The conversion of lignocellulose biomass to value-added chemicals is challenging. In this paper, the conversion process of diphenyl ether (DPE) as a model lignin compound to phenol and vanillin compounds involved a bifunctional catalyst in reaching the simultaneous one-pot reaction in mild conditions with a high yield product. The catalysts used in this conversion are hierarchical ZSM-5 zeolites and their cobalt oxide and molybdenum oxide impregnated derivate. The ZSM-5 zeolites were synthesized using alternative precursors from natural resources, i.e., Indonesian natural zeolite and kaolin. The physicochemical properties of the catalysts were determined with various characterization methods, such as: X-ray Diffraction (XRD), Fourier Transform Infra Red (FT-IR), Scanning Electron Microscope - Energy Dispersive X-ray (SEM-EDX), X-ray Fluorescence (XRF), Surface Area Analyzer (SAA), and NH$_3$-Temperature Programmed Desorption (NH$_3$-TPD). The catalytic activity on conversion of DPE substrates showed that the MoO$_x$/HZSM-5 produced the highest %yield for phenol and vanillin products; 31.96% at 250 °C and 7.63% at 200 °C, respectively. The correlation study between the physicochemical properties and the catalytic activity shows that the dominance of weak acid (>40%) and mesoporosity contribution (pore size of ~ 9 nm) play roles in giving the best catalytic activity at low temperatures.

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**Keywords:** Diphenyl ether; Co oxide/ZSM-5; Mo oxide/ZSM-5; Vanillin and Phenol production; catalytic conversion; natural sourced ZSM-5

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**1. Introduction**

The main challenge in fine chemical industrial development is the replacement of fossil resources with sustainable resources. The utilization of lignocellulosic biomass has recently shown a rapid development due to being the only renewable resource of organic carbon in nature, which provides advantages in value-added chemical production [1]. The chemical structure of lignin has many aromatic structures with specific ether bonding for each monolignol [2].
that become a source of high-value compounds, such as vanillin and phenol [3]. However, regarding the complexity of the lignin structure, the conversion mechanism becomes unclear. The simplification of the complexity of the lignin fraction can be seen in several existing model compounds, such as diphenyl ether (DPE) as a representative of 4-O-5 bonding, phenethyl phenyl ether (PPE) as representative of β-O-4 bonding and benzyl phenyl ether (BPE) as representative of a-0-4 bonding [4].

ZSM-5 as a heterogeneous catalyst is commonly used in biomass conversion because of its porosity, leading to a good shape selectivity of products and good thermal stability [5]. Deepa et al. reported that the presence of conventional HZSM-5 shows that biomass depolymerization produced around 60% of aromatic monomers [6]. Hereafter, several modifications in ZSM-5, such as modification of the pores into hierarchical pores and the addition of metal oxides, have shown to increase the catalytic effectiveness in biomass conversion, especially to improve the selectivity of the reaction product.

CoOx/HZSM-5 in the pyrolysis reaction produced the highest distribution yield for monocyclic aromatic compounds [7] and facilitated the conversion of bio-oil into phenolic and guaiacol products with the increasing selectivity of 9.2% and 15.3% compared with the non-catalyzed reaction [8]. Also reported, the pyrolysis reaction’s selectivity to produce phenolic derivative products facilitated by Mo modified ZSM-5 was 30% [9]. The impregnation of the Mo oxide on ZSM-5 produced monocyclic aromatic with the highest yield, and selectivity was 84.5% in fast pyrolysis reaction [10]. Hydrogenolysis of aryl ether bond over heterogeneous cobalt-based catalysts also show the 97% selectivity of C–O bond ruptured products was achieved from DPE model lignin compound, with the major product were phenol and benzene [11]. Also reported that Mo-based catalysts leading the effective hydrodeoxygenation of biomass-derived oxygenates, such as lignin model compounds [12,13]. Based on these several reports, it is shown that combination of acid sites in zeolite and metal oxide species, such as cobalt oxides and molybdenum oxides can effectively improve the lignin conversion.

For research purposes, the synthesis of ZSM-5 catalysts usually uses pro analyst precursors. Nonetheless, taking into account the environmental, economic, and abundances in nature, the use of natural resources as alternative precursors can be a distinct added value. It has been studied the success of zeolite synthesis from alternative resources, for example, kaolin [14,15], rectorite with diatomite [16], and a combination of Indonesia zeolite and kaolin [17]. In this work, the ZSM-5 catalyst was synthesized using the alternative precursor, i.e. Indonesian natural zeolite and kaolin. The as-synthesized ZSM-5 then was converted to HZSM-5, followed by modification with molybdenum and cobalt oxides to provide more active sites in the catalyst.

In this present work, we aimed to study the conversion of diphenyl ether (DPE), one of the lignin models, to more useful chemicals, such as phenolic compounds and vanillin using Mo-oxides and Co-oxides-modified HZSM-5 catalysts (MoOx/HZSM-5 and CoOx/HZSM-5). The correlation between physicochemical properties and activity of catalyst on DPE conversion, as well as the optimum conditions to obtain the highest %yield of vanillin and phenol are discussed.

2. Materials and Methods

2.1 Materials

Indonesian natural zeolite was from Bayat Klaten, Central Java. The kaolin used was provided by PT Aneka Kaolin Utama, Belitung Indonesia. NaOH pellet 99 %, nitric acid, hydrochloric acid, hydrogen peroxide 30%, glacial acetic acid, sodium acetate tetrahydrate, sodium bicarbonate, ethanol, trisodium citrate dihydrate, CO(NO3)2·6H2O, NH4NO3, and methanol were purchased by Merck (Germany). Tetra-propylammonium hydroxide (TPAOH 40%), (NH4)6Mo7O24·4H2O, and polydiallyldimethylammonium chloride acrylamide (PDDAM, 10 %) purchased from Sigma Aldrich, US. And the phosphoric acid (97 %) was purchased from PT. Smart Lab Indonesia.

2.2. Synthesis of Hierarchical ZSM-5 Catalyst from Natural Resources

Natural zeolite and kaolin were pre-treated with the activation, purification, fragmentation, and calcination processes following the procedure from Rohayati et al. [18]. The synthesis of hierarchical ZSM-5 using a molar ratio of 3 Al2O3: 64.35 SiO2: 10.07 (TPAO): 3571.66 H2O. Fragmented Indonesia zeolite and extracted silica from kaolin as the precursors were mixed with H2O, stirred overnight. Furthermore, TPAOH and TEOS were added dropwise into the mixture while stirring at 100 °C. Then, the pH solution was adjusted to ±11 using acetic acid glacial followed by aging for three hours. Afterward, a certain amount of PDD-AM was slowly added into the reaction
mixture at room temperature and stirred for 24 h. After stirring, the mixture was transferred into an autoclave for further crystallization at 170 °C for 144 h. The crystals were washed with H₂O and then dried in the oven at 60 °C, then calcined in the atmospheric pressure at 550 °C for five hours [19]. The as-synthesized hierarchical ZSM-5 then was named ZSM-5.

2.3. Preparation of Hierarchical HZMS-5 Catalyst

Multiple ammonium exchange was carried out using a solution of NH₄⁺ 1 M at 90 °C for two hours under stirring for three repetitions. The resulting NH₄/ZSM-5 then was calcined gradually at 550 °C for 5 hours to produce H/ZSM-5 [20] and named as HZSM-5.

2.4 Preparation of Hierarchical CoOₓ/ZSM-5 and MoOₓ/ZSM-5 Catalysts

Catalyst modification was carried out by wet impregnation for 10 %wt metal loaded by adding 1.1313 M of Co(NO₃)₂·6H₂O or 0.0355 M of (NH₄)₆MoO₄·4H₂O into 1 gram of ZSM-5 or HZSM-5 using spraying method multiple times to form a paste [21] and left for 24 hours before it was calcined gradually at 550 °C to obtained CoOₓ/ZSM-5 [22] and at 500 °C to obtained MoOₓ/ZSM-5 [23]. Furthermore, the as-prepared catalysts were named CoOₓ/ZSM-5, CoOₓ/HZSM-5, MoOₓ/ZSM-5, and MoOₓ/HZSM-5.

2.5. Characterization of Catalysts

All catalysts were then characterized using XRD, FT-IR, XRF, SEM, EDS, SAA, and NH₃ TPD. The FT-IR analysis used Alpha – Bruker, while the XRD was carried out in PANalytical X’Pert PRO 2318 diffractometer with Cu-K radiation (λ = 1.5418 Å) as the incident beam. Analysis XRF using PANanalytical epsilon1. The SEM-EDS measurement using FE-SEM JIB-4610F, Schottky electron gun rote current (200nA), electron backscatter diffraction (EBSD), cathodoluminescence (CLD). Moreover, for the surface area analyzer, use Quantachrom-Evo Surface Area and Pore Analyzer. And for the acidity properties was analyzed using NH₃-TPD Chemisorb 2750 micrometric, with the sample heated at 350 °C for 60 min under He gas (inert) as the pre-treatment, followed by the NH₃ adsorption was carried out at 100 °C for 30 minutes using NH₃ 5% in He (v/v), then purged with He gas (inert) at the same temperature, for 30 minutes. Afterward, the NH₃ desorption was carried out at a temper-}

2.6. Catalytic Activity Test

The conversion reaction was performed in a batch reactor shown in Figure 1. The procedure was following Deepa et al. [6] and Pratama et al. [17] with modification. The reaction was carried out under an inert condition with 2 atm of N₂ at room temperature. The solvent was water: ethanol (1:1 v/v) mixture in a total volume of 25 mL. The amount of DPE and the catalyst added was 0.25 g and 0.125 g, respectively. The reaction was performed under a stirring condition with 500 rpm for 30 min [17]. The reaction temperature varied at 150, 200, and 250 °C.

After the reaction, the filtrate was separated and prepared for analysis with the HPLC using LC PG equipped with C18 column, and a mixture of methanol: distilled water (80:20) as eluent. The % conversion of DPE, and the % yield of phenol and vanillin are calculated using the standard calibration curve and determined using following equations:

\[
\text{%DPE Conversion} = \frac{\text{Init. Substrate Mass (g) - Residual Mass (g)}}{\text{Substrate Mass (g)}} \times 100\
\]

\[
\text{%Yield} = \frac{\text{Product Concent. (mg / L) x Solution Volume (L)}}{\text{Substrate Mass (g)}} \times 100\
\]

3. Results and Discussion

3.1. Catalyst Characterizations

Figure 2 shows the diffractogram of all as-prepared catalysts, which reveals the specific

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pattern for ZSM-5 based on JCPDS 49-0657 [24] that in angel 2θ = 7-10°, 22-25° [25,26]. It depicts that the MFI (Mordenite Framework Inverted) as the pentasil framework was successfully synthesized. Moreover, as-synthesized ZSM-5 also has another phase as the presence of a strong peak around the angle of 26.7 which is probably the quartz phase. This due to the precursor from the natural resources, so the quartz phase of unreacted silica can be found in the material.

Furthermore, Figure 2 shows new diffraction as Co3O4 phase (2θ = 19°, 31°, 37°, 45°, 56°, 59°) in cobalt oxide modified catalysts referred to JCPDS No. 42-1467 [27]. The XRD patterns of Mo oxide modified catalysts also show new diffraction peaks for MoO3 phase (2θ = 13°, 23°, 27°, 34°, 38°, 46°, 49°, 50°, 51°, 53°, 54°, 56°, 59°, 64°) as referred to JCPDS No. 05-0508 [28]. These results inform that the incorporation of Co-oxide or Mo-Oxide into ZSM-5 was done successfully.

FT-IR spectra for the as-prepared catalysts can be seen in Figure 3. In the wavenumber around 3500 cm⁻¹ a broad band appeared in all spectra, which is assigned to water molecules that are hydrogen-bonded to silanol groups (Si-OH) from the surface of ZSM-5 [22,29]. There were differences in its intensity in the spectra of Mo and Co impregnated ZSM-5 and HZSM-5, indicating the closure of the area due to the metal impregnation process in ZSM-5 zeolite. Furthermore, the other typical peaks of the MFI structure of ZSM-5 zeolite are shown as the absorption band of asymmetric stretching from the T-O at 1075-1250 cm⁻¹, symmetric stretching of T-O at 820-650 cm⁻¹, and at 650-500 cm⁻¹ assigned as pentasil double five rings [29].

Additional peaks appear in the fingerprint area between 1000-500 cm⁻¹ for all the as-prepared catalysts, indicating the presence of metal oxide in ZSM-5. The characteristic bands of MoO3 show absorbance bands around 999-995, 900-877, 561-554 cm⁻¹ [30]. Furthermore, the additional characteristic peaks for Co3O4 show around 667, 626, and 580 cm⁻¹ [31,32]. This FT-IR analysis provides additional data implementation for as-prepared catalysts and supports the characterization of the XRD diffractogram, which shows the successful process of preparation catalysts.

Scanning Electron Microscopy (SEM) characterization provides information on the catalyst morphology. Figure 4 informs the morphology of all as-prepared catalysts showing the coffin-like or hexagonal crystal geometry [33]. Specific to the Figure 3 (c)-(f), the Co or Mo oxides anchoring to the catalyst’s surface contributes to changing the surface of the ZSM-5 catalysts to become slightly rougher.

The elemental composition of the catalyst is analyzed by XRF and EDS methods. The XRF data reveals the element composition in a
bulky state, while the EDS data show the composition of the elements on the surface. The summary of the Si/Al ratio and the loaded metal of the catalysts are shown in Table 1. Generally, based on XRF data, there was no significant change in the Si/Al ratio of the catalyst after the preparation of HZSM-5 and the metal oxide impregnation process. In addition, the EDS data showed that the %wt of Na content was significantly decreased in HZSM-5, indicating an effective cation exchange process. Furthermore, the %wt loading of the Co-oxide and Mo-oxide is close to the expected amount of metal oxide. As for metal oxides that are not incorporated into the catalyst, it could be caused by the aggregation of metal oxide groups on the outside of the catalyst.

Furthermore, the porosity and textural properties of the catalyst were analyzed using the BET and BJH methods. The adsorption-desorption isotherm graphs (Figure 5) show that as-prepared catalysts have a type IV isotherm curve, which indicates monolayer adsorption at low pressure and multilayer adsorption in high pressure, and with the existence of hysteresis loop that indicates the hierarchical porosity [33-35]. The adsorption and desorption isotherm curves show small hysteresis, that could be due to the existence of impurities from the natural precursors which influenced the formation of pores in ZSM-5. Furthermore, from discussion in XRD data, it can also be seen that there is a quartz phase that might cause pore-blocking within the ZSM-5 framework.

Tabel 1. Summary Si/Al and metal loading (%wt) in catalysts by XRF and EDS method

| Catalyst       | XRF       | EDS       |
|----------------|-----------|-----------|
|                | Mo | Co | Si/Al Ratio | Na | Mo | Co | Si/Al Ratio |
| ZSM-5          | -  | -  | 12.11       | 1.20| -  | -  | 14.12       |
| HZSM-5         | -  | -  | 13.20       | 0.50| -  | -  | 14.65       |
| CoOx/ZSM-5     | 7.94| -  | 11.44       | -  | -  | 7.00| 12.04       |
| MoOx/ZSM-5     | -  | 8.30| 11.30       | -  | 9.60| -  | 11.32       |
| CoOx/HZSM-5    | -  | 7.36| 12.12       | -  | -  | 7.80| 10.11       |
| MoOx/HZSM-5    | 8.19| -  | 11.19       | -  | 10.30| -  | 12.00       |

Figure 4. SEM images for (a) ZSM-5, (b) MoOx/ZSM-5, (c) CoOx/ZSM-5, (d) HZSM-5, (e) MoOx/HZSM-5, (f) CoOx/HZSM-5 catalyst
The process of cation exchange showed not to significantly change the structural porosity of the catalyst and the textural properties tended to be preserved. Meanwhile, the incorporation of metal oxides in catalysts shows that all the catalysts experienced a reduction in BET surface area except the CoOx/HZSM-5. This decrease was mainly due to solid metal species at the pores and/or the external surface of zeolites [21]. Meanwhile, the MoOx/ZSM-5 experiences a significant decrease in BET surface area and pore volume. This condition is because of the agglomeration of Mo oxide in the pore.

In contrast, the increase of surface area in CoOx/HZSM-5 due to the aggregation of Co-oxides on the external zeolite surface, which leads to the creation of more volume and pore. This phenomenon was also observed by Krisnandi et al. when preparing iron oxide modified NaY Zeolite [36]. Moreover, the t-Plot analysis showed the metal oxides reside in both micropores and mesopores catalysts. The textural properties of the catalysts are summarized in Table 2.

Data from Table 2 show that Mo impregnated HZSM-5 led to the pore opening in the mesopore site of catalysts which made a larger size in the distribution pores. Seen also in XRF data of MoOx/HZSM-5, that experienced a decrease of Si/Al ratio from 13.20 to 11.19 compared to the HZSM-5 was assumed due to de-silication. It was also reported by Kosinov et al. that most of the initially aggregated Mo-oxide at the external surface are dispersed into the pore upon calcination, resulting in the reaction of mobile MoO3 species with framework Al, aluminium molybdate formation, and produced the amorphous SiO2 [37].

The acidity of ZSM-5 and modified ZSM-5 catalysts was determined by NH3-TPD as de-

Tabel 2. Summary of textural properties catalysts based on N2-sorption analysis

| Catalyst      | Surface Area (m²/g) | Volume @STP (cc/g) | Pore Distribution (nm) |
|---------------|---------------------|--------------------|------------------------|
|               | ^aBET | ^bMicro | ^cMeso | ^dTotal | ^eMicro | ^fMeso | Micro | Meso |
| ZSM-5         | 159   | 75     | 84     | 0.11 | 0.04 | 0.07 | 1.93 | 3.12 |
| HZSM-5        | 149   | 70     | 79     | 0.10 | 0.04 | 0.07 | 1.94 | 2.73 |
| CoOx/ZSM-5    | 152   | 72     | 80     | 0.11 | 0.04 | 0.07 | 1.93 | 2.16 |
| MoOx/ZSM-5    | 58    | 25     | 34     | 0.04 | 0.01 | 0.03 | 1.94 | 2.16 |
| CoOx/HZSM-5   | 193   | 84     | 110    | 0.13 | 0.04 | 0.08 | 1.93 | 2.16 |
| MoOx/HZSM-5   | 139   | 54     | 85     | 0.14 | 0.03 | 0.11 | 1.94 | 9.28 |

^aBET surface area; ^bMicropore surface area evaluated by t-plot method; ^cBET surface area, ^dMicropore surface area evaluated by t-plot method; ^eMesopore surface area calculated using S_BET-S_micro; ^fTotal pore volume at P/P0 ~ 0.99; ^gMesopore surface area calculated using S_BET-S_micro; ^hTotal pore volume at P/P0 ~ 0.99; ^iMicropore volume calculated by t-plot method; ^jMesopore volume calculated using V_total-V_micro; ^kMicropore volume calculated by t-plot method; ^lMesopore volume calculated using V_total-V_micro; ^mPore distribution based on BJH analysis.

Figure 5. (a) Isotherm of adsorption-desorption curves and (b) pore size distribution of as-prepared catalysts
The temperature-programmed desorption of a basic molecule, such as ammonia (NH$_3$-TPD), is one of the most commonly used methods for measuring the surface acidity of porous materials such as zeolites [21,38-39]. With the NH$_3$-TPD analysis, the acid site distribution in catalysts could be estimated. Generally, the acidity distribution can be divided into three regions by Gaussian function as a weak acid, moderate acid, and strong acid site [21,46]. Specific to the ZSM-5 and HZSM-5 acidity profile, the peaks of acid distribution usually appear in two temperature regions [47] or three temperature regions [21,46].

In Figure 6, each curve was divided into three peaks as Gaussian function; the peaks centered ca. 100-250 °C, 250-600 °C, and 600-800 °C pointing to the desorption of NH$_3$ in weak acid, medium acid, and strong acid positions [21]. The low Si/Al ratio (Si/Al ratio = 12) in as-prepared catalysts caused the NH$_3$ desorption in medium and strong acid sites was found in high temperature regions. It was also reported by Lonyi et al. that the NH$_3$-TPD curve of HZSM-5 with Si/Al ratio = 15 have a high temperature region around 550-700 °C [39]. Table 3 shows the summary of detailed catalysts acidity information of as-prepared catalysts.

Furthermore, Mo incorporated ZSM-5 and HZSM-5 has interestingly changed the acid site property from the strong acid to weak acid, with the % weak acid content being 48% and 42%, respectively. Meanwhile, the CoO/ZSM-5 has strong acid as the dominant acid sites, while CoO/HZSM-5 is predominated with medium acid sites.

The change in the acidity of the catalyst is associated with the closure of the acid sites on the surface and the reaction between metal species and the acid site on the outer surface or in the channels [21,38,40]. In addition, the data shows the impregnation lead reaction between metal species and protonic acid and would have converted the strong acid into a medium or weak acid.

3.2. Catalytic Activity

The % conversion of the DPE substrate was displayed in Figure 7, showing that the % conversion of DPE was about 89-91% conversion for the uncatalyzed reaction, and 96-100% conversion when catalysts were added, with the highest using the MoO$_x$/HZSM-5 catalyst at 200 °C was 100% conversion.

Figure 8 reveals the % yield of the desired compounds of this reaction, phenol and vanillin. The Figure 7(a) shows without a catalyst, the % yields of phenol fall in the range of 10% - 18%, the highest was 17.65% at 200 °C, while in the presence of catalysts, the % yield of phenol was increased, with the highest yield of
31.96 % was achieved using MoO₃/HZSM-5 catalyst at 250 °C. On the other hand, for vanillin, as shown in Figure 8(b), the highest yield was 7.63% over MoO₃/HZSM-5 catalyst at a temperature of 200 °C.

3.3. Correlation of Physicochemical Properties of Catalysts and the Catalytic Activity

The reaction of DPE molecules as organic molecules is influenced by temperature, so as expected the % conversion of DPE at the reaction temperature (150-250 °C) was high, nearly 100%. It has also been reported that the breaking of C=O–C and aryl ether bonds can occur in the temperature range of 150-300 °C without using a catalyst [41]. Yao et al. reported that over numerous heterogenous catalysts the DPE conversion above 70% in 120 °C [42], furthermore, Zhao et al. reported over Pd/C and HZSM-5 in aqueous solution, DPE are converted 100% at 200 °C [43]. However, it becomes important to use a catalyst in the reaction to increase the selectivity of desired products, such as vanillin and phenol. In addition, this study showed that phenol and vanillin are the major products from DPE substrate over the as-prepared catalysts. The other possible products are benzene, cyclohexane, cyclohexanol and cyclohexanone, as reported in [44,45]. Thus, further product analysis using other standard compounds or with Liquid Chromatography-Mass Spectrometry (LC-MS) is suggested to be carried out if necessary. According to the catalytic activity and the physicochemical properties, the character of the catalyst that has a significant influence on the production of phenol and vanillin is the composition of the catalyst acidity and the textural/porosity properties.

As observed in this study, where ZSM-5 has two desorption peaks and HZSM-5 has three desorption peaks in NH₃-TPD curve as depicted in Figure 6. Furthermore, Engtrakul et al. reported that

Table 3. Acidity profile by NH₃-TPD measurement of as-prepared catalysts

| Catalyst    | Acid Amount (mmol/g) | *Acid Site Content (%) | Peak Position (ºC) |
|-------------|----------------------|------------------------|--------------------|
|             |                      | Weak | Medium | Strong | Weak | Medium | Strong |
| ZSM-5       | 0.2870               | 38   | 62     | 0      | 207  | 568    | -      |
| HZSM-5      | 0.2199               | 6    | 8      | 85     | 221  | 510    | 703    |
| CoOₓ/ZSM-5  | 0.1803               | 19   | 15     | 66     | 220  | 557    | 726    |
| MoOₓ/ZSM-5  | 0.0532               | 48   | 12     | 41     | 207  | 502    | 635    |
| CoOₓ/HZSM-5 | 0.2595               | 15   | 72     | 13     | 214  | 475    | 732    |
| MoOₓ/HZSM-5 | 0.1512               | 42   | 36     | 22     | 224  | 526    | 676    |

*Acid Content determined by NH₃-TPD profile deconvolution with Gaussian peaks (R² > 0.95)

Figure 7. DPE conversion over as-prepared catalysts; reaction condition: P N₂ = 2 atm DPE : catalyst ratio = 0.25 g : 0.125 g, solvent used (ethanol: H₂O) = 1:1 in total volume was 25 mL.
reported that the temperature peaks are influenced by the Si/Al ratio of the catalysts, which the lower Si/Al can shift the peaks to higher temperature region [39,48].

In addition, the incorporation of metal oxides in zeolite has been reported can change the catalysts' acidity, such as new peaks appearing at high-temperature regions [47] and changing the dominant composition of the acid sites [21,28,49,50]. Specific to incorporated with molybdenum oxide, the low temperature desorption peak experienced an increase [28,49]. Meanwhile, the incorporation with cobalt oxide tends to increase desorption peak at higher temperature region [50]. This phenomenon is similar to what was found in this study, that incorporating molybdenum oxide can increase acidity in the low-temperature region. In contrast with the cobalt oxides can increase acidity in relatively high temperature region.

Specific to the expected mild conditions in this study, where the reaction temperature is low, ranging from 150-250 °C, it is seen that the catalyst with the high weak acid content can facilitate the reaction optimally. The modified Mo catalyst with the weak acid content
above 40% shows the highest production of phenol and vanillin at a reaction temperature of 200-250 °C. It was also reported by Jiang et al. that cleavage of diphenyl ether C=O bond optimally facilitated over weakly acidic catalyst in 220 °C [51].

Moreover, in more detail on the NH\textsubscript{3}-TPD analysis, apart from the number of catalyst acid sites, the ability of the modified Mo oxide catalyst in adsorbing and desorbing substrate molecules (base species) from the surface greatly supports the performance of heterogeneous catalysts, where the ability of the active site of the catalyst to adsorb-desorb substrates and products is one of the important factors. Furthermore, the Navajas et al. also reported that the Molybdenum oxides have interesting activity regarding the acid sites as the Lewis acid and the Brönsted acid in the conversion of vegetable oil [52]. Considering the Lewis acidity, the molybdenum species could provide the orbital d and can form the reactive transition state with the substrate and lead the lower energy pathway in the reaction. It showed that increasing acidity in the low-temperature region could support the conversion reaction in mild conditions due to the ability to give the hydrogen from the surface to react with the substrate. Furthermore, supported by Ben et al. the existence of hydrogen as the Brönsted acid site in catalyst can facilitate some reactions in lignin conversions, such as hydrodeoxygenation (the carbocation formed by dehydration), followed by cleavage ether bond, decarboxylation, or cleavage of the C−C bond [53].

In addition to the acidity of the catalyst, it is also seen that the mesopore size influences the tendency for the formation of phenol and vanillin products in the catalyst. The presence of mesopore in the catalyst increases the catalytic effectiveness, where the larger the size of the mesopore, the higher the yield of the desired product [54,55]. In this study, the mesopore size above 9 nm gives the highest production of phenol and vanillin.

Interestingly, although it has a dominance of a weak acid, if the catalyst does not have a large mesopore size, then the production of phenol and vanillin is not optimal. It can be seen in catalytic activity, where MoO\textsubscript{x}/ZSM-5 with 48% weak acid but only 2.16 nm mesopore size resulted in the production of phenol and vanillin under the MoO\textsubscript{x}/HZSM-5 catalyst, which had 42% weak acid content with 9.28 nm mesopore size. The size of the mesopore greatly affects the ability of the substrate and product to diffuse into the pore. Kantarelis et al. also reported that the coke formation formed during the reaction and led to the blockage in the pore [7]. Meanwhile, with the larger pore size (by introducing mesoporosity), this drawback can be overcome. Therefore, this work revealed that the yield of phenol and vanillin products in the catalytic reaction of DPE as a lignin model compound was correlated with the content of weak acid on the catalyst and, at the same time, the mesopore size in the catalyst. Therefore, this study can recommend that ZSM-5 synthesized with higher weak acid content and large mesoporosity can facilitate the conversion of lignin at the mild condition with low temperatures, ranging from 200-250 °C.

3.4 Proposed Reaction Mechanism

Based on Figure 9 and considering the resulting yield, the DPE conversion mechanism is thought to be initiated by the formation of phenol followed by vanillin. This reaction is fa-
cilitated by hydrogen on the catalyst surface and breaks the ether bond [44]. It is similar to the observation by Yao et al. that phenol is the major product of conversion DPE in 140 °C in one hour reaction by the hydrodeoxygenation pathway [39]. This reaction begins with the adsorption of the substrate molecule on its oxygen (base substituent) on the acidic side of catalyst, probably the Mo oxide on the surface of the catalyst and is followed by a chemical reaction on the surface due to the presence of hydrogen in the catalyst surface. It has been reported the Mo-based catalysts selectively break C−O bond, meanwhile preserve the aromatic ring [53]. Moreover, Mo oxide species is generally considered as the originate of high hydrodeoxygenation activity over Mo-based catalysts [54]. The reaction continues to produce vanillin, the presence of supported Mo oxide facilitates the reaction of the oxidation from ethanol as a solvent to an aldehyde substituent, supported by report in [11,55]. The presence of Brönsted acid in the catalyst surface leads to the formation of a carbocation and termination of the C−C bond to produce methoxy, similar to the report in [50]. The description of these stages can be seen in Figure 10.

4. Conclusions

In this study, the as-synthesized and modified ZSM-5 catalysts from alternative precursors i.e Indonesian zeolite and Kaolin showed physicochemical properties that have met the criteria for good heterogeneous catalyst in DPE lignin model compound conversion to phenol and vanillin. The relationship between the physicochemical properties of the catalysts has been investigated. To conclude, MoOx/HZSM-5 catalyst, which has dominance of weak acid composition above 40% and with the mesopore size of 9 nm, showed the highest % yields of phenol and vanillin, at reaction temperature of 200-250 °C in 30 minutes reaction.

![Figure 10. Proposed mechanism to produce vanillin from DPE with phenolic compound as the intermediate over MoOx/HZSM-5 catalyst](image-url)
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