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Synthesis of basic zeolite from coal fly ash and its reactivity in Knoevenagel reaction

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ABSTRACT

Zeolite was hydrothermally synthesized from coal fly ash in NaOH solution and static condition, at various times of crystallization and treatment. Gel treated with ultrasonication before heating resulted in the formation of pure zeolite P (Na-P) while untreated gel formed a mixture of sodalite and Na-P. Pure zeolite P was produced in 5 days and stable up to 31 days of crystallization time without the trace of sodalite formed. The synthesized Na-P was then ion-exchanged with potassium (K-P) and cesium (Cs-P) ions in order to increase the basicity of the Na-P obtained. The reactivity of the catalysts was tested in Knoevenagel reaction between benzaldehyde and malononitrile, producing solid benzylidenemalononitrile as single product. The reactivity was measured by the time when the first solid product formed. K-P catalyst was found to be the most reactive followed by Cs-P and Na-P in which the reactivity depends more on the number of base sites as well as the basic strength of zeolite. In conclusion, zeolites synthesized from CFA is potential catalysts for the Knoevenagel reaction.

| coal fly ash| zeolites| ultrasonic treatment | Knoevenagel reaction | basic zeolite |

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1. INTRODUCTION

Coal fly ash (CFA) discharged from coal electric power plant occupies a great part of the total amount of coal ash causing problematic issues to the environment if disposed in the landfill due to its higher silica and heavy metals contents [1]. Due to this, the conversion of CFA to other materials such as zeolite as a new recycling material has become an interest to researchers. Zeolite synthesized from coal fly ash could be applied to various fields such as agricultural and environment. However interest on zeolite from CFA as catalyst is not widely known may be due to the impurities associated with the as-synthesized zeolites.

The production of synthetic zeolite from coal fly ash by hydrothermal reaction with alkaline solutions is a well known process that has been used for a long time [2,3]. The conversion of CFA to zeolite involved aluminosilicate which is main component of coal fly ash into zeolite crystal by alkali hydrothermal reaction [3]. Hollman *et al.* [4] has developed a two stages synthesis procedure that enables the synthesis of almost hundred percent of pure zeolite A and X from high Si solutions obtained from a light alkaline attack of fly ash. The alkali hydrothermal method has been improved by varying the parameter to obtain different results. The zeolite P which usually formed in static cond-

dition converted to sodalite as the synthesis time increased[1,5].

Zeolite synthesized from alkaline NaOH usually is in the form of Na-zeolite and posses basic property. In this condition it can be applied as basic catalyst [6] in catalyzed based reaction such as Knoevenagel reaction [3,7]. Knoevenagel reaction was usually used in the organic synthesis producing unsaturated compound from reaction containing carbonyl as base catalysis in the reaction [8-10]. Nowadays, there was an extensive interest of Knoevenagel condensation usage for industrial application especially in pharmaceutical area since it is a key step in the preparation of several pharmaceuticals including the antimalarial drug, lumefantrineas. Zeolite having basic site has high probability to be used as base catalyst in the reaction which favors base in its reaction. This paper discussed the formation and the reactivity of zeolite from CFA in NaOH solution in which the gel was treated with ultrasonication before heating. The obtained zeolites was further ion exchanged with K and Cs ions to study the effect of the strength of alkalinity of the zeolite formed in Knoevenagel reaction initiated by benzaldehyde and malononitrile to form benzylidenemalononitrile.

2. EXPERIMENTAL

Coal Fly ash, CFA (5g) obtained from Kapar Power Station Klang Selangor, was immersed in NaOH solution

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(100 mL, 3 M). The mixture was treated with ultrasonication for 1 hr at 50 °C followed by heating at 5, 10 and 31 days respectively. Another set of CFA and NaOH solution mixture was prepared but gel was aged without ultrasonication treatment. The solid product obtained was dried at 100°C overnight. The resulting product formed from CFA with ultrasonic treatment (3 g) was further ion exchanged for 24 hours at ambient temperature in CH₃COOK (100 ml, 1M) solution in round bottom flask while ion exchanged in CH₃COOCs (50 ml, 1M) solution were done to synthesized zeolite sample (2 g) in round bottom flask. The resulting K- and Cs- exchanged products were dried at 100°C for one day. All zeolite samples obtained were characterized by X-Ray Diffraction (XRD-Diffractometer model Bruker D8) with radiation source Cu K_α, λ= 1.5406 Å at current of 10 mA was used. The diffractogram was scanned at 2θ at the range of 2 - 60° with step size 0.05°/s to obtain the crystallographic and types of zeolite formed. Characterization using Fourier transformed infrared spectroscopy (FTIR- Perkin Elmer series 1600) was prepared by grinding a portion of sample together with KBr (1:100) which then assembled to form a thin pallet that was then transferred to disc holder before loaded into the spectrometer. Elemental analysis was performed by using Energy Dispersion X-Ray Analysis (EDAX) and flame photometry to determine the elemental of the surface and bulk samples respectively. Qualitative analysis of the basicity of the zeolite produced was done by touching wet red litmus paper into the dry samples in which the red litmus turned to blue.

The reactivity of Na-zeolite, K-zeolite and Cs-zeolite as base catalysts in the Knoevenagel reaction was tested in Knoevenagel condensation between benzaldehyde and malononitrile to produce benzylidenemalononitrile. The catalysts were activated at 500 °C for 5 hours before used. An equimolar solution of benzaldehyde (0.03 mol, 3.1836 g) and malononitrile (0.03 mol, 1.9818 g) were put in a round bottom flask (25 mL) batch reactor which connected to the condenser in the flow of nitrogen gas.

The activated zeolite (0.1g) was then added to the reactants mixture and left reacted at ambient temperature for five hours. The reactivity of the catalyst was determined by the time when the first solid product started to form.

3. RESULTS & DISCUSSION

The presence of silica (65.7 %) and alumina (15.5%) in coal fly ash which is suitable as starting material for synthesis of zeolites was fully utilized in this study. The XRD of CFA in Figure 1, indicates a mixture of silica in the form of quartz and amorphous silica, as shown by the elevated based line between 2θ 20-30°. Formation of zeolites are highly depends on the temperature and concentration of alkali medium used. Crystallization of zeolitic material occurred through nucleation aluminosilicates ions and crystal growth. Nucleation depends on alkalinity; therefore high concentration of alkalinity was used in the reaction in order to ensure the dissolution of silica and alumina of CFA to form aluminate and silicates ions. Types of zeolite form also depend on the treatment on the gel mixture before or during the hydrothermal treatment. Figure 2 shows the diffractograms of zeolite formed from the gel in ultrasonic treatment at different times of crystallization. It showed that pure zeolite P or Na-P has been formed within 5 days crystallization whereas quartz of CFA was still present in the product. The absence of elevated based line in the diffractogram and the decrease of the intensity of quartz lines suggested that all the amorphous silica of CFA has been used to form zeolite P while part of quartz has been converted to zeolite P as well. As the time of crystallization increased the crystallinity of the Na-P formed increased while the quartz intensity gradually decreased to a trace level at 31 days crystallization. It indicated that at high alkalinity and temperature, quartz gradually dissolved to polymeric silicates and help in the growth of Na-P crystal. Table 1 listed the phase formation and the treatment of CFA in its transformation to zeolite

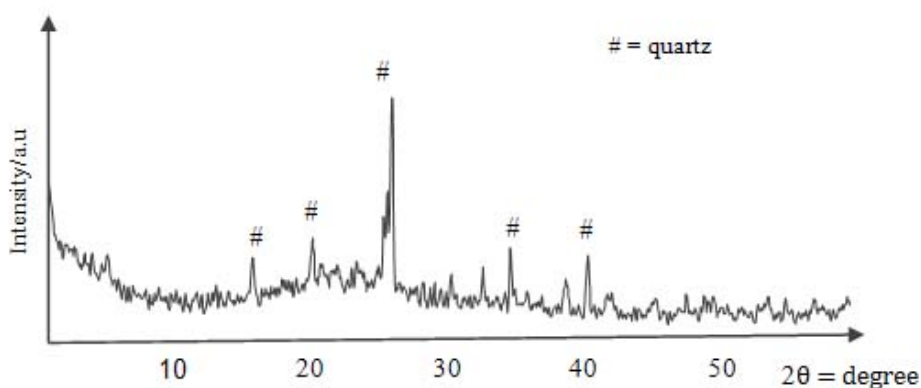


Figure 1 : XRD of coal fly ash

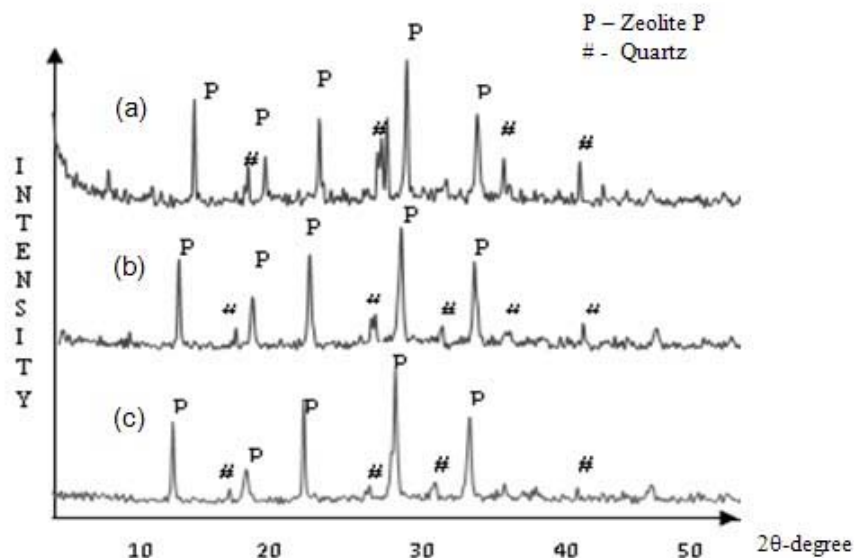


Figure 2 : Diffractogram of zeolite formed from treated coal fly ash with ultrasonic (a) 5 days, (b) 10 days, (c) 31 days.

Table 1: List of treatment, types of phases and relative crystallinity of zeolites formed from coal fly ash in different treatments.

Sample	Treatment	X-Ray Diffraction (XRD)			
		Crystal phase	Maximum peak (2θ)	Intensity (Cps)	Relative crystallinity (%)
Zeo-CFA	Hydrothermal, 5 days	Sodalite	24.282	24.7	24.4
		Zeolite P	28.033	48.4	47.8
		Quartz	26.216	28.2	27.8
Zeo-aging-CFA	Aging 1 day + hydrothermal, 5 days	Sodalite	24.253	20.4	19.9
		Zeolite P	27.969	49.2	48.0
		Quartz	26.163	32.9	32.1
Zeo-ultra-CFA	Ultrasonic + hydrothermal 5 days	Zeolite P	28.078	69.0	57.7
		Quartz	26.642	50.5	42.3
	+ 10 days	Zeolite P	28.07	69.1	75.8
		Quartz	26.2	22.1	24.2
	+ 31 days	Zeolite P	28.117	106	89.3
Quartz		26.215	12.7	10.7	

Diffractograms of Na-P samples exchanged with K and Cs ions are shown in Figure 3. The crystallinity of K-P sample is almost similar with that of Na-P showing the larger size of K⁺ ion has no significant effect to changes of zeolite structure as a whole. However, in Cs-P sample, the

peak at low angle at 2θ, ~ 12° was found to be missing. This indicated that the preferred orientation Cs⁺ ion occurs at low angle that affect the diffraction line. This is due to the large Cs⁺ size causing the distortion of the framework at the surface of the crystal.

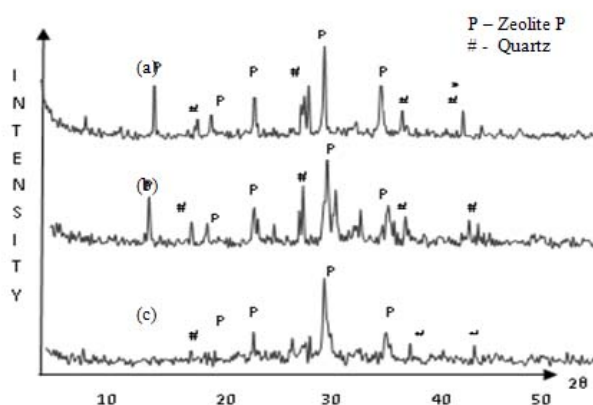


Figure 3 : Diffractogram of zeolite ion exchange (a) Na-P. (b) K-P. (c) Cs-P

3.1 Infrared spectroscopy (IR)

IR spectra for ion exchanged zeolite were compared and Table 2 presents the vibration of all the ion exchanged zeolite P. All zeolites were observed to have the same IR vibration pattern and peak position. The IR shows the peaks of external linkage, internal tetrahedral of TO₄ (T=Si, Al) symmetric and asymmetric stretching, T-O bending and double ring in the area of 1500 cm⁻¹ to 400 cm⁻¹. This indicated that different sizes of cations have no significant effect to the changes of the framework of zeolite P.

Table 2 : Summary of IR vibration of ion exchanged zeolite (cm⁻¹)

Sample	External linkage (cm ⁻¹)		Internal tetrahedral (cm ⁻¹)	
	TO ₄ symmetric stretch	double ring	TO ₄ asymmetric stretch	T-O bending
Na-P	738.01	569.13	994.31	439.87
K-P	741.87	564.19	994.67	443.17
Cs-P	739.43	567.37	990.99	438.86

3.2 Qualitative analysis of zeolite basicity

The analysis of zeolite basicity was conducted using wet litmus paper where all red litmus paper have turn into blue due to the basic site existed on the zeolite. This analysis has confirmed that the zeolite have possessed basic properties.

3.3 Elemental analysis

Elemental analysis by EDX method on samples Na-P, K-P and Cs-P is presented in Table 3. The fact that no Na⁺ ion was detected in sample K-P and Cs-P showed all Na⁺ on the surface of the crystal has been successfully replaced by K⁺ or Cs⁺. A small amount of Na⁺ can still be

detected in Cs-P indicated that not all Na⁺ can be exchanged by Cs⁺ due to the space limitation of larger size of Cs as shown in Table 2 because of its larger size than K which prevent from entering the zeolite cavities.

Table 3 : Type of elements and its weight percentage in zeolite P

Element	Weight Percentage (%)		
	Na-P	K-P	Cs-P
Sodium	6.64	0.00	2.20
Potassium	0.00	10.14	0.00
Caesium	0.00	0.00	10.30
Aluminium	17.28	15.13	14.18
Silica	14.98	16.13	23.24
Calcium	0.50	0.56	0.84
Iron	2.20	3.15	1.53
Carbon	9.43	11.81	12.73

3.4 Quantitative analysis of cations in Zeolite P

Result of the elemental analysis to determine the concentration of cations present in the zeolite P presented in Table 4. The result indicated that concentration of Na⁺ has decreased in both K-P and Cs-P samples. This suggested that Na⁺ ion has successfully exchanged with K⁺ and Cs⁺. K-P sample showed the increased in K⁺ concentration indicating that considerable amount of K⁺ ion has replaced Na⁺ ion that present in the Na-P. This is due to the less difference in size between Na⁺ and K⁺ ion. Compared with Cs-P sample, less Na⁺ ion had been replaced by Cs⁺ ion, due to the much larger size of Cs⁺ ion, hinders it entering the framework to be exchanged with Na⁺, thus the exchanged only occurred on the surface of the crystal. This is in agreement with the result obtained from EDAX where no Na⁺ ion was detected in Cs-P sample. This suggests that different size of the cations affect the ion exchanged process in sample having framework structure such as zeolite.

Table 4 : Elemental analysis of cations in zeolite P

Sample	Na ⁺ ion (ppm)	K ⁺ ion (ppm)
Coal fly ash	1.425	0.4868
Na-P	56.425	1.145
K-P	38.925	68.908
Cs-P	48.925	0.4868

3.5 Reactivity of zeolites in Knoevenagel reaction

Reactivity of ion exchanged zeolites as catalyst in Knoevenagel reaction was determined by the duration of time for the first solid product formed. Theoretically, the

increased of basicity in zeolite will increase the activity of the catalyst. In this case we would expect that the reactivity should be in the sequence of Cs-P > K-P > Na-P based on the basicity strength of the cations. However, the result in Table 5 shows that K-P was more active based on the shortest time obtained to form the product compared to Cs-P and Na-P. It suggests more basic active sites present in K-P sample as proven by elemental analysis shown in Table 4. Meanwhile, Cs-P is more active than Na-P even though the amount of Cs is small in zeolite due to its higher basic strength than Na. Na-P is the least active because of the less basic strength among the zeolite P used. This result has proven the significance of the number of basic sites and the strength of cations in the zeolite framework in the reactivity in Knoevenagel reaction. Knoevenagel reaction of benzaldehyde and malononitrile is shown in the Equation 1. Using gas chromatography, all the catalyzed reaction shows the same pattern of chromatograms as shown in Figure 4(b) where the reaction shows a high selectivity with only one product peak was observed.

This proved that this reaction produced 100 percent of yield. No product was formed for reaction without catalyst in 5 hours as proven by chromatogram in Figure 4 (a). It showed that all zeolite samples obtained by using CFA and its ion exchanged modification are basic catalyst that has successfully catalysed Knoevenagel reaction of benzaldehyde and malononitrile.

Table 5: The time required for product formation

Samples	Intermediate (hours)	Solid state (hours)
Coal Fly Ash	>5.00	>5.00
Na-P	1.50	1.67
K-P	1.00	1.17
Cs-P	1.17	1.33

Equation 1 : Knoevenagel reaction between benzaldehyde and malononitrile

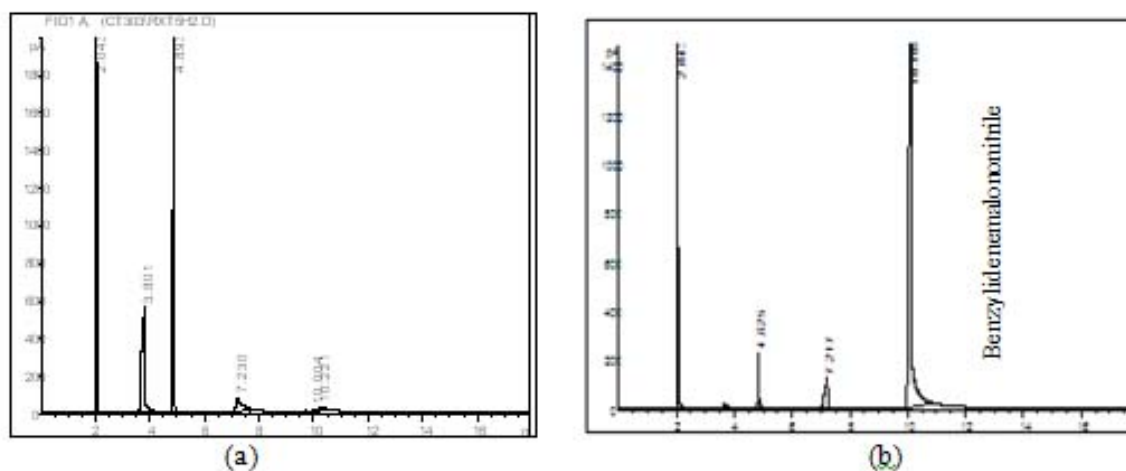
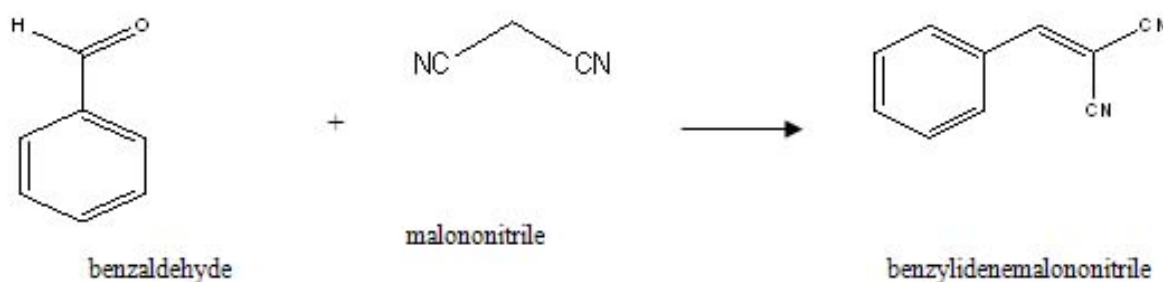


Figure 4 : Chromatogram of uncatalyzed (a) and catalyzed Knoevenagel reaction (b).

4. CONCLUSION

Synthesis of CFA treated with ultrasonic by hydrothermal reaction yielded pure Na-P is stable up to 31 days. Ion exchange of Na-P to K-P and Cs-P has successfully increased the basicity strength of zeolite P as proven by the reactivity shown in the Knoevenagel reaction of benzaldehyde and malononitrile giving 100% selectivity

of benzylidenemalononitrile product. Na-P, K-P and Cs-P were all active catalyst in the Knoevenagel reaction. This present study has shown that the number of basic sites presence in zeolite and the strength of cations played a significant role in enhancing the reactivity of basic catalyst in Knoevenagel reaction.

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