

# Kaliophilite from fly ash: synthesis, characterization and stability

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MS received 12 October 2009

**Abstract.** Kaliophilite was synthesized by fusion method using fly ash as starting material. In this method, at first, alkaline fusion of fly ash with KOH occurs, followed by hydrothermal treatment in KOH medium. Scanning electron microscopy (SEM) observations revealed that the synthesized kaliophilite (S-KAL) was a plate-like crystal. X-ray diffraction (XRD) results showed three characteristic diffraction peaks located at  $2\theta = 19.56^\circ$ ,  $20.78^\circ$  and  $28.71^\circ$ , respectively. The thermal analysis indicated that the S-KAL had remarkable thermal stability when heated to  $1000^\circ\text{C}$ . Leaching test confirmed the high retention rate of potassium for S-KAL in boiling water for 10 h.

**Keywords.** Fly ash; kaliophilite; carbonaceous deposit; catalyst support.

## 1. Introduction

As is well known, the active phases of catalysts are very susceptible to the formation of carbonaceous deposits in contact with hydrocarbons and their derivatives (Denis *et al* 2008). This phenomena may pose a very significant problem. Therefore, it is necessary for catalysts to have properties, such as high activity, remarkable stability and the resistance to carbon deposition, especially. In addition, the formation of coke is easier for catalysts with strong acid centre than with strong base centre, so it would seem advantageous to employ supports promoted by alkali metals (Fatsikostas *et al* 2001; Marino *et al* 2003; Frusteri *et al* 2004a, b; Vaidya and Rodrigues 2006; Ni *et al* 2007; Subramani and Song 2007; Denis *et al* 2008), modified by additions of oxides, pure oxides of alkaline or weakly alkaline nature (Srinivas *et al* 2003; Velu *et al* 2005; Barroso *et al* 2006; Liberatori *et al* 2007; Sánchez-Sánchez *et al* 2007). Applying catalyst supports, modified by the addition of kaliophilite ( $\text{KAlSiO}_4$ ) would neutralize acid centre of catalysts and inhibit hydrocarbon cracking reaction. Moreover, these supports slowly release free potassium and promote steam gasification reaction (Juntgen and Van Heek 1985; Song *et al* 1997; Thierry *et al* 2004; Zheng and Ma 2006), thus avoiding carbonaceous deposit. Kaliophilite has recently been used in many catalysis reactions, such as dehydrogenation of ethylbenzene to styrene, hydrocarbon steam reforming for hydrogen production, ammonia synthesis and catalytic combustion of diesel soot (Juntgen 1985). As for the synthesis, kaliophilite was mostly synthesized using flint

clay or sodalite (Juntgen 1985) as raw materials and synthesis from fly ash has not been reported yet.

Fly ash is a by-product derived from the combustion of coal in electric power plants. Approximate 500 million tonnes of fly ash are discharged per year throughout the world (Cho *et al* 2005; Wang *et al* 2008). However, the utilization rate for fly ash is far less than that of the ash being generated. The rest is discharged into ash ponds or landfills. In the future, the lacking of landfill space and escalating disposal costs are anticipated, so new recycle technologies for fly ash are desired to develop (Nihon and Kankyogijyutsu 2005). In the present study, we report the synthesis of kaliophilite by fusion method using fly ash as raw material (Molina and Poole 2004). The synthesized product (S-KAL) was characterized by scanning electron microscopy (SEM), X-Ray diffraction (XRD) and Fourier transform infrared spectroscopy (FT-IR) analysis. Its stability was also investigated by thermal analysis (TG-DTA) and leaching test in boiling water.

## 2. Experimental

### 2.1 Materials

The fly ash was obtained from Hangzhou thermoelectric plant in China. The chemical compositions were undertaken by X-ray fluorescence (XRF, Shimadzu XRF-1800) and the results were as follows (in wt.%):  $\text{SiO}_2$  50.5%,  $\text{Al}_2\text{O}_3$  35.9%,  $\text{Fe}_2\text{O}_3$  5.3%,  $\text{CaO}$  4.6%,  $\text{TiO}_2$  1.5%,  $\text{K}_2\text{O}$  1.3% and others 0.9%. XRD analysis revealed that the major crystalline phases of fly ash were mullite, quartz and magnetite together with amorphous component (figure 1).

The magnetite content in fly ash influences the product properties, so the fly ash was pretreated by magnetic

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separation. The process was performed on WCF-2 multi-purpose magnetic analytical meter (Beijing Geological Instrument Factory, China) with a constant magnetic current of 2.8 A.

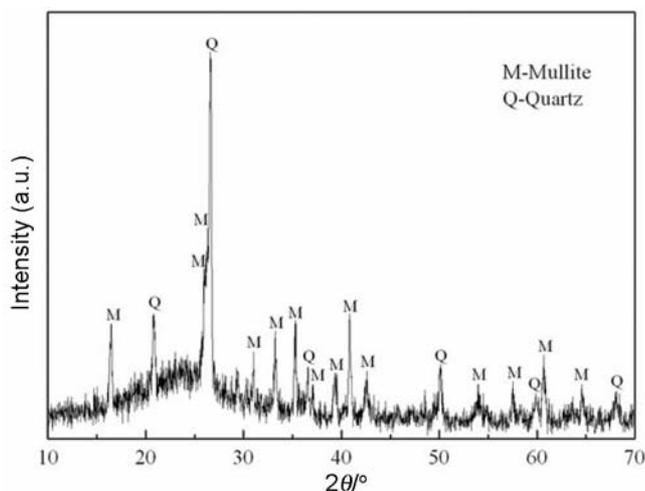
## 2.2 Kaliophilite synthesis

A series of preliminary experiments were conducted to find out the optimal conditions. The process comprises two stages. At the first stage, the pretreated fly ash was mixed and ground with 10% KOH to obtain a homogeneous mixture. The mixture was then heated in a crucible in air at 950°C for 1.5 h. In the second stage, 50 g of the fusion products were ground and dissolved in 100 ml of 2 M KOH solution. The mixture was put into an autoclave made of stainless steel and a hydrothermal treatment was conducted. The reaction temperature and time were set as 180°C and 12 h, respectively. At the end of the process the solid was separated by filtration, washed several times with distilled water and then dried at 80°C for 10 h.

## 2.3 Material characterization

Crystalline phase analysis by XRD was carried out with CuK $\alpha$  as the radiation source. A Rigaku Denki diffractometer model D/max-IIB operated at 40 kV and 30 mA in the range of 10–70°. Particle morphology was observed by a Hitachi S-4800 scanning electron microscope. Transmission IR spectra were recorded by a Nicolet Nexus-670 FT-IR using a KBr disc method.

The thermal stability of the S-KAL was investigated by TG-DTA analysis. It was conducted by a ZRY-2P simultaneous thermal analyser (Precision and Science Instrument Co. Ltd., Shanghai, China). The sample was heated in air from ambient temperature to 1000°C at a heating rate of 10°C/min.



**Figure 1.** XRD pattern of the fly ash.

The higher loss rate of potassium in catalysts has a negative effect on catalyst performance. In this study, the loss rate of potassium for the S-KAL was determined by leaching test. The S-KAL sample was put into a distillation flask and the distilled water was added with L/S ratio of 10 extracting for 1–10 h. The concentration of potassium in the leached solution was determined by an atomic absorption spectrometry (Hitachi, Model 180-50). The retention rate of potassium was calculated according to the formula:

$$A = \frac{B - C}{B} \times 100\%$$

$A$  is the retention rate of potassium (%) and  $B$  and  $C$  are the concentrations of potassium in the S-KAL before and after leached.

## 3. Results and discussion

### 3.1 SEM results

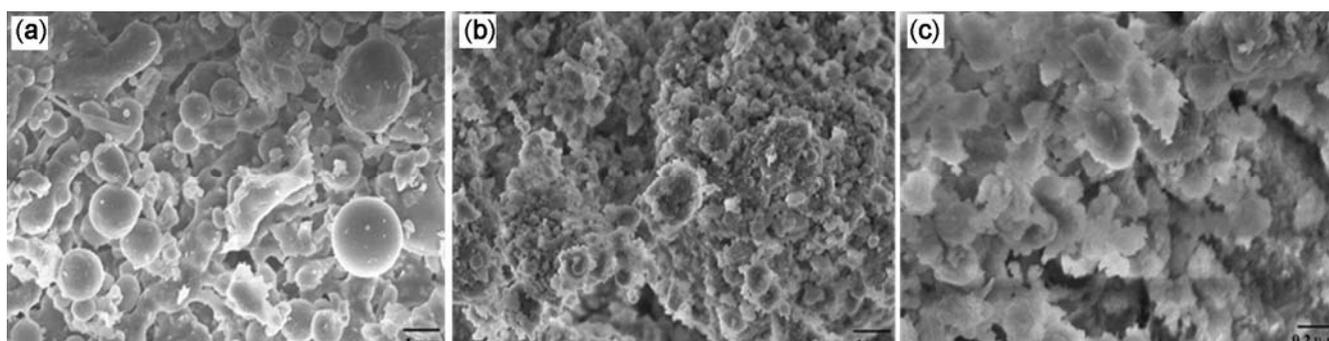
SEM investigations were conducted to explore the microstructure evolution. For a comparison, the SEM image of the fly ash is also included in figure 2. The fly ash particles showed approximately spherical shapes with smooth surface, while other particles had irregular shapes (figure 2a). From figure 2b–c, the S-KAL showed as plate-like crystal. It is worth mentioning that the morphology of S-KAL differed from the irregular round-shaped for fly ash. The fused fly ash sample was dissolved primitively from the particle surface under alkaline hydrothermal conditions. Then, the dissolved silica and alumina chemicals in solution were re-crystallized (Murayama *et al* 2002).

### 3.2 XRD results

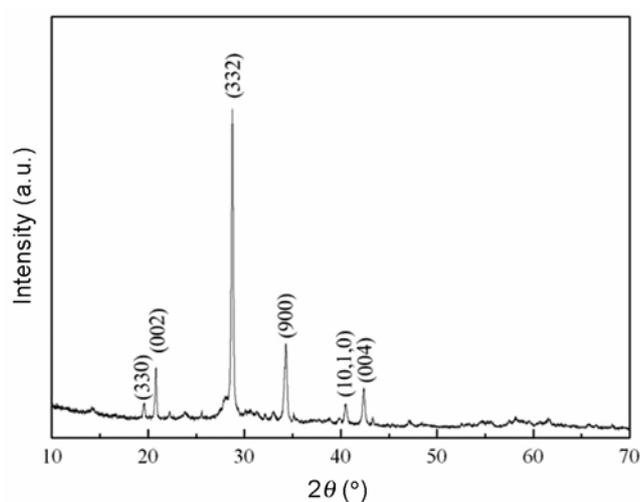
Figure 3 shows characteristic diffraction peaks located at 19.56°, 20.78°, 28.71°, 34.28°, 40.49° and 42.34° in the XRD pattern. All peaks could be indexed to kaliophilite, which are in good agreement with the literature values (JCPDS card no. 11-313). No peaks from other phases were detected, indicating the high purity of the S-KAL.

### 3.3 FT-IR results

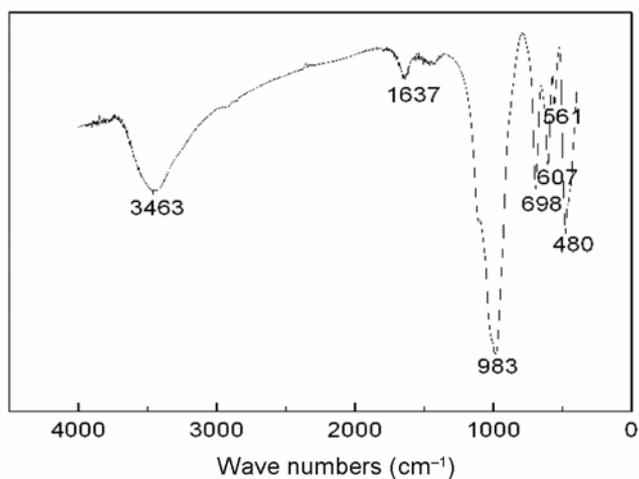
The FT-IR spectrum of the S-KAL is illustrated in figure 4. The significant broad peaks are located at approximately 3463 cm<sup>-1</sup> and 1637 cm<sup>-1</sup> for O–H stretching and O–H bending, respectively (He *et al* 2000). The absorption peak located at 983 cm<sup>-1</sup> belongs to the asymmetric stretching vibration of Si–O–Si bond. Peak positions at



**Figure 2.** SEM images of the fly ash (a) and the S-KAL (b–c).

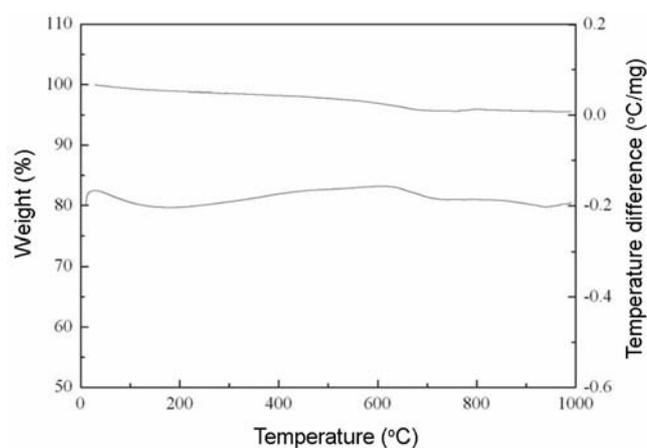


**Figure 3.** XRD pattern of the S-KAL.

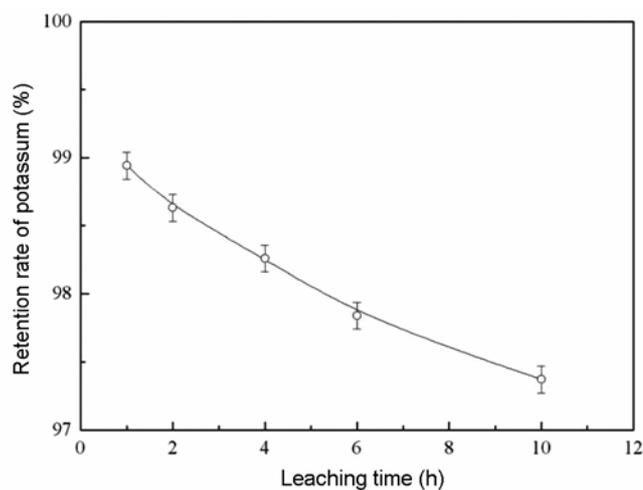


**Figure 4.** FT-IR spectrum of the S-KAL.

$698\text{ cm}^{-1}$  and  $607\text{ cm}^{-1}$  are both assigned to symmetric stretching vibration, while peak positions at  $561\text{ cm}^{-1}$  and  $480\text{ cm}^{-1}$  correspond to bending vibration of Si–O and stretching vibration of Al–O bond, respectively (Carpenter and Cellai 1996).



**Figure 5.** TG-DTA curves of the S-KAL.



**Figure 6.** The retention rate of potassium for different leaching time.

### 3.4 Stability analysis of S-KAL

TG–DTA studies of the S-KAL are shown in figure 5. It indicates a two-stage mass loss. At the first stage, about 1.693% mass loss was occurred between  $0^{\circ}\text{C}$  and  $400^{\circ}\text{C}$ ,

accompanied by an endothermal peak. This is reasonable due to the loss of the occluded water molecules in the crystal. The second occurred continuously between 400°C and 800°C with a mass loss of 2.548%. The loss was not accompanied by significant exothermal or endothermal peaks. The results indicated that the S-KAL had remarkable thermal stability.

Figure 6 shows that the retention rates of potassium maintained at 98.26% and 97.84% leaching for 4 h and 6 h, respectively. The leaching rate was only 0.47% extracting for 10 h. These results indicated that the S-KAL has high retention rate of potassium.

#### 4. Conclusions

This study has clearly shown that the synthesized kaliophilite was synthesized from fly ash by the fusion method. On the basis of results reported in this study, the following conclusions can be drawn:

(I) Characterized by X-ray diffraction, the synthesized kaliophilite was shown to be mono-phase. The diffraction pattern could be perfectly indexed to the kaliophilite.

(II) Scanning electron microscopy observations revealed that the synthesized kaliophilite had irregular shapes with plate-like crystal.

(III) The thermal analysis indicated that the synthesized kaliophilite had remarkable thermal stability.

(IV) The leaching test showed that the synthesized kaliophilite had high retention rate of potassium. It could be employed as a catalyst support.

#### Acknowledgments

This work was financially supported by Chinese National 863 High Technology (Grant No. 2007AA06Z128) and the Fundamental Research Funds for the Central Universities.

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