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# Role of copper- or cerium-promoters on NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts in hydrodeoxygenation of guaiacol and bio-oil



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#### ABSTRACT

Effect of copper (Cu) or cerium (Ce) as promoters for nickel-molybdenum/ $\gamma$ -alumina (NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) catalyst on the hydrodeoxygenation (HDO) of guaiacol (GUA), a model oxygenated compound found in a bio-oil derived from woody biomass, was comparatively investigated. The addition of Cu- or Ce-promoters affected the physicochemical properties of the NiMo catalyst. The NiMo catalyst promoted by Cu showed the higher reducibility, whilst the Ce-promoter (2-8 wt% based on Y-Al<sub>2</sub>O<sub>3</sub> content) provided the NiMo catalyst with a higher distribution of active metals and induced a greater difficulty in the reduction under hydrogen (H<sub>2</sub>) atmosphere. For the HDO of GUA at a mild reaction condition (10 bar initial H<sub>2</sub> pressure and 300 °C) in the absence of solvent, the Cu-promoter enhanced the hydrogenation activity of the NiMo catalyst to convert GUA to phenol and methylphenols, one-atomic oxygen species. Whereas, the addition of Ce obviously inhibited the formation of coke on the catalyst surface after a long reaction period (6 h) and gave a higher GUA conversion level with increasing yield of phenols. For the HDO of real bio-oil obtained from the fast pyrolysis of cassava rhizome, the NiMo catalysts promoted by Cu or Ce at 4 wt% based on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> content showed a higher performance at eliminating the oxygenated compounds in the bio-oil, reducing the oxygen/carbon (O/C) molar ratio by over sevenfold from 1.75 to 0.24-0.25. Moreover, the gross heating value of the bio-oil was improved from 21.5 to ca. 29.0 MJ/kg after the HDO process. However, the addition of the Cu or Ce promoter did not inhibit coke deposition, possibly due to the acidic properties of the bio-oil that deteriorated the catalyst performance by metal leaching.

#### 1. Introduction

The expanding global population and increasing economic development results in a rapidly increasing level of energy consumption, while the reliance on non-renewable fossil fuels as the sole or principal energy source leads to increasing environmental, economic and geopolitical concerns. The liquid fuels generated from biomass pyrolysis, called as "bio-oil", have potential as prospective replacement for conventional gasoline and diesel. Moreover, they provide the environmental benefit in terms of having lower emission levels of sulfur dioxide and nitrogen oxides than fossil fuels and have a zero net carbon dioxide  $(CO_2)$  release due to the  $CO_2$  consumption of plants during photosynthesis [1]. Bio-oil is classified as a multi-component mixture that mainly consists of water (10–30 wt%) and oxygenated compounds (30–40 wt%) derived from the depolymerization and fragmentation of cellulose, hemicellulose and lignin during the biomass pyrolysis. These oxygenated components in the bio-oil induce undesirable properties, such as low energy density, high thermal instability and high acidity, which make bio-oil inappropriate for direct application in current combustion engines [1–4].

To improve the quality of bio-oil, hydrodeoxygenation (HDO) is a promising method to reduce the level of those oxygenated molecules by conversion to water under a hydrogen ( $H_2$ ) atmosphere, as presented in the conceptual reaction shown in Eq. 1,

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$$CH_{1.4}O_{0.4} + 0.7H_2 \rightarrow 1CH_2 + 0.4H_2O,$$
 (1)

where  $CH_2$  represents unspecified hydrocarbon products [2]. The HDO process consists of the two steps of (i) the stabilization step, operated at a low hydrotreating temperature to convert some reactive groups in the bio-oil such as methoxyphenol, biphenols and others to less active compounds and thus provide the better quality of bio-oil and (ii) the deep deoxygenation step, which is performed under more severe condition to complete the HDO process [4]. Among the oxygenated compounds in bio-oil, guaiacol (GUA; 2-methoxyphenol), which is derived from the decomposition of lignin is normally selected as a model compound of bio-oil due to its relatively high content in bio-oil and it also contains two oxygenated functional groups: phenolic and methoxy groups, which can form high molecular weight compounds and so reduces the stability of the bio-oil [3,4].

Normally, two main groups of catalysts are applied for the HDO process [5]; (i) the noble transition metal catalysts such as palladium (Pd), platinum (Pt), ruthenium (Ru) or rhodium (Rh) supported on  $\gamma$ -alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>), zirconium oxide (ZrO<sub>2</sub>) or carbon and (ii) non-noble metal catalysts in the sulfide or oxide form such as metallic nickel (Ni) and molybdenum (Mo) and bimetallic catalysts such as Ni-Mo or cobalt (Co)-Mo supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>, which are the typical catalysts used for hydrotreating processes [2,6]. Although the latter catalyst type is more attractive and practical due to its lower cost than the noble metal-based catalysts, they need to be activated first by sulfidation or reduction.

The conventional NiMo or CoMo catalysts are normally sulfided in the presence of sulfur containing agents (hydrogen sulfide or carbon disulfide) to maintain the catalyst activity before use in the hydrodesulfurization (HDS) or HDO reactions. However, they are toxic and can contaminate the obtained products [7,8]. Without the sulfidation, the reduction performed under H<sub>2</sub> atmosphere can be applied to activate the metal-oxide catalyst precursor. Jahromi and Agblevor [9,10] reported that the reduction of Ni supported on red mud catalyst (Ni/ RM) in the presence of 10% H<sub>2</sub> and 90% nitrogen (N<sub>2</sub>) mixed gas at 450 °C for 6 h yielded an effective catalyst for the HDO of both lowmolecular-weight oxygenate compounds and bio-oil derived from the catalytic pyrolysis of pinyon-juniper. Moreover, there are some reports that unsulfided NiMo in a reduced form is an effective catalyst for the HDO of anisole [8], glacial acetic acid and the bio-oil obtained from pine sawdust pyrolysis [11]. However, the Ni-based catalysts generally suffer from a high level of coke formation that results in severe catalytic deactivation [12].

The addition of promoters is recommended to suppress coke deposition on the catalyst surface and to increase the catalytic activity. In the  $CO_2$  reforming of methane (CH<sub>4</sub>), it was observed that the addition of 1 wt% copper (Cu) onto the Ni/Al<sub>2</sub>O<sub>3</sub> enhanced the catalytic activity and stability by reducing the amount of carbon deposition [13]. This behavior was also found in the CH<sub>4</sub> and methanol steam reforming reaction. The use of a Ni-Cu/Al<sub>2</sub>O<sub>3</sub> catalyst generated only 8.9 wt% coke formation, which was almost 3.2-fold lower than that with a Ni/Al<sub>2</sub>O<sub>3</sub> catalyst (28.3 wt% coke formation) [12]. Moreover, the combination of Ni-Cu-Mo on the Al<sub>2</sub>O<sub>3</sub> support resulted in an efficient catalyst for promoting high alkane production during the HDO of fatty acid esters [14].

With respect to the use of rare earth elements as a promoter, it has been reported that a small amount of basic rare earth oxide, such as cerium (Ce), could be applied as the promoter for Ni-based catalysts, such as Ni/Al<sub>2</sub>O<sub>3</sub>, Ni supported on ZrO<sub>2</sub> or a catalyst comprised of Ni, Co and manganese supported on ZrO<sub>2</sub>, to inhibit coke formation and sintering of metallic species during the methane (CH<sub>4</sub>) reforming reaction or autothermal CO<sub>2</sub> reforming of CH<sub>4</sub> [15–17]. It also promoted a better dispersion of the metallic active sites throughout the surface of the catalyst [17].

Considering the above points, the aim of this research was to comparatively investigate the effect of Cu- and Ce-promoters on the catalytic efficiency and coke formation of NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst in the

HDO of GUA, used as a model oxygenated compound, in the absence of solvent so as to avoid the formation of byproducts generated from solvent cracking. This process was operated at a mild condition to study the catalytic performance in the stabilization step of HDO. Moreover, the promoted catalysts were applied for the HDO of real bio-oil, derived from the fast pyrolysis of cassava rhizome in order to comparatively investigate the potential to remove the oxygenated compounds in a real system.

#### 2. Experimental

#### 2.1. Chemicals and materials

The GUA ( $\geq$  99% purity) and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> ( $\emptyset$  = 150 µm) were purchased from Sigma-Aldrich (China) and Nippon Light Metal Co., Ltd. (Japan), respectively. The metal precursors used for catalyst preparasuch ammonium molybdate tetrahydrate tion. as ((NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O), nickel (II) nitrate hexahydrate (Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, extra pure), copper (II) nitrate trihydrate (Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, AR grade) and cerium (III) nitrate hexahydrate (Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O, 99% purity), were obtained from Macron Fine Chemical<sup>™</sup> (USA), Ajax Finechem Pty Ltd. (Australia), QRëC (New Zealand) and Sigma-Aldrich (China), respectively. The  $\geq$  99.99% purity H<sub>2</sub>, argon (Ar), helium (He) and 1/9 (v/v) H<sub>2</sub>/Ar mixed gases were supplied from Praxair Co. Ltd., (Thailand). Tetrahydrofuran (THF) (Fisher Scientific, Leicestershire, UK) and 2-propanol (QRëC, New Zealand) were analytical grade.

#### 2.2. Catalyst preparation

The catalyst preparation in this research was performed by the successive incipient wetness impregnation adapted from the previous literature [18]. Briefly, the 0.87 M (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>.4H<sub>2</sub>O solution (4.2 ml) and 2.02 M Ni(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O solution (4.2 ml) were sequentially impregnated onto the dried  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support (5.0 g). At each step, the obtained catalyst was dried using a rotary evaporator at 65 °C for 30 min, and then finally calcined in a furnace at 520 °C for 6 h to obtain the calcined NiMo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (hereafter referred to simply as NiMo omitting the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support designation).

For the promoted catalysts, the calcined NiMo catalyst was then further impregnated with 4.2 ml Cu(NO<sub>3</sub>)<sub>2</sub>.3H<sub>2</sub>O solution or Ce (NO<sub>3</sub>)<sub>3</sub>.6H<sub>2</sub>O solution at the desired concentrations to produce the NiMoCu or NiMoCe catalyst, respectively. The obtained promoted catalysts were also dried and calcined again as described above. The nominal amount of Cu- or Ce-promoter in the NiMo catalysts was controlled at 2, 4, 8 and 10 wt% based on the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> content and were denoted as NiMo2X or NiMo4X, NiMo8X and NiMo10X, respectively, where X was Cu or Ce-promoter.

#### 2.3. HDO of GUA

The HDO of GUA was performed in a 250-mL high pressure stirring batch reactor (Parr Instrument Company, USA) in the absence of solvent. The oxygen content in the GUA molecule was ca. 25.8%. The glass liner ( $\emptyset = 6 \text{ cm}$ ; height = 6.5 cm) containing the studied catalyst (15 wt% based on the GUA content) was put in the reactor. The air inside the reactor was removed by flushing with H<sub>2</sub> gas for 5 min before in situ reduction of the catalyst for 1 h under 10 bar initial H<sub>2</sub> pressure at 300 °C. This temperature was the maximum attainable due to the limitation of the reactor. The temperature and pressure of the system were then decreased to slightly above ambient condition and GUA (30 ml or 33.87 g) was charged into the reactor using a syringe. After purging the system with H<sub>2</sub> for 5 min, the system was pressurized to 10 bar initial H<sub>2</sub> pressure and heated up to 300 °C for 1-6 h under a constant agitation rate of 300 rpm, and then the reaction was stopped by cooling to 20 °C. The liquid and solid products were separated using a suction filtration apparatus. The solid product was then dried at 120 °C for 24 h,

while the liquid product was stored in an amber bottle and kept in the refrigerator prior to subsequent analysis.

#### 2.4. Preparation of bio-oil and HDO of the bio-oil

Typically, GUA is used as a representative compound of lignin-derived bio-oil [3]. This research used cassava rhizomes as the raw material for bio-oil production since they are an abundant renewable product including as a waste product in Thailand and contain a high portion of lignin (21.7 wt%) [19]. To prepare the bio-oil, the dried cassava rhizome powder ( $\emptyset = 212-600 \,\mu\text{m}$ ) containing 2.5 wt% moisture, 75.7 wt% volatile matter, 10.5 wt% fixed carbon and 11.3 wt % ash was pyrolyzed in the fluidized bed reactor with a feed rate capacity of 100 g/h, while silica sand ( $\emptyset = 212-600 \,\mu\text{m}$ , 150 g) was used as the fluidizing and heat transfer material.

The biomass particles were continuously fed into the reactor with the aid of a preheated  $N_2$  gas (300–400 °C) at a flowrate of 7 L/min. The pyrolysis temperature was kept constant at 500 °C. During pyrolysis, the pyrolysis vapor together with char fines was filtered by a hot vapor filtration unit using glass wool (5 g). The obtained pyrolysis vapor was rapidly condensed in a series of condensation devices using ethanol as a coolant and was then passed through an electrostatic precipitator to collect most of the aerosols by condensing into a liquid at the wall and flowing downwards into a glass bottle. The residue vapor was further cooled by two dry-ice/acetone condensers and the non-condensable gas stream was filtered by a cotton wool filter before leaving the unit. This pyrolysis condition yielded 43 wt% bio-oil, 32 wt% char and 25 wt% gas products.

The HDO of the obtained bio-oil (33 g) was also performed in the same reactor used for the HDO of GUA without the assistance of any solvent. This reaction was comparatively catalyzed by 15 wt% NiMo, NiMo4Cu or NiMo4Ce based on the bio-oil content under 10 bar initial H<sub>2</sub> pressure at 300 °C for 1 h. The procedure was similar to the HDO of GUA as described above. The mixture of liquid and solid products were dissolved in THF (50 ml) over 24 h and then separated by suction filtration and dried at 120 °C in the oven. The liquid product was purified using a rotary evaporator in order to remove THF.

#### 2.5. Catalyst characterization

The surface area, pore volume and average pore size of the prepared catalysts (0.5 g/each) were determined from N<sub>2</sub> physisorption evaluated by Micromeritics ASAP-2020 following the Brunauer-Emmett-Teller (BET) equation for calculation of the surface area and the Barrett-Joyner-Halenda (BJH) method on the N<sub>2</sub> desorption stage for the evaluation of the average pore size.

Type and crystalline matters of each calcined catalyst were evaluated by X-ray diffractometry (XRD) (Bruker, D8 Advance) using CuK $\alpha$ radiation ( $\lambda = 1.54^{\circ}$ A; 40 kV; 40 mA). The 2 $\theta$  range was scanned between 5 and 80° at a rate of 1°/s. The crystallite size (d<sub>p</sub>) of nickel oxide (NiO) and molybdenum oxide (MoO<sub>3</sub>) of all samples was calculated following the Scherrer equation [13], shown in Eq. (2);

$$d_{p} = \frac{\kappa \lambda}{\beta \cos \theta}$$
(2)

where  $\kappa$  is the Scherrer constant (0.9),  $\lambda$  is the wavelength of X-ray (1.54°A),  $\theta$  is the diffraction angle and  $\beta$  is the half-peak width (radian) [16].

The reduction temperature of all prepared catalysts was measured by H<sub>2</sub>-temperature-programmed reduction (TPR) using Micromeritics AutoChem II 2920. A 0.1 g portion of the calcined catalyst was dried under an Ar atmosphere at a flow rate of 50 ml/min from room temperature to 100 °C at a heating rate of 10 °C/min for 1 h. Then, the reduction step was performed in the presence of a 1/9 (v/v) H<sub>2</sub>/Ar mixed gas and heated from 100 °C to 900 °C at the same gas flow and heating rates. The acidic properties of the prepared catalysts were analyzed by temperature-programmed desorption of ammonia (NH<sub>3</sub>-TPD) using Belcat-Basic Chemisorption analyzer. The calcined catalyst (0.05 g) was dried using He gas at a flow rate of 50 ml/min for 30 min and then heated from ambient temperature to 300 °C at 10 °C/min and held at 300 °C for 1 h. After cooling down to 100 °C, the treated sample adsorbed NH<sub>3</sub> in the presence of 7/3 (v/v) NH<sub>3</sub>/He fed into the system at 50 ml/min for 30 min. At this temperature, non-adsorbed NH<sub>3</sub> was flushed out from the system using He gas at a flow rate of 50 ml/min for 15 min. The desorption of NH<sub>3</sub> adsorbed in the sample was performed from 100 to 600 °C at a heating rate of 10 °C/min. The eluted NH<sub>3</sub> was analyzed using a thermal conductive detector (TCD) and He gas was used as the carrier at a flow rate of 30 mL/min.

X-ray photoelectron spectroscopy (XPS) was performed on an Axis Ultra DLD spectrometer (Kratos, Manchester, UK) equipped with monochromated Al-K $\alpha$  X-ray source (h $\nu$  = 1486.6 eV) and fixed analyzer pass energy of 40 eV under ultrahigh vacuum conditions (UHV;  $3 \times 10^{-9}$  Torr). The XPS spectra were recorded using an analysis area of 700 x 300  $\mu m.$  The spectrometer also consisted of a high pressure cell (HPC) used for reduction of the prepared catalysts, which were in the oxide forms. Each catalyst sample was put into the HPC and sealed from UHV chamber. It was then reduced under 1 bar H<sub>2</sub> pressure (99.999% purity) at 300 °C for 30 min in the HPC. After reduction, the sample was transferred under UHV to the electron spectrometer for analysis. The binding energy (BE) of samples was calibrated using the C1s peak attributed to carbon surface impurities at 284.6 eV. For analysis, the background was subtracted by the Shirley method and curve-fitting was performed with the convolution of Gaussian-Lorentzian functions in the Vision 2 Processing software.

#### 2.6. Product characterization

The degree of GUA conversion, product distribution and compositions of the liquid product generated from the HDO of GUA were calculated from material balance and the peak area obtained from gas chromatography-mass spectrometry (GC-MS; Shimadzu-2010) equipped with a DB-5 column ( $\emptyset = 0.25 \text{ mm}$ ; L = 30 m) using He as the carrier gas at a flow rate of 1.65 mL/min. The initial column temperature was controlled at 40 °C for 3 min before ramping to 150 °C at 10 °C/min and then held at 150 °C for 16 min. The injection and detector temperatures were kept at 200 and 230 °C, respectively. Before analyzing, the liquid product was diluted 10<sup>3</sup>-fold using 2-propanol and then 1 µL was injected into the system with a split ratio of 1:30. The GUA conversion level and yield of each component in the liquid product were calculated following Eqs. (3) and (4), respectively:

$$GUA \text{ conversion } (\%) = \left[1 - \frac{\text{Unreacted GUA } (g)}{\text{Fed GUA } (g)}\right] \times 100$$
(3)  
Yield  $(g/g_{\text{reacted GUA}}) = \frac{\text{Selectivity} \times \text{Reacted GUA in liquid form } (g)}{\text{Total reacted GUA } (g)}$ 

(4)

where "Total reacted GUA" was the summation of the reacted GUA in liquid, solid and gas forms.

For calculation of the solid product, thermogravimetric analysis (TGA) performed by Perkin Elmer (Pyris Diamond Model) of spent catalysts under an air atmosphere was used to determine the coke formation deposited on the surface of the catalysts during the HDO of GUA. The spent catalyst (15 mg) was heated from 40 to 900 °C at 10 °C/ min in the presence of air at a flow rate of 50 mL/min. The percentage of weight loss between 200–700 °C was attributed to coke formation [20]. However, this weight loss was only a rough estimation of the amount of coke deposition, and potentially an underestimatation, due to the potential oxidation of the reduced catalysts during the TGA analysis, which could result in a marked gain in the catalyst weight.

The compositions of the liquid products, except the unreacted GUA,

were mainly classified into the two groups of (i) single oxygenated compounds (phenol + methylphenols and methoxybenzenes) and (ii) two oxygenated compounds (methoxy methylphenols, 1,2-benzenediol and 1,2-dimethoxybenzene). The selectivity of each composition obtained from any given HDO condition was calculated from the peak area of the respective GC-MS chromatograms.

#### 2.7. Characterization of real bio-oil and catalyst before and after HDO

Elemental compositions as carbon (C), hydrogen (H) and nitrogen (N) in the real bio-oil before and after HDO were measured using a CHN analyzer (Perkin-Elmer 2400 Series CHN/O Analyser), while the oxygen (O) content was calculated by difference. The gross calorific value of the bio-oil was also investigated using bomb carolimetry following ASTM 5865. The coke deposition on the surface of catalysts after reaction was analyzed by TGA as described above.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

From the textural properties of the prepared catalysts (Table 1), the NiMo catalyst had a surface area of  $34.3 \text{ m}^2/\text{g}$  with a pore volume and a pore size of  $0.08 \text{ cm}^3/\text{g}$  and 72.8 Å, respectively. The addition of Cu or Ce as a promoter (2–10 wt% based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) on the NiMo catalyst affected the textural properties of each obtained catalyst. It was observed that the addition of the Cu- or Ce-promoter at high loading levels decreased the surface area and pore volume of the catalysts with slightly decreasing the pore size when compared to the unpromoted one. This implied that the over-loading of promoters could block the pores of the NiMo catalyst resulting in a marked reduction in the surface area, pore volume and pore size of the catalysts [21].

The effect of the Cu- or Ce-promoter content on the crystalline size of MoO<sub>3</sub> and NiO of the NiMo catalyst was evaluated by XRD analysis using Scherrer's equation, with the results shown in Fig. 1 and Table 1. For the unpromoted NiMo catalyst (Fig. 1a), the diffraction peaks at a 20 of 46.0° and 49.4 corresponded to  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> [22–24]. The signals of the MoO<sub>3</sub> phase were found at a 20 of 12.7°, 23.5°, 25.8°, 27.3° and 33.9° [25], while the diffraction peaks of NiO (20 of 39.0°) [24] and nickel molybdenum oxide (NiMoO<sub>4</sub>; 20 of 14.6° and 29.4°) were also detected [26,27]. The average crystallite diameter, as calculated from the Scherrer's equation, of MoO<sub>3</sub> and NiO was 68.7 and 49.2 nm, respectively.

When the Cu-promoter was loaded onto the NiMo catalyst, new diffraction peaks at a  $2\theta$  of  $35.4^{\circ}$  and  $38.9^{\circ}$ , which corresponded to copper oxide (CuO), were observed (Fig. 1b–e). This position



**Fig. 1.** XRD patterns of the NiMo catalysts with and without the addition of Cu or Ce promoters: (a) without promoter, (b) NiMo2Cu (c) NiMo4Cu, (d) NiMo8Cu, (e) NiMo10Cu, (f) NiMo2Ce, (g) NiMo4Ce, (h) NiMo8Ce and (i) NiMo10Ce.

overlapped with that of the NiO species resulting in their difficulty to be distinguished, and was possibly due to the high dispersion degree of metals on the support [28]. This explanation is in agreement with the reduced crystallite size of the NiO and MoO<sub>3</sub> in the NiMo2Cu catalyst to 34.0 and 56.3 nm, respectively (Table 1). Thus, the addition of the appropriate Cu content could suppress the size of the active metal particles and promote a high degree of dispersion. However, the increasing amount of Cu to 10 wt% increased the crystallite size of MoO<sub>3</sub> and NiO to 70.9 and 56.5 nm, respectively.

For the NiMoCe catalyst (Fig. 1f–i), the very small diffraction peak of cerium oxide (Ce<sub>2</sub>O<sub>3</sub>) appeared at a 2 $\theta$  of 28.5° [29], which indicated the high dispersion level of CeO<sub>2</sub> throughout the surface of the catalyst. Moreover, the increasing Ce-promoter level to 8 wt% (NiMo8Ce) decreased the crystallite size of both MoO<sub>3</sub> and NiO to 52.5 and 35.3 nm,

#### Table 1

Textural properties and reduction temperature of active metals for each catalyst.

Catalyst	Textural properties			Crystallite size (nm)		Reduction temperature (°C)		
	$\frac{S_{BET}^{a}}{(m^{2}/g)}$	V <sub>p</sub> <sup>b</sup> (cm <sup>3</sup> /g)	Pore size (°A)	MoO <sub>3</sub>	NiO	$Mo^{6+} \rightarrow Mo^{4+}$	NiO	$Mo^{4+} \rightarrow Mo^{0}$ or NiAl <sub>2</sub> O <sub>4</sub>
NiMo	34.3	0.08	72.8	68.7	49.2	442	600	852
NiMo2Cu	30.1	0.06	76.3	56.3	34.0	443	516	832
NiMo4Cu	38.7	0.08	63.7	67.6	41.2	458	511	809
NiMo8Cu	25.8	0.06	69.6	69.1	45.2	451	516	838
NiMo10Cu	25.6	0.06	71.1	70.9	56.5	439	521	846
NiMo2Ce	39.7	0.08	64.2	76.5	46.4	473	670	884
NiMo4Ce	29.8	0.07	71.3	70.4	47.4	467	650	861
NiMo8Ce	27.2	0.06	71.2	52.5	35.3	470	636	833
NiMo10Ce	26.0	0.06	66.5	67.0	46.3	472	679	> 900

<sup>a</sup> BET surface area.

<sup>b</sup> Pore volume.



Fig. 2.  $H_2$ -TPR profiles of the oxide forms of NiMo catalysts with and without the addition of Cu or Ce-promoter: (a) without promoter, (b) NiMo2Cu (c) NiMo4Cu, (d) NiMo8Cu, (e) NiMo10Cu, (f) NiMo2Ce, (g) NiMo4Ce, (h) NiMo8Ce and (i) NiMo10Ce.

respectively. This result is consistent with the previous report that the use of CeO<sub>2</sub> as a promoter for CeO<sub>2</sub>-Ni/Mo/SBA-15 and Ni-Ce/MgAl<sub>2</sub>O<sub>4</sub> catalysts improved the Ni dispersion and resulted in a reduction in the metals' agglomeration [30,31]. However, the increase in the Ce content to 10 wt% (NiMo10Ce) resulted in an increased crystallite size of MoO<sub>3</sub> and NiO to 67.0 and 46.3 nm, respectively. Koo et al. [31] explained that an excess Ce content could induce Ni agglomeration resulting in the reduction of metal dispersion and specific surface area.

To test the reducibility of the prepared catalysts, the H<sub>2</sub>-TPR of all catalysts was performed with the results shown in Fig. 2 and summarized in Table 1. The results showed that the NiMo catalyst clearly exhibited three major peaks of H<sub>2</sub> consumption at 442, 600 and 864 °C (Fig. 2a). The first low-temperature peak at 442 °C was attributed to the reduction of Mo<sup>6+</sup> to Mo<sup>4+</sup> [14,22], while the intermediate reduction temperature (peak at 600 °C) was assigned to the reduction of the Ni<sup>2+</sup> on the alumina surface [22]. The highest reduction temperature (852 °C) was attributed to the reduction of the NiAl<sub>2</sub>O<sub>4</sub> spinal structure due to the strong interaction between nickel species and alumina [12,13]. However, this position could also be ascribed to the reduction of Mo<sup>4+</sup> to Mo<sup>0</sup> [22].

For the H<sub>2</sub>-TPR profile of the NiMo catalysts promoted by Cu (Fig. 2b–e), the addition of 2–10 wt% Cu significantly shifted the NiO reduction peak at the intermediate reduction temperature from 600 °C to a lower temperature in the range of 511–521 °C. Moreover, the reduction temperature of NiAl<sub>2</sub>O<sub>4</sub> or Mo<sup>4+</sup> at the highest temperature zone in the TPR profiles was also decreased to 805–846 °C, suggesting that the addition of Cu enhanced the reducibility of the NiO, NiAl<sub>2</sub>O<sub>4</sub> and Mo<sup>4+</sup> phases. This phenomenon has been observed previously in the HDO of GUA and anisole catalyzed by Ni-Cu bimetallic catalysts [32,33], where the oxides of Ni-Cu catalysts had a lower molar free energy for reduction (-100.65 kJ/mol at 25 °C) than NiO (-12.31 kJ/mol at 25 °C) [33,34].

With respect to the NiMo catalysts promoted by Ce, three major peaks of  $H_2$  consumption appeared (Fig. 2f–i), which indicated that the increasing Ce content markedly increased the reduction temperature of both MoO<sub>3</sub> and NiO phases. This implied that the addition of Ce could promote a strong interaction between NiO and CeO<sub>2</sub> and between MoO<sub>3</sub>



Fig. 3. Ni 2p XPS spectra of the reduced (a) NiMo, (b) NiMo4Cu and (c) NiMo4Ce catalysts.

and CeO<sub>2</sub>. This observation was also consistent with a previous study using a Ce-promoted NiCoMn/ZrO<sub>2</sub> catalyst for the autothermal CO<sub>2</sub> reforming of CH<sub>4</sub> [16] and Ce-promoted Ni/SBA-15 catalyst for hydrogenolysis of glycerol [35]. Thus, it could be concluded that the reducibility was ordered from high to low as: NiMoCu > NiMo > NiMoCe.

Since the addition of Cu or Ce mainly affected the reduction temperature of the NiO phase of the calcined catalysts, the chemical states of the Ni in the NiMo, NiMo4Cu and NiMo4Ce catalysts in the reduced form were evaluated by XPS analysis. After deconvolution, the bands of Ni 2p3/2 at a BE of 852, 856, 858 and 862 eV, which corresponded to the Ni<sup>0</sup>, NiAl<sub>2</sub>O<sub>4</sub>, Ni<sup>2+</sup> or very small NiO particles found at the walls of mesopores and the shake-up satellite peak, respectively [16,35-37] were observed for all samples, but at different quantities as presented in Fig. 3 and Table 2. The NiMo and NiMo4Ce catalysts had a low peak area for the band at 852 eV (6.5% and 13.2%, respectively) indicating the incomplete Ni reduction under the given reduction condition in the XPS analysis. Likewise, Jiang et al. [38] reported that the addition of Ce could strongly interact with Ni and promote NiAl<sub>2</sub>O<sub>4</sub> formation. Considering the use of a Cu-promoter, it was clearly observed that NiMo4Cu had a larger area of metallic Ni at a BE of 852 eV (64.5%). This result was consistent with the H2-TPR analysis, where the addition of Cu had the potential to promote the reducibility of Ni species in the catalysts.

The number and strength of the acid sites in the solid catalysts was evaluated by NH<sub>3</sub>-TPD analysis (Table 3). Generally, acid sites are classified according to the desorption temperature of NH<sub>3</sub> as weak (< 200 °C) medium (200–350 °C) and strong (350–600 °C) [16]. The weak, medium and strong acid sites of the unpromoted NiMo catalyst were 54, 89 and 239 µmol NH<sub>3</sub>/g, respectively. The addition of Cu at 2 wt% reduced the number of strong acid sites to 198 µmol NH<sub>3</sub>/g, while the level of weak and medium acid sites increased. The increase in the Cu loading to 4 wt% decreased the level of all acid sites and reduced the total acidity to 299 µmol NH<sub>3</sub>/g. However, a Cu loading

Table 2

Relative peak area of Ni at various BEs in the reduced catalysts, as detected by XPS analysis.

Catalyst	Peak area (%	b)				
	Ni <sup>0</sup>	Ni <sup>2+</sup>				
	852 eV	856 eV	858 eV	862 eV		
NiMo	6.5	56.2	7.4	29.9		
NiMo4Cu	64.5	18.4	13.7	3.4		
NiMo4Ce	13.2	45.5	8.5	32.8		

#### Table 3

Surface acidity of the calcined catalysts with different types and contents of promoters.

Catalyst	Acidity (mmol NH <sub>3</sub> /g)					
	Weak (< 200 °C)	Medium (200–350 °C)	Strong (350–600 °C)	Total		
NiMo	54	89	239	382		
NiMo2Cu	90	152	198	440		
NiMo4Cu	46	82	171	299		
NiMo8Cu	82	131	161	374		
NiMo10Cu	84	21	207	312		
NiMo2Ce	79	134	263	476		
NiMo4Ce	57	85	264	406		
NiMo8Ce	46	81	169	296		
NiMo10Ce	89	147	32	268		

level of 8–10 wt% increased the total acidity of the catalysts to  $312-374 \,\mu$ mol NH<sub>3</sub>/g. In particular, the increase in the Cu loading to 10 wt% markedly decreased the level of medium acid sites to 21  $\mu$ mol NH<sub>3</sub>/g, while the amount of strong acid site increased to 207  $\mu$ mol NH<sub>3</sub>/g. This was possibly due to the higher formation of copper oxide crystallites at high Cu loading level. This behavior has also been observed in Cu/Al<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> catalysts [39], where the total acidity and medium acid site of catalysts decreased with increasing Cu content up to 5 wt%.

For the NiMo catalysts promoted by Ce, the addition of 2 wt% Ce resulted in a higher total acidity (476 µmol NH<sub>3</sub>/g) due to an increase in all three acid sites. However, the increase in the Ce content to 4 or 8 wt % decreased the total acidity of the catalysts to 406 and 296 µmol NH<sub>3</sub>/g, respectively with a decreased level of all three types of acidic sites on the catalyst surface. This was due to the basic properties of Ce. In the case of NiMo10Ce, the total acidity was the lowest at 268 µmol NH<sub>3</sub>/g resulting from the marked reduction in the strong acid sites to 32 µmol NH<sub>3</sub>/g. This indicated that the high loading level of Ce (10 wt%)

promoted the strength of basic sites on the catalyst [31].

## 3.2. Proposed reaction network and effects of promoters and reaction time on the HDO of GUA

After the *in-situ* reduction of the respective catalyst under 10 bar initial H<sub>2</sub> pressure at 300 °C for 1 h, the HDO of GUA was started by charging pure GUA (30 ml) into the reactor using a syringe. The effects of the promoter type and content and the reaction time on the HDO of GUA in terms of the GUA conversion level, product distribution and composition of the liquid product were studied using univariate analysis with a central condition of 15 wt% catalyst concentration based on the GUA content and 4 wt% promoter loading based on the amount of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> under 10 bar initial H<sub>2</sub> pressure at 300 °C for 1 h. The proposed reaction network shown in Scheme 1 was derived from the compositions found in the liquid product, as evaluated by GC–MS analysis (Fig. 4) and the data available in previous literatures [3,4,40].

#### 3.2.1. Proposed reaction mechanism

Under the central condition, Fig. 4 shows representative GC-MS chromatograms of the liquid products obtained from the HDO of GUA catalyzed by NiMo, NiMo4Cu and NiMo4Ce catalysts. The liquid products contained a mixture of one-atomic oxygen products such as phenol + methylphenols (cresol), methoxybenzene (anisol) and the methyl substituted derivatives (2-methyl-methoxybenzene (o-anisole) and 4-methyl-methoxybenzene (p-anisole)) and two-atomic oxygen species such as 1,2-benzenediol (catechol), 1,2-dimethoxybenzene (2methoxyanisole) and two methyl-substituted GUAs (2-methoxy-4-methylphenol (creosol) and 2-methoxy-5-methylphenol (6-methoxy-mcresol). It was previously reported that the GUA conversion via HDO is comprised of three competing reaction pathways: the anisole, catechol and phenol production pathways [41]. However, methyl substitution of GUA was also observed in this research. Thus, phenol, catechol, methylsubstituted GUA, 1,2-dimethoxybenzene and anisole were reported as the primary products in the presence of H<sub>2</sub> atmosphere as shown in Scheme 1 for route 1-5, respectively.



Scheme 1. Proposed reaction network of the HDO of GUA using NiMo catalysts with and without the addition of a Cu- or Ce-promoter under a mild reaction condition.



Fig. 4. GC–MS chromatograms of the liquid products obtained from the HDO of GUA using the (a) NiMo, (b) NiMo4Cu and (c) NiMo4Ce catalysts (Central condition: catalyst concentration = 15 wt% based on the GUA content at 10 bar H<sub>2</sub> pressure and 300 °C for 1 h).

Although the HDO of GUA under a mild condition would be expected to be directly transformed as phenol with the formation of methanol via demethoxylation (route 1 in Scheme 1) [4], Runnebaum et al. [40] reported that the HDO route catalyzed by  $Pt/\gamma$ -Al<sub>2</sub>O<sub>3</sub> had a pseudo-first-order rate constant of 4.4 L/gcatalyst h, which was lower than that of the demethylation via hydrogenolysis of the methyl-oxygen bond in the methoxy functional group to form 1,2-benzenediol and methane  $(6.5 \text{ L/g}_{catalyst} \cdot h)$  as shown in route 2 in Scheme 1. One of the hydroxyl groups of 1,2-benzenediol was subsequently eliminated to form phenol later. Moreover, it was observed that the formation of methoxy methylphenols and 1,2-dimethoxybenzene occurred via methyl substitution or transalkylation of GUA (routes 3 and 4 in Scheme 1). A small amount of methoxybenzene was also detected after a long reaction time (see Fig. 6, Section 3.2.2), which was possibly due to the slow reaction rate resulting in a low content of its methyl-substituted derivatives [40]. In addition, the methoxybenzene and its methyl-derivatives were intermediates that could be converted to phenol and methylphenols via hydrogenolysis and transalkylation or demethylation, respectively [40].

#### 3.2.2. Effect of the promoter type and content

The effect of the Cu- and Ce-promoter content (2–8 wt% based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> content) on the catalytic activity of the NiMo catalyst for GUA conversion, product distribution and composition of the liquid product is summarized in Fig. 5. The NiMo catalyst provided a GUA conversion level of 29.4% with 52.7, 42.5 and 4.79 wt% liquid, gas and solid products, respectively (Fig. 5a). With respect to the quality of the obtained liquid product (Fig. 5b), a low content of phenol + methylphenols (0.08 g/g<sub>reacted GUA</sub>) was observed.

With 2–4 wt% Cu loaded as the promoter for the NiMo catalyst, the GUA conversion level was decreased to 17.5–21.8% with a higher liquid (60.6–66.3 wt%) and lower gaseous (29.2–36.0 wt%) product levels than that with the unpromoted NiMo catalyst. Moreover, the solid product was 3.45–4.49 wt%, which was lower than that with the unpromoted NiMo catalyst. It was possible that the addition of Cu retarded the hydrogenolysis activity and CH<sub>4</sub> formation by the Ni portion in the catalyst and so resulted in the lower amount of gaseous product [32,42].

Considering the liquid product, the addition of 2–4 wt% Cu increased the yield of phenol + methylphenols to 0.17-0.25 g/g<sub>reacted GUA</sub>, while the formation of methoxybenzenes (0.04-0.05 g/g<sub>reacted GUA</sub>) was observed. This indicated that the addition of the appropriate amount of Cu-promoter enhanced the hydrogenation activity of Ni in the bimetallic Ni-Cu catalyst to convert GUA into phenol derivatives and

methoxybenzenes resulting in a higher HDO efficiency (route 1 and 5 in Scheme 1) [33]. Although it has previously been reported that the addition of Cu could provide a higher catalyst stability by inhibiting coke formation and sintering [33,42], an overdose of Cu (8 wt%) generated a high gaseous product level (51.3 wt%) and a higher amount of solid product (5.41 wt%) with a decreased total content of one-oxygen atom species in the liquid product to 0.18 g/g<sub>reacted GUA</sub>. This could be explained from the XRD results, where the excess Cu loading accumulated on the surface of the catalyst and induced a large size of active metals that resulted in a reduced HDO catalytic activity and enhanced



**Fig. 5.** Effect of the promoter type and content on the (a) GUA conversion and product distribution and (b) liquid compositions obtained from the HDO of GUA (Condition: catalyst concentration = 15 wt% based on GUA content at 10 bar H<sub>2</sub> pressure and 300 °C for 1 h).



**Fig. 6.** Effect of the reaction time on the (a) GUA conversion and product distribution and (b) liquid compositions obtained from the HDO of GUA (Condition: catalyst concentration = 15 wt.% based on the GUA content at 10 bar H<sub>2</sub> pressure and 300 °C).

carbon deposition [13].

For the Ce-promoter, the addition of 2-8 wt% Ce into the NiMo catalyst increased the GUA conversion level to 21.8-34.5% with a higher amount of liquid product at 59.5-75.0 wt%. Thus, the increased basicity of the catalysts may result in a lower amount of gaseous product and so a reduced pyrolytic carbon formation [30]. However, the addition of the Ce-promoter under this central condition did not promote the HDO reaction and resulted in a lower content of phenol + methylphenols (0.02–0.05 g/ $g_{reacted GUA}$ ). Rather the NiMoCe catalysts mainly converted GUA into 1,2-benzenediol (catechol) and 1,2-dimethoxybenzene depending on the Ce content. The formation of 1,2benzenediol from GUA as one of the primary products has also been observed previously in the HDO of GUA using a CeO<sub>2</sub>-ZrO<sub>2</sub> catalyst [43]. The production of 1,2-benzenediol from GUA in the presence of hydrochloric acid at 280 °C was also promoted in the presence of H<sub>2</sub> to give CH<sub>4</sub> as a by-product [44]. Thus, the conversion of GUA to 1,2benzenediol was shown as route 2 in Scheme 1. Moreover, it was reported that the addition of Ce at an appropriate content increased the Ni dispersion and resulted in a higher level of CH<sub>4</sub> formation via CO<sub>2</sub> methanation [45]. The obtained CH<sub>4</sub> then possibly further reacted with GUA to form 1,2-dimethoxybenzene (route 4 in Scheme 1).

Considering the solid product generated during the HDO catalyzed by the Ce-promoted NiMo catalysts, the addition of Ce at 2 wt% increased the solid product level from 4.79 to 7.06 wt%, whereas the increasing Ce content to 8 wt% markedly decreased the solid product level to 3.78 wt%. This phenomenon could be explained by three reasons. Firstly, the coke formation might be related to the size of the Ni particles as seen in XRD analysis (Table 1), where the addition of 2–4 wt % Ce was insufficient to decrease the size of the Ni particles and resulted in a high amount of coke on the surface of the catalysts. However, the increase in the Ce content to 8 wt% effectively reduced the size of the Ni particles and provided a lower carbon deposition on the catalyst surface. Secondly, although the smaller size of Ni particle might provide more CH<sub>4</sub> formation, the produced CH<sub>4</sub> during the HDO of GUA was consumed in methyl-substitution or transalkylation to form 1,2dimethoxybenzene or methoxy methylphenols (route 4 and 3, respectively in Scheme 1). Lastly, the lower level of coke formation in Ni-Mo8Ce might relate to the reduction step, which provided Ce with electron-rich oxygen vacancies. The released free electrons possibly migrated from the Ni-CeO<sub>2</sub> interface to Ni<sup>0</sup> resulting in a higher electron density that inhibited the CH<sub>4</sub> cracking reaction and so reduced the coke formation [15,30]. This observation was consistent with previous reports that Ce-promoted Ni/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts produced less coking (2.64 wt%) than the unpromoted one (3.45 wt%) during the catalytic reforming of wood vinegar to H<sub>2</sub> [46].

#### 3.2.3. Effect of the reaction time

The influence of the reaction time on the HDO of GUA was assayed with 15 wt% NiMo, NiMo4Cu or NiMo4Ce catalysts based on GUA content using 10 bar initial  $H_2$  pressure and 300 °C for 1–6 h. The longer reaction time enhanced the GUA conversion level for all applied catalysts and provided a higher and lower amount of liquid and gaseous products, respectively (Fig. 6a). This implied that the longer reaction time had a positive effect on the GUA conversion level and achieved a higher quantity of liquid product under low  $H_2$  pressure.

Considering the liquid product composition obtained from the HDO of GUA catalyzed by the NiMo and NiMo4Cu catalysts, the increase in the reaction time from 1 to 3 h increased the total content of oneoxygen atom products (phenol + methylphenols and methoxybenzenes) from 0.09 to  $0.18\,g/g_{reacted\ GUA}$  and 0.27 to  $0.35\,g/g_{reacted}$ <sub>GUA</sub>, respectively (Fig. 6b). However, further increase in the reaction time to 6 h decreased the amount of phenol + methylphenols to 0.13 and 0.27 g/g<sub>reacted GUA</sub> for NiMo and NiMo4Cu, respectively. Moreover, a markedly increased content of 1,2-benzenediols was observed with longer reaction time, and could be explained via the pseudo-first-order rate constants for the reaction network of GUA conversion using Pt/y- $Al_2O_3$  catalyst in the presence of  $H_2$  [40]. In that study, GUA was preferentially converted to 1,2-benzenediol via hydrogenolysis (route 2 in Scheme 1) at a faster rate (pseudo-first-order rate constant of 6.5 L/ g<sub>catalvst</sub>·h) than the HDO reaction for converting GUA into phenol (4.4 L/g<sub>catalyst</sub>·h). Thus, it was possible that the amount of  $H_2$  remaining after the hydrogenolysis of GUA might not be sufficient to further convert 1,2-benzenediol to phenol under the given reaction condition. However, the amount of 1,2-benzenediol generated with NiMo4Cu was lower than that with NiMo because Cu can suppress the CH<sub>4</sub> production from hydrogenolysis [14,42]. Subsequently, a low content of methoxy methylphenols (route 3 in Scheme 1) was generated from transalkylation at the slower rate (pseudo-first-order rate constant of only 0.50 - $0.21 \text{ L/g}_{\text{catalyst}} \cdot h)$  [40].

For the Ce-promoter, Fig. 6b indicated that the NiMo4Ce catalyst gave different results to the NiMo and NiMo4Cu catalysts. The increase in the reaction time from 1 to 6 h with NiMo4Ce markedly increased the total amount of phenol + methylphenols and methoxybenzene from 0.03 to  $0.24 \text{ g/g}_{\text{reacted GUA}}$ . This indicated that the NiMo4Ce catalyst required a longer reaction time for activation since Ce could increase the metal dispersion throughout the catalyst surface resulting in retardation of the reduction of the active metals, as described in Section 3.1. Moreover, a higher amount of phenol + methylphenols with the reduction of 1,2-dimethoxybenzene was observed at long reaction time. This could be explained from the proposed reaction mechanism in Scheme 1, where a longer reaction time promoted a higher conversion of 1,2-dimethoxybenzene to methoxybenzene, which could then be transalkylated to obtain a higher amount of methylphenols.

Table 4 shows the comparative conversion and product selectivity in the HDO as the function of the reaction time. The NiMo and NiMoCu catalysts preferred the hydrogenation pathway (route 2 in Scheme 1) to convert GUA to 1,2-benzenediol. The addition of Cu also increased the hydrogenation ability of Ni in the catalyst to further convert 1,2-benzenediol as phenol. Whereas, the use of Ce-promoter might activate

Table 4

Comparative conversion and product selectivity in the HDO of GUA catalyzed by NiMo, NiMo4Cu and MiMo4Ce under 10 bar initial H<sub>2</sub> pressure at 300 °C for 6 h.

(·	-)		Product selectivity (%)						
		Phenols (Route 1)	1,2-Benzenediol (Route 2)	Methoxy methylphenols (Route 3)	1,2-Dimethoxybenzene (Route 4)	Methoxybenzenes (Route 5)			
NiMo 62 NiMo4Cu 43 NiMo4Ce 56	$2.8 \pm 0.58$ $3.3 \pm 0.58$ $6.7 \pm 3.70$	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$	$58.3 \pm 0.33 \\ 42.9 \pm 0.54 \\ 38.9 \pm 1.03$	$\begin{array}{rrrr} 9.42 \ \pm \ 0.08 \\ 7.12 \ \pm \ 0.51 \\ 8.22 \ \pm \ 0.41 \end{array}$	$9.92 \pm 0.00$ 16.1 ± 0.18 20.8 ± 2.45	$\begin{array}{rrrr} 4.76 \ \pm \ 0.01 \\ 2.11 \ \pm \ 0.38 \\ 2.56 \ \pm \ 0.01 \end{array}$			

transalkylation (route 4 in Scheme 1) to firstly obtain 1.2-dimethoxybenzene, which could then be converted to methoxybenzene and methanol. The methoxybenzene could be further converted to phenol and methylphenols via hydrogenolysis and transalkylation, respectively. Runnebaum et al. [40] reported that the hydrogenolysis of methoxybenzene had a greater pseudo-first-order rate constant as 12 L/ g<sub>catalyst</sub>·h for the HDO of GUA catalyzed by Pt/γ-Al<sub>2</sub>O<sub>3</sub>. However, the direct transformation of GUA to phenol or methoxybenzene via HDO had lower pseudo-first-order rate constant of 4.4 and 0.11 L/gcatalyst-h, respectively. Thus, it was possible that the NiMoCe preferred to the transalkylation pathway to promote a higher production of 1,2-dimethoxybenzene from GUA, which was easier to be converted to methoxybenzene and phenol. This observation was confirmed using NiMo8Ce (Fig. 6b), where the long reaction time (6 h) gave a higher yield of liquid product (91.8 wt%) with lower gas formation (6.46 wt %). The amount of methoxybenzene increased with increasing amounts of phenol + methylphenols, while a lower content of 1,2-benzenediol was noticed. It was possible that the 1,2-benzenediol was converted to phenol in this long reaction time. The CH<sub>4</sub> generated during hydrogenolysis of GUA to 1,2-benzenediol was then reacted with GUA to produce methoxy methylphenols, which were further hydrogenated to methylphenols.

Considering the solid product, the addition of Cu or Ce as a promoter on the NiMo catalyst could effectively inhibit the formation of coke in the long term operation (6 h). The HDO of GUA catalyzed by NiMo4Ce or NiMo4Cu produced a solid product of only 2.46 and 3.49 wt%, respectively. Moreover, the increase in Ce loading to 8 wt% based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> content generated a lower solid product of only 1.72 wt%, whereas the HDO of GUA catalyzed by NiMo provided 4.82 wt% solid after 6 h. Thus, it was concluded that the addition of Cu or Ce promoter into the NiMo catalyst inhibited coke formation via suppression of CH<sub>4</sub> formation by reducing the hydrogenolysis of Ni or enhancing the electron density of Ni, respectively.

The thermal decomposition of the carbon deposited on the catalyst surface was analyzed by TGA. The derivative thermogravimetric (DTG) curves (Fig. 7) showed that all the used catalysts exhibited one



Fig. 7. DTG of TGA thermograms of the spent NiMo, NiMo4Cu and NiMo4Ce catalysts after the HDO of GUA.

exothermic peak obtained from the oxidation of coke formed on their surface at a moderate temperature in the range of 200–500 °C. The maximum temperature of the coke decomposition was ca. 330-340 °C, attributed to soft coke, which would be easy to remove for catalyst regeneration [20,47].

#### 3.3. HDO of bio-oil

To compare the efficiency of the NiMo catalysts with and without the addition of Ce or Cu promoters at 4 wt% based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> on the HDO of real bio-oil, the reaction was performed at 10 bar initial H<sub>2</sub> pressure and 300 °C for 1 h and the amount of catalyst was kept constant at 15 wt% based on bio-oil. The results (Table 5) indicated that the real bio-oil, derived from the fast pyrolysis of cassava rhizome, had a high O/C mole ratio (1.75) with a low gross heating value (21.5 MJ/kg) due to the low contents of both C and H atoms. After the catalytic HDO, the quality of the bio-oil was improved in terms of the lower content of oxygenated compounds and higher heating value of the obtained hydrogenated bio-oil (HBO). Without the use of promoters, the HDO using the NiMo catalyst provided a HBO with 52.5% lower oxygen content than the original one. The addition of 4 wt% Cu or Ce based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> improved the efficiency of the NiMo catalyst in terms of a higher elimination of oxygenated compounds (ca. 66% reduction) due to the ability of Cu and Ce to promote hydrogenation [33] and hydrodecarboxylation [24], respectively. This also provided a higher gross heating value in the HBO (ca. 29 MJ/kg) than that in the untreated biooil (21.5 MJ/kg).

Although the results from the HDO of GUA indicated the efficiency of Cu and Ce on the suppression of carbon formation, the HDO of bio-oil catalyzed by NiMo promoted by Cu or Ce induced a higher amount of coke formation from 40.9 wt% to 51–54 wt% based on the spent catalyst content. The large amount of coke significantly decreased the surface area of the catalysts and induced the catalyst deactivation, as reported by Jahromi and Agblevor [48]. Although deactivation of a Ni-

Table 5

Analysis of the bio-oil properties before and after HDO using NiMo catalyst with and without the addition of Cu- or Ce-promoter.

	Bio-oil	HDO-bio-oil				
		NiMo	NiMo4Cu	NiMo4Ce		
Elemental analysis (wt%)						
С	28.2	59.2	67.7	67.8		
Н	4.6	6.8	7.1	7.1		
Ν	1.3	2.7	2.9	2.9		
O <sup>a</sup>	65.9	31.3	22.3	22.2		
		(52.5% O-	(66.2% O-	(66.3% O-		
		removal)	removal)	removal)		
O/C (by mole)	1.75	0.40	0.25	0.24		
Gross heating value (MJ/kg)	21.5	25.8	29.2	29.0		
Coke (wt%) <sup>b</sup>	-	40.9	51.1	54.3		

<sup>a</sup> Calculated from difference.

<sup>b</sup> Based on the weight of the spent catalyst.

based catalyst was reported to result from the coke deposition and the lost interaction between Ni particles and support inducing the oxidation of Ni [48], the Ni oxidation might be a less important factor for catalyst deactivation during HDO of real bio-oil since the residual water in the bio-oil could inhibit the oxidation of Ni particles [48]. Moreover, it was possible that some active metals or promoters might have been leached from the catalyst due to the high acidity of the bio-oil, which would result in a lower efficiency of the promoters to retard coke formation [32].

#### 4. Conclusions

This study investigated the effect of Cu and Ce as a promoter for a NiMo catalyst in the HDO of GUA and bio-oil. The addition of Cu enhanced the reducibility of the NiMo catalyst, whilst the addition of Ce at an appropriate quantity (< 10 wt% based on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> content) induced a higher dispersion of active metals and provided a difficulty to reduce the catalysts. For the HDO of GUA under a mild reaction condition (10 bar initial H<sub>2</sub> pressure and 300 °C for 1 h), the use of NiMo4Cu catalyst exhibited the highest yield of phenol and methylphenols formation (0.31 g/g<sub>reacted GUA</sub>) reflecting the high HDO performance due to the ability of Cu to catalyze the hydrogenation of GUA to phenol compounds. For the addition of Ce as a promoter, the NiMo4Ce catalyst required a long reaction time (6 h) to provide a liquid product with a higher content of one-oxygenated species. Moreover, it was clear that the addition of Ce could effectively inhibit coke formation during the HDO of GUA at this longer reaction time (6 h). It was possible that the migration of electrons from CeO<sub>2</sub> during the reduction could induce a higher electron density of Ni° to suppress CH<sub>4</sub> formation, the source of coke deposition on the catalyst surface. For the HDO of real bio-oil obtained from pyrolysis of cassava rhizomes, the NiMo4Cu and NiMo4Ce catalysts could eliminate more oxygenated compounds and provide a bio-oil with a higher gross heating value (from 21.5 to 29 MJ/kg). However, they did not inhibit the coke formation, which was possibly due to the acidity of the bio-oil leaching the promoters from the catalysts.

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