Study on the Reduction Behaviour of Nickel Doped Molybdenum Trioxide by Using Carbon Monoxide as Reductant

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Abstract—The reduction behaviour of molybdenum trioxide, (MoO₃) and nickel (Ni) doped MoO₃ using carbon monoxide (CO) as reductant was investigated by temperature programmed reduction (TPR) and characterized by X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and transmission electron microscope analysis (TEM). The reduction characteristics of MoO₃ to MoO₂ were examined up to temperature 700 °C and continued with isothermal reduction by 20 vol. % CO in nitrogen. The studies show that, TPR spectra of doped MoO₃ slightly shift to a lower temperature as compared to the undoped MoO₃ which begins at 630 °C. The interaction between nickel and molybdenum ions leads to this slightly decrease of the reduction temperature of Ni doped MoO₃. Analysis using XRD confirmed, the addition of Ni enhances the reducibility of MoO₃. By addition of Ni, complete reduction to MoO₂ were take place at only 30 minutes starting of the isothermal reduction at 700 °C. Whereas, for undoped MoO₃ it takes about 60 minutes to completely reduce to MoO₂. However, excess of CO brings to the formation of molybdenum carbide (Mo₂C). Based on the results, it is confirmed addition of Ni to MoO₃ has a remarkable influence by reducing temperature in the reduction process. The ability to enhance the reducibility involved in MoO₃ may be associated to the presence of nickel molybdate, NiMoO₄ compound.

Index Terms—Carbon monoxide, molybdenum trioxide, nickel, reduction.

I. INTRODUCTION

Metallic molybdenum, having a body centered cubic crystal structure with a melting point of 2619 $^{\circ}$ C and a density of 10.22 g/cm³ [1]. Due to superior properties such as excellent in mechanical, thermal and electric properties and

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Fairous Salleh, Tengku Shafazila Tengku Saharuddin, Rizafizah Othaman, and Mohd. Ambar Yarmo are with School of Chemical Science & Food Technology, Faculty of Science and Technology, Universiti Kebangsan Malaysia, 43600 Bangi, Selangor, Malaysia (e-mail: fairoussalleh@gmail.com, tengkushafazila@gmail.com, rizafizah@ukm.edu.my, ambar@ukm.edu.my). good corrosion resistance make them ideally 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 [2].

As a catalyst, the reduction behaviour and the degree of reduction of the molybdenum species were highly important in such application. The reduction process of MoO₃ is not a simple process and involved different mechanism depending on various factors such as temperature, concentration of reduction gas used and additives to the MoO₃. In general, the two-stage flow scheme (MoO₃ \rightarrow MoO₂, MoO₂ \rightarrow Mo) is employed in order to minimize the formation of volatile molybdenum species that would be generated at high temperature required to obtain molybdenum in a single stage conversion of the molybdenum precursor [3].

Reduction of MoO_3 by hydrogen is one of the methods used to obtain metallic molybdenum of high purity. Many excellent reports studying reduction of MoO_3 to Mo with hydrogen have been published [4]–[6]. Generally, the two-step hydrogen reduction process to produce pure molybdenum powders is well known [7]. First stage reduction occurs in the temperature range of 450 - 650 °C, and reduces the input material to MoO_2 . Second stage reduction is performed in the 1000 - 1100 °C range, and this process results in molybdenum metal. Nevertheless, hydrogen used as a reducing agent of MoO_3 reduction is expensive.

Carbon is also used to reduce MoO_3 at elevated temperature (600 - 1200 °C). When metal oxides react with carbon, one of the reaction products would be gaseous and could be readily separated from the solid reaction products [8], [9]. This means that the use of carbon as a reducing agent can eliminate the need for an additional process that is a challenging task with reactive metals to separate the reaction products.

Therefore, it would be highly desirable to develop an alternative process to manufacture molybdenum. Reduction of MoO_3 by using CO as reductant was recommended as an alternative process for producing molybdenum. Reduction of MoO_3 to MoO_2 by CO was suggested to follow two reduction stages which are shown as equation (1) and (2). However, it is limited of studies to use CO as reductant for reduction of MoO_3 to MoO_2 .

$$4\text{MoO}_3 + \text{CO} \rightarrow \text{Mo}_4\text{O}_{11} + \text{CO}_2 \tag{1}$$

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

The reduction of MoO_3 to MoO_2 is the crucial stage in the production of metallic molybdenum. Reference [10] reported

that the reduction of MoO_3 to MoO_2 by using hydrogen consists of two reduction stages, namely $Mo^{6+} \rightarrow Mo^{5+}$ and $Mo^{5+} \rightarrow Mo^{4+}$. It seems that during the reduction of MoO_3 , MoO_3 is firstly reduced to Mo_4O_{11} , then continued to MoO_2 .

Different reducing agent would give different reducibility effect. However, other elements are also needed to enhance the reducibility of metal oxide. For hydrogen reduction, other elements can generally influence MoO_3 reduction by altering the reaction sequence by chancing nucleation and growth. Moreover, trace elements such as lanthanum, La and yttrium, Y are able to enhance the reduction rate of MoO_3 [10]. Moreover, the addition of Ni to MoO_3 can enhance their catalytic activity and stability by improving their oxygen storage capacity, reducibility, and resistance to sintering [11]. Hence, the used of Ni will encourage the reduction behaviour of MoO_3 .

The objective of this work is to study the reduction behaviour of MoO_3 and to enhance the reduction performance of MoO_3 by addition of other metal additive using mixture gas of 20 vol.% CO in nitrogen as a reducing agent. In this study we report the preferable effects of the addition of different percentage of Ni species into MoO_3 powders. The TPR and XRD analysis was performed to investigate the reduction behaviour of Ni doped MoO_3 by comparing it to undoped species.

II. EXPERIMENTAL PROCEDURE

A. Material

All chemicals and solvents that have been used in these experiments e.g. commercially MoO_3 powders from BDH Chemicals Ltd.., nickel nitrate, Ni(NO₃)₂.6H₂O from Merck and ethanol, C₂H₆O (99.5%) from Systerm[®] are pure and used as supplied.

B. Catalyst Preparation

Nickel doped molybdenum oxide were prepared by impregnation method using a Ni $(NO_3)_2.6H_2O$ and MoO_3 powder. The amount of Ni added was adjusted to be 3 and 9 mol% of total metal cation or known as 3% Ni-MoO₃ and 9% Ni-MoO₃. The both compounds were dissolved in water with additional of ethanol at 80 °C with stirring for 3 hours, producing a viscous mixture. The mixture was placed in an oven, dried at 110 °C overnight and finally calcined at 400 °C for 4 hours in air and then cooled to room temperature.

C. Reduction of Molybdenum Trioxide, MoO₃

Reduction of the undoped MoO₃ and Ni doped MoO₃ was carried out 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 vol.% CO in 80 vol.% nitrogen was introduced into the reaction cell 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 at 700 °C for 30 and 60 minutes.

D. Characterization

The crystal structures of the catalysts before and after

reactions were determined by XRD's Bruker AXS D8 Advance type. The radiation used was Cu K α (40 kV, 40 mA) to record the 2 θ diffraction angle 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. The Brunauer-Emmett-Teller (BET) surface areas of the catalysts were measured using a Micromeritics ASAP 2010 instrument after the catalyst was evacuated at 200 °C for 4 hours. The TEM analysis was performed using a Philips CM12 transmission electron microscope with an electron gun at 200 kV. Samples were dispersed in ethanol using supersonic waves and then placed on Cu grids under atmospheric condition.

III. RESULT AND DISCUSSION

A. Characterisation of Undoped and Doped Molybdenum Trioxide, MoO₃ Using XRD

XRD patterns of as prepared undoped and doped MoO_3 with 3 and 9 mol% Ni obtained after calcination at 400 °C for 4 hours are shown in Fig. 1. It shows that molybdenum largely exists as MoO_3 (JCPDS 05-0508). With addition of 3 mol% Ni there was a minimal change observed with respect to presence of NiMoO₄ (JCPDS 086-0361). Further increased addition of Ni to 9 mol% displays an appearance of crystalline of NiMoO₄ which is considered to be the reaction products of MoO_3 with Ni(NO₃)₂.6H₂O.



Fig. 1. XRD patterns of the undoped MoO₃, 3% Ni-MoO₃ and 9% Ni-MoO₃ samples obtained after calcination at 400 ℃ for 4 hours.

B. Physical Surface Analysis (BET)

BET analysis of the undoped MoO₃ and Ni doped MoO₃ samples are summarized in Table I. Surface area of undoped MoO₃ was 6.85 m²/g while surface areas of doped MoO₃ with 3 and 9 mol% Ni were 11.35 and 19.64 m²/g respectively. It was found that the surface area was increased with increasing loading of Ni to MoO₃. This could suggest that there are more active sites that might be attributed to the lower temperature reduction of MoO₃ after doping. Hence, Ni addition can significantly increase the surface area of MoO₃.

Pore size of undoped MoO₃ was 20.36 nm, by addition of Ni to 3 and 9 mol% were 24.89 and 27.75 nm respectively. It was found that the pore size decreased by increasing of Ni loading to MoO₃. Moreover the pore volume for undoped MoO₃ was 0.035 cm³/g, while by increasing the addition of Ni

from 3 to 9 mol%, the pore volume was increased to 0.071 and 0.087 cm^3/g respectively.

TABLE I. BET ANALYSIS OF UNDOPED MOO3 AND NICKEL DOPED MOO3				
Catalyst	Surface area	Pore size	Pore volume	
	(m^2/g)	(nm)	(cm^3/g)	
Undoped MoO ₃	6.85	20.36	0.035	
3% Ni-MoO ₃	11.35	24.89	0.071	
9% Ni-MoO3	19.64	27.75	0.087	

TABLE I: BET ANALYSIS OF UNDOPED MOO3 AND NICKEL DOPED MOO

C. Surface Morphology by TEM

An investigation on structural of doped catalysts was attempted with TEM. Fig. 2 shows TEM image of undoped MoO_3 and doped MoO_3 with Ni samples. It seems that the powder can be clearly differentiated because of the different particle sizes of support (MoO_3) and dope (Ni). MoO_3 cluster comprised larger molecule compared to Ni cluster. Tiny spots were revealed in the images which represent Ni cluster that were seen located around the MoO_3 particles. It showed that the Ni was successfully intercalated into MoO_3 powder during impregnation process. Moreover, effect of addition of 3 and 9 mol% Ni resulted in presence of new peaks of Ni which is supported with XRD result shown in Fig. 1.



Fig. 2. TEM images of (a) undoped MoO_3 (b) 3% Ni-MoO_3 calcined at 400 $\,^\circ C$ for 4 hours.

D. Temperature Programmed Reduction (TPR)

Reduction of MoO₃ to MoO₂ needs to complete at temperature lower than its melting point (795 °C) since MoO₃ will end up as an alloy fused mass when it is taken to its melting point [8]. The reduction behaviour of undoped MoO₃ sample and Ni (3 and 9 mol%) doped MoO₃ samples was studied using TPR. Fig. 3 shows the TPR profile of nonisothermal reduction until 700 °C continued with isothermal reduction at 700 °C for 60 minutes by using 20% CO in nitrogen.

The TPR profile of undoped MoO_3 sample represents two reduction stages (denoted I and II) which stage I owing to peak displayed at early reaction time may regard to the reduction of MoO_3 to Mo_4O_{11} , while stage II is subsequent to reduction steps of Mo_4O_{11} to MoO_2 . Meanwhile, with excess of CO brings to the formation of Mo_2C [12], [13]. The profile monitor CO consumption peaks by using 20 vol.% of CO in nitrogen which started at about 630 °C was pointed to the first stage of reduction in agreement with [3], 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 60 minutes, new peak started forming at minutes 40 due to sample changes that occurred, reflecting to second stage reduction of Mo_4O_{11} to MoO_2 .

On the other hand, Fig. 3 also indicates clearly that the reduction process of doped MoO₃ with 3 and 9 mol% of Ni can be divided into two stages. In each stage, there is a peak of CO consumption and the TPR peaks have been shifted to lower temperatures. By additional 3 mol% of Ni, the reduction peaks are leading to low temperature to 570 °C, while second peak can be monitored after 20 minutes, starting off with isothermal reduction at 700 °C. Then, for the reduction of doped MoO₃ with 9 mol% of Ni, TPR profile is almost similar showing two peaks where the first reduction peak starts at about 460 °C which is much lower compared to undoped MoO₃, while the second peak started forming at minutes 10 during isothermal reduction at 700 °C.

From Fig. 3, it may be concluded that the reduction of MoO_3 is observed to occur with a shift to lower temperature by increasing of additions of Ni. It could be found that doping with Ni had a remarkable influence on the reduction process of the MoO_3 by improving their oxygen storage capacity and reducibility. The strong interaction between nickel ions and molybdenum ions in the samples leads to changes in the coordination environment of molybdenum and the strength of Mo–O bonds [10]. The catalytic effect of Ni which enhances CO absorption and C deposition also causes the decreasing of reduction temperature [14]. The phases formed after the reduction by TPR were analysed by recording XRD pattern of the residual obtained after selected reduction condition.



Fig. 3. TPR profile of undoped MoO₃, 3% Ni-MoO₃ and 9% Ni-MoO₃ samples under 20 vol.% CO at 40-700 °C and then hold at 700 °C for 60 minutes.

E. Reduction Based on Crystallinity

To investigate the reduction behaviour of MoO₃ by using 20 vol.% CO in 80 vol.% nitrogen, the samples were collected and XRD patterns were measured. The XRD profile obtained in Fig. 4 revealed the undoped MoO₃ sample was not yet reduced to MoO₂ even after flowing with 20 vol.% of CO until 700 °C. It is due to insufficiency of CO and heat supply

to the reaction. Since undoped MoO₃ is not completely reduced to MoO₂ after nonisothermal reduction until 700 °C, reaction continued with isothermal reduction with 20 vol.% of CO in 80 vol.% of nitrogen at 700 °C for 30 minutes. From the XRD profile obtained in Fig. 4, it is seen that the complete reduction to MoO₂ was not achieved. However, the MoO₂ (JCPDS 76-1807) peaks start to appear and MoO₃ (JCPDS 74-7383) peaks nearly disappear. Most of the peaks are intermediate phases of Mo₄O₁₁ (JCPDS 89-0687). It is comparable with literature reported by [15] that suggested formation of Mo₄O₁₁ as the earliest reduction of MoO₃. As it is shown in Fig. 4, undoped MoO₃ was completely reduced to MoO₂ after increasing isothermal reduction at 700 °C for 60 minutes.



Fig. 4. XRD patterns of reduction of undoped MoO₃ sample with 20 vol.% CO in nitrogen until 700 ℃ and hold at 700 ℃ for 30 and 60 minutes.

The comparison of XRD pattern for the nonisothermal reduction of 3 and 9 mol% Ni-MoO₃ samples with 20 vol.% CO in nitrogen until 700 °C is shown in Fig. 5. Analysis of the patterns revealed, the reduction product of 3 and 9 mol% Ni-MoO₃ samples were rather similar with formation of intermediate phases of Mo_4O_{11} and a few peaks of NiMoO₄ (JCPDS 086-0361). However, reduction products of 3 mol% Ni-MoO₃ sample showed some remaining unreduced MoO₃ peaks but are less than undoped MoO₃ sample. For 9 mol% Ni-MoO₃ sample, no remaining unreduced MoO₃ peaks observed. It can be seen that additional of Ni is capable to speedup the reduction process of MoO₃.

As shown in Fig. 5, doped MoO₃ with Ni is not completely reduced to MoO₂ even after nonisothermal reduction until 700 °C. To complete the reduction, reaction continued with isothermal reduction with 20 vol.% of CO in 80 vol.% of nitrogen at 700 °C for 30 minutes. XRD profile obtained in Fig. 6 shows that the complete reduction to MoO_2 was achieved by addition of 9 mol% of Ni to MoO₃. Meanwhile, for 3 mol% Ni-MoO₃ sample, the MoO₂ peaks start to appear and MoO₃ peaks completely disappear. Most of the peaks are intermediate phases of Mo₄O₁₁. Moreover, a few peaks of NiMoO₄ observed in both samples and new peaks of Mo_{0.09}Ni_{0.91} (JCPDS 071-9766) observed in 9 mol% Ni-MoO₃ sample. It could be found that by doping with 9 mol% of Ni, complete reduction would be achieved only after 30 minutes, with the starting of isothermal reduction process compared with undoped MoO₃ sample that would take about 60 minutes of isothermal reduction to completely reduce to MoO₂.



Fig. 5. XRD patterns of nonisothermal reduction of 3% Ni-MoO₃ and 9% Ni-MoO₃ samples with 20 vol.% CO in nitrogen until 700 °C.



Fig. 6. XRD patterns of nonisothermal reduction of 3% Ni-MoO₃ and 9% Ni-MoO₃ samples with 20% CO in nitrogen until 700 °C and hold at 700 °C for 30 minutes.



Fig. 7. XRD patterns of nonisothermal reduction of 3% Ni-MoO₃ and 9% Ni-MoO₃ samples with 20 vol.% CO in nitrogen until 700 °C and hold at 700 °C for 60 minutes.

Referring to results in Fig. 6, 3 mol% Ni-MoO₃ sample is not completely reduced to MoO₂. Therefore, isothermal reduction was increased to another 30 minutes. Since the 9 mol% Ni-MoO₃ sample was completely reduced to MoO₂, effect of excess of CO was studied. Fig. 7 shows the XRD patterns of isothermal reduction of 3 and 9 mol% Ni-MoO₃ samples for 60 minutes by using 20 vol.% CO in nitrogen. As it is shown, 3 mol% Ni-MoO₃ samples were completely reduced to MoO₂ after isothermal reduction for 60 minutes. Peaks of NiMoO₄ completely disappeared and peaks of $Mo_{0.09}Ni_{0.91}$ are observed in both samples. Somehow, Fig. 7 shows the formation of carbide will take place when excess of CO was introduced to the system. This was confirmed by the XRD patterns of both samples which displayed a new formation peaks of Mo_2C (JCPDS 071-0242) when the isothermal reduction prolongs until 60 minutes. XRD patterns match well to previously reported pattern for processing of Mo_2C [16].

Based on the characterization of the reaction products using XRD, it is concluded that the reduction of MoO₃ to MoO₂ by CO consists of two reduction stages, namely, Mo⁶⁺ \rightarrow Mo⁵⁺ and Mo⁵⁺ \rightarrow Mo⁴⁺ [10]. Reduction of MoO₃ to MoO₂ was a consecutive reaction with the intermediate product Mo₄O₁₁. By addition of Ni, the completed reduction to MoO₂ becomes faster compared to undoped MoO₃ samples. The MoO₂ peaks sharply increase and intermediate Mo₄O₁₁ phases become less and totally disappear. With excess of CO supplied, Mo₂C formation will take place. It can be seen that doping with nickel has a remarkable influence in the reduction process of the MoO₃.

IV. CONCLUSION

The reduction behaviour of undoped MoO₃ and Ni doped MoO₃ samples were investigated and compared using TPR technique and characterized by XRD, BET and TEM analysis. The findings in this research revealed that reduction reaction of MoO₃ obeys the consecutive mechanism, namely, MoO₃ is firstly reduced to Mo₄O₁₁ and then Mo₄O₁₁ is reduced to MoO₂. Furthermore, addition of Ni to MoO₃ give higher surface area and for TEM it is clearly shown the Ni was well disperse on the surface of MoO₃. The addition of Ni to the MoO₃ shifted the TPR peaks to the lower temperature side. It can be concluded that the reduction temperature of MoO₃ decreased by increasing Ni addition. Ni change the coordination environment of molybdenum and the strength of Mo-O bonds, leading to a decrease of the reduction temperature of doped MoO₃.

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