

PREPARATION, CHARACTERIZATION AND CATALYTIC ACTIVITY OF CuO/TS-1 ON BENZENE HYDROXYLATION REACTION

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Abstract

CuO/TS-1 catalysts have been prepared and tested in the benzene hydroxylation. TS-1 was synthesized by hydrothermal method, while CuO/TS-1 was prepared by impregnation method using $\text{Cu}(\text{NO})_2 \cdot 3\text{H}_2\text{O}$ as precursor. Catalysts were characterized by using X-ray diffraction (XRD), infrared spectroscopy (IR), and N_2 adsorption-desorption techniques. The catalytic activity was tested in the hydroxylation reaction of benzene. The products were analyzed using gas chromatography. Catalyst characterization by XRD and IR techniques have showed that the catalyst structure was a MFI type of zeolite. XRD pattern have showed the orthorombic structure and indicated the presence of CuO aggregation. The results of the pyridine adsorption have found that the acidity of TS-1 and CuO/TS-1 were a Lewis acid and it's increased with an increasing amount of CuO loading. The results of nitrogen adsorption analysis have showed decreasing of surface areas of catalyst with increasing amount of CuO loading. The optimum conditions of benzene hydroxylation was observed by 1%CuO/TS-1 catalyst at 70 °C, reaction time 2 h and acetic acid as the solvent yielded 27.6% of phenol with phenol selectivity was 75.5%.

Keywords: acetic acid, benzene hydroxylation, CuO/TS-1, TS-1

1. Introduction

Hydroxylation of benzene to phenol with one-stage process has been developed over the last ten years [1]. In this reaction, oxidant and catalyst are required. Oxidant that was commonly used in this reaction is hydrogen peroxide (H_2O_2). H_2O_2 is an oxidant that is stable, has higher content of active oxygen, as well as is environmentally friendly, so it is suitable to be used as oxidant in the hydroxylation of benzene [2]. In the beginning the catalysts used was homogeneous catalyst, such as palladium acetate-fenantroline that was used to produce phenol (100% selectivity) at 180 °C [3]. However, homogeneous catalysts are now started to be left behind because it has some disadvantages, such as difficult to separate from products that are in one phase, thus requiring additional costs to separate the catalyst from the reactants and products. Therefore, the scientists then turned to the use of heterogeneous catalysts, which have several advantages such as it can be separated from the reactants and products, and can be reused in the next reaction [4].

The use of heterogeneous catalysts in direct benzene hydroxylation reaction has been developed in recent

years. Several heterogeneous catalysts used in benzene hydroxylation reactions include $\text{VO}_x/\text{MCM-41}$ with 10% benzene conversion and selectivity to phenol 38%, as well as a mixture of Fe/cerium oxide with 29% conversion and 73% selectivity to phenol [5]. TS-1 has been used to catalyze the hydroxylation reaction of benzene with H_2O_2 with the conversion and selectivity of phenol as high as 74% and 4 hour reaction time [6]. Hydroxylation reaction of benzene with other TS-1 catalyst yielded products up to 97% [7]. Of several examples of catalysts that have been developed, TS-1 is the best catalyst in direct hydroxylation reaction of benzene to phenol.

Titanium silicate (TS-1), $\text{Si}_{96-x}\text{Ti}_x\text{O}_{192}$, is a molecular sieve with microporous structure of MFI. As in ZSM-5 zeolite, MFI structure has two channels containing ten oxygen atoms, with the size of: 0.51 x 0.55 nm (100) and 0.53 x 0.56 nm (010). Titanium silicate-1 (TS-1) is a micro-channel catalyst, which can increase the contact efficiency between the catalyst and reactants. Titanium silicate-1 can catalyze the oxidation of various organic compounds such as epoxydation of alkenes, oxidation of aromatics, phenol hydroxylation, and hydroxylation of benzene with H_2O_2 as oxidant. The ability of TS-1 as

catalyst is due to its tetrahedral Ti^{4+} active site isolated from each other, which could enhance its catalytic activity.

TS-1 catalytic activity in benzene hydroxylation reaction is influenced by the amount of Ti loading in the MFI framework. The increase in titanium concentration can improve the catalytic activity of TS-1 [8]. Titanium in tetrahedral coordination is the key of TS-1 catalysis reaction because it acts as the active site of the catalyst [9]. However, there is a certain rule that the amount of titanium incorporated within the framework of TS-1 should not exceed 3% [10]. The higher concentration of titanium, the more TiO_2 in the extra-framework. The existence of TiO_2 outside the framework can cause H_2O_2 decomposition into water and oxygen [11], which lead to obstruction of the interaction between the reactant molecules and the Ti^{4+} sites in the framework so that it can reduce the catalytic activity of TS-1.

An effort to improve the catalytic activity of TS-1 on the production of phenol can be done by changing the nature of TS-1 which was originally hydrophobic to hydrophilic by adding metal oxides that has acidic properties. Synthesis of vanadium oxide impregnated on TS-1 and used as a catalyst for hydroxylation of benzene have been carried out giving 95.50% selectivity to phenol [12]. The catalytic activity of TS-1 can also be improved by increasing the active site of the transition metal ions or metal oxides. Metal oxides have properties that can increase the acidity of the catalyst support, while the metal ion can add active sites in catalyst through the formation of double active sites.

Copper has been developed as a catalyst in the hydroxylation of benzene. Some of the Cu catalysts have been reported including Cu/Al_2O_3 with phenol yield as much as 1.49% [13], and $CuO-Al_2O_3$ with phenol yield of 0.9% [14]. The use of MCM-41 supported CuO with catalyst ratio of 4 wt%, resulting in a conversion of 21% and 94% selectivity to phenol, in the reaction time of 70 minutes at 70 °C [15]. In that reaction Cu acted as an active site reducing H_2O_2 to the hydroxyl radical OH· on non active MCM-41 support, and oxidized benzene to phenol [15]. The results of other study also showed that Cu catalyst supported by Al pillared catalyst could improve the catalytic activity giving 55% phenol conversion and selectivity to phenol of 80% [16]. From several studies that have been reported, copper, either as metal ion or metal oxides, have a role as an active site in the catalytic reaction of hydroxylation of phenol, as well as benzene. In this research an effort to improve the catalytic activity of TS-1 was done by adding active sites of the Cu metal ions from CuO metal oxides through the formation of Cu and Ti double active sites.

2. Experiment

TS-1 (1 mol% titanium) was synthesized according to the patented procedure [17] using tetraethyl ortosilicate (TEOS) and tetrabutyl ortotitanate (TBOT) as titanium source. The gel to synthesize the TS-1 (1 mol% titanium) was made from 66.86 grams TEOS, 1.1 grams of TBOT in 2-propanol (10 mL) and 60 g of TPAOH. CuO/TS-1 catalysts were prepared by impregnation method based on the procedure reported in [16] with various composition of 0%, 1%, 2%, 4, and 8 wt% CuO: TS-1. The impregnation was done by immersing TS-1 powder to a solution of $Cu(NO_3)_2 \cdot 3H_2O$ as CuO source. The mixture was stirred with a magnetic stirrer at room temperature for 3 hours, then evaporated to remove water content. The solid catalyst was then dried at a temperature of 100 °C for 24 hours and calcined at 550 °C for 5 hours.

TS-1, and XCuO/TS-1 (0%, 2%, 4% and 8% CuO/TS-1) catalysts were characterized using FTIR KBr pellet method and the spectra were obtained at wavenumber 4000-400 cm^{-1} . Analysis of the solid structure of TS-1 and CuO/TS-1 was performed with X-ray diffraction with Cu K α radiation ($\lambda = 1.5405 \text{ \AA}$) at 40 kV and 30 mA, $2\theta = 5-50^\circ$, scan speed of 0.04°/sec. Determination of catalyst surface area was performed using nitrogen adsorption-desorption method in Quantochrome NovaWin instrument with a temperature bath of 77.3 K.

Catalysis reaction was performed by a method that has been used previously [18]. Catalyst activity test experiments were carried out with 17% catalyst/total number of reactants as in the following procedure: 1 g of benzene was dissolved in 5 g of solvent in a round flask, followed by addition of 0.15 g of catalyst. The mixture is stirred for 10 minutes and 1.5 g of H_2O_2 , 30%, was added, then was stirred with a speed of 250 rpm for 3 h. After the mixture was reacted for 3 h, samples were taken for analysis of the resulting reaction product using gas chromatography (GC).

3. Results and Discussion

X-ray diffraction. X-ray diffraction patterns of TS-1, ZSM-5 (Si: Al = 25:1) and CuO/TS-1 synthesis results were shown in Figure 1, having high peaks at $2\theta = 7.92$; 8.82; 23.09; 23.29; 23.68, and 23.92°. These peaks correspond to the results published by the International Zeolite Association [19] for the diffraction pattern of ZSM-5 with the MFI structure type and orthorhombic symmetry. The TS-1 also have single diffraction line at $2\theta = 23.09$; 23.29; 23.68, and 23.92° which is the typical peaks of symmetry orthorhombic of TS-1, the peaks were formed due to titanium were in the framework of TS-1 [9]. The existence of tetrahedral

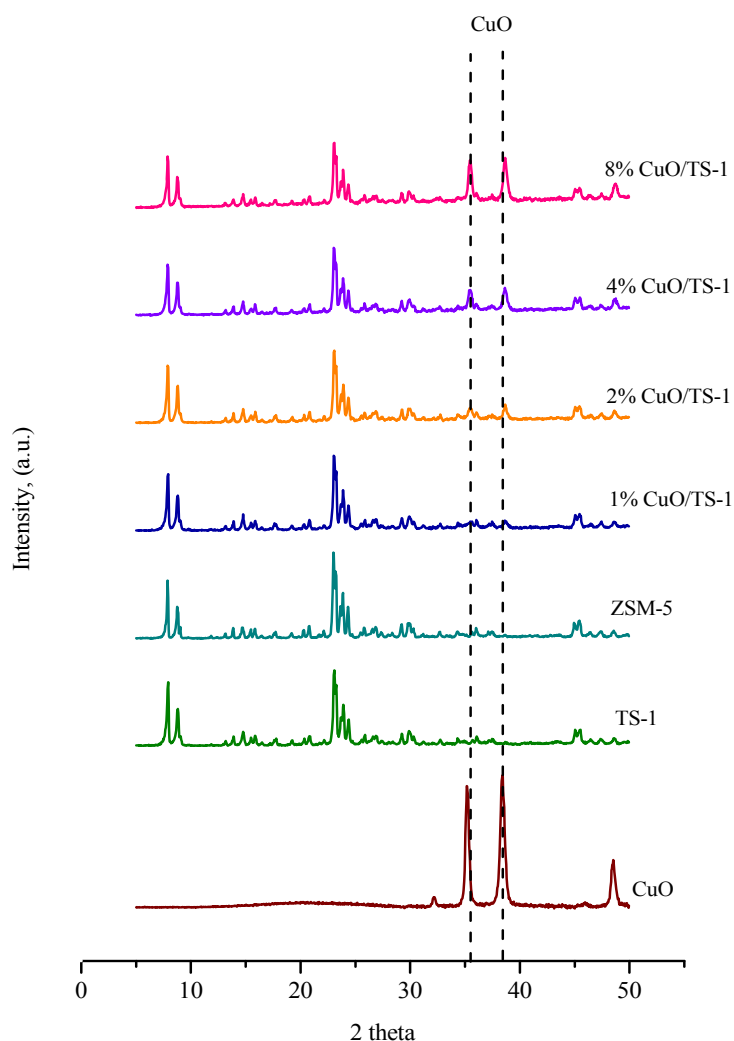


Figure 1. XRD Patterns of CuO, TS-1, ZSM-5, 1%, 2% 4%, and 8% CuO/TS-1

coordinated titanium in the framework structure of TS-1 is acting as the active catalyst [20]. As the active catalyst, titanium is coordinated in a tetrahedral framework of TS-1 is in an isolated state with the $[-\text{Si-Ti-O}(\text{OSi})_3]$ matrix, and not in a state of the Ti-O-Ti matrix [21].

Diffraction lines of crystalline CuO after calcination of the precursor $\text{Cu}(\text{NO}_3)_2 \cdot \text{H}_2\text{O}$ at 550°C for 5 hours appeared at $2\theta = 35.4$, and 38.6 (Figure 1), while the X-ray diffraction pattern of CuO/TS-1 showed combined diffraction pattern between CuO and TS-1. Crystalline CuO diffraction peaks indicated by the diffraction peak $2\theta = 35.4$ and 38.6° was started to appear at the addition of 1% CuO. This indicates that the copper oxide has covered the entire surface of TS-1. The presence of CuO impregnated on TS-1 resulted in reduced crystallinity of TS-1, as shown by the decrease in diffractogram peak intensity at $2\theta = 23.09$ (Table 1). The decrease of this peak can be caused by the content of copper oxide (CuO) has been dispersed on the surface and covered the entire surface of TS-1.

Table 1 shows the diffraction pattern of the all catalysts. The TS-1, and x CuO/TS-1 catalysts still showed the characteristics of the MFI structure which are not affected by the presence of copper oxide on their surfaces. The amount of CuO loading on TS-1 only affects the crystallinity of TS-1, which further decreased significantly with the increasing amount of added CuO.

FTIR spectroscopy. Infrared spectra of TS-1 and CuO/TS-1 having absorption bands on the same wavenumber region, namely 1230 , 1100 , 800 , 550 and 450 cm^{-1} are shown in Figure 2. These bands are from different vibration of tetrahedral structure typical of MFI zeolite. The main absorption band is at wave number around 1100 cm^{-1} with a shoulder around 1230 cm^{-1} which is assigned to the asymmetric stretching vibration of Si-O-Si, while the 800 cm^{-1} region is for vibration of stretching/bending symmetry of the Si-O-Si bridge. Absorption band around 552 and 457 cm^{-1} is attributed to rocking vibration of Si-O-Si [21]. Absorption bands that appear on the wavenumber

around 1230 and 547 cm^{-1} are attributed to the characteristic vibration in the tetrahedral structure of the zeolite framework type MFI [22], whereas the absorption band appears at 970 cm^{-1} is characteristic of TS-1, which indicates the presence of titanium atoms in the structure of TS-1 [7]. Absorption tape at wavenumber region around 970 cm^{-1} is the stretching vibration mode of Si-O-group of the $[\text{SiO}_4]$ unit bound to the Ti(IV) atoms with tetrahedral coordination in TS-1 framework [19]. However, according to Boccuti and Thangaraj *et al.* [23-24], this band is assigned to the asymmetric stretching vibration mode of the bridge Si-O-Ti.

Infrared spectra indicated by all CuO/TS-1 samples showed similar spectra with those given by TS-1. The characteristic peak of TS-1 is shown with a small peak at around 970 cm^{-1} is unchanged. This is shown by the relative number of moles of titanium remains around 1.64 to 1.69 mol%. The total mole% of Ti in TS-1 and XCuO/TS-1 could be obtained by comparing the relative intensity at wave number 970 and 800 cm^{-1} , respectively, and then enter the ratio value in the linear regression equation. The relatively fixed amount of titanium on the TS-1 and xCuO/TS-1 indicates that TS-1 structure is not influenced by the presence of copper oxide on the surface. Thus the amount of Ti in TS-1

does not exceed the maximum ring Ti certainty determined that is 3 mol (%) [10].

Infrared spectra of all xCuO/TS-1 samples showed the no presence of characteristic peaks of crystalline CuO phase, as existed in the previous XRD analysis. This is due to low CuO content at CuO/TS-1 that caused lower CuO vibration intensity than that in the TS-1. This is comparable with the results reported in [25], in which infrared spectroscopy techniques cannot detect niobat acid in Nb/TS-1 samples because of low intensity of pure acid niobat vibration compared with TS-1. These results show that the addition of CuO does not affect the

Table 1. Crystallinity of the Sample TS-1, ZSM-5, and XCuO/TS-1 (X = 1, 2, 4 and 8%)

Sample Code	Intensity at $2\theta = 23.09^\circ$, Cps	Crystallinity (%)	Phase
TS-1	1414	100	MFI
1% CuO/TS-1	1406	99,43	MFI
2% CuO/TS-1	1362	96,32	MFI
4% CuO/TS-1	1274	90,10	MFI
8% CuO/TS-1	1218	86,14	MFI

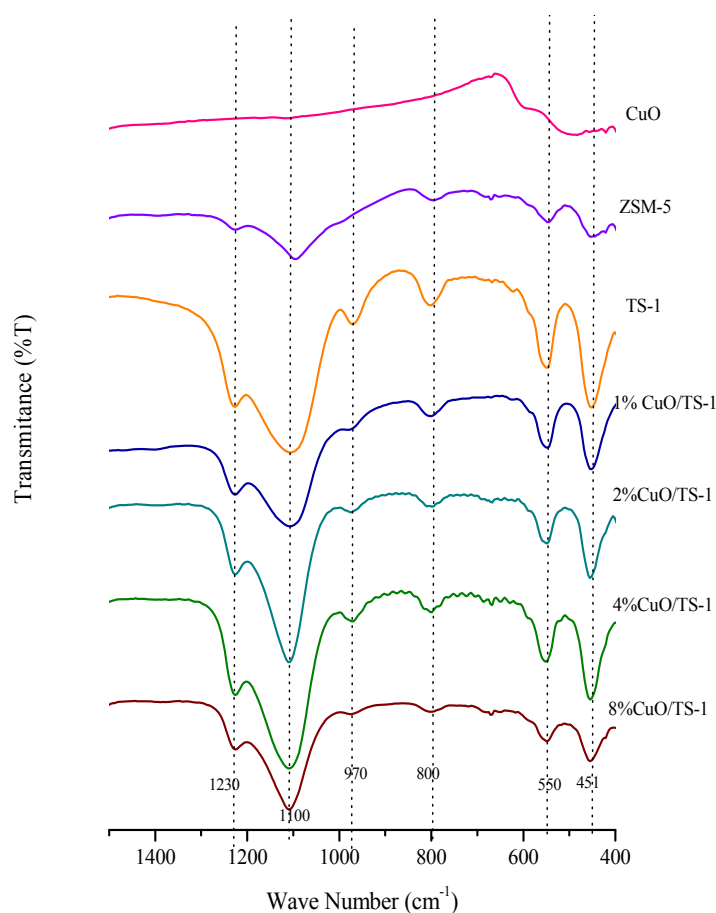


Figure 2. Infrared Spectra of CuO, ZSM-5, TS-1, and CuO/TS-1

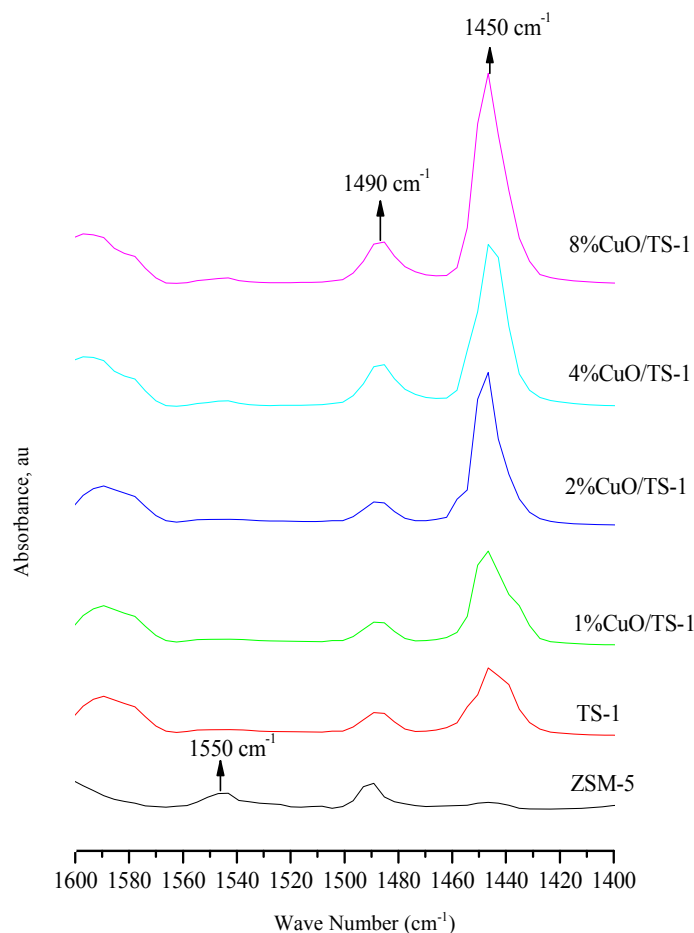


Figure 3. Infrared Spectra of Pyridine Adsorption at ZSM-5 Samples, TS-1, and $x\text{CuO}/\text{TS-1}$ ($x = 1, 2, 4,$ and 8)

MFI structure of TS-1. The characterization results obtained from XRD and infrared spectra showed that the as-synthesized catalysts had MFI type.

Acidity test. FTIR spectra of pyridine from TS-1 and $x\text{CuO}/\text{TS-1}$ which showed the absorption bands at 1446 cm^{-1} and 1490 cm^{-1} wavenumbers are shown in Figure 3. The absorption band at $1446\text{--}1450\text{ cm}^{-1}$ indicated the presence of Lewis acid site, while the absorption band around 1490 cm^{-1} is the total combination of Lewis and Brønsted acid sites. The results of FTIR analysis showed that TS-1 has only Lewis acid site and no Brønsted acid site, because it only gives absorption at 1450 cm^{-1} and 1490 cm^{-1} , whereas the absorption band showing the presence of Brønsted acid at 1540 cm^{-1} peak did not exist. This result is in accordance with [26] which states that the pyridine absorption bands from TS-1 and $\text{SO}_4/\text{TS-1}$ only appeared on the Lewis acid site. Lewis acid site of the TS-1 appeared due to titanium atom coordinated in a tetrahedral lattice structure of the TS-1 [27].

The addition of copper oxide (CuO) on the surface of TS-1 did not result in the appearance of Brønsted acid

on TS-1, but increased the Lewis acid site. This can be seen on the increase of the intensity of absorption band of Lewis acid site along with the increase in loading amount of CuO on the TS-1. This increase, according to Acta Crystallography, because CuO is a metal oxide that has only weak Lewis acid site, which is according to data from the state of the copper oxide crystallography is one of the metal oxides which have only weak Lewis acid site. Other metal oxides are of MgO, CaO, SrO, BaO, CoO, NiO, ZnO, and Cu_2O .

Nitrogen adsorption. Nitrogen adsorption-desorption isotherms of all TS-1 catalyst samples and $x\text{CuO}/\text{TS-1}$ ($x = 1, 2, 4,$ and 8 (% mass)) are shown in Figure 4 which shows similar pattern of N_2 adsorption-desorption between TS-1 with $x\text{CuO}/\text{TS-1}$. This pattern shows the adsorption of nitrogen at a pressure $P/P_0 = 0.0$ to 0.05 . N_2 adsorption-desorption curve in Figure 4 also shows the adsorption curve of type I, which is a special type of microporous solids and chemical adsorption isotherm. The large nitrogen adsorption at partial pressure from 0 to 0.05 and the shape of the curve type I in TS-1 and $\text{CuO}/\text{TS-1}$ indicate that material catalyst synthesis results are included in microporous size.

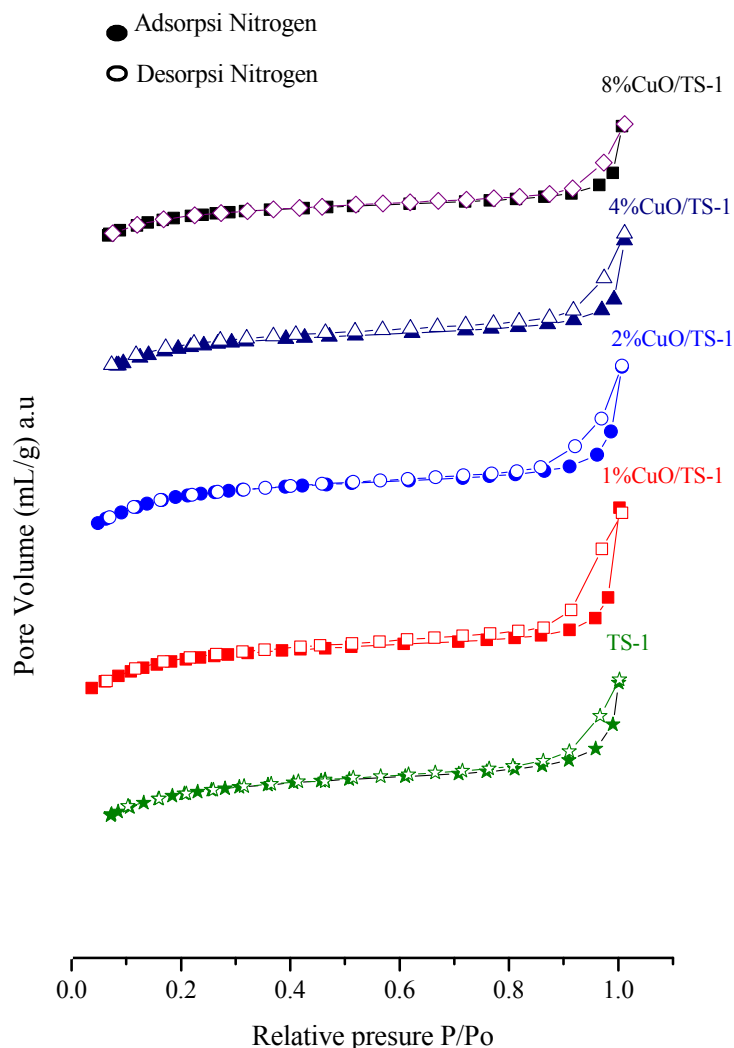
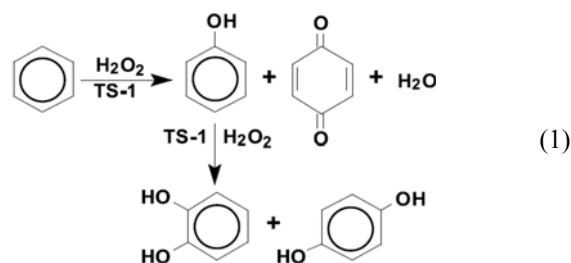


Figure 4. Graphic of N₂ Adsorption-desorption Isotherm of TS-1 and X CuO/TS-1

Table 2 shows the surface area of ZSM-5, TS-1, and xCuO/TS-1 catalysts, as measured by the BET method. The table shows that the surface area of TS-1 catalyst is between 310-463 m²/g which is in accordance with the surface area of zeolites, in general [9]. The existence of the impregnated CuO on the surface of TS-1 affected the surface area of the catalysts, with a reduced surface area of 1.69-13.41%. The decrease in surface area due to surface pores xCuO/TS-1 of TS-1 was blocked by CuO.

Effect of catalysts. Catalyst activity test was performed on all catalysts: CuO, TS-1, ZSM-5 and xCuO/TS-1 in benzene hydroxylation reaction. Analysis of the reaction was carried out using gas chromatography (GC). Data of overall reaction products (phenol (Phe), hydroquinone (HQ), catechol (Kat) and benzoquinone (BZ)) yielded was calculated using nitrobenzene as an internal standard, and moles of each product was

calculated using calibration curve method. In general, the reaction equation of benzene hydroxylation is formula (1):



Catalytic activity of ZSM-5, copper oxide, TS-1, and xCuO/TS-1 expressed in number of moles of reaction products of catalytic hydroxylation of benzene and the H₂O₂ oxidant were shown in Table 3 and Figure 5. Based on Figure 5, it is observed that the hydroxylation

Table 2. BET Specific Surface Area in TS-1, and x CuO/TS-1 Samples (x = 1, 2, 4, and 8% Loading)

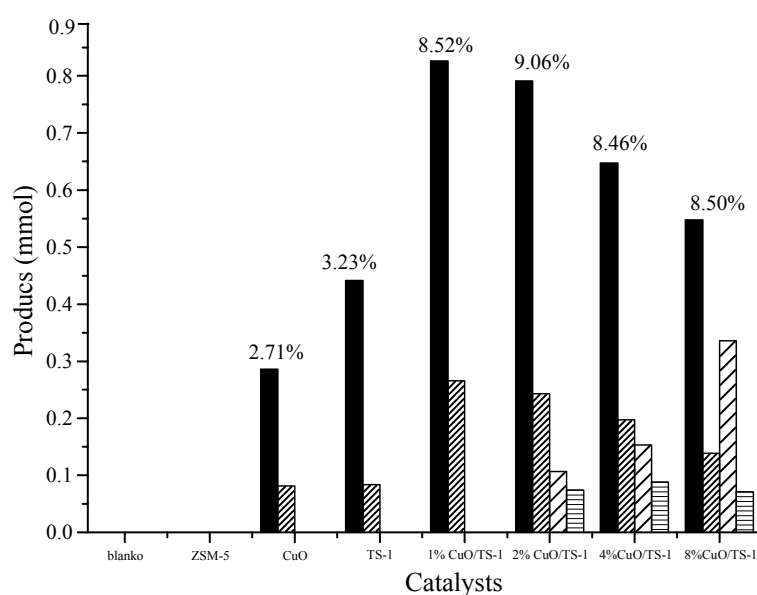
Sample	Surface area (BET) m ² /g
ZSM-5	357
TS-1	374
1% CuO/TS-1	354
2% CuO/TS-1	348
4% CuO/TS-1	328
8% CuO/TS-1	284

Table 3. The products of Catalytic Benzene Hydroxylation Reaction with H₂O₂ Oxidant on the Optimization of the Type of Catalyst, with Acetonitrile as Solvent

Catalyst	Phe (mmol)	BQ (mmol)	HQ (mmol)	Cat (mmol)	Conv (%)	Select (%)
Blanko	0.00	0.00	0.00	0.00	0.00	0.00
ZSM-5	0.00	0.00	0.00	0.00	0.00	0.00
CuO	0.29	0.08	0.00	0.00	2.71	77.28
TS-1	0.44	0.08	0.00	0.00	3.23	78.81
1% CuO/TS-1	0.83	0.27	0.00	0.00	8.52	75.68
2% CuO/TS-1	0.79	0.22	0.11	0.07	9.06	68.01
4% CuO/TS-1	0.65	0.19	0.15	0.09	8.46	59.66
8%CuO/TS-1	0.55	0.14	0.34	0.07	8.50	50.13

reaction of benzene with H₂O₂ oxidant carried out without catalyst did not produce a reaction product due to the absence of interaction between the oxidant H₂O₂ with stable benzene [24]. Similarly, the catalyst ZSM-5, also produced no reaction product. In the hydroxylation reaction of benzene, ZSM-5 is a non-active catalyst at conditions of low temperature and liquid phase. ZSM-5 is generally used as catalysts in the hydroxylation reaction of benzene in the gas phase conditions, temperatures above 200 °C and in form of modified ZSM-5 catalyst. The amount of phenol produced in reaction catalyzed by ZSM-5 was very small because of ZSM-5 strongly adsorbed the reactants but weak in diffusing produced phenol [28].

Hydroxylation reaction of benzene, began to produce the product when CuO catalyst was used with the ratio of CuO : benzene = 0.15 : 1 (g). With this catalyst, 0.29 mmol of phenol, 0.08 mmol benzoquinone were produced and 2.71% conversion achieved. Compared with other catalysts, CuO is the catalyst with the lowest activity. As an active catalyst TS-1 with weight ratio of 0.15: 1 gram TS-1/benzene produced 0.44 mmol of phenol. The optimal amount of phenol produced was obtained when using 1%CuO/TS-1 catalyst, producing 0.82 mmol phenol (6.5%). The high amount of phenol obtained on the catalyst CuO/TS-1 indicates the contribution of copper oxide on the catalyst TS-1. The existence of the active Cu and Ti enhance the catalyst activity in benzene hydroxylation reaction. However, the amount of phenol produced was significantly decreased when the percentage of CuO is added to the TS-1 is increasing from 1% to 8% (Tabel 3). The decrease is due to the formation of benzoquinone,


Figure 5. Products of Catalytic Hydroxylation Benzene with H₂O₂ Oxidant with 3 h Reaction Time, at 60 °C, and Acetonitrile Solvent, Phenol (■), Benzoquinon (▨), Hydroquinon (▩), Catecol (▤), Conversion %

hydroquinone and catechol, which are the results of further oxidation of phenol [29]. Figure 5 also shows the influence of the amount of CuO loading on TS-1 on the formation of hydroquinone and benzoquinone as byproducts from the reaction of benzene hydroxylation. Hydroquinone was started to be produced on the 2% CuO/TS-1 catalyst, whereas benzoquinone formation has occurred when the catalyst CuO and TS-1 were employed. Hydroquinone formation can be seen increased from 0.11 to 0.34 mmol (0.85 to 2.65%) with an increase in the percentage of CuO loading on TS-1. The formation of hydroquinone not only decreased the amount of phenol but also the amount of benzoquinone as a byproduct. Benzoquinone was seen to decrease from 0.27 to 0.14 mmol (2.10 to 1.09%) with increasing amounts of hydroquinone. The formation of hydroquinone only affected benzoquinone formation but had no effect on catechol product which was relatively small quantity. Catechol produced in this reaction was very small compared with hydroquinone and benzoquinone.

One of the parameters that the catalyst has high catalytic activity is its product conversion to the reactants. Product conversion ratio is calculated based on the ratio of number of moles of all products to the initial moles of benzene with the assumption that all benzene reacts with the catalyst and oxidant H_2O_2 [29]. In this catalytic benzene hydroxylation reaction, the optimum conversion was reached by using 2% catalyst CuO/TS-1

but with the increasing number of CuO loading up to above 4% in the TS-1, the conversion of benzene to become products benzene decreased. Besides the conversion, the catalyst activity was also determined by the size selectivity of each reaction product. From several types of catalysts used, TS-1 was the catalyst that had the greatest selectivity towards phenol, 78.81%. TS-1 catalyst modified by impregnation with 1%wt CuO gave 75.68% selectivity to phenol.

Figure 6 shows that the increasing number of added CuO caused the benzene conversion increased and reached the optimum conversion of 9.06% when using the 2%wt CuO loading. This optimum conversion was due to the surface of support (TS-1) is covered by a CuO layer consisting of a single layer (monolayer), while the CuO loading above 2% cause the entire surface of TS-1 was closed and caused blocking of the pores of TS-1. As results, the Ti^{4+} as the isolated active sites is difficult to react with H_2O_2 to form $\cdot OH$ free radicals and $\cdot O_2H$, where $\cdot OH$ radicals will attack the benzene ring and formed phenol through free radical reactions. Blocking of the pores also causes the amount of benzene molecules adsorbed into the pores of TS-1 limited so that only few amount of benzene was in contact with the active site. Another phenomenon that could occur is benzene molecules which have been on the active sites are difficult to be released as reaction products (e.g. phenol), so the conversion also decreased with increase in the amount of CuO loaded in TS-1.

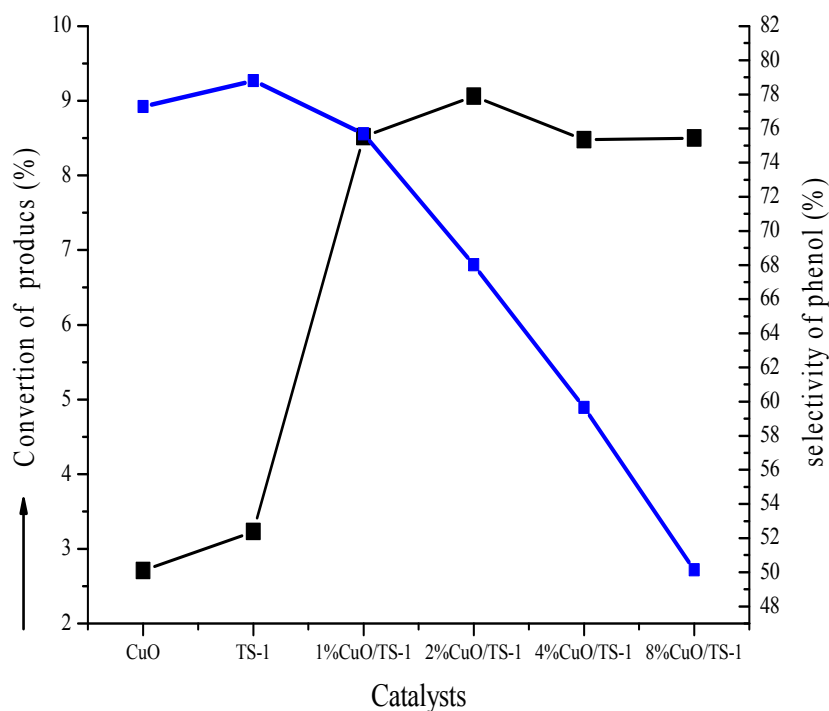


Figure 6. The Chart of Conversion and Selectivity towards Phenol Produced in the Hydroxylation Reaction of Benzene to Phenol with Acetonitrile as Solvent, Reaction Temperature 60 °C

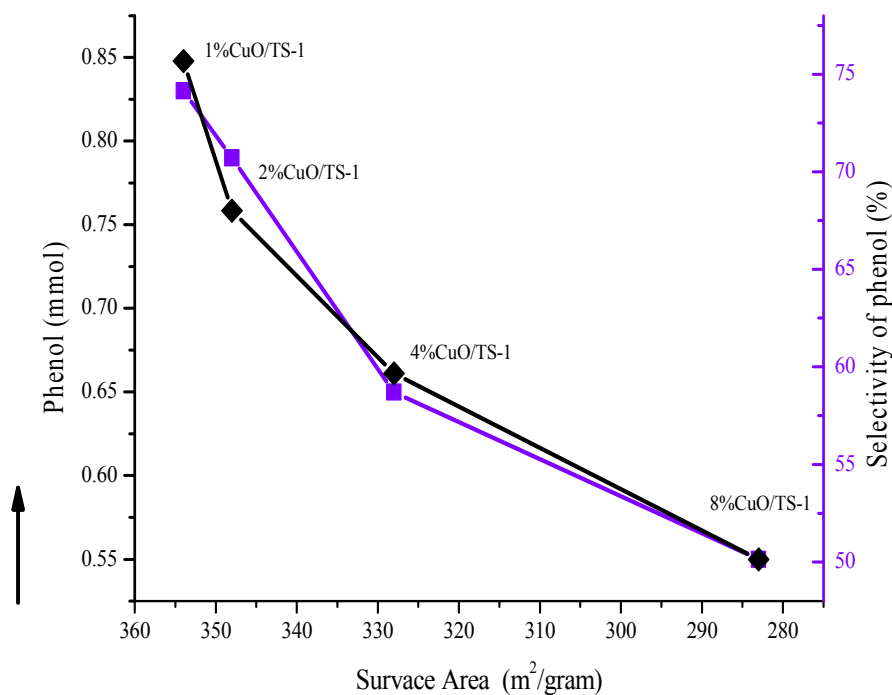


Figure 7. Graph Showing the Relationship between the Catalyst Surface Area CuO/TS-1 with the Phenol Selectivity in Hydroxylation Reaction of Benzene

Figure 6 also shows that the selectivity of phenol that decreased with increasing amount of CuO added to TS-1 by impregnation. This low selectivity due to the byproducts produced because of the oxidation of benzene. These byproducts are produced because phenol is an intermediate of benzene oxidation that is easily oxidized to hydroquinone, and benzoquinone [15]. Based on the conversion and selectivity to produced phenol then the phenol yield can be obtained. The highest yield of phenol was obtained by using the 1%CuO/TS-1 catalyst, 6.44%, while the yield of phenol on the catalyst 2%CuO/TS-1 was 6.16%. Phenol yield was also reduced due to higher amount of CuO loading on TS-1, which also means that the catalytic activity of CuO/TS-1 also decreased with the increasing CuO amount on the TS-1.

The decrease in catalytic activity of the hydroxylation reaction of benzene is also closely related to the surface area of the catalyst. The surface area of xCuO/TS-1 catalysts, measured by nitrogen adsorption techniques and BET methods, show to decrease with the increment of CuO loading on TS-1.

Figure 7 shows that with lower surface area, catalyst activity of CuO/TS-1 on benzene hydroxylation reactions are also getting smaller. The decrease in catalyst surface area is because the whole Surface TS-1 has been covered by copper oxide, and formation of aggregate (bulk CuO) on the surface. Aggregation of CuO present on the surface of TS-1 may cover most of

the active sites of TS-1 which play an important role in the catalysis reaction, as supported by the results of the study [16] which states decrease the catalytic activity of Cu-PILCs is caused by the formation of aggregation on the surface of Al-PILCs. The presence of CuO aggregate on the catalyst surface caused the effectiveness of product formation was reduced [16]. CuO aggregate or cluster formation is also possible to occur in TS-1. This aggregation caused the formation of the phenol hydroxylation reaction of benzene with the catalyst CuO/TS-1 became ineffective. The formation of CuO aggregate can be seen from the X-ray diffraction pattern showing the crystalline CuO peaks at $2\theta = 35.6$ and 38.6° with higher peak intensity along with the increase in percentage loading CuO/TS-1 (Figure 1).

Effect of reaction temperature. Temperature optimization was performed to determine the optimum reaction temperature which produced the maximum amount of phenol, as well as to observe the resulted impacts when the temperature used was not suitable for the catalysis reaction. The catalyst activity test was performed on 1%CuO/TS-1 catalyst, with variation temperature at 50, 60, 70 and 80 °C and 3-hour reaction time.

Table 4 and Figure 8 show an increase in conversion and selectivity of the products are proportional to the increase in reaction temperature from 50 to 70 °C, and then decreased at 80 °C. At low temperature the amount of phenol formed is not maximal due to the benzene

ring is stable at low temperature, making it difficult to be attacked by OH \cdot radical. In addition, at low temperature selectivity to phenol was also low due to the fact that phenol is an intermediate compound that is more easily oxidized than benzene compounds. Thus, byproducts, is easier to form. At 70 °C conversion and product selectivity to phenol reached optimal, because the rate of formation of \cdot OH radicals is very large so that benzene was easily dissolved in H₂O₂-water phase.

This situation is favorable towards \cdot OH radical attacking on benzene ring, thus increasing the conversion products of benzene [16]. At 80 °C the selectivity to phenol decreased due to at higher temperature the thermal decomposition of H₂-O₂ led to the formation of by-products of stable water (H₂O) and O₂ [16], while the selectivity to phenol decreased due to at high temperature phenol is more easily hydroxylated

Table 4. Products of Benzene Hydroxylation Using 1%CuO/TS-1 Catalyst and H₂O₂ Oxidant with Temperature Variation at 50, 60, 70, and 80 °C in Acetonitrile

Temperature (°C)	Phenol (mmol)	Bz (mmol)	Hq (mmol)	Cat (mmol)
50	0.64	0.19	0.27	0.08
60	0.69	0.16	0.34	0.08
70	1.16	0.17	0.10	0.08
80	1.12	0.14	0.25	0.08

to hydroquinone and benzoquinone [30]. Besides, at 80 °C benzene is evaporated before reacting with H₂O₂ resulting in lower yield of the reaction [15].

Effect of reaction time. Catalytic reaction time greatly affects the outcome of the reaction. Optimization of the reaction is carried out to determine the most efficient duration of the hydroxylation reaction of benzene with CuO/TS-1 catalyst, as well as the factors that affect the catalytic reaction rates. To determine the effect of reaction time on products, benzene hydroxylation reaction was carried out on 1%CuO/TS-1 catalyst at reaction temperature of 70 °C which was obtained in the previous optimization stage. Table 5 shows the catalytic activity of 1%CuO/TS-1 at reaction time of 0 to 6 hours. Hydroxylation reaction of benzene with the 1%CuO/TS-1 catalyst was started to produce the reaction products (phenol, benzoquinone, hydroquinone and catechol) after the reaction runs for 1 hour. Based on these data, it is indicative that the presence of copper oxide in the TS-1 could enhance the catalytic activity of the catalyst within shorter reaction time. The existence of the active site of Cu²⁺ from CuO and Ti⁴⁺ also affected the rate of phenol formation.

The amount of phenol increased sharply after 2-hour reaction time as well as the conversion benzene, but these increases are small after the reaction run for more than 2 hours. This suggests that the effective rate of phenol formation is at the beginning of the reaction. The reaction time of 2 hours is the optimal time of phenol formation at the hydroxylation reaction of benzene with

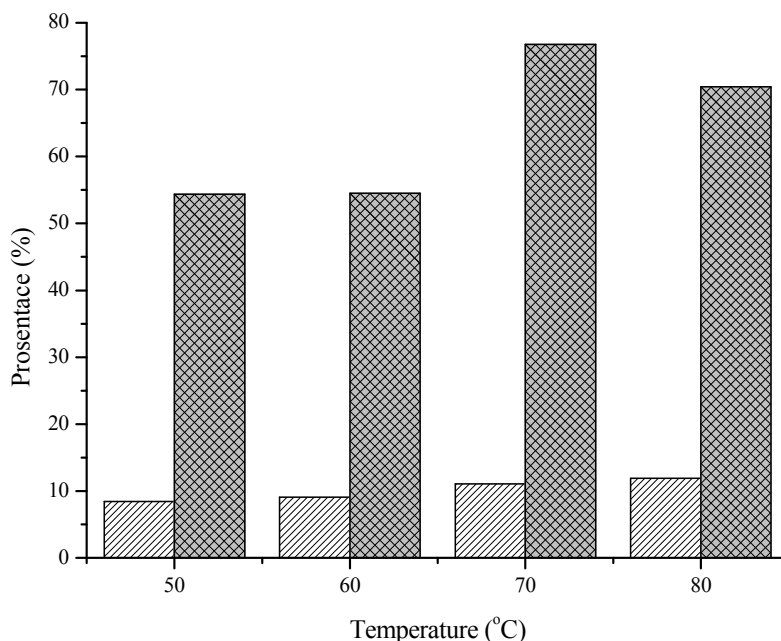


Figure 8. Conversion and Selectivity to Phenol, the Results of Catalytic Tests with 1%CuO/TS-1 Temperature Variation at 50, 60, 70, and 80 °C in Acetonitrile, Conversion (▨), Selectivity (▩)

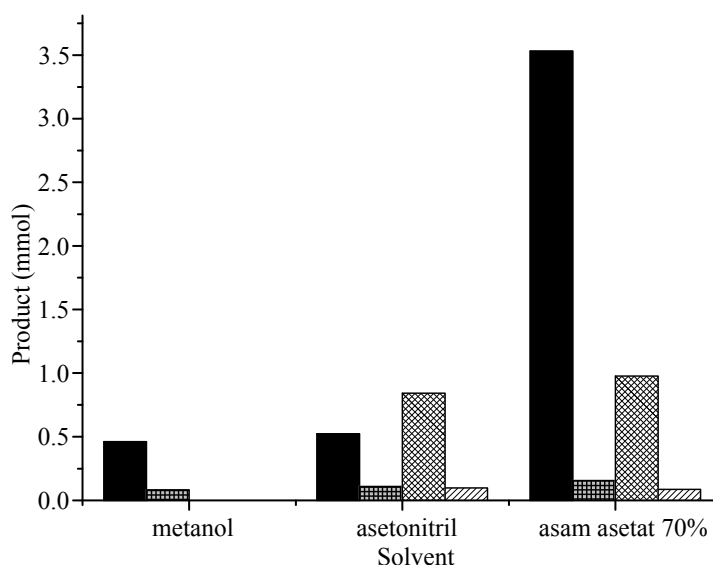


Figure 9. The Products of Benzene Hydroxylation Reaction Using the 1%CuO/TS-1 Catalyst on the Reaction Conditions of Temperature at 70 °C, 2 Hour-Reaction Time, in Various Solvents: Methanol, Acetonitrile and Acetic Acid, and 12.8 mmol Benzene, , Phenol (■), Benzoquinon (▨), Hydroquinon (▩), Catecol (▧)

CuO/TS-1 catalyst and H_2O_2 oxidant. When the reaction time is longer, the amount of phenol produced was decrease, followed by lower selectivity to phenol. This occurred because the formation of by-products such as hydroquinone, benzoquinone, and catechol as reported [31].

Effect of solvents. The hydroxylation reaction of benzene to phenol with H_2O_2 oxidant and catalyst is strongly influenced by the type of solvent used. The use of unsuitable solvents can result in no formation of the desired reaction product. The catalytic activity test on solvent optimization was performed on 1%CuO/TS-1 catalyst, reaction temperature at 70°C and reaction time of 2 hours with variation of the solvent used: methanol, acetonitrile, and 70% acetic acid. The analysis on results of the catalytic test of hydroxylation reaction of benzene with various solvents can be seen in Figure 9.

Hydroxylation reaction of benzene with acetic acid solvent yield 3.53 mmol of phenol (27.54%) and 75.5% selectivity to phenol. Significant increase in the amount of phenol produced is due to the role of acetic acid in the reduction of Cu^{2+} to Cu^+ [15]. Through redox reactions, Cu^+ reacts with H_2O_2 to form $\cdot OH$ and $\cdot O_2H$ radicals. Furthermore $\cdot OH$ free radicals will attack the benzene ring to form phenol. In acetic acid media, the amount of H_2O_2 decomposed into oxygen and water was less than that in acetonitrile. Thus, the formation of phenol is more effective because more amount of $\cdot OH$ radicals produced from the oxidation-reduction reaction between Cu^{2+} with H_2O_2 [19]. Acidic media (e.g. ascorbic acid) is a good reducing agent, which reduces

Fe^{3+} ions to Fe^{2+} [16], which is analogous to the reduction of Cu^{2+} to Cu^+ by acetic acid.

The data obtained indicates that the catalytic activity of TS-1 is determined by several factors in the reaction conditions such as the amount of CuO loaded on TS-1, the catalytic reaction temperature, the reaction time and the solvent used. The catalytic activity in benzene hydroxylation reaction with $xCuO/TS-1$ catalyst and H_2O_2 oxidant was higher than that of just the TS-1. In addition, the phenol was obtained faster, and the amount of phenol produced was more optimum. The addition of metal oxides on the catalyst TS-1 was associated with the transformation properties of TS-1, which was originally hydrophobic to hydrophilic. The hydroxylation reaction of benzene to phenol is easier on the hydrophilic catalyst. In addition to changing the hydrophilicity of TS-1, CuO also serves as the active sites as found in some hydroxylation and oxidation reaction of benzene with non-active catalysts such as MCM-41, Al_2O_3 , and Clay. Through redox reaction, Cu^{2+} reacts with H_2O_2 to form free $\cdot OH$ radicals directly without going through the formation of peroxy, followed by $\cdot OH$ free radical attacking on the benzene ring to form phenol. On the catalyst $xCuO/TS-1$ there are two active sites and each contributes in benzene hydroxylation reaction resulting in a maximum product of phenol. The contribution of the double active sites can be seen in Table 5 which shows that the amount of phenol produced by the catalyst $xCuO/TS-1$ is larger than in CuO and TS-1 alone. This shows the contribution of CuO in forming the double active site in the hydroxylation reaction of benzene with H_2O_2 oxidant.

However the activity xCuO/TS-1 catalyst cannot produce phenol when the catalytic reaction is not performed in an appropriate reaction conditions. Temperature of 70 °C is the optimal reaction conditions of temperature on the reaction of benzene hydroxylation with H₂O₂ oxidant. At low temperatures small phenols obtained because of the stability of the benzene ring are not easily attacked by OH radical and phenol as the nature of the intermediates are more easily oxidized to hydroquinone, catechol and benzoquinone. However, at high temperatures above 70 °C phenol produced is also not optimal. This happens because at higher temperatures the decomposition of H₂O₂ to form the competition of oxygen and water as byproducts. Decrease in selectivity to phenol occurs because of the advanced oxidation of hydroquinone and phenol to benzoquinone is more apt to occur at high temperatures. The acidity of the catalyst and the surface area also play a role in the hydroxylation reaction of benzene. The addition of natural copper oxide TS-1 increases the amount of the acid through the addition of the Lewis acid, but the addition of acid on this catalyst was not much influence on catalytic activity for benzene hydroxylation reaction. This was shown by the greater amount of CuO loading on TS-1 and followed by a rise in the amount of acid is not accompanied by a rise in the amount of phenol produced. A very influential factor in the hydroxylation reaction of benzene in this study is the use of a suitable solvent. The use of acetic acid as the solvent can enhance the catalytic activity with increasing amounts of phenol CuO/TS-1 generated 27.61% than the solvent acetonitril that only 3.9%. The increase in the amount of phenol produced is due to the role of acetic acid in the reduction of Cu²⁺ to Cu⁺ [15], and in the medium of acetic acid decomposition of H₂O₂ into oxygen and small amount of water so that the formation of phenol is more effective as radical OH resulting from the oxidation-reduction reaction between Cu²⁺ with H₂O₂ more.

4. Conclusion

Based on the results and discussion, it can be concluded that the CuO/TS-1 catalysts has the same characteristics as the TS-1 which has orthorombic structure with MFI type. The presence of CuO impregnated on TS-1 does not result in changes in structure and properties of TS-1. The addition of CuO only lead to lower catalyst surface area and increase the amount of the Lewis acid on the catalyst. Increases the catalytic activity of CuO/TS-1, due to the contribution of Cu²⁺ ions and Ti⁴⁺ double-sided active catalyst.

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