HYDROGENATION KINETIC OF CARBON DIOXIDE USING MICROWAVE INDUCED ALLOYING Mo_2C AS CATALYST.

Hainorita Hairon and Abdul Rahim Yacob
Department of Chemistry, Faculty of Science, UniversitiTeknologi Malaysia, 81310 Johor Bahru.

Abstract

Due to overwhelming issues on greenhouse effects, there are many approaches to convert the greenhouse gas, carbon dioxide to reduce global warming. Based on this problem, a kinetic study of hydrogenation of carbon dioxide via prepared microwave induced alloying (MIA) molybdenum carbide was conducted. The MIA technique that had been employed supported the "green chemistry" theme. Prepared Mo_2C catalyst was characterized using Nitrogen Adsorption Analysis (NAA), X-Ray Diffraction (XRD), and Ammonia-Temperature Desorption (TPD) analysis. The catalyst was used in the hydrogenation of carbon dioxide to carbon monoxide in a modified household microwave oven and the product was characterized by Fourier Transform Infrared Spectroscopy (FTIR). The nitrogen adsorption analysis showed that the surface are of the prepared molybdenum carbide is $76.70m^2/g$ which is higher than the commercial. XRD analysis indicated the peaks that represent the carbides formation. NH_3-TPD analysis showed the present of weak, medium, and strong acid site for the prepared molybdenum carbide. In the application of the prepared catalyst, our finding suggested that the minimum starting temperature for the reaction is 350°C, which proved the catalyst was indeed effective. The kinetic analysis of the IR spectrum concludes that the order of reaction is second order with the activation energy lower than non-catalytic reaction that is 128.26 kJ/mol.

Keywords: Microwave induce alloying, molybdenum carbide, hydrogenation, reaction order

---

INTRODUCTION

Carbon dioxide, CO_2 gas is the widely known as the greenhouse gas as it causes global warming. Researchers have done studies on how to convert the greenhouse CO_2 gas to valuable or useful chemicals. It can be used as the starting materials for the production of valuable chemicals [1]. There are many kinds of reaction to convert CO_2 gas to useful gas or chemicals, including methanation, hydrogenation and reverse water gas shift reaction. One of the valuable chemical is the SYNGAS, carbon monoxide, CO that has been studied extensively.

Carbon monoxide is a gas that has many applications in industry in bulk chemical manufacturing. As an example, the production of detergent from the hydroformylation reaction of alkene, CO and H_2 gas to produce a large quantity of aldehydes to couple with Shell Higher Olefin Process. Besides that, the production of methanol also can be formed by the hydrogenation reaction of carbon monoxide. The hydrogenation of CO could also formed diesel by conversion of coal or biomass that produced in the coupled C-C bond formation in this reaction based on Fischer-Trophsch Process where CO is hydrogenated with hydrocarbon fuels [2].

In this study, molybdenum carbide, Mo_2C catalyst supported by commercial activated carbon is used.The introduction of molybdenum carbide as an alternative catalyst in the hydrogenation of carbon dioxide to produce carbon monoxide gas will be looked into. As this catalyst has characteristic that similar to the noble metal for surface catalyst, molybdenum carbide has gained attention as a substitute for this reaction to increase the reaction forward. The ability of this catalyst is proven when it more active than Fe_3C, WC and TaC [3]. The microwave induced alloying (MIA) technique used in the preparation of the catalyst is a very easy and cheap method where it applies the simple modified household microwave oven that successfully produced tungsten carbide, WC alloys and therefore, this technique looks promising for the preparation of molybdenum carbide,Mo_2C catalyst [8]. The hydrogenation of global warming gas, carbon dioxide to produced syngas, carbon monoxide is promoted to convert the harmful gas into useful one and the kinetic analysis on the reaction was conducted.

EXPERIMENTAL

Preparation of molybdenum carbide catalyst

17.65g of ammonium heptamolybdate (AHM) was transferred into a 100 mL volumetric flask and distilled water was added to the mark for the preparation of 1 M of the molybdenum standard solution. Next, 0.5g of carbon (7mol) was added into the 11.91 mL solution of 1M molybdenum standard solution in a three-neck round bottom flask. To make sure that the reaction free from oxygen atmosphere, the nitrogen gas was bubbled for 30 min in the flask. Then, by using 800 W and 2 min radiation, the microwave induced alloying was conducted in modified domestic microwave oven (Figure 1) until the sample dried. Lastly, the excess molybdenum was removed by washing the product obtained with hot water and dried in an oven at 105±5°C overnight [4].

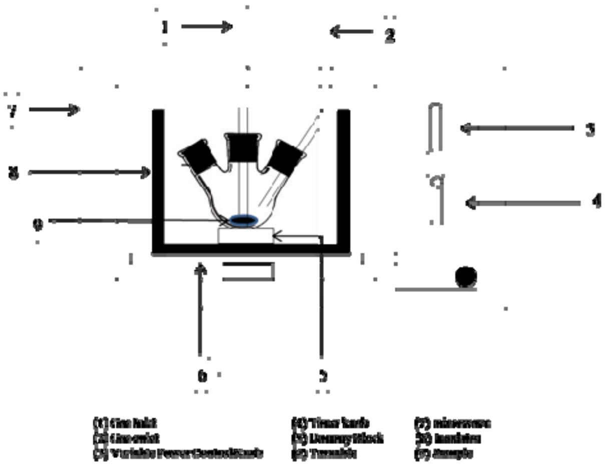


Figure 1: The schematic diagram of modified microwave oven [4]

Hydrogenation of carbon dioxide

A glass tube was used for the catalytic reaction. The prepared catalyst was placed in the tube and embedded between wools and silica powder. To get an optimum reaction of the gas, the materials were arranged and packed in the glass tube to avoid any air inside it (Figure 2). Adsorbed gas and moisture in the catalyst could distract the reaction. To avoid this problem, the catalyst was pre-heated with N_2 gas at 400°C. The catalyst is then cooled down at room temperature but still under N_2 atmosphere. Before the reaction started, H_2 and CO_2 gases are allowed to flow into the reaction vessel for 30 minutes. The temperature 300°C, 350°C, 400°C and 450°C were used for this reaction. The flow ratio of CO_2:H_2gas is 1:4. The IR spectrum was taken after the desired temperature and continues for 60 min, with 10 min interval.

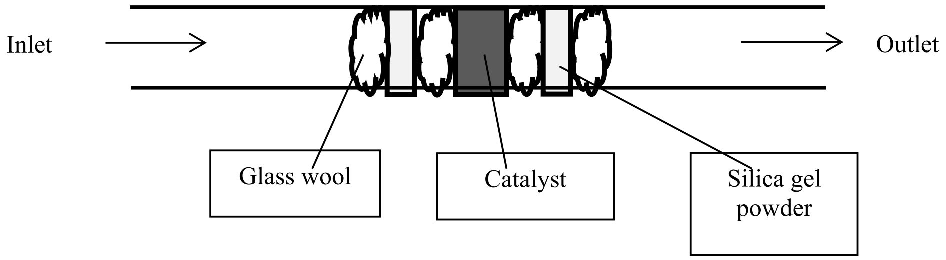


Figure 2: Catalyst arrangement in glass tube

RESULT AND DISCUSSION

Characterization of Prepared Mo_2C

From the figure 3 above, it can be clearly shown that the highest peak was at 39.4° followed by 38.0°, 34.4°, 61.5°, 69.6° and 74.6° which represent the molybdenum carbide, Mo_2C. The slightly peaks of 26.2°, 37.0, and 53.5° proposed that there was molybdenum oxide, MoO_2 present in the sample. This was due to the lack of molybdenum presented in the sample that causes the reaction to stop at the formation of MoO_2 [4]. It can be conclude that there was small amount of MoO_2 that is not completely converted to molybdenum carbide.

This event happened due to the formation of MoO_3 from the decomposition of precursor AHM and then it was reacted with carbon to form MoO_2. Most of the molybdenum oxide was successfully converted into molybdenum carbide while some of it only stops at MoO_2. This may also be due to the lack of time of exposure in microwave which limited the conversion of molybdenum oxide to molybdenum carbide as desired. Finally, the MoO_3 and most of MoO_2 were successfully converted to the hexagonal β-Mo_2C when using the molybdenum to carbon of 2:7. The stoichiometric 2:7 showed all six characteristics peaks belong to hexagonal Mo_2C. The reaction mechanisms are as stated below [5,6]:

$$(NH_4)_6Mo_7O_{24}.4H_2O \longrightarrow MoO_3 + 6NH_3 + 7H_2O \qquad \text{(Eq. 1)}$$

$$2MoO_3 + 7C \longrightarrow 2MoO_2 + 2CO + 5C \longrightarrow Mo_2C + 6CO \qquad \text{(Eq. 2)}$$

From the equations above, the AHM was firstly converted to MoO_3 (Eq. 1) and then it was reacted with carbon to form MoO_2. The MoO_2 was further reacted with carbon and finally produced the desired product that is Mo_2C (Eq. 2).

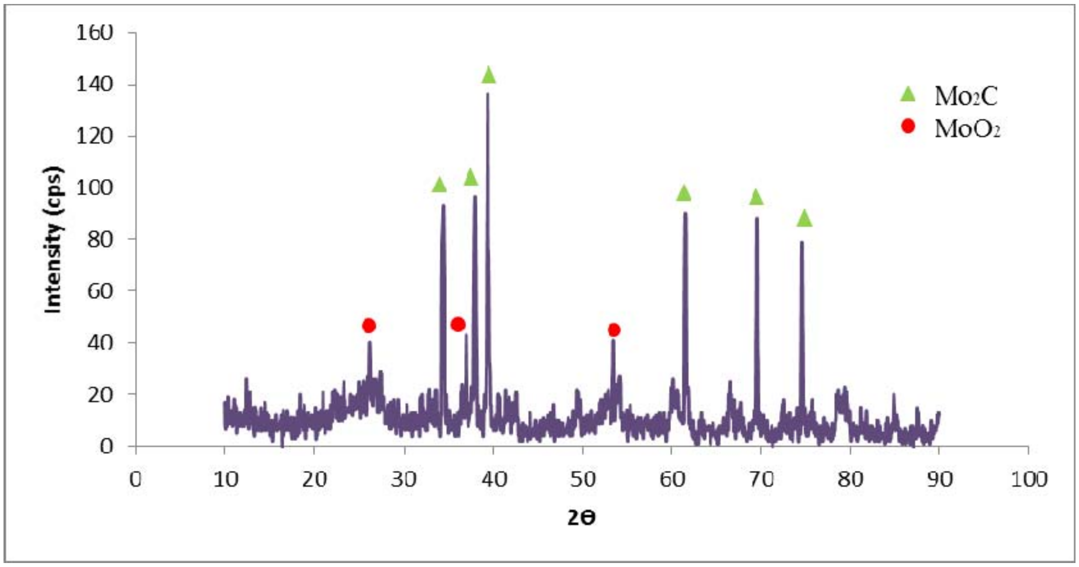


Figure 3: XRD pattern for the prepared MIA molybdenum carbide, Mo_2C

For the crystallity of the catalyst, the size of the particles is calculated by using Scherrer equation:

$$\tau = \frac{K\lambda}{\beta cos\theta} \qquad \text{(Eq. 3)}$$

Where, τ = mean size of the ordered (crystalline) domains
K= dimensionless shape factor
λ= X-ray wavelength
β= line broadening at half the maximum intensity (FHWM)

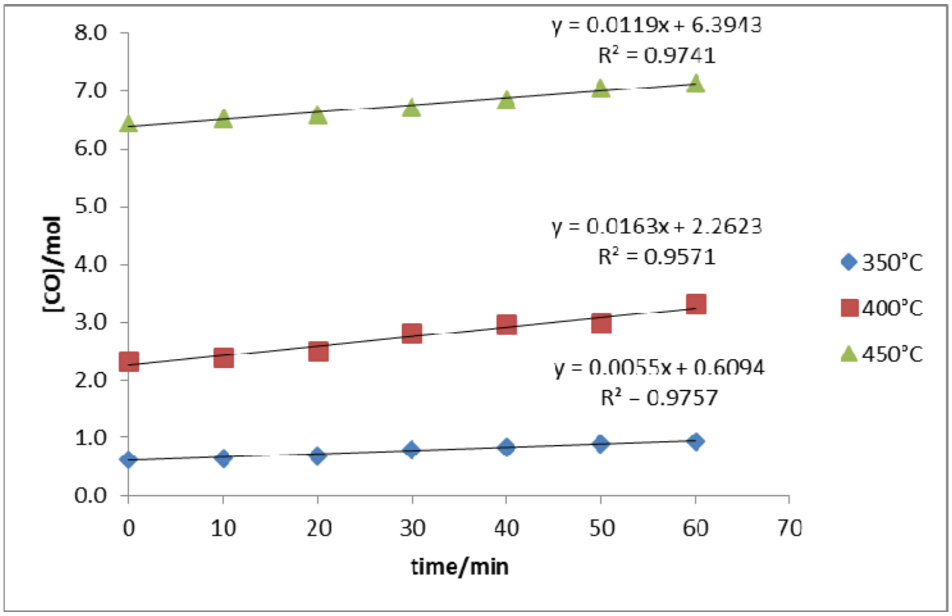
From the formula, the average size calculated is 26.762 nm which is considered as nanoscale sized particles. The size is much larger than the molybdenum carbide prepared using temperature programmed reaction conducted by Gerardo *et al* (2015) which is 1.4 nm [9]. However, this result cannot be the absolute fact to conclude that the particle size isnanoscale. Further analysis should be conducted to support this statement such as Transmission Electron Microscopic (TEM) method.

Kinetic Analysis of Hydrogenation of CO_2 using Prepared Mo_2C

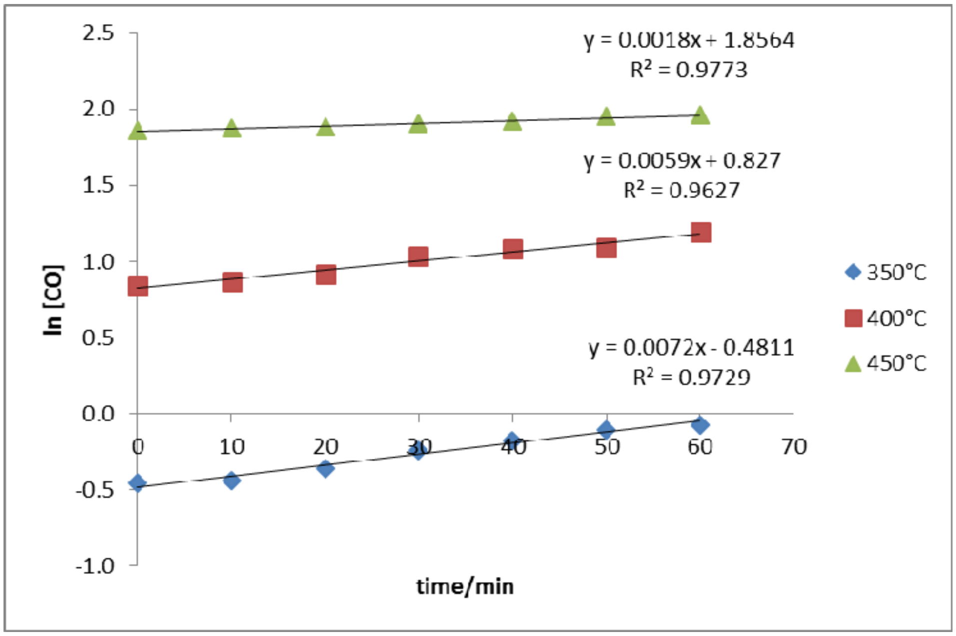
Order of Reaction

Based on the line graphs plotted, the straight regression line was represented as the rate coefficient, *k* (gradient). The zero order graph (Figure 4(a)) shows that the relationship between time and the concentration of CO have good correlation in all temperatures. As can be seen, the R^2 values for 350°C, 400°C, and 450°C are 0.9757, 0.9571, and 0.9741 respectively. Besides, the rate of zero order reaction for 350°C is 0.0055μmol^{-1}s^{-1}, 0.0163μmol^{-1}s^{-1} for 400°C, and 0.0119μmol^{-1}s^{-1}for 450°C.

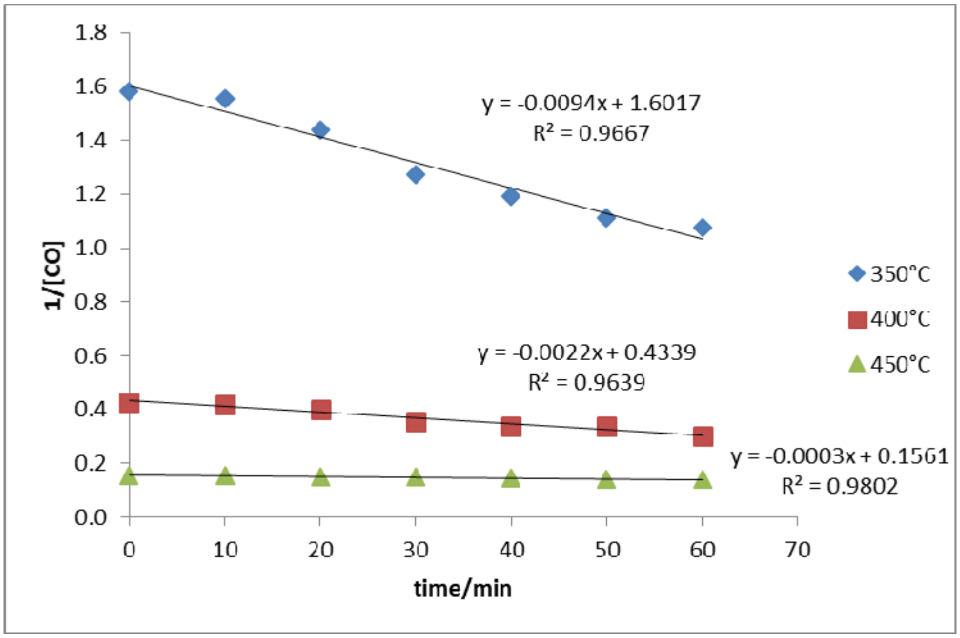
Same goes with first order of reaction graph (Figure 4(b)). Each temperature shows R^2 value higher than 0.9 which means a good correlation between the axes. The rate of reaction is 0.0072s^{-1}, 0.0058s^{-1}, and 0.0018s^{-1} for temperature 350°C, 400°C, and 450°C respectively. The correlation value, R^2 for the first order is 0.9279 at 350°C, 0.9627 at 400°C, and 0.9773 at 450°C.For the second order of reaction, figure 4(c) illustrated shows decline pattern with negative value of coefficient rate, *k*. The rate is 0.0094μmol^{-1}s^{-1}, 0.0022μmol^{-1}s^{-1}, and 0.0003μml^{-1}s^{-1} with the R^2 value of 0.9667, 0.9639, and 0.9802 for temperature 350°C, 400°C and 450°C respectively.



(a)



(b)



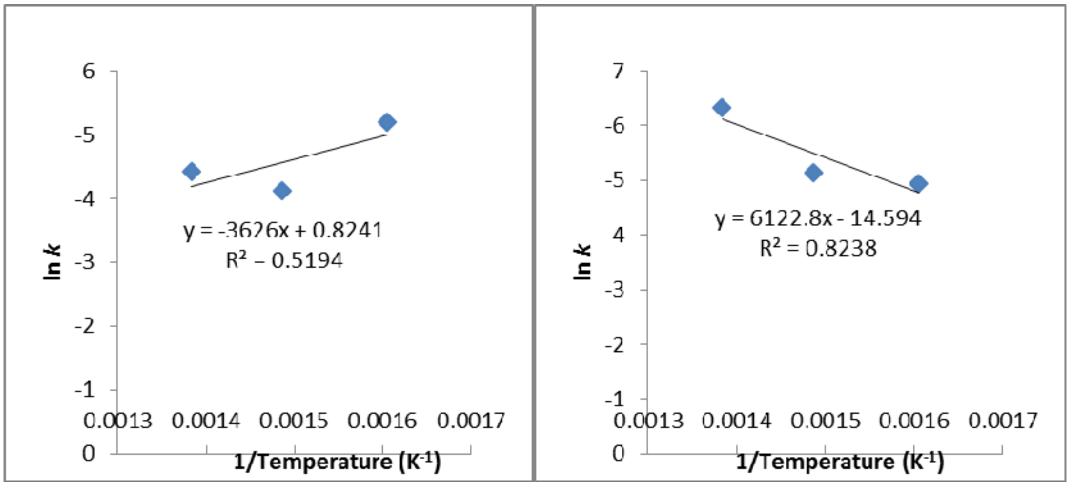
(c)

Figure 4: The graph of **(a)** zero order, **(b)** first order, and **(c)** second order of hydrogenation reaction

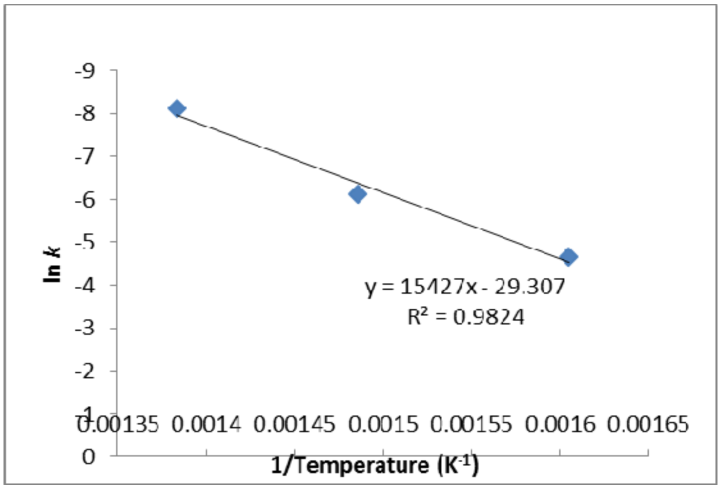
From the graph shown in Figure 4, it can be concluded that the order of the hydrogenation of CO_2 by using Mo_2C prepared by MIA method at 400°C was second order which can be indicated by the highest value of correlation coefficient, R^2 of 0.9667 for 350°C, 0.9639 for 400°C, and 0.9802 for 450°C. The highest value of R^2 represented the best fit of the line which indicating the order of reaction. However, this result still needs to be confirmed by the thermodynamic analysis to strengthen the fact that the order of reaction is second order.

Activation Energy, E_A

From the linear equation derived from the graph in Figure 5, the gradient that indicate the value of constant, *k*. can be used to plot the graph of ln*k* against 1/temperature to determine the activation energy by using the Arrhenius equation.



(a) **(b)**



(c)

Figure 5: Arrhenius Law graph for (a) zero order, (b) first order, and (c) second order of reaction

Figure 5 (a,b, and c) shows the graph oh Arrhenius law for zero order, first order, and second order respectively. Based on this graph, it can be seen that the second order graph have the highest correlation coefficient, R^2 which is 0.9824 compared to zero order and first order which is 0.5194 and 0.8238 each. By using the same determination as graphical method in previous sub-section, the order of the hydrogenation reaction is second order. Thus, the activation energy is calculated based on Arrhenius Law of second order graph.

Based on the calculation, the activation energy, E_A and pre-exponential, A were 128.26 $kJmol^{-1}$ and 5.34 x 10^{12} $mols^{-1}$ respectively. Interestingly, the activation is lower than the activation of non-catalytic reaction conducted by Bustamante *et al* (2004) which is 222.00 $kJmol^{-1}$[10]. This statement shows that the prepared MIA Mo_2C is successful in lowering the activation energy of the hydrogenation of CO_2 to CO reaction. Figure below shows the energy profile diagram of the reaction:

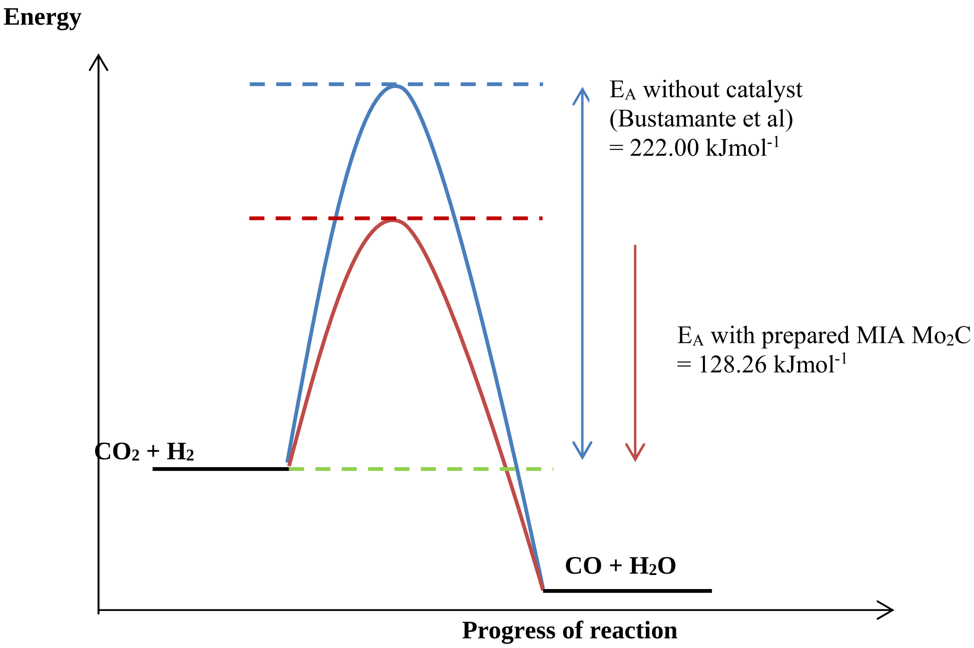


Figure 6: Energy profile diagram of a reaction

Repeatability of Catalyst

Repeatability or reusability of the catalyst was determined by repeating the hydrogenation reaction up to five times for every temperature. The experiment was conducted at temperature 350°C, 400°C, and 450°C by 1:4 continuous flow of CO_2:H_2 gas until an hour. Figure 7.1, 7.2, and 7.3 indicate the percentage conversion of carbon dioxide into carbon monoxide at different temperature 350°C, 400°C, and 450°C respectively. From figure 7.1, it can be seen that there is no significant different between the first (R1) and second (R2) cycle of the reaction using the prepared molybdenum carbide catalyst. The percentage conversion started to increase at the third cycle followed by the fourth cycle. Unfortunately, the increments stop at the last cycle (R5) which it can be seen at the graph that the percentage conversion started to drop except at the 10 and 60 minute of the reaction.

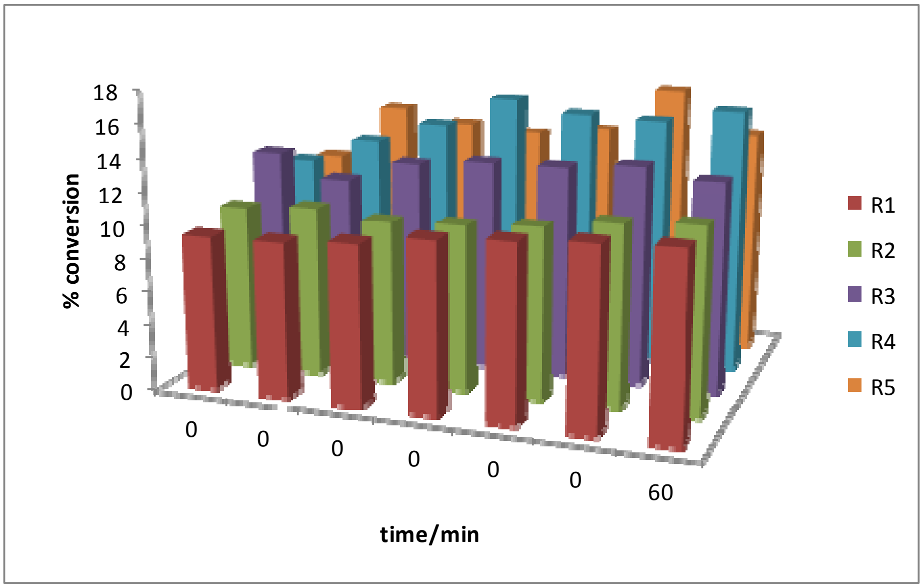


Figure 7.1: The repeatability of the prepared molybdenum carbide in the hydrogenation of carbon dioxide at temperature 350°C

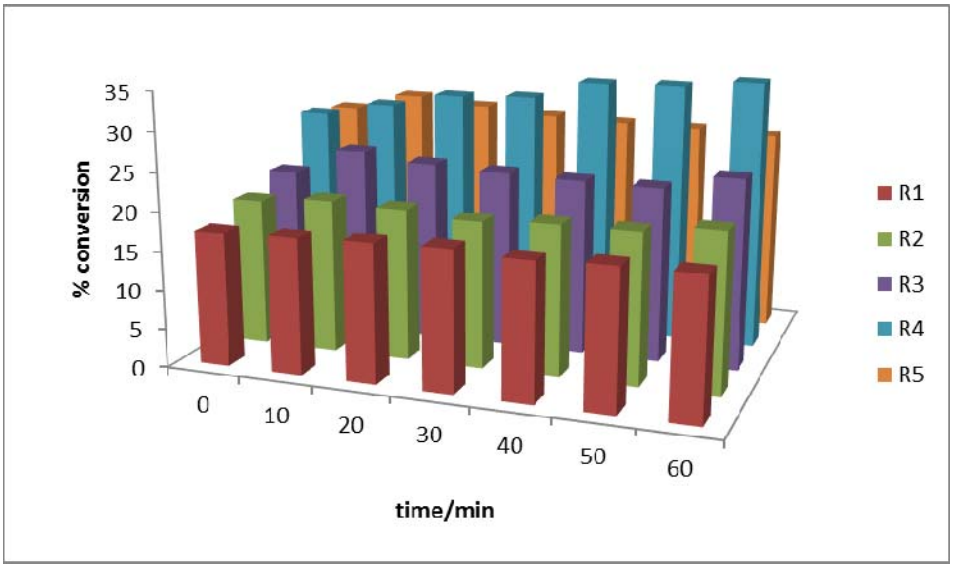


Figure 7.2: The repeatability of the prepared molybdenum carbide in the hydrogenation of carbon dioxide at temperature 400°C

For the reaction at 400°C (refer Figure 7.2), the percentage conversion of carbon dioxide into carbon monoxide increased gradually from R1 to R3. The percentage conversion continues to increase sharply at R4 followed by decrement at final cycle of the reaction. There are no big changes of increasing pattern shows at the first to fourth cycle of the reaction conducted at 450°C (refer Figure 7.3). However, the percentage conversion to product also declined at the fifth cycle of the reaction.

Based on the findings, it can be concluded that the prepared MIA Mo_2C catalyst was able to be reused up to four times for the hydrogenation of carbon dioxide reaction. This finding has proved that the molybdenum carbide can be classified as heterogeneous catalyst as the reusability is one of an important characteristic of a catalyst [7]. However, this statement is not the final fact that the catalyst is cannot be used for the fifth cycle at all. The catalyst still can be used for the small amount of desired product and it is expected that the percentage conversion to product will continue to decrease.

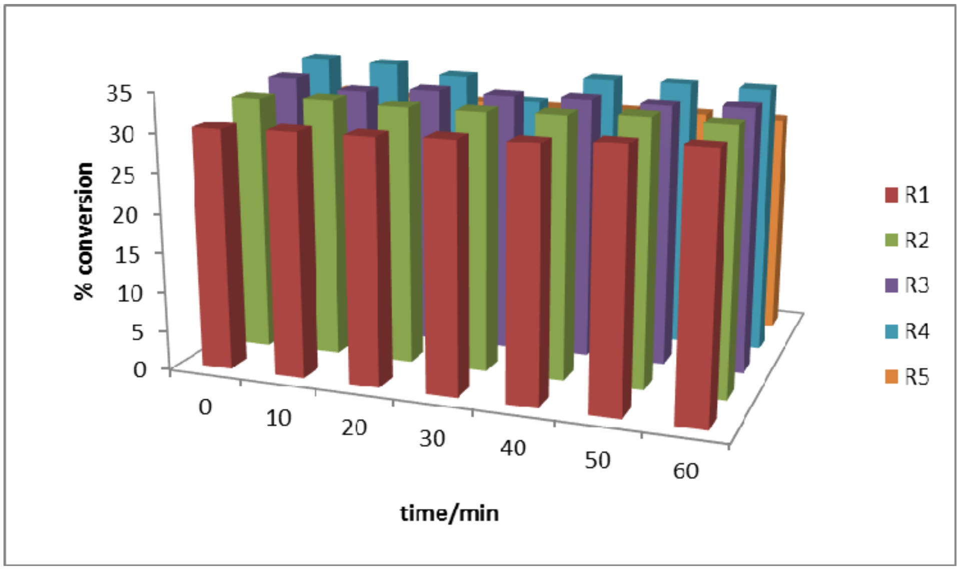


Figure 7.3: The repeatability of the prepared molybdenum carbide in the hydrogenation of carbon dioxide at temperature 450°C

CONCLUSION

Generally, the study of catalytic activity using the in-house built reactor shows that the conversion of CO_2 in producing CO gas started at temperature 350°C by using the prepared MIA molybdenum carbide, Mo_2C catalyst. The characterization of the prepared catalyst shows that the molybdenum oxide MoO_3 was successfully converted into MoO_2 and further reacted with carbon to produce the desired molybdenum carbide, Mo_2C with crystallite size 26.762 nm. From the graphical method to determine the order of the hydrogenation of carbon dioxide to carbon monoxide reaction by using the prepared Mo_2C catalyst, it shows that the order of reaction is second order. From this finding, the activation energy was calculated by using Arrhenius Law equation which is 128.26 $kJmol^{-1}$and the catalyst can be reused for maximum four times of hydrogenation of CO_2 to CO reaction cycle.

REFERENCES

1. Wang, W., Wang, S.P., Ma, X.B., Gong, J.L. (2011). Recent advances in catalytic hydrogenation of carbon dioxide. Chem. Soc. Rev. 40, 3703–3727.
2. Klaus, W., Hans, J.A., John, W. (1997). Industrial Organic Chemistry. 3rd Ed. New York, USA: VCH Publishers, Inc. 13-55.
3. Kubo, M., Ando, M., Sakahara, S., Jung, C., Seki, K., Kugasaya, T., Endou, A., Takami, S., Imamura, A., Miyamoto, A. (2004). Development of tight-binding, chemical-reaction-dynamics simulator for combinatorial computational chemistry.Appl. Surf. Sci. 223, 188-195.

4. Yacob A. R.,Mutajab, M.K.A.A. (2012). Preparation of molybdenum carbide via Microwave Induced Alloying. JurnalTeknologi (Sains&Kej)57(1), 155 - 162.
5. Vallance, S.R., Kingman, S., Gregory, D.H. (2007). A New Method for the Synthesis of Molybdenum Carbide. Material Letters61, 5173-5174.
6. Parviz, D., Kazemeini, M., Rashidi, A. M., Jozani, K. (2010). Synthesis and Characterization of MoO3 Nanostructures by solution Combustion Method Employing Morphology and Size Control. Journal of Nanoparticle Research12, 1509-1521.
7. Fernandes, R., Patel, N., Miotello, A., Jaiswal, R., Kothari, D.C. (2010). Stability, durability, and reusability studies on Transition Metal-Doped Co-B Alloy Catalyst for Hydrogen Production. International Journal of Hydrogen Energy36(21), 13379-13391
8. Yacob, A. R., Hanapi, S. Z., Masrom, N. I. (2010). Tungsten Carbide Synthesis by Microwave-Induced Alloying Using Phosphoric Acid Activated Palm Kernel Shell Carbon. Journal of Material Science and Engineering4(12), 1509-1521.
9. Gerardo, V., Hector, G., Maria, L.F., Frauwallner, C.E., Scott, P.P. (2015). Synthesis of nanocrystalline molybdenum carbide materials and their characterization. Catalyst Today250, 123-133.
10. Bustamante, F., Enick, R. M,.Cunigi, A. V., Killmeyer, R. P., Howard, B. H., Rothenberger, K. S., Ciocco, M. V., Morreale, B. D., Chattopadhyay, S., Shi, S. (2004). High Temperature Kinetics of the Homogeneous Reverse Water-Gas Shift Reaction. American Institute of Chemical Engineer50, 1028-1041.