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Nuclear Magnetic Resonance Spectroscopic Study on the Grafting of Ethylene Oxide onto the Interlayer Surface of γ-Zirconium Phosphate

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The reaction products of γ-zirconium phosphate with ethylene oxide were analyzed by solid-state ^{31}P magic-angle spinning (MAS) NMR, and ^{31}P and ^{13}C solution NMR spectroscopy. γ-Zirconium phosphate can be formulated as $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$. Ethylene oxide molecules react with the interlayer H_2PO_4 groups, forming diester derivatives of ethylene and/or diethylene glycols.

There are two types of layer-structured zirconium phosphates, $Zr(HPO_4)_2\cdot nH_2O$: a monohydrtate, α and a dihydrate, γ.[1,2] The γ phase having a larger basal spacing is more reactive for intercalation reactions. In a previous study[3] on the preparation of organic derivatives of zirconium phosphate, the γ phase was used, and the phosphate groups on the interlayer surface were subjected to reaction with ethylene oxide. It was concluded that all of the monohydrogenphosphate groups in the structure were involved in the formation of P-O-C ester bonds since about two moles of ethylene oxide reacted with one mole of zirconium phosphate

$$Zr(HPO_4)_2 \quad + \quad 2\,\overline{C_2H_4O} \quad \longrightarrow \quad Zr(HOC_2H_4OPO_3)_2$$

Similar types of organic derivatives were prepared by an ion exchange of the interlayer phosphate groups with various phosphoric ester groups:[1]

$$Zr(HPO_4)_2 \quad + \quad RO\text{-}PO_3^- \quad \longrightarrow \quad Zr(ROPO_3)(HPO_4) \quad + \quad HOPO_3^-$$

where R are organic functional groups, but only half of the phosphate groups could be exchanged with the ester groups. The reason why only half of the phosphate groups are exchanged, while all of them are used in the grafting reaction with ethylene oxide, has not been explained yet.

Recently, Clayden[4] investigated the ^{31}P MAS NMR spectra of α- and γ-zirconium phosphates. The former showed only one ^{31}P resonance, whereas the latter two resonances. After the detailed analysis of the spectra, he concluded that there were two chemically distinct types of phosphate groups in the γ phase, and that it should be formulated as $Zr(PO_4)(H_2PO_4)\cdot 2H_2O$ rather than $Zr(HPO_4)_2\cdot 2H_2O$. The crystal structure of γ-titanium phosphate, which is isomorphous with γ-zirconium phosphate was analyzed on the basis of the X-ray powder diffraction data by Christensen et al.[5] The structural model proposed was in agreement with the NMR data; the phosphate is present as equal number of PO_4 and H_2PO_4 groups, only the latter phosphate groups being on the interlayer surface.

In this study, the reaction of ethylene oxide (EO) with γ-zirconium phosphate is re-examined by using ^{31}P MAS NMR spectroscopy. The resulting organic derivatives are hydrolyzed with alkaline solutions into zirconium hydroxy precipitate and phosphoric esters. The esters are analyzed by ^{31}P and ^{13}C solution NMR spectroscopy.

γ-Zirconium phosphate was supplied from Daiichi-kigenso Kagaku Kogyo Co.. The reaction with ethylene oxide was carried out by using the 1 and 3 M (1 M = 1 mol dm^{-3}) aqueous solutions according to the procedures described in a previous paper.[3)] Samples of three different degrees of reactions with basal spacings, d = 1.63, 1.85 and 1.94 nm were separated, washed with water, and air-dried. The molar ratios of ethylene oxide taken up by γ-zirconium phosphate (n = EO/Zr) were determined to be 0.70, 1.75 and 2.30, respectively by thermogravimetric analysis. Standard samples of phosphoric esters for reference were prepared by the reaction of phosphorous oxychloride with different amounts of ethylene glycol. The esters were separated by a fractional precipitation with $Ba(OH)_2$ as the barium salts. The solid-state as well as solution NMR spectra were collected on a Bruker AMX400 NMR spectrometer. A 85% H_3PO_4 was used as reference for ^{31}P and sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) for ^{13}C nuclei.

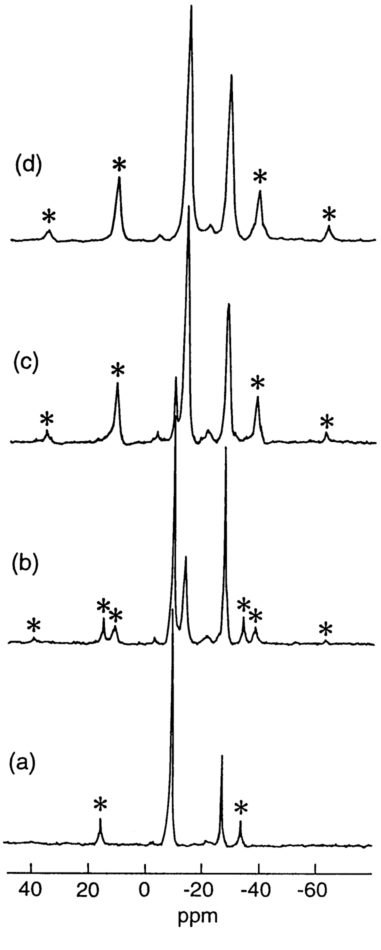


Fig. 1. ^{31}P CP MAS NMR spectra of (a) γ-zirconium phosphate and its organic derivatives with different degrees of reaction, (b) n = 0.70, (c) 1.75, and (d) 2.30. * indicates spinning side bands.

^{31}P cross-polarization (CP) MAS-NMR spectra were measured on the samples of different degrees of reaction, and are shown in Fig. 1. Two sharp ^{31}P resonance peaks are clearly seen in the spectrum of the starting γ-zirconium phosphate at -8.90 and -26.83 ppm, which were respectively assigned to H_2PO_4 and PO_4 by Clayden.[4)] As the reaction with ethylene oxide proceeded, the intensity of the former peak due to H_2PO_4 was reduced and a new peak appeared at -13.24 ppm; the peak due to PO_4 remained unshifted at -26.9 ppm. This finding indicates that only half of the phosphate groups are used for the grafting reaction, though about two moles of ethylene oxide reacted with one mole of γ-zirconium phosphate. It is reasonable to assign the new peak to the ^{31}P of the phosphate groups with P-O-C ester bonds. Intense spinning side bands

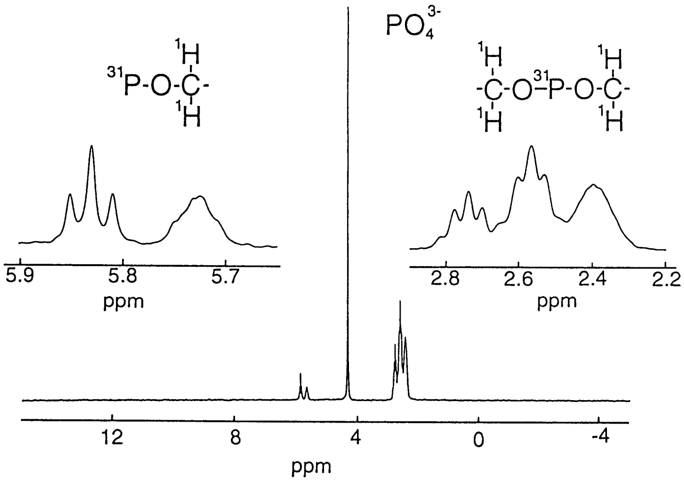


Fig. 2. ^{31}P NMR non-decoupled spectrum of the supernatant solution of the hydrolized product.

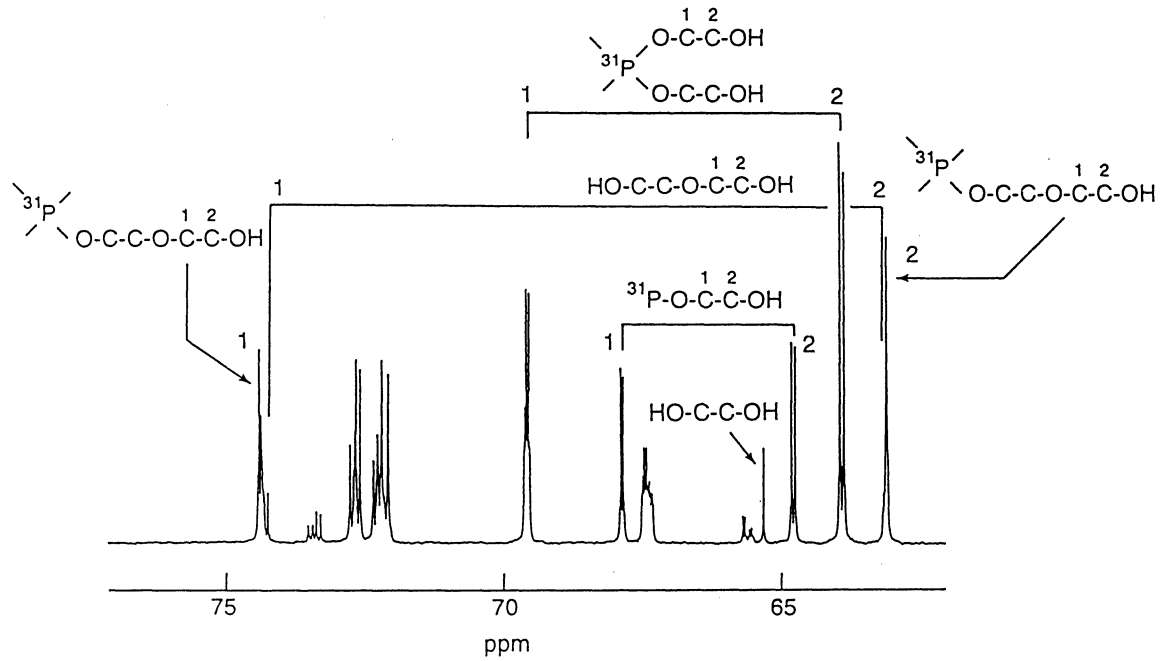


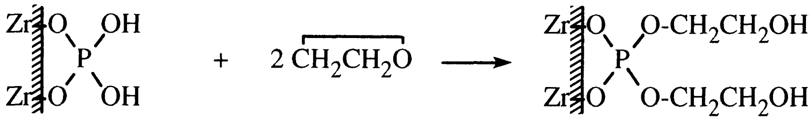
Fig. 3. ^{13}C NMR spectrum of the supernatant solution of the hydrolyzed product with 1 M NaOH at 323 K for 3 h.

were associated with the ^{31}P resonance peaks of the ester and H_2PO_4. This also suggests that the new phosphate groups are in an asymmetrical environment as that of the H_2PO_4 groups. The increased linewidth of the spectra of the organic derivatives are interpreted in terms of a reduction in the crystallinity of the samples.

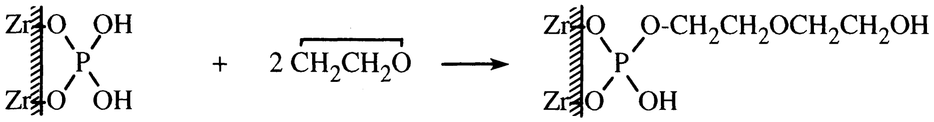
The reaction product (n = 1.75, d = 1.85 nm) was hydrolyzed with a 1 M NaOH solution at 323 K for 2 h. Figure 2 shows ^{31}P non-decoupled NMR spectra of the supernatant solution of the hydrolyzed product. A sharp singlet peak at 4.31 ppm is assigned to orthophosphate ions. The presence of multipulet peaks can be interpreted in terms of the formation of several kinds of phosphate esters;6) more than two kinds of monoesters (triplets in the lower field), and more than three kinds of diesters (quintets in the higher field). It should be noted that the peak intensity of the diesters is much larger than that of the monoesters. If a small amount of NaOH (molar ratio of NaOH/Zr < 2) was used for the hydrolysis, the formations of monoesters and orthophosphate ions in the hydrolyzed products were much smaller.

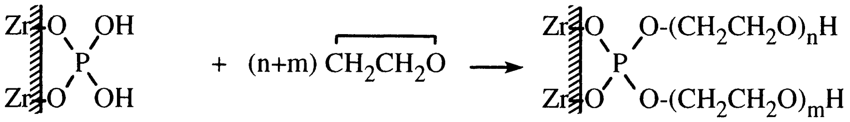
Figure 3 shows the ^{13}C NMR spectra of the supernatant solution obtained by a similar hydrolysis. It is well known that the coupling constant of ^{31}P-O-^{13}C is about 4.5-6 Hz, which is smaller than that of ^{31}P-O-C-^{13}C, 6.5-7.5 Hz.7) A large number of doublet peaks observed in the figure suggest that there are a number of different types of phosphoric esters, in accordance with the findings by the ^{31}P non-decoupled NMR spectra of the solution. The singlet ^{13}C resonance peaks due to ethylene and diethylene glycols8) were assigned as shown in Fig. 3. The intensities of these peaks greatly increased on further hydrolysis of the solution with NaOH at 373 K. The assignments of the resonance peaks for the mono- and di-esters of ethylene glycol were made on the basis of the spectra of the standard samples and the coupling behaviors described above. Singlet resonance peaks near those of diethylene glycol are tentatively assigned to O-C-^{13}C-OH and O-^{13}C-C-OH groups of the diethylene glycol esters. It is likely that the rest of the doublet resonance peaks are attributed to ^{31}P-O-^{13}C-C-O- and ^{31}P-O-C-^{13}C-O- groups of a mixture of mono- and di-esters of diethylene glycols and/or ethylene glycols. More detailed analysis of the spectra and the preparation of standard esters will be necessary for further discussion.

From the NMR spectroscopic data presented here, the following structural model is proposed for the reaction of ethylene oxide with the interlayer surface of γ-zirconium phosphate. γ-Zirconium phosphate has two types of phosphate groups; PO_4 and H_2PO_4, and only the interlayer H_2PO_4 groups react with ethylene oxide. The reason why one mole of γ-zirconium phosphate can react with two moles of ethylene oxide is found in the formation of diesters;



In parallel, diethylene glycol esters are formed, and the formation of more complicated esters will also be possible;





The hydrolysis products include all kinds of the combinations of phosphoric esters. The ^{13}C NMR spectra shown in Fig. 3 is still more complicated than expected from the structural model proposed here. It is likely that some new esters are formed during the hydrolysis such as P-O-CH_2CH_2-O-P-O-CH_2CH_2OH. Further studies are now under way.

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