# Anion Exchange between Sulfate Ion and Hydrogenphosphate Ion to Form Mesoporous Zirconium-Phosphorus Complex Oxide

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Formation of zirconium-phosphorus complex oxide with stable hexagonal pore structure has been clarified to result from anion exchange of $HPO_4^{2-}$ ions for $SO_4^{2-}$ ions in surfactant-assisted zirconium oxide during phosphoric acid treatment.

Since the discovery of a new family of silica-based mesoporous materials, M41S,[1] various mesostructured materials have been reported for non-silica metal oxides of Ti,[2] V,[3] W,[4] Ta,[5] Nb,[6] and Zr.[7,8] This is due to new opportunities in design of innovative materials with potential application as catalysts, sorbents, and solid electrolyte devices. The mesostructured oxides consist of cooperative assemblies of surfactant ions and inorganic species.[9] A common problem of the non-silica hexagonal materials is destruction of their mesostructures upon heating treatment to eliminate the surfactant. In case of titania, for example, the hexagonal pore system was maintained even after the calcination, but the BET surface area was only about 200 $m^2g^{-1}$.[2] A solvent extraction technique,[6] successfully applied to remove the surfactant from $Nb_2O_5$, seems not to be generalized on the others. Mesostructured zirconium oxide has given porous material with random pore structure upon the calcination,[7] while zirconium oxide having hexagonal pore system has not been obtained yet. In contrast, it has recently been reported that phosphoric acid treatment can stabilize the hexagonal pore structure of zirconium oxide.[8a] This is an interesting method but the reason for the stabilization of hexagonal structure upon the treatment remains unresolved. In this study, we have tried to resolve the issue and found novel anion exchange between $SO_4^{2-}$ and $HPO_4^{2-}$ during the phosphoric acid treatment. The findings would result in development of new preparation method of various porous materials.

Hexagonally mesostructured zirconium oxide, abbreviated as ZO, was synthesized from $Zr(SO_4)_2 \cdot 4H_2O$ and hexadecyltrimethylammonium bromide ($C_{16}$TMABr) by the procedure reported previously.[8] The parent ZO was treated with a phosphoric acid solution of 0.01-2 M at ambient temperature for 2 h. The treatment was repeated 1-6 times. The samples were characterized with XRD, ICP, elemental analysis, TEM, $N_2$ adsorption and IR before and after the calcination at 723 K. The zirconium-phosphorus complex oxide obtained was abbreviated as ZP($n$) where $n$ indicates the atomic ratio of P/Zr.

The parent ZO showed characteristic (100), (110) and (200) XRD diffractions of the hexagonal structure with $d$ spacings of 4.06, 2.36 and 2.03 nm before the calcination. The change in the structure of ZO upon the phosphoric acid treatment has first been examined as a function of acid concentration. When ZO was treated with 0.5, 1.0, and 2.0 M $H_3PO_4$ solutions for 2 h, the relative (100) XRD intensities to that of the parent ZO were 1.12, 1.24, and 0.29, respectively. It is clear that adequate treatment with the phosphoric acid solution increased the ordering of the hexagonal structure but too high concentration of phosphoric acid solution resulted in destroying structure. The $d$ spacing slightly decreased by *ca.* 0.1 nm on all ZP samples. To prepare ZP samples with high P/Zr ratio and good hexagonal structure, repetition of the treatment with 0.5 M $H_3PO_4$ was tried. The P/Zr ratios were 1.20, 1.42, 1.50, 1.60, 1.67, and 1.67 after the 1st, 2nd, 3rd, 4th, 5th, and 6th treatments. The relative XRD intensity of ZP treated six times was 1.21. These indicate the limit of P/Zr=1.67 and no collapse of the hexagonal structure.

The samples were calcined at 723 K for 6 h (Table 1). The BET surface area increased with increasing P/Zr ratio and reached 456-547 $m^2g^{-1}$ at P/Zr > 1.0. Their TEM images also confirmed the hexagonal pore structure of the calcined ZP. These findings conclude that the phosphoric acid treatment is really effective to produce hexagonally porous materials and the stability of the structure was dependent on the amount of P incorporated.

**Table 1.** Characterization of zirconium-phosphorus oxides[a]

| Sample (P/Zr ratio) | C/N ratio | Elemental analysis $C_{16}$TMA[b] | Br[b] | S[b] | P[b] | Surface area[c] /$m^2 g^{-1}$ |
|---|---|---|---|---|---|---|
| ZO | 18.4 | 1.43 | 0.05 | 2.35 | 0 | 16 |
| ZP(0.08) | 17.2 | 1.35 | 0.01 | 2.09 | 0.19 | 17 |
| ZP(0.32) | 19.0 | 1.30 | 0 | 1.49 | 0.83 | 38 |
| ZP(0.62) | 18.7 | 1.27 | 0 | 0.81 | 1.71 | 181 |
| ZP(1.07) | 17.2 | 1.26 | 0 | 0.40 | 2.66 | 456 |
| ZP(1.22) | 18.2 | 1.27 | 0 | 0.19 | 2.95 | 470 |
| ZP(1.50) | 21.2 | 1.21 | 0 | 0.02 | 3.58 | 536 |
| ZP(1.67) | 17.2 | 1.18 | 0 | 0.05 | 3.65 | 547 |

[a] The data were all for uncalcined samples except for the surface area. [b] mmol $g^{-1}$. [c] after the calcination at 723 K for 6 h.

The mechanism of phosphorus incorporation has next been investigated. The results of elemental analysis are summarized in Table 1. The amounts of $C_{16}$TMA were roughly constant regardless of the P/Zr ratio, and the C/N atomic ratios were approximately equal to the theoretical value of 19. These indicate neither any loss nor any decomposition of the surfactants during the acid treatment. The phosphorus incorporation is hard to be due to the exchange or reaction of $H_3PO_4$ with the surfactant.

Elemental analyses shown in Table 1 reveal that the amount of sulfur decreased with incorporation of phosphorus. This correlation can be recognized more clearly when the amount of P incorporated was plotted against that of S released (Figure 1). Below 1.2 mmol $g^{-1}$ of P incorporated (P/Zr < 0.6), the amount of P incorporated were almost precisely proportional to those of S released. Above 2.0 (P/Zr > 0.8), P atoms were incorporated into ZO with little release of S.

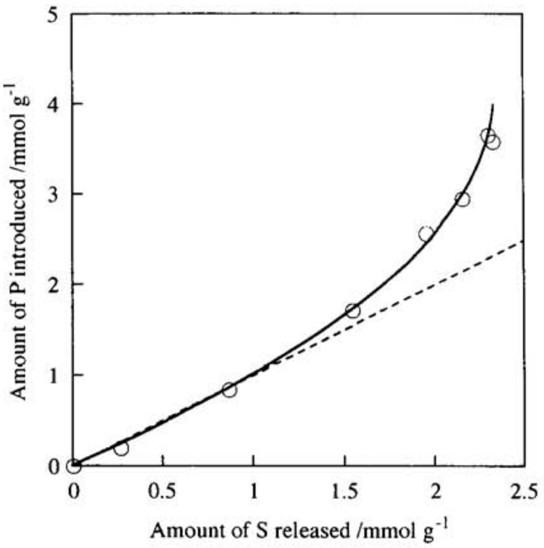

**Figure 1.** Correlation of amount of P incorporated with that of S released. The dotted line indicates the 1/1 atomic ratio of P/S.

IR spectra provided further information concerning the above issue. As shown in Figure 2, the 1229 $cm^{-1}$ band due to S-O vibration of sulfates[10] decreased with increasing P/Zr ratio, while the new band attributable to P-O stretching or bending vibration[11] appeared gradually at 1036 $cm^{-1}$. It should be noted that the intensity of the 1229 $cm^{-1}$ band almost disappeared at $P/Zr > 1.0$, while the intensity of the P-O bands always increased in the P/Zr range 0-1.67.

All of these results allow us to propose a mechanism that the phosphorus incorporation during the $H_3PO_4$ treatment proceeds through novel anion exchange of $HPO_4^{2-}$ ions for $SO_4^{2-}$ ions (Scheme 1). This is the case for the region $P/Zr < 0.6$.

$$\text{Zr-SO}_4\text{-C}_{16}\text{TMA} + \text{H}_3\text{PO}_4 \longrightarrow \text{Zr-HPO}_4\text{-C}_{16}\text{TMA} + \text{H}_2\text{SO}_4 \quad (1)$$

The $SO_4^-$ may interact with Zr species and surfactants through $I^+X^-S^+$ mechanisum.[8, 9] Figures 1 and 2 suggest that there must be another route for the phosphorus incorporation at $P/Zr > 0.6$. Although there is no direct evidence for this route, the reaction of $H_3PO_4$ with Zr-OH groups could be suggested to correspond to another part of phosphorus incorporation.

It follows that there are two kinds of phosphorus incorporation and the first step is the anion exchange between sulfate and hydrogenphosphate ions. The phosphoric acid treatment makes it possible to remove the surfactants without structure destruction and produce porous zirconium phosphate with high surface area.

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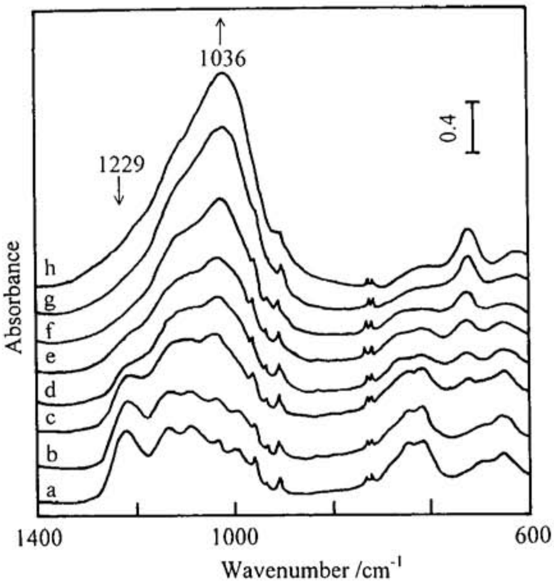

**Figure 2.** IR spectra of the parent ZO (a), and the ZP samples with P/Zr ratio of 0.08 (b); 0.32 (c); 0.62 (d); 1.07 (e); 1.22 (f); 1.50 (g) and 1.67 (h).

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