Catalytic Performance of NiO Modified on Refluxed Chicken Eggshell Waste for Pyrolysis of High-Density Polyethylene

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Keywords: eggshells, nickel oxide, plastic waste, hydrocarbons, pyrolysis oil
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Chicken eggshells are rich in calcium carbonate ($CaCO_3$) that can be highly converted into calcium oxide (CaO) via one-step calcination. However, chicken eggshells were often discarded as wastes from food and agriculture sector. Recently, chicken eggshells wastes were recovered and used as support catalyst in biodiesel production (Sulaiman et al., 2021; Erchamo et al., 2021). To the best of our knowledge the application of metal modified chicken eggshell waste as calcium oxide-based catalyst is still lacking in pyrolysis area. Currently, active metal loading such as nickel oxide (NiO) is commonly used in catalytic pyrolysis of plastic wastes. Thus, the main objective of this work is to investigate the effect of NiO modified on refluxed chicken eggshell waste for pyrolysis of high-density polyethylene (HDPE) via fixed-bed reactor. HDPE was selected as plastic wastes for pyrolysis. The temperature, pressure, and catalyst to feedstock mass ratio for pyrolysis was kept constant at 500 °C, 1 atm, and 1:1 respectively for all investigated samples. CaO commercial (CaO-cc) was purchased from Sigma-Aldrich for benchmarking with CaO chicken eggshell waste (CaO-es) which were recovered from local food stores. To obtain CaO-es, first the collected chicken eggshell was rinsed, crushed, and dried in an oven at 105 °C for 24 hours and later calcined in muffle furnace at 900 °C (5 °C/min) for 4 hours. For the preparation of refluxed catalyst, CaO-es undergoes reflux by mixing with de-ionized water and stirred at 60 °C for 2 hours. Later, dried in an oven at 105 °C for 24 hours before undergoes calcination at 600 °C (5 °C/min) for 4 hours and finally labelled as CaO-esR. NiO/CaO-es, and NiO/CaO-esR catalysts were prepared via incipient-wetness-impregnation (IWI) method with fixed NiO loading of 5 wt.%. All the catalyst samples were then characterized via Brunauer-Emmett-Teller (BET) for textural properties and x-ray diffraction (XRD) for phase analysis.

Table 1 shows the textural properties of synthesized catalysts such as BET surface area (S_{BET}), total pore volume (V_{total}), and pore diameter (D). It can be observed that the CaO-esR has higher pore diameter (3.91 nm) and total pore volume (0.0875 cm^3/g) compared to CaO-cc and CaO-es. This could be due to the influence of refluxed process in which aligned to the occurrence of sediment mud-crack (Hirose and Matsubara, 2018). Similar results were obtained by Nawar et al. (2021), in which they reported that the original fibre-rod porous structure in chicken eggshell waste has altered into hexagonal mud-crack like structure after undergone refluxed process.

Table 1. Textural properties of synthesized catalysts.

Catalysts	[a]S_{BET} (m^2/g)	[b]V_{total} (cm^3/g)	[c]D (nm)
CaO-cc	3.80	0.0063	3.58
CaO-es	8.72	0.0156	3.87
CaO-esR	10.23	0.0875	3.91
NiO/CaO-es	9.12	0.0181	3.78
NiO/CaO-esR	11.28	0.0881	3.89

[a]S_{BET} (BET surface area) were obtained by the BET method.
[b]V_{total} (total pore volume) were obtained from the adsorbed amount at P/P0 = 0.99.
[c]D (pore diameter) was obtained from the adsorption branches of the isotherms by the BJH method.

However, CaO-cc, CaO-es, and CaO-esR exhibits similar XRD patterns as shown in Figure 1. Thus, it can be concluded that the chicken eggshell waste (before and after refluxed) is highly contained calcium oxide in which aligned with XRD peaks of commercial CaO. In addition, the refluxed process did not alter the crystallography properties of chicken eggshell waste but only the textural properties. The interconnected porous structure with IWI process in which NiO is embedded, it creates a structural networks channel for higher rate conversion of heavy carbon compound to lighter carbon compound (Erchamo et al., 2021). Based on Figure 2, it can be observed that the commercial CaO-cc and CaO-es has almost similar percentage of pyrolysis products. Hence, it can be concluded that CaO-cc and CaO-es has similar catalytic cracking activity. Slight reduction in pyrolysis oil and increment in non-condensable gas was observed for CaO-esR sample. This might be due to the high total pore volume in CaO-esR (0.0875 cm_3/g) that leads to the secondary cracking of primarily produced vapour molecules into non-condensable gas. Generally, NiO favours the gas products due NiO capable of cracking heavy compounds into light (Sulaiman et al., 2021). Thus, in this study, similar results were observed for NiO/CaO-es and NiO/CaO-esR catalyst in which the non-condensable gas has achieved at 45% and 48% respectively compared to CaO-es (26%) and CaO-esR (36%).

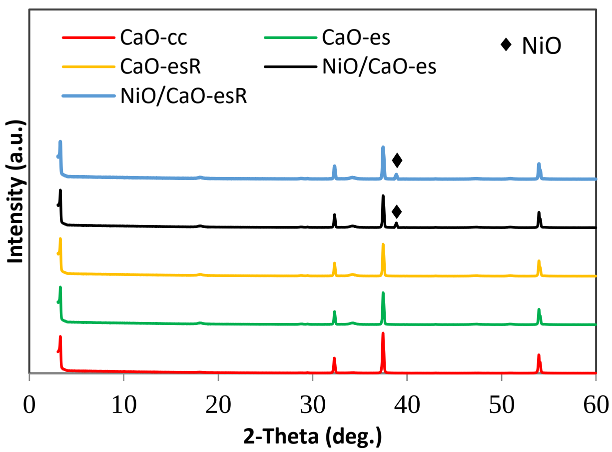

Figure 1. XRD results of synthesized catalysts.

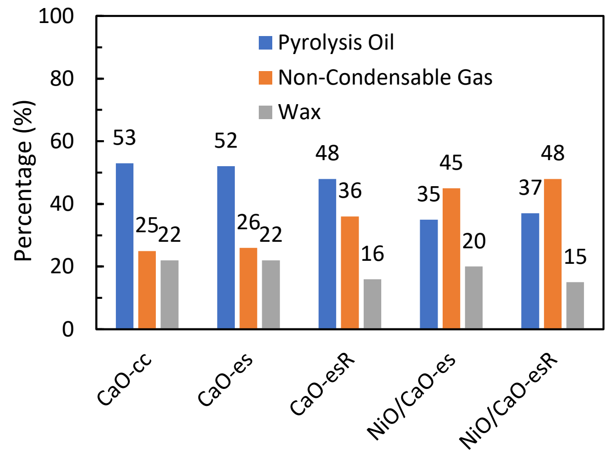

Figure 2. The effect of synthesized catalysts on pyrolysis of HDPE.

In conclusion, CaO-esR, did no change the properties of crystallography of CaO and in pyrolysis had slight reduction in pyrolysis oil but increment in non-condensable gas due to more pores leading to secondary cracking of primarily produced vapour molecules. NiO favours the gas products; resulted in more non-condensable gas for both NiO/CaO-es and NiO/CaO-esR; additionally, CaO-es has potential to produce pyrolysis oil from pyrolysis of HDPE It’s an interesting attempt using CaO-esR to replicate zeolite characteristics in catalytic pyrolysis while achieving United Nation sustainable development goal category 7 in affordable and clean energy.

Acknowledgment

A special thanks to the Ministry of Higher Education of Malaysia for the financial support to carry out this research project under the Fundamental Research University Grant (FRGS), Registration Proposal No: FRGS/1/2020/TK0/UTM/02/113 and Universiti Teknologi Malaysia (UTM) for the opportunity to carry out the research works.

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