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Effect of cobalt oxide on surface structure of alumina supported molybdena catalysts studied by in situ Raman spectroscopy

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A set of Co promoted 10% Mo/Al_2O_3 samples have been characterized by means of Raman spectroscopy under ambient as well as in situ dehydrated conditions. Under ambient conditions, the degree of the polymerization of surface molybdenum oxide species decreases with increasing Co loading. Under dehydrated conditions, the polymeric molybdenum oxide species is absent with the addition of only 0.2% Co. At low Co loadings ($\leqslant 2\%$), before the formation of $CoMoO_4$ compound, the spectral features are very similar under ambient conditions. Dehydration causes the upward shift of the Mo=O symmetric stretching mode. A broad band around 920–930 cm^{-1} was thus observed. This band has been suggested to be associated with the Co–Mo interaction species. In contrast to crystalline $CoMoO_4$, this species shows a reversibility on H_2 reduction–O_2 reoxidation treatments. From the results obtained, it is proposed that cobalt oxide interacts with the most polymerized molybdenum oxide species to form Co–Mo interaction species and/or crystalline $CoMoO_4$; therefore, the amount of the surface molybdenum oxide species decreases with a change in the molecular structure as a function of the Co concentration.

Keywords: Interaction; molybdenum oxide; cobalt oxide; alumina; dehydration; Raman spectroscopy

1. Introduction

Numerous investigations using a variety of experimental techniques for characterization of hydrodesulfurization (HDS) catalysts have been reported in literature. Among them, Raman spectroscopy has been proved to be a very powerful one. The identification of surface species for molybdenum oxide precursor (mainly on Al_2O_3) by Raman spectroscopy was first reported by Brown et al. as early as 1977 [1]. Subsequently, a number of studies were conducted on MoO_3/Al_2O_3,

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Co–Mo/Al_2O_3 in which Raman spectra were used to follow the genesis of surface and crystalline species as a function of metal loading, metal impregnation sequence, and method of impregnation [2–8].

However, most of the previously reported Raman studies were carried out under ambient conditions. It is known that Raman technique is highly sensitive to the composition and structure of oxidic and sulfided HDS catalysts. Thus, much interesting information could be covered or blurred because of the influence of ambient conditions. Recently, some in situ Raman studies on supported molybdenum oxide were performed [9–14]. Upon dehydration, the symmetric stretching frequency of the Mo=O bond shifts upward. This frequency difference was attributed to a change in structure due to the effect of moisture which is present on the oxide support surface under ambient conditions [14]. No characterization studies, however, have been reported for the Co promoted MoO_3/Al_2O_3 system under dehydrated conditions.

It is well known that the optimal catalysts typical for application in HDS have composition and loadings as: MoO_3 contents near the monolayer capacity and promoter/(promoter + Mo) ratios r near 0.3 [15]. Raman spectra of these materials under ambient conditions were very similar, almost identical to those of unpromoted Mo/Al_2O_3 catalysts [2,16–18]. Moreover, the oxide and molybdate of promoter elements are not normally formed except at high ratios r [15]. Therefore, little is known, by Raman spectroscopy, about the interaction between Co promoter and surface molybdenum oxide species at low ratios r. In this paper, the baseline 10 wt% Mo/Al_2O_3 sample was prepared near the theoretical Mo monolayer coverage. The Raman spectra, presented for the dehydrated Co promoted 10% Mo/Al_2O_3 samples, will yield more information about the influence of the presence of cobalt oxide on molybdenum oxide species.

The present work deals with the determination of the molecular structure of Co promoted 10% Mo/Al_2O_3 HDS catalyst oxide precursor under both hydrated and dehydrated conditions by Raman spectroscopy. The purpose of this work is to reveal the structural change of alumina supported molybdenum oxide as a function of cobalt loading. Since most polymeric molybdate species were found to be extractable by ammonia solution at a pH above 12.0 [19, 20], characterization of the Co–Mo/Al_2O_3 system after extraction by ammonia solution can also provide useful information for understanding the surface structure of such catalysts.

2. Experimental

Sample preparation: A commercial γ-Al_2O_3 was used with S_{BET} of 200 $m^2\ g^{-1}$, pore volume of 0.51 $cm^3\ g^{-1}$, ground and seived to 100 mesh. 10 wt% Mo/Al_2O_3 sample was prepared by incipient wetness impregnation from aqueous solution of ammonium heptamolybdate, followed by drying at 393 K and calcining at 723 K for 10 h. Co promoted samples were prepared by two-step impregnation from aqueous solution containing the appropriate amounts of Co nitrate. A set of samples were prepared based on 10 wt% Mo/Al_2O_3 with Co varying from 0.2 up to 6 wt% (all concentrations were expressed as wt% metal loading). These samples were further dried at 393 K and calcined at 723 K in air for 5 h.

Raman spectral acquisition: Samples were pressed into self-supporting wafers with 13 mm diameter and put into quartz cell which was connected to a gas handling system so that the sample could be subjected to various pretreatments. The cell was first purged with dry O_2 (99.99%) at room temperature, then the temperature was incrementally increased in O_2 (30 ml/min) to 700 K and kept there for 1 h. Afterward, the sample was cooled to room temperature to obtain Raman spectra. It was found that the Raman spectra obtained in dry O_2 at 700 K are almost exactly the same as the spectra obtained after cooling to room temperature, indicating that temperature on such scale has very little influence on the spectra recorded. Thus, for comparison with the spectra taken under ambient conditions, all our spectra shown were collected at room temperature. The redox treatments were performed as follows: after dehydration, the sample was reduced at 700 K in H_2 (30 ml/min) for 1 h, then reoxidized at 700 K in O_2 for another 1 h. The Raman spectra were collected using a Jobin-Yvon U-1000 spectrometer. The 488.0 nm line of an argon-ion laser (Spectra Physics) was used as excitation source. The laser power at the source was 200 mW.

Extraction of molybdenum; Extraction of Mo by solubilization was carried out by treating 0.5 g samples with 120 ml of 0.3% ammonia (pH 12.6) solution for 0.5 h. After filtration the extracted samples were dried at 393 K and further calcined at 723 K for 4 h.

3. Results

Fig. 1 presents the Raman spectra of (0–6)% Co–10% Mo/Al_2O_3 samples under ambient conditions. The spectrum of the uncalcined wet 10% Mo/Al_2O_3 sample (fig. 1a) consists of bands at 940, 879, 555, 359 and 219 cm$^-$1 which are characteristic of adsorbed octahedrally coordinated $Mo_7O_{24}^{6-}$ species [7,21,22]. For the calcined 10% Mo/Al_2O_3 sample, the Raman bands are observed at 961, 854, 358 and 210 cm^{-1}. The bands at 961 and 358 cm^{-1} are attributed to the symmetric stretching and bending mode of the Mo=O bond of octahedrally coordinated polymeric molybdenum oxide species, respectively [17,18,21–23]. The bands at ~ 854 and 210 cm^{-1} are ascribed to the Mo–O–Mo asymmetric stretches and Mo–O–Mo deformations of polymeric molybdenum oxide species [24]. These results indicate that 10% Mo/Al_2O_3 possesses mostly polymeric molybdenum oxide species. With the addition of cobalt from 0.2 to 6%, the Raman band of the Mo=O symmetric stretching mode decreases and shifts downwards from 961 to ~ 947 cm^{-1}. In addition, the bands at 210 and 358 cm^{-1} also decrease and disappear above 2% Co loading. At 4% Co loading and higher, a sharp band at 938 cm^{-1} predominates in the

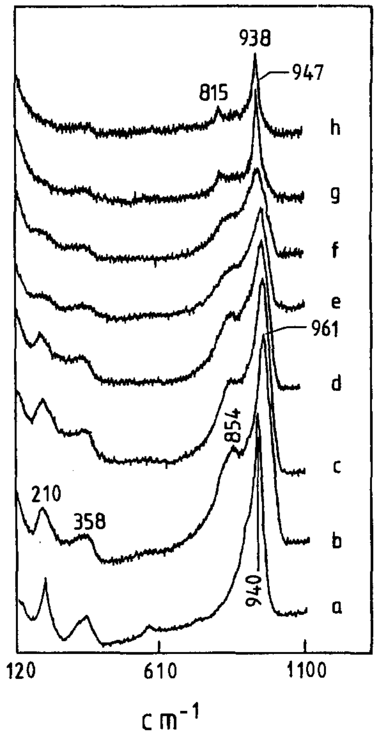

Fig. 1. Raman spectra of (a) uncalcined wet 10% Mo/Al_2O_3, (b) 10% Mo/Al_2O_3, (c) 0.2% Co–10% Mo/Al_2O_3, (d) 0.5% Co–10% Mo/Al_2O_3, (e) 1% Co–10% Mo/Al_2O_3, (f) 2% Co–10% Mo/Al_2O_3, (g) 4% Co–10% Mo/Al_2O_3, (h) 6% Co–10% Mo/Al_2O_3 under ambient conditions.

spectra, together with two weak bands at ~ 815 and ~ 360 cm^{-1}, which are due to crystalline $CoMoO_4$ [25]. Besides, the band in the 850–870 cm^{-1} region is almost invisible in these two spectra.

The Raman spectra of the same samples under dehydrated conditions are shown in fig. 2. The 10%Mo/Al_2O_3 sample possesses a sharp Raman band at 1000 cm^{-1}, a broad band at ~ 866 cm^{-1}, a weak band at ~ 210 cm^{-1} and a broad, ill-defined band at ~ 300 cm^{-1}. The 1000 and ~ 300 cm^{-1} bands have been assigned to the isolated monooxo molybdenum oxide species. The band at ~ 210 cm^{-1} is attributed to the polymeric molybdenum oxide species [14]. But it is difficult to define other bands which might be associated with the polymeric molybdenum oxide species because of not so good a signal to noise ratio and a low fraction of this species. The broad band observed at ~ 866 cm^{-1} can be ascribed to a regular MoO_4 tetrahedron due to microcrystalline molybdates formed from small amounts of cationic impurities (such as K^+, Na^+, Ca^+, Sr^+, or Ba^+) present on alumina surface [26]. Spectral features are changed with the addition of cobalt oxide. As Co loading increases from 0.2 to 6%, the Mo=O stretching mode decreases and shifts downwards from 1000 to ~ 987 cm^{-1}. The band at ~ 210 cm^{-1} disappears with the addition of only

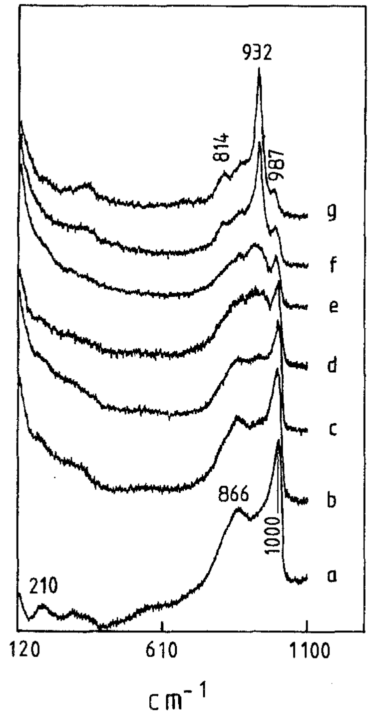

Fig. 2. Raman spectra of (a) 10% Mo/Al_2O_3, (b) 0.2% Co–10% Mo/Al_2O_3, (c) 0.5% Co–10% Mo/Al_2O_3, (d) 1% Co–10% Mo/Al_2O_3, (e) 2% Co–10% Mo/Al_2O_3, (f) 4% Co–10% Mo/Al_2O_3, (g) 6% Co–10% Mo/Al_2O_3 under dehydrated conditions.

0.2% Co. In the 0.2–2% Co concentration region, a broad Raman band appears at $\sim$ 927 cm^{-1} and becomes more pronounced with increasing Co loading. This broad band is probably being overlapped by the Mo=O stretching band under hydrated conditions. At 4 and 6% Co loadings, a sharp band at 932 cm^{-1} shows up, together with two weak bands at $\sim$ 814 and $\sim$ 360 cm^{-1}, which are due to the presence of crystalline $CoMoO_4$. The small frequency difference for crystalline $CoMoO_4$ under hydrated and dehydrated conditions might be associated with the change in position of the Mo=O symmetric stretching mode. The results presented above propose that the broad band around 920–930 cm^{-1} at low Co loadings ($\leqslant 2\%$) is most likely associated with cobalt and molybdenum oxide interaction species.

It is noted for the 4 and 6% Co–10% Mo/Al_2O_3 samples that, after dehydration, the Raman band in the 850–870 cm^{-1} region becomes observable. Dehydration may change the Raman cross sections of the hydrated molybdate species. In MoO_3/SiO_2 system, the Raman cross section of the dehydrated molybdate surface species has been proposed to be much smaller than the cross section of the hydrated molybdenum oxide cluster [27]. However, in this work, the Raman cross section of the dehydrated molybdate species appears to be higher than that of the hydrated molybdate species. It is argued that the 850–870 cm^{-1} band observed under hydrated conditions which is assigned to the Mo–O–Mo asymmetric stretching mode should be absent after dehydration [14,24], while in the same region, the band due to microcrystalline molybdates should be unaffected by the moisture [26]. Comparison of the spectra presented in figs. 1 and 2 reveals the difference as a function of Co loading under hydrated and dehydrated conditions. The 850–870 cm^{-1} band due to the Mo–O–Mo asymmetric stretching mode under ambient conditions decreases with increasing Co loading and almost disappears at 4% Co loading, which is accompanied by the decrease of the terminal Mo=O stretching band. On the other hand, the 850–870 cm^{-1} band due to microcrystalline molybdates observed under dehydrated conditions is little affected by the presence of Co oxide. Thus, it is proposed that the Raman cross section of the dehydrated microcrystalline molybdates is much higher than the cross section of the hydrated microcrystalline molybdates. The fact that only the relative intensity in the 850–870 cm^{-1} region is greatly affected by the moisture can be accounted for by the presence of two bands due to two types of surface molybdate species which possess different Raman cross sections under hydrated and dehydrated conditions.

Fig. 3 shows the Raman spectra of the 2 and 4% Co–10% Mo/Al_2O_3 samples before and after reduction–reoxidation treatments under dehydrated conditions. No significant change was observed for the spectra of 2% Co–10% Mo/Al_2O_3, indicating the reversibility of surface species upon redox treatments. On the contrary, a change in the spectral feature of 4% Co–10% Mo/Al_2O_3 occurs after the redox treatments. Simultaneously with the intensity decrease at 932 cm^{-1}, a new band appears at ~ 692 cm^{-1}, which is due to $CoAl_2O_4$ and/or Co_3O_4 [28]. This result shows that crystalline $CoMoO_4$ is unstable upon hydrogen treatments, with some octahedrally coordinated Co ions in the $CoMoO_4$ structure transforming into tetrahedrally coordinated Co ions in $CoAl_2O_4$ and/or Co_3O_4. The different behaviors of these two samples on redox treatments suggest that the Co–Mo interaction species might be a highly dispersed phase.

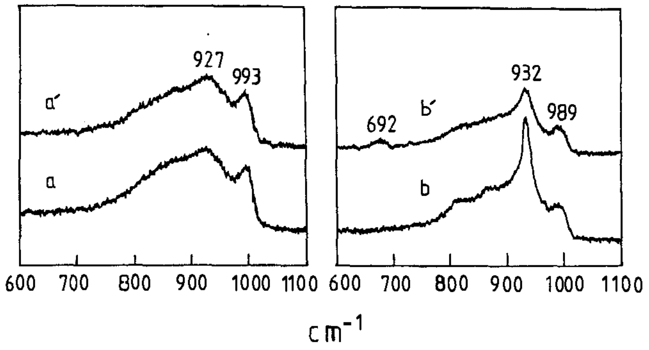

Fig. 3. Raman spectra of the dehydrated (a, a') 2% Co–10% Mo/Al_2O_3 and (b, b') 4% Co–10% Mo/Al_2O_3 before and after H_2 reduction and O_2 reoxidation treatments, respectively.

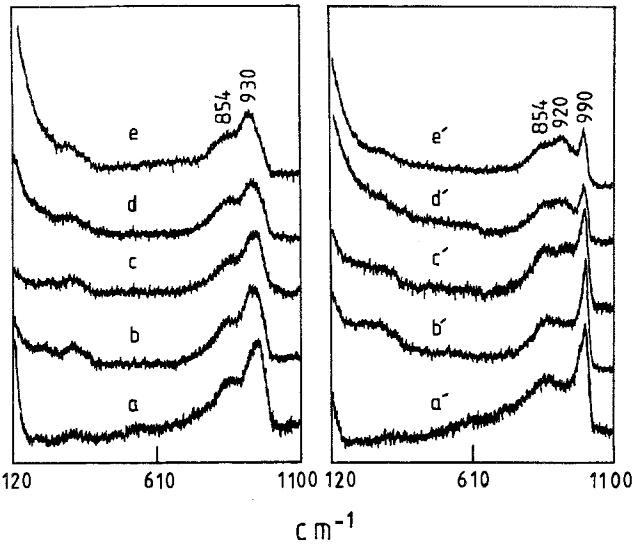

Fig. 4. Raman spectra of the extracted (0, 0.5, 1, 2, 4)% Co–10% Mo/Al_2O_3 samples taken under ambient (a, b, c, d, e) and dehydrated (a′, b′, c′, d′, e′) conditions, respectively.

Fig. 4 shows the Raman spectra of the samples after extraction by ammonia solution. The spectral features taken under ambient conditions are very similar, as shown in figs. 4a–4e. As compared to the corresponding unextracted samples, the Raman band of the Mo=O symmetric stretching mode decreases and shifts 10–17 cm^{-1} downwards, and the band at 210 cm^{-1}due to polymeric molybdenum oxide species is absent. Additionally, the ~ 854 and ~ 320 cm^{-1} bands are observed in all these spectra. The broad weak band at ~ 320 cm^{-1} is due to the Mo–O bending mode of isolated and tetrahedrally coordinated MoO_4^{2-} species [7,22]. The sharp band at 938 cm^{-1} for 4% Co–10% Mo/Al_2O_3 is absent after extraction, indicating the disruption of the molecular structure of crystalline $CoMoO_4$. The Raman spectra of the extracted samples after dehydration are presented in figs. 4a′–4e′. All the spectra exhibit a sharp band in the Mo=O stretching region at 995–990 cm^{-1} and a possibly very weak band at ~ 300 cm^{-1}, which are due to the monooxo molybdenum oxide species. The Raman bands in 920–940 cm^{-1} region which are associated with Co–Mo interaction species and $CoMoO_4$ crystallites decrease greatly and shift downwards to relatively lower positions as compared to the corresponding unextracted samples.

4. Discussion

The molecular structures of supported molybdenum oxides have been studied extensively under ambient conditions with Raman techniques. For the

MoO_3/Al_2O_3 system, it is now generally accepted that at low Mo loadings a hydrated tetrahedrally coordinated MoO_4^{2-} species and at higher Mo loadings hydrated polymolybdate species are present [10,29]. In all cases, the Raman frequency of the Mo=O symmetric stretching mode increases with Mo coverage, so does the degree of the polymerization of the surface molybdenum oxide species. The results presented above indicate that the Raman bands due to the polymeric molybdenum oxide species decrease with increasing Co loading. Additionally, the symmetric stretching mode of the terminal Mo=O bond shifts downwards from 961 to 947 cm^{-1}. This behavior is similar to that of decreasing molybdenum oxide coverage on alumina surface. The degree of polymerization of the molybdenum oxide species is therefore a function of Co content, so is the molecular structure.

Under dehydrated conditions, three surface molybdenum oxide species are present on 10% Mo/Al_2O_3, i.e., the isolated monooxo molybdenum oxide species, the octahedrally coordinated polymeric molybdenum oxide clusters and the microcrystalline molybdates formed from cationic impurities. The polymeric molybdenum oxide species disappears with the addition of only 0.2% Co. Subsequently, the Mo=O symmetric stretching band decreases and shifts downwards with increasing Co loading. This result is also consistent with that of decreasing molybdenum oxide coverage as discussed above. Meanwhile a broad band becomes more pronounced at $\sim$ 927 cm^{-1} with increasing Co loading and finally a sharp band appears at 932 cm^{-1} at 4% Co and higher. Taking into account the previously reported EXAFS results that Co had very little effect on the local structure around the Mo atoms [16], the current results suggest that cobalt oxide might first interact with the most polymerized molybdenum oxide species to form Co–Mo interaction species. The broadening of the $\sim$ 927 cm^{-1} band indicates that we are not dealing with well-defined molybdenum compounds. Therefore a normal formula could not suit the structure of this species. However, its frequency shows a resemblance to that of crystalline $CoMoO_4$. In $CoMoO_4$, the structure of the molybdates is that of distorted octahedra, and Mo octahedra are bridged by Co octahedra [2]. This resemblance in the band position suggests that the Co–Mo interaction species has a two- and/or three-dimensional structure with Mo octahedra being bridged by Co octahedra in the cluster. As a result of the structure similarity, the frequency of the Co–Mo interaction species should tend to agree with that of crystalline $CoMoO_4$. When Co loading is high enough to reach an appropriate concentration, these isolated Co–Mo clusters would aggregate together to form $CoMoO_4$ compound. Even a higher calcination temperature would give rise to aggregation of these isolated clusters to form crystalline $CoMoO_4$, as evidenced by some other experimental results [21]. This interpretation would also be compatible with the proposed distorted polymolybdate in which Co ions in calcined catalysts are located in highly disordered phase [16].

Recently, a model has been put forward to explain the surface structures of supported metal oxides under ambient conditions [24,30]. It has been proposed that the surface of the oxide support is hydrated and the surface metal oxides are essentially in an aqueous medium. Consequently, the structure of the metal oxide follows the metal oxide aqueous chemistry as a function of the net pH at the point of zero charge (PZC) and the metal oxide concentration. Since cobalt oxide is basic in character [31], the presence of cobalt oxide should increase the pH at PZC of the hydrated surface. This will result in the decrease of the degree of polymerization of the molybdenum oxide species. The current results for Co promoted molybdenum oxide species appear to be consistent with the net surface pH in the PZC model. It might be coincidental that cobalt oxide interacts with the most polymerized molybdenum oxide species to form Co–Mo interaction species and/or $CoMoO_4$ crystallites.

Extraction by ammonia solution at a pH above 12.0 greatly decreases the Mo coverage on alumina surface and thus changes the molecular structure of the Co–Mo/Al_2O_3 catalysts. The extracted samples contain a higher fraction of tetrahedrally coordinated molybdenum oxide species, as evidenced by the broad band at $\sim 320\ cm^{-1}$. This can also be explained by the increase of the net surface pH at PZC because of the adsorption of NH_4OH on the hydrated surface. In this case, the Co ions on the surface after extraction should associate with the remained less polymerized molybdenum oxide species, thus resulting in a shift of the band of the Co–Mo interaction species to a relatively lower position as compared to their corresponding unextracted samples.

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References

[1] F.R. Brown, L.E. Makovsky and K.H. Rhee, J. Catal. 50 (1977) 162.

[2] J. Medema, C. van Stam, V.H.J. de Beer, A.T.A. Konings and D.C. Koningsberger, J. Catal. 53 (1978) 386.

[3] H. Jeziorowski and H. Knözinger, J. Phys. Chem. 83 (1979) 1166.

[4] D.S. Zingg, L.E. Makovsky, R.E. Tischer, F.R. Brown and D.M. Hercules, J. Phys. Chem. 84 (1980) 2898.

[5] B. Sombret, P. Dhamelincourt, F. Wallart, A.C. Muller, M. Bouquet and J. Grosmangin, J. Raman Spectry. 9 (1980) 291.

[6] L. Salvatti, L.E. Makovsky, J.M. Stencel, F.R. Brow and D.M. Hercules, J. Phys. Chem. 85 (1980) 3700.

[7] L. Wang and W.K. Hall, J. Catal. 66 (1980) 251.

[8] C.H. Chang and S.S. Chan, J. Catal. 72 (1981) 139.

[9] G.L. Sahrader and C.P. Cheng, J. Catal. 80 (1983) 369.

[10] J.M. Stencel, L.E. Makovsky, T.A. Sarkus, J. De Vries, R. Thomas and J.A. Moulijn, J. Catal. 90 (1984) 314.

[11] E. Payen, S. Kasztelan, J. Grimblot and J.P. Bonnell, J. Raman Spectry. 17 (1986) 273.
[12] E. Payen, S. Kasztelan, J. Grimblot and J.P. Bonnell, J. Mol. Struct. 143 (1986) 259.
[13] T. Machej, J. Haber, A.M. Turek and I.E. Wachs, Appl. Catal. 70 (1991) 115.
[14] M.A. Vuurman and I.E. Wachs, J. Phys. Chem. 96 (1992) 5008.
[15] B. Delmon, in: *Proc. Climax 3rd Int. Conf. on Chemistry and Uses of Molybdenum*, eds. H.F. Barry and P.C.H. Mitchell (Climax Molybdenum Comp., Ann Arbor, 1979) p.73.
[16] B.S. Clausen, B. Lengeler and H. Topsøe, Polyhedron 5 (1986) 199.
[17] S. Kasztelan, E. Payen, H. Touhoat, J. Grimblot and J.P. Bonnelle, Polyhedron 5 (1986) 157.
[18] S. Kasztelan, J. Grimblot, J.P. Bonnelle, E. Payen, H. Toulhoat and Y. Jacquin, Appl. Catal. 7 (1983) 191.
[19] F.J. Gil, A.M. Escudey Castro, A. Lopez Agudo and J.L.G. Fierro, J. Catal. 90 (1984) 323.
[20] C.V. Caceres, J.L.G. Fierro, A.L. Agudo, M.N. Blanco and H.J. Thomas, J. Catal. 95 (1985) 501.
[21] L.E. Makovsky, J.M. Stencel, F.R. Brown, R.E. Tischer and S.S. Pollack, J. Catal. 89 (1984) 334.
[22] K.Y.S. Ng and E. Gulari, J. Phys. Chem. 89 (1985) 2479.
[23] L. Wang and W.K. Hall, J. Catal. 77 (1982) 232.
[24] D.S. Kim, K. Segawa, T. Soeya and I.E. Wachs, J. Catal. 136 (1992) 539.
[25] E. Payen, J. Grimblot and S. Kasztelan, J. Phys. Chem. 91 (1987) 6642.
[26] F.D. Hardcastle and I.E. Wachs, J. Raman Spectry. 21 (1990) 683.
[27] M. de Boer, A.J. van Dillen, D.C. Koningsberger, J.W. Geus, M.A. Vuurman and I.E. Wachs, Catal. Lett. 11 (1991) 227.
[28] E. Payen, J. Barbillat, J. Grimblot and J.P. Bonnelle, Spectrosc. Lett. 11 (1978) 997.
[29] C.C. Williams, J.G. Ekerdt, J.M. Jeng, F.D. Hardcastle and I.E. Wachs, J. Phys. Chem. 95 (1991) 8791.
[30] G. Deo and I.E. Wachs, J. Phys. Chem. 95 (1991) 5889.
[31] G.A. Park, Chem. Rev. 65 (1965) 177.