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CHARACTERIZATION K_3PO_4/NaZSM-5 USING XRD AND FTIR AS A CATALYST TO PRODUCE BIODIESEL

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Abstract

Synthesis of NaZSM-5 and impregnation of K_3PO_4 catalyst with concentration 5, 10, and 15 wt.% on the resulting NaZSM-5 as a catalyst to produce biodiesel have been done in this study. This study is an experimental study, the research stages include the synthesis and characterization NaZSM-5 and K_3PO_4/NaZSM-5. Characterization by X-Ray Diffraction (XRD) was conducted to determine the X-ray diffraction patterns and the percentage crystallinity of the samples. X-ray diffraction pattern of the resulting sample showed the emergence of diffraction peaks with high intensity at 2θ = 7.8; 8.8; 23.0; 23.2, and 24.3° are specifically indexed to the structure of the MFI topology. The percentage crystallinity of the sample becomes smaller with increasing number of K_3PO_4 impregnated on NaZSM-5 synthesis. Characterization of the samples by Fourier Transform Infra Red (FTIR) aims to determine the type of functional groups present in a compound. FTIR spectra of samples NZ, NZK5, NZK10 and NZK15 have absorption bands in the region 1220 and 547 cm^{-1} which shows the absorption characteristics of vibration T - O - T on NaZSM-5 type zeolite which distinguish the other and sensitive to changes in structure. The results of characterization using XRD and FTIR showed that the structure of NaZSM-5 remained unchange after impregnated with K_3PO_4.

Keyword: K_3PO_4/NaZSM-5, the diffraction pattern, the percentage crystallinity, absorption characteristics

INTRODUCTION

Biodiesel, a mixture of fatty acid alkyl esters, has been developed as one of the most promising alternative fuel for fossil fuels regarding the limited resources of fossil fuels and the environmental concerns [1]. Almost all commercial biodiesel is currently produced by using homogeneous catalyst (i.e., KOH, NaOH and H_2SO_4). Even though homogeneous catalyzed biodiesel production processes are relatively fast and achieve high conversions, the removal of the homogeneous catalyst after reaction may be a significant problem. This is a concern, since aqueous quenching causes the formation of stable emulsions and saponification, making separation of alkyl-esters difficult, resulting in the generation of large amounts of waste water, and need a high cost in operation especially for waste water treatment [1-3]. For this reason, heterogeneous catalyst is likely to be used replacing homogeneous catalyst in the near future.

Heterogeneous base catalysts are more effective than acid catalysts and enzymes. From the economic standpoint, it would be ideal if solid base catalysts could work efficiently at temperatures below 150°C and low pressure. On the other hand, solid acid catalysts, enzymes and non-catalytic supercritical transesterification have been largely ignored in biodiesel research due to pessimistic expectations in terms of reaction rates, undesirable side reactions and high costs [4].

Several heterogeneous base catalysts that used for biodiesel production are ZnO-Al_2O_3/ZSM-5 yield 99,00% [2], K_3PO_4 yield 97,30% [5], KF/Ca-Al hidrotalcite yield 97,14% [6], Mg/MCM-41 yield 85,00% [7], KI/silika mesopori yield 90,09% [3]. In this experiment, K_3PO_4 is chosen as catalysts because yield of biodiesel 97,30%, relatively insoluble in methanol and oil [5]. NaZSM-5 supported K_3PO_4 were prepared by impregnation. Thus the aim of this work is to evaluate character of NaZSM-5 and K_3PO_4/NaZSM-5 by XRD and FTIR.

RESEARCH METHOD

Synthesis

The NaZSM-5 crystals were prepared by procedure similar to that described by Khalifah [8]. The seeding gels were prepared by dissolving 1.28 gram sodium aluminate in a solution (12.6 mL TPAOH and 62.5 mL water). After its complete dissolution, 28.2 ml TEOS was added in a solution. This solution was stirred for 15 min and heated at 60 ^oC for 6 h. After gel formed, was added 11.952 gram CTABr little by little and was stirred until its complete dissolution. Subsequently the crystallisation of the seeding gels was carried out using autoclave for 24 h at 150 ^oC. Finally the solid was separated by filtration, washed with distilled water until pH neutral and dried, firstly for 24 h at 60 ^0C and subsequently for 24 h at 110 ^0C. The occluded surfactant (CTA^+) and the organic template (TPA^+) were removed by calcination in air at 550 ^oC for 10 h.

The K_3PO_4 solution was impregnated on NaZSM-5 by impregnation with concentration of K_3PO_4 at 5, 10, and 15 wt.%. The catalyst was dried at 110 °C for 24 h followed by calcining at 550 °C for 10 h so that produce K_3PO_4/NaZSM-5 catalyst. The resulting NaZSM-5 and K_3PO_4/NaZSM-5 catalyst with concentration of K_3PO_4 at 5, 10, and 15 wt.% are labeled NZ, NZK5, NZK10 and NZK15.

Characterisation

The X-ray diffraction patterns and the percentage of crystallinity of NZ, NZK5, NZK10 and NZK15 were characterized by Phillips Expert X-Ray Diffraction (XRD) with Cu K_α radiation (40 kV, 30 mA) at scale 2θ = 5-40^o and rate of scan 0,04 ^{o}/second. The infrared spectra were recorded using the KBr pellets and Shimadzu Instrument Spectrum One 8400S Fourier Transform Infrared (FTIR) Spectrometer in the range between 4000 and 400 cm^{-1}.

RESULT AND DISCUSSION

X-ray Diffraction

The X-ray diffraction pattern of K_3PO_4, the resulting samples (NZ, NZK5, NZK10 and NZK15) and ZSM-5 was producted by Zhu et al. [9] are shown in Fig. 1. The XRD pattern of the resulting sample showed the emergence of diffraction peaks that similar with high intensity at 2θ = 7.8; 8.8; 23.0; 23.2, and 24.3°.

This XRD resulting is similar as the XRD patterns of ZSM-5 was reported by Zhu et al. [9] with high intensity at 2θ = 7.8; 8.8; 23.1; 23.4, and 24.4° are specifically indexed to the structure of the MFI topology. On the basis of this characterization, NZ, NZK5, NZK10 and NZK15 included the structure of the MFI topology and not be found the another ZSM-5 type.

Fig. 1 also show diffraction pattern of the K_3PO_4 with high intensity at $2\theta = 31.8^0$. The presence of K_3PO_4 impregnated on NaZSM-5 does not show new peak of K_3PO_4 at NZ, NZK5, NZK10 and NZK15, suggesting that the structure of NaZSM-5 is not destroyed during the process of catalyst preparation and K_3PO_4 has well dispersed on NaZSM-5. Zhang et al. [10] observe nothing diffraction peak of PtSnNa catalyst after impregnated on ZSM-5, suggesting that the structure of ZSM-5 is not destroyed during the process of catalyst preparation. Some parts of Na^+ and Sn^{4+} could enter the zeolite main channels, while Pt particles were located mainly on the external surface of the zeolite.

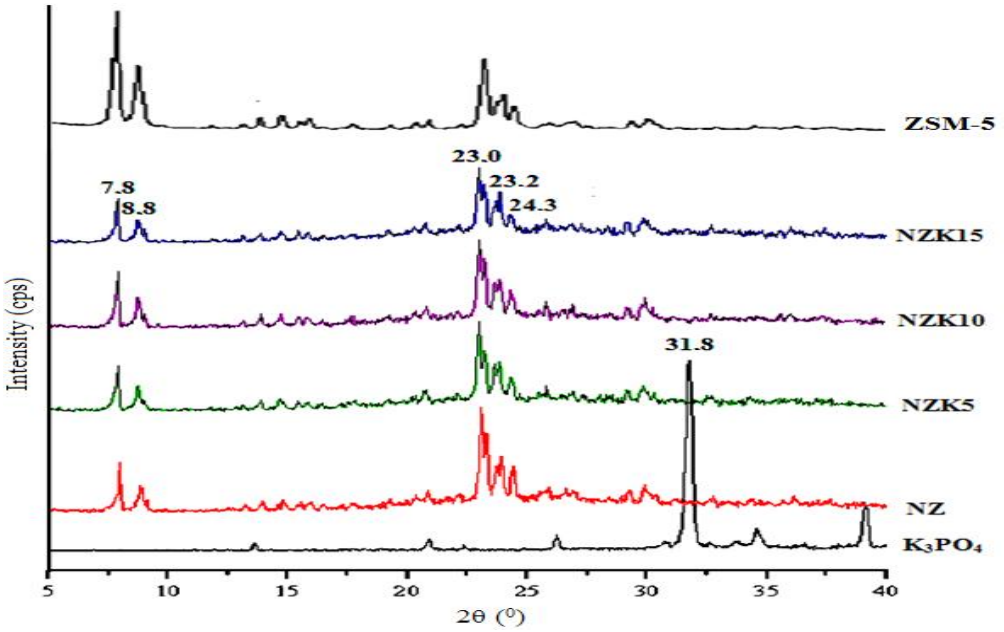

Fig. 1. The X-ray diffraction pattern of K_3PO_4, the resulting samples (NZ, NZK5, NZK10 and NZK15) and ZSM-5 was producted by Zhu et al. [9]

The intensities of NaZSM-5 characteristic peaks were decreasing caused by increasing of K_3PO_4 concentration. The phenomenon decreasing of the intensities of ZSM-5 characteristic peaks also reported by Kim et al. [2] after $ZnO\text{-}Al_2O_3$ and $SnO\text{-}Al_2O_3$ was impregnated on ZSM-5.

Table 1 show relationship percentage crystallinity with percentage K_3PO_4 impregnated on NaZSM-5, that calculated based on intensity main peak at $2\theta = 23°$ using highest intensity sample (NaZSM-5) as comparator standard that assumed has percentage crystallinity = 100. The percentage crystallinity of the samples becomes smaller with increasing number of K_3PO_4 impregnated on NaZSM-5 synthesis.

Table 1. Relationship percentage crystallinity with percentage K_3PO_4 impregnated on NaZSM-5

Sample	2θ	Intensity, I	I/Io	% Crystallinity
NZ	23.10	376.70*	1.00	100
NZK5	23.00	334.18	0.89	89
NZK10	23.01	314.18	0.83	83
NZK15	23.00	271.50	0.72	72

* comparator standard (Io)

FTIR Spectra

FTIR spectra between 400–1300 cm^{-1} of K_3PO_4 and the resulting samples (NZ, NZK5, NZK10 and NZK15) are shown in Fig. 2. In this range all resulting samples possess one broad band at 1000–1200 cm^{-1}, and three bands around 795, 547, and 455 cm^{-1}. FTIR spectra of samples NZ, NZK5, NZK10 and NZK15 have absorption bands in the region 1220 and 547 cm^{-1} which shows the absorption characteristics of vibration T-O-T on NaZSM-5 type zeolite which distinguish the other and sensitive to changes in structure.

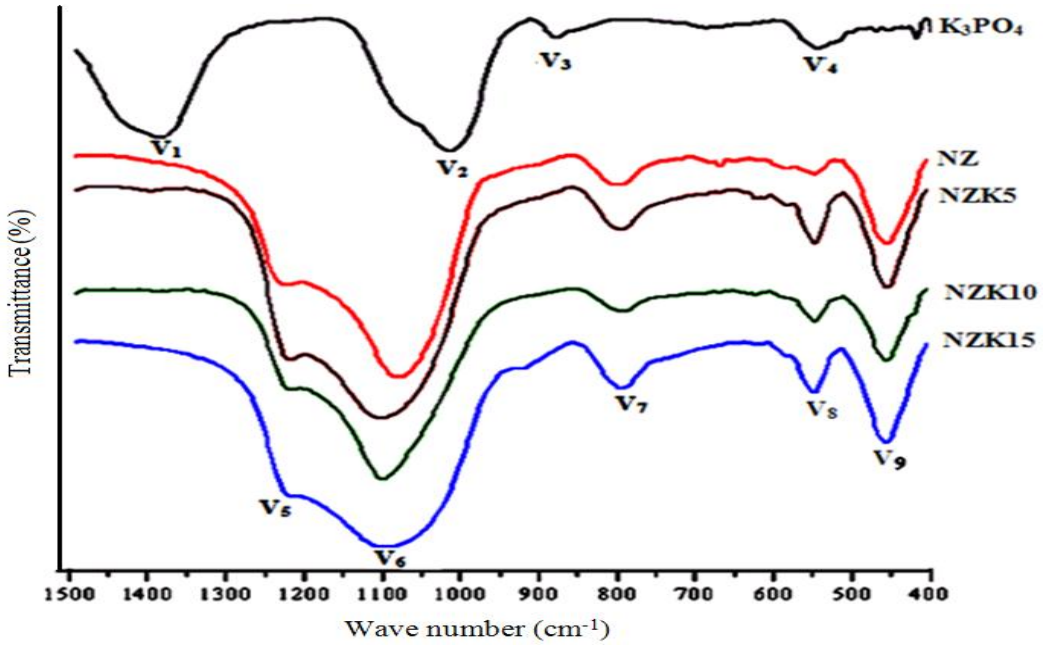

Fig. 2. FTIR spectra of K_3PO_4 and the resulting samples (NZ, NZK5, NZK10 and NZK15)

Traditionally [8,11], the bands in the range at around 1000–1200 and 455 cm^{-1} are attributed to the structure insensitive internal tetrahedron asymmetric stretching vibrations T-O-T and bending vibrations Si-O-Si, respectively. The band at around 795 cm^{-1} can be attributed to both structure insensitive internal tetrahedron and structure sensitive external tetrahedron symmetric stretching vibrations Si-O-Si. The structure sensitive band, appearing in the presented spectra around 547 cm^{-1}, is attributed to five-ring units in the structures of pentasil zeolites like ZSM-5 (Table 2).

FTIR spectra of K_3PO_4 have absorption bands in the region 1396, 1000 and 551 cm^{-1}. The bands at 1396 and 879 cm^{-1} is attributed to vibrations of carbonate ion from CO_2 gas adsorbed by K_3PO_4 [12-14]. The bands at 1000 and 551 cm^{-1} is attributed to stretching vibrations and bending vibrations of phosphate ion on K_3PO_4 [12].

Building on FTIR spectra, the presence of K_3PO_4 impregnated on NaZSM-5 does not show new bands of K_3PO_4 at NZ, NZK5, NZK10 and NZK15. So, the analysis resulting of characterization using XRD and FTIR show that the structure of NaZSM-5 remained unchange after impregnated with K_3PO_4.

Table 2. Wave number of of K_3PO_4, ZSM-5 and the resulting samples (NZ, NZK5, NZK10 and NZK15)

Bands	Wave number (cm^{-1})						Absorption characteristics
	K_3PO_4	ZSM-5 Gonçalves, et al [11]	NZ	NZK 5	NZK 10	NZK 15	
V_1	1396	-	-	-	-	-	Vibrations of carbonate ion
V_2	1014	-	-	-	-	-	Stretching vibrations of phosphate ion
V_3	879	-	-	-	-	-	Vibrations of carbonate ion
V_4	551	-	-	-	-	-	Bending vibrations of phosphate ion
V_5	-	1220	1222	1219	1215	1215	Structure insensitive internal tetrahedron asymmetric stretching vibrations T-O-T
V_6	-	1100	1103	1103	1099	1099	Structure insensitive internal tetrahedron asymmetric stretching vibrations Si-O-T
V_7	-	795	802	795	795	795	Structure insensitive internal tetrahedron and structure sensitive external tetrahedron symmetric stretching vibrations Si-O-Si
V_8	-	546	547	547	548	548	Five-ring units in the structures of pentasil
V_9	-	450	455	455	459	459	Bending vibrations Si-O-Si

CONCLUSION AND SUGGESTION

Characterization by XRD and FTIR of the NaZSM-5 and K_3PO_4/NaZSM-5 catalyst with concentration of K_3PO_4 at 5, 10, and 15 wt.% was investigated. The XRD pattern of the resulting sample (NZ, NZK5, NZK10 and NZK15) showed the emergence of diffraction peaks that similar with high intensity at 2θ = 7.8; 8.8; 23.0; 23.2, and 24.3° that are specifically indexed to the structure of the MFI topology and not be found the another ZSM-5 type. The percentage crystallinity of the sample becomes smaller with increasing number of K_3PO_4

impregnated on NaZSM-5 synthesis. FTIR spectra of resulting samples have absorption bands in the region 1220 and 547 cm^{-1} which shows the absorption characteristics of vibration T-O-T on NaZSM-5 type zeolite which distinguish the other and sensitive to changes in structure. The analysis resulting of characterization using XRD and FTIR show that the structure of NaZSM-5 remained unchange after impregnated with K_3PO_4.

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