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Ionothermal Synthesis of Layered Zirconium Phosphates and Their Tribological Properties in Mineral Oil

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In an attempt to synthesize novel zirconium phosphate materials, a series of syntheses have been performed in a deep eutectic solvent (DES), composed of tetrapropylammonium bromide (TPABr) and oxalic acid. As a result, this DES does not act as a template provider in reaction probably owing to the steric effects of the longer chains of the TPA cation, and only the α-$Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP) phase has been achieved. However, after organic amine was added to the initial reaction mixture in a normal way, the additives did act as a template to induce the zirconium phosphate framework. For example, with 1,4-dimethylpiperazine as an additive, a novel layered compound, $[C_6H_{16}N_2]_{0.5}Zr(H_{0.5}PO_4)_2 \cdot H_2O$ (denoted as $ZrPO_4$-DES8) was obtained. Its structure was determined from single-crystal X-ray diffraction (XRD) data and consists of zirconium phosphate layers with the protonated 1,4-dimethylpiperazine and water molecules in between. Interestingly, the two layered materials as additives in a liquid lubricant exhibit excellent friction behavior with higher load-carrying and antiwear capacities in comparison to typical lubricant additives such as MoS_2 and graphite, increase the P_B value of the base oil by 27.2% and 8.5%, and decrease the wear scar diameter of the base oil by 43% and 36%, respectively. Scanning electron microscopy, XRD, and energy-dispersive X-ray spectrometry are used to investigate the lubricant behavior of those materials.

Introduction

Zirconium phosphates are an important class of compounds owing to their potential applications in proton ion conductivity, ion exchange, adsorption, and catalysis.[1−3] These materials are usually prepared by solvothermal synthesis using an amine as a structure-directing agent (SDA) or template. Recently, ionothermal synthesis,[4−6] a novel method for the preparation of aluminophosphate molecular-sieve analogues, was developed by Morris et al., where an ionic liquid or a deep eutectic solvent (DES) functions as the reaction medium and, in some cases, acts as the SDA provider during the reaction process. This new synthetic methodology promises exciting possibilities for the preparation of hitherto unknown materials,[7,8] for the improved preparation of previously synthesized materials, and for mechanistic studies.[9,10]

One class of DESs is usually composed of organic halide salt and an organic compound capable of forming a hydrogen bond with the halide ion, such as amides, amines, carboxylic acids, and alcohols.[11,12] Such DESs are usually liquid at a temperature of 100 °C or below and exhibit solvent properties similar to those of conventional ionic liquids. In contrast to ionic liquids, the advantages of DESs are their ease of preparation as pure phases from easily available components and their relative nonreactivity with water. They could also be used in ionothermal synthesis as an alternative to conventional ionic liquids.[13,14] Besides $AlPO_4$ or

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$MeAlPO_4$ materials, some other metal phosphates such as $ZnPO_4$ and $GaPO_4$ could be synthesized from DESs.[15,16] More recently, using a DES consisting of urea and tetramethylammonium chloride (TMACl), our group prepared two different zirconium phosphates, $(NH_4)_4[Zr(PO_4)_2F_2]$ and $(NH_4)_3[Zr(PO_4)_2F]$, in which urea-derived ammonium cations showed a stronger structure-directing role compared to tetramethylammonium (TMA) cations.[17] To avoid competition between the two ammonium cations, the urea was replaced by oxalic acid to form a DES with TMACl. This allowed for the synthesis of open-framework zirconium phosphate using TMA cations as an SDA.

Templating or a structure-directing effect is an important issue for the synthesis of zeolites or metal phosphate zeolite analogues. To further investigate the effects of the quaternary ammonium cation in ionthermal syntheses, TMACl was replaced by tetrapropylammonium bromide (TPABr) to form a DES with a melting point below 100 °C. When the solvent was used for the attempted preparation of novel zirconium phosphates, only α-$Zr(HPO_4)_2 \cdot H_2O$ (α-ZrP) was formed. However, when some 1,4-dimethylpiperazine (DMP) was added to the initial mixture, a new layered zirconium phosphate, denoted as $ZrPO_4$-DES8, was successfully synthesized. The crystal structure for the new solid product was determined from single-crystal X-ray diffraction (XRD) data. In addition, we investigated the lubricant properties for the two layered compounds by means of a point contact test. To understand the friction behavior of the layered materials, the states of the mating surface of the steel balls and the solid samples before and after the friction tests were studied by powder XRD, scanning electron microscopy (SEM), and energy-dispersive X-ray spectrometry (EDS).

Experimental Section

Raw Chemicals. Orthophosphoric acid (85 wt % in water), zirconium(IV) oxychloride octahydrate (99 wt %, Fluka), hydrofluoric acid (40 wt % in water), 1,4-dimethylpiperazine (DMP; 98 wt %, Aldrich), tetrapropylammonium bromide (TPABr; 99 wt %, Fluka), oxalic acid dihydrate (99 wt %, Aldrich), graphite (Shanghai Graphite Factory), and MoS_2 (SCM Industrial Chemical Co., Ltd.) were purchased from commercial sources and used in all syntheses without further purification. The base oil employed in this work was mineral oil (100 SN) with a viscosity of 16.27 mm^2/s at 40 °C, a viscosity index of 68, and a flash point of 196 °C. The balls (diameter = 12.7 mm) used in the test were made of GCr15 bearing steel (SAE52100 steel) with an HRc of 59−61.

Synthesis. The typical synthesis condition for $ZrPO_4$-DES8 was as follows: a Teflon-lined autoclave (total volume 23 mL) was charged with DES [made from oxalic acid (1.0 g, 7.94 mmol) and TPABr (3.2 g, 12.01 mmol)], $ZrOCl_2$ (250 mg, 0.76 mmol), H_3PO_4 (177 mg, 1.54 mmol), HF (66 μL, 1.52 mmol), and DMP (175 mg, 1.53 mmol). The autoclave was then heated at 180 °C for 3 days. After the autoclave was cooled to room temperature, the solid product was recovered by dissolution of the eutectic mixture in distilled water and subsequent filtration. The white solid was then washed thoroughly with acetone and dried at room temperature. ***Caution!*** *HF* (*40 wt % in water*) *is very toxic if inhaled, contacted with skin, and swallowed. When used, please wear suitable protective clothing, gloves, and eye/face protection.*

Table 1. Experimental and Crystallographic Data for $ZrPO_4$-DES8

compound	$ZrPO_4$-DES8
empirical formula	$C_3NH_{11}ZrP_2O_9$
fw	358.29
temperature (K)	93
wavelength (Å)	0.710 73
cryst syst	monoclinic
space group	$P2_1/c$
a (Å)	11.372(5)
b (Å)	10.613(4)
c (Å)	9.281(5)
β (deg)	109.236(16)
volume (Å ^{3})	1057.6(8)
Z	4
ρ_{calc} (g/cm^3)	2.250
μ (mm^{-1})	1.378
F(000)	712
cryst size (mm)	0.05 × 0.03 × 0.01
θ range (deg)	3.0 − 27.5
index ranges	$-12 \leq h \leq 14$ $-13 \leq k \leq 13$ $-11 \leq l \leq 10$
reflns collected	6838
indep reflns	2206 [R_{int} = 0.0408]
abs corrn	Multiscan
refinement method	full-matrix least squares on F^2
GOF on F^2	1.178
final R indices [$I > 2\delta(I)$]	R1 = 0.0300, wR2 = 0.0954
R indices (all data)	R1 = 0.0347, wR2 = 0.0979
largest diff peak and hole [e/Å^3]	+0.805 and −0.765

Characterization. Powder XRD patterns were recorded on a Rigaku D/max 2500 diffractometer with Cu Kα_1 radiation (λ = 1.5406 Å) at room temperature. The crystal morphology and size were checked with a JEM-6700F scanning electron microscope. CHN analysis was carried out on an Elementar Vario EL analyzer. Thermogravimetric analysis (TGA) was obtained on a NETZSCH STA409C thermogravimetric analyzer in an air atmosphere with a heating rate of 10 °C/min over the temperature range 30−1000 °C. Mass spectrometric (MS) analysis of the effluent gas was performed with an online-coupled quadrupole mass spectrometer (OmniStar).

Structural Determination. The single-crystal XRD data for $ZrPO_4$-DES8 were collected with a Rigaku MM007/RA and a Mercury CCD with confocal optics, Mo Kα radiation (λ = 0.710 73 Å), and a rotating-anode generator at a temperature of 93 K. All of the data sets were corrected for absorption via multiscan methods. The structures were solved by direct methods and refined by full-matrix least-squares techniques, using the *SHELXS*, *SHELXL*, and *WinGX* packages. Nonhydrogen atoms were refined anisotropically. Crystal data and refinement parameters for the structure determination are presented in Table 1. CCDC 752594 contains the supplementary crystallographic data for this paper.

Lubrication Properties. The antiwear properties of the samples used as additives in the base oil were evaluated with a four-ball tester at 1200 rpm and room temperature (25 °C). The maximum nonseizure loads (P_B) and load-carrying capacities of α-ZrP and $ZrPO_4$-DES8 were determined according to the China National Standard method GB/T3142-90, which is similar to those determined by ASTM D2783. For each sample, they were carefully milled prior to use until an edge length of about several micrometers was obtained. Prior to and after each test, the steel balls were each cleaned with petroleum ether and then dried in air at ambient conditions. The wear scar diameters (WSDs) on the three stationary balls were measured on a digital-reading optical microscope with an accuracy of 0.01 mm in the directions parallel and perpendicular to the sliding motion. Three identical tests were performed for an average so as to

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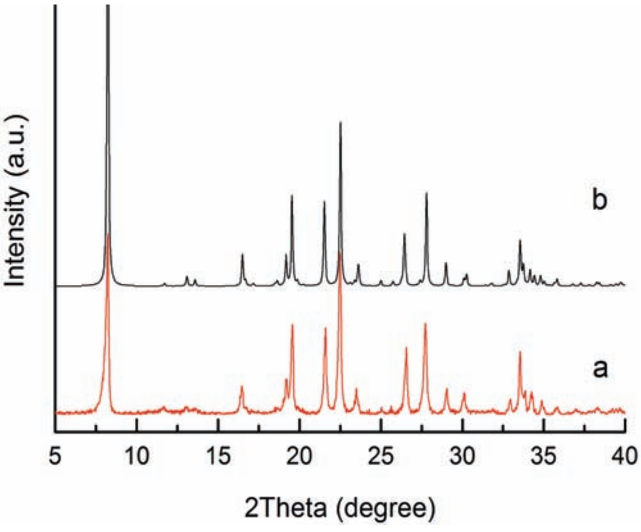

Figure 1. Experimental (a) and simulated (b) power XRD patterns for $ZrPO_4$-DES8.

minimize data scattering, and the estimated errors on the WSD values were less than 1.0%.

Results and Discussion

1. Synthesis and Structural Characterization. A series of syntheses has been performed to investigate the effect of the synthetic conditions on the final products (Table S1, Supporting Information). In the DES comprised of oxalic acid and TPABr, only the layered α-ZrP phase was formed. Phase recognition was achieved by powder XRD (Figure S1, Supporting Information). The templating ability of the tetrapropylammonium (TPA) cation component of this DES was not observed in these syntheses. By contrast, an open-framework zirconium phosphate templated TMA cation was synthesized from a DES consisting of oxalic acid and TMACl.[17] This is likely due to the steric effects produced by the longer chains of the TPA cation compared to the TMA cation. However, such a DES is predominantly an ionic liquid with properties that differ markedly from those of molecular liquids and salts dissolved in molecular solvents. A DES brings with it significant advantages over other types of ionic liquids, particularly its ease of preparation as a pure phase from easily available and cheap components. This feature therefore makes the present DES an excellent choice to be used as an ionic solvent in the ionothermal synthesis of zirconium phosphate materials.

By the initial introduction of some DMP to the initial mixture for the preparation of the α-ZrP phase, a new layered zirconium phosphate, $ZrPO_4$-DES8, was synthesized. Single-crystal XRD analysis indicated that $ZrPO_4$-DES8 crystallizes in the monoclinic space group $P2_1/c$ with the formula $[C_6H_{16}N_2]_{0.5}Zr(H_{0.5}PO_4)_2 \cdot H_2O$. The experimental XRD pattern of $ZrPO_4$-DES8 is in good agreement with the simulated results generated on the basis of the single-crystal structure analysis (Figure 1), proving the phase purity of the as-synthesized product.

The inorganic layer of $ZrPO_4$-DES8 (Figure 2) is similar to that found in α-ZrP (Figure S2, Supporting Information). For each ZrO_6 octahedron, the zirconium atom is octahedrally coordinated by six oxygen atoms from the different phosphate groups, with Zr−O bond lengths in the range of 2.037(3)−2.110(2)Å. For each PO_4 tetrahedron, three of its coordinating oxygen atoms bridge to zirconium atoms with P−O bond lengths in the range of 1.513(2)−1.534(2) Å. The fourth oxygen atom exists in the terminal form of $P{-}O^-$ and P−OH, which interacts with the interlayer protonated DMP and water molecules, with an N···O distance of 2.700 Å and a O···O distance of 2.622−2.955 Å. Compared with the typical α-ZrP compound, $ZrPO_4$-DES8 can be described as a pillared α-ZrP with an organic amine of DMP, where the guest molecules are in a chair conformation to form an organic monolayer and the amino groups are protonated by protons from the −POH groups belonging to two facing layers.

α-ZrP has been intensively studied as a host for intercalation reactions in the past few decades.[1,18] Now a large number of pillared α-ZrP compounds have been produced using postprocessing techniques, where species with sites that can be protonated are the preferred intercalation guests. For these intercalation compounds, it is difficult to obtain highly crystalline materials for structure determination; therefore, the manner of arrangement of interlayer guest molecules is usually estimated from the observed intercalation parameters on the basis of their host crystal structure and the amine molecule dimensions. Generally, it was proposed that a bilayer was formed for monamines and a monolayer for di- or polyamines between layers, and the terminal amino groups are protonated by the −POH groups of adjacent layers.[19−21] For $ZrPO_4$-DES8, it seems that DMP with two amino groups has a manner of arrangement between layers similar to that of di- or polyamine intercalation compounds. However, following the previous intercalation methods,[19,21] the intercalation reaction for α-ZrP in an aqueous DMP or DMP hydrochloride solution could not lead to the $ZrPO_4$-DES8 solid material. Also, on the basis of typical synthetic conditions for $ZrPO_4$-DES8, XRD patterns were recorded for samples after different crystallization times to investigate the ionothermal crystallization process (Figure S3, Supporting Information). Interestingly, at the earlier crystallization process (30 min), the intermediate product is an unknown phase and not the expected α-ZrP compound, and the target product could be quickly formed after reaction for 3 h, indicating that the formation of $ZrPO_4$-DES8 probably proceeded in a manner different from the intercalation reaction of α-ZrP. CHN elemental analysis indicates that the C, N, and H contents are 10.2, 3.8, and 2.9%, respectively, corresponding to a C/N molar ratio of 3.1. This ratio is quite close to that of the free DMP molecule (calculated at 3.0), showing the added DMP retained its integrity in $ZrPO_4$-DES8 between inorganic layers.

The TGA curve of $ZrPO_4$-DES8 consists of three main steps showing a total mass loss of 21.4% from 30 to 650 °C (Figure 3). The first step of ca. 5.7% between 30

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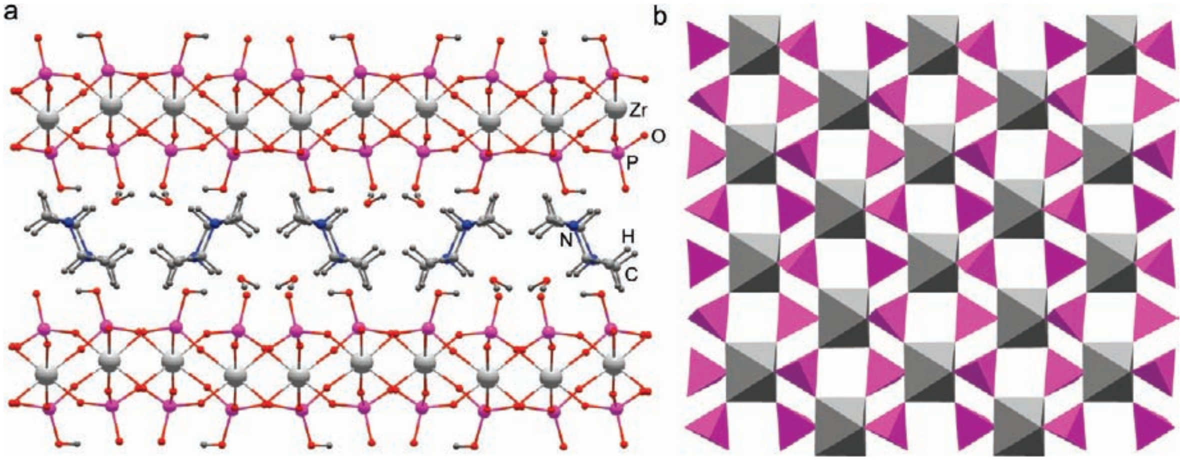

Figure 2. Layered structure of $ZrPO_4$-DES8 viewed parallel to the *c* axis (a) and a single inorganic layer viewed parallel to the *a* axis (b). Color code: PO_4, pink; ZrO_6, gray.

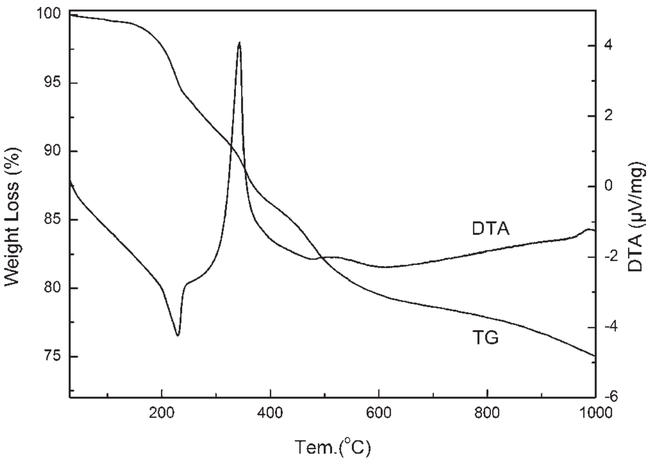

Figure 3. TGA curves for $ZrPO_4$-DES8.

and 230 °C, accompanied with a small endothermic peak, can be attributed to the loss of structural water and surface adsorption water. The weight loss for the second and third steps amounted to 15.7% between 230 and 600 °C, accompanied by a marked exothermic peak, resulting from the removal of organic species between layers with a calculated value of 15.9%. Further heating of the sample shows a gradual weight loss, and the sample was transformed to the ZrP_2O_7 phase (JPCDS 73-2297) at higher temperature. The removal of the water and organic species between layers was confirmed by online MS detection in the effluent gas (Figure S4, Supporting Information). The observed characteristic ion of H_2O (m/z 18) around 210 °C results from the removal of water; at higher temperature (below 600 °C), the MS peaks of $N(CH_3)_3$ (m/z 59), H_2O (m/z 18), CO_2 (m/z 44), and NO_2 (m/z 46) are caused by thermal decomposition of organic species (DMP) and further combustion. The fragment ions of DMP (m/z 114) in the effluent gas have not been observed, showing that the intercalated DMP could not be removed as a whole and was decomposed into small organic molecules upon heating. Powder XRD patterns recorded on samples treated with different temperatures (Figure S5, Supporting Information) show that the structure undergoes phase transformation at 250 °C and finally transformed to the ZrP_2O_7 product above 700 °C.

Table 2. P_B Values and WSDs in Oil and Oil + Layered Materials

lubricant	P_B (N)	WSD (mm)
pure oil	470	0.58
oil + 1.0 wt % α-ZrP	598	0.33
oil + 1.0 wt % $ZrPO_4$-DES8	510	0.37
oil + 1.0 wt % MoS_2	549	0.37
oil + 1.0 wt % graphite	510	0.42

2. Lubrication Properties. Wear limits the life span of many mechanical devices with moving parts; thus, lubricants are frequently used for reducing wear. When service conditions in tribological applications become severe, solid lubricants may be the only choice for controlling friction and wear. Most solid lubricants and additives in liquid lubricants, which include graphite and MX_2 (M = Mo or W; X = S or Se), belong to a specialized class of materials known as lamellar solids.[22−24] Recently, studies showed that α-layered sodium disilicate (α-$Na_2Si_2O_5$) exhibits good tribological properties as an additive in liquid paraffin.[25] Considering that both α-ZrP and $ZrPO_4$-DES8 have similar inorganic layered structures, whether or not the two compounds will also exhibit good tribological behavior as additives in liquid lubricants will be interesting to determine. In this regard, some studies that aimed to determine the tribological properties, such as load-carrying and antiwear capacities, of these two layered materials have been carried out.

The P_B value is an important index to evaluate the load-carrying capacity of a lubricant. Data for pure oil and oil + different layered materials are shown in Table 2. It should be noted that using α-ZrP and $ZrPO_4$-DES8 as additives can considerably improve a lubricant's P_B value. The P_B values were improved by 8.5% and 27.2% after $ZrPO_4$-DES8 and α-ZrP were added to oil, respectively. For comparison, the data for graphite and MoS_2 were also measured under identical conditions. Among the four solid lubrication additives, the P_B value for the

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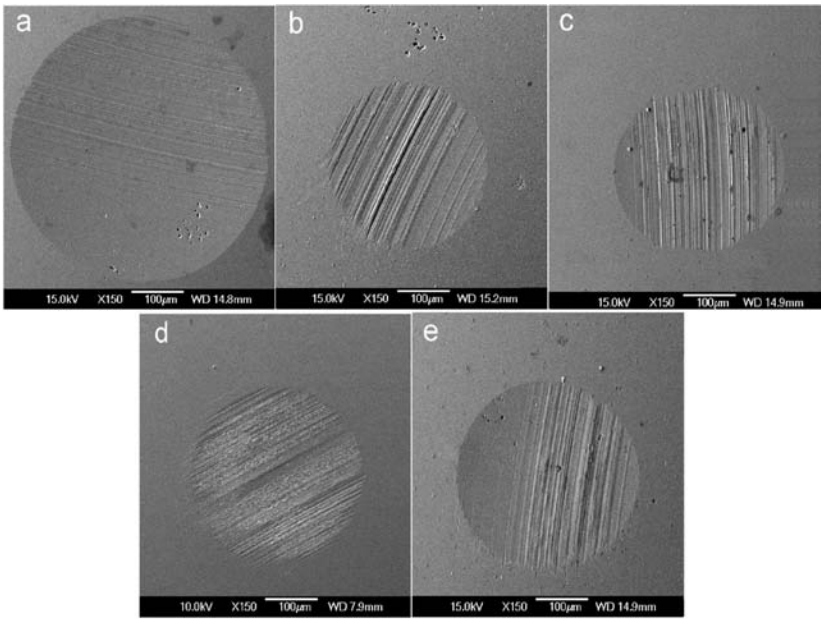

Figure 4. SEM images of worn surfaces on balls lubricated with (a) pure oil and containing different additives: (b) α-ZrP; (c) $ZrPO_4$-DES8; (d) MoS_2; (e) graphite.

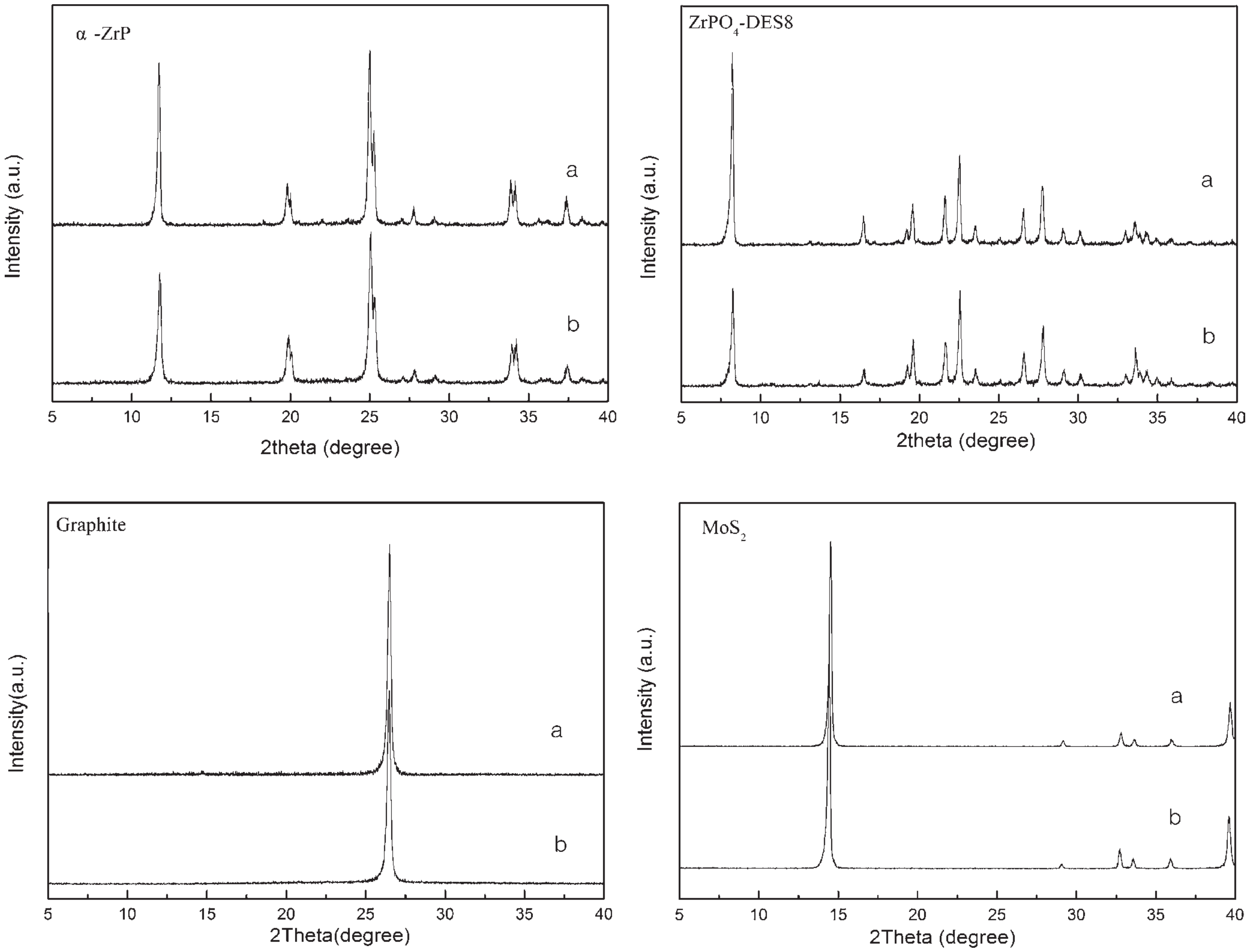

Figure 5. XRD patterns for the four additives before (a) and after (b) antiwear tests.

α-ZrP material was found to be able to reach 598 N, higher than that for typical solid lubrication additives (549 N for MoS_2 and 510 N for graphite), thus showing a good load-carrying capacity.

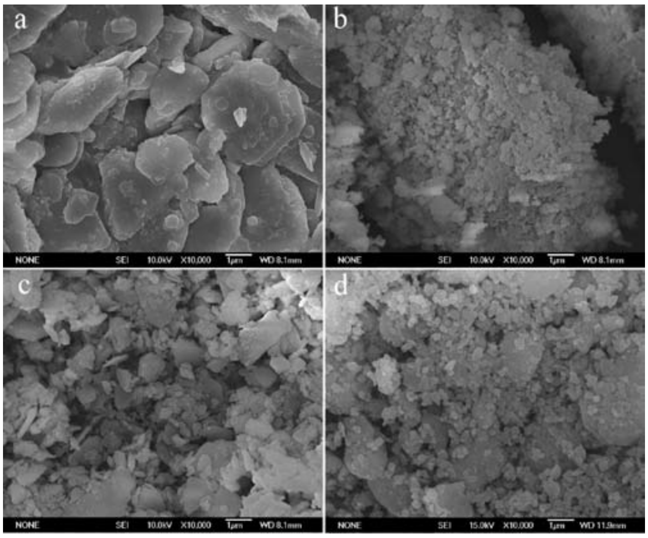

Figure 6. SEM images for the two zirconium phosphates before and after antiwear tests: α-ZrP (a and b); $ZrPO_4$-DES8 (c and d).

The WSD is usually used to evaluate the antiwear property of a lubricant; thus, antiwear tests were performed, and the WSD of the experimental balls were recorded (see Table 2). In all tests, the additives made up 1.0 wt % of the tested material, a value that is based on most industrial applications. It can be seen that the WSDs obviously decreased after the two layered zirconium phosphate materials were added to oil. For α-ZrP and $ZrPO_4$-DES8, the WSDs are 0.33 and 0.37 mm, respectively. These values correspond to decreases of 43% for α-ZrP and 36% for $ZrPO_4$-DES8 based on the pure oil. The observed wear scar area and wear degree in SEM images (Figure 4) also show that the steel ball lubricated with pure oil was damaged more seriously in comparison to oil + additives. The presented results show that both zirconium phosphate materials exhibit excellent antiwear capacities when used as additives in liquid lubricants, particularly in comparison to the typical lurication additives, MoS_2 and graphite.

To understand the friction behavior of the layered materials, the states of the mating surface of the steel balls and the solid samples before and after the friction tests were studied by SEM, XRD, and EDS. The XRD results show that there was no change in the crystalline framework of the two zirconium phosphates (Figure 5) and they maintained their original layered structures. In addition, SEM images (Figure 6) show that the additive underwent severe deformation and fracture after antiwear testing, becoming smaller in size. Some tiny particles in the samples were believed to have resulted from the strong interaction between the steel balls during the friction process. EDS (Figure S6, Supporting Information) shows that, except for iron, no other compositions were detected on the wear scar surface of the steel balls. This indicates that no chemical reactions between the additive and steel ball took place to form a protective film on the rubbing surfaces. On the basis of these experimental results, we are inclined to believe that the friction behavior of a layered zirconium phosphate proceeds with a third-body model; it has been speculated for years that "third bodies" control the friction and wear behavior of solid lubricants.[26,27] In the friction process, once the thickness of the lubricant film (1−100 nm) is less than that of the additive particles, a third body will be formed. The third body in our case is thought to be composed of a mixture of oil, wear particles, and tiny zirconium phosphate particles. As shown in the SEM images (Figure 4), in comparison to the surfaces lubricated with pure oil, the rougher surfaces (featuring many thick and deep furrows) rubbed with oil + additives probably are associated with the dragging of agglomerated and compressed particles, as well as wear debris in the interface. The straight asperity contact is limited by the presence of additive particles, which are partially confined in the valleys of the contacting surfaces and can be furnished from the valleys to the contact surface, thereby improving the friction behavior.

Conclusion

In conclusion, DES made from oxalic acid and TPABr could be used as an ionic reaction medium for the synthesis of zirconium phosphate materials in the presence of an organic amine, in which the structure-directing ability of the TPA cation could not be observed. Following the addition of DMP, a new layered zirconium phosphate was obtained by using DMP as a template or SDA. Its inorganic layer is similar to that found in α-ZrP, and it can also be regarded as a DMP pillared α-ZrP compound. Interestingly, the two layered zirconium phosphate materials, α-ZrP and $ZrPO_4$-DES8, as additives in a liquid lubricant, exhibit excellent friction behavior with higher load-carrying and antiwear capacities in comparison to typical lubricant additives such as MoS_2 and graphite. The friction behavior of the two layered materials in our case could be understood by using a third-body model.

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Supporting Information Available: Table of detailed synthetic conditions, powder XRD patterns, MS spectrum, view of an α-ZrP inorganic layer, EDS, and a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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