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Kinetics of Formation of Molybdenum Carbide (Mo_2C) by Reaction between Carbon Monoxide and Molybdenite or Molybdenum

P. Suryaprakash Rao†, T. R. Mankhand and P. M. Prasad

Centre of Advanced Study in Metallurgy, Department of Metallurgical Engineering,
Institute of Technology, Banaras Hindu University, Varanasi 221 005, India

Investigations have been conducted on the reactions between molybdenite (technical grade MoS_2) and molybdenum metal powders with carbon monoxide in the temperature range 1123 to 1298 K. The rates of both MoS_2+CO and Mo+CO reactions have been found to increase significantly with temperature. XRD examination of the reaction products reveal the formation of Mo_2C directly by the reduction-carburization of MoS_2. The said carbide is also observed to be the dominant product of molycarburization (Mo+CO) reaction. The MoS_2 conversion has been found to be a slow process, whose results fit into a linear rate law with a high activation energy value (230 kJ mol^{-1}). In contrast, the carburization of Mo powder has been observed to be a fast process, initially rapid upto about 30% conversion and subsequently progress in accordance with parabolic kinetics (low activation energy values of 76 and 33.5 kJ mol^{-1}, respectively for initial and parabolic stages). Since no elemental Mo has been detected in the products of the MoS_2+CO reaction, it is not possible to separate it from the subsequent *in-situ* molycarburization (Mo+CO) reaction. An indepth analyses of the findings indicate that the linear kinetics and the high activation energy value (230 kJ mol^{-1}) determined for the overall reduction-carburization of MoS_2 may pertain to the pre-requisite reaction (namely, $MoS_2+2CO=Mo+2COS$) itself.

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I. Introduction

Traditional methods of producing molybdenum carbide from molybdenite concentrate suffer from many inherent limitations such as several processing steps, expensive SO_2 pollution abatement measures, low recoveries and need for residue processing(1)-(3). A few new routes based on molten salt electrowinning from complex baths have also been reported(4)-(6) from time to time by several researchers but no electrowinning route has yet been commercialized. Because of the growing interest in molybdenum carbide which finds numerous applications(1)(2)(7)-(9) (*e.g.* speciality cutting tools, heat-resistant hard alloys, catalyst, etc.), the authors have taken up investigations on an alternative method for preparing the said carbide, In an earlier communication(10), we suggested a simple and non-polluting route that may be useful for the direct (single step) synthesis of Mo_2C from molybdenum sulphide (MoS_2) by its carbon monoxide reduction in the presence of lime. Our researches on the MoS_2+CaO+CO reaction have indicated that it is feasible to achieve 99% reduction-carburization of MoS_2 and prepare a carbide product of at least 98% purity(10)(11). Hence it was considered interesting and useful to understand the kinetics and mechanism of the reduction-carburization of molybdenite by carbon monoxide.

The lime-scavenged reduction of molybdenite (MoS_2) by carbon monoxide in the presence of lime resulting in Mo_2C formation can be represented by the equation:

$$2MoS_2(s)+4CaO(s)+6CO(g) = Mo_2C(s)+4CaS(s)+5CO_2(g). \quad (1)$$

The above reaction can be considered to be an appropriate sum of two successive solid-gas reactions given below:

$$2MoS_2(s)+6CO(g) = Mo_2C(s)+4COS(g)+CO_2(g) \quad (2)$$

and

$$CaO(s)+COS(g)=CaS(s)+CO_2(g). \quad (3)$$

By itself the reduction-carburization reaction (2) is highly unfeasible thermodynamically under standard conditions but becomes feasible on account of the consecutive lime-sulphidation reaction (3). For example at 1200 K, ΔG^0 values were calculated (from the data taken from Refs. (12) and (13)) to be +348.5, −90.0 and −11.6 kJ mol^{-1}, respectively for reactions (2), (3) and (1). Lime is a potent scavenger for sulphur bearing gases and the CaO(s)+COS(g) reaction (3) has been reported to be very rapid in practice(14). Further, reaction (2) itself consists of two consecutive gas-solid reactions viz.,

$$MoS_2(s)+2CO(g)=Mo(s)+2COS(g) \quad (4)$$

and

$$2Mo(s)+2CO(g)=Mo_2C(s)+CO_2(g). \quad (5)$$

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† QIP Fellow from REC, Warangal 506 004, India.

Literature survey on the carburization of molybdenum shows that kinetic information/data is available only on the reactions between Mo sheets or powder with graphite(15), CH_4+H_2(16), CH_4 in the presence of graphite(17) and on the chemical vapour depositon (CVD) of Mo on graphite(15). Thus the present paper deals with kinetic investigations on the direct carburization of molybdenite (MoS_2) as well as molybdenum powders by CO gas.

II. Experimental

1. Materials

Molybdenite: Technical grade Climax molybdenite powder (procured from M/s Minworth Metals Ltd., U.K.) analyzing 58.8% Mo, 39.44% S, 0.17% Fe, 1.00% C and 0.27% insolubles was used. 98.5% of it is of minus 100 μm size.

Molybdenum powder of over 99.9% purity (supplied by M/s Miller Thermal Inc., U.S.A.) whose average particle size was 4–6 μm was used.

Carbon monoxide gas was generated by CO_2-charcoal (devolatilized) reaction at 1323 K as described in an earlier publication by Mohan, Mankhand and Prasad(18).

2. Procedure

The carburization experiments on the MoS_2 as well as Mo powders were conducted under pre-planned experimental conditions using a locally fabricated thermogravimetric (TG) assembly. In each test run the sample pan was connected to a CAHN-1000 recording microbalance. Initially the TG system was flushed with high purity nitrogen gas and after attainment of the required temperature, CO gas was admitted into the experimental set-up. The progress of each reaction [$MoS_2(s)+CO(g)$ or $Mo(s)+CO(g)$] under study was followed by mass change measurements. The procedures employed are essentially the same as those described in our earlier publications(19)(20). Effects of CO gas flow rate, temperature and time were investigated.

3. Fraction reacted

For estimating the fraction of MoS_2 or Mo reacted, it is necessary to know what type of products are formed in our carburization studies. Hence phase identification studies were carried out on the reactant solids as well as the reacted products by employing the X-ray diffraction (XRD) technique. JEOL-8030 computer controlled powder diffractometer was used.

Typical results of the XRD tests are given in Table 1. Besides unreacted MoS_2, the products of MoS_2+CO reaction (2) are seen to consist of Mo_2C; moreover no elemental Mo or the other carbide MoC have been detected. On the other hand, XRD tests on the products of the Mo+CO reaction indicate that the metal powder is converted essentially to Mo_2C and a little MoC is also formed. Such observations are understandable because MoC is unstable and decomposes readily to Mo_2C at higher temperatures(21)(22) (equilibrium constant at 1200 K for the reaction $2MoC=Mo_2C+C$ has been calculated to be 14.2).

Table 1 XRD studies on the reacted products.
CO gas flow rate: 8.33 $cm^3\,s^{-1}$

Temp. (K)	Time (ks)	Fraction converted	Phases Identified			
			MoS_2	Mo	Mo_2C	MoC
A. MoS_2+CO reaction						
1173	21.6	0.055	*vs*	*nd*	*nd*	*nd*
1223	21.6	0.083	*vs*	*nd*	*vw*	*nd*
1248	21.6	0.162	*vs*	*nd*	*w*	*nd*
1273	21.6	0.206	*vs*	*nd*	*m*	*nd*
B. Mo+CO reaction						
1173	5.4	0.90	—	*w*	*vs*	*vw*
1223	6.0	0.99	—	*nd*	*vs*	*vw*
1248	5.4	0.99	—	*nd*	*vs*	*vw*
1273	4.2	>0.99	—	*nd*	*vs*	*vw*

Note: Intensities of XRD peaks have been comparatively ranked
vs: very strong, *s*: strong, *m*: medium, *w*: weak, *vw*: very weak, *nd*: not detected.

From eq. (2), it is clear that the conversion of two moles of MoS_2 to one mole of Mo_2C results in a net mass loss equivalent to the removal of four atoms of sulphur and gain of one atom of carbon; the net mass loss will be 116.27 g for every 128.28 g sulphur in the MoS_2 sample. The molybdenite used in our studies contains 39.44% S. Hence the theoretically expected maximum mass loss is calculated to be 35.75% of the mass of MoS_2 used in any test run. On the other hand in the case of CO carburization of Mo metal powder, if the reaction proceeds ideally as per the stoichiometry dictated by reaction (5), there will be a mass gain of one atom of carbon for every two atoms of Mo. Hence the maximum mass gain will be approximately 6.26% of the mass of Mo used (approx. because of the small presence of MoC).

In view of the above, the fraction of MoS_2 converted to carbide (R) and the fraction of Mo carburized (R') have been calculated by using the relationships given below.

Reduction-carburization of molybdenite (MoS_2)

$$R=\frac{W_e}{0.3575W_s}$$

Carburization of molybdenum metal powder

$$R'=\frac{W_e}{0.0626W_s}$$

where

W_s: mass of sample (MoS_2 or Mo) used in any test run.
W_e: experimentally recorded mass change in the concerned test run.
R, R': both are dimensionless quantities.

III. Results

Results of the studies on the direct reduction-carburization of MoS_2 by CO have been taken up first followed by those on the carburization of Mo powder by CO. In both cases the influences of CO flow rate and temperature on the concerned conversion process have been discussed. Results depicting temperature dependence have been analyzed for determining the probable rate laws and the activation energies associated with them assuming that the unreacted core model for spherical particles can be applied to the molybdenite as well as molybdenum powders. Kinetic results of the studies on $MoS_2(s)+CO(g)$ and $Mo(s)+CO(g)$ have then been discussed together to understand rate-governing mechanism of the reduction-carburization of MoS_2.

1. Direct conversion of MoS_2 by CO

(1) Effect of CO flow rate

The effect of carbon monoxide flow rate on the direct conversion of molybdenite powder to Mo_2C is shown in Fig. 1. It is obvious that the MoS_2 conversion rate increases appreciably with gas flow rate upto a limiting value of 8.33 $cm^3\ s^{-1}$ beyond which there is no significant improvement.

(2) Effect of temperature

Results on the influence of temperature on the direct conversion of MoS_2 by carbon monoxide (flow rate 8.33 $cm^3\ s^{-1}$) are presented in Fig. 2. The fraction of MoS_2 converted has been found to increase with temperature upto 1298 K (maximum temperature of this study). The pronounced effect of temperature is evident from the fact that under identical conditions, only 5.5% of MoS_2 has been converted at 1173 K in 21.6 ks whereas 22.2% conversion has taken place by increasing the temperature to 1298 K in the same treatment time.

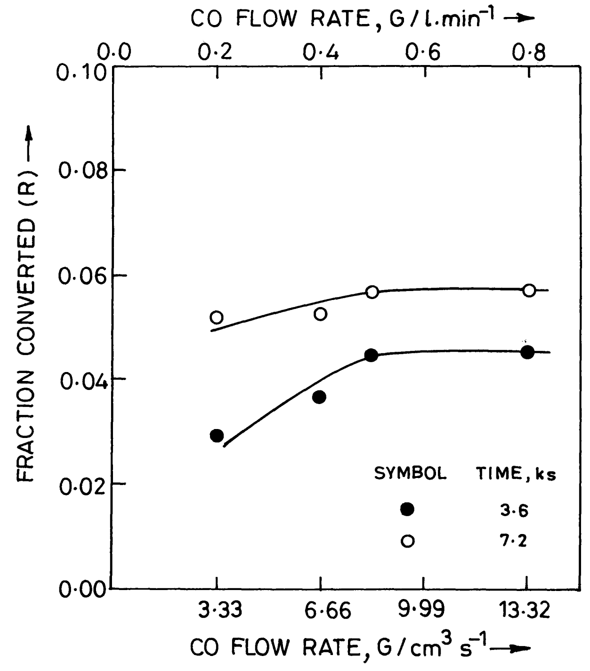

Fig. 1 Effect of CO flow rate on MoS_2+CO reaction at 1223 K.

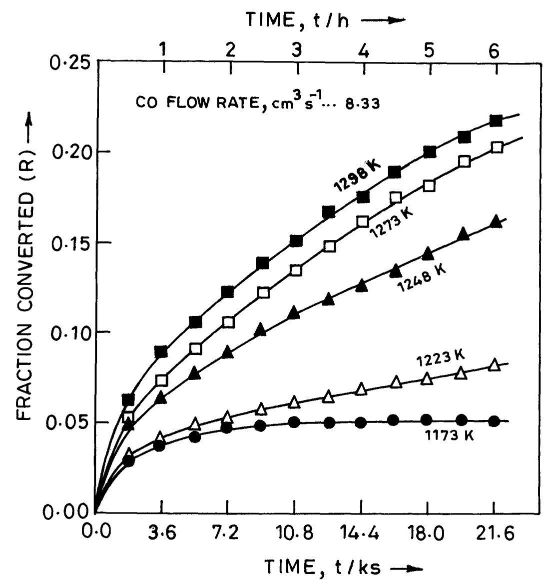

Fig. 2 Effect of temperature on MoS_2+CO reaction.

(3) Temperature dependence

The MoS_2 conversion results have been tested for the observance of the Jander's linear rate law:

$$[1-(1-R)^{1/3}]=k_1t$$

where

R = fraction of MoS_2 converted
k_1 = specific rate constant
t = time of reaction.

From Fig. 3 it is clear that the above rate law is valid upto all levels of reduction tested in this work. Further, a plot of $\log k_1$ vs $1/T$ (Fig. 4) indicates a good observance of Arrhenius relationship, the regression analysis of which yields an activation energy of 230±4 $kJ\ mol^{-1}$ for the reduction-carburization of MoS_2 by CO gas.

2. Carburization of Mo powder by CO

(1) Effect of CO flow rate

The influence of CO flow rate on the carburization of

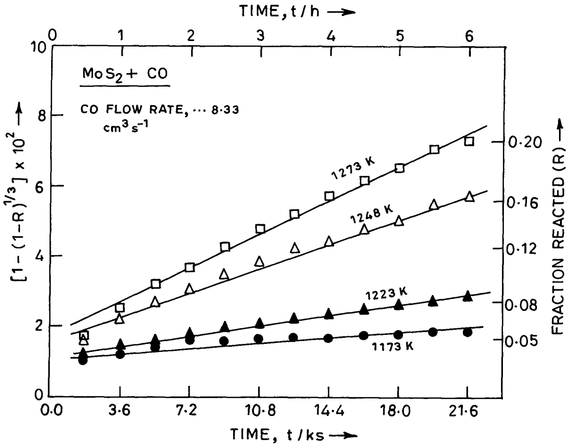

Fig. 3 $[1-(1-R)^{1/3}]$ vs time plots for MoS_2+CO reaction.

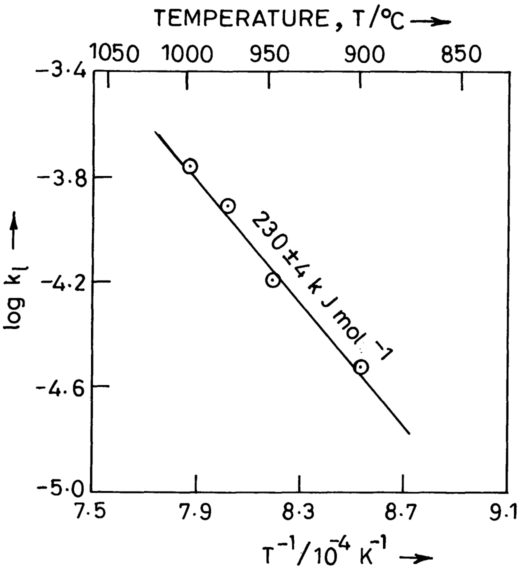

Fig. 4 Arrhenius plot for the MoS_2+CO reaction.

Mo powder at 1173 K is presented in Fig. 5. The conversion rate is seen to increase substantially with CO gas flow rate upto a limiting value of 8.33 $cm^3\ s^{-1}$. Increased levels of Mo carburization achieved using high CO gas flow rates may be attributed to the decrease in gas boundary layer resistance. However, we note that further increase in gas flow rate (to say, 13.33 $cm^3\ s^{-1}$) does not result in any appreciably improved conversion.

(2) Effect of temperature

Results on the effect of temperature on Mo conversion by CO (flow rate 8.33 $cm^3\ s^{-1}$) are given in Fig. 6. Even at a low temperature of 1123 K, over 92% conversion took place within 5.4 ks and it has been found to increase further with temperature upto 1273 K. For achieving near complete conversion (over 99%) a treatment time of 4.2 ks at 1273 K is considered adequate.

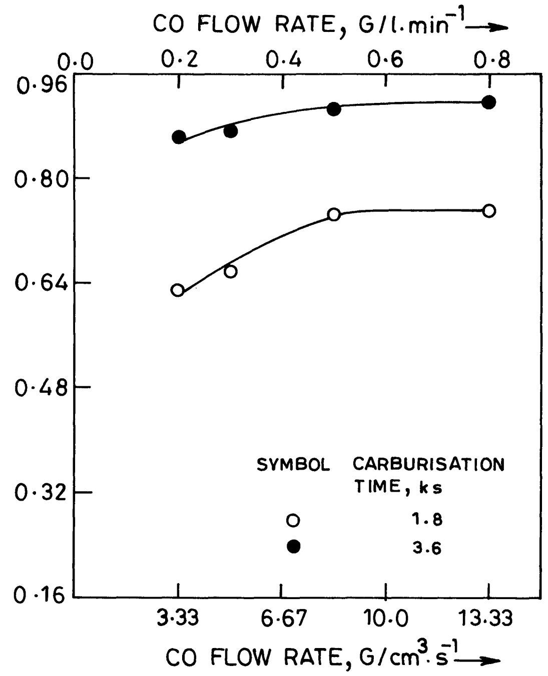

Fig. 5 Effect of CO flow rate on Mo+CO reaction at 1173 K.

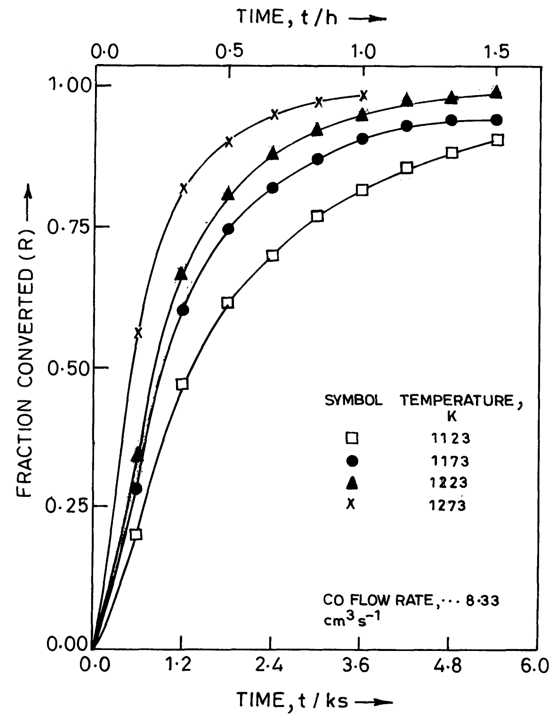

Fig. 6 Effect of temperature on Mo+CO reaction.

(3) Temperature dependence

It is interesting to note from Fig. 6 that at all temperatures of our study the Mo powder gets carburized very rapidly in the beginning at all temperatures of this study. For the initial regime (~30% conversion) an activation energy of about 76 kJ mol^{-1} has been estimated. From Fig. 7 it is obvious that results of Mo powder carburization fit into the modified parabolic rate law (Cranck, Ginstling and Brounshtein equation) given below:

$$[1-(2/3)R'-(1-R')^{2/3}]=k_p t$$

where

R' = fraction of Mo carburized
k_p = specific rate constant
t = time of reaction.

Further a plot of log k_p vs $1/T$ (Fig. 8) is seen to be linear and by regression an activation energy value of 33.5 kJ mol^{-1} has been obtained for the CO-carburization of Mo powder.

IV. Discussion

The above results show that molybdenite (MoS_2) as well as molybdenum powders can be carburized by carbon monoxide to form molycarbide (Mo_2C). As stated earlier, the direct formation of Mo_2C from MoS_2 can be represented by the overall reaction

$$2MoS_2(s)+6CO(g) = Mo_2C(s)+4COS(g)+CO_2(g). \quad (2)$$

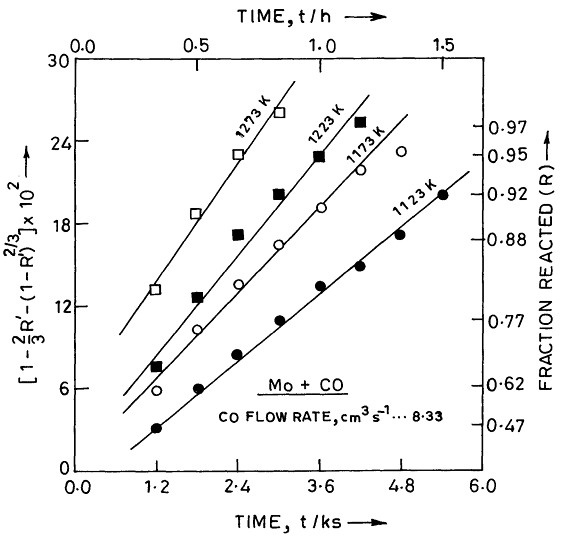

Fig. 7 $[1-(2/3)R'-(1-R')^{2/3}]$ vs time plots for Mo+CO reaction.

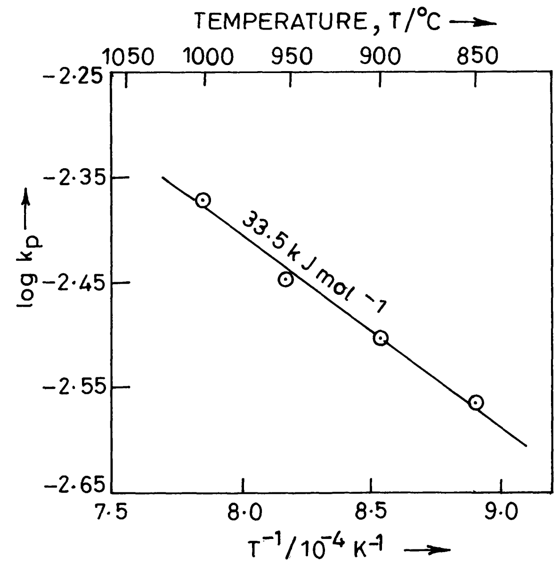

Fig. 8 Arrhenius plot for Mo+CO reaction.

Since no elemental molybdenum has been detected in the products of the said reaction, it does not seem possible to isolate the sulphide reduction (MoS_2+CO reaction resulting in Mo metal) from the molycarburization (Mo+CO) process. The two concerned consecutive solid-gas reactions that constitute the above overall reaction are recapitulated below:

$$MoS_2(s)+2CO(g)=Mo(s)+2COS(g) \qquad (4)$$

and

$$2Mo(s)+2CO(g)=Mo_2C(s)+CO_2(g). \qquad (5)$$

Thermodynamic considerations indicate that, under standard conditions, both reactions (2) and (4) are not feasible, reaction (5) may take place (ΔG^0 values at 1200 K are +348.5, +179.9 and −11.3 kJ mol^{-1}, respectively for reactions (2), (4) and (5)). The present studies show that the molycarburization reaction (5) proceeds rapidly and goes to near completion at 1273 K in just 3.6 ks. On the other hand, the overall MoS_2+CO reaction (2) has been found to be kinetically slow, *e.g.*, only 22% conversion at 1273 K even after a long treatment time of 21.6 ks. Thus the Mo+CO reaction (5) is not only highly feasible thermodynamically (ratios of equilibrium constants $K_5/K_2=4.57\times 10^{15}$ and $K_5/K_4=2.1\times 10^8$ at 1200 K), but also very much faster in practice under identical conditions (ratio of apparent reaction rates at 1173 K calculated to be $k_5/k_2=20.4$; see Table 2). Therefore, the progress of MoS_2 reduction-cum-carburization reaction (2) must be ascribed to the fact that being a solid-gas reaction, the rapid *in-situ* conversion of product Mo to Mo_2C as per reaction (5), virtually amounting to the removal of the product Mo of reaction (4), must be driving reaction (4) forward on account of the operation of the LeChatelier's principle.

The present work shows that the MoS_2 conversion data for the overall reaction (2) fits into a linear rate law with a high activation energy value (230 kJ mol^{-1}). In constrast to this, the molycarburization reaction (5) has been observed to be relatively fast upto about 30% conversion and thereafter progress in accordance with parabolic kinetics which is understandable because the molar volume ratio of the carbide product to reactant Mo metal is closer to unity (see Table 2). At this juncture we note that the formation of Mo product on MoS_2 as per reaction (4) must obey linear kinetics on account of the very low molar volume ratio of Mo/MoS_2 (0.282). Even the direct conversion of MoS_2 to Mo_2C as per reaction (5) does not seem to alter the kinetics of the $MoS_2(s)+CO(g)$ reaction because though the molar volume ratio in this case (0.343 for $Mo_2C/2MoS_2$) is slightly higher than that for reaction (4), it is still not adequate. Thus whether CO reduction of molybdenite results in moly metal or molycarbide, in either case the product layers formed on the reactant MoS_2 particles are bound to be porous and hence expected to conform to linear kinetics.

According to the traditional chemical kinetics, generally the rates of consecutive reactions or steps may be governed by the rate of the slower one among them. Based on this premise, it appears that the progress of the reduction-carburization of MoS_2 by CO will be governed by the rate of the former, viz. MoS_2 reduction reaction (4). Moreover, the consecutive solid-gas reaction (5) between Mo+CO which is characterized by low activation energy values (76 and 33.5 kJ mol^{-1}, respectively, for the initial and the subsequent stages) is unlikely to be a bottle-neck to the overall progress of MoS_2 carburization. In the light of such an analysis, one may conclude that the estimated activation energy value (230 kJ mol^{-1}) and the linear rate law (indicative of phase-boundary or chemical reaction control) may pertain to reaction (2), namely, MoS_2+CO reaction resulting in moly metal formation.

V. Conclusion

(1) The reaction between $MoS_2(s)$ and CO(g) results

Table 2 Summary of the kinetic studies and other relevant aspects.

Reactions of interest:

$$2MoS_2(s)+6CO(g)=Mo_2C(s)+4COS(g)+CO_2(g) \qquad (2)$$

$$MoS_2(s)+2CO(g)=Mo(s)+2COS(g) \qquad (4)$$

$$2Mo(s)+2CO(g)=Mo_2C(s)+CO_2(g) \qquad (5)$$

	Item	Reaction (2)	Reaction (4)	Reaction (5)
1.	ΔG^0 at 1200 K, kJ mol^{-1}	+348.5	+179.9	−11.3
2.	Equil. Const. (K) at 1200 K	6.76×10^{-16}	1.48×10^{-8}	3.09
3.	Reaction product (identified by XRD)	Mo_2C	—	Mo_2C (dominant)
4.	Molar volume ratio (product/reactant)	0.343 ($Mo_2C/2MoS_2$)	0.282 (Mo/MoS_2)	1.217 ($Mo_2C/2Mo$)
5.	Rate law observed	Linear	—	Parabolic
6.	Activation energy kJ mol^{-1}	230	—	33.5*
7.	Fraction reacted employing CO flow rate of 8.33 cm^3 s^{-1}			
	(a) at 1273 K in 3.6 ks	0.070	—	0.99
	(b) at 1173 K in 6 ks	0.045	—	0.92
8.	Apparent reaction rate at 1173 K ($k=R/t$), mol·s^{-1}	7.5×10^{-6}	—	1.53×10^{-4}

*76 kJ mol^{-1} for the initial carburization of Mo (rapid upto about 30%).

in the formation of Mo_2C directly. No elemental Mo or the other carbide (MoC) have been detected in the reaction products.

(2) Reduction-carburization of molybdenite (technical grade MoS_2 powder) by CO has been found to be a slow process *e.g.* only 22% conversion even at high temperature (1298 K) and long treatment time (21 ks).

(3) Carburization of Mo powder by CO gas has been observed to be relatively fast. Near complete (99%) conversion takes place at 1273 K in a short duration of 4.2 ks only.

(4) Results of the MoS_2+CO reaction have been found to fit into linear rate law with an activation energy of 230 kJ mol^{-1}. On the other hand carburization of Mo powder has been observed to be initially rapid (upto about 30% conversion; apparent activation energy estimated to be 76 kJ mol^{-1}) and thereafter progress according to parabolic kinetics with a low activation energy of 33.5 kJ mol^{-1}.

(5) Based on a critical analyses of the results on the MoS_2+CO and the Mo+CO reactions, the progress of the reduction-carburization of MoS_2 by CO gas is considered to be governed by the rate of the molybdenite reduction reaction (MoS_2+CO) resulting the initial formation of Mo metal which then gets carburized *in-situ* (Mo+CO reaction) to form the product carbide.

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