Synthesis, Characterisation and Mechanism of Novel Ca-ZSM-5 Zeolite Nanocomposite from Eggshell using Simple Co-Precipitation Method

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Abstract. In this study, Ca-ZSM-5 zeolite nanocomposite was synthesised as controlled-released fertiliser due to the excess of nutrients leaching in the soil which has caused serious environmental problem such as eutrophication. The zeolite nanocomposite was first synthesised using a simple co-precipitation template method. The zeolite nanocomposite was then impregnated with calcium, originated from chicken eggshell powder, at a molar ratio of 1:1. The physical and chemical properties of Ca-ZSM-5 zeolite nanocomposite were characterised using several analytical instruments such as Fourier Transform Infrared (FTIR) Spectrometer, Scanning Electron Microscope (SEM), Energy Dispersive X-ray (EDX) Spectrometer and Transmission Electron Microscopy (TEM). Based on SEM analysis, the porosity of mesoporous H-ZSM-5 nanozeolite was in the range of 31.7 to 190 nm. Meanwhile, the porosity of macroporous eggshell was 71.4 to 230 nm and mesoporous H-ZSM-5 nanozeolite material was impregnated into the macroporous eggshell due to porosity of eggshell was larger than porosity of H-ZSM-5 nanozeolite. Ca-ZSM-5 zeolite nanocomposite with porosity of 71.4-198 nm was successfully synthesised by simple co-precipitation method. While the results obtained from FTIR analysis confirmed the presence of tetrahedral (TOx, x = Si or Al) stretching. Overall, the synthesised Ca-ZSM-5 zeolite nanocomposite possess key characteristic as a precursor for various applications.

1. Introduction

Organic waste like eggshell can be used as natural biomaterials in various applications. For an example, it is used as catalysts in industrial field while dental, bone implantation and wound dressings in biomedical field. Meanwhile, in agricultural sector the residue of eggshell is suitable for microbial application because it can supply nutrients required by plants for growth [1]. Furthermore, eggshell waste is used in various applications because of high content of calcium carbonate (CaCO3) in the form of calcite which can be utilised as nutrients [1]. Moreover, organic waste from eggshell contains many tiny holes which called as pore canals on the surface layer which can allow air to follow through easily [2]. An interesting template synthetic routes show high level interest of scientists in cutting edge technology to prepare and impregnate synthetic alumina-silicate materials in nanoscale [3]. Zeolite is well defined as crystalline aluminosilicate with different pore sizes which classified as microporous (pore size smaller than 2 nm), mesoporous (pore size between 2 to 50 nm) and macroporous (pore size...
larger than 50 nm) [3]. Ethylene glycol is commonly used as a ‘soft’ material to create the template of H-ZSM-5 due its ability to form inter and intramolecular forces of hydrogen bonding (–OH) with HCl [3]. Many researchers have used several materials such as NPK and Ag for impregnation of zeolite [4]. Chicken eggshell was used as an impregnation agent in this study because it contains ceramic materials such as cuticle, calcareous and mammillary which are considered as environmentally friendly [1]. In this study, we present the synthesis of nanozeolite using simple co-precipitation method using ethylene glycol as organic soft template as well as impregnation of calcium derived from white chicken eggshell powder with H-ZSM-5 nanozeolite.

2. Materials and methods

2.1 Materials
Sodium silicate (Fisher Scientific), ethylene glycol (Merck), aluminium sulfate 98 % (Sigma-Aldrich), commercial zeolite (Merck), commercial ZSM-5 zeolite (Merck), sodium hydroxide (Bendosen) and acid hydrochloric 37 % (R&M Chemicals) were used to synthesise H-ZSM-5 nanozeolite.

2.2 Preparation of H-ZSM-5 and Ca-ZSM-5 Zeolite Nanocomposite
H-ZSM-5 nanozeolite was prepared by simple co-precipitation method using ethylene glycol as organic soft template [3]. White precipitates of sodium silicate solution (55 g/100 mL deionised water) and 25 mL of ethylene glycol were mixed together and stirred for 2 h while the temperature maintained at 50-60 °C to obtain a homogenous mixture. Aluminium sulfate (39.35 g/100 mL) and sodium hydroxide (15 g/100 mL) were added dropwise until the final pH of the mixture reached to 12 and adjusted to neutral using 1 M HCl. The mixture was then filtered using a filter paper (Smith 102, 110 mm) and white colour precipitate was obtained. The precipitate underwent drying process in an oven set at 105 °C for 1 h and purification using 25 mL of ethanol solution. Grey colour H-ZSM-5 nanozeolite was produced after calcination at 650 °C for 2 h. H-ZSM-5 nanozeolite was impregnated with eggshell powder at a molar ratio of 1:1 using simple suspension method in 20 mL deionised water. The mixture was stirred for 3 h to attain maximum impregnation of calcium. The resulting suspension underwent vacuum filtration using a filter paper (Double Rings 203, 90 mm) followed by drying in an oven set at 50 °C for 24 h. The light grey coloured Ca-ZSM-5 zeolite nanocomposite was obtained after the drying process was completed.

2.3 Characterisation study
In this study, materials were characterised using several analytical instruments. The FTIR spectra were recorded using a Thermo Nicolet 6700 FTIR spectrometer at wavenumbers range between 4000 and 400 cm⁻¹ with over 32 cumulative scans. A Hitachi SU8020 UHR was used to obtain TEM images, STEM images and EDX spectra of the materials. The SEM was operated at an acceleration of 5.0 kV.

3. Results and discussion

3.1. FTIR analysis
The FTIR spectra of commercial zeolite, H-ZSM-5 nanozeolite and commercial ZSM-5 zeolite which was purchased from Merck are presented in figure 1. From figure 1, absorption bands observed at 788-618 cm⁻¹ can be assigned to internal and external of asymmetrical tetrahedral linkages [3]. On the other hand, strong absorption bands at wavenumber of 1040 cm⁻¹ (figure 1(b)) and 1062 cm⁻¹ (figure 1(c)) can be attributed to tetrahedral \((\text{TO}_x, x = \text{Si or Al})\) stretches [4]. The discernible peaks at 788 cm⁻¹ (figure 1(c)) and 785 cm⁻¹ (figure 1(c)) are correspond to external symmetry \((-\text{OTO})\) [4]. The appearance of these peaks is imperative in order to proof that the occurrence of nucleation process in simple co-precipitation method, which was conducted at low temperature. Meanwhile, the weak bands at 1652 cm⁻¹ (figure 1(a)) and 1634 cm⁻¹ (figures 1(b) and 1(c)) showed deformation mode of water. This observation suggests that Si was not bonded with OH in H-ZSM-5 nanozeolite [3]. Overall, the absorption bands observed in FTIR spectra of commercial zeolite and ZSM-5 zeolite were well
matched with FTIR spectrum of synthesised H-ZSM-5 nanozeolite. Figure 2 shows FTIR spectra of H-ZSM-5 nanozeolite, eggshell and Ca-ZSM-5 zeolite nanocomposite. A shown in figure 2(b), the prominent peaks observed at 1393, 871 and 711 cm\(^{-1}\) was due to the presence of carbonate minerals in the eggshell [5]. Following impregnation with eggshell, there was a significant change in FTIR spectrum of H-ZSM-5 nanozeolite (figure 2(c)), of which the features of carbonate minerals were appeared at absorption bands at 1404, 872 and 711 cm\(^{-1}\) [6]. This strongly supports that calcium was successfully impregnated to H-ZSM-5 nanozeolite. Additionally significant peaks at 3200-3600, 1652 and 1393 cm\(^{-1}\) which expected the presences of positively charged functional group of amine and amide [5]. Overall the synthesised Ca-ZSM-5 zeolite nanocomposite possesses key characteristics as a precursor for various applications.

![Figure 1](image1.png)

**Figure 1.** FTIR spectra of (a) commercial zeolite, (b) H-ZSM-5 nanozeolite and (c) commercial ZSM-5 zeolite.

![Figure 2](image2.png)

**Figure 2.** FTIR spectra of (a) H-ZSM-5 nanozeolite (b) eggshell and (c) Ca-ZSM-5 zeolite nanocomposite.

### 3.2. SEM analysis

The surface morphology of commercial ZSM-zeolite, H-ZSM-5 nanozeolite, eggshell and Ca-ZSM-5 zeolite nanocomposite was observed using SEM analysis at 25,000x magnification as presented in figure 3. It was found that commercial ZSM-5 shows a well-defined structure (figure 3(a)). After
conducting simple co-precipitation procedure of which ethylene glycol (25 mL, 0.72 M) was added as a soft template material to the synthesised H-ZSM-5 nanozeolite, the size of porosity of this material was developed into mesoporous structure [7][8]. As shown in figure 3(b), the size of porosity of H-ZSM-5 nanozeolite was estimated between 31.7 and 190 nm. In the context of eggshell (figure 3(c)), shell unit between calcite and membrane was well-organised [3][9]. Furthermore, SEM analysis showed that the porosity of eggshell can be classified as macroporous with the size ranging from 71.4 to 230 nm. The surface morphology and porous structure of Ca-ZSM-5 zeolite are shown in figure 3(d) [10]. It is apparent that the mesoporous H-ZSM-5 nanozeolite material was impregnated into the macroporous eggshell due to porosity of eggshell was larger than porosity of H-ZSM-5 nanozeolite [8]. Moreover, smooth calcite membrane was formed when ethylene glycol was used as a soft template material in H-ZSM-5 nanozeolite [11][12].

**Figure 3.** SEM images of (a) commercial ZSM-5 zeolite (b) H-ZSM-5 nanozeolite (c) eggshell and (d) Ca-ZSM-5 zeolite nanocomposite at 25,000x magnification.

3.3. **EDX analysis**
Energy Dispersive X-ray (EDX) analysis was performed in order to identify the element present in H-ZSM-5 nanozeolite and Ca-ZSM-5 zeolite nanocomposites. As shown in figure 4(a), the EDX spectrum of H-ZSM-5 nanozeolite showed strong peaks represent Si, Na and Al. The presence of these three elements suggests the similarity in composition of commercial ZSM-5 zeolite [13]. Meanwhile additional peaks of 56.40 % O and 2.59 % Cl correspond to ethylene glycol and HCl, which were used to synthesise H-ZSM-5 nanozeolite. Furthermore, figure 4(b) presents the elemental composition of H-ZSM-5 nanozeolite following impregnation with eggshell. From figure 4(b), it is clear that 86.84 % Ca mineral from eggshell already impregnated into mesoporous structure of H-ZSM-5 nanozeolite [5]. In addition, 29.69 % of Si composition (figure 4(a)) reduced to 11.59 % suggesting that 18.10 % of Si was used to substitute Ca in order to produce Ca-ZSM-5 zeolite nanocomposite. Results from EDX
analysis corroborate the results obtain from SEM analysis conformi
ng that Ca has successfully impregnated into H-ZSM-5 nanozeolite (figure 3(d)) [14].

![Figure 4](image)

**Figure 4.** EDX spectra of (a) H-ZSM-5 nanozeolite, (b) Ca-ZSM-5 zeolite nanocomposite at 1 micrometer magnification.

3.4. TEM analysis

Figure 5 shows the TEM images of H-ZSM-5 at 200,000x and 500,000x magnifications. It is obvious that the particles of H-ZSM-5 zeolite nanocomposite were distributed so uniformly. This was expected because the H-ZSM-5 nanozeolite was surrounded by soft template which was prepared during simple co-precipitation step [15]. From figures 5(a) and 5(b), the size of these particles was in the range between 2.38 nm and 26.8 nm. In addition, from figure 5(b) it can be observed that disaggregate crystallites were formed in H-ZSM-5 nanozeolite [16].

![Figure 5](image)

**Figure 5.** TEM images of H-ZSM-5 nanozeolite at (a) 200,000x, and (b) 500,000x magnifications.
3.5. XRD analysis

Figure 6 shows phase study of synthesised (a) H-ZSM-5 nanozeolite and (b) Ca-ZSM-5 zeolite nanocomposite diffractograms. After undergoing calcination at 600 °C, 2 major peaks in H-ZSM-5 nanozeolite can be observed at 22.0°, 25.0° and 28.5° which characteristic primary nanocrystals structure of Mordenite Framework Inverted (MFI) [17]. Furthermore synthesised H-ZSM-5 nanozeolite show a high intensity peak at 25.0°. Characteristic peaks of XRD patterns Ca-ZSM-5 zeolite nanocomposite were identify existence of calcium from eggshell as crystalline phase from CaCO$_3$ which present in the form of calcite [18]. Moreover, major peaks in Ca-ZSM-5 zeolite nanocomposite observed at 29.0° well-fitted with characteristic of CaCO$_3$ in a stable calcite phase [19]. This result confirmed that solid phase between H-ZSM-5 nanozeolite and CaCO$_3$ in calcite phase formed at the surface layer of eggshell with saturated Ca$^{2+}$ [20]. Furthermore, figures 3(b) and (d) and XRD patterns in figure 6 showed that the framework of H-ZSM-5 nanozeolite remains unchanged after undergoing Ca$^{2+}$ ion-exchange process.

![Figure 6](image)

**Figure 6.** XRD patterns of (a) H-ZSM-5 nanozeolite and (b) Ca-ZSM-5 zeolite nanocomposite.

3.6. Reaction mechanism

Scheme 1 shows that in ZSM-5 framework where two primary unit of SiO$_4$ and AlO$_4^-$ will gathered in particular structures named Secondary Building Unit (SBU) based on Lowenstein rule to form aluminosilicate polyhedral structure [21]. The polyhedral aluminosilicate framework showed in tetrahedral which substituted by Si$^{4+}$ and Al$^{3+}$ occupied as central atoms with negative charge while in the vertices contains four oxygen atoms which can be balanced by monovalent or divalent cations and can be used as cation exchange site [21].

![Scheme 1](image)

**Scheme 1.** Schematic of Possible Structure of Polyhedral Aluminosilicate with Cation Exchange Site

Possible mechanism for the formation of H-ZSM-5 nanozeolite is shown in scheme 2. Figures 1(b) and (c) show hydrogen-bonded interaction of ZSM-5 in acidic sites (1040 and 1062 cm$^{-1}$) [21]. Due to
the porous structure in the ZSM-5 framework refer to figure 3(a), and scheme 1, H⁺-ZSM-5 nanozeolite was prepared which can act as ion-exchange sites for mono or divalent cations and the chemical equation is given below [22]:

\[
\text{ZSM-5 zeolite (s) + H}^+ (\text{aq}) \rightleftharpoons \text{H}^+\text{-ZSM-5 nanozeolite (s)} \quad (1)
\]

Scheme 2. Schematic of Possible Mechanism for the Formation of H⁺-ZSM-5 Nanozeolite (NZ)

Scheme 3 illustrates the possible mechanism for the formation of Ca²⁺-ZSM-5 Zeolite Nanocomposite (ZNC). Ion-exchange process will occur between the H⁺ from HCl and calcium ion from eggshell in calcite form and act as cation which going to exchange [22][23]. Chemical equation calcium ion-exchange is given in Equation 2 below:

\[
2\text{H}^+\text{-ZSM-5 nanozeolite (s) + Ca}^{2+} (\text{aq}) \rightleftharpoons \text{Ca-ZSM-5 zeolite nanocomposite (s) + 2H}^+ (\text{aq}) \quad (2)
\]

When the ion-exchange process took place, the Ca²⁺ ions are substituted with H⁺ ions. EDX spectrum displayed in figure 4(b) reveals that 86.84% of Ca²⁺ ions were successfully exchanged into H-ZSM-5 nanozeolite. Furthermore, this calcium ion-exchange level was supported by the data from figure 6 in XRD patterns showed that high intensity peak at 29.0° which corresponding calcium ions from CaCO₃ in calcite crystalline phase from eggshell.

Scheme 3. Schematic of Possible Mechanism for the Formation of Ca²⁺-ZSM-5 Zeolite Nanocomposite (ZNC)
4. Conclusion
Ca-ZSM-5 zeolite nanocomposite with porosity of 71.4-198 nm has successfully prepared by simple co-precipitation method using ethylene glycol as organic soft template. The FTIR, SEM, EDX, TEM and XRD results proved that calcium from chicken eggshell was impregnated into H-ZSM-5 nanozeolite with particle size of 2-26 nm. Zeolites are commonly used as catalysts for hydrocarbon application. Due to the ion-exchange capability, Ca-ZSM-5 zeolite nanocomposite has been developed as controlled-release fertiliser for agricultural usage particularly in plant growth. This study also emphasises the utilisation of waste-based materials that can be converted into innovative high technology materials. This is in line with national policy on waste-to-wealth.

5. References
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