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Catalytic Behaviors of Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ during the Hydrodeoxygenation of Palm Oil

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Abstract

The deactivation and regeneration behaviors of the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts in the hydrodeoxygenation (HDO) of palm oil were investigated at 573 K and 5 MPa in a trickle bed reactor. The catalysts were prereduced at 773 K for 3 h before the HDO experiments. The catalysts exhibited good catalytic activity (>90% yield) and remained stable for 100 h on-stream. Nevertheless, after 150 h on-stream, the product yield gradually decreased from 92.2 to 76.2% over the Ni catalyst and dramatically declined from 88.6% to ca. 56.6% over the Co catalyst. The combined decarbonylation and/or decarboxylation (DCOₓ) reactions were dominant over the HDO reaction when the reaction was catalyzed by the Ni catalyst. Meanwhile, the contribution of DCOₓ and HDO reactions were nearly comparable over the Co catalyst. The XRD and XANES analyses confirmed the partial formation of metallic nickel or cobalt after prereduction, and the further in situ reduction during the HDO experiments, suggesting the coexistence of the metal and metal oxides on the catalyst surfaces. The XRD and TEM analyses revealed some sintering of the nickel and cobalt particles during the time course of reaction. Based on the TPO analysis, the carbon deposition rate on cobalt catalyst was faster than that on nickel catalyst and would be a major reason for the catalyst deactivation, and the sintering was a minor one. Additionally, the regeneration under air at 773 K followed by reduction in H₂ at 773 K can completely restore the catalytic activity.

Keyword: Deactivation, Regeneration, Hydrodeoxygenation, Green diesel, Palm oil

1. Introduction

The development of liquid transport fuels from renewable bioresources is an important key to future energy sources due to the depletion of petroleum fuels. Biomass
feedstocks can be divided into three categories: carbohydrates (i.e., starch and sugar), lignocellulose materials, and animal fats/vegetable oils composed of triglycerides and free fatty acids ranging from $C_{10}-C_{20}$ \(^1\). Triglycerides have been used as important renewable feedstocks for the production of liquid biofuels because of their low degree of functionalization and simple structure compared with cellulosic biomass \(^2, \, 3\). In particular, palm oil contains primarily $C_{16}$ and $C_{18}$ fatty acids, making it a promising feedstock for green diesel and biodiesel production. The conventional technology for conversion of animal fats/vegetable oils into the diesel-like fuels is a transesterification of triglycerides and methanol that produces the fatty acid methyl esters (FAMEs), which is called biodiesel \(^1, \, 4\). However, some disadvantages of biodiesel compared with petroleum diesel are the $C=\text{C}$ bonds and $C=\text{O}$ bonds that remain in the molecules of FAMEs, which leads to low thermal and oxidation stability because of its high oxygen content, high viscosity, and low heating value \(^5, \, 6\).

Another effective way to use triglycerides for the production of diesel fuel is through hydrodeoxygenation, which removes oxygen functionalities from the triglycerides/free fatty acids at 573–623 K with $\text{H}_2$ at 5–15 MPa in the presence of heterogeneous catalysts \(^7, \, 8\). Green diesel, which provides better diesel properties, such as high cetane number, zero oxygen content \(^9\), and high thermal and oxidation stability \(^10\), can be produced by the catalytic deoxygenation of triglycerides through 3 major reaction pathways, including decarbonylation, decarboxylation, and hydrodeoxygenation \(^3, \, 11, \, 12\), thus producing straight-chain alkanes ranging from $C_{15}$ to $C_{18}$. First, the reaction proceeds via hydrogenation of unsaturated triglycerides ($C=\text{C}$ double bond) to form saturated triglycerides \(^13\), followed by hydrogenolysis of saturated triglycerides resulting in fatty acids and propane. Finally, the fatty acid undergoes the following reactions: (1) hydrodeoxygenation (HDO), an exothermic reaction, which removes oxygen in the form of water and yields n-alkanes with the same
carbon number as the corresponding fatty acid, (2) decarbonylation (DCO) and (3) decarboxylation (DCO₂), endothermic reactions, which lead to elimination of oxygen in the form of CO and water or CO₂, respectively. The resulting n-alkane has one carbon atom less than the original fatty acid. 

The Ni- and Co-promoted molybdenum sulfide catalysts have been typically used in the hydrodeoxygenation of triglycerides, fatty acids, and esters. The conventional metal sulfide catalysts, which are less expensive catalysts, showed high activity in the deoxygenation of triglycerides and model compounds; nevertheless, sulfur leaching lead to catalyst deactivation and sulfur contamination in the liquid products. It should be noted that the metal sulfide catalysts require the addition of sulfiding agents e.g., CS₂ and DMDS, to the liquid feed to avoid catalyst deactivation during the deoxygenation reactions. Furthermore, the trace amount of water that is produced from the DCO and HDO reactions would hasten the sulfur leaching and rigorously shorten the lifetime of catalysts.

To develop the next generation of hydrodeoxygenation catalysts, the metal catalysts or sulfur-free catalysts in reduced states, such as Ni, Co, Pd, and Pt, are good candidates for the deoxygenation reactions. Some metal catalysts, such as Ni, Pd, and Pt, are favorable in the DCO and DCO₂ pathways. The hydrogen consumption for the deoxygenation of triglycerides/fatty acids/esters decreased in the order of HDO > DCO > DCO₂; thus the DCO and DCO₂ routes may be more theoretically economical than the HDO route. The noble metal catalysts imply an extremely high cost in green diesel production, thus limiting their use in the large-scale applications. Accordingly, the transition metal catalysts, such as Ni and Co, which also display a good catalytic activity, have been employed as great catalysts in the deoxygenation process. However, only a few studies have been reported on the deoxygenation of triglycerides. Peng et al. investigated the catalytic deoxygenation of crude microalgae oil with a Ni/ZrO₂ catalyst in a trickle bed reactor at 543
K and 4 MPa. A 70 wt.% yield of \( n \)-heptadecane was obtained, and the catalyst did not significantly deactivate after 72 h on stream. Kim et al.\(^{36}\) reported the effect of temperature and pressure on the hydrotreating of soybean oil over a Ni/SiO\(_2\)-Al\(_2\)O\(_3\) catalyst in batch and continuous flow reactors in the range of 573-713 K and 2.5 – 15 MPa. Stusentschnig and co-workers\(^4\) hydrotreated the crude palm oil with the commercial Raney nickel catalyst at 633 K and 9 MPa in batch mode. After 5 h of reaction time, 100% conversion with alkanes yields of mainly \( n \)-heptadecane and \( n \)-octadecane between 54 and 60% were achieved. In addition, the mixed metal and metal oxide catalysts, e.g. Pt/Nb\(_2\)O\(_5\)\(^{37}\) and FeNi/SiO\(_2\)\(^{38}\), have been recently developed for deoxygenation. The unique performance of the mixed metal and metal oxide phases could be ascribable to their cooperation in which the H\(_2\) is dissociated by metallic sites and carboxylic acid is adsorbed at the oxygen vacancy of metal oxide sites\(^{37,38}\). Nevertheless, to the best of our knowledge, the deactivation and regeneration in the hydrodeoxyg enation reaction over metal catalysts has certainly not been reported in the literature. Consequently, the understanding of the deactivation and regeneration processes is important for improving and optimizing the process conditions.

In the present work, the deactivation behavior of Ni/\( \gamma \)-Al\(_2\)O\(_3\) and Co/\( \gamma \)-Al\(_2\)O\(_3\) catalysts in palm oil hydrodeoxyg enation was studied in a continuous-flow trickle bed reactor at 573 K and 5 MPa over a reaction time of 150 h. Their catalytic performances were evaluated according to the triglyceride conversion, product yield, and the contribution of HDO (hydrodeoxyg enation) and DCO\(_x\) (decarbonylation and/or decarboxylation), which were estimated based on the mole balance corresponding to the fatty acids in the oil feed. The calcined, prereduced, spent and regenerated catalysts were subsequently characterized to clarify the origin of deactivation and regeneration characteristics using a combination of techniques: temperature programmed reduction (TPR), N\(_2\) sorption, CO pulse chemisorption, X-ray diffraction (XRD), X-ray absorption near edge structure (XANES), transmission
electron microscopy (TEM) and temperature programmed oxidation (TPO). Furthermore, the regenerability of the spent catalysts after the long-term tests was also reported.

### 2. Experimental

#### 2.1 Catalyst preparations

The γ-Al$_2$O$_3$ support (1.8 mm diameter, Sasol Company, Germany, purity 99.9%) was crushed and sieved to 0.5 – 1.0 mm diameter. The Co and Ni supported on the γ-Al$_2$O$_3$ catalysts (10 wt % of Ni and Co loading) were prepared by the incipient wetness impregnation method using cobalt (II) nitrate hexahydrate [(Co(NO$_3$)$_2$.6H$_2$O), Sigma-Aldrich, purity ≥98%] and nickel (II) nitrate hexahydrate [(Ni(NO$_3$)$_2$.6H$_2$O), Sigma-Aldrich, purity 99.999%] as the corresponding metal salt precursors. After impregnation, the resultant samples were dried at 393 K for 12 h and then calcined at 773 K for 5 h.

#### 2.2 Catalyst characterizations

Powder X-ray diffraction (XRD) patterns of the samples were collected on an X-ray diffractometer (D8 ADVANCE, Bruker, Ltd., Germany) using Cu Kα radiation. The measurement was operated at 40 kV and 40 mA in steps of 0.02° s$^{-1}$ with a step time of 0.5 s over the range of 20° < 2θ < 80°.

The X-ray absorption near edge structure (XANES) technique at Ni K-edge (8333 eV) and Co K-edge (7709 eV) were acquired at the SUT-NANOTEC-SLRI XAS Beamline (BL-5.2) of the Synchrotron Light Research Institute (Public Organization), Thailand using a double Ge (2 2 0) crystal monochromator for the selection of photon energy. The data were obtained at room temperature in the transmission mode using a 13-element Ge detector. The samples were pressed into a frame covered by polyimide tape before mounting to the sample holder. The NiO, Ni foil, Co$_3$O$_4$, CoO, and Co foil were used as the reference standards for
the XANES analysis. The XANES spectra by linear combination fitting were analyzed through the Athena program.

The specific surface area, total pore volume, and pore diameter of the samples were measured at 77 K with a nitrogen adsorption-desorption technique (Nova 2000e, Quantachrome Instruments, Germany). Prior to measurement, the samples were degassed at 393 K for 3 h. Pore size distributions of the samples were determined from the desorption branch of the isotherms using the Barrett-Joyner-Hallenda (BJH) method. The specific surface area was estimated based on the BET approach. The total pore volume was measured at the relative pressure (P/P₀) of 0.98.

The H₂ temperature programmed reduction (H₂-TPR) was carried out using a CHEMBET-Pulsar Quantachrome Instruments in a quartz U-tube reactor with 20 mg of sample. Prior to the experiments, the samples were pre-treated at 393 K for 1 h at a He flow rate of 30 cm³/min. The reduction was conducted in a 5 vol% H₂/Ar flow rate of 30 cm³/min at a heating rate of 10 K/min from 373 to 1273 K. The hydrogen consumption was analyzed using a thermal conductivity detector (TCD). The representative metallic sites of the catalysts were determined by CO pulse chemisorption experiments with the same apparatus as used for H₂-TPR. A 50 mg quantity of catalyst was reduced with a 5 vol% H₂/Ar flow rate of 30 cm³/min at 973 K for 3 h. The pulses of CO (0.05 cm³) were injected through the sample until CO saturation was attained. Temperature-programmed oxidation (TPO) combined with a mass spectroscopy detector was used to determine the amount of coke deposited on the spent catalyst using the same apparatus used for the H₂-TPR experiment. Prior to the TPO experiments, the spent catalyst samples (50 mg) were pre-treated at 673 K for 1 h under a He flow rate of 30 cm³/min. The oxidation was conducted by raising the temperature from 373 to 1073 K at a heating rate of 10 K/min in a 5% O₂/He flow rate of 30
The product gases were detected by online mass spectroscopy.

The morphology and particle size of the catalysts were examined by transmission electron microscopy (TEM) at 200 kV on an FEI TECNAI G2-20S-TWIN instrument equipped with an energy dispersive spectrum (EDS) analysis facility.

2.3 Catalytic hydrodeoxygenation tests-durability evaluation

Long-term durability reaction tests to investigate the deactivation and regeneration behaviors were evaluated in a custom-made down-flow trickle-bed reactor with an internal diameter of 7 mm, length of 210 mm, and a volume of 8 cm$^3$. The effect of external mass transfer resistance in the catalyst bed was negligible under the working conditions as a further increase in the space velocity with a fixed WHSV has no impact on the conversion and product yield. The details of the reactor apparatus are presented elsewhere.\textsuperscript{11} A palm oil feedstock (a high purity refined palm olein type with a free fatty acid content <1 wt %) was commercially obtained from a local market in Thailand. The fatty acid compositions of refined palm olein (wt %), determined through the fatty acid methyl esters (FAMEs) obtained from the transesterification of triglycerides with methanol using a base catalyst, were as follows: lauric acid (C12:0) 0.4%; myristic acid (C14:0) 0.8%; palmitic acid (C16:0) 37.4%; palmitoleic acid (C16:1) 0.2%; stearic acid (C18:0) 3.6%; oleic acid (C18:1) 45.8%; linoleic acid (C18:2) 11.1%; linolemic acid (18:3) 0.3%; arachidic acid (C20:0) 0.3%; and eicosenoic acid (C20:1) 0.1%.\textsuperscript{39} The catalysts (5.5 g) were loaded into the reactor and then were in situ prereduced with a flow of pure H$_2$ (200 cm$^3$/min, Praxair, purity 99.99%) at 773 K for 3 h. In the reaction testing, the reactor was heated to the desired temperature and was pressurized with H$_2$ to the desired pressure controlled by a back pressure regulator. An HPLC pump was used to introduce the oil feed, and the H$_2$ feed was controlled by mass flow controllers. The deactivation and regeneration experiments in the palm oil hydrodeoxygenation were
conducted at a temperature of 573 K, H\textsubscript{2} pressure of 5 MPa, liquid hourly space velocity (LHSV) of 1 h\textsuperscript{-1}, and a H\textsubscript{2}/oil feed ratio of 1,000 N(cm\textsuperscript{3}/cm\textsuperscript{3}). Note that after a long-term reaction test was completed, the catalysts were cooled to room temperature under N\textsubscript{2} flow before exposition in air and being further characterized by various techniques. Furthermore, the regeneration experiments were conducted by calcination in air at 773 K for 5 h and reduction in H\textsubscript{2} at 773 K for 3 h.

2.4 Product analysis

After the separation of the water and oil-phase products obtained from the hydrodeoxygenation experiments, they were analyzed offline by a gas chromatography (GC) equipped with a capillary column (DB-1HT, 30 m × 0.32 mm × 0.1 μm) and a flame ionization detector (FID) (GC-2014, Shimadzu). The calibration curve of standards was used to quantify a composition of n-alkanes (n-C\textsubscript{8} to n-C\textsubscript{18}) in the liquid products. Briefly, 50 mg of sample was diluted with 1 cm\textsuperscript{3} of hexane and 0.001 cm\textsuperscript{3} of sample was injected into the GC with a split ratio of 100. High injection and column temperatures were used to directly analyze the triglyceride without chemical derivatization \textsuperscript{20, 40}. The injection and detector temperatures were 613 and 643 K, respectively. The temperature program was increased from 313 to 543 K at a rate of 8 K/min, and held for 11 min, followed by an increase of 15 K/min to 643 K, and held for 15 min. The composition of gas products (C\textsubscript{3}H\textsubscript{8}, C\textsubscript{2}H\textsubscript{6}, CH\textsubscript{4}, CO, CO\textsubscript{2}, and H\textsubscript{2}) was analyzed by an online GC equipped with two packed columns (molecular sieve 5A and Porapak Q) and a thermal conductivity detector (TCD) (GC-14B, Shimadzu).

For an in-depth analysis of the catalyst performance evaluation, the mole balance of organic liquid products was used to determine the conversion and product yields; the mole balance was always above 95% for all conditions. The conversion was defined as the moles of reactants (triglyceride) converted to others (intermediates and hydrocarbons). The product
yields were theoretically determined based on the mole balance of n-alkanes in the product corresponding to the moles of fatty acids in the oil feed. The product yield of n-C$_{15}$ to n-C$_{18}$ fraction and conversion were calculated using the following equations:

\[
\text{Conversion (\%) = } \left( \frac{\text{mole of triglycerides in feed} - \text{mole of triglycerides in product}}{\text{mole of triglycerides in feed}} \right) \times 100
\]

(1)

\[
\text{Product yield (\%) = } \left( \frac{\text{Total mole of n-alkanes (n-C$_{15}$ to n-C$_{18}$) in product}}{\text{Total mole of C$_{16}$ and C$_{18}$ fatty acid in feed}} \right) \times 100
\]

(2)

The relative activity of decarbonylation and decarboxylation reactions could not be directly correlated to the amount of CO and CO$_2$ detected in the gas phase due to the possible gas-phase reactions involved, such as methanation and water-gas shift reactions. Consequently, the percent contribution of hydrodeoxygenation (HDO) and combined decarbonylation and/or decarboxylation (DCO$_x$) reactions were also calculated based on the mole balance, using the total moles of n-alkanes with even numbers (HDO) or odd numbers (DCO$_x$) of carbon atoms in the liquid product, to the moles of fatty acids in the oil feed using the following equations:

\[
\text{HDO (\%) = } \left( \frac{\text{Total mole of n-alkanes (n-C$_{16}$ and n-C$_{18}$) in product}}{\text{Total mole of C$_{16}$ and C$_{18}$ fatty acid in feed}} \right) \times 100
\]

(3)

\[
\text{DCO$_x$ (\%) = } \left( \frac{\text{Total mole of n-alkanes (n-C$_{15}$ and n-C$_{17}$) in product}}{\text{Total mole of C$_{16}$ and C$_{18}$ fatty acid in feed}} \right) \times 100
\]

(4)
3. Results and discussions

3.1 Deactivation behaviors

The long-term reaction tests were performed for 150 h on-stream to examine the changes in the activity, performance, and selectivity of Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts in the palm oil hydrodeoxygenation. The reaction conditions were as follows: reaction temperature = 573 K, H₂ pressure = 5 MPa, H₂/oil ratio = 1000 N(cm³/cm³), and LHSV = 1 h⁻¹. Fig. 1 shows the triglyceride conversion and product yield on the catalytic performance of Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts as a function of reaction time. It should be noted that the hydrodeoxygenation reaction over pure γ-Al₂O₃ resulted in 56% conversion of the triglyceride without a liquid alkane product yield. The results suggested that only saturated triglyceride scission to free fatty acids and propane occurred. Therefore, γ-Al₂O₃ played no catalytic role in the hydrodeoxygenation of the triglycerides. Interestingly, the product yield was achieved when the reaction was catalyzed by the metallic species, confirming the hydrodeoxygenation activity of the metallic sites of Ni or Co species. The triglyceride conversion, shown in Fig. 1, remained steady at ~100% throughout the 150 h reaction time during the test. Over the Ni catalyst, the product yield was generally between 85.7 – 94.4%, with an average value of 92.2 ± 2.2%. Meanwhile, over the Co catalyst, the product yield was also between 83.8 – 93.8% with an average value of 88.6 ± 3.6% at the first 100 h reaction time. Furthermore, the slight increase of product yield observed during the first 24-h reaction time was likely due to the formation of metallic Ni or Co by the in situ reduction during working conditions. As demonstrated in Fig. 1, at reaction times > 100 h, a decrease in product yield from 92.2 to 75.6% was observed over the Ni catalyst, whereas, a dramatic drop in product yield from 88.6% to ca. 56.6% could be noticed over the Co catalyst. These results indicated that the Ni and Co catalysts showed a significant catalyst deactivation over 100 h of reaction time. It should be noted that the catalytic activity on the palm oil
hydrodeoxygenation over the Ni catalyst seems to be greater than the Co catalyst. Furthermore, the percent deactivation of the catalysts was evaluated based on the product yield after 150 h compared with the average product yield during the first 100 h of reaction. The deactivation of the Ni and Co catalysts was 19.8% and 36.6%, respectively. It is clear that the Co catalyst was faster deactivated than the Ni one.

Although the triglyceride conversion remained constant throughout the 150 h reaction experiment, the changes in the liquid product properties were observed at reaction times in the range of 100-150 h (Fig. 1). The liquid product solidified at room temperature and was comprised of n-alkanes and oxygenated intermediates (i.e., free fatty acids, alcohols, and esters) including a small amount of triglycerides. This finding indicated that the Ni and Co metallic sites became deactivated and the reaction mainly proceeded through the hydrogenation of the C=C bonds in the unsaturated triglycerides, followed by C-O bond cleavage via the hydrogenolysis of the saturated triglyceride to produced free fatty acids and propane, indicating incomplete hydrodeoxygenation activity. The actual operation should avoid these conditions due to the strong adsorption of the oxygenated intermediates on the catalyst active sites, thus providing that the catalysts underwent rapid deactivation.

When the Ni was used, at 100 h of reaction time, DCO$_x$ (decarbonylation, DCO and/or decarboxylation, DCO$_2$ pathways) (89.2 ± 2.4%) were a major reaction pathway, whereas, HDO, hydrodeoxygenation, (2.1 ± 0.3%) was a minor reaction pathway (Fig. 2). Interestingly, the dominant contribution over the Co catalyst during 100 h of reaction time was from both DCO$_x$ (43.0 ± 3.3%) and HDO (45.8 ± 3.0%) pathways, suggesting that the triglycerides were deoxygenated through DCO, DCO$_2$, and HDO (Fig. 2). This finding indicated that the metallic sites of the Co catalyst were responsible for all three major reaction pathways, whereas, the metallic sites of Ni, strongly promoted DCO and/or DCO$_2$
reactions. The palm oil used in this study was mainly composed of C_{16} and C_{18} fatty acids (>98.4 wt %). Thus, the main composition of the liquid product was n-C_{15} and n-C_{17} due to highly selective DCO and DCO_2 reactions over the Ni catalyst (Fig. 3). On the contrary, n-C_{15}, n-C_{16}, n-C_{17}, and n-C_{18} were a major product composition when the Co catalysts were used (Fig. 3). Moreover, a small amount of light hydrocarbon compositions (n-C_8 to n-C_{14}) (results not shown) was observed during the hydrodeoxygenation, suggesting that the cracking reaction proceeded over the Ni and Co catalysts by C-C bond cleavage. It should be noted that the contribution and liquid product composition were also observed to change in a similar way to that of the product yield.

The gas product compositions as a function of reaction time are represented in Fig. 4. When the Ni and Co catalysts were used, CH_4 was a major gas composition (≈20 mole % for Ni catalyst; ≈10 mole % for Co catalyst) as a result of the methanation reaction between CO or CO_2 with H_2, as well as the cracking reaction, implying that the metallic sites of the Ni and Co catalysts strongly promoted methanation and cracking reactions. The CO and CO_2 were not detected during the hydrodeoxygenation. When the reaction was catalyzed by Ni, the amount of C_3H_8 (< 1 mole %), produced by the hydrogenolysis of triglycerides, was lower than that of the Co catalyst, suggesting that the cracking reaction of C_3H_8 to C_2H_6 and CH_4 by C-C cleavage occurs over the Ni catalyst. Furthermore, the formation of the CH_4, C_2H_6, and C_3H_8 species in the gas product could be associated with the cracking reaction in the liquid phase. As seen in Fig. 4, the activity in the gas phase reactions (mainly methanation and cracking reactions) was not strongly affected as a function of time on stream over the Ni catalyst; nevertheless, the composition of gas product mainly CH_4, C_2H_6, and C_3H_8, slightly decreased after 80 h of reaction time over the Co catalyst. It should be deduced that the decay of the metallic sites of Ni catalyst showed a milder effect on the gas phase reactions.
3.2 Catalyst characterizations

In order to understand the deactivation and regeneration behaviors, as well as a reason for the activity decline, in the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts used in the hydrodeoxygenation, the calcined, prereduced, spent and regenerated catalysts were characterized by temperature programmed reduction, N₂ sorption, CO pulse chemisorption, X-ray diffraction, X-ray absorption near edge structure, transmission electron microscopy, and temperature programmed oxidation.

The H₂-TPR experiments were conducted to investigate the reducibility of Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts, as well as to study the interaction between metal species and γ-Al₂O₃ support in the catalysts (Fig. 5). Firstly, the reduction peak of both pure NiO and Co₃O₄ catalysts revealed a broad peak at approximately 750 K, indicating the nature of the reduction behavior of the pure metal oxide. The reduction profile of Ni/γ-Al₂O₃ showed a broad peak composed of three contributions (~943, ~1033, and ~1153 K), representing the presence of different nickel species. The peak at 943 K was attributed to the reduction of bulk NiO species to Ni⁰, which have a weak interaction with the support. The second peak at 1033 K also represented the NiO species, which have stronger metal and support interactions, or smaller particles located inside the pore. In addition, the reduction peak at the high temperature of 1153 K could be assigned to stronger Ni and γ-Al₂O₃ interactions or nickel aluminate phases with a spinel structure (NiAl₂O₄)²⁶,⁴¹. On the other hand, the TPR profile of Co/γ-Al₂O₃ showed a broad curve from 703 to 1073 K with three different peaks at ~793, ~898, and ~1023 K. The transformation of Co₃O₄ to Co⁰ occurred in two steps; the first peak, at 703–823 K, was ascribed to the reduction of Co₃O₄ to CoO and the second one, at 823–953 K, to the subsequent reduction of CoO to Co⁰. Additionally, the peak at higher temperature (1023 K) may be assigned to the existence of a Co species with smaller crystallite sizes or stronger metal-support interactions.¹³,⁴² Note that a high reduction temperature for catalyst
activation should be avoided due to the formation of large metal particle size and/or the transformation of $\gamma$-$\text{Al}_2\text{O}_3$ to other $\text{Al}_2\text{O}_3$ phases, thus providing the low activity and stability toward the reaction of catalysts. Therefore, the Ni and Co catalysts were in situ prereduced at a lower temperature (773 K) with pure $\text{H}_2$ for 3 h before catalytic hydrodeoxygenation testing.

To investigate possible changes in the catalyst texture, the BET specific surface area, total pore volume, and average pore diameter of bare $\gamma$-$\text{Al}_2\text{O}_3$, prereduced, spent, and regenerated catalysts are summarized in Table 1. The surface area of bare $\gamma$-$\text{Al}_2\text{O}_3$ was 201.1 m$^2$/g with a total pore volume of 0.55 cm$^3$/g. The BET surface area and pore volume typically decreased by 10% after metal loading. The decrease of the specific surface area and total pore volume of the catalysts would be due to the metal converging on the $\gamma$-$\text{Al}_2\text{O}_3$ support and blockage of the pores by metal species. Interestingly, the observed pore sizes of all the catalysts were approximately 7.5 nm and did not change significantly after metal loading in the range studied. $\text{N}_2$ adsorption–desorption isotherms (results not shown) of $\gamma$-$\text{Al}_2\text{O}_3$ and the catalysts exhibited type-IV isotherms, a typical characteristic of a mesoporous structure. As seen in Table 1, the BET surface area of prereduced Ni/$\gamma$-$\text{Al}_2\text{O}_3$ did not significantly differ when compared with the calcined catalysts; whereas, the surface area of pre-reduced Co/$\gamma$-$\text{Al}_2\text{O}_3$ catalysts was somewhat less than that of the calcined catalysts. This may be due to the sintering of cobalt particles during $\text{H}_2$ reduction at 773 K. A significant decrease in BET surface area, pore volume, and pore diameter was observed from both spent Ni/$\gamma$-$\text{Al}_2\text{O}_3$ and Co/$\gamma$-$\text{Al}_2\text{O}_3$ catalysts after 150 h on-stream. It should be noted that the changes in the physical structural properties of the spent catalyst were possibly caused by carbonaceous deposits on the pore channels and/or external surface of catalysts, thus leading to pore blocking. In addition, the pore blocking could result in catalyst deactivation due to limiting diffusion of the reactants or intermediates and the products dispersion from the catalysts active sites$^{43,44}$. 
However, the texture properties of the catalysts after regeneration by calcining in air at 773 K for 5 h were similar to the prerduced catalysts, indicating that the carbon deposited on the catalyst was completely removed, and the pore structure did not change under the hydrodeoxygenation experiments.

CO uptake, which represents a number of active sites on a catalyst, was used to elucidate the loss of catalyst active sites (Table 1). The CO uptake of Ni/γ-Al₂O₃ was typically higher than that of Co/γ-Al₂O₃. It should be confirmed that the decrease in catalyst active sites after a 150 h experiment was likely due to the coking or catalyst sintering. Furthermore, the increase in the CO uptake after regeneration may be due to the redispersion of the Ni and Co species during the carbon burning.

The phase identity and crystallinity of the calcined, prerduced, spent, and regenerated catalysts were revealed through XRD patterns (Figs. 6 and 7). Three peaks at \(2\theta=37.5^\circ, 46^\circ\) and \(67^\circ\) assigned to the γ-Al₂O₃ phase with low crystallinity were observed for all catalysts.\(^{45}\) The calcined Ni/γ-Al₂O₃ catalyst (Fig. 6, pattern a) exhibited three diffraction peaks at \(2\theta=37.4^\circ, 44^\circ\), and \(63^\circ\) which correspond to NiO (111), NiO (200), and NiO (220), respectively, which approximately disappeared after pre-reduction in pure H₂ at 500 °C (Fig. 6, pattern b)\(^{21}\). The diffraction peak of metallic Ni at \(2\theta=44.6^\circ, 52.2^\circ\), and \(76.5^\circ\) could be attributed to the reflection of (111), (200), and (220) planes, respectively\(^ {46}\). As represented in Fig. 7, pattern a, the diffraction peaks at \(2\theta=31.3^\circ, 37.7^\circ, 59.5^\circ\) and \(65.4^\circ\), which were seen in calcined Co/γ-Al₂O₃ catalysts, were assigned to those of spinel Co₃O₄; meanwhile, the pre-reduced catalyst (Fig. 7, pattern b) exhibited a diffraction peak for CoO at \(2\theta=37.2^\circ\) and metallic Co at \(2\theta=44.2^\circ\) and \(52.3^\circ\).\(^ {47}\) The XRD patterns of the catalysts after the hydrodeoxygenation reaction, shown in Figs. 6, pattern c and 7, pattern c, revealed the increase in the intensity of the diffraction peak of metallic Ni and Co peaks, indicating that
the crystallinity size of the Ni and Co crystallites slightly increased. Thus, the phenomena implied that metallic Ni and Co particles start to aggregate during the 150 h hydrodeoxygenation reaction experiment. Additionally, the XRD patterns of regenerated Ni and Co by calcining in air at 500 °C for 5 h (Figs. 6, pattern d and 7, pattern d) illustrated that the regenerated catalysts exhibit crystalline structures of NiO and Co$_3$O$_4$ for the regenerated Ni and Co catalysts, respectively. Generally, in the hydrodeoxygenation reaction, a water content of 10-15 wt % was found in the liquid product. The transformation of $\gamma$-Al$_2$O$_3$ into $\gamma$-AlOOH in the presence of water under hydrothermal conditions has been reported by some researchers. As demonstrated in the XRD patterns of the catalysts after reaction, the transformation of $\gamma$-Al$_2$O$_3$ into $\gamma$-AlOOH did not occur during 150 h on-stream. The $\gamma$-Al$_2$O$_3$ has been stabilized in the presence of the palm oil, alkanes, oxygenated intermediates, and water products under the working conditions.

The fist-row transition metal elements revealed well-defined site symmetry spectra in the X-ray absorption near edge structure (XANES) characteristics. Normalized Ni and Co K-edge XANES spectra of the calcined, prerduced, and spent Ni/$\gamma$-Al$_2$O$_3$ and Co/$\gamma$-Al$_2$O$_3$ catalysts are displayed in Figs. 8 and 9, respectively. The standard edge energy was calibrated at the first inflection point in the metal foil calibration spectrum (8333.0 eV for Ni, 7709.0 eV for Co) as reported in the literature. The intensity of the pre-edge peak and white line was used to consider the main features, reflecting the oxidation state of the Ni and Co catalysts on the $\gamma$-Al$_2$O$_3$ support. Firstly, the shape and features of the calcined Ni (Fig. 8) and Co (Fig. 9) catalysts were similar to the spectra of NiO and Co$_3$O$_4$ spinel, respectively, indicating that the samples were in the form of NiO and Co$_3$O$_4$ on the $\gamma$-Al$_2$O$_3$ support, which was consistent with the XRD patterns. In the case of the Ni catalysts, shown in Fig. 8, after being prerduced and tested in the hydrodeoxygenation, the edge energy of the prerduced and spent Ni catalysts shifted to that of Ni foil and the intensity of the white line decreased,
whereas the pre-edge increased. This suggested that the NiO on the $\gamma$-Al$_2$O$_3$ species were not completely reduced so oxides of Ni existed. In the case of the Co catalysts (Fig. 9), it is clear from the XANES data that it is easy to distinguish between metallic Co, CoO, and Co$_3$O$_4$ phases. After being prereduced, the edge energy of the prereduced Co catalyst shifted to that of CoO, whereas the intensity of the line decreased and the pre-edge increased when CoO species transformed into Co metallic species were observed. The transformation of Co$_3$O$_4$ to Co$^0$ occurred in two steps: the first step, the transition of Co$_3$O$_4$ to CoO and the second one, the reduction of CoO to Co$^0$, which is consistent with what was observed in the TPR experiments.

To quantify the amount of Ni and Co species in the prereduced, calcined and spent catalysts, a linear combination fit (LCF) of the XANES spectra was applied and performed using the XANES data of standard materials (NiO and Ni foil for Ni; Co$_3$O$_4$, CoO, and Co foil for Co) as possible compositions. This procedure yielded the percentage of the catalyst species on the $\gamma$-Al$_2$O$_3$ support. The weight percentages are summarized in Table 3 for the Ni and Co species. The statistical goodness-of-fit parameter with R-factor (coefficient of determination) shows that the fit is reasonably good. The LCF confirmed that the NiO and Co$_3$O$_4$ species are the dominant metal phases in the calcined Ni/$\gamma$-Al$_2$O$_3$ and Co/$\gamma$-Al$_2$O$_3$ catalysts, respectively. After being prereduced, some of the NiO species were transformed to metallic Ni, whereas, the Co$_3$O$_4$ species were first transformed to CoO before being transformed to metallic Co. It is evident from the XANES data that the nickel oxide and cobalt oxide were not completely reduced to the metallic form at 773 K for 3 h in the presence of pure H$_2$. In addition, it could be observed that the amount of metallic Ni and Co increased with an increase in the reaction time, indicating that the reduction continued to occur during the hydrotreating process.
The combined XRD and XANES data confirmed that the nickel and cobalt oxides were not completely reduced to metallic phases. To confirm the role of metal oxides, the effect of prereduction temperature was conducted over Ni/γ-Al₂O₃ catalysts. As demonstrated in Fig S1, the metal oxide catalyst without prereduction exhibited much lower activity than that with prereduction. The result suggested that the metallic phase was the dominant active site for the reaction. In addition, the HDO activity remained almost constant, although the ratio of metal to metal oxide would change during the time course of reaction, especially the first few days. Therefore the role of metal oxide was not significant in the present HDO experiments. It should be noted that the increase in reduction temperature from 773 to 973 K to completely reduce the NiO phase drastically suppressed the catalytic activity due to the aggregation of metal particles.

To investigate the metal particle growth or sintering effect on the palm oil hydrodeoxygenation activity, typical TEM images and particle size distribution of prereduced, spent, and regenerated Ni and Co catalysts are represented in Figs. 10 and 11. The TEM images of the Ni catalysts (Fig. 10) display an uneven metal particle size, whereas, a less clear distinction between the metal and alumina was observed in TEM images of the Co catalysts (Fig. 11). Nonetheless, the most aggregation of Co particles could be distinguished due to the darkest contrast. The Co particles were less dispersed on the γ-Al₂O₃ support than the Ni particles, and most of the Co particles were clustered into large particles. The average particle size of the Ni and Co catalysts after the reaction somewhat increased from 10.7 ± 2.3 to 12.7 ± 2.1 nm and from 11.8 ± 3.9 to 12.2 ± 4.9 nm, respectively. This finding indicated that the average metal particle size increased slightly after the reaction, suggesting that the metal sintering occurred during the hydrodeoxygenation reaction. Furthermore, it should be noted that the metal particle sizes of the Ni and Co were much larger than the pore size of γ-Al₂O₃, suggesting that most particles would be located outside
the pore of alumina. Interestingly, the TEM images of the catalysts regenerated at 773 K in air for 5 h, followed by prereduction in H₂ at 773 K for 3 h also showed that the metal particles size of Ni and Co were 12.5 ± 2.4 and 10.5 ± 3.5, respectively. The particle size was not significantly changed before and after the regeneration under the thermal treatment. It should be deduced that the sintering may not be the main reason for catalyst deactivation because the reaction temperature 573 K was significantly lower than the melting point of the Ni and Co catalysts. The combination data of the XRD and TEM analyses showed the catalyst sintering was a reason for the catalyst deactivation during the palm oil hydrodeoxygenation. Note that the average metal particle size was measured from 50-100 particles to ensure a significant population variance.

Furthermore, the pre-reduced, spent, and regenerated Ni and Co catalysts were characterized by FE-SEM. As shown in Fig. S2, the morphology of the catalysts did not obviously change after the deoxygenation for 150 h and the regeneration process. Meanwhile, the elemental mapping analysis for the pre-reduced, spent, and regenerated Ni and Co catalysts (Fig. S3) based on SEM-EDX analysis revealed that distribution of the Ni species on the γ-Al₂O₃ support was more uniform than that of Co species. The agglomeration of some Ni species in the spent catalyst was observed which was consistent to the particles size of the spent Ni catalysts based on the TEM analysis.

The amount of carbonaceous species deposited on the spent catalysts was determined by temperature-programmed oxidation. The desorption curves of CO₂ measured by mass spectrometry, shown in Fig. 12, indicated that a large amount of CO₂ was released from the spent catalysts. According to the literature, the peaks at low temperature approximately 573 K correspond to more reactive amorphous carbon which adsorbed on the metallic sites; meanwhile, the oxidation of crystalline or graphitic carbon occurs at temperatures above 773
K\textsuperscript{53-55}. The TPO profile of the spent Ni and Co catalysts showed a wide peak in the temperature range of 573–913 K with a peak maximum at ca. 813 K and ca. 763 K, respectively. The carbonaceous species deposited during hydrodeoxygenation could be removed above 773 K, suggesting that the formed carbon species were both amorphous and graphitic carbons. As summarized in Table 3, the carbon content of the spent Ni and Co was determined to be 34.88 mg/g\textsubscript{cat} and 49.51 mg/g\textsubscript{cat}, respectively; whereas, only trace amounts were detected in regenerated catalysts. It should be confirmed that the Co catalyst deactivated faster than the Ni catalysts due to the higher carbon formation rate on the catalyst surface. Thus TPO analysis indicated carbon deposition was a main cause for the catalysts’ deactivation.

3.3 Regeneration behaviors

After the 150 h on-stream experiment, the product yield decreased from 92.2 to ca. 75.6% over the Ni catalyst and from 88.6% to ca. 56.6% over the Co catalyst. As discussed above, the major reason for catalyst deactivation was caused by the formation of carbonaceous species on the catalyst, and the minor reason was likely the partial sintering of the metal particles. At first, to find out the suitable temperature for the effective removal of the carbonaceous species, TGA (results not shown) was investigated in the range of 473-1073 K in the presence of air. The complete decomposition of carbon was observed at the temperature of 773 K, suggesting that the appropriate regeneration temperature was 773 K. Therefore, the spent catalysts after 150 h on-stream were regenerated by calcining at 773 K for 5 h. A higher regeneration temperature should be avoided due to the formation of large metal particle sizes, and the transformation of Ni and Co on \(\gamma\)-Al\textsubscript{2}O\textsubscript{3} to metal aluminate phases. After regeneration, the catalysts exhibited the crystalline structures of metal oxide phases, which implied that the pre-reduction under H\textsubscript{2} at 773 K for 3 h was necessary. It should be deduced that the physical and chemical properties such as BET surface area, pore
volume, pore diameter, and metal particles size were not significantly different after the regeneration as shown in Figs. 1-4, indicating that the catalytic performance can be essentially restored after the regeneration. This suggests that the carbon deposited on the catalyst surfaces was completely removed and was the origin of the deactivation.

4. Conclusions

The deactivation and regeneration behaviors of the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts during palm oil hydrodeoxygenation in a trickle bed reactor have been studied and the concluding remarks are as follows:

- On the hydrodeoxygenation reaction test for 150 h, the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts exhibited good catalytic activity and stable performance for 100 h on-stream under the reaction conditions of temperature = 573 K, H₂ pressure = 5 MPa, H₂/oil ratio = 1000 N(cm³/cm³), and LHSV = 1 h⁻¹.

- After 100 h on-stream, the catalyst activity over the Ni catalyst gradually dropped; whereas, a dramatic decline can be observed over Co catalysts. According to the characterization data, the carbonaceous species deposited on the catalysts seemed to be the main cause of catalyst deactivation, and metal particle size growth was deduced to be the minor reason.

- The spent catalyst can be fully regenerated by calcination in air at a temperature of 773 K for 5 h, followed by prereduction in H₂ at 773 K for 3 h, resulting in a complete recovery of the catalytic performance.

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References


**Figure captions**

**Fig. 1.** Triglyceride conversion and product yield over time on stream during palm oil hydrodeoxygenation on the catalytic performance and regeneration of the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts. Reaction conditions: 573 K, 5 MPa, LHSV of 1 h⁻¹, and H₂/oil ratio of 1,000 N(cm³/cm³)

**Fig. 2.** Contribution of HDO and DCOₓ over time on stream during palm oil hydrodeoxygenation on the catalytic performance and regeneration of the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts. Reaction conditions: 573 K, 5 MPa, LHSV of 1 h⁻¹, and H₂/oil ratio of 1,000 N(cm³/cm³)

**Fig. 3.** Liquid product composition over time on stream during palm oil hydrodeoxygenation on the catalytic performance and regeneration of the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts. Reaction conditions: 573 K, 5 MPa, LHSV of 1 h⁻¹, and H₂/oil ratio of 1,000 N(cm³/cm³)

**Fig. 4.** Gas product composition over time on stream during palm oil hydrodeoxygenation on the catalytic performance and regeneration of the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts. Reaction conditions: 573 K, 5 MPa, LHSV of 1 h⁻¹, and H₂/oil ratio of 1,000 N(cm³/cm³)

**Fig. 5.** H₂-TPR profiles of the catalysts, (a) Ni/γ-Al₂O₃, (b) Co/γ-Al₂O₃, (c) NiO, (d) Co₃O₄

**Fig. 6.** XRD patterns of the (a) calcined, (b) prereduced, (c) spent, and (d) regenerated of Ni/γ-Al₂O₃ catalysts.

**Fig. 7.** XRD patterns of the (a) calcined, (b) prereduced, (c) spent, and (d) regenerated of Co/γ-Al₂O₃ catalysts.
Fig. 8. Normalized Ni K-edge XANES spectra of the calcined, prereduced, and spent Ni catalysts and the reference standards.

Fig. 9. Normalized Co K-edge XANES spectra of the calcined, prereduced, and spent Co catalysts and the reference standards.

Fig. 10. TEM images of the (a) prereduced, (b) spent, and (c) regenerated Ni/γ-Al₂O₃ and the particle size distribution of the (d) prereduced, (e) spent, and (f) regenerated Ni/γ-Al₂O₃.

Fig. 11. TEM images of the (a) prereduced, (b) spent, and (c) regenerated Co/γ-Al₂O₃ and the particle size distribution of the (d) prereduced, (e) spent, and (f) regenerated Co/γ-Al₂O₃.

Fig. 12. Temperature programmed oxidation profiles of the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts after 150 h on-stream.
Table 1 Physicochemical properties of the calcined, prereduced, spent, and regenerated catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Metal content(^a) (wt.%)</th>
<th>(S_{\text{BET}})(^b) (m(^2)/g)</th>
<th>Total pore volume(^c) (cm(^3)/g)</th>
<th>Pore diameter (BJH)(^d) (nm)</th>
<th>CO uptake (umol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\gamma)-Al(_2)O(_3)</td>
<td>-</td>
<td>201.1</td>
<td>0.549</td>
<td>7.53</td>
<td>-</td>
</tr>
<tr>
<td>Calcined Ni/(\gamma)-Al(_2)O(_3)</td>
<td>9.42</td>
<td>178.1</td>
<td>0.454</td>
<td>7.51</td>
<td>-</td>
</tr>
<tr>
<td>Prereduced Ni/(\gamma)-Al(_2)O(_3)</td>
<td>-</td>
<td>177.2</td>
<td>0.497</td>
<td>7.51</td>
<td>26.5</td>
</tr>
<tr>
<td>Spent Ni/(\gamma)-Al(_2)O(_3)</td>
<td>-</td>
<td>105.1</td>
<td>0.236</td>
<td>5.44</td>
<td>18.7</td>
</tr>
<tr>
<td>Regenerated Ni/(\gamma)-Al(_2)O(_3)</td>
<td>-</td>
<td>178.6</td>
<td>0.519</td>
<td>7.51</td>
<td>32.5</td>
</tr>
<tr>
<td>Calcined Co/(\gamma)-Al(_2)O(_3)</td>
<td>9.05</td>
<td>181.2</td>
<td>0.470</td>
<td>7.51</td>
<td>-</td>
</tr>
<tr>
<td>Prereduced Co/(\gamma)-Al(_2)O(_3)</td>
<td>-</td>
<td>172.7</td>
<td>0.469</td>
<td>7.51</td>
<td>9.4</td>
</tr>
<tr>
<td>Spent Co/(\gamma)-Al(_2)O(_3)</td>
<td>-</td>
<td>100.8</td>
<td>0.239</td>
<td>5.44</td>
<td>0</td>
</tr>
<tr>
<td>Regenerated Co/(\gamma)-Al(_2)O(_3)</td>
<td>-</td>
<td>171.8</td>
<td>0.502</td>
<td>7.51</td>
<td>12.6</td>
</tr>
</tbody>
</table>

\(^a\) Metal content determined by ICP-OES

\(^b\) BET surface area calculated from the adsorption branch of the \(N_2\) isotherm

\(^c\) Total pore volumes calculated from the \(N_2\) adsorption at a relative pressure of 0.98

\(^d\) Pore diameter calculated from the desorption branch using the BJH method
Table 2 Phase compositions obtained from linear combination fitting of the XANES spectra of the Ni and Co catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R-factor*</th>
<th>Ni</th>
<th>NiO</th>
<th>Co</th>
<th>CoO</th>
<th>Co$_3$O$_4$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Calcined Ni/γ-Al$_2$O$_3$</td>
<td>0.01605</td>
<td>0.3</td>
<td>99.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Prereduced Ni/γ-Al$_2$O$_3$</td>
<td>0.00522</td>
<td>31.7</td>
<td>68.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Spent Ni/γ-Al$_2$O$_3$</td>
<td>0.00575</td>
<td>45.5</td>
<td>54.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Calcined Co/γ-Al$_2$O$_3$</td>
<td>0.00721</td>
<td>-</td>
<td>-</td>
<td>0</td>
<td>4.9</td>
<td>95.1</td>
</tr>
<tr>
<td>Prereduced Co/γ-Al$_2$O$_3$</td>
<td>0.00899</td>
<td>-</td>
<td>-</td>
<td>22.7</td>
<td>74.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Spent Co/γ-Al$_2$O$_3$</td>
<td>0.00395</td>
<td>-</td>
<td>-</td>
<td>67.7</td>
<td>32.3</td>
<td>0</td>
</tr>
</tbody>
</table>

* R-factor (coefficient of determination) is the statistical goodness-of-fit parameter
Table 3 Total coke contents before and after regeneration by calcining in air at 773 K for 5 h as obtained from temperature programmed oxidation

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Carbon amount remained after the reaction (mg/g_{cat})</th>
<th>Carbon amount remained after the regeneration (mg/g_{cat})</th>
<th>Carbon amount removed after the regeneration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spent Ni/γ-Al$_2$O$_3$</td>
<td>34.88</td>
<td>0.02</td>
<td>99.94</td>
</tr>
<tr>
<td>Spent Co/γ-Al$_2$O$_3$</td>
<td>49.51</td>
<td>0.02</td>
<td>99.95</td>
</tr>
</tbody>
</table>
Fig. 1. Triglyceride conversion and product yield over time on stream during palm oil hydrodeoxygenation on the catalytic performance and regeneration of the Ni/γ-Al₂O₃ and Co/γ-Al₂O₃ catalysts. Reaction conditions: 573 K, 5 MPa, LHSV of 1 h⁻¹, and H₂/oil ratio of 1,000 N(cm⁻³/cm⁻³)
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