

Synthesis, characterization and intercalation property of layered zirconium benzylamino-*N,N*-dimethylphosphonate phosphate materials

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ABSTRACT

Layered zirconium benzylamino-*N,N*-dimethylphosphonate phosphate (ZBMPA) was prepared by the reaction of zirconyl chloride with benzylamino-*N,N*-dimethylphosphonic acid (H₂BMPA) and phosphoric acid in the presence of hydrofluoric acid. The intercalation of *n*-alkylamines (*n*-butylamine, *n*-heptylamine and *n*-decylamine) into ZBMPA was primarily investigated at room temperature. These materials were characterized by elemental analysis, ICP, XRD, SEM, FT-IR, Raman spectra, TG and DSC. The composition of ZBMPA is Zr(HPO₄)(C₆H₅CH₂N(CH₂PO₃)₂)_{0.5} · 2.0H₂O. The interlayer distance of ZBMPA, *n*-butylamine, *n*-heptylamine and *n*-decylamine intercalation compounds is 2.03, 2.58, 2.52 and 3.17 nm, respectively. ZBMPA and the *n*-alkylamine intercalation compounds are different in the morphology and vibration spectra. Thermogravimetric analyses of all materials obtained reveal three step mass losses at temperatures of up to 1000 °C. These results indicate that *n*-alkylamines are intercalated into the galleries of host ZBMPA.

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1. Introduction

Zirconium phosphate, phosphonate and phosphonate phosphate have been the object of a growing interest in the fields of ion exchange [1,2], catalyst or catalyst support [3,4] for their desirable properties of high thermal stability and structural versatility.

Organic derivatives of α -zirconium phosphate (Zr(HPO₄)₂ · H₂O) were synthesized by direct reaction of tetravalent zirconium ions with organophosphoric or phosphonic acids in 1978, this method had been applied to preparation of layered compounds with different properties and functionalities [5–7]. In recent years, we and several research groups have reported a variety of hybrid zirconium phosphonate phosphates Zr(HPO₄)_{2-x}(O₃P-G)_x · nH₂O ($x = 0-2$, G: organic groups) such as zirconium sulphophenylphosphonate phosphate Zr(HPO₄)_{2-x}(O₃PC₆H₄SO₃H)_x · H₂O [8,9], zirconium sulphotolylphosphonate phosphate Zr(HPO₄)_{2-x}[O₃PC₆H₃(CH₃)SO₃H]_x · H₂O [10], zirconium sulfonated 1,4-phenylenediphosphonate phosphate Zr(HPO₄)_{2-2x}[O₃PC₆H₃(SO₃H)PO₃]_x, zirconium sulfonated 4,4'-bisphenylene(phosphonate) phosphate Zr(HPO₄)_{2-2x}[O₃PC₆H₄(SO₃H)C₆H₄(SO₃H)PO₃]_x [11,12], zirconium [N-(phosphonomethyl)morpholine-phosphate] Zr(HPO₄)[O₃PCH₂-

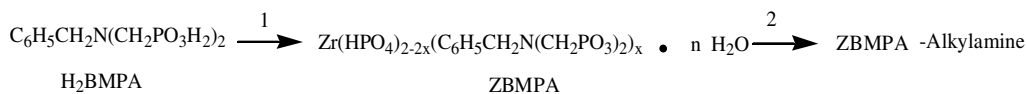
N(CH₂CH₂)₂O] · nH₂O and zirconium [N-(phosphonomethyl)imino-diacetic acid-phosphate] Zr(HPO₄)[O₃PCH₂N(CH₂COOH)₂] · nH₂O [13], zirconium substituted aminoethyl phosphonate phosphate Zr(HPO₄)_{1.35}[O₃PCH₂CH₂N(CH₃)₂]_{0.65} · H₂O, Zr(HPO₄)_{1.35}[O₃PCH₂CH₂NHC(=NH)NH₂]_{0.65} · H₂O and Zr(HPO₄)_{1.35}[O₃PCH₂CH₂NHCH(CH₃)₂]_{0.65} · H₂O [14], these zirconium phosphonate phosphate materials have been applied in heterogeneous catalysis. Interestingly, the organic groups of these materials can be designed for special purpose, and organic/inorganic molar ratio (x value) may vary and optimize from 0 to 2.

Layered zirconium phosphate can also be used as host material to intercalate guest species, such as alkylamines, diamines and poly-amines, alkanols, glycols, urea and its derivatives, hydrazine, piperidine, dimethyl sulfoxide, dimethyl formamide, heterocyclic bases (imidazole, benzimidazole, alcohols and histamine), metal complexes, porphyrins, amino azobenzene [15–23]. These intercalation compounds are very attractive materials, which may be applied in many fields such as special absorbent [24], chemical separation and catalysis [25,26], and as nonlinear optical materials [27]. However, the hybrid zirconium phosphonate phosphate as host material has been paid less attention. Layered zirconium benzylamino-*N,N*-dimethylphosphonate phosphate was prepared (as seen Scheme 1), and the intercalation of *n*-alkylamines into the layered host material was primarily studied in the present paper. Hereafter, the intercalation compound of *n*-butylamine, *n*-heptylamine and *n*-decylamine into ZBMPA is abbreviated to ZBMPA-BA, ZBMPA-HA, ZBMPA-DA, respectively.

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Scheme 1.

2. Results and discussion

2.1. Synthesis, composition and schematic structure of ZBMPA

Zirconium phosphonate phosphate was prepared from a mixture of H₂BMPA and H₃PO₄ under the appropriate reaction conditions. Amorphous zirconium phosphonate phosphate was obtained in the absence of HF. The crystalline zirconium phosphonate phosphate can be prepared by adding a strong complexing agent such as HF. Zr⁴⁺ ions form soluble complexes [ZrF₆]²⁻ with excess HF which can prevent premature precipitation. When [ZrF₆]²⁻ decomposes with loss of HF at elevated temperatures, the hybrid zirconium phosphonate phosphate slowly crystallizes, and it is extremely insoluble. The characteristic diffraction peak becomes increasingly sharp as HF/Zr ratio increases (as shown by XRD in Fig. 1), indicating an increase in crystallite size and the crystalline degree of ZBMPA, but HF/Zr ratio is greater than 15:1, crystalline zirconium phosphonate phosphate has not been obtained for 30 days. Maybe, low HF/Zr ratio gives a low concentration of [ZrF₆]²⁻ in the reaction mixture and a relatively rapid precipitation of ZBMPA, high HF/Zr ratio gives a high concentration of [ZrF₆]²⁻ in the reaction mixture and a relatively slow precipitation of ZBMPA.

Using a polypropylene vessel, with HF/Zr = 8, reaction mixtures with [Zr⁴⁺] = 0.1, 0.2 and 0.4 M were prepared and the reaction carried out at 70 °C as described in Section 3. At higher Zr⁴⁺ concentration, the rate of precipitation of ZBMPA is presumably faster, and prevents the growth of larger crystals observed at lower Zr⁴⁺ concentration.

Reaction mixtures with [Zr⁴⁺] = 0.1 M and HF/Zr = 8 were prepared in glass and polypropylene vessels carried out at 70 °C as described in Section 3. The reaction of HF with the silicate in the glass vessel reduces the degree of complexation of the Zr⁴⁺ by F⁻ ions and accelerates the precipitation process, resulting in smaller crystallites than in the polypropylene vessel. In addition, the majority of the dissolved silicon is slowly removed as a volatile silicon fluoride in the glass vessel, the possibility of contamination of ZBMPA by silica cannot be excluded.

Reaction mixture with [Zr⁴⁺] = 0.1 M and HF/Zr = 8 was prepared in polypropylene vessel carried out at room temperature as described in Section 3. No precipitation was observed after 40

days, presumably the rate of decomposition of [ZrF₆]²⁻ is too slow under these conditions.

In a word, the crystallite size and the crystalline degree of ZBMPA have been shown to depend on a number of factors including the HF/Zr ratio, the concentration of Zr⁴⁺ ions, the material of the reaction vessel and the reaction temperature.

On the basis of C H N elemental analysis, ICP, TG, the composition of ZBMPA is formulated as Zr(HPO₄)[C₆H₅CH₂-N(CH₂PO₃)₂]_{0.5} · 2.0H₂O.

In α-zirconium phosphate, each layer may be regarded as sandwich consisting of a plane of zirconium atoms between two layers of tetrahedral HPO₄²⁻. Three oxygens of each HPO₄²⁻ are linked to three zirconium atoms, while the fourth oxygen bears a proton [28]. If the two phosphonate groups of a diphosphonate are located far from each other, a pillared structure can be formed, where the molecule has one of the phosphonates attached to one layer and the other phosphonate attached to an adjacent layer. Some of these pillared compounds have been made from mixture a diphosphonate and a monophosphonate (or phosphate like phosphoric acid) [1,3,29–31]. In the present paper, the two phosphonates are only three atoms away from each other, so it is almost impossible to form pillared structure. Instead, the two phosphonates might bind to the same layer. The interlayer distance as observed by X-ray diffraction is 2.03 nm, which is similar to the calculation value of 2.07 nm when benzylamino groups of adjacent two layers face opposite each other, suggesting that ZBMPA is a layered structure similar to that of α-zirconium phosphate, the benzylamino groups (A) and P–OH (B) arranged as ABBABB alternatively (Fig. 2). Although the lamellar surface –OH of α-zirconium phosphate are partially substituted by benzylamino groups of ZBMPA, which may accept guest molecules to form intercalation compounds.

2.2. Morphology of ZBMPA and the *n*-alkylamine intercalation compounds

SEM images of ZBMPA and its *n*-butylamine intercalation compound have significant difference in morphology (as shown in Figs. 3a and 3b). ZBMPA consists of thin plates with the size of 5–10 μm. The *n*-butylamine intercalation compound appears to be aggregate

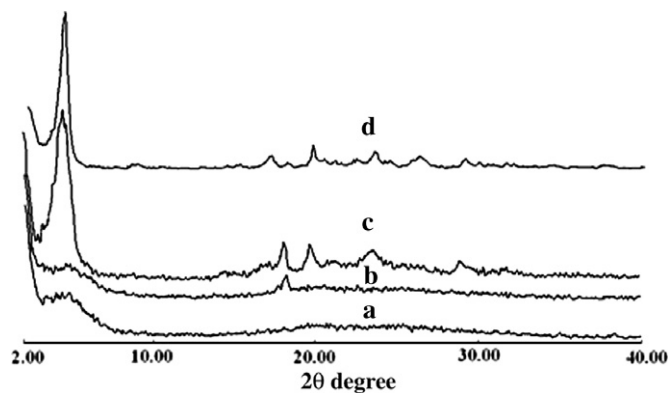


Fig. 1. XRD pattern of ZBMPA (mole ratio of HF/Zr) 1 (a), 2 (b), 5 (c) and 10 (d).

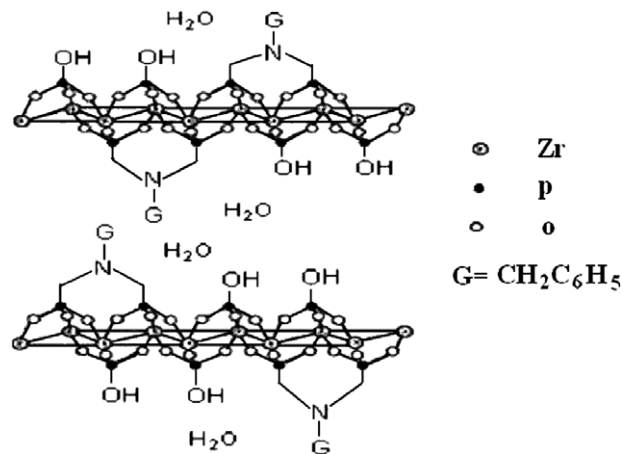


Fig. 2. Schematic structure representation of ZBMPA.

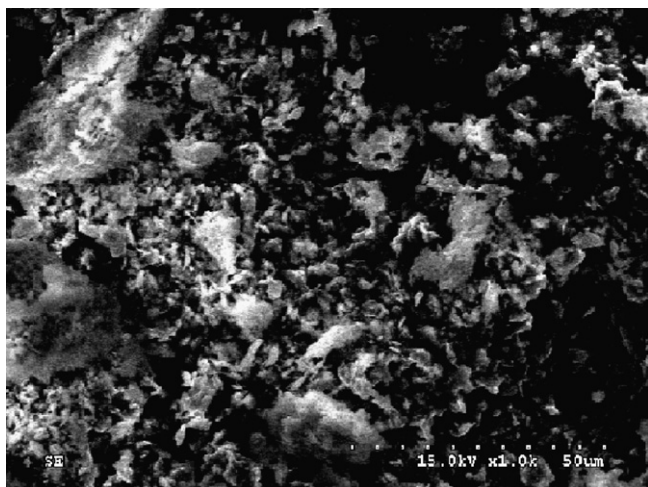


Fig. 3a. SEM image of ZBMPA (1000 times).

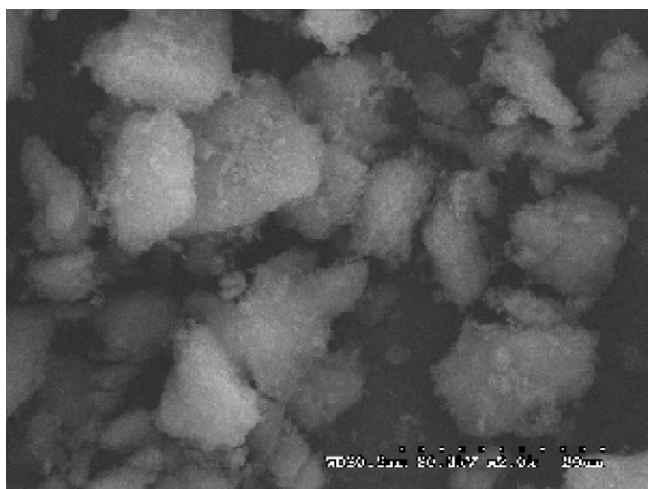


Fig. 3b. SEM image of ZBMPA-BA (2000 times).

of much small particles, the morphology of the other alkylamine intercalation compounds is similar to that of the *n*-butylamine intercalation compound.

2.3. XRD of ZBMPA and the *n*-alkylamine intercalation compounds

The characteristic diffraction peak with the interlayer distance of 2.03 nm of ZBMPA in Fig. 4a appears at $2\theta = 4.3^\circ$, which is much larger than that ($d = 0.76$ nm) of α -zirconium phosphate, and is attributed to the effect of benzylamino groups in the interlayer region. The new major diffraction peak of *n*-butylamine intercalation compound splits into two peaks, indicating the intercalation compound contains more than two phases with two different interlayer distance, but the lowest diffraction peak with the interlayer distance of 2.58 nm in Fig. 4b is observed at $2\theta = 3.4^\circ$. The *n*-heptylamine intercalation compound gives a single peak with the interlayer distance of 2.52 nm in Fig. 4c at $2\theta = 3.5^\circ$. The new major diffraction peak of the *n*-decylamine intercalation compound is similar to that of the *n*-butylamine intercalation compound, the lowest diffraction peak with the interlayer distance of 3.17 nm in Fig. 4d is observed at $2\theta = 2.8^\circ$. The characteristic diffraction peak of host ZBMPA disappears in all intercalation compounds. Thus the X-ray powder diffraction patterns clearly demonstrate that alkylamines are intercalated into the galleries of host ZBMPA and

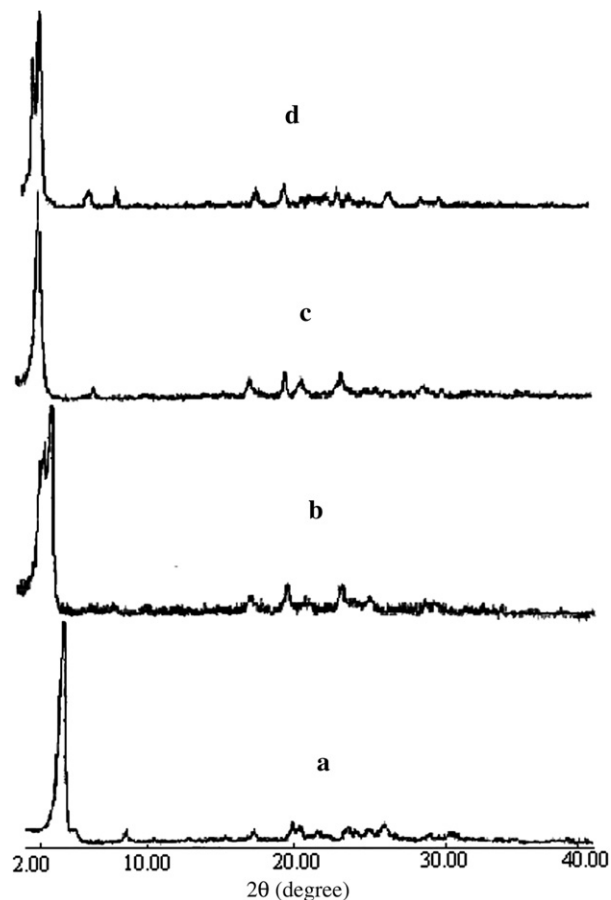


Fig. 4. XRD patterns of ZBMPA (a), ZBMPA-BA (b), ZBMPA-HA (c) and ZBMPA-DA (d).

form intercalation compound along with the expansion interlayer distances at low angles [32].

2.4. Infrared and Raman spectra of ZBMPA and the *n*-alkylamine intercalation compounds

The character of the interactions between the guest molecules and the host ZBMPA layers in the intercalation compounds was studied using FT-IR and Raman spectra.

The two bands near 2928 and 2856 cm^{-1} are due to asymmetric and symmetric stretching vibrations of the NH_3^+ , the corresponding deformation vibration being observed at about 1560 cm^{-1} in the infrared spectra of the intercalation compounds, which clearly indicates that some proton transfer from host ZBMPA layers to alkylamine has taken place. Note that, the stretching vibration of $-\text{NH}_2$ observed at about 3280 cm^{-1} in the intercalation compounds is probably overlapped by the stretching vibration of P–OH, and the band at 1632 cm^{-1} can be caused either by the deformation vibration of $-\text{NH}_2$ or by the deformation vibration of cointercalated H_2O in the infrared spectra, indicating that proton transfer from host ZBMPA layers to alkylamine is incomplete. The band at 1250 cm^{-1} is caused by stretching vibration of C–N or in-plane deformation vibration of P–OH. The bands at 980 cm^{-1} can be attributed to out-plane deformation vibration of P–OH in the infrared spectra. Suggesting that some alkylamine molecules are involved in NH_3^+ ionic bonding to PO^- of the host ZBMPA layers, the other alkylamine molecules are involved in NH_2 van der Waals bonding to POH of the host ZBMPA layers.

The FT-IR and Raman spectra of the host ZBMPA and the intercalation compounds exhibit many common features. The strong

bands near 1160 and 1050 cm^{-1} are probably caused by stretching vibration of P–O in the infrared spectra, these bands are in good with 1155 and 1052 cm^{-1} in the Raman spectra. The multiple bands between 2856 and 3100 cm^{-1} can be assigned to the stretching vibration of saturated hydrocarbon and arene C–H in the infrared and Raman spectra. The band at 1460 cm^{-1} is due to the deformation vibration of C–H in the infrared spectra, and the corresponding band is shifted to 1435 cm^{-1} in the Raman spectra. The characteristic band at 699 cm^{-1} is the result of deformation vibration of mono-substituted arene C–H in the infrared spectra (see Figs. 5 and 6).

2.5. TG–DSC of ZBMPA and the *n*-alkylamine intercalation compounds

The TG curve of ZBMPA indicates three step mass losses at temperatures of up to 1000 °C, as shown in Fig. 7a, the DSC curve is in agreement with TG data. The first mass loss at below 250 °C is due to dehydration of interlayer water, the endothermic peaks at 106 and 200 °C corresponding to the loss of water. The second in the range of 250–610 °C is ascribed to decomposition of the organic moiety and dehydration of structural water, the exothermic peaks

at 334 and 509 °C are evidently related to the decomposition of the organic moiety and the condensation of hydroxyl groups. The third at above 610 °C is primarily due to decomposition of the residual organic moiety. The total mass loss is found (cacl.) to be 39.7 (39.3)%.

The TG curve of *n*-butylamine intercalation compound reveals three steps mass loss at temperatures of up to 1000 °C in Fig. 7 b. The first mass loss at below 250 °C is probably assigned to dehydration of interlayer water and desorption of *n*-butylamine, the second in the range of 250–575 °C and the third at above 575 °C are the same as the mass loss of ZBMPA. The total mass loss is found (cacl.) to be 37.5 (37.8)%. The DSC curve clearly confirms all losses, the endothermic peaks at about 110 and 186 °C, and the exothermic peaks at about 332, 524 and 621 °C, respectively. The similar TG curves of *n*-heptylamine and *n*-decylamine intercalation compounds are obtained, the total mass loss is found (cacl.) to be 45.7 (45.2) and 42.3 (41.9)%, as shown in Fig. 7c and d. The intercalation of alkylamine into the galleries of host ZBMPA is also confirmed by TG–DSC. Interestingly, the TG–DSC measurements show very similar results for the *n*-butylamine intercalation compound and the compound without intercalation. Butyl amine is volatile and is expected to escape from the host very easily when heated.

2.6. Arrangement of the *n*-alkylamine in the interlayer region of ZBMPA

It is very difficult to prepare a single crystal of intercalation compound suitable for the diffraction analysis. The X-ray powder diffraction patterns are in addition influenced by a strong preferred orientation. Therefore, the arrangement of guest molecules in the interlayer region is usually suggested on the basis of steric demands of the guest molecules, the composition of intercalation compound, the experimentally found interlayer distance and host layer thickness.

Combination of elemental and thermogravimetry analysis, the compositions of intercalation compounds are $\text{Zr}(\text{HPO}_4)[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3)_2]_{0.5} \cdot 0.34\text{BA} \cdot 0.4\text{H}_2\text{O}$, $\text{Zr}(\text{HPO}_4)[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3)_2]_{0.5} \cdot 0.28\text{HA} \cdot 1.1\text{H}_2\text{O}$ and $\text{Zr}(\text{HPO}_4)[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3)_2]_{0.5} \cdot 0.25\text{DA} \cdot 0.66\text{H}_2\text{O}$, respectively.

When the alkyl chain of amine has a trans, trans conformation and the guest molecules are intercalated perpendicular to the host layers, the length of alkyl chain should increase by 0.127 nm for each additional carbon atom [33], in comparison with observation value of the interlayer distance, the calculation value of the interlayer distance for *n*-butylamine, *n*-heptylamine, *n*-decylamine intercalation compound is 2.54, 2.92 and 3.30 nm, respectively.

On the basis of these results, there are more than two phases in the *n*-butylamine intercalation compound, and they are probably different in the arrangement and the content of *n*-butylamine in the interlayer space. But there is single phase in the *n*-heptylamine intercalation compound, *n*-heptylamine may be arranged monolayer according to the interlayer distance. The arrangement of *n*-decylamine intercalation compound is similar to that of the *n*-butylamine intercalation. This is in striking contrast that alkylamines usually form an inclined bilayer in interlayer regions of α -zirconium phosphate and zirconium phosphonate [34,35].

3. Experimental

3.1. Synthesis of zirconium benzylamino-*N,N*-dimethylphosphonate phosphate

Benzylamino-*N,N*-dimethylphosphonic acid $(\text{H}_2\text{O}_3\text{PCH}_2)_2\text{-NCH}_2\text{C}_6\text{H}_5$ was synthesized according to Ref. [36]. A white solid was recrystallized from ethanol-water (1:1, v/v) in yield of 83%.

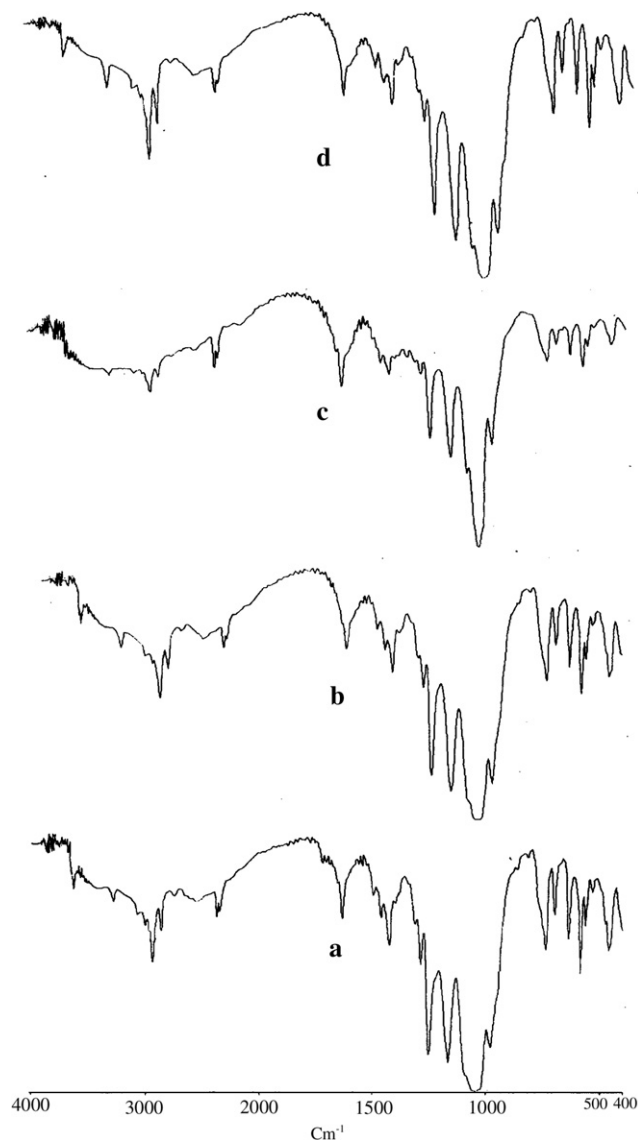


Fig. 5. FT-IR spectra of ZBMPA (a), ZBMPA-BA (b), ZBMPA-HA (c) and ZBMPA-DA (d).

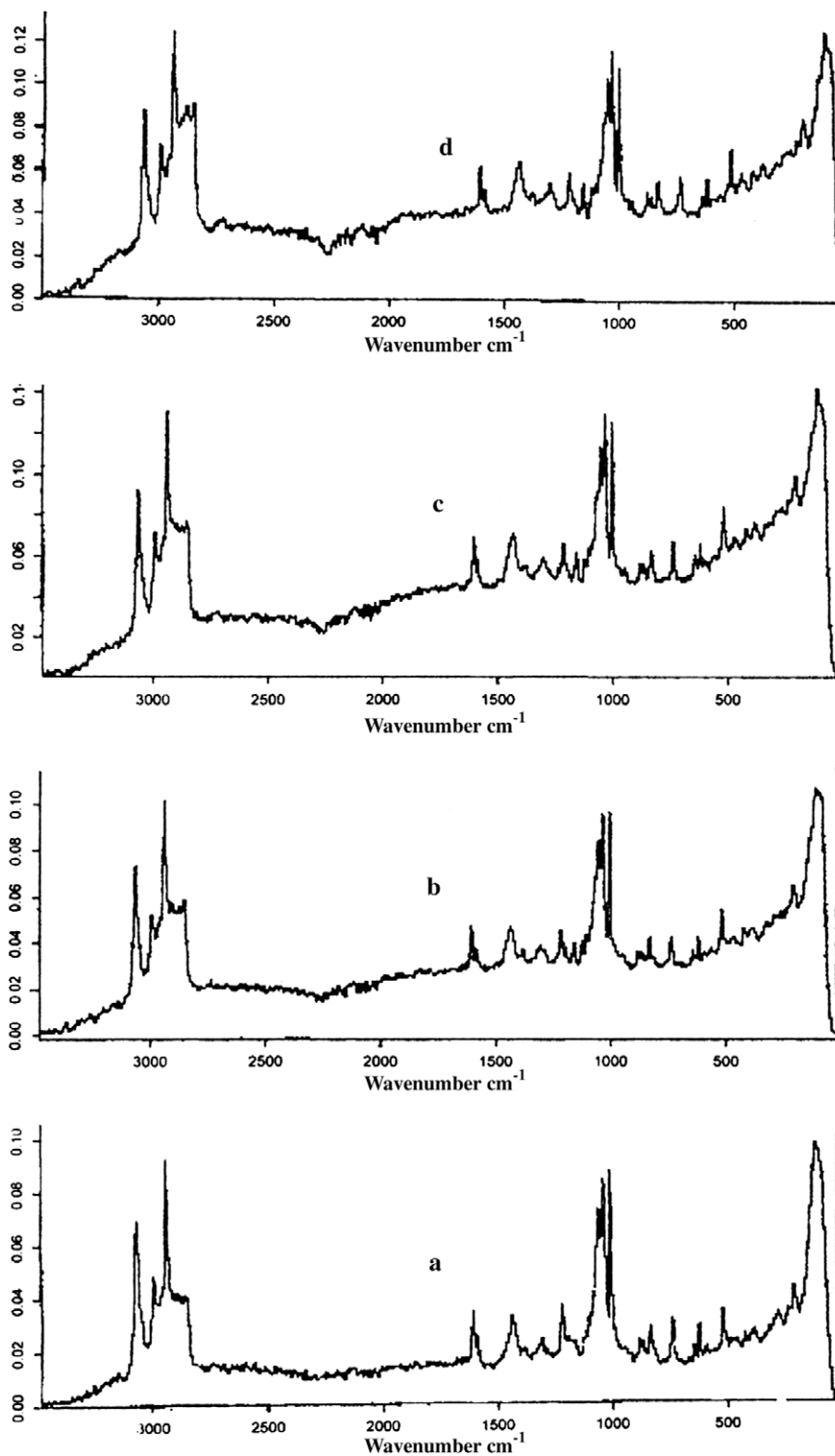


Fig. 6. Raman spectra of ZBMPA (a), ZBMPA-BA (b), ZBMPA-HA (c) and ZBMPA-DA (d).

m.p.: 247–249 °C, and the purity was confirmed by NMR and elemental analysis. Elemental analysis for $C_9H_{15}NO_6P_2$: found (cacl.) C 36.50 (36.62), H 5.08 (5.12), N 4.74 (4.78)%. 1H NMR: δ = 7.30–7.35 ppm (C_6H_5 , m, 5H), 4.20 ppm (ph- CH_2-N , s, 2H), 3.46–3.50 ppm (N- CH_2-PO_3 , d, 4 H). ^{31}P NMR: δ = 8.19 ppm.

$ZrOCl_2 \cdot 8H_2O$ (20 mmol) was dissolved in 50 ml of distilled water, followed by the addition of 0.16 mol of 40% HF, then

10 mmol of H_2BMPA and 40 mmol of 85% H_3PO_4 dissolved in 200 ml of distilled water were added with stirring, the reaction mixtures had been stirred at 70 °C for 72 h in polypropylene vessel, white solid was centrifuged, washed with distilled water to pH 5 and dried in vacuo, ZBMPA was obtained in yield of 66% [10]. Elemental analysis for $ZrC_{4.5}H_{10.5}N_{0.5}O_9P_2$: found (cacl.) Zr 24.61 (24.73), C 14.53 (14.65), H 3.01 (2.92), N 1.84 (1.90)%.

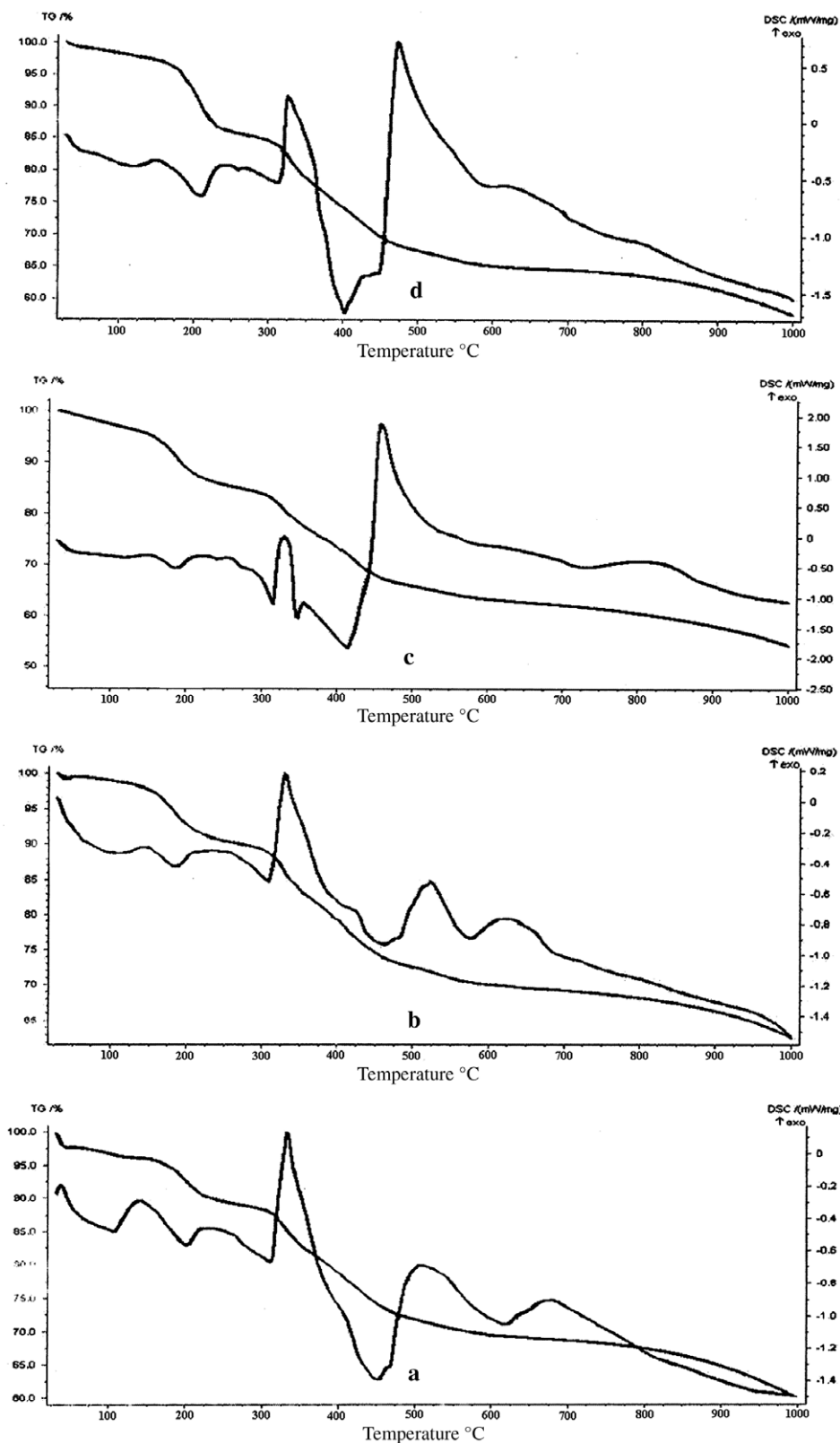


Fig. 7. TG–DSC curve of ZBMBA (a), ZBMBA-BA (b), ZBMBA-HA (c) and ZBMBA-DA (d).

3.2. Intercalation reactions

Fifty millilitre of 0.01 mol dm^{-3} of *n*-alkylamines (*n*-butylamine, *n*-heptylamine or *n*-decylamine) was added to 0.5 g of ZBMBA, the mixtures had been shaken at 25°C for 7 d, after

which the solids were centrifuged, washed with petroleum ether and dried at room temperature. Elemental analysis for ZBMBA-BA, ZBMBA-HA, ZBMBA-DA: found (calcd.) Zr 24.88 (25.00), C 19.41 (19.29), H 2.94 (3.05), N 3.17 (3.22)%; Zr 23.62 (23.70), C 20.27 (20.16), H 3.44 (3.52), N 2.76 (2.84)%; Zr 23.63

(23.76), C 21.76 (21.89), H 3.61 (3.56), N 2.80 (2.73)%, respectively.

3.3. Analytical and instrumental procedures

C, H, N elemental analysis were carried out with a Perkin–Elmer 2400 analyzer, and Zr analysis by TPS-7000 ICP analyzer. ^1H and ^{31}P NMR were recorded on a Bruker AV-300 NMR instrument. Micrographs were taken by S3000 scanning electron microscope. FT-IR spectra were recorded on Spectrum GX instrument (KBr pellet). Raman spectra were recorded on Bruker RFS 100/S instrument. X-ray powder diffraction is performed with a D/MAX-3C automatic diffractometer with Cu $K\alpha$ radiation. TG–DSC was performed with Netzsch STA449C thermoanalyzer.

4. Conclusion

Layered zirconium benzylamino-*N,N*-dimethylphosphonate phosphate material $\text{Zr}(\text{HPO}_4)[\text{C}_6\text{H}_5\text{CH}_2\text{N}(\text{CH}_2\text{PO}_3)_2]_{0.5} \cdot 2.0\text{H}_2\text{O}$ was prepared. *n*-Butylamine, *n*-heptylamine and *n*-decylamine are incorporated in the interlayer region of the ZBMPA, which is a new type of hybrid layered material with intercalation performance. Furthermore, the *n*-alkylamine intercalation compound as absorbent will be investigated.

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References

- [1] G. Alberti, U. Costantino, J. Mol. Catal. 27 (1984) 235.
- [2] A.A. Marti, J.L. Colon, Inorg. Chem. 42 (2003) 2830.
- [3] A. Clearfield, D.S. Thakurb, Appl. Catal. 26 (1986) 1.
- [4] I.O. Benfetz, B. Bujoli, L.J. Camus, C.M. Lee, F. Odobel, D.R. Talham, J. Am. Chem. Soc. 124 (2002) 4363.
- [5] G. Alberti, U. Costantino, S. Alluilli, N. Tomassini, J. Inorg. Nucl. Chem. 40 (1978) 1113.
- [6] M.B. Dines, P.M. Digiaco, Inorg. Chem. 20 (1981) 92.
- [7] M.B. Dines, R.E. Cooksey, P.C. Griffith, R.H. Lane, Inorg. Chem. 22 (1983) 3104.
- [8] C.Y. Yang, A. Clearfield, React. Polym. 4 (1987) 3.
- [9] X.K. Fu, B.K. Luo, Q.Y. Lei, Chin. J. Appl. Chem. 8 (1991) 5.
- [10] X.K. Fu, S.Y. Wen, Y.Q. He, Chinese Patent 96117605.9, 1996.
- [11] A. Clearfield, Z. Wang, P. Bellinghausen, J. Solid State Chem. 167 (2002) 376.
- [12] Y. Sui, X.K. Fu, R.Q. Zeng, X.B. Ma, J. Mol. Catal. A Chem. 217 (2004) 133.
- [13] X.B. Ma, X.K. Fu, J. Mol. Catal. A Chem. 208 (2004) 129.
- [14] R.Q. Zeng, X.K. Fu, C.B. Gong, Y. Sui, X.B. Ma, X.B. Yang, J. Mol. Catal. A: Chem. 229 (2005) 1.
- [15] A. Clearfield, Chem. Rev. 88 (1988) 125.
- [16] D. Behrendt, K. Beneke, G. Lagaly, Angew. Chem., Int. Ed. Engl. 15 (1976) 544.
- [17] U. Costantino, J. Chem. Soc., Dalton Trans. (1979) 402.
- [18] L.A. Vermeulen, M.E. Thompson, Nature 358 (1992) 656.
- [19] G.B. Hix, S.J. Kitchin, K.D.M. Harris, J. Chem. Soc., Dalton Trans. (1998) 2315.
- [20] T. Kijima, K. Ohe, F. Sasaki, M. Yada, M. Machida, Bull. Chem. Soc. Jpn. 71 (1998) 141.
- [21] L. Benes, K. Melanova, V. Zima, P. Patrono, P. Galli, Eur. J. Inorg. Chem. (2003) 1577.
- [22] P.L. Gentili, U. Costantino, R. Vivani, L. Latterini, M. Nocchetti, G.G. Aloisi, J. Mater. Chem. 14 (2004) 1656.
- [23] C.V. Kumar, A. Chaudhari, J. Am. Chem. Soc. 122 (2000) 830.
- [24] H. Nakayama, A. Hayashi, T. Eguchi, N. Nakamura, M. Tshuhako, J. Mater. Chem. 12 (2002) 3093.
- [25] G. Alberti, M. Casciola, U. Costantino, R. Vivani, P. Zappelli, Mater. Sci. Forum 91 (1992) 147.
- [26] U. Costantino, J. Inorg. Nucl. Chem. 43 (1981) 147.
- [27] M. Ogawa, M. Takahashi, K. Kuroda, Chem. Mater. 6 (1994) 715. 1063.
- [28] A. Clearfield, G. Smith, Inorg. Chem. 8 (1969) 431.
- [29] A. Clearfield, Curr. Opin. Solid State Chem. 1 (1996) 268.
- [30] G. Alberti, R. Vivani, F. Marmottini, P. Zappelli, J. Porous Mater. 5 (1998) 205.
- [31] A. Clearfield, Z.K. Wang, J. Chem. Soc., Dalton Trans. (2002) 2937.
- [32] M. Danjo, A. Hayashi, H. Nakayama, Bull. Chem. Soc. Jpn. 72 (1999) 2079.
- [33] K. Nakamura, K. Matsuyama, I. Tomita, Y. Hasegawa, J. Incl. Phenom. Mol. Recog. Chem. 31 (1998) 351.
- [34] M.T. Robert, D.K. Ellis, G. Peng, A. Clearfield, J. Chem. Soc. Faraday Trans 81 (1985) 545.
- [35] T. Kijima, S. Watanabe, K. Ohe, M. Machida, J. Chem. Soc., Chem. Commun. (1995) 75.
- [36] K. Moedentzer, R.R. Irani, J. Org. Chem. 31 (1966).