In situ carburization of metallic molybdenum during catalytic reactions of carbon-containing gases

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Supported molybdenum clusters were prepared by sublimation of $Mo(CO)_6$ onto dehydroxylated alumina followed by decomposition in flowing dihydrogen at 970 K. These alumina-supported molybdenum clusters were found by XAFS to transform into Mo_2C if heated in a 20% methane/H_2 mixture at 950 K. For the hydrogenolysis of *n*-butane at 510 K and CO–H_2 reactions at 570 K, both at atmospheric pressure, molybdenum and carburized molybdenum showed similar, but different for each reaction, turnover rates. The product distribution was the same for each reaction on Mo and Mo_2C. In both reactions, in situ XAFS data for fresh and used catalysts indicated that Mo clusters progressively transformed into Mo_2C under the reaction conditions

Keywords: Molybdenum carbide catalysts; alumina-supported; *n*-butane hydrogenolysis; CO hydrogenation; in situ carburization; XAFS

1. Introduction

In the past decade, carbides of Mo and W have been tried as substitute catalytic materials for noble metals. New methods for the preparation of supported and unsupported metal carbides with high specific surface areas have been reviewed [1]. For reactions in which ruthenium is an active catalyst such as CO–H_2 reactions, hydrogenation and hydrogenolysis of hydrocarbons, and hydrotreating, molybdenum carbide is also a catalyst of comparable activity [1].

Historically, catalysis by metal carbides was discovered during studies starting with the parent metals. First, Muller and Gault investigating reactions of 1,1,3-trimethylcyclopentane on a W film found that selectivity toward xylene as found

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on Pt became observable only after an induction period [2]. The in situ formation of W carbide by a reaction between W and the reactant was suggested. Later, Sinfelt and Yates prepared Mo powders by reduction of MoO_2 in H_2: the rate of ethane hydrogenolysis on these powders increased 60 times in 5 h of reaction, after which the formation of a bulk molybdenum carbide Mo_2C was confirmed by X-ray diffraction [3]. Then, a study of surface chemistry and catalysis with WC powders led to an analogy in catalytic behavior between WC and Pt [4]. This analogy was based on the simple idea that carbon atoms in the interstitial sites of W temper the surface reactivity of the host metal. Thus, a WC surface could bind reactant molecules strongly enough but not too strongly, an essential property of good catalysts like Ru, Rh, Pd, Ir or Pt. More recently, Burwell and coworkers prepared Mo clusters supported on alumina (Mo/Al_2O_3) by decomposition of $Mo(CO)_6/Al_2O_3$. These Mo clusters showed activity in hydrogenolysis of alkanes, exceeded only by Ru [5,6].

In view of the brief review of previous works, the following question then arises: was Mo or Mo_2C the catalyst in the work of Burwell and collaborators? To answer this question, we prepared Mo and Mo_2C supported on Al_2O_3, and compared them as catalysts for hydrogenolysis of *n*-butane and CO–H_2 reactions. In particular, we examined the catalysts by X-ray absorption fine structure (XAFS) carried out in the reaction cell before and after reaction.

2. Experimental

Metallic molybdenum Mo/Al_2O_3 was prepared following the method of Burwell and coworkers [5,6] and as reported in our laboratory [7]. The $Mo(CO)_6$ was sublimed at room temperature (RT) and carried in flowing H_2 onto dehydroxylated γ-alumina kept at 320 K. The dehydroxylation required to obtain zero-valent molybdenum clusters was accomplished by heating the alumina at 1170 K for 1 h in flowing He. The resulting $Mo(CO)_6/Al_2O_3$ was decomposed by temperature-programmed reaction with flowing H_2 at a heating rate of 430 K s^{-1} up to 970 K and maintaining this temperature for 1 h to yield Mo/Al_2O_3. The Mo_2C/Al_2O_3 was obtained by carburization of Mo/Al_2O_3 at 950 K for 0.5 h in a CH_4–H_2 mixture.

Chemisorption of CO at RT was employed to titrate the exposed Mo atoms. In a conventional volumetric adsorption system, two isotherms separated by evacuation at RT were obtained and the difference between the values of amount adsorbed extrapolated to zero pressure was taken as the amount of irreversibly chemisorbed CO. Catalytic reactions were carried out at atmospheric pressure in a typical flow system with quartz reaction cell for the preparation and CO chemisorption. Samples in the reaction cell were not exposed to air at any time. Products of the reaction were analyzed by gas chromatography. Details are given in ref. [7].

A controlled atmosphere cell (fig. 1) was used for the collection of XAFS data

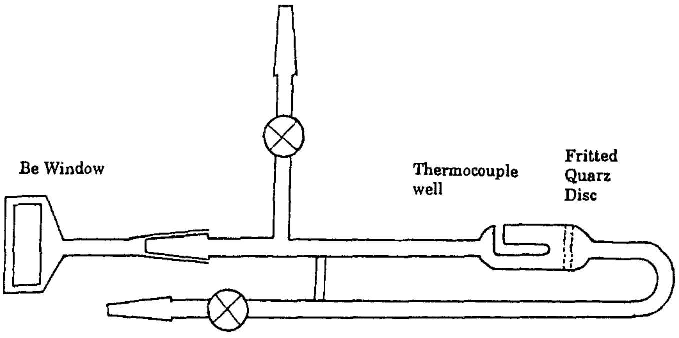


Fig. 1. A controlled atmosphere powder XAFS cell.

on powder samples. Following gas treatments, the cell was cooled to RT for transportation to the spectrometer. Prior to XAFS measurements, the cell was inverted and the sample powders were poured into the space between the Be windows. This spectroscopic cell was a modification of a standard design used for wafer samples. The modification was needed to deposit $Mo(CO)_6$ uniformly onto the alumina support. However, care must be taken to avoid the distortion of spectra due to a nonuniform thickness across the beam when the powders were loosely packed into the window end of the cell. The XAFS spectra were collected in a transmission mode at the Stanford Synchrotron Radiation Laboratory (SSRL). The data were analyzed by an in-house program in our laboratory.

3. Results and discussion

3.1. SAMPLE CHARACTERIZATION

Deposition and thermal decomposition of $Mo(CO)_6$ is a complicated process. The process was followed by chemical and physical methods including XAFS and the results have been presented elsewhere [7]. Of particular interest is the formation of highly carbon deficient Mo_2C (molar ratio of $C/Mo = 0.1–0.2$) during decomposition of $Mo(CO)_6/Al_2O_3$ in H_2 above 800 K. This carbide is destroyed to form the metal only when heated up to 970 K in H_2. One reason why $Mo(CO)_6$ is convenient as a catalyst precursor is that it leads to metallic Mo under mild conditions by a simple decomposition. But, because of the formation of carbide during the decomposition, a high temperature treatment is needed following the decomposition.

Fig. 2 shows the X-ray absorption near-edge structure (XANES) obtained near the Mo K-edge for the prepared samples and reference materials of Mo foil and Mo_2C powder mixed with γ-alumina. As evidenced from the reference spectra, Mo and Mo_2C could be easily differentiated by a separation of the two broad peaks above the absorption edge. The Mo spectrum shows a larger separation than that

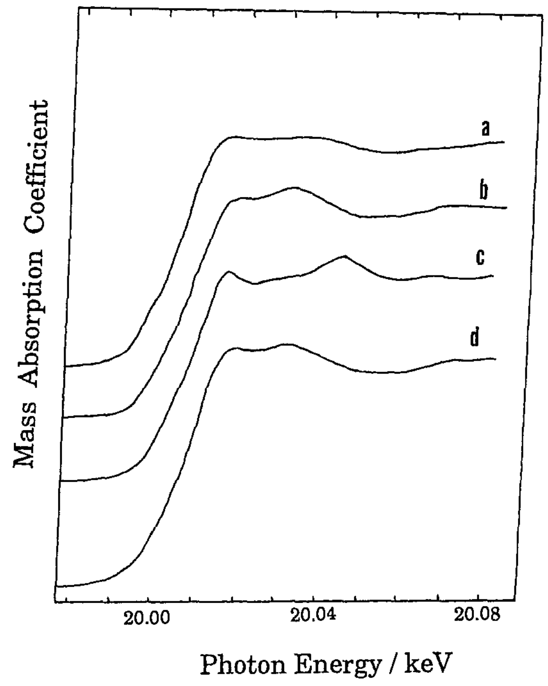
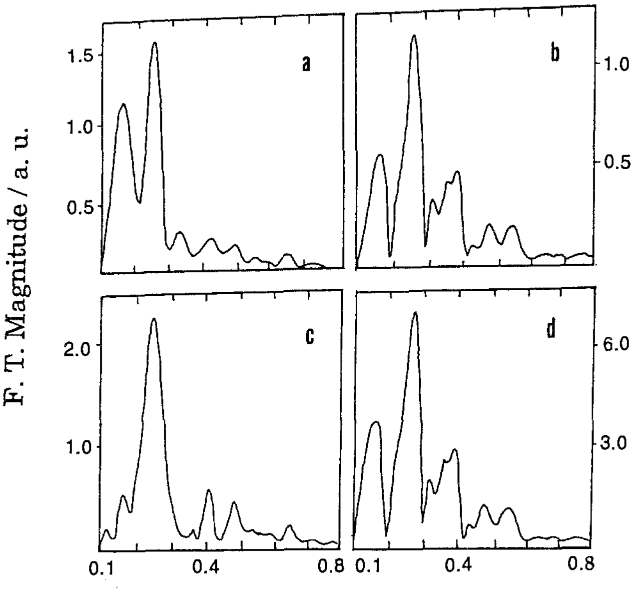


Fig. 2. XANES spectra of Mo/Al_2O_3 (a), Mo_2C/Al_2O_3 (b), Mo foil (c), and Mo_2C powder (d).

for the Mo_2C spectrum. The Mo/Al_2O_3 and Mo_2C/Al_2O_3 showed expected XANES spectra of metallic Mo and Mo_2C, respectively.

The extended X-ray absorption fine structure (EXAFS) spectra of the same samples are shown in fig. 3 and structural information abstracted from EXAFS is tabulated in table 1. The EXAFS spectrum of Mo_2C/Al_2O_3 is identical to that of Mo_2C powder in every detail except for the peak heights, indicating that small Mo_2C clusters are present in Mo_2C/Al_2O_3. The situation with Mo/Al_2O_3 is not as simple. Unlike the case of XANES, the EXAFS spectrum of Mo/Al_2O_3 is not the same as that of Mo foil. An EXAFS peak is seen near the Mo–C position and the position of the Mo–Mo peak (280 pm) lies between the positions expected for Mo (272 pm) and Mo_2C (296 pm).

The amount of carbon retained in Mo/Al_2O_3 was determined to be about 0.01 C/Mo by measuring the methane produced when the sample was treated with H_2 up to 1170 K. The amount of carbon appears to be too small to account for the substantial disturbance in the structure of Mo clusters. At these low levels of carbon, the concentration is difficult to determine accurately and it is likely that the carbon content is underestimated. Furthermore, trace oxygen may remain in the structure together with carbon. In any case, Mo/Al_2O_3 is essentially metallic Mo with a carbide or perhaps oxycarbide impurity. The greatly reduced average Mo–Mo coordi-



Distance / nm

Fig. 3. EXAFS spectra of Mo/Al_2O_3 (a), Mo_2C/Al_2O_3 (b), Mo foil (c), and Mo_2C powder (d).

nation numbers for the supported samples as compared to those for the references indicate that the Mo and Mo_2C in the samples are in the form of small clusters.

Table 2 shows the amount of CO irreversibly chemisorbed on the samples at RT expressed as the number of CO molecules divided by total Mo in the system (CO/Mo). The Mo_2C/Al_2O_3 chemisorbed about twice as much CO as Mo/Al_2O_3. Since the carburization temperature was always lower than that required for the initial preparation of Mo/Al_2O_3, Mo is not likely to have sintered during carburization. Hence, the different amounts of chemisorption are believed to reflect the different stoichiometries of CO chemisorption. Indeed, chemisorption of CO on single crystals [8] indicates that a metallic Mo surface adsorbs CO dissociatively while the metal with a carbide overlayer does so molecularly. The results also indicate that the surface of Mo/Al_2O_3 is completely reduced.

Table 1
Structure of fresh catalysts determined by EXAFS

Sample	Interatomic distance (pm)		Coordination number	
	Mo–C	Mo–Mo	Mo–C	Mo–Mo
Mo/Al_2O_3	215	280	2	4
Mo_2C/Al_2O_3	209	295	2	4
Mo foil	–	272	–	8
Mo_2C	209	296	3	12

Table 2
Irreversible chemisorption of CO at room temperature (CO molecule/ Mo atom)

Mo loading (wt%)	Mo/Al_2O_3	Mo_2C/Al_2O_3
0.9	0.14	0.20
2.7	0.14	0.28
4.5	0.06	0.14

3.2. HYDROGENOLYSIS OF n-BUTANE AND HYDROGENATION OF CO

Catalysis by Mo and Mo_2C of n-butane hydrogenolysis and CO hydrogenation have been or will be discussed elsewhere in detail [7,9]. In the present letter, we will focus only on the difference in catalytic behavior of Mo without precarburization and carburized Mo. Table 3 summarizes the results of n-butane hydrogenolysis at 510 K and atmospheric pressure. The reaction rate is expressed as turnover rate v_t, defined as the number of carbon-containing reactant molecules converted to products per CO-titrated surface metal atom per second. The stoichiometry of CO chemisorption per exposed metal site was assumed to be 1 for Mo_2C/Al_2O_3 and 0.5 for Mo/Al_2O_3 as explained earlier in this letter.

The values of v_t for supported Mo and Mo_2C are all very high. Under the same conditions, 0.5% Ru/Al_2O_3, with Ru being one of the most active catalysts for hydrogenolysis of alkanes, showed a v_t value of 0.82 s^{-1} [7]. Nakamura et al. [6] reported a v_t value of 0.08 s^{-1} for propane hydrogenolysis at 523 K over Mo/Al_2O_3 which is close to the v_t value for our 0.9% Mo/Al_2O_3. Carbide catalysts showed higher v_t values than noncarbided catalysts by factors of 4–6 (table 3). Except for the difference in v_t, Mo/Al_2O_3 and Mo_2C/Al_2O_3 exhibited remarkable similarity in product distributions and kinetic parameters. The product distribution shows similar cracking probability for the terminal and internal C–C bonds in the n-butane molecule. This is also true for Ru. Kinetic studies for n-butane hydrogenolysis over the group VIII metals have usually indicated negative reaction orders

Table 3
Hydrogenolysis of n-butane at 510 K and atmospheric pressure

Catalyst	v_t[a] (s^{-1})	Product distribution (%)				Kinetic parameters[b]		
		C_1	C_2	C_3	i-C_4	m	n	E_a (kJ mol^{-1})
0.9% Mo/Al_2O_3	0.047	41.4	31.0	25.0	2.6	–	–	–
1.0% Mo_2C/Al_2O_3	0.290	41.5	31.6	24.9	2.0	–	–	–
2.7% Mo/Al_2O_3	0.007	54.0	26.0	16.8	3.2	0.29	1.37	87
2.9% Mo_2C/Al_2O_3	0.026	44.8	32.8	19.0	3.4	0.40	1.58	81

[a] Turnover rate based on CO-titrated sites after 0.5 h on stream, with n-butane/H_2 ratio of 0.11 and n-butane conversion less than 8.8%.

[b] Rate $= k_0 \exp(E_a/RT)[n\text{-butane}]^m[H_2]^n$, where k_0 is a constant.

with respect to H_2 and apparent activation energies E_a of 120–200 kJ mol^{-1} [9]. Hence strong positive orders in H_2 and the low E_a values observed for Mo and Mo_2C are different from those observed for group VIII metals.

In CO hydrogenation, Mo_2C/Al_2O_3 also showed a v_t value higher than that for Mo/Al_2O_3 (table 4). However, product distribution (table 4) was again very similar in both cases but different from those for group VIII metals. Namely, Mo and Mo_2C produced a large amount of CO_2, reflecting their high activity in water–gas shift reaction. They also produced large amount of C_2–C_4 hydrocarbons consisting mostly of paraffins. The difference in the C_2H_6/C_2H_4 ratio is a result of the higher CO conversion on Mo_2C/Al_2O_3 (0.8%) than on Mo/Al_2O_3 (0.2%).

3.3. ACTIVE PHASE OF MOLYBDENUM CATALYSTS WORKING UNDER CARBON-CONTAINING REACTANTS

In agreement with the results of Burwell and coworkers, initially noncarbided molybdenum is an active catalyst for both reactions studied here. Poor activity may have been due to incomplete reduction or contamination [7]. Noncarbided Mo is very susceptible to contamination by O_2, CO, H_2O and even to some extent by N_2 [6]. Carburization of Mo provides an even better catalyst, although the effect is not as dramatic as in the observation by Sinfelt and Yates [3], whose Mo may have been only partially reduced at 870 K.

The most interesting observation in the comparison of the supported Mo and Mo_2C catalysts appears to be the striking similarity in their product distribution and kinetic parameters in both *n*-butane hydrogenolysis at 510 K and CO hydrogenation at 570 K. To explain this finding, the structure of Mo/Al_2O_3 was monitored by XAFS before and after the catalytic reaction. Since results for *n*-butane hydrogenolysis have already been published [7], only the data for CO hydrogenation are presented here in fig. 4 and table 5. The XANES spectrum of the fresh Mo/Al_2O_3 shows a large separation of two broad post-edge peaks, characteristic of Mo. Following 2 h of reaction, the high energy peak in the spectrum of Mo/Al_2O_3 shifts

Table 4
CO hydrogenation at 570 K and atmospheric pressure

Catalyst	v_t [a] (s^{-1})	HC selectivity [b]	Methane selectivity [c]	C_2/C_1 [d]	C_2H_6/C_2H_4 [e]
2.7% Mo/Al_2O_3	0.009	0.5	0.5	0.4	2.1
2.9% Mo_2C/Al_2O_3	0.040	0.5	0.4	0.4	7.5

[a] Turnover rate based on CO-titrated sites after 0.5 h on stream, with H_2/CO ratio of 3, and CO conversion of less than 1%.

[b] Fraction of CO converted to hydrocarbons (HC). Remaining CO was converted to CO_2.

[c] Weight fraction of CH_4 in hydrocarbon products.

[d] Weight ratio of C_2H_6 and C_2H_4 to CH_4.

[e] Molar ratio of ethane to ethylene.

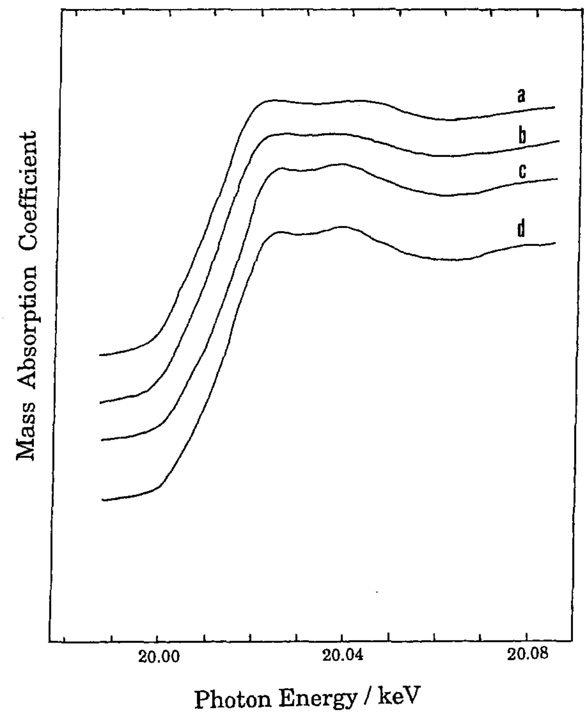


Fig. 4. Change in XANES spectra during CO hydrogenation at 570 K for 2 h. Fresh Mo/Al_2O_3 (a), Mo/Al_2O_3 after reaction (b), fresh Mo_2C/Al_2O_3 (c), and Mo_2C/Al_2O_3 after reaction (d).

closer to the lower energy peak, thus making the spectrum very similar to the Mo_2C spectrum. The carburization of the same sample in CH_4/H_2 at 950 K makes the XANES features identical to those found for Mo_2C powder spectrum. These features are unaltered during reaction. The results of EXAFS are also summarized in table 5. The EXAFS of Mo/Al_2O_3 showed negligible change during reaction. The carburized catalyst shows the EXAFS features of bulk Mo_2C and remains unchanged during reaction.

The XAFS data demonstrate that the initially noncarbided Mo clusters trans-

Table 5
Change in structural parameters during CO hydrogenation at 570 K for 2 h

Catalyst	Interatomic distance (pm)		Coordination number	
	Mo–C	Mo–Mo	Mo–C	Mo–Mo
2.7% Mo/Al_2O_3, fresh	207	280	2	4
2.7% Mo/Al_2O_3, after reaction	211	278	2	4
2.9% Mo_2C/Al_2O_3, fresh	209	295	2	6
2.9% Mo_2C/Al_2O_3, after reaction	211	295	2	6

form progressively into Mo_2C during the catalytic reactions of carbon-containing gases. In related work, Overbury showed that noncarbidic surface carbon formed by dissociative adsorption of ethylene on Mo(111) was transferred to a subsurface position to form a carbide near 600 K [10]. Hence, the activity and product distribution observed for MO/Al_2O_3 must be due to the carbide as the catalytic reaction proceeds.

The last question then is to explain why the value of v_t for Mo clusters is a few times lower than that for Mo_2C. This is true not only for *n*-butane hydrogenolysis (table 3) but also for CO–H_2 reactions (table 4). In the case of *n*-butane hydrogenolysis, this situation was explained by the deposition of carbonaceous residues on the Mo surface before it was carbided [7]. Is this explanation also valid for CO–H_2 reactions? One difficulty is that alkane hydrogenolysis is a structure sensitive reaction on metals while CO–H_2 reactions are structure insensitive as established by studies on single crystals of metals [11]. Thus, at first glance, it would seem that a given amount of carbon deposition on Mo would depress v_t for hydrogenolysis on Mo more than for CO–H_2 reactions as compared to the values of v_t on Mo_2C. This is not so. But another factor must be considered. The evolution of v_t with time on stream was quite different for both reactions. In the case of hydrogenolysis, the rate stabilized itself at about 70% of initial value. This is because the "coke" producing reactions are suppressed as the rate of hydrogenolysis is decreasing because of the elimination of ensembles at the surface of the metal. Thus, coking stops when the rate of hydrogenolysis stabilizes. By contrast, in CO–H_2 reactions, the rate decreased rapidly to 40% of its initial value in the first 10 min, but continued to decrease slowly but steadily after that. Therefore it is possible that more carbonaceous residues were formed on Mo during equal period of CO–H_2 reactions than during hydrogenolysis. In this way, even though a given amount of carbonaceous residues would depress the rate of hydrogenolysis more than that of CO–H_2 reactions, the situation could be very similar for both reactions as observed, if the amount of carbonaceous residues were larger for CO–H_2 reactions than for hydrogenolysis.

In any event, as was concluded earlier [7], the active catalytic phase of molybdenum appears to be molybdenum carbide, as evidenced by XAFS, and also by the very similar selectivity and/or kinetic parameters obtained for both reactions on both Mo and Mo_2C clusters.

4. Conclusion

Both Mo and Mo_2C clusters exhibit similar turnover rates and nearly identical product distributions in *n*-butane hydrogenolysis at 510 K and CO hydrogenation at 570 K. For both reactions, noncarbided Mo clusters are transformed progressively into Mo_2C by carburization during the reactions as shown by in situ XAFS data.

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