spectra have been used to investigate the interactions between molybdena and ceria in MoO_3/CeO_2 samples with different Mo loadings. The spectra exhibit a weak Mo=O broad band of surface species at *ca.* 920–970 cm^{-1}, which reveals that the interaction between dispersed

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* To whom correspondence should be addressed at Department of Chemistry, Nanjing University, Nanjing 210093, China.

molybdena and ceria could be mainly ionic in nature. With the increasing of Mo loadings, the observed Mo=O band broadening and frequency shifting are due to the overlapping and condensation of different hydrated surface species. On the basis of the measured surface dispersion capacity of molybdena and the structure of the preferentially exposed (111) plane of ceria, it is reasonable to suggest that the Mo^{6+} cations and the accompanying O^{2-} anions are incorporated into the surface available vacant sites of CeO_2, accordingly the dispersed molybdena species are interacted electrostatically with the support instead of only physically dispersed on the surface of it.

1. INTRODUCTION

Molybdena dispersed on various oxide supports are widely used as catalysts in different chemical reactions,[1] and the structures of surface interaction species on different supports have been studied extensively through various physicochemical techniques.[2-8] Among them, the surface structure and hydration of the dispersed molybdena on γ–alumina have been studied systemically.[9-11] Raman spectroscopy was usually used to study these systems as MoO_3 possesses a large scattering cross section.[3] A broad Raman band around 920–970 cm^{-1} formed by molybdena dispersed on different supports has been detected, and the structures of the corresponding surface species have been identified using the model compounds with known structures.[4,12]

As a support ceria has drawn growing interest, as its supported noble metal catalysts have shown promising application in the treatment of automobile exhaust gas. However, few studies on the MoO_3/CeO_2 system have been reported.[13,14] In this work, DRIFT and FT-Raman spectra of a series of MoO_3/CeO_2 samples with different Mo loadings have been investigated. The results demonstrate that with the dispersion of MoO_3 on CeO_2 surface electrostatic interaction species are formed. The spectroscopic properties of the surface Mo=O species are discussed by the measured vibrational bands and the expected structure of the dispersion species.

2. EXPERIMENTAL

MoO_3 and $Ce(NO_3)_3 \cdot 6H_2O$ were AR grade (Shanghai Chemical Reagent Company); MoO_3 was preheated at 723 K for 5 h before use and a thermodynamically stable orthorhombic structure was obtained with a BET surface of 2 m^2/g. CeO_2 support, with a BET surface area of 72 m^2/g, was prepared by calcining $Ce(NO_3)_3 \cdot 6H_2O$ at 823 K for 4 h in air.

MoO_3/CeO_2 samples were prepared by heating the mechanical mixtures with the required amounts of MoO_3 and CeO_2 at 693 K for 18 h in air. The Mo loadings of the mixtures are (a) 0.3, (b) 0.5, (c) 1.0 and (d) 1.4 $mmol/100m^2$, respectively.

DRIFT spectra were recorded using a Nicolet 170 SX FT-IR spectrometer connected to a DTGS detector, and Spectra were accumulated for 200 scans at 4 cm^{-1} resolution.

FT-Raman spectra were taken with a Bruker RFS 100 spectrometer fitted with an InGaAs detector cooled by liquid nitrogen. Raman excitation at 1064 nm was provided by a Nd: YAG laser. The laser power measured at the sample was 100 mW, and Spectra were accumulated for 50 scans at 4 cm^{-1} resolution in back scattering geometry.

3. Results and Discussion

3.1. DRIFT spectra

Fig. 1 shows the DRIFT spectra in 4000-700 cm^{-1} region of MoO_3 with surface area of 2m^2/g, CeO_2 and the calcined mixture samples as a function

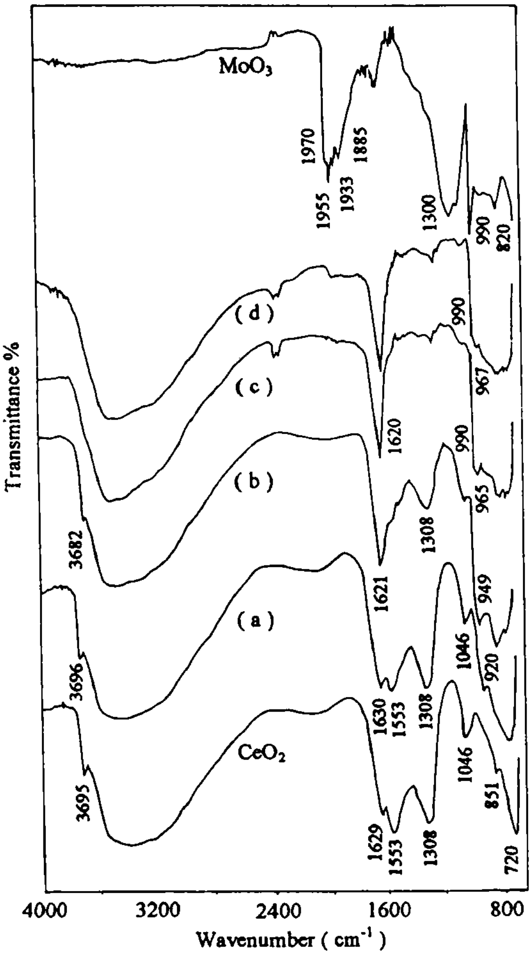


FIG. 1 The DRIFT spectra of MoO$_3$, CeO$_2$ and the MoO$_3$/CeO$_2$ samples at different loadings (mmol MoO$_3$/100m^2): (a) 0.3; (b) 0.5; (c) 1.0 and (d) 1.4

of the Mo loadings (a-d). The spectrum of MoO_3 is consistent with the reported one using a sample with a surface area of 1.8 m^2/g.[15] The bands centered at 990 cm^{-1} and near 820 cm^{-1} have been ascribed to the stretching vibration of Mo=O and the stretching vibration of Mo-O-Mo, respectively. Two groups of absorption at *ca.* 1300-1010 cm^{-1} and 1970-1885 cm^{-1} are attributed to the combination modes arising from stretching fundamentals. Noticeably, MoO_3 samples with low surface areas, i.e., 2 and 1.8 m^2/g, exhibit no distinct absorption around 3400 cm^{-1} suggesting that crystalline MoO_3 with such a small surface area was little affected by the moisture in air. However, the band around 3400 and 1630 cm^{-1} ascribed respectively to the stretching and deformation vibrations of the associated H_2O molecules are observed for MoO_3 samples which have a surface areas greater than 3 m^2/g, and the intensity of these bands enhanced rapidly with the increasing of the surface area of MoO_3.[15] The above results can be understood as crystalline MoO_3 with small surface area has a chain-layer structure which was formed through edge-linked octahedra,[16] and the valent states of Mo, O atoms tend to be saturated and shielded. Thus, the influence of the moisture from air could not be detected. However, with the increasing of the surface area of MoO_3, i.e., the decrease in particle size, part of the Mo-O chain-layer structure was broken leading to the exposure of Mo and O atoms, which are easier to interact with the moisture from air. In turn, by dispersing MoO_3 on CeO_2, the exposed Mo and O atoms in the surface species are increasing, causing them to be easily hydrated.

Generally, the surface of CeO_2 support is sensitive to H_2O and CO_2 in air resulting in several strong absorption bands in its spectra.[17,18] These absorbed species can be removed by calcination at 1073 K with subsequent vacuum treatment,[17] but are not affected by vacuum treatment at lower temperatures, e.g., at 673 K[18]. As can be seen from the spectrum of CeO_2 in Figure 1, the broad band near 3400 cm^{-1} together with a overlapping peak around 3695 cm^{-1} are due to the stretching vibration of associated and isolated hydroxyl groups respectively, and the band at *ca.* 1630 cm^{-1} is assigned to the deformation mode of the surface absorbed water.[19] The strong bands at *ca.* 1553, 1308, 1046 and 851 cm^{-1} are the contributions of different carbonate species formed on ceria surface due to the chemisorption of CO_2 in air.[17,19]

Results of both XRD and XPS[14] have shown that the dispersion capacity of MoO_3 on CeO_2 is 0.80 mmol/100m^2. As can be seen from the spectra of MoO_3/CeO_2 samples shown in Fig. 1, two groups of combination modes and the terminal Mo=O band (near 990 cm^{-1}) of crystalline MoO_3 disappear, indicating the absence of crystalline MoO_3 in samples a and b. The peak intensities of the carbonate species on CeO_2 decreased gradually with increasing Mo loading, meanwhile, the intensity of a new band around 920-965 cm^{-1}, similar to the terminal Mo=O band produced by the surface species in MoO_3 /γ-Al_2O_3 samples, increases gradually. These results suggest that during the dispersion of molybdenum in CeO_2, the interaction between the acidic dispersed MoO_3 and the basic support CeO_2 is strong enough to cause the desorption of the surface carbonates. For samples containing MoO_3 lower than 0.80 mmol/100 m^2, with the increase of Mo loading (Fig. 1a,b), the intensity of isolated hydroxyl group at 3695 cm^{-1} decreases and its frequency shifts to lower wavenumber. In contrast, the intensities of the stretching mode near 3400 cm^{-1} and deformation mode near 1630 cm^{-1} corresponding to the associated hydroxyl group are kept almost unchanged, but the shape of broad band near 3400 cm^{-1} changes gradually, and the frequencies of the above two bands shift to a higher and lower wavenumbers, respectively. When MoO_3 loading exceeds its dispersion capacity (Fig. 1c,d), the band ascribed to isolated hydroxyl group disappears. However, the stretching and deformation modes of the associated hydroxyl (shape, intensity, frequency) keep unchanged. generally, it is known that the frequency of the basic hydroxyl group (M•••OH) is higher than that of acidic hydroxyl group (M-O•••H). The above results indicate that with the increasing Mo loading, the isolated and associated hydroxyl groups on ceria surface gradually interact with the dispersed phase in different ways leading to the formation of hydrated surface species. As shown in Fig. 1c and d displaying the result of samples with molybdenum loading beyond its dispersion capacity, a shoulder near 990 cm^{-1} attributed to crystalline MoO_3 is observed showing the coexistence of MoO_3 crystalline with interacted species on the surface. As mentioned above, the remained crystalline MoO_3 is probably not affected by the moisture. Thus, the band ascribed to associated water basically maintains constant same in c and d of Figure 1. In addition, the fact that after the amount of MoO_3 exceeds its dispersion capacity the frequency corresponding to the surface species Mo=O does not change any more, indicating that the frequency shift of surface species Mo=O vibration is correlated with hydration. The results are consistent with the studies on $MoO_3/\gamma-Al_2O_3$ systems which have also clarified that the surface species terminal Mo=O takes part in different hydration.[20]

3.2. *FT-Raman spectra*

The FT-Raman spectra of MoO_3, CeO_2 and MoO_3/CeO_2 samples with different Mo loading are shown in Figure 2. No distinct absorption in

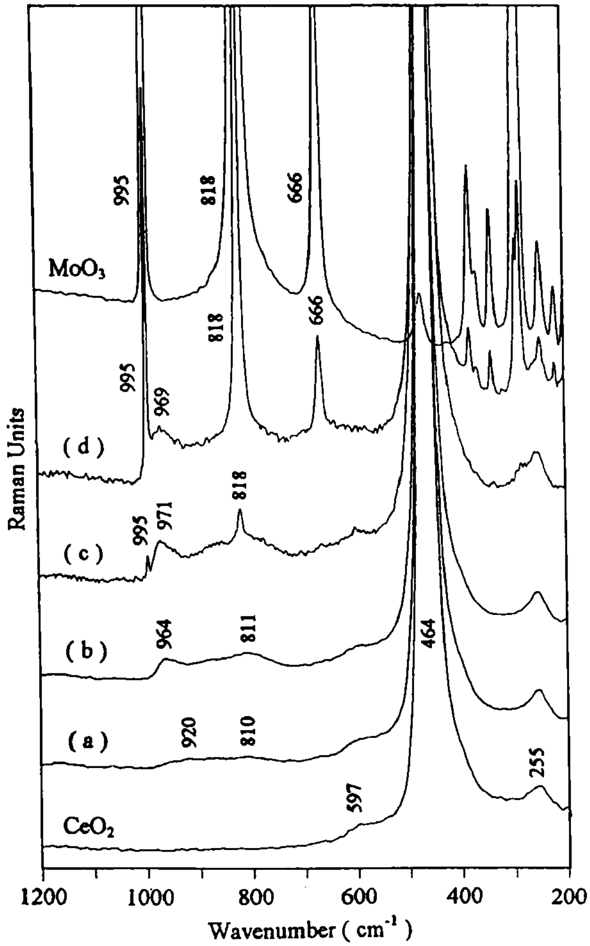


FIG. 2 The FT Raman spectra of MoO_3, CeO_2 and the MoO_3/CeO_2 samples at different loadings (mmol $MoO_3/100m^2$): (a) 0.3; (b) 0.5; (c) 1.0 and (d) 1.4

4000-1500 cm^{-1} region has been detected due to the weak scattering of H_2O molecules. For CeO_2, there is a characteristic band near 464 cm^{-1} accompanying by the weak bands, which can be assigned to the vibration of Ce-O (T_{2g})[21] and to the corresponding phonon vibrations[22] respectively. It is known that, generally speaking, the band of a polar bonding is strong in IR absorption and weak in Raman scattering, in contrast, for a nonpolar bonding the situation is reversed. Thus, strong absorbed carbonate species on CeO_2 formed by the chemisorption of CO_2 as well as the associated H_2O can be detected in DRIFT spectra, but not in FT-Raman spectra. In comparison, MoO_3 with the chain-layer structure formed by the Mo-O coordination edge-linked octahedra has a large Raman scattering cross section in Laser Raman. The spectrum of MoO_3 shown in Figure 2 is coincident with the literature.[15,23] In general, only fundamental modes of vibration can be observed in Raman, whereas combination modes in IR spectra (cf. Fig. 1). Thus, IR and Raman spectroscopies are complementary methods for the study of the interaction of MoO_3 on CeO_2. The strong Raman bands of MoO_3 at ca. 995, 818 and 666 cm^{-1} are the main characteristic bands of the chain-layer structure of crystalline MoO_3, which have commonly been accepted as the evidence of the existence of crystalline MoO_3 in surface study. Furthermore, from the combination of the vibration modes[24] and bond orders[25] of these three bands, the following conclusion can be drawn: The band near 995 cm^{-1} is ascribed to the stretching vibration of terminal Mo=O which has a bond order of 2.04, and that at *ca.* 818 cm^{-1} to the stretching vibration of Mo•••O-Mo which has an intrachain bond order of 1.63 (O-Mo) and an interchain bond order of 0.34 (Mo•••O) respectively, whereas that near 666 cm^{-1} to the stretching vibration of Mo-O-Mo with an intrachain bond order of 0.81 and an interchain bond order of 0.28. The bands below 500 cm^{-1} are mainly attributed to the deformation modes of Mo-O.[23]

Shown in Fig. 2 a,b are FT-Raman spectra of samples with MoO_3 loadings below its dispersion capacity, no scattering band corresponding to crystalline MoO_3 is detected. Noticeably, in Fig. 2 c, a sample with MoO_3 loading beyond the dispersion capacity, the overlapping bands near 995 and 818 cm^{-1} evidence the presence of a small amount of crystalline MoO_3, while for the sample with MoO_3 loading of 1.4 mmol/100m^2, in Fig. 2d, all characteristic bands of crystalline MoO_3 can clearly be seen. All spectra at MoO_3 loading no matter higher and lower than its dispersion capacity are apparently diversified indicating that MoO_3 is strongly interacted with CeO_2. In addition, as no new vibrational bands corresponding to the covalent structure has been detected in the spectra as shown in Fig. 2a-d, which suggests that the surface species are mainly ionic in nature, i.e., they are formed through the electrostatic interaction between the dispersed MoO_3 and CeO_2.

As seen from Fig 2, the intensities of the weak broad bands near 920-970 and 810 cm^{-1} increase with the increase of MoO_3 loadings, which indicates that the surface species with mainly ionic character might still have some covalent component. Considering the relationship between MoO_3 vibrational frequency and bond order,[25] the band near 920-970 cm^{-1} with calculated bond order of 1.68-1.84 is attributed to the terminal Mo=O stretching vibration, while the band near 810 cm^{-1} is assigned to the Mo-O-Mo stretching mode. However, in spectra d and b, the distinct difference between the intensities of bands near 995, 818 and 964, 810 cm^{-1}

demonstrates that the above covalent component in Mo=O and Mo-O-Mo vibration are relatively low. The decreasing of the vibrational frequency and the broadening of the Mo=O band of the surface species indicate that the surface species are affected by several interactions with the environment.

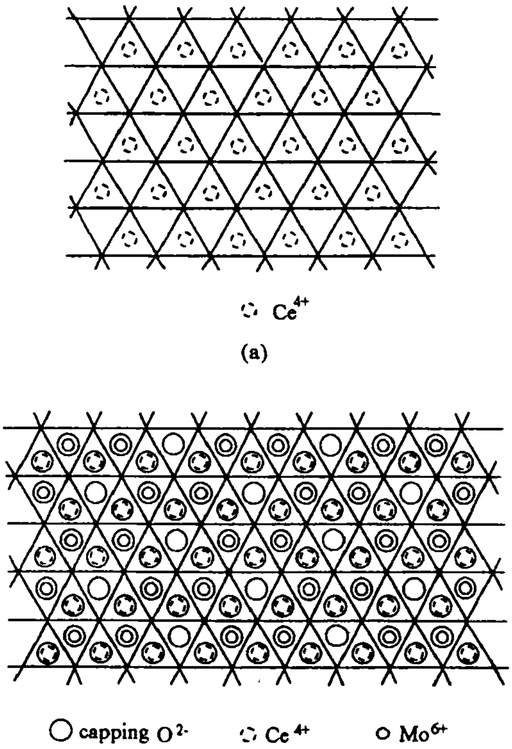
It is noticed that the MoO_3/CeO_2 samples have an orange red color under calcination temperature and turn into light yellow after cooling in air, which is similar to that of the dehydrated and hydrated CrO_3/TiO_2-SiO_2 catalysts,[26] indicating that the ambient atmosphere might cause the hydration of the MoO_3/CeO_2 surface species, which is consistent with the above DRIFT analysis. Earlier studies on $MoO_3/\gamma-Al_2O_3$ samples have revealed that a broad band attributed to hydrated Mo=O at 920-970 cm^{-1} is transformed to a sharp band at ca. 1000 cm^{-1} by dehydration,[20,27,28] and this process is reversible in addition to its bandwidth reproducible. These results are in support of the above IR and Raman spectroscopic analysis concerning the hydration and dehydration of the Mo=O surface species.

A similar changeable tendency in the terminal Mo=O bands has been observed in our samples with different Mo loadings as shown in Fig. 1 (DRIFT) and Fig. 2 (FT-Raman). The Mo=O band of the sample with low MoO_3 loading, i.e., 0.3 mmol/100m^2, is around 920 cm^{-1} in IR and Raman spectra. In comparison with the crystalline MoO_3 which has a Mo=O band of 995 cm^{-1} in Raman and 990 cm^{-1} in IR, a vibrational frequency shift about 70 cm^{-1} to the lower wavenumber is apparent in the supported sample. As will be discussed in the next section, that the orientation of terminal Mo=O group of the surface species is almost perpendicular to the surface of CeO_2 and exposed to outer space. This configuration predicts a decrease both in the bond order and the vibrational frequency of the terminal Mo=O of the surface species due to the formation of the hydrated Mo=O•••HOH species through hydrogen bonding between terminal Mo=O and water under ambient atmosphere. With the increase of Mo loading, as shown in spectra a-c, the intensity of the surface Mo=O increases gradually and its vibrational frequency shifts upwards 965 (IR) and 970 cm^{-1} (Raman). Accompanying with the change of the vibrational frequency of Mo=O, the changes of the IR bands around 3695, 3400 and 720 cm^{-1} (corresponding respectively to the isolated and associated hydroxyl group and the rocking vibration of the coordinated H_2O on CeO_2) have also been detected, reflecting that the absorbed water on CeO_2 are getting involved in the formation of the hydrated Mo=O•••HOH and H_2O•••Mo=O coordination species from the terminal group of the interacted species. Moreover, with the increasing of the amount of hydrated surface species, the condensation between them occurs leading to the deformation on their structure. On the other hand, the formation of polymerized surface species by condensation process will cause the increase of the bridging oxygen atoms in the surface species. Both of these two effects tend to shift the vibrational frequency of surface M-O upwards.[11-13,29]

In short, with the increase of Mo loadings in the samples, the condensation of different hydrated surface species will proceed gradually, resulting in the Mo=O band and the shift of its vibrational frequency. For MoO_3/CeO_2 samples with MoO_3 loading beyond its dispersion capacity (Fig. 1c,d) , the vibrational frequency of Mo=O and associated hydroxyl group around 3400 cm^{-1} remain mostly unchanged. The above results lead to the conclusion that the extra amount of the added MoO_3 will maintain its crystalline form which is not interacted with the associated hydroxyl groups in the sample. In addition, the fact that both the vibrational band of the Mo=O from the surface species and the characteristic bands of crystalline MoO_3 are detected in the spectra of FT-Raman (Fig. 2c,d) and DRIFT (Fig. 1c,d), further indicating the coexistence of the highly dispersed surface species and crystalline MoO_3 in those samples.

3.3. Possible structure for surface species

To get a deeper insight into the nature of the dispersed species, the interaction between the dispersed species and the support should be taken into consideration. It has been well accepted that CeO_2 has a fluorite structure with its (111) plane preferentially exposed for samples prepared by the calcination of $Ce(NO_3)_3 \cdot 6H_2O$. As schematically shown in Fig. 3a, this plane is terminated by oxygen anions located at the cross points of the surface and a subsurface layer of Ce^{4+} cations. Both the surface oxygen anions and cerium cations are each vacant one nearest neighbor in their respective coordination spheres. According to the incorporation model, the above vacant sites available in the surface can be used for the incorporation of the dispersed ions, and the sites available for the cations is expected to be 1.22 mmol/100m^2 as reported elsewhere.[30] Concerning the dispersion of MoO_3 on CeO_2, the chain layer structure of MoO_3, as discussed in the above section, is dissembled by calcination with the formation of surface species through electrostatic interaction, which is consistent with the expectation of the incorporation model, i.e., the incorporation of Mo^{6+} cations into the available vacant sites in the surface. However, as each incorporated Mo^{6+} cations is accompanied by three oxygen anions positioning on its top for charge compensation, the shielding effect of the



(a)

(b)

FIG. 3 The incorporation of MoO$_3$: (a) The structure of the (111) plane of Ceria; (b) MoO$_3$ fully incorporated

accompanied oxygen anions will prevent part of the available vacant sites from being occupied by the Mo^{6+} cations. A conclusion can be withdrawn from the above considerations that only 2/3 of the available sites for cations can be occupied by the incorporated Mo^{6+} cations when the loading amount of MoO$_3$ reaches its dispersion capacity, and all the vacant sites for anions are being occupied by the accompanied oxygen anions with the formation of a close packed monolayer oxygen anions on the surface. A schematically picture of the above discussion is drawn in Fig. 3b, from which by knowing the structure factors of ceria, it can be estimated that upon full occupation of the available sites on the surface, the loading amount of MoO_3 should be 0.81 mmol/100m^2 which is in excellent agreement with the results measured by XPS and XRD[2,14]. From the above description, it is clear that one of the capping O^{2-} is locating directly on the top of the incorporated Mo^{6+} cation and the terminal Mo=O thus formed is perpendicular to the (111) plane, while the other capping oxygen anions might lead to the formation of linkages between the cations on the surface, as shown in Fig. 3b, with the contribution of a weak broad band around 810 cm^{-1}.

Usually, the electrostatic interaction may comprise some of the covalent component and vice versa. The weak broad Raman scattering of the surface species at ca. 920-970 and 810 cm^{-1}, as shown in Figure 2, might be attributed to the ionic nature of the dispersed molybdenum species. Apparently the interactions between the incorporated Mo^{6+} cation and its nearest capping O^{2-} anion is the strongest one since it has the shortest distance in comparison with other O^{2-} anion. Therefore, it is reasonable to consider that some covalent character is composed in the Mo=O terminal group of the highly dispersed species. In addition, the O^{2-} anion capping on the coordinately unsaturated Ce^{4+} cation is also interacted with the nearest neighbor cations leading to the formation of M-O-M bands, such as Mo-O-Ce, Mo-O-Mo etc., with some extent of covalent character.

In light of the structure of dispersion species discussed above, it may be a general phenomenon that the terminal Mo=O is comparatively less affected by the support. Its Mo and O atoms are exposed to the ambient atmosphere, and will easily interact with the moisture in air. Thus, the

Raman spectra exhibit a similar overlapping and condensation broad band of hydrated Mo=O species, which is often observed in samples prepared by the dispersion of MoO_3 on various oxides supports (Fe_2O_3, SnO_2, ZrO_2, TiO_2 etc.), i.e., with a given Mo loading a weak broad band near 950 cm^{-1} in their Raman spectra. Similar results have been observed in MoO_3 supported on Al_2O_3 samples. Finally, it should be recalled that although similarities in the Mo=O terminal group of the dispersed molybdenum species have been discussed in this paper, yet the properties of the dispersed species is critically determined by the intrinsic nature of the support in producing different catalysts possessing their own specific characteristics.

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