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TEMPERATURE PROGRAMMED REDUCTION AND X-RAY DIFFRACTOMETRY STUDIES OF MoO_3 REDUCTION BY DIFFERENT CONCENTRATIONS OF CARBON MONOXIDE

(Kajian Penurunan Suhu Berprogram dan Pembelauan Sinar-X Terhadap Penurunan MoO_3 Menggunakan Kepekatan Karbon Monoksida Berbeza)

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Abstract

Reduction of molybdenum trioxide, MoO_3 to molybdenum dioxide, MoO_2 by using carbon monoxide, CO has been studied by temperature programmed reduction (TPR) and X-ray diffraction spectroscopy (XRD). The influence of carbon monoxide concentration on the reduction of MoO_3 have been investigated by comparing the reduction behaviour of MoO_3 to MoO_2 with 20 vol.% and 40 vol.% of CO concentration. The XRD results show that by using 20% of CO, reduction to MoO_2 takes place at 700°C in 60 minutes. However, by using 40% of CO, complete reduction to MoO_2 takes place at 700°C in only 30 minutes. Moreover, excess of CO results in the formation of molybdenum carbide, Mo_2C. It is suggested that by using CO, complete reduction from MoO_3 to MoO_2 gives two-steps reduction ($MoO_3 \rightarrow Mo_4O_{11} \rightarrow MoO_2$) with Mo_4O_{11} as an intermediate product. It can be concluded that the reducing behavior of MoO_3 is strongly dependent on the concentration of CO and reaction time.

Keywords: molybdenum trioxide, molybdenum dioxide, molybdenum carbide, carbon monoxide

Abstrak

Penurunan molibdenum trioksida, MoO_3 kepada molibdenum dioksida, MoO_2 dengan menggunakan karbon monoksida, CO telah dikaji menggunakan suhu penurunan berprogram (TPR) dan spektroskopi pembelauan sinar-X (XRD). Kesan kepekatan karbon monoksida terhadap penurunan MoO_3 telah dikaji dengan membandingkan kesan penurunan MoO_3 kepada MoO_2 menggunakan kepekatan karbon monoksida di antara 20 % dan 40 %. Keputusan XRD menunjukkan bahawa dengan menggunakan 20 % kepekatan CO, penurunan kepada MoO_2 berlaku pada suhu 700 °C dalam masa 60 minit. Walau bagaimanapun, dengan menggunakan 40 % kepekatan CO, penurunan lengkap kepada MoO_2 berlaku pada suhu 700 °C dalam masa hanya 30 minit. Selain itu, pendedahan kepada CO berlebihan akan menyebabkan pembentukan molibdenum karbida, Mo_2C. Adalah dicadangkan bahawa dengan menggunakan CO, penurunan lengkap daripada MoO_3 kepada MoO_2 terdiri daripada dua peringkat penurunan ($MoO_3 \rightarrow Mo_4O_{11} \rightarrow MoO_2$) dengan menghasilkan Mo_4O_{11} sebagai produk perantara. Ini boleh disimpulkan bahawa kelakuan penurunan MoO_3 adalah amat bergantung kepada kepekatan CO dan tempoh masa tindak balas.

Kata kunci: molibdenum trioksida, molibdenum dioksida, molibdenum karbida, karbon monoksida

Introduction

Metallic molybdenum offers excellent mechanical, thermal and electric properties and good corrosion resistance and is widely used as an alloying agent for manufacturing steels, cast irons and super-alloys to increase their mechanical strength, hardness, swiftness and resistance to corrosion and wearing [1]. Molybdenum powder is manufactured in two-step process starting from MoO_3. The first step reduction is exothermic in nature that is carried out at lower temperatures and involves transformation of MoO_3 to MoO_2. The second step reduction is endothermic in nature where MoO_2 is further reduced to Mo [2]. The reduction of MoO_3 to MoO_2 is a crucial stage in the production of metallic molybdenum. The reduction of MoO_3 to MoO_2 by using hydrogen consists of two reduction stages, namely $Mo^{6+} \rightarrow Mo^{5+}$ and $Mo^{5+} \rightarrow Mo^{4+}$ [3]. It seems that during the reduction of MoO_3, MoO_3 is first reduced to Mo_4O_{11}, then to MoO_2. Generally, pure molybdenum powders are produced using the well known two-step hydrogen reduction process [4]. The first step occurs in the temperature range of 450 - 650 °C and reduces the input material to MoO_2. The second step reduction is performed in the 1000 - 1100 °C range and this process results the formation of molybdenum metal. Nevertheless, usage of hydrogen as a reducing agent of MoO_3 reduction is expensive. Carbon is also used to reduce MoO_3 at elevated temperature (600 - 1200 °C) [5]. When metal oxides react with carbon, one of the reaction products would be gaseous and could be readily separated from the solid reaction products [6]. Therefore, it would be highly desirable to develop an alternative process to manufacture molybdenum. Reduction of MoO_3 by using CO as reductant was suggested as an alternative process for producing molybdenum. However, currently there are limited number of studies using CO for reduction of MoO_3 to MoO_2. In this study, we report the influence of CO content on the reduction behaviour of MoO_3. The isothermal and non-isothermal temperature programmed reduction (TPR) was performed to investigate the reduction behaviour of MoO_3 to MoO_2 by using CO as a reducing agent and later characterizing by XRD. Reduction of MoO_3 to MoO_2 by CO was suggested to follow two reduction stages which are shown as Equation 1 and Equation 2.

$$4MoO_3 + CO \rightarrow Mo_4O_{11} + CO_2 \tag{1}$$

$$Mo_4O_{11} + 3CO \rightarrow 4MoO_2 + 3CO_2 \tag{2}$$

Materials and Methods

Chemicals and raw materials

Commercial molybdenum trioxide, MoO_3 (AnalaR) powder was obtained from BDH Chemicals Ltd.. The gas mixture of carbon monoxide (CO) in nitrogen (20 and 40 vol % of CO) from Linde Malaysia was used.

Reduction of molybdenum trioxide

The commercially bought MoO_3 powder was calcined to remove impurities at 400 °C for 4 hours in air and then cooled to room temperature before undergo the reduction process by using a Micromeritic Autochem 2920 Chemisorption Analyzer apparatus. The completeness of the reduction of the powder was analysed using a temperature programmed reduction (TPR) method. In this experiment, a mixed gas of 20 % CO in 80 % nitrogen and 40 % CO in 60 % nitrogen was introduced into the apparatus at an effective flow rate of 20 mL/min. Then, temperature was increased from 40 to 700 °C with a heating rate of 10 °C/min and continued with isothermal reduction for 30 and 60 minutes at 700 °C.

Characterization method

The crystal structures of the MoO_3 powder before and after reactions were determined by XRD's Bruker AXS D8 Advance type. The radiation source used was Cu Kα (40 kV, 40 mA) to record the 2θ diffraction angles from 10° to 80° at wavelength ($\lambda = 0.154$ nm). For identification purposes of crystalline phase composition, diffraction patterns obtained were matched with standard diffraction data (JCPDS) file.

Results and Discussion

Thermodynamic Consideration Data

According to the thermodynamic analysis for the reduction of MoO_3 by using CO as a reducing agent to the reaction in Equation 3 and Equation 4, the Gibbs free energy changes due to reaction and the equilibrium composition of the oxides was calculated.

$$MoO_3 + CO \rightarrow MoO_2 + CO_2 \tag{3}$$

$$2MoO_2 + 6CO \rightarrow Mo_2C + 5CO_2 \tag{4}$$

From the calculation, the Gibbs free energy for formation of MoO_2 for reaction Equation 3 is $\Delta G_{(298\ K)} = -29.8$ kcal/mol which clearly indicates that the reaction is favorable. However, if excess CO is introduced to the reduction system, the formation of Mo_2C will take place according to reaction Equation 4 with the $\Delta G_{(298\ K)} = -34.9$ kcal/mol which means the reaction is very spontaneous.

Characterization by TPR

The reduction behaviour of MoO_3 to MoO_2 was studied using TPR. Figure 1 shows the TPR profile of non-isothermal reduction of MoO_3 until 700 °C continued with isothermal reduction at 700 °C for 60 minutes by using 20% and 40% of CO in nitrogen. Complete reduction to MoO_2 needs to complete at temperature lower than its melting point (795 °C) since MoO_3 will end up as an alloy fused mass when it is taken to its melting point [5].

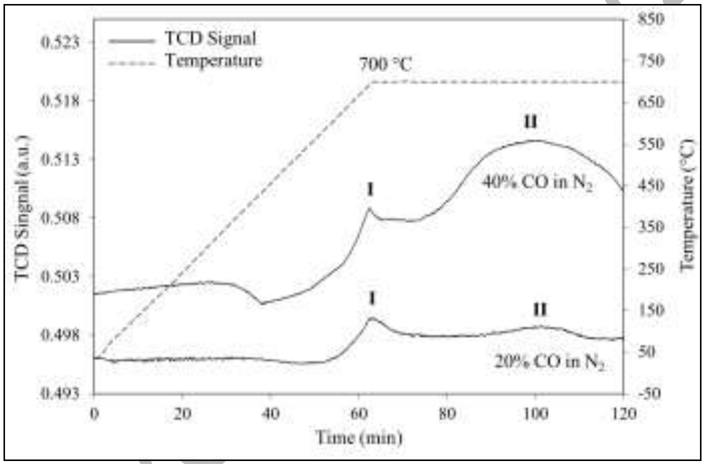

Figure 1. TPR profile of non-isothermal reduction of MoO_3 with 20% and 40% of CO in nitrogen at 40-700 °C and continued with isothermal reduction at 700 °C for 60 minutes.

The TPR profile of MoO_3 represents two reduction events (denoted I and II) which event I owing to peak displayed at early reaction time may regard to the reduction of MoO_3 to Mo_4O_{11}, while event II is subsequent to reduction steps of Mo_4O_{11} to MoO_2. However, with excess of CO supply to the reduction system, it brings to the formation of Mo_2C. The profile monitor CO consumption peaks by using 20 % of CO in nitrogen which started at about 530 °C was pointed to the first stage of reduction (event I) in agreement with Dang et al. [7], as mentioned that the MoO_3 is firstly reduced to Mo_4O_{11}, then to MoO_2. After continuing the reaction with isothermal reduction at 700 °C for 40 minutes, new broad peak is observed due to sample changes that occurred, reflecting to second stage reduction of Mo_4O_{11} to MoO_2.

Then, for the reduction of MoO_3 in 40 % of CO atmosphere, the TPR profile shows two peaks that reflect the two stages of reduction. By increasing concentration of CO to 40 % CO, the reduction peaks are leading to a low temperature to 420 °C, while the second peak can be monitored after 10 minutes, starting off with isothermal reduction at 700 °C. It seems that, the reduction of MoO_3 is observed to occur with a slight shift to lower temperature by increasing the concentration of CO. In addition, it shows that the reducing behaviour of MoO_3 is strongly dependent on the concentration of CO. The phases formed after the reduction by TPR were analysed by recording XRD pattern of the residual obtained after selected reduction condition.

Characterization by XRD

To investigate the reduction behaviour of MoO_3 by using different concentration of CO, the samples were collected and XRD patterns were measured. The XRD profile obtained in Figure 2 revealed the MoO_3 (JCPDS 74-7383) was not yet reduced to MoO_2 even after flowing with 20 % of CO until 700 °C. It is due to insufficient of CO and heat supply to the reaction. However, by flowing with 40% of CO the XRD patterns showed peaks that identified with MoO_2 phases (JCPDS 76-1807). From the results, the reduction of MoO_3 by using 20% and 40% of CO concentration shows two stages process ($MoO_3 \rightarrow Mo_4O_{11} \rightarrow MoO_2$) in respect to a trace of intermediate Mo_4O_{11} (JCPDS 89-0687) which presence is identified at 700 °C. It is comparable with literature reported by Lalik [8] that suggested formation of Mo_4O_{11} as the earliest product in the reduction of MoO_3.

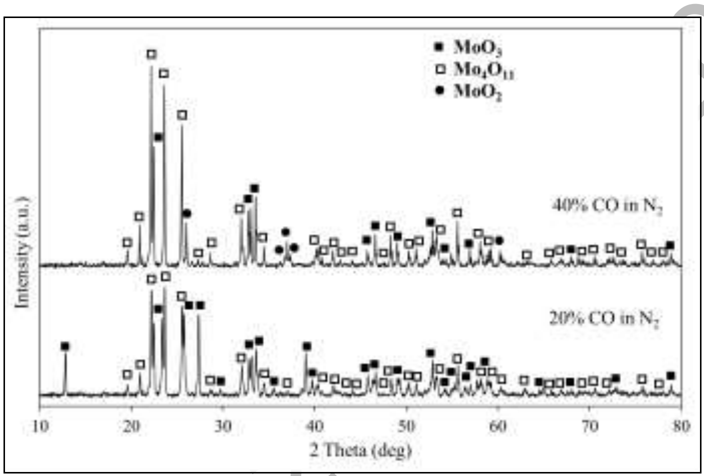

Figure 2. XRD patterns of non-isothermal reduction of MoO_3 with 20 % and 40 % of CO in nitrogen until 700 °C

Since MoO_3 is not completely reduced to MoO_2, isothermal reduction with 20 % and 40 % of CO in nitrogen was conducted at 700 °C for 30 minutes to complete reduction to MoO_2. From the XRD profile obtained in Figure 3, it is seen that by using 20% of CO, the MoO_2 peaks start to appear and MoO_3 peaks nearly disappear. Most of the peaks are intermediate phases of Mo_4O_{11}. However, by using 40 % of CO, the intensity of MoO_2 peaks sharply increase and intermediate phases of Mo_4O_{11} completely disappear. It shows that, reduction to MoO_2 in 20 % of CO concentration required higher heat supply to be accomplished compared by using 40 % of CO. It is seen that the higher concentration of CO will give the higher reduction to MoO_3.

Isothermal reduction at 700 °C was increased to 60 minutes to study the reduction behaviour by excessing the CO supplied. Figure 4 shows the XRD patterns of isothermal reduction for 60 minutes by using 20 % and 40 % of CO. As it is shown, MoO_3 was completely reduced to MoO_2 after isothermal reduction using 20 % of CO at 700 °C for 60 minutes. Figure 4 show the formation of carbide will take place in excess of CO. This was confirmed by the XRD profile of 40 % of CO displayed a decrease in the intensity of the MoO_2 peaks and new formation peaks of Mo_2C (JCPDS 65-8766) when the isothermal reduction prolongs until 60 minutes. This XRD patterns match well to previously reported pattern for processing of Mo_2C [9].

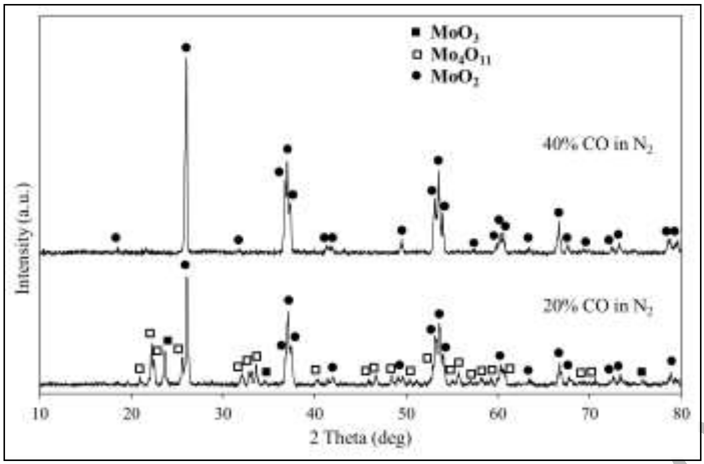

Figure 3. XRD patterns of non-isothermal reduction of MoO_3 with 20 % and 40 % of CO in nitrogen until 700 °C and continued with isothermal reduction at 700 °C for 30 minutes

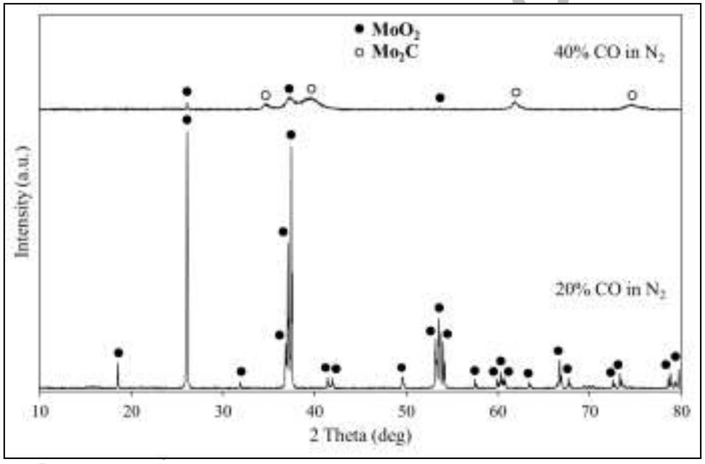

Figure 4. XRD patterns of non-isothermal reduction of MoO_3 with 20% and 40% of CO in nitrogen until 700 °C and continued with isothermal reduction at 700 °C for 60 minutes

Conclusion

In conclusion, the reduction behaviour of MoO_3 by TPR technique and XRD characterization shows that the reduction reaction of MoO_3 is strongly dependent on the concentration of CO and reaction time. The reduction reaction follows the consecutive two-steps mechanism, namely, MoO_3 is firstly reduced to Mo_4O_{11} and then Mo_4O_{11} is reduced to MoO_2. However, if excess of CO is introduced to the system, the formation of Mo_2C will take place.

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