

XPS study of the basic aluminium sulphate at room temperature and after calcination at 200° and 400°C

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Introduction

Basic aluminium sulphate is a complex salt of the Keggin complex Al_{13} $[\text{AlO}_4][\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$. The structure of this complex was first studied by X-ray diffraction by Johansson and co-workers after precipitation in the form of two different basic aluminium sulphates in which the Al_{13} structure is retained and is linked by H-bonding to the O-atoms of the SO_4 -groups. The Al_{13} complex is one of the important large inorganic complexes that can be used to prepare so-called pillared clays, where the clay layers are propped apart by cation exchange of the hydrated interlayer cation such as Na^+ by Al_{13} followed by a calcination step around 400 to 500°C to convert the complex to an strongly bonded oxidic form. To get a better understanding of the processes that take place during the transformation of the Al_{13} -expanded clay to the final pillared clay a detailed knowledge of the behaviour of the Al_{13} Keggin structure itself is a necessity.

The Al_{13} Keggin structure can be prepared in solution by a number of methods. The most common methods are forced hydrolysis by a base of an aluminium salt solution or by homogeneous hydrolysis through the decomposition of urea. Initially the presence of this very large complex plus other large complexes was shown by colorimetry based on complexation with hydroxyquinone. Later ^{27}Al NMR showed the presence of both tetrahedral and octahedral Al in the complex. Earlier work on the ^{27}Al solid state NMR confirmed that the configuration of the Keggin structure with a central four-coordinated Al surrounded by 12 six-coordinated Al is preserved in the basic aluminium sulphate. Earlier work in our laboratory focussed on the vibrational spectroscopy of the basic aluminium sulfate. Kloprogge et al. [9,10] described the precipitation of monoclinic basic aluminium sulphate $\text{Na}_{0.1}[\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}](\text{SO}_4)_{3.55}\cdot 9\text{H}_2\text{O}$. ^{27}Al Solid-state Magic-Angle Spinning Nuclear Magnetic Resonance spectroscopy showed that the tridecameric was preserved in the crystal structure. Kloprogge *et al.* [10] and Teagarden *et al.* [11]

reported the infrared spectrum of Al₁₃-sulfate with typical adsorption bands of OH at 3440, 1085, and 980 cm⁻¹, H₂O at 3247 and 1640 cm⁻¹, and SO₄²⁻ at 1135, 980, 715, 610, and 566 cm⁻¹. The Raman spectra of basic aluminium sulphate [13,14] are dominated by two broad bands, which have been assigned to the ν_1 and ν_3 sulphate modes around 981 and 1051 cm⁻¹. In addition, the band around 724 cm⁻¹ has been assigned to an Al-O mode of the polymerised Al-O-Al bonds in the Al₁₃ structure. A sharp band at 1066 cm⁻¹ and a minor band at 1384 cm⁻¹ were assigned to minor NO₃⁻ impurities in the Al₁₃-sulfate crystals.

In this paper we describe for the first time the XPS spectra of basic aluminium sulphate after preparation at room temperature and after calcination at 200° and 400°C in order to obtain more information about the possible structural changes that can take place. This information can later be used in order to obtain a better understanding of the effect of calcination on the preparation of pillared clays.

Methods

The synthesis and characterisation of the monoclinic basic aluminium sulphate used in this study has been extensively described by Kloprogge et al. [2,8,9,18,19]. The tridecameric aluminium polymer was obtained by forced hydrolysis of a 0.5 M aluminium nitrate solution with a 0.5 M sodium hydroxide solution until an OH/Al molar ratio of 2.2 was reached. Next, the basic aluminium sulphate was precipitated by the addition of the appropriate amount of 0.5 M sodium sulphate and aged for 42 days before removal from the solution. Crystals collected from the wall of the container were shown to be phase pure by X-ray diffraction, ²⁷Al solid state nuclear magnetic resonance spectroscopy and chemical analysis.

Scanning electron microscopy

Scanning electron microscope (SEM) images were obtained on a FEI Quanta 200 Environmental Scanning Electron Microscope (FEI Company, USA) operated at an accelerating voltage of 20 kV.

XPS analysis

The samples were analyzed in freshly powdered form. Prior to the analysis the samples were out gassed under vacuum for 72 hours. The XPS analyses were performed on a Kratos AXIS Ultra with a monochromatic Al X-ray source at 150 W. Each analysis started with a survey scan from 0 to 1200 eV with a dwell time of 100 milliseconds, pass energy of 160 eV at steps of 1 eV with 1 sweep. For the high resolution analysis the number of sweeps was increased, the pass energy was lowered to 20 eV at steps of 100 meV and the dwell time was changed to 250 milliseconds.

Results and discussion

Table 1. Chemical analysis (atom %) of the basic aluminium sulphates before and after heat treatment based on the XPS analysis

	25°C	200°C	400°C
O	73.79	71.08	68.68
Al	19.03	18.86	21.85

S	5.03	7.22	3.42
Na	2.29	2.66	6.05

Table 2 Binding energies of the basic aluminium sulphates before and after heat treatment

a) Oxygen 1s

	25°C			200°C			400°C		
	Binding energy (eV)	FWHM (eV)	Rel. %	Binding energy (eV)	FWHM (eV)	Rel. %	Binding energy (eV)	FWHM (eV)	Rel. %
O 1	532.521	1.295	18.72	532.813	1.300	14.10	532.812	1.324	20.99
O 2	531.458	1.230	63.30	531.579	1.497	73.59	531.870	1.371	58.54
O 3	530.519	1.142	17.98	530.280	1.554	12.31	530.774	1.391	20.47

b) Aluminium 2p

	25°C			200°C			400°C		
	Binding energy (eV)	FWHM (eV)	Rel. %	Binding energy (eV)	FWHM (eV)	Rel. %	Binding energy (eV)	FWHM (eV)	Rel. %
Al 1	74.187	1.397	88.28	74.247	1.340	89.10	74.594	1.350	87.63
Al 2	73.714	1.257	11.72	73.448	1.269	10.90	73.861	1.036	12.37

c) Sulphur 2p

	25°C			200°C			400°C		
	Binding energy (eV)	FWHM (eV)	Rel. %	Binding energy (eV)	FWHM (eV)	Rel. %	Binding energy (eV)	FWHM (eV)	Rel. %
S 2p _{1/2}	169.128	1.464	50.11	169.513	1.554	40.21	169.927	1.266	43.26
S 2p _{3/2}	168.008	1.080	49.89	168.319	1.291	59.79	168.749	1.062	56.74

d) Sodium 1s

	25°C		200°C		400°C	
	Binding energy (eV)	FWHM (eV)	Binding energy (eV)	FWHM (eV)	Binding energy (eV)	FWHM (eV)
Na 1	1071.014	1.722	1071.38	2.102	1071.563	1.637