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Fe₂O₃ on Zeolite NaY Synthesized from Rice Husk as Catalyst for Oxidation of Styrene

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Received 14 May 2018; Revised 18 June 2018; Accepted 25 June 2018

Abstract

In this research, zeolite NaY is successfully synthesized from rice husk silica as agricultural waste material. Iron catalysts on zeolite NaY from wet impregnation, Fe/NaY with Fe loading 0.5-10.0 wt% are characterized and investigated for the oxidation of styrene to benzaldehyde. The characterization with wide angle X-ray scattering (WAXS) suggest that loaded iron dispersed on external surface and inside pore of NaY. Moreover, the formation of γ -Fe₂O₃ phase is observed on NaY, as indicated by soft X-ray absorption spectroscopy. TGA and FTIR measurements of the Fe/NaY also show the formation of nitrate ion. Over the catalysts, the oxidation of styrene is enhanced with benzaldehyde being the major whereas styrene glycol, acetophenone, phenylacetaldehyde, styrene oxide and benzoic acid being the minor products. The 2.5wt% Fe/NaY show the good catalytic selectivity in catalytic oxidation of styrene using H₂O₂ and reaction time at 6 h, and the selectivity of the benzaldehyde reached 75%.

Keywords : Fe Oxide; Zeolite NaY; Benzaldehyde; Oxidation of Styrene

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1. Introduction

NaY is a type of zeolite molecular sieve which is crystalline aluminosilicates with faujasite (FAU) structure. It has a three-dimensional large pores which include uniform channels with 7.4 Å diameter and cavity with 12 Å diameter [1], [2]. NaY have potential applications in fields including catalysis, adsorption and ion exchange due to their properties such as molecular sieving, high thermal stability and acidity [1]. Because of its shape selectivity and large internal surfaces, NaY has also been used as catalysts and catalyst supports. Researchers report the application of NaY zeolite as excellent catalyst in hydrolysis of nitrile [3] and cracking of petroleum [4], [5]. Meanwhile, NaY supported metal catalysts, which ZnS and ZnO [6], Ir [7], Rh [8], TiO₂ [9] VO, Cu and Ni complexes [10] have been used in varied application such as pharmacological, hydrogenolysis of *n*-butane, hydro generation of CO₂, degradation of dye and oxidation of VOCs, etc.

In organic synthesis, products from oxidation of styrene are important in chemical industry such as benzaldehyde, styrene glycol, styrene oxide and benzoic acid, especially benzaldehyde is a very valuable chemical because it has widespread applications in perfumery, dyestuff, and agro chemical industries, etc [11]-[13]. Many research interest to study catalytic for products selectivity

of styrene oxidation. PMo/modified MCM-41 [13] has been used as a catalyst for styrene oxidation to styrene oxide selectivity with H₂O₂. Meanwhile, V/MCM-41 [14] showed good catalytic selectivity for phenylacetic acid and benzaldehyde. Hence the catalyst is an effective to product selectivity in the styrene oxidation, moreover, the type of oxidant is quite interest. α-Fe₂O₃ nanoparticle [15] and g-Fe₂O₃/NaY [12] have been used as a catalyst for styrene oxidation to styrene oxide selectivity with tert-BuOOH as the oxidant.

Iron catalyst that can catalyze the selective oxidation of several other hydrocarbons. Iron(II, III) is oxidized by hydrogen peroxide to iron(III, IV), forming a hydroxyl radical and a hydroxide ion in the process. Hydroxyl radical is used to oxidize contaminants or waste waters and catalyze in hydroxylation of benzene to phenol [16]. When iron oxide is deposited on a NaY support with high surface area, the catalytic performance could be improved because of an improvement in iron oxide dispersion.

In the present work, the NaY was synthesized from rice husk silica by hydrothermal method [17]. Rice husk silica is good choice for the production of cheap because it is a by-product of rice milling and can be considered as an agricultural waste, in addition, rice husk contains more than 95 wt% silica after acid leaching and calcination [18].

The NaY was used as a support material for catalysts consisting of Fe oxides loading of 0.5-10.0 wt%. Characteristics of the NaY and catalysts as well as the investigate for styrene oxidation in the presence of H_2O_2 were studied.

2. Research Methodology

2.1 Research Processes

The NaY was synthesized from rice husk silica by hydrothermal method and then 0.5, 1.0, 2.5, 5.0 and 10.0 wt% Fe were loaded onto NaY by incipient wetness impregnation method. The Fe_2O_3/NaY catalyst was characterized by Fourier transform infrared spectroscopy (FTIR), thermogravimetric analysis (TGA), wide angle X-ray scattering (WAXS) and soft X-ray absorption spectroscopy. The catalyst was used for the catalytic oxidation of styrene in the present of H_2O_2 as the oxidant. The effect of the amount of iron on NaY and reaction time on styrene oxidation were investigated.

2.1.1 Materials and Methods

The chemical for rice husk silica preparation was hydrochloric acid (HCl, 37%, Carlo Erba). The chemicals for NaY synthesis were sodium hydroxide, anhydrous pellet (NaOH, Carlo Erba) and sodium aluminate ($NaAlO_2$, Sigma-Aldrich). The chemical for catalyst preparation was Iron (III) nitrate nonahydrate ($Fe(NO_3)_3 \cdot 9H_2O$, Merck). The chemicals for catalytic testing were

hydrogen peroxide (H_2O_2) 30%, styrene ($C_6H_5CH=CH_2$) 99% and styrene oxide (C_8H_8O) 97% supplied by ACROS Organics, acetonitrile (C_2H_3N) and benzaldehyde (C_7H_6O) supplied by RCI Labscan. The IR spectra were recorded on a Perkin elmer spectrum 100 over the 4,000-400 cm^{-1} range for KBr pellets. The thermal behavior of the samples were analyzed by thermogravimetric analysis (TGA) (Perkin elmer; STA 6000) under a flow of N_2 at a heating rate of 10°C/min in the range 50- 900°C. The degree of crystallinity of the samples were measured with wide angle X-ray scattering (WAXS) technique at Beamline 1.3W, SLRI using hard X-ray synchrotron with the energy of 9 keV. The scattering data were collected using a charge-coupled detector (CCD) (MAR SX165) with 2theta-diffraction angle ranging from 0°-70°. For soft X-ray absorption, the samples (2x2 cm^2 in dimension) were mounted on the tantalum sample holder inside ultrahigh vacuum chamber with the base pressure of 1×10^{-9} mbar. The samples were excited by the synchrotron beam with the energy range near the XANES of the iron L-edge. The energy step was 0.1 eV. The XANES spectra were analyzed in total electron yield (TEY) mode by recoding the sample current at Beamline 3.2Ua, SLRI.

2.1.2 NaY Synthesis

The NaY zeolite was synthesized from a seed gel and feedstock gel under

hydrothermal condition as previously reported [17].

The seed gel with a molar ratio of $10.67\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 180\text{H}_2\text{O}$ was prepared by adding Na_2SiO_3 solution (Na_2SiO_3 was prepared by mixing 27 g of rice husk silica with a NaOH solution) to the solution of NaAlO_2 . The mixture was stirred until homogeneous and transferred into a polypropylene (PP) bottle, capped, and aged at room temperature for 24 h.

The feedstock gel with molar ratio $4.30\text{Na}_2\text{O} : \text{Al}_2\text{O}_3 : 10\text{SiO}_2 : 180\text{H}_2\text{O}$ was prepared in similar to that of the seed gel except that it was used immediately without aging.

The NaY synthesis was carried out by a slow addition of the seed gel into the feedstock gel under stirring. The mixture was transferred into a PP bottle, capped, and crystallized at 90°C for 24 h. After cooling to room temperature, the solid product, as-synthesized NaY was separated by centrifugation, washed thoroughly with DI water and dried at 100°C for 24 h. The resultant solid was white in color.

2.1.3 Catalyst preparation

Catalysts were prepared with a varied loading of iron (Fe) to 0.5, 1.0, 2.5, 5.0 and 10.0 wt% on NaY support by incipient wetness impregnation method. 10.0 mL of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ aqueous solution in different Fe^{3+} concentration was added dropwise to 5.0 g of NaY zeolite. The impregnated catalysts were

dried in an oven at 100°C for 6 h and then calcined in a furnace at 450°C for 5 h.

2.1.4 Catalytic oxidation of styrene

The oxidation of styrene was carried out in a round bottom flask with a reflux condenser. 17.3 mmol styrene, 10 ml acetonitrile and 100 mg of catalyst were mixed in the flask and heated to 80°C . Then 44.1 mmol H_2O_2 (30%) was added to the flask. The reaction was carried out for the different loading of iron and reaction time. The reaction products were analyzed with a gas chromatograph (Shimadzu GC-2014) equipped with a thermal conductivity detector and a capillary column (Rtx_WaX, 30 m, 0.25 mm, 0.5m).

3. Results and Discussion

3.1 Characterization of catalysts

The FTIR spectra for catalysts were shown in Fig. 1. The broad peak around $3,450$ and sharp peak at $1,640\text{ cm}^{-1}$ were ascribed to the stretching vibration of OH and bending of adsorbed molecular water, respectively. The bands at 1010 , 780 and 480 cm^{-1} can be attributed to T–O (T = Si or Al) internal tetrahedral asymmetrical, symmetrical stretching and bending vibration of NaY structure, respectively. The zeolite bands at $1,125$ and 700 cm^{-1} correspond to external linkages between tetrahedral asymmetrical and symmetrical stretching [19]-[21]. The FTIR spectra of $\text{Fe}_2\text{O}_3/\text{NaY}$ catalysts

were similar to pure NaY except that the peak intensity decreased with increasing the amount of iron. This result confirmed incorporation of Fe ions into zeolite channels. Additional band at $1,400\text{ cm}^{-1}$ was observed, which can be assigned to vibrational of NO_3^- ion from iron(III) nitrate. The intensity of band increased with increasing amount of iron that result indicated the calcination temperature was not sufficient to decomposition of nitrate ion.

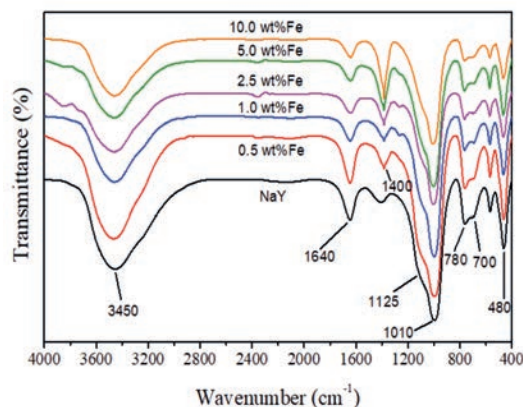


Fig. 1 FTIR spectra of the samples

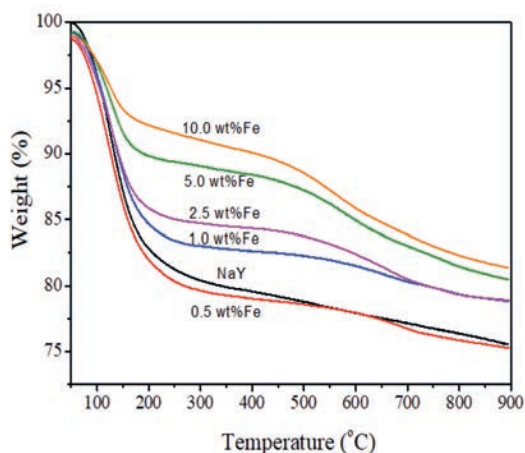


Fig. 2 TGA spectra of the samples

The TGA spectra of pure NaY and $\text{Fe}_2\text{O}_3/\text{NaY}$ catalysts were shown in **Fig. 2**. All samples showed rapid weight loss at under 150°C because moisture in catalyst desorbed in this range [22]. Moreover, the amount of moisture loss of Fe_2O_3 catalysts decreased with increasing iron loading. This result indicated that the hydroxyl groups on NaY were replaced by Fe ion. The weight loss of Fe catalysts with 2.5, 5.0 and 10.0 wt% loading clearly showed the second region of ca. 3.0, 5.8 and 6.3 wt%, respectively at around 550°C . These regions were corresponding to the nitrate decomposition since it remained from catalyst preparation process.

Fig. 3 showed the XRD patterns of $\text{Fe}_2\text{O}_3/\text{NaY}$, typical peaks of NaY zeolite were observed at 2θ values of 6.6° , 10° , 12° , 16° , 24° and 27° and can be assigned to (111), (220), (311), (331), (533), and (642) planes, respectively, as confirmed by reported values [23]. After deposition with iron, the intensity of NaY pattern decreased with increasing the iron loading due to the presence of Fe_2O_3 on the support surface could scatter out the X-ray resulting in lower diffracted intensity. In addition, the spectra were not occurred XRD patterns of Fe_2O_3 because Fe_2O_3 clusters may located within the pores of NaY zeolite [6]. As shown in **Fig. 3B**, the peak position of the (111) plane of the supported catalysts shifted slightly toward the higher angle

suggesting that some iron oxide settled in the supercage or blocked micropores of NaY [24]. Furthermore, the brown color of the obtained Fe/NaY together with the soft X-ray absorption spectroscopy verified the presence of iron in the catalyst.

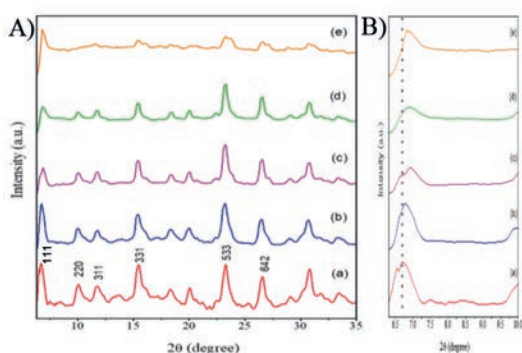


Fig. 3 A) XRD pattern of the samples

- (a) 0.5wt%Fe/NaY,
- (b) 1.0wt%Fe/NaY,
- (c) 2.5wt%Fe/NaY,
- (d) 5.0wt%Fe/NaY and
- (e) 10.0wt%Fe/NaY,

B) the enlarge (111) peaks for the samples

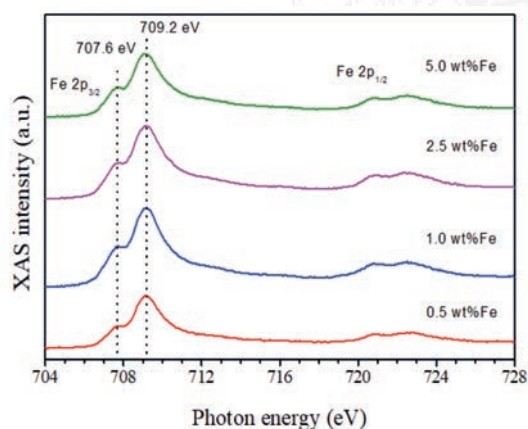


Fig. 4 XAS spectrum at Fe *L*-edge of the samples

Fig.4 showed the Fe 2*p* XAS spectra of 0.5-5.0 wt% Fe/NaY, which presented Fe *L*₃-edge (*2p*_{3/2}) located at 707.6 and 709.2 eV and, moreover, Fe *L*₂-edge (*2p*_{1/2}) located at 720-725 eV. The *2p*_{3/2} edge of all catalysts showed a peak similar to *g*-Fe₂O₃ [25],[26] indicating that Fe atoms on NaY were mostly Fe³⁺ of *g*-Fe₂O₃.

3.2 Catalytic oxidation of styrene

Fig.5 showed the effect of iron loading on styrene oxidation for reaction time 8 h at 80°C using 100 mg catalyst and H₂O₂ as the oxidant. The main product of Fe₂O₃ catalysts was benzaldehyde while styrene oxide, styrene glycol, phenylacetaldehyde, acetophenone and benzoic acid were detected as minor products. The results of **Fig. 5**, the styrene conversion decreased with increasing amount of iron on NaY. 5.0 wt% and 10.0 wt% Fe on NaY, especially, had low styrene conversion about 22% and 14%, respectively because the formation of nitrate ion probably blocked the active site of catalysts. Moreover, high amount of iron loading can led to aggregation, which would make the catalyst not active due to poor dispersion of iron oxide. The pure NaY showed the high styrene conversion (55%) whereas showed the less benzaldehyde selectivity (10%) and, moreover, the main products of pureNaY were styrene oxide and phenylacetaldehyde. In this case, H₂O₂

was decomposed into free radicals and then which interacted with the C=C double bond of styrene to form styrene oxide. The formation of phenylacetaldehyde may be formed through further isomerization by ring opening of styrene oxide on bronsted acid site of NaY [27]. In present of Fe catalyst, role of Fe^{3+} was decomposition of H_2O_2 into free radicals on the surface catalyst ($\text{Fe}^{4+}\text{-O}\cdot$) [22]. Afterwards, $\text{Fe}^{4+}\text{-O}\cdot$ interacted with styrene followed by cleavage of the C=C double bond to form styrene oxide as intermediate in formation of benzaldehyde. Benzaldehyde can be formed by oxirane ring opening by nucleophilic attack of H_2O_2 and followed by C-C cleavage of intermediate substance. Styrene glycol may be formed through hydrolysis of styrene oxide due to the water present in process. Afterward, rearrangement of electrons and C-C bond breakage of styrene glycol would give benzaldehyde [28]. This result indicated that iron content would have notable influence on the benzaldehyde selectivity. From **Fig. 5** result, that showed 2.5 wt% Fe/NaY providing the highest benzaldehyde selectivity about 61%. This result indicated that Fe_2O_3 catalysts with 2.5 wt% loading was optimum catalyst for styrene oxidation.

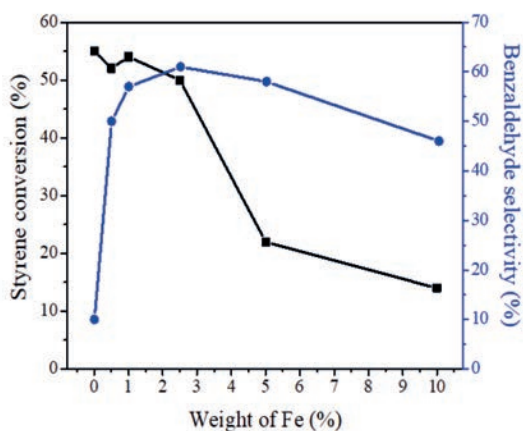


Fig. 5 Oxidation of styrene with H_2O_2 over x wt% Fe/NaY (x = 0, 0.5, 1.0, 2.5, 5.0 and 10.0). (square) styrene conversion, (circle) benzaldehyde selectivity. [Reaction condition: 17.3 mmol styrene, 44.1 mmol H_2O_2 , 10 mL acetonitrile, catalyst 100 mg, temperature 80°C , reaction time 8 h]

The styrene conversion and product selectivity were done by carrying out the reaction time from 2 h - 8 h, at 80°C using 100 mg of 2.5 wt% Fe/NaY. The conversion increased with increasing reaction time while products selectivity of 2.5 wt% Fe/NaY exhibited the similar trend at each time except for reaction time at 2 h were presented in **Fig. 6**. The amount of styrene oxide decreased and disappeared at 8 h because it can be transferred to benzaldehyde and styrene glycol with increasing reaction time. Meanwhile, other products such as benzoic acid and phenylacetaldehyde might be form through oxidation of benzaldehyde and isomerization of styrene oxide, respectively [10].

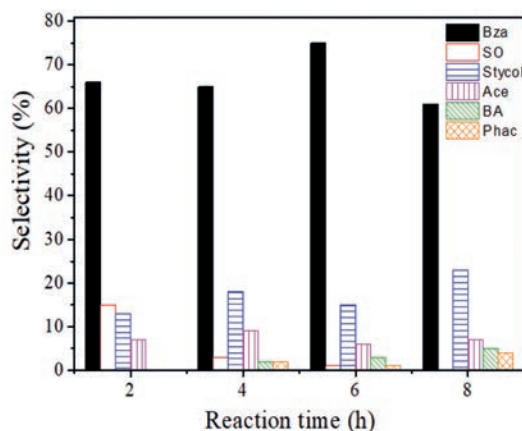


Fig.6 Effect of reaction time on oxidation of styrene with H_2O_2 over 2.5% Fe/NaY. (Bza) benzaldehyde, (SO) styrene oxide, (Stycol) styrene glycol, (Ace) acetophenone, (BA) benzoic acid and (Phac) phenylacetaldehyde selectivity

The reaction time was 6 h, that was optimum time for 2.5 wt% Fe/NaY because it had highest benzaldehyde selectivity about 75% and by-products include styrene oxide (1%), styrene glycol (15%), acetophenone (6%), benzoic acid (3%) and phenylacetaldehyde (1%).

4. Conclusion

NaY zeolite was synthesized with rice husk silica by hydrothermal method and used as a catalyst support for iron oxide. The form of Fe confirmed by soft X-ray absorption was $\gamma\text{-Fe}_2\text{O}_3$. The activity of catalyst decreased with the poor dispersion of iron oxide on NaY after high degree of iron loading and also with formation of nitrate ion. Styrene oxidation testing, the

mainly product as a benzaldehyde and by-products e.g. styrene glycol, acetophenone, phenylacetaldehyde, styrene oxide and benzoic acid were detected. The iron loading at 2.5 wt% on catalyst can promoted the selectivity of styrene oxidation to benzaldehyde under temperature at 80°C for reaction time 6 h that gave highest benzaldehyde selectivity about 75%.

5. Acknowledgement

We are grateful to thank Dr. Ratchadaporn Supruangnet and Mr. Surachet Rattanasuporn for help with the XAS experiments. We would like to thank Dr. Nuntaporn kamonsutthipajit and Dr. Siriwat Soontaranon for helpful discussions for the SAXS measurements. We would like to thank Dr. Natkanin Supamathanon and Dr. Areeporn Ontam for his kind assistance all through the project.

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