

SOLID STATE NMR STUDY OF PHOSPHATE ADSORPTION ON NATURAL MICROPOROUS MATERIALS

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1. Introduction

Phosphates are important ingredients, especially in agricultural fertilizers or in detergents, but when their concentrations in aquatic environments (where they may be present in the form of anions PO_4^{3-} , HPO_4^{2-} , H_2PO_4^-) are high, they are usually responsible for the eutrophication of these surface waters [1,2]. The mobility of dissolved phosphates may be regulated by their adsorption, e.g. on iron oxyhydroxides [3] or by their precipitation as calcium phosphates under appropriate operating conditions. The latter technique may not only remove the phosphate anions from waters, but also enable recycling of resulting calcium phosphate precipitate back into the fertiliser industry [4].

The present paper deals with the ^{31}P NMR study of potential phosphate adsorbents, basically natural microporous materials like clinoptilolite, montmorillonite and slovakite, which were used in laboratory conditions for adsorption of phosphate from model solutions [5]. They are considerably cheaper than commercial adsorbents, for example iron oxyhydroxides or other synthetic polymeric ion exchangers. The aim of the ^{31}P NMR measurements reported in this paper was to demonstrate the formation of surface calcium precipitates on the examined materials, responsible for phosphate adsorption especially on the surface of natural zeolite.

2. Experimental

^{31}P NMR measurements were carried out on natural clinoptilolite, montmorillonite and slovakite with adsorbed phosphates denoted as P-clinoptilolite, P-montmorillonite and P-slovakite. The measurements were also performed on a sample of pure $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ which was used for the preparation of a model solution for adsorption. ^{31}P NMR chemical shifts in the measured spectra were determined using pure $\text{NH}_4\text{H}_2\text{PO}_4$ as a secondary standard for which the chemical shifts of 0.7 ppm [6], 0.8 ppm [7], and 0.9 ppm [8] with respect to the primary standard 85% H_3PO_4 were published. For this reason the values of chemical shifts in our spectra are determined with accuracy ± 0.1 ppm.

^{31}P NMR measurements were carried out on a 400 MHz Varian spectrometer with a superconducting wide-bore magnet generating a magnetic field of 9.4 T. The measurements were performed at room temperature using a probehead with a 4 mm rotor spinning at the magic angle with a rate of 10 kHz. The spectra were measured at a resonance frequency of 161.6 MHz, the 90° pulse duration was 3.8 μs , and the recycle delay 300 s. Between 13-35 scans were sufficient to obtain spectra of good quality for pure chemical compounds, while 250-300 scans were necessary for accumulation in order to obtain well-resolved spectra for phosphates adsorbed on clinoptilolite, montmorillonite and slovakite. The spectra were processed using MestReNova software.

3. Results

^{31}P MAS NMR spectra of all samples are characterized by one central signal with symmetrically positioned spinning sidebands (Fig. 1a).

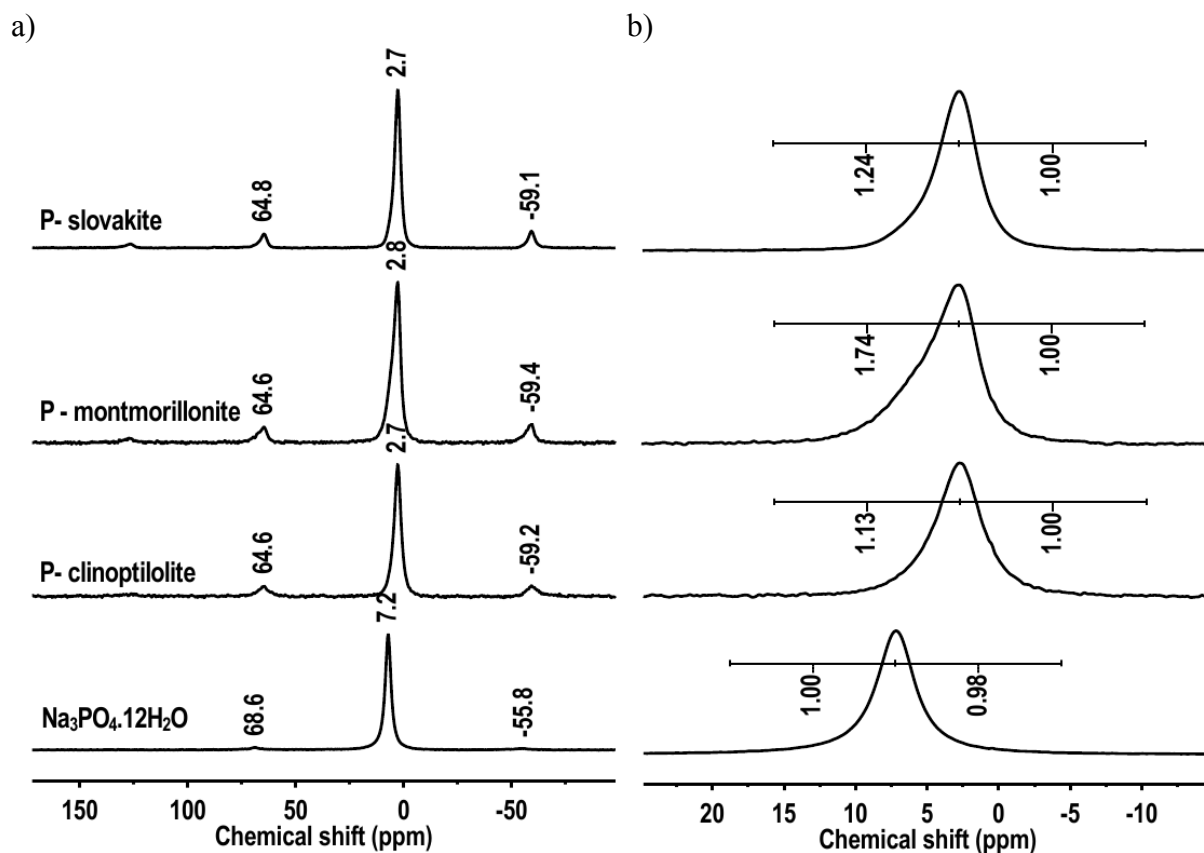


Fig.1 ^{31}P MAS NMR spectra of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$, P, clinoptilolite, P-montmorillonite and P-slovakite a), central lines of ^{31}P MAS NMR spectra with the integrals of the left and right part of the line with respect to the peak of the central line b).

The chemical shift of the central line in the spectrum $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ is 0.4 ppm lower than the value reported in the literature [9], which could be caused by partial hydration of this

sample. The chemical shifts of central lines in the spectra measured for adsorbents which are of 2.7-2.8 ppm, are in good agreement with the value of 2.8 ppm obtained for pure $\text{Ca}_3(\text{PO}_4)_2$ [9]. From this it can be deduced that the dominant signal at chemical shift of 2.7-2.8 ppm in the spectra measured on these adsorbents can be assigned to surface precipitate $\text{Ca}_3(\text{PO}_4)_2$.

The central signal in the spectra of adsorbents is not symmetrical, as can be seen in Fig. 1b. This asymmetry can be quantified by integration of the left and right parts of the line with respect to the peak of the signal. Pure $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ produces a symmetrical signal, since the left and right integral values are the same. In the case of adsorbents the left integrals are always larger than right ones, and the largest asymmetry is observed for P-montmorillonite. From this it can be inferred that PO_4^{3-} anions can react not only with Ca^{2+} cations but very probably also with other cations, e.g., K^+ , Mg^{2+} , Na^+ , which can be present in the outer pores of adsorbents and form compounds with higher ^{31}P chemical shift. The relatively high symmetry of the spectrum of P-clinoptilolite indicates that Ca^{2+} cations are dominant in clinoptilolite structure.

The signal with the greatest asymmetry in the spectrum of P-montmorillonite can be deconvoluted into three lines (Fig. 2a) with the same Lorentzian/Gaussian ratio of 0.4 and with chemical shifts of 2.8 ppm, 5.8 ppm and 9 ppm. The lines can be assigned to surface precipitates – $\text{Ca}_3(\text{PO}_4)_2$ with chemical shift of 2.8 ppm as mentioned above, K_2HPO_4 , which as pure chemical has chemical shift of 4.0 ppm [9] or $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ with chemical shift of 4.6 ppm [10], and probably also $\text{Na}_3\text{PO}_4 \cdot x\text{H}_2\text{O}$ ($x < 12$), which without crystalline water produces a line with chemical shift of 13.7 ppm [11]. The higher chemical shift for $\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$ can also be caused by the partial absence of crystalline water, because deprotonation of ^{31}P nuclei results in higher chemical shift values [10]. The spectrum of P-slovakite can be deconvoluted into two lines (Fig. 2b). The results of deconvolutions are listed in Table 1. The area under line (line intensity) is proportional to the amount of precipitate.

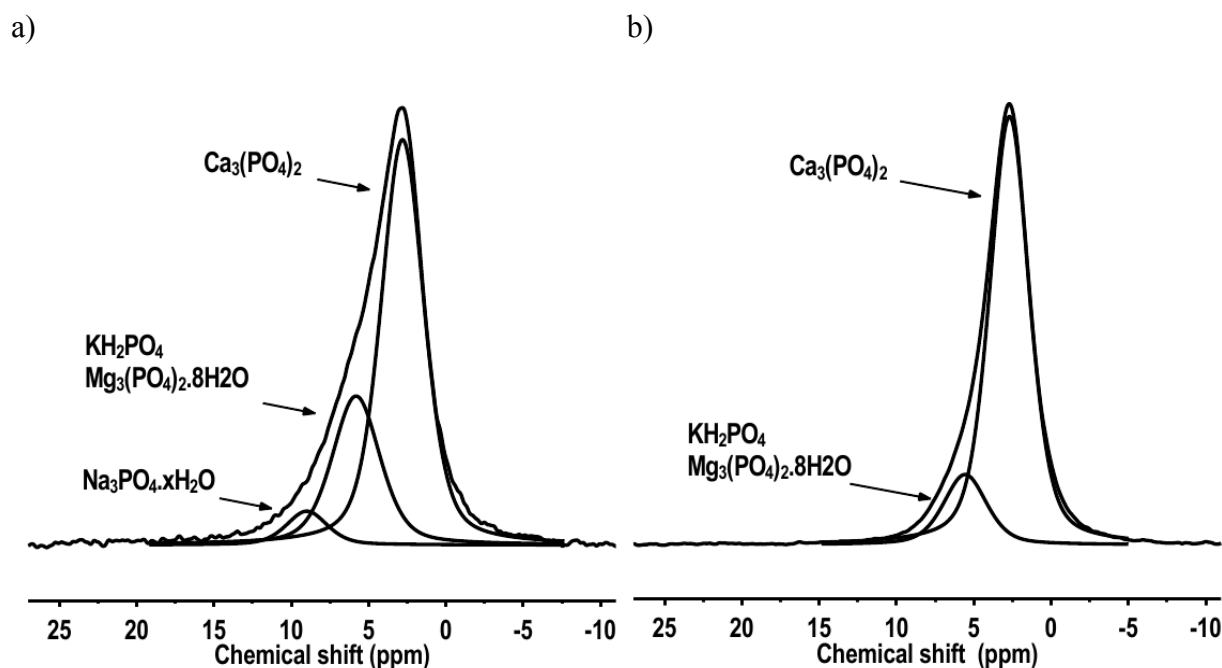


Fig. 2 ^{31}P MAS NMR spectra of P-montmorillonite a) and P-slovakite b).

Tab. 1. The results of deconvolutions of ^{31}P MAS NMR spectra of P-montmorillonite and P-slovakite

Material	δ_{iso} (ppm)	Assignment	Area %
P-montmorillonite	2.8	$\text{Ca}_3(\text{PO}_4)_2$	67.2
	5.8	$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	27.4
	9.0	$\text{Na}_3\text{PO}_4 \cdot x\text{H}_2\text{O}$	5.4
P-slovakite	2.7	$\text{Ca}_3(\text{PO}_4)_2$	85.0
	5.6	$\text{Mg}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$	15.0

4. Conclusion

^{31}P MAS NMR spectra measured on natural clinoptilolite, montmorillonite and slovakite with adsorbed phosphates confirmed that the phosphate anions in solution can react with Ca^{2+} and Mg^{2+} cations present on the surface of adsorbent particles and form surface precipitates. The most beneficial from the practical point of view is the formation of calcium phosphate precipitates, since calcium phosphate may be used as stock for the fertilizer industry.

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