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CHARACTERIZATION AND GRAVIMETRIC ANALYSIS OF THE DISSOLVED QUARTZ IN THE CONVERSION OF COAL FLY ASH TO SODALITE

(Pencirian dan Analisis Gravimetri Kuarza Terlarut dalam Pertukaran Abu Terbang Batu Arang ke Sodalit)

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Abstract

Coal fly ash (CFA) is a waste product produced from the electrical power plant and hazardous towards the environment. However, the high composition of silica and alumina in the CFA makes it useful as raw materials in the zeolite synthesis. However, the presence of silica in the form of quartz in the CFA does not facilitate the transformation of CFA to zeolite at 100^{o}C and autogeneous pressure. In this study, CFA was converted to zeolites in various NaOH concentrations by microwave heating at various heating time. All synthesized product were characterized by X-ray diffraction(XRD), and gravimetric analysis. XRD has shown that quite pure sodalite in nanosize has been formed as early as 15 minutes and increase with time. Prolong heating up to 45 minutes has reduced the content of quartz to *ca* 20%. Gravimetric analysis performed on the liquor of the reaction showed that the dissolved silica decrease with increase of heating time indicating that most of the dissolved quartz is used up to form sodalite framework. Hence, quartz of CFA did help in enhancing the crystallinity of the formed sodalite after prolong heating.

Keywords: Coal fly ash, Sodalite , Dissolved quartz, Gravimetric analysis

Abstrak

Abu terbang batu arang (CFA) ialah sisa buangan yang dihasilkan dari stesen janakuasa elektrik dan ia berbahaya terhadap persekitaran. Walau bagaimana pun, komposisi silika dan alumina yang tinggi dalam CFA membuatkan ia berguna sebagai bahan mentah dalam sintesis zeolit. Silika dalam bentuk kuarza dalam CFA tidak membantu transformasi CFA kepada zeolit pada 100^{o}C and tekanan *outogeneous*. Dalam kajian ini, CFA bertukar kepada zeolit dalam pelbagai kepekatan larutan NaOH melalui pemanasan mikrogelombang pada pelbagai masa pemanasan. Semua produk dicirikan melalui pembelauan sinar-X(XRD) dan analisis gravimetri. XRD telah menunjukkan sodalit yang agak tulin dalam saiz nano telah diperoleh seawal 15 minit dan mencapai kehabluran maksimum dalam 30 minit. Pemanasan selama 45 minit telah menurunkan kandungan kuarza kepada 20%. Analisis gravimetri ke atas likur tindak balas menunjukkan kuarza CFA membantu dalam meningkatkan kehabluran sodalit yang terbentuk selepas pemanasan yang panjang.

Kata kunci: Abu terbang batu arang, Sodalit , Kuarza terlarut, Analisis gravimetri

Introduction

Coal combustion by-products production is estimated to about 600 million tons worldwide [1]. A large number of the portion of this production is coal fly ash (CFA). Fly ash particles are also considered highly contaminating due to the presence of toxic trace elements that condense from flue gas. The cement industry used CFA as raw material for the production of concrete [2]. Besides that, it is also utilized as recycling material for agriculture and engineering [2]. CFA contains mainly of silica (60-65%), and alumina (25-30%) and Fe_2O_3 (6-15%) [3] besides other traces of metal oxides. Since it contain silica and alumina are the two most important ingredients makes fly ash a suitable starting materials for zeolite synthesis [4].

Querol *et. al.* [2,3] has reported an improvement synthesis process of zeolite using CFA as precursor by applying e microwave synthesis. The application of microwave heating [5] instead of conventional hydrothermal heating for the synthesis of zeolite, has opens up a new opportunity in the synthesis process in term of short crystallization time needed. Synthesis and yield of zeolite obtained from the microwave and conventional synthesis were very similar, but the activation time was drastically reduced by using microwave [4].

The silica in the CFA is in the form of quartz, which is the most stable form of silica crystal. By using CFA as precursor for the synthesis of zeolite, the difficulty of dissolving the quartz into silicate ion hinders it becoming important for the zeolite synthesis. In order to dissolve quartz, microwave-assisted heating has been applied to decrease the time taken for the quartz to dissolve. This paper reported the use of microwave-assisted heating for the conversion of CFA into pure zeolite phase. The transformation of quartz into zeolite was monitored by XRD and gravimetric analysis of the dissolved silica in the reaction mixture after the synthesis.

Materials and Methods

Materials

Coal fly ash was obtained from Kapar power station located in Klang, Selangor. The composition of CFA is listed in Table 1. Alkaline source used was NaOH (Merck, 98%w/w) while sulphuric acid (Qrec,98% w/w) was used in the gravimetric analysis of silica.

Table 1. Composition of coal fly ash

Composition	Percentage (%)
SiO_2	65.7± 0.02
Al_2O_3	15.5± 0.01
Fe_2O_3	15.7± 0.01
K_2O	1.43± 0.01
CaO	1.16± 0.01
TiO_2	0.34± 0.01
MnO_2	0.09± 0.01
Na_2O	0.13± 0.01

Synthesis of Zeolite from Coal Fly Ash

Coal fly ash (CFA), a gray powder was calcined at 550^{o}C for 12 hours before undergone synthesis process. In the experiment, CFA (2.5 g) was mixed with NaOH solution (100 mL, 3 M) and the mixture was stirred for 2 hours. After 2 hours, the mixture was put into the microwave oven (Samsung, power: 850 Watt) for 15, 30 and 45 minutes. At the end of each heating time, the solid sample was separated from its liquor solution by centrifuging (Kubota, 3,000 rpm) where the liquor solution was collected for gravimetric analysis of the dissolved silica, while the solid was washed with distilled water until the pH of 7 was reached. The solid obtained was then dried in an oven for overnight to obtain whitish grey powder.

Characterization of Samples

The XRD of the sample was carried out to determine the crystallinity of the product formed. XRD of the sample were recorded on Bruker Advance D8 using Siemens diffractometer with Cu Kα radiation (λ= 1.5418Å, 40kV). The powder was spread equally on the sample holder to form a thin layer with smooth surface. The sample was then scanned in the 2θ scale (degree) from 5^o to 50^o with step size 0.02^o per second. Infrared spectra were obtained by Perkin Elmer 1600 series spectrometer using the KBr wafer technique. The solid sample was ground together with KBr in the ratio of sample to KBr 1:100. Then, the fine powder was pressed under 5 tons of pressure for a few minutes to acquire a thin transparent pallet. The spectra were recorded at room temperature with 4 cm^{-1} resolution between 4000 cm^{-1} - 400cm^{-1}.

Gravimetric Analysis of Silica in the Reaction Liquor

The liquor solution obtained after separating from the solid product was analysed for the dissolved silica. The liquor was titrated with 1.5 M sulphuric acid until pH 7 or slightly acidic to ensure complete precipitation of the silica. The silica obtained was recovered by filtering, followed by drying in an oven for 24 hours and weighted. This silica was the dissolved silica which still remained in the reaction mixture and did not being used up to form zeolite crystal.

Results and Discussion

Microwave conversion of CFA to zeolite yielded sodalite as the main zeolite phase with some other phases. Figure 1 shows the X-ray diffractogram of samples at various heating time. The diffraction peaks observed at 2θ around 16.40°, 29.40°, 33.24°, 35.27° and 42.66° are similar to those of reference peaks which belong to sodalite [9] with the d-value 3.66, 3.04, 2.70, 2.54 and 2.12. The sodalite crystal appeared to be formed as early as 15 minutes, together with zeolite A. The presence of diffraction peak for quartz with an appreciated intensity indicated that a large amount of CFA was still not being converted to zeolite phases . The crystallinity of sodalite was found to increase with the increase of heating time as shown by the increased in the peaks intensity of sodalite in samples heated for 30 and 45 minutes, suggesting that sodalite is more stable zeolite phase as compared to zeolite A. This is indeed the case because zeolite A has more open structure as compared to the dense sodalite framework that makes aluminosilicate framework of zeolite A prone to redissove in the highly alkali medium of the reaction mixture. The quartz phase was also decrease as the heating time increased suggesting that the dissolved silica from quartz phase might have been used in the growth of sodalite crystal. High concentration of the alkaline medium promotes the dissolution of quartz phase but the increase rate of dissolution of the quartz was assisted by the microwave heating. Relative percentage of phases in samples at various heating times calculated based on the highest peak intensity of each phase in a sample are shown in Table 2.

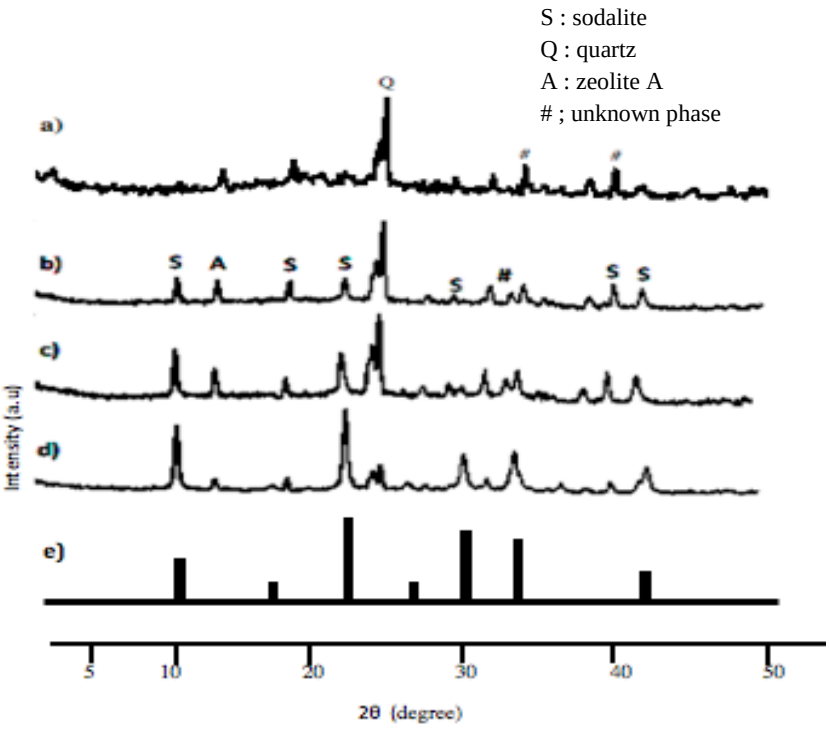

Figure 1. XRD patterns of microwave synthesis of zeolite with 3 M of NaOH at various heating time; (a) before heating (b) 15 minutes, (c) 30 minutes, (d) 45 minutes, (e) XRD of reference sodalite [9].

Table 2. Percentage of phases existed in each samples calculated based on the XRD results

Samples	Heating time (minutes)	Products/phases	Peak Intensity, I_{100} (Count/second)	% phase
SOD3-15MV	15	Sodalite	1370	22
		Zeolite A	1317	22
		Quartz	3317	55
SOD3-30MV	30	Sodalite	1823	29
		Zeolite A	1404	22
		Quartz	2998	48
SOD3-45MV	45	Sodalite	1797	60
		Zeolite A	442	15
		Quartz	718	24

Table shows the increase percentage of sodalite formation in each sample with increasing heating time, with more than 50% sodalite in sample is obtained from heating for 45 minutes. By this time, more than 70% of quartz has been dissolved. Significant decreased in the amount of quartz as the time increased indicated that microwave heating has capable of dissolving stable quartz. The capability of the microwave heating in rapid zeolite formation was also proven when sodalite phase was observed to appear as early as 15 minutes of heating time. Similar result was reported by Querol *et al*. for the synthesis of Na-zeolites from coal fly ash [2].

Figure 2 presents the FTIR spectra of samples obtained at various heating times while Table 3 listed the value of IR vibration bands. The vibration band pattern showing for all samples is the typical vibration pattern for sodalite framework. The vibration peak related to the asymmetric stretching occurs at 987 cm^{-1} in samples SOD3-15MV, 990cm^{-1} in SOD3-30MV and 980 cm^{-1} in SOD3-45MV. Compared to the CFA before synthesis where the asymmetric stretching for SiO_4 tetrahedral in CFA at 1091.16 cm^{-1}, the band has shifted to lower frequency in sodalite framework, indicating that Al has replaced some of the Si in the Si-O-Si bond to for Si-O-Al bond. The shifting of the band to lower frequency is due to longer Al-O bond compared to Si-O bond. The fact that the asymmetric stretching vibration for all as-prepared samples appear at *ca* 1000 cm^{-1} suggest that the framework of the sodalite formed may has Si/Al equal to 1. Peak vibration at *ca* 430 cm^{-1} is assigned to pores opening of sodalite framework whereby the peak intensity increases with heating time, indicating the increasing perfectness of the crystal formed. Similar result was obtained by Wakihara and Okubo on the hydrothermal synthesis of nanosodalite [7].

Table 3**.** FTIR assignment of vibration bands of samples heated at various heating times

Sample	Insensitive to framework structure (cm^{-1})			Sensitive to framework structure (cm^{-1})
	Asymmetric stretching (Si-O-T)	Symmetric stretching (Si-O-T)	T-O bending	Pore opening
SOD3-15MV	987	670	462	432
SOD3-30MV	990	664	462	434
SOD3-45MV	980	664	462	433

T= Al or Si

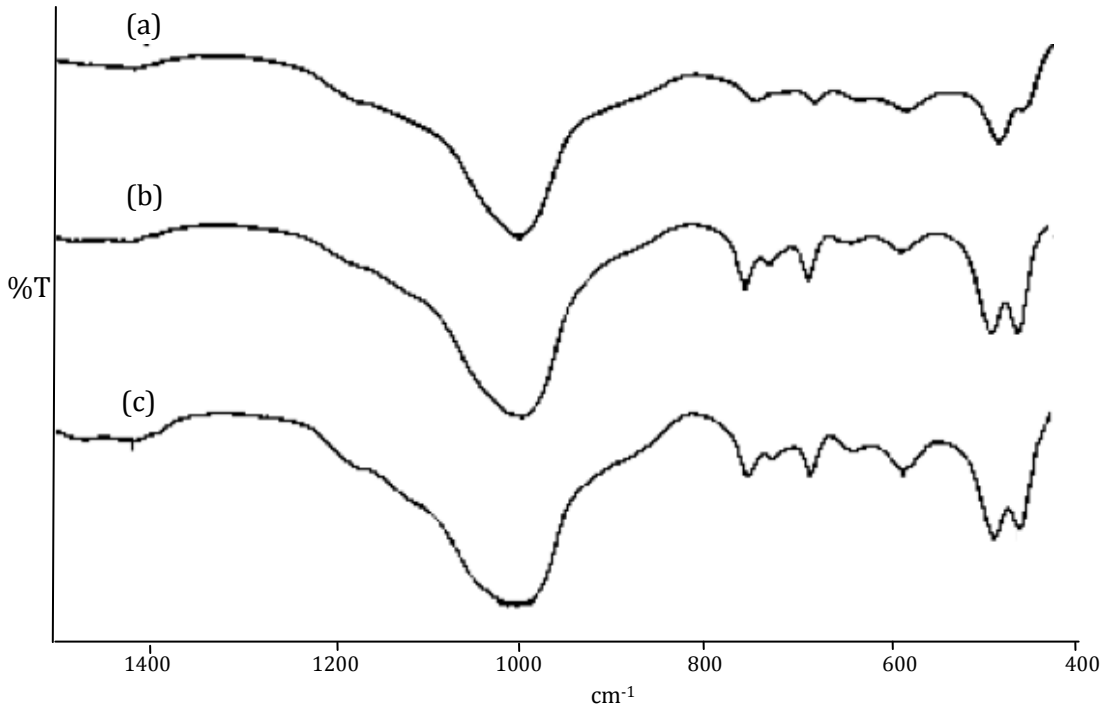

Figure 2. FTIR of samples obtained by microwave synthesis of zeolite (a) 15 minutes (b) 30 minutes (c) 45 minutes

Gravimetric Analysis of Silica in the Reaction Liquor

The weight of the silica that has not been used to form zeolites phases at the end of the synthesis time was determine in order to monitor the dissolution rate of quartz in the reaction alkaline medium and the used up of this dissolved silica in the formation of the zeolite framework. Table 4 listed the weight of the dissolved silica that still remained in the liquor after heating of the synthesis end.

Table 4. Result of gravimetric analysis of silica in the reaction liquor

Sample	Dissolved silica (g)
SOD3-15MV	0.49
SOD3-30MV	0.20
SOD3-45MV	0.09

A significant decreases of the amount of silica content in the reaction liquor proved that most the dissolved silica from quartz has been used up in the formation of zeolite framework as the time of heating increased. This is due to the dissolved amorphous silica has changed into more stable form of zeolite in the alkaline condition. Furthermore, the basicity of the alkaline solution does help in the conversion of quartz to more stable form of zeolite. Graph in Figure 3 shows the relationship of the remaining silica obtained from gravimetric analysis, with that of the percentage of sodalite phase formed based on the XRD result. The rate of dissolution of quartz in the first 30 minutes is higher than the formation of sodalite crystal. This is the stage where the formation of zeolite nucleus and redissolution process took place until stable nucleus of sodalite is formed. That explained the large amount of dissolved silica that still present in the reaction liquor while only small percentage of sodalite was formed. The next 15 minutes involved crystal growth in which rapid used up of silica occurred for the formation of sodalite crystal which left only small amount of dissolved silica remained at the end of 45 minutes of heating time. Significant increased of the percentage of sodalite formed was observed at this heating time.

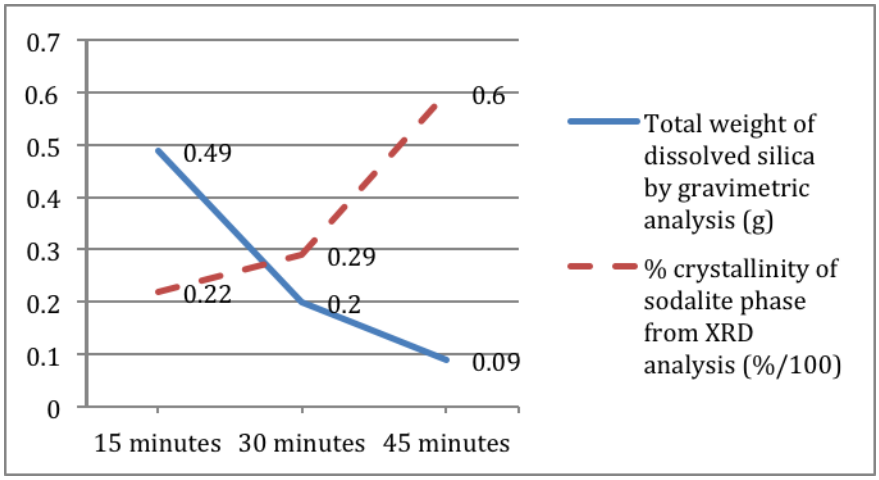

Figure 3. Relationship of the remaining dissolved silica with that of the percentage formation of sodalite.

Conclusion

The zeolite with sodalite as the main stable zeolite has been successfully formed from coal fly ash via microwave heating method. More than 60% of sodalite has been formed in NaOH medium in less than 1 hour. heating time. With the microwave-assisted heating, quartz of CFA has rapidly dissolved and transformed it into the more stable sodalite phase. The study has demonstrated the importance of microwave heating method in shortening the time for the transformation of CFA to zeolite phase.

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