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Synthesis, Characterisation and Catalytic Activity of NiO supported Al₂O₃ for CO₂ Hydrogenation to Carboxylic Acids: Influence of Catalyst Structure

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Abstract. Utilisation and conversion of carbon dioxide into valuable chemicals and fuels are the promising ways to reduce carbon dioxide concentration in the atmosphere. In addition, the conversion of carbon dioxide into fuels, such as methane, methanol and formic acid has been proven a good method for hydrogen storage. In this work, the catalyst structure plays an important role in the production of formic acid and acetic acid at low temperature. Nickel oxide supported alumina catalysts were synthesised by using the solid-state fusion method at 550 °C and 700 °C. Calcined catalysts were characterised by X-ray diffraction, Brunauer-Emmett-Teller surface area, high-resolution field emission scanning electron microscopy, Auger electron spectroscopy with X-ray photoelectron spectrometer and transmission electron microscopy. Carbon dioxide hydrogenation was performed in the batch reactor. The products obtained were analysed by using high-performance liquid chromatography and gas chromatography with a thermal conductivity detector. The highest levels of formic acid and acetic acid production were 4.08 and 1.58 mmol/L, respectively.

Keywords: CO₂ utilisation, heterogeneous catalyst, NiO/Al₂O₃, formic acid, acetic acid.

1. Introduction

Global warming is a critical issue affecting the world nowadays. The main cause of global warming is attributed to the increase in greenhouse gases mainly from CO₂ (65 %) [1]. At present, the concentration of CO₂ has increased up to 406 ppm in 2018 and from the last five years, the increment is about 3–4 ppm, as measured at Mauna Loa [2]. This phenomenon is something to worry about since global warming causes climate change, which in turn results in (1) tropical storms, (2) rise in sea level and coastal flooding, (3) El Nino and La Nina that may affect rainfall and water supplies (4) threat to inland plants and animals, and (5) worsened human health [3]. Therefore, something should be done to reduce atmospheric CO₂ concentration.

CO₂ conversion and utilisation are two different terms with the same meaning that are used to mitigate CO₂ in atmosphere space. The term CO₂ conversion refers to the transformation of CO₂ into chemically different forms that contain the carbon of CO₂ or that make use of its active ‘oxygen atom’ [4]. On the other hand, CO₂ utilisation is the use of CO₂ in both physical and chemical processes [4]. Compared to other methods (CO₂ capture and CO₂ storage), CO₂ conversion and utilisation not only reduce atmospheric CO₂ concentration, but also convert CO₂ into other valuable chemicals and fuels. CO₂ is a simple molecule that consists of two oxygen atoms that are covalently bonded to one carbon atom. However, this molecule is thermodynamically very stable to be reduced to another valuable chemical. Therefore, the presence of a catalyst is very important since it can speed up the rate of reaction by reducing the activation barrier for the reaction to proceed.

Currently, formic acid production from CO₂ as the main feedstock has attracted scientists’ attention globally [5, 6]. Formic acid production from CO₂ not only reduces atmospheric CO₂ concentration, but



also stores H_2 in the form of liquid, which is safe and non-toxic. It is known that formic acid can be applied as a fuel in direct formic acid fuel cells (DFAFCs) and can also be used as a potential chemical hydrogen storage material [7, 8]. Therefore, the state-of-the-art of this study is to reduce CO_2 into formic acid under a low-temperature reaction with the presence of the good activity of a low-cost catalyst.

The use of noble metals as catalysts was applied many years ago. According to previous research, palladium (Pd), aurum (Au), and ruthenium (Ru) have been investigated in heterogeneous catalytic of CO_2 hydrogenation into formate and formic acid products [9–15]. However, these catalysts are expensive and have limited availability, thus making them impractical to be used in catalytic hydrogenation from the industrial point of view. The use of non-noble metals is a good alternative in replacing noble metals since they exhibit both high activity and stability.

In this work, NiO-based catalysts were used for hydrogenation of CO_2 at low temperature. The low-cost catalysts showed good catalytic activity in CO_2 hydrogenation at low temperature and under mild condition. The effect of calcination temperature on structure and catalytic activity of alumina supported NiO catalysts were investigated. The techniques of X-ray diffraction (XRD), Brunauer-Emmett-Teller (BET) surface area, high-resolution field emission scanning electron microscopy (FESEM), Auger electron spectroscopy with X-ray photoelectron spectrometer (AES-XPS) and transmission electron microscopy (TEM) were performed to report the phenomenon and effect.

2. Experimental Methods

2.1. Catalyst synthesis and characterisation

NiO-C/ Al_2O_3 catalysts were synthesised by fusion solid-state method as reported by Pudukudy et al. [16]. After being well-mixed by using mortar, the catalyst samples were fused at 100 °C in an oven and later calcined in air at 550 °C and 700 °C for 4 h. The catalysts were labelled as NiO-C/ Al_2O_3 -550 and NiO-C/ Al_2O_3 -700 according to their calcination temperature.

XRD was used to identify the phase structures of the catalysts (D8 Advanced, Bruker AXS Germany). High resolution FESEM (Merlin Compact) was used to investigate the morphologies of the catalysts and TEM analysis was performed on TEM Philips CM-12. A small quantity of the catalysts was dispersed in ethanol and dried on the copper grids for the next measurement. For the specific surface area of the catalysts, Micromeritic ASAP 2020 with BET method was used. The chemical state information of the element was investigated by using AES-XPS (Axis Ultra DLD, Kratos/Shimadzu).

2.2. Hydrogenation of CO_2

CO_2 hydrogenation was performed in a high-pressure stainless steel autoclave reactor (250 mL; internal diameter, 60 mm) with a mechanical stirrer. In each experiment, 0.2 g of the catalyst was inserted into a batch reactor with 35 mL of 1,4-dioxane as a solvent. The reactor was purged with H_2 for 1 min and pressurised with 10 bar of CO_2 . H_2 was filled up to the initial pressure of 35 bar. The system was heated to 130 °C by a mantle fitted with a digital temperature controller. The reaction was conducted for a few hours. Next, the reactor was cooled down to room temperature naturally, and the pressure was released to ambient condition.

The liquid products obtained were filtered and analysed with Agilent LC1100/1200 series high-performance liquid chromatography (HPLC) system with RP80 column (250 mm) at 30 °C by using 0.1% H_3PO_4 as an eluent. The flow rate was maintained at 1 mL/min with a run time of 20 min and a UV detector of 210 nm. For gaseous products, the gas chromatography (GC) system from Agilent Technologies (6890N) with thermal conductivity detector (TCD) was used to identify the gas composition from the reaction. Propack Q and molecular sieve column were used for the GC system.

3. Results and Discussion

3.1 Characterisation of nano-NiO supported Al_2O_3

Figure 1(a) shows the XRD spectra for both NiO-C/ Al_2O_3 -550 and NiO-C/ Al_2O_3 -700 recorded in the range of 5–80°. The patterns were very different for both catalysts. However, they exhibited peak characteristics of NiO and γ - Al_2O_3 . NiO-phase peaks were detected at 37.18° (111), 43.52° (200), 63.22° (220), 75.83° (311) and 79.54° (222). The presence of NiO in NiO-C/ Al_2O_3 -550 was confirmed to be nickel oxide with monoclinic system (PDF 03-065-6920). After calcined at 700 °C, the diffraction pattern changed to the bunsenite type of NiO and was confirmed with the database (PDF 01-071-1179). Besides that, the peaks for the amorphous carbon were detected together with NiAl_2O_4 at 19.74° and 31.75° [17, 18]. Carbon was generated from the addition of citric acid as a gelling agent in the catalyst preparation. However, from the XRD diffraction line for NiO-C/ Al_2O_3 -550, the peak for carbon was not detected due to the structure formation of the catalyst as illustrated in Figure 1(b). The illustration shows that the NiO nanoparticles had covered the Al_2O_3 surface and were connected with a carbon layer in between.

The crystallite size of both samples can be calculated by using the Scherrer's formula [19]. As temperature increases, the crystallite size of the catalyst increased from 4.6–12.9 nm (NiO-C/ Al_2O_3 -550) to 5.6–78.6 nm (NiO-C/ Al_2O_3 -700). In addition, the percentage crystallinity values recorded in the range of 5–80° for NiO-C/ Al_2O_3 -550 and NiO-C/ Al_2O_3 -700 were found to be 53.4% and 43.1%, respectively. The increase in temperature would produce more crystalline structure of Al_2O_3 [20]. However, this study obtained a contradicted result and the decrease in crystallinity may be attributed to the exposed mesoporous carbon detected by the XRD analysis. The XPS analysis of the catalysts was performed at the oxidised state as shown in Figure 1(c). From the result obtained, the binding energy values for $\text{Ni}2p_{3/2}$ and $\text{Ni}2p_{1/2}$ were 854.41 eV and 871.6 eV, respectively, and there were satellite peaks at 861.08 eV and 877.28 eV. These results indicated that the nickel species was Ni^{2+} .

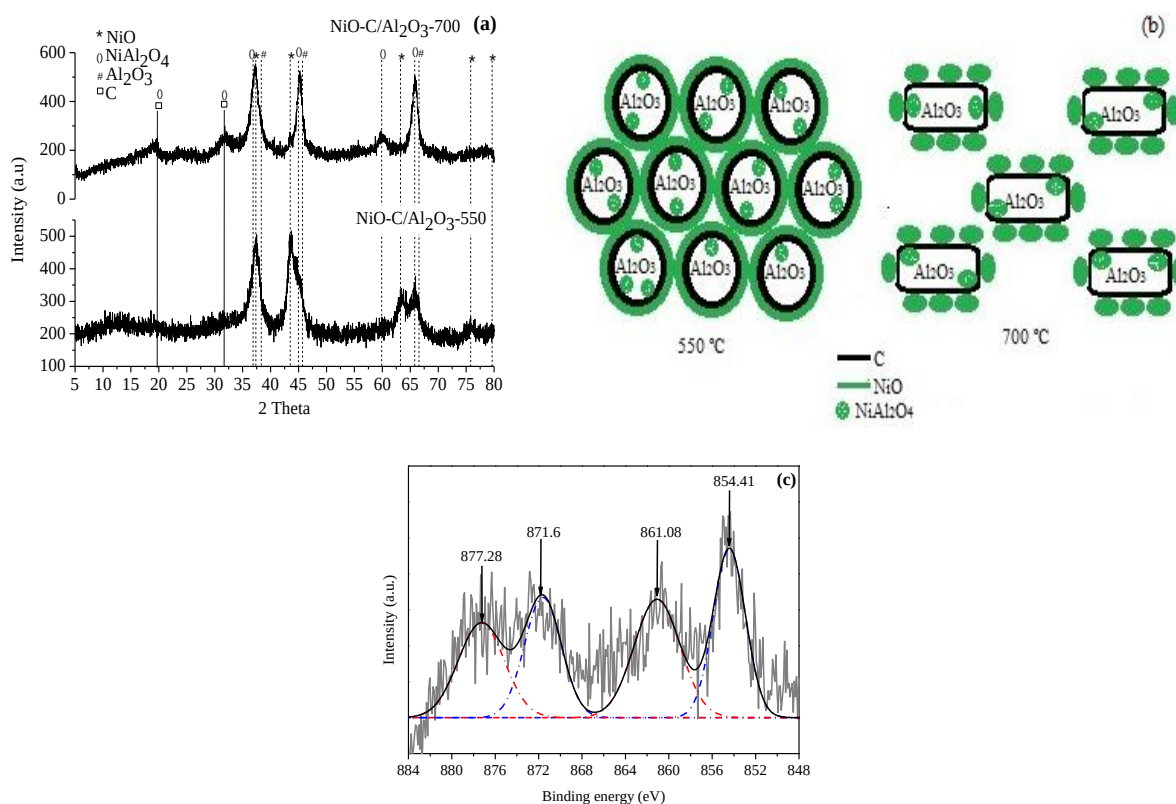


Figure 1(a). XRD spectra, (b) structure illustration of NiO-C/ Al_2O_3 -550 and NiO-C/ Al_2O_3 -700, and (c) XPS spectrum of NiO-C/ Al_2O_3 -550.

Figure 2(a–b) show the FESEM images of both catalysts. The sample, which was calcined at 550 °C, exhibited a group of closely arranged spore-like morphology. In contrast to NiO-C/Al₂O₃-550, NiO-C/Al₂O₃-700 exhibited the characteristic of a non-uniform rod-like morphology. The results showed that the morphologies of the products were affected by the calcination temperature.

To study the structure and size of synthesised catalysts under nanometer scale, TEM analysis was performed as shown in Figure 2(c–d). For NiO-C/Al₂O₃-550, the NiO nanoparticles were well distributed on the support surface from smaller to bigger sizes as shown by the red circle. The sizes of NiO nanoparticles from NiO-C/Al₂O₃-550 and NiO-C/Al₂O₃-700 were in the range of 40–55 nm and 12–35 nm, respectively. These results showed that the size of NiO nanoparticles became smaller as temperature increased.

Table 1 shows the physisorption measurement results for NiO-C/Al₂O₃-550 and NiO-C/Al₂O₃-700. The NiO-C/Al₂O₃-550 exhibited a larger specific surface area of 160.2953 m²/g as compared to NiO-C/Al₂O₃-700 at 80.6227 m²/g. The results showed that the surface area of the catalyst decreased as temperature increased. From the results mentioned above, the increase in temperature from 550 °C to 700 °C had changed the morphology, size, crystallinity and surface area of the catalyst.

Table 1 BET surface are of NiO-C/Al₂O₃-550 and NiO-C/Al₂O₃-700

Sample	Surface area (m ² /g)
NiO-C/Al ₂ O ₃ -550	160.2953
NiO-C/Al ₂ O ₃ -700	80.6227

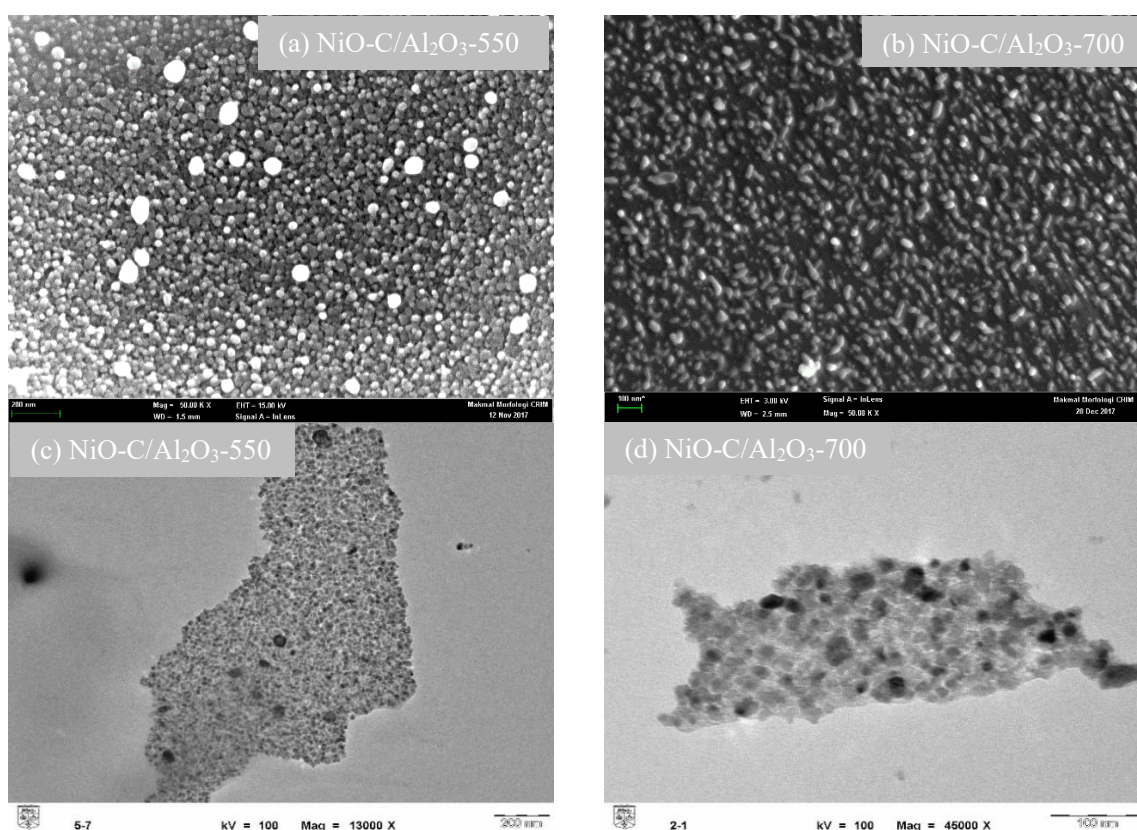


Figure 2. SEM and TEM images of NiO-C/Al₂O₃-550 and NiO-C/Al₂O₃-700.

3.2 Catalytic performance for CO₂ hydrogenation to carboxylic acids

The hydrogenation reaction of CO₂ was carried out in a batch reactor at 130 °C for the evaluation of catalytic performance. The reactions were performed at different reaction time, from 2 h to 12 h for both

catalysts. At the end of the reaction, liquid and gaseous products were analysed by using HPLC and GC-TCD detector. Only liquid products were detected and no gaseous products were detected except for CO_2 and H_2 . In this study, with the presence of $\text{NiO-C/Al}_2\text{O}_3$ in 1,4-dioxane, CO_2 was reduced to formic acid and acetic acid only, and the product yield was calculated with an internal standard. Figure 3 shows the product yield obtained from the CO_2 hydrogenation by using both catalysts. For the $\text{NiO-C/Al}_2\text{O}_3$ -550 catalyst, the formic acid production increased from 2 h to 12 h and the highest concentration of product obtained was 0.61 mmol/L. However, this result was in contrast with that of acetic acid because as time increases, the concentration of acetic acid started to decrease from 0.04 to 0 mmol/L. Compared to $\text{NiO-C/Al}_2\text{O}_3$ -550, the product obtained for $\text{NiO-C/Al}_2\text{O}_3$ -700 was higher. The optimum yield of formic acid obtained at 6 h was 4.08 mmol/L. However, the yield of acetic acid was not comparable to formic acid because the significant concentrations obtained were 1.43 mmol/L and 1.58 mmol/L at 6 h and 10 h, respectively. The catalytic activity of $\text{NiO-C/Al}_2\text{O}_3$ -700, which was better than that of $\text{NiO-C/Al}_2\text{O}_3$ -550, was attributed to the structure of the catalyst and size of NiO. As illustrated in Figure 1, the rod-like structure provides a good catalytic activity due to the separation of NiO from carbon. Based on the result, when NiO completely linked together with carbon, the production of carboxylic acids was quite low. The interaction between NiO with carbon might be the main reason for the low production of carboxylic acids since carbon is known to deactivate the catalyst and slow down the reaction rate [21]. Besides, the small size of NiO nanoparticles provided a large active site for the adsorption of CO_2 and H_2 on the nickel surface to produce more carboxylic acids [22]. Although the surface area of $\text{NiO-C/Al}_2\text{O}_3$ -700 was smaller than that of $\text{NiO-C/Al}_2\text{O}_3$ -550, the production of carboxylic acids was high. This result proves that surface area is not the main factor that is affecting catalytic activity [23].

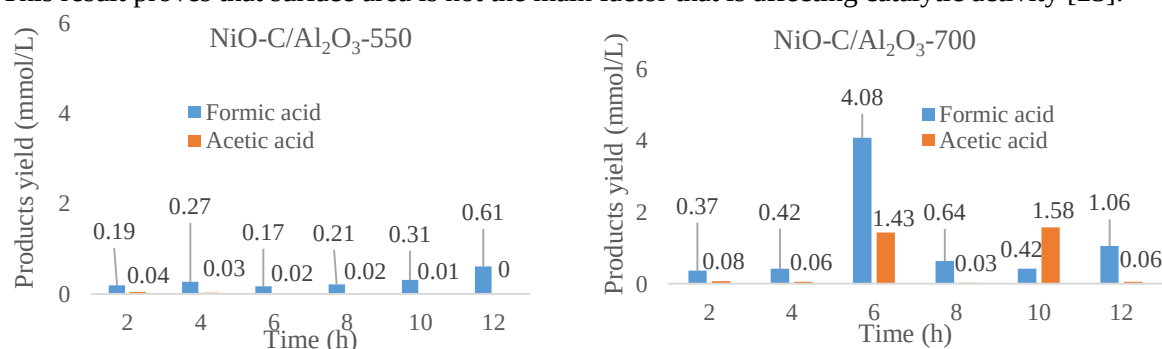


Figure 3. Formic acid and acetic acid yield as a function of $\text{NiO-C/Al}_2\text{O}_3$. Reaction conditions: 0.2 g of catalyst, 35 mL of 1,4-dioxane, pressure of 35 bar and temperature of 130 °C.

Currently, there are no established technologies that can transform CO_2 from air into formic acid and use it directly in a fuel cell system. Researchers reported that in future, it is possible to combine separate processes to produce an integrated system, which can utilise CO_2 as the raw material to generate electricity by using a fuel cell system [24–26]. Therefore, the findings of this study can be used as additional knowledge for the production of formic acid from CO_2 under low temperature and mild condition with the presence of a low-cost catalyst.

4. Conclusions

In conclusion, nano-nickel (II) oxide supported alumina catalysts were successfully synthesised at 550 °C and 700 °C by using the fusion solid-state method. The X-ray diffraction results showed the presence of nickel (II) oxide and alumina mixture in the samples and only nickel (II) species was detected for nickel. As temperature increased, the morphology, size, crystallinity and surface area changed. The temperature calcination played an important role in carbon dioxide hydrogenation. Nickel (II) oxide supported alumina that was calcined at 700 °C presented a better activity for carbon dioxide hydrogenation to carboxylic acids, at mild condition pressure and low temperature of 35 bar and 130 °C, respectively. Nickel (II) oxide supported alumina that was calcined at 700 °C exhibited a rod-like

morphology and smaller sized nickel (II) oxide nanoparticles (12–35 nm) produced the highest formic acid and acetic acid with values of 4.08 mmol/L and 1.58 mmol/L, respectively.

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