Hydrocracking of α-Cellulose Using Co, Ni, and Pd Supported on Mordenite Catalysts

Wega Trisunaryanti[*], Triyono, Ria Armunanto, Lathifah Puji Hastuti, Desinta Dwi Ristiana, and Resi Vita Ginting

Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Gadjah Mada, Sekip Utara, Yogyakarta 55281, Indonesia

ABSTRACT

Hydrocracking of α-cellulose has been conducted in a semi-batch reactor at 400, 450, and 500 °C with hydrogen flow (30 mL/min.) for 4 h. Mordenite (MOR) and Co, Ni and Pd metal supported on the MOR were used as solid catalysts. The catalysts were characterized using X-ray Diffractometer (XRD), Fourier Transform Infrared (FTIR) spectroscopy, and Scanning Electron Microscopy (SEM) to evaluate the physical-chemical properties. Energy Dispersive X-ray (EDX) and Inductively Coupled Plasma (ICP) were used to analyze the amount of metal impregnated on the catalysts. The liquid product was analyzed using Gas Chromatograph-Mass Spectroscopy (GC-MS). Thermal hydrocracking was also conducted at 450 °C with the amount of liquid product was 37.86 wt.%. The highest liquid conversion obtained by mordenite catalyst was 94.66 wt.% at 450 °C and the highest liquid conversion (98.08 wt.%) was reached by Pd/MOR catalyst at 400 °C.

Keywords: *hydrocracking; α-cellulose; mordenite*

ABSTRAK

Hidrorengkah α-selulosa telah dilakukan dalam reaktor semi-batch pada temperatur 400, 450, dan 500 °C dengan aliran hidrogen (30 mL/menit) selama 4 jam. Mordenit (MOR) dan logam Co, Ni, Pd teremban pada MOR digunakan sebagai katalis. Karakterisasi katalis dilakukan dengan difraksi sinar-X (XRD), FTIR, dan SEM untuk mengetahui sifat fisika dan kimia katalis. EDS dan ICP digunakan untuk menganalisis kandungan logam yang terimpregnasi dalam katalis. Analisis komposisi produk cair dilakukan dengan GC-MS. Perengkahan termal juga dilakukan pada 450 °C dengan total produk cair sebesar 37,86% b/b. Produk cair tertinggi yang diperoleh dengan penggunaan mordenit sebagai katalis sebesar 94,66% b/b pada 450 °C dan konversi produk cair tertinggi (98,08% b/b) diperoleh dengan penggunaan katalis Pd/MOR pada 400 °C.

Kata Kunci: *hidrorengkah; α-selulosa; mordenit*

INTRODUCTION

Cellulose is the most abundant renewable carbon resource on the planet and has great potential to be used as an alternative feedstock for the production of bio-based valuable platform molecule [1]. The conversion of cellulose not only into fuel-based but also high-value chemical is equally important. Hence, the conversion of cellulose into value-added fuel and chemicals has received increasing attention [2-5].

Cellulose exists mainly as aggregates due to its complex intermolecular and intramolecular hydrogen bonding network, which make cellulose is very difficult to depolymerized and convert into a low mass molecule compound. To overcome the problem, dissolution of cellulose in suitable solvents could promote the conversion because cellulose chains are well-extended and -dispersed in such conditions beside the reaction run in extreme conditions [6-7]. In this context, ionic liquids and alkaline aqueous solutions are generally employed for dissolution of cellulose [8-10]. For example, ionic liquids have been used as solvent to convert cellulose into HMF [11]. Oxalic and glycolic acids have been obtained from cellulose by alkali fusion or nitric acid oxidation processes [12]. However, this process required high concentrations of nitric acid (ca. 40 wt.%), which was very costly, corrosive, require special reaction apparatus in terms of scaling up for industrial production and dangerous for environmental.

Despite the great success achieved with small molecule biomass derivatives (e.g., mono- and disaccharides) in these studies, the direct catalytic conversion of cellulose remains a challenge, mainly because cellulose is highly stable and insoluble to most solvents. Direct catalytic in conversion of cellulose expected run without any-solvent.

Fukuoka and Dhepe [13] first reported the direct conversion of cellulose to hexytols on Pt/Al_2O_3 in water

without using any mineral acids. In order to improve product selectivity, various bifunctional catalysts with acid and metal sites, including Ni/CNT [14-15], Ni_2P/C [16], Ru/CNT [17], Rh-Ni/MC [18] and $Ru/Cs_3PW_{12}O_{40}$ [19] have been designed and studied. In addition, transition metal carbide catalysts, Ni-WC/activated carbon, Ni-W/SBA-15, Ni-WxC/CMK-3, Raney Ni with tungstic acid, and a CuCr catalyst were reported to be active for the production of diols from cellulose [20]. Efficient reaction processes and catalysts for the selective degradation of cellulose, however, have been difficult to identify because of the robust crystalline structure and high chemical stability of cellulose [21] and further work is therefore needed to explore this area in greater detail.

Zeolite catalyst is the most frequently used catalyst in biomass conversion due to its excellent deoxygenation ability. Zeolite is a porous, acidic catalyst and its active sites can promote a number of reactions, especially hydrocracking [22-23]. Mordenite is a well-known zeolite used in many catalytic reactions such as cracking, hydrocracking, isomerization, alkylation, dehydrogenation, and dehydration [24]. Mordenite is a very strong acid catalyst that has two channel type: larger and smaller channel. The main channels measuring 6.5 × 7.0 Å, which are connected by tortuous pores measuring 2.6 × 5.7 Å that form the so-called side pockets [25]. The side pockets are too small for most organic molecules, resulting in a quasi-unidirectional microporous system that makes as-synthesized H-MOR susceptible to mass transport limitations and rapid deactivation [26]. Due to their microporous structure, the coke formed is not only covering active site but also blocking the pores [27].

Mordenite is widely used in catalysis and in separation and purification because of its uniform, small pore size, high internal surface area, flexible framework, and controlled chemistry [28]. It had been proved that mordenite could be used as catalyst in hydrocracking process to convert low density polyethylene (LDPE) and tire waste to fuel fractions [29-31]. Tortuous pores are too small for most molecules to enter, for this reason mordenite is generally regarded as a mono-dimensional zeolite. The major drawback of mordenite is generally a result of the limited size of the channels and cavities, and the lack of interconnectivity. This imposes diffusional limitations on reactions, limiting their activity, selectivity, and stability [32]. These can be improved by scattering metal either on the surface or in the pore of zeolites. There are many report concerning the influence of metal on the activity of mordenite catalyst. Ribeiro and Ribeiro [33] has reported the influence of metal loaded on mordenite. The presence of metal has positive effect that is hydrogenating the coke precursors. The activity and selectivity increase with the increase in platinum

concentration using Pt/H-MOR to produce light isomers [34-36]. Majdan et al. [37] had studied the influence of metals (Mn, Co, Ni, Cu, Zn and Cd) loaded on mordenite on the resulted characteristic. Ni and Co loaded on natural zeolite has been used for hydrocracking of LDPE [30], coconut oil [38] and polypropylene [39]. Burbidge et al. [40] reported that Pd/H-MOR has greater activity rather than Pd/H-Y.

Since mordenite is greatly deactivated during the run, optimum temperature become important thing to be specified. The conversion of heavy n-alkanes using H-MOR catalyst is active at temperatures higher than 523 K, presenting a maximum in activity near 673 K [34].

Based on the description above, the authors examined the characters of three kind of metals (Co, Ni and Pd) loaded on mordenite i.e. Co/MOR, Ni/MOR and Pd/MOR as catalysts for hydrocracking of α-cellulose under variation of temperature (400, 450, and 500 °C). The liquid products were compared to those of thermal and non-impregnated mordenite catalyst in the same condition of the hydrocracking.

EXPERIMENTAL SECTION

Materials

α-cellulose powder was purchased from Sigma-Aldrich (#C8002), zeolite mordenite (HSZ 640-HOA) was purchased from Catalyst & Chemical Ind.Co.Ltd., $PdCl_2$ (with 59% Pd), $NiCl_2 \cdot 6H_2O$ and $CoCl_2 \cdot 6H_2O$ were purchased from Merck, methanol 98% were purchased from Sigma-Aldrich.

Instrumentation

Scanning electron microscope with Energy Dispersive X-Ray Analysis (SEM-EDX) series JEOL JSM-6510LA, inductively coupled plasma (ICP) series Shimadzu ICPE 9820, FTIR series Shimadzu 21, X-ray diffractometer (XRD) series Rigaku Miniflex 600, gas chromatography mass spectrometer (GC-MS) series Shimadzu QP2010S.

Procedure

Catalyst preparation and characterization

Metals (Co, Ni and Pd) were loaded onto mordenite (MOR) were prepared by wet impregnation method using salt precursor of $CoCl_2 \cdot 6H_2O$, $NiCl_2 \cdot 6H_2O$, $PdCl_2$, respectively. An amount of 3.33 mg of $PdCl_2$, 8.20 mg of $NiCl_2 \cdot 6H_2O$, and 8.07 mg of $CoCl_2 \cdot 6H_2O$ were respectively mixed with 2.0 g of the MOR in 200 mL of methanol, followed by filtered and evaporated at 100 °C, then calcined at 450 °C for 3 h

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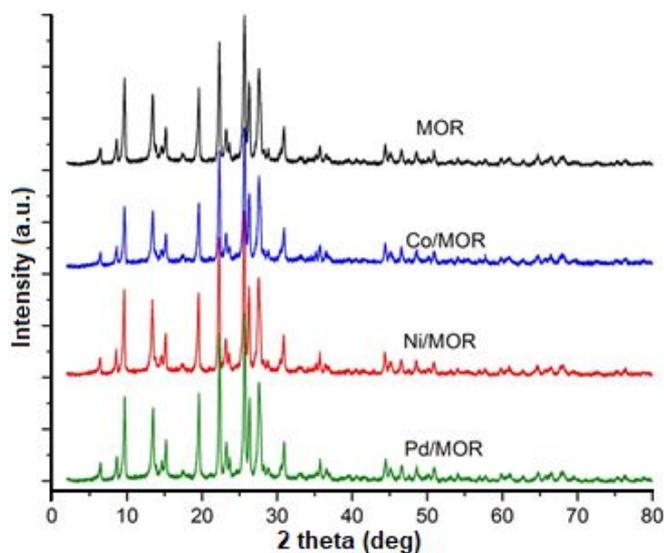
Fig 1. XRD pattern of mordenite catalysts
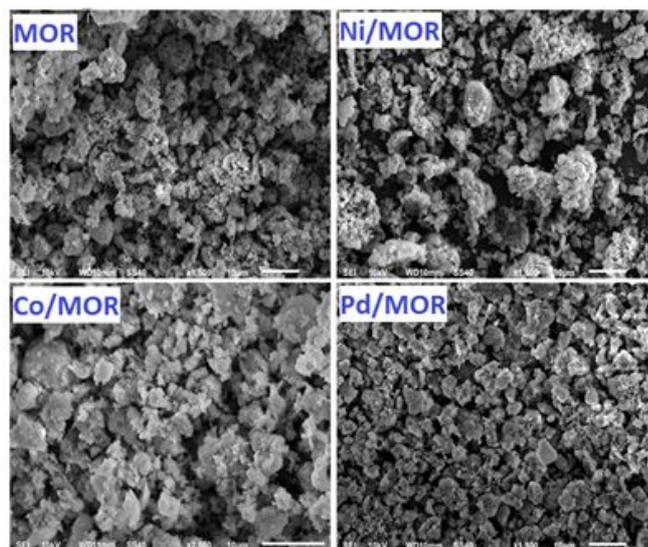
Fig 2. SEM images of mordenite catalysts

and continued by reduction (20 mL/min of H_2 flow) for 3 h to produce Co/MOR, Ni/MOR and Pd/MOR catalyst, respectively. Surface morphology of catalyst was analyzed using SEM (JEOL JSM-6510LA). The amount of metal impregnated on the MOR was investigated qualitatively using EDX and quantitatively using ICP (Shimadzu ICPE-9820). Catalyst's powder was pelleted using KBr and analyzed at 4000–300 cm^{-1} using FTIR (Shimadzu Prestige 21) spectrometer. The crystallinity of catalysts was investigated by XRD using Rigaku Miniflex 600 instrument.

Hydrocracking α-Cellulose

α-cellulose and catalyst in a weight ratio of 10:1 were loaded in a semi-batch reactor (h: 30.0 cm; l: 30.0 cm; o.d.: 4.50 cm; i.d.: 3.75 cm). The reaction temperature was varied under 400, 450, and 500 °C for 4 h with 30 mL/min of hydrogen flow. The reactor was connected with condenser and the liquid product was collected in an ice-bath system and investigated by GC-MS.

RESULT AND DISCUSSION

Catalysts Characterization

The X-ray diffractogram of mordenite, Co/MOR, Ni/MOR and Pd/MOR were shown in Fig. 1. The metal support did not affect the crystallinity of mordenite. The SEM images of the mordenite, Co/MOR, Ni/MOR and Pd/MOR were shown in Fig. 2. The morphology of mordenite catalysts after metal loaded did not defect the morphology with respect to those of mordenite, indicating that no crystalline transformations occurred during the impregnation of metals onto mordenite. The
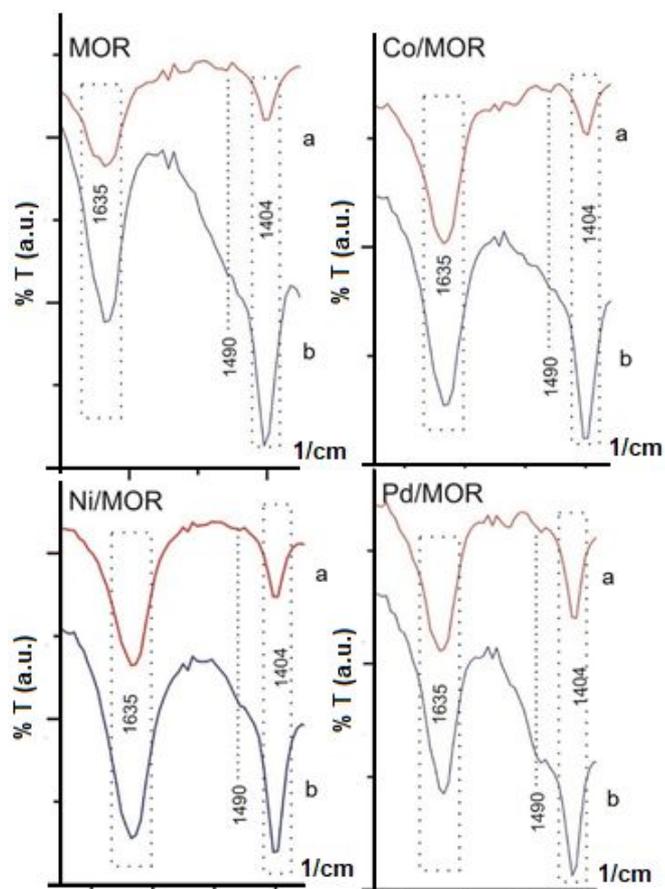
Fig 3. FTIR spectra of mordenite catalysts: (a) before and (b) after pyridine adsorption

availability of Co, Ni, and Pd indicated qualitatively by EDX and quantitatively analyzed by ICP were 0.56, 0.32 and 0.49 wt.%, respectively.

Table 1. Liquid product and residue distribution of α-cellulose hydrocracking

Catalyst	Liquid Product (wt.%)			Residue (wt.%)		
	400 °C	450 °C	500 °C	400 °C	450 °C	500 °C
Thermal	-[a]	37.86	-[a]	-[a]	23.69	-[a]
Mordenite	52.71	94.66	79.77	32.38	25.43	25.40
Co/MOR	59.57	90.48	73.05	26.49	23.56	21.51
Ni/MOR	28.97	73.43	71.18	24.44	22.89	21.40
Pd/MOR	98.08	67.38	58.77	23.60	22.72	21.91

[a] not detected

The existence of Brønsted and Lewis acid sites on mordenite, Co/MOR, Ni/MOR, and Pd/MOR analyzed by FTIR was shown in Fig. 3. From the Figure, the peaks at 1404 and 1635 cm^{-1} indicated Brønsted and Lewis acid sites. The metal loading increased Brønsted and Lewis acid sites [41-45]. This result was in agreement with the result obtained by Kaneda and coworkers [46] that loading of Pd-Ni metals onto the Y-zeolite increased both of Brønsted and Lewis acid sites.

Activity and Selectivity of Catalysts

Liquid product conversion and residue of α-cellulose hydrocracking at 400, 450, and 500 °C was shown in Table 1. It can be seen from this Table that the liquid product of catalytic hydrocracking were higher than thermal cracking (37.86 wt.%). The highest liquid product obtained by mordenite catalyst was 52.7, 94.66, and 79.77 wt.% at 400, 450, and 500 °C, respectively. The mechanism of thermal cracking proceeds through radical formation that initiates the new radical with lower C atom forming the gaseous product [47]. Meanwhile, the catalytic hydrocracking was taken place through carbonium ion mechanism at active sites of catalyst [48]. The highest liquid product obtained using Co/MOR of 90.48 wt.% at 450 °C while using Ni/MOR produced 73.43 wt.% at 450 °C respectively. The liquid products obtained by metal loaded-mordenite catalysts at temperature of 400 °C were higher than that obtained by mordenite, except for the Ni/MOR. This result may be due to the increasing performance of metal-loaded catalyst that indicated by the increased of the catalyst acidity [49] as shown in Fig. 3. Pd/MOR catalyst produced the highest liquid conversion of 98.08 wt.% at 400 °C. This phenomena may be caused by excellent performance of Pd that was also showed by others [50-52]. On the other hand, the liquid produced by the metal loaded-mordenite at 450 and 500 °C were lower than that obtained by mordenite. This may be due to the power of heat that increase the thermal cracking mechanism to produce more gas than liquid [47].

The residue for thermal cracking and catalytic hydrocracking of all variation temperature was shown in Table 1. The increase of temperature toward the amount of residue for thermal cracking and catalytic hydrocracking generally decreased in percent unit (wt.%). This phenomenon can be explained that the increase in temperature supplied more energy for vaporization of α-cellulose to undergo reaction with catalyst. The lowest and highest residues are reached by Ni/MOR at 500 °C (21.40 wt.%) and MOR at 400 °C (32.38 wt.%).

The composition of liquid product was shown in Table 2. Thermal cracking of α-cellulose produced 2-propanone-1-hydroxy of 85%. Meanwhile, hydrocracking using mordenite catalyst produced 1-propanol-2-methyl (66%) at 400 °C, methanol (58%) at 450 °C and ethanoic acid (83%) at 500 °C. Carboxylates acid (ethanoic and propanoic acid) were mainly produced using Co/MOR catalyst. The Ni/MOR catalyst obtained alcohol and 2-propanone. Pd/MOR catalyst mainly produced 2-propanone at all various temperatures.

The result indicated that both thermal cracking and catalytic hydrocracking produced relatively low carbon number compounds with molecular formula of C_2-C_3 hydrocarbons. Mordenite is microporous type zeolite. This result may be caused by the micropores characters of mordenite as a support catalyst. Thermal cracking also produced low carbon number compounds be caused the thermal cracking proceed via radical mechanism. The formation of radical by thermal can affect the formation of other radical from hydrocarbon feed caused continue cracking process until the smallest carbon number hydrocarbons was formed, thus produced more gaseous fractions [47].

CONCLUSION

The characteristic, selectivity, and activity evaluation of MOR, Co/MOR, Ni/MOR, and Pd/MOR catalysts for α-cellulose hydrocracking under variation of reaction temperatures as well as thermal cracking had been investigated. The highest liquid fraction produced by mordenite catalyst was 94.66 wt.% at 450 °C and the highest liquid conversion (98.08 wt.%) was performed by Pd/MOR catalyst at 400 °C. Thermal cracking at 450 °C produced liquid fraction of 37.86 wt.%.

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