

Article

CO₂ Conversion to Methanol over Novel Carbon Nanofiber-Based Cu/ZrO₂ Catalysts—A Kinetics Study

Israf Ud Din ^{1,2,*}, Maizatul S. Shaharun ³ , Abdul Naeem ², Mshari A. Alotaibi ¹, Abdulrahman I. Alharthi ¹ and Qazi Nasir ⁴

¹ Department of Chemistry, College of Science and Humanities, Prince Sattam Bin Abdulaziz University, P.O. Box 173, Al-Kharj 11942, Saudi Arabia; alosaimi@psau.edu.sa (M.A.A.); a.alharthi@psau.edu.sa (A.I.A.)

² National Centre of Excellence in Physical Chemistry, University of Peshawar, Peshawar 25120, Pakistan; naeem@uop.edu.pk

³ Department of Fundamental and Applied Sciences, Universiti Teknologi Petronas, Bandar Seri Iskandar, Tronoh 31650, Perak, Malaysia; maizats@utp.edu.my

⁴ Department of Chemical Engineering, University of Nizwa, Nizwa 616, Oman; qazinasir@unizwa.edu.om

* Correspondence: i.din@psau.edu.sa

Received: 28 April 2020; Accepted: 15 May 2020; Published: 19 May 2020



Abstract: Ongoing industrialization has deteriorated the global environment. Global warming is a human-induced issue affecting the environment. The alarming increase in CO₂ emissions is among the major contributors to global warming. The conversion of CO₂ to methanol is an economically viable and environmentally friendly solution to mitigate its concentration. Here, hydrogenation of CO₂ was studied over carbon nanofiber-based Cu/ZrO₂ catalysts. Kinetics investigations were carried out for the reaction. Overall, kinetics data indicated that CO₂ conversion follows a pseudo-first-order reaction. The kinetics studies were further modeled by using an artificial neural network, which supported the experimental kinetics study.

Keywords: CO₂ conversion; pseudo-first-order; activation energy

1. Introduction

Rapid industrialization to cope with growing population demands has adversely affected the natural environment. The rise in CO₂ concentration as a result of industrialization is considered to be a major contributor to global warming [1]. CO₂ hydrogenation to methanol provides a win–win situation by diminishing CO₂ concentration on the one hand while producing fuel in the form of methanol on the other [2–5].

CO₂ hydrogenation to methanol is given by Reaction 1 [6].



To support methanol synthesis on an industrial scale, many kinetics models have been proposed in the literature for CO₂ conversion to methanol. Kinetic investigations of low-temperature CO₂ conversion have a potential impact on designing and controlling the reactor systems for such processes [7]. Several kinetic models with variant reaction mechanisms have been reported for methanol synthesis by CO₂ conversion. The Langmuir–Hinshelwood–Hougen–Watson model was applied over a CuO/ZnO/Al₂O₃ catalyst by Skrzypek et al. [8]. Similarly, a dual-site mechanism-based kinetic model was developed [9]. Likewise, a kinetic model with three-site adsorption was applied over a copper–zinc catalyst [10].

Recently, Díez-Ramírez et al. [11] documented the application of a three-site mechanism-based model over a Pd–Cu–Zn/SiC catalyst.

The early-stage kinetics model assumes that methanol synthesis is only possible from CO, where CO₂ cannot be used in the synthesis of methanol [12–15]. More recently, complex kinetics models have been introduced based on experimental findings that indicate that methanol is not produced mainly from CO but in fact from CO₂ [8,15–17].

An artificial neural network (ANN) model has been applied for CO₂ hydrogenation to methanol. The application of this model has been found to be very promising for describing the chemistry of complex reactions. Similarly, the model also helps understanding of the reaction mechanism where exact mechanisms of reactions are not well comprehended. The application of this model is therefore best suited in the case of complex CO₂ hydrogenation with non-univocal reaction mechanisms. Furthermore, an ANN model has been recorded as 120–5000 times faster when compared to phenomenological models, giving extra advantage to this model regarding computation time [18]. Therefore, the ANN model has found wide application in kinetics investigations in chemical and biological reactors [19,20]. The ANN model was applied to investigate kinetics study over the Al₂O₃ catalyst for methanol dehydration by Alamolhoda et al. [21] in using a slurry reactor. The study found that the experimental kinetics data was significantly matched by ANN model estimations. In this approach, which is considered to be very effective due to the involvement of computer architecture, the ANN model uses the numerical input and output values obtained from experimental data.

Carbon nanofibers (CNFs), due to high surface area, are considered to be a good catalyst support [22,23]. The application of CNFs is further amplified in liquid-phase reactions due to the complete absence of bottle-like pores which ultimately mitigate mass transfer limitations [24,25]. Therefore, CNF-supported catalysts have been reported to have better catalytic profiles compared to traditional metal oxide-based catalysts [1]. In the current work, kinetics studies of CNF-supported Cu/ZrO₂ catalysts in terms of CO₂ conversion have been undertaken. The significance of the current study can be comprehended by the fact that it can potentially be applied for the understanding of a detailed reaction mechanism of CO₂ conversion to methanol over CNF-supported Cu/ZrO₂ catalysts, which is one of the hypotheses of the current work.

The goal of the current work is a kinetics study of CO₂ conversion. Based on our previous work, the catalyst with optimum activity (Cu.ZrO₂/CNFs with 15 wt.% of Cu and ZrO₂ each) was used. The catalyst was characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques to assess the phase and morphology of the catalyst, respectively. Furthermore, the reported kinetics data was supported by the application of an ANN model in the current work.

2. Results and Discussions

2.1. XRD and TEM Investigations

The XRD spectrum and transmission electron microscopy (TEM) image of the CZC450 catalyst are displayed in Figure 1. Hexagonal graphitic planes of CNFs are confirmed by two prominent XRD diffraction peaks at 2θ values of 26° and 44° (JCPDS No. 41-1487) [25]. Similarly, small diffraction lines at 36°, 50°, 54°, 63°, and 78° indicate the presence of CuO. TEM investigation revealed the successful deposition of zirconia and copper on the surface of the support. The existence of individual metals is identified by arrows based on their shapes.

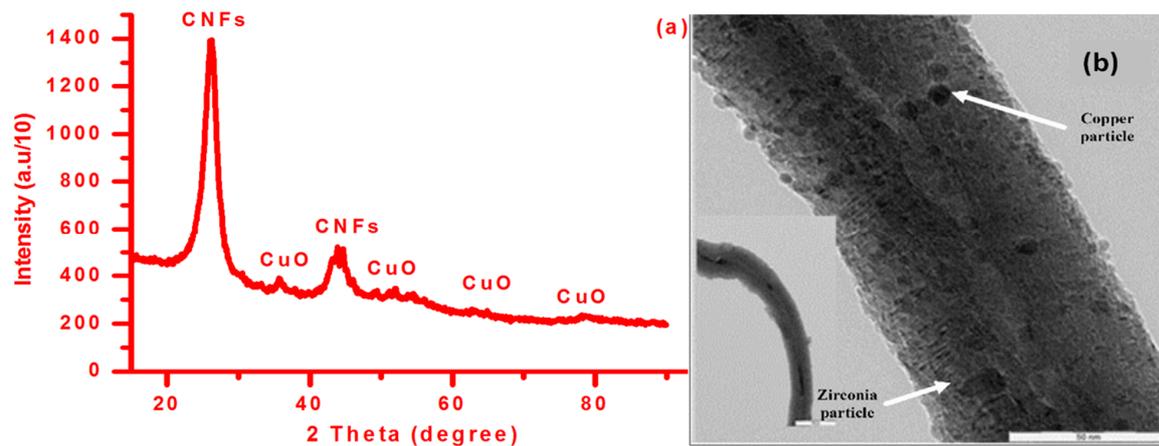


Figure 1. (a) X-ray diffraction (XRD) spectrum; and (b) transmission electron microscopy (TEM) image of CZC450 catalyst.

2.2. Kinetics Study

A slurry reactor was employed to evaluate the kinetics study for CO₂ hydrogenation to methanol. To evaluate the rate of CO₂ conversions, the concentrations of H₂ and H₂O were neglected.

For the concentration ratio $M = \frac{C_{CH_3OH^0}}{C_{CO_2^0}}$, the reaction rate is given as follows:

$$\begin{aligned} \frac{dC_{CH_3OH}}{dt} &= -\frac{dC_{CO_2}}{dt} = C_{CO_2^0} \frac{dX_{CO_2}}{dt} = k_1 C_{CO_2} - k_2 C_{CH_3OH} \\ &= k_1 (C_{CO_2^0} - C_{CO_2^0} X_{CO_2}) - k_2 (M C_{CO_2^0} + C_{CO_2^0} X_{CO_2}) \end{aligned} \quad (1)$$

where $C_{CO_2^0}$, $C_{CH_3OH^0}$ and X_{CO_2} is the initial concentration of CO₂, initial concentration of CH₃OH and CO₂ conversion fraction, respectively.

$$k_c = \frac{C_{CH_3OH^e}}{C_{CO_2^e}} = \frac{M + X_{CO_2^e}}{1 - X_{CO_2^e}} \quad (2)$$

$X_{CO_2^e}$, $C_{CO_2^e}$ and $C_{CH_3OH^e}$ and are equilibrium CO₂ conversion, equilibrium CO₂ concentration and equilibrium CH₃OH concentration, respectively.

The equilibrium constant (k_c) is given by

$$k_c = \frac{k_1}{k_2} \quad (3)$$

Combining Equations (1)–(3) CO₂ conversion at equilibrium is obtained as

$$\frac{dX_{CO_2}}{dt} = \frac{k_1(M+1)}{M+X_{CO_2^e}} (X_{CO_2^e} - X_{CO_2}) \quad (4)$$

Integration of Equation (4) gives

$$-\ln\left(1 - \frac{X_{CO_2}}{X_{CO_2^e}}\right) = -\ln\frac{C_{CO_2} - C_{CO_2^e}}{C_{CO_2^0} - C_{CO_2^e}} = \frac{M+1}{M+X_{CO_2^e}} k_1 t \quad (5)$$

A graph plotted between $-\ln\left(1 - \frac{X_{CO_2}}{X_{CO_2^e}}\right)$ against reaction time for the kinetics data obtained at different reaction temperatures resulted in a straight line as depicted in Figure 2, therefore supporting a pseudo-first-order kinetics hypothesis for CO₂ conversion.

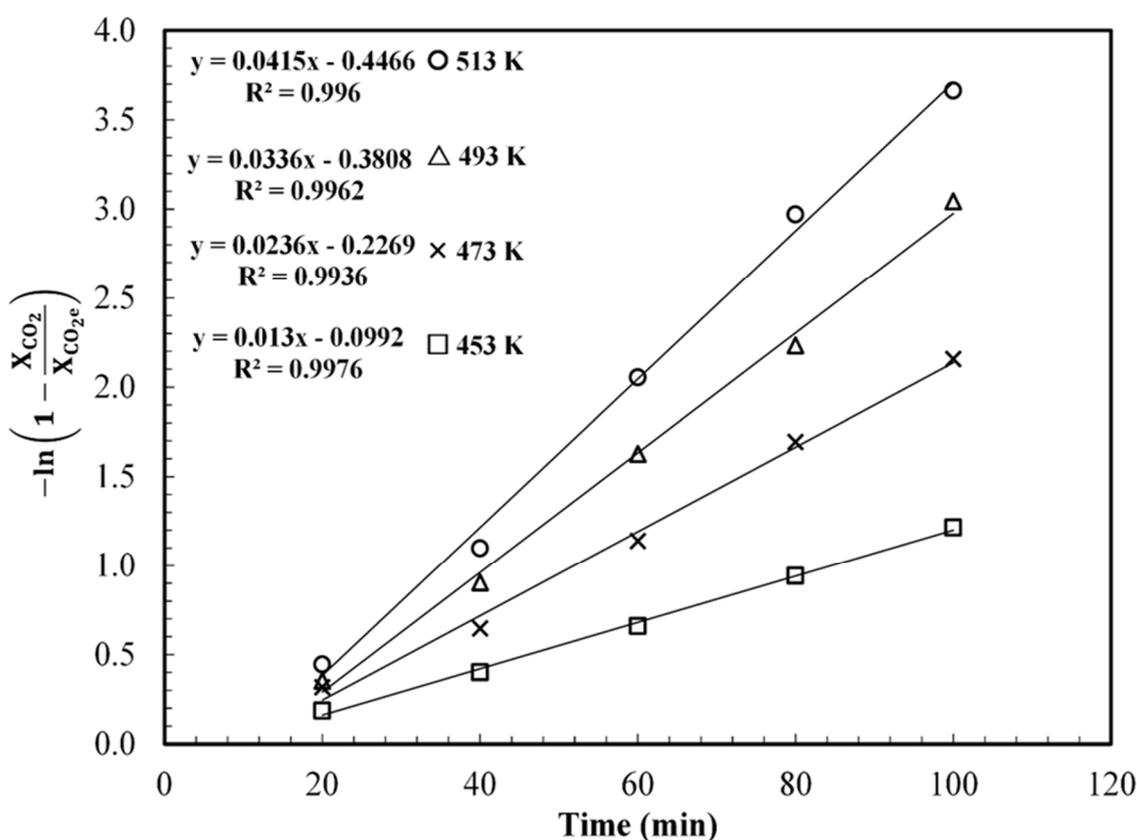


Figure 2. Plots of $-\ln(1 - X_{CO_2}/X_{CO_2e})$ versus reaction time at variant reaction temperatures.

The magnitudes of k_1 , obtained from slope are documented in Table 1.

Table 1. Rate constants at different reaction temperature.

| Reaction Temperature (K) | Rate Constant k_1 |
|--------------------------|---------------------|
| 453 | 0.0015 |
| 473 | 0.0033 |
| 493 | 0.0055 |
| 513 | 0.008 |

2.3. Activation Energy

The Arrhenius equation was used to calculate activation energy as depicted in Equation (6).

$$k_1 = Ae^{-\frac{Ea}{RT}} \quad (6)$$

where k_1 shows rate constant, representing effective collisions between the reactants. R represents the universal gas constant, while Ea stands for activation energy.

Integrating Equation (6), we get the linearized Arrhenius Equation (7),

$$\ln k_1 = \ln A - \frac{Ea}{R} \cdot \frac{1}{T} \quad (7)$$

$\ln k_1$ was plotted versus $1/T$ to measure the activation energy as shown in Figure 3. A value of 54 kJ/mole activation energy was found in the current case, very close to the reported data in Table 2.

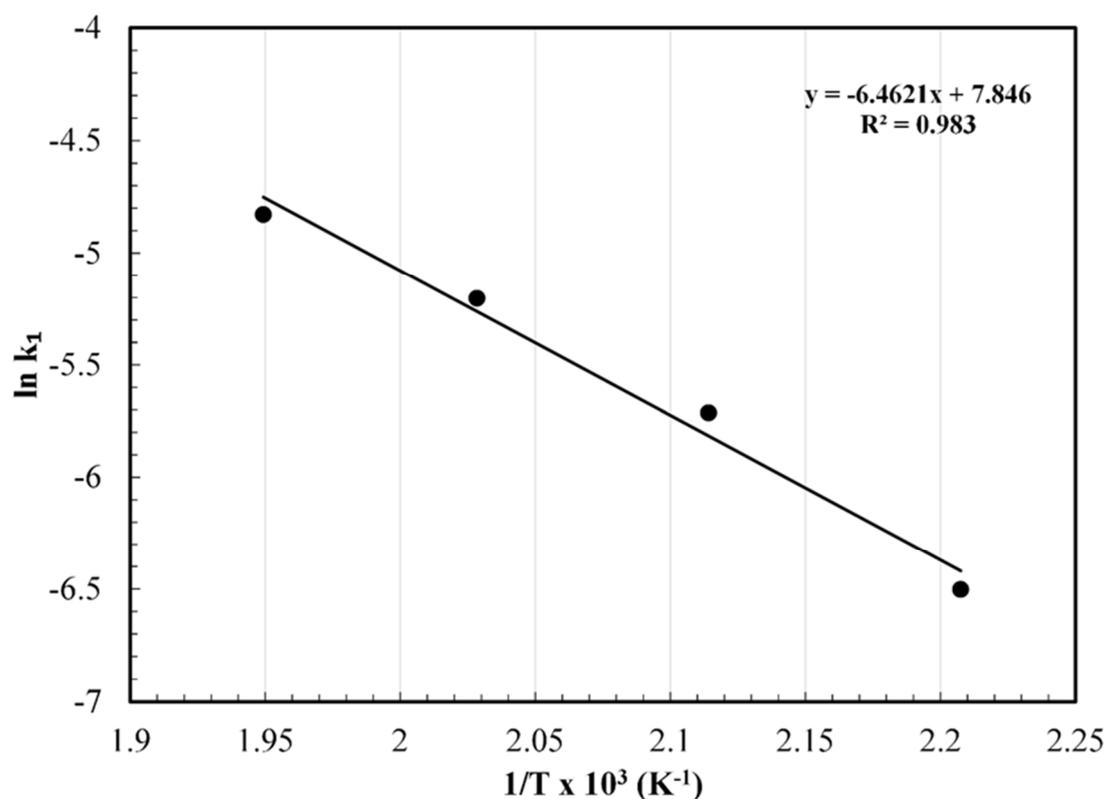


Figure 3. Arrhenius plot of CO₂ hydrogenation.

Table 2. Activation energy of CO₂ hydrogenation.

| Catalyst | Activation Energy (kJ/mole) | Reference |
|---|-----------------------------|-----------|
| Cu/ZrO ₂ /CNFs | 54 | This work |
| Cu/ZnO/Al ₂ O ₃ | 68 | [26] |
| Cu/ZnO/ZrO ₂ | 52 | [10] |
| Cu/ZnO/ZrO ₂ /Al ₂ O ₃ /SiO ₂ | 32 | [18] |
| Ga ₃ Ni ₅ /SiO ₂ | 64 | [27] |
| Cu–Zn–Al | 65 | [9] |

2.4. Application of Artificial Neural Networks

An ANN model with a feed-forward back-propagation network was employed in the current study. Four algorithms, namely *trainbr*, *trainlm*, *traingdm*, and *traingda*, were used to evaluate the experimental data.

Figure 4 shows good agreement between the experimental and predicted data, indicating the accuracy of the kinetics data. Such agreement between the experimental data and ANN-predicted data was reported for Pt–Sn/c–Al₂O₃ catalyst-based propane dehydrogenation by Amini et al. [28].

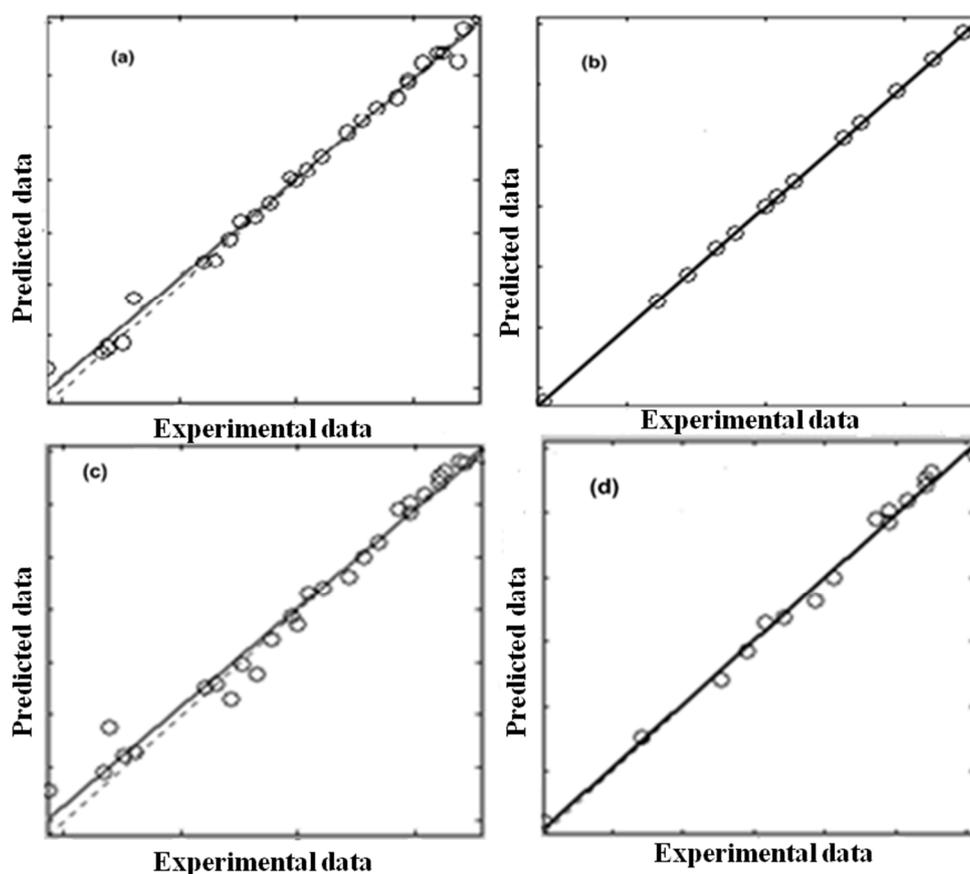


Figure 4. Experimental versus predicted data for (a) LM, (b) SCG, (c) BR, and (d) GDA algorithm.

3. Experimental

3.1. Catalysts Synthesis

CNF GNF-100 type, acquired from Carbon Nano-material Technology Co. Ltd., Korea was used as the catalyst support. Deposition precipitation method was used for catalyst synthesis [25,29,30]. Copper nitrate tri-hydrate (R&M Chemicals, London, UK) and zirconyl nitrate hydrate (Sigma–Aldrich, St. Louis, MO, USA) were used as starting materials for Cu and ZrO₂, respectively. In a typical experiment, the required quantities of copper nitrate trihydrate and zirconyl nitrate hydrate were dissolved in distilled water. Upon total dissolution of the nitrate salts, the required amount of pH was adjusted to 8 by urea solution. The slurry was stirred for 18 h at 85–90 °C.

Catalyst Cu.ZrO₂/CNFs with 15 wt.% each (Cu and ZrO₂) with CNFs as a support was synthesized. The synthesized catalyst was cooled to avoid leaching of active catalyst components, filtered, washed, and dried overnight at 100 °C. The dried catalyst was calcined at N₂ flow at 450 °C for 3 h and labeled as CZC450 catalyst. The catalyst underwent reduced H₂ flow with rate of 2000 cm³ h⁻¹ for 6 h at 380 °C before kinetics investigations.

3.2. Characterization

The PANalytical X-ray diffractometer model Empyrean (Malvern Panalytical Ltd., Malvern, UK) was employed to investigate phase studies of catalyst. Room-temperature XRD studies were conducted from 20 to 80 at 2θ Bragg angle.

Zeiss LIBRA 200TEM TEM (A Carl Zeiss SMT AG Company, Oberkochen, Germany) was employed to investigate catalyst morphology in the current work.

3.3. Kinetics Study

Slurry reactor model Parr 4593 was used in the current study. A kinetics investigation for CO₂ conversion was conducted at 453, 473, 493, and 513 K reaction temperature with constant 40 bar pressure. 0.5 g of catalyst was placed in a reactor vessel containing 25 mL ethanol, used as the reaction solvent [31]. The reaction was stirred at 1300 rpm to avoid mass transfer limitations [32,33]. The kinetics of the process was investigated in a dynamic mode by taking the sample at different time intervals. The samples were analyzed at reaction times of 20, 40, 60, 80, 100, 120, 140, 160, and 180 min and gas samples were studied by GC TCD for CO₂ conversion. The experiment lasted for 3 h.

3.4. Artificial Neural Networks for Kinetics Estimations

An ANN model with back-propagation method was used as a supporting tool in the current work (Figure 5). Hence, as predicted, the kinetics data performed at 40 bar constant reaction pressure. The role of pressure in the reaction helps in the kinetics of the reaction, but higher pressure is usually not recommended in industry. Therefore, optimum pressure value is adopted in this study and, while keeping it constant, temperature varies, to find the rate of the reaction. The adopted ANN procedure replicated our experimental finding and, in comparison with the experimental data, the predicted results show a reasonable estimate.

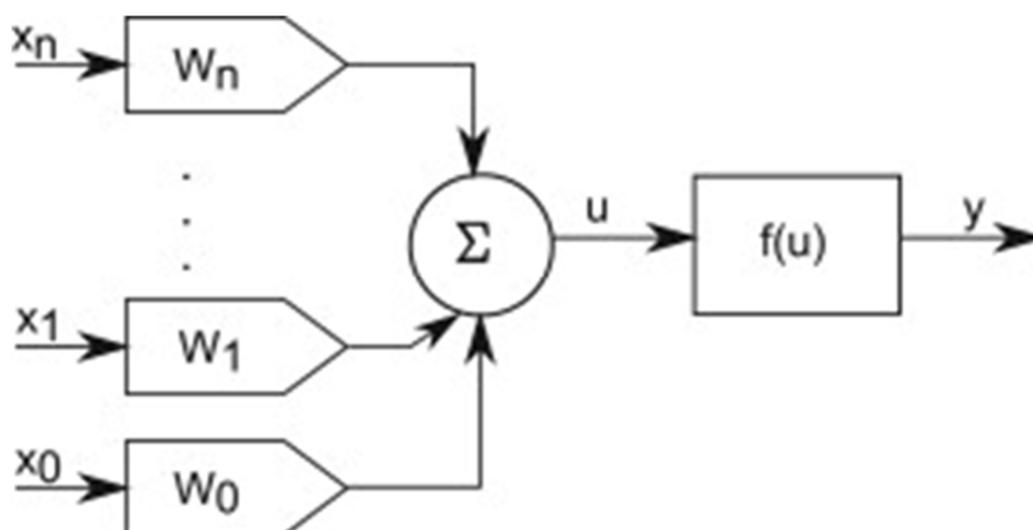


Figure 5. Scheme for application of ANN in kinetics modeling.

In addition, four algorithms were used in a MATLAB platform for CO₂ conversion. The “trainlm” and “trainbr” types are the network training updates bias and weight value of your input and target data, based on the Levenberg–Marquardt optimization procedure. The algorithm type “trainlm” is considered to be the fastest back-propagation algorithm and recommended to be the first-choice supervised algorithm that does not require memory as compared to other algorithms. The algorithm type “trainbr” curtails the combination of both weights and squared errors; by doing that, it determines the correct combination so that the network can produce a correct generalization of the input and output data. This process is known as Bayesian regularization. The type “traingda” is the network training function, which operates by updating the weight and bias based on output and input data according to gradient descent with adaptive learning rate procedure. The performance of this algorithm is sensitive to the proper setting of the learning rate. Setting learning to high creates unstable and oscillated algorithms, whereas setting the learning rate to low can take the algorithm too long to converge. The type “traingdm” is the network training function, which updates weight and bias values using gradient decent with momentum procedure.

4. Conclusions

In the current work, CO₂ conversion has been reported using a CNF-supported Cu/ZrO₂ catalyst. Kinetics investigations were carried out for the title reaction. The overall kinetics studies revealed that CO₂ conversion follows pseudo-first-order kinetics. Similarly, the Arrhenius model was used to calculate the activation energy of the reaction. The kinetics data were supported using an ANN model.

Author Contributions: I.U.D. designed the experiment; performed and collected data; M.S.S. and A.N. supervised and administrated the work; M.A.A. and A.I.A. wrote the original draft preparation revised, reviewed and edited the paper, Q.N. performed modeling work. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the deanship of research, Prince Sattam bin Abdulaziz University via research grant number 2019/01/10916.

Acknowledgments: Authors acknowledge the financial support provided by the deanship of research, Prince Sattam bin Abdulaziz University via research grant number 2019/01/10916. The research facilities provided by the chemistry department, college of science and humanities, Prince Sattam bin Abdulaziz university are also acknowledged.

Conflicts of Interest: The authors declare no conflict of interest

References

1. Din, I.U.; Shaharun, M.S.; Naeem, A.; Tasleem, S.; Ahmad, P. Revalorization of CO₂ for methanol production via ZnO promoted carbon nanofibers based Cu-ZrO₂ catalytic hydrogenation. *J. Energy Chem.* **2019**, *39*, 68–76. [[CrossRef](#)]
2. Ahmad, K.; Upadhyayula, S. Influence of reduction temperature on the formation of intermetallic Pd₂Ga phase and its catalytic activity in CO₂ hydrogenation to methanol. *Greenh. Gases Sci. Technol.* **2019**, *9*, 529–538. [[CrossRef](#)]
3. Centi, G.; Perathoner, S. CO₂-based energy vectors for the storage of solar energy. *Greenh. Gases Sci. Technol.* **2011**, *1*, 21–35. [[CrossRef](#)]
4. Sun, Q.; Ye, J.; Liu, C.-j.; Ge, Q. In₂O₃ as a promising catalyst for CO₂ utilization: A case study with reverse water gas shift over In₂O₃. *Greenh. Gases Sci. Technol.* **2014**, *4*, 140–144. [[CrossRef](#)]
5. Pereira, S.C.; Ribeiro, M.F.; Batalha, N.; Pereira, M.M. Catalyst regeneration using CO₂ as reactant through reverse-Boudouard reaction with coke. *Greenh. Gases Sci. Technol.* **2017**, *7*, 843–851. [[CrossRef](#)]
6. Tada, S.; Satokawa, S. Effect of Ag loading on CO₂-to-methanol hydrogenation over Ag/CuO/ZrO₂. *Catal. Commun.* **2018**, *113*, 41–45. [[CrossRef](#)]
7. Wang, G.; Zhang, J.; Shao, J.; Liu, Z.; Wang, H.; Li, X.; Zhang, P.; Geng, W.; Zhang, G. Experimental and modeling studies on CO₂ gasification of biomass chars. *Energy* **2016**, *114*, 143–154. [[CrossRef](#)]
8. Skrzypek, J.; Lachowska, M.; Moroz, H. Kinetics of methanol synthesis over commercial copper/zinc oxide/alumina catalysts. *Chem. Eng. Sci.* **1991**, *46*, 2809–2813. [[CrossRef](#)]
9. Graaf, G.; Stamhuis, E.; Beenackers, A. Kinetics of low-pressure methanol synthesis. *Chem. Eng. Sci.* **1988**, *43*, 3185–3195. [[CrossRef](#)]
10. Portha, J.-F.O.; Parkhomenko, K.; Kobl, K.; Roger, A.-C.C.; Arab, S.; Commenge, J.-M.; Falk, L. Kinetics of methanol synthesis from carbon dioxide hydrogenation over copper–zinc oxide catalysts. *Ind. Eng. Chem. Res.* **2017**, *56*, 13133–13145. [[CrossRef](#)]
11. Díez-Ramírez, J.; Díaz, J.; Dorado, F.; Sánchez, P. Kinetics of the hydrogenation of CO₂ to methanol at atmospheric pressure using a Pd-Cu-Zn/SiC catalyst. *Fuel Process. Technol.* **2018**, *173*, 173–181. [[CrossRef](#)]
12. Villa, P.; Forzatti, P.; Buzzi-Ferraris, G.; Garone, G.; Pasquon, I. Synthesis of alcohols from carbon oxides and hydrogen. 1. Kinetics of the low-pressure methanol synthesis. *Ind. Eng. Chem. Process Des. Dev.* **1985**, *24*, 12–19. [[CrossRef](#)]
13. Bart, J.C.J.; Sneed, R.P.A. Copper-zinc oxide-alumina methanol catalysts revisited. *Catal. Today* **1987**, *2*, 1–124. [[CrossRef](#)]

14. Skrzypek, J.; Lachowska, M.; Grzesik, M.; Słoczyński, J.; Nowak, P. Thermodynamics and kinetics of low pressure methanol synthesis. *Chem. Eng. J. Biochem. Eng. J.* **1995**, *58*, 101–108. [[CrossRef](#)]
15. Bussche, K.M.V.; Froment, G.F. A Steady-State Kinetic Model for Methanol Synthesis and the Water Gas Shift Reaction on a Commercial Cu/ZnO/Al₂O₃ Catalyst. *J. Catal.* **1996**, *161*, 1–10. [[CrossRef](#)]
16. Chinchén, G.C.; Denny, P.J.; Parker, D.G.; Spencer, M.S.; Whan, D.A. Mechanism of methanol synthesis from CO₂/CO/H₂ mixtures over copper/zinc oxide/alumina catalysts: Use of ¹⁴C-labelled reactants. *Appl. Catal.* **1987**, *30*, 333–338. [[CrossRef](#)]
17. Kubota, T.; Hayakawa, I.; Mabuse, H.; Mori, K.; Ushikoshi, K.; Watanabe, T.; Saito, M. Kinetic study of methanol synthesis from carbon dioxide and hydrogen. *Appl. Organomet. Chem.* **2001**, *15*, 121–126. [[CrossRef](#)]
18. Fontaine, J.L.; Germain, A. Model-based neural networks. *Comput. Chem. Eng.* **2001**, *25*, 1045–1054. [[CrossRef](#)]
19. Larachi, F. Neural network kinetic prediction of coke burn-off on spent MnO₂/CeO₂ wet oxidation catalysts. *Appl. Catal. B* **2001**, *30*, 141–150. [[CrossRef](#)]
20. Fullana, M.; Trabelsi, F.; Recasens, F. Use of neural net computing for statistical and kinetic modelling and simulation of supercritical fluid extractors. *Chem. Eng. Sci.* **2000**, *55*, 79–95. [[CrossRef](#)]
21. Alamolhoda, S.; Kazemeini, M.; Zaherian, A.; Zakerinasab, M.R. Reaction kinetics determination and neural networks modeling of methanol dehydration over nano γ -Al₂O₃ catalyst. *J. Ind. Eng. Chem.* **2012**, *18*, 2059–2068. [[CrossRef](#)]
22. Din, I.U.; Shaharun, M.S.; Subbarao, D.; Naeem, A. Synthesis, characterization and activity pattern of carbon nanofibres based Cu-ZrO₂ catalyst in the hydrogenation of carbon dioxide to methanol. *Adv. Mater. Res.* **2014**, *925*, 349–353. [[CrossRef](#)]
23. Din, I.U.; Shaharun, M.S.; Subbarao, D.; Naeem, A. Physicochemical investigations of carbon nanofiber supported Cu/ZrO₂ catalyst. In Proceedings of the 3RD International Conference on Fundamental and Applied Sciences (ICFAS 2014): Innovative Research in Applied Sciences for a Sustainable Future, Kuala Lumpur, Malaysia, 3–5 June 2014.
24. Ud Din, I.; Shaharun, M.S.; Subbarao, D.; Naeem, A. Homogeneous deposition precipitation method for synthesis of carbon nanofibre based Cu-ZrO₂ catalyst for hydrogenation of CO₂ to methanol. *Appl. Mech Mater.* **2013**, *446*, 83–87. [[CrossRef](#)]
25. Ud Din, I.; Shaharun, M.S.; Subbarao, D.; Naeem, A. Synthesis, characterization and activity pattern of carbon nanofibers based copper/zirconia catalysts for carbon dioxide hydrogenation to methanol: Influence of calcination temperature. *J. Power Sources* **2015**, *274*, 619–628. [[CrossRef](#)]
26. Park, N.; Park, M.-J.; Lee, Y.-J.; Ha, K.-S.; Jun, K.-W. Kinetic modeling of methanol synthesis over commercial catalysts based on three-site adsorption. *Fuel Process. Technol.* **2014**, *125*, 139–147. [[CrossRef](#)]
27. Ahmad, K.; Upadhyayula, S. Kinetics of CO₂ hydrogenation to methanol over silica supported intermetallic Ga₃Ni₅ catalyst in a continuous differential fixed bed reactor. *Int. J. Hydrogen Energy* **2020**, *45*, 1140–1150. [[CrossRef](#)]
28. Amini, Y.; Fattahi, M.; Khorasheh, F.; Sahebdelfar, S. Neural network modeling the effect of oxygenate additives on the performance of Pt-Sn/ γ -Al₂O₃ catalyst in propane dehydrogenation. *Appl. Petrochem. Res.* **2013**, *3*, 47–54. [[CrossRef](#)]
29. Din, I.U.; Shaharun, M.S.; Naeem, A.; Tasleem, S.; Johan, M.R. Carbon nanofiber-based copper/zirconia catalyst for hydrogenation of CO₂ to methanol. *J. CO₂ Util.* **2017**, *21*, 145–155. [[CrossRef](#)]
30. Din, I.U.; Shaharun, M.S.; Subbarao, D.; Naeem, A.; Hussain, F. Influence of niobium on carbon nanofibres based Cu/ZrO₂ catalysts for liquid phase hydrogenation of CO₂ to methanol. *Catal. Today* **2016**, *259*, 303–311. [[CrossRef](#)]
31. Din, I.U.; Shaharun, M.S.; Naeem, A.; Tasleem, S.; Rafie Johan, M. Carbon nanofibers based copper/zirconia catalysts for carbon dioxide hydrogenation to methanol: Effect of copper concentration. *Chem. Eng. J.* **2018**, *334*, 619–629. [[CrossRef](#)]

32. Reubroycharoen, P.; Yamagami, T.; Vitidsant, T.; Yoneyama, Y.; Ito, M.; Tsubaki, N. Continuous low-temperature methanol synthesis from syngas using alcohol promoters. *Energy Fuels* **2003**, *17*, 817–821. [[CrossRef](#)]
33. Tsubaki, N.; Zeng, J.; Yoneyama, Y.; Fujimoto, K. Continuous synthesis process of methanol at low temperature from syngas using alcohol promoters. *Catal. Commun.* **2001**, *2*, 213–217. [[CrossRef](#)]



© 2020 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).