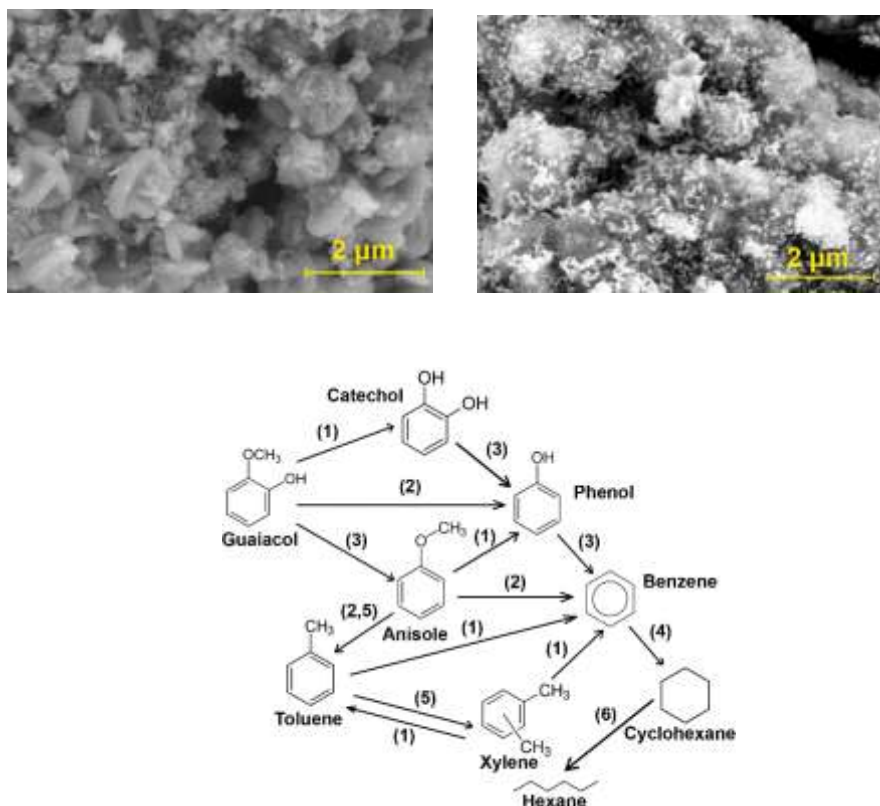


Hydrotreating of guaiacol: A comparative study of Red Mud-supported nickel and commercial Ni/SiO₂-Al₂O₃ catalysts

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Graphical abstract



Highlights

- Red Mud can serve as nickel catalyst support for hydrodeoxygenation reactions.
- Ni/RM improves deoxygenation over hydrogenation compared to commercial Ni/SiO₂-Al₂O₃.
- Ni/RM catalyst moderates hydrocracking and coke formation versus commercial Ni/SiO₂-Al₂O₃.
- Coke deposition, oxidation of nickel, and formation of iron nickel oxide contribute to deactivate Ni/RM catalyst during HDO.

Abstract

Upgrading of bio-oil through catalytic hydrotreating was investigated with guaiacol as a model compound. A nickel supported on red mud (Ni/RM) hydrotreating catalyst was developed and compared to the standard Ni/SiO₂-Al₂O₃ catalysts under similar experimental conditions. The Ni/RM catalyst was characterized by inductively coupled plasma atomic emission spectrometry (ICP-AES), X-ray diffraction analysis (XRD), scanning electron microscopy (SEM), BET specific surface area, and temperature programmed reduction (TPR). The effects of reaction temperature (300, 350, 400 °C) and initial hydrogen pressure (4.83 MPa (700 psi), 5.52 MPa (800 psi), and 6.21 MPa (900 psi)) on products distribution were investigated. The major products of hydrotreating process were catechol, anisole, phenol, cyclohexane, hexane, benzene, toluene, and xylene. Increasing the reaction temperature and hydrogen pressure improved HDO

reactions. Complete HDO was achieved at reaction temperature of 400 °C and initial hydrogen pressure of 6.21 MPa (900 psi). Under these conditions, the selectivity to cyclohexane, benzene, toluene, and xylene over Ni/RM catalyst were 38.8, 24.5, 18.1, and 7.9% respectively, whereas these values were 62.2, 15.9, 8.4, and 4.5% respectively over Ni/SiO₂-Al₂O₃. Reaction network and the kinetics of guaiacol HDO were proposed according to analysis of the products. The Ni/RM catalyst was more effective for deoxygenation reactions than hydrogenation while commercial Ni/SiO₂-Al₂O₃ was more effective for hydrogenation than deoxygenation. Thus, hydrogen consumption per gram of bio-oil was lower for the Ni/RM catalyst compared to the Ni/SiO₂-Al₂O₃. There was less hydrocracking and coke formation for the Ni/RM compared to the commercial catalyst and this resulted in higher liquid yield for the new catalyst.

Keywords: Guaiacol; hydrodeoxygenation; red mud; nickel catalyst; pyrolysis

1. Introduction

Biofuels are emerging as a promising substitute to fossil fuels, as they are renewable and contribute to lower CO₂ emissions [1-4]. Fast pyrolysis is an attractive thermochemical conversion process to generate alternative liquid fuels from biomaterials [5, 6]. These pyrolysis oils (crude bio-oils) are multicomponent mixtures of a large number of oxygenated compounds. However, the high oxygen content of crude bio-oils, usually 20 to 50 wt. %, results in a low heating value, poor stability, poor volatility, high viscosity and corrosiveness [7-12]. Therefore, oxygen removal from bio-oils is necessary for further application as liquid fuels.

Noble metal [13-16] and transition metal sulfide [17-20] catalysts have been studied for this purpose. Noble metals are relatively costly and they catalyze hydrogenation of aromatic rings [21, 22], which is undesirable in fuel production. Noble metal catalysts suffer from deactivation due to oxidation or hydrolysis of the active phase unless a sulfiding agent is added [1, 23-25] which increases the risk of product contamination. Thus, it is vital to find alternative catalysts for HDO applications in bio-oil upgrading.

Red mud (RM) is a caustic by-product of processing of bauxite that is generated in the industrial production of alumina using the Bayer process [26]. There are many problems with managing RM slurry including costly maintenance of RM ponds, risk of caustic pollutants for all living organisms, and leakage of alkaline contaminants into groundwater resources [26, 27]. The main chemical components of RM are Fe_2O_3 , Al_2O_3 , SiO_2 , CaO , Na_2O , and a number of minor metal oxides of Cr, V, S, Ni, Cu, Mn, Zn, Mg etc. [27]. RM has been tested as catalyst for various applications, including pyrolysis of biomass [28, 29], hydrogenation and liquefaction of coal and biomass [30-35], hydrodechlorination and desulfurization reactions [36-38], methanogenesis reaction [39] and exhaust gas clean-up [40, 41]. The RM conversion into a value added product such as heterogeneous catalyst will be a desirable technology for the final fate of the residue.

Bio-oil is a complicated mixture of more than two hundred compounds such as aromatics, aliphatics, aldehydes, ketones, and ethers. Therefore it is difficult to interpret the HDO results of the actual bio-oil [12]. Although there are too many cross-interactions between bio-oil compounds, guaiacol is a suitable model compound representing the decomposition products of lignin pyrolysis, as it contains phenolic hydroxyl and methoxy groups like many degradation products of lignocellulose [2, 3, 42, 43]. It has been reported that incorporation of Mo and V in Ni/TiO₂ catalyst improved the catalyst performance for the HDO of guaiacol. In aqueous

medium, Ni-V/TiO₂ was more effective resulting in better guaiacol conversion than Ni-Mo/TiO₂ and showing more tolerance for water [44]. Ni metal was effective for ring opening activity while Co favored deoxygenation activity. The Ni catalyst favored the multiple hydrogenolysis of C-C bond, leading to carbon loss via methanization. Cobalt not only facilitated the reduction and dispersion of nickel metal oxides but also enhanced the HDO activity of bimetallic Ni-Co catalyst [45]. Hydrodeoxygenation of guaiacol using silica alumina supported Ni-Pd and Ni-Pt overlayer catalysts under atmospheric pressure showed that Pd and Pt active sites of overlayer catalysts significantly enhanced deoxygenation activity and the BTX selectivity could be up to 80% on Ni-Pd overlayer catalyst [46]. HDO of guaiacol over NiB/SiO₂-Al₂O₃ and Ni/SiO₂-Al₂O₃ catalysts showed that the conversion of guaiacol and the selectivity to cyclohexane were much higher on the former than the latter [47]. However, SiO₂-supported Ni-Mo bimetallic catalyst showed high selectivity towards AR-O bond cleavage in the HDO reactions of anisole, phenol and guaiacol, giving BTX selectivity more than 96% [48]. Lately, Mora-Vergara et al. [49] showed that the addition of potassium to alumina-supported NiMo and CoMo catalysts promoted selectivity to deoxygenated compounds in the HDO of guaiacol.

A potential method of reducing the cost of HDO process, is the development of new HDO catalysts from low cost materials. Red mud has interesting properties such as active components and relatively large surface area. The main objective of this research work is to evaluate the performance of RM-supported nickel catalyst for hydrodeoxygenation of bio-oils and guaiacol was used as a model compound for biomass pyrolysis oil. In view of the stability and poisoning resistance of RM, it can be a catalyst support for Ni in HDO process and it would be potentially much more cost-effective in comparison with other catalyst supports such as Al₂O₃, SiO₂, and

TiO₂ that require complicated preparation procedures. In this paper the performance of the Ni/RM is compared with commercial Ni/SiO₂-Al₂O₃ obtained from Sigma Aldrich.

2. Material and methods

2.1. Material

Guaiacol, anisole, catechol, and nickel nitrate hexa hydrate (Ni(NO₃)₆H₂O) were purchased from Alfa Aesar (Haverhill, MA, USA). Cyclohexane and toluene were bought from Pharmco-Aaper (Brookfield, CT, USA). Commercial nickel on silica/alumina (~65% wt. % Ni loading) catalyst powder, benzene, and phenol were purchased from Sigma Aldrich (St. Louis, MO, USA). Hexane and xylene were obtained from Fisher Scientific (Hampton, NH, USA). All chemicals were analytical grade and were used as received without any further purification. High purity (99%) hydrogen (Airgas, PA, USA) was used for HDO experiments.

2.2. Preparation and characterization of Ni/RM catalyst

Ni/RM catalysts were prepared at 40 wt. % nickel metal loading using wet impregnation method [50, 51]. The calculated amount of Ni(NO₃)₆H₂O equivalent to 40 wt. % nickel metal loading was dissolved in 100 ml deionized water and then mixed with red mud (particle size < 90 μm). The mixture was heated to 70 °C and continuously stirred for 5 hours to prepare the catalyst precursor. The catalyst precursor was dried at 105 °C for 10 hours and then calcined in air at 620 °C in a muffle furnace (Thermo Scientific, Inc., Waltham, MA, USA) for 5 hours. The calcined material was reduced for 6 hours at 450 °C using a reducing gas mixture of 10% H₂ and 90% N₂ at flow rate of 20 ml/min to obtain the final catalyst.

The Brunauer-Emmet-Teller (BET) specific surface area of the catalysts were determined on a MS-16 BET analyzer (Quantachrome Instruments, Boynton Beach, FL, USA). About 0.1 g catalyst sample was used in each measurement. Prior to the analysis, the catalyst samples were milled into fine powder using a SPEX Certiprep 6750 cryogenic miller (Metuchen, NJ, USA). All samples were degassed at 300 °C for 4 hours prior to duplicate measurements. A porous Al₂O₃ standard was measured along with each run to ensure consistency between the different samples.

Metal loading determination was carried out using inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis. For this purpose, 0.5 g catalyst sample was digested in nitric acid at 95 °C for 1 h. Then 12 ml, 30 wt. % hydrogen peroxide was added to the digestion tube and cooled to room temperature [52]. The extracts were measured using a Thermo iCAP 6300 ICP-OES Inductively-Coupled Plasma Spectrophotometer (Thermo Fisher Scientific, Waltham, MA, USA) with Optical Emission.

Thermo gravimetric-temperature programmed reduction (TG-TPR) studies were carried out using a TGA Q500 (TA Instruments, Lindon, UT, USA). Twenty-five milligrams of catalyst (calcined form) was heated in a flow of 10% H₂ / 90% N₂ (20 ml/min) from room temperature to 700 °C at a heating rate of 10 °C/min. Hydrogen uptake was monitored by the change in sample weight according to the plot of derivative weight vs. temperature.

X-ray powder diffraction (XRD) analyses were carried out by Hazen Research Inc. (Golden, CO, USA). The samples were ground in a mortar and pestle with isopropyl alcohol and analyzed using a Bruker D8 Advance with Davinci design and a Lynxeye detector. The diffraction pattern was measured in the interval from 5 to 85 in 2 θ using a 0.02 step size and 40 s of counting time.

Scanning electron microscopy (SEM) analysis was conducted on a FEI Quanta FEG-650 (Thermo Fisher Scientific, MA, USA). For preparation of the specimens a small amount of catalyst was placed on a two-sided sticky tape resting on an aluminum holder and observed at different magnifications. Images were recorded using low vacuum secondary electron (LFD) detector.

2.3. Hydrodeoxygenation (HDO) experiments

All experiments were conducted in a Parr Series 4560 300 mL autoclave reactor (Parr Instruments, Moline, IL, USA). This reactor had a variable speed magnetic drive and turbine agitator. A temperature sensor, immersed in the reactor content, was used to measure the liquid temperature. The reaction temperature was maintained at its desired value with an accuracy of ± 1 °C. The setup had an electrically heated jacket to ensure isothermal conditions. The temperature and speed of agitation were controlled by using a Parr 4848 controller. In each experiment, the reactor was charged with guaiacol (30 g) and catalyst (4.5 g). The reactor was then purged with N₂ to ensure an inert atmosphere. The reactor was then charged with high purity hydrogen supplied from a reservoir tank to desired pressures of 4.83, 5.52, or 6.21 MPa (700, 800, or 900 psi) via a pressure regulator. A gas sample was taken from a gas release valve from the gas sampling port for gas analysis when the reactor was at room temperature. The reactor was then heated to reaction temperature (300, 350, or 400 °C) at heating rate of 15 °C/min. The reaction time was recorded when the set temperature was reached. The reactor content was stirred at the desired speed of agitation (~1000 rpm) for all experiments. Seven liquid samples were collected at fixed time intervals for kinetic studies. Every time, a sample volume equal to 0.3 cm³ was collected. The change in volume of liquid inside the reactor was negligible. After the desired

reaction time (30 minute), the reactor was cooled to room temperature using the internal cooling coil and an external air fan simultaneously. A gas sample was collected in a tedlar bag for gas analysis when the reactor was cooled to room temperature. The reproducibility of experiments was checked and the error in all experimental measurements was found to be less than 3%.

In a blank experiment (without catalyst) 30 g of guaiacol was charged into the reactor and the reactor was pressurized to 6.2 MPa (900 psi) with hydrogen and allowed to react for 30 minutes at 400 ° C. All experiments were conducted in triplicate.

2.4. Analysis of HDO products

Hydrogen consumption, gas analysis, and product yields were determined as described in previous work [12]. The liquid products of HDO experiments were analyzed by HPLC (Shimadzu Scientific, Columbia, MD) using a RID-10A detector and a Kromasil 100-5-C18 column obtained from AkzoNobel (Amsterdam, Netherlands). The HPLC was equipped with a LC-10AT pump, SCL-10Avp controller, and SIL-10A autosampler. CLASS-VP 7.3 SP1 software was used to analyze HPLC chromatograms. A CTO-10A column oven was used to maintain the column temperature at 55 °C during the analysis. The injection volume was 0.25 µl and acetonitrile at flow rate of 0.6 ml/min was used as the mobile phase. Data acquisition time was 60 minutes for all analyses.

The liquid samples were analyzed for guaiacol, anisole, catechol, phenol, cyclohexane, hexane, benzene, toluene, and xylene. To quantify the amount of each compound, five solutions of 20, 40, 60, 80, and 100 wt. % of each compound were prepared and injected to HPLC system and peak area vs. concentration was plotted to obtain the calibration curve of the compounds.

The elemental composition of HDO products were determined using ThermoFischer Scientific Flash 2000 organic elemental analyzer (ThermoFisher Scientific, Waltham, MA, USA), and the oxygen content was calculated by difference according to ASTM D5291.

Conversion of guaiacol and product selectivity were calculated using equations (1) and (2) respectively [53]:

$$\text{Conversion \%} = \frac{\text{Moles of guaiacol reacted}}{\text{Moles guaiacol fed}} \times 100 \quad (1)$$

$$C_p \text{ Selectivity \%} = \frac{\text{moles } C_p}{\sum \text{moles } C_p} \times 100 \quad (2)$$

Where C_p represents the content of products.

Kinetic studies using integral method was perform to estimate the reaction rate equations according to equation (3) [54].

$$-r_G = \frac{dC_G}{dt} = k \cdot C_G^n \quad (3)$$

Where r_G is the rate of disappearance of guaiacol, C_G is the concentration of guaiacol at time t , k is the reaction rate constant and n is the reaction order.

The water content of the aqueous products were determined by Karl-Fischer titration method using Hydranal® -composite 5 solution. A Metrohm 701KF Titrino and 703 titration stand setup (Brinkmann Instruments, Riverview, FL, USA) were used for the volumetric Karl Fischer titration.

3. Results and discussion

3.1. Characterization of Ni/RM catalyst

RM (in reduced form) was tested in HDO experiment to investigate whether the support had HDO activity or it acted as an inert support. The BET specific surface area of RM support (calcined form) was relatively low ($37.5 \text{ m}^2/\text{g}$). Reduction of the calcined RM increased its specific surface area to $54.3 \text{ m}^2/\text{g}$. The increase in specific surface area was attributed to reduction of some metallic oxides.

The specific surface area of the Ni/RM catalyst precursor (calcined form) was $51.3 \text{ m}^2/\text{g}$ while after activation by reduction, the BET specific surface area increased to $79.3 \text{ m}^2/\text{g}$. The increase in BET specific surface area after the reduction was attributed to the pores that were created to accommodate the shrinkage in the catalyst precursor associated with reduction of NiO to Ni [55-58]. These results are in agreement with those reported in literature [59].

The ICP analysis of the RM and 40%Ni/RM catalyst showed that the major metals present in RM were Al, Ca, Fe, Na, Si and Ti and trace amounts of other metals such as As, Cd, Cu, Mo, Zn etc. (Table 1). The Ni content of the red mud was negligible but after the impregnation the Ni content was 40.8%, which was close to the estimated amount incorporated. The Ni loading of the commercial Ni/SiO₂-Al₂O₃ catalyst was 63.3% (Table 1) which was close to the 65 wt. % stated on the sample bottle by the manufacturer.

TG-TPR was performed to investigate the reducibility of nickel oxide, RM support, and the interaction between nickel and the RM support. The TPR profile of RM showed three major reduction peaks at 279.9, 542.7, and 694.6 °C (Fig. S1 in supplementary material). The peak at 279.89 °C could be due to the reduction of Fe₂O₃ to Fe₃O₄ and the unresolved peaks centered at 542.68 °C and 694.6 °C could be due to reduction of Fe₃O₄ to FeO and then to elemental Fe [27].

The TPR profiles of Ni/RM catalyst showed two major reduction peaks at 442.22 and 583.11 °C (Fig. S2 in supplementary material). The peak at 442.22 °C was attributed to reduction of nickel oxide, but this peak also indicated a possible interaction with RM support since its intensity increased with increasing the Ni content (data not reported) and its reduction temperature shifted towards that of nickel oxide (347.89 °C according to Fig. S3 in supplementary data). This observation will be in agreement with Jeangros et al. who observed interaction between SiO₂ and NiO during the reduction of NiO to Ni [57]. The peak at 583.11 °C was attributed to the reduction of RM components (mostly Fe₂O₃) since its intensity decreased as Ni loading increased (data not provided). Ni supported on Fe₂O₃ was prepared using wet impregnation method to investigate the effect of the presence of Fe₂O₃ (which was the major RM component) on the reducibility of Ni. The TPR profile of NiO/Fe₂O₃ (Fig. S4 in supplementary material) showed interaction between NiO and Fe₂O₃ at 390.03 °C. The peak at 522.67 °C was ascribed to reduction of Fe₂O₃ to magnetite. These results suggested that, besides Fe₂O₃, Ni interacted with other components of RM too.

Fig. 1 shows the XRD pattern of fresh Ni/RM catalyst. Distinct sharp peaks observed at 2 θ 52.2°, 61° were attributed to elemental Ni from the reduction of NiO. The detection of NiO signal at 2 θ 43.7°, 50.9°, and 74.7° showed that nickel oxide was not completely reduced to elemental Ni after treatment with H₂ (Fig. 1) which is in agreement with Jeangros et al (2013) who reported that total NiO reduction does not occur until the reduction temperatures is above 600 C [57]. Detection of magnetite (Fe₃O₄) peaks at 2 θ 21.6°, 35.1°, 41.7°, and 74.3° were due to reduction of hematite (Fe₂O₃) that was present in the original RM [28].

XRD pattern of used Ni/RM catalyst (Fig. 2) showed stronger NiO peaks compared to fresh catalyst suggesting that Ni was partially oxidized during HDO. This could be one reason for the

partial deactivation of the catalyst. Additionally, iron nickel oxide (trevorite) (Fe_2NiO_4) peaks were also detected after HDO that could be another reason for partial deactivation of active Ni sites. The detection of weak elemental nickel peaks (2θ 52.1° and 61°) in the used catalyst suggested that the catalyst was only partially deactivated.

In order to recycle the catalyst, the used catalyst was regenerated in muffle furnace to burn off the deposited carbonaceous compounds (coke) at 400 °C for 4 h. The XRD pattern of the regenerated catalyst (Fig. 3) showed strong NiO diffraction peaks at 2θ 43.9°, 50.8°, and 75° which was due to the oxidation of nickel to NiO under heat treatment in air. Existence of hematite (Fe_2O_3) diffraction peaks in regenerated catalyst was ascribed to oxidation of magnetite. Furthermore, it was interesting to note that weak elemental Ni diffraction peaks were present in the XRD pattern of the regenerated catalyst (Fig. 3). This suggested that some Ni particles in the interior of the RM were not exposed to oxygen due to mass transfer limitations.

The regenerated catalyst was then activated by reduction in H_2 . The XRD pattern of the regenerated and activated catalyst (Fig. 4) showed similar diffraction peaks as the fresh catalyst (Fig. 1) suggesting complete regenerability of the catalyst which was in contrast to the commercial catalyst that could not be regenerated using similar procedure. More detailed information on catalytic activity of the used catalyst and the recycled catalyst are discussed in section 3.6.

The surface morphology of the catalyst was studied by using scanning electron microscopy (SEM). The SEM images of the Red Mud support, Ni/RM catalyst precursor (calcined form), fresh Ni/RM catalyst (reduced form), and used 40% Ni/RM catalyst are presented in Fig. 5. In the case of RM support (Fig. 5a), in addition to amorphous looking particles, crossed cocentric discs and spherical-shaped particles were observed. The SEM image of Ni/RM catalyst in

calcined form is shown in Fig. 5b. Ni particles with relatively uniform morphology and approximate mean diameter of 90 nm were dispersed on the surface of RM components in the case of activated Ni/RM (Fig. 5c). The SEM picture for the used catalyst (Fig. 5d) showed that the catalyst was coated with coke after HDO process, which could inhibit the hydrogen transfer and partially deactivate the catalyst.

3.2. HDO products yield distribution and selectivity

In the blank experiment without catalyst, the guaiacol did not convert to any other compounds and neither did it produce any gas nor coke, hence the reactor was not catalytically active and did not influence the HDO experiments.

The major HDO liquid products using the nickel catalysts were catechol, anisole, phenol, cyclohexane, hexane, benzene, toluene, and xylene. CO, CO₂ and C₁–C₅ hydrocarbon gases as well as water and coke. When RM was treated using similar reaction conditions as Ni/RM catalyst and used in HDO experiment, the guaiacol conversion was only 2.7%. A relatively high amount of coke was formed (18.3 wt. %) and 96.3 wt. % of the final liquid products was unreacted guaiacol and small amounts of benzene, phenol, and anisole. The results of HDO experiments using RM support are summarized in Table S1 in supplementary material. Therefore the RM support contribution to HDO process was very low. The effects of reaction temperature and hydrogen pressure are discussed in subsections 3.2.1 and 3.2.2 respectively.

3.2.1. Reaction temperature effect

Fig. 6 shows the overall products yield distribution of guaiacol HDO as a function of reaction temperature. At all reaction temperatures, Ni/RM catalyst produced higher organic liquid yield compared to Ni/SiO₂-Al₂O₃. In contrast higher amounts of gas and coke were formed in the case of Ni/SiO₂-Al₂O₃, which could be due to the higher specific surface area and higher Ni content of the catalyst. The aqueous liquid yield at reaction temperatures of 300, 350, and 400 °C were 9.8, 12.4 and 16.7 % respectively for Ni/RM catalyst while those for Ni/SiO₂-Al₂O₃ were 11.3, 15.6, and 21.1 % respectively. The higher aqueous liquid yield was due to increased methanation of carbon dioxide over the commercial Ni/SiO₂-Al₂O₃ (Table 2) [12, 60]. The aqueous phase was 99.9 wt. % H₂O.

Pressure changes during the HDO of guaiacol at different reaction temperatures are shown in Fig. S5 (supplementary material). The total pressure profile using Ni/SiO₂-Al₂O₃ fell below the pressure profile of Ni/RM catalyst due to higher hydrogen consumption in the case of the commercial catalyst (Table 2).

Fig. 7 and 8 show the HDO product selectivity and guaiacol conversion as a function of reaction temperature for Ni/RM and Ni/SiO₂-Al₂O₃ catalysts respectively. Increasing the reaction temperature improved the conversion of guaiacol in all HDO experiments. At reaction temperatures of 300 and 350 °C; catechol, anisole, and phenol were produced due to demethylation, dehydroxylation, and demethoxylation of guaiacol respectively, however the selectivity to these compounds were lower for Ni/RM compared to Ni/SiO₂-Al₂O₃ (Fig. 7 and 8). In contrast the selectivity to benzene, toluene, and xylene (BTX) was lower for Ni/SiO₂-Al₂O₃ suggesting that Ni/RM was more effective in hydrodeoxygenation than Ni/SiO₂-Al₂O₃.

When the reaction temperature was increased from 300 °C to 400 °C the selectivity to oxygenated intermediates (catechol, anisole, and phenol) decreased significantly indicating that

guaiacol was first converted to catechol, anisole, and phenol via demethylation, dehydroxylation, and demethoxylation, and subsequently to cyclohexane, benzene, toluene, and xylene. Hexane was also obtained in relatively lower selectivity as a result of ring opening. At reaction temperature of 400 °C complete hydrodeoxygenation of guaiacol was achieved with both catalysts. However, Ni/SiO₂-Al₂O₃ was more effective in hydrogenation of aromatic ring compared to Ni/RM resulting in benzene, toluene, and xylene selectivities of 24.5, 17.1, and 7.9 % respectively for Ni/RM while these values were 15.9, 8.4, and 4.5 % respectively for Ni/SiO₂-Al₂O₃. Higher rates of hydrogenation reaction over Ni/SiO₂-Al₂O₃ resulted in cyclohexane selectivity of 62.2 % versus 38.8 % for Ni/RM at 400 °C (Fig. 7 and 8). This result is also reflected in higher hydrogen consumption over Ni/SiO₂-Al₂O₃ compared to Ni/RM (Table 2). The major gas product was methane for both catalysts.

3.2.2. Hydrogen pressure effect

The influence of hydrogen pressure on the guaiacol HDO products yield distribution is shown in Fig. 9. Increasing the initial hydrogen pressure from 4.83 to 6.21 MPa increased the liquid product yield for both catalysts, however the organic liquid yield was much higher over Ni/RM. The increase in organic liquid yield could be due to an increase in concentration of adsorbed hydrogen on the catalyst surface and an increase in the amount of dissolved H₂ in the organic phase, as hydrogen pressure was increased [12, 61, 62]. For Ni/RM, the gas yield decreased from 23.7% to 8.4% over this pressure range while the gas yield decreased from 41.4% to 16.6% for Ni/SiO₂-Al₂O₃. The coke yield decreased from 6.4% to 2.1% for Ni/RM and from 9.5% to 5.5% using Ni/SiO₂-Al₂O₃ (Fig. 9). This would suggest that higher levels of hydrogen pressure helped HDO reactions to predominate cracking and (re)polymerization reactions that produce gas and

coke [63]. The increase in aqueous liquid yield by increasing hydrogen pressure could also confirm that higher H_2 pressures favored HDO reactions. Pressure profile during the HDO of guaiacol at different hydrogen pressures are shown in Fig. S6 in supplementary material. The reaction pressure in the case of $Ni/SiO_2-Al_2O_3$ was lower than that of Ni/RM due to higher hydrogen consumption by the commercial catalyst (Table 3).

During the catalytic hydrotreatment processes, multiple reactions may occur, including hydrogenation, hydrogenolysis, hydrodeoxygenation, hydrocracking, and polymerization [5, 9]. Hydrogenation for ring saturation, hydrocracking for gasification, and methanation made hydrogen consumption exceed the deoxygenated stoichiometric ratio [9]. In order to reduce the hydrogen consumption, the direct deoxygenation without ring saturation is desirable in HDO. Figs 10 and 11 show the guaiacol conversion and evolution of products as a function of hydrogen pressure over Ni/RM and $Ni/SiO_2-Al_2O_3$ respectively. At initial H_2 pressures of 4.83 MPa and 5.52 MPa, oxygenated intermediates (catechol, anisole, and phenol) were produced while these compounds were completely deoxygenated when the initial H_2 pressure was 6.21 MPa. However, higher selectivity to benzene, toluene, and xylene were observed (24.5, 18.1, and 7.9% respectively) for Ni/RM compared to $Ni/SiO_2-Al_2O_3$ (15.9, 8.4, and 4.5% respectively) resulting in less hydrogen consumption in the case of Ni/RM (Table 3). This result was attributed to higher ring hydrogenation activity of $Ni/SiO_2-Al_2O_3$ since this catalyst had higher Ni loading (63.3% according to Table 1) than Ni/RM (40%). Furthermore, higher catalytic activity of $Ni/SiO_2-Al_2O_3$ led to higher cyclohexane selectivity of 62.2 % (Fig 11) because of the hydrogenation of the aromatic ring and demethylation reaction resulting in lower BTX selectivity.

The major gas product for both catalysts was methane for both catalysts (Table 3) because of demethylation, methanation and cracking reactions. It is interesting to note that at all temperatures and pressures, the Ni/RM produced CO, whereas the Ni/SiO₂-Al₂O₃ did not produce any CO probably because of the methanation reaction that was stronger in this catalyst than the Ni/RM.

Guaiacol HDO liquid products (organic and aqueous phases) were analyzed for Ni using ICP in order to investigate leaching effect. The Ni content of HDO products were below detection limit (0.05 mg/kg) suggesting that Ni did not leach into the HDO products (data not reported).

3.3. Evaluation of HDO process

To accurately visualize and extrapolate trends from elemental analysis, the elemental composition of the products were plotted in Van Krevelen-type diagrams. The molar O/C versus molar H/C ratios of the feed guaiacol and the HDO products are shown in Figs. 12 and 13 at different temperatures and initial hydrogen pressures respectively. The O/C ratio of HDO products decreased as a function of reaction temperature for both catalysts, however, higher hydrogenation occurred over Ni/SiO₂-Al₂O₃. At 300 °C the O/C ratio of HDO products of Ni/RM was 0.18 versus 0.22 for Ni/SiO₂-Al₂O₃. At 350 °C this value was relatively the same for Ni/RM and Ni/SiO₂-Al₂O₃ (0.09 and 0.10 respectively) however the H/C ratio at 300, 350, and 400 °C were 1.40, 1.46, and 1.59 respectively for Ni/RM versus 1.42, 1.63, and 1.93 respectively for Ni/SiO₂-Al₂O₃ HDO products. Thus, there was more hydrogenation with Ni/SiO₂-Al₂O₃ than Ni/RM. Moreover, the Van Krevelen plot of HDO products over Ni/RM catalyst at different H₂ pressures (Fig. 13) fell below the HDO products over Ni/SiO₂-Al₂O₃ showing that for HDO of guaiacol, less saturation of double bonds took place over Ni/RM catalyst resulting in lower hydrogen consumption which is desirable in HDO process. These results were mainly attributed

to higher catalytic activity of Ni/SiO₂-Al₂O₃ because of the higher Ni loading that favored hydrogenation and hydrocracking reactions. Also, to a lesser extent, silica and alumina can catalyze demethylation reaction [1, 20, 64] contributing to increased hydrogen consumption in the case of Ni/SiO₂-Al₂O₃.

3.4. Reaction pathways

For the study of HDO pathways of guaiacol over Ni/RM and Ni/SiO₂-Al₂O₃, HDO of catechol, anisole, phenol, cyclohexane, benzene, toluene, and xylene were carried out under the same conditions as the HDO of guaiacol. These reaction results are shown in Table 4. Guaiacol was first converted to catechol, anisole, and phenol via demethoxylation and dehydroxylation reactions. The selectivity to catechol, anisole, and phenol were 1.5, 2.3, 9.5 % respectively for Ni/RM and 3.4, 4.7, and 10.8 % respectively for the commercial catalyst after HDO of guaiacol. Anisole underwent demethylation, demethoxylation, and alkylation to produce phenol, benzene, and toluene respectively. Catechol was first converted to phenol via dehydroxylation and then converted to benzene. Benzene was initially formed via demethoxylation of anisole, dehydroxylation of phenol, and demethylation of toluene, and then hydrogenated to cyclohexane. At relatively lower selectivity compared to other intermediates, xylene was formed via a transalkylation reaction [45, 46]. HDO of benzene produced cyclohexane through ring hydrogenation at selectivity of 88.2% and 67.6% over Ni/RM and Ni/SiO₂-Al₂O₃ respectively but ring opening was more pronounced over the commercial catalyst (32.4% selectivity) compared to Ni/RM (11.8% selectivity) (Table 4). A summary of the HDO pathways of guaiacol based on the observed product distribution is proposed in Fig. 14. Pathways 1, 2, and 3 are demethylation, demethoxylation, and dehydroxylation processes, respectively. Pathway 4 is

hydrogenation which was more pronounced over Ni/SiO₂-Al₂O₃ than Ni/RM. Pathway 5 is a transalkylation reaction in which the methyl group is transferred to the aromatic ring [65]. In conclusion, similar reaction pathways over both catalysts were observed while products selectivity were quite different as discussed in section 3.2. Overall, the conversion of oxygenated compounds (guaiacol, catechol, anisole, and phenol) were higher for Ni/RM compared to the commercial catalyst suggesting higher activity of Ni/RM catalyst for deoxygenation than hydrogenation (Table 4). The Ni/SiO₂-Al₂O₃ showed higher conversion for hydrogenation of BTX and ring opening compared to Ni/RM.

3.5. Kinetic studies

In order to determine the reaction order and rate constant of the reaction, the activity data (concentration and time) was fitted to power-law equation [54]. As shown in Fig. 15, the slope of a plot of $1/C_{\text{guaiacol}}$ as a function of reaction time is linear with slope of k , hence, HDO of guaiacol global kinetics followed the second order mechanism which was in agreement with other studies [44]. The rate constant of Ni/SiO₂-Al₂O₃ (55.8 ml/mol.s) was more than two times higher than the Ni/RM catalyst (24.4 ml/mol.s), which explains the higher activity of Ni/SiO₂-Al₂O₃ compared to Ni/RM. Ni/RM has shown better performance over Ni/SiO₂-Al₂O₃ since the latter favored ring hydrogenation reaction. Since the support was different for both catalysts, the activity difference could be due to both Ni loading and interaction with support. In the case of Ni/RM the elemental Ni loading was less than the nominal 40% because the XRD pattern showed the presence of NiO after the reduction with H₂. Apparent activation energy for each catalyst was calculated based on the Arrhenius-type plots (equation 4) [54] (Fig. 16). The apparent activation energy for the Ni/RM and Ni/SiO₂-Al₂O₃ catalysts were 97.5 KJ/mol and 90.3 KJ/mol, respectively. These values were within the range of various values reported in

literature [44, 46, 66]. Therefore the global kinetic model over Ni/RM and Ni/SiO₂-Al₂O₃ catalysts had the forms of equations (5) and (6) respectively:

$$\ln(k) = \ln(k_0) - \frac{E}{RT} \quad (4)$$

$$-r_G = 56.26 e^{(-\frac{97.5}{RT})} \cdot C_G^2 \quad (5)$$

$$-r_G = 51.42 e^{(-\frac{90.3}{RT})} \cdot C_G^2 \quad (6)$$

The development of a more detailed kinetic model is out of the scope of this article.

3.6. Catalyst deactivation and regeneration

As discussed in section 3.1, three mechanisms contributed to catalyst deactivation; coke formation, oxidation of Ni, and formation of iron nickel oxide. In order to evaluate the catalyst life, the recovered catalysts after HDO experiments were washed using a solution of 1:1 (wt. ratio) toluene/methanol and consecutively used in further HDO tests without any catalyst regeneration. The selectivity of HDO products changed as the catalyst deactivated. A summary of the results of these experiments is shown in Table 5. Metal loading, and pore structure of support have been proposed to affect coke deposition [9, 16]. After four consecutive runs using Ni/RM, the catalyst completely deactivated due to coking and possible oxidation of active Ni sites both of which can contribute to the reduction of BET specific surface area from 79.3 m²/g to 59.2 m²/g. After the fifth run the catalyst did not indicate any activity and the guaiacol did not undergo any HDO reactions. There was more coke built up on the catalyst surface that further reduced the BET specific surface area to 56.4 m²/g. The Ni/SiO₂-Al₂O₃ completely deactivated after five consecutive runs and its BET specific surface area reduced from 118.4 m²/g to 77.9 m²/g. After the sixth run the catalyst did not show any activity for HDO reactions however its

BET specific surface area further reduced to 72.2 m²/g. The reduction in BET specific surface area suggested that coke was formed in the pores of the catalyst.

The spent catalysts were placed in muffle furnace to burn off the deposited coke at 400 °C for 4 h followed by reduction as explained in section 3.1. The regenerated/activated catalyst was used in HDO experiments. A summary of these HDO test results are shown in Table 6. Guaiacol conversion and HDO products selectivity over Ni/RM were similar to that of fresh catalyst (Table 5). These result indicated that the Ni/RM catalyst regained its activity after the regeneration/activation process. However, the regeneration of the commercial Ni/SiO₂-Al₂O₃ was not possible following the same procedure and the catalyst did not show HDO activity after regeneration/reduction. The BET specific surface area of the regenerated Ni/SiO₂-Al₂O₃ catalyst was 88.8 m²/g which was much lower than the fresh catalyst (118.4 m²/g) suggesting that some Ni particles probably formed stable compounds with the support phase during regeneration. Additionally, when exposed to air, the reduced Ni/SiO₂-Al₂O₃ catalyst underwent spontaneous oxidation that could be due to oxidation of free Ni particles that were not interacting with the support phase.

4. Conclusion

Red mud, which is a waste material from the aluminum industry, was used as support material for preparation of nickel hydrogenation/hydrodeoxygenation catalyst. Hydrodeoxygenation of guaiacol as lignin model compound was investigated over red mud-supported nickel catalyst. For comparison, commercial Ni/SiO₂-Al₂O₃ was tested in HDO process under similar conditions. Unlike traditional HDO catalysts (CoMo/Al₂O₃ and NiMo/Al₂O₃), this catalyst did not require

any pre-treatments such as sulfidation and it can be used as received. Also this catalyst is much cheaper than typical noble metal catalysts that are widely used for HDO reactions. The Van-Krevelen diagrams of HDO products at different reaction temperatures and hydrogen pressures showed that increasing the reaction temperature and hydrogen pressure improved HDO reactions. Complete deoxygenation of guaiacol was achieved at a reaction temperature of 400 °C when the initial hydrogen pressure was 6.21 MPa (900 psi). Ni/RM showed higher activity for deoxygenation while hydrogenation of the aromatic ring was more pronounced for the commercial Ni/SiO₂-Al₂O₃. Consequently, the Ni/RM consumed less hydrogen than Ni/SiO₂-Al₂O₃. Hydrocracking and coke formation were significantly lower in the case of Ni/RM catalyst which is desirable in HDO process. The kinetics of guaiacol HDO followed second order model for both catalysts while higher rate constant and lower activation energy were determined for Ni/SiO₂-Al₂O₃ catalyst compared to Ni/RM. The increased catalytic activity of Ni/SiO₂-Al₂O₃ was ascribed to higher Ni loading and higher BET specific surface area of the catalyst. Coke formation was the major mechanism of catalyst deactivation, although oxidation of active Ni sites and formation of iron nickel oxide could also contribute to catalyst deactivation. After regeneration by burning off the coke and reducing with hydrogen, the activity of the Ni/RM catalyst was completely restored in contrast to the commercial catalyst that was not regenerable. This study showed that Red Mud can serve as a nickel catalyst support for HDO process.

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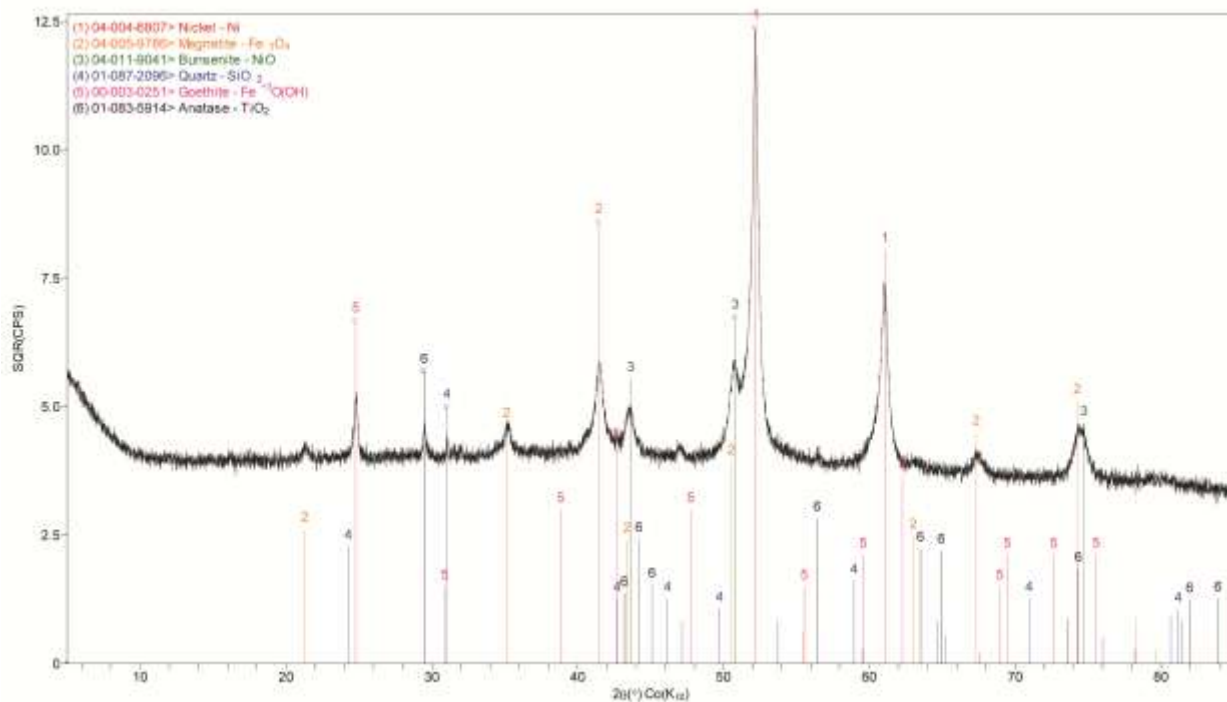


Fig. 1: XRD pattern of fresh Ni/RM catalyst.

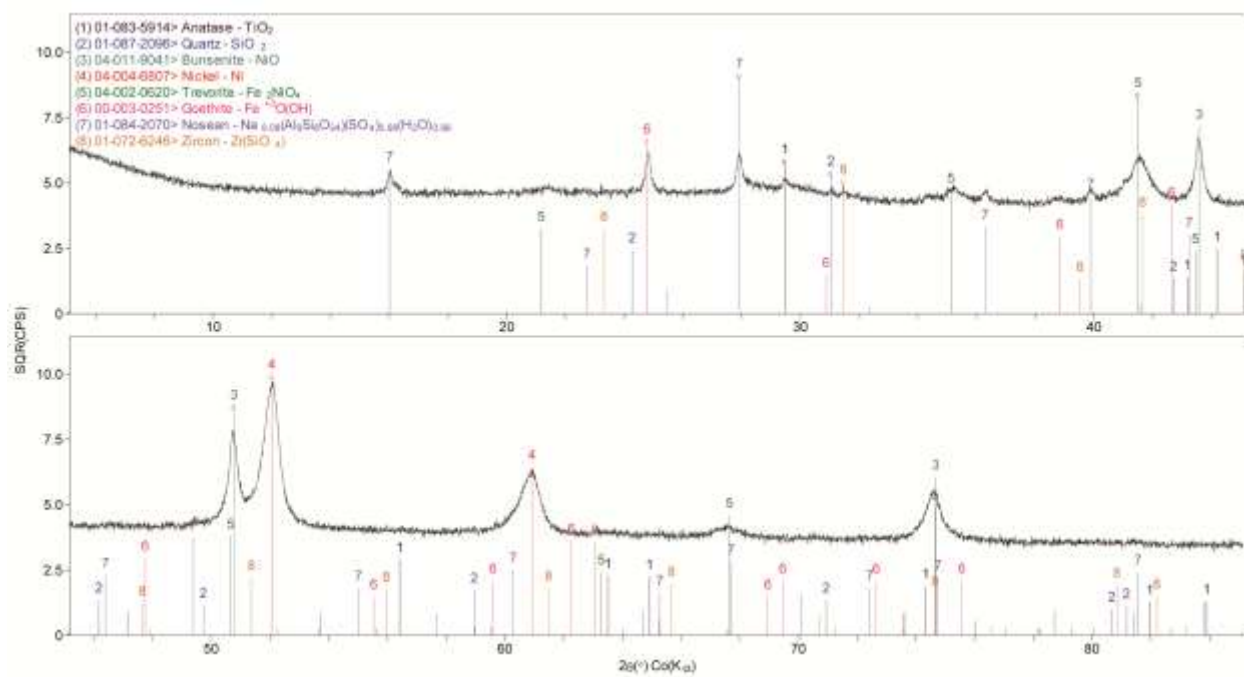


Fig. 2: XRD pattern of used Ni/RM catalyst.

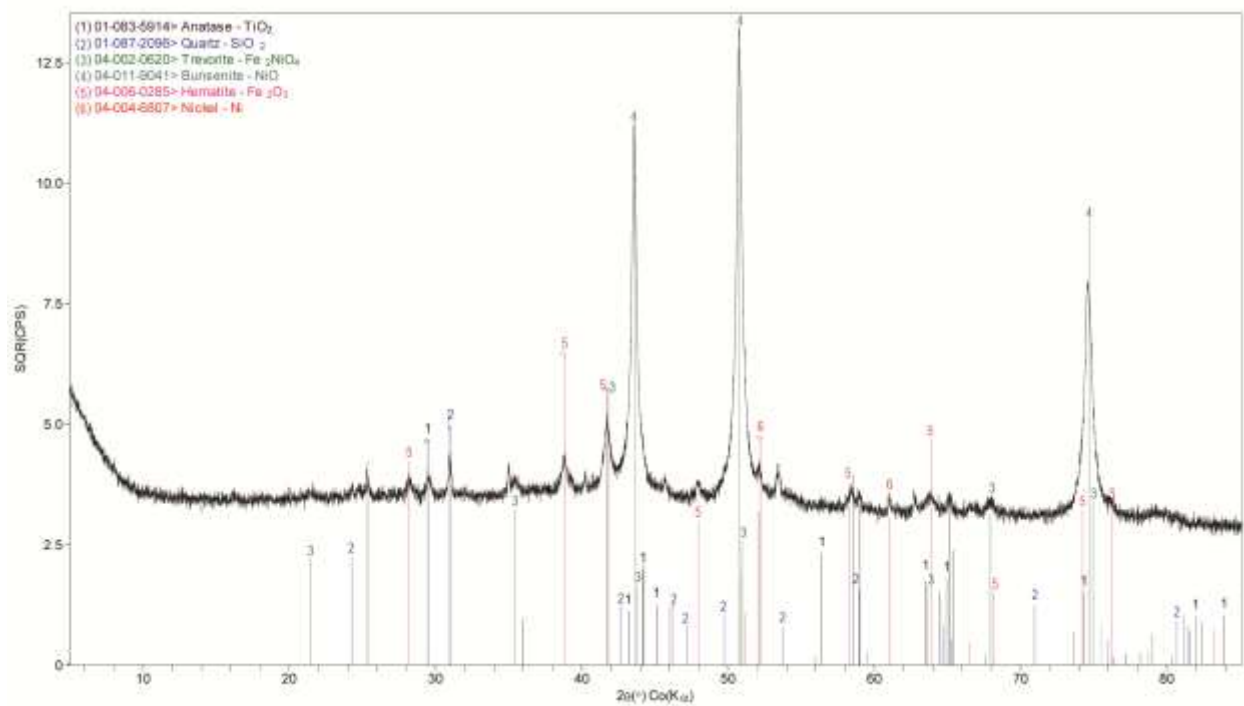


Fig. 3: XRD pattern of regenerated Ni/RM catalyst.

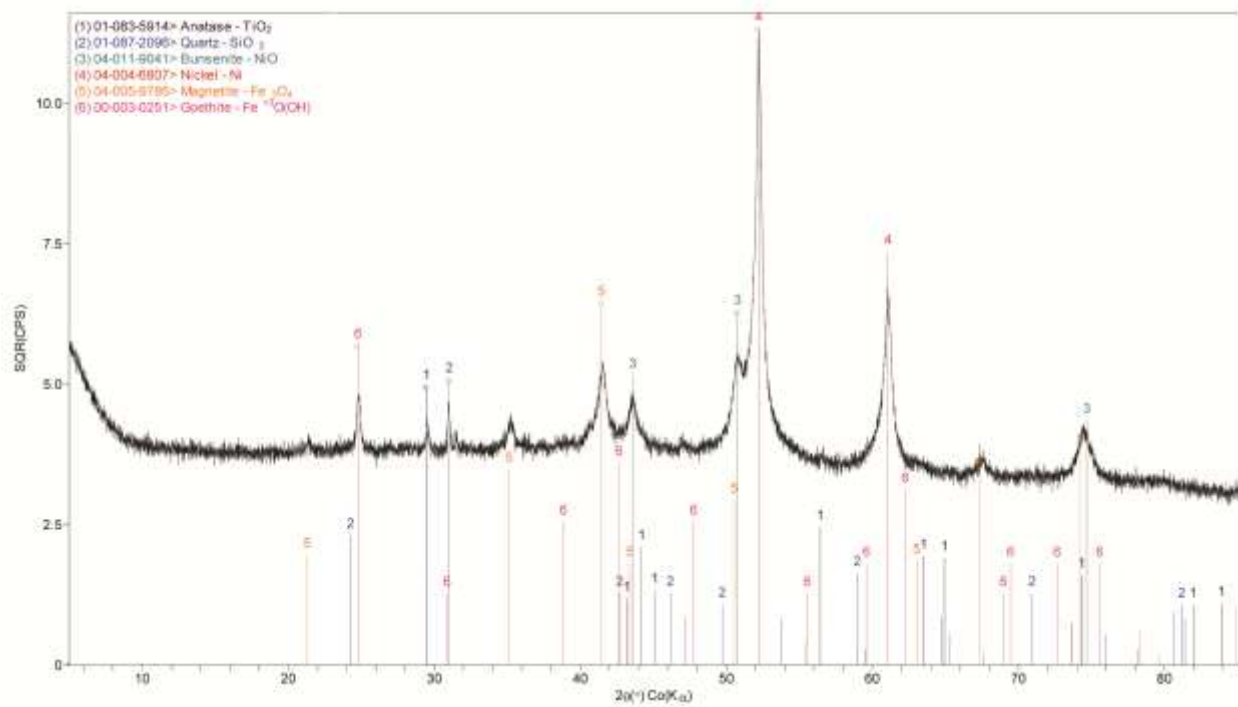


Fig. 4: XRD pattern of regenerated and reduced Ni/RM catalyst.

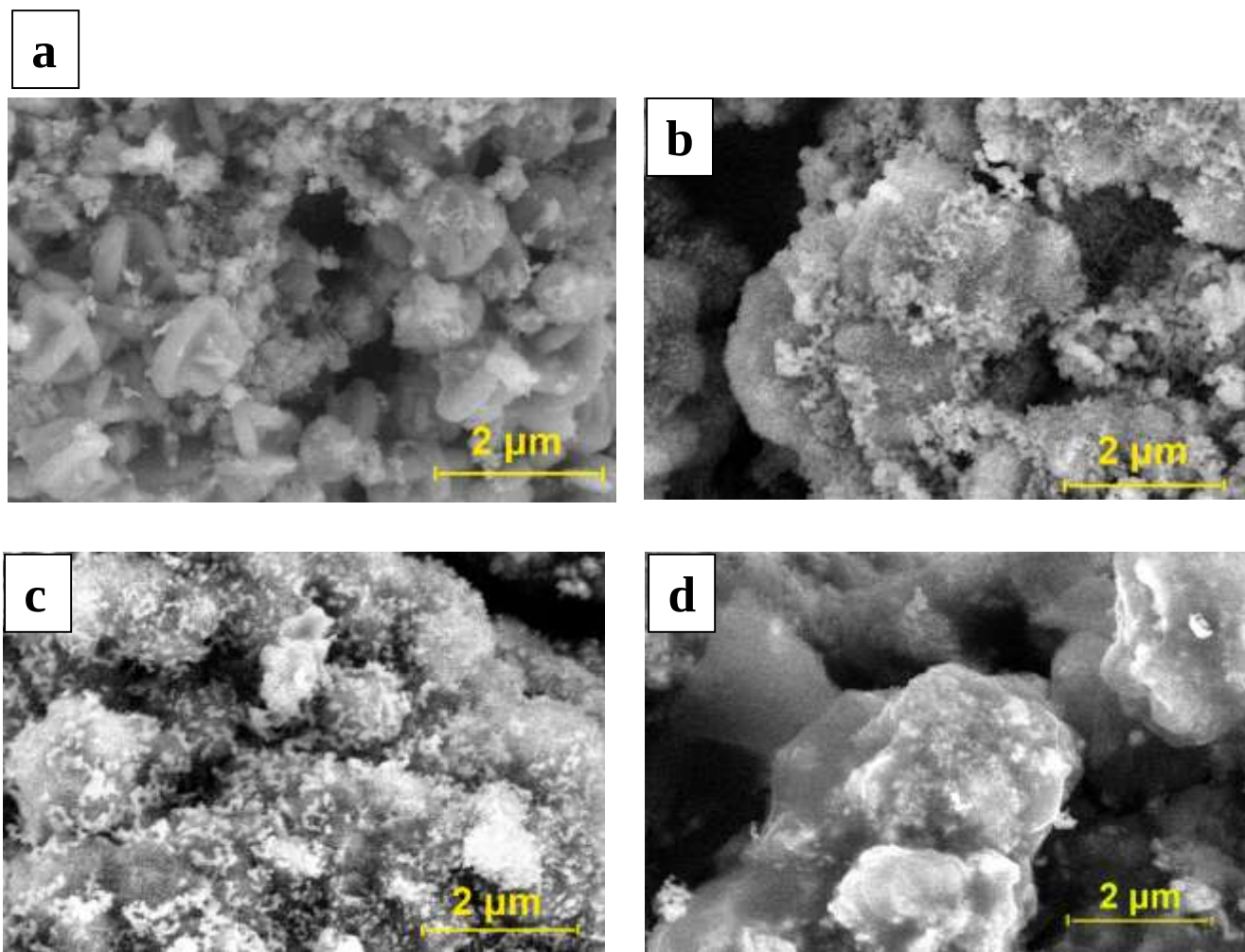


Fig. 5: SEM images of a) Red Mud support, b) Ni/RM (calcined form), c) Ni/RM (reduced form), d) Used Ni/RM catalyst.

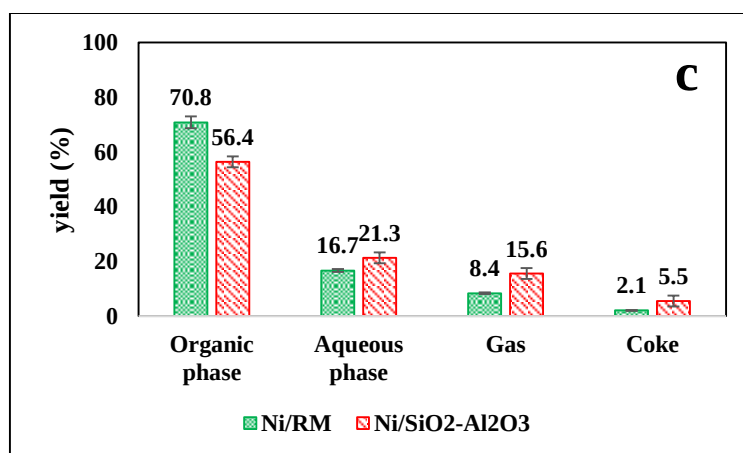
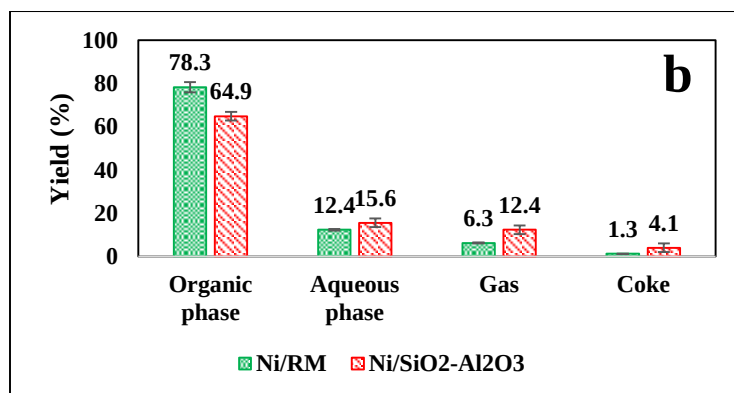
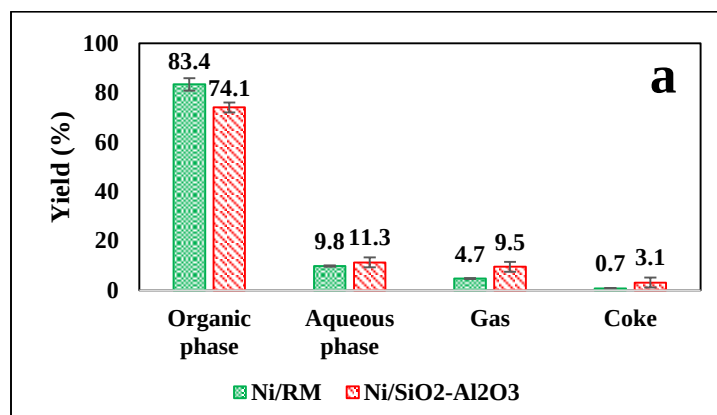


Fig. 6: Products yield distribution using Ni/RM and Ni/SiO₂-Al₂O₃ at a) 300 °C, b) 350 °C, and c) 400 °C (error bars show the standard deviation of three measurements).

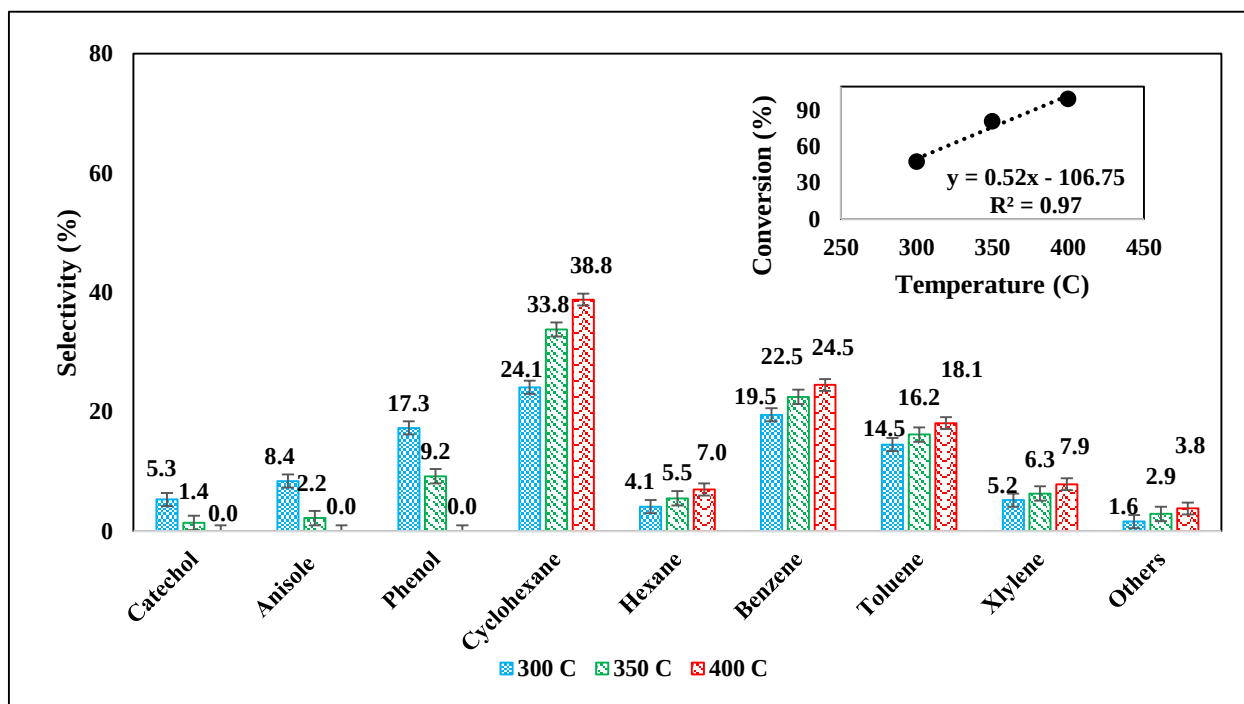


Fig. 7: Guaiacol conversion and products selectivity at different temperatures using Ni/RM catalyst (error bars show the standard deviation of three measurements).

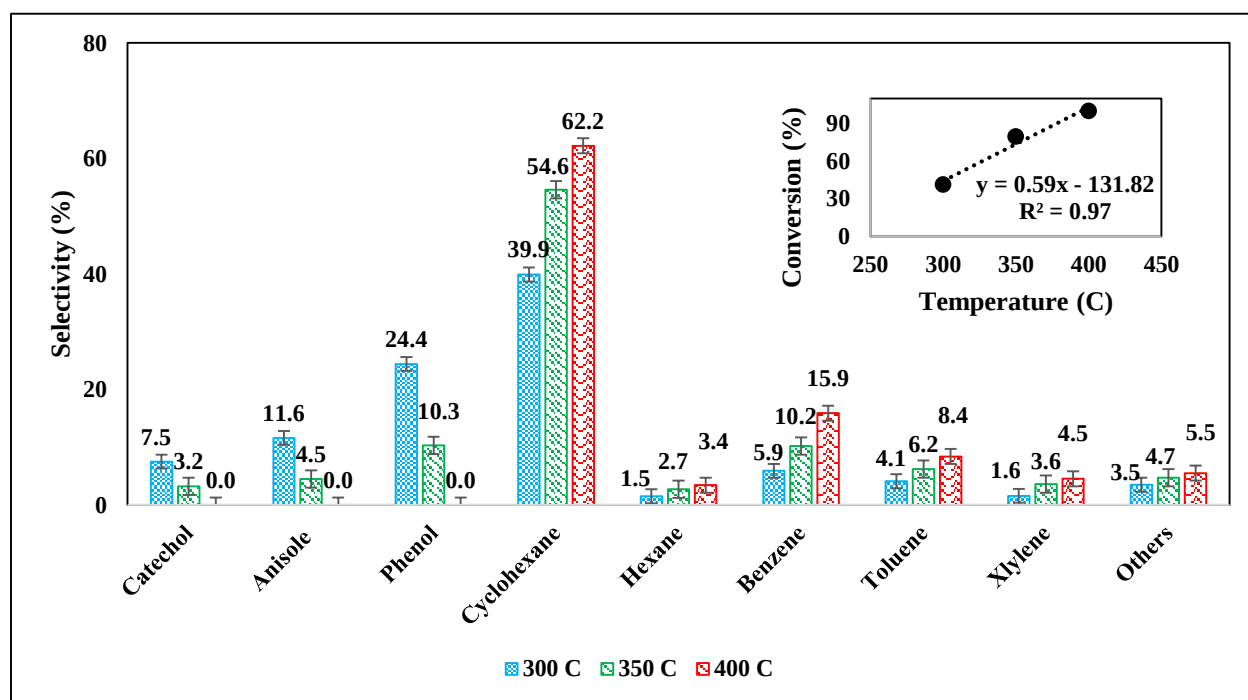


Fig. 8: Guaiacol conversion and products selectivity at different temperatures using Ni/SiO₂-Al₂O₃ catalyst (error bars show the standard deviation of three measurements).

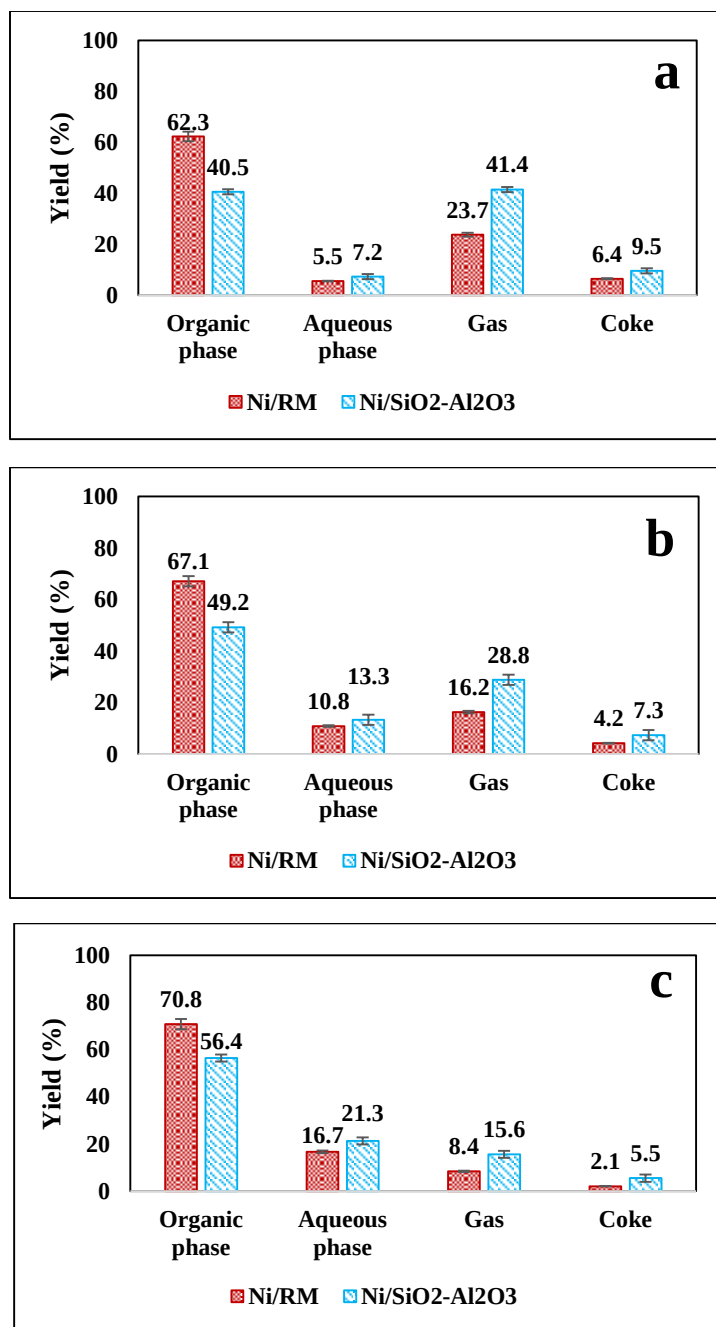


Fig. 9: Products yield distribution using Ni/RM and Ni/SiO₂-Al₂O₃ at a) 4.83 MPa (700 psi), b) 5.52 MPa (800 psi), and c) 6.21 MPa (900 psi) (error bars show the standard deviation of three measurements).

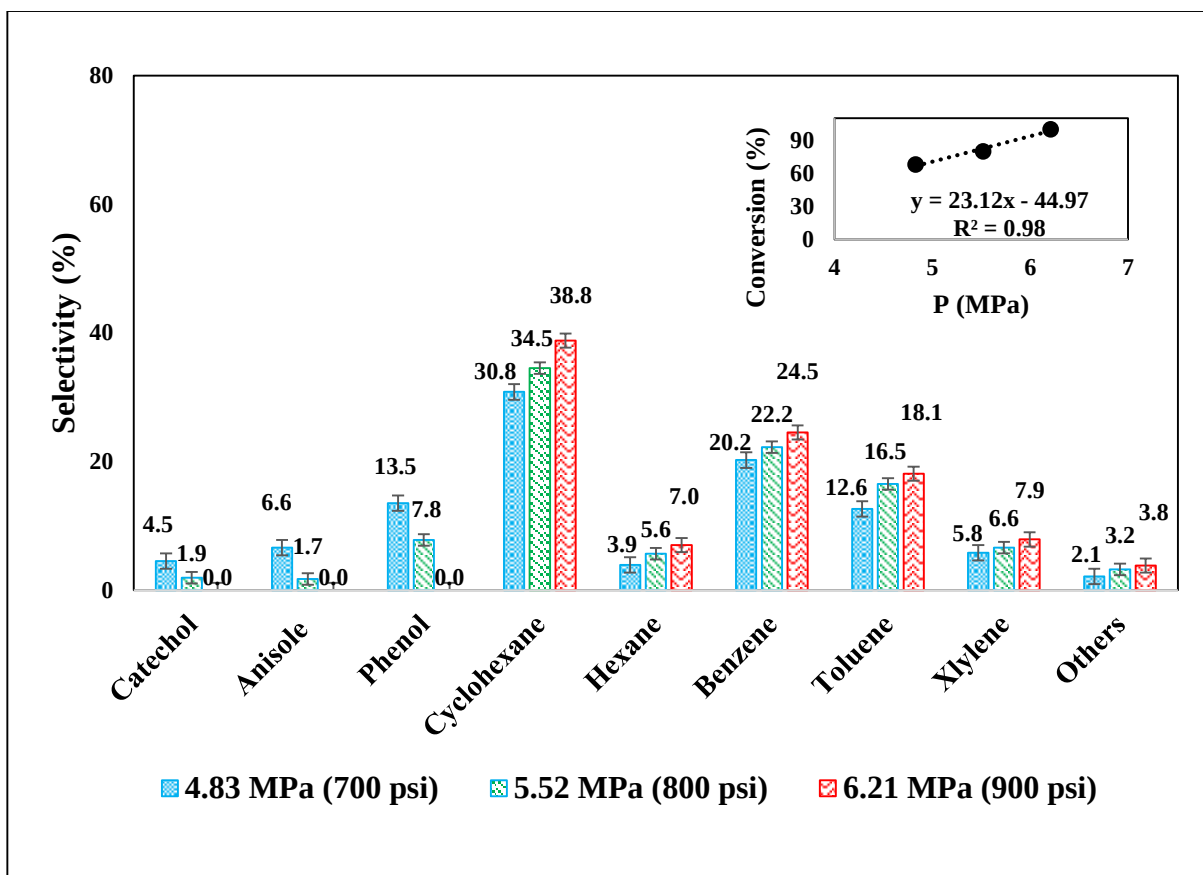


Fig. 10: Guaiacol conversion and products selectivity at different hydrogen pressures using Ni/RM catalyst (error bars show the standard deviation of three measurements).

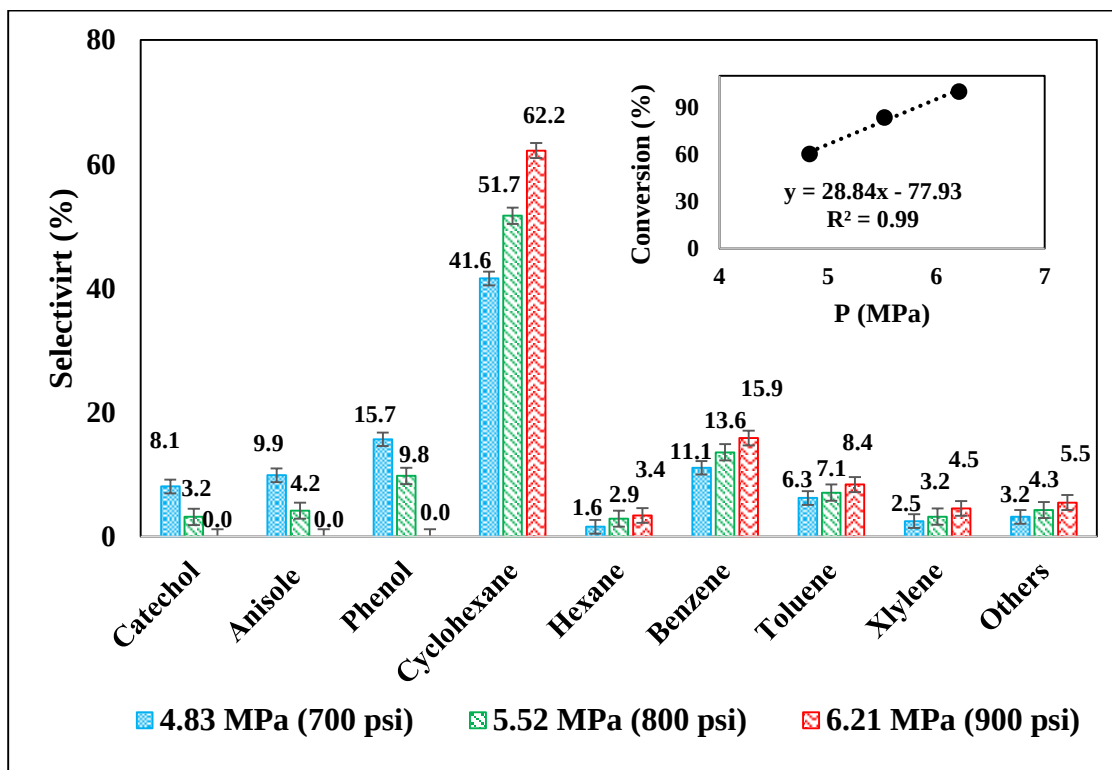


Fig. 11: Guaiacol conversion and products selectivity at different hydrogen pressures using Ni/SiO₂-Al₂O₃ catalyst (error bars show the standard deviation of three measurements).

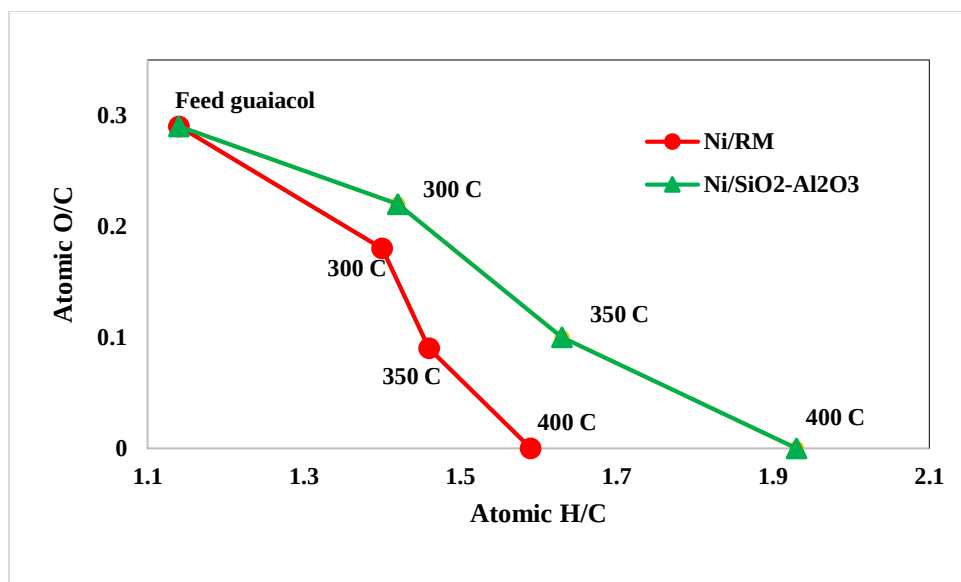


Fig. 12: Van-Krevelen diagram of guaiacol HDO products at different reaction temperatures.

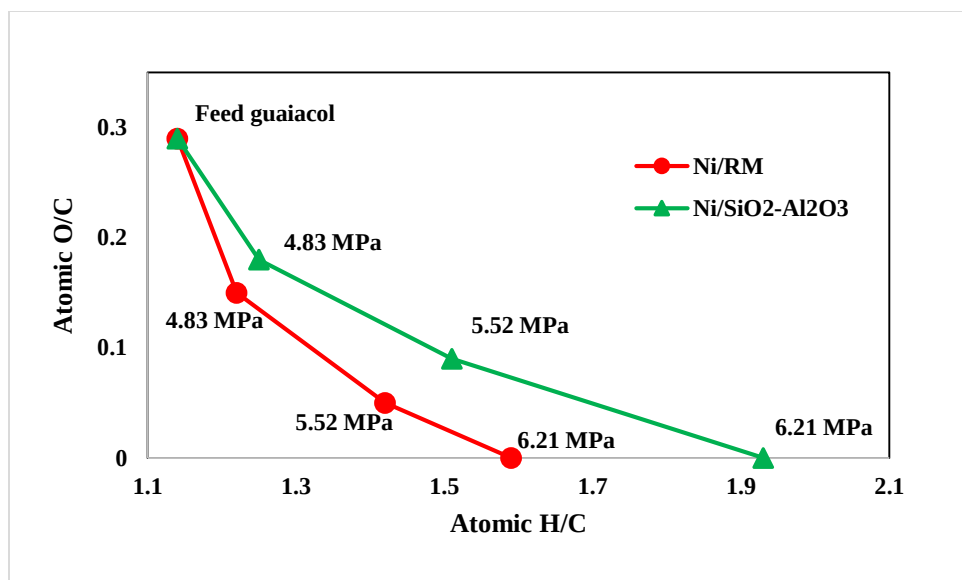


Fig. 13: Van-Krevelen diagram of guaiacol HDO products at different initial hydrogen pressures.

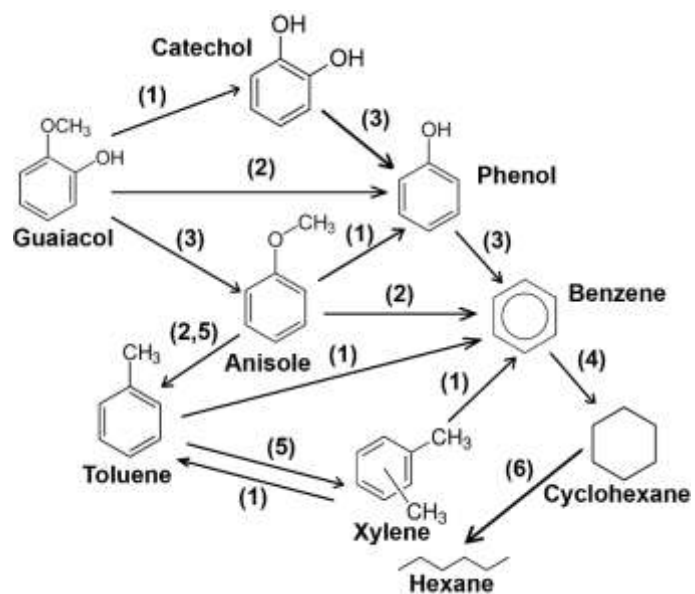


Fig. 14: Reaction network of guaiacol HDO. 1: demethylation, 2: demethoxylation, 3: dehydroxylation, 4: hydrogenation, 5: transalkylation, 6: ring opening.

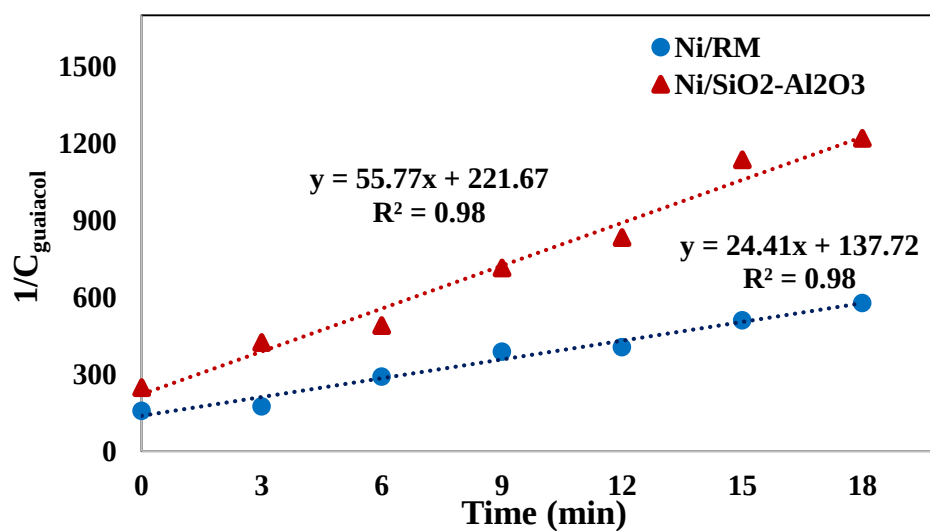


Fig. 15: Determination of reaction order and rate constant by integral method: reaction temperature 400 °C, H₂ pressure 6.21 MPa (900 psi)

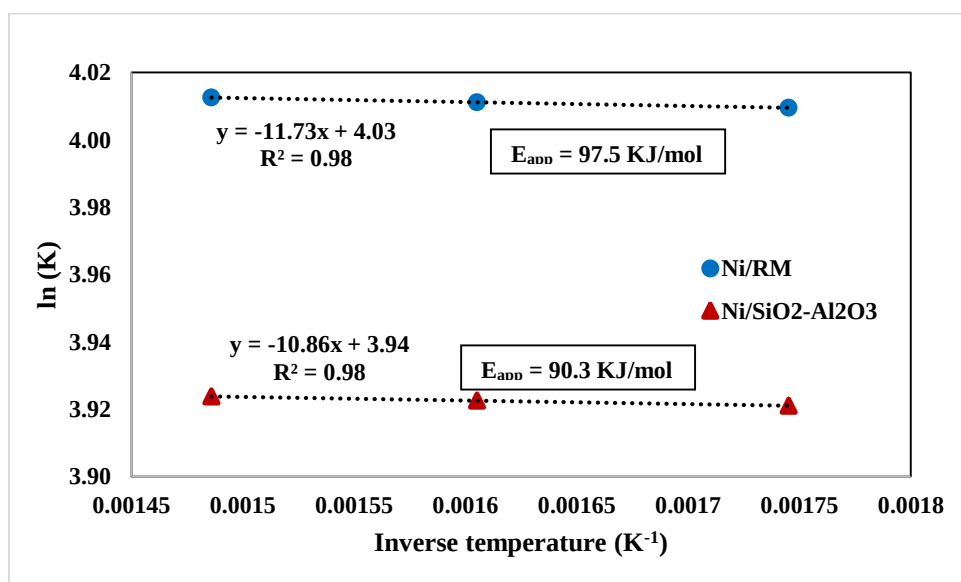


Fig. 16: Arrhenius-type plot for guaiacol HDO on Ni/RM and Ni/SiO₂-Al₂O₃.

Table 1: ICP analysis of RM support, Ni/RM, and Ni/SiO₂-Al₂O₃ catalysts.

Metal (wt. %)	RM	Ni/RM	Ni/SiO ₂ -Al ₂ O ₃
Al	9.08	4.44	16.17
Ca	1.20	0.65	0.25
Fe	21.56	9.47	1.21
K	0.03	0.02	0.01
Mg	0.07	0.04	0.07
Na	7.17	3.51	0.05
Ni	<0.01	40.8	63.3
P	0.03	0.01	0.02
S	0.10	0.06	0.04
Si	4.35	2.53	12.71
Ti	4.10	1.53	0.35
Metal (mg/kg)	RM	Ni/RM	Ni/SiO ₂ -Al ₂ O ₃
As	0.87	<DL *	<DL
B	9.41	0.85	<DL
Ba	10.4	4.55	7.27
Cd	5.79	3.37	<DL
Co	278	12.3	226
Cr	245	132	5.69
Cu	3.13	<DL	21.3
Mn	<DL	<DL	24.1
Mo	1.62	0.48	1.06
Pb	156	7.09	140
Se	<DL	<DL	<DL
Sr	23.1	2.28	9.57
Ti	<DL	<DL	<DL
Zn	2105	26.1	2994

* Less than detection limit (0.05 mg/kg)

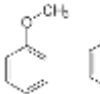
Table 2: Hydrogen consumption and gas composition of guaiacol HDO at different temperatures (the initial hydrogen pressure was 6.21 MPa) (the standard deviation of all data were within ± 0.05).

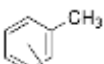
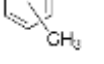
Catalyst	Temperature ($^{\circ}\text{C}$)					
	300		350		400	
	Ni/RM	Ni/SiO ₂ -Al ₂ O ₃	Ni/RM	Ni/SiO ₂ -Al ₂ O ₃	Ni/RM	Ni/SiO ₂ -Al ₂ O ₃
H ₂ Consumption (mol H ₂ /kg guaiacol)	0.19	0.24	0.29	0.38	0.37	0.45
Gas composition (mol %)						
CO	6.8	0	5.4	0	4.4	0
CO ₂	10.4	8.5	9.8	6.2	8.2	2.3
CH ₄	42.2	57.3	49.6	66.9	55.8	71.5
C ₂ H ₆	9.3	7.4	11.5	9.6	13.4	11.6
C ₃ H ₈	17.3	15.4	11.6	9.8	9.6	8.4
C ₄ H ₁₀	9.2	6.6	7.4	4.3	5.3	3.2
C ₅ H ₁₂	4.1	3.7	3.7	2.1	2.1	1.7

Table 3: Hydrogen consumption and gas composition of guaiacol HDO at different pressures (the reaction temperature was 400 °C)(the standard deviation of all data were within ± 0.05).

Catalyst	Pressure (MPa)					
	4.83		5.52		6.21	
	Ni/RM	Ni/SiO ₂ -Al ₂ O ₃	Ni/RM	Ni/SiO ₂ -Al ₂ O ₃	Ni/RM	Ni/SiO ₂ -Al ₂ O ₃
H ₂ Consumption (mol H ₂ /kg guaiacol)	0.22	0.29	0.31	0.36	0.39	0.45
Gas composition (mol %)						
CO	10.4	0	7.6	0	4.4	0
CO ₂	18.7	14.4	10.1	7.7	8.2	2.3
CH ₄	42.8	61.3	51.9	68.6	55.8	71.5
C ₂ H ₆	10.2	8.7	11.5	9.3	13.4	11.6
C ₃ H ₈	7.8	6.6	8.2	6.5	9.6	8.4
C ₄ H ₁₀	5.7	4.2	5.5	3.7	5.3	3.2
C ₅ H ₁₂	4.3	2.8	3.3	2.4	2.1	1.7

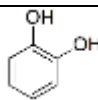
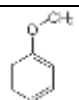
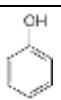
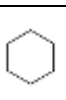
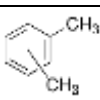
Table 4: Conversion and selectivity of guaiacol and intermediates HDO (the standard deviation of all data were within ± 0.5).

Sub.	Catalyst	Conv. (%)	Selectivity (%)							
										
	Ni/RM	83.2	1.5	2.3	9.5	34.8	5.7	23.1	16.6	6.5
	Ni/SiO ₂ -Al ₂ O ₃	78.6	3.4	4.7	10.8	57.3	2.8	10.7	6.5	3.8
	Ni/RM	81.4	-	-	21.6	19.6	11.5	47.3	-	-
	Ni/SiO ₂ -Al ₂ O ₃	76.4	-	-	36.9	31.4	7.6	24.1	-	-
	Ni/RM	71.3	-	-	14.5	17.4	4.9	38.1	15.7	9.4
	Ni/SiO ₂ -Al ₂ O ₃	66.7	-	-	22.7	32.8	8.3	20.4	10.6	5.2
	Ni/RM	85.6	-	-	-	31.6	9.8	58.6	-	-
	Ni/SiO ₂ -Al ₂ O ₃	74.9	-	-	-	58.3	5.4	36.3	-	-
	Ni/RM	68.2	-	-	-	-	100	-	-	-
	Ni/SiO ₂ -Al ₂ O ₃	76.4	-	-	-	-	100	-	-	-
	Ni/RM	71.4	-	-	-	88.2	11.8	-	-	-

	Ni/SiO ₂ -Al ₂ O ₃	89.3	-	-	-	67.6	32.4	-	-	-
	Ni/RM	78.6	-	-	-	34.4	15.6	44.4	-	5.6
	Ni/SiO ₂ -Al ₂ O ₃	91.1	-	-	-	66.5	9.8	21.3	-	2.4
	Ni/RM	74.3	-	-	-	26.7	13.6	37.3	22.4	-
	Ni/SiO ₂ -Al ₂ O ₃	80.2	-	-	-	56.8	8.7	20.6	13.9	-

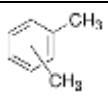
Reaction conditions: 350 °C, 6.21 MPa, 30 min

Table 5: Catalyst recyclability results (reaction temperature 400 °C, H₂ initial pressure 6.21 MPa) (the standard deviation of conversion and selectivity data were within ± 0.5 , and the standard deviation of BET data were within ± 1.5).

Catalyst/Reuse #	BET surface area (m ² /g)	Conv. (%)	Selectivity (%)							
										
Ni/RM										
Fresh	79.3	100	0	0	0	40.2	7.3	25.5	18.8	8.2
Reuse 1	71.2	100	4.2	3.2	7.1	35.5	6.7	23.6	15.4	4.3
Reuse 2	67.5	81.4	7.9	8.9	5.6	32.8	4.9	21.9	14.8	3.2

Reuse 3	63.5	47.5	10.5	17.1	3.5	31.4	2.6	20.7	12.5	1.7
Reuse 4	59.2	23.7	15.8	19.9	1.2	30.1	1.5	19.4	11.3	0.8
Reuse 5	56.4	0	-	-	-	-	-	-	-	-
Ni/SiO₂-Al₂O₃										
Fresh	118.4	100	0	0	0	65.9	3.6	16.8	8.9	4.8
Reuse 1	107.4	100	2.5	3.2	5.5	59.8	3.3	12.6	8.8	4.3
Reuse 2	100.3	68.8	5.7	5.9	8.3	53.4	3.1	11.2	8.5	3.9
Reuse 3	91.6	54.3	6.6	9.4	9.5	51.5	2.8	8.7	7.9	3.6
Reuse 4	84.4	34.7	7.5	10.6	10.9	50.8	2.5	7.5	7.4	2.8
Reuse 5	77.9	17.2	10.9	11.7	11.7	48.6	2.1	6.6	6.3	2.1
Reuse 6	72.2	0	-	-	-	-	-	-	-	-

Table 6: HDO results of regenerated catalysts (the standard deviation of conversion and selectivity data were within ± 0.5 , and the standard deviation of BET data were within ± 1.5).

Catalyst	BET surface area (m ² /g)	Conv. (%)	Selectivity (%)							
										
Ni/RM	79.9	100	0	0	0	39.7	7.5	26.2	19.1	7.5
Ni/SiO ₂ -Al ₂ O ₃	88.8	0	-	-	-	-	-	-	-	-