XPS investigations on the feasibility of isomorphous substitution of octahedral Al^{3+} for Fe^{3+} in Keggin ion salts

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Investigation of Keggin ion salts prepared by partial hydrolysis of Al^{3+} and Fe^{3+} ions followed by addition of sodium sulfate solution to generate the sulfate salt of the Keggin ion was carried out. Characterization of the salts was performed by classical analytical methods and FTIR and XP spectroscopy. Incorporation of iron in the Keggin ion produced a new photoemission peak probably as a satellite in the Fe(2p) XP spectrum. The results suggest that a small portion of Al^{3+} is replaced by Fe^{3+} in an octahedral position.

Introduction

In recent decades, increasing attention has been paid to the synthesis of materials with pores of molecular dimensions. Pillared clays, where nanoscale polyoxometallate ions are intercalated between the smectite layers, proved to be a promising solution. Most frequently, aluminium-containing polyhydroxy species of Keggin structure were used as intercalates. The composition of this ion can be given as $[AlO_4Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$, where 12 aluminium ions of octahedral coordination surround the 13th Al^{3+} of tetrahedral coordination.[1] It was also reported that both the tetrahedrally and the octahedrally coordinated aluminium may be replaced by other ions such as Fe^{3+}, Cr^{3+}, Ga^{3+}, V^{3+}, Re^{3+}, La^{3+}, Ge^{4+} and Mg^{2+}. The feasibility of these substitutions has been questioned, although the preparation of multicomponent metal oxide pillars has been accepted.[2,3]

One of the origins of the polemic is that generally the pillared clay material has been studied instead of the Keggin ion salts and/or solutions. Looking through the preparation procedure for pillared clays, the last stage where the Keggin structure of the intercalated ion can be recognized is the suspension of the clay and the polyhydroxometallate solution where the ion exchange takes place, or after the next step consisting of drying at ambient temperature where only partial dehydration of the intercalated material takes place, excluding those cases where the clay itself contains iron. Calcining the material in order to fix the pillars at given positions between the clay layers, the Keggin structure can no longer be recognized, since metal oxide or oxides formed during the heat treatment are present instead of Keggin ions. Therefore, studies on the feasibility of isomorphous substitution of octa- and tetrahedrally coordinated aluminium atoms in Keggin ions are at the focus of the solution to the problem.

Ge^{4+} substitution in tetrahedral coordination in Keggin ions has been reported by Bertram et al.[4] The replacement of an Al^{3+} ion in a tetrahedral position of a Keggin ion was suggested on the basis of IR spectroscopic measurements[5] and was proved by Parker et al.[6] using both ^{71}Ga NMR and X-ray diffraction methods.

The incorporation of other metal ions is still ambiguous. In the case of iron substitution, two opinions can be found. One group of researchers think that iron can be isomorphously substituted both in the tetrahedral and in the octahedral position of the Al_{13} Keggin ions and the formation of the mixed metal pillars takes place in this way.[7-14] Others think it is not feasible, and there is no substitution of iron in the tetrahedral position, but the formation of mixed oxide pillars is not excluded.[15-17] These researchers accept the feasibility of substitution in the octahedral position but reject its possibility in tetrahedral coordination.[15-17]

This paper reports on the results obtained by XPS on the feasibility of the substitution of Fe^{3+} ions into the octahedral position of Keggin ions. To our knowledge, this is the first paper in which an XPS study on Keggin ion salts has been presented.

Experimental

Preparation of Keggin ion salts

For the preparation of Al_{13} Keggin ion, partial hydrolysis of $AlCl_3$ solution of 0.25 mol dm^{-3} concentration was used. NaOH solution (1 mol dm^{-3}) was used for the hydrolysis of $AlCl_3$ solution until the ratio OH:Al = 2 was reached. The solutions were aged at 333 K overnight. The Keggin ion salt was prepared by adding excess sodium sulfate solution to the Keggin ion solution. After 1 week the crystals were separated, flushed with slightly acidic solution, dried and stored (this sample is denoted Al_{13}).

The same preparation procedure was applied starting with 0.25 mol dm^{-3} $FeCl_3$ solution. Here a precipitate was formed after the partial hydrolysis (crystal formation was not observed even after the addition of sodium sulfate solution). The precipitate was filtered, washed with distilled water and dried at room temperature (this sample is denoted Fe_{13}).

The third group of samples was prepared by co-hydrolysis of solutions containing both $AlCl_3$ and $FeCl_3$ with $Fe^{3+}:Al^{3+}$ ratios of 0.5:12.5, 1:12 and 4:9. The OH:metal ratio was 2 in all cases. The preparation steps were identical with those applied for Al_{13} Keggin ion salt (these samples are denoted $Fe_{0.5}Al_{12.5}$, Fe_1Al_{12} and Fe_4Al_9).

Elemental analysis

After dissolving the samples in distilled water, the solution was analyzed for Al^{3+} and Fe^{3+} using classical titrimetry.

XPS method

The experiments were performed in an ultra-high vacuum system with a background pressure of 10^{-9} mbar, produced by an iongetter pump. The photoelectrons generated by Mg Kα primary radiation (14 kV, 15 mA) were analyzed with a hemispherical electron energy analyzer (Kratos XSAM 800). To compensate for possible charging effects, binding energies were normalized with respect to the position of the C(1s) peak. These values were kept constant at 285.1 eV. Before taking the XP spectra, the samples were evacuated for 30 min at 300 K in the sample preparation chamber and then introduced into the analyzing chamber by a sample transfer system. The pass energy was set to 40 eV. An energy step width of 50 meV and a dwell time of 300 ms were used. Typically 10 scans were accumulated for each spectrum. Fitting and deconvolution of the spectra were performed with the help of VISION software.

FTIR method

IR spectroscopic measurements were performed using the KBr matrix technique. A 2 mg amount of the sample was homogenized in 200 mg of KBr and pressed into pellets while the die was evacuated. Spectra were registered with a Mattson Genesis FTIR spectrometer. In each case 32 scans were accumulated.

Results

The chemical analysis of the samples showed Fe:Al ratios as follows. No iron or aluminium was found in the Al_{13} and Fe_{13} samples, respectively. Keggin ion salts generated from solutions containing mixed Al–Fe ions gave Fe:Al ratios of 0.006 for $Fe_{0.5}Al_{12.5}$, 0.01 for Fe_1Al_{12} and 0.0125 for Fe_4Al_9. These values are much smaller than expected from the solution composition.

The IR spectra of Al_{13} and Fe_1Al_{12} samples are identical, as Fig. 1 shows. The band positions observed are in good agreement with those reported in the literature. The assignment of the bands is as follows: bands at 727 (729), 628 (627), 547 (546) and 493 (492) cm^{-1} are due to $(Al-O)_{Td}$, $(Al-OH)_O$, $(Al-O)_O$ and $(Al-OH_2)_O$ bond vibrations, respectively (figures in brackets are from ref. 5). However, no bands appeared at 606 and 465 cm^{-1} where the $(Fe-O)_{Td}$ and $(Fe-OH)_O$ bonds absorb.

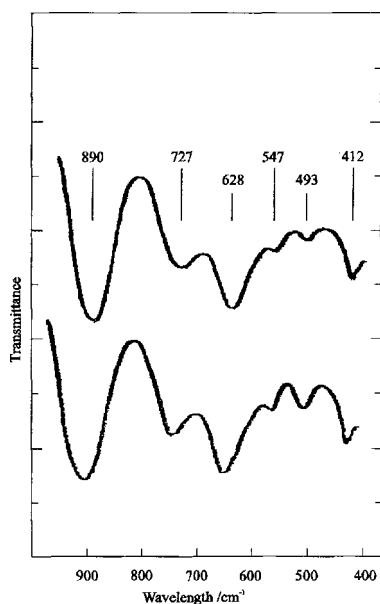Before investigating the incorporation of iron into the pure Keggin ion, we determined first the Al(2p) and O(1s) XPS

positions in the Al_{13} Keggin ion. Al(2p) exhibited a single peak at 74.95 eV. The tetrahedral and octahedral positions cannot be distinguished by XPS. O(1s) also produced a symmetric peak at 532.15 eV. This position is higher by 0.5 eV than for pure Al_2O_3[18] and lower by 1.1 eV than for $Al(OH)_3$.[19] The observed intermediate value between pure oxide and hydroxide may represent a uniform composition for XPS.

Fe(2p) energy levels were also monitored by XPS in the Fe_{13} sample. $Fe(2p_{1/2})$ appeared at 725.05 eV, and $Fe(2p_{3/2})$ at 711.2 eV. The positions and energy separation are very close to that observed either for FeO(OH) or for Fe_2O_3 structures.[20-22] The spectrum is displayed in Fig. 2(A). A broad shake-up satellite appeared at 719.8 eV which is also characteristic of Fe^{3+}.[22] In order to differentiate between FeO(OH) and Fe_2O_3 we also monitored the O(1s) region. The photoemission peak is centered at 531.5 eV. This value is higher by 1.2 eV than for Fe_2O_3 or for Fe_xO.[22] The peak could be deconvoluted to two components with peak positions at 530.0 and 531.7 eV, respectively [Fig. 2(B)]. This structure is very close to that of FeO(OH). Allen et al.[20] found a broad O(1s)
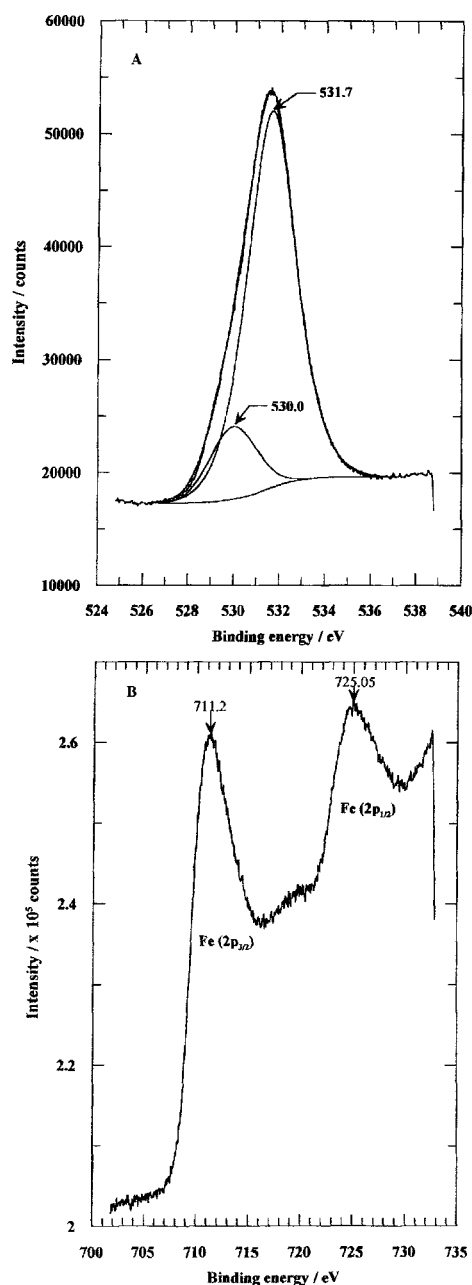

Fig. 1   FTIR spectra of Al_{13} and Fe_1Al_{12} Keggin ions.

Fig. 2   (A) Oxygen 1s and (B) iron 2p X-ray photoelectron spectra of Fe_{13} sample.

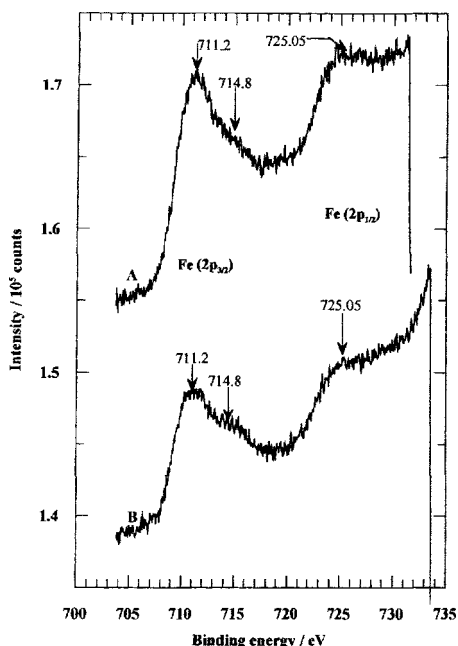**Fig. 3** Iron 2p X-ray photoelectron spectra of (A) $Fe_{0.5}Al_{12.5}$ and (B) Fe_4Al_9 Keggin ions.

peak for FeO(OH) at 531.0 eV. High resolution (monochromatized Al Kα) O(1s) core level spectra from various iron oxide and hydroxide samples were measured by Brundle et al.[21] For FeO(OH) two well resolved peaks were observed at 530.3 and 531.5 eV. The O(1s) for Fe_2O_3 was found at 530.3 eV. Taking these data into account, we may conclude that the Fe_{13} sample consists of FeO(OH) rather than pure oxide.

In subsequent measurements we investigated the incorporation of Fe^{3+} in the Al_{13} Keggin ion. At low loading $(Fe_{0.5}Al_{12.5})$ photoemission appeared at 711.2 eV for $Fe(2p_{3/2})$, similarly to FeO(OH), and an additional shoulder was observed at the high energy side of this peak at 714.8 eV (Fig. 3). The deconvoluted peak ratio was 5.28. When the iron content was increased, this higher binding energy peak intensified further (Fig. 3); the intensity ratio was calculated to be 2.85 for Fe_4Al_9. In parallel with these changes, the $Fe(2p_{1/2})$ region was also modified.

The Al(2p) photoemission peaks remained in unchanged positions after incorporation. Also, the Fe^{3+} loading did not alter the O(1s) peak determined in pure Al_{13} Keggin ion.

Discussion

Among the papers published in the field of pillared interlayer clays, several studies have dealt particularly with the feasibility of the isomorphous substitution of tetrahedrally coordinated aluminium ion in the Keggin structure. Other publications discuss the differences in the interlayer distances, BET areas and adsorption or catalytic characteristics of iron and aluminium pillared smectites.

There are several ways to prepare iron oxide pillared materials. The most frequently used, well described procedures are as follows. Rightor et al.[23] used partially hydrolyzed Fe^{3+} ion solutions with different anions, such as Cl^-, NO_3^- or ClO_4^-. They identified polynuclear iron hydrocomplexes containing 6–8 iron ions depending on the counterion of the salt. A similar conclusion was drawn by Govea and Steinfink.[24] Ion exchange of trinuclear acetatohydroxoiron(II) nitrate, $[Fe_3(OCOCH_3)_7OH]NO_3$, followed by decomposition of the acetate groups by heat treatment, has also been a frequently

applied method.[25] A Keggin-like structure of the ion used for exchanging the iron compound into the layer was claimed. Bradely and Kydd[5] reported the preparation of a Keggin structure containing iron, but pillaring of smectites with this ion was unsuccessful. These preparation methods give iron oxide pillared smectites with small interlayer distances. The distance determined was smaller in each case than that of the aluminium oxide pillared material produced from a Keggin ion-containing solution. In addition to these small intercalant compounds, partial hydrolysis of iron salts results in the formation of polyoxoironates characterized by particle sizes around 3–10 nm, and with molecular masses $>1 \times 10^5$.[26–28] However, these species are much larger than the Keggin ions, and consequently they prop the layers apart even above 7.6 nm.

When both iron and aluminium are present in the exchange solution, mixed oxide pillars can be expected as a product. Mössbauer spectroscopic investigations of alloy pillared interlayer clays were not free of difficulties since the iron content of the montmorillonite itself disturbed the precise determination of the coordination of iron in the pillar.[29] It was also difficult to characterize generally the interactions between the pillar and the layer.[30] Among the products of the partial hydrolysis of iron ions in the presence of aluminium salts, FeOOH phases were found. Singh and Kodama[31] observed that Fe oxyhydroxides crystallize readily in acidic media in the presence of aluminium ions. Immediate formation of akaganeite (β-FeOOH) was detected from chloride solution, whereas from nitrate salts γ-FeOOH was generated. Using Mössbauer spectroscopy, Bakas et al.[32] unambiguously identified the formation of lepidocrocite (γ-FeOOH) species in a pillared clay prepared in a solution containing partially hydrolyzed iron and aluminium ions. They investigated the intercalated clay before heat treatment, when the building blocks of the material could still be recognized. The Mössbauer parameters were attributed to a severely distorted octahedral environment of γ-FeOOH due either to the replacement of Al with Fe somewhere in the structure or/and to the small size of the Fe oxohydroxy particles. These layers may cover the particles.

On the basis of ^{27}Al magic angle spinning NMR spectroscopic studies, Nagy et al.[33] concluded that no isomorphous substitution of Al in the tetrahedral position of Keggin ion by iron took place.

The chemical analysis of Keggin ion salts prepared from solutions containing iron and aluminium ions in different ratios showed that iron appeared in the salts at concentrations which were at least one order of magnitude smaller than expected from the starting compositions of the solutions. From this it follows that the amount of the iron incorporated in the Keggin ions should be very small, if any. Therefore, isomorphous substitution in the tetrahedral position should be excluded from the real opportunities. Octahedral substitution is also improbable, but it may not be disregarded.

IR spectroscopy is assumed to be sensitive enough for the detection of the presence of a very small amount of iron–oxygen bonds. The iron content of a KBr pellet pressed from 2 mg of Fe_1Al_{12} Keggin salt and 200 mg of KBr is around 50 nmol, which may fall below the detection limit of the method. Therefore, the isomorphous substitution of iron either in the tetrahedral or in the octahedral position of Keggin ions cannot be strictly excluded and also cannot be unambiguously confirmed on the basis of IR spectroscopic results.

The appearance of the high binding energy peak in XPS at 714.8 eV (more than 3 eV higher than in the Fe_{13} sample) for Fe(2p) seems to be a very unique case. This new feature demonstrates that the chemical environment of the iron ion has been changed in the Keggin ion. Seemingly it would be easy to attribute this new peak to the formation of simple Fe_xO during incorporation. This form exhibited a broad shake-up satellite centered at 715 eV which is characteristic of

Fe^{2+} species.[22] This explanation, however can be disregarded because the Fe(2p$_{3/2}$) and Fe(2p$_{1/2}$) peaks remained in unchanged positions after incorporation and are characteristic of Fe^{3+} (711.2 and 725.0 eV). For Fe^{2+} the 2p$_{3/2}$ orbital should be detected below 710 eV.[21,34] In our case there is no emission at this energy.

Although the octahedrally and tetrahedrally coordinated Fe^{3+} species are hardly distinguished in pure iron oxide by their core level XP spectra,[21] we consider that a certain fraction of iron cations can be incorporated in the octahedral position in a Keggin ion where the oxygen coordination is the highest. The formation of this highly coordinated species is represented by the appearance of a new photoemission peak at 714.8 eV. It is still an open question whether this new peak represents a real 2p$_{3/2}$ or a new shake-up satellite induced by an excess of oxygen. Novakov and Prins[35] have shown that the presence of an excess of oxygen may greatly enhance shake-up (e.g. transition from d^8 to d^{8*}). Regardless of the nature of the photoemission process, we suggest that a small fraction of Fe^{3+} could replace Al^{3+} in the octahedral position.

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