Raman spectroscopic studies on tetragonal $\text{ZrO}_2$ supported MoO$_3$ and ZnO–MoO$_3$ systems

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A series of samples of MoO$_3$ and/or ZnO supported on tetragonal $\text{ZrO}_2$ (t-$\text{ZrO}_2$) have been investigated by laser Raman spectroscopy and XRD. For these supported binary-oxide systems, the loading sequence of the oxide and the calcination temperature have notable effects on the interactions of the oxides and support and hence the nature of the catalysts. The experimentally measured dispersion capacities of ZnO or MoO$_3$ on t-$\text{ZrO}_2$, and ZnO on two MoO$_3$-modified t-$\text{ZrO}_2$ are consistent with the values predicted by the incorporation model. The dispersion capacity of MoO$_3$ on ZnO-modified t-$\text{ZrO}_2$ has not been measured due to the strong interaction between MoO$_3$ and the supported ZnO, leading to the formation of a ZnMnO$_3$ phase. The results are further proof of the effect of the nature and, in particular, the surface structure of the support on the dispersion behavior and the surface structure of the dispersed oxides. The effect of calcination temperature on the dispersion state of the oxides is also discussed.

Introduction

Supported molybdenum oxides catalysts are widely used in various catalytic processes. The structure of the surface molybdenum oxide species on different oxide supports has been extensively investigated by various techniques, e.g., Fourier transform infrared (FTIR), solid-state $^{95}$Mo nuclear magnetic resonance (NMR), extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), X-ray photoelectron spectroscopy (XPS), and ultraviolet/visible diffuse reflectance spectroscopy (UV/VIS-DRS). It has been concluded that the structures of the supported molybdenum oxide species are closely related to the nature of the specific support, the loading amount of molybdenum oxide, the preparation procedures and, in particular, the calcination temperature.

Several models have been proposed to explain the dispersion state of the ionic compounds on oxide supports. As we reviewed briefly in a previous paper, these models can be tentatively divided into two categories: the first suggests that under appropriate conditions a monolayer of the dispersed ionic compound is formed on the surface of the support, the second proposes that instead of forming an overlapping monolayer, the dispersed metal cations are incorporated into the surface vacant sites of the support with their accompanying anions staying on the top of them for charge compensation. According to the monolayer model, a close-packed monolayer of MoO$_3$ can be formed on the surface of $\gamma$-alumina, and the dispersion capacity of MoO$_3$ thus calculated is consistent with the experimental data. However, for metal oxides of lower valence types, e.g., $\text{M}^{1+}$ and $\text{M}^{2+}$ oxides, the experimental results are always notably lower than the values expected by the close-packed monolayer. On the other hand, the dispersion capacities of a series of ionic compounds, e.g., Li$_2$O, NiO, MgO, NaCl, KCl and MoO$_3$, on various supports, e.g., $\gamma$-alumina, ceria and titania, predicted by the incorporation model are consistent with the experimental data. For MoO$_3$ on $\gamma$-alumina, the incorporation model expects that upon reaching its dispersion capacity, the accompanying oxygen anions should arrange themselves into a close-packed monolayer whereas no such close-packed monolayer can be formed on $\gamma$-alumina by the dispersion of metal oxides of lower valence types. Experimental results in support of the incorporation of Mo$^{6+}$ cations into the vacant surface sites of $\gamma$-alumina can be found in the literature. However, comparatively few studies have been carried out concerning the structure of surface molybdenum oxides on $\text{ZrO}_2$, especially on t-$\text{ZrO}_2$.

Various combinations of Mo, W, Co or Ni oxides supported on $\gamma$-alumina are frequently used as catalyst precursors for either hydrodesulfurization (HDS) or hydrodenitrogenation (HDN) reactions. A great deal of research has been done to explore the promoting effect of Co and Ni oxides. However, little attention has been paid to the other oxide additives. It has been reported that the addition of ZnO into the supported Mo catalysts can improve its hydrodesulfurization activity. Patzer et al. have found that the ZnO-modified $\gamma$-alumina is a promising support for HDS. To the best of our knowledge no similar studies have been done with Zn as an additive to zirconia. As part of the efforts to investigate the nature of interactions between metal oxide and oxide supports, this work intends to (1) investigate the surface species and their structures in the Zn–Mo–t-$\text{ZrO}_2$ system by the combination of laser Raman and XRD results, (2) determine the influence of the loading sequence of ZnO and MoO$_3$ on the dispersion state of the oxides on the zirconia and (3) understand the interactions between the supported Zn and/or Mo oxide and the support as well as the interactions between these supported oxide species. The effect of the surface structure of the support and the calcination temperature on the dispersion and nature of the dispersed oxides, i.e., Mo and Zn oxides, are discussed.

Experimental

Sample preparation

Tetragonal zirconia (t-$\text{ZrO}_2$) was prepared by the method reported elsewhere. After calcining at 773 K for 4 h, it has a BET surface area of 65 m$^2$g$^{-1}$.

Two MoO$_3$-modified t-$\text{ZrO}_2$ (designated as Mo$_1$Zr and Mo$_2$Zr) and two ZnO-modified t-$\text{ZrO}_2$ (designated as Zn$_1$Zr and Zn$_2$Zr) samples were prepared by impregnating the t-$\text{ZrO}_2$ with aqueous solutions of ammonium heptamolybdate.
Sample characterization

XRD results were obtained using a Shimadzu XD-3A diffractometer employing Ni-filtered Cu-Kα radiation (1.5418 nm). The X-ray tube was operated at 35 kV and 20 mA. XRD quantitative results were obtained by using γ-alumina powder as reference.

FT-Laser Raman spectra (LRS) were recorded on a Bruker RFS-100 spectrometer with a wavenumber accuracy of 4 cm⁻¹. An Nd:YAG crystal laser was used for excitation and the laser power measured at the sample was 100 mW. Powder samples were used for all the measurements.

Results and Discussion

MoO₃/t-ZrO₂ system

Fig. 1 shows the relationship of residual crystalline MoO₃ with the total amount of MoO₃ in the MoO₃/t-ZrO₂ samples, as determined by XRD quantitative analysis. The straight line in Fig. 1 does not go through the origin and gives an intercept corresponding to a dispersion capacity of ca. 4.5 Mo⁶⁺ mm(t-ZrO₂)⁻². Crystalline MoO₃ is detected in samples with Mo loading higher than its dispersion capacity.

Raman spectroscopy has been widely used to characterize the chemical states of molybdenum oxide supported on various oxide supports, such as γ-Al₂O₃, TiO₂, ZrO₂ (monoclinic), MgO, and CeO₂. Raman bands between 910 and 980 cm⁻¹ are usually assigned to the terminal Mo=O vibration of the isolated or polymerized (e.g., tetrahedral or octahedral) Mo species. The Raman spectroscopic results of MoO₃/t-ZrO₂ samples are shown in Fig. 2. Data below 600 cm⁻¹ were not collected due to the interference of the strong background of tetragonal zirconia. The band at 642 cm⁻¹ caused by t-ZrO₂ decreases with the increase of MoO₃ loading. A broad band centered around 932–940 cm⁻¹ observed in the low Mo loading samples [Fig. 2(a) and (b)] indicates the existence of an isolated molybdate species in these samples. With the increase of Mo loading, this band shifts from 932 to 975 cm⁻¹, which is assigned to the terminal Mo=O vibration of the polymerized Mo species. The broad Raman band around 827–830 cm⁻¹ is tentatively attributed to the Mo=O—Mo Raman stretching mode, and with the increase of Mo loading no significant shift of this band is observed. When the loading of MoO₃ is higher than its dispersion capacity, crystalline MoO₃ can be identified by its characteristic bands at 666, 820 and 994 cm⁻¹ [Fig. 2(d) and (e)]. For the high loading sample with 10 Mo⁶⁺ mm(t-ZrO₂)⁻², raising the calcination temperature to 823 K leads to the formation of the ZrMoO₃ phase identified by its characteristic Raman bands at 748, 946, and 1003 cm⁻¹, as shown in Fig. 2(f).

To gain a deeper insight into the nature of the dispersed species and the features of their Raman spectra, the interaction between the dispersed species and the support should be taken into consideration. It is known that t-ZrO₂ has a slightly distorted fluorite structure and only one half of its distorted cube sites surrounding by oxygen anions is occupied by zirconium cations. With the assumption that (111) planes are preferentially exposed on the surface of the t-ZrO₂, the surface vacant site density is calculated to be 8.6 mm(t-ZrO₂)⁻². According to the incorporation model, the crystalline MoO₃ is dispersed by the incorporation of Mo⁶⁺ cations into the available vacant sites on the surface of the support. Taking into consideration the shielding effect produced by the three oxygen anions accompanying each incorporated Mo⁶⁺ cation, only some of the available vacant sites can be used for the incorporation of the Mo⁶⁺ cations. When the loading amount of MoO₃ reaches its dispersion capacity, a close-packed monolayer of capping oxygen anions is formed on the surface of the zirconia. It can thus be estimated that the dispersion capacity of MoO₃ on t-ZrO₂ should be around 4.8 Mo⁶⁺ mm(t-ZrO₂)⁻², which is in agreement with the results of XRD and LRS.

In the light of the structure of dispersion species discussed above, it is suggested that one of three accompanying cations with the formation of Mo=O—Zr bonds, and the linkage between the incorporated Mo⁶⁺ with its nearest incorporated Mo⁶⁺ (if it is available), i.e., Mo⁶⁺—O—Mo⁶⁺, might also occur through the intermediate...
lattice oxygen anions. These kinds of linkages between the cations on the surface might result in a weak broad band at 827–830 cm$^{-1}$. The terminal Mo=O bonding with oxygen anions exposed to the ambient atmosphere easily interacts with the moisture in the air leading to the formation of hydrated surface species. When Mo loading is low, the isolated molybdenum oxide species are mainly formed on the surface of zirconia (Raman bands at 932–940 cm$^{-1}$). As the Mo loading increases, the polymerized Mo species are formed on the surface due to the linkages of the isolated molybdate species. In fact, the so-called isolated and polymerized species are more or less distorted due the strong electrostatic interaction between the incorporated Mo$^{6+}$ cation and the O$^{2-}$ anions around the surface vacant site of zirconia. This kind of distortion should be responsible for the rather broad Raman stretching band of the terminal Mo=O as compared with the spectra of the corresponding molybdate species in solution.\textsuperscript{27}

**MoO$_3$/ZnO-modified t-ZrO$_2$ system**

It is known that the HDS activity of supported molybdenum catalysts can be improved significantly by adding some metal oxides as promoters. Such a synergetic effect is believed to have a direct relation with the surface structure of the catalyst. In order to understand the interactions between the t-ZrO$_2$ supported Zn and Mo oxides as well as the interactions between them and the zirconia, a series of samples of Mo supported on ZnO-modified t-ZrO$_2$ were prepared and studied. Two ZnO-modified t-ZrO$_2$ samples (Zn$_i$Zr and Zn$_j$Zr) with loadings of 8.3 and 4.2 Zn$^{2+}$ nm(t-ZrO$_2$)$^{-2}$, respectively, were used as supports. Apparently, the surface structure of these supports are different from that of t-ZrO$_2$ due to the presence of ZnO. As discussed in the previous section, by considering that its (111) plane is preferentially exposed on t-ZrO$_2$ the surface available vacant sites are estimated to be 8.6 nm(t-ZrO$_2$)$^{-2}$, which is in good agreement with the dispersion capacity measured by XRD quantitative analysis, i.e., 8.5 Zn$^{2+}$ nm(t-ZrO$_2$)$^{-2}$, as shown in Fig. 3. Along this line, there are almost no surface vacant sites available on the Zn$_i$Zr sample, which has a ZnO loading of 8.3 Zn$^{2+}$ nm(t-ZrO$_2$)$^{-2}$, a value very close to its dispersion capacities as shown in Fig. 3. On the other hand, for Zn$_j$Zr only about half of its available vacant sites are being occupied by the incorporated Zn$^{2+}$ cations, there are still plenty of vacant sites available for the incorporation of MoO$_3$. The structure of the ZnO-modified (111) plane of t-ZrO$_2$ is shown in Fig. 4.

Fig. 5 shows the Raman spectra of a model compound ZnMoO$_4$ and MoO$_3$/Zn$_j$Zr samples calcined at 773 K. Two weak Raman bands at 969 and 946 cm$^{-1}$ are observed for the sample with a loading of 2.5 Mo$^{6+}$ nm(t-ZrO$_2$)$^{-2}$. With the increase of Mo loading, the intensities of these two bands gradually increases, and a new sharp band at 932 cm$^{-1}$ is gradually intensifies [Fig. 5(a)–(d)]. In comparison with the Raman spectra of the model compound ZnMoO$_4$ [Fig. 5(e)], the presence of the sharp bands at 969, 946 and 932 cm$^{-1}$ are attributed to the presence of crystalline ZnMoO$_4$. Its existence in this series of samples has also been identified by XRD measurement, i.e., by the three main diffraction peaks at $2\theta = 24.1$, 26.1, and 26.4$^\circ$. It is noteworthy that almost all the incorporated surface Zn species on the zirconia can be converted into the ZnMoO$_4$ phase by adding MoO$_3$. After that, further addition of MoO$_3$ leads to the formation of crystalline MoO$_3$ particles and a ZrMoO$_4$ phase due to the reaction between MoO$_3$ and zirconia [Fig. 5(d)]. The formation of a ZnMoO$_4$ phase implies that the interaction of the surface Zn species with MoO$_3$ is stronger than that with t-ZrO$_2$. In addition, it appears that a weak broad Raman band is included in the characteristic bands of MoO$_3$ suggesting that the coexistence of a small amount of dispersed Mo species can not be excluded.

To understand further the influence of the surface structure of the support on the dispersion state of MoO$_3$ and ZnO, the Raman spectra of the series of MoO$_3$/Zn$_j$Zr samples calcined at 773 K were also measured and are shown in Fig. 6. For the

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**Fig. 3** Amount of residual crystalline ZnO [Zn$^{2+}$ nm(t-ZrO$_2$)$^{-2}$] ex. Zn content [Zn$^{2+}$ nm(t-ZrO$_2$)$^{-2}$] in ZnO/t-ZrO$_2$ (□), ZnO/Mo$_i$Zr (○) and ZnO/Mo$_j$Zr (△)

**Fig. 5** Raman spectra of MoO$_3$/Zn$_j$Zr samples calcined at 773 K with different Mo loadings [Mo$^{6+}$ nm(t-ZrO$_2$)$^{-2}$]: (a), 2.5; (b), 5.0; (c), 6.5; (d), 9.0; and (e), ZnMoO$_4$

**Fig. 4** Structure of the ZnO-modified (111) plane of t-ZrO$_2$ derived from the incorporation model
Fig. 6 Raman spectra of MoO$_3$/Zn$_x$Zr samples calcined at 773 K with different Mo loadings [Mo$^{6+}$ nm(t-ZrO$_2$)$^{-2}$]: (a), 2.5; (b), 4.4; (c), 6.8; and (d), 10.5.

low loading sample of 2.5 Mo$^{6+}$ nm(t-ZrO$_2$)$^{-2}$, only the isolated surface molybdate species identified by 932 and 836 cm$^{-1}$ Raman bands [Fig. 5(a)] are detected by LRS. The fact that both XRD and LRS show no evidence of the formation of a ZnMoO$_4$ phase in this sample is apparently different from that of the Zn$_x$Zr supported sample with the same Mo loading [Fig. 5(a)]. The absence of a ZnMoO$_4$ phase indicates that MoO$_3$ is preferentially dispersed on the surface of Zn$_x$Zr by incorporating Mo$^{6+}$ cations into the unoccupied surface vacant sites of the t-ZrO$_2$ surface. The conclusion is then evident: the interaction between MoO$_3$ and t-ZrO$_2$ is stronger than that between MoO$_3$ and the dispersed Zn species. After the available surface vacant sites on Zn$_x$Zr are occupied, further increase of Mo loading leads to the formation of the ZnMoO$_4$ phase [Fig. 6(b)–(d)]. When the surface Zn species on Zn$_x$Zr have completely reacted with molybdenum oxide, crystalline MoO$_3$ and ZrMoO$_4$ will finally appear in the higher loading sample, as can be seen from Fig. 6(d).

To discuss the effect of calcination temperature on the nature of these samples, laser Raman spectra of MoO$_3$ on ZnO-modified t-ZrO$_2$ samples calcined at different temperatures are shown in Fig. 7. For the MoO$_3$/Zn$_x$Zr system, the results of the 9.0 Mo$^{6+}$ nm(t-ZrO$_2$)$^{-2}$ sample is listed as a representative. At relatively lower calcination temperature (673 K) the characteristic bands of crystalline MoO$_3$ and ZnMoO$_4$, i.e., bands around 994, 818, 666 cm$^{-1}$ and 969, 946 and 932 cm$^{-1}$, respectively, reveal the coexistence of these two species in the sample. With the increase of the calcination temperature to 773 K, as can be seen from Fig. 7(b), the disappearance of characteristic MoO$_3$ bands and the increase in the intensities of the ZnMoO$_4$ bands are obviously due to the interaction between MoO$_3$ and the dispersed ZnO with the formation of ZnMoO$_4$. Besides, a small amount of Zr$^{4+}$O$_4$$^{2-}$ phase is also detected in this sample. With the calcination temperature further raised to 823 K, as shown by Fig. 7(c), the amount of ZnMoO$_4$ phase does not increase further, suggesting that the surface Zn species were completely converted into the ZnMoO$_4$ phase at 773 K. For the Zn$_x$Zr supported sample with a same Mo loading after calcination at 773 K, as shown in Fig. 7B crystalline MoO$_3$ species still remained and coexisted with the newly formed ZnMoO$_4$ because the amount of dispersed ZnO species in Zn$_x$Zr is only half that in Zn$_x$Zr. The presence of a weak band at 748 cm$^{-1}$ indicates the formation of a ZrMo$_2$O$_6$ phase in this sample, and almost all the residual MoO$_3$ is converted into a ZrMoO$_3$ phase when the calcination temperature is further increased to 823 K [Fig. 7(c)].

Fig. 7 Raman spectra of MoO$_3$/ZnO-modified t-ZrO$_2$ samples with Mo loading of 9.0 Mo$^{6+}$ nm(t-ZrO$_2$)$^{-2}$ calcined at different temperatures (K): (a), 673; (b), 773; (c), 823. A, Samples supported on Zn$_x$Zr; and B, on Zn$_x$Zr.

ZnO/MoO$_3$-modified t-ZrO$_2$ system

Based on the above results, it is interesting to make a comparative study of the ZnO/MoO$_3$-modified t-ZrO$_2$ samples. For this purpose two MoO$_3$-modified t-ZrO$_2$ samples, i.e., Mo$_2$Zr [4.2 Mo$^{6+}$ nm(t-ZrO$_2$)$^{-2}$] and Mo$_2$Zr [2.2 Mo$^{6+}$ nm(t-ZrO$_2$)$^{-2}$], were used as supports. XRD results reveal that ZnO can be dispersed on Mo$_2$Zr without the formation of ZnMoO$_4$ phase. As shown in Fig. 3, the dispersion capacity of ZnO on this modified support is 4.5 Zn$^{2+}$ nm$^{-2}$ measured by quantitative XRD analysis. According to the incorporation model, there are 8.6 vacant sites nm$^{-2}$ on the (111) plane of t-ZrO$_2$ and on Mo$_2$Zr only 4.2 sites nm$^{-2}$ are occupied by the incorporated Mo$^{6+}$ cations, i.e., about 4.4 sites nm$^{-2}$ are still empty but covered by the capping oxygen anions. The experimentally measured dispersion capacity of ZnO on Mo$_2$Zr is 4.5 Zn$^{2+}$ nm$^{-2}$, which seems to suggest that high-temperature calcination has promoted the diffusion of Zn$^{2+}$ cations through the capping layer leading to the occupation of these unoccupied vacant sites on the surface of zirconia. The presence of these newly incorporated Zn cations as the near neighbors of the surface Mo species existing on the surface might induce a structural reorganization of the surface species. Indeed, a corresponding modification of the Raman spectra of
this series of samples has been observed as shown in Fig. 8. With the increase of ZnO loading, from Fig. 8(b) to 8(f), the Mo=O terminal stretching band not only is enhanced but also shifts gradually from 969 to 921 cm⁻¹. No significant change has been observed for the broad Mo=O Mo stretching band around 828 cm⁻¹. The obvious change in the Mo=O terminal stretching frequency between 0 and 5.0 Zn²⁺ nm(t-ZrO)² samples suggests that by adding ZnO the isolated Mo species (ca. 921 cm⁻¹) gradually becomes predominant at the expense of the surface polymerized Mo species (ca. 969 cm⁻¹). It is noteworthy that both the intensity and frequency of the isolated Mo species band stop changing as soon as the amount of Zn loading reaches saturation, at which point the atom ratio of Zn to Mo is close to 1:1. Further addition of ZnO has no effect on this band. In comparison with a greater dispersion capacity of ZnO on MoₙZr, it is expected as there are more surface vacant sites MoₙZr available. XRD results have shown that the measured dispersion capacity of Zn is 6.2 MoₙZr on (Fig. 3), which is consistent with the value expected by the incorporation model.

Raman spectra of the two series of samples calcined at different temperatures (K): (a), 673; (b), 723; (c), 773; and (d), 823. A, ZnO/MoₙZr with Zn loading of 4.0 Zn²⁺ nm(t-ZrO)²; and B, ZnO/MoₙZr with Zn loading of 1.8 Zn²⁺ nm(t-ZrO)².

that with ZnO. The results are obviously different from those of the MoₙZr/ZnO-modified t-ZrO₂ system, in which a ZnMoO₄ phase has been clearly detected (Fig. 5 and Fig. 6). Hence, we can conclude that the species formed on t-ZrO₂ strongly depend on the loading sequence of the supported oxides. Similar results have been obtained on samples of the ZnO/MoₙZr series, as shown in Fig. 9. It can be seen that after the loading of ZnO reaches a value of about 2.5 Zn²⁺ nm, i.e., an atom ratio of Zn to Mo close to 1:1, the terminal Mo=O=O=O stretching vibration band shifts to 921 cm⁻¹. Further addition of ZnO has no effect on this band. In comparison with MoₙZr, a greater dispersion capacity of ZnO on MoₙZr is expected as there are more surface vacant sites available. XRD results have shown that the measured dispersion capacity of Zn is 6.2 MoₙZr on MoₙZr (Fig. 3), which is consistent with the value expected by the incorporation model.

Raman spectra of the two series of samples calcined at different temperatures are also measured and shown in Fig. 10A and B, respectively. No significant difference is observed after these thermal treatments. Thus the dispersion state of the surface species support on Mo-modified t-ZrO₂ samples appears to be independent of the calcination temperature in the range of 673–823 K.

Conclusions

The following conclusions on the dispersion and interaction of metal oxides, i.e., MoO₃ and/or ZnO, on t-ZrO₂ can be drawn from this study.


Fig. 8 Raman spectra of ZnO/MoₙZr samples calcined at 773 K with different Zn loadings [Zn²⁺ nm(t-ZrO)²]: (a), 0 (MoₙZr); (b), 1.9; (c), 4.0; (d), 5.0; (e), 6.2; and (f), 8.5

Fig. 9 Raman spectra of ZnO/MoₙZr samples calcined at 773 K with different Zn loadings [Zn²⁺ nm(t-ZrO)²]: (a), 0 (MoₙZr); (b), 0.9; (c), 1.8; (d), 2.5; (e), 4.5; and (f), 8.1

Fig. 10 Raman spectra of ZnO/MoO₃-modified t-ZrO₂ samples calcined at different calcination temperatures (K): (a), 673; (b), 723; (c), 773; and (d), 823. A, ZnO/MoₙZr with Zn loading of 4.0 Zn²⁺ nm(t-ZrO)²; and B, ZnO/MoₙZr with Zn loading of 1.8 Zn²⁺ nm(t-ZrO)².
(1) The loading sequence of the metal oxides has an important effect on the nature of the dispersed oxide species. The interaction of between MoO$_3$ and ZnO is stronger than that between ZnO and t-ZrO$_2$ but weaker than that between MoO$_3$ and t-ZrO$_2$. As a consequence, adding ZnO before MoO$_3$, i.e., MoO$_3$ on ZnO modified t-ZrO$_2$, might result in the formation of a ZnMoO$_4$ phase after calcination at 773 K; in comparison, this phase is not formed for samples prepared by adding MoO$_3$ before ZnO, i.e., ZnO on MoO$_3$-modified t-ZrO$_2$. The dispersion capacity of MoO$_3$ on ZnO-modified t-ZrO$_2$ has not been measured due to the strong interaction between MoO$_3$ and ZnO, leading to the formation of a ZnMoO$_4$ phase.

(2) The surface structure of the support is critical for the dispersion of the metal oxide. ZnO can disperse on the unoccupied surface vacant sites of MoO$_3$-modified t-ZrO$_2$ leading to the formation of a two-dimensional surface species with an atomic ratio of Zn to Mo similar to that of ZnMoO$_4$. In addition, the experimentally measured dispersion capacities of MoO$_3$ on t-ZrO$_2$ as well as ZnO on the two MoO$_3$-modified t-ZrO$_2$ supports are consistent with the values expected by the incorporation model.

(3) The surface structure of the supports and their interaction with the supported species have a great influence upon the nature of the dispersed species. The Raman spectra of MoO$_3$/t-ZrO$_2$ samples are significantly different from those of MoO$_3$/monoclinic zirconia, and the terminal stretching Mo=O bands of the supported isolated and polymerized Mo species are different from those of the tetrahedral and octahedral species that exist in a solution of ammonium polymolybdates. Moreover, the calcination temperature has a strong effect on the dispersion state of MoO$_3$ supported on ZnO-modified t-ZrO$_2$, whereas no detectable change on the dispersion of ZnO supported on MoO$_3$ has been observed in the temperature range of 673–823 K.

References

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