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The Effect of Vanadium Oxide on The Catalytic Activity of Titanium Silicalite in Conversion of Benzene to Phenol

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Abstracts

Phenol is one of the most important intermediate for petrochemical, agrochemical, and plastics industries. Almost *95% phenol is* produced using cumene method. Cumene method is a multi-stage process with many disadvantages including the difficulties to gain phenol product in maximum quantities and production of co-product such as acetone which has great amount in market nowadays. One of the alternative routes to produce phenol which has more advantages is through benzene hydroxylation reaction using H_2O_2 as oxidant agent and Titanium Silikalit-1 (TS-1) as catalyst. TS-1 catalyst has high catalytic activity and selectivity in selective oxidation reaction of aromatic compounds with H2O2 which important for commercial industries. However, the reaction rate is tend to be low because TS-1 has hydrophobic nature and as the result H2O2 adsorption which has hydrophilic nature towards active sites of TS-1 is also become slower. Addition of metal oxide V2O5 could enhance hydrophilicity of TS-1 catalyst. Liquid phase catalytic benzene hydroxylation using hydrogen peroxide as oxidant was carried out over vanadium (V) oxide-modified TS-1 catalyst (V_2O_5/TS-1), that were prepared by impregnation method using vanadium methavanadate as precursor and characterized by pyridine adsorption and hydrophilicity techniques.

Keywords: Titanium silicalite (TS-l), V_2O_5/TS-l, acidity, hydrophilicity

1. Introduction

Phenol is an important intermediate compound for the synthesis of petrochemicals, agrochemicals, and plastics. Nowadays approximately 95 % of phenol production was produced by cumene process consisting of three main reaction steps (alkylation of benzene with propylene to cumene, oxidation of cumene to cumene hydroperoxide and decomposition to phenol and acetone)[1]. The advantage of the cumene process is that it takes two inexpensive starting materials, benzene and propylene and converts them into two high value useful products, phenol and acetone, using air. Despite its great success, the cumene process has some disadvantages such as the production of an explosive intermediate (cumene hydroperoxide), it has a high environmental impact, and it uses a corrosive

catalyst. It is multi-step process, which makes it difficult to achieve high phenol yields in relation to benzene used and which leads to a high capital investment. It requires the uses of aggressive media (dilute sulphuric acid at 60-70oC) and has a high acetone production as a co-product which results in an over supply in the market [2]. This situation encouraged scientists to develop other methods for producing phenol from benzene, preferably via a single-step and free of co-products reaction, which thus would be economically favorable.

The direct hydroxylation of benzene to phenol is an attractive alternative to phenol production for economically and environmentally reason [3]. One of the alternative routes to produce phenol which has more advantages is through benzene hydroxylation reaction using H_2O_2 as oxidant agent and Titanium Silicalite-1 (TS-1) as catalyst. TS-1 is known to be an excellent catalyst for hydroxylation of benzene with selectivity to phenol reach 97 % [4]. TS-1 catalyst has high catalytic activity and selectivity in oxidation reaction of aromatic compounds with H_2O_2 which important for commercial industries [5]. However, the reaction rate of benzene hydroxylation is tend to be low [6]. It is because TS-1 has hydrophobic nature [5] and as the result H_2O_2 adsorption which has hydrophilic nature towards active sites of TS-1 is also become slower.

Meanwhile, in the hydroxylation reaction, it is well kwown that the interaction between titanium and oxidizing agents (H_2O_2) to form titanium-peroxo species as intermediate species from reaction between H_2O_2 and TS-1 catalyst, should occur before the reaction with benzene to produce phenol. The rates of the formation of titanium-peroxo depend on the rate of H_2O_2 reach to active site in TS-1. One of the ways to increase benzene hydroxylation reaction rate with TS-1 catalyst is by making TS-1 become more hydrophilic, and the reaction rate of benzene hydroxylation will be much faster, and it's 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 metal oxide in TS-1 catalyst which act as acid site capable to increase catalyst hydrophilicity, so that reactant adsorption in catalyst becomes faster [7, 8]. The improvement of hydrophilic character of MoO_3/TS-1 catalyst is also accompanied with the improvement of its catalytic activity. In this research, TS-1 catalyst was modified by addition of metal oxide V_2O_5 on the surface of TS-1 catalyst. The existence of V_2O_5 on the TS-1 surface was observed to make this catalyst (V_2O_5/TS-1) has higher hydrophilic character as compared to TS-1.

2. Experiments Procedure

2.1 Samples Preparation

Titanium silicalite (TS-1, 3% of titanium, mol%) was prepared according to a procedure described earlier [9]. The V_2O_5/TS-1 catalysts were prepared by wetness impregnation of TS-1 with an aqueous solution containing sufficient amount of ammonium methavanadate (NH_4VO_3), to yield materials with loading in the ranges of 0.5 – 4 wt% of V_2O_5. The suspension was heated at 80oC for 3 h under stirring condition, followed by evaporation of water, draining at 110oC for 24 h, and calcination at 500oC for 5 h. The samples were denoted by their weight percentage of V_2O_5 on TS-1.

2.2 Characterizations

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 oC under nitrogen flow for 4 h, continued by adsorption of pyridine at room temperature. After evacuation at 150oC for 3 h, infrared spectra of the sample were recorded at room temperature in the region of 1400 - 1700 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 V_2O_5/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.

2.3 Catalytic Activity

The catalyst performance was tested in the hydroxylation of benzene using aqueous H2O2 (30%) as oxidant. The reaction mixture containing benzene (1 g), H_2O_2 (1.32 ml), and acetonitrile (5 g) as solvent was put together in a round bottom flask equipped with a condenser. The catalyst (0.15 g TS-1 based) was then added to the mixture. The reaction was carried out in an oil bath under stirring at 70oC. The products of the reaction were analyzed by a Agilent gas chromatograph using an HP 5 non polar column with FID detector.

3. Result and Discussion

The acidity of V2O5/TS-1 catalyst samples were investigated by infrared spectroscopy using pyridine as the probe molecule. Fig. 1 shows the infrared spectra of the samples at various V_2O_5 loadings after evacuation at 150oC under vacuum for 3 h.

Sample TS-1 shows peaks at around 1490 and 1445 cm-1. The peak at around 1445 cm-1 is assigned to Lewis acid sites, suggesting that TS-1 possesses only Lewis acid. Similar finding has been reported by Drago [10]. Meanwhile, all V_2O_5/TS-1 samples show peaks at around 1546, 1490, and 1445 cm-1. The small peak at around 1546 cm-1 and the strong peak at around 1445 cm-1 indicate that all the samples contain both Brønsted and Lewis acid sites. The calculated amount of Lewis and Brønsted acid sites in the TS-1 and V_2O_5/TS-1 catalyst samples is tabulated in Table 1, which is calculated according to the equation method introduced by Emeis [11]. The impregnation of V_2O_5 in TS-1 results in the existence of interaction between V2O5 and hydroxyl group

at solid surface of TS-1, and gives acid sites to solid itself. According to Nur *et all* [7] and Prasetyoko, *et all* [8], the existence of acid sites can enhanced hydrophilicity of TS-1 catalyst, which can be carried out by addition of metal oxide to catalysts. Table 2 also shows the area of the peak at around 1490 cm-1 that can be assigned to total amount of acid sites (Brønsted and Lewis). The table shows that the area increases as V_2O_5 loading increases up to 4 wt%. In this study, it is suggested that the coordinately bonding of vanadium species with hydroxyl groups on the surface of TS-1 can be correlated with Brønsted acid sites.
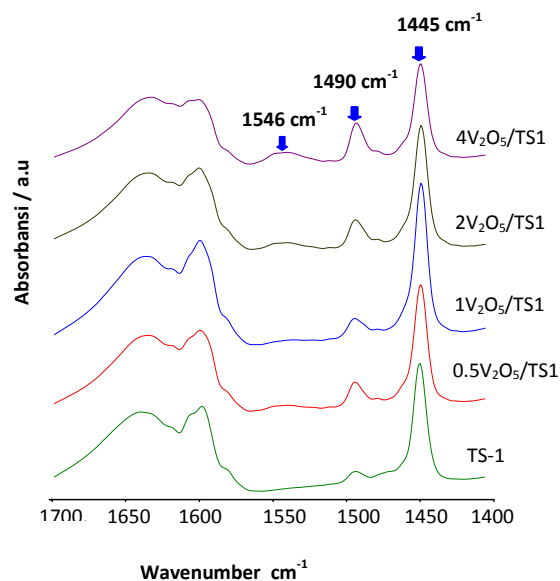

Figure 1. Infrared spectra of the TS-1 and X V_2O_5/TS-1 (X = 0.5, 1, 2, and 4) catalyst samples after evacuation at 400oC in the nitrogen flow, followed by pyridine adsorption at room temperature and desorption at 150oC for 3 h.

The results of hydrophobic tests are shown in Table 1. TS-1 and V_2O_5/TS-1 catalyst samples seem to show similar behavior during the hydrophilicity test. It indicates that the addition of metal oxide V_2O_5 on TS-1 surface didn't give too much effect in TS-1 catalyst properties, which is partially hydrophobic.

Table 1. Hydrophobicity character of the TS-1 and X V2O5/TS-1 (X = 0.5, 1, 2, and 4) catalyst samples

Sampel	Indeks	Sifat	Waktu tenggelam dalam air (dtk)
TS-1	5		72
0.5 V_2O_5 /TS-1	5		63
1 V_2O_5/TS-1	5	Partial hydrophobic.	54
2 V_2O_{53}/TS-1	5		35
4 V_2O_5/TS-1	5		24

Nevertheless, the addition of metal oxide V_2O_5 on TS-1 surface resulted higher hydrophilicity of V_2O_5/TS-1 catalysts than that of TS-1 catalyst. Table 1 shows that the higher V_2O_5 loading in TS-1 catalyst resulted in the faster sinks of V_2O_5/TS-1 catalysts into water. It suggested that the increasing of the catalyst hydrophilicity character is accompanied with the increasing of metal oxide V_2O_5 content at TS-1 catalyst.
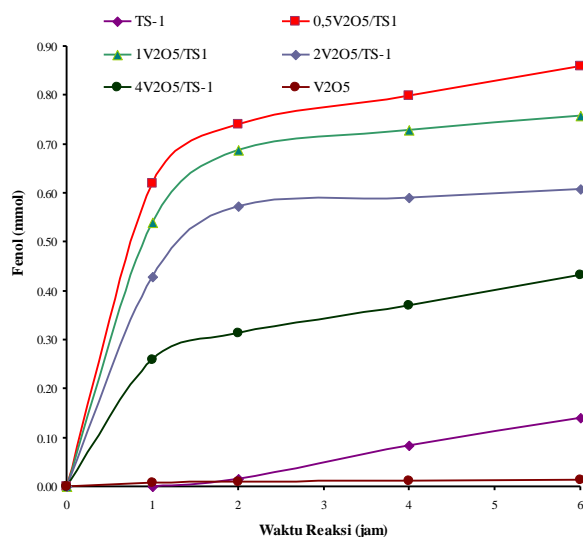

Figure 2. The formation of phenol from benzene hydroxylation using aqueous H_2O_2 at 70^0C catalyzed by TS-1 and V_2O_5/TS-1

The catalytic activity of the V_2O_5, TS-1, and V_2O_5/TS-1 catalysts were tested in the hydroxylation of benzene using H_2O_2 as oxidant and acetoneitrile as solvent at 70^oC. The main product of the reaction was phenol. Fig. 2 shows the graph of the rate of formation of phenol versus reaction time in the hydroxylation of benzene using acetoneitrile as solvent.

All of samples show activity towards the the hydroxylation of benzene. Compared to V_2O_5/TS-1 catalysts, sample TS-1 shows the lowest rate of the formation of phenol. Therefore, the high rate of phenol formation observed in the reaction mixture catalyzed by samples V_2O_5/TS-1 may be due to the presence of V_2O_5 in the catalysts. However, the yield of phenol decreased as V_2O_5 loading increased in all reaction time.

Since among the catalysts was used in the reaction have the similar amount of TS-1, this finding suggest that in this condition, the V_2O_5 is not active in the hydroxylation of benzene , but low concentration of V_2O_5 improves catalytic activity. Furthermore, for the activity of V_2O_5/TS-1 catalysts, as can be seen in Fig. 2 that the rate of phenol formation increased very rapidly at the initial stage, and then further increased gradually with the reaction time up to 6 h. The high rate of the formation of phenol observed in the initial stage of reaction time on V_2O_5/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, the benzene is a non-polar molecule, while H_2O_2 a polar molecule. Therefore, benzene will be adsorbed immediately at the catalyst with high hydrophobicity. Sample TS-1 has higher hydrophobic properties than V_2O_5/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 benzene, the active sites is peroxo-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 peroxo-titanium species. As a results, the

formation of phenol was found to be increased. Based on these finding, it is concluded that the high rate of the formation of phenol observed on V_2O_5/TS-1 catalysts may due to the higher hydrophilicity of these catalysts as compare with sample TS-1.

Among the V_2O_5/TS-1 catalysts, it is found that the rate of the formation of phenol decreased sharply with an increasing amount of V_2O_5 loading. This finding suggests that the capability of substrate to access the peroxo-titanium active sites inside the pore of TS-1 is easier at lower amount of V_2O_5 loading. The pore opening of TS-1 is blocked by vanadium oxide at the high amount of V_2O_5 loading. Meanwhile, the higher activity observed in the sample with lower V_2O_5 loading indicated that only small amount of V_2O_5 is needed to increase the hydrophilicity of TS-1 for the formation of peroxo-titanium species. Similar findings have been reported by Prasetyoko et al 2005, which reported that the yield of 1,2-epoxyoctane from 1-octene epoxidation decreased as WO_3 loading in TS-1 increased higher that 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.

4. Conclusion

Impregnation of vanadium oxides (V_2O_5) onto titanium silicalite (TS-1) was studied.. Brønsted acid sites have been generated in the V_2O_5/TS-1 catalysts. It was suggested that the Brønsted acid sites were formed due to formation of Si–O–V bond in the V_2O_5/TS-1 catalysts. The increasing of the acid sites both Lewis and Brønsted acids are accompanied with the increasing of metal oxide V_2O_5 content at TS-1 catalyst. Catalyst hydrophilicity character increases successively from TS-1, $0,5V_2O_5$/TS-1, $1V_2O_5$/TS-1, $2V_2O_5$/TS-1, and $4V_2O_5$/TS-1. In the hydroxylation of benzene with aqueous H_2O_2 in acetoneitrile as a solvent, the V_2O_5/TS-1 catalysts showed higher activity than the unloaded TS-1 due to higher hydrophylicity of the V_2O_5/TS-1 catalysts.

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