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The Effect of Calcium Oxide from Waste Chicken Eggshell on HZSM-5

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The main objective of the current work is to investigate the influence of waste chicken eggshell (WCE) as an alternative source of calcium oxide (CaO) on Hydrogen exchanged Zeolite Socony Mobil-5 catalyst (HZSM-5). WCE as promoter was loaded at 1wt.% on HZSM-5 catalyst which act as support via incipient wetness impregnation method. The HZSM-5, commercial CaO, and WCE were individually prepared for comparison with WCE/HZSM-5. Synthesized catalysts were characterized via X-Ray Diffraction to analyse the phase purity, Field Emission Scanning Electron Microscopy to analyse the surface morphology, and Brunauer-Emmett-Teller to analyse the surface area and pore size. The addition of WCE on HZSM-5 has significantly affected the framework structure of HZSM-5 where the crystallinity percentage and average crystal size of HZSM-5 drastically dropped to 44.97 % and 45.00 nm. The original cubic-like structure in HZSM-5 has significantly altered into a netlike structure after the impregnation of WCE. A similar effect of alteration was observed on BET surface area dropped from 365.81 m^2/g (HZSM-5) to 292.14 m^2/g (WCE/HZSM-5). Interestingly, the pore diameter of WCE/HZSM-5, WCE, and HZSM-5 catalysts was similar at 3.88 nm, 3.87 nm, and 3.87 nm respectively. WCE and commercial CaO almost share similar textural properties. Hence, the addition of WCE as an alternative source of calcium oxide into HZSM-5 can provide a high catalytic reaction and stable surface in catalytic cracking of heavy hydrocarbons into small hydrocarbons with longer catalyst lifetimes.

1. Introduction

Zeolite catalysts are widely employed in catalytic cracking in petroleum refining to the possible high production of hydrocarbons (Galadima and Muraza, 2015). Zeolite catalysts such as SBA-15, HZSM-5, β-zeolite, MCM-41, and novel zeolite catalysts such as mordenite, ITQ-2, and faujasite (Cai et al., 2016). The differences in all type of zeolite catalysts are in terms of acidic and textural properties. Zeolite catalysts exhibited different crystalline structures and open cavities that attributes their shape-selectivity during catalytic cracking (Veses et al., 2015). Zeolite catalysts were widely considered than other acid catalysts due to higher catalytic cracking property on heavy compounds (Mayorga et al., 2019). Several measurements of zeolites properties such as amount of acid sites, porosity property, and shape selectivity of catalyst are influenced in the catalytic cracking process (Balasundram et al., 2019). HZSM-5 is highly preferable in the catalytic cracking process due to thermally stable, cost-effective, and higher cracking ability with some drawbacks such as short lifetime due to high coking rate, low organic liquid yield, and low selectivity (Doluda et al., 2019). The formation coke covers the acid sites of HZSM-5 and eventually decrease its cracking abilities (Balasundram et al., 2018). The catalyst properties are known as critical factors in catalytic cracking process due to the significant effect on the product distribution and coking rate (Chico-Proano et al., 2021).
Calcium oxide (CaO) has offered great potentials as a heterogeneous catalyst in many processes due to considered as a low-cost catalyst that has long lifetimes (Casa et al., 2021). CaO is naturally known for its basic

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properties that could fine-tune the acidic properties of HZSM-5. The catalyst with acid and basic sites show synergistic action in improving the fuel properties rich in hydrocarbons (Galadima and Muraza, 2015). The heavy compounds can enter the narrow pores of the HZMS-5 catalyst to be efficiently cracked by C-C cleavage into smaller compounds, afterwards converted to aromatics over CaO catalyst. Ahmad et al. (2020) reported the potential of extracting CaO from waste chicken eggshell as a natural source of calcium oxide. This naturally derived CaO has low surface area that restricts the exposure of active basic sites (Rahman et al., 2018). High loading of catalyst and long reaction time is needed for completion of catalytic cracking of heavy compounds in petroleum. The waste chicken eggshell which is a naturally derived source of calcium oxide should be utilized as a promoter into HZSM-5 which act as support. The WCE could alter the framework of HZSM-5 that will have longer lifetimes. Although many studies have firmly established the application of waste chicken eggshell as CaO-based catalyst in many processes, the modification HZSM-5 framework using waste chicken eggshell is still unclear and has not yet been well clarified.

To the best of our knowledge, the study on the effect of WCE on the framework of HZSM-5 is still lacking in the literature. The objective of this study is to obtain an in-depth understanding of the WCE and its effect on HZSM-5 physicochemical properties. The incipient wetness impregnation method was successfully applied to produce a novel WCE/HZSM-5 catalyst. The findings of this study offer a potential solution for existing catalyst in catalytic cracking such as pyrolysis of biomass from both economic and environmental points of view. This is because WCE is a low-cost material and can be considered as an alternative source of calcium oxide to be applied as a base catalyst in the catalytic cracking process. All the synthesized catalysts including HZSM-5, WCE, and commercial CaO were characterized by XRD, BET, and FESEM to examine and compare their physical and geometric properties.

2. Methodology

2.1 Catalyst preparation

The ZSM-5 (SiO_2/Al_2O_3=23) (Purity = 100 %) in ammonium form was purchased from Alfa Aesar and calcium oxide (CaO) (Purity = 100 %) from ACROS Organics. The waste chicken eggshell (WCE) was purchased from the local market, Malaysia. ZSM-5 was converted from its original ammonium form into the HZSM-5 by calcination at 600 ºC for 4 h (5 ºC/min) in a muffle furnace. WCE was calcined in a muffle furnace at 900 ºC for 4 h (5 ºC/min) to convert the calcium carbonate ($CaCO_3$) in WCE into calcium oxide (CaO). The impregnation of WCE (1 wt%) was achieved on HZSM-5 via incipient wetness impregnation method. The deionized water (80 mL) was added with calcined WCE (rich in CaO) and HZSM-5 in a beaker and continuously stirred for homogenous solution using hot plate magnetic stirrer at 80 ºC for 4 h. The formed paste was filtered and washed with deionized water. The paste was dried in a microwave oven at 100 $\pm$ 2 ºC for an overnight. The dried solid catalyst was calcined at 600 ºC for 4 h (5 ºC/min). The solid catalyst was labelled as WCE/HZSM-5.

2.2 Catalyst characterization

WCE/HZSM-5 catalyst was characterized to investigate its phase purity, surface morphology, and textural properties. The HZSM-5, CaO, and WCE catalysts were also characterized to compare the physicochemical properties with the WCE/HZSM-5 catalyst. X-Ray Diffraction (XRD) (PANalytical, Empyrean, Japan) was used to analyse the phase purity of synthesized catalysts. The catalyst samples were irradiated using CuKα1 radiation with a wavelength (λ) of 0.15405 nm at 30mA and 40 kV. Sample scanning was carried out over 2θ range from 3° to 60° (5 °/min). The average crystal size (D) of the synthesized catalysts is calculated by Debye-Scherrer equation [$D = K\lambda / \beta cos\theta$, where K is the Scherrer constant, λ is the X-ray wavelength, β is the full width at the half-height of the measurement sample and θ is the Bragg's diffraction angle]. Field Emission Scanning Electron Microscopy (FESEM) (SEM, CARL-ZEISS) was used to characterize the surface morphology of the synthesized catalysts. The catalysts were placed on the carbon stub in a high-resolution coater of platinum/palladium (Pt/Pd). The accelerating voltage was set to 7 kV with a working distance of 8 – 8.5 mm in a vacuum condition. Brunauer-Emmett-Teller (BET) (ThermoScientific, Waltham, MA, USA) was used to analyse the surface area and pore size by adsorption of N_2 gas. The surface area and pore analyser were used to measure the BET surface area, total pore volume, and average pore diameter of synthesized catalysts by N_2 adsorption and desorption at –196 °C. Before measurement, the catalyst samples were degassed under a vacuum at 300 °C for about 8 h to remove adsorbed compounds. The total pore volume (estimated at a relative pressure (P/P_0) of 0.99) and average pore diameter were calculated based on Barrett-Joyner-Halenda (BJH) method.

3. Results and discussions

3.1 Phase analysis

Phase analysis of HZSM-5, CaO, WCE, and WCE/HZSM-5 catalysts were determined by X-ray diffraction (XRD) is shown in Figure 1. The XRD patterns were examined at degrees ranging from 3° to 60° for all the synthesized catalysts due to no diffraction peaks were found in the catalyst above 60°. The main peaks of HZSM-5 were presented at the 2θ of 7.94°, 8.85°, 23.10°, 23.96°, and 24.01°. The main XRD peaks of HZSM-5 from this study are in consistent with the XRD peak range (2θ = 7° - 25°) from previous work by Balasundram et al. (2018). It can be concluded that the synthesized HZSM-5 catalyst in this work is highly crystalline. The degree of crystallinity is significant because there is a potential for an amorphous phase, which indicates impurities that may affect the catalytic properties of HZSM-5 (Veses et al., 2015).
The WCE/HZSM-5 catalyst exhibits the similar patterns of diffraction of HZSM-5. The impregnation of WCE on HZSM-5 has a significant effect in lowering the amount of intensity. This might be due to the formation of the amorphous phase by WCE on the external surface of HZSM-5 that lowers the crystallinity percentage. As shown in Table 1, it can be observed that the crystallinity percentage of HZSM-5 (99.90 %) had significantly reduced to 44.97 % after the impregnation of WCE into HZSM-5. It can be concluded that the impregnation of WCE at a small amount of 1 wt.% had greatly affected the crystallinity percentage of HZSM-5 support. The average crystal size of HZSM-5 has increased from 42.90 nm to 45.00 nm after the impregnation of WCE into HZSM-5. This increment might be due to the WCE nanoparticles combined and lumped with HZSM-5 nanoparticles on the catalyst's surface. HZSM-5 and WCE/HZSM-5 catalysts exhibited as nanoparticle due to the average crystal size lies in the range between 1 nm – 100 nm as shown in Table 1.

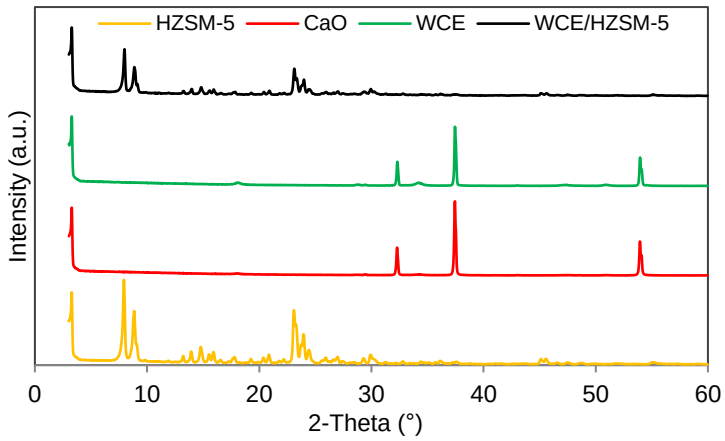

Figure 1: XRD patterns of synthesized catalysts

Table 1: Crystallinity and average crystal size of synthesized catalysts

Catalysts	Crystallinity (%)	Average crystal size (nm)
HZSM-5	99.90	42.90
CaO	40.22	53.97
WCE	40.42	45.13
WCE/HZSM-5	44.97	45.00

The main peaks of WCE and CaO catalysts have similar diffraction peaks at the 2θ of 32.25°, 37.43°, and 53.91° (refer Figure 1). Similar results of diffraction peaks for waste chicken eggshell were previously reported by Rahman et al. (2018), in which they suggested that these diffraction peaks are cubic configuration of CaO. WCE and CaO also have similar crystallinity percentage of 40.22 % and 40.42 % but with different crystal size at 45.13 nm and 53.97 nm as shown in Table 1. The lower average crystal size in WCE than CaO could be due to the higher calcination temperature of 900 °C used in converting calcium carbonate ($CaCO_3$) in WCE into calcium oxide (CaO). At higher calcination temperature, the phase transition has occurred that leads to reducing the crystal size. The lower crystallinity percentage of WCE, CaO, WCE/HZSM-5 than HZSM-5 shows that there might there is a potential of an amorphous phase, which indicates the impurities.

3.2 Surface morphology

The FESEM images were taken to better explain the morphological changes happening on the synthesized catalyst's surface. The FESEM micrographs of the HZSM-5, WCE, CaO, and WCE/HZSM-5 are shown in Figure 2 (a-d). Based on Figure 2 (a), it can be seen that the shape of the HZSM-5 zeolite grains is noted to be heterogeneous and has an irregular morphology. Figure 2 (a) depicts that the synthesized HZSM-5 zeolites have cubic-like particle morphology that varies in size with the individual crystal sizes of approximately 50-80 nm which is aligned with the XRD result that obtained with the crystal size of 54.36 nm. Similar results were obtained by Balasundram et al. (2018) where the HZSM-5 has a cubic-like structure.

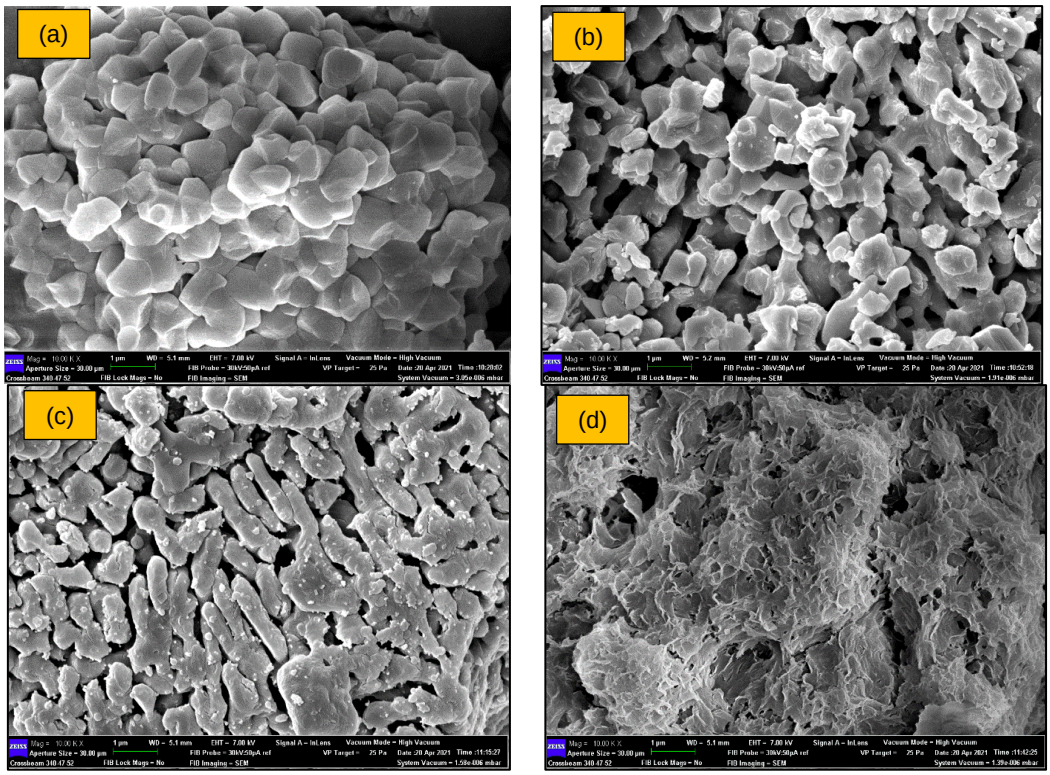

Figure 2: Surface morphology of (a) HZSM-5, (b) CaO, (c) WCE, and (d) WCE/HZSM-5

According to Figure 2, it was discovered that HZSM-5 has agglomerated, apparently due to the interconnection of small particles. HZSM-5 catalyst tend to agglomerate into microsized agglomerates and these microsized zeolites seem to just stack loosely together to create bigger stacks with visibly vast gaps between the individual crystals (Veses et al., 2015). Based on Figure 2, it can be observed that the HZSM-5 were densely packed. The tunable microscopic crystalline structure of HZSM-5, as shown in Figure 2a, with its interconnected porous network, regular pore size, and high surface area is of great industrial importance as good candidates of catalyst in catalytic cracking process.

As shown in Figure 2b and 2c, it can be seen that the CaO has spherical morphology, while WCE has plate-like particles. CaO and WCE exhibits irregular and smooth surface. Similar results of surface morphology for WCE and CaO were previously reported by Khan et al. (2020) and Casa et al. (2021). It can be seen that the particles in WCE are randomly oriented with some particles are large having dimension in 2.0-3.0 μm range, while few particles are small in size which might be due to broken pieces of large particles. Almost similar particles size range of WCE can be seen for CaO (refer Figure 2 (b). This indicates that WCE resembles the surface morphology of commercial CaO due to highly composed of calcium oxide in WCE. The calcination of raw WCE was successfully converted into calcium oxide. The impregnation of WCE into HZSM-5 had significantly altered the original cubic-like structure of HZSM-5 as shown in Figure 2 (d). Although the WCE was impregnated at a small amount of 1 wt.% into HZSM-5, the cubic particles of HZSM-5 and plate particles of WCE were hardly seen in WCE/HZSM-5 and has drastically changed to netlike porous structure (refer Figure 2a, 2c, and 2d)).

3.3 Surface area and pore analysis

The importance of BET analysis is to characterize the textural and porosity properties of synthesized catalysts that greatly influence the reaction mechanism during catalytic cracking process. The measurements of BET surface areas, total pore volumes, and pore diameters of all the synthesized catalysts were shown in Table 2. The BET surface area, total pore volume, and average pore size of the HZSM-5 catalyst were reported to be 365.81 m^2/g, 0.2291 cm^3/g, and 3.87 nm (refer Table 2). It can be concluded that HZSM-5 has a large surface area with a microporous structure which is aligned with the surface morphology of HZSM-5 as shown in Figure 2 (a). According to Galadima and Muraza (2015), a large surface area boosts the zeolite catalyst's cracking capacity. Since the average pore diameter of all the synthesized catalysts were in between 2 nm to 50 nm then it is said to fall under the mesoporous category, while below 2 nm is known for microporous.

Table 2: Textural properties of synthesized catalysts

Catalysts	[a] S_{BET} (m^2/g)	[b] V_{total} (cm^3/g)	[c] D (nm)
HZSM-5	365.81	0.2291	3.87
CaO	3.80	0.0063	3.58
WCE	8.72	0.0156	3.87
WCE/HZSM-5	292.14	0.2663	3.88

[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 $P/P_0 = 0.99$.
[c] D (pore diameter) was obtained from the adsorption branches of the isotherms by the BJH method.

The WCE and CaO have a very small surface area at 8.72 m^2/g and 3.80 m^2/g compared to HZSM-5 catalyst. Rahman et al. (2018) reported a small surface area for waste eggshell at 2.98 m^2/g. The wide gap of surface area between WCE and CaO in this study might be due to the higher calcination temperature of 900 °C that has a different surface area. Lani et al. (2019) stated that catalyst with low surface area limits the exposure of active basic sites. A smaller surface area of catalyst reduces the reaction rate during the cracking process (Badnore et al., 2018). WCE has a similar pore diameter of 3.87 nm with HZSM-5 catalyst, unlike commercial CaO slightly has a smaller pore diameter at 3.58 nm. It can be observed that the total pore volume of WCE is higher than CaO at 0.0156 cm^3/g and 0.0063 cm^3/g (refer Table 2). WCE as an alternative source of CaO, it has better textural properties than commercial CaO. This might be due to the presences of other elements in the WCE such as silicon, magnesium, potassium, and iron which was previously reported by Ahmad et al. (2020).
The WCE/HZSM-5 catalyst has BET surface area and total pore volume at 292.14 m^2/g and 0.2663 cm^3/g as shown in Table 2. It can be seen that the impregnation of WCE on HZSM-5 has a significant effect of decreased BET surface area from 365.81 m^2/g to 292.14 m^2/g and increased total pore volume from 0.2291 cm^3/g to 0.2663 cm^3/g. The decrease in BET surface area might be due to the good dispersion of WCE on the surface of HZSM-5 during the incipient wetness impregnation method. The increase in the total pore volume might be due to the WCE had enlarged the pore of HZSM-5 during the preparation process. The pore diameter of HZSM-5 was not much affected after the impregnation of WCE into HZSM-5, in which it retains the pore diameter at 3.88 nm while HZSM-5 at 3.87 nm. It can be concluded that the addition of WCE into the framework of HZSM-5 has a great effect on the BET surface area and total pore volume but less effect on the pore diameter.

4. Conclusions

The waste chicken eggshell (WCE) was successfully impregnated on the HZSM-5 via the incipient wetness impregnation method which was labelled as WCE/HZSM-5. All the synthesized catalysts such as HZSM-5, WCE, commercial CaO, and WCE/HZSM-5 were also successfully characterized via XRD, FESEM, and BET to investigate the effect of calcium oxide from WCE on the HZSM-5 framework. Based on the obtained XRD data, WCE were well dispersed on the surface of HZSM-5. The crystallinity percentage drastically dropped to 44.97 % and the average crystal size increased to 45 nm. WCE and commercial CaO exhibits almost similar phase purity in which the crystallinity percentage was observed at 40.42 % and 40.22 % , while the average crystal size at 45.13 nm and 53.97 nm. Based on FESEM images, it was observed that HZSM-5 has a cubic like structure, while WCE and CaO share almost similar surface morphology of plate-like structure. The addition of WCE into HZSM-5 had significantly modified the surface morphology of HZSM-5 into a netlike structure. The addition of WCE into HZSM-5 has lowered the BET surface of HZSM-5 from 365.81 m^2/g to 292.14 m^2/g. The pore diameter of WCE/HZSM-5, WCE, and HZSM-5 was at a closed value at 3.88 nm, 3.87 nm, and 3.87 nm. The WCE/HZSM-5 catalyst with acid and basic sites will have a synergistic effect in catalytic cracking of heavy compounds into hydrocarbons with longer catalyst lifetimes. The effect of WCE/HZSM-5 on catalytic cracking of heavy compounds from pyrolysis of biomass couldn’t be conducted at recent times due to Movement Control

Order that has restricted in carrying further investigation. In future, the HZSM-5, WCE, commercial CaO, and WCE/HZSM-5 catalysts will be used in catalytic cracking of biomass to investigate the product distribution of pyrolysis products and the percentage of hydrocarbons produced via fixed-bed reactor.

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