Reaction kinetics of direct hydrogen reduction of molybdenum disulfide in the presence of lime: A single pellet experimental investigation

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ABSTRACT

Recovery of pure molybdenum from molybdenum disulfide (MoS_2) was studied by following the progress of reduction of molybdenum disulfide with hydrogen in the presence of calcium oxide. The reaction was conducted on solid reactants comprised in a pellet and monitored using thermogravimetric method. The influence of important parameters such as temperature (1123–1373 K), thickness of the pellet (2–11 mm), concentration of hydrogen, molar mixing ratio of the solid reactants and purity of the starting MoS_2, on the reaction was experimentally investigated. Lime was found to enhance the reduction rate of MoS_2 significantly while substantially reducing emissions of hydrogen sulfide.

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1. Introduction

Molybdenum is a refractory metal characterized by high strength of the inter-atomic bond and consequently by a high melting point (over 2700 K), sustained high temperature strength and other physical properties such as high thermal conductivity, low specific heat and low coefficient of expansion. The conventional method for producing this important metal is based upon roasting molybdenite concentrate, followed by purification of the resultant oxide (MoO_3), and a final step consisting of reduction of purified molybdenum oxide to metallic Mo, using hydrogen [1]. Overall the process suffers from serious disadvantages such as complex-multi-steps sequence and emissions of gaseous sulfur dioxide arise from sulfide raw materials such as chalcopyrite and chalcocite. These factors have motivated several researchers to consider new and alternative processes to produce Mo metal from molybdenite concentrate. Among the proposed methods, leaching [2–4], electro-oxidation [5–10], bioleaching [11–13], and chlorination [14,15], appear to be potential routes for treating molybdenite concentrates. However, another concept for extraction of metals from their sulfides is their direct reduction in the presence of a suitable metal oxide with desulfurizing capability [16–23]. This general scheme, for reduction of molybdenum sulfide with lime as the desulfating metal oxide [16–19] can be represented by the following reactions:

$$MoS_2 + 2H_2 = Mo + 2H_2S \tag{1}$$

$$2H_2S + 2CaO = 2CaS + 2H_2O \tag{2}$$

Afsahi et al. [24] reported that molybdenum sulfide particles (using 5 mg powder samples without presence of any lime) can be completely reduced to molybdenum metal at a temperature of 1173 K within a short time of 8 min at a hydrogen flow rate of 700 ml min^{-1}. They also performed experiments on a thin cylindrical pellet of MoS_2 of 0.26 mm thickness [25] and reported that time for completion of the reaction (1) was 90 min using otherwise the same conditions as in ref. [24]. It should be emphasized that short reaction time in ref. [25] has been arisen from lack of pellet form and the very low amount of molybdenum sulfide as fine powders in the experiments.

The following reaction is the summation of reactions (1) and (2).

$$MoS_2 + 2CaO + 2H_2 = Mo + 2CaS + 2H_2O \tag{3}$$

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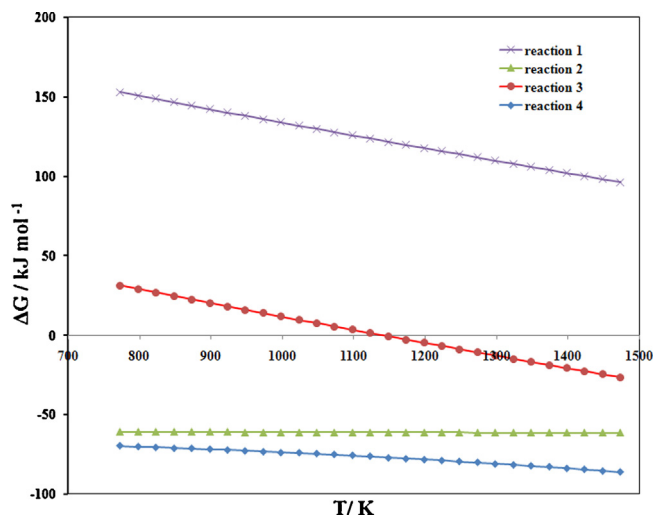E-mail address: afsahi@uk.ac.ir (M.M. Afsahi).

Fig. 1. Ellingham lines for reactions (1)–(4).

A side reaction, reaction (4), consecutively with reaction (3) can take place and as a result, calcium molybdate, instead of molybdenum metal can be formed in the final product.

$$MoS_2 + 3CaO + H_2O(g) = CaMoO_4 + 2CaS + H_2(g) \qquad (4)$$

Kay and Habashi reported 82 and 40 percent conversion for reaction (3), at low ratio of the solids (1:1 ratio) and at low temperatures (800 °C and 1:1 ratio) respectively [16,17].

To the authors' knowledge, Mankhand and Prasad reported the only other published study on reduction of MoS_2 by hydrogen in the presence of lime whereby the solid reactant is completely converted to metallic molybdenum [19]. Their work was related to reduction experiments on a mixture of lime and molybdenite powder. The present work is the first research on the reduction of molybdenum sulfide in presence of lime in the pellet form.

Prasad et al. [26] did not report finding any calcium molybdate in phase identification of their reacted samples as analysis by XRD at 1173 K. They used high grade and low-grade molybdenite concentrate with commercial grade lime in the form of fine powders for the reaction. It is quite possible that their reaction conditions were such to avoid the molybdate phase region; either because the fine powder reactants and the gases were ultra-dry or contact between water vapor and the powders was negligible. Thus conditions for forming molybdenum without any molybdate were met.

2. Thermodynamic aspects

Equilibrium constant for reducing molybdenum disulfide increases by 6 orders of magnitude at 1273 K, in presence of calcium oxide as the sulfur-scavenging agent as in reaction (3), in comparison with direct reduction shown in (1), from a value of 2.5×10^{-5} to 2.8 [27].

The graphical representation of change in Gibbs free energy versus temperature for reactions (1)–(4) [27] is shown in Fig. 1.

As can be noted in Fig. 1, reaction (3) is thermodynamically favorable only for temperatures greater than 1143 K. Therefore, in order to successfully produce metallic Mo, experiments should be carried out at temperatures >1143 K. Given that water vapor is produced during reaction (3), and that reaction (4) is thermodynamically favorable at all temperatures, it is crucial to determine the thermodynamic conditions that will favor the formation of molybdenum metal rather than calcium molybdate. Phase stability diagram, depicting the phase regions for metallic Mo and for the calcium molybdate, arising from reactions (3) and (4) is shown in Fig. 2 within a temperature range of 1153–1473 K and ratios of H_2O/H_2 of $10–10^{-5}$.

In the bottom part of the figure, below the line for reaction (3) as highlighted by the hatched part is the stable region for molybdenum formation and the hatched part above the line for reaction (4) identifies the stable region for the calcium molybdate phase. As can be observed from Fig. 2, at a temperature of 1153 K, if partial pressure of H_2O in the pellet is higher than hydrogen partial pressure, only calcium molybdate is produced and if partial pressure of hydrogen is more than 3160 times of water vapor, only molybdenum metal is produced. Therefore controlling the amounts of the
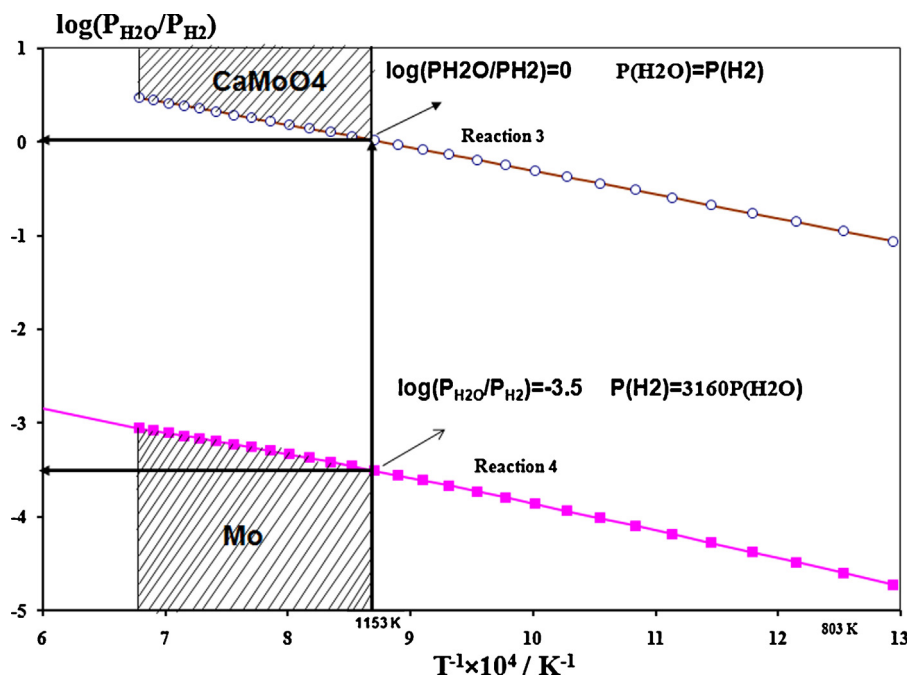

Fig. 2. Stability diagram for reactions (3) and (4).