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Surface Properties of Supported Molybdenum Catalysts

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Heterogeneous catalysts consisting of highly dispersed supported molybdenum have been investigated. Hexacarbonylmolybdenum(0) catalysts supported on TiO_2, Al_2O_3, ZrO_2, MgO, and SiO_2 were characterized by temperature-programmed decomposition (TPDE), XPS, and catalytic activity for CO shift reaction, metathesis, and hydrogenation of alkenes. Mo catalyst supported on TiO_2 showed higher catalytic activity than that of the Mo catalysts on other supports. The TPDE spectrum of $Mo(CO)_6$ on TiO_2, which was pretreated at 773 K, showed two-stage decomposition peaks due to the elimination of CO ligands with very little evolution of H_2, which resulted in a low-valent catalyst. After the first stage of TPDE, $Mo(CO)_3$ species were formed on TiO_2. Those species gave higher catalytic activity for CO shift reaction at 403 K, but not for hydrogenation and metathesis. Metathesis of propene at 323 K and hydrogenation of 1,3-butadiene at 273 K showed higher activity only after the second stage. Those catalytic activities are one or two orders of magnitude higher than those of corresponding oxide catalysts. When the catalyst was pretreated at 600–773 K, slight oxidation of Mo occurred due to the presence of hydroxyls of TiO_2; this suppresses the catalytic activities for CO shift reaction and hydrogenation. However, the activity of metathesis increased with increasing evacuation temperatures. The results suggest that metathesis requires a higher oxidation state of Mo than do CO shift reaction and hydrogenation.

Recently, there has been growing interest in the study of transition metal complexes, especially mononuclear carbonyl complexes, supported on various inorganic supports, such as alumina, zeolites, and silica gel (*1*). The transition metal complexes, as precursors, can give highly dispersed and low-valent metal catalysts without reduction treatments (*2*, *3*). These catalysts can be much more active for metathesis of alkenes (*4*, *5*), hydrogenation of CO (*6*) or alkenes (*7*), and hydrogenolysis of alkanes (*8*) than their corresponding supported metal oxide systems, which have higher average valence states.

Other promising features include the possibility of studying the catalytic activities and selectivities of supported metal complexes without dissociation of CO ligands. Previously, we reported the catalytic activities of $Mo(CO)_3$ subcarbonyls on various supports for allylic alkylation in liquid phase (*9*, *10*). The $Mo(CO)_3/TiO_2$ catalyst exhibited higher activity with regio- and stereoselectivity.

Metal carbonyls can be immobilized by impregnating inorganic oxide (*11*). The method involves evacuation of the support to ensure penetration of the solution into the pores. An alternative procedure that can be used with volatile carbonyls involves sublimation in a flow of inert gas onto support (*12*), or under vacuum conditions (*9*). The preparation of a supported transition metal catalyst from carbonyl precursor involves several steps: pretreatment of support, contact with or adsorption on the support with the carbonyl complex, and decomposition of the complex to the desired extent by suitable heat treatment. Our

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work elucidates the higher activity of molybdenum on TiO_2 catalysts not only for the subcarbonyl stage but also for the low-valent metallic state which is obtained after decomposition at higher temperatures.

EXPERIMENTAL

Catalysts were prepared by dispersing $Mo(CO)_6$ (Strem Chemicals, 6.5 mg, 5×10^{-5} mol) on 0.5 g of various inorganic supports by sublimation at 343 K for 1 h under vacuum conditions. The inorganic supports in this work were SiO_2 (Degussa, Aerosil-200), TiO_2 (Degussa, P-25), Al_2O_3 (JRC-ALO-4), MgO (JRC-MgO-1), and ZrO_2. Al_2O_3 and MgO were the Japan Reference Catalysts (*13*) and ZrO_2 was prepared by the method of Tanabe and co-workers (*14*). Prior to sublimation, all supports were dehydrated at 773 K and treated with 39.9 kPa (300 Torr) of O_2 for 1 h, followed by evacuation at 773 K for 30 min. After sublimation at 343 K, the catalyst was evacuated at 343 K for 30 min except for TPDE measurements, which were started from room temperature. The amount of Mo loading of each catalyst was determined by chemical analysis as oxide base after treatment with flowing O_2 at 773 K (*15*).

For temperature-programmed decomposition (TPDE) experiments, the sample was heated from room temperature to 773 K at a linear rate of 5 K min^{-1} under vacuum conditions. The catalyst was evacuated at 273 K after sublimation of $Mo(CO)_6$ on the support at 343 K until the pressure reached 1.3×10^{-3} Pa (1×10^{-5} Torr); the TPDE run followed. The pressure change from the elimination of CO was monitored by an ionization gauge (ULVAC, GI-K) and was recorded automatically on a desktop recorder.

For X-ray photoelectron spectroscopy (XPS) measurements, the fresh catalysts or pretreated catalysts were sealed in a Pyrex ampoule under vacuum conditions. The ampoule was transferred to the preparation chamber of XPS, and then the seal of the ampoule was broken under purified Ar atmosphere. The samples of XPS were measured on a spectrometer (Shimadzu, ESCA 750) under minimum contamination with air. The binding energies of XPS spectra of $Mo(3d_{5/2})$ and $Mo(3d_{3/2})$ were calibrated by the observed binding energy of C(1*s*).

The catalytic activities of the CO shift reaction at 403 K, hydrogenation of 1,3-butadiene at 273 K, and metathesis of propene at 323 K were studied by a closed recirculation system (150 cm^3). The reaction products were analyzed on a gas chromatography (Ohkura, Model-701) which was equipped with a 2-m column of activated charcoal at 313 K for CO shift reaction and a 6-m column (Gaskuro Kogyo, VZ-7) at 273 K for hydrogenation and metathesis.

RESULTS AND DISCUSSION

The TPDE spectra of $Mo(CO)_6$ supported on SiO_2, TiO_2, Al_2O_3, ZrO_2, and MgO are shown in Fig. 1. Prior to sublimation of $Mo(CO)_6$, all supports were oxidized with O_2 and evacuated at 773 K until the pressure of the vacuum system reached 1.3×10^{-3} Pa (1×10^{-5} Torr). Two or three decomposition peaks, due to the elimination of CO, appeared at below 373 K for the first

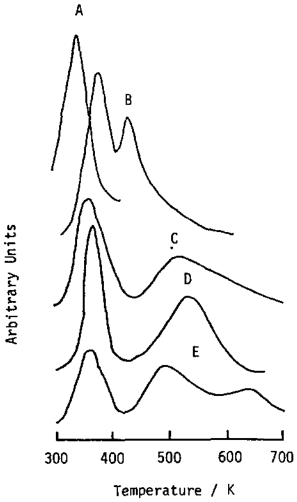

FIG. 1. TPDE spectra of $Mo(CO)_6$ after sublimation at 343 K on various supports: (A) SiO_2, (B) TiO_2, (C) Al_2O_3, (D) ZrO_2, (E) MgO. (All supports were evacuated at 773 K prior to the sublimation.)

TABLE 1

Amount of CO Evolution after Sublimation at 343 K, and Mo Loading after Evacuation at 773 K on Various Supports

Support[a]	Specific area (m^2 g^{-1})	CO evolution[b] at different temp. (10^{-5} mol)		Mo loading[c] (10^{-5} mol)
		343–413 K	413–773 K	
MgO	149	4	11	4.9
ZrO_2	69	10	10	5.0
Al_2O_3	157	5	14	4.8
TiO_2	55	5	16	4.9
SiO_2	191	0	0	—

[a] Support, 0.5 g.
[b] $Mo(CO)_6$, 5.0×10^{-5} mol.
[c] Determined by chemical analysis.

stage and at above 443 K for the second and/or third stages on TiO_2, Al_2O_3, ZrO_2, and MgO. The TPDE spectrum of $Mo(CO)_6$ on SiO_2 (Fig. 1A) showed only one peak at 343 K. After the TPDE experiment, the amount of Mo was measured by chemical analysis. In the case of SiO_2, no Mo was detectable. This result suggests that $Mo(CO)_6$ cannot be supported on SiO_2 by this method. The lower temperature peak at around 343 K on SiO_2 can be assigned as due to the evolution of $Mo(CO)_6$ itself.

Table 1 shows the amount of CO evolution after sublimation of $Mo(CO)_6$ and evacuation at 343 K, as determined by volumetric measurements of CO evolution between 343 and 773 K. $Mo(CO)_6$ (5.0×10^{-5} mol) was sublimed and evacuated at 343 K on each 0.5-g sample of support; then the amounts of CO evolution during the heat treatments at 343–413 and 413–773 K were measured. During the sublimation and the subsequent evacuation at 343 K, three CO ligands per Mo were already eliminated on MgO, and two CO ligands per Mo were eliminated on ZrO_2, Al_2O_3, and TiO_2. But on SiO_2, $Mo(CO)_6$ could not adsorb on the surface, since no evolution of CO was observed. Then, after evacuation at 413 K (after the first stage in TPDE), $Mo(CO)_2$ species were formed on MgO and ZrO_2, and $Mo(CO)_3$ species were formed on Al_2O_3 and TiO_2. These results may be due to the replacement of CO ligands with supports by oxidative addition to stabilize the Mo subcarbonyls, such as $Mo(CO)_2$ or $Mo(CO)_3$ on the surfaces of supports.

After the measurements of CO evolution, the Mo loadings were also measured. Table 1 shows the Mo loading on various supports, which were determined by chemical analyses after evacuation at 773 K. Except for SiO_2, the Mo loading showed almost constant values within the experimental errors, which were almost the same as the amounts of Mo at the start of preparation. The results suggest that, during the evacuation up to 773 K, the Mo did not evaporate under vacuum conditions after sublimation of $Mo(CO)_6$ on various supports.

Table 2 summarizes the catalytic activity of the CO shift reaction at 403 K and the oxidation state of Mo on the catalyst after pretreatment at different temperatures. The oxidation state of each catalyst was determined by the O_2 consumption at 773 K by separate experiments after pretreatment at different temperatures. After pretreatment of each catalyst, 26.6 kPa (200 Torr) of CO

TABLE 2

Catalytic Activity for CO Shift Reaction and Oxidation State of $Mo(CO)_x$ Catalyst on Various Supports after Pretreatment at Different Temperatures

Support	Activity for CO shift reaction[a] (10^{-7} s^{-1}) at evacuation temp. (K)			Oxidation state[b] at evacuation temp. (K)	
	413	573	773	573	773
MgO	3	13	46	4.0+	4.2+
ZrO_2	20	23	59	3.5+	4.3+
Al_2O_3	2	0	0	3.7+	4.7+
TiO_2	150	470	190	1.8+	2.8+
SiO_2	0	0	0	—	—

[a] Reaction temperature, 403 K.
[b] Determined by O_2 consumption at 773 K after pretreatment.

TABLE 3

Catalytic Activities on $Mo(CO)_3/TiO_2$ Catalyst Pretreated under Different Conditions

Pretreatment	Catalytic activities (10^{-3} s^{-1})		
	CO shift reaction at 403 K	Hydrogenation at 273 K	Metathesis at 323 K
Evacuated at			
413 K	0.015	0	0.18
573 K (1.8+)	0.047	12	0.70
773 K (2.8+)	0.019	9.0	2.1
Reduced at 773 K[a] (1.6+)	0.046	12	0.69
Oxidized at 773 K[b]	0	0	0
Reduced at 773 K[c] (2.6+)	0.0012	0.26	0.043
Oxidized at 773 K[c]	0	0	0

Note. Number in parentheses is oxidation state of Mo determined by O_2 consumption at 773 K after pretreatment of catalyst.

[a] The catalyst was evacuated at 773 K and then reduced.

[b] The catalyst was evacuated at 773 K and then oxidized.

[c] The reduced oxide catalyst (MoO_3, 2.5 wt%) prepared by a standard impregnation method.

was admitted to the reaction system; 0.7 kPa of H_2O was always supplied to the system during reaction. At the subcarbonyl stage after evacuation at 413 K, all catalysts were active except on SiO_2, since $Mo(CO)_6$ could not be supported on SiO_2 support (Fig. 1 and Table 1). The catalysts supported on TiO_2 after evacuation at different temperatures from 413 to 773 K showed higher activity for CO shift reaction than the catalysts on other supports. However, after pretreatment at 773 K, the catalytic activity of the CO shift reaction was suppressed; this may be due to the oxidation of Mo by surface hydroxyls of TiO_2. The Mo catalysts on other supports, such as on MgO, ZrO_2, and Al_2O_3, have lower activity than those on TiO_2; that would be due to the higher extent of oxidation of Mo by surface hydroxyls of supports other than TiO_2.

Table 3 shows catalytic activity on $Mo(CO)_3/TiO_2$ for CO shift reaction (CO, 26.6 kPa; H_2O, 0.7 kPa) at 403 K, hydrogenation of 1,3-butadiene (1,3-butadiene, 2.7 kPa; H_2, 5.4 kPa) at 273 K, and metathesis of propene (propene, 26.6 kPa) at 323 K, after pretreatment under different conditions. The $Mo(CO)_3/TiO_2$ catalyst obtained after evacuation at 413 K showed activity for CO shift reaction and metathesis. With evacuation at 573 K, the catalytic activities for all reactions were enhanced. On the other hand, after evacuation at 773 K, the activities for CO shift reaction and hydrogenation were suppressed, but that for metathesis was not suppressed. When the catalyst was reduced with H_2 at 773 K after evacuation at 773 K, the catalytic activities for CO shift reaction and hydrogenation became higher than those of the catalyst evacuated at 773 K. However, when the catalyst was oxidized with O_2 at 773 K, it had no catalytic activity for all reactions. If we compare it with the oxide catalyst (MoO_3/TiO_2, prepared by the standard impregnation method), it also has no catalytic activity. In addition, the reduced MoO_3/TiO_2 (MoO_3, 2.5 wt%, 2.6+ state) catalyst showed lower activity for all reactions than the catalysts prepared by this method.

Figure 2 shows the catalytic activities of CO shift reaction at 403 K, hydrogenation of 1,3-butadiene at 273 K, and metathesis of propene at 323 K on $Mo(CO)_3/TiO_2$ cata-

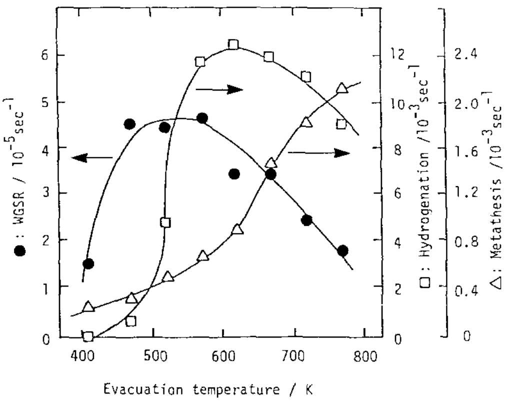

FIG. 2. Catalytic activities of CO shift reaction at 403 K, hydrogenation of 1,3-butadiene at 273 K, and metathesis of propene at 323 K as a function of pretreatment temperatures.

lysts as a function of pretreatment temperatures. For the CO shift reaction, the catalyst showed activity both on the subcarbonyl stage and on the metallic state, while for hydrogenation, it has no activity on the subcarbonyl stage (after evacuation at 413 K). After dissociation of CO ligands at higher temperatures, the activity for hydrogenation was drastically enhanced, since the number of coordinatively unsaturated sites of Mo increased. However, at pretreatment temperatures above 600 K, CO shift reaction and hydrogenation were suppressed. During the evacuations from 600 to 773 K, 4.8 × 10^{-6} mol of H_2 was evolved, as determined by volumetric measurements and GC analysis. Such an amount of H_2 evolution corresponds to only 9.6% of Mo, which was adsorbed on TiO_2 after sublimation of $Mo(CO)_6$. While on Al_2O_3 support, the amount of H_2 which evolved was much larger (5.11 × 10^{-5} mol) than the amount for the Mo on TiO_2. The results suggest that the Mo species can be more oxidized on Al_2O_3 than on TiO_2 (see Tables 2 and 3). For metathesis, the activity increased almost monotonically with increasing pretreatment temperatures. Even if the catalysts had been oxidized after evacuation at 773 K, they only became 3+ state. Those higher oxidation states enhance the activity of metathesis but suppress hydrogenation.

The TPDE of $Mo(CO)_3/TiO_2$ catalysts before and after CO shift reaction have been examined; the results are shown in Fig. 3. As was stated previously, $Mo(CO)_3$ species were adsorbed on TiO_2 surface after evacuation at 413 K. Those CO ligands of $Mo(CO)_3/TiO_2$ have been easily removed below 573 K (Fig. 3A). The TPDE spectrum of $Mo(CO)_3/TiO_2$ after CO shift reaction (Fig. 3B) showed a spectrum similar to that of (A). In spectrum (C), the catalyst was evacuated at 573–773 K; no peak appeared for TPDE, since the catalyst has no CO ligands. After this spectrum was taken, the catalyst was exposed and recirculated to 1.3 kPa of H_2 at 403 K and evacuated at 300 K; the spectrum also did not show any peak. However, after CO shift reaction, the TPDE spectrum of the catalyst (Fig. 3D), which was pretreated at 573–773 K, was quite similar to those for spectra (A) and (B). When the water vapor was allowed to touch the catalyst which was pretreated at 573–773 K, one broad peak appeared at around 533 K (Fig. 3E). Therefore, the shoulder peak in spectra (B) and (D) at around 540 K can be assigned to water evolution. The main peak in spectra (A), (B), and (D) can be assigned to CO evolution; this was also confirmed by MS and GC

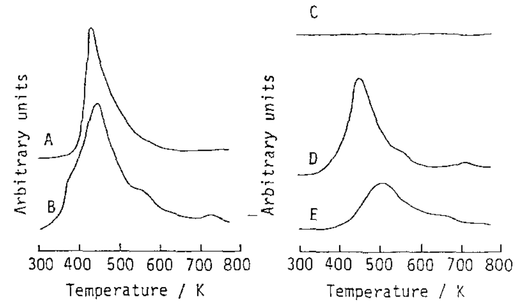

FIG. 3. TPDE spectra of $Mo(CO)_x/TiO_2$ (x = 3–0) before and after CO shift reaction: (A) $Mo(CO)/TiO_2$ (evacuated at 413 K), (B) after CO shift reaction on $Mo(CO)_3/TiO_2$, (C) Mo/TiO_2 (evacuated at 573–773 K), (D) after CO shift reaction on Mo/TiO_2, (E) after exposure to water vapor at the temperature of CO shift reaction on Mo/TiO_2.

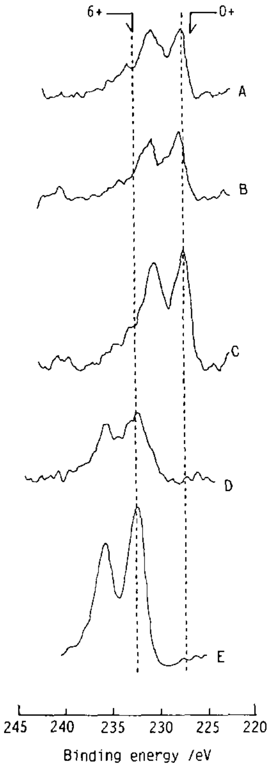

FIG. 4. Mo(3*d*) XPS spectra of $Mo(CO)_3/TiO_2$ evacuated at different temperatures: (A) evacuated at 573 K, (B) evacuated at 773 K, (C) evacuated and reduced at 773 K, (D) oxidized and evacuated at 773 K, (E) MoO_3/TiO_2 (MoO_3, 2.5 wt%) prepared by standard impregnation method.

analysis after each TPDE run. Either at the subcarbonyl stage (pretreated at 413 K) or at the low-valent metallic stage (pretreated above 573 K), the catalyst on TiO_2 showed higher activity for CO shift reaction than that of the catalysts on other supports (see Table 2). Even at the low-valent metallic stage, Mo subcarbonyls were easily reproduced on the surface during the CO shift reaction (Figs. 3C and 3D).

The XPS spectra of $Mo(CO)_3/TiO_2$ catalyst, which exhibited higher activity for CO shift reaction, are shown in Fig. 4. Spectrum D in Fig. 4 was obtained from the catalyst which was treated with O_2 for 3 h at 773 K, followed by evacuation at the same temperature. The $Mo(3d_{5/2})$ binding energy of (D) was 232.6 eV; this is about 6 eV higher than that of $Mo(CO)_6$ (226.6 eV) (*16*). The spectrum of oxide catalyst (Fig. 4E), which has 2.5 wt% of MoO_3 on TiO_2 prepared by the standard impregnation method, also showed the same binding energy as D. Thus, the catalyst after O_2 treatment at 773 K came to be in the 6+ state. On the other hand, $Mo(CO)_3/TiO_2$ which was evacuated at 573 and 773 K (Figs. 4A and 4B) had a binding energy about 2 or 3 eV higher than that of $Mo(CO)_6$. In this case, Mo became slightly oxidized (presumably 2+ or 3+ state), due to the oxidation of Mo subcarbonyls with hydroxyls of titania on the surface. When the catalyst was evacuated at 773 K and then reduced with H_2 at 773 K, the spectrum became narrower (Fig. 4C) than spectra (A) and (B) in Fig. 4. The broader spectra may include small amounts of oxidized species of Mo. In addition, the $Mo(3d_{5/2})$ binding energy of spectrum C became lower than that for spectra (A) and (B).

CONCLUSIONS

The results allow us to account for the genesis of the $Mo(CO)_3/TiO_2$ catalysts prepared by the sublimation method of hexacarbonylmolybdenum(0) on TiO_2. Mononuclear molybdenum carbonyl complexes seem to be bound on the titania surfaces and to be anchored by oxygens bridged with Ti atoms when the catalyst precursor is evacuated above 413 K. After sublimation of $Mo(CO)_6$ (5.0×10^{-5} mol) on 0.5-g samples of TiO_2 surfaces and evacuation at 413 K, the Mo carbonyls changed to the $Mo(CO)_3$ stage on TiO_2 by the elimination of three CO ligands per Mo. Burwell and Brenner have reported that $Mo(CO)_3$ species are formed after the first decomposition peak in the case of Al_2O_3 support (*17*). The catalyst at this stage showed activity for CO shift reaction and for metathesis.

When the catalyst is evacuated at 573 K, three CO ligands are eliminated. At this stage, the catalyst on TiO_2 showed higher activity for CO shift reaction and hydrogenation than that of the Mo catalysts on other supports. From the results of TPDE, Mo subcarbonyls were easily reproduced during CO shift reaction, which was followed by the formation of H_2 and CO_2 by water vapor. In the homogeneous system, two types of reaction mechanisms have been proposed previously; one is an associative mechanism (*18*) which proceeds via carboxylic acid with Mo, and the other is a dissociative mechanism (*19*) which proceeds via formate ion with Mo. In this work, we could not discriminate such intermediates for CO shift reaction. Studies using infrared spectroscopy can identify such intermediates.

The higher catalytic activity for CO shift reaction was almost equivalent to or slightly higher than that for the homogeneous catalytic system of $Mo(CO)_6$ which was reported previously (*20*). In comparison with industrial applications in heterogeneous systems (*21, 22*), the reaction temperatures for CO shift reactions on $Mo(CO)_3/TiO_2$ catalyst were about 200 K lower.

During the evacuation at 573–773 K, very small amounts of H_2 (4.8×10^{-6} mol) were evolved. Thus relatively slight oxidation would occur in comparison with that for the catalyst on other supports; this would suppress the activity for CO shift reaction and for hydrogenation. However, the activity for metathesis was enhanced with increasing pretreatment temperatures. This is because metathesis would require a higher oxidized state (presumably 4+ state) than hydrogenation (*23*). The Mo catalysts on other supports, such as on Al_2O_3, ZrO_2, and MgO, showed higher oxidation states after being evacuated at 773 K; this result reflects their lower activity.

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