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; artikelisa@mail.ntust.edu.tw * Correspondence: sandy@ukwms.ac.id; Tel.: +62-31-389-1264 Abstract: The fast depletion of fossil fuels has attracted researchers worldwide to explore alternative biofuels, such as biodiesel. In general, the production of biodiesel is carried out via transesterification processes of

5**vegetable oil with the presence of a** suitable **catalyst. A**

mixed metal oxide has shown to be a very attractive heterogeneous catalyst with a high performance. Most of the mixed metal oxide is made by using the general wetness impregnation method. A simple route to synthesize silane-modified mixed metal oxide (CaO-CuO/C6) catalysts has been successfully developed. A fluorocarbon surfactant and triblock copolymers (EO)106(PO)70(EO)106 were used to prevent the crystal agglomeration of carbonate salts (CaCO3-CuCO3) as the precursor to form CaO-CuO with a definite size and morphology. The materials show high potency as a catalyst in the transesterifi- cation process to produce biodiesel. The calcined co-precipitation product has a high crystallinity form, as confirmed by the XRD analysis. The

10**synthesized catalyst was** characterized **using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray**

(EDX). The mechanism of surface modification and the effects of the catalytic activity were also discussed. The biodiesel purity of the final product was analyzed by gas chromatography. The optimum biodiesel yield was 90.17% using the modified mixed metal oxide CaO-CuO/C6. Keywords: hydrophobic surface modification; mixed metal oxide; biodiesel; transesterification; silanization 1. Introduction The demand of a large amount of energy to sustain world economic development causes the requirement of

13**fossil fuels, such as petroleum, coal and natural gas**

, to con- tinuously increase [1–4]. There are various

13**renewable energy resources**, namely **solar, wind, hydropower, geothermal and biomass. Biomass**

can be converted to biofuels, such as biodiesel [3]. Biodiesel is very promising due to its quality: it is renewable, highly degradable, has zero toxicity and is environmentally friendly [4]. Biodiesel is typically formed as a methyl ester; therefore, it can be produced from vegetable oil or fats through a transesterification and/esterification reaction in the presence of a catalyst [5,6]. Homogeneous catalysts are widely used for transesterification reactions. However, the separation of homogeneous catalysts from the final product is a major disadvantage. In order to solve this problem, heterogeneous catalysts such as metal oxides are applied in biodiesel synthesis [7]. Heterogeneous catalysts are known for their preferable properties, namely being non-corrosive, green, eco-friendly and having a high catalytic efficiency [8].

3**Nanomaterials 2022, 12**, 245. **https://doi.org/10.3390**/nano12020245 **https://www.mdpi.com/journal/nanomaterials**

12**CaO is the most** widely **used alkaline** earth **metal oxide** as a catalyst **for**

transesteri- fication [9,10]. CaO has a strong basic catalytic performance, low solubility in methanol and low toxicity [9,10]. The main factor in CaO-based catalyzed transesterification is to increase its basic catalyst sites. The catalytic activity of metal oxide particles is influenced by their size and morphology. CaO catalysts present as aggregated particles consisting of small crystals. A smaller particle size has a higher surface area, which causes a greater exposure

17**of active sites on the surface of the**

catalysts [11]. The aggregation of particles during synthesis needs to be minimized. CaO can be synthesized from the calcination of CaCO3 precursors. However, the synthesis of carbonate salts by using a direct precipitation can be a complex process [12,13]. Previously, Hai et al. used a simple mixing of CaCl2 and Na2CO3 to produce CaCO3, and followed with calcination to finally form CaO [5]. The direct mixing of CaCl2 and Na2CO3 without any additional surfactant caused the production of CaCO3 with a very large particle size of around 8–10 μm. The calcination of the synthesized CaCO3 created large and irregular CaO particles with sizes in the range of 4–8 μm. These micron-sized CaO particles are aggregate particles consisting of interconnected small CaO nanoparticles [5]. The catalyst performance highly depends on the exposure

15**of active sites on the** catalyst surface. **The reduction of**

aggregated particle sizes causes the exposure of active sites to increase, which finally enhances the catalyst performance. It is crucial to control the size of the aggregated catalyst particle. A single particle CaCO3 is formed through the aggregation of smaller crystals. The small crystals tend to bind with other crystals, causing aggregation and growth in the particle size. Different additives have been used to control the growth of the particle size, such as organic solvents and macromolecules. Various polymers can act as barriers between tiny crystals to prevent agglomeration. Hanafy et al. used

19**poly (sodium 4-styrenesulfonate) (PSS), poly (allylamine hydrochloride) (PAH), chitosan (CHI**) and **poly acrylic acid (PAA**

) to control the colloidal CaCO3. Each polymer influences the final shape and diameter of the CaCO3 [14]. Different ranges of particle sizes can be produced, with the largest particle size at 3 μm. Poly (acrylic acid) and sodium dodecyl benzene sulfonate have been used to control the morphology and particle size of CaCO by inhibiting the growth of calcite. The concentration of the polymer in the mixture affects the particle sizes. The increase in the amount of poly (acrylic acid) might form particles with a diameter of 8 μm [15]. Song et al. used lecithin to control the nucleation of CaCO3 to produce microsphere CaCO3 with a particle size of around 2 μm [16]. Previously, a fluorocarbon surfactant and triblock copolymers have been used as a template to form monodisperse mesoporous silica nanoparticles [17]. Both surfactants have never been used to control the formation of CaCO3 as a precursor in the production of CaO or other mixed metal oxides, such as CaO-CuO. There are several limiting factors with the use of pure CaO as a catalyst that can deteriorate its catalytic performance, such as its moderate basicity and stability. CaO is rapidly hydrated upon contact with air, which can reduce its activity as a catalyst [10]. The drawback of pure CaO can be overcome

7**by doping with alkali and organic compounds** or **mixing with metal**

oxide [9].

17**A combination of CaO with** other **transition metal oxides**

5**would increase the basicity and reduce the particle size**

[18]. In a recent study, CaO was mixed with NiO, CuO and ZnO by using

5**a simple wetness impregnation method**. All of **the**

mixed metal oxides had high catalytic activities. However, the synthesis method resulted in large aggregate particles. The irregular particle shape and large particle size might reduce the optimum exposure of the catalyst active basic sites [18]. Copper catalysts were shown to have high catalytic activities and selectivity, and are also less expensive [19,20]. Niju et al. were the first to report the synthesis of mixed metal oxide CuO-CaO. They used a general wetness impregnation to form CuO and then doped the particles with CaO. The synthesized aggregated catalysts had no defined shape and appeared as large agglomerate particles (~10 µm) [20]. The mixed metal oxide CaO-CuO can

7**improve the catalytic** performance **of CaO**. The **CaO**

-CuO has also been used

7**as a catalyst in** transesterifying **waste** cooking **oil**

. Most of the mixed metal oxide was

7**synthesized by using wet impregnation**. This **method**

mainly produces large aggregates particles, which might block catalyst active sites and reduce the catalytic performance. Another approach to producing mixed metal oxide with a controllable particle size and morphology is highly required. In addition, surface characteristics of the catalyst also influence the interaction with reactants, which affects the final result. The modification of the catalyst with hydrophobic characteristics can enhance the catalyst–substrate interaction, which finally leads to a higher yield [21].

2**To the best of our knowledge, there is no** study in **the synthesis of**

CaO-CuO particles by using a surfactant (fluorocarbon surfactant and triblock copolymers) controlled precipitation and their modification with an organosilane to form modified CaO-CuO particles as a catalyst in the transesterification process. The catalytic activity of surfactant- based synthesized CaO was compared with CaO (from commercial $CaCO_3$), CaO-CuO (mixed metal oxide) and organosilane-modified CaO-CuO/C6. 2. Materials and Methods

14**2.1. Materials Commercial soybean oil (purchased from local store**

) and methanol (CH_3OH, pur- chased from Merck, Darmstadt, Germany; CAS: 67-56-1) were used as the feedstocks for transesterification reactions. n-Hexane (C_6H_{14}; CAS: 110-54-3) was purchased from Merck, Darmstadt, Germany for final product purification purposes. The materials for particles synthesis were as follows: calcium chloride ($CaCl_2$; CAS: 10043-52-4) and sodium carbonate (Na_2CO_3; CAS: 497-19-8) were purchased from Merck, Darmstadt, Germany. Fluorocarbon FC-4 was purchased from Yick-Vic Chemicals and Pharmaceutical, Hong Kong, China, and PF-127 (CAS: 9003-11-6) was purchased from Sigma Aldrich, Singapore. For surface modification purposes, trichlorohexylsilane (CAS: 928-65-4) was purchased from Sigma Aldrich, Singapore, Singapore. All materials were used as purchased. Deionized water (DO) was employed for glassware washing purposes only. 2.2. Synthesis of Calcium Oxide (CaO) The template solution (3% wt) was made by mixing FC-4 and PF127 (1:3 w/w) in 100 mL DO water. A total of 0.005 mol of $CaCl_2$ was mixed under stirring for 30 min to form a homogeneous solution. Then, 100 mL sodium carbonate 0.1 M was added under vigorous stirring (±300 RPM) for 10 min and left for 24 h. The formed calcium carbonate ($CaCO_3$) was separated from the liquid using a centrifugation at 5000 RPM for 15 min. The solid particles were washed with ethanol (96% purity) 3 times and

8**dried at** 75 ◦**C for** 6 **h. The dry** particles **were calcined at** 1000 ◦**C for** 2 **h** and stored **in**

desicators. The synthesized particle was denoted as CaO-E. For comparison, we also prepared CaO made from commercial CaCO3, denoted as CaO-R. 2.3. Synthesis of Calcium-Oxide–Copper-(II)-Oxide (CaO-CuO) The template solution (3% wt) was made using the same method as the template of CaO preparation. A total of 0.005 mol of CaCl2 was mixed under stirring for 30 min to form a homogeneous solution, and then the 0.005 mol copper (II) sulfate was added. The stirring was continued for an hour to obtain a clear blue solution. The 100 mL sodium carbonate 0.1 M was added into the vigorous stirring (±300 RPM) for 10 min and left for

15**24 h. The** formed **particles were separated from the** liquid **using a**

centrifugation at 5000 RPM for 15 min. The solid particles were washed with ethanol (96% purity) 3 times and

8**dried at** 75 ◦**C for** 4 **h. The dry** particles **were calcined at** 700 ◦**C for** 6 **h** and stored **in**

desicators. The synthesized particle was denoted as CaO-CuO. 2.4. Surface Modification of CaO-CuO Various stock solutions were prepared by dissolving trichlorohexylsilane into toluene AR (0.1:10, 0.25:10, and 1:10 v/v) under stirring conditions at 70 ◦C to form homogeneous solution. The solution was stored at room temperature. The 0.5 g of dry mixed metal oxide was added into the 30 mL solution and stirred for 4 h at 80 ◦C under closed system. After the silanization was finished, the solid phase was separated by centrifugation at 5000 RPM and washed with ethanol (96% purity) for 5 times. The particles were dried at 75 ◦C under vacuum conditions for 6 h. The modified CaO and CaO-CuO were denoted as CaO-E/C6 and CaO-CuO/C6, respectively. 2.5. Transesterification Reaction The transesterification reaction was carried out in a 100 mL sealed flask bottle (Schott Duran) under mechanical stirring. In typical assay, 8 g of soybean oil and methanol (alcohol:oil molar ratio = 12) were added into the reaction bottle (the transesterification reactor). Using catalyst (3% of oil by weight), the reaction was performed for 7 h at 70 ◦C under constant stirring (500 RPM). Afterwards, the reactor was cooled at room temperature before collecting the final products. The reaction was repeated with the same operation condition using different types of catalysts as follows: commercial CaO (denoted as CaO-R), CaO-E, CaO-CuO, CaO-E/C6 and CaO-CuO/C6. The solid catalyst was separated by centrifugation at 5000 RPM for 10 min. The liquid product was dissolved in n-hexane (liquid product: n-hexane = 2:3 v/v) to form 2 layers. The top layer was taken out and evaporated at 70 ◦C under vacuum conditions to separate the n-hexane from the final product. The remained insoluble oil was also

2**separated by centrifugation at** 5000 **RPM for 5 min**

. 2.6. Characterization of Synthesized Solid Catalysts The morphology of synthesized solid

14**catalyst was observed by scanning electron microscopy (SEM**

) (JEOL JSM 6390, Peabody, MA, USA with 20 kV accelerating voltage. The crystalline phase of the samples was observed by X-ray diffraction (Philips PANalytical X'Pert powder X-ray diffractometer), Brighton, UK) (15◦ ≤ 2θ ≤ 60◦) with Cu Kα radiation (λ = 1.5406 Å) at 40 kV and 30 mA. Fourier transform infrared (FTIR Shimadzu 8400S, Kyoto, Japan) analysis was employed to determine the functional groups contained on the surface of synthesized solid catalyst (KBr was used as a blank, 1% of sample were mixed in KBr). A shimadzu TGA 50H, Kyoto, Japan

2**was used for thermogravimetric analysis (TGA) at a heating rate of 2** ◦**C/min under a nitrogen flow of** 50 **mL/min**

. 2.7. Characterization of Transesterification Product The FAME's composition was determined by GC method. A 100 mg transesterifica- tion final product was dissolved in n-heptane containing an inner standard (C17:0), and was quantitatively identified by gas chromatograph (Shimadzu GC-2014, Kyoto, Japan)

18**equipped with a DB-5HT column** (15 **m × 0**.32 **mm × 0.1 μm, Agilent, Santa Clara**

, CA,

11**USA) and FID detector. The operating conditions** took place **as follows: carrier gas = He, injection temperature = 250** ◦**C and detector temperature** = 300 ◦**C. The** initial column

6**temperature was programmed at** 60 ◦**C** for 2 **min and increased to 200** ◦**C at a rate of 10** ◦**C/min**; afterwards, it **increased to** 300 ◦**C at a rate of** 5 ◦**C/min** and **was** maintained **for** 7 **min. The**

external reference FAME (47885 U, containing thirty-seven elements of the FAME standard mixture) was used for the identification of the peak of the methyl group organic compound in the sample, together

4**with methyl heptadecanoate as** the **internal standard**. To calculate **the purity of FAME in the sample**, the following equation **was**

used: Fame Purity Fp, % = ∑ AFAME − AMH CMHVMH × 100% × (1) ( ) (AMH m) where: Nanomaterials 2022, 12, x FOR PEER REVIEW 5 of 14 where: ∑AFAME = Total area of FAME peaks;
∑AMAHFA=MAEr=eaTooftaMlaHrepaeoafkF;AME peaks; AVMMHH= VAorlueamoefoMfHMHpesaokl;ution
(mL); VCMH = AVcotuluamlceoonfcMenHtrastoioluntioofnM(mHLs)o;lution (g/mL);
CmM=HA=ctAucatluwaelicgohntcoenfttrhaetiFoAnMofEMsaHmspolleut(igo)n. (g/mL); m =
AFcutruthalewrmeoigrhe,t toof dtheeteFrAmMinEe tshameypileeld(go).f FAME, the following equation was
used: Furthermore, to determine the yield of FAME, the following equation was used: $YieldofFame$ =?
M????×F??×100% (2) where: Yieldof Fame= MFAMM?E??×Fp ×100% (2) (MOil) wMhFAeMreE:=

4**Weight of FAME obtained after the reaction and separation process (g**

); MMoFiAl=MWE=eiWghetigohftthoef FinAitMiaEl ooibltsaaimnepdlea(fgte)r; the reaction and separation process (g); FMpo=il F=AWMeEigwhteoigfhthtefriancittiioanl ooibltsaaimnepdlefr(ogm); FAME purity. Fp =

4**FAME weight fraction obtained from** FAME purity. **3. Results and** Discussion
3.1R.SeysuntlhtsesainsdanDdiMscoudsisfiicoantion **of**

Modified Mixed Metal Oxide (CaO-CuO/C6) 3.1. SIynnthesistahnisd Modifiwcoatriko,n of Mowdeified
MiuxseeddMetal Oaxide (CflauOo-rCoucaOr/bCo6n) surfactant
[C3F7IOn(tChFis(CwFo3r)kC,Fw2Oe)u2CseFd-
(aCflFu3)oCrOocNarHbo(CnHsu2)rf3Nac+tan2tH[C5)32CF7HO3(]Cl−,F(wChFi3c)hCFis2Ode)2nCoFte-
(dCFa3s)
CFCO4N,Han(CdHtr2i)b3lNoc+k(CP2EHO5)-2PCPHO3-]PI−EO,wchoipcholiysmdeenroste(EdOas)1F06C(P4O,a)n70d(EtrOib)l1o06ck(FP1E2O7)-
PtoPOco-nPtEroOl cthoepoplyremcieprista(tEioOn)1o0f6(PthOe)m70(iExtOu)r1e06o(fFC12a7C)Oto3-
CcuonCtOro3lotrheCpaCreOci3poitnaltyio.nCaoCfOth3e-CmuCixOtu3rewoasf CusaeCdOa3s-
CaupCrOec3ursoCratCoOfo3romnlyC.aCOa-CCOuO3-C,wuChOer3eawsaCsauCseOd3
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2tob,tdh)e. precursor (CaCO3-CuCO3) (Figure 2b,d). Figure 1. Synthesis of CaO-CuO by using the
surfactant-controlled precipitation. Nanomaterials 2022, 12, x FOR PEER REVIEW 6 of 14 Figure 1.
Synthesis of CaO-CuO by using the surfactant-controlled precipitation. FFigiguurere22..
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tTehmepvleasteic.leThteemvpelsaitcilnegteampppprloataicnhgliamppitreodatchhelgimroiwtetdhtohreaggrgorwegthatioorn
a2t
µarmou.nTdhe2smµmal.leTrhpeasrmticallelesrizpeaerntiaclbelessizaegerneaabtelresexapgorseuarteerofexcaptoasluyrset
aocfticvaetasliytesst,awcthiviceh abgegtrwegeaetniosninbgeltewpeaerntiscilnesglaenpdarletidclteos
athnedfloerdmtoattiohne foofrmsizaeti-oconnotfroslilzeed-cpoanrtrtiocllleesdaptaarrtoiculensd

sfiitnesa,llwyhleicahdsfitnoamllyulcehadimsptoromvuedchcaimtaplyrtoicveadctcivaittaileyst.ic activities.
largeTThahenedssuiurrrfreafgacctuatlananrttvpvaeesrtsiciicclleleе-
sb-.baTassehedisdmimsesetohtmhoodedtphpirnergevvetenhnatsttstchtahenenaoaggtggbrereegagacathitoiieonvnoeodffsisifniongngllelyecucrrysyisnstgata
ladrigreecatnpdrecirirpeigtautliaorn p[1a2r,t1ic3l]e.sP.rTevhiiosuiss sstoumdieetshisnhgowtheadt
tchaantndoitrebcetparcehciiepviteadtioifnolenalydsutsointhge
sifmorpmleatidoinreocftlaprrgeeciapgigtarteigoante[s1o2f,1p3a].rtPicrleesvioofuCsasOtu[d5]ieasndshCouwOed[12th].aTthdeidreircetcptprerceicpipitiattaitc
lemadetshtoodthreeqfuoirrmedataiomnoorfelacorgmepalgegxrpergoacteedsuorfepfaorrticcolenstrooflICinagOth[5e]
panardtiCclueOsiz[1e2[]1.3T]h.e direct precipTithaetionnexmtesthteopd
riseqtuoiremdoadimfyortehceommpelteaxl porxoicdeedu(CreaOfo)r
cwonitthrotlrliinchgltohreo(phaerxtiycll)esisliaznee [1((3C].H3(CH2)5SiCl3). Helmy et al. [24] found that
organosilane with Cl (chloro) as head grouTphsewnaesxtthesmteopstisreatcotivmeoidnitfhye
trheaectmioentawlitohxmideetal(CoaxOid)e (wTiiOth2).trTircihclholroor(oh(hexeyxyl)ls)islialannee
((CH3(3C(CHH2)25)S5iCl3)3. wHaeslmfiyrstehtyadl.ro[2ly4z]efdoubyndadtshoartbeodrgwanatoesril[a1n0e].
wThitehsiClaln(echwlaosroth)eans ahbeleadto gfroorumpscrowssa-
slintkhinegmthorsotugrheahcytidvreogienn btohnedirnegacwtiiothn
hwyditrhoxymle(OtaHl)ogxriodueps(ToniOt2h)e. sTurrifcahceloo-f
rom(heteaxlyolx)sidilae.nTeh((eCrHea3c(CtioHn2)f5oSrimCle3dwCasa-fOir-
sStihbyodnrdoilnygz,ewdhbiychadinstorrobdeudcewdatthere[(1h0e]x.yTlh)seilsainlaenoen wthaes
stuhrefnacaebolfethtoe cfaotramlysctr.oTshs-islinmkaidnge
tthherocautgahlyshtymdororegehnydbroonpdhionbgicw[2i4th]. Thhyedraobxoyvle(mOeHch)- garonuispms
donoetshneostuprefarcfoeromf mweeltlalwoitxhidCeu.OTh.eThreisacistidonuefotormtheedcChaa-rOac-
tSeirbisotincdsionfgC,wuOhi,cwhhinic-h
trhoadsuacleodwthheyg(rhoesxcyolp)siciilatyneatoannothrmeasulhrfuamceidoiftyt.hTehecalotawlyasmt.oTuhnist
omfaaddesotrhbeedcawtaaltyesrthminodreers hoyrdgraonpohiloabniec
h[2y4d].roTlhyesiasbaonvdefmuretchhearnhiisnmdedrocersonsso-
tlipnekrinfogrmwiwthetlhlewmithetCaluoOx.idTehi(sCiusOd)u[e25to]. the characteristics of CuO, which has a
low hygroscopicity at a normal humidity. The low amount of adsorbed water hinders organoilane hydrolysis
and further hinder Nanomaterials 2022, 12, c2r4o5ss-linking with the metal oxide (CuO) [25]. 3.2.
Charaterization of Silane-Modified Mixed Metal Oxide (CaO-CuO/C6) Figure 3.23. Chsahroawtersizattihoen
ofFSTiIlaRne-Manoadliyfiseids Mioxfed Mtheetal sOyxnitdhee(sCizaeOd-CuCOa/OC6,) trichlo-
ro(hexyl)silane-modified CaO particles (CaO-E/C6), CaO-CuO and trichlo- ro(hexyl)silane-mFiogduirfeied3
CshaoOw-CsuthOe(CFTaOIR-CaunOal/yCs6i)s
poafrttihceless.yCntahOeseizxehdibCitsaOse,vterricahllvoirbor(ah-exyl)silane- tions. Ca-
OmboonddifiseadreCsahOowpanrtbicylethse(CwaiOd-eEb/aCn6d),aCtaaOro-
uCnudO5a0n0dcmtri−c1,hwlohroe(rheaesxythl)esi8la6n6ec-mm−o1dified CaO- and 1417
cmCth−1ueObwa(niCddeasObca-oCnrdrueOaspt/aoCrno6d)upntoadrC5ti0-
cO0lecbsm.oCn−ad1,Osw.Tehxheheriebsatisrtsotnhseegv8be6ar6anlcdmvai−btr13a6at4nio3dnc1sm4.1C−17acc-
omOrr−be1ospnboadnnsddassrecosrhroewspnonbdy to the O-HtoboCn-
Odsb,ownhdisc.hThinedstircoantegsbtahnedraetm36a4in3icnmg−h1ycdorrorexsyplognrdosutposthoenOt-
hHe bsounrdfasc,ewhofich indicates synthesizedthCearOem[2a6i]n.ing hydroxyl groups on the surface of
synthesized CaO [26]. Figure 3. FTIFRigaunraely3s.isFoTfIRthaencaalytasliyssot:f CthaeOc-aEt,aClyasOt:-
CE/aCO6-,EC,aCoa-OCu-EO/,CC6a,OC-aCou-COu/CO6,.CaO-CuO/C6. particles. ThpearCtiacl-eOs.
bTahnedCwa-aOs baalnsod fwoausnadlsaotfaoruonudnadt
a5r0o0ucnmd−510,0wchme−re1a,swthheerebaasntdheabta8n6d6at 866 cm−1 CaO-E/C6 spCeacOtr-
aEs/hCo6wspthecetFraTsIRhoawnatlhyesiFsToIfRthaenatrlyicshisloorfot(hheextryilc)hsilolarnoe(h-
mexoydl)isfiieladnCe-amOodified CaO cm−1 and 14a1n7dc1m4−117ccomnf−ir1mcotnhfierCm-OtheboCn-
dOs.bConodmsp.aCroemdptoarCedaOto-ECsapOe-cEtrsap,eacntraad,danitiaodndailtional band band
appeaarpedpeaatre9d91atcm99−11.cTmh−e1. Thcem99−11bcamn−d1cboarnrdescpoornredssptoonSdis-
Oto-mSi-eOta-lmbeotnaldbso[n2d7]s,[i2n7-], indicating dicating thatthtahtetShie-OSi--COa-Cwaaswas
successfuflolrymfoerdmbeydthbeystihlaenization reactrioeanc.tTiohne.sTtrhoengstrong band band at
theartatnhgeeraonfg1e00o0f–11010000–c1m10−01schmo−w1ssthhoewpsrethseenpcreeosefnthceeoSfi-
tahlekoSxi-yalgkrooxuypg.rInoutph.isIn this case, case, the
batnhdeabta1n0d79atcm10−719incdmic−a1teisntdhiecapteresstehneceproefstehneceSio-Oft-hheexSyi-
lOgr-houexpyolngrtohuepsuornfatchee surface of of
modifiedmhoyddirfioepdhohbyidcrpoaprhtiocbleics.pTahreticslteros.nTghbeanstdroantg36b4a3ncdma−t13c6o4rr3ecsmpo−n1dcsotroretshpeoOn-
dHs to the O-H bonds
[26],bwohnidchs[i2n6d]i,cwatheischthienrdeimcaateinsitnhgehryemdraoixnyinlggrhoyudprsooxynltghreosuuprsfaocne
tohfethsuerpfaarcteicolfesthe particles after the silaanftiezrattihoensrileaancitzioanti.on reaction. CaO-CuO
sCpaecOtr-
CaushOoswpeactsriamsilhaoriwtyawsiitmhilCaarOityswpeitchtrCa,awOitshpeacdtdrait,iwoniathlvaidbdraittiioonnaaltvibration
at 533 cm−1 rep5r3e3scemnti−n1greCpurOese[2n8ti]n.gTrCicuhOlo[r2o8(h].eTxryicl)hsliolarnoe(h-
mexoydl)isfiieladnCe-amOo-dCiufiOedpCaartOic-lCesuOhapdarticles had typical
specttyrpaictahlastpwecetrreasthimatilwarerteosCimaOila-rCtuoOC.aTOh-
eCumOa.inThdeifmfearienndceiffiesrtehnecepirsetsheenpcereosfenace of a band band at
107a9tc1m07−19,wcmhi−c1h, winhdiicchatiensdtihceatpersetsheenpcereosfetnhceeSoif-Oth-eheSxi-yOl-
ghreoxuyplg[2r7o]u.p [27]. In
agreemenIntwagitrheetmheeFntTwIRitahntahleysFiTs,ItRheanTaGlyAsirse,stuhletsTsGhAowretshueltesxsihstoewnctehoefetxhiesthenexceylof
the hexyl silane on thseilcaonmepoonstihteeCcoamO-pCousiOte. FCiagOu-
rCeu4Osh.oFwigsurTeG4AshfoorwCsaTOG-ACufoOraCnadOC-CaOuO-CaunOd/CC6a.O-CuO/C6. A
previous study showed that the degradation of various organosilanes was completed at around 550 ◦C. The
CaO-CuO/C6 had around a 10% weight loss compared to the CaO- CuO. The weight loss between 40–200
◦C is related

9**to the desorption of** physisorbed **water**, whereas **the weight loss** between 200–550 ◦**C is due to the** decomposition **of** hexylsilane [29]. A previous study showed that the degradation of various organosilanes was completed at around 550 °C. The CaO-CuO/C6 had around a 10% weight loss compared to the CaO-CuO. The weight loss between 40–200 °C is related

9**to the desorption of** physisorbed **water**, whereas **the weight loss** between 200–550 °**C is due to the** decomposition **of**

h8eoxf-14 ylsilane [29]. Figure 4. TGA analysis of the catalyst: Cao-CuO and CaO-CuO/C6. Figure 4. TGA analysis of the catalyst: Cao-CuO and CaO-CuO/C6. Figure 5 shows the X-ray diffractograms of the CaCO3, synthesized CaO (CaO-E), CaOFi-gCuurOe 5ansdhohwexsytlhsielaXn-er-amyoddiiffifreadctCoagOra-mCusOofptahreticCleasC.OTh3,esCynatChOes3izdeidffrCacatOion(CinaOdi-cEa)t,es CathOe-CpureOseanncde hofexcyallcsiiltaen(e2-7m◦,o2d9i◦fi,e3d9◦C,a4O8◦-C)uanOdpvaartteicrlietes. (T27h.e5◦C,a2C8O.5◦3)d.iTffhraecXtiRonDinpdaticteartnesof thCeapOrepseonssceessoefdcaalcsiimtei(la2r7i°t,y2w9°i,th39p°u,b4l8is°h)eadndXRvDatepraitteter(2n7d.5a°t,a2[81.35,°1)4.]T.hTeheXpReDakpsattearrno Ca2O8.5p1o◦s,s3e2s.s1e4d◦,a3s7i.m32i◦la,r4i7ty.2w1◦itahnpdu5b3l.i8s3h◦edexXhRibDitpthatetefarnced-caetnat[e1r3e,d14c]u.Tbihcecpryesatkasl asttraurcotuunredof 28C.5a1O°,. 3B2a.s1e4d°,o3n7.t3h2e°,X4R7D.21p°aattnedrn5,3th.8e3r°eeisxhniobirtetmhaeinfaicneg-cCeanCteOre3dinctuerbmicecdriyastetadlusterutocttuhreehoifgh CateOm.pBearsaetduroenin theXcRaDlcinpaattitoenrnp,rtohceerses.is no remaining CaCO3 intermediate due to the high teTmhpeeXraRtuDreaninaltyhseiscaslhcionwatsiothnaptrCocaeOss-C.uO particles contain CaO, Ca(OH)2 and also CuO. Specifically, the peaks at around 35.4◦, 38.6◦ and 48.6 represent CuO. The peaks at around 28◦, 46.5◦, 52◦ and 54.8◦ indicate a hexagonal crystal structure from portlandite (Ca(OH)2) [11], which could occur from the spontaneous reaction of CaO and the mois- ture [15]. The presence of Ca(OH)2 as a result of the spontaneous reaction between CaO and the moisture is also supported by the FTIR data (Figure 3). In general, CaO-CuO/C6 had a similar crystal structure to CaO-CuO. The

5**crystallite size of the** catalyst **was** calculated **by** using **Scherrer's equation** (Table 1). **The** crystallite size **of**

CaCO3 was 39.53 nm. CaO made from surfactant-controlled precipitation (CaO-E) had a smaller crystallite size compared to CaO-R. Pure CaO (CaO-E, CaO-R) had a higher size compared to CaO in the composite of CaO-CuO. These results are in agreement with a previous study by Sulaiman et al. [18]. It was reported the introduction of different transition metal oxides affects the CaO crystallite size. The Ca(OH)2 particles co-existed with all CaO particles, with crystallite sizes of around 20 nm. Analyses for the CaO-CuO samples show crystallite sizes of 26.82 and 27.75 nm. Previous studies show that different synthesis parameters, including precursors, affect the formation catalyst with different crystallite sizes: CaCO3 (12–282 nm) [30], CaO (15–20 nm) [31], Ca(OH)2 (16–21 nm) [18] and CuO (10–22 nm) [32]. All of the synthesized catalysts in this study had crystallite sizes that were relatively small. These small crystallite sizes influence the performance of the synthesized catalysts.

3**Nanomaterials 2022, 12, x FOR PEER REVIEW 9 of 14 Figure** 5. **XRD** analysis **of**

synthesized particles: CaCO3, CaO-E, CaO-CuO, CaO-CuO/C6. Figure 5. XRD analysis of synthesized particles: CaCO3, CaO-E, CaO-CuO, CaO-CuO/C6. Table 1. Crystallite sizes of synthesized catalyst. The XRD analysis shows that CaO-CuO particles contain CaO, Ca(OH)2 and also CuOS.oSlipdePciafritciaclleys, the peaks at around 35.4°, 3C8r.y6s°taalnlidte 4S8i.z6e r(enpmr)esent CuO. The peaks at around 28°, 46.5°, 52° anCda5C4O.83° indicate a hCeaxOagonal crystaClas(OtrHuc)t2ure from poCrutlOandite (Ca(OHC)2a)C[O113], which cou3ld9.5o3ccur from the sp-ontaneous reactio-n of CaO and the- mois- ture [15C].aTOh-Re presence of Ca-(OH)2 as a resu1l8t.9o9f the spontane1o8u.0s5reaction betwee-n CaO and theCmaOoi-sEture is also sup-ported by the F2T4I.R10data (Figure 32)1..9In0 general, CaO-C-uO/C6 had a sCimaOi-lCarucOrystal structur-e to CaO-CuO. 11.36 20.25 26.82 TChaeCucrOy2s/taCl6lite size of the catalyst was ca1l1c.7u3lated by using2S7.c3h1errer's equati2o7n.7(5Table - 1). The crystallite size of CaCO3 was 39.53 nm. CaO made from surfactant-controlled precipiTtaabtiloen2 d(CisapOla-yEs) thhaedresaulstmsoafllEerDXcraynsatalyllsities fosirzCeacCoOm3p,CaraeOd, CtoaOC-aCO6,-RC.aCPOur3e-CCuaCOO3, (CCaaOO-E-C,CuaOOa-nRd)hCaadOa-hCiugOhe/rCs6iz.eTchoemwpeairgehdttopeCrcaeOnitnagtehse ocofmCapowsietreeohfiCgahOer-CcoumOp.Tahreedseto reCsuultfsoarrtehien magirxeeedmmenettawliothxiadeprceavtiaolyussts.tuTdhye baynaSluylsaiismoafntreitcahll.o[r1o8(]h.eltxwyla)ssilraenpeo-rmteoddtihfieed inptraordtiuclcetsio(nCaoOf/dCif6fearnedntCtarOan-CsiutiOon/Cm6)etinaldiocxaitdeessthaeffpercetssenthcee oCfaSOi, wcrhyiscthalilsitreelsaitzeed. tTohtehe Caa(tOtaHch)m2peanrttsicolfehsecxoy-lesxiliastneedmwoiitehtieaslloCnatOhepcaarttailcylests,suwriftahcec.rystallite sizes of around 20 nm. Analyses for the CaO-CuO samples show crystallite sizes of 26.82 and 27.75 nm. Table 2. EDX analysis of synthesized catalyst. %wt Atom CaCO3 -E CaO-E CaO-E/C6 CaCO3 -CuCO3 CaO-CuO CaO-CuO/C6 C 20.97% O 50.65% Ca 28.39% Cu - Si - 100.00% 17.19% 48.94% 33.87% - - 100.00% 26.43% 47.58% 25.72% - 0.28% 100.00% 51.53% 10.67% 28.36% 9.44% - 100.00% 11.58% 8.70% 68.17% 11.54% - 100.00% 13.87% 6.71% 57.49% 13.62% 8.30% 100.00% The catalytic performance of different catalysts in converting vegetable oil into biodiesel (FAME) can be seen in Table 3. Pure CaO had the lowest yield compared to other modified catalysts. There were two types of pure CaO particles. The main difference is in the source of CaCO3 as the main precursor to form CaO. CaO made from surfactant-based controlled precipitation CaCO3 particles had a higher yield of FAME compared to the commercial CaCO3. The use of surfactants enables better control over the CaCO3 particle size and morphology. The surfactant prevents the formation of large aggregate particles [16]. The smaller particle size improves the exposure of catalyst basic active sites, which leads to a better catalytic performance. The combination of CaO with CuO further increased the yield of FAME. Table 3. Yield of FAME from different catalysts. Catalyst Yield (%) Purity of FAME (%) Yield of FAME (%) CaO-R CaO-E2 CaO-E2 /C6 CaO-CuO CaO-CuO/C6 60.10 96.80 70.51 92.54 74.28 96.75 83.80 96.50 92.48 97.53 58.18 65.22 71.90 80.87 90.17 The combination of CaO with CuO formed mixed metal oxide CaO-CuO, which had a higher activity compared to pure CaO. Pure CaO is one of the most widely used alkaline earth catalysts. However, the spontaneous reaction of CaO and moisture during contact with air might deteriorate the catalyst performance. The addition of CuO increases the CaO stability and basicity and can also reduce the CaO crystallite size. These factors made the mixed metal oxide (CaO-CuO) superior to pure CaO [20]. In this study, the CaO-CuO enabled the yield of FAME at 80.87%. This result is considerably high compared to the previous study. The study indicated the variety of yields that can be achieved by using the CaO-CuO catalyst from 56 to 95% [20]. It is interesting to note that trichloro(hexyl)silane-modified CaO-CuO (CaO-CuO/C6) had the highest activity. Trichloro(hexyl)silane (CH3(CH2(5SICl3) was used to introduce hydrophobic properties to the catalyst. The hydrophobic characteristics improve the wetting of the entire surface of the catalyst with the hydrophobic soybean oil. The presence of hydrophobic moieties intensifies the interactions between the hydrophobic oil and the catalyst [21,33]. A previous study showed that a poor wetting of hydrophobic vegetable oil might even cause the inactivation of the catalyst. Furusawa et al. studied silane-modified CaO-loaded alginate capsules in the . The silane-modified catalyst had the highest oil permeation rate, which affected the production of a reasonably high yield of FAME (66%) [33]. A recyclability test was conducted to test the stability of the CaO-CuO/C6. The testing was conducted by repeating the use of the CaO-CuO/C6 in the transesterification process three times. Figure 6 shows that the catalyst had a high catalytic activity, even after a three-time usage, and that the catalyst activity can be maintained at around 80–90%. The yield from the first run to the fourth run is 90.17%, 90%, 85.50% and 80%. highest oil permeation rate, which affected the production of a reasonably high yield of FAME (66%) [33]. A recyclability test was conducted to test the stability of the CaO-CuO/C6. The test- ing was conducted by repeating the use of the CaO-CuO/C6 in the transesterification process three times. Figure 6 shows that the catalyst had a high catalytic activity, even after a three-time usage, and that the catalyst activity can be maintained at aroun1d1 o8f01–4 90%. The yield from the first run to the fourth run is 90.17%, 90%, 85.50% and 80%. Figure 6. Reusability testing over the CaO-CuO/C66 catalyst. 3.3. Transesterification Mechanism ttooProduce Biodiesel from Vegetable Oil Triglycerides bbyyUussiinngg SSiillaannee--MMooddiifiifieeddMMiixxeeddMMeettaallOOxxiiddee((CCaaOO--CCuuOO//CC66)) TThheeffoollllloowwiinnggiisstthheeccaattaallyyttiiccmmeecchhaanniissmmooffCCaaOO--CCuuOO//CC66iinntthheettrraannsseesstteerriifificcaattiioonnooff vveeggeettaabblleeooiilllttrriiggllyycceerriiddeess((FFiigguurree77))[[99,,3344]]:: SStteepp C1:6C((6h(e(xhyelx)syill)asnilea)nien)crienacsreesasthesetwheetnweestsnoefstshoefbtahseicbcaastiaclycsattmalyixsetdmmixeetdalmoxeitdael (oCxaidOe- 1SS:tteepp (rCfM2Cer:uomaeMmOOtohe)-vomCtwahxuelioittdfOxhhreio)ahdmnawyenodimalitronh(oeCniphtosHhhnya(o3dsCnbOr(oHioCHclp3Hs()hOoCt3oyo−OHba) −f3i)oocOirniislHnm.iotiT)iytamihtaatoeeteoetfbitholrta.rorasmaTxninchisdmseCeeesaebstaOtteanhers-roiiiCioficxfunciiCcdaOsaate(tiOcCioaoan-HntnCai3bolubyOynyOs−stbbc) (iin;CianndtHddauili3ncyOnegsgs−t)t;tpionordotthtuhoeecneccsraaeprrmbbroooontvnoyaynlll 2: ccaarrbboonn ooff ttrriiggllyycceerriiddeess aanndd ccrreeaattiinngg aann aallkkooxxyy ccaarrbboonnyyll iinntteerrmmeeddiiaattee;; SS3Stt:teeeppp 3TT:hhTeehafeolkramolkxaoytxicoyanrcboaorfbnfaoytnltyyinlaticenirtdmermemdeeitahdtyiealtteersattnreasrfn(oFsrfAmoMrsmvEsi)av(Ribao1CbnodOniOn The 4S:tep s4e:qTuheenfcoerimsraetipoenatoefdftaottfyoramcida mfatettyhyacliedstferorm(FAR2MaEn)d(RR13C.OOCH3) and diglycerides. The sequence is repeated to form a fatty acid from R2 and R3. Nanomaterials 2022, 12, x FOR PEER REVIEW 12 of 14 Nanomaterials 2022, 12, 245 12 of 14 FiguFriegu7.reTr7a.nTsreasntseersitfiecraiftiicoantioonf torfigtrliygcleyrciedreidseisntinotboiboidoideiseesleblybyuusisninggbbaassicic CaO-CuO/C66cacatatalylysts.t. 4. C4o.nclusions A faAcilfeacmileetmhoedthhoads hbaeesnbdeeenvedloevpeeldoptoedprtoodpurcoedmucoenodisperse CaCCOa3CO3-Cu3CpOa3rtpicalre-s as atpicrleescuarssaorptroecfuorrsmormtoixfeodrmmemtaixleodximdeetCalaoOx-iCdueOC.aTOh-CeutrOa.nTsehsetetrriafincsaetsitoenrifsitcuadtiyonshsotuwdeyd thatsChoaOw-eCdutOhaptaCratiOcl-eCsuwOerpeahrtigichlelys wcaetarelyhtiicgahlllyy acacttaivlyet.icAalfluyrathcteirvme.oAdiffiucrathtieornmoofCdiafiOca-CtiounO withofoCrgaaOn-oCsuilOanwei(t(hheoxrgyal)nsoilsainlaen)ee(n(hheaxnycle)sdiltahnee)caetnahlaynticcepdetrhfeorcmataanlycteicopfetrhfeorpmaartnicceleos.f Tthhee hexypla-rstiilcalnese. iTmhperhoevxeydl-tshileaninetiemrapcrtoiovnedbethtweeinetnertahcetiroenacbteatnwteseanntdhethreeaccattaanlytsstasnudrftahceec.aTtah-e synelyrgstisstuicrfeafcfee.ctTshferosmyntehrgeiustsiec oefffaecctosmfrboimnatthioenuosef CofaOa-cComuObinanatdiohnyodfroCpahOo-bCiucOpraonpderhtiye-s signdifirocpahnotlbyicepnrhoapnecretidesthsiegncoifnicvaenrtslyioennohfantcheedvtehgeetcaobnlveerosiilosninotfothbeiovdeiegseetal.bleThoiislsfainctiol appbroioadchiescaeln. 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12**synthesis of fatty acid methyl esters** (FAME) from **the methanolysis of** rapeseed **oil**

—,rseuvpieerwviasinodn;eMdi.tYin.:gc,osnucpeeprtvuisailoizna;tiFo.En.,Sr.e:sroeusorcuersc,evs,isvuiasuliazlaitziaotnio,nw;rSit.Ii.n:gr
—esroeuvriceews, avnadlideadtiitoinng;,
supeSr.vB.iHsio.:nre;vFi.eEw.S,.:varelisdoautirocne,ss,uvpiseurvailsiizoant.ioAnl;l
Sau.It.h:orerssohuarvceerse,avdalainddataiognre;eSd.Bto.Hth.:erpevubielwish,evdalviderastiioonn,
supeorfvtihseiomn.aAnullscaruiptht.ors

3**have read and agreed to the published version of the manuscript**

. FundFuinngd:inTgh:isThreissearch wawsfausnded bybTyhTehIendonesian Ministry of Research and Technology and HighHeirgEhedrucation through WoWrIdorCldlaCslsaRssesearch wiwthitThhTehCeontract nnoo150B/WM01.5/N/2021. Institutional RevRieewvieBwoaBrodarSdtatement: NoNtoatpplicable. InfoIrnmfoerdmCedonCsoennsteSnttaStetmateemnte:nNt:oNtoatpplicable. DataDAatvaaAilvabaiillaibtyilSittyatSetmateemnte:nDt:aDtaaitsa cisoncotanitnaeindedwwithitihninthtehearatritcilceless.. Conflicts of Interest: The authors declare no conflict of interest.

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