



TEMPERATURE PROGRAMMED REDUCTION AND X-RAY DIFFRACTOMETRY STUDIES OF MoO₃ REDUCTION BY DIFFERENT CONCENTRATIONS OF CARBON MONOXIDE

(Kajian Penurunan Suhu Berprogram dan Pembelauan Sinar-X Terhadap Penurunan MoO₃
Menggunakan Kepekatan Karbon Monoksida Berbeza)

Alinda Samsuri^{1, 2*}, Tengku Shafazila Tengku Saharuddin¹, Fairous Salleh¹, Rizafizah Othaman¹,
Mohamed Wahab Mohamed Hisham¹, Mohd. Ambar Yarmo¹

¹Catalysis Research Group, School of Chemical Sciences and Food Technology,
Faculty of Science and Technology,

Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia.

²Centre for Defence Foundation Studies,
Universiti Pertahanan Nasional Malaysia, Kem Sungai Besi, 57000 Kuala Lumpur, Malaysia

*Corresponding author: alindasamsuri@gmail.com

Received: 24 February 2015; Accepted: 27 October 2015

Abstract

Reduction of molybdenum trioxide, MoO₃ to molybdenum dioxide, MoO₂ 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 MoO₃ have been investigated by comparing the reduction behaviour of MoO₃ to MoO₂ with 20 vol.% and 40 vol.% of CO concentration. The XRD results show that by using 20% of CO, reduction to MoO₂ takes place at 700°C in 60 minutes. However, by using 40% of CO, complete reduction to MoO₂ takes place at 700°C in only 30 minutes. Moreover, excess of CO results in the formation of molybdenum carbide, Mo₂C. It is suggested that by using CO, complete reduction from MoO₃ to MoO₂ gives two-steps reduction (MoO₃ → Mo₄O₁₁ → MoO₂) with Mo₄O₁₁ as an intermediate product. It can be concluded that the reducing behavior of MoO₃ is strongly dependent on the concentration of CO and reaction time.

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

Abstrak

Penurunan molibdenum trioksida, MoO₃ kepada molibdenum dioksida, MoO₂ dengan menggunakan karbon monoksida, CO telah dikaji menggunakan suhu penurunan berprogram (TPR) dan spektroskopi pembelauan sinar-X (XRD). Kesan kepekatan karbon monoksida terhadap penurunan MoO₃ telah dikaji dengan membandingkan kesan penurunan MoO₃ kepada MoO₂ menggunakan kepekatan karbon monoksida di antara 20 % dan 40 %. Keputusan XRD menunjukkan bahawa dengan menggunakan 20 % kepekatan CO, penurunan kepada MoO₂ berlaku pada suhu 700 °C dalam masa 60 minit. Walau bagaimanapun, dengan menggunakan 40 % kepekatan CO, penurunan lengkap kepada MoO₂ berlaku pada suhu 700 °C dalam masa hanya 30 minit. Selain itu, pendedahan kepada CO berlebihan akan menyebabkan pembentukan molibdenum karbida, Mo₂C. Adalah dicadangkan bahawa dengan menggunakan CO, penurunan lengkap daripada MoO₃ kepada MoO₂ terdiri daripada dua peringkat penurunan (MoO₃ → Mo₄O₁₁ → MoO₂) dengan menghasilkan Mo₄O₁₁ sebagai produk perantara. Ini boleh disimpulkan bahawa kelakuan penurunan MoO₃ 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 MoO₃. The first step reduction is exothermic in nature that is carried out at lower temperatures and involves transformation of MoO₃ to MoO₂. The second step reduction is endothermic in nature where MoO₂ is further reduced to Mo [2]. The reduction of MoO₃ to MoO₂ is a crucial stage in the production of metallic molybdenum. The reduction of MoO₃ to MoO₂ by using hydrogen consists of two reduction stages, namely Mo⁶⁺ → Mo⁵⁺ and Mo⁵⁺ → Mo⁴⁺ [3]. It seems that during the reduction of MoO₃, MoO₃ is first reduced to Mo₄O₁₁, then to MoO₂. 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 MoO₂. 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 MoO₃ reduction is expensive. Carbon is also used to reduce MoO₃ 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 MoO₃ 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 MoO₃ to MoO₂. In this study, we report the influence of CO content on the reduction behaviour of MoO₃. The isothermal and non-isothermal temperature programmed reduction (TPR) was performed to investigate the reduction behaviour of MoO₃ to MoO₂ by using CO as a reducing agent and later characterizing by XRD. Reduction of MoO₃ to MoO₂ by CO was suggested to follow two reduction stages which are shown as Equation 1 and Equation 2.



Materials and Methods

Chemicals and raw materials

Commercial molybdenum trioxide, MoO₃ (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 MoO₃ 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 MoO₃ powder before and after reactions were determined by XRD's Bruker AXS D8 Advance type. The radiation source used was Cu K α (40 kV, 40 mA) to record the 2 θ diffraction angles from 10° to 80° at wavelength (λ = 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 MoO₃ 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.



From the calculation, the Gibbs free energy for formation of MoO_2 for reaction Equation 3 is $\Delta G_{(298\text{ K})} = -29.8$ 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 $\Delta G_{(298\text{ K})} = -34.9$ 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 $700\text{ }^\circ\text{C}$ continued with isothermal reduction at $700\text{ }^\circ\text{C}$ 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 ($795\text{ }^\circ\text{C}$) since MoO_3 will end up as an alloy fused mass when it is taken to its melting point [5].

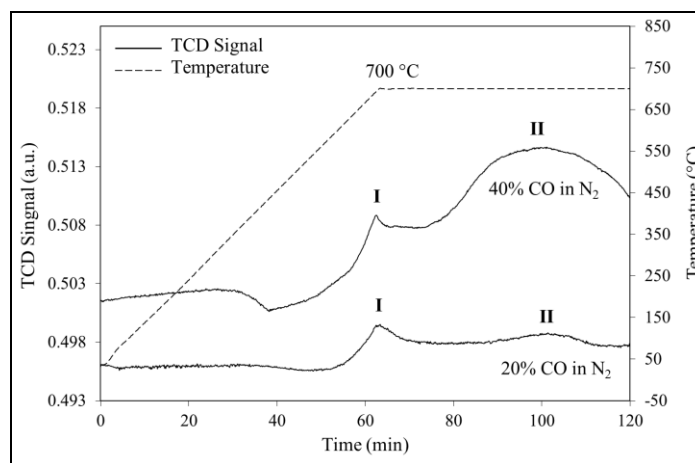


Figure 1. TPR profile of non-isothermal reduction of MoO_3 with 20% and 40% of CO in nitrogen at $40\text{-}700\text{ }^\circ\text{C}$ and continued with isothermal reduction at $700\text{ }^\circ\text{C}$ for 60 minutes.

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 $530\text{ }^\circ\text{C}$ 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 $700\text{ }^\circ\text{C}$ 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 $420\text{ }^\circ\text{C}$, while the second peak can be monitored after 10 minutes, starting off with isothermal reduction at $700\text{ }^\circ\text{C}$. 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 MoO₃ by using different concentration of CO, the samples were collected and XRD patterns were measured. The XRD profile obtained in Figure 2 revealed the MoO₃ (JCPDS 74-7383) was not yet reduced to MoO₂ 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 MoO₂ phases (JCPDS 76-1807). From the results, the reduction of MoO₃ by using 20% and 40% of CO concentration shows two stages process (MoO₃ → Mo₄O₁₁ → MoO₂) in respect to a trace of intermediate Mo₄O₁₁ (JCPDS 89-0687) which presence is identified at 700 °C. It is comparable with literature reported by Lalik [8] that suggested formation of Mo₄O₁₁ as the earliest product in the reduction of MoO₃.

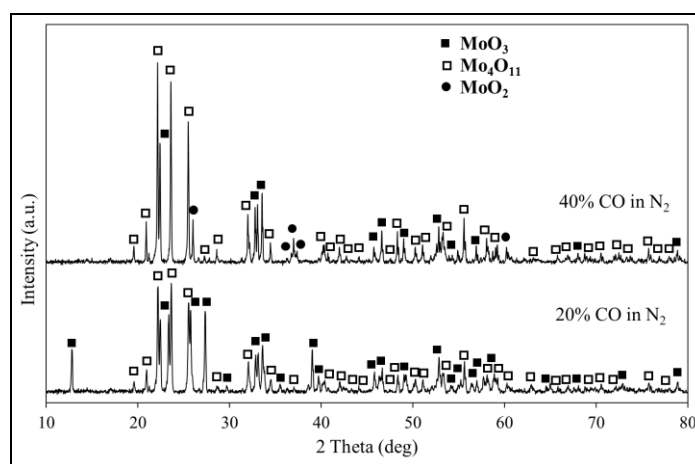


Figure 2. XRD patterns of non-isothermal reduction of MoO₃ with 20 % and 40 % of CO in nitrogen until 700 °C

Since MoO₃ is not completely reduced to MoO₂, isothermal reduction with 20 % and 40 % of CO in nitrogen was conducted at 700 °C for 30 minutes to complete reduction to MoO₂. From the XRD profile obtained in Figure 3, it is seen that by using 20% of CO, the MoO₂ peaks start to appear and MoO₃ peaks nearly disappear. Most of the peaks are intermediate phases of Mo₄O₁₁. However, by using 40 % of CO, the intensity of MoO₂ peaks sharply increase and intermediate phases of Mo₄O₁₁ completely disappear. It shows that, reduction to MoO₂ 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 MoO₃.

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, MoO₃ was completely reduced to MoO₂ 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 MoO₂ peaks and new formation peaks of Mo₂C (JCPDS 65-8766) when the isothermal reduction prolongs until 60 minutes. This XRD patterns match well to previously reported pattern for processing of Mo₂C [9].

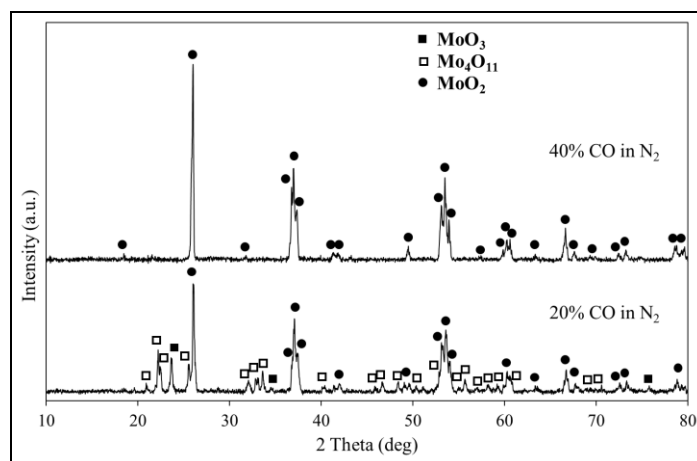


Figure 3. XRD patterns of non-isothermal reduction of MoO_3 with 20 % and 40 % of CO in nitrogen until 700 °C and continued with isothermal reduction at 700 °C for 30 minutes

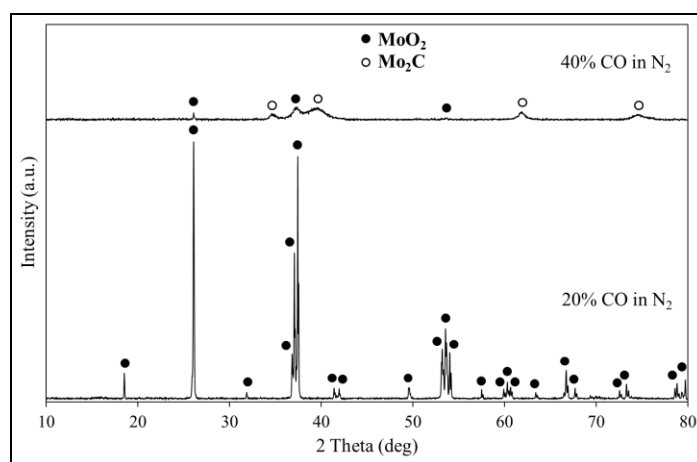


Figure 4. XRD patterns of non-isothermal reduction of MoO_3 with 20% and 40% of CO in nitrogen until 700 °C and continued with isothermal reduction at 700 °C for 60 minutes

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.

Acknowledgement

The authors wish to thank the Ministry of Higher Education (MOHE) and Universiti Pertahanan Nasional Malaysia for funding staff's scholarships and also Universiti Kebangsaan Malaysia (UKM) for funding this project under research grant number LRGS/BU/2011/USM-UKM/PG/02, BKBP-FST-K003323-2014, FRGS/2/2013/TK06/UKM/02/3, ETP-2013-066 as well as the Centre of Research and Innovation Management (CRIM) for the instruments facilities.

References

1. Manukyan, K., Davtyan, D., Bossert, J. and Kharatyan, S. (2011). Direct reduction of ammonium molybdate to elemental molybdenum by combustion reaction. *Chemical Engineering Journal*, 168 (2): 925 – 930.
2. Enneti, R. K. and Wolfe, T. A. (2012). Agglomeration during reduction of MoO₃. *International Journal of Refractory Metals and Hard Materials*, 31: 47 – 50.
3. Wang, J., Ren, Z., Liu, W., Gao, F. and Zhou, M. (2009). Effects of RE₂O₃ doping on the reduction behavior of molybdenum oxide and properties of molybdenum powder. *International Journal of Refractory Metals and Hard Materials*, 27 (1): 155 – 158.
4. Saghafi, M., Heshmati-Manesh, S., Ataie, A. and Khodadadi, A. A. (2012). Synthesis of nanocrystalline molybdenum by hydrogen reduction of mechanically activated MoO₃. *International Journal of Refractory Metals and Hard Materials*, 30 (1): 128 – 132.
5. Saghafi, M., Ataie, A. and Heshmati-Manesh, S. (2011). Effects of mechanical activation of MoO₃/C powder mixture in the processing of nano-crystalline molybdenum. *International Journal of Refractory Metals and Hard Materials*, 29 (4): 419 – 423.
6. Satyajeet Chaudhury, V. V., Mukerjee, S. K. and Vaidya, V. N. (1997). Kinetics and mechanism of carbothermic reduction of MoO₃ to Mo₂C. *Journal Alloys Compounds*, 261: 105 – 113.
7. Dang, J., Zhang, G.-H., Chou, K. C., Reddy, R. G., He, Y. and Sun Y. (2013). Kinetics and mechanism of hydrogen reduction of MoO₃ to MoO₂. *International Journal of Refractory Metals and Hard Materials*, 41: 216 – 223.
8. Lalik, E. (2011). Kinetic analysis of reduction of MoO₃ to MoO₂. *Catalysis Today*, 169: 85 – 92.
9. Claridge, J. B., York, A. P. E., Brungs, A. J., Marquez-Alvarez, C., Sloan, J., Tsang, S. C. and Green, M. L. H. (1998). New Catalysts for the Conversion of Methane to Synthesis Gas : Molybdenum and Tungsten Carbide. *Journal of Catalysis*, 180: 85 – 100.