Solvothermal synthesis and removal capacity for hydrogen chloride gas of Zn(OH)(NO$_3$) with a rare (10,3)-*d* net

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Abstract

A basic zinc nitrate, [Zn(OH)(NO$_3$)]$_n$ with a novel framework reported herein is prepared by solvothermal synthesis, and holds a rare three-dimensional (10,3)-*d* net called by Wells. It crystallizes in orthorhombic, space group, *Pna*2$_1$ (No. 33), $a = 9.148(3)$ Å, $b = 7.596(3)$ Å, $c = 5.500(2)$ Å, $Z = 4$, $V = 382.2(2)$ Å^3, $\rho_{calcd} = 2.509$ Mg/m^3, $\mu = 6.290$ mm^{-1}, $3.49 < \theta < 27.51$, $T = 293$ K, $R_1 = 0.029$, w$R_2 = 0.0773$ for 697 ($I > 2\sigma(I)$) of 1728 [$R_{(int)} = 0.0246$] unique reflections and 59 parameters. GOF = 1.073. Interestingly this basic zinc nitrate, [Zn(OH)(NO$_3$)]$_n$ behaves well at removal capacity for hydrogen chloride gas, 20.3 g HCl/100 g, and its framework is not destroyed yet. This adsorption character may be useful for the removal of toxic gases in the environment.
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1. Introduction

The reticular inorganic open framework materials have gained more interest all the time for their potential applications in the field of catalysis, adsorption, and separation and sensor [1], such as aluminosilicate, phosphate, phosphite, arsenicate, germanate, sulphate, and so on [2,3]. Most of the network materials are characteristic of four-connected nodes. Recently, much attention has been paid to such facile and versatile triangular building blocks such as carbonates, borates, 1,3,5-benzenetricarboxylate [4–7,8], for these triangular 3-connected nodes can result in some networks such as (12,3), (10,3), (8,3)-net with intrinsic helical channels. Although nitrate anion possesses such structure parameter, it is seldom observed in the reticular structure except for C$_{60}$[Ag(NO$_3$)]$_5$ in the template of C$_{60}$ [9]. Since hydrosoluble metal nitrate salts exhibit the character of strong ionic bond, it still is of great difficulty to covalently form a network between metal and nitrate.

Solvothermal synthesis acts as a powerful and successful strategy [10], it has widely been used in microporous materials with new reticular structures, such as JDF-20 with 20-membered rings in glycol, GeO$_2$ (FDU-4) with 24-membered rings in DMF solvents, anion framework [(Me$_2$NHCH$_2$)$_2$]·[Ga$_4$P$_5$O$_{20}$H] (Me stands for methyl group) in butanol, [NH$_3$(CH$_2$)$_6$NH$_3$]·[Zn$_4$(PO$_4$)$_2$(HPO$_4$)$_2$] with 20-membered rings in glycol [11–15], to name a few. Thus it is shown that lower polarity, and higher viscosity of the organic solvents than aqueous media seems to be helpful for synthesizing more new phases. So we attempt to obtain complex structure of hydrosoluble metal nitrate in the solvothermal condition of non-aqueous media.

Herein we report on solvothermal synthesis of a basic zinc nitrate [Zn(OH)(NO$_3$)]$_n$ with a novel framework prepared by using organic amine as a structure-directing agent in the non-aqueous media. [Zn(OH)(NO$_3$)]$_n$ has a rare three-dimensional (3D) structure with (10,3)-*d* net called Wells and large adsorption capacity of hydrogen

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chloride gas (20.3 g HCl/100 g). This property may be useful for the removal of toxic gases in environment.

2. Experimental section

2.1. Synthesis

[Zn(OH)(NO$_3$)]$_n$ with (10,3)-*d* net structure was synthesized by solvothermal method. For a typical procedure, 1 mmol Zn(NO$_3$)$_2$ · 6H$_2$O (0.301 g) was dissolved in 10 mL DMF with stirring to form a clear solution. Then 10 mmol TBA (1.01 g) was added to the above transparent solution, stopped stirring and retained for 30 min until the solution formed into a gel. Finally the resulting gel was sealed in a 25-ml teflon-lined bomb, and placed in a oven at 120 °C. After 3 days, the large colorless block crystals were collected and washed with DMF. A suitable single crystal with the size of $0.1 \times 0.1 \times 0.1$ mm was selected for single-crystal X-ray diffraction (XRD) measurement. Elemental analysis (%) calcd. for the title compound: H 0.70, N 9.70, Zn 45.28; found: H 0.97, N 9.62, Zn 45.42, IR spetrum (KBr): v (Br, OH) of terminal hydroxyl group 3507.7 cm^{-1}, 3434 cm^{-1}, v_s (NO$_2$) and v_{as} (NO$_2$) for nitrate group, 1631, 1305 cm^{-1}, v (NO) for nitrate group, 1032.6 cm^{-1}.

2.2. X-ray single-crystal diffraction

The full hemisphere of data was collected on a Brucker SMART Apex CCD diffractometer with Mo$K\alpha$ radiation ($\lambda = 0.71073$ Å). The frames were integrated with the Saint Software Package. The structure was solved by direct method and the subsequent difference Fourier synthesis, and refined by full-matrix least-squares method on F^2 with the SHELXTL (Version 5.10) software package. X-ray data for HNO$_4$Zn, crystal size, $0.1 \times 0.1 \times 0.1$ mm, orthorhombic, space group, *Pna*2$_1$ (No. 33), $a = 9.148(3)$ Å, $b = 7.596(3)$ Å, $c = 5.500(2)$ Å, $Z = 4$, $V = 382.2(2)$ Å^3, $\rho_{calcd} = 2.509$ Mg/m^3, $\mu = 6.290$ mm^{-1}, $3.49 < \theta < 27.51$, $T = 293$ K, $R_1 = 0.029$, w$R_2 = 0.0773$ for 697 ($I > 2\sigma(I)$) of 1728 [$R_{(int)} = 0.0246$] unique reflections and 59 parameters. GOF = 1.073. Further details can be obtained from Fachinformationszentrum Karlsruhe, Hermann-von-Helmholtz-Platz 1, D-76344, Eggenstein-Leopoldshafen, Germany (Fax: + 49 7247 808 132, e-mail: crysdata@fiz-karlsruhe.de) on quoting the depository number CSD-415537.

2.3. Chloride determination

Potentiomatric titration of chloride ion deposited in the adsorbent and the residual HCl of outlet were preformed by Mettler DL-21 titrator with a Ag electrode as a work electrode and 0.1 mol/L and 1×10^{-4} mol/L AgNO$_3$ solution as titrant, respectively.

3. Result and discussion

3.1. Synthesis

The colorless transparent block crystalline products of compound [Zn(OH)(NO$_3$)]$_n$ suitable for single-crystal XRD studies were obtained easily by solvothermal treatment at 120 °C from a *N,N'*-dimethylformamide (DMF) solution containing Zn(NO$_3$)$_2$ · 6H$_2$O, tributylamine. To estimate the role of tributylamine in this reaction, we carried out experiments to find if the mixture did contain it or not. The results showed that the compound [Zn(OH)(NO$_3$)]$_n$ could not be obtained in the absence of tributylamine. Using other organic amines such as triethylamine, tripropylamine instead of tributylamine, the compound [Zn(OH)(NO$_3$)]$_n$ was still obtained. Furthermore, it is shown that the organic amine appears to act as a catalyst in the ionization of water, and produce more hydroxyl ions so as to form a large number of intermediate species, Zn(OH)$^+$, of the compound [Zn(OH)(NO$_3$)]$_n$. We ever attempted to utilize other organic solvents as non-aqueous media such as ethanol, ether and DMSO to prepare the novel phase of Zn(OH)(NO$_3$), and failed to obtain it. Thus it is shown that DMF is an efficient solvent, so that metal centers may bind covalently to nitrates, and form a complex 3D network.

3.2. Structure

The compound [Zn(OH)(NO$_3$)]$_n$ crystallizes in orthorhombic, space group *Pna*2$_1$, $a = 9.148(3)$ Å, $b = 7.596(3)$ Å, $c = 5.500(2)$ Å. The asymmetric unit of this compound [Zn(OH)(NO$_3$)]$_n$ contains seven non-hydrogen atoms, of
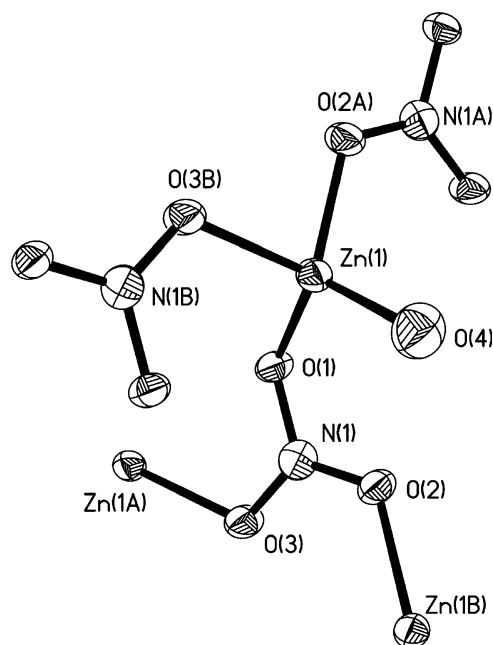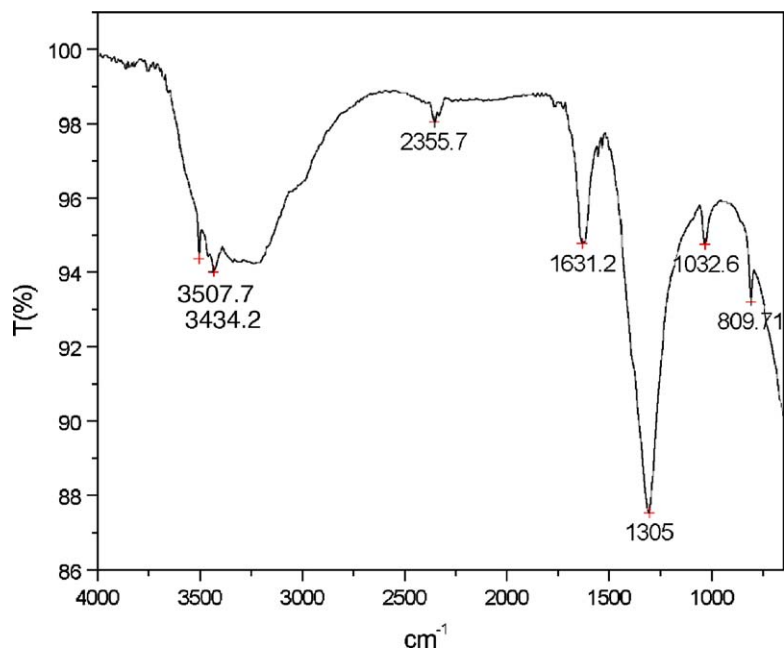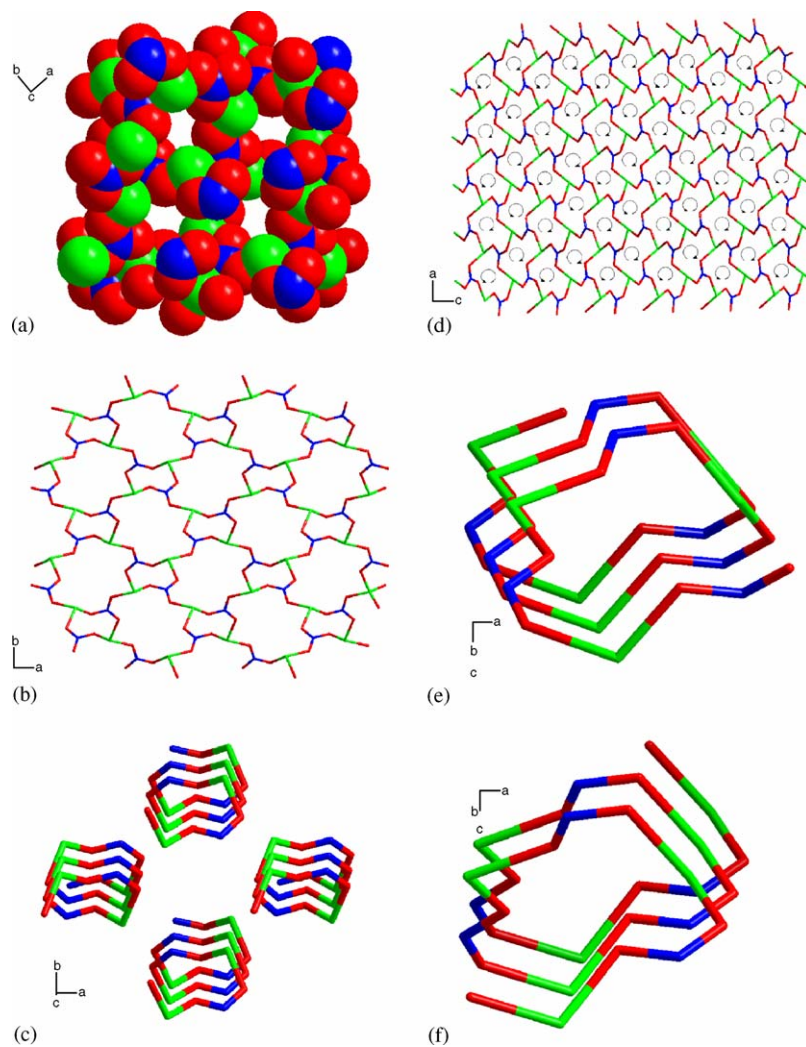

Fig. 1. The molecular structure of [Zn(OH)(NO$_3$)]$_n$, hydrogen is omitted for clarity.

Fig. 2. IR spectrum of $[Zn(OH)(NO_3)]_n$.

Fig. 3. The crystal structure of $[Zn(OH)(NO_3)]_n$: (a) the CPK drawing; (b) the project in the c direction; (c) the intersecting array of left- and right-handed 2_1 helix; (d) the b project in which arrows showing chiral orientation of helix channel; (e) right-handed helix in the b direction; (f) left-handed helix in the b direction.

which six atoms constitute the polymeric framework, another atom belongs to the terminal oxygen atom of hydroxyl group shown in Fig. 1. The Zn atom is tetrahedrally coordinated by four oxygen atoms from three nitrates and one hydroxyl group. The geometric parameters of tetrahedral zinc ion are very unusual, and the bond distances match well with those reported for the compounds of similar geometry [17], where the distances of Zn–O are 1.950, 1.956, 1.982, 2.008 Å respectively, but the bond angles do not, and whose angles of $\angle$O–Zn–O are 112.67(19), 109.61(17), 89.58(16), 117.79(19) individually. In contrast with the compound of $Zn(OH)(NO_3) \cdot H_2O$ with the same composition [18], the difference in their bond parameters may result from different geometries of zinc ions. In the structure of the compound $[Zn(OH)(NO_3)]_n$, the nitrate group exhibits a 3-connected node, of which all binding sites appear in the mono-dentate form, which is further confirmed by the IR spectra as a symmetric unit (Fig. 2) [19]. Such a coordination mode has seldom been observed in other basic zinc nitrate reported [18,20]. Its bond lengths of N–O range from 1.259 to 1.305 Å (O(2)–N(1) = 1.259(7) Å; O(1)–N(1) = 1.305(6) Å, O(3)–N(1) = 1.276(6) Å), its bond angles of $\angle$O–N–O is near to $120°$, slightly different from that of nitrate chelate in $C_{60}[Ag(NO_3)]_5$ [9]. The framework structure of the title compound consists of $ZnO_4(OH)$ tetrahedral units and NO_3 trigonal planer units linked by sharing their oxygen vertices (Fig. 3).

Fig. 3a and 3b shows that a framework made up of $ZnO_4(OH)$ tetrahedral units and NO_3 planar trigonal units belongs to an extended 3D network. Only if the terminal hydroxyl groups are removed, the network exhibits a zeotype structure containing 1D channels of 8-membered rings with the pore size of 7.2×6.5 Å (4.0×3.2 Å calculated as Van der Waals radii). Viewing from the c-axis (Fig. 3b), the project may look as the plane 48^2 net, in which 4-membered ring contain a 2_1-helical chain along the c-axis, and the 4-membered ring of the same chirality arranges in the cross linkage (Fig. 3c). However, Fig. 4a shows the project of the doubled 410^2 net along the a-axis, in which the 4-membered rings only contain a crankshaft chain, but the repeatable unit of this crankshaft chain is similar to such repeatable unit of helical chain in the c project as T_{Zn}–T_N–T_{Zn}–T_N (T is the triangular unit herein), and interestingly it contains two conformational isomers A and B which array in a cross linkage in the structure of $[Zn(OH)(NO_3)]_n$ (Fig. 4b). In the b direction, a project of plane (6,3) net can be seen (Fig. 3d), and each 6-membered ring comprises a 3_1-helix chain (Fig. 3e, 3f). The 6-membered ring constructed from the same chiral chains array alternately along the a-axis (Fig. 3d). These observations indicate that the compound $[Zn(OH)(NO_3)]_n$ possesses a very interesting 3-connected 3D network structure. Only viewing from the c direction, it seems to be one of three nets such as (10,3)-a, (10,3)-d, (10,3)-f. However, compared with those prototypes derived by Wells [16], it is different from them in the a and b project.
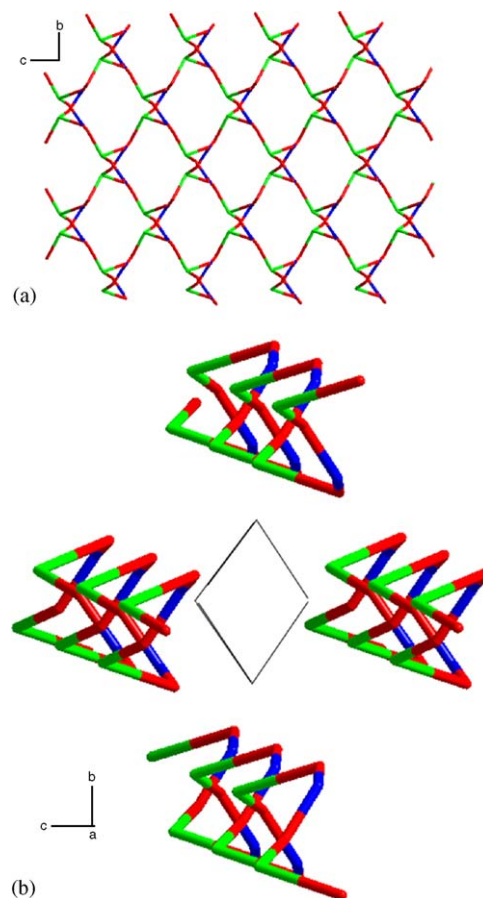

Fig. 4. (a) The a project of $[Zn(OH)(NO_3)]_n$; (b) intersecting array of A and B configuration of crankshaft chain in the a direction.

To fully evaluate the structure of the compound $[Zn(OH)(NO_3)]_n$, and its topology, it is instructive to connect all the extended points only containing zinc atoms and the nitrate N atoms in the structure. This gives a 3-connected net with the zinc (green) and N (blue) atoms at the vertices (Fig. 5a). In this network, these tetrahedral zinc nodes akin to those nitrogen ones act all as 3-connected ones. Both zinc and nitrogen 3-connected nodes are pyramidal ($\angle$N–Zn–N angles are 135, 118, 97.4° and $\angle$Zn–N–Zn angles are 128, 113.8, 111°). In the c direction the project of plane 48^2 net is comparable to that of net (10,3)-a, d, f (Fig. 5b–f), only the nonequivalence between Zn and N atoms as 3-connected nodes reduces four-fold screw axis into two-fold screw axis (Fig. 5c). The fact that both right-hand and left-hand 2_1 helixes arrange in the cross linkage further indicates this network should be the (10,3)-d net (Fig. 5f). Closer examination of this net shows that there are ten smallest 10-gon circuits (the red line marked in Fig. 5a) through each point of N or Zn atom, while the number of such 10-gon circuits including each a linker (Zn–N) of a given N (or Zn) atom are 8, 6 and 6, respectively. This precisely shows it really is the (10,3)-d net predicted by Wells [16]. However, the projects of the net along the [100] and [010] directions exhibit 'double layer' 410^2 net and plane (6,3) net, respectively, different from its
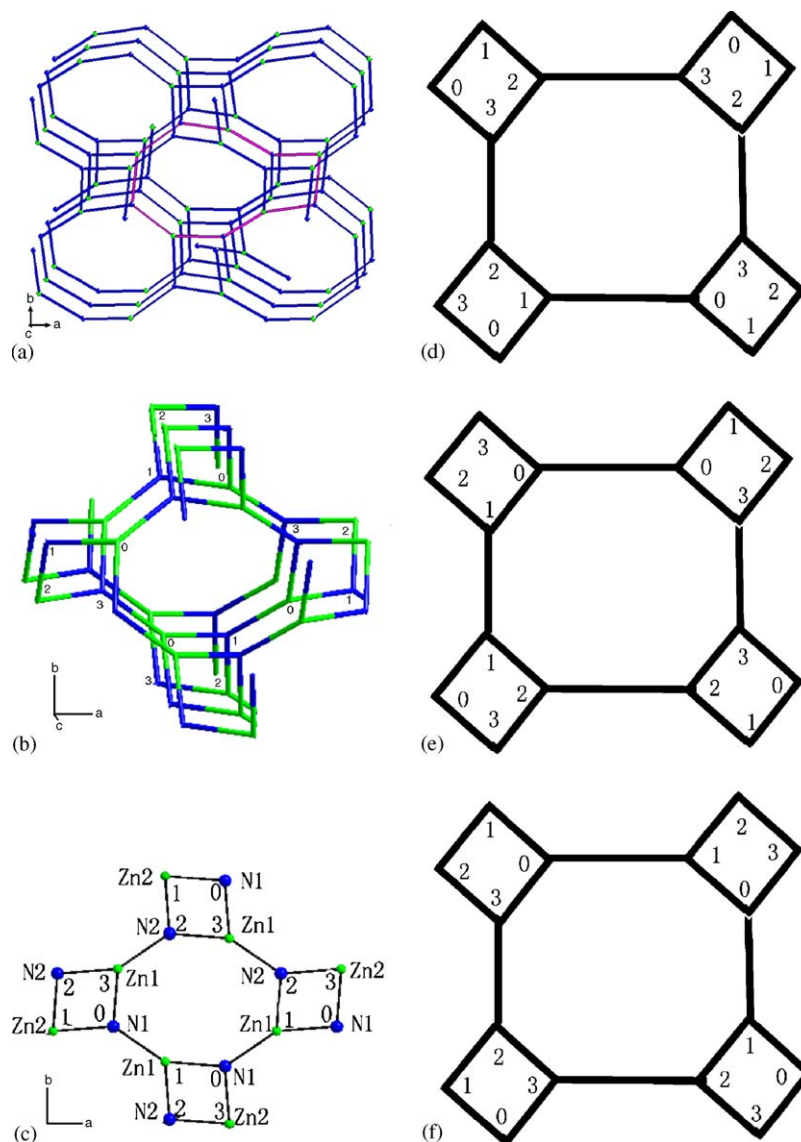
Fig. 5. (a) Topological structure of $[Zn(OH)(NO_3)]_n$, red line showing one 10-membered ring; (b) showing 2_1 helix chain arrangement from topological form of $[Zn(OH)(NO_3)]_n$; (c) the simplified helix chain arrangement project in the c direction when these helix chain motifs in Fig. 5b are marked by such a sequence as 0, 1, 2, 3; (d) helix chain arrangement project of (10,3)-f in the c direction; (e) helix chain arrangement project of (10,3)-a in the c direction; (f) helix chain arrangement project of (10,3)-d in the c direction.

prototype from the geometrical view (Fig. 3d and 4a), this may be related to the pyramidal distortion of 3-connected nodes. These pyramidal remodelments of trigonal planar nodes on the (10,3)-d net result in geometrical change of (10,3)-d net, and enlarge the distinction that should be drawn between geometry and topology. The net appears to be very different from (10,3)-d net, but from a point of topological view, they are identical. This phenomenon was observed by Robson in (10,3)-a net [21].

3.3. Physical properties

TG-DTA analyses of the title compound $[Zn(OH)(NO_3)]_n$ show that there is one step of 46.2% weight loss

along with the corresponding endothermic effects at about $210\,°C$, and this may be attributed to the loss of a nitric acid molecule in its decomposition into the ZnO (Fig. 6c). Thus it is seen that anhydrous $[Zn(OH)(NO_3)]$ with (10,3)-d 3D net may thermally stabilize to $210\,°C$. Compared with the layered hydrate $[Zn(OH)(NO_3)]\cdot H_2O$, it does not exhibit phase transformation.

To evaluate the chemical adsorption capability of HCl gas for the title compound at room temperature, we do such an experiment that a N_2 dry gas mixed with 2000 ppm dry HCl $(3.25\,g/m^3)$ runs through the cleaning trap $(\phi = 1.0\,cm)$ filled with $10\,g$ $[Zn(OH)(NO_3)]/50\,g$ glass wool at a flux speed of $2\,cm/s$. The contents of chloride ion absorbed in the absorbent and the residual HCl
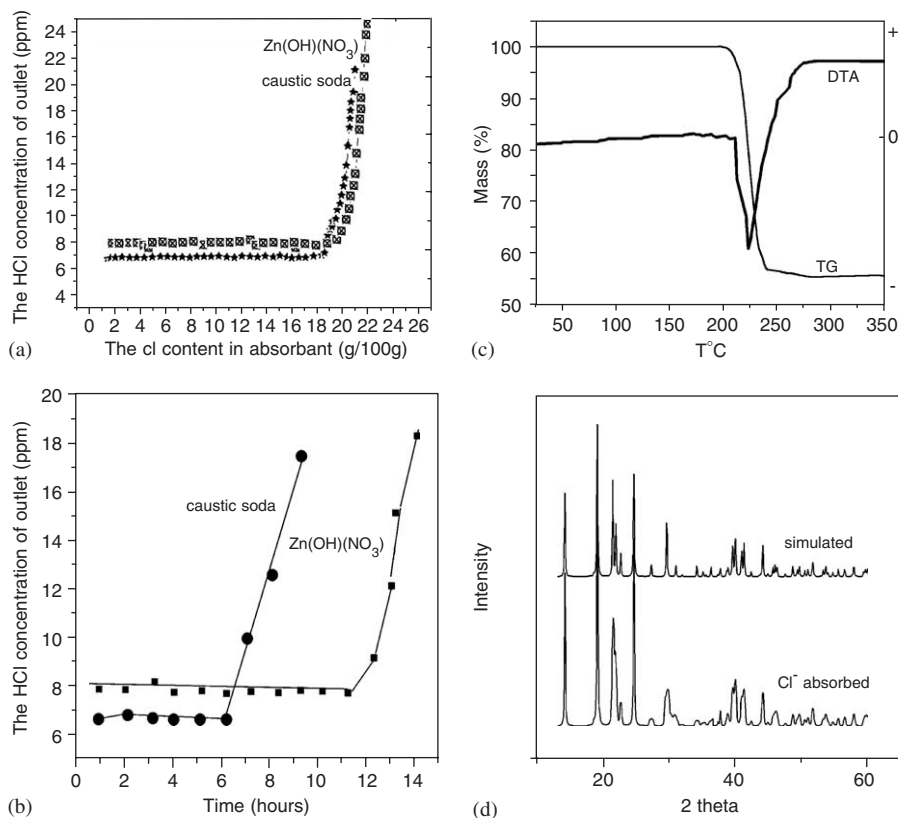
Fig. 6. (a) Absorbed capacity-dependant breakthrough curve of of [Zn(OH)(NO$_3$)]$_n$ and caustic soda illustrated by the residual HCl content of trap outlet vs. chloride ion contents absorbed in the absorbent; (b) time-dependant breakthrough curve of [Zn(OH)(NO$_3$)]$_n$ and caustic soda expressed by the residual HCl content of trap outlet vs. the durable time of adsorbents, The thermal-analytic curves of [Zn(OH)(NO$_3$)]$_n$; (b) XRD pattern of [Zn(OH)(NO$_3$)]$_n$ after HCl gas is absorbed.

content of trap outlet are measured by potentiometric titration. The results showed in Fig. 6a and b indicate that this material is comparable to caustic soda in terms of both efficiency and effective capacity for hydrogen chloride adsorption. The title compound achieves an effective capacity of 20.3 g Cl/100 g of its as-synthesized product with a concentration of residual HCl in the cleaned outlet gas of <10 ppm, and generally keeps outlet concentration in the 7–8 ppm limit as available in Fig. 6a. This effective capacity corresponds to a conversion of approximately 82.56%, and the time to breakthrough of 100 g [Zn(OH)(NO$_3$)] was about 12 h (Fig. 6b). To our surprise, the basic zinc nitrate [Zn(OH)(NO$_3$)]$_n$ does not act only as a base to remove the HCl molecule, but it also retains its perfect structure after the removal of HCl, indicated further by XRD (Fig. 6d). From its structure, its static channel is too small to adsorb into the HCl molecule. However, its lager adsorption capacity seems to suggest that this reaction does not only occur on its surface. The IR spectrum of its adsorbed samples further showed the characteristic of hydroxyl group or water is weakened sharply. Furthermore, we do such a hypothesis that this spring-like reactive structure might absorb the HCl gas in the swollen form, then react with the hydroxyl group, and release equivalent water

molecules. This water is then taken away by a dry gas flux simultaneously. This hypothesis can give a good explanation for its XRD pattern.

4. Conclusion

A basic zinc nitrate, [Zn(OH)(NO$_3$)]$_n$ with novel frameworks reported herein is prepared by solvothermal synthesis, and holds a rare 3D Wells'(10,3)-d net. Interestingly this basic zinc nitrate, [Zn(OH)(NO$_3$)]$_n$ behaves well at removal capacity for hydrogen chloride gas, and its framework is not destroyed yet. This adsorption character may be useful for the removal of toxic gases in the environment.

Appendix. Supplementary materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2006.01.039.

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