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Research paper

Interaction of metakaolin-phosphoric acid and their structural evolution at high temperature

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ABSTRACT

In the present study metakaolin (MK), prepared by calcination of a natural tunisian kaolin at 750 °C, was mixed with different amounts of phosphoric acid (11–48 wt% P_2O_5) and heated at various temperatures (250, 500, 750 and 1000 °C) for 4 h. The structure of materials was characterized by X-ray diffraction, Fourier transform infrared spectroscopy, scanning electron microscopy (MEB), thermal analysis (DTA/TGA). The XRD results showed the formation of an $AlPO_4$ phase for the MK-H_3PO_4 mixtures containing 11, 17 and 27 wt% P_2O_5 independently of the heating temperature. While with 48 wt% of P_2O_5 two major phases have been formed $Al(PO_3)_3$ at 500 °C and $AlSi_2(PO_4)_3$ at 1000 °C. These results were confirmed by ^{27}Al, ^{31}P and ^{29}Si MAS-NMR techniques.

1. Introduction

In recent years much work has been done in the field of developing and investigating of aluminosilicates- phosphate compounds. These materials present various advantages such as better thermal, chemical, high density and mechanical resistance. These properties give them a wide range of applications such as geopolymers products refractory ceramics and biomaterials (Davidovits, 1989; Chiou and Chung, 1993; Le-ping et al., 2010; Tchakoutéa and Rüscherb, 2017).

The kaolin and metakaolin have simpler chemical compositions compared to other common precursor materials. Therefore, it will be very attractive to use it as alternative sources of aluminosilicate. While, the phosphoric acid is commonly used as a phosphate source (Duxson et al., 2007; Le-ping et al., 2010; Douiri et al., 2014; Louati et al., 2014), However, it is interesting to note that the clay component has a significant effect on their interaction so that the investigation of this interaction deserves to be investigate by theoretical and practical studies. Mamykin et al. (1974), show that the reaction at 1000 °C of the kaolinite with orthophosphoric acid at a molar ratio Al_2O_3/P_2O_5 of unity or lower produces the aluminophosphates $AlPO_4$ and ortho aluminophosphates $Al(PO_3)_3$. Sahnoun and Bouaziz (2012) showed that the phosphoric acid reacts with aluminum from kaolin to produce the $Al(H_2PO_4)_3$ phase at room temperature and $AlPO_4$ phase above 800 °C. Moreover, Louati et al. (2014) studied the effect of phosphoric acid on the properties of geopolymer based on metakaolin. Their results show the formation of $AlPO_4$ and $(Al_2(PO_4)(OH)_3)$ phases at room temperature.

The objective of this paperwork is to study the effect of the phosphoric acid added at different percentages (11, 17, 27 and 48 wt% P_2O_5) to the metakaolin powder. The structural transformations taking place during thermal-treatment have been studied by different instrumental techniques such as SEM, XRD, FTIR, TGA–DTA and MAS-NMR.

2. Experimental

2.1. Materials

The clay used in this project is raw kaolinitic clay collected from Tabarka (Northern Tunisia). It was first dried at 110 °C for a period of 24 h to facilitate its grinding. It was crushed in a mortar with a pestle and finally sieved to obtain particles smaller than 106 µm. The chemical composition of the raw clay, determined by chemical analysis, is shown in Table 1. The percentage of SiO_2 is relatively high (53%) due to the presence of quartz. The amount of alumina is also quite high (27.7%). The high contents of silica and alumina content explain why this material was chosen as a source of aluminosilicates. Note that the content of K_2O is relatively high is in relation with the presence of illite in the sample. From the potassium content and from the empirical formula of illite $K_{0.6}(H_3O)_{0.4}Al_{1.3}Mg_{0.3}Fe^{2+}0.1Si_3{\cdot}5O_{10}(OH)_2$ (H_2O), the quantity of illite may be estimated at 13.2% with the hypothesis that all potassium is brought by illite (Nahdi et al., 2003; Emeruwa and Kouadio, 2008).

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Table 1
Chemical composition (percentage weight: % wt) of kaolin.

Oxyde	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	LOI
% wt	53	27.7	1.7	0.07	0.33	1.38	1.92	13.89

LOI: Loss of ignition.

Table 2
Chemical composition of experimental mixes prepared (percentage weight: % wt).

Oxyde	SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O	P_2O_5	H_2O
MKP1	48.52	28.06	3.13	0.06	0.31	1.37	0.89	11	5.41
MKP2	43.7	25.24	2.83	0.06	0.28	1.24	0.81	17	7.48
MKP3	35.93	20.65	2.30	0.04	0.23	1	0.66	27	11.2
MKP4	19.32	11.10	1.24	0.02	0.12	0.54	0.35	48	18.8

2.2. Material preparation

The parent clay was submitted to heating at 750 °C, during 2 h, to give the corresponding metakaolin. The obtained material, was mixed with different amounts of phosphoric acid corresponding of P_2O_5 range between 11 and 48 wt% (Table 2) and followed by heating at various temperatures (250, 500, 750 and 1000 °C) during 4 h. The samples were identified as [MKPx-T], where MK represents the metakaolin used to prepare the materials, "P" represents the P_2O_5 and "T" represents the temperature. For example, MKP_{11}-500 °C stands for the product prepared with metakaolin containing 11 wt% P_2O_5 and heat-treated at 500 °C.

2.3. Characterization of the samples

The XRD patterns were measured from 5° to 70° 2θ. The phase composition was quantitatively determined by X-ray powder diffraction (Rigaku Miniflex, CuKα radiation) with the reference intensity ratio method (Al_2O_3 as internal standard).

FT-IR spectra were recorded in the region 4000–400 cm^{-1} in a Perkin-Elmer 180 infrared Fourier transform spectrometer, using the KBr pellet technique (about 1 mg of sample and 300 mg of KBr were used in the preparation of the pellets).

Differential thermal analysis (DTA) and thermal gravimetric (TG) were performed on a SETSYS Evolution-1750 instrument. Approximately 10–20 mg samples were placed in a platinum crucible on the pan of a microbalance and then heated from room temperature up to 1000 °C at a heating rate of 10 °C/min. The NMR studies were carried out on an MSL 400 Bruker spectrometer using the MAS technique (spinning rate: 4 kHz). To have an idea about the morphology, the sample was characterized by scanning electron microscopy (SEM Philips XL 30).

3. Result and discussion

3.1. Raw material characterization

Fig. 1 presents XRD patterns of a raw and kaolinitic clay specimen heat-treated at 750 °C for 2 h. The X-ray diffractogram of the kaolinitic clay is shown in Fig. 1. It exhibits the characteristic reflections of kaolinite (7.11 Å; 3.56 Å) (Brown and Brindley, 1980; Dudkin et al., 2004). It also shows the presence of the characteristic reflections of quartz (3.34 Å, 2.45 Å, 1.81 Å) and of illite (10.01 Å). After heating at 750 °C, the transformation of the kaolin into a typical metakaolin has been confirmed by the appearance of a hallo between 20 and 40° 2θ and the total disappearance of the reflections corresponding to kaolinite. The remaining reflections were attributed to quartz (24.24°; 30.94°, 42.64°; 58.85°) and illite (10.28°) (Chakchouk et al., 2006).

Fig. 2 illustrates the IR spectra of natural kaolin (K) and metakaolin

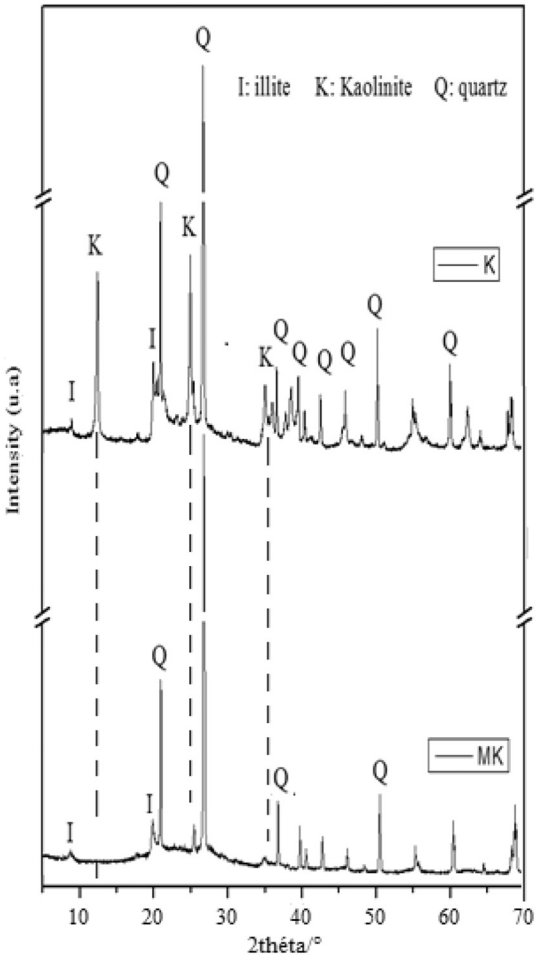

Fig. 1. XRD patterns of the parent kaolin (K) and the metakaolin (MK).

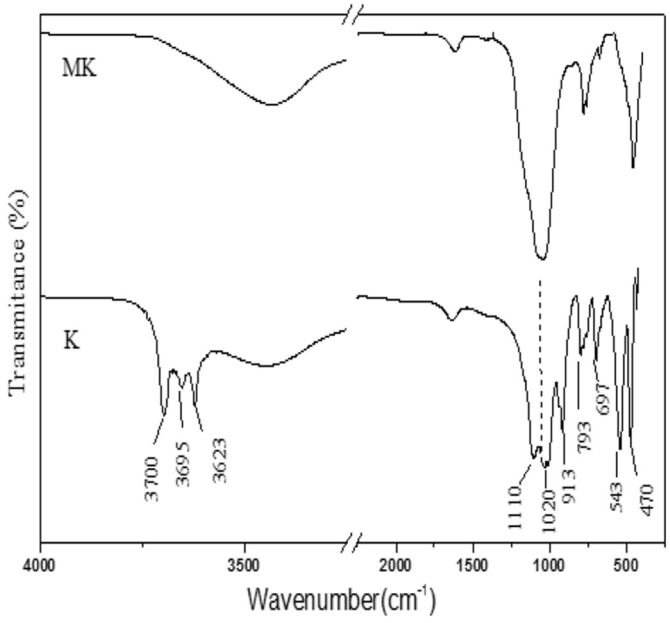

Fig. 2. FT-IR spectra of the kaolin (K) and the metakaolin (MK).

(MK). The kaolin spectrum showed the typical bands of this material at 3700, 3695 and 3623 cm^{-1}, characterized the stretching bands of the OH groups coordinated to the octahedral cations. The water stretching vibration appeared at 3459 cm^{-1}, while the band at 1633 cm^{-1}