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O-Methylation Of Phenol With Methanol In Liquid Phase Over KNaX Zeolite Synthesized From Kaolin

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Abstract: KNaX zeolite catalyst, with a Si/Al ratio of approximately 1.33, was synthesized from kaolin, originating from Belitung island in Indonesia. The synthesized KNaX zeolite was applied for O-methylation of phenol with methanol in a liquid phase to produce anisole, using dimethylsulfoxide as solvent, which may facilitate to achieve reaction temperature from 135°C up to 155°C. The reaction was conducted using 5% up to 25%-w of catalyst and the molar ratio of phenol over methanol was varied from 1:10 to 1:50. It was found that the optimum results were at a temperature of 155°C, in the presence of 15%-w of catalyst and the molar ratio phenol/methanol 1:20, in which 85.40% phenol was converted into 84.60% anisole yield. The selectivity in producing anisole was observed as 99.10% in 10 h reaction period. In addition, this heterogeneous catalysis O-methylation reaction was applied on the methylation of cashewnut shell liquid, in which the successful of the reaction was shown on the FTIR-spectra.

Key words: Heterogeneous catalysis · KNaX zeolite · O-methylation · Liquid phase · Methanol as methylating reagent · Cashewnut shell liquid

INTRODUCTION

The preferences on using solid catalysts are more in demand recently, because heterogeneous catalysis reaction is capable of minimizing reactants usage, waste of side products, energy consumption and eventually the product cost [1]. A solid catalyst such as zeolite is favorable for shaping selective catalytic reactions, including for alkylation of phenol and its derivates. Low cost zeolite catalysts can be prepared from materials which contain silica and alumina components such as kaolin. Clay minerals, namely kaolin is found in some areas in Indonesia, for example in East and West Java, in South Sumatra (Lampung) and in Bangka-Belitung island. Modification of kaolin into zeolite can be conducted by hydrothermal process in basic solution, without using a template agent to produce low-silica X-zeolite [2, 3] and using structure-directing agent tetraethylammonium hydroxide (TEAOH) to prepare meso-structured β-zeolite [4]. In this research, kaolin originating from the Belitung region was used to synthesize KNaX zeolite catalyst, which was used for O-methylation of phenol with methanol in liquid phase to produce anisole.

Anisole or methyl phenol ether and its derivates are important intermediates in the fine chemicals industries for the synthesis of dyes, fragrance, pharmaceutical chemicals and agrochemicals. Selective methylation of phenol involves C-methylation of the benzene ring and O-methylation of the side chain molecule, which depends on the acid-base characters of the used catalysts. Alkylation of phenol is very sensitive toward the acidic and basic properties of the catalysts [5-9]. Strong acid catalysts are found to promote C-alkylation of the benzene ring [10] and basic catalysts to promote the side-chain O-alkylation. Increased catalysts basic activities had been studied by loading basic zeolite NaY with molybdenum oxide [11] and KNaX zeolite with impregnated alkaline metal hydroxides [12].

To improve the performance of the heterogeneous catalytic reaction rate, most studies on the selective methylation of phenol were conducted in the vapor phase at a higher temperature range than the reaction in liquid phase, using dimethyl carbonate (DMC) as a methylating reagent. Normally, the high reaction temperatures lead to deactivation of the catalysts. Zi-Hua Fu *et al.* [7], who conducted the O-methylation of phenol with DMC in

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the vapor phase, obtained 76% yield of anisole and 93% selectivity over NaX zeolite at 280°C. Su Chui Lee *et al.* [6] conducted the O-alkylation of phenol derivatives in the slurry phase in an autoclave reactor at 300°C over basic CsNaX zeolite and obtained only 2.6% conversion with 100% selectivity. N. Ballarini *et al.* [13] studied the transformation involving methanol in the acid-and base-catalyzed gas-phase methylation of phenol and found that basic catalysts transformed methanol to formaldehyde, which generated the active species for the methylation of phenol. Whereas the acid-type activation of methanol led to the development of an electrophylic species to the formation of anisole and cresols.

In this research methanol was used as the methylating agent and DMSO as a solvent over KNaX zeolite synthesized from kaolin to produce anisole. Since Indonesia is developing cashew tree (*Anacardium occidentale* L.) plantations, the importance of this research is its application in transforming cashewnut shell liquid, which contains phenol-formaldehyde compounds, into valuable intermediate products.

Experimental

Materials: Mineral kaolin, used as the alumina and silica sources in the synthesis of KNaX zeolite, is a commercial grade product in fine powder produced by PT Kaolindo Sakti Perkasa, Belitung, Indonesia. Other chemicals employed were sodium and potassium hydroxides (NaOH 97% and KOH 86%) from Merck and demineralized water. The chemicals used in the catalytic reaction were phenol (99%) from Aldrich, methanol (99%) and dimethylsulfoxide, DMSO (99%) from Merck. Anisole (99%) from Merck was used for the quantitative standard determination of products yield and selectivity.

Catalyst Preparation and Characterization: Kaolin was first calcined at 750°C for 24 h to obtain meta-kaolin and then NaOH in 50% weight ratio of kaolin was mixed and was further calcined at 850°C for 6 h. X-ray diffraction analysis were conducted to observe the transformation of kaolin to meta-kaolin. KNaX zeolite was prepared by mixing 7.5 g calcined kaolin with 14 g NaOH, 6.73 g KOH and 98.64 g demineralized water. The mixture was homogenized by stirring for 24 h at room temperature and the crystallization was carried out under hydrothermal condition in a tightly closed polypropylene bottle at 90°C for 72 h. The precipitate was filtered and washed with demineralized water until the pH of the washing water reached below 10, then it was dried at 110°C for 12 h. As a comparison, KNaX zeolite with Si/Al = 1.0 was prepared following the same preparation method with the addition of 16.9 g $Al_2(SO_4)_3.18H_2O$.

KNaX zeolite was characterized by X-ray diffraction (XRD) measurements, which were performed on a XRD Phillips PW 2213/20 with Cu K_α radiation and a Ni filter. The scanning range of 2θ was set between 10° and 80°. The chemical compositions of kaolin, meta-kaolin and KNaX zeolite were determined using X-ray fluorescent (XRF) measurements, which were performed on a Jeol Element Analyzer JSX-321. The surface area and pore diameter measurements were conducted using a Quantachrome NovaWin2.

Catalytic Reactions and Analysis: The catalytic reactions in liquid phase were carried out in a two-necked glass reactor fitted with two step condensers to prevent the loss of volatile compounds and equipped also with a thermometer. The reaction was performed at atmospheric pressure using DMSO as a solvent to maintain the reaction temperature at 150-155°C and using methanol as the methylating agent. The reactants mixtures of phenol and methanol were varied at mole ratios of 1/10, 1/20, 1/30, 1/40 and 1/50. The solvent/reactants mixtures were prepared in weight ratio of 10:1, whereas the catalyst was added in 10%-w of reactants. The reactions mixtures were heated at a variation of temperature ranging from 135°C to 155°C with a variation of reaction times from 6 h up to 24 h. For a comparative study, O-methylation reaction of phenol with methanol was conducted with and without KNaX zeolite catalyst. Furthermore, the influence of weight ratio of catalyst toward weight of reactants was studied in the presence of 5%, 10%, 15% and 25%-w of catalyst.

The reactions products were analyzed by Gas Chromatography Shimadzu GC-9A (column: INNOWAX), using phenol and anisole as standard references and by Gas Chromatography Mass Spectrometric GC Agilent 6890N (column: Hewlett Packard-5 MS). The phenol conversion and the yield and selectivity of anisole were defined as follows: phenol conversion (%) = moles of consumed phenol/moles of fed phenol x 100, yield of anisole (%) = moles of produced anisole/moles of fed phenol x 100 and selectivity of anisole (%) = moles of produced anisole/moles of converted phenol x 100.

RESULTS AND DISCUSSION

Zeolite Synthesis and Characterization: The hydrothermal process is usually applied to produce synthetic zeolite, whether it uses soluble forms of silica and alumina under highly alkaline conditions, or it uses minerals, which contain silica and alumina, such as kaolin. E.I. Basaldella and J.C. Tara [2] studied the influence of the Na/K ratio on the hydrothermal synthesis of low silica

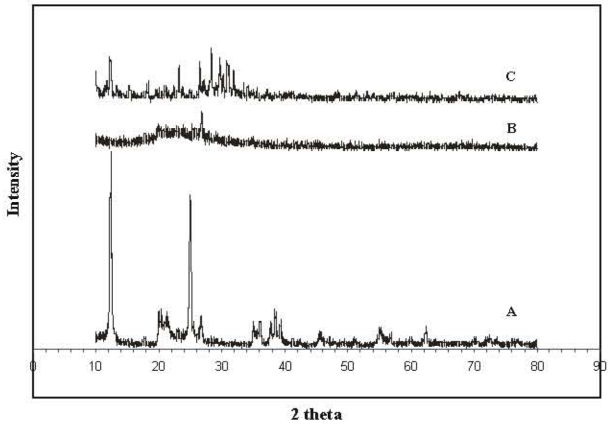

Fig. 1: X-ray diffractograms of (A) Kaolin (originating from Belitung) ; (B) Meta-kaolin and (C) synthesized KNaX zeolite (Si/Al ratio = 1.33)

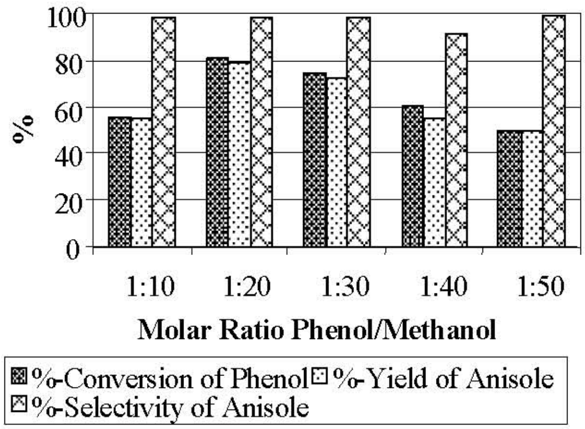

Fig. 2: The influence of molar ratio phenol/methanol on the catalysis reaction (reaction temperature 150°C; reaction time 10 h ; 10%-w of catalyst)

X zeolite (LSX zeolite) using quartz-contaminated kaolin clay, heated with Na_2CO_3 in a highly alkaline-mixed Na/K medium. The ratio Na/K has an importance role on the crystallization reaction of zeolite X and the cocrystallization of zeolite A. Pure LSX zeolite was obtained with the ratio $K_2O/(K_2O+Na_2O) = 0.18$ at 56°C for 96 h hydrothermal condition. D. Akolekar *et al.* [3] studied the transformation of kaolin extrudates to low-silica X zeolite, especially studied on the crystallization time of the macroporous metakaloin.

Indonesian red soils are rich in kaolin group minerals, which consist of tubular halloysite in the range of 40-60% and up to 90% [14]. In this research, mineral kaolin originating from Belitung region was used for the synthesis of KNaX zeolite. Kaolin was first transformed into meta-kaolin before it was modified into KNaX zeolite under hydrothermal conditions. Basic zeolite KNaX was prepared by adding a mixture of NaOH and KOH at a certain ratio to confirm the formation of zeolite X, in which the molar ratio gel composition was $3.83Na_2O$: $1.17K_2O$: Al_2O_3: $2.97SiO_2$: $118H_2O$. The XRF analysis results of kaolin, meta-kaolin and KNaX zeolite showed that the Si/Al ratio of KNaX zeolite was 1.33 and the %-weight K/(K+Na) ratio was 0.36. The higher K/Na ratio was preferred to minimize the cocrystallization of zeolite A, but it needed higher temperature of 90°C and longer crystallization time of 72 h. Fig. 1 shows the diffractograms of kaolin, meta-kaolin and KNaX zeolite. It shows that kaolin had been successfully transformed into meta-kaolin and into KNaX zeolite, which resembled the diffractogram of commercial NaX [15]. Since KNaX zeolite was synthesized from kaolin, peak signals of mica and zeolite A were found in the diffractogram. As reported by E.I. Basaldella and J.C. Tara, zeolite X and zeolite A are zeolites with low Si content and usually can be formed together in the synthesis of zeolite X. Surface area analysis showed that KNaX zeolite (Si/Al ratio = 1.33) had surface area 128.9 m^2/g, average pore diameter 2.43 nm and total pore volume 0.078 cm^3/g.

O-methylation Catalysis Reaction: O-methylation of phenol in liquid phase was studied by Maria D. Romero *et al*, who conducted the O-methylation of phenol with DMC in liquid phase using DMSO as a solvent over KNaCeX zeolite [12]. The highest yield of anisole (around 85%) was obtained with DMC/phenol molar ratio of 2.0 and 0.3%-w of catalyst at 155°C. 100% phenol conversion was reached after 3-5 h reaction period. Using DMC as the methylating agent, methanol is produced as a byproduct and it was found that methanol did not interfere O-methylation of phenol in liquid phase.

In this research, the O-methylation catalysis reaction of phenol was conducted at atmospheric pressure in DMSO solvent with methanol as the methylation agent. The boiling point of DMSO is 198°C at atmospheric pressure and to achieve the reaction temperature of 150-155°C, DMSO and phenol were first heated at around 195°C before methanol was added. Since the kinetic of phenol conversion is very slow, the catalytic methylation reactions were first studied for the influence of reagents molar ratio at 150°C for 10 h (Fig. 2) and the comparison of the methylation reaction with and without catalyst KNaX zeolite (Fig. 3). Figure 2 shows the highest phenol conversion and the yield of anisole were achieved with phenol/methanol molar ratio of 1/20. Basic KNaX zeolite showed very high selectivity toward anisole. Low conversion of phenol in molar ratio phenol/methanol of 1/10 is caused by the strong bound of phenol to the basic sites on the catalyst surface in the condensed phase.

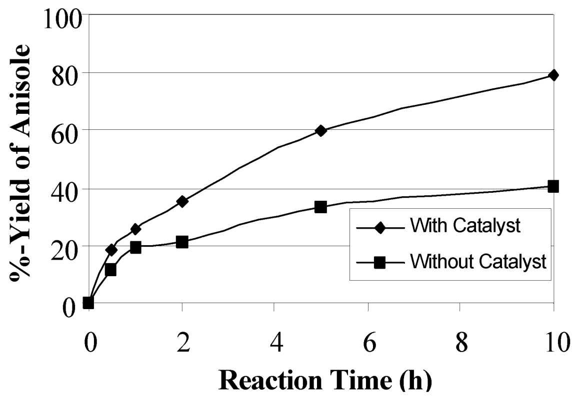

Fig. 3: Comparison yield of anisole with and without catalyst KNaX zeolite (phenol/methanol molar ratio = 1/20 ; reaction temperature 150°C ; 10%-w of catalyst)

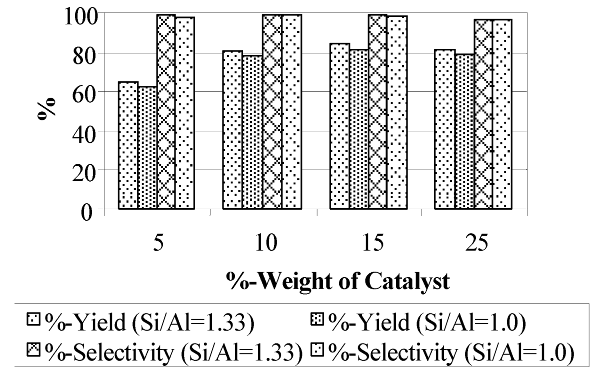

Fig. 4: The comparison activity and selectivity of KNaX zeolites (phenol/methanol molar ratio = 1/20; reaction temperature 155°C; reaction time 10 h)

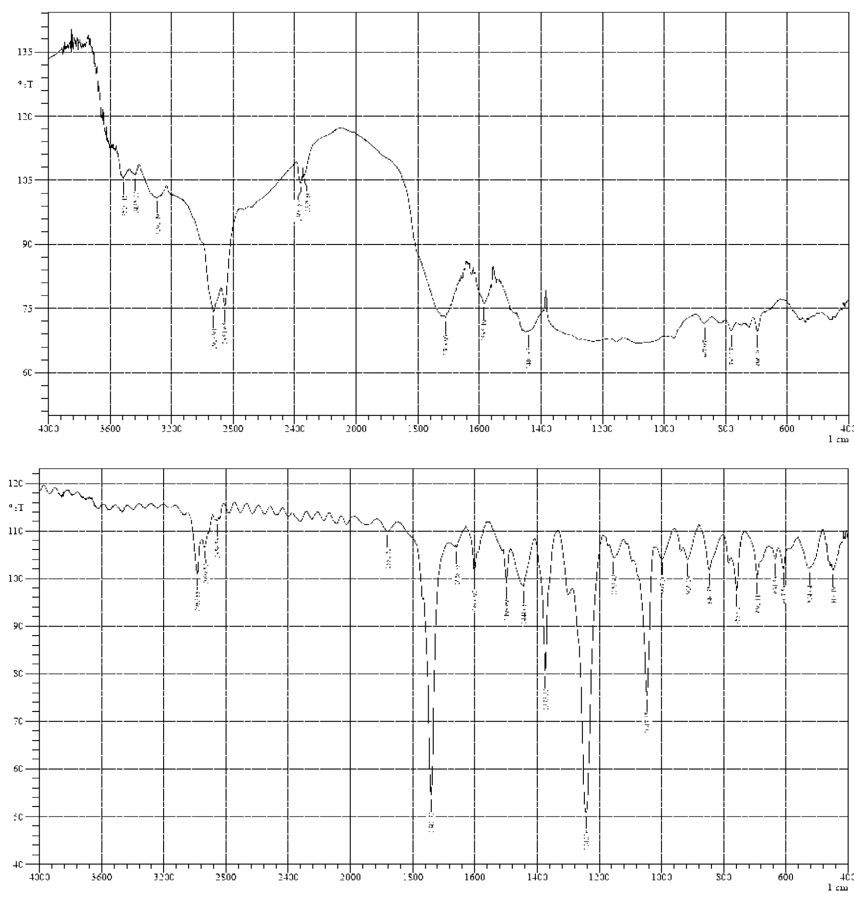

Fig. 5: FTIR spectra of cashewnut shell liquid before (spectrum above) and after the catalysis reaction with methanol as the methylating agent and DMSO as the solvent over KNaX zeolite (Si/Al = 1.33) at 155ºC for 10 h.

Figure 3 shows that O-methylation reaction of phenol can proceed without a basic catalyst through the formation of phenoxyl ion, but without a catalyst higher activation energy is needed. The GC chromatogram methylation reaction without a catalyst showed the product of C-methylation. The influence of reaction temperature and reaction time were studied respectively at a variation of temperature ranging from 135°C to 155°C and for a variation of reaction times from 6 h to 24 h. These results showed that the highest selectivity of anisole 99.3% was achieved at 155°C for 10 h reaction time. The catalysis reaction conducted at longer reaction period showed already the decreased selectivity of anisole, due to the product of C-methylation. These KNaX zeolite catalyst activity and selectivity toward anisole were studied using 10%-w of catalyst to weight of reactants at 155°C. The catalysis reactions in the presence of 15%-w and 25%-w of catalyst showed a slightly decreased in catalyst selectivity, because of the presence of more basic sites availabilities to produce C-methylation and other side products. The KNaX zeolite catalyst activity and selectivity toward anisole were also studied by comparing the Si/Al ratio of 1.33 with Si/Al ratio of 1.0. Since Aluminium atoms in the framework of zeolite produce negative charges, which are balanced by the Na and K cations, more Al atoms in the KNaX zeolite with Si/Al =1.0 lead to less basic properties than KNaX zeolit with Si/Al = 1.33. The decreased basicity of KNaX zeolite with Si/Al = 1.0 showed the decreased of catalyst activity and selectivity as shown in Figure 4.

The interaction between phenol and methanol without a catalyst are intermolecular acid-base reactions, in which the phenoxyl and the methoxyl ions are the reactive intermediates. The mechanism reaction of O-methylation of phenol with methanol over basic KNaX zeolite is suggested to follow the bimolecular nucleophilic substitution, since phenol is more strongly interacted to the basic sites of the catalyst than methanol. In this study, the O-methylation reaction depends strongly on the basic sites of the catalyst, rather than on the catalyst surface characteristics of surface area and pore volume, as shown in the successful methylation of cashewnut shell liquid, which contains 90% anacardic acid and 10% cardol. This additional pre-study on the O-methylation of cashewnut shell liquid with methanol was conducted with 15%-w of KNaX zeolite catalyst (Si/Al = 1.33) at 155°C in 10 h reaction period. Figure 5 shows the FTIR spectra of the cashewnut shell liquid before and after the catalysis reaction, in which the broad band of -OH group at 3292 cm^{-1} is vanished and is replaced by the peak of $-OCH_3$ group at 2869 cm^{-1}. The broad band at 3000-2500 cm^{-1} and the peak at 1708 cm^{-1} of the carboxylic groups of the anacardic acid are replaced by the peak of its ester at 1741 cm^{-1}. Further study is needed to investigate the reaction side products.

CONCLUSION

Synthesized KNaX zeolite (Si/Al 1.33) from kaolin was successfully used as a basic catalyst for O-methylation of phenol with methanol as a methylating agent in DMSO solvent. The catalytic reaction in liquid phase of reactants mixture phenol/methanol in molar ratio of 1:20 showed the highest reactivity and selectivity toward anisole at 155°C in the present of 15%-w of catalyst. Although O-methylation reaction can proceed without catalyst, but it only produced 40.48% anisole.

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