The dispersion and surface structure of molybdena supported on ceria have been studied by using XRD, XPS, LRS and FTIR spectroscopies. The samples were prepared by mixing MoO₃ and CeO₂ and by impregnating CeO₂ with an aqueous solution of ammonium polymolybdate. The results indicate that the dispersion capacity of MoO₃ is 4.8 Mo⁶⁺ nm⁻²(CeO₂) and the structure of molybdena depends on the loading of molybdenum on ceria. At low loadings, only a surface species was formed, possibly resulting from the incorporation of Mo⁶⁺ into the surface vacant sites of CeO₂. Beyond the dispersion capacity, the excess bulk MoO₃ remained in the samples. The Raman spectra of MoO₃/CeO₂ samples prepared with different precursors show that calcination dramatically affects the state of molybdenum and results in the formation of the same surface species, indicating that the structure of the surface species depends on the surface structure of the support. The comparison of the XRD results of MoO₃/CeO₂ and MoO₃/ZnO-modified CeO₂ leads to the conclusion that the surface vacancies play the key role in determining the dispersion of MoO₃ on CeO₂. In addition, the coordination environment of the surface molybdenum species is discussed according to the incorporation model.

Supported molybdenum catalysts have been studied extensively owing to their well known applications in various important reactions, e.g. hydrodesulfurization, hydrodenitrogenation, methanation, Fischer–Tropsch and water gas shift reactions. Different views concerning the nature of the interactions between metal oxides and supports are often attributed to the complexity of these systems and differences in the experimental conditions adopted. In addition, as mentioned by Massoth, the techniques used commonly for characterizing these systems might cause some confusion. Xie and Tang were the first to measure quantitatively the dispersion capacities of a series of metal oxides on γ-alumina using an XRD method. They claimed that a close-packed monolayer of MoO₃ can be formed on the surface of γ-alumina by a spontaneous dispersion process. Leyrer et al. suggested a theoretical monolayer capacity of about 3.6 Mo⁶⁺ nm⁻² for MoO₃ on γ-alumina, CeO₂, ZrO₂ and TiO₂, etc. The structure of MoO₃/γ-alumina has been the subject of numerous publications, and in a recent review paper, Knöninger and Taglauer attributed the dispersion of MoO₃ on γ-alumina to the wetting and spreading of the metal oxide on the support. They concluded that the presence of water vapour is not essential for the dispersion of MoO₃ to occur, but the nature of the molybdenum species formed is determined by the presence or absence of water vapour. Furthermore, Liu et al. reported that the surface molybdenum species, Al₂[MoO₄]₃, can react with water to form MoO₂(OH)₂, which is more volatile than MoO₃.

Several models concerning the interactions between supported molybdenum oxide and γ-alumina have been proposed. As we reviewed briefly in our previous paper, these models can be tentatively divided into two categories: one suggesting that under appropriate conditions, MoO₃ might cover the support with the formation of a monolayer on the surface, and, in contrast, the other proposing that the Mo⁶⁺ cations might be incorporated into the vacant sites on the surface of the support. The structure of the dispersed oxide species on γ-alumina has been investigated extensively using various surface sensitive techniques. For example, XPS, ISS (ion-scattering spectroscopy), LRS (laser Raman spectroscopy), IR and UV–VIS reflectance spectroscopies have been used to probe the structure of Mo⁶⁺ ions on the surface and to determine the dispersion capacity of MoO₃ on γ-alumina. In fact, many authors have provided evidence to support the suggestion that metal cations are incorporated into the surface vacant sites of γ-alumina. However, few studies on the MoO₃/CeO₂ system have been reported in the literature. In this work, we studied the interactions between molybdena and ceria in a series of MoO₃/CeO₂ samples. In particular, the dispersion capacity of MoO₃ on CeO₂ was determined and the structure of the surface Mo⁶⁺ species is discussed. Furthermore, a ZnO-modified CeO₂ has been used as a support to investigate the influence of the surface structure change on the dispersion of MoO₃ on the support.

**Experimental**

**Instrumentation**

X-Ray diffraction patterns were obtained with a Shimadzu XD-3A diffractometer employing Ni-filtered Cu-Kα radiation (0.15418 nm). The X-ray tube was operated at 35 kV and 20 mA. The amount of residual crystalline MoO₃ was determined by XRD quantitative analysis as reported elsewhere, in which α-alumina powder was used as the reference.

X-Ray photoelectron spectra were recorded with a VG Escabab MK II spectrometer equipped with a hemispherical electron analyser. The spectrometer was operated at 15 kV and 20 mA and an aluminium anode (Al-Kα = 1486.6 eV) was used. C 1s (285 eV) was taken as a reference to calculate the binding energies ($E_b$).

Laser Raman spectra were obtained with a Spex Ramalog-1403 equipped with a triple monochromator. The 514.5 nm line of a Spectra Physics model 2000 Ar⁺ laser was used for excitation. A laser power of 20 mW at the sample was applied. The spectral slit width was 300 nm with a wavenumber accuracy of ±2 cm⁻¹. All IR spectra were taken with a Nicolet 510P Fourier-transform IR spectrometer operating at a spectral resolution of 4 cm⁻¹. Samples were pressed into self-supporting wafers and placed into an IR cell equipped with CaF₂ windows.

**Sample preparation**

The CeO₂ support with a BET surface area of 73 m² g⁻¹ was prepared by the calcination of Ce(NO₃)₃·6H₂O (A.R.) in air at 823 K for 4 h.

MoO₃ (A.R.) was purchased from the Shanghai Chemical Reagent Company. It was heated at 723 K for 5 h before being used for the preparation of MoO₃/CeO₂ samples.

MoO₃/CeO₂ samples were prepared by two methods: (1) heating the mechanical mixtures of the required amounts of MoO₃ and CeO₂ at 693 K in air for 24 h, and (2) impregnating CeO₂ with aqueous solutions of ammonium paramolybdate at pH 2 or 9, followed by drying at 373 K for 10 h and then calcination in air at 693 K for 2 h.

The ZnO-modified ceria support was prepared by impregnation of CeO₂ with an aqueous solution containing the zinc nitrate hexahydrate [73 Zn²⁺ nm⁻²(CeO₂)] (A.R.). The sample was dried under an IR lamp followed by calcination in air at 723 K for 4 h.

Results and Discussion

Characterization of molybdena on ceria

All the samples discussed in this section were prepared by heating mechanical mixtures of MoO₃ and CeO₂ [preparation method (1)].

Fig. 1 shows the XRD patterns of a series of MoO₃/CeO₂ samples containing different Mo loadings before and after the heat treatment. The XRD patterns for the mixtures as given in Fig. 1(a–c) exhibit sharp peaks of crystalline MoO₃ (2Θ = 25.72 and 27.33°). After the heat treatment, the bulk MoO₃ completely disappeared from the samples with low MoO₃ loadings, e.g., 3.0 and 4.6 Mo⁶⁺ nm⁻²(CeO₂) (Fig. 1a' and b'). However, when the MoO₃ loading exceeded a critical amount, i.e., the dispersion capacity, the bulk MoO₃ remained but decreased markedly after the heat treatment as shown in Fig. 1c' for the sample containing 6.0 Mo⁶⁺ nm⁻²(CeO₂). In addition, the intensity of the XRD peaks for the bulk MoO₃ in the 6.0 Mo⁶⁺ nm⁻²(CeO₂) sample was not decreased further by increasing the heating time. This indicates that the heat treatment only caused the dispersion of MoO₃ on the surface of CeO₂, but did not cause the diffusion of Mo⁶⁺ cations into the bulk CeO₂.

Fig. 2 shows the relationship between the amount of residual crystalline MoO₃ and the total amount of MoO₃ in the MoO₃/CeO₂ samples as determined by XRD quantitative analysis. When the loading of MoO₃ in the samples is below the dispersion capacity, no crystalline MoO₃ can be detected. However, when the MoO₃ loading exceeds the dispersion capacity, the residual MoO₃ is as shown as in Fig. 2 by the straight line. This straight line does not go through the origin but gives an intercept corresponding to the dispersion capacity. In the ideal case the slope of this line is unity. Results of the quantitative analysis of MoO₃/CeO₂ by XRD show that the dispersion capacity of MoO₃ supported on CeO₂ is 4.8 Mo⁶⁺ nm⁻².

The binding energies of Mo 3d₅/₂ and Ce 3d₅/₂ for MoO₃/CeO₂ samples with different Mo loadings are listed in Table 1. Fig. 3 shows the spectra of Mo 3d and Ce 3d of the MoO₃/CeO₂ sample with a Mo loading of 3.8 Mo⁶⁺ nm⁻² (CeO₂) (sample 3); the spectra of this sample before (B and b) and after (A and a) calcination are shown in Fig. 3. The binding energies of Mo 3d₅/₂ and Ce 3d₅/₂ in the calcined sample are 232.4 and 882.7 eV, which means that the valences of molybdenum and cerium are +6 and +4, respectively. The Mo 3d/Ce 3d XPS intensity ratios of the mechanical mixtures (A) and calcined samples (B) as a function of Mo loadings are shown in Fig. 4. For the calcined sample the intensity ratio is larger than that of the corresponding uncalcined mixture. Obviously, the heat treatment has caused MoO₃ to disperse onto the surface of CeO₂ and hence gives a stronger XPS

![Fig. 1 XRD patterns for MoO₃/CeO₂ samples with different Mo loadings (Mo⁶⁺ nm⁻²) before (a, b, c) and after (a', b', c') heat treatment at 93 K for 24 h. a, a': Mixture of 3.0 Mo⁶⁺ nm⁻²; b, b': mixture of 4.6 Mo⁶⁺ nm⁻²; c, c': mixture of 6.0 Mo⁶⁺ nm⁻².](image)

![Fig. 2 Amount of residual crystalline MoO₃ vs. Mo content in MoO₃/CeO₂ samples, as determined by XRD quantitative analysis.](image)

![Fig. 3 Mo 3d and Ce 3d spectra of sample 3 in Table 1. A, a: after calcination at 93 K for 24 h. B, b: mixture of MoO₃ and CeO₂.](image)
signal. The same phenomenon has also been reported by Gui et al. \(^4\) The turning point corresponds to a dispersion capacity of 4.8 Mo\(^{6+}\) nm\(^{-2}\) (CeO\(_2\)). The Mo/Ce intensity ratio at high Mo loading (>4.8 Mo\(^{6+}\) nm\(^{-2}\) (CeO\(_2\))) increases more slowly than that obtained at lower loading and retains the same ratio as that of the mixture sample. This indicates that crystalline MoO\(_3\) exists as well as surface Mo\(^{6+}\) species in the samples with high Mo loadings, and the result is in good agreement with that of XRD. XPS peak intensities are influenced not only by the surface concentration but also by other factors such as the physical properties of the support, especially the pore size distribution and the particle size of the metal oxide. Nevertheless, in our case, the changes in surface areas and in the pore size distribution were insignificant, indicating that the particle size and pore size are not responsible for the distinct change of the slopes in the intensity ratio vs. loading plots.

Fig. 5a–d show the representative Raman shifts for the calcined mixture samples as a function of the Mo loadings. For the samples with loadings of 1.4 and 3.7 Mo\(^{6+}\) nm\(^{-2}\), two peaks at 963 and 800 cm\(^{-1}\) are clearly visible in Fig. 5a and b, and for the samples with loadings of 5.8 and 7.8 Mo\(^{6+}\) nm\(^{-2}\) (Fig. 5c and d, respectively), sharp bands at 818 and 994 cm\(^{-1}\) can be observed, which indicate that some residual bulk MoO\(_3\) exists in the samples. This can be identified by comparing spectra c and d with that for pure MoO\(_3\) (Fig. 5e). Note that the peak frequencies of the bands at 963 and 800 cm\(^{-1}\) do not change with the increasing Mo loading from a to d, and the intensities of the two bands also remain the same once the dispersion capacity is reached, as shown in Fig. 5c and d. The above results indicate that the surface Mo\(^{6+}\) species are formed after the heat treatment.

Fig. 6a–d show the peak wavenumbers of the FTIR bands for the MoO\(_3\)/CeO\(_2\) samples with different Mo loadings, where the spectra of the mixture of MoO\(_3\) and CeO\(_2\) (e) and pure CeO\(_2\) (f) are also presented for comparison. For the samples with Mo loadings less than the dispersion capacity, two peaks at 958 and 1050 cm\(^{-1}\) are distinct (Fig. 6a and b). By comparison of spectra a, e and f, it is reasonable to suggest that the peak frequency of 958 cm\(^{-1}\) is associated with the formation of surface Mo species. For the MoO\(_3\)/CeO\(_2\) sample with a loading of 5.8 Mo\(^{6+}\) nm\(^{-2}\), Fig. 6c exhibits a new peak at 995 cm\(^{-1}\), indicative of the presence of bulk MoO\(_3\). As shown in Fig. 6a and b, only the surface Mo species (958 cm\(^{-1}\)) exist in the samples with Mo loadings below the dispersion capacity. Beyond the dispersion capacity, the bulk MoO\(_3\) and surface Mo\(^{6+}\) species both exist, as shown in Fig. 6c and d. This is in good agreement with the LRS, XPS and XRD results. Note that the peak intensities at 1050 cm\(^{-1}\) for CeO\(_2\) in Fig. 6c and d are weaker than those in Fig. 6a and b, which can be ascribed to the coverage of the surface Mo species on the CeO\(_2\) support.

An incorporation model for the surface Mo species on the CeO\(_2\) support

It has been proven that LRS is sensitive to the coordination environment of Mo\(^{6+}\) cations. The LRS technique has been

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**Table 1** Binding energies of Mo 3d\(_{5/2}\) and Ce 3d\(_{5/2}\) for samples with various Mo loadings

<table>
<thead>
<tr>
<th>sample number</th>
<th>Mo loading /Mo(^{6+}) nm(^{-2}) (CeO(_2))</th>
<th>E(_{3d})/eV</th>
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<tr>
<td>1</td>
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<td>232.7</td>
</tr>
<tr>
<td>6</td>
<td>9.7</td>
<td>232.5</td>
</tr>
</tbody>
</table>

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**Fig. 4** XPS peak intensity ratio I(Mo 3d)/I(Ce 3d) vs. MoO\(_3\) content in the samples before (A) and after (B) calcination at 693 K for 24 h

**Fig. 5** Raman spectra of calcined MoO\(_3\)/CeO\(_2\) samples as a function of Mo loadings (Mo\(^{6+}\) nm\(^{-2}\)). a, 1.4; b, 3.7; c, 5.8; d, 7.8; e, pure MoO\(_3\); f, CeO\(_2\) support.

**Fig. 6** IR spectra of calcined MoO\(_3\)/CeO\(_2\) samples as a function of Mo loadings (Mo\(^{6+}\) nm\(^{-2}\)). a, 0.2; b, 1.4; c, 3.7; d, 5.8; e, 7.8; f, pure MoO\(_3\); g, pure CeO\(_2\).
used often to study the state of surface Mo species on γ-
alumina\textsuperscript{15,16} and TiO\textsubscript{2}.\textsuperscript{17} Perhaps the biggest difficulty facing any investigation dealing with the vibrational spectroscopy of dispersed species is the assignment of bands. This is because the dispersion of molybdena onto a support provides a distribution of chemical environments and strains. Since the general coordinate analysis of surface species is not possible, the band assignments are usually made by comparison with the spectra of model compounds with known structures. This method has been used often by many authors, although it does not yield clear-cut answers since the vibrational frequencies of the stretching modes of the terminal and bridging molybdenum oxygen groups frequently overlap.\textsuperscript{18}

It is known that MoO\textsubscript{2}\textsuperscript{-} and MoO\textsubscript{2}\textsuperscript{2-} species exist in equilibrium in molybdate solution, and the ratio of these two species depends on the pH and the concentration of the molybdenum. The impregnation and drying steps would induce modifications of the structure of the precursors fixed on the support. Fig. 7 shows the effects of the heat treatment on the MoO\textsubscript{3}/CeO\textsubscript{2} samples with different preparation methods, i.e., the precursors of molybdenum in the samples are bulk MoO\textsubscript{3}, MoO\textsubscript{2}\textsuperscript{6-} and MoO\textsubscript{2}\textsuperscript{2-}, respectively for Fig. 7A–C.

In Fig. 7, the differences in spectra B and C are attributed to the different pH values upon impregnation; however, it is clear that no MoO\textsubscript{3} crystallites are detected for these two samples. Note that calcination has a dramatic effect on the samples, as indicated by the similarity of spectra A', B' and C', in which new peaks around 963 and 800 cm\textsuperscript{-1} are evident. This means that sufficient calcination has induced the formation of new surface species and eliminated the effect of the different precursors because of the strong metal oxide-support interactions. These spectra imply that the surface molybdenum species may have a similar coordination environment. The above Raman results for the calcined MoO\textsubscript{3}/CeO\textsubscript{2} samples basically agree with those of Knözinger \textit{et al.}, who observed bands at 959 and ca. 790 cm\textsuperscript{-1} but assumed the existence of both poly- and mono-metric surface molybdates in their samples with the assignment of the bands above 900 cm\textsuperscript{-1} to Mo=O terminal stretching modes of the molybdenum species while the origin of the band around 790 cm\textsuperscript{-1} remained unsolved.\textsuperscript{3}

Considering that CeO\textsubscript{2} prepared by calcining Ce(NO\textsubscript{3})\textsubscript{3}\cdot6H\textsubscript{2}O has the (111) plane preferentially exposed,\textsuperscript{19} and CeO\textsubscript{2} has the fluorite structure, the incorporation model\textsuperscript{30} was used to discuss the surface species on CeO\textsubscript{2}. Fig. 8 is the deduced configuration of the dispersed molybdena and the same coordinated Mo\textsuperscript{6+} species formed in all calcined samples, an asymmetric seven-coordinate molybdenum species formed by the incorporation of Mo\textsuperscript{6+} into the surface vacant sites of ceria. In this case, the asymmetric seven-coordinate molybdenum species should be both Raman and IR active. The transmittance FTIR spectra (see Fig. 6) of the calcined MoO\textsubscript{3}/CeO\textsubscript{2} samples with MoO\textsubscript{3} loadings greater or less than the dispersion capacity displayed a peak at 958 cm\textsuperscript{-1}, corresponding to the band of 963 cm\textsuperscript{-1} in the LRS spectra. The LRS and IR results lead to the suggestion that the seven-coordinate molybdenum is the major surface species.

**Influence of the ZnO-modified ceria on the dispersion of MoO\textsubscript{3}**

To study the effect of the surface structure (the surface vacant sites) on the dispersion of MoO\textsubscript{3}, a ZnO-modified ceria with a BET surface area of 58 m\textsuperscript{2} g\textsuperscript{-1} was used as a support. The XRD patterns of a mechanical mixture of the ZnO-modified ceria and MoO\textsubscript{3} before and after heat treatment are shown in Fig. 9. The XRD results (b, b') of the sample with the same Mo loading [4.0 Mo\textsuperscript{6+} nm\textsuperscript{-2} (support)] using ceria without modification are also shown for comparison. It is interesting to note that little dispersion of crystalline molybdena can be detected on the ZnO-modified ceria after treatment at 693 K for 24 h, whereas the dispersion of molybdena on unmodified ceria have been studied by Raman spectroscopy and X-ray diffraction (XRD) methods. The results show that the dispersion of molybdena is significantly enhanced by the presence of ZnO-modified ceria, with a peak at 963 cm\textsuperscript{-1} in the Raman spectra attributed to Mo=O terminal stretching modes of the molybdenum species while the origin of the band around 790 cm\textsuperscript{-1} remained unsolved. Considering that CeO\textsubscript{2} prepared by calcining Ce(NO\textsubscript{3})\textsubscript{3}\cdot6H\textsubscript{2}O has the (111) plane preferentially exposed, and CeO\textsubscript{2} has the fluorite structure, the incorporation model was used to discuss the surface species on CeO\textsubscript{2}. Fig. 8 is the deduced configuration of the dispersed molybdena and the same coordinated Mo\textsuperscript{6+} species formed in all calcined samples, an asymmetric seven-coordinate molybdenum species formed by the incorporation of Mo\textsuperscript{6+} into the surface vacant sites of ceria. In this case, the asymmetric seven-coordinate molybdenum species should be both Raman and IR active. The transmittance FTIR spectra (see Fig. 6) of the calcined MoO\textsubscript{3}/CeO\textsubscript{2} samples with MoO\textsubscript{3} loadings greater or less than the dispersion capacity displayed a peak at 958 cm\textsuperscript{-1}, corresponding to the band of 963 cm\textsuperscript{-1} in the LRS spectra. The LRS and IR results lead to the suggestion that the seven-coordinate molybdenum is the major surface species.

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig8.png}
\caption{A tentative model of the surface Mo species formed on the (111) plane of CeO\textsubscript{2} support}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.8\textwidth]{fig9.png}
\caption{XRD patterns of MoO\textsubscript{3}/ZnO-modified CeO\textsubscript{2} (a, a') and MoO\textsubscript{3}/CeO\textsubscript{2} (b, b') samples with a loading of 4.0 Mo\textsuperscript{6+} nm\textsuperscript{-2} (support) before (a, b) and after (a', b') heat treatment at 693 K for 24 h}
\end{figure}

![Fig. 8](figure8.png)

**Fig. 8** A tentative model of the surface Mo species formed on the (111) plane of CeO\textsubscript{2} support.

![Fig. 9](figure9.png)

**Fig. 9** XRD patterns of MoO\textsubscript{3}/ZnO-modified CeO\textsubscript{2} (a, a') and MoO\textsubscript{3}/CeO\textsubscript{2} (b, b') samples with a loading of 4.0 Mo\textsuperscript{6+} nm\textsuperscript{-2} (support) before (a, b) and after (a', b') heat treatment at 693 K for 24 h.

ceria before and after modification. The surface vacant sites can be explained by the changes of the surface structure of plane is exposed preferentially on the CeO$_2$ surface and the ceria under similar conditions is apparent. This phenomenon are calculated to be 7.3 nm$^2$ by considering that the (111) incorporates model since the three capping radius of O$_2^-$ is 0.14 nm. The dispersion capacity of MOO$_x$ associated with each incorporated Mo$^{6+}$ have an area of (111) plane of a ZnO-modified ceria is shown in Fig. 10. It is evident that there are almost no surface vacant sites left on the ZnO-modified ceria since the loading of ZnO was 7.3 Zn$^{2+}$ (support), just enough to fill all the available vacant sites on the ceria (111) plane. The results support the incorporation model which emphasizes the importance of the surface vacant sites of the support for the dispersion of metal oxides.

Conclusions

XRD and XPS data have shown that the dispersion capacity of MoO$_3$ supported on ceria is 4.8 Mo$^{6+}$ nm$^{-2}$. Below the dispersion capacity only the surface Mo species exists but both bulk MoO$_3$ and the surface molybdenum species have been identified beyond the dispersion capacity, which are also demonstrated by LRS and FTIR results.

The LRS results for molybdena in the calcined samples prepared by different methods show that the same coordinated Mo$^{6+}$ species formed irrespective of the different precursors of molybdenum used, which can be interpreted as an asymmetric seven-coordinate Mo$^{6+}$ species formed by the incorporation of Mo$^{6+}$ cations into the CeO$_2$ (111) plane.

The comparison of the differences between the dispersions of MoO$_3$ in MoO$_3$/ZnO-modified CeO$_2$ and MoO$_3$/CeO$_2$ samples by XRD shows the important role of the surface vacant sites in the dispersion process of molybdena onto the surface of ceria.

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References


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