

CATALYTIC PERFORMANCES OF $\text{Fe}_2\text{O}_3/\text{TS-1}$ CATALYST IN PHENOL HYDROXYLATION REACTION

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ABSTRACT

Hydroxylation reaction of phenol into diphenol, such as hydroquinone and catechol, has a great role in many industrial applications. Phenol hydroxylation reaction can be carried out using Titanium Silicalite-1 (TS-1) as catalyst and H_2O_2 as an oxidant. TS-1 catalyst shows high activity and selectivity for phenol hydroxylation reaction. However, its hydrophobic sites lead to slow H_2O_2 adsorption toward the active site of TS-1. Consequently, the reaction rate of phenol hydroxylation reaction is tends to be low. Addition of metal oxide Fe_2O_3 enhanced hydrophilicity of TS-1 catalyst. Liquid phase catalytic phenol hydroxylation using hydrogen peroxide as oxidant was carried out over iron (III) oxide-modified TS-1 catalyst ($\text{Fe}_2\text{O}_3/\text{TS-1}$), that were prepared by impregnation method using iron (III) nitrate as precursor and characterized by X-ray diffraction, infrared spectroscopy, nitrogen adsorption, pyridine adsorption, and hydrophilicity techniques. Catalysts $1\text{Fe}_2\text{O}_3/\text{TS-1}$ showed maximum catalytic activity of hydroquinone product. In this research, the increase of hydroquinone formation rate is due to the higher hydrophilicity of $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalysts compare to the parent catalyst, TS-1.

Keywords: $\text{Fe}_2\text{O}_3/\text{TS-1}$, hydrophilic site, phenol hydroxylation

INTRODUCTION

Widespread contamination of water by phenol and phenolic compounds has been recognized as an issue of growing importance in recent years. Phenol and phenolic compounds are a group of organic pollutants that often appear in wastewaters from many heavy chemical, petrochemical, and oil refining industries. Phenol is carcinogenic and is a considerable health concern, even at low concentration. Because of their toxicity and poor biodegradability, phenolic wastewaters must be specially treated before disposing off.

Various treatment techniques have been applied to remove or eliminate phenolic compounds from wastewaters, including chemical oxidation [1], solvent extraction [2], membrane techniques [3], adsorption [4], photo degradation [5], coagulation flocculation [6], and biological process [7] and so on. Ozone, oxygen, hydrogen peroxide or a combination of them are frequently used as oxidant. However, such technologies usually involve complicated procedures and are not economically viable. The catalytic oxidation process is a well-established technique to decompose toxic and/or non-biodegradable organic compounds in wastewaters [8], which is able to oxidize organic pollutants into products that can be very useful for humankind.

Earlier studies reported in the literature deal mainly with hydroxylation of phenol, whereas the oxidation of

the latter using a heterogeneous catalyst in the aqueous phase with hydrogen peroxide opens up a new field of investigations. Nowadays, an investigation of catalysts, which would have a high activity for oxidation of phenols in aqueous solutions, is the objective of many scientists and engineers working in the wastewater treatment field. As known, hydroxylation reaction of phenol to produce diphenol (catechol and hydroquinone) and its isomers is one of important reaction because phenol has various important functions such as antioxidant, polymerization inhibitor, photography, rubber production, antiseptic, reducing agent, intermediate in pharmacy, and many others. Hydroxylation reaction of phenol to produce diphenol had draws many attentions since 1970s and some catalysts, both homogeneous and heterogeneous have been applied in this reaction. One of the promising catalysts for the phenol hydroxylation is TS-1 zeolite with MFI structure synthesized by hydrothermal crystallization. Hydroxylation reaction of phenol becomes environmentally friendly reaction when TS-1 (Titanium Silicalite-1) is applied as catalyst and aqueous H_2O_2 as oxidant [9]. TS-1 had draws many attention since last decade because its unique catalytic characters to selective oxidation reaction of organic compounds like aromatic hydroxylation, alkenes epoxidation, cyclohexanone ammoximation and oxidation of alkene and alcohol with hydrogen

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peroxide as oxidant [10]. TS-1 has been commercialized in hydroxylation reaction of phenol with high hydroquinone selectivity (hydroquinone/catechol ratio = 1) and high H_2O_2 efficiency [11]. Hydroxylation reaction of phenol with TS-1 catalyst shows high activity and selectivity, become clean reaction with low H_2O_2 non-productive decomposition, and high catalyst stability [12].

TS-1 can lessen tar product and side products which have potential as pollutant. Reaction mechanism of phenol hydroxylation is as follows: (1) TS-1 will decompose H_2O_2 (oxidation agent) which has hydrophilic character to form titanium-peroxo radical (initiation step), then (2) propagation step in solution [13]. This mechanism can be explained via titanium-peroxo complex formation mechanism as intermediate from reaction between H_2O_2 and TS-1 catalyst [10, 14-17]. The rate of the formation of titanium-peroxo depended on the rate of H_2O_2 reach to active site in TS-1. H_2O_2 is hydrophilic, that is quite different from hydrophobic character of TS-1 [18], consequently the reaction rate of phenol hydroxylation reaction is tends to be low [15]. One of the way to increase phenol hydroxylation reaction rate with TS-1 catalyst is by making TS-1 become more hydrophilic character, and the reaction rate of phenol hydroxylation will be much faster and shows increasing of catalytic activity and selectivity higher than TS-1. Hydrophilic improvement of catalyst can be carried out by addition of metal oxide which leads to increasing of acidity properties. The existence of metal oxide in TS-1 catalyst can gives acid site which capable to increase catalyst hydrophilicity, so that reactant adsorption in catalyst becomes faster [19-20]. Heterogeneous catalytic process in phenol hydroxylation reaction can be carried out with pure metals oxide or supported oxide such as MoO_3 , CuO/SiO_2 , Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$, Co_3O_4 , V_2O_5 and colloid particle of TiO_2 . However, this metal oxides show very low catalytic activity and selectivity [21].

In previous research by Indrayani [22], synthesis and catalytic activity were carried out with low-loading of $\text{MoO}_3/\text{TS-1}$ catalyst in phenol hydroxylation reaction. $\text{MoO}_3/\text{TS-1}$ catalysts have showed improvement of hydrophilicity along with the increasing of MoO_3 content in $\text{MoO}_3/\text{TS-1}$ catalyst. The improvement of hydrophilic character of $\text{MoO}_3/\text{TS-1}$ catalyst is also accompanied with the improvement of its catalytic activity in phenol hydroxylation reaction. In this paper, TS-1 catalyst was modified by addition of metal oxide Fe_2O_3 on the surface of TS-1 catalyst. The existence of Fe_2O_3 on the TS-1 surface is expected to make this new catalyst ($\text{Fe}_2\text{O}_3/\text{TS-1}$) has higher hydrophilic character compared to TS-1, and the rate of phenol hydroxylation reaction becomes faster than TS-1.

EXPERIMENTAL SECTION

Materials

Materials that have been used in this study are as follows, i.e. tetraethyl orthosilicates, TEOS (Merck, 98%), tetraethyl orthotitanate, TEOT (Merck, 95%), isopropyl alcohol, tetrapropylammonium hydroxide, TPAOH (Merck, 20% TPAOH in water), distilled water, and iron (II) nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

Instrumentation

The solid structure of catalyst TS-1 and $\text{Fe}_2\text{O}_3/\text{TS-1}$ was determined using X-ray diffraction (XRD) and infrared spectroscopy technique, X-ray powder diffraction (XRD) patterns were collected using the Ni-filtered $\text{Cu-K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) as the diffracted monochromatic beam at 40 kV and 40 mA. The pattern was scanned in the 2θ ranges from 5° to 50° at a step size 0.010° and step time 1s. Infrared spectra of the catalyst TS-1 and $\text{Fe}_2\text{O}_3/\text{TS-1}$ samples were collected on a Shimadzu Fourier Transform Infrared, with scans 20 s by KBr pellet method. The framework spectra were recorded in the region of $1400\text{--}400 \text{ cm}^{-1}$. The acidity of samples were determined by infrared spectroscopy technique using pyridine as probe molecule. The wafer of the sample (10–12 mg) was locked in the cell equipped and evacuated at 400°C under vacuum condition for 4 h, continued by adsorption of pyridine at room temperature. After evacuation at 150°C for 3 h, infrared spectra of the sample were recorded at room temperature in the region of $1400\text{--}1700 \text{ cm}^{-1}$ using Shimadzu Fourier Transform Infrared (FTIR). The catalysts hydrophilicity is analyzed by catalyst sample powder dispersion method at water phase and organic phase mixture (water and xylene). A mixture of xylene and water, which do not mix with each other, is employed to test the hydrophobic characteristics of the samples. Xylene and water of the same volume are added into a test tube to form a stable phase interface. TS-1 and $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalyst samples are, respectively, dispersed in the xylene–water system and stirred. After the mixture has stabilized, the hydrophobic characteristics can be qualitatively evaluated by inspecting the state of the floating/sinking of samples at the interface [24].

Procedure

Catalysts Preparation

Samples TS-1 were prepared according to a procedure described earlier by Taramasso et al. [23]. Tetraethyl orthosilicates, TEOS (Merck, 98%)

containing 0.3145 mol of silicon was placed into a Teflon beaker and vigorously stirred, tetraethyl orthotitanate, TEOT (Merck, 95%) containing 0.0032 mol of titanium in isopropyl alcohol was carefully added dropwise into this TEOS. The beaker was covered with parafilm to avoid hydrolysis. The temperature of the mixture was raised to 35 °C and the reactants were mixed homogeneously for 1 h to obtain depolymerisation of the titanate oligomers that may be present in TEOT. Then the mixture was cooled to about 0 °C. The solution of tetrapropylammonium hydroxide, TPAOH (Merck, 20% TPAOH in water), which was used as template, was also cooled to 0 °C. After a few minutes, TPAOH containing 0.1287 mol of TPAOH was added drop-wise slowly into the mixture of TEOS and TEOT. At first, one should wait a few minutes after addition of a few drops of TPAOH solution before more TPAOH solution is added, to avoid precipitation. Stirring and cooling were continued during this process. After the addition of about 10 mL the addition rate of TPAOH solution was increased. When the addition of TPAOH was completed, the mixture was heated in the temperature range of 80–90 °C for about 4 h in order for the hydrolysis of TEOS and TEOT to take place. Distilled water was added to increase the volume of the mixture to about 127 mL, after which a clear gel was obtained. The gel was transferred into a 150 mL autoclave and heated at 175 °C under static condition. The material was recovered after 4 days of hydrothermal crystallization by centrifugation and washing with excess distilled water. A white powder was obtained after drying in air at 100 °C overnight [23].

The Fe₂O₃/TS-1 catalysts were prepared by incipient wetness impregnation of TS-1 with an aqueous solution containing sufficient amount of iron (II) nitrate Fe(NO₃)₃ · 9H₂O, to yield materials with loading in the ranges of 0.5–4 wt% of Fe₂O₃ in the calcined state. The suspension was heated at 80 °C for 3 h under stirring condition, followed by evaporation of water, drying at 100 °C for 7 h, and calcination at 500 °C for 3 h. The samples were denoted by their weight percentage of Fe₂O₃ on TS-1.

Catalytic Performance

The catalyst performance was tested in the hydroxylation of phenol using aqueous H₂O₂ (30%) as oxidant. The reaction mixture containing phenol, H₂O₂, and solvent (methanol and acetone) was put together in a round bottom flask equipped with a condenser. The catalyst was then added to the solution. The reaction was carried out in an oil bath under stirring at 70 °C. The products of the reaction were analyzed by an Agilent gas chromatograph using an HP 5 non polar column with FID detector.

RESULT AND DISCUSSION

Characterization

TS-1 and Fe₂O₃/TS-1 catalysts were characterized by X-ray diffraction technique. The XRD patterns of the Fe₂O₃, TS-1 and Fe₂O₃/TS-1 samples with various iron loading are shown in Fig. 1. Characteristic diffraction lines of TS-1 is observed at 2θ = 7.94; 8; 23.08; 23.62; 23.88; 23.92°. The peak at 2θ around 24° is observed for the orthorhombic symmetry, which is symmetry of TS-1. This phenomenon indicates that titanium atom is already exist

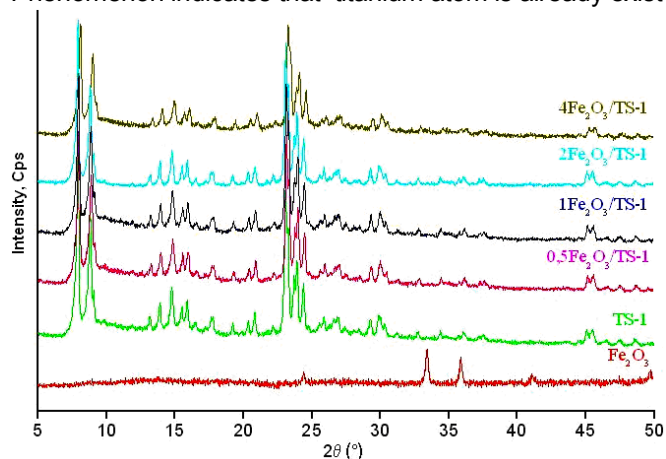


Fig 1. X-ray Diffraction Pattern of the Fe₂O₃, TS-1, and XFe₂O₃/TS-1 (X = 0.5, 1, 2, and 4) catalyst samples

Table 1. Physical and chemical properties of the TS-1, and XFe₂O₃/TS-1 (X = 0.5, 1, 2, and 4) catalyst samples

Sample	Surface area (m ² /g)	Number of Lewis acid sites (μmol/g)	Intensity at 2θ = around 23.00°, Cps	Hydrophilicity		
				Character	Index	Water submerged time (s)
TS-1	431.00	0.066	3288	Partially Hydrophobic	5	68.4
0,5Fe ₂ O ₃ /TS-1	400.29	0.059	3030	Partially Hydrophobic	5	62.4
1Fe ₂ O ₃ /TS-1	390.57	0.075	2964	Partially Hydrophobic	5	47.2
2Fe ₂ O ₃ /TS-1	380.73	0.030	2349	Partially Hydrophobic	5	36.9
4Fe ₂ O ₃ /TS-1	374.13	0.042	2332	Partially Hydrophobic	5	34.1

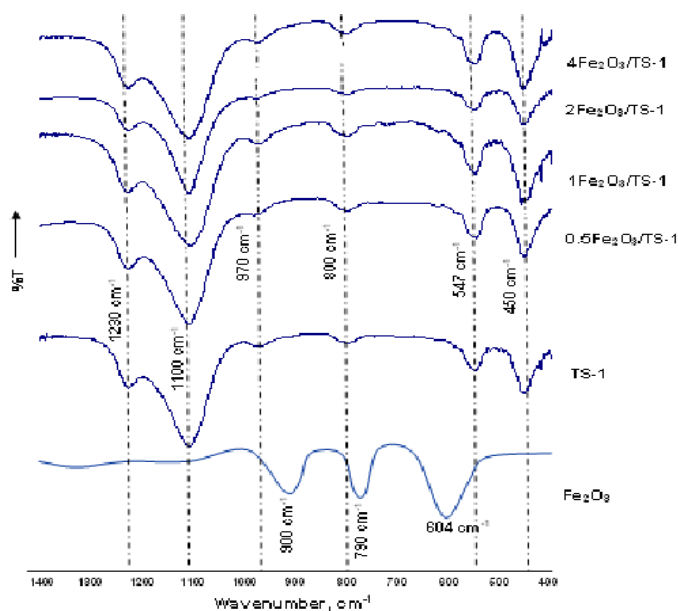


Fig 2. IR Spectra of TS-1 and $X\text{Fe}_2\text{O}_3/\text{TS-1}$ ($X = 0.5, 1, 2,$ and 4) catalyst samples

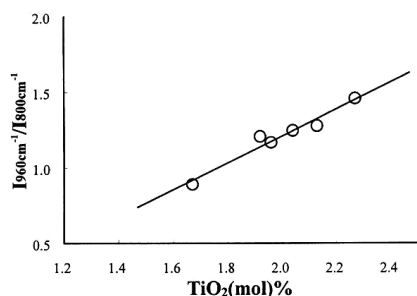


Fig. 3. Ratio intensity of I_{970}/I_{800} with TiO_2 content (mol %) with titanium content ($\circ = \text{Ti}^{4+}$) in zeolite framework [26]

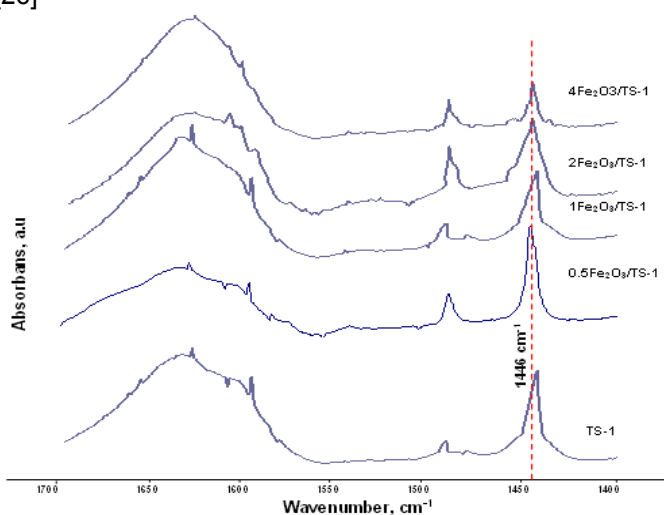


Fig 4. Infrared spectra of the TS-1 and $X\text{Fe}_2\text{O}_3/\text{TS-1}$ ($X = 0.5, 1, 2,$ and 4) catalyst samples after evacuation at 400°C in vacuum followed by pyridine adsorption at room temperature and desorption at 150°C for 3 h

in the framework structure of TS-1 [25]. No diffraction line assigned for crystalline phase of the iron (II) oxide is present in the XRD pattern of $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalysts; and generally, the MFI structure of TS-1 still retained after dispersion of Fe_2O_3 to TS-1. This finding indicated that the MFI structure of TS-1 is not collapsed after impregnation of Fe_2O_3 .

However, the peak intensities of the $\text{Fe}_2\text{O}_3/\text{TS-1}$ samples decrease with the increase of Fe_2O_3 loading, due to the increase concentration of the Fe_2O_3 on the surface of the TS-1. It is suggested that Fe_2O_3 could be located on the surface of TS-1 or covering the surface of TS-1. The crystallinity of $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalysts (based on the highest diffraction line of TS-1) are summarized in Table 1.

The infrared spectra of the samples (Fig. 2) showed absorption band at around 970 cm^{-1} and 800 cm^{-1} , which absorption band at around 970 cm^{-1} is characteristic of TS-1 in vibration mode of stretching Si-O from unit $[\text{SiO}_4]$, which tied at atom Ti^{4+} with tetrahedral coordination in TS-1 framework. Absorption band at this wavenumber is an evidence that titanium atom has already stayed inside the structure of catalyst framework [26]. Absorption band at around 800 cm^{-1} is symmetrical vibration mode of SiO_4 or AlO_4 tetrahedral. No additional band after impregnation of Fe_2O_3 into TS-1 can be observed. This finding shows that impregnation of Fe_2O_3 has not affected the MFI structure of TS-1 significantly. Relative intensity at I_{970}/I_{800} shows the titanium content in zeolite framework, and it described by the ratio between 970 cm^{-1} and 800 cm^{-1} line area. Fig. 3 shows ratio intensity of I_{970}/I_{800} with TiO_2 content (mol %) in zeolite framework. I_{970}/I_{800} value of TS-1 is found 0.97, and it resulted in 1.70 (mol)% of titanium content of TS-1.

The acidity of $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalyst samples were investigated by infrared spectroscopy using pyridine as the probe molecule. Fig. 4 shows the infrared spectra of the samples at various Fe_2O_3 loadings after evacuation at 150°C under vacuum for 3 h. TS-1 and $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalyst samples shows the peak adsorption at around 1446 cm^{-1} , which assigned to Lewis acid sites, and no peak adsorption assigned for Brønsted acid sites is present at around 1540 cm^{-1} . It suggests that TS-1 and $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalysts possesses only Lewis acid. Similar findings have been reported by Kung [27] for TS-1 and Fe_2O_3 acid, respectively. It has been reported that TS-1 and Fe_2O_3 has only Lewis acid sites. The calculated amount of Lewis acid sites in the TS-1 and $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalyst samples is tabulated in Table 1, which is calculated according to the equation method introduced by [28]. The impregnation of Fe_2O_3 in TS-1 results in the existence of interaction between Fe_2O_3 and hydroxyl group at solid surface of TS-1, and gives acid sites to

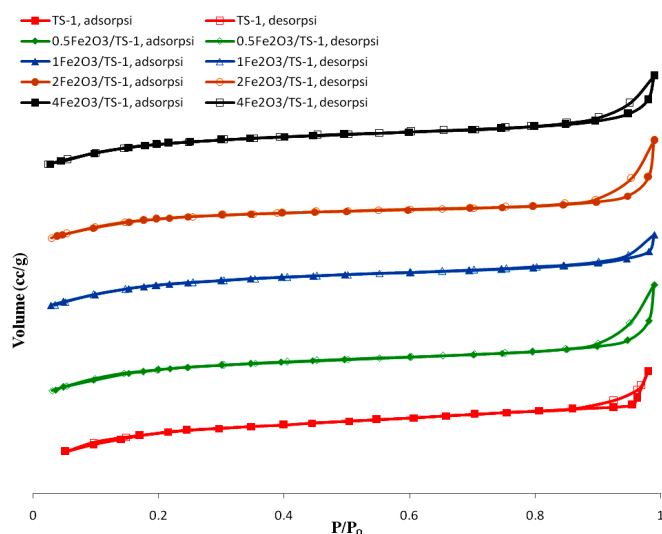


Fig 5. N_2 adsorption–desorption isotherms of the calcined TS-1 and $XFe_2O_3/TS-1$ ($X = 0.5, 1, 2,$ and 4) catalyst samples

solid itself. According to Nur et al. [29] and Prasetyoko et al. [30], the existence of acid sites can enhanced hydrophilicity of TS-1 catalyst, which can be carried out by addition of metal oxide to catalysts. Therefore, reactant adsorption to catalyst become much faster.

According to Table 1, $1Fe_2O_3/TS-1$ catalyst tends to have higher Lewis acid sites amount than TS-1 and other $XFe_2O_3/TS-1$ catalyst ($0.028 \mu\text{mol/g}$). This finding has also affirmed by the result of catalysts hydrophilicity test, which will be discussed later in this paper. The random amount of Lewis acid sites indicates that there was no chemical bonding formed between Fe_2O_3 and TS-1, and possibly the interaction between Fe_2O_3 and TS-1 was unfavourable dispersion phenomenon.

TS-1 and $Fe_2O_3/TS-1$ catalysts specific surface areas were measured based on the Brunauer-Emmett-Teller (BET) isotherm using nitrogen adsorption. Fig. 5 illustrates the N_2 adsorption/desorption isotherm of TS-1 and $Fe_2O_3/TS-1$ catalyst samples. The isotherm of TS-1 and $Fe_2O_3/TS-1$ catalyst samples exhibits a sharp transition in adsorption branch followed by a linear section with a very gentle slope, which indicates its microporous structure. This result was confirmed with The Barrett–Joyner–Halenda (BJH) analysis of the desorption isotherms in Fig. 6. Single significant peak is found in the BJH pore size distribution plots of $XFe_2O_3/TS-1$ ($X = 0.5, 1, 2,$ and 4) catalyst samples. As shown in Fig. 6, the pores are distributed in ranges below 2 nm (20 \AA), which is the ranges characteristic for microporous material. The hysteresis loop at high P/P_0 ($0.9\text{--}1.0$) can be attributed to the interparticle spaces formed by the nanometer sized particles [31]. Surface area progressively decreased with increasing Fe_2O_3 concentration. The results of catalyst samples surface

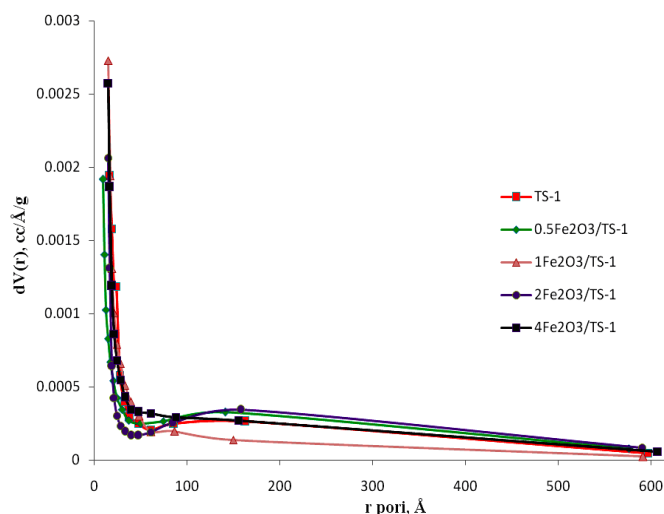


Fig 6. Pore size distribution of the calcined TS-1 and $XFe_2O_3/TS-1$ ($X = 0.5, 1, 2,$ and 4) catalyst samples

area are presented in Table 1. Similar findings have been reported by Li et al. [25], which reported that specific surface area of TS-1 catalyst is approximately $310\text{--}463 \text{ m}^2/\text{g}$.

The results of hydrophobic tests are shown in Table 1. TS-1 and $Fe_2O_3/TS-1$ catalyst samples seem to show similar behavior during the hydrophilicity test. It indicates that the addition of metal oxide Fe_2O_3 on TS-1 surface didn't give too much effect in TS-1 catalyst properties, which is partially hydrophobic. Nevertheless, the addition of metal oxide Fe_2O_3 on TS-1 surface makes $Fe_2O_3/TS-1$ catalysts has higher hydrophilicity than TS-1 catalyst. Table 1 show that the higher Fe_2O_3 loading in TS-1 catalyst resulted in the faster sinks of $Fe_2O_3/TS-1$ catalysts into water. It suggested that the increasing of the catalyst hydrophilicity character is accompanied with the increasing of metal oxide Fe_2O_3 content at TS-1 catalyst. However, $1Fe_2O_3/TS-1$ catalyst tends to show significant increasing of hydrophilicity character. Which shown in the higher speed of samples to sink in the water.

Catalytic Performance

The catalytic activity of the Fe_2O_3 , TS-1, and $Fe_2O_3/TS-1$ catalysts were tested in the hydroxylation of phenol using H_2O_2 as oxidant and methanol as solvent at $70 \text{ }^\circ\text{C}$. The main product of the reaction is hydroquinone. Fig. 7 shows the graph of the rate of formation of hydroquinone vs. reaction time in the hydroxylation of phenol using methanol as solvent. Fe_2O_3 did not show activity towards the hydroxylation of phenol, this finding suggest that in this condition, the

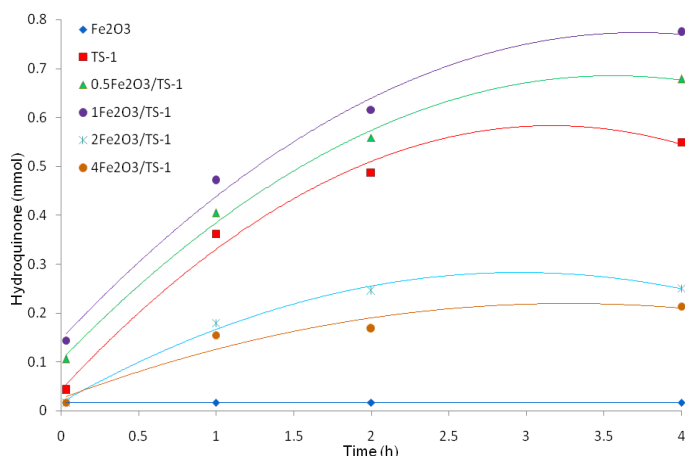


Fig 7. Yield of hydroquinone from phenol hydroxylation using H_2O_2 as oxidant and methanol as solvent at 70°C catalyzed by Fe_2O_3 , TS-1 and $X\text{Fe}_2\text{O}_3/\text{TS-1}$ ($X = 0.5, 1, 2, \text{ and } 4$) catalyst samples

Fe_2O_3 is not active in the hydroxylation of phenol. All samples except Fe_2O_3 show activity towards the hydroxylation of phenol. $1\text{Fe}_2\text{O}_3/\text{TS-1}$ shows the highest rate of formation of hydroquinone up to 4 h reaction time, follows by $0.5\text{Fe}_2\text{O}_3/\text{TS-1}$. The high rate of formation of hydroquinone observed in the reaction mixture catalyzed by samples $\text{Fe}_2\text{O}_3/\text{TS-1}$ may due to the presence of Fe_2O_3 in the catalysts. It can be seen in Fig. 7 that the rate of formation of hydroquinone increased very rapidly at the initial stage, and then further increased gradually with the reaction time up to 4 h. The highest hydroquinone formed in phenol hydroxylation is obtained by using $1\text{Fe}_2\text{O}_3/\text{TS-1}$ as catalyst compare to other catalysts up to 0.774 mmol in 4 h reaction. The high rate of the formation of hydroquinone observed in the initials stage of reaction time on $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalysts can be explained in term of the hydrophilicity of the catalysts. Generally, in the catalytic reaction by heterogeneous catalysts, the first step of the reaction involve adsorption of the substrate on the surface of the catalysts to form intermediate, followed by reaction in the catalyst, and finally desorption of the product from the catalyst. In this reaction, phenol is a non-polar molecule, while H_2O_2 is a polar molecule. Therefore, phenol will be adsorbed immediately at the catalyst with high hydrophobicity. Sample TS-1 has higher hydrophobic properties as compare to samples $\text{Fe}_2\text{O}_3/\text{TS-1}$. Consequently, when catalyst TS-1 is added into the solution of phenol and H_2O_2 , the adsorption of phenol on the TS-1 is faster than that of H_2O_2 . Meanwhile, it is known that in the hydroxylation of phenol, the active site is peroxy-titanium complex which form by interaction of titanium species of TS-1 with hydrogen peroxide. Therefore, it is expected that the faster interaction of H_2O_2 with titanium in the TS-1 result the faster formation of peroxy-titanium species.

As a result, the formation of hydroquinone was found to be increased. Based on these finding, it is concluded that the high rate of the formation of hydroquinone observed on $\text{Fe}_2\text{O}_3/\text{TS-1}$ catalysts may due to the higher hydrophilicity of these catalysts as compare with sample TS-1.

Meanwhile, $2\text{Fe}_2\text{O}_3/\text{TS-1}$ and $4\text{Fe}_2\text{O}_3/\text{TS-1}$ shows the rate decreasing of the formation of hydroquinone. It suggested that the pore opening of TS-1 is blocked by iron (II) oxide at the high amount of Fe_2O_3 loading. This explanation is supported by the finding of the rate decreasing of formation of hydroquinone on $2\text{Fe}_2\text{O}_3/\text{TS-1}$ and $4\text{Fe}_2\text{O}_3/\text{TS-1}$ samples compare to TS-1 sample (Fig. 7). This explanation is also affirmed by the surface area of $2\text{Fe}_2\text{O}_3/\text{TS-1}$ and $4\text{Fe}_2\text{O}_3/\text{TS-1}$ catalysts, whereas the surface area of $2\text{Fe}_2\text{O}_3/\text{TS-1}$ and $4\text{Fe}_2\text{O}_3/\text{TS-1}$ catalysts is decreasing along with the increasing of Fe_2O_3 content in TS-1. The yield of hydroquinone decreased as Fe_2O_3 loading increased higher than 1 wt% in all reaction time. This finding suggests the capability of substrate to access the peroxy-titanium active sites inside the pore of TS-1 is easier for lower amount of Fe_2O_3 loading. Similar findings have been reported by Prasetyoko et al. [30], which reported that the yield of 1,2-epoxyoctane from 1-octene epoxidation decreased as WO_3 loading in TS-1 increased higher than 7 wt% due to the blocking pores of TS-1 by tungsten oxide WO_3 at the high amount of WO_3 loading in TS-1.

CONCLUSION

Catalyst TS-1 and $\text{Fe}_2\text{O}_3/\text{TS-1}$ show the catalytic activity towards the hydroxylation of phenol. $1\text{Fe}_2\text{O}_3/\text{TS-1}$ catalyst shows the highest rate of formation of hydroquinone due to the presence of Fe_2O_3 in the catalysts in term of the hydrophilicity of the catalysts. $4\text{Fe}_2\text{O}_3/\text{TS-1}$ catalyst shows the lowest rate decreasing of the formation of hydroquinone due to the blocking pores of TS-1 by Fe_2O_3 at the high amount of Fe_2O_3 loading in TS-1.

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