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Phenol hydroxylation on Al-Fe modified-bentonite: Effect of Fe loading, temperature and reaction time

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Abstract. The present work reflects the study of the phenol hydroxylation reactions to synthesize hydroquinone and catechol on Al-Fe modified-bentonite. This study started with synthesizes the catalyst material based on the modified bentonite. Natural bentonite from Pacitan, Indonesia was intercalated with Cetyl-TetramethylammoniumBromida (CTMA-Br) followed by pillarization using Alumina. The pillared bentonite was then impregnated with Fe solution (0.01 M, 0.05 M, and 0.1 M). The solid material obtained was calcined at 723 K for 4 hours. All the materials were characterized using BET N₂ adsorption. Their catalytic activity and selectivity were studied for phenol hydroxylation using H₂O₂ (30%). The reaction conditions of this reaction were as follows: ratio of phenol/ H₂O₂ = 1:1 (molar ratio), concentration of phenol = 1 M and ratio of catalyst/phenol was 1:10. Reaction temperatures were varied at 333, 343 and 353 K. The reaction time was also varied at 3, 4 and 5 hours. The result shows that the materials have potential catalyst activity.

Keywords: betonies; phenol; Fe; hydroxylation

1. Introduction

Hydroquinone is used extensively as a photography chemicals, antioxidants, polymerization inhibitors, flavoring agents and drug intermediates [1]. Several utilizations reflect that hydroquinone is one of the important chemicals that have gained interest from many researchers. There are a lot of efforts on catalyst synthesis development for improving the phenol conversion and hydroquinone selectivity. The reaction might be oxidizing the reaction products, catechol and hydroquinone, synthesizing undesirable heavy molecules, like benzoquinones. Phenol hydroxylation has become an important industrial process to synthesize hydroquinone and catechol. This process involves the reaction of phenol with H₂O₂ which is simple and environmental friendly. The reaction has been widely investigated using various homogenous and heterogeneous catalysts. The heterogeneous catalysts are preferred over the homogeneous ones because they give a high phenol conversion with high product selectivity and can be separated easily from the reaction mixture. Some researchers use titanium silicate [2–4], TiO₂ in supports such as silica [5], alumina [6], zeolite [7, 8], and activated carbon [9], zeolite MCM [10], copper-iron complexes [11, 12] as a heterogeneous catalyst for phenol hydroxylation. The other researchers also examined the activity of phenol hydroxylation on zeolite MCM [10] and copper-iron complexes [11, 12].



Among several heterogeneous catalysts, supported Fe is widely used. Fe has been a catalyst of interest for the reaction over other metals because it gives high phenol conversion at mild reaction conditions and high product selectivity. There are several ways to improve the catalytic performance of Fe catalysts, such as immobilization of Fe on MCM [13, 14] and on wood-based activated carbon [15].

In our previous work we described that use of modified betonies as a Fe supporting material to facilitate Fe dispersion depicted promising catalysts for the phenol hydroxylation with hydrogen peroxide [16, 17]. We used betonies as it is abundant material in Indonesia and it has special characteristic in its porous structure to facilitate Fe dispersion. In this paper we report more focus on the effect of Fe loading into the modified betonies, and the effect of temperature and reaction time toward catalyst activity on phenol hydroxylation.

2. Experimental

2.1. Materials

Clay (natural Pacitan bentonite), FeCl_2 (Merck), Cetyl-Tetramethylammonium Bromida, CTMA-Br (Merck), Noah (Merck), $\text{Al}(\text{OH})_3$ (Merck).

2.2. Instrumentation

The chemical analysis of the solids was carried out by Fourier Transform Infra Red Spectrophotometer (FTIR, Broker Tensor 27, Germany). The specific surface areas were obtained from the BET method. Nitrogen adsorption was determined with an ASAP 2010 Adsorption Analyzer from Micrometrics. The concentration of phenol, hydroquinone and cathecol was measured by High Performance Liquid Chromatography (HPLC) from Knauer.

2.3. Procedure

The starting clay was a natural Pacitan bentonite, extracted from Pakistan, Indonesia. Noah and Al (molar ratio of OH to Al = 0.8) was mixed to generate the pillaring agent solution. Modification of betonies was carried out by mixing betonies, pillaring agent solution and intercalating agent (Cetyl-TetramethylammoniumBromida, CTMA-Br) with ratio [gram bentonite/ volume of solution] = 1 gram/50 mL, and it was heated at 343 K for 5 hours. The obtained solid was dried and calcined at 773 K for 4 hours with nitrogen and oxygen stream. This modified bentonite was then impregnated with Fe solution. The Fe concentrations were 0.01 M, 0.05 M, and 0.1 M. After impregnation process, Al-CTMA bentonite was calcined at 773 K for 4 hours with nitrogen and oxygen stream. The catalytic oxidation reaction of phenol in a diluted aqueous medium was carried out in a batch glass reactor equipped with thermometer and reflux condenser. It was open to the atmosphere and thoroughly stirring with magnetic stirrer. The temperature was varied at 333 K, 343 K and 343 K for 3, 4 and 5 hours. The hydrogen peroxide solution was added stepwise during a reaction time. The molar ratio of phenol to hydrogen peroxide was 1:1. The weight ratio of catalyst to phenol was 1:10. The course of the phenol conversion and selectivity was followed by high performance liquid chromatography (HPLC). For all chromatographic separations, a Knavery HPLC System was used, including Euros her II 100-3 C18, 100 x 3 mm ID column. The mobile phase was methanol:water (40:60 v/v) with the flow rate was 0.5ml/min at room temperature. UV 254 nm (10 mm cell, 5 Hz, 0.2 sec.) was used as detector. Conversion is defined as the ratio of consumed phenol over the fed phenol for the reaction. Selectivities of products are the ratio of produced product over the consumed phenol. The desired product was hydroquinone.

3. Results and discussion

3.1. Catalyst characterization

Figure 1 shows the FTIR spectra of fresh (unmodified) bentonite and CTMABr-Al-Fe modified bentonite before and after calcinations. The absorption peak in the region 3623.05 cm^{-1} indicates --OH asymmetric stretching from Al--OH , Si--OH and H--O--H in bentonite. The presence of alkyl groups were shown by absorption peak in the region 2920.25 cm^{-1} (--CH_3 stretching asymmetric), 2851.20 cm^{-1} (--CH_2 stretching symmetric), and supported by absorption peak of 1471.28 cm^{-1} (--C--H bending vibration). These peaks proved that CTMABr molecules might lay on the bentonite surface to form pillared bentonite. The absorption peak in the region $1030 - 1040\text{ cm}^{-1}$ indicated asymmetric stretching O--Si--O , O--Fe--O and O--Al--O group in material. These bands exhibited a slight shift to the higher wave numbers due to the formation of new system polymerization of shifted to the O--Al--O and O--Si--O in the pillared bentonite. The difference of width absorption region in the range of $950 - 1200\text{ cm}^{-1}$ proved that the Fe pillars are formed permanently in the bentonite. The FTIR spectra and X-Ray diffractogram characterizations and its analysis have been described in more detail before [16, 17].

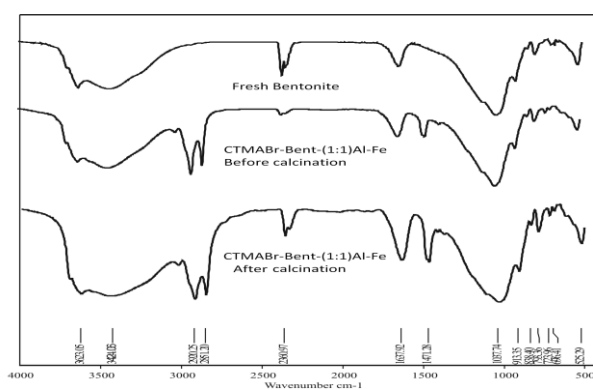


Figure 1. FTIR spectra fresh (unmodified) bentonite and CTMABr-Al-Fe modified bentonite before and after calcinations.

The determination of distribution of pore size and surface area of pillared bentonite can be done by using adsorption N_2 gas analysis. The observation focused on the influence of existing Fe metal to pillar height and porous size of bentonite. The success of intercalating, pillarization and impregnation process can be indicated by increasing of porous size and its distribution. The created material will be better, if the number of mesopore ($> 20\text{ \AA}$) is higher. The high surface area and mesopore size distribution allowing the dispersion of a large number of catalytically active species [18]. The effect of Fe concentration to created pore is shown by figure 2 and table 1.

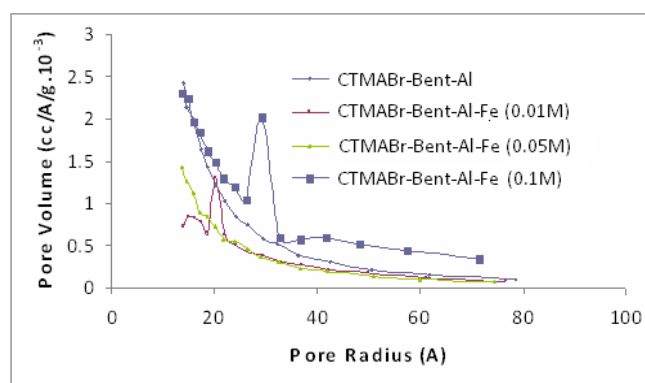
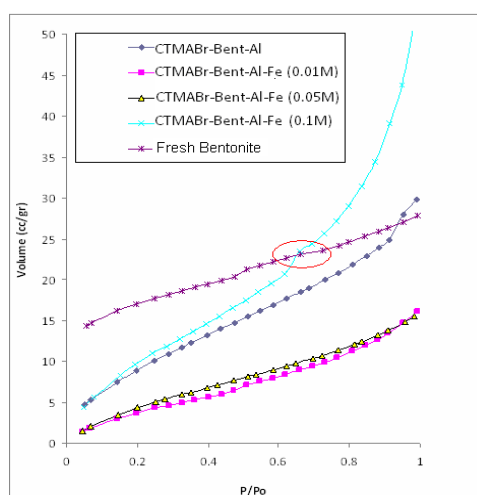


Figure 2. Pore size distribution of modified-bentonite.

Table 1. The effect of Fe concentration on average pore radius of modified-bentonite.

Sample	Average Pore Radius (Å)	Specific Surface Area (m ² /g)
Fresh bentonite	14,380127	59,746942
CTMABr-Bent-Al	24,203416	38,039192
CTMABr-Bent-Al-Fe (0,01 M)	26,112431	19,024643
CTMABr-Bent-Al-Fe (0,05 M)	21,235114	22,589425
CTMABr-Bent-Al-Fe (0,1 M)	35,919653	44,333773

BET analysis which is listed on table 6 shows that fresh bentonite pores are distributed in the micro size (≤ 20 Å) and has high specific surface area (59.75 m²/g). The disadvantage of fresh bentonite is that it has impermanent porosity. Fresh bentonite will swell when it is hydrated and collapse when it is dehydrated. Increasing Fe concentration along impregnation process will affect the increase of the average pore radius. Figure 2 shows that pore size distribution tend to increase in the range of micropore to mesopore. Fe impregnated bentonite that has been calcinated, the bentonite structure change into amorphous. It has lower crystallinity but the pore volume is getting higher as shown by XRD [16, 17] and BET analysis. Table 1 show that the biggest average pore radius is that of CTMABr-Bent-Al-Fe (0.1 M). This phenomenon was supported by data in figure 3 which showed that CTMABr-Bent-Al-Fe (0.1 M) had pore size distribution in the range of mesopore.

**Figure 3.** N₂ isotherm adsorption on fresh and modified bentonite.

3.2. Catalytic activity test

The phenol hydroxylation reaction follows the proposed reaction mechanism below (scheme 1).

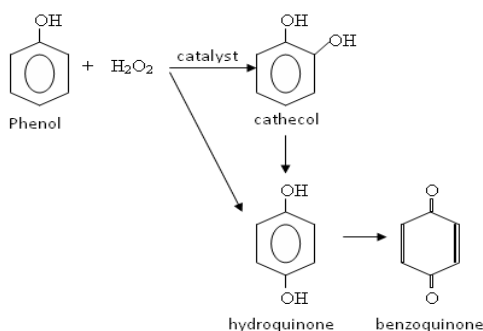
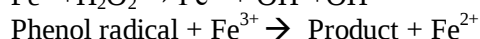
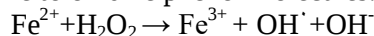
**Figure 4.** Proposed reaction pathway of phenol hydroxylation

Figure 5 depicts the result of phenol hydroxylation reaction at 333 K. This result describes that the most active catalyst was Comair-Bent-Al-Fe (0.1M), since this catalyst gave the highest propane conversion and hydroquinone selectivity. This result is consistent with the BET data showing that the catalyst CTMABr-Bent-Al-Fe (0.1M) has the biggest pore radius and specific surface area. This characteristic of the catalyst leads the phenol reactant to be adsorbed and could be contacted in longer time with peroxide. In addition, this data are also consistent with the previous work which described that the more Fe is loaded, the more active is the catalyst since the catalytic activity needs the presence of ion Fe to oxidize phenol molecules. The mechanism of oxidation of phenol is as follows [19]:



Catechu has been postulated to be produced in the catalyst external surface while hydroquinone is formed inside the pores [20]. The barrier of reactants to diffuse into the porous network of the pillared bentonite can be the reason for reduced hydroquinone selectivity, although thermodynamically *o*- and *p*-products have equal possibility.

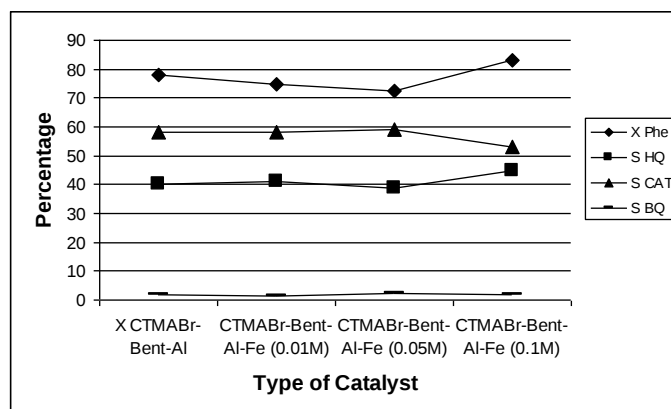


Figure 5. Phenol hydroxylation on different type of catalyst at 333K for 3 hours (X Phe = Conversion of Phenol; S HQ = Selectivity of Hydroquinone; S CAT = Selectivity of Cathecol; S BQ = Selectivity of Benzoquinone).

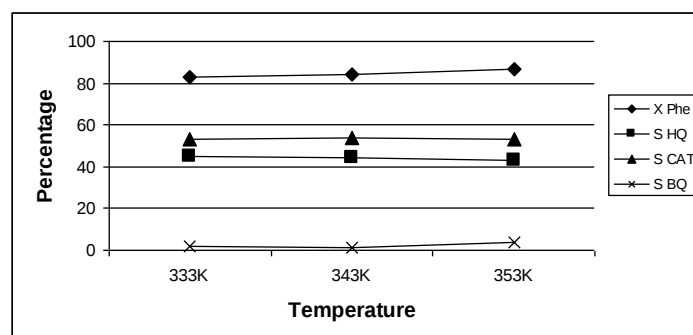


Figure 6. Effect of reaction temperature on Phenol hydroxylation on CTMABr-Bent-Al-Fe (0.1M) for 3 hours (X Phe = Conversion of Phenol; S HQ = Selectivity of Hydroquinone; S CAT = Selectivity of Cathecol; S BQ = Selectivity of Benzoquinone).

Figure 6 shows that phenol conversion increased, in line with increasing reaction temperature. Increasing reaction temperature affected the phenol conversion. This is due to the fact that energy given to the system is high enough resulting in the increase in the reaction rate.

The effect of reaction time is shown in figure 7. It can be observed the phenol conversion reached a maximum value of 78% with the reaction time of 4 hours. However, the phenol conversion slightly decreased when reaction time further increased to 5 hours. It can also be described that selectivity of hydroquinone decreased when reaction time increased, which may be attributed to the fact that hydroquinone was further oxidized to generate more by-product, i.e. 1,4-benzoquinone, in a longer time. Over-oxidation of hydroquinone occurred because more energy was needed to form 1,4-benzoquinone due to its low structure stability. The results show that higher phenol conversion did not tend to produce high amount of hydroquinone. It is probably because of the energy given to the system was excessive and enhanced the over-oxidation to produce 1,4-benzoquinone.

4. Conclusion

In general, the modification of bentonite shows prospective support material for Fe as catalyst. The catalytic activity tests for phenol hydroxylation show that Fe loading plays an important role to the catalytic performance. Reaction conditions are very important to get the best result in term of the highest phenol conversion and also the highest selectivity to hydroquinone. Besides the composition of the catalyst precursor, synthesis method, drying method, activation method, all reaction parameters (such as, reactant ratio, reactant-catalyst ratio, reaction time and reaction temperature) are important variables that require further research in obtaining optimized combination for the best phenol hydroxylation to hydroquinone.

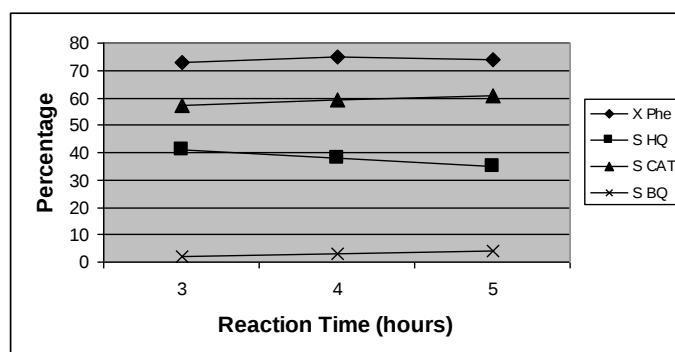


Figure 7. Effect of reaction time on Phenol hydroxylation on CTMABr-Bent-Al-Fe (0.1M) at 333K (X Phe = Conversion of Phenol; S HQ = Selectivity of Hydroquinone; S CAT = Selectivity of Cathecol; S BQ = Selectivity of Benzoquinone).

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