

On the Feasibility of Iron or Chromium Substitution for Aluminium in the Al₁₃-Keggin Ion

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²⁷Al NMR measurements in the liquid and the solid state supplemented with chemical analysis of the mixed salts unambiguously reveal that neither tetrahedral nor octahedral aluminium can be substituted by either iron or chromium in Al₁₃-Keggin ion salts prepared by conventional methods.

Modification of microporous materials often lead to substances with unusual physical and chemical properties. One such property, the ability to catalyse various transformations, can be drastically influenced by the isomorphous substitution of atoms in the framework or pillars of, for instance, zeolites and pillared layer materials, respectively. Isomorphous substitution changes catalytic properties in various ways, e.g. the size and acidity of the active sites may be altered or elements with redox properties can be incorporated.

For pillared layer clays (PILCs), it is hard to tell whether isomorphous substitution does indeed occur, or whether merely co-hydrolysis and then co-pillaring takes place resulting in the formation of mixed pillars. Although ions of virtually every element have been claimed to be introduced into the tetrahedral as well as octahedral positions of the Al₁₃-Keggin ion [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺,¹ the highly cited patent did not give any clear-cut evidence for this. Direct proofs for isomorphous substitution are accumulating slowly and only for ions of certain elements such as germanium² and gallium.³ Papers have appeared in the literature reporting the success of substituting iron or chromium into the tetrahedral as well as the octahedral positions in the Al₁₃-Keggin ion;⁴⁻⁹ proof, however, is vague, especially since the pillared materials were investigated instead of the salt containing the polyhydroxy cations used for pillaring. This is clearly inadequate because the pillaring agents for Fe-PILC or Cr-PILC are anything but ions of Keggin type. In two extreme cases reported by the same authors (one for iron⁸ and another for chromium⁹), the only proof presented was by citing ref. 1.

Thinking over the problem, suspicion should arise at least for incorporating Fe³⁺ or Cr³⁺ to any of the positions, but especially the tetrahedral positions of the Al₁₃-Keggin ion, since their large size [Cr³⁺ octahedral (0.76 nm), ionic radius for tetrahedral coordination is not given; Fe³⁺ tetrahedral (0.63 nm, high-spin complex), octahedral (0.69 nm, low-spin complex, 0.79 nm, high-spin complex) compared to Al³⁺, tetrahedral (0.53 nm), octahedral (0.68 nm)¹⁰] should introduce considerable strain to the polyhydroxy ion. While successful incorporation of Fe³⁺ into zeolitic frameworks (isomorphous substitution of iron for aluminium) is well proven, in this instance, the whole crystal can help release any strain. There is another problem

with iron substitution. Each study reports the partial hydrolysis of Fe^{III} in the presence of Al^{III}. It has been shown that in such a system the hydrolysis of the iron salt becomes extremely rapid, leading to various forms of iron hydroxous oxides.¹¹ Hydrolysis, however, can be slowed down when an iron(II) salt is applied, since Fe^{II}-Fe^{III} oxidation must precede hydrolysis. Thus, only by use of an iron(II) salt can one have a chance to incorporate iron into the Al₁₃-Keggin structure.

As far as Cr³⁺ is concerned, octahedral coordination is usually adopted. There are only very few examples of tetrahedrally coordinated Cr³⁺ and in such cases, the Cr³⁺ ion is at the centre of complex anion and the tetrahedron is highly distorted.¹²

In this contribution we show that, contrary to widespread belief, co-pillaring is a feasible way of modifying Al₁₃-pillared layer clays when chromium or iron ions are the modifiers. Also in contrast to widespread practice we provide results obtained mostly on pillar precursors (ions in solution as well as in the crystalline state) instead of for pillared clays.

For the preparation of the Al₁₃-Keggin ion partial hydrolysis of AlCl₃ was applied, while for the synthesis of mixed or isomorphously substituted pillar ions the partial co-hydrolysis of AlCl₃ and CrCl₃, or AlCl₃ and FeCl₂, of varying composition were applied. The solution ²⁷Al NMR measurements were applied (i) for checking the formation of the Keggin unit after the partial hydrolysis of AlCl₃ and (ii) studying the composition of the filtrate after treating the solution containing the partially hydrolysed AlCl₃ with Na₂SO₄ solution. This treatment led to the precipitation of a white crystalline material which was further studied by ²⁷Al MAS NMR spectroscopy. The sulfate salts of the co-hydrolysed AlCl₃ + CrCl₃ or AlCl₃ + FeCl₂ mixtures were also studied by ²⁷Al MAS NMR spectroscopy and the ratio of octahedral to tetrahedral aluminium was calculated from the integrated areas of the relevant resonances. Data are listed in Table 1.

Data in Table 1 clearly show that the Keggin unit was formed in solution (entry 1) and was precipitated by Na₂SO₄ (entries 2 and 3). Although the solid-state NMR spectra of the 'isomorphously substituted' Keggin-sulfate salts are complex, resonances belonging to aluminium sitting in octahedral or tetrahedral positions can be easily identified.

Table 1 Data obtained by quantitative ²⁷Al NMR measurements

Entry	Nominal composition	δ ^o (ΔH/Hz)	δ ^T (ΔH/Hz)	Al _o /Al _T
Samples in the solution phase				
1	Al ₁₃ -Keggin-Cl (K1)	-0.1 (25)	62.8 (9)	14.0
2	K1 + Na ₂ SO ₄ filtrate ^a	0.0 (25)	—	—
Samples in the solid state				
3	Al ₁₃ SO ₄	4.8	61.7	11.9
4	Al ₁₂ CrSO ₄ ^b	-1.2, -10.1, -64.3, -107.4	61.4	11.5
5	Al ₁₂ FeSO ₄ ^c	-10.0, -49, -107.2	60.6	8.0
6	Al ₁₁ Fe ₂ SO ₄ ^d	-12.0, -64.9, -109.2	61.4	6.5

^a After partial hydrolysis of the AlCl₃ solution it was treated with Na₂SO₄ solution resulting in the precipitation of a solid material and the filtrate was subjected to NMR measurement. ^b Initial AlCl₃:CrCl₃ ratio of 12:1. ^c Initial AlCl₃:FeCl₂ ratio of 12:1. ^d Initial AlCl₃:FeCl₂ ratio of 11:2.

After integration the Al_O/Al_T ratio decreases, instead of showing the tremendous increase that should occur if substitution in the tetrahedral position really takes place.

Incorporation of Cr (entry 4) seems to be negligible by comparison of the Al_O/Al_T ratio with that for $Al_{13}-SO_4$ (entry 3) assuming that tetrahedral sites are not occupied by Cr.

Similar Al_O/Al_T ratios to those listed in Table 1 (entries 5 and 6) would be obtained for Fe,Al salts if some degree of tetrahedral and significant octahedral substitution occurred. The ionic radius of octahedrally coordinated low-spin Fe^{3+} indicates that the octahedral positions may be accessible. However, chemical analysis of the Fe,Al salts (dissolving the salt, titrating the iron and aluminium content) gave very low iron to aluminium ratios of 1:80–100 instead of 1:12 or 2:11 (entries 5 and 6). FT-IR¹³ on co-hydrolysed Keggin salts and ⁵⁷Fe Mössbauer measurements on Fe,Al co-pillared montmorillonite¹⁴ also revealed that overwhelmingly co-precipitation occurred instead of tetrahedral or octahedral substitution and that a small amount of iron hydrous oxide covers the Al_{13} -Keggin salt. This oxide, however, contains the iron in octahedral coordination.

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