Effect of Nickel Loading on the Isothermal Carburation of Molybdenum Trioxide Catalyst

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Abstract. The carburization behaviour of nickel molybdenum trioxide (Ni-MoO_3) catalyst with different loadings of Ni has been studied by using temperature programmed reduction (TPR) with exposure of 60 vol. % carbon monoxide (CO) in helium atmosphere as a reductant. The Ni-MoO_3 catalysts were prepared by using the conservative wet impregnation method. The carburization characteristics of prepared catalysts were examined by isothermal carburization mode at 700°C for 90 minutes. The carburized phases were characterized by using X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) and field emission scanning electron microscopy (FE-SEM). XRD pattern of undoped MoO_3 show the formation of molybdenum dioxide (MoO_2) ($2\theta = 37°$ and 74.10°) and Mo_2C ($2\theta = 33.63°$ and 62.50°). After addition of nickel at higher loading which is 3% (wt./wt.) of Ni-MoO_3 show the XRD pattern obtained Mo_2C at $2\theta = 61.47°$, showing that the higher loading of nickel in MoO_3 lead to higher reducibility compared to 1% (wt./wt.) of Ni-MoO_3 indicated by the broad and weak peak resulted from XRD pattern. By calculating the crystallites size 7.11 nm for 3% (wt./wt.) Ni-MoO_3 catalyst give the higher crystallinity compared to 1% (wt./wt.) Ni-MoO_3 catalyst which is 5.70 nm. Physical properties analysis by using BET showed an increasing in surface area and pore size of MoO_3 catalyst after addition of Ni metal loading. This proves that the higher loading of nickel might attribute to the increasing in active site for enhancing the carburization process which lead to the formation of Mo_2C. The slightly phase covering the surface of the particles or seemed like an agglomerate is amorphous deposited carbon that formed between the platelet shape on Ni-MoO_3 surfaces were observed through the FE-SEM images indicating some morphology modification occurred on MoO_3. Based on these results, it is interesting to address that the addition of Ni metal to MoO_3 has a remarkable influence on carburization process. The 3% (wt./wt.) of Ni on MoO_3 catalyst was sufficient to promote the formation of Mo_2C.

Introduction

Molybdenum (Mo) is a transition element and categorized as a metal refractory that used in high-temperature applications such as the chemical industries, metallurgical, electrical, aerospace and sputtering target materials [1]. The main characteristics of Mo are hardness, good thermal and electrical conductivity, high melting point (2615°C) and resistance to corrosion and resistance to high temperatures [2]. Molybdenum trioxide (MoO_3) powder is the main raw material used to produce molybdenum and alloy products.

As a catalyst, the reduction behavior and reduction rate of Mo species are very important in such applications. For example, molybdenum carbide is a good catalyst but has a dense surface (low porosity) and a specific surface area less than 10 m^2/g. As a result, surface area is largely reliant on the synthesis method [3]. As a result, several investigations on the synthesis of metallic Mo and molybdenum carbide have been done for different applications. Based on carbon recourse, the synthesis pathway may be separated into three categories: solid-gas reactions, solid-liquid reactions, and solid-solid processes.

In general, the MoO_3 reduction reaction is synthesized by a solid gas reaction involving different metals powders and MoO_3. The reduction of MoO_3 using hydrogen is one of the methods of production of high purity Mo metal. The production of Mo metal through this method is a staged process and occurs separately starting with the reduction of MoO_3 to MoO_2 and followed by the reduction of MoO_2 to Mo metal as summarized in Eq. 1 and Eq. 2, respectively. Generally, a two-step reduction flow scheme ($MoO_3 \rightarrow MoO_2$, $MoO_2 \rightarrow Mo$) was used to reduce the formation of the volatile element Mo at high temperatures if MoO_3 reduction is carried out using a single step of metal Mo production. The reduction of MoO_3 to MoO_2 is the first important stage in metal Mo production [5].

$$MoO_3\,(s) + H_2\,(g) \rightarrow MoO_2\,(s) + H_2O\,(g) \quad (1)$$
$$MoO_2\,(s) + H_2\,(g) \rightarrow Mo\,(s) + 2H_2O\,(g) \quad (2)$$

The reduction is demonstrated in detail by using the hydrogen-temperature programmed reduction (H_2-TPR) profile of the MoO_3 catalyst employing by 10% H_2 as a reducer which shows a wide utilization of hydrogen peaks, showing that three phases of MoO_3 reduction have been combined into one broad peak (Mo^{6+} to Mo^{5+} to Mo^{4+} to Mo^0) [6]. According to Zhang et al., [7] three reduction advances peaks may be involved during MoO_3 reduction by hydrogen as a reductor, at 640°C, where the first reduction peak involves the reduction of Mo^{6+} to Mo^{5+}. At the peak of 680°C refers to the reduction of the species Mo^{5+} to Mo^{4+}, and at temperature above 800°C, hydrogen consumption is associated with the development of the reduction of the Mo^{4+} species to the metal Mo. However, hydrogen is used as a reducing agent for MoO_3 reduction is expensive.

Other techniques for MoO_3 reduction can also use carbon or known as carbothermal reduction which can also be used for Mo production. Carbon monoxide (CO) is one of the possible reducers that may be employed for metal oxide reduction [8]. CO reduction has several significant advantages, including low cost, convenience, and strong reproducibility in commercial applications [9]. At high temperatures (600-1200°C), carbon is also employed to reduce MoO_3. This technique is expected to be practical because when a metal oxide reacts with the element carbon, one of the results obtained is in the gaseous state which is easily separated from the other if in the solid state [10]. This means that the reduction technique using carbon can eliminate the additional methods required to separate the mixed solid product after the reaction. CO reductors are suggested to reduce MoO_3 to MoO_2 in a succession of reduction phases as described in Eq. 3 and Eq. 4.

$$4MoO_3\,(s) + CO\,(g) \rightarrow Mo_4O_{11}\,(s) + CO_2\,(g) \quad (3)$$
$$Mo_4O_{11}\,(s) + 3CO\,(g) \rightarrow 4MoO_2\,(s) + 3CO_2\,(g) \quad (4)$$

Different reducing agents have varying reduction effects. However, other elements are required to improve metal oxide deficient. Due to the high possibility of carbide production, which might

interfere with or slow down the reduction reaction, studies on the reduction of MoO_3 to MoO_2 using CO as a reducer are restricted. However, there is another way that can be used such as increasing the reaction temperature will increase the stability of the CO and theoretically heating up to the optimum high temperature with the present of carbon is able to separate oxygen from the metal oxide. The addition of additional element can typically impact the reduction of MoO_3 by modifying the reaction sequence by changing nucleation and growth. According to previous research, Ni-based catalysts have better catalytic activity, due to the superior dispersion of active sites caused by Ni/Zn interactions, leading in decreased hydrogen chemisorption capacity and reducibility [11].

Furthermore, by enhancing their oxygen storage capacity, ductility, and resistance to sintering, the addition of Ni to MoO_3 can improve their catalytic activity and stability [12]. As a result, the application of Ni will enhance MoO_3 reduction behavior. The goal of this research is to examine effect of nickel additions to the carburation behavior of the MoO_3 catalyst that would have by utilizing a mixed gas reducing agent of 60% CO in helium. TPR analysis was used to investigate the carburation behavior of nickel doped MoO_3 catalysts in comparison to non-doped species.

Materials and method

Materials. All chemicals and solvents that have been used in this research such as commercially MoO_3 powders from BDH Chemicals Ltd., nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$) from Sigma-Aldrich and ethanol (C_2H_5OH) (95%) from John Kollin Chemicals are pure and used exactly as given.

Catalysts preparation. MoO_3 catalysts modified with other metals were prepared using the impregnation technique reported by Ma et al., [13] with slightly modification. In this study, $Ni(NO_3)_2.6H_2O$ as precursor of other metals in the form of salt was used for the preparation of a modified MoO_3 catalyst and while for Mo metal the precursor used is molybdenum trioxide (MoO_3). As much as 1% (wt./wt.) and 3% (wt./wt.) of $Ni(NO_3)_2.6H_2O$ known as 1% Ni-MoO_3 and 3% Ni-MoO_3 were added to the desired mass of MoO_3 catalyst and then dissolved in distilled water and ethanol. Next the slurry was mixed with MoO_3 catalyst and stirred at 40°C for 4 hours. The mixture was then dried at 110°C overnight and calcined at 400°C for 4 hours.

Carburization of catalyst. The TPR technique was utilized to analyse the carburization of undoped MoO_3, and nickel doped MoO_3 utilizing a Micromeritic Autochem 2920 Chemisorption Analyzer. The catalyst was isothermally carburized at 700°C for 90 min with a heating rate of 10°C/min under stream of mixed gas 60 vol. % CO in 40 vol. % helium at a flow rate of 20 mL/min.

Characterization. Structural characterization and degree of crystallinity of catalysts were performed using XRD technique. In this study a Bruker AXS D8 Advance type X-ray diffractometer was used with a Cu Kα X-ray radiation source (40 kV, 40 mA) and recorded a diffraction angle of 2θ at a wavelength (λ) of 0.154 nm. The diffraction data obtained from this technique will be supported by comparative data from standard peak data available at the International Centre for Diffraction Data (ICDD). Further sample characterization was performed using field emission scanning electron microscopy (FE-SEM) to analyze the surface morphology of the samples at different magnifications. In this study, morphological images of the sample surface were taken using Merlin ultra-high resolution instrument operates at 3.0 kV equipped with energy dispersive x-ray detector (EDX). Nitrogen adsorption/desorption analysis (Brunauer-Emmet-Teller, BET) was used to investigate the surface area, pore volume and pore size of catalysts by using a Micromeritics ASAP 2020 instrument. Before the analysis is carried out, gaseous molecules that were chemically bound to the metal surface were removed by degassing at 300°C for 6 hours before analysing all samples under 77K liquid nitrogen environment to acquire adsorption isotherms.

Results and discussions

XRD patterns were recorded to evaluate the carburization behaviour of undoped MoO_3, 1% Ni-MoO_3 and 3% Ni-MoO_3. Fig. 1 depicts the XRD patterns of fresh and prepared samples with different nickel loading. It shows that undoped MoO_3 largely exists as MoO_3 with reference code (01-076-1003).

Meanwhile, $Ni(MoO_4)$ with reference code (00-045-0142) existed after calcined with addition of 1% (wt./wt.) nickel from MoO_3. Further increased addition of nickel to 3% (wt./wt.) displays an appearance of crystalline of $Ni(MoO_4)$ and $Mo_{1.24}Ni_{0.76}$ which is the reaction products of MoO_3 with $Ni(NO_3)_{2.6}H_2O$ during wet impregnation process.

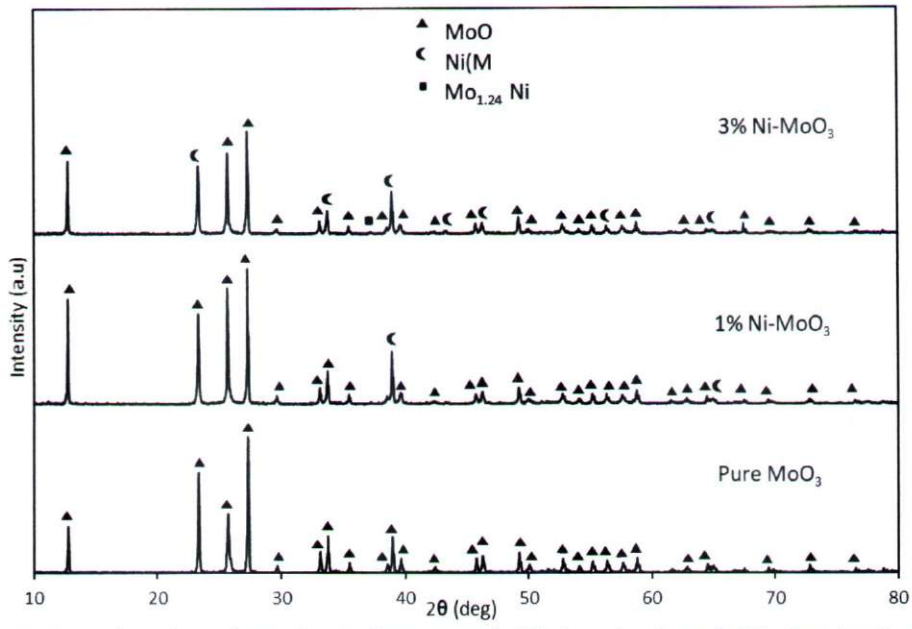

Fig. 1 XRD patterns of undoped MoO_3 and prepared 1% (wt./wt.) and 3% (wt./wt.) of nickel doped MoO_3

The isothermal carburization process of undoped MoO_3 and prepared MoO_3 with 1% (wt./wt.) and 3% (wt./wt.) nickel loading to MoO_3 catalysts in the CO atmosphere were studied by using CO-TPR under a flow of 60 vol.% CO in helium (20 mL/min) at 700°C for 90 min. Since MoO_3 will become an alloy fused mass when heated to its melting point (795°C), the reduction of MoO_3 to MoO_2 must be completed at a temperature lower than its melting point [10]. In order to investigate the influence of nickel loadinf on carburization process, all samples were collected according to the designed carburization mode and samples was analyzed by XRD. XRD analysis was performed in the range 2θ between 10°-80° for undoped and prepared MoO_3 catalysts as shown in Fig. 2. XRD pattern for isothermal carburization behaviour of undoped MoO_3 at 700°C for 90 min indicates a phase change occurred from MoO_3 to MoO_2 (2θ = 36.96° and 73.96°) and Mo_2C (2θ= 34.49° and 61.63°). This can infer that the average crystallinity size of undoped MoO_3 was 54.81 nm calculated by using Scherrer equation. A study conducted by Alinda et al., [14] showed MoO_3 completely changed phase to MoO_2 using 20 vol.% CO in 60 vol.% nitrogen by using isothermal reduction mode for 60 min. This result showed that higher volume of CO and increased the isothermal carburized time have the higher ability for formation of Mo_2C.

Besides, 1% (wt./wt.) and 3% (wt./wt.) nickel loading to MoO_3 in the same carburization condition with undoped MoO_3 shows the broad and weak peak of XRD pattern (Fig. 2). These results proved that average crystallinity decreases after isothermal carburized from 35.03 nm to 5.70 nm for 1% (wt./wt.) nickel doped MoO_3. While, for 3% (wt./wt.) nickel doped MoO_3 give the average crystallinity 41.06 nm to 7.11 nm after isothermal carburization. By increasing the load of nickel doped in MoO_3, the crystallinity also increases. Similar results were reported by Ma et al., [13] they stated that 15% (wt./wt.) nickel doped Mo_2C and 10% (wt./wt.) nickel doped Mo_2C give crystallinity both as 7.8 nm and if the lower nickel content were approximately lower than 7.8 nm, $Ni(MoO_4)$ and Mo_2C appeared at 2θ = 61.65° approximately after addition of nickel doped in the MoO_3. This is showing the $Ni(MoO_4)$ change phase to Mo_2C after increases the loading of nickel doped from 1% (wt./wt.) to 3% (wt./wt.) nickel doped. Therefore, further enhancing the MoO_3 carburization effect.

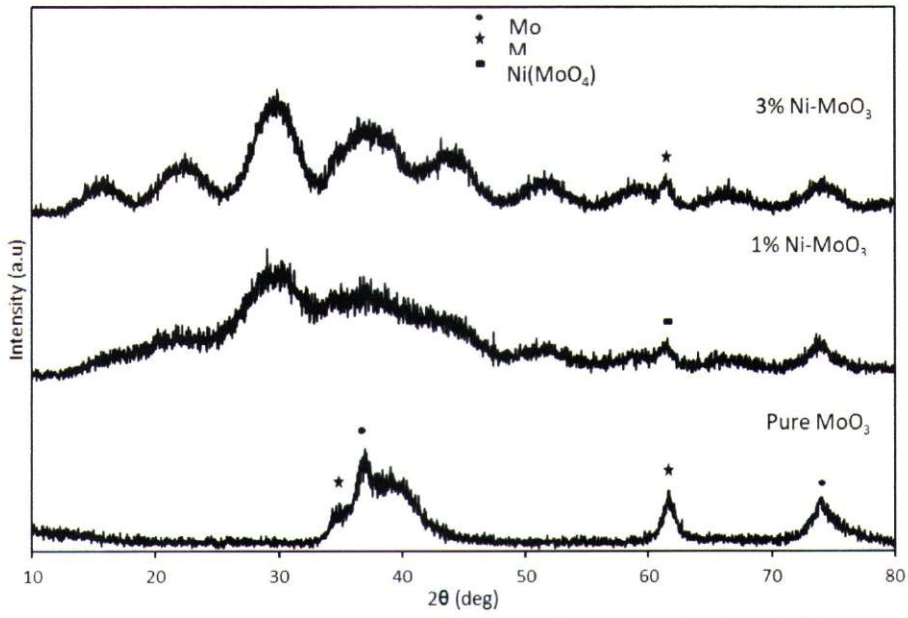

Fig. 2 XRD patterns of carburized undoped and prepared 1% (wt./wt.) and 3% (wt./wt.) of nickel doped MoO_3

Based on the CO-TPR and XRD studies, the characterization of catalyst surface morphology was employed using FE-SEM. Fig. 3 shows the FE-SEM images of the catalyst after isothermal carburization process. FE-SEM images was used to investigate the evolution of structural properties undoped and doped MoO_3 catalysts towards carburization process. Because of the different particles formed after the addition of nickel to MoO_3, it appeared that the morphology evolution could be distinctly distinguished by using instrument FE-SEM. Fig. 3 (a) shows the irregular platelet shape of MoO_2. While in Fig. 3 (b) and (c) both shows after the addition of nickel in MoO_3 it appeared that the phase covering the surface of the particles is amorphous deposited carbon that formed between the platelet shape [15]. This is also showing the product shape becomes irregular and the particles size becomes much smaller which is agreement with the XRD patterns in Fig. 2.

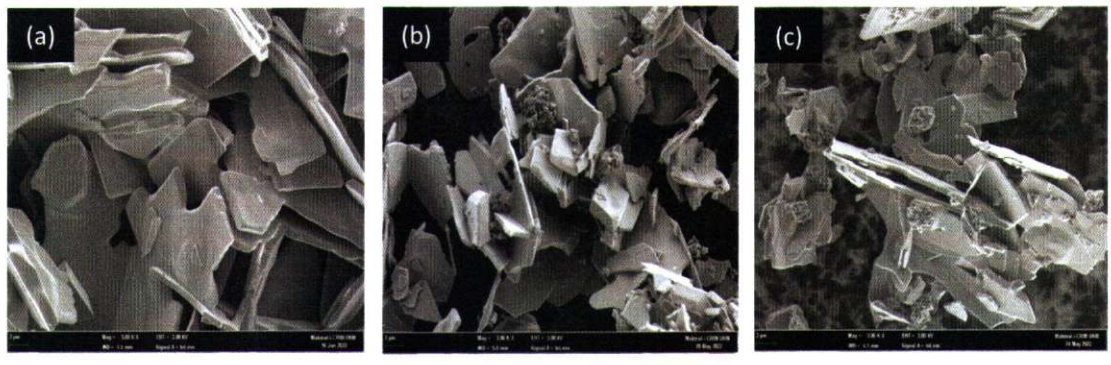

Fig. 3 FE-SEM images of (a) undoped MoO_3, (b) 1% (wt./wt.) of nickel doped MoO_3 and (c) 3% (wt./wt.) of nickel doped MoO_3 after isothermal carburization for 90 minutes at 700°C.

BET surface area (S_{BET}) of undoped MoO3 and prepared nickel doped MoO_3 catalysts are summarised in Table 1. As compared to undoped MoO3, the BET surface area of undoped MoO_3 3.0628 m^2/g was higher compared to nickel doped MoO_3. This is because surface area of undoped MoO_3 is higher due to the more actives sites formed. After addition of 3% (wt./wt.) nickel doped to MoO_3 the surface area was 1.8573 m^2/g higher compared to 1% (wt./wt.) nickel doped to MoO_3 which is 0.2072 m^2/g. This is due to some additional metal oxide namely nickel, expected to have partially filled the pores of MoO_3 and partially formed a new surface outside the pores of MoO_3. This

phenomenon is due to the larger size of the additional cluster metal and its quantity in excess of the pore volume. The larger pore size of 3.1623 nm for 1% (wt./wt.) nickel doped MoO_3 indicates a smaller surface area (0.2072 m^2/g) and pore volume (0.0002 cm^3/g).

Table 1 BET analysis of undoped MoO_3 and nickel doped MoO_3 before isothermal carburized.

Catalysts	$S_{BET}(m^2/g)$	Pore size (nm)	Pore volume (cm^3/g)
Undoped MoO_3	3.0628	2.2751	0.0017
1% Ni-MoO_3	0.2072	3.1623	0.0002
3% Ni-MoO_3	1.8573	2.8590	0.0013

While Table 2 summarizes the BET analysis of undoped MoO_3 and nickel doped MoO_3 following isothermal carburization. The surface area of undoped MoO_3 was 2.1617 m^2/g, while doped MoO_3 with 1% (wt./wt.) and 3% (wt./wt.) nickel was 3.7544 m^2/g and 12.5828 m^2/g, respectively, demonstrating that increasing the addition of nickel to MoO_3 improved the surface area. This might mean that there are more active sites, which could be related to the 90 min isothermal carburization at 700°C, which is an optimum temperature to reduced MoO_3 after doping. As a result, addition of nickel can greatly enhance the surface area of MoO_3. However, when the molar ratio of nickel doped MoO_3 is more than 5/95, the surface area is drastically reduced. This is due to the covering of nickel particles on the surface of Mo_2C in the case of higher nickel loading amounts [13]. The pore size of undoped MoO_3 was 2.2670 nm, while the pore size after nickel addition at 1 % (wt./wt.) and 3% (wt./wt.) was 5.6889 and 3.5789 nm, respectively. The results revealed that adding the nickel loading to MoO_3 reduced the pore size. Furthermore, the pore volume of undoped MoO_3 was 0.0012 cm^3/g, however increasing the addition of nickel from 1 % (wt./wt.) and 3% (wt./wt.) raised the pore volume to 0.0053 cm^3/g and 0.0113 cm^3/g, respectively.

Table 2 BET analysis of undoped MoO_3 and nickel doped MoO_3 after isothermal carburized.

Catalysts	$S_{BET}(m^2/g)$	Pore size (nm)	Pore volume (cm^3/g)
Undoped MoO_3	2.1617	2.2670	0.0012
1% Ni-MoO_3	3.7544	5.6889	0.0053
3% Ni-MoO_3	12.5828	3.5789	0.0113

Conclusion

TPR was used to analyze and compare the carburization behavior of undoped MoO_3 and nickel doped MoO_3 samples, which were characterized by XRD, FE-SEM and BET analysis. The resilts revealed that a higher volume of CO and an enhanced isothermal carburized time of 90 min have a greater potential to produce Mo_2C supported by XRD analysis. Furthermore, when nickel was added to MoO_3, it was discovered that the phase covering the surface of the particles is amorphous deposited carbon that developed between the platelet shape in the FE-SEM morphology. When the nickel loading is higher, BET analysis show increasing in the surface area of catalyst. It may be deduced that increasing nickel addition not only reduced the reduction temperature of MoO_3, but also enhance the carburization of catalyst. Nickel influences molybdenum's coordination environment and the strength of Mo-O bonds which lowering the reduction temperature of doped MoO_3.

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