On the Feasibility of Iron or Chromium Substitution for Aluminium in the \( \text{Al}_{13} \)-Keggin Ion

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\( ^{27}\text{Al} \) 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 \( \text{Al}_{13}\)-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 \( \text{Al}_{13}\)-Keggin ion \( [\text{AlO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}\), 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 germanium\(^2\) 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 \( \text{Al}_{13}\)-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 in the crystalline state) instead of for pillared clays.

For the preparation of the \( \text{Al}_{13}\)-Keggin ion partial hydrolysis of \( \text{AlCl}_3 \) was applied, while for the synthesis of mixed or isomorphously substituted pillar ions the partial co-hydrolysis of \( \text{AlCl}_3 \) and \( \text{CrCl}_3 \), or \( \text{AlCl}_3 \) and \( \text{FeCl}_2 \), of varying composition were applied. The solution \( ^{27}\text{Al} \) NMR measurements were applied (i) for checking the formation of the Keggin unit after the partial hydrolysis of \( \text{AlCl}_3 \) and (ii) studying the composition of the filtrate after treating the solution containing the partially hydrolysed \( \text{AlCl}_3 \) with \( \text{Na}_2\text{SO}_4 \) solution. This treatment led to the precipitation of a white crystalline material which was further studied by \( ^{27}\text{Al} \) MAS NMR spectroscopy. The sulfate salts of the co-hydrolysed \( \text{AlCl}_3 + \text{CrCl}_3 \) or \( \text{AlCl}_3 + \text{FeCl}_2 \) mixtures were also studied by \( ^{27}\text{Al} \) 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 \( \text{Na}_2\text{SO}_4 \) (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>
<thead>
<tr>
<th>Entry</th>
<th>Nominal composition</th>
<th>( \delta^0 ) (( \Delta H/\text{Hz} ))</th>
<th>( \delta^1 ) (( \Delta H/\text{Hz} ))</th>
<th>( \text{Al}_{12}/\text{Al}_1 )</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>( \text{Al}_{13})-Keggin-Cl (K1)</td>
<td>-0.1 (25)</td>
<td>62.8 (9)</td>
<td>14.0</td>
</tr>
<tr>
<td>2</td>
<td>( \text{K} + \text{Na}_2\text{SO}_4 ) filtrate(^*)</td>
<td>0.0 (25)</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>Samples in the solid state</td>
<td>4.8</td>
<td>61.7</td>
<td>11.9</td>
</tr>
<tr>
<td>4</td>
<td>( \text{Al}_{13}\text{CrSO}_4)(^d)</td>
<td>-12.0, -10.1, -64.3, -107.4</td>
<td>61.4</td>
<td>11.5</td>
</tr>
<tr>
<td>5</td>
<td>( \text{Al}_{13}\text{FeSO}_4)(^c)</td>
<td>-10.0, -49.0, -107.0</td>
<td>60.6</td>
<td>8.0</td>
</tr>
<tr>
<td>6</td>
<td>( \text{Al}_{13}\text{Fe}_2\text{SO}_4)(^d)</td>
<td>-12.0, -64.9, -109.2</td>
<td>61.4</td>
<td>6.5</td>
</tr>
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</table>

\(^a\) After partial hydrolysis of the \( \text{AlCl}_3 \) solution it was treated with \( \text{Na}_2\text{SO}_4 \) solution resulting in the precipitation of a solid material and the filtrate was subjected to NMR measurement. \(^b\) Initial \( \text{AlCl}_3 : \text{CrCl}_3 \) ratio of 12:1. \(^c\) Initial \( \text{AlCl}_3 : \text{FeCl}_2 \) ratio of 12:1 \(^d\) Initial \( \text{AlCl}_3 : \text{FeCl}_3 \) ratio of 11:2.
After integration the Al$_2$/Al$_1$ 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$_2$/Al$_1$ ratio with that for Al$_{13}$-SO$_4$ (entry 3) assuming that tetrahedral sites are not occupied by Cr.

Similar Al$_2$/Al$_1$ 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-IR$^{13}$ on co-hydrolysed Keggin salts and $^{57}$Fe Moessbauer measurements on Fe,Al co-pillared mottormorillonite$^{14}$ 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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References