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Production of Biodiesel and Hydrogen from Plant Oil Catalyzed by Magnetic Carbon-Supported Nickel and Sodium Silicate

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Abstract

A novel magnetic carbon-based nickel and sodium silicate catalyst (Na₂SiO₃@Ni/C) was prepared by precipitation of Ni(OH)₂ on bamboo powders, pyrolysis and loading of Na₂SiO₃ for biodiesel and hydrogen co-production. The catalyst had strong magnetism (magnetic saturation, Ms of 15.7 Am^2/kg) from Ni and basicity (3.18 mmol/g) from Na₂SiO₃ for magnetic separation and biodiesel production. In the presence of Na₂SiO₃@Ni/C, biodiesel yield of 98.1% was achieved from soybean oil under the best conditions (9/1 methanol/oil molar ratio, 7 wt% catalyst, 65 °C for 100 min) optimized by single-factor experiments. The catalyst was cycled 4 times with biodiesel yield > 93%, but the yield dropped to 80.9% with 85.3% catalyst recovery rate at the fifth cycle. The deactivated catalyst after 5 cycles catalyzed the hydrothermal gasification of biodiesel by-product (crude glycerol) at 350 °C for 5 min with gasification rate of 80.1% and 82.7% H₂ purity. The role of Ni is to catalyze H₂ production while Na₂SiO₃ is to absorb CO₂ to achieve high H₂ concentration. After gasification, the structure of Ni/C changed slightly and can be still cycled to load Na₂SiO₃ for biodiesel production and subsequent gasification.

Keywords: Biodiesel; Magnetic catalyst; Crude glycerol; Hydrothermal gasification; Hydrogen.

1. Introduction

Utilization of renewable and clean fuels is an attractive option for reducing greenhouse gas emissions and improving energy security,¹ many countries have been directed towards the exploitation of alternative biofuels,² such as bioethanol³, biodiesel⁴ and biogas⁵. Biodiesel has attracted great attentions in recent years because of its similar properties to fossil diesel and gained widespread acceptance as its sustainability.⁶ Most common method in biodiesel industry is transesterify crude oil to biodiesel with liquid potassium or sodium hydroxide⁷, but the liquid catalysts are difficult to be recycled as they are soluble in methanol and glycerol mixture. So, they are usually neutralized that increases wastewater treatment cost⁸. Heterogeneous catalysts, such as hierarchically ordered nanoporous base catalyst⁹, activated Zn-Al hydrotalcites¹⁰, MgO nanocrystals¹¹ Li-CaO¹², CaO-La₂O₃ and CaO-CeO₂¹³ are widely studied to replace homogeneous bases. Na₂SiO₃¹⁴ and Na doped SiO₂ solid bases¹⁵ were used for biodiesel synthesis, and the deactivated Na₂SiO₃ could be still applied for the hydrothermal production of hydrogen from by-product glycerol combined with addition of nickel catalyst¹⁶. However, the separation of these heterogeneous catalysts needs filtration or centrifugation that is energy and time consuming.⁹⁻¹⁶

Magnetic heterogeneous catalysts were easily separated from product mixture by a magnet¹⁷ with high mass recovery rate, e.g., the rate for Na₂SiO₃/Fe₃O₄ magnetic catalyst is 1.7 times that for non-magnetic base Na₂SiO₃ (92.2 *vs.* 54.4 wt%)¹⁸. It was found that the recovery rate of magnetic carbon-based Na₂SiO₃@Fe₃O₄/C catalyst after 5 cycles is even higher than that of Na₂SiO₃/Fe₃O₄ after 1 cycle (96.1 *vs.* 92.2 wt%) because active carbon has good loading capacity besides as reducing agent for Fe₂O₃.¹⁹ Magnetic Na₂SiO₃@Fe₃O₄/C is active for biodiesel production and easily separated, but after deactivation from biodiesel production, the remained Fe₃O₄ core is not active for

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glycerol conversion to other value-added products. It is found that Ni (besides magnetic properties²⁰) can catalyze glycerol to hydrogen²¹, acetol and syngas²². For carbon supported nickel catalyst (Ni/C), NiO could be reduced by carbon carrier to active metal Ni directly without using reducing gas during pyrolysis at 700 °C for the production of porous char for catalyst loading, while commercial Ni/Al₂O₃ catalyst for H₂ production *via* steam methane reforming reaction was prepared with reducing gas (e.g., 3/7 mixture of H₂/N₂) at 750 °C for 20 h²³.

This work is to synthesize a magnetic base catalyst ($Na_2SiO_3@Ni/C$) that is active for biodiesel production, easily separated for recycles, and H_2 production from glycerol after deactivation. The catalyst was tested in biodiesel production from soybean oil and further for the hydrothermal production of hydrogen from by-product (crude glycerol) in biodiesel production.

2. Experimental

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2.1. Materials

Bamboo powders [49.4 C, 6.0 H and 43.4 O, wt%; analyzed by Elemental Analyzer (Vario EL III CHONS, Elementar Analysensysteme GmbH, Hanau, Germany)] were purchased from Zhili Hongqiang bamboo processing plant (Huzhou, Zhejiang), dried in an oven (WFO-710, EYELA, Tokyo Rikakikai Co., Ltd.) at 105 °C for 24 h, ball-milled (SHQM-0.4L, Chunlong Petroleum Instrument Co., Ltd., Lianyungang, Jiangsu) and passed through a 200-mesh sieve for experiments. Deionized water was obtained by a water purification system (electrical conductivity is 18.2 M Ω ·cm, Milli-Q Academic, Merck Millipore, Darmstadt, Germany). Analytical reagents Ni(NO₃)₂·6H₂O (\geq 98.0%), urea (\geq 99.0%), sodium silicate nonahydrate (Na₂SiO₃·9H₂O, 19.3-22.8 wt% Na₂O, weight ratio of Na₂O/SiO₂ = 1.03±0.03), dehydrated methanol (\geq 99.5%), glycerol (\geq 99.0%), Na₂CO₃

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(99.8%) and potassium hydrogen phthalate [C₆H₄(COOK)(COOH), 99.5%] were purchased from

Xilong Chemical Factory Co., Ltd. (Shantou, Guangdong). Soybean oil [refined, molecular weight of 881.2 g/mol, acid value (AV) of 0.6 mg KOH/g] was bought from Jiali Cereal & Oil Co., Ltd. (Fangchenggang, Guangxi). Standard heptadecanoic acid methyl ester ($C_{17:0}$) and other methyl esters [palmitate ($C_{16:0}$), linolenate ($C_{16:1}$), stearate ($C_{18:0}$), oleate ($C_{18:1}$), linoleate ($C_{18:2}$) and linolenate ($C_{18:3}$)] (\geq 99.0%) were purchased from Sigma (Shanghai). Crude glycerol [94.7 wt% glycerol, 5.3 wt% unreacted oil, biodiesel and methanol; TOC (total organic carbon) of 32.7 mmol/g] was produced during soybean biodiesel production catalyzed by Na₂SiO₃@Ni/C during 1-4 catalyst cycles and distilled at 65 °C for 2 h by a rotary evaporator (RE-52AA, Shanghai Yancheng Instrument Co., Ltd.).

2.2. Catalyst preparation

Similar to previous work¹⁹, aqueous solution (500 mL) of Ni(NO₃)₂·6H₂O (145.5 g), solid urea (60 g) and bamboo powders (24 g) were added into a three-neck flask (1 L) with a water-cooled condenser. The flask was submerged in oil bath at 135 °C with vigorous mechanical stirring for 10 h for reaction to form Ni(OH)₂ by ammonium hydroxide caused by slow urea decomposition in hot water [CO(NH₂)₂ + H₂O \rightarrow NH₃↑ + CO₂↑ + NH₄OH; Ni(NO₃)₂ + NH₄OH \rightarrow Ni(OH)₂ ↓ + NH₄NO₃]. After filtered (pore size 1-3 µm) and washed with deionized water, solid product was dried at 105 °C and heated 2 h to reach 700 °C for 2 h calcination in a tubular furnace (SGL-1100, Shanghai Daheng Optics and Fine Mechanics Co., Ltd.) under nitrogen flowing (200 mL/min) to form Ni particles (Ni plays both roles as magnetic carrier and catalytic site for H₂ production) by dehydration and reduction [Ni(OH)₂ \rightarrow NiO + H₂O; NiO + C \rightarrow Ni + CO/CO₂↑] while the formed porous char is as

support to load Na₂SiO₃. Ni/C particles (20 g) were put into aqueous sodium silicate solution (150 mL containing 60 g Na₂SiO₃·9H₂O) in a flask (1 L) and stirred at 85 °C in oil bath to achieve a gel by evaporation. The dried gel was heated 2 h to reach 400 °C for 2 h calcination in the tubular furnace under nitrogen flowing (200 mL/min), and milled by the above ball-mill with ZrO₂ balls at spinning speed of 230 rpm for 12 h, and sieved through 200-mesh. The obtained catalyst (powders) was designated as Na₂SiO₃@Ni/C (containing 56.0 wt% Na₂SiO₃). Na₂SiO₃ catalyst was prepared by calcining Na₂SiO₃·9H₂O at 400 °C for 2 h, and then passed through 100-mesh sieve after ground by a mortar.

After biodiesel reaction in a sealed glass reactor, liquid products were decanted, catalyst remained in the reactor attracted by a magnet (NeFeB, Ø37 mm×H18 mm) was directly used for next runs without any treatment. After 5 cycles, the catalyst was washed by ethanol under magnetic stirring thoroughly, dried at 105 °C until consistent weight (denoted as deactivated Na₂SiO₃@Ni/C) for hydrothermal gasification, and recovery rate was calculated as:

Recovery rate (wt %) = (weight of deactivated $Na_2SiO_3@Ni/C$) / (weight of fresh $Na_2SiO_3@Ni/C \times 100\%$ (1)

After gasification, the deactivated Na₂SiO₃@Ni/C catalyst was separated by the magnet, washed by water, dried at 105 °C until consistent weight, and denoted as used deactivated Na₂SiO₃@Ni/C for characterization.

2.3. Catalyst characterization

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Ni/C, fresh, deactivated and used deactivated Na₂SiO₃@Ni/C catalysts were analyzed by X-ray diffraction (XRD; Rigaku Rotaflex RAD-C, Tokyo) using a CuKα radiation source. Their functional

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groups were detected by Fourier transform-infrared spectroscopy (FT-IR; Nicolet iS10, Thermo Fisher Scientific Co., Ltd., Waltham, MA) over the range from 400 to 4000 cm⁻¹ with a resolution of 0.4-4 cm⁻¹ using the standard KBr disk method. Magnetic properties of catalysts were measured by using a vibrating sample magnetometer (VSM; lakeshore7407, Lake Shore Cryotronics, Inc., Westerville, OH). Their morphologies were examined using a scanning electron microscope (SEM; Ouanta 200, FEI, Hillsboro, OR). Selected surface areas in samples were analyzed by energy-dispersive X-ray spectrometry (EDX; Quanta 200, Hillsboro, OR) to obtain semi-quantitative elemental compositions (C, O, Ni, Na and Si excluding H). Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES; Optima 5300 DV, PerkinElmer Inc., Waltham, MA) was used to analyze inorganic Ni, Na and Si compositions of catalysts after dissolved by HCl. Specific surface area and pore volume of samples were determined by Bruner Emmett and Teller (BET) method (Tristar II 3020, Micromeritics Instrument Co., Ltd., Northcross, GA). Temperature programmed desorption (TPD; Chemisorption analyzer, Quantachrome Instruments, Boynton Beach, FL) was applied to assess the basicity of catalysts. In TPD analysis, sample (about 50-100 mg) was degassed by heating to 400 °C (5 °C/min) and cooled to 50 °C exposed with He flowing (85 mL/min), and absorbed CO₂ by flushing pure CO₂ (85 mL/min) for 80 min. The sample was subsequently desorbed by heating to 400 °C (5 °C/min) and kept for 60-90 min under He flowing (85 mL/min). Four different volumes (0.5, 1, 1.5 and 2 mL) of standard CO₂ gas (10% CO₂ and 90% helium) were used to calibrate the basicity.

2.4. Biodiesel production and analysis

Biodiesel production was carried out in a 20 mL glass reactor (Ø25 mm×H55 mm). Refined

soybean oil (4.4-4.6 g), a relevant amount of dehydrated methanol and catalyst were mixed and stirred by a magnetic bar (15 mm length) in the glass that was sealed by a cover with silicon rubber washer (Fig. 1a) and immersed in oil bath at 55-75 °C for reaction. All the experiments were repeated at least two times, and the reported biodiesel yields were averaged data with standard deviation (σ) of 0.05-4.25 %.

After reaction, crude biodiesel at upper layer (Fig. 1b) was collected and filtered (pore size 0.22 μ m) for analysis by Gas Chromatography (GC; GC-2014, Shimadzu, Kyoto) with a capillary column of Rtx-Wax (30 mר0.25 mm×0.25 μ m) under analytical conditions of column temperature 220 °C, injector temperature 260 °C, detector temperature 280 °C, carrier gas (He) with flow rate 1 mL/min and split ratio 40/1. Biodiesel yield (weight calculated by GC peaks/actual weight of crude biodiesel ×100%, wt%) was determined by using heptadecanoic acid methyl ester (HDAM; C_{17:0}) as internal standard. The relative response factor of six standard methyl esters [palmitate (C_{16:0}), linolenate (C_{16:1}), stearate (C_{18:0}), oleate (C_{18:1}), linoleate (C_{18:2}) and linolenate (C_{18:3})] to that of HDAM was calibrated as 1.014, 1.023, 1.076, 1.038, 1.019 and 0.926 in previous work¹⁷.

2.5. Hydrothermal gasification of glycerol and analysis

Similar to previous work¹⁶, subcritical water gasification of glycerol was conducted in a Hastelloy (HC-276) autoclave (25 mL with 8.4 mL headspace, Parr Instrument Co., Moline, IL). The autoclave can reach temperature and pressure up to 500 °C and 34.5 MPa, respectively. In each experiment, water (15 g), glycerol (0.41-0.49 g) and a relevant amount of catalyst were added to the autoclave and sealed. Then, nitrogen (99.999% purity) was added and purged for 3 times to remove air, and an initial nitrogen pressure of 8.0 MPa was used to avoid water vaporization during

gasification. The autoclave was heated from room temperature (20 °C) and took 55 min to reach 350 °C and 21.5-22.0 MPa and kept for 5 min reaction time with magnetic stirring (250 rpm). The reactor was powered off and immediately cooled down to room temperature by an electric fan for 2 h. Gas volume (about 2.44-3.12 L) was measured using a wet gas meter (LMF-1, Shanghai A.K. Instruments Co., Ltd.), where water was saturated by NaHCO₃ to avoid absorption of CO₂. Gas was collected in a gas bag for GC analysis. The aqueous sample was collected and centrifuged for further analysis. Each experiment was repeated at least two times, and the reported data were averaged values.

Produced gas (H₂, CO₂, C₂H₆, C₂H₄ and C₂H₂) was analyzed by GC (7820A, Agilent, Palo Alto, CA) with a packed column Porapak N (3 ft × 1/8 in.) and a thermal conductivity detector (TCD). CH₄ and CO were analyzed by the same GC with a packed column Molecular Sieve 5A (6 ft × 1/8 in.) and a TCD. Helium and N₂ (99.999% purity) were used as carrier gas. Gas sample was calibrated with three different concentrations diluted with N₂ from a standard gas mixture (9.082% H₂, 6.063% CO, 6.013% CH₄, 6.029% CO₂, 0.100% C₂H₆, 0.106% C₂H₄ and 0.100% C₂H₂; vol%) (Yunnan Messer Co., Ltd., Kunming) (with R² of 0.9837 for H₂, 0.9906 for CO₂, 0.9967 for CH₄ and CO for 0.9970).

Mole of gas (n_i) was calculatd as:

$$n_i \text{ (mole)} = P_0 V_i / (RT)$$
(2)

Where n_i (mole) and V_i (m³) are mole and volume of H₂, CO, CH₄ and CO₂; P₀ (0.8 × 10⁵ Pa) is atmospheric pressure at altitude 1886.5 m in Kunming²⁴ (north latitude 25.00°, east longitude 102.39°) calculated by Barometric formula²⁵; R is gas constant (8.31 mol·K/Pa·m³) and T is gas temperature (298 K).

Gas composition was defined as:

Gas (mol%) = (mole of gas) / (total mole of H₂, CO₂, CH₄ and CO) \times 100% (3)

Where gas is for H_2 , CO_2 , CH_4 and CO, respectively (C_2 gases < 0.01%).

Gasification rate was defined as:

Gasification rate (mol%) = (carbon mole of CO₂, CH₄, CO and inorganic carbon) / (carbon mole of crude glycerol) \times 100% (4)

Inorganic carbon (IC) and TOC of aqueous products and crude glycerol were measured with a TOC analyzer (TOC-V_{CPN}, Shimadzu, Kyoto) using Na₂CO₃ and C₆H₄(COOK)(COOH) as standard IC (25, 50 and 100 ppm; $R^2 \ge 0.999$) and TOC (250, 500 and 1000 ppm; $R^2 \ge 0.999$) calibrants. Crude glycerol produced was determined with a high performance liquid chromatography (HPLC; LC-20A, Shimadzu) fitted with an HPX-87H column and a reflex index (RI) detector.

3. Results and discussion

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Biodiesel from soybean oil was produced in the glass reactor and its by-product glycerol was further gasified in the autoclave. Experimental setup and catalyst separation for biodiesel production with Na₂SiO₃@Ni/C catalyst are given in Fig. 1. Figs. 2 shows biodiesel yield versus variables according to single-factor experiments. Characteristic results of XRD, FT-IR, VSM, SEM, EDX, BET and CO₂-TPD for catalysts are presented in Figs. 3-8, respectively. Elemental compositions of catalysts by ICP-OES and EDX are listed in Table 1. Temperate and pressure profiles, and gas products from hydrothermal gasification of glycerol are illustrated in Figs. 9-11. Glycerol gasification rate, gas concentrations and carbon balance in hydrothermal gasification of glycerol are summarized in Tables 2 and 3. Deactivated catalyst after gasification is characterized with results given in Fig. 12.

3.1. Biodiesel production

Effects of variables [i.e., methanol/oil molar ratio (3/1-15/1), catalyst dosage (3-11 wt%) reaction temperature (55-75 °C), and reaction time (40-120 min)] on biodiesel yield from soybean oil were optimized according to single-factor experiments in the glass reactor (Fig. 1).

3.1.1. Methanol/oil molar ratio

In Fig. 2a, biodiesel yield was just 55.1% when theoretical methanol/oil molar ratio of 3/1 was used at 65 °C for 100 min with 7 wt% catalyst owing to the heterogeneous reaction conditions and insufficient methanol for transesterification caused by methanol evaporation and mixture.¹⁹ As methanol/oil molar ratio rose from 6/1 to 9/1, biodiesel yield reached the highest of 97.9% from 90.2%, and dropped gradually to 93.9% and 87.9% at methanol/oil ratio of 12/1 and 15/1. This might be due to the relative low concentration of catalyst in the reaction system caused by excess methanol. Methanol/oil molar ratio of 9/1 is selected as the best value for the next experiments.

3.1.2. Catalyst dosage

In Fig. 2b, catalyst increased from 1 to 9 wt% for biodiesel production under conditions of methanol/oil molar ratio of 9/1, reaction temperature of 65 °C and reaction time of 100 min. Biodiesel yield jumped sharply from 84.2% to 91.0% as catalyst rose from 1 to 3 wt%, and grew slightly to 94.9% at 5 wt% before reached the highest value of 97.9% at 7 wt% catalyst. Low amount of solid catalyst 1 wt% was insufficient for transesterification, and > 5 wt% catalyst was required for

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reaction. However, as catalyst increased further from 7% to 9 wt%, biodiesel yield declined slightly because of the difficult mixing of liquid reactants with high concentration of catalyst under magnetic stirring. Catalyst of 7 wt% with the highest yield of 97.9% is selected as the best value for the next optimization.

3.1.3. Reaction temperature

Temperature from 55 to 75 °C was optimized for biodiesel production under conditions of reaction time of 100 min, methanol/oil molar ratio of 9/1 and catalyst of 7 wt% (Fig. 2c). Biodiesel yield reached 92.6% at 55 °C due to long reaction time (100 min) for transesterification at low temperature. The yield increased slowly from 95.9% to the highest value of 97.9% as temperature grew from 60 to 65 °C, and gradually decreased to 96.3% and 94.3% at 70 and 75 °C. This is because that high temperature promoted reaction to reach higher biodiesel yield, but liquid methanol vaporized into gas phase at much higher temperature, and resulted in lower yield^{26, 27}. Therefore, in this work, the best temperature is chosen as 65 °C.

3.1.4. Reaction time

Effect of reaction time on transesterification was studied from 40 to 120 min under conditions of methanol/oil molar ratio of 9/1, catalyst of 7 wt% and reaction temperature of 65 °C (Fig. 2d). As time rose from 40 to 60 min, biodiesel yield increased from 85.7% to 93.7% sharply, and gradually grew to 96.5% at 80 min and the highest value of 97.9% at 100 min. There is no obvious rise (98.5% *vs.* 97.9%) when time rose further to 120 min. The best reaction time is chosen as 100 min.

Therefore, the best conditions are 9/1 methanol/oil molar ratio and 7 wt% catalyst at 65 °C for

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100 min with biodiesel yield of 97.9%.

3.1.5. Catalyst cycles

Recycle studies of Na₂SiO₃@Ni/C catalyst were carried out under the best conditions (i.e., 65 °C for 100 min, 9/1 methanol/oil molar ratio and 7 wt% catalyst) optimized by the above single-factor experiments. Magnetically separated catalyst was directly used for next runs without any treatment. Biodiesel yield decreased little for the first 3 cycles (97.9±0.60%, 98.1±0.345 % and 97.0±0.265 %), but the yield dropped to 93.1±0.575 % and 80.9±1.91 % at the fourth and fifth cycle. After 5 cycles, recovery rate of Na₂SiO₃@Ni/C was 85.6±2.97 wt%. The deactivation of catalyst might be caused by the leaching of active component (Na₂SiO₃) in methanol¹⁹ that also catalyzed transesterification. Previous work¹⁴ showed that calcined sodium silicate (Na₂SiO₃) after washed for 5 times with methanol still had high activity with biodiesel yield > 90% from soybean oil at 60 °C for 120 min, but the corresponding recovered methanol with leached active component had a lower biodiesel yield (< 65%). It also confirmed that the main transesterification reaction started on the surface of Na₂SiO₃.

In this work, magnetic stirring was applied in biodiesel experiments. Although there were numerous Na₂SiO₃@Ni/C particles attached on the magnetic bar's surface before and after reaction (Fig. 1), but the particles were dispersed well during stirring at about 750 rpm by centrifugal force to promote biodiesel production. For industry application, mechanical stirring can be used with electromagnet recovered system. On the other hands, electromagnetic reactor could be designed to have better mixing for reactants and catalyst. Characterization of catalysts before and after reaction was studied further in the next section.

The crystalline phases of Ni and Na₂SiO₃ in the Ni/C particles and catalysts were determined by XRD analysis (Fig. 3) as compared with the cards from Joint Committee on Powder Diffraction Standards (JCPDS: 04-0850, 16-0818). Ni/C particles have well-crystallized Ni structures with characteristic and symmetric reflections, but there is no peak from the active carbon because of its undefined structure (Fig. 3a). Fresh Na₂SiO₃@Ni/C has well-crystallized structures of Na₂SiO₃ and Ni (Fig. 3b). But, the characteristic reflections from Na₂SiO₃ almost disappeared after 5 cycles (Fig. 3c), proving its leaching into methanol.

3.2.2. FT-IR

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In Fig. 4, absorptions at 3424 and 1637 cm⁻¹ are observed for all samples due to the stretching and bending vibrations of –OH groups²⁸ from physically adsorbed water, and their intensity could be reduced by heat treatment.²⁹ Ni/C particles have no other obvious absorption except those for –OH (Fig. 4a). This means that carbon support in Ni/C particles (12.7%, Table 1) was almost carbonized completely, and NiO was reduced by carbon completely because of no absorption found at 430 cm⁻¹ for Ni-O.³⁰ After loading Na₂SiO₃, Na₂SiO₃@Ni/C catalyst has many obvious absorptions at 1025, 960, 889 and 710 cm⁻¹ from Si-O bending, Si-O-Na, Si-O-H and Si-O-Si stretching, respectively.¹⁴ The bands from 745 to 467 cm⁻¹ are contributed from symmetric stretching and bending vibrations of Si-O-Si bond³¹. Furthermore, an absorption at 1462 cm⁻¹ from $CO_3^{2^2}$ groups was possibly from the reaction of CO₂ in air with Na₂SiO₃ during sample

preparation.²⁹ However, absorptions for deactivated Na₂SiO₃@Ni/C catalyst became weak (Fig. 4c), because Na₂SiO₃ was leached after 5 cycles, which was also confirmed by XRD analysis (Fig. 3a).

3.2.3. VSM

Hysteresis loops measurement gives specific magnetic saturation values (Ms). Ms of fresh Na₂SiO₃@Ni/C (15.7 Am²/kg) is lower than that of Ni/C particles (41.8 Am²/kg) after covered with 130 wt% Na₂SiO₃ (Fig. 5a and b) but with much stronger magnetism than that of Na₂SiO₃/Fe₃O₄ catalyst prepared in previous work (15.7 *vs.* 0.5 Am²/kg)¹⁸. So, the prepared catalyst is easily separated by a magnet for recycles (Fig. 1b). After 5 cycles, its Ms slightly decreased to 15.3 Am²/kg (Fig. 5c *vs.* b). The magnetism of Na₂SiO₃@Ni/C catalyst is strong and stable.

3.2.4. SEM, EDX and ICP-OES

In Fig. 6A-a, Ni/C particles have bulk structure of fibrous shape (< 100 μ m) similar to that of original bamboo. At larger magnification, numerous spherical Ni particles (0.3-1 μ m) are found, demonstrating they were well-precipitated on the surface of carbon support. EDX spectrum (Fig. 6A-b) shows that they were mainly composed of (wt%) 96.4 Ni and 2.60 C with minor of O (0.70) and trace of Na (0.10) and Si (0.20) (Na and Si were apparently from inorganics in bamboo as ash). EDX data were semi-quantitative for the selected surface areas.^{32, 33} ICP is for the whole bulk sample analysis, and it revealed much lower Ni content (87.3 wt%) for Ni/C particles (Table 1) because Ni(OH)₂ was precipitated and concentrated on the surface of bamboo powders. Ni/C particles contained 12.7 wt% (100% - Ni%) bamboo char for subsequent loading base Na₂SiO₃.

Na2SiO3@Ni/C catalyst doesn't have uniformed particle size in bulk (< 50 µm) with small

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particles agglomerated by Na₂SiO₃ gel (Fig. 6B-a). It was composed of (wt%) C (5.00), O (18.1), Na (30.7), Si (14.3) and Ni (31.9) analyzed by EDX in a selected area (Fig. 6B-b). Na/Si molar ratio of Na₂SiO₃@Ni/C by EDX is 2.0/0.8 (higher than 2/1 for Na₂SiO₃ and for ICP analysis in Table 1). This is because Na₂SiO₃ solution was hydrolyzed to NaOH and H₂SiO₃ [Na₂SiO₃ + H₂O \rightarrow NaOH + H₂SiO₃], more of H₂SiO₃ or SiO₂ remained on the core of Na₂SiO₃@Ni/C catalyst after dry and calcination.

After 5 cycles, the morphology of Na₂SiO₃@Ni/C catalyst changed little (Fig. 6C-a), but its C increased to 28.5 wt% from 5.00 wt% by EDX analysis because residual glycerol, biodiesel and oil deposited on the surface of catalyst. ICP analysis shows that its Ni also rose to 75.6 wt% from 38.4 wt%, and Na and Si decreased to 8.21 and 5.09 wt% from 20.6 and 12.5 wt% (Table 1) because Na₂SiO₃ was leached, that was also confirmed by XRD pattern in Fig. 3c.

3.2.5. BET

Nitrogen adsorption-desorption isotherm (Fig. 7a) shows that Ni/C particles exhibited a clear hysteresis loop with high adsorption capacity (76.1 m²/g specific surface area and 0.101 cm³/g pore volume). The high specific surface area was caused by pyrolysis of bamboo and reduction of NiO with carbon at 700 °C to form numerous micropores in biochar by vaporization of volatiles and gases. After loading Na₂SiO₃, the specific surface area and pore volume of Na₂SiO₃@Ni/C were significantly declined to 8.24 m²/g and 0.047 cm³/g because pores were filled by Na₂SiO₃ as compared with specific surface area of 2.42 m²/g for calcined Na₂SiO₃. After 5 cycles, they increased to 14.3 m²/g and 0.052 cm³/g because Na₂SiO₃ was leached.

3.2.6. CO₂-TPD

In Fig. 8, Ni/C particles have no obvious CO_2 desorption with a very weak basicity of 0.01 mmol/g. Na₂SiO₃@Ni/C catalyst has two peaks at 260-300 °C and 360-400 °C for CO₂ desorption with total basicity of 3.18 mmol/g. But, the basicity reduced significantly to 0.29 mmol/g after 5 cycles because some Na₂SiO₃ was leached and the active sites were covered by glycerol, oil and soap.

3.3. Hydrothermal gasification

After 5 cycles, deactivated Na₂SiO₃@Ni/C was ethanol-washed and selected as catalyst for H₂ production in the autoclave from biodiesel byproduct glycerol (both pure and crude glycerol were used as feedstocks in the experiments) at 350 °C under 21.5-22.0 MPa for 5 min (heating time from 20 to 350 °C need 55 min under 8.0 MPa initial N₂ pressure. Fig. 9 shows that reaction temperature and pressure rapidly rises to 340 °C and 21.8 MPa at 31 min from 25 °C and 8 MPa, and gradually increases further to 350 °C and 22.0 MPa at 55 min for 5 min in a typical run.

3.3.1. Gasification of pure glycerol

In Fig 10a, a blank experiment was conducted to gasify pure glycerol (total carbon of 15 mmol) without catalyst, and results showed very low gas yield produced (0.102 mmol H₂, 0.00352 mmol CO, 0.0702 mmol CH₄, and 0.468 mmol CO₂). However, when 10 wt% deactivated Na₂SiO₃@Ni/C catalyst was added, H₂, CO, CH₄ and CO₂ sharply jumped to 5.59, 0.989, 1.60 and 4.08 mmol, respectively. As catalyst rose to 20 and 30 wt%, H₂ production increased further to 7.17 and 11.7 mmol, CO₂ to 5.43 and 6.62 mmol, but slight rise for CH₄ (2.13 and 2.28 mmol). These results indicated that hydrothermal gasification was efficiently promoted by Na₂SiO₃@Ni/C catalyst that

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had a good activity for C-C scission followed by water-gas shift reaction ($C_3H_8O_3 + H_2O \rightarrow CO_2 + H_2$).^{25, 34} As catalyst rose to 40 and 50 wt%, H₂ grew slightly to 12.1 and 12.4 mmol, CO₂ to 6.80 and 7.72 mmol, but CH₄ increased obviously to 6.80 to 7.72 mmol, and CO reached a peak of 0.989 mmol and decreased to 0.0364 mmol because of methanation reaction (CO + H₂ \rightarrow CH₄ + H₂O³⁵). So, 30 wt% deactivated Na₂SiO₃@Ni/C catalyst was fixed for hydrothermal gasification to study the effect of addition of calcined Na₂SiO₃.

Low H₂ concentration (56.2 mol%) was obtained with relative high concentrations of CO₂ (31.8 mol%) and CH₄ (10.9 mol%) with 30 wt% deactivated Na₂SiO₃@Ni/C (Table 2), calcined Na₂SiO₃ (20, 40, 60, 80 and 100 wt%) was added for glycerol hydrothermal gasification to promote H₂ production (Fig. 10b). H₂ production only increased slightly from 11.7 to 12.1 and 12.9 mmol, but CO₂ decreased from 6.62 to 6.31 and 1.60 mmol as Na₂SiO₃ rose from 0 to 20 and 100 wt%. Na₂SiO₃ had little promotion for H₂ production but could absorb CO₂ by dissolving it into the basic hydrothermal solution to form Na₂CO₃ (CO₂ + H₂O + Na₂SiO₃ \rightarrow Na₂CO₃ + H₂SiO₃). The CO₂ absorption was also confirmed by IC in aqueous-phase increasing from 9.50 to 63.5 mol% as Na₂SiO₃ rising from 0 to 100 wt%. At the same time, carbon in gas-phase decreased from 60.8 to 17.1 mol% with low CO₂ concentration (11.8 mol%) and high H₂ concentration (83.4 mol%) (Table 2). Glycerol gasification rate also rose to 80.6 mol% from 70.3 mol% without adding Na₂SiO₃. This is because Na₂CO₃ could inhibit glycerol carbonizing³⁶ and promote glycerol gasification similar to the case of hydrothermal gasification and liquefaction of biomass.³⁷ Total carbon in gas and aqueous-phases is higher (99.0 vs. 93.5 mol%) but organic carbon in aqueous-phase is lower (18.4 vs. 23.2 mol%) with addition of 100 wt% Na₂SiO₃ as compared without Na₂SiO₃, suggesting Na₂SiO₃ promoted gasification and inhibited char formation (Table 3).

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3.3.2. Gasification of crude glycerol

Crude glycerol (total carbon 15.0 mmol) from the above biodiesel production was hydrothermally gasified with deactivated Na₂SiO₃@Ni/C (30 wt%) and Na₂SiO₃ (100 wt%), hydrogen rich gas (12.8 H₂, 0.0214 CO, 0.859 CH₄ and 1.80 CO₂, mmol) was produced (Fig. 11). There were no significant changes in gasification rate and gas composition between crude glycerol (80.1% with 82.7 H₂, 0.14 CO, 5.56 CH₄ and 11.6 CO₂, mol%) and pure glycerol (80.6% with 83.4 H₂, 0.11 CO, 4.72 CH₄ and 11.8 CO₂, mol%) (Tables 1 and 2). This proves that by-product crude glycerol is suitable for hydrothermal hydrogen production.

3.4. Stabilization of Ni/C after gasification

After gasification, XRD pattern shows that the used deactivated Na₂SiO₃@Ni/C after dried at 65 °C still had well-crystallized structures of Ni but without characteristic peaks of Na₂SiO₃ because the crystal structure of Ni is stable and Na₂SiO₃ dissolved in water after hydrothermal gasification (Fig. 12a). IR spectrum also proves the disappearance of absorptions from Na₂SiO₃ (Fig. 12b). After gasification, its Ms increased to 28.7 Am²/kg (Fig. 12c) from 15.3 (Fig. 5c), lower than that for Ni/C (41.8 Am²/kg). Its specific surface area and pore volume also rose from 14.3 m²/g and 0.052 cm³/g (Fig. 7c) to 63.7 m²/g and 0.086 cm³/g (Fig. 12d), slightly lower than the values for Ni/C particles (76.1 m²/g and 0.101 cm³/g). These results confirmed that the Ni/C structure is relative stable after biodiesel production and gasification.

The deactivated Na₂SiO₃@Ni/C after gasification was recycled for hydrothermal gasification of glycerol at the same condition [Experimental conditions: 0.46 g (total carbon 15 mmol) pure glycerol, 15 g H₂O, 30 wt% used deactivated Na₂SiO₃@Ni/C, 100 wt% Na₂SiO₃, 55 min heating

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time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, 22.0 MPa highest reaction pressure]. Slight higher H₂ (13.6±0.219 *vs.* 12.9±0.178 mmol) and CO₂ (1.79±0.169 *vs.* 1.60±0.257 mmol), and little change in CO (0.017±0.00436 *vs.* 0.018±0.00169 mmol) and CH₄ (0.665±0.129 *vs.* 0.661±0.106 mmol) were found as compared with that for the first used deactivated Na₂SiO₃@Ni/C. This indicates that the catalyst is still active for H₂ production.

4. Conclusions

Magnetic Na₂SiO₃@Ni/C catalyst was successfully synthesized for biodiesel and H₂ co-production from soybean oil. The catalyst was active to produce biodiesel with maximum yield of 98.1% at 65 °C and was easily separated by a magnet for 4 cycles (biodiesel yield > 93%). After 5 cycles, the deactivated catalyst successfully catalyzed gasification of biodiesel by-product (crude glycerol) with 80.6 mol% gasification rate and 83.4 mol% H₂ concentration in compressed water at 350 °C. After gasification, it is found that the structure of Ni/C changed slightly and can be re-loaded Na₂SiO₃ for both biodiesel and H₂ production from soybean oil without pollutants produced.

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References

1 M. Z. Jacobson, Review of solutions to global warming, air pollution, and energy security. *Energy Environ. Sci.*, 2009, **2**, 148-173.

2 Y. Zhang, L. Jin, K. Sterling, Z. Luo, T. Jiang, R. Miao, C. Guild and S. L. Suib, Potassium modified layered $Ln_{(2)}O_{(2)}CO_{(3)}$ (Ln: La, Nd, Sm, Eu) materials: efficient and stable heterogeneous catalysts for biofuel production. *Green Chem.*, 2015, **17**, 3600-3608.

3 M. Guo, J. Littlewood, J. Joyce and R. Murphy, The environmental profile of bioethanol produced from current and potential future poplar feedstocks in the EU. *Green Chem.*, 2014, **16**, 4680-4695.

4 D. Kralisch, C. Staffel, D. Ott, S. Bensaid, G. Saracco, P. Bellantoni and P. Loeb, Process design accompanying life cycle management and risk analysis as a decision support tool for sustainable biodiesel production. *Green Chem.*, 2013, **15**, 463-477.

5 S. E. Evans, J. Z. Staniforth, R. J. Darton and R. M. Ormerod, A nickel doped perovskite catalyst for reforming methane rich biogas with minimal carbon deposition. *Green Chem.*, 2014, **16**, 4587-4594.

6 E. Lois, Definition of biodiesel. Fuel, 2007, 86, 1212-1213.

7 Q. Kwok, B. Acheson, R. Turcotte, A. Janès, G. Marlair, Thermal hazards related to the use of potassium and sodium methoxides in the biodiesel industry. *J. Therm. Anal. Calorim.*, 2013, **111**, 507-515.

8 A. Singhabhandhu, T. Tezuka, A perspective on incorporation of glycerin purification process in biodiesel plants using waste cooking oil as feedstock, *Energy*, 2010, **35**, 2493-2504.

9 J. J. Creasey, C. M. A. Parlett, J. C. Manayil, M. A. Isaacs, K. Wilson and A. F. Lee, Facile route to conformal hydrotalcite coatings over complex architectures: a hierarchically ordered nanoporous base catalyst for FAME production. *Green Chem.*, 2015, **17**, 2398-2405.

10 Q. Liu, B. Wang, C. Wang, Z. Tian, W. Qu, H. Ma and R. Xu, Basicities and transesterification activities of Zn-Al hydrotalcites-derived solid bases. *Green Chem.*, 2014, **16**, 2604-2613.

11 J. M. Montero, P. Gai, K. Wilson and A. F. Lee, Structure-sensitive biodiesel synthesis over MgO nanocrystals. *Green Chem.*, 2009, **11**, 265-268.

12 R. S. Watkins, A. F. Lee and K. Wilson, Li-CaO catalysed tri-glyceride transesterification for biodiesel applications. *Green Chem.*, 2004, **6**, 335-340.

13 M. Kim, C. DiMaggio, S. Yan, S. O. Salley and K. Y. Simon Ng, The effect of support material on the transesterification activity of CaO-La₂O₃ and CaO-CeO₂ supported catalysts, *Green Chem.*, 2011,

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13, 334-339.

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14 F. Guo, N. N. Wei, Z. L. Xiu and Z. Fang, Transesterification mechanism of soybean oil to biodiesel catalyzed by calcined sodium silicate. *Fuel*, 2012, **93**, 468-472.

15 E. Akbar, N. Binitha, Z. Yaakob, S. K. Kamarudin and J. Salimon, Preparation of Na doped SiO₂ solid catalysts by the sol-gel method for the production of biodiesel from jatropha oil. *Green Chem.*, 2009, **11**, 1862-1866.

16 Y. D. Long, Z. Fang, T. C. Su and Q. Yang, Co-production of biodiesel and hydrogen from rapeseed and *Jatropha* oils with sodium silicate and Ni catalysts. *Appl. Energy*, 2014, **113**, 1819-1825.

17 B. J. Xue, J. Luo, F. Zhang and Z. Fang, Biodiesel production from soybean and *Jatropha* oils by magnetic CaFe₂O₄-Ca₂Fe₂O₅-based catalyst. *Energy*, 2014, **68**, 584-591.

18 P. M. Guo, F. H. Huang, M. M. Zheng, W. L. Li and Q. D. Huang, Magnetic solid base catalysts for the production of biodiesel. *J. Am. Oil Chem. Soc.*, 2012, **89**, 925-933.

19 F. Zhang, Z. Fang and Y. T. Wang, Biodiesel production directly from oils with high acid value by magnetic Na₂SiO₃@Fe₃O₄/C catalyst and ultrasound. *Fuel*, 2015, **150**, 370-377.

20 N. E.Rajeevan, V. Kumar, R. Kumar, R. Kumar and S. D. Kaushik. Neutron diffraction studies of magnetic ordering in Ni-doped LaCoO₃. *J. Magn. Magn. Mater.*, 2015, **393**, 394-398.

21 Y. L. Zhang, Z. Shen, X. F. Zhou, M. Zhang and F. M. Jin, Solvent isotope effect and mechanism for the production of hydrogen and lactic acid from glycerol under hydrothermal alkaline conditions. *Green Chem.*, 2012, **14**, 3285-3288.

22 D. Hernandez, D. López and J. J. Fernández. Catalytic performance of Ni/La₂O₃ materials in glycerol valorization for acetol and syngas production. *Appl. Catal. A*, 2015, **499**, 13-18.

23 T. Numaguchi, K. Shoji, S. Yoshida, Hydrogen effect on α -A1₂O₃ supported Ni catalyst for steam methane reforming reaction. *Appl. Catal. A*, 1995, **133**, 241-262.

24 X. Qian, Y. Q. Yao, J. R. Li, J. Yin, Y. J. Zhang, L. Y. Liu, H. S. Wang, Y. H. Zhou, L. Li, X. L. You and J. L. Ma, Distribution of atmospheric water vapor content over china. *Chinese Astron. Astr.*, 2013, **37**, 212-229.

25 N. Sissenwine, M. Dubin and S. Teweles. U.S. Standard Atmosphere. U.S. Government Printing Office, Washington, D.C., 1976.

26 F. Zhang, Z. Fang and Y. T. Wang, Biodiesel production direct from high acid value oil with a

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novel magnetic carbonaceous acid. Appl. Energy, 2015, 155, 637-647.

27 X. Deng, Z. Fang, Y. H. Liu and C. L. Yu, Production of biodiesel from *Jatropha* oil catalyzed by nanosized solid basic catalyst. *Energy*, 2011, **36**, 777-784.

28 A. P. Rao, A. V. Rao and G. M. Pajonk. Hydrophobic and physical properties of the ambient pressure dried silica aerogels with sodium silicate precursor using various surface modification agents. *Appl. Surf. Sci.*, 2007, **253**, 6032-6040.

29 S. S. Kouassi, M. T. Tognonvi, J. Soro and S. Rossignol. Consolidation mechanism of materials obtained from sodium silicate solution and silica-based aggregates. *J. Non-Cryst. Solids*, 2011, **357**, 3013-3021.

30 D. Varshney and S. Dwivedi. Synthesis, structural, Raman spectroscopic and paramagnetic properties of Sn doped NiO nanoparticles. *Superlattices Microstruct.*, 2015, **86**, 430-437.

31 Y. Chen, G. Yu, F. Li and J. Wei. Structure and photoluminescence of amorphous silicate composites containing ZnO particles synthesized from layered sodium silicate. *J. Non-Cryst. Solids*, 2012, **358**, 1772-1777.

32 M. C. Zuluaga, A. Alonso-Olazabal, X. Murelaga and L. A. Ortega. A comparison of scanning electron microscopy energy dispersive X-ray (SEM/EDX) and inductively coupled plasma optical emission spectrometry (ICP-OES) for provenance inferences of grog-tempered Bronze Age pottery. *Microchem J.*, 2011, **99**, 443-448.

33 L. Wang, T. Li, B. M. Güell, T. Løvås and J. Sandquist. An SEM-EDX study of forest residue chars produced at high temperatures and high heating rate. *Energy Procedia*, 2015, **75**, 226-231.

34 Z. Fang, T. Minowa, C. Fang, R. L. Smith Jr., H. Inomata and J. A. Kozinski, Catalytic hydrothermal gasification of cellulose and glucose. *Int. J. Hydrogen Energy*, 2008, **33**, 981-990.

35 N. Shimoda, D. Shoji, K. Tani, M. Fujiwara, K. Urasaki, R. Kikuchi and S. Satokawa, Role of trace chlorine in Ni/TiO₂ catalyst for CO selective methanation in reformate gas. *Appl. Catal. B*, 2015, **174-175**, 486-495.

36 Z. Fang and C. Fang, Complete dissolution and hydrolysis of wood in hot water. *AIChE J.*, 2008, **54**, 2751-2758.

37 Z. Fang, T. Minowa, R. L. Smith Jr., T. Ogi and J. A. Kozinski, Liquefaction and gasification of cellulose with Na₂CO₃ and Ni in subcritical water at 350 °C. *Ind. Eng. Chem. Res.*, 2004, **43**, 2454-2463.

Figure Captions:

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Fig. 1 Biodiesel production and catalyst separation in a glass reactor: (a) before and (b) after transesterification.

Fig. 2 Effects of variables on the soybean biodiesel production with $Na_2SiO_3@Ni/C$ catalyst: (a) methanol/oil molar ratio, (b) catalyst dosage, (c) reaction temperature, and (d) reaction time.

Fig. 3 XRD patterns of (a) Ni/C particles, (b) fresh and (c) deactivated Na₂SiO₃@Ni/C catalysts.

Fig. 4 FT-IR spectra of (a) Ni/C particles, (b) fresh and (c) deactivated Na₂SiO₃@Ni/C catalysts.

Fig. 5 Hysteresis loops of (a) Ni/C particles, (b) fresh and (c) deactivated Na₂SiO₃@Ni/C catalysts.

Fig. 6 (a) SEM images and (b) EDX spectra of (A) Ni/C particles, (B) fresh and (C) deactivated Na₂SiO₃@Ni/C catalysts (H is undetectable by EDX, and excluded in elemental composition).

Fig. 7 Nitrogen adsorption/desorption isotherms of (a) Ni/C particles, (b) fresh and (c) deactivated Na₂SiO₃@Ni/C catalysts.

Fig. 8 CO₂-TPD profiles of (a) Ni/C particles, (b) fresh and (c) deactivated Na₂SiO₃@Ni/C catalysts.

Fig. 9 Temperature and pressure versus time (0-60 min) in hydrothermal gasification of crude glycerol with deactivated Na₂SiO₃@Ni/C catalyst

[Experimental conditions: 0.46 g (total carbon 15 mmol) crude glycerol, 15 g H_2O , 55 min heating time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, 22.0 MPa highest reaction pressure.]

Fig. 10 Gas products from hydrothermal gasification of pure glycerol with various dosage of (a) deactivated $Na_2SiO_3@Ni/C$ catalyst, and (b) Na_2SiO_3 with 30 wt% deactivated $Na_2SiO_3@Ni/C$ catalyst.

[Experimental conditions: 0.46 g (total carbon 15 mmol) glycerol, 15 g H_2O , 55 min heating time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, 21.5-22.0 MPa highest reaction pressure.]

Fig. 11 Gas products from hydrothermal gasification of glycerol with 30 wt% deactivated Na_2SiO_3 @Ni/C and 100 wt% Na_2SiO_3 .

[Experimental conditions: 0.46 g (total carbon 15 mmol) glycerol, 15 g H_2O , 55 min heating time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, 22.0 MPa highest reaction pressure.]

Fig. 12 Characterization of used deactivated Na₂SiO₃@Ni/C after gasification: (a) XRD, (b) FT-IR, (c) VSM, and (d) nitrogen adsorption/desorption isotherms.

Table Captions:

Table 1 Elemental compositions (C, O, Na, Si and Ni) of Ni/C, fresh and deactivated Na₂SiO₃@Ni/C catalysts.

Table 2 Gas products from hydrothermal gasification of glycerol with deactivated $Na_2SiO_3@Ni/C$ and Na_2SiO_3 catalysts.

Table 3 Carbon balance and glycerol gasification rate in hydrothermal gasification of glycerol with deactivated Na₂SiO₃@Ni/C and Na₂SiO₃ catalysts.

Wt%	Ni/C	Fresh Na ₂ SiO ₃ @Ni/C	Deactivated Na ₂ SiO ₃ @Ni/C
C^{a}	2.60	5.00	28.5
O^a	0.70	18.1	20.9
Na ^a	0.10	30.7	18.7
Si ^a	0.20	14.3	11.7
Ni ^a	96.4	31.9	20.2
Na/Si mole ratio ^a	-	2.0/0.8	2.0/1.0
Na ^b	0.06	20.6	8.21
Si ^b	0.15	12.5	5.09
Ni ^b	87.3	38.4	75.6
Char	12.7	-	-
Na/Si mole ratio ^b	-	2.0/1.0	2.0/1.0

Table 1 Elemental compositions (C, O, Na, Si and Ni) of Ni/C, fresh and deactivated Na₂SiO₃@Ni/C catalysts.

^a analyzed by EDX, H is undetectable.

^b analyzed by ICP-OES, for Ni/C, char (%) was calculated by (100% - Ni%) (Na and Si were from char as inorganic ash).

Gas-phase composition (mol%)	Deactivated Na ₂ SiO ₃ @Ni/C ^a	Deactivated Na ₂ SiO ₃ @Ni/C and Na ₂ SiO ₃ ^a	Deactivated Na ₂ SiO ₃ @Ni/C and Na ₂ SiO ₃ ^b			
H_2	56.2±2.50	83.4±1.17	82.7±2.11			
СО	1.10±0.85	0.11 ± 0.01	$0.14{\pm}0.02$			
CH_4	10.9±0.05	4.72±0.70	5.56±0.52			
CO_2	31.8±2.97	11.8±1.69	11.6±0.88			
$C_2(C_2H_2, C_2H_4, C_2H_6)$	< 0.01	< 0.01	< 0.01			

Table 2 Gas products from hydrothermal gasification of glycerol with deactivated Na₂SiO₃@Ni/C and Na₂SiO₃ catalysts.

Experimental conditions: 0.46 g glycerol (total carbon 15 mmol), 30 wt% deactivated Na₂SiO₃@Ni/C after 5 cycles, 100 wt% Na₂SiO₃, 15 g H₂O, 55 min heating time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, and 22.0 MPa highest pressure.

^a with pure glycerol.

^b with crude glycerol.

	Deactivated Na ₂ SiO ₃ @Ni/C ^a	Deactivated Na ₂ SiO ₃ @Ni/C and Na ₂ SiO ₃ ^a	Deactivated Na ₂ SiO ₃ @Ni/C and Na ₂ SiO ₃ ^b
Carbon in aqueous-phase (mol%)	32.7	81.9	80.8
Inorganic carbon	9.50±0.57	63.5±2.50	62.3±2.05
Organic carbon	23.2±1.03	18.4±0.95	18.5±0.87
Carbon in gas-phase (mol%)	60.8	17.1	17.8
Total (mol%)	93.5	99.0	98.6
Glycerol gasification rate (mol %)	70.3	80.6	80.1

Table 3 Carbon balance and glycerol gasification rate in hydrothermal gasification of glycerol with deactivated Na₂SiO₃@Ni/C and Na₂SiO₃ catalysts.

Experimental conditions: 0.46 g glycerol (total carbon 15 mmol), 30 wt% deactivated Na₂SiO₃@Ni/C after 5 cycles, 100 wt% Na₂SiO₃, 15 g H₂O, 55 min heating time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, and 22.0 MPa highest pressure.

^a with pure glycerol.

^b with crude glycerol.



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Fig. 5 Hysteresis loops of (a) Ni/C particles, (b) fresh and (c) deactivated Na₂SiO₃@Ni/C catalysts.



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Fig. 7 Nitrogen adsorption/desorption isotherms of (a) Ni/C particles, (b) fresh and (c) deactivated $Na_2SiO_3@Ni/C$ catalysts.



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Fig. 9 Temperature and pressure versus time (0-60 min) in hydrothermal gasification of crude glycerol with deactivated Na₂SiO₃@Ni/C catalyst

[Experimental conditions: 0.46 g (total carbon 15 mmol) crude glycerol, 15 g H_2O , 55 min heating time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, 22.0 MPa highest reaction pressure.]

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Fig. 10 Gas products from hydrothermal gasification of pure glycerol with various dosage of (a) deactivated Na₂SiO₃@Ni/C catalyst, and (b) Na₂SiO₃ with 30 wt% deactivated Na₂SiO₃@Ni/C catalyst.

[Experimental conditions: 0.46 g (total carbon 15 mmol) glycerol, 15 g H₂O, 55 min heating time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, 21.5-22.0 MPa highest reaction pressure.]

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Fig. 11 Gas products from hydrothermal gasification of glycerol with 30 wt% deactivated Na₂SiO₃@Ni/C and 100 wt% Na₂SiO₃.

[Experimental conditions: 0.46 g (total carbon 15 mmol) glycerol, 15 g H_2O , 55 min heating time from 20 to 350 °C and 5 min holding time, 8.0 MPa initial pressure, 22.0 MPa highest reaction pressure.]

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Fig. 12 Characterization of used deactivated Na₂SiO₃@Ni/C after gasification: (a) XRD, (b) FT-IR, (c) VSM, and (d) nitrogen adsorption/desorption isotherms.

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Production of Biodiesel and Hydrogen from Plant Oil Catalyzed by Magnetic Carbon-Supported Nickel and Sodium Silicate

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Production of biodiesel from plant oil catalyzed by magnetic $Na_2SiO_3@Ni/C$ catalyst, and H_2 by the deactivated catalyst from by-product glycerol.