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FT-IR Studies of Molybdena Supported on Titania

Kwan Kim* and Soon-Bo Lee[†]

Department of Chemistry, Seoul National University, Seoul 151-742

[†]Department of Chemistry, Sung Kyun Kwan University, Suwon 440-746

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Fourier transform infrared spectroscopy has been applied to the characterization of titania supported molybdena. The equilibrium adsorption method seemed to produce molybdena species homogeneously dispersed on the support. Even under an oxidizing environment, molybdena species appeared to be able to possess coordinatively unsaturated Mo^{5+} ions owing to the natures 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+} . The carbonyl bands at 2198 and 2190 cm^{-1} observed after CO exposure were attributed to the $\text{Mo}^{5+}\cdots\text{CO}$ and $\text{Mo}^{4+}\cdots\text{CO}$ complexes, respectively, while the band pair at 2136 and 2076 cm^{-1} to $\text{Mo}^{4+}(\text{CO})_2$.

Introduction

There is considerable current interest in the strong interaction between certain oxide support and metal phase (SMSI)¹⁻³. In addition, the interaction between oxide supports and highly dispersed oxide phases is receiving increasing attention⁴⁻⁷.

Supported oxides of transition metals of group VIb (Cr, Mo, W) are widely used as catalysts for various reactions. For example, alumina-supported molybdenum based catalysts are extensively used in the hydrotreating processes such as hydrodesulfurization, hydrodenitrogenation and hydrodemetalization of petroleum or coal products⁸⁻¹². The oxidation of hydrocarbons, carbon monoxide hydrogenation and water gas shift reaction are also catalyzed by supported molybdena. Reviews and useful discussions of various aspects of the alumina supported molybdena catalyst have been published⁸⁻¹², but conclusions tend to be controversial and contradictory. The confusion is attributable, in part, to the variety of catalysts studies and to differences in preparation and/or pretreatment of catalysts of similar composition.

Titania is a typical SMSI oxide. SMSI is characterized by the loss of a supported metal's ability to chemisorb CO or H_2 following high temperature reduction¹. Early explana-

tions of the SMSI effect centered on an electronic model wherein the chemical properties of metal were altered via a charge transfer between the support and the metal². More recently, there is a growing body of evidence that a reduced form of titania migrates onto the metal surface during high temperature reduction³. The origin of chemisorption suppression is explained in terms of a simple loss in surface adsorption sites. The detailed mechanism of TiO_x -overlayer formation, occurring within minutes at moderate temperatures¹³ is still obscure, however³.

Based on the above description, one may expect that titania would modify the surface state of the supported molybdena. In fact, Segawa *et al*¹⁴ reported that titania supported molybdena catalyst exhibited two types of active sites after reduction: one site was active for hydrogenation, and the other site was active either for isomerization or metathesis.

Many spectroscopic techniques have been applied to the study of molybdena/titania catalysts, including ESCA^{15,16}, ISS¹⁷ and laser Raman^{17,18}. These methods, however, do not yield information on specifically those surface atoms which are "exposed" or "coordinatively unsaturated" (cus), among which, presumably, are to be found the sites active for catalysis.

Among the spectroscopic techniques most useful for sur-

face characterization of catalysts, infrared spectroscopy remains preeminent^{19,20}. Infrared study of adsorbed "probe" molecules such as CO, NO, and O₂ can yield information on the atoms which are actually exposed on the surface under fairly realistic conditions. A number of plausible arguments reported earlier²¹ have favored CO as a probe molecule for molybdate catalysts since it is more easily accessible to molecular spectroscopy than O₂, and more selective and stable than NO.

Surprisingly infrared spectroscopic investigation of titania-supported molybdena catalyst using CO probe has been published, to our knowledge, only by Zaki *et al.*²². They prepared samples using the incipient wetness method. It has been well-known that highly dispersed catalyst can be prepared by an equilibrium adsorption method^{23,24}. On the other hand, the reduction conditions employed Zaki *et al.* were so severe that samples became highly opaque in the CO stretching region. Accordingly, the identification of oxidation state and coordination number of cation sites remains intriguing. In order to understand better the surface Lewis acidic centers we have investigated the adsorption of CO on mildly reduced titania-supported molybdena catalyst using a Fourier transform infrared instrument.

Experimental

Supported molybdena catalyst was prepared by an equilibrium adsorption method²⁵. The titania support was P-25 titania from Degussa, with a surface area of ca. 50 m²g⁻¹. One gram of titania was impregnated at 300 K for a week with 0.007 M aqueous solution of ammonium heptamolybdate. The pH of the impregnating solution was adjusted with HNO₃ to 2.94. After adsorption, the wet solid was separated from the impregnating solution by filtration. The prepared catalyst was dried overnight in an oven at 400 K, and then ground. The catalyst powder was spread uniformly on paraffin paper to prevent metal contamination, placed in a 2.5-cm diameter die pellet press, and pressed at 10 kg cm⁻². The self-supporting wafer (~20 mg cm⁻²) thus obtained was mounted into a specially designed transmission cell with KBr windows^{26,27}, and treated in situ in heating zone of the cell as described in the "Results and Discussion" section.

Oxygen (99.998%), nitrogen (99.999%), hydrogen (99.999%), and carbon monoxide (99.997%) obtained from Messer Griesheim GmbH (FRG) were used as received. The gas pressure was measured with either 0–100 or 0–1000 torr (1 Torr = 133.3 Pa) transducer gauge (Datametrics).

Infrared spectra were recorded on the vacuum-purged Bruker IFS 113 spectrometer at spectral resolution of 2 cm⁻¹. One hundred scans with a liquid N₂-cooled MCT (Mercury Cadmium Telluride) detector were used for an individual spectrum. The wavenumber accuracy from the spectra is better than ±0.5 cm⁻¹. All spectra taken at the ambient temperature have been corrected by subtraction for absorption of the gas phase and the KBr windows.

Results and Discussion

A number of studies relating to the behavior of molybdate in solution have been reported^{28,29}. At high pH only monomeric species exist in the form of MoO₄²⁻. However, with dec-

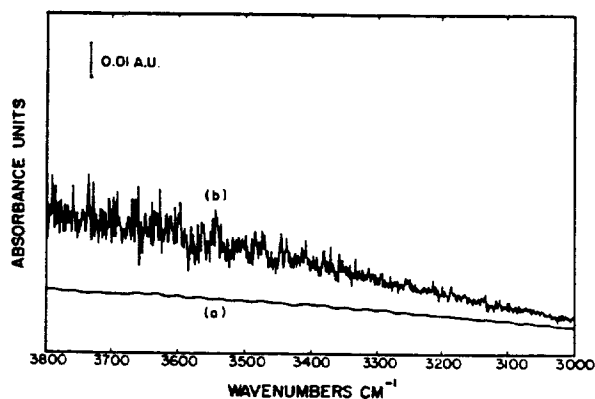
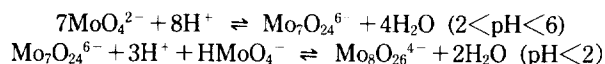


Figure 1. Infrared spectra of (a) "oxidized" and (b) slightly "reduced" molybdena supported on titania in the hydroxyl stretching region. The featureless noise in (b) is due to the opaque character of the reduced sample.

rease of pH in solution, MoO₄²⁻ is protonated and polymerization equilibria are established as follows:



On the other hand, the surface hydroxyl groups of titania in solution tend to be polarized and electrically charged^{30,31}. The hydroxyls of titania are protonated and positively charged below its isoelectric point (IEP) of pH = 6.2:



But above its IEP, deprotonation of surface hydroxyls of titania causes the ion to be negatively charged. From this we can understand the adsorption phenomena of molybdena species on titania surfaces. At acidic pH values, polymeric species seem to be adsorbed on the positively charged titania surface, whereas above the IEP the hydroxyls of titania tend to be negatively charged, so that it is relatively hard for the molybdena species to be adsorbed on titania due to the electrical repulsion in the solution.

Prior to taking infrared spectra a titania supported molybdena pellet was evacuated in the IR cell at 295 K overnight, and then dehydrated at 773 K for 2 hrs. This treatment was followed by calcination with 160 Torr of O₂ at 773 K for 1 hr so as to produce an "oxidized" sample. The sample was outgassed at 773 K for 2 min, and then kept under dynamic vacuum (10⁻⁵ Torr) at 295 K to ensure stoichiometry. After these oxidation/evacuation treatments the sample was a bright white color indicating that the bulk was fully oxidized (this does not mean the sample to be completely stoichiometric). Segawa *et al.*¹⁴ investigated the molybdena species adsorbed on the titania surface, and found that at pH = 2.9 (we used the same condition) the Mo loading was 7.7 wt%. On the basis of UV spectroscopy and CO₂ chemisorption, molybdena species were reported to be homogeneously dispersed on the titania surface. No CO₂ chemisorption was detected on the oxidized catalyst implying that free hydroxyl was no longer available. In fact, we could not observe any infrared band in the O-H stretching region attributable to titania after the oxidation treatment as can be seen in Figure 1 (a). On the other hand, the uptake of CO₂ was found by Segawa *et al.* to increase with increasing extent of reduction.

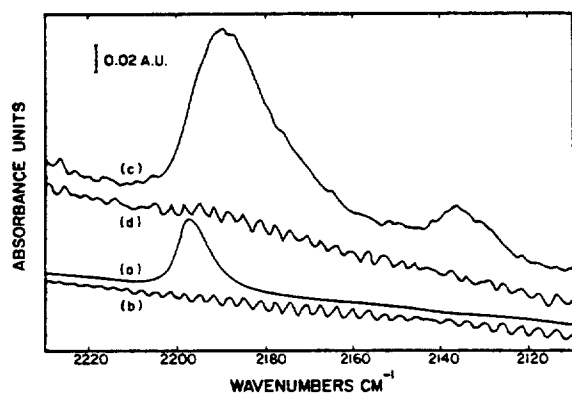


Figure 2. Infrared spectra of carbon monoxide adsorbed on (a) "oxidized" and (c) slightly "reduced" molybdena supported on titania in the region of 2230~2110 cm^{-1} . Gas-phase contributions have been eliminated. (b) and (d) are the spectra corresponding to (a) and (c), respectively, after evacuation at 295 K for 10 min. The oscillatory features in (b) and (d) arose from the incomplete evacuation of gas phase.

They have thus proposed that at the initial stage of reduction a part of the Mo-O-Ti and Mo-O-MO bondings were removed, with subsequent appearances of the Mo^{4+} sites and the Ti-OH groups. One may then expect appearance of infrared bands in the O-H stretching region as reduction proceeds. To our knowledge, any infrared spectroscopic evidence has not been reported yet, however, for the generation of free surface hydroxyls upon the thermal reduction in hydrogen. Neither could we observe any ν_{OH} bands after reducing the oxidized sample with 8 Torr of H_2 at 773 K for 15 min [see Figure 1 (b)], although the sample exhibited a dark brown color indicating that fair amount of reduction has indeed occurred. This may indicate that the reduction condition employed in this work is in fact quite milder than that of Segawa *et al.*

We have previously³² studied the titania surface by FT-IR spectroscopy. After the calcination of TiO_2 with 160 Torr of O_2 at 773 K for 1 hr, four OH stretching bands were observed, namely at 3719, 3689, 3673, and 3661 cm^{-1} . As the "oxidized" titania was treated with 8 Torr of H_2 at 773 K for 15 min, its color changed from white to blue-gray, and the OH stretching bands became more distinct without any shift in their positions. This means that the exposed H_2 produced the free surface hydroxide groups. Similar observation could be made even after the reduction for less than 1 min. Hence, the titania-supported molybdena catalyst prepared in this work is believed certainly not to possess any bare titania protruded beyond molybdena even after the H_2 treatment.

Figures 2 and 3 show the spectra of CO adsorbed on the molybdena sample in the regions of 2230-2110 and 2120-1900 cm^{-1} , respectively. The spectra have been taken at 295 K and 10 Torr of CO. When CO was adsorbed on the oxidized molybdena [see Figure 2 (a) and 3 (a)], one intense band appeared at 2198 cm^{-1} in Figure 2 (a). The band centered at 1977 cm^{-1} in Fig. 3 (a) has nothing to do with the presence of CO.

When CO was adsorbed on an "oxidized" titania, two intense bands were reported³² to appear at 2209 and 2187 cm^{-1} . Hence the fact that only one band appeared at 2198 cm^{-1}

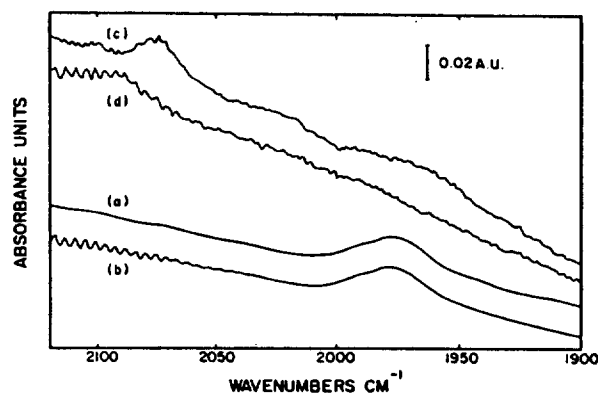


Figure 3. Infrared spectra of carbon monoxide on (a) "oxidized" and (c) slightly "reduced" molybdena supported on titania in the region of 2120~1900 cm^{-1} . Gas-phase contributions have been eliminated. (b) and (d) are the spectra corresponding to (a) and (c), respectively, after evacuation at 295 K for 10 min. The oscillatory features near 2100 cm^{-1} in (b) and (d) are due to the incomplete evacuation of gas phase.

for the oxidized molybdena sample in this work seems to support the aforementioned argument that the molybdate species are well-dispersed on the titania support surface and that they have substituted the titania hydroxyl groups to a large extent. In fact, this observation is correlated with the absence of any O-H stretching bands in the infrared spectra. Above discussions suggest that the band at 2198 cm^{-1} must be due to $\text{Mo}^{n+} \cdots \text{CO}$ complex. It should be pointed out, however, that such a species disappeared immediately upon moderate evacuation as can be seen in Figure 2 (b). This observation may imply that the adsorption strength is very weak.

When 10 Torr of CO was exposed to a molybdena sample treated with 8 Torr H_2 at 773 K for 1 min, no significant spectral change occurred in comparison with an "oxidized" sample. However, as can be seen in Figure 2 (c) and 3 (c), dramatic spectral changes were followed after a 15 minute-reduction at 773 K. First of all, the 1977 cm^{-1} band was no longer observable in the reduced sample. Secondly, the C-O stretching band at 2198 cm^{-1} observed in the oxidized sample [Figure 2 (a)] disappeared. Instead, a very strong band appeared at 2190 cm^{-1} (one may prefer the concept of peak shift rather than to use the terms like "appearance" and "disappearance"). Additional carbonyl bands began to show up clearly at 2136 and 2076 cm^{-1} . Moreover, very weak bands can be noticed to grow near 2020 and 1970 cm^{-1} . Nevertheless, all the carbonyl bands were completely removed by evacuation at the ambient temperature as can be seen in Figure 2 (d) and 3 (d). We believe that the carbonyl bands in Figure 2 (c) and 3 (c) are also due to $\text{Mo}^{n+} \cdots \text{CO}$ complexes. A possibility of the presence of $\text{Ti}^{n+} \cdots \text{CO}$ complexes should be scarce. If titania surfaces were regenerated as the catalyst was reduced, we could have observed, as discussed earlier, a series of rather strong O-H stretching bands. In our previous work³², the infrared spectra of CO adsorbed on a reduced titania exhibited two C-O stretching bands (2209 and 2187 cm^{-1}) whose positions were in fact hardly different from those on an oxidized titania. For the reduced molybdena sample in this work no band near 2209

cm^{-1} was observed. Accordingly, titania is believed to be covered, as concluded previously, by molybdena species still in the reduced state.

It seems to be very informative that the band near 1977 cm^{-1} disappears at the relatively early stage of reduction. The origin of this band is not unambiguously clear yet. When titania alone was oxidized or reduced, similar band has never been observed. It has been generally accepted that for molybdate species the Mo=O terminal stretching mode appears in the $900\text{--}1000\text{ cm}^{-1}$ range³³. Furthermore, as monomeric species become polymerized, the Mo=O stretching mode is known to have a higher wavenumber^{34,35}. For instance, the Mo=O stretching bands of the molybdate anions MoO_4^{2-} and $\text{Mo}_7\text{O}_{24}^{6-}$ and MoO_3 appear at 896 , 938 , and 996 cm^{-1} , respectively³⁶⁻³⁸. Owing to the strong TiO lattice vibration below 1000 cm^{-1} , we could not obtain any direct information regarding the polymerized surface species. Nevertheless, it is tempted in this work to assign the 1977 cm^{-1} peak in Figure 2 (a) due to the overtone of the Mo=O stretching mode in the supported molybdena species (we could not find any literature regarding to the overtone bands of molybdenum oxide species). Based on this assignment, it can be said that the terminal double bond oxygens (Mo=O) are removed at the initial stage of reduction. At the moment we can not provide a concrete evidence to support the present view. However, it may be worth to mention that the present view is in good accord with the two-dimensional model of molybdena-titania catalyst proposed by Segawa *et al.*¹⁴.

Prior to assigning the carbonyl bands, in Figure 2 (c) and 3 (c), on the reduced sample, it may be adequate to give a brief discussion on the infrared spectra obtained after CO admission onto oxidized supported-molybdena catalysts. Louis *et al.*³⁹ reported the absence of infrared bands in the carbonyl region after CO exposure to an oxidized Mo/SiO₂. Based on this observation, the Mo⁶⁺ ions were suggested by them not to be able to adsorb CO. Absence of carbonyl band was also reported by Zaki *et al.*²² when CO was admitted to an oxidized alumina-supported molybdena. On the other hand, Zaki *et al.* could observe a carbonyl band when the molybdena species being oxidized was supported on either titania or ceria. The band at 2196 cm^{-1} observed on oxidized Mo/TiO₂ was attributed by them to Mo⁵⁺(CO), and the band at 2186 cm^{-1} observed on oxidized Mo/CeO₂ to Mo⁴⁺(CO). As mentioned earlier, in the present work one single band appeared as well at 2198 cm^{-1} when a Mo/TiO₂ sample oxidized was exposed to CO [see Figure 2 (a)]. CO adsorption on oxidized molybdena seems thus to occur only when the molybdena is supported on a so-called SMSI support like TiO₂ and CeO₂. This may imply that surface characteristics of molybdena is affected by the nature of its support material. Titania and ceria are generally known for their oxygen-deficiencies (TiO_{2-x} and CeO_{2-x})^{40,41}, and their high permeabilities toward oxygen diffusion⁴². Accordingly, the formation of Moⁿ⁺ with $n < 6$ in molybdena would be facilitated by the presence of titania or ceria surface.

Several attempts have been made to correlate carbonyl stretching frequencies of adsorbed CO and enthalpies of adsorption. Soltanov *et al.*⁴³ reported a linear correlation, whereas Morterra *et al.*⁴⁴ found a parabolic dependence of $\nu(\text{CO})$ on the enthalpy of adsorption. Hush and Williams⁴⁵ have shown theoretically that the carbonyl stretching frequen-

cy should monotonously increase with the electric field strength of the cation center of d^0 electron configuration. Angell and Schaffer⁴⁶ found cation-sensitive carbonyl bands in ion-exchanged zeolite, whose frequency was an almost linear function of the calculated electric field strength at the cation site. Larsson and coworkers⁴⁷ investigated the effect of cation sites anchored onto SiO₂ surfaces, and Harrison and Thornton⁴⁸ performed a similar study using SnO₂ as a support for surface metal cations. Knözinger *et al.*^{49,50} have recently modified the approach of Harrison and Thornton in calculating the electric field strength by accounting for the coordination of the central ion. According to their report, a universal correlation seemed to exist. It had been argued that the frequencies of Moⁿ⁺...CO complexes for $n=3, 4$ and 5 correlated with the electric field strength at the cation. Judging from their correlation curve, the peak at 2198 cm^{-1} in Figure 1 (a) should be attributed to a Mo⁵⁺...CO complex with the Mo⁵⁺ being coordinated to five O²⁻ ions. This assignment is in fact the same as that made in the experimental work of Knözinger *et al.*²².

It is rather difficult to assign the carbonyl bands observed during CO adsorption on the reduced molybdena. Peri⁵¹ studied impregnated Mo/Al₂O₃ catalyst and detected three carbonyl bands after exposure of thermally reduced sample to CO; 2190 cm^{-1} , attributed to Mo⁴⁺(CO) and 2040 and 2025 cm^{-1} , assigned to Mo⁰(CO). On the other hand, Guglielminotti and Giamello⁵² and Louis *et al.*³⁹ have independently studied the CO adsorption on the reduced molybdena on silica. The former authors attributed the bands at 2203 and 2181 cm^{-1} to Mo⁵⁺(CO) and Mo⁴⁺(CO), respectively. The latter authors assigned the corresponding bands to appear at 2224 and 2196 cm^{-1} , respectively. Based on these reports, we tend to attribute the band at 2190 cm^{-1} in Figure 2 (c) to Mo⁴⁺...CO. The Mo⁴⁺ ion in this complex is supposed further to be coordinated to five O²⁻ ions according to the correlation curve^{49, 50} between carbonyl stretching frequency and coordination number of central ion. Nevertheless, the 2190 cm^{-1} band in Figure 2 (c) may contain the contributions of both the Mo⁵⁺...CO and Mo³⁺...CO complexes although their portions are not significant. Such possibilities can be inferred from the fact that the band centered at 2190 cm^{-1} in Figure 2 (c) is very broad and asymmetric covering the spectral regions corresponding to the Mo⁵⁺(CO) and Mo³⁺(CO) complexes. For the case of silica-supported molybdena catalyst, the Mo³⁺C-O monocarbonyl stretching vibration was suggested to appear at 2167 cm^{-1} by Louis *et al.*³⁹ In fact, the low frequency side of the 2190 cm^{-1} band in Figure 2 (c) extends down to 2153 cm^{-1} . On the other hand, the high frequency side has tails up to $\sim 2206\text{ cm}^{-1}$, nearly the same as that observed in the oxidized sample [see Figure 2 (a)]. Earlier XPS study¹⁶ revealed that TiO₂ facilitated the reduction of the supported molybdena to Mo (IV) and Mo (III). However, considering that molybdena sample in the present work was just slightly reduced, the preferential population of Mo⁴⁺ ion compared with either Mo⁵⁺ or Mo³⁺ is believed to be realistic. It may be informative that Leyrer *et al.*³³ observed from a study on the monolayer formation in MoO₃/Al₂O₃ physical mixtures that Mo⁶⁺ were reduced only to Mo⁴⁺. Hence, it is supposed that the reduced molybdena in this work contains lots of Mo⁴⁺ ion along with some Mo⁵⁺ and Mo³⁺ ions, being exposed as surface species. As

the oxidation number decreases, the coordinatively unsaturated (cus) sites are expected to become more available. That is, the surface Mo^{4+} and Mo^{3+} ions would possess more than one cus sites. Based on this view, it may also be expected to observe the carbonyl bands arising from multiply coordinated complexes such as $\text{Mo}^{4+}(\text{CO})_2$. In their study on the Mo/SiO₂ system, Guglielminotti and Giamello⁵² attributed the carbonyl bands at 2140 and 2108 cm⁻¹ to $\text{Mo}^{4+}(\text{CO})_2$. Referring to this assignment, we attribute tentatively the band pair at 2136 and 2076 cm⁻¹, observed after CO exposure to a reduced molybdena [see Figure 2 (c) and 3 (c)], to $\text{Mo}^{4+}(\text{CO})_2$ complex. On the other hand, the very weak band pair near 2020 and 1970 cm⁻¹ may be assigned to arise from the multiply coordinated Mo^{3+} complex. The possibility of an alternative assignment such as $(\text{Mo}^{4+})_2\text{CO}$ can not be ruled out. In order to confirm, at least, the specific molybdenum oxidation state, we plan to investigate the present system by X-ray photoelectron spectroscopy (XPS). Nevertheless, it may be appropriate to mention that Zaki *et al.*²² reduced the Mo/TiO₂ catalyst at 773 K for 2 hrs, and spectra of CO adsorption was recorded under 40 Torr of CO using a dispersive IR spectrometer. When the CO adsorption was performed at 77 K, three bands centered at 2186, 2160, and 2140 cm⁻¹ could be observed, while only one band appeared distinctly at 2190 cm⁻¹ as the adsorption temperature was increased to 298 K. In contrast to the present observation the latter peak has not disappeared completely upon evacuation at 298 K. This may indicate that our reduction condition was, in fact, very mild. On the other hand, FT-IR spectroscopy seems to be very useful in detecting the very weakly bound adsorbate species. The present work dictates that the lower oxidation species like Mo^{4+} and Mo^{3+} appears to form at the early stage of reduction. The less sensitive dispersive spectrometer may not provide such observation. However, we believe that more systematic investigation has to be performed than that provided here to enhance our knowledge on the physico-chemical properties of surface molybdena species. Based on the present result, we'll perform the FT-IR spectroscopic study under more various experimental condition. The XPS study is hoped to be carried out at the same time.

In summary, we have applied Fourier transform infrared spectroscopy to the characterization of molybdena supported on titania. The equilibrium adsorption method appeared to produce molybdena species homogeneously dispersed on the titania surface. Even under an oxidizing atmosphere molybdena species seemed to contain cus Mo^{5+} ions. This is attributed to the nature of support material, TiO₂, which is well known for its oxygen deficiency and its permeability toward oxygen diffusion. These characteristics are believed to have relevance to the SMSI effect of titania. At the initial stage of reduction, the terminal double bond oxygens ($\text{Mo}=\text{O}$) seemed to be removed, producing presumably Mo^{4+} . Accordingly, the band at 2198 cm⁻¹ observed after CO exposure to an oxidized molybdena was assigned to the $\text{Mo}_{5\text{c}}^{5+}\cdots\text{CO}$ complex (subscript indicates the coordination number of the coordinatively unsaturated cation by oxygen ions). On the other hand, the 2190 cm⁻¹-peak observed on a reduced sample was attributed to CO coordinated to $\text{Mo}_{5\text{c}}^{4+}$, while the band pair at 2136 and 2076 cm⁻¹ to a $\text{Mo}^{4+}(\text{CO})_2$ complex.

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Ab initio SCF Calculations of Potential Energy Surfaces for the Proton Transfer in a Formamide Dimer

Young Shik Kong and Mu Shik Jhon*

Institute of Basic Science, Chonbuk National University, Chonju 560-756

**Department of Chemistry, and Center for Molecular Science, Korea Advanced Institute of Science and Technology, Seoul 130-650. Received July 6, 1990*

Potential energy surfaces for the proton transfer in a formamide dimer have been obtained by *ab initio* SCF calculations with STO-3G, 3-21G, and 4-31G basis sets and several features have been discussed. Energy minima for a formamide dimer and its tautomer are varied with basis sets. But the general features of the potential energy surfaces are similar among them.

Introduction

The hydrogen bond and the proton transfer are very important to understand various phenomena in many chemical and biological systems. Due to those importances, there are many studies on the single or multiple and the inter or intramolecular hydrogen bonds and the proton transfers¹⁻¹³. Löwdin suggested that the proton transfer in a DNA base pair might be an origin of the mutation³ and Clementi *et al.* performed an *ab initio* study for the hydrogen bond in the guanine-cytosine base pair⁴. Del Bene *et al.* and other groups also performed an *ab initio* calculations for the proton transfers in a formic acid dimer and other systems⁵. The study on the potential energy surface of the proton transfer is very important as a starting point for the theoretical study of the proton transfer rate. In this study, the potential energy surfaces for the proton transfer in a formamide dimer have been obtained by *ab initio* SCF calculations with three kinds of basis sets, such as STO-3G, 3-21G, and 4-31G. The

proton transfer in formamide dimer can be considered as a simple model for the asymmetric intermolecular double proton transfer whereas the proton transfer in a formic acid dimer can be considered as a simple model for the symmetric intermolecular double proton transfer. As mentioned above, there are some studies on the proton transfer in a formic acid dimer. But in the case of the proton transfer in a formamide dimer, it is not so. That is the direct motive of this study. Therefore, the results obtained in this study have been compared with other's results.

Methods of Calculations

All *ab initio* calculations in this study have been performed on a Cray-2 computer using the program of Gaussian-86 version. Three kinds of basis sets, such as STO-3G, 3-21G, and 4-31G, have been used. The initial geometry for a formamide dimer is taken from Ottersen *et al.*¹⁴ The schematic structures of a formamide dimer (A) and its tautomer (B), which