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Carboxymethyl Cellulose Photocracking by Magnetic Recoverable Photocatalyst to Produce Biofuel in Ambient Condition

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Abstract: Synthesis of $Fe_3O_4/SiO_2/TiO_2$ nanocomposite and its application as photocatalyst in Carboxymethyl Cellulose (CMC) photocracking had been conducted. Magnetite preparation was carried out by sono-coprecipitation method. The deposition of SiO_2 and TiO_2 were performed by sol-gel method under ultrasonic irradiation. All material products were characterized by X-ray diffraction (XRD), Fourier transform infra-red spectrophotometry (FT-IR), and transmission electron microscopy (TEM). The final material product was also analysed by specular reflectance UV-Visible (SR-UV-Vis). The product of photocracking was analysed by gas chromatography – mass spectrometry (GC-MS).The XRD diffractogram and FT-IR spectra confirmed the presence of Fe_3O_4, SiO_2, and anatase phase of TiO_2. The TEM image revealed the presence of nanocomposite with core-shell structure. The SR-UV-Vis spectrum was used to determine band gap energy of the photocatalyst and it gave a result of 3.22 eV. The GC chromatogram of photocracking product indicated some major fractions. The MS spectra showed that some major fractions were smaller molecules including methanol, the component of biofuel.

Keywords: Biofuel, CMC, $Fe_3O_4/SiO_2/TiO_2$, Nanocomposite, Photocatalyst, Photocracking

***Abstract*:** *Sintesis nanokomposit $Fe_3O_4/SiO_2/TiO_2$ dan aplikasinya sebagai fotokatalis telah dilakukan dalam fotorengkah Carboxymethyl Cellulose (CMC). Magnetit dipreparasi melalui metode sono-koprepitisasi. SiO_2 dan TiO_2 dideposisi melalui metode sol-gel dengan paparan radiasi ultrasonik. Semua produk telah dikarakterisasi dengan X–ray diffraction (XRD), Fourier transform infra-red (FTIR), dan transmission electron microscopy (TEM). Material produk akhir juga dianalisis menggunakan specular reflectance UV-Visible (SR-UV-Vis). Produk hasil fotorengkah juga dianalisis menggunakan gas chromatography – mass spectrometry (GC-MS). Hasil difraktogram XRD dan spektra FTIR mengkonfirmasi keberadaan Fe_3O_4, SiO_2, dan TiO_2 fasa anatase. Citra TEM menunjukkan penampakan nanokomposit dengan struktur core-shell. Spektra SR-UV-Vis digunakan untuk penentuan energi celah pita dari foto katalis dan memberikan hasil 3,22 eV. Kromatogram GC dari produk fotorengkah menunjukkan beberapa puncak utama dan melalui spektra MS diketahui puncak-puncak tersebut adalah molekul yang lebih kecil termasuk metanol, komponen dari biofuel.*

Kata kunci: *Biofuel, CMC, $Fe_3O_4/SiO_2/TiO_2$, Fotokatalis, Fotorengkah, Nanokomposit*

INTRODUCTION

The problems caused by the incresment of CO_2 concentration in atmosphere became a main concern in many countries. These problems induced climate change and became huge challenge in humanity (Friedlingstein *et al*. 2014). Core ice expedition revealed that the CO_2 concentration in the atmosphere becomes steady state until industrial revolution (Jouzel 2013; Kohler *et al*. 2011; Nomura *et al*. 2013). After that, the CO_2 concentration significantly increases with exponential trend. This condition already reaches two third of critical value where humanity could not be existed anymore. Up to 1,430 Giga ton of CO_2 has been released annually from 1870 to 2013 and would be increase up to 1,670 Giga ton in 2019 (Friedlingstein *et al*. 2014).

Some researches deal with transform CO_2 into fuel either methanol fuel or natural gas. Those actions are taken to resolve another problem, energy crisis. Energy becomes primary needs to support humanity, Industry, hospitality, and education depend on energy supply (Richardson *et al*. 2010). In this searching of new energy resources, biomass give an opportunity. Biomass have short energy cycle that make this new energy resource became renewable and zero emission (Vyas *et al*. 2010).

Some researches work with biodiesel that made from transesterification of vegetable oil. This method will give fatty acid methyl esters (FAMEs) (Henando *et al*. 2007). The disadvantages are low energy will release from long chain carbon and also FAMEs only satisfied Diesel engine (Vyas *et al*. 2010). The general automotive in the city applied Otto engine, so engine modification is required to apply FAMEs in civilization.

The other researches work with biofuel. Biofuel have higher energy compared to biodiesel in the same volume and also biofuel suitable to Otto engine (Borges & Diaz 2012). The problem was in biofuel preparation from biomass. Natural biomass made from biomolecule that included long chained polymer. To make smaller molecules usually needs high temperature and high pressure of H_2 (Dhepe & Fukuoka 2007). This step neither sustainable nor green.

This research develops heterogeneous catalyst that can crack CMC, as biomass model, into smaller molecules. These smaller molecules desired to be resource of biofuel. To develop catalyst with that criteria, this research designed nanocomposite material that have photocatalytic activity. For another advantage, this nanocomposite has magnetite core that make this material has magnetic recoverability property. To improve reusability of this material, this material laminated by SiO_2 to avoid Fe_3O_4 contact to TiO_2 and caused photodissolution. Photocatalyst will generate electron-hole pair where the hole has strong Lewis acid behavior and can be used to make photocracking could happened in ambient condition.

MATERIALS AND METHODS

Materials

Most of reagents are pro-analysed grade and were purchased from Merck. Technical grade methanol and the other synthesis grade chemical reagents were purchased from Sigma-Aldrich.

Instrumentation

FTIR spectra were recorded on a Shimadzu Prestige-21 FT-IR spectro-photometer with KBr pellets method. XRD diffractograms were recorded on a Shimadzu XRD 6000. SR-UV-Vis spectrum was recorded on a Pharmaspec UV 1700 spectrophotometry. GC chromatogram and MS spectra were recorded on a Shimadzu QP-2010S gas chromatography – mass spectroscopy. TEM images were recorded on a JEOL JEM-1400 transmission electron microscopy. Sonication run in a Bransonic CPX2800H ultrasonic cleanser. Calcination run in Vulcan A-130 furnace.

Synthesis of Fe_3O_4 nanoparticle

As much as 6.02 g of $FeCl_3{\bullet}6H_2O$ and 4.08 g of $FeSO_4{\bullet}7H_2O$ dissolved into 60 mL of ion free water and then aerated by N_2 along synthesis. The solution stirred and added by 25 % NH_3 solution until the pH was 10 and then the mixture was sonicated for an hour until the solid was formed. After that, the solid was separated by external magnet and washed until the pH was 7. The solid was soaked into 100 mL of sodium citrate 0.2 M and soaked for overnight. After that, the solid was washed until the pH was 7 and dried overnight. The solid preparation was characterized by XRD, FTIR and TEM.

Synthesis of Fe_3O_4/SiO_2

An amount of 0.1 g of Fe_3O_4 soaked into 60 mL of technical grade methanol. The solution stirred and added by 1 mL of tetraethyl ortosilicate (TEOS) and then the mixture was sonicated for three hours. After that, the solid was separated by external magnet and dried overnight. The solid prepared was characterized by XRD, FTIR and TEM.

Synthesis of $Fe_3O_4/SiO_2/TiO_2$

Fe_3O_4/SiO_2(0.1 g) soaked into 60 mL of technical grade methanol. The solution stired and added by 1 mL of titanium tetraisopropoxide (TTIP) and then the mixture was sonicated for three hours. After that, the solid was separated by external magnet and dehydrated overnight. The old calcinated over 500°C for three hours. The solid preparation was characterized by XRD, FTIR and TEM.

Photocracking

Some of CMC 10 ppm (100 mL) added by 50 mg of $Fe_3O_4/SiO_2/TiO_2$. After that, the mixture stirred for 10 minutes in the dark and then illuminated by UV lamp for an hour. The photocatalyst was separated from product by external magnet. The product was analysed by GC-MS.

Reusability and Magnetic Recoverability

As much as 10 mL of CMC 10 ppm added by 50 mg $Fe_3O_4/SiO_2/TiO_2$. The mixture was stirred for 10 minutes and then illuminated with UV lamp for an hour. Before the solid separated from a mixture, the absorbance of the mixture measured by UV-Vis spectrophotometer and then the solid separated by external magnet. After a cycle, the solid soaked to a fresh 10 mL of CMC 10 ppm and run to another catalytic cycle until 10 catalytic cycle. Each product from a catalytic cycle analysed by GC-MS.

RESULTS AND DISCUSSION

Preparation of $Fe_3O_4/SiO_2/TiO_2$ Nanocomposite

This research develops the nanocomposite with Fe_3O_4 core to gives magnetic recoverability property to the photocatalyst and laminated by TiO_2 give the ability as photocatalysis and SiO_2 coated give an electronic barrier to avoid contact between Fe_3O_4 and TiO_2. This combination gives a good magnetic recoverability and reusability properties. TEM images (Figure 1) revealed the nanocomposite structure with core-shell structure. The FT-IR spectra (Figure 2) and XRD diffractogram (Figure 3) confirmed the presence of Fe_3O_4 (M), SiO_2 (S), and anatase phase of TiO_2 (A) with composite trend. This result confirmed the synthesis of $Fe_3O_4/SiO_2/TiO_2$ nanocomposite had been done. The SR-UV-Vis spectrum of this material determined this material band gap and it gave 3.22 eV.

Previous research used metal (such as Pt and Ru) support material to cracking cellulose and only get sorbitol, another saccharide, under 250°C and H_2

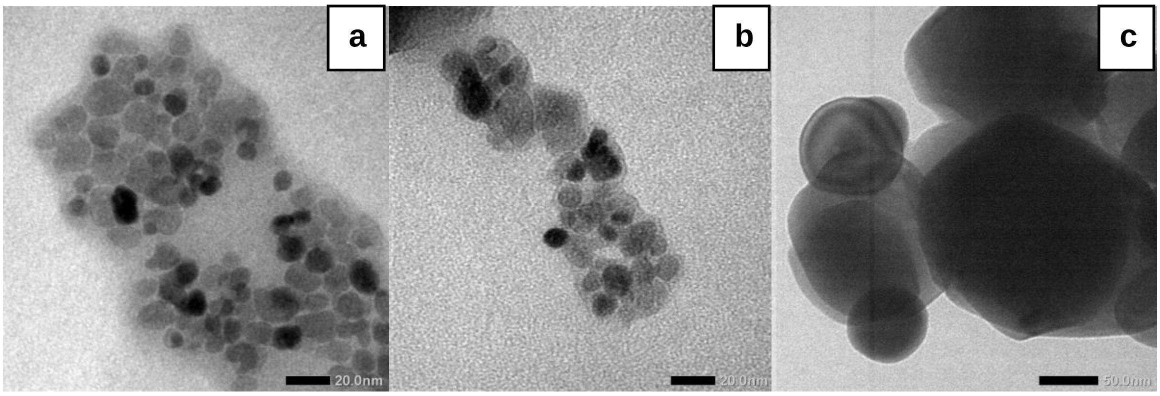

Figure 1. TEM images of (a) Fe_3O_4 nanoparticle (b) Fe_3O_4/SiO_2 nanocomposite (c) $Fe_3O_4/SiO_2/TiO_2$ nanocomposite

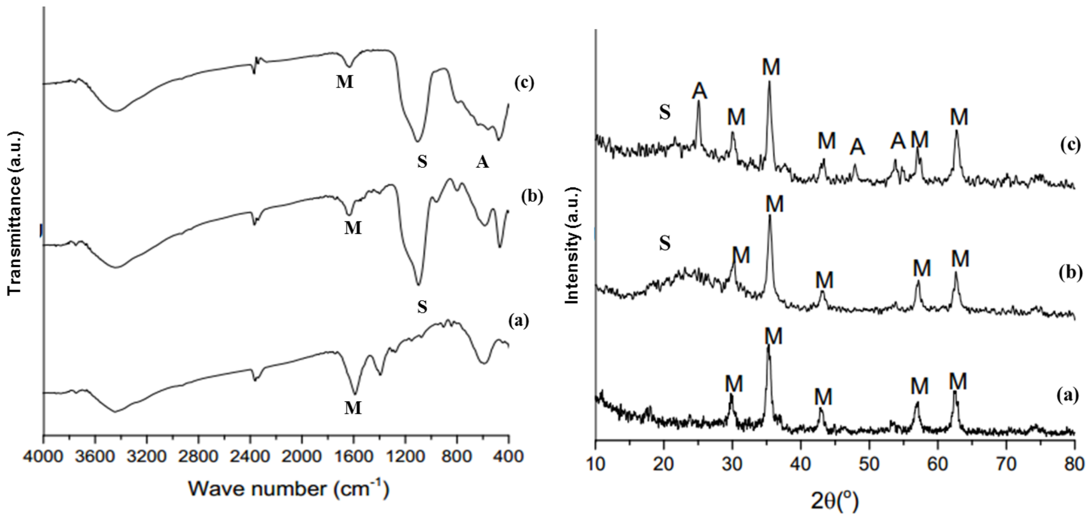

Figure 2. FT-IR spectra (left) and XRD pattern (Right) of (a) Fe_3O_4 nanoparticle (b) Fe_3O_4/SiO_2 nanocomposite (c) $Fe_3O_4/SiO_2/TiO_2$ nanocomposite

pressure [9]. Even this metal not strong enough to make smaller molecules that can be used as fuel. In this research, photocatalyst also induced H_2 generating from H_2O photolysis so H_2 pressure condition does not required anymore. This research also used simple metal oxide thathave higher availability than transition metals like Ru and Pt. $Fe_3O_4/SiO_2/TiO_2$ nanocomposite also has magnetic recoverability property to improve recovery system and enhance the sustainability.

Study of Photocatalytic Activity

The photocatalytic activity of $Fe_3O_4/SiO_2/TiO_2$ nanocomposite was tested as photocatalyst in CMC photocracking. Cracking mechanism required Lewis acid to run. Photocatalyst can generate hole that has character as strong Lewis acid. This is the reason why photocracking could be run in ambient condition without high temperature and pressure. This becomes major advantages of photocracking compare to thermal cracking and normal catalytic cracking. This method also greener and more sustainable than conventional method because needs less energy and give better product.

CMC has been chosen as feed because huge abundance and not consumed by human so this feed does not have issue with starving and food crisis. The challenge about CMC is the polymeric structure inhibit cracking processes. This problem can be resolved with application photocatalyst as heterogeneous catalyst. Photocatalyst in this research have band gap around 3.22 eV. That make the hole of electron has potential electron around 3.22 V because in one photoexciting proses only involved by an electron. This hole strong enough to cut polymeric chain to make smaller molecules.

The product of photocracking was analysed by GC-MS and gives result in Table 1. From Table 1 we can conclude that photocracking of CMC had been done and make some smaller molecules. One of that molecule is methanol the main component of biofuel. This result revealed that $Fe_3O_4/SiO_2/TiO_2$ nanocomposite could be a potential photocatalyst in CMC photocracking to produce biofuel.

Magnetic Recoverability and Reusability

The magnetic recoverability and reusability was studied under ten catalytic cycles. As seen in Figure

Table 1. Component of photocracking product

Peak Number	Retention Time (minutes)	Peak area (%)	MS prediction
1	1.874	15.18	Oxalic Acid
2	1.950	13.59	Methanol
3	1.992	71.22	Acetone

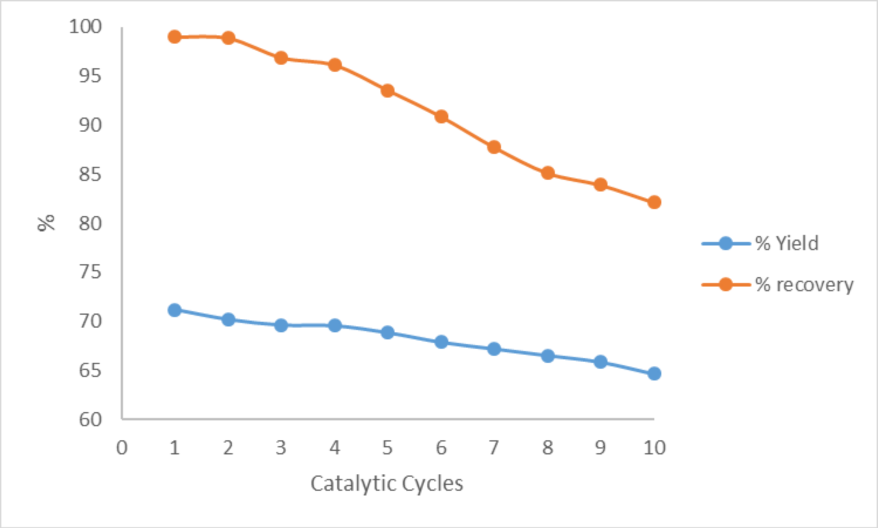

Figure 4. Reusability and recovery diagram

4, after ten catalytic cycles the catalytic activity does not decreased significantly. This trend can be seen from yield percentage diagram, that decreased only 5% after ten catalytic cycles. The recovery percentage determined by turbidimetry that measure the absorbance of the substrate after a catalytic cycle. The λ in this method set to the visible spectrum to avoid photocatalytic reaction during the measurement. This method gives that only 20 % of catalytic loss during ten catalytic cycles. This result confirmed the good magnetic recoverability of this photocatalyst.

CONCLUSIONS

The synthesis of $Fe_3O4/SiO_2/TiO_2$ nanocomposite had been done and characterized by XRD, FT-IR, and TEM confirmed the appearance of Fe_3O_4, SiO_2, TiO_2 in core-shell structure. This material can be used as photocatalyst in CMC photocrackingunder UV irradiation and gives 73.91% yields. The products of photocracking were smaller molecules including methanol, the component of biofuel. This material also had good magnetic recoverability and good reusability.

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