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The Adsorption of CO and Hydrogen on Reduced Molybdenum Catalysts Used for CO Hydrogenation

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The adsorption of CO and H_2 on reduced Mo catalysts derived from the reduction of various heteropoly molybdates has been studied. Both CO and H_2 were adsorbed on a well-reduced metallic Mo surface. However, only a portion of the surface was reduceable to the zero valent state and was thus available for adsorption. Turnover frequencies for CO hydrogenation calculated on the basis of CO adsorption are comparable to those observed on Ni even though Mo is reported to be a poor catalyst for CO hydrogenation. The effect of the countercations of HPMo on the selectivity for olefin formation is explained by considering the relative affinity of the surface for CO and hydrogen. The results of TPD and TPR experiments suggest that CO is adsorbed nondissociatively. The surface-CO bond appears to be considerably weaker than that observed for noble metals.

INTRODUCTION

CO hydrogenation studies on supported group VIII metals abound in the literature. In contrast, similar studies on metals other than those in group VIII are less numerous. CO hydrogenation studies on Re (*1*), W (*2*), and Mo (*3–9*) suggest that Mo not only shows promise as a CO hydrogenation catalyst but also has a high tolerance toward sulfur poisoning (*3*). Recently, Mo has been incorporated into multimetallic catalysts used for the synthesis of alcohols from CO and H_2 (*7, 8*). However, there are relatively few studies which relate the surface properties of Mo to its catalytic activity for the hydrogenation of CO.

In a previous study (*9*) we reported the Fischer–Tropsch reaction over reduced Mo derived from heteropoly compounds as catalyst precursors. We found that the reducibility was improved when heteropoly compounds were used and that a metallic Mo powder having a very large surface area was obtained by the reduction of $H_3PMo_{12}O_{40}$ (HPMo). Its catalytic activity was found to be about an order of magnitude than that observed on conventional Mo catalysts. Using different salts of 12-molybdophosphoric acid, various additives were introduced as countercations under equivalent conditions and their additive effects were studied.

In this paper we report on the adsorption of CO and hydrogen on various Mo catalysts derived from the reduction of MoO_3 and heteropoly compounds. The study is aimed at clarifying the relationship between surface properties and catalytic activity for CO hydrogenation. The following points will be addressed: (1) a clarification of the nature of the active sites which promote CO hydrogenation, (2) the measurement of the number of active sites in order to compare turnover frequencies to those obtained over supported group VIII metals, (3) the relation between countercations in various salts of HPMo, the chemisorptive properties of CO, and the activity and selectivity in CO hydrogenation, and (4) the nature of the surface-CO bond, including the adsorbed state of CO.

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EXPERIMENTAL

Catalyst Preparation

MoO_3. Reagent grade ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24} \cdot xH_2O$, Wako Pure Chem.) was calcined in flowing dry air at 773 K for 5 h. The resulting grey powder was used in subsequent catalytic studies.

HPMo($H_3PMo_{12}O_{40} \cdot xH_2O$). 12-Molybdophosphoric acid was prepared by the method described by Tsigdinos (*10*) and Drechsel (*11*) as follows: 2.46 g of phosphoric acid (reagent grade, Wako Pure Chem.) was added to 150 ml of pure water and boiled for 30 min while refluxing. Fifty grams of MoO_3 was added in a stepwise manner and the mixture was allowed to boil for 6 h. Following cooling, insoluble contaminants were removed by filtration. The desired compound was extracted using ether and the filtrate was dried. A yellow powder was obtained.

KPMo($KH_2PMo_{12}O_{40} \cdot xH_2O$). The amount of K_2CO_3 (reagent grade, Wako Pure Chem.) required to ensure a K/Mo atomic ratio of 1/12 was added to an aqueous solution of HPMo. The solution was heated in a water bath until CO_2 was no longer evolved. After drying, a yellow powder was obtained.

MePMo($MeH_2PMo_{12}O_{40} \cdot xH_2O$, Me = Na, Cs, Mg, Ni, Co). Additional salts of HPMo were prepared in a similar fashion to that of KPMo in accord of the method of Tsigdinos (*10*). The atomic ratio, Me/Mo was fixed at 1/12. The designation of the precursor is used to denote each catalyst even though the chemical composition may be changed substantially during the reduction process.

Pretreatment

Each catalyst was evacuated for 10 min at room temperature. Its temperature was increased at a constant rate of 10 K/min by means of a temperature controller. This was followed by evacuation at 453 K for 1 h. The dry weight was obtained following cooling to room temperature. The temperature of the catalyst was then increased at a rate of 10 K/min to 773 K in flowing H_2. Reduction was at 773 K for 4 h. Both the rate of heating and the reduction temperature are of the utmost importance in ensuring reproducibility in catalytic activity. Following reduction in hydrogen, the catalyst was evacuated at 773 K for 0.5 h ($<10^{-4}$ Torr). The temperature of the catalyst was then reduced to room temperature and the weight was measured. The extent of reduction was obtained from the weight loss during the reduction process. In general, there was good agreement on the extent of reduction of MoO_3 and HPMo determined from loss during the reduction process and hydrogen consumption.

Hydrogen and CO adsorption

Chemisorption experiments were performed at room temperature (Table 1). Because the amount of gas adsorption differed significantly between catalysts, both the volumetric and the dynamic pulse adsorption methods were used.

On HPMo, CoPMo, and NiPMo, the adsorption was sufficient to enable the use of a conventional adsorption apparatus. On alkali metal and alkali earth metal salts adsorption was small and only the dynamic pulse method could be used. Agreement between the volumetric and the dynamic

TABLE 1

CO and Hydrogen Adsorption on Various Heteropoly Molybdates at Room Temperature

Catalyst	BET area (m^2/g)	Degree of reduction (%)	CO ads. ($\mu mol/g$)	H_2 ads. ($\mu mol/g$)
HPMo	64.7	98.1	166	26.0
NaPMo	14.0	61.3	26.0	0.33
KPMo	54.6	86.0	42.9	2.13
CsPMo	54.6	90.9	28.7	0.15
MgPMo	63.1	92.1	67.9	5.07
NiPMo	56.4	100	102	21.4
CoPMo	64.4	100	157	26.4
MoO_3[a]	15.6	97.8	15.3	5.71

[a] Reduction at 873 K, others at 773 K.

pulse methods was confirmed using MoO_3.

When the dynamic pulse method was used a helium carrier gas was used for CO adsorption and an argon carrier gas was used for hydrogen adsorption. The purity of the carrier gas was checked by means of an O_2–CO titration technique on supported Pt. The procedure has been described in the literature (*12*). Because the amount of CO_2 evolved was small, it was assumed that only trace amounts of O_2 were present in the carrier gas.

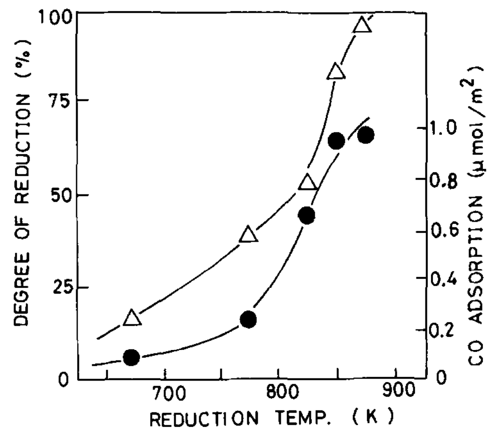

FIG. 1. Effect of the reduction temperature of MoO_3 on the degree of reduction and the amount of CO adsorption. (△) Degree of reduction. (●) amount of CO adsorption.

Temperature-Programmed Desorption (TPD) and Temperature-Programmed Reaction (TPR) of CO

The catalyst was reduced and evacuated at 773 K. It was then exposed to 100 Torr of CO at room temperature for 15 min. This CO exposure was followed by evacuation for 5 min. During the TPD experiments, helium was passed over the catalyst at a rate of 20 ml/min while the temperature was raised at a rate of 5 K/min from room temperature to 773 K. The desorption products were periodically injected into a gas chromatograph through a six-port valve. In the case of the TPR measurements a hydrogen carrier gas was used instead of helium. Other conditions were identical to those in the TPD experiments.

RESULTS AND DISCUSSION

Chemisorption of CO and H_2

The relationship between the extent of reduction and CO chemisorption on MoO_3 reduced at different temperatures was studied. The extent of reduction of MoO_3 as a function of temperature, together with CO chemisorption per BET surface area, is shown in Fig. 1. The extent of reduction increased monotonically with an increase in the reduction temperature. CO chemisorption was observed to increase sharply when the extent of reduction exceeded 40%, suggesting that relatively high reduction temperatures are required in order to expose metallic Mo. The adsorption of CO on HPMo was observed to be about an order of magnitude higher than on MoO_3. Because HPMo is about 98.1% reduced, it appears that CO is preferentially adsorbed on metallic Mo. This was substantiated by X-ray diffraction measurements on reduced HPMo and MoO_3 (873 K reduction). These results suggested that Mo was reduced to the zero valent state. However, surface area measurements of MoO_3 and HPMo calculated from CO chemisorption were 0.68 and 12.4 m^2/g, respectively. This area is significantly smaller than that calculated from BET surface area measurements (15.6 and 64.7 m^2/g, respectively). A similar behavior was observed by Ramakrishnan and Weller (*14*) on alumina-supported Mo catalysts. In addition, Kelly *et al.* (*2*) reported a similar behavior on tungsten surfaces. Both Mo and W have high heats of sublimation, and consequently, high surface energy. If the reduction of bulk and surface Mo—O is considered according to the following equations:

$$\text{Mo—O} + H_2 \xrightarrow{\Delta G_s} \text{Mo (surface)} + H_2O \quad (1)$$

$$\text{Mo—O} + H_2 \xrightarrow{\Delta G_b} \text{Mo (bulk)} + H_2O \quad (2)$$

it is immediately apparent that the temperature required to reduce surface Mo is considerably higher than that required for bulk Mo.

The adsorption of CO on various salts of HPMo was studied as a function of reduction temperature. Following reduction at 773 K, the extent of reduction to Mo° was observed to vary from between 60 to 100%. Figure 2 shows that both CO and H_2 chemisorption increase sharply when the extent of reduction approaches 100%. From this reason, we conclude that CO is chemisorbed only on highly reduced Mo surfaces. Under these conditions, BET surfaces still did not agree with surface areas measured using CO adsorption. This suggests that even under extreme reduction conditions, only a portion of the surface can be reduced to metallic Mo and is, therefore, accessible to CO chemisorption. The remainder of the surface appears to be covered by oxide ions, even though the X-ray diffraction patterns show that the bulk is reduced to metallic Mo. Additionally, hydrogen adsorption was considerably less than CO adsorption. Measured surface areas, therefore, decreased in the following order:

BET area > area based on CO adsorption
> area based on hydrogen adsorption.

Similar trends have been observed on Ru/SiO_2. In the presence of chloride on the Ru surface, hydrogen adsorption was more seriously affected than CO adsorption. This is due to the dual site adsorption requirement for H_2 as compared to a single site adsorption requirement for CO.

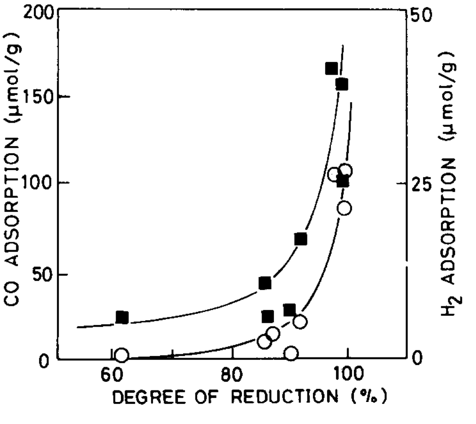

FIG. 2. The amount of CO or H_2 adsorption on various salts of HPMo at room temperature as a function of the reduction temperature. (■) CO adsorption, (○) H_2 adsorption.

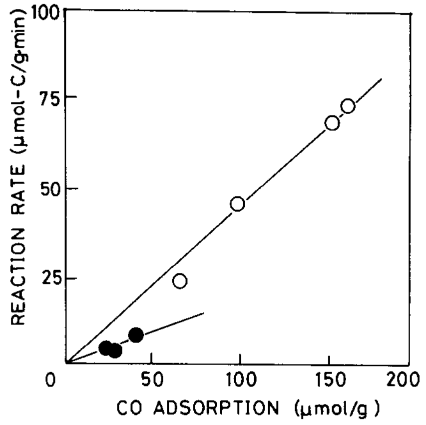

FIG. 3. Relation between the amount of CO adsorption and the rate of CO hydrogenation (at 503 K) on various salts of HPMo. (○) HPMo, CoPMo, NiPMo, MgPMo. (●) NaPMo, KPMo, CsPMo.

The Activity and Selectivity for CO Hydrogenation

In a previous study (*9*) we reported results on the hydrogenation of CO over a series of salts of HPMo. Both the activity and the selectivity were observed to depend on the particular choice of counteraction. It is of interest, therefore, to relate the catalytic activity to the surface properties.

A comparison between the reaction rate and the BET surface area was attempted. However, the relationship between the two was not of much interest. Figure 3 shows that the reaction rate was proportional to the amount of CO chemisorbed for catalysts classified into two groups: highly active (○) and less active (●). There was no clear relationship between reaction rate and hydrogen adsorption. For this reason, we concluded that CO adsorption gives a much better indication of the sites which are active for CO hydrogenation than does hydrogen chemisorption.

In a previous paper (*9*) we reported that the TOF for CO hydrogenation on HPMo as calculated from the measured BET surface area was comparable to that observed for Ir, the least active of the group VIII metals (*13*). However, we now know that the entire surface area as measured by the BET method is not available for reaction. When the TOF is based on CO adsorption, a rate of 0.44 min^{-1} (503 K) is obtained. This rate is comparable to that observed for Ni which is an active catalyst for CO hydrogenation. According to Vannice (*13*), the TOF for CO hydrogenation on group VIII metals decreases in the following sequence:

Ru> Fe> Ni> Mo (present study) >
Co> Rh> Pd> Pt> Ir

Because only a small portion of the surface is active for the reaction, Mo was considered to be a rather poor methanation catalyst. When the activity is considered on the basis of reduced Mo sites as measured by CO chemisorption, the picture appears to be quite different.

Turnover frequencies for CO hydrogenation on the various salts of HPMo were found to decrease in the following order:

(HPMo, CoPMo, NiPMo) > MgPMo
> (NaPMo, KPMo) > CsPMo.

This decrease in activity correlates well with the decreasing electronegativity of the cations.

The ability to chemisorb CO is generally reflected in a high CO hydrogenation activity. However, the selectivity for olefin formation is increased considerably when hydrogen chemisorption is suppressed. This data is shown in Table 2 in which the amount of olefin formation ($C_2^{=}$ + $C_3^{=}$) is shown to increase sharply for high CO/H_2 adsorption ratios. Apparently, when the active sites have a low affinity for hydrogen adsorption, paraffin formation is sharply increased.

TABLE 2

CO/H_2 Ratio of Adsorption and Selectivity of CO Hydrogenation over Various Heteropoly Molybdates

Catalyst	CO/H_2 ratio	Selectivity of $C_2^{=}$ + $C_3^{=}$ (%)	Selectivity of C_1 (%)
HPMo	6.38	2.08	36.1
NaPMo	79.0	29.9	18.1
KPMo	20.1	29.9	21.0
CsPMo	19.7	32.7	24.5
MgPMo	11.4	6.5	26.8
CoPMo	5.93	8.3	20.9
NiPMo	4.77	7.9	25.3
MoO_3	2.68	3.1	36.9

Selectivity differences were also observed when different cations were introduced. Unfortunately, a clear cut relationship between adsorption data and C_1 selectivity was not found. HPMo and CoPMo, for example, showed similar adsorptive behavior. However, HPMo had the highest C_1 selectivity while that of CoPMo was quite poor. The chemisorptive properties of the adsorbed intermediate species such as alkyl groups or methylene, may be more important bearing on C_1 selectivity than the CO/H_2 adsorption ratios.

TPD and TPR Experiments

The TPD spectrum of CO adsorbed on HPMo is shown in Fig. 4A. CO desorption from HPMo occurred with the formation of only trace amounts of CO_2. This behavior is quite different from that observed for supported Ru or Pt (*16*) in which relatively large amounts of CO_2 were formed. The formation of CO_2 is believed to be associated with the ability of the metal to promote the rupture of the CO bond. CO_2 is then formed as a result of the Boudouard reaction. The desorption of CO from HPMo was observed to take place at relatively low temperatures. In the case of Ru or Pt, CO desorption continued to occur up to about 750 K. CO desorption from HPMo, on the other hand, was virtually complete at 600 K. The maximum in the rate of desorption of CO occurred at 380 K, which was significantly lower than that observed on Ru. For this reason we conclude that CO is much more weakly bound to the surface of Mo than to noble metals.

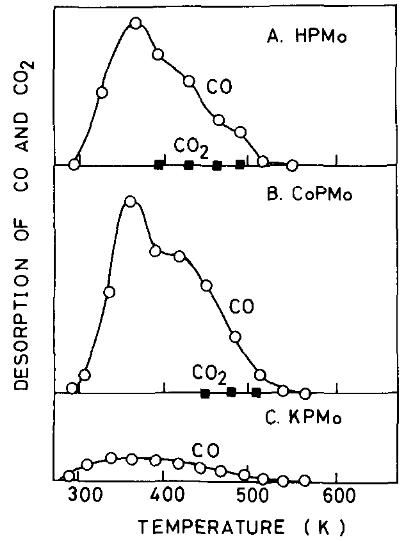

FIG. 4. Temperature-programmed desorption spectra of adsorbed CO on HPMo (A), CoPMo (B), and KPMo (C). Carrier gas, He 20 ml/min; program rate; 5 K/min. Amount of desorption in arbitrary units. (○) CO, (■) CO_2.

Following the TPD experiments, CO adsorption was performed at room temperature. Because the amount of adsorbed was comparable to that observed for the fresh catalyst we conclude that the CO desorption occurred reversibly during the TPD experiments.

The TPD spectrum of Ni-, Fe-, and CoPMo was similar to that observed for HPMo (Fig. 4B). The effect of transition metals on the desorption behavior of CO was, therefore, not clear. Alkali metal salts of HPMo were observed to desorb relatively small amounts of CO and the TPD spectra of CO were rather defined. Even though the CO peak height was much smaller on KPMo than on HPMo or CoPMo, the desorption of CO continued to occur up to 560 K. For this reason, the introduction of K appears to increase the strength of the surface-CO bond.

Temperature-programmed reaction spectra of CO adsorbed on HPMo, CoPMo, and KPMo are shown in Fig. 5. In contrast to similar studies on noble metals (*17*) which show that methane is the primary desorption product, the desorption products from HPMo and CoPMo consist predominantly of CO. Methane appears to be only a minor desorption product. These results also show that the bonding of CO to the surface of Mo is considerably weaker than that observed on noble metals. Two distinct methane desorption peaks were observed on HPMo and CoPMo. These peaks were centered at 400 and 500 K. Three distinct desorption states of CO are observed, one of which leads to the reversible desorption of CO and the other two, lead to the formation of methane which are observed as separate desorption maxima.

The low-temperature methane peak occurs in the same temperature range as that reported for Ru and Rh (*17*). It is, therefore, reasonable to assume that this desorption state of CO is responsible for the CO hydrogenation activity. On KPMo only the high-temperature methane desorption peak centered at 500 K was observed.

The adsorption of CO on clean, well-defined Mo surfaces has been the subject of considerable surface science studies. A clean Mo (100) surface reportedly dissoci-

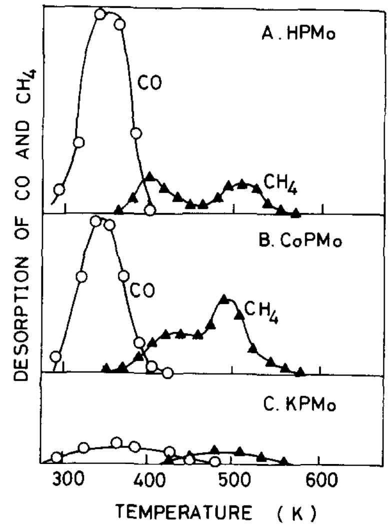

FIG. 5. Temperature-programmed reaction spectra of adsorbed CO on HPMo (A), CoPMo (B), and KPMo (C). Carrier gas, H_2 20 ml/min; program rate, 5 K/min. Amount of desorption in arbitrary units. (○) CO, (▲) CH_4.

ates CO at room temperature (*18–22*). The adsorption of molecular CO has been observed only at temperatures below 200 K. However, CO is also molecularly adsorbed at relatively high surface coverages following the dissociative adsorption of CO. Following the flash desorption of CO, at least three CO desorption maxima are observed. These are centered at: 300–600 K (α-CO) which is molecularly adsorbed: and 900–1500 K (β_1 and β_2-CO) which is due to dissociatively adsorbed CO. However, if the surface is modified by an oxygen adlayer or by the addition of a carbonaceous layer, the dissociation of CO is significantly suppressed and CO is adsorbed only nondissociatively giving rise only to the α-CO peak (*23, 24*).

In the present study, CO is adsorbed on only a small fraction of the Mo surface. Additionally, the surface appears to be strongly perturbed by the presence of an oxygen adlayer. It is therefore reasonable to assume that CO is adsorbed nondissociatively on the surface of the Mo catalyst. The TPD results are consistent with this interpretation for the following reasons: (1) only trace amounts of CO_2 were observed and (2) the CO desorption maximum was consistent with that observed for α-CO.

CONCLUSIONS

Several important conclusions emerge from this study as follows:

(1) The surface is only partially reduced to Mo. The hydrogenation activity of CO increases substantially with the extent of reduction. However, enhanced olefin formation can be related to a drop in hydrogen adsorption.

(2) When the CO hydrogenation activity is based on CO chemisorption which presumably counts the number of reduced Mo sites, turnover frequencies are comparable to those obtained on group VIII metals.

(3) The CO hydrogenation activity correlates well the electronegativity of the countercations for a series of HPMo salts.

(4) TPD and TPR spectra suggest the reversible nature of CO adsorption on Mo. This compares well with α-CO observed on clean Mo surfaces. The surface-CO bond appears to be considerably weaker than that observed on noble metals.

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