

Interaction of Molybdenum Oxide with Titania: Raman Spectroscopic Study

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Laser Raman spectroscopy has been used to study the interaction of MoO_3 with TiO_2 . The bulk molybdenum oxide appeared to spread on the surface of titania under the submonolayer coverage. The surface polymolybdate was observed to be very stable with respect to the repeated treatment of reduction and subsequent calcination. Owing to the interaction of molybdate and titania, the phase transformation of TiO_2 seemed to be strongly retarded. The additives such as Co and Ni reacted readily with MoO_3 to form the corresponding molybdate salts. Nevertheless, the polymolybdate species appeared to be more stable on the titania surface than the molybdate salts.

Introduction

Alumina-supported molybdenum oxide catalysts are well-known as the hydrosulfurization catalyst. Various spectroscopic methods have been applied in order to identify active species and to understand why a small amount of additives has a profound effect on catalytic activities. In spite of the abundance of the work on alumina-supported Mo catalyst, titania-supported Mo catalysts have attracted much less attention. One reason is that the catalytic activity was considered to be much lower compared with the alumina-supported catalysts. Recently, however, titania-supported molybdenum catalysts are reported to be active for a wide range of important industrial reactions such as olefin hydrogenation and isomerization.¹ Accordingly, several research groups have characterized the catalyst by various spectroscopic methods.²⁻⁶ The active surface species is not yet, however, clearly understood.

Raman spectroscopy is effective in detecting the presence of the crystalline as well as amorphous oxide. Consequently, alumina-supported Mo catalysts have been extensively studied by Raman spectroscopy.⁷⁻¹² On the other hand, Raman spectroscopic study on titania-supported catalysts is scarce and little is known about the structure of surface species.^{2,6} The role of various additives such as Co and Ni has not been investigated by Raman spectroscopy.

The dispersion or spreading of metal oxide on supports is one of the problems currently being investigated in the supported catalysts. Xie and co-workers¹³ first showed that heating a physical mixture of crystalline MoO_3 and $\gamma\text{-Al}_2\text{O}_3$ at temperature near 670 K for typically 24 hrs led to the disappearance of the X-ray diffraction pattern of MoO_3 . This observation was interpreted as monolayer dispersion of MoO_3 on the surface of $\gamma\text{-Al}_2\text{O}_3$. Later, the same group reported supportive data for crystalline MoO_3 physically mixed with TiO_2 . However, they were unable to analyze the nature and structure of the dispersed oxide due to the experimental technique applied.¹⁴ Stampfl *et al.*¹⁵ and Leyrer *et al.*¹⁶ have subsequently applied laser Raman spectroscopy to the study on the interaction of MoO_3 with TiO_2 . It was shown that MoO_3 spreaded over the surface of TiO_2 at 720 K and tended to form "monolayer" on the support.

The purpose of this work is to investigate by Raman spectroscopy the stability of surface species in physical mixtures

of MoO_3 and TiO_2 . Since most of the previous works have been focused on the nature of the surface molybdate formed merely by calcination, we have attempted to know how the surface species are affected by the congruent treatments of calcination, reduction, and subsequent recalcination. The effect of the presence of additives, Co and Ni, on the stability of surface molybdate has been considered. The phase transition of titania has also been considered in conjunction with the interaction between molybdenum oxide and titania support.

Experimental

The titania and silica supports, P-25 titania and Aerosil 130 from Degussa with surface areas of ca. 50 and 130 m^2/g , respectively, were dried overnight in oven at 400 K before use. The MoO_3 was obtained by thermal decomposition of reagent grade ammonium heptamolybdate in air at 773 K for 6 hrs. The formation of orthorhombic MoO_3 was confirmed by the X-ray diffraction analysis. Initially, a series of mechanical mixture of MoO_3 and $\text{TiO}_2(\text{SiO}_2)$ were weighed. After a thorough grinding, each sample has been pelletized and then subjected to calcination for 24 hrs. To prepare the sample containing either Ni or Co, the corresponding reagent grade nitrate salt has been added in the mixture. The reduction treatment has been performed under flowing hydrogen (flow rate: 30 ml/min) for 24 hrs. For a comparative work, a few samples have been prepared by the so-called impregnation method.

Raman spectra were obtained with a Japan Spectroscopic Model R-300 laser Raman spectrometer. 514.5 nm radiation from an argon ion laser (Spectra Physics Model 164-06) was used to excite the Raman spectra. Raman scattering was observed at 90° geometry with a commercial photon counting system. The typical laser power was 20-40 mW at the sample position. The sampling pellet was rotated at 2000 rpm during the Raman measurement to prevent any decomposition reaction due to local heating. All the spectra were recorded under the ambient condition.

Results and Discussion

In order to facilitate the interpretation of the Raman spectra of molybdenum catalysts, spectra of various reference

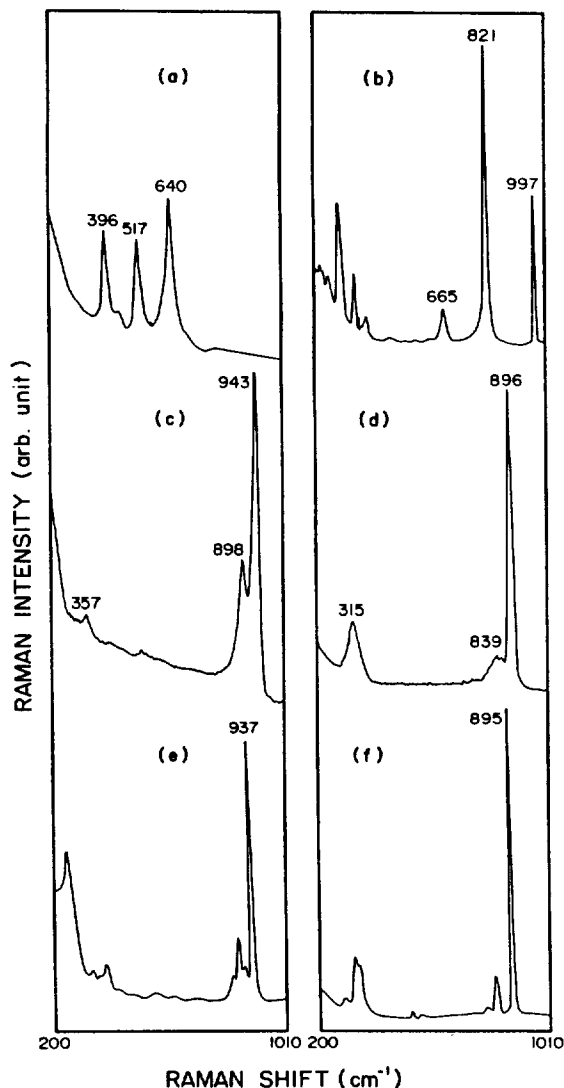


Figure 1. Raman spectra of reference compounds; (a) TiO_2 , (b) MoO_3 , (c) $\text{Mo}_7\text{O}_{24}^{6-}$ and (d) MoO_4^{2-} ions in aqueous solution, (e) $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot x\text{H}_2\text{O}$, (f) $\text{Na}_2\text{MoO}_4 \cdot x\text{H}_2\text{O}$.

compounds have been recorded. Figure 1a represents the Raman spectrum of titania support. The major anatase bands occur at 396, 517 and 640 cm^{-1} , while the bands due to rutile at 448 and 611 cm^{-1} . It is seen that the spectrum is dominated by the anatase feature.¹⁶ As shown in Figure 1b, MoO_3 can be characterized by the prominent peaks at 997 and 821 cm^{-1} which are attributed to the stretching vibrations of the terminal $\text{Mo}=\text{O}$ and the bridging $\text{Mo}-\text{O}-\text{Mo}$ bonds, respectively.¹⁷ Figure 1c and 1d exhibit, respectively, the Raman spectra of $\text{Mo}_7\text{O}_{24}^{6-}$ and MoO_4^{2-} ions in aqueous solution. For comparison, the Raman spectra of polycrystalline ammonium heptamolybdate and sodium molybdate are also shown in Figure 1e and 1f, respectively. The characteristic wavenumber regions of molybdate species are 200-250, 310-370, 700-850 and 900-1,000 cm^{-1} , which are to be assigned respectively to $\text{Mo}-\text{O}-\text{Mo}$ deformation, terminal $\text{Mo}=\text{O}$ bending, antisymmetric $\text{Mo}-\text{O}-\text{Mo}$ stretching, and symmetric and antisymmetric terminal stretching modes.¹⁸

The Raman spectra of conventionally prepared molybdate catalysts are very similar to those of polymolybdate anions

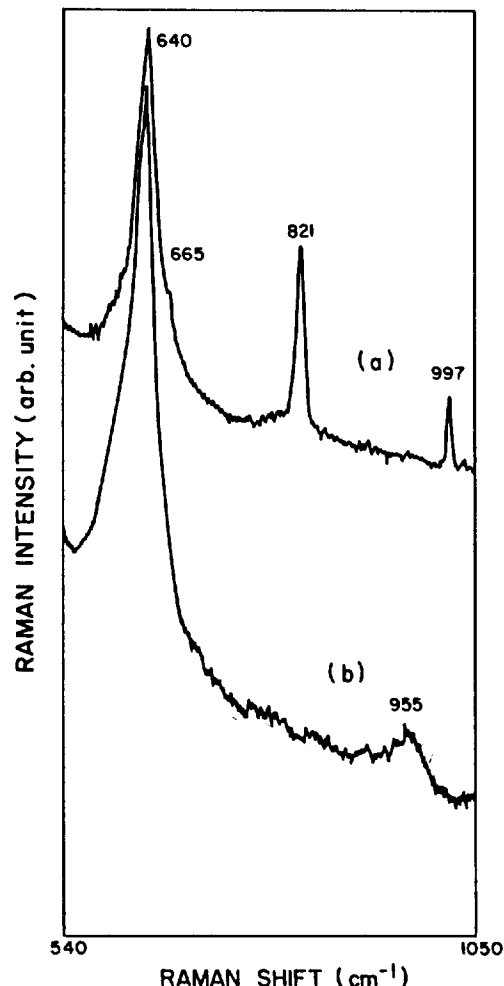


Figure 2. Raman spectra of mechanical mixture containing 2.9 wt% MoO_3 in TiO_2 . (a) Untreated and (b) calcined at 773 K in air for 24 hrs.

and have been interpreted in terms of surface analogues of highly condensed polyanions.¹⁹ This interpretation was based on the appearance of the 220 cm^{-1} band, which suggests the presence of $\text{Mo}-\text{O}-\text{Mo}$ linkages, and on the high wavenumber of the $\text{Mo}=\text{O}$ terminal stretching mode in the 940-960 cm^{-1} range. Jannibello *et al.*²⁰ have argued against this interpretation in their work on $\text{MoO}_3/\gamma\text{-Al}_2\text{O}_3$ catalyst by mentioning that both monomeric and polymeric species should be present on the alumina surface after calcination. These authors emphasized the difficulty of distinguishing between $\text{Mo}-\text{O}-\text{Mo}$ and $\text{Mo}-\text{O}-\text{Al}$ linkages, the more so as spectra of well-characterized molecular compounds containing similar $\text{Mo}-\text{O}-\text{Al}$ bonds are not available. Jannibello *et al.* concluded that the high wavenumber values in the $\text{Mo}=\text{O}$ stretching region were not sufficient to justify the polymerized surface species of octahedrally coordinated molybdenum-oxygen species, since a similar wavenumber shift was observed and attributed to an increase of the polarization of terminal $\text{Mo}=\text{O}$ bonds of monomeric tetrahedral structures as a result of progressive surface dehydration. However, angular correlation studies²¹ have provided unequivocal evidence for the fact that condensed polymeric surface species with molybdenum in octahedral coordination are the majority species

in $\text{Mo}/\gamma\text{-Al}_2\text{O}_3$ catalysts after calcination at 773 K. Hence, most of the Raman spectroscopic studies on the supported molybdenum catalysts have been interpreted in terms of surface analogues of highly condensed polyanions. In accordance with this view, the spectral feature of the region above 600 cm^{-1} was mainly used in this work regarding to the interaction between molybdenum oxide and titania support.

The spectra for the $\text{MoO}_3/\text{TiO}_2$ system are displayed in Figure 2. The system contains 2.9 wt% MoO_3 in TiO_2 , which is far below the amount of MoO_3 needed for the monolayer coverage in TiO_2 (monolayer coverage is calculated to form at near 6 wt% in the present catalyst).²² The peak at 640 cm^{-1} is associated with anatase. The characteristic MoO_3 peak at 821, 997 and 665 (small shoulder) cm^{-1} are clearly present in spectrum 2a for the mechanical mixture of MoO_3 and TiO_2 . When the mechanical mixture was calcined in air at 773 K, the peaks due to MoO_3 disappeared as shown by spectrum 2b. Instead, a small broad feature appeared at 955 cm^{-1} in spectrum 2b. Although the exact nature of the band is not known, one can speculate that the band is associated with a surface polymolybdate species based on the characteristics of heptamolybdate ion mentioned above. These results are consistent with the previous idea of the bulk molybdenum oxide spreading on the surface of the titanium oxide under the submonolayer coverage.^{14,15}

The spreading of one oxide over the surface of a second oxide can occur *via* the three ways²³: (1) gas-phase transport and redeposition on the support surface, (2) transport by surface diffusion in a concentration gradient, (3) solid-solid wetting with a gradient of the surface free energy as the driving force. As reported by Leyrer *et al.*¹⁰, gas-phase transport may be unlikely under the experimental condition applied in this work. If this mechanism was the most favorable one, the surface polymolybdate should also occur in the $\text{MoO}_3/\text{SiO}_2$ system. In a separate experiment, we have calcined the physical mixture containing 5 wt% MoO_3 in SiO_2 in air at 773 K for 24 hrs. The Raman spectrum of the thermally treated material was found to be identical to that of the uncalcined physical mixture. These results suggest that there is no interaction between MoO_3 and the silica support. The observation made on the $\text{MoO}_3/\text{SiO}_2$ system seems to dictate further that surface diffusion is also not a major process for the formation of surface polymolybdate. Hence, it appears that solid-solid wetting would be the most likely and dominant process for the spreading of MoO_3 over TiO_2 and the subsequent formation of polymolybdate species.

Low energy ion scattering spectroscopy (ISS) is known to be a useful method for analyzing the chemical composition of the first layers of heterogeneous catalysts because of its sensitivity for the outermost atomic layer. Leyrer *et al.*¹⁶ has recently applied ISS to $\text{MoO}_3/\text{SiO}_2$ and $\text{MoO}_3/\text{TiO}_2$ systems. According to their report, MoO_3 spreads on the surface of TiO_2 upon calcination at 720 K even in the absence of water vapor. On the other hand, when SiO_2 was used as a support no indication could be obtained for spreading of MoO_3 even though the calcination had been performed in moist atmosphere. Hence, it appears that MoO_3 spreads over the surface of TiO_2 prior to the formation of surface polymolybdate species. Above discussions suggest that the interaction energy between MoO_3 and TiO_2 is greater than that between MoO_3 and SiO_2 . The interaction energy should contain the adhesion

energy and chemical contributions. Nevertheless, it is difficult at the present time to quantify each contribution considering that the solid state reaction between MoO_3 and TiO_2 can occur to produce a compound $\text{Ti}(\text{MoO}_4)_2$ while not feasible between MoO_3 and SiO_2 , the chemical contribution seems to be an important factor for the solid-solid wetting process to occur.

Leyrer *et al.*¹⁶ reported that when a physical mixture of 4.1 wt% $\text{MoO}_3/\text{TiO}_2$ was calcined in a flow of dry O_2 at 720 K, the polycrystalline MoO_3 was exclusively present in the Raman spectrum. Hence, they concluded that H_2O vapor was absolutely essential for the polymolybdate formation on the titania surface. In the present work, we have performed the calcination treatment exclusively in air. Under this environment, the MoO_3 appeared to transform completely into surface polymolybdate as long as the molybdena loading was submonolayer and the calcination temperature was at 773 K (*vide infra*). In a separate experiment, we have calcined a physical mixture of MoO_3 and TiO_2 under dry O_2 at 773 K and taken the Raman spectrum immediately after the preparation. It was very interesting to observe that the Raman spectrum was rather similar to that for a sample prepared by air-calcination. At the present time, we are not equipped with a Raman cell which can be operated under in-situ condition at a higher temperature. However, we believe that MoO_3 spreads over the surface of TiO_2 irrespective of the presence of H_2O vapor. At any rate, it is hardly conceivable that the spreaded MoO_3 would react immediately with the water vapor in air at room temperature to result in the formation of surface polymolybdate species. Regarding to this matter, we plan to make an in-situ Raman cell in order to elucidate the role of H_2O vapor. Nevertheless, it may be supposed²⁴ that the spreaded MoO_3 would react with H_2O to give $\text{MoO}_2(\text{OH})_2$. This intermediate may react further with surface hydroxyls to form monomeric tetrahedral surface molybdate species which would then polymerize to yield the surface polymolybdate species.¹⁰ In these reaction steps, TiO_2 would provide an active surface sites. It is well known that in basic aqueous solution, molybdate exists as a monomeric species in the form of MoO_4^{2-} . However, with decrease of pH in solution, MoO_4^{2-} is protonated and polymerization equilibria are established.²⁵ For instance, $\text{Mo}_7\text{O}_{24}^{4-}$ is stable at pH region, 2-6, and MoO_5^{2-} at below pH 2. On the other hand, the isoelectric point²⁶ of TiO_2 is known to be of pH = 6.2. Hence, at acidic pH values, polymeric molybdate species are favorably adsorbed on the positively charged titania surface, whereas at basic pH values, monomeric species are stable on titania.¹ Based on these arguments, it appears that the surface of TiO_2 provides an acidic environment for the polymolybdate species to form on TiO_2 . It would be informative to notice that in normal aqueous solution the molybdena species adsorb hardly on the silica surface, however, since the pH value corresponding to its isoelectric point is too low.

Figure 3 shows the Raman spectra for the system containing 4.8 wt% MoO_3 in TiO_2 after calcination at different temperatures. After calcination at 573 K in air for 24 hrs, MoO_3 peaks at 821 and 997 cm^{-1} are barely changed. As the calcination temperature increases to 673 K, a peak attributable to surface polymolybdate species is clearly seen. Nevertheless, the surface transformation of MoO_3 into a surface poly-

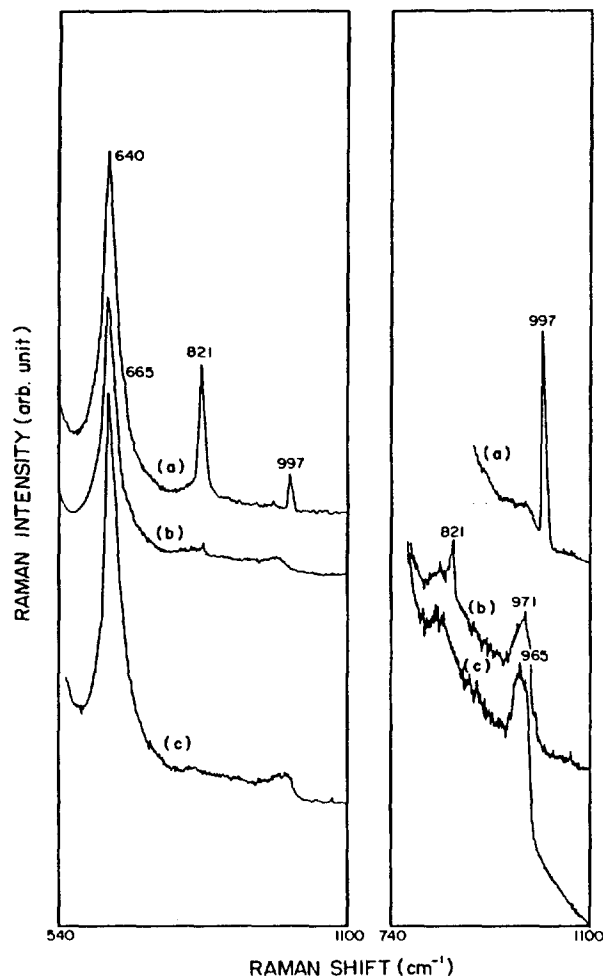


Figure 3. Raman spectra of mechanical mixture containing 4.8 wt% MoO_3 in TiO_2 . Calcined at (a) 573, (b) 673, and (c) 773 K in air for 24 hrs.

molybdate is not complete at 673 K. When the calcination temperature reaches to 773 K, peaks arising from the vibrations of MoO_3 are no longer present and the peak due to polymolybdate is exclusively observed at 965 cm^{-1} . It may be interesting to observe, instead, that the peak position related to the surface polymolybdate species seems to be affected by the molybdenum loading. As the loading increases, the corresponding $\text{Mo}=\text{O}$ stretching band appears at a relatively higher wavenumber. This may be understood on the basis that as monomeric species become polymerized, the $\text{Mo}=\text{O}$ stretching mode assumes in general to have higher frequency. Hence, it is conjectured that the degree of polymerization in the calcined state is more or less greater for the sample with 4.8 wt% MoO_3 than that with 2.9 wt% MoO_3 considered earlier. As the calcination temperature was increased to 873 K, the spectral feature due to the surface polymolybdate has barely changed. However, it could be seen that substantial amount of phase transition has occurred in TiO_2 from anatase to rutile. Considering that such a phase transformation proceeds significantly even at 773 K for TiO_2 itself, the surface polymolybdate species seem to retard the structural changes in TiO_2 . This observation supports that the interaction between MoO_3 and TiO_2 is, in fact, fairly strong. Nevertheless, the interaction looks to be active in the

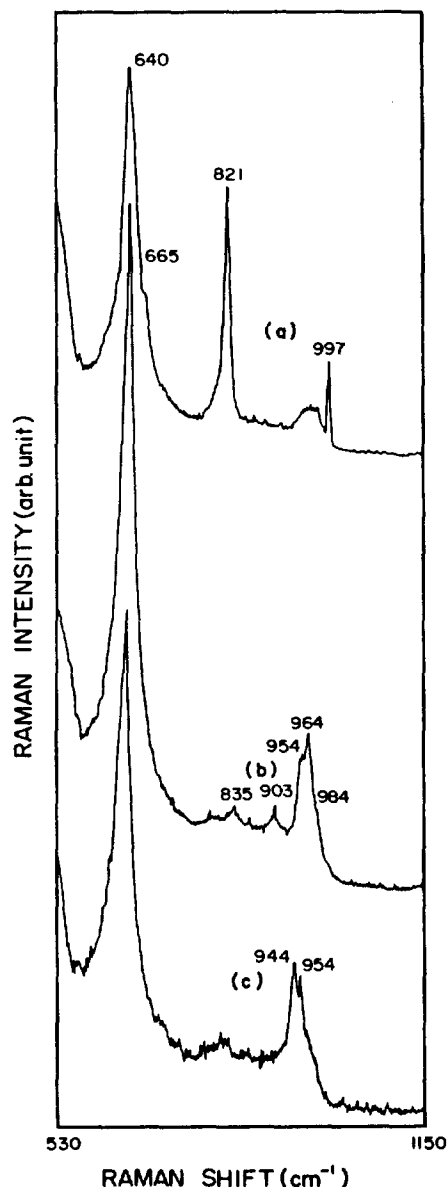


Figure 4. Raman spectra of mixtures calcined at 773 K in air for 24 hrs. (a) 13.0 wt% MoO_3 in TiO_2 , (b) 3.4 wt% NiO plus 13.0 wt% MoO_3 in TiO_2 , and (c) 3.4 wt% CoO plus 13.0 wt% MoO_3 in TiO_2 .

interfacial region since the MoO_3 phase can be seen in the Raman spectra for the $\text{MoO}_3/\text{TiO}_2$ system in the calcined state as long as the molybdenum loading exceeds the monolayer coverage. The presence of water vapor is not enough to produce the surface polymolybdate species. Under the condition of multilayer coverage, free surface hydroxyls of titania may not be available. Accordingly, it appears that surface hydroxyl group of TiO_2 is involved directly in the formation of surface polymolybdate species.

The surface polymolybdate species are observed to be very stable with respect to the repeated treatment of reduction under H_2 and subsequent calcination in air. As the calcined physical mixture of MoO_3 and TiO_2 was treated with dry H_2 at 673 or 773 K, the sample became dark and any Raman spectral pattern could not be observable. The Raman spectrum of the sample after recalcination in air at 673 or 773

K exhibited, however, the same characteristics as that observed prior to the reduction process. The spectral feature in the calcined state is hardly dependent on the number of such a combined treatments. We could evidence the stability of surface polymolybdate even for the $\text{MoO}_3/\text{TiO}_2$ sample prepared by impregnation wetness method.

Figure 4 shows the Raman spectra of the mechanical mixture containing 13.0 wt% MoO_3 and 3.4 wt% NiO (or CoO) in TiO_2 after calcination at 773 K in air for 24 hrs. For comparison, the Raman spectrum of a sample without $\text{Ni}(\text{Co})$ is also shown in the figure. As can be seen in Figure 4a, the calcined $\text{MoO}_3/\text{TiO}_2$ sample consists of both the surface polymolybdate species and the bulk MoO_3 phase since the molybdenum loading exceeds the amount necessary for the monolayer coverage on TiO_2 . It is very interesting, however, to observe that there are not any peaks attributable to MoO_3 for the sample containing either Ni or Co. The band attributable to the surface polymolybdate was observed to occur as a shoulder in the high frequency side of the prominent peak at 964 cm^{-1} for the nickel containing sample and at 954 cm^{-1} for the cobalt containing sample. The peaks at 964, 954, 903 and 835 cm^{-1} in Figure 4b can be attributed to the formation of NiMoO_4 . Similarly, the peaks at 954 and 944 cm^{-1} would be attributed to the polycrystalline cobalt molybdate. The same spectral pattern could be observed irrespective of the sample preparation methods, mechanical mixing and impregnation. After the repeated treatment of reduction under H_2 and subsequent calcination in air, the phase attributed to either nickel molybdate or cobalt molybdate was recovered without any noticeable spectral change. Hence, in the calcination process the additives such as Co and Ni appear to react readily with MoO_3 to form the corresponding molybdate salts. However, it is seen that the surface polymolybdate is relatively more stable on the titania surface than the molybdate salts. When a physical mixture of $\text{Ni}(\text{NO}_3)_2$ ($\text{Co}(\text{NO}_3)_2$), MoO_3 and TiO_2 with the molybdenum loading not enough for the monolayer coverage was calcined, its Raman spectrum was much the same as that shown in Figure 2b. Any peak attributable to the formation of molybdenum salt could be hardly discerned. Even after the combined treatment of reduction and recalcination, the peak due to polymolybdate species appeared only at 955 cm^{-1} as a broad band. Nevertheless, it is not known yet how much of the added $\text{Ni}(\text{Co})$ incorporates into the surface polymolybdate species. The X-ray diffraction (XRD) analysis could not be applied to determine the structure of surface polymolybdate. Only the structureless features are seen; because of the low concentration, the presence of any crystalline phase due to nickel oxide (cobalt oxide) or nickel molybdate (cobalt molybdate) can not be examined by the XRD method. In order to determine, at least, the specific nickel (cobalt) oxidation state we plan to investigate the composite system by X-ray photoelectron spectroscopy.

Although the polymolybdate species seems to be very stable on the surface of titania, its detailed structure is still a matter of conjecture. Various structural models have been proposed by several research groups. We have recently applied the Fourier transform infrared spectroscopy to characterize the titania supported molybdenum.²⁷ The equilibrium adsorption method was used to prepare molybdena species homogeneously dispersed on the support. The samples have

been oxidized at 773 K in dry O_2 and then slightly reduced for 15 min at 773 K in dry H_2 . Even under an oxidizing environment, molybdena species appeared to be able to possess coordinatively unsaturated Mo^{5+} ions owing to the nature of TiO_2 , *i.e.* oxygen deficiency and permeability toward oxygen diffusion. At the initial stage of reduction, the terminal double bond oxygen ($\text{Mo}=\text{O}$) seemed to be removed, generating presumably Mo^{4+} . These experimental results seemed to be in good accord with the two-dimensional model of molybdena-titania catalyst proposed by Segawa *et al.*¹ Although the calcined physical mixture of MoO_3 and TiO_2 prepared in this work may possess a different structure from that obtained by the equilibrium adsorption method, we are preferably in a position to favor the model proposed by Segawa *et al.* for the structure of surface polymolybdate species.

In summary, we have applied Raman spectroscopy to the characterization of physical mixture of MoO_3 and TiO_2 . The bulk molybdenum oxide appeared to spread on the surface of the titanium oxide under the submonolayer coverage. It seemed that surface hydroxyl group of TiO_2 took part in the formation of surface polymolybdate species. Besides, the surface polymolybdate was observed to be very stable with respect to the repeated treatment of reduction and subsequent calcination. Owing to the interaction of molybdate and titania, the phase transformation of TiO_2 seemed to be strongly retarded. The additives such as Co and Ni reacted readily with MoO_3 to form the corresponding molybdate salts. Nevertheless, the polymolybdate species appeared to be more stable on the titania surface than the molybdate salts. Although the detailed structure of surface polymolybdate is not known, we prefer the two dimensional model proposed by Segawa *et al.*¹

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Conformation of L-Ascorbic Acid in Solution

2. L-Ascorbic Acid Anion

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In the unhydrated and hydrated states, conformational free energies of L-ascorbic acid anion (AAA) were computed with an empirical potential function and the hydration shell model (a program CONBIO). The conformational energy was minimized from possible starting conformations expressed with five torsion angles of the molecule. The conformational entropy of each low energy conformation in both states was computed using a harmonic approximation. As found in L-ascorbic acid (AA), intramolecular hydrogen bonds (HBs) are proved to be of significant importance in stabilizing the overall conformations of AAA in both states, and give the folded conformations, which are quite different from those in crystal. There are competitions between HBs and hydration around O3 atom of the lactone ring and hydroxyls of the acyclic side chain. Especially, the whole conformation of AAA is strongly dependent on the water-accessibility of O3 atom. Though there is a significant effect of the hydration on conformational surface, the lowest energy conformation of the unhydrated AAA is conserved. The different patterns of HBs and hydration result in the conformations of AAA in both states being different from those of AA. It can be drawn by several feasible conformations obtained in the hydrated state that there exists an ensemble of several conformations in aqueous solution.

Introduction

L-Ascorbic acid (vitamin C, hereafter abbreviated to AA) was isolated first by Szent-Györgyi in 1928¹ and it became apparent that this molecule takes a part in a number of physiological processes.² It is found that L-ascorbic acid anion (hereafter abbreviated to AAA) has the same effect *in vivo* as the vitamin itself, presumably because of the reversible equilibrium between two substances, and that the anion form exists as the single species at physiological pH of AA. Electrochemists³ found intermediates in the oxidation pathway from AA to dehydroascorbic acid (DHA); one of considerable interest is the radical anion of DHA, and oxalic acid is the final stable product of AA oxidation.

There are some theoretical studies with MO methods on AAA, which include a modified CNDO with CI,⁴ INDO,⁵ and *ab initio* STO-3G^{5,6} calculations, and were based on standard geometry or very limited geometry optimization. The MNDO calculation on AA radicals⁷ showed that DHA anion was found to be thermodynamically the most stable species, due to a significant increase in π -electron delocalization in the five-membered ring. Hvorslef confirmed the crystal and molecular structure of AAA by X-ray diffraction analysis.⁸ Berger measured the pH dependence of the ¹³C chemical shifts of AA and interpreted it in terms of protonation sites.⁹ The radicals produced in the radiolysis of aqueous solution of AA were examined with the radiolysis-ESR method by Laroff *et al.*¹⁰ However, there are no detailed studies on the conformation of AAA in aqueous solution yet.

In this work, the conformational study of AAA in aqueous

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