Supported Molybdenum Oxide Catalyst
—Structure and Chemistry of
Oxidized, Reduced, and Sulfided Surfaces—

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Highly dispersed molybdena–titania catalyst can be prepared by an equilibrium adsorption method. In this method, molybdate anions adsorb onto positively charged titania surfaces via electrostatic attraction by controlling pH of the impregnating solution. The amounts of absorbed molybdate anion are strongly dependent on pH of the impregnating solution and they increase as an inverse function of pH. XRD, Raman, and XPS data of the calcined samples show that monolayer coverage of molybdenum oxide over-layer possesses a highly distorted MoO$_6$ group with a molecular geometry resembling a distorted square pyramid. The Mo species are fixed by an oxygen bridge with Ti, as Mo–O–Ti, or with neighboring Mo, as Mo–O–Mo.

The catalytic oxidation of methanol over the surface molybdate species on titania possess higher turnover numbers and higher selectivities of partial oxidation products than do the catalysts exceeding monolayer coverage which possess the crystalline MoO$_3$ phase. Changes of the surface properties either, after reduction and sulfiding treatment over monolayer catalyst, have also been investigated. The NO chemisorption and XPS studies show that two types of active sites appeared after reduction treatment: one site is active for hydrogenation of 1,3-butadiene and the other site is active for metathesis of propene. A higher degree of coordinative unsaturations of Mo is required for hydrogenation than for metathesis. After subjecting sulfiding treatments to the catalyst, hydrogenolysis of thiophene requires the ensemble of doubly or triply coordinative unsaturations.

1. Introduction

Molybdenum oxide catalysts are widely used in hydrodesulfurization and hydrocracking of heavy fractions of crude oil, for partial oxidation of aliphatic alcohols, and in polymerization, metathesis, isomerization and hydrogenation of alkenes in the petroleum industry. They are also known to be active in coal liquefaction reactions. The distinct features of molybdena catalysts include higher catalytic activities in oxidized, reduced, and sulfided states, with a wide range of oxidation states (from Mo$^{6+}$ to Mo$^{0+}$).

Catalysts are usually used by supporting the catalytically active species on an inorganic support (Al$_2$O$_3$, TiO$_2$, SiO$_2$, ZrO$_2$, and MgO) for the purposes of (1) increasing the catalytic activity and selectivity, (2) extending the life of catalysts, and (3) increasing the mechanical strength of catalysts. Alumina-supported molybdena catalysts are extensively used in the industrial processes. Recently, titania-supported molybdena catalysts have become important due to their higher reducibility to lower valence state of Mo, and because their hydrodesulfurization and hydrocracking activities were higher than those of alumina-supported molybdena catalysts. In addition, titania support itself does not have any strong acidic sites or other active sites which would result in side reactions.

Supported molybdena catalysts have usually been prepared by coprecipitation or impregnation and/or incipient wetness methods. Recently, an equilibrium adsorption method was devised to overcome the drawbacks of these methods. In this method, molybdate anions are adsorbed from solution onto positively charged support surfaces due to the electrostatic attraction.

In the oxidized state, molybdena catalysts are active for oxidation reactions. For example, oxidation of methanol into formaldehyde is an important industrial process. The catalytic activity and selectivity of oxidation reactions are strongly dependent on the surface morphology.

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Changes of the surface properties either after subjecting reduced or sulfided pretreatments over the two-dimensional molybdena over-layer on the titania surfaces have been also investigated.

The objectives of this study are (1) to elucidate the adsorption phenomena in the impregnating solution and (2) to determine the influence of the structure and corresponding surface properties of the adsorbed molybdena species on the catalytic activities in oxidized, reduced, or sulfided states.


Recently, an equilibrium adsorption method on various oxide supports was devised to make highly dispersed catalysts. In this method, the pH of the impregnating solution and the isoelectric point (IEP) of a support are essential parameters for regulating the surface properties of the catalyst. A number of studies relating to the behavior of molybdate in solution have been reported. Haight and Boston pointed out that at high pH regions (pH>6), MoO42- ions are generally present in solution. With decrease of pH in solution, however, MoO42- is protonated and polymerization equilibria are established as follows:

\[
7\text{MoO}_4^{2-} + 8\text{H}^+ \rightleftharpoons 3\text{MoO}_2^{6-} + 4\text{H}_2\text{O} \quad (2<\text{pH}<6), \quad (1)
\]

\[
\text{Mo}_7\text{O}_{24}^{6-} + 3\text{H}^+ + \text{HMoO}_4^- \rightleftharpoons 2\text{MoO}_2^{6-} + 2\text{H}_2\text{O} \quad (\text{pH}<2). \quad (2)
\]

On the other hand, the hydroxyl groups of the titania surface in solution tend to be either positively or negatively charged below or above the IEP of titania (anatase: pH=6.2, rutile: pH=4.8–5.6).

\[
\text{Ti-OH}_2^+ + \text{H}^+ \rightleftharpoons \text{Ti-OH} \rightleftharpoons \text{Ti-O}^- + \text{H}^+ \quad (3)
\]

This conception allows us to explain the adsorption phenomena of molybdate anions on titania support. The amounts of adsorbed molybdate anion are controlled by the number of positively charged hydroxyl groups on the titania surface. Above the IEP of titania, the hydroxyls of titania tend to be negatively charged, so that it is relatively hard for the molybdena species to be adsorbed on the titania surface, attributed to the electrostatic repulsion in the solution.

2.1 The Effect of pH of the Impregnating Solution

The 95Mo-NMR spectra of the impregnating solution at different pH values are obtained at 17.4 MHz on a Fourier transform pulsed spectrometer (JEOL, JNM-GX270); the results are shown in Fig. 1. In the basic solutions (pH>7.61), only the sharp resonance line of tetrahedrally coordinated Mo species (MoO262-) is observed at -1.75 ppm. In the acidic solutions region (pH<5.26), a broad resonance peak is observed at 33.3 ppm; this is attributed to octahedrally coordinated Mo species (MoO265-). In the intermediate pH region (6.45>pH>5.42), both tetrahedral and octahedral Mo species are observed in the spectra; and the relative intensities of each peak vary as a function of pH. The linewidth of the MoO262- lies in the range of 11 to 170 Hz with the narrowest signal being observed at pH above 9.31, where the molybdate ion is completely ionized. At that point, the electric field is close to zero as a result of

![Fig. 1 95Mo-NMR Spectra of Impregnating Solution at Different pH Values](image)
the tetrahedral symmetry of the anion. At lower pH, the protonation of the anion results in the loss of symmetry which increases the electric field gradient and causes an increase in the linewidth. No significant change in the linewidth is observed for Mo7O246– for pH values greater than 4.64.

The UV spectra of the impregnating solutions were also measured after the samples were equilibrated (ca. 100 h) at different pH values. Typical spectra are shown in Fig. 2. The spectra of the acidic solutions differ from those of the basic solutions. At acidic pH values (D, E, F in Fig. 2), two characteristic bands were observed at about 260 nm and 315 nm. The band at 260 nm is attributed to the charge transfer band of Mo6+=O2– and the band at 315 nm is that of bridged Mo–O–Mo10. As the pH values increased, however, the 315 nm band decreased in intensity, and at basic pH values (A, B in Fig. 2), only the 260 nm band remained.

The NMR and UV spectroscopic studies suggest that polymeric species (Mo7O246–) in the acidic pH regions (pH<5.26) and the monomeric species (MoO42–) in the basic pH regions (pH>7.61) were preferentially equilibrated with titania surface in the impregnating solution.

2.2 Surface Properties of Calcined MoO3/TiO2

The titania support employed in this study was P–25 titania from Degussa, with a surface area of ca. 51 m2 g–1. The titania support was composed of ca. 66% anatase and 34% rutile, as determined by XRD. 5 g of titania was impregnated at 323 K for 100 h with 0.007 M aqueous solution of ammonium heptamolybdate. The pH of the impregnating solution was adjusted with HNO3 or NH4OH solution. After adsorption, the solids were separated from the solution by filtration. All the wet catalysts were dried at 373 K for 24 h and then calcined in air at 773 K for 24 h. The adsorbed amounts of molybdenum as oxide base (wt% of MoO3) were determined by chemical analysis.

The effect of pH on the surface properties of MoO3/TiO2 after calcination at 773 K is shown in Table 1. The initial pH value of the impregnating solution tends to shift towards IEP (pH=6.2) of the TiO2 in order to compensate the net charge of the titania surface. The amounts of adsorbed molybdate anions were strongly dependent on the final pH of molybdic solution and these increased as the pH values decreased. The amounts of

![UV Spectra of Impregnating Solutions of Molybdate Anion after Equilibrium Adsorption for 100 h](A) pH=9.69, (B) pH=7.28, (C) pH=6.47, (D) pH=5.26, (E) pH=3.98, (F) pH=2.86

**Table 1** Surface Properties of MoO3/TiO2 Catalysts Prepared by an Equilibrium Adsorption Method

<table>
<thead>
<tr>
<th>Mo loading [wt%]</th>
<th>Initial pH</th>
<th>Final pH</th>
<th>CO2 uptake [mmol·g–1]</th>
<th>% of free titania</th>
<th>Surface area [m2·g–1]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO2</td>
<td>2.4</td>
<td>9.77</td>
<td>9.69</td>
<td>0.142</td>
<td>51.0 (51.0a)</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>8.81</td>
<td>8.68</td>
<td>0.975</td>
<td>49.4 (50.6b)</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>7.86</td>
<td>7.28</td>
<td>0.674</td>
<td>47.5 (51.1b)</td>
</tr>
<tr>
<td></td>
<td>6.4</td>
<td>5.06</td>
<td>5.72</td>
<td>0.476</td>
<td>33.5 (51.4b)</td>
</tr>
<tr>
<td></td>
<td>6.6</td>
<td>3.91</td>
<td>3.98</td>
<td>0.103</td>
<td>7.3 (49.6b)</td>
</tr>
<tr>
<td></td>
<td>7.1</td>
<td>2.53</td>
<td>2.61</td>
<td>0.058</td>
<td>4.1 (49.7b)</td>
</tr>
<tr>
<td></td>
<td>20.0</td>
<td>0.99</td>
<td>1.24</td>
<td>0.0</td>
<td>0.0 (45.4b)</td>
</tr>
</tbody>
</table>

a: Initial and final pH values in impregnating solution. b: (CO2 uptake of catalyst/CO2 uptake of parent titania)×100 [%]. c: Numbers in the parenthesis represent surface areas per gram of titania.
chemisorbed CO$_2$ decreased concomitantly as the Mo loading increased and approached zero at about 6.6 wt%. Segawa and Hall$^{11}$ previously showed that CO$_2$ chemisorbs selectively on the hydroxyls of the Al$_2$O$_3$ support surface but does not show any chemical interaction with surface molybdena species; similar behavior$^9$ was found for the MoO$_3$/TiO$_2$. The surface area per gram of TiO$_2$ instead of per gram of catalyst was constant, regardless of Mo loading, up to 6.6 wt%. This result indicates that the catalysts dispersed homogeneously on TiO$_2$ surface up to 6.6 wt%.

The XPS Mo(3d)/Ti(2p) peak area intensity ratios as a function of Mo loading for the calcined catalysts are shown in Fig. 3. The Mo(3d)/Ti(2p) ratios increased linearly up to ca. 6.6 wt% and then leveled off from the linear relationship for further increases of Mo loadings. The result indicates that the molybdena species adsorbed homogeneously on the titania surface and reached monolayer coverage at about 6.6 wt%, and above 6.6 wt% some aggregation of Mo species occurred on TiO$_2$ surfaces during the calcination process, which results in the crystalline MoO$_3$.

The laser Raman spectra of the calcined catalysts were obtained under ambient conditions and are presented in Fig. 4. The TiO$_2$ support exhibits strong Raman bands at 996, 516, and 637 cm$^{-1}$ and weak Raman bands at 446 and 790 cm$^{-1}$ (B—E in Fig. 4). The strong bands originate from the anatase phase and the weak band at 446 cm$^{-1}$ is due to the rutile phase$^{12}$. The weak band at 790 cm$^{-1}$ is due to the first overtone of the 395 cm$^{-1}$ band of anatase. The adsorption of Mo oxide on TiO$_2$ introduced a new Raman feature in the 940—970 cm$^{-1}$ range for the 2.4 to 7.1 wt% of MoO$_3$/TiO$_2$ catalysts. The intensity of the Raman band of surface Mo oxide is increased with Mo loading. The 7.1 wt% of MoO$_3$/TiO$_2$ catalyst also exhibits a very weak Raman band at 823 cm$^{-1}$, which is characteristic of crystalline MoO$_3$ particles. Thus, the 7.1 wt% MoO$_3$/TiO$_2$ catalyst possesses a molybdenum oxide coverage slightly in excess of a monolayer, and about 6.6 wt% of MoO$_3$/TiO$_2$ corresponds to a monolayer of surface Mo oxide on TiO$_2$. The 20 wt% MoO$_3$/TiO$_2$ catalyst (A in Fig. 4) exhibits significantly strong Raman bands at 996 and 822 cm$^{-1}$, as well as additional bands at ca. 294 cm$^{-1}$, which are due to the presence of crystalline MoO$_3$.$^{13,14}$

The structure of the surface molybdenum oxide species on the TiO$_2$ support can be determined from comparison of the Raman vibrational data of the MoO$_3$/TiO$_2$ with reference Mo oxide compounds$^9$. An ideal MoO$_6$ octahedron would be expected to exhibit a stretching mode at ca.
351 cm\(^{-1}\) wavenumber\(^{19}\). This information regarding the Mo–O stretching vibrations for the molybdena reference compounds are used to identify molybdate functionalities and to aid in determination of molybdate species present on the titania support. The Raman spectra of calcined MoO\(_3/\)TiO\(_2\) catalysts exhibit bands in the 948—965 cm\(^{-1}\) region (see Fig. 4). The position of the Mo–O stretch for MoO\(_3/\)TiO\(_2\) is much higher than that for the ideal tetrahedral structure of MoO\(_4^{2-}\) (aq) (897 cm\(^{-1}\)) or the distorted tetrahedral structures of \((\text{NH}_4)_2\text{Mo}_2\text{O}_7\) (910 cm\(^{-1}\)) and \(\text{K}_2\text{Mo}_2\text{O}_7\text{KBr}\) (928 cm\(^{-1}\)). The position of the band for MoO\(_3/\)TiO\(_2\) is also much higher than that of the slightly distorted MoO\(_6\) octahedra of Ba\(_2\)CaMoO\(_6\) (812 cm\(^{-1}\)). The position of the Raman bands for MoO\(_3/\)TiO\(_2\), however, falls in the region observed for a highly distorted MoO\(_6\) octahedron such as Mo\(_7\text{O}_{24}^{6-}\) (aq) (940 cm\(^{-1}\)), Mo\(_8\text{O}_{26}^{4-}\) (aq) (961 cm\(^{-1}\)), and \((\text{NH}_4)_4\text{Mo}_6\text{O}_{26}\text{H}_2\text{O}\) (963 cm\(^{-1}\)). Thus, it appears that the surface molybdenum oxide species on TiO\(_2\) possess a highly distorted square pyramidal structure.

In Scheme 1, we propose a two-dimensional monolayer model in the oxidized state of MoO\(_3/\)TiO\(_2\) (6.6 wt\%, pH=3.98) on the basis of CO\(_2\) chemisorption and Raman spectroscopic studies. The Mo species are fixed by bridged oxygens with Ti, Mo–O–Ti, and with neighboring Mo, Mo–O–Mo. The majority of molybdena octahedra possess a highly distorted MoO\(_6\) group containing one very short Mo–O bond (<0.18 nm), Mo=O, and one very long Mo–O bond (>0.23 nm), Mo–O–Mo, with a molecular geometry resembling the distorted square pyramid; stretching frequencies for the short Mo–O bond are in the 940—1000 cm\(^{-1}\) range.

3. Catalytic Reactions over MoO\(_3/\)TiO\(_2\)

3.1 Oxidation of Aliphatic Alcohol over Oxidized Surfaces

Oxidation of methanol was carried out at 423—548 K by using a standard flow reaction system with a mixture of methanol and oxygen in the ratio of 1/5 (mole/mole) diluted with 82% of nitrogen. The reaction products were analyzed by an on-line gas chromatograph, which was installed at the outlet of the reactor. The column packings were 1.5-m of Porapak T at 413 K for separation of CO\(_2\), HCHO, CH\(_2\)OCH\(_3\), H\(_2\)O, CH\(_3\)OH, HCOOCH\(_3\), and (CH\(_2\)O\(_2\))\(_2\)CH\(_2\) and 3-m of Porapak T at 213 K for separation of O\(_2\) and CO. The catalytic activity (TON) was calculated from the initial rate of methanol consumption per Mo atom.

The titania support itself is inert for the methanol oxidation at 473 K. High catalytic activities up to monolayer coverage (6.6 wt\%) are observed regardless of Mo loading. Regarding the above monolayer coverage, however, activities decreased as the Mo loading was increased. The decrease in catalytic activity of above monolayer is attributed to the increase of MoO\(_2\) crystallites which are less active than surface molybdate species\(^{4}\). The selectivity of CH\(_3\)OCH\(_3\), which cannot be formed via oxidative dehydrogenation, increases as the Mo loadings increased. The formation of CH\(_3\)OCH\(_3\) may be facilitated by the acidic sites of catalyst surfaces. Segawa and Hall\(^{10}\) have reported that both Lewis-bound pyridine (LPy) and pyridium ion (BPy) occur on the oxide form of molybdena–alumina catalysts. The catalyst prepared at high pH region showed no Brønsted acidity, but Brønsted acidity increased linearly when Mo loading increased. Kataoka and Dumesci\(^{17}\) have also found that, although no Brønsted acidic sites were observed on 1 wt\% Mo/SiO\(_2\) under water-free conditions, small amounts of Brønsted acidic sites were detected with the 6.4 wt\% Mo/SiO\(_2\) sample. The origin of acidic sites on the MoO\(_3/\)TiO\(_2\) catalysts is the presence of the acidic hydroxyl groups which are thought to be generated on the surface of catalyst by the hydration of polymeric Mo clusters.

The selectivity of each product of methanol oxidation over 6.6 wt\% catalyst as a function of the reaction temperatures is shown in Fig. 5. At lower reaction temperatures, the main product is (CH\(_3\)O\(_2\))\(_2\)CH\(_2\), but at above 473 K, HCHO was mostly formed; HCOOCH\(_3\) was next in abundance. The selectivity for HCHO increases with rise in reaction temperatures. This result suggests that the formation of HCHO is more likely than that of (CH\(_3\)O\(_2\))CH\(_2\) and HCOOCH\(_3\) at the higher reaction temperatures used in this investigation. Only trace amounts of CO and CO\(_2\) were formed over the whole range of reaction.

When (CH\(_3\)O\(_2\))CH\(_2\) and HCOOCH\(_3\) are used as the reactant for oxidation, as shown in Figs. 6 and 7, the oxidation products were CH\(_3\)OCH\(_3\), HCHO, and CH\(_3\)OH for oxidation of HCOOCH\(_3\) and, as well as, additional HCOOCH\(_3\) for oxidation of (CH\(_3\)O\(_2\))CH\(_2\), and the major product was HCHO at higher reaction temperatures. Tatibouet et al.\(^{18}\)
have proposed that the product distributions of methanol oxidation over orthorhombic MoO₃ single crystals are strongly dependent on the crystal face: namely, HCHO, (CH₃O)₂CH₂, and CH₃OCH₃ are produced on the (010), (100), and (001)+(101) faces, respectively, as shown in Fig. 8.

Epitaxial growth of two solids on the crystal surface requires a crystallographic match between their crystal structures. Delmon et al. have found that there is a crystallographic fit between the (010) face of MoO₃ and the (001) face of TiO₂ (anatase). This result indicates that the epitaxial growth of crystal on TiO₂ occurs between the (010)
face of MoO₃ and (001) face of TiO₂ face. Thus (010) face of MoO₃ preferentially appeared over MoO₃/TiO₂ catalysts’ surface after calcination at 773 K. The higher selectivity of HCHO in the methanol oxidation can be understood in terms of the crystal growth between MoO₃ and TiO₂.

The reaction pathway of methanol oxidation previously proposed for the V₂O₅ system²⁰, is shown in Scheme 2. On the MoO₃/TiO₂ catalyst, dissociative adsorption of methanol produces methoxy intermediates. Then, abstraction of hydrogen atom from the methoxy group by an adjacent oxygen can result in the formation of oxymethylene intermediates. Either desorption or condensation of oxymethylene intermediates may produce the gaseous HCHO and/or (CH₃O)₂CH₂. Desorption of oxymethylene is much faster than that of condensation with methanol at higher reaction temperatures. Thus oxymethylene intermediates desorb readily to give HCHO, preferentially, at high conversion regions. In addition, further oxidation of the oxymethylene produces adsorbed formate intermediates via dioxy-methylene intermediates; these react with methoxy groups to give HCOOCH₃. In summary, the catalytic active sites of methanol oxidation are proposed to be double bond oxygens (Mo=O) or bridged oxygens (Mo–O–Mo) on surface molybdate species that gives Mo–CH₃ and Mo–OH, simultaneously. The selectivity of CH₃OCH₃, which is produced by acidic sites on the MoO₃/TiO₂ surface, increases as Mo loading is increased.

3.2 Metathesis and Hydrogenation of Alkenes over Reduced Surfaces

3.2.1 Surface Properties of Reduced Catalysts

The catalysts were treated in flowing O₂ for 12 h and then reduced with a gas flow of 5% H₂ in 95% N₂ at a constant rate of temperature increase (2.5 K min⁻¹) from 423 K to a specific temperature to reach the desired extent of reduction.

To investigate the changes in the titania surface as a function of the extent of reduction, CO₂ chemisorption has been measured at 293 K for 6.6 wt% of MoO₃/TiO₂. As was stated previously, CO₂ does not show any chemical interaction with the molybdenum portions of catalysts even after subjecting to reduction treatment of such catalysts³,¹¹. During the preparation of this catalyst, the free hydroxyl groups of titania are fully covered with polymeric molybdate over-layer (see Scheme 1); therefore, no CO₂ chemisorption is detected on the oxidized form of this catalyst. As shown in Fig. 9, the uptake of CO₂ is seen to increase as the extent of reduction increases; it reached a maximum at about MoO₃₄ and stayed.

Scheme 2 Reaction Pathway of Methanol Oxidation over MoO₃/TiO₂ Catalysts

Fig. 9 CO₂ Chemisorption on Molybdena–Titania Catalyst (6.6 wt%, pH=3.98) at Different Extents of Reduction (The closed circles represent the uptake CO₂ after NO adsorption.)
constant during further reduction. NO is selectively adsorbed on coordinatively unsaturated sites (CUS) of molybdena portion to produce coordinatively covalent bonds with Mo21). After undergoing reduction treatment, the catalyst was exposed to 1.3 kPa of NO and then evacuated at 293 K; the CO2 chemisorption was then measured. The uptake of CO2 chemisorption, which is represented by closed circles in Fig. 9, was similar to that of standard CO2 chemisorption (open circles). The results suggest that NO and CO2 are chemisorbed on different portions of the catalysts. The maximum uptake of CO2 corresponds to about 60% recovery of the parent titania, since the CO2 uptake of parent titania alone was 0.142 mmol·g⁻¹. This result indicates that about 60% of the Mo–O–Ti bondings have been removed and that the hydroxyls of titania have reappeared. The remaining Mo–O–Ti bondings were stable, even after reduction at 973 K. When the most deeply reduced catalyst (reduction temperature: 973 K) was reoxidized, and the catalyst was then reduced again, the amount of CO2 chemisorption showed the same value at the same extent of reduction. Thus, no serious aggregation or sintering occurred after the reduction treatment.

The catalytic active sites of molybdenum catalysts, which are called coordinatively unsaturated sites (CUS), were developed by reduction treatments. An attempt was made to use NO chemisorption to discriminate the catalytic active sites of molybdena, as a function of extent of reduction, since NO was selectively adsorbed on CUS of molybdena as dinitrosyl or NO dimer to produce coordinative covalent bonds with Mo21).22). In the temperature programmed desorption (TPD) spectra of NO in Fig. 10, two types of desorption peaks (designated α and β) were observed at each extent of reduction. The results suggest that two types of adsorption sites may exist on the reduced molybdena–titania. The α peak appeared at lower temperature (ca. 360 K), and the β peak appeared at higher temperatures (500 K). The contribution of each peak per total uptake of NO was studied; it was found that each α peak reached its maximum at about MoO1.9, while each β peak reached its maximum at MoO3.0.

The X-ray photoelectron spectra (XPS) of the Mo(3d) level for the reduced molybdena–titania catalysts (6.6 wt%) are shown in Fig. 11. The XPS value of the Mo(3d) level shift to the lower binding energies, as a function of extents of reduction. The broader spectra of the Mo(3d) level may indicate the presence of Mo species of different oxidation states on the reduced catalysts. The binding energies of Mo(3d) levels for the various oxidation states show a shift of 5.1 eV between Mo6+ and Mo0+. The distribution of Mo valence states, determined from the curvefitted XPS Mo(3d) envelope, are shown in Table 2. It can be

![Fig. 10 TPD Spectra of NO Adsorbed on Reduced Molybdena–Titania Catalyst (6.6 wt%, pH=3.98) at Different Extents of Reduction](image1)

(A) MoO1.30, (B) MoO1.84, (C) MoO2.27

![Fig. 11 XPS of Mo(3d) Levels for Reduced Molybdena–Titania Catalyst (6.6 wt%, pH=3.98) at Different Extents of Reduction](image2)

(A) MoO1.20, (B) MoO1.87, (C) MoO2.31, (D) MoO3.0

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seen that the percentage of Mo⁶⁺ decreased and those of Mo⁵⁺, Mo⁴⁺, Mo³⁺, Mo²⁺, and Mo⁰⁺ increased, as a function of extents of reduction. The relative abundances of Mo⁴⁺ and Mo³⁺ reach maxima at MoO₁.87 and MoO₁.50, respectively.

### 3.2.2 Hydrogenation and Metathesis of Alkenes

The catalytic activities for metathesis of propene at 373 K and hydrogenation of 1,3-butadiene at 323 K were studied by a micro-catalytic pulse method. The catalytic activity of each reaction (TOF) was calculated from the number of molecules which reacted in one pulse (average number of first five pulses) per one Mo atom.

Siegel proposed that some specific catalytic reactions may occur on the particular CUS of cobalt which appear on the surface. For example, the hydrogenation of alkenes requires triply CUS in one Co atom, one site for adsorption of alkene and two sites for the homolytic dissociation of H₂. The catalytic activities on 6.6 wt% of molybdena-titania as a function of extent of reduction are shown in Fig. 12. Metathesis of propene showed the maximum catalytic activities at about MoO₁.9, hydrogenation of 1,3-butadiene showed the maximum at about MoO₁.5. It is interesting to note that the catalysts at higher extent of reduction were less active for all reactions. When the deeply reduced catalyst was reoxidized and then reduced to some desired extent of reduction, the activities were not changed. Thus, no irreversible aggregations or sinterings have been observed under those reduction conditions. In addition, no catalytic activities for metathesis and hydrogenation reactions was observed on the lower extent of reduction. The reaction pathway of propene metathesis (A in Scheme 3) is known to proceed via metallo-cyclobutane intermediates, so that doubly CUS (Mo⁴⁺) of Mo is required to form the those intermediates. On the other hand, for the hydrogenation of 1,3-butadiene (B in Scheme 3),

![Scheme 3](image_url)
H₂ is dissociatively adsorbed on some CUS and 1,3-butadiene is adsorbed on the remaining CUS to produce butenes via σ-alkyl intermediates. Therefore, a higher degree of coordinative unsaturation, such as triply CUS (Mo³⁺), is required for hydrogenation than metathesis. This result indicates that different types of reaction required different extents of reduction.

3.3 Hydrogenolysis of Thiophene over Sulfided Surfaces

3.3.1 Surface Properties of Sulfided Catalysts

The catalyst was treated in O₂ flowing for 12 h and then sulfided with a gas flow of 3% H₂S in 20% H₂/77% N₂ at constant rate of temperature increase (2.5 K min⁻¹) from 323 K to a specific temperature.

The XPS of Mo(3d) level for sulfided molybdena–titania catalysts are shown in Fig. 13. In the sulfided catalysts, the binding energies of Mo(3d⁵/₂) and Mo(3d³/₂) are 228.7 and 231.8 eV, respectively. A shoulder peak which can be attributed to the S(2s) line is observed at 225.8 eV. The observed binding energies of Mo(3d) and S(2s) for the sulfided

(A) crystalline MoS₂, (B) 923 K, (C) 873 K, (D) 773 K, (E) 673 K, (F) 573 K

Fig. 13 XPS of Mo(3d) and S(2s) Levels for Sulfided Molybdena–Titania Catalyst (6.6 wt%, pH= 3.98) at Different Sulfiding Temperatures

(A) 873 K, (B) 773 K, (C) 673 K, (D) 573 K

Fig. 14 TPD Spectra of NO Adsorbed on Sulfided Molybdena–Titania Catalyst (6.6 wt%, pH= 3.98) at Different Sulfiding Temperatures
molybdena–titania catalysts are in good agreement with those of MoS\(_2\) single crystal (see A in Fig. 13). Therefore, a MoS\(_2\)-like structure is formed by sulfiding treatment\(^{25,26}\). In contrast with the case of molybdena–alumina catalysts, molybdena–titania catalysis did not show any peak [\(\text{Mo(3d}_{3/2})=234.6\text{ eV}\)] for Mo\(^{5+}\) \(^{25,26}\). This result suggests that molybdena species supported on the TiO\(_2\) are more readily sulfided than those on Al\(_2\)O\(_3\).

As shown in Fig. 14, in the TPD spectra of adsorbed NO, two types of desorption peaks were observed at each extent of sulfiding. The NO species adsorbed on \(\alpha\) (CUS 3) and \(\beta\) (CUS 2) sites desorbed at about 372 K and 510 K, respectively. The desorption peaks of NO adsorbed on sulfided catalysts shift to a higher temperature region than that of reduced catalysts. In addition, more \(\alpha\) sites are selectively present in the sulfided states than in reduced states, in the lower temperature regions.

### 3.3.2 Hydrogenolysis of Thiophene and Hydrogenation of Alkene

The catalytic activities for hydrogenation of 1,3-butadiene at 323 K and hydrogenolysis of thiophene at 673 K were studied with a micro-catalytic pulse method.

As shown in Table 3, hydrogenation of 1,3-butadiene showed maximum catalytic activity at 623 K. The catalytic activity of hydrogenation shows a linear correlation with the number of \(\alpha\) sites (triply CUS). Therefore, triply CUS are active sites for the hydrogenation of 1,3-butadiene. The hydrogenolysis of thiophene shows a broad maximum in catalytic activity between 623 K and 723 K. No linear correlation of hydrogenolysis was observed with the number of \(\alpha\) or \(\beta\) sites, but there was a correlation with the total amount of NO. A similar trend was observed for sulfided molybdena–alumina and molybdena–titania catalysts\(^{27,28}\). Recently, Markel et al.\(^{29}\) observed that the catalytic activity of 2,3-dihydrothiophene (2,3-DHT) is much higher than that of thiophene over sulfided Mo/Al\(_2\)O\(_3\) and Re/Al\(_2\)O\(_3\), but the distributions of C\(_4\) products are similar to each other. Based on this result, they proposed that 2,3-DHT is an intermediate for thiophene hydrodesulfurization. H\(_2\) is heterolytically adsorbed on sulfided catalyst to produce the Mo–S–H or Mo–H species. Thiophene is adsorbed on some CUS to form \(\eta\)-bound thiophene intermediates. These intermediates are hydrogenated by adjacent Mo–S–H and Mo–H species and subsequently transformed to 2,3-DHT. The C–S cleavage of 2,3-DHT by the adjacent Mo–H and formation of the 1,3-butadiene follow. The produced 1,3-butadiene is hydrogenated and isomerized to produce the 1-butene and 2-butenes. These results for hydrogenolysis and hydrogenation indicate that hydrogenolysis of thiophene requires two adjacent CUS (\(\alpha\)-\(\alpha\), \(\alpha\)-\(\beta\), or \(\beta\)-\(\beta\)) and hydrogenation of 1,3-butadiene requires a triply CUS on the sulfided catalysts.

### 4. Conclusions

The results obtained in this study are summarized as follows:

1. Highly dispersed molybdena–titania catalysts can be prepared by an equilibrium adsorption method.
2. The amounts of adsorbed molybdate species are increased as an inverse function of the final pH of the impregnating solution.
3. Monolayer coverage of molybdenum oxide was established at pH=3.98 (6.6 wt%). Above monolayer coverage, crystalline MoO\(_3\) is formed on the titania surface.
4. The surface Mo oxide over-layers possess a highly distorted square pyramidal structure, regardless of the final pH of the impregnating solution.
5. The catalytic activity and selectivity for methanol oxidation are strongly dependent not only on the surface morphology but also on the reaction temperature.
6. Two types of catalytically active sites (designated \(\alpha\) and \(\beta\)) appeared after subjecting to reduction treatment: each \(\alpha\) site (CUS 3, Mo\(^{3+}\)) is active for hydrogenation of 1,3-butadiene and each \(\beta\) site (CUS 2, Mo\(^{4+}\)) is active for metathesis of propene.
7. A Mo\(_2\)-like structure is formed by sulfiding treatment with H\(_2\)S.
8. Hydrogenolysis of thiophene required an ensemble of two adjacent doubly and triply CUS.

### References


| Table 3 Hydrogenation of 1,3-Butadiene and Hydrogenolysis of Thiophene on Sulfided Molybdena–Titania Catalyst (6.6 wt%, pH=3.98) |
|-----------------|------------------|-------------------|-------------------|
| Sulfiding temp. [K] | S/Mo | HYD | TON | HDG |
| 573 | 1.84 | 0.112 | 0.041 (31.2) |
| 623 | 1.79 | 0.178 | 0.049 (37.8) |
| 673 | 1.54 | 0.104 | 0.050 (38.2) |
| 723 | 1.77 | 0.070 | 0.049 (37.4) |
| 773 | 1.80 | 0.037 | 0.044 (33.6) |
| 823 | 1.85 | 0.022 | 0.041 (31.8) |
| 873 | 2.11 | 0.012 | 0.033 (25.1) |
| 923 | 2.06 | 0.006 | 0.025 (19.0) |
| 973 | 2.16 | 0.001 | 0.022 (17.1) |

a: S(2p)/Mo(3d) peak area ratios determined from XPS.
b: Numbers in parentheses represent conversion (%) of thiophene.

HYD: hydrogenation of 1,3-butadiene at 323 K.
HDG: hydrogenolysis of thiophene at 673 K.
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要 旨

担持酸化モリブデン触媒
—酸化、還元、硫化状態の構造及び表面化学—

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平衡吸着法を用いてモリブデンを高分散した MoO_3/TiO_2 触媒を調製した。チタニア表面上のモリブデンアニオンの吸着量は含浸液の pH に強く依存し、チタニア担体の等電点（pH = 6.2）より塩基性側では吸着量は少なく、酸性側になるにつれて増加した（Table 1）。XRD，XPS（Fig. 3）およびラマン（Fig. 4）の結果から、モリブデン酸化物 MoO_3（pH = 3.98（6.6wt%））付近でノレイヤーを形成し、それより低い pH では多分子層（結晶性 MoO_3）で存在していることが分かった。なお、表面モリブデン酸化物は含浸液の pH と関係なく、すべて四角形で存在することが明らかになり、Scheme 1 にノレイヤー触媒の酸化表面モデルを提案した。

773 K で焼成して得た触媒を用いてメタノールの酸化反応を行った結果、触媒活性および選択性は触媒の表面状態および反応温度に強く依存することを分かった。反応主生成物は低い反応温度では (CH_3O)_2CH_2 であり、473 K より高い反応温度では HCHO であった（Fig. 5）。本反応条件では CO と CO_2 はほとんど生成せず、本触媒は新規性の一部酸化触媒であることを示した。反応副生成物である CH_3COCH_3 の選択率は担持率が増加するにつれて増大した。

CO_2 がチタニア表面に選択的に吸着する性質を用いて、各々の還元状態における触媒表面の変化を調べた（Fig. 9）。モノレイヤー触媒は酸化状態ではチタニア表面がモリブデン酸化物に覆われているため CO_2 はまったく吸着せず、還元が進行するにつれ吸着量は増加した。これは還元処理によって再びチタニア表面が現れてくることを示唆している。NO は還元処理により生じたモリブデンの配位不飽和サイトに選択的に吸着する。吸着 NO の TPD スペクトルからはいずれの場合でも二種類の脱離ピークが得られ、還元により構造が異なる二種類の活性サイトが生成することが分かった（Fig. 10）。例えば、水素化反応は配位不飽和度 3 のサイト（Mo^4+）が、メタノールは配位不飽和度 2 のサイト（Mo^4+）が最も活性が高く、反応の種類によって要求される活性点の構造が異なることを示した。

還元処理することにより、モリブデン酸化物 MoO_3 と類似な構造に変化することが XPS スペクトルから明らかにされ、NO の TPD スペクトルからは DOCO の脱離が観察され、配位不飽和度 3 のサイトは硫化処理した方が還元処理した場合より低い温度で発現することが分かった（Fig. 14）。一方、チオフェンの水素化分解反応に関与した二種類の配位不飽和度サイトが必要であることが分かった。

Keywords
Molybdenum oxide, Equilibrium adsorption method, Methanol oxidation, Methathesis, Hydrogenation, Hydrogenolysis