Supplementary Information

Disproportionation of hypophosphite and phosphite

Dapeng Liu,[a,b,c] Xiang Li,[c] Ling Wei,[b] Tingting Zhang,[b] Anjie Wang,[c] Chenguang Liu,[b] Roel Prins[d,*]

a College of Science, China University of Petroleum (East China), Qingdao 266580, PR China
b State Key Laboratory of Heavy Oil Processing, College of Chemical Engineering, China University of Petroleum (East China), Qingdao 266580, PR China
c State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, PR China
d Institute of Chemical and Bioengineering, ETH Zurich, 8093 Zurich, Switzerland

*Corresponding author
E-mail address: **prins@chem.ethz.ch** (R. Prins)

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An indication of what happens with the water that does not escape to the gas phase can be obtained from the stoichiometry of the solid and gaseous products. Heating NaH_2PO_2 leads to the formation of solid sodium phosphites and phosphates and gaseous PH_3. Furthermore, gaseous H_2O and H_2 may be formed; H_2O by condensation and H_2 by reaction of H_2O with phosphite, as we will see in the following. These gases are responsible for the weight decrease observed in the TG (Fig. 1). At the same time, the Na/P ratio of the solid products increased, as the LS ^{31}P NMR spectra demonstrated (Fig. 4). The changes in the P/Na, O/Na and H/Na ratios indicate how much PH_3 and H_2O or H_2 escape to the gas phase in the decomposition of hypophosphite and phosphite. When hypophosphite and phosphite were heated to high enough temperature (e.g. 400 °C), none of the P(V) products ($Na_3P_3O_9$, $Na_5P_3O_{10}$, $Na_4P_2O_7$, Na_3PO_4) contained hydrogen, which means that it is removed as PH_3, H_2O or as H_2. This enables us to determine the coefficients a, b, c, d and e in the equation NaH_2PO_2 ♍ aPH_3 + $bNaPO_3$ + cNa_3PO_4 + dH_2 + eH_2O from the mass balances for the Na, H, P and O atoms and the formal charge balance on the P atoms. Only two P(V) compounds need to be considered as independent components, e.g. $NaPO_3$ and Na_3PO_4, because the other two can be written as a combination of these two compounds (e.g. $Na_4P_2O_7 = NaPO_3 + Na_3PO_4$ and $Na_5P_3O_{10} = Na_3PO_4 + 2NaPO_3$). Because sodium atoms do not escape to the gas phase, all Na atoms present in the reactant end up in the P(V) products. When H_2O is not a product, also all O atoms of NaH_2PO_2 must be in the P(V) products and the above equation becomes $5NaH_2PO_2$ ♍ $2PH_3 + 2NaPO_3 + Na_3PO_4 + H_2 = 2PH_3 + Na_5P_3O_{10} + H_2$. When H_2O is a product, the equation becomes $4NaH_2PO_2$ ♍ $2PH_3 + NaPO_3 + Na_3PO_4 + H_2O = 2PH_3 + Na_4P_2O_7 + H_2O$. The results of all possible reactions for hypophosphite, phosphite and mixtures, with either H_2 or H_2O as product, are presented in Table S1. For each reaction the theoretical weight losses due to the formation of PH_3, H_2O and H_2 are presented, as well as the observed values. Furthermore, the Na/P ratios in the solid product are presented.

Table S1 Total decomposition reactions of NaH_2PO_2, NaH_2PO_3 and Na_2HPO_3

Reaction	Na/P Ratio	weight loss (%) theory	exper.

	Pure compounds			
1.	$5NaH_2PO_2 \not\rightarrow 2PH_3 + Na_5P_3O_{10} + 2H_2$	1.67	16.4	16.6 ± 0.5
	$4NaH_2PO_2 \not\rightarrow 2PH_3 + Na_4P_2O_7 + H_2O$	2.0	24.4	
2.	$2NaH_2PO_3 \not\rightarrow Na_2H_2P_2O_5 + H_2O$			
	$15Na_2H_2P_2O_5 \not\rightarrow 6PH_3 + 3Na_5P_3O_{10} + 5Na_3P_3O_9 + 6H_2$	1.25	7.6	7.5 ± 0.2
	$4Na_2H_2P_2O_5 \not\rightarrow 2PH_3 + Na_5P_3O_{10} + Na_3P_3O_9 + H_2O$	1.33	1	1.3
3.	$5Na_2HPO_3 \not\rightarrow PH_3 + 2Na_3PO_4 + Na_4P_2O_7 + H_2$	2.5	5.7	
	$5Na_2HPO_3 \not\rightarrow P + 2Na_3PO_4 + Na_4P_2O_7 + 2.5H_2$	2.5	0.8	0.5 ± 0.4
	$8Na_2HPO_3 \not\rightarrow 2PH_3 + 4Na_3PO_4 + Na_4P_2O_7 + H_2O$	2.67	8.5	
	Mixtures			
4.	$2NaH_2PO_3 + 2Na_2HPO_3 \not\rightarrow Na_2H_2P_2O_5 + 2Na_2HPO_3 + H_2O$	1.5		
	$^*5Na_2H_2P_2O_5 + 10Na_2HPO_3 \not\rightarrow$			
	$\not\rightarrow 4PH_3 + 5Na_4P_2O_7 + 2Na_5P_3O_{10} + 4H_2$	1.87	6.5	
	$\rightarrow 5Na_2H_2P_2O_5 + 10Na_2HPO_3 \not\rightarrow$			
	$\not\rightarrow 2PH_3 + 2P + 5Na_4P_2O_7 + 2Na_5P_3O_{10} + 7H_2$	1.87	3.7	
	$\uparrow 5Na_2H_2P_2O_5 + 10Na_2HPO_3 \not\rightarrow$			
	$\not\rightarrow 2PH_3 + Na_5P_3O_{10} + 5/3Na_3P_3O_9 + 10Na_2HPO_3 + 2H_2$	1.67	3.3	3.2 ± 0.4
5.	$2Na_2HPO_3 + 2NaH_2PO_4 \not\rightarrow 2Na_2HPO_3 + Na_2H_2P_2O_7 + H_2O$			
	$2Na_2HPO_3 + Na_2H_2P_2O_7 \not\rightarrow Na_5P_3O_{10} + NaPO_3 + 2H_2$	1.5		

*both reactants react and are oxidized by water, →both reactants react and are oxidized by water, 50% of PH_3 decomposes, ↑only $Na_2H_2P_2O_5$ reacts.

Table S2 Possible mechanisms for the first step of the disproportionation of NaH_2PO_2

Mechanisms	**↑W-loss**	***R1**	**→R2**
1. Disproportionation and condensation of NaH_2PO_3			

$6NaH_2PO_2$ ↛ $2PH_3 + Na_2H_2P_2O_5 + 2Na_2HPO_3 + H_2O$	16.3	1	0
2. 1. and oxidation NaH_2PO_2 to P(III)			
$4NaH_2PO_2$ ↛ $PH_3 + Na_2H_2P_2O_5 + Na_2HPO_3 + H_2$	12.3	0.5	0
3. 1. and oxidation NaH_2PO_2 to P(V)			
$20NaH_2PO_2$ ↛ $6PH_3 + 3Na_2H_2P_2O_5 + 6Na_2HPO_3 + Na_2H_2P_2O_7 + 4H_2$	12.0	1	0.33
4. 1. and oxidation NaH_2PO_2 to P(V) and H-Na exchange			
$10NaH_2PO_2$ ↛ $3PH_3 + 2Na_2H_2P_2O_5 + Na_2HPO_3 + Na_4P_2O_7 + 3H_2$	12.3	0.25	0.5
5. 1. and oxidation NaH_2PO_2 and Na_2HPO_3			
$14NaH_2PO_2$ ↛ $4PH_3 + 3Na_2H_2P_2O_5 + 3Na_2HPO_3 + Na_2HPO_4 + 3H_2$	11.5	0.5	0
6. 1. and oxidation $Na_2H_2P_2O_5$			
$12NaH_2PO_2$ ↛ $4PH_3 + Na_2H_2P_2O_5 + Na_2H_2P_2O_7 + 4Na_2HPO_3 + 2H_2$	13.3	2	1
7. 1. and oxidation $Na_2H_2P_2O_5$ and H-Na exchange with $Na_2H_2P_2O_7$			
$12NaH_2PO_2$ ↛ $4PH_3 + 2Na_2H_2P_2O_5 + 2Na_4P_2O_7 + 4H_2$	13.6	0	1
8. 1. and oxidation of $Na_2H_2P_2O_5$ and Na_2HPO_3			
$24NaH_2PO_2$ ↛ $8PH_3 + 3Na_2H_2P_2O_5 + 6Na_2HPO_3 + Na_2H_2P_2O_7 + 2Na_2HPO_4 + 4H_2$	13.3	1	0.33
9. 1. and oxidation of $Na_2H_2P_2O_5$ and Na_2HPO_3 and H-Na exchange			
$18NaH_2PO_2$ ↛ $6PH_3 + 3Na_2H_2P_2O_5 + 2Na_2HPO_3 + 2Na_2HPO_4 + Na_4P_2O_7 + H_2$	13.4	0.33	0.33
10. 1. and oxidation of Na_2HPO_3			
$12NaH_2PO_2$ ↛ $4PH_3 + 2Na_2H_2P_2O_5 + 2Na_2HPO_3 + 2Na_2HPO_4 + 2H_2$	13.3	0.5	0
Experiment in N_2	12.6	0.6	0.6
Experiment in H_2	13.2	0.4	0.25

↑Weight loss by PH_3, H_2O and H_2 (%), *$Na_2HPO_3/2(Na_2H_2P_2O_5)$, →$(Na_2H_2P_2O_7+Na_4P_2O_7)/Na_2H_2P_2O_5$

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Several mechanisms can be written in which NaH_2PO_2, $Na_2H_2P_2O_5$ or Na_2HPO_3 are oxidized by water (Table S2), but not all mechanisms agree with the experimental results. The LS NMR spectra (Fig. 4) show that $Na_2H_2P_2O_7$ appears immediately at 300 °C, simultaneously with $Na_2H_2P_2O_5$ and phosphite,

as if it is a primary product. Therefore, only mechanisms in which water oxidizes hypophosphite or pyrophosphite to pyrophosphate need to be considered. Mechanisms in which Na_2HPO_3 is oxidized to Na_2HPO_4 can be omitted, because Na_2HPO_4 does not condense to $Na_4P_2O_7$ below 370 °C. This means that mechanisms 1, 2, 5 and 10 of Table S1 can be disregarded. Furthermore, already at the start of the reaction at 300 °C the intensity of the phosphite NMR peak at 3.25 ppm is smaller than that of the pyrophosphite peak at -4.99 ppm (Fig. 4). This means that less Na_2HPO_3 is formed than $Na_2H_2P_2O_5$ (Fig. 4), meaning that mechanisms 3, 6 and 8 can be disregarded as well. Mechanism 7 cannot explain the results either, because it does not predict any formation of Na_2HPO_3. At higher temperature (310-360 °C) the intensity of the phosphite NMR peak, and thus the concentration of Na_2HPO_3, decreases strongly. This indicates that, once formed, Na_2HPO_3 reacts to Na_2HPO_4 by oxidation by water (H_2O + Na_2HPO_3 ♑ H_2 + Na_2HPO_4) or to NaH_2PO_3 by H-Na exchange ($2Na_2HPO_3$ + $Na_2H_2P_2O_7$ ♑ $2NaH_2PO_3$ + $Na_4P_2O_7$). The exchange transforms Na_2HPO_3, which itself does not react below 450 °C, into reactive NaH_2PO_3. The required $Na_2H_2P_2O_7$ can be formed by oxidation of NaH_2PO_2 and $Na_2H_2P_2O_5$ by water.

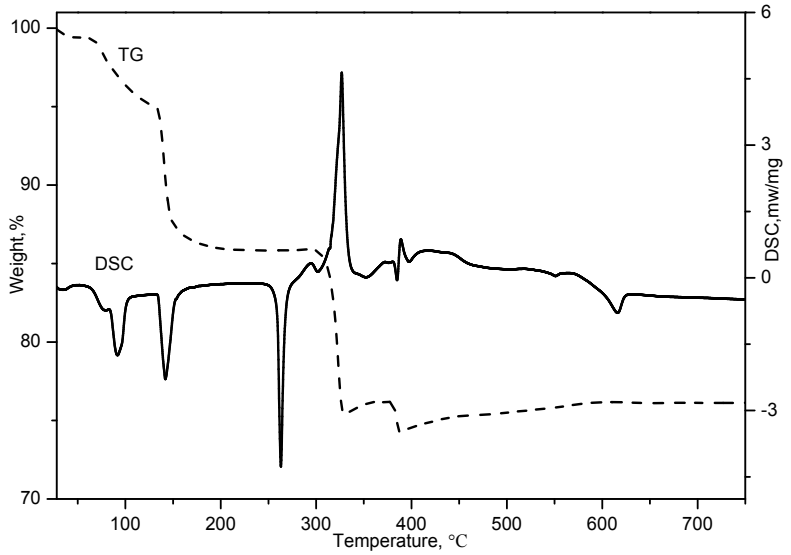

Fig. S1 TG-DSC curves of $NaH_2PO_2 \cdot H_2O$ in N_2.

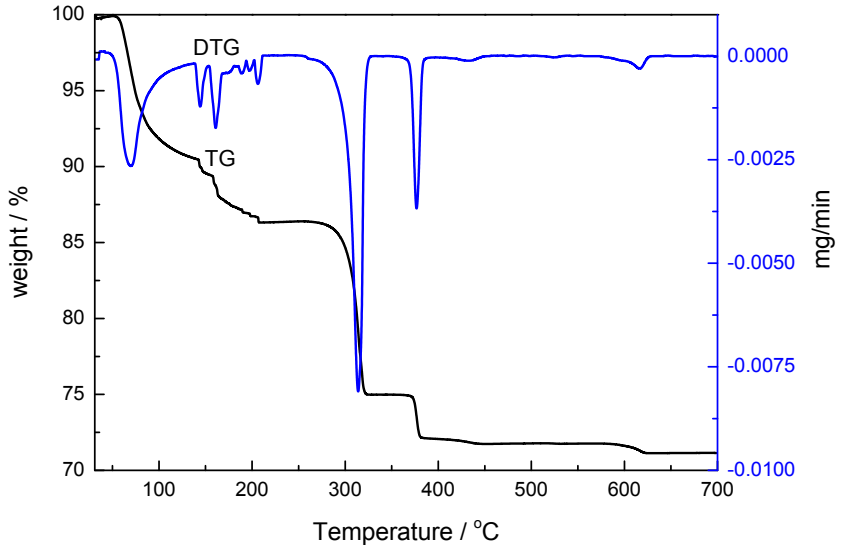

Fig. S2 TG-DTG curves of $NaH_2PO_2 \cdot H_2O$ in 10% H_2 in N_2 (v/v).

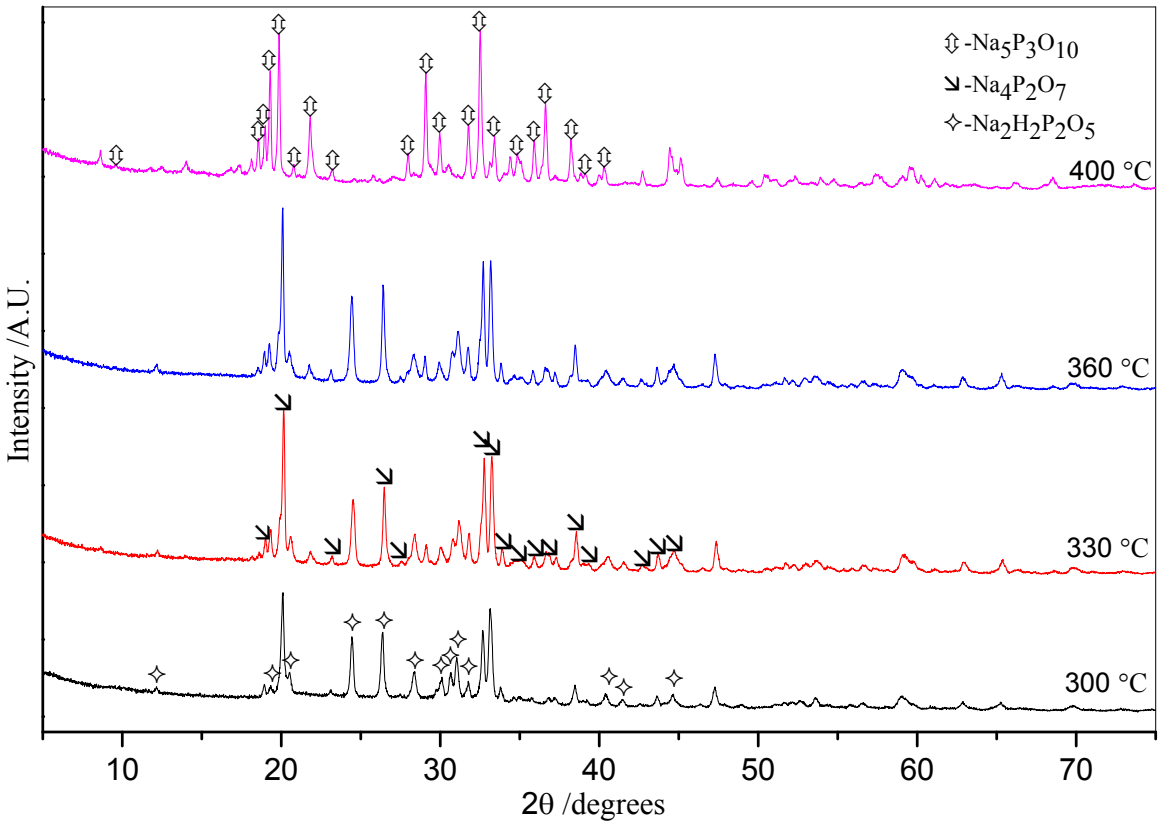

Fig. S3 XRD patterns of the products of heating NaH_2PO_2 in H_2 to different temperatures.

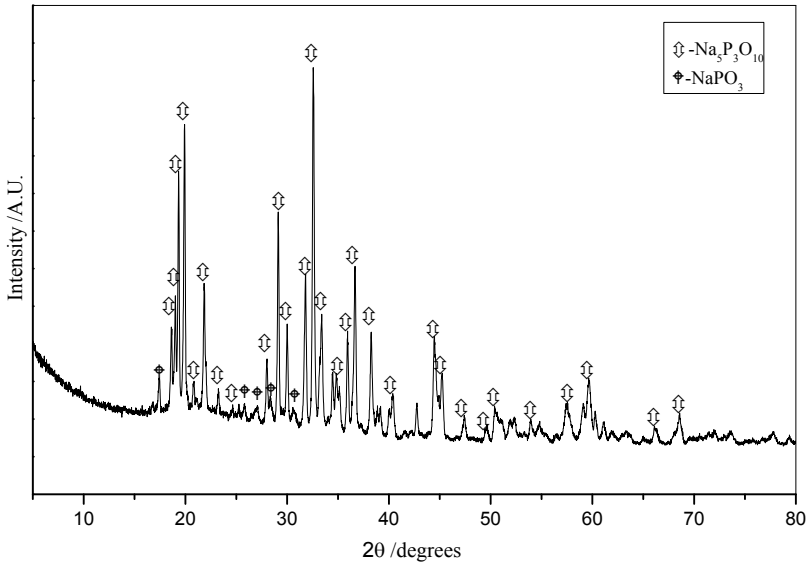

Fig. S4 XRD pattern of the product of heating Na_2HPO_2 at 360 °C in N_2 for 1 h.

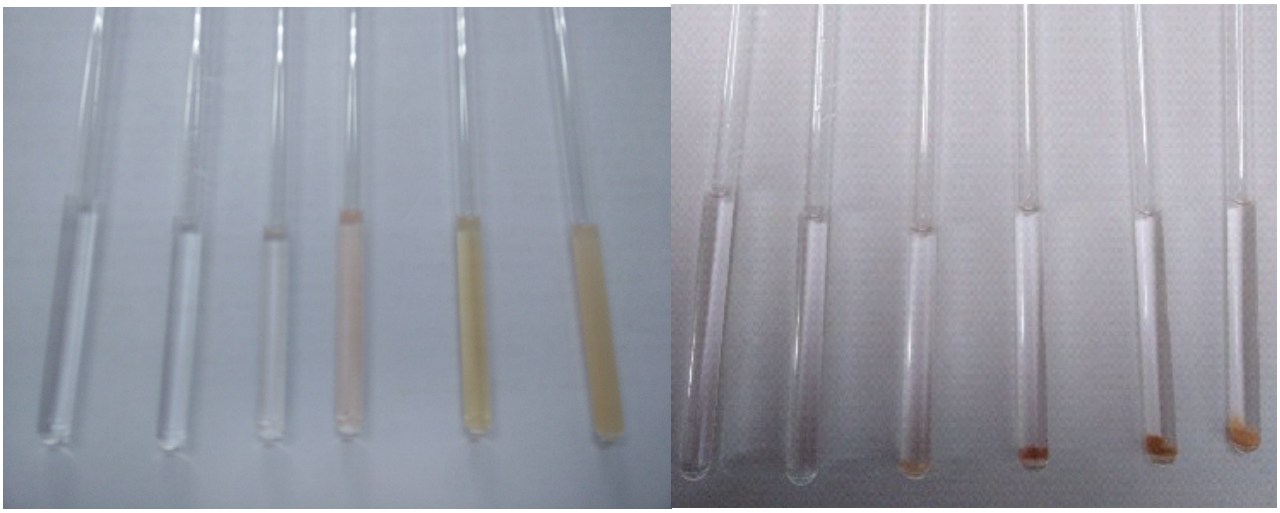

Fig. S5 Solutions and suspensions of 30 mg of the solids obtained after heating NaH_2PO_2 in N_2 to 260, 280, 300, 330, 360 and 400 °C (from left to right) dissolved in D_2O, after shaking (left) and after settling for two days (right).

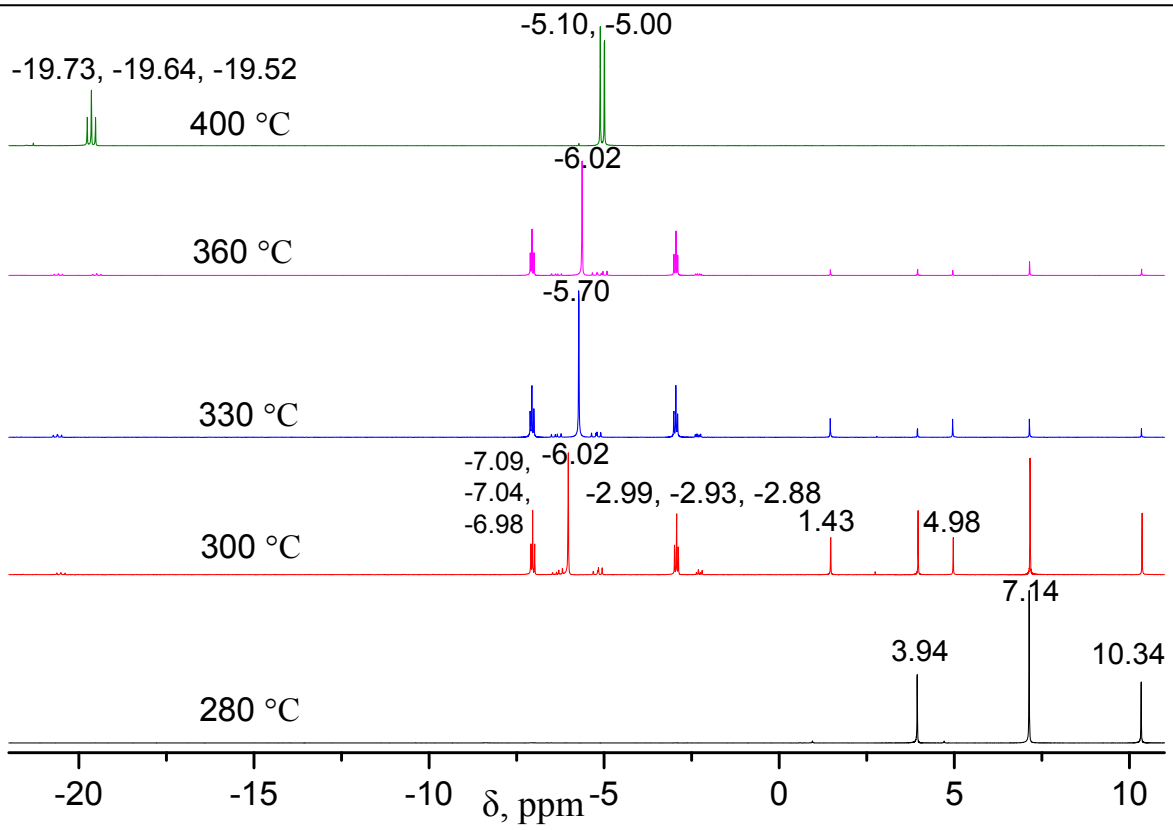

Fig. S6 Normal ^{31}P NMR spectra of solutions of the products of heating $NaH_2PO_2 \cdot H_2O$ in N_2 to 280, 300, 330, 360 and 400°C.

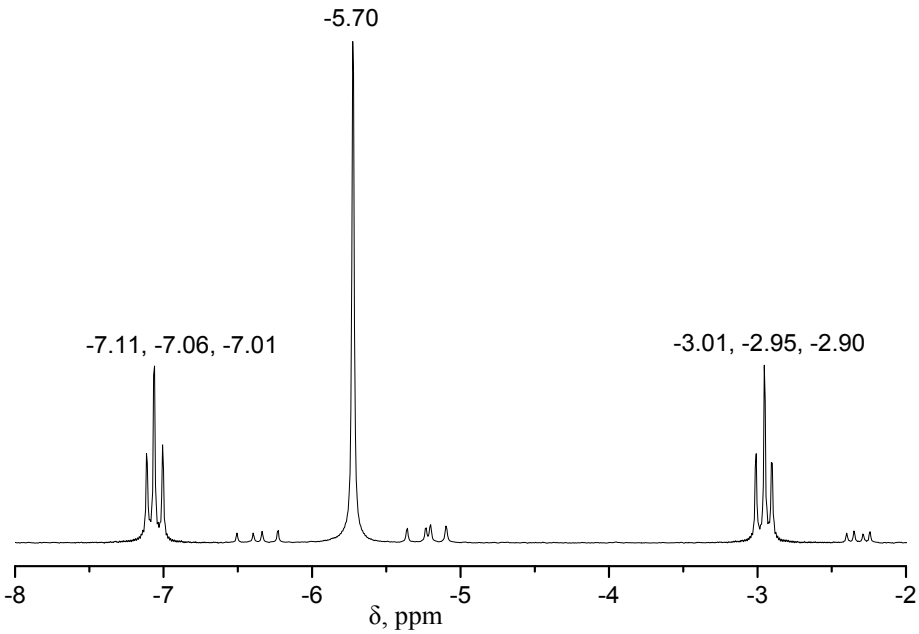

Fig. S7 Expansion of the normal ^{31}P NMR spectrum of the product of heating $NaH_2PO_2 \cdot H_2O$ in N_2 to 330 °C.

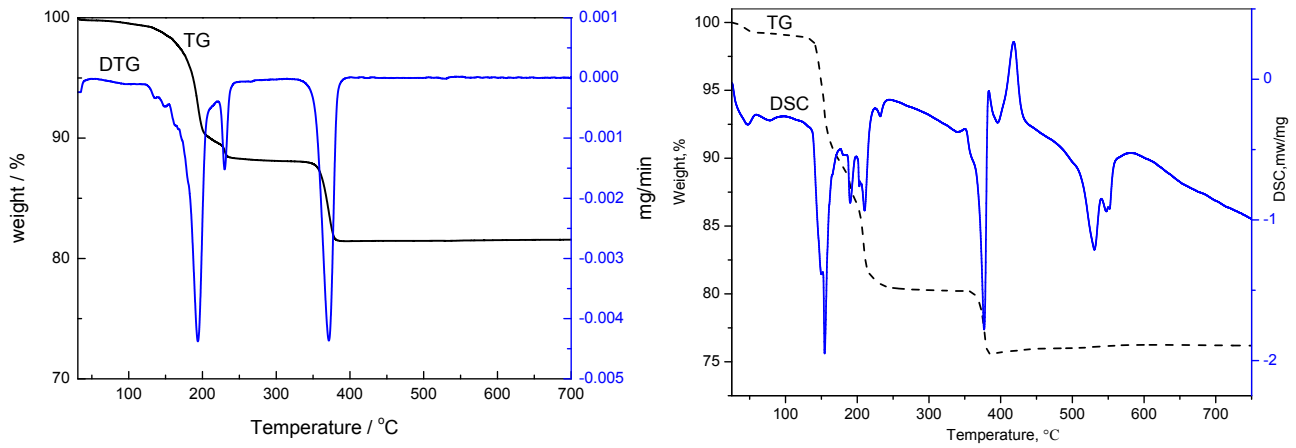

Fig. S8 TG-DTG (left) and TG-DSC (right) curves of $NaH_2PO_3 \cdot H_2O$ in N_2.

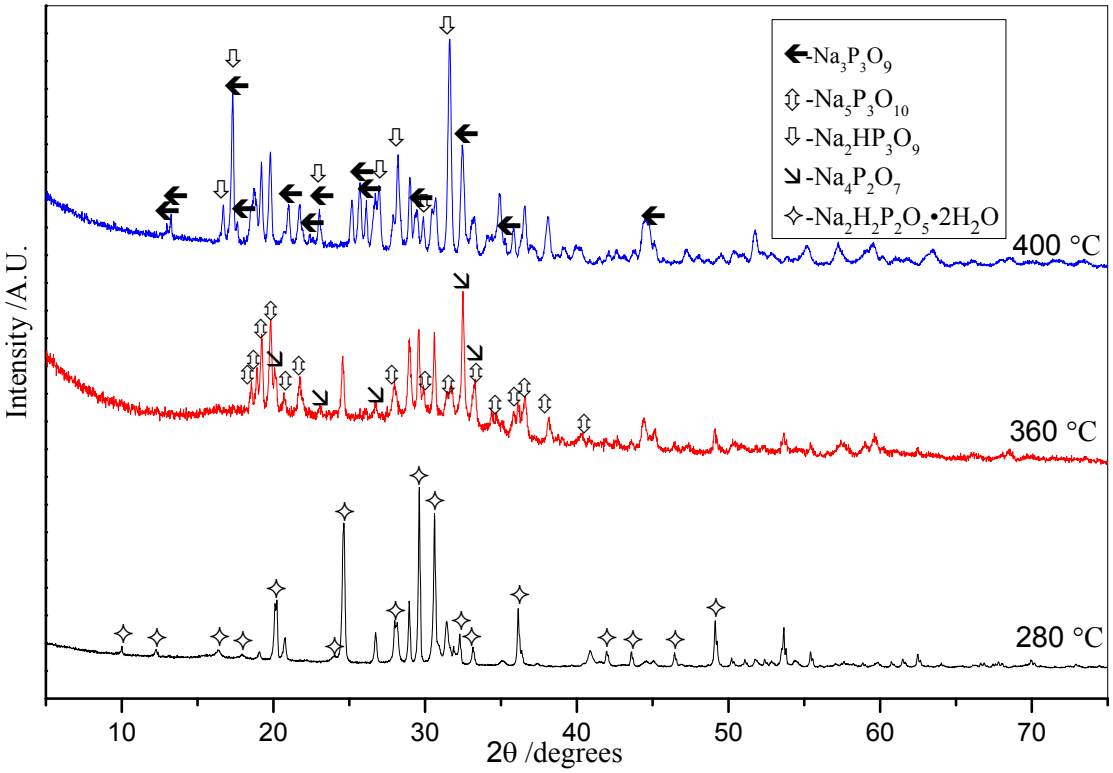

Fig. S9 XRD patterns of the products of heating NaH_2PO_3 in N_2 to 280, 360 and 400 °C.

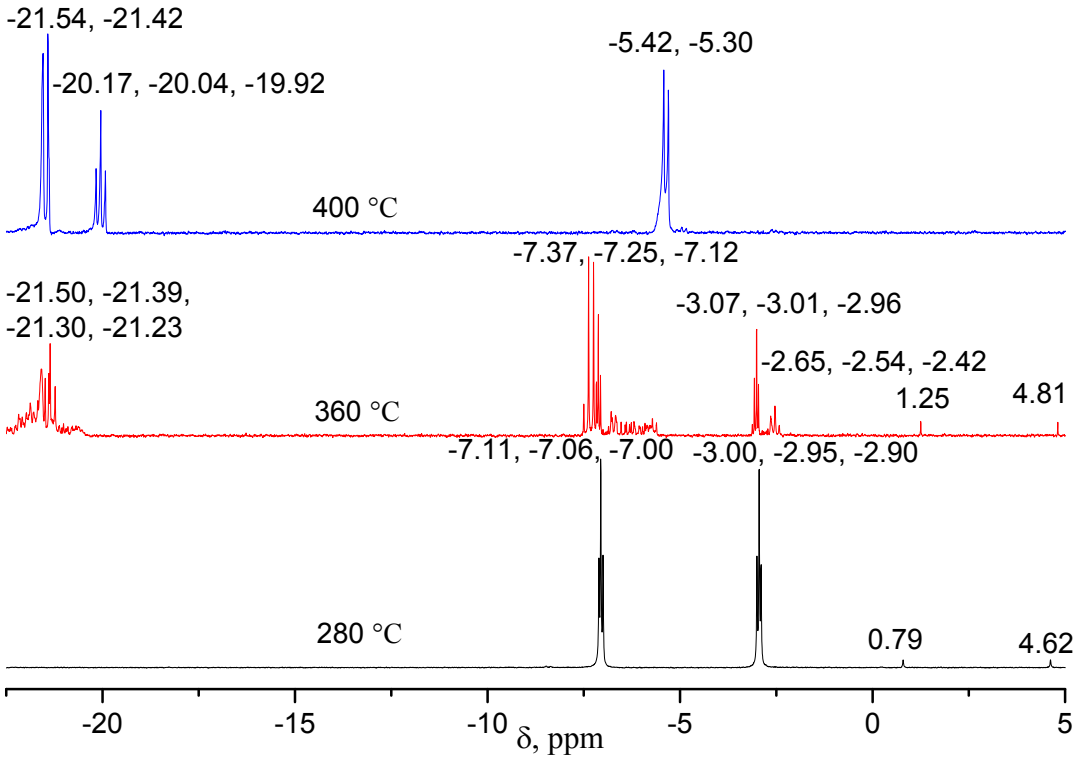

Fig. S10 Normal ^{31}P NMR spectrum of the product of heating NaH_2PO_3 in N_2 to 280, 360 and 400 °C.

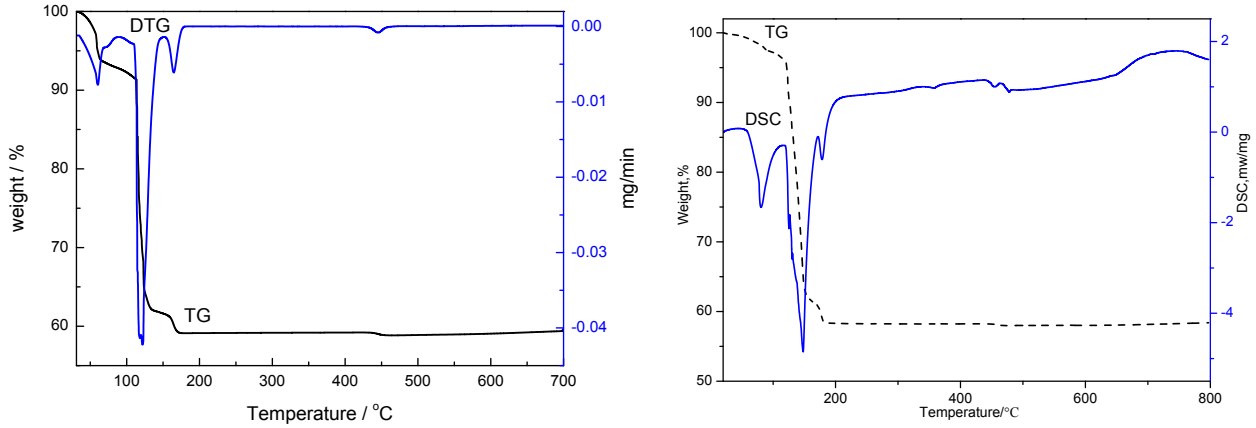

Fig. S11 TG-DTG (left) and TG-DSC (right) curves of $Na_2HPO_3 \cdot 5H_2O$ in N_2.

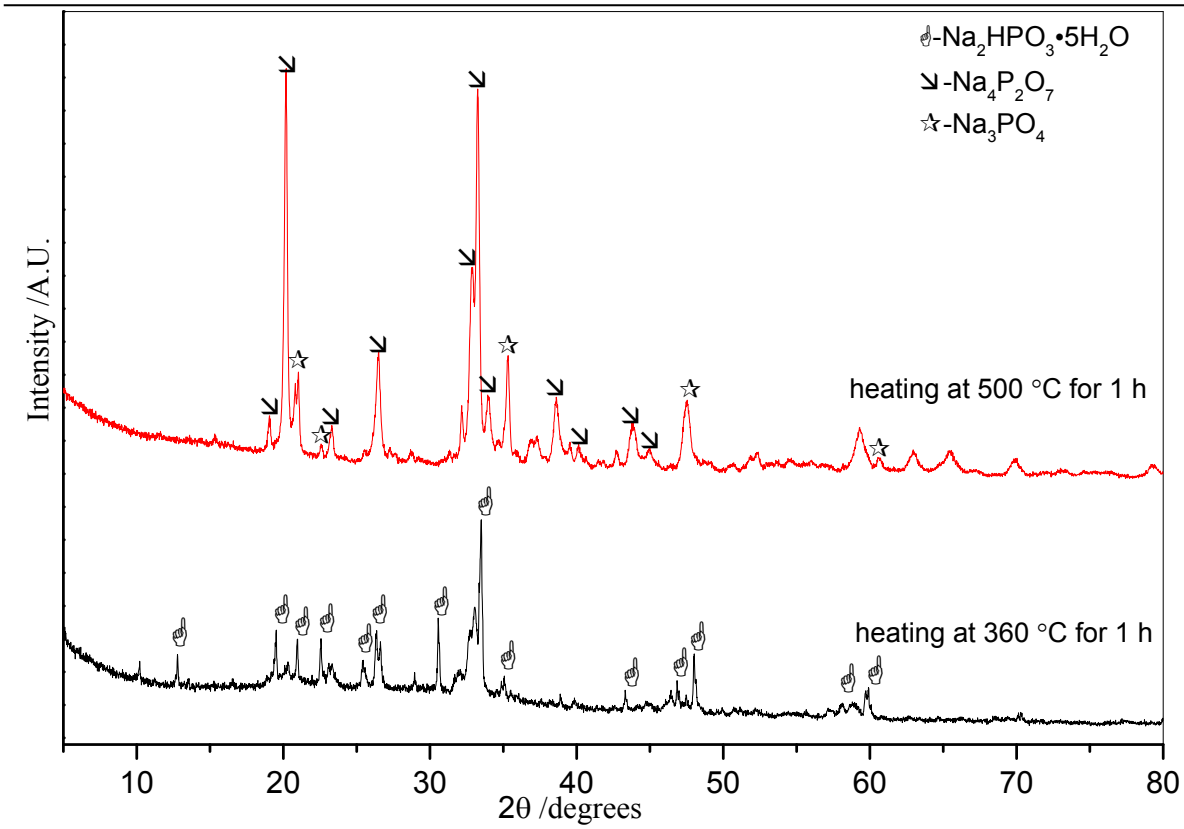

Fig. S12 XRD patterns of the products of heating Na_2HPO_3 in N_2 at 360 and 500 °C for 1 h.

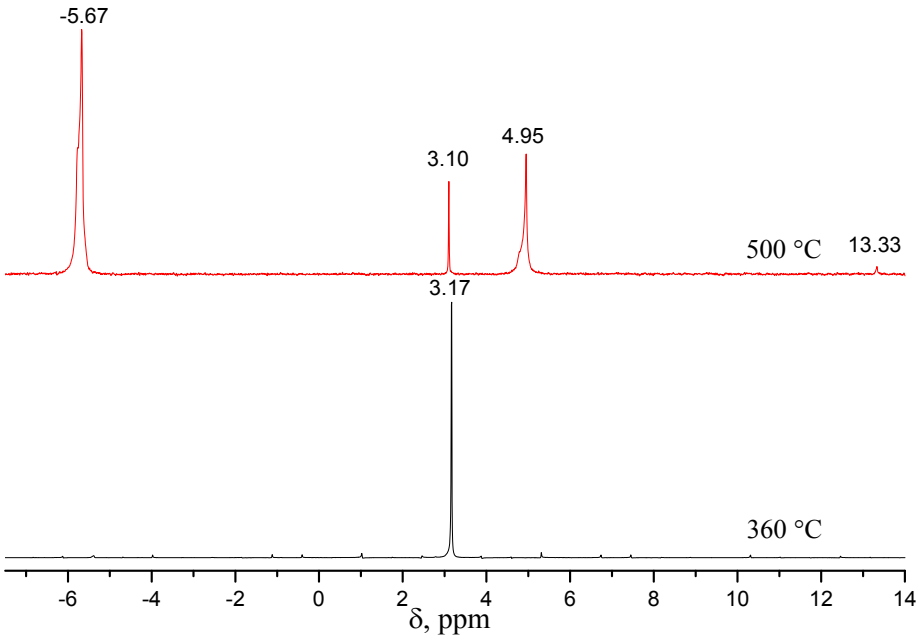

Fig. S13 The proton-decoupled ^{31}P LS-NMR of the products of heating Na_2HPO_3 in N_2 to 360 and 500 °C.

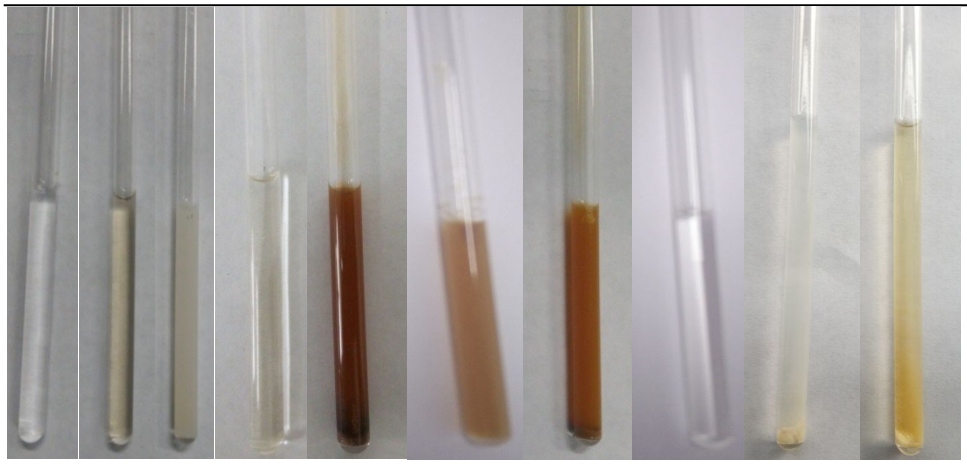

Fig. S14 The solutions and suspensions of the products of heating NaH_2PO_3 to 280, 360 and 400 °C (the first three from left to right); heating Na_2HPO_3 to 360 and 500 °C (4^{th}-5^{th}); Na_2HPO_3 + NaH_2PO_3 (1:1) to 360 and 400 °C (6^{th}-7^{th}); Na_2HPO_3 + NaH_2PO_4 (1:1) 360 and 400 °C (8^{th}-9^{th}); Na_2HPO_3 + Na_2HPO_4 (1:1) to 400 °C (10^{th}) (all samples were heated in N_2).

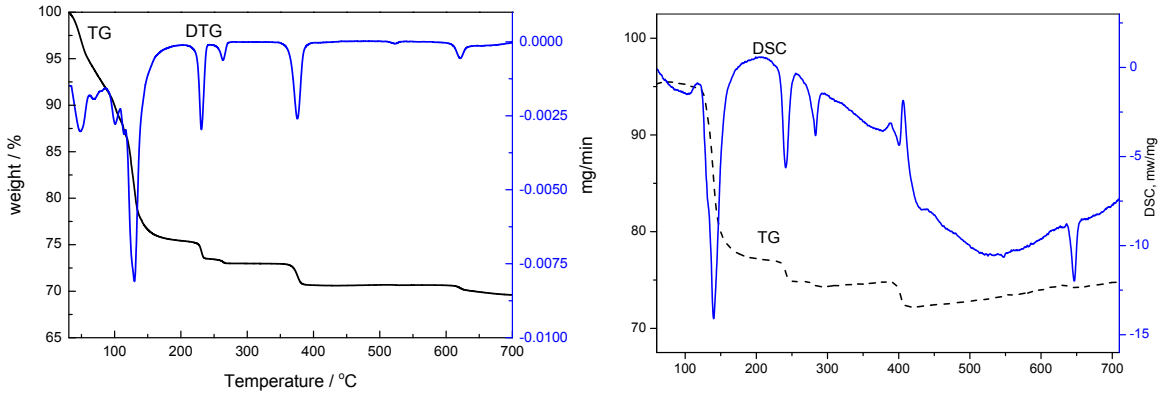

Fig. S15 TG-DTG (left) and TG-DSC (right) of a 1:1 mixture of $NaH_2PO_3 \cdot H_2O$ and $Na_2HPO_3 \cdot 5H_2O$ in N_2.

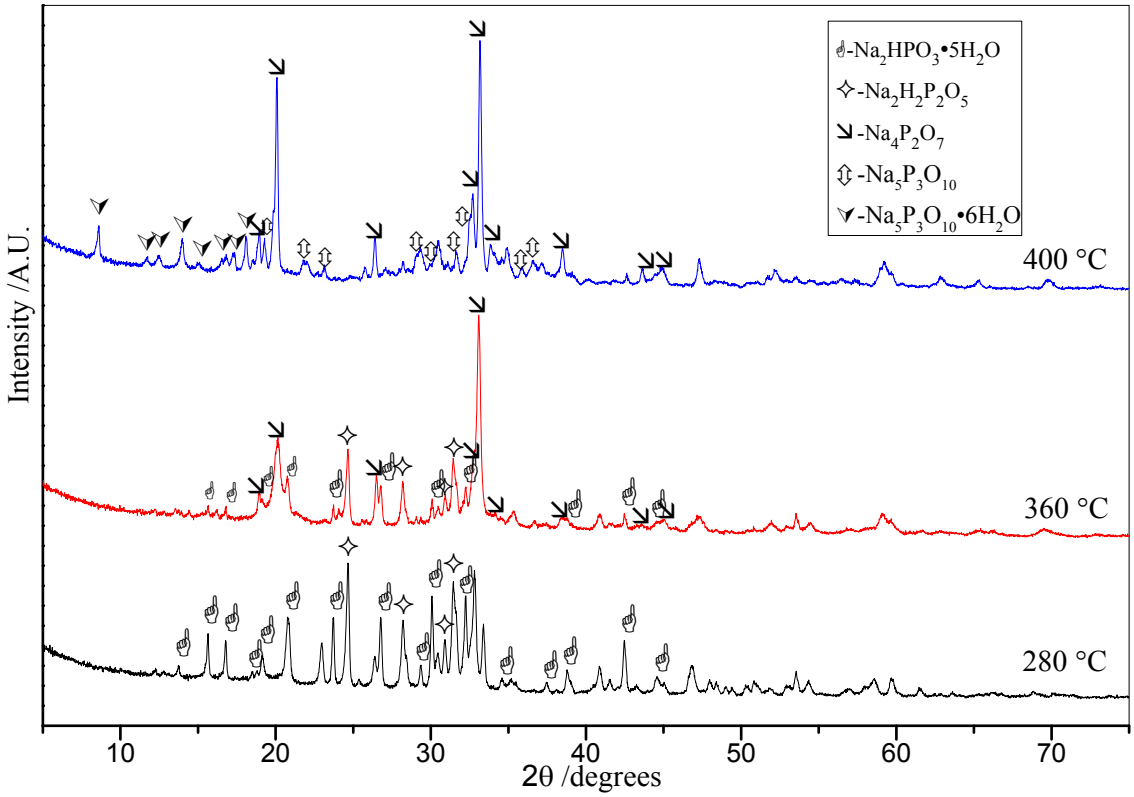

Fig. S16 XRD patterns of the products of heating a 1:1 mixture of Na_2HPO_3 and NaH_2PO_3 in N_2 to 280, 360 and 400 °C.

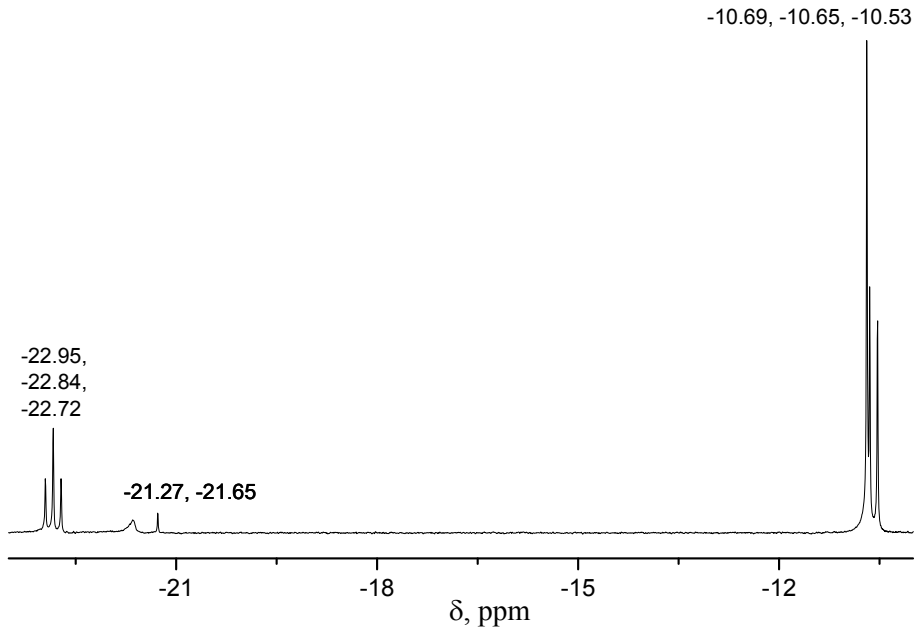

Fig. S17 Normal ^{31}P NMR spectrum of the solution of the product of heating a 1:1 mixture of Na_2HPO_3 and NaH_2PO_3 in N_2 to 400 °C after adding one drop concentrated HCl (before adding HCl, pH=9; after addition, pH=1).

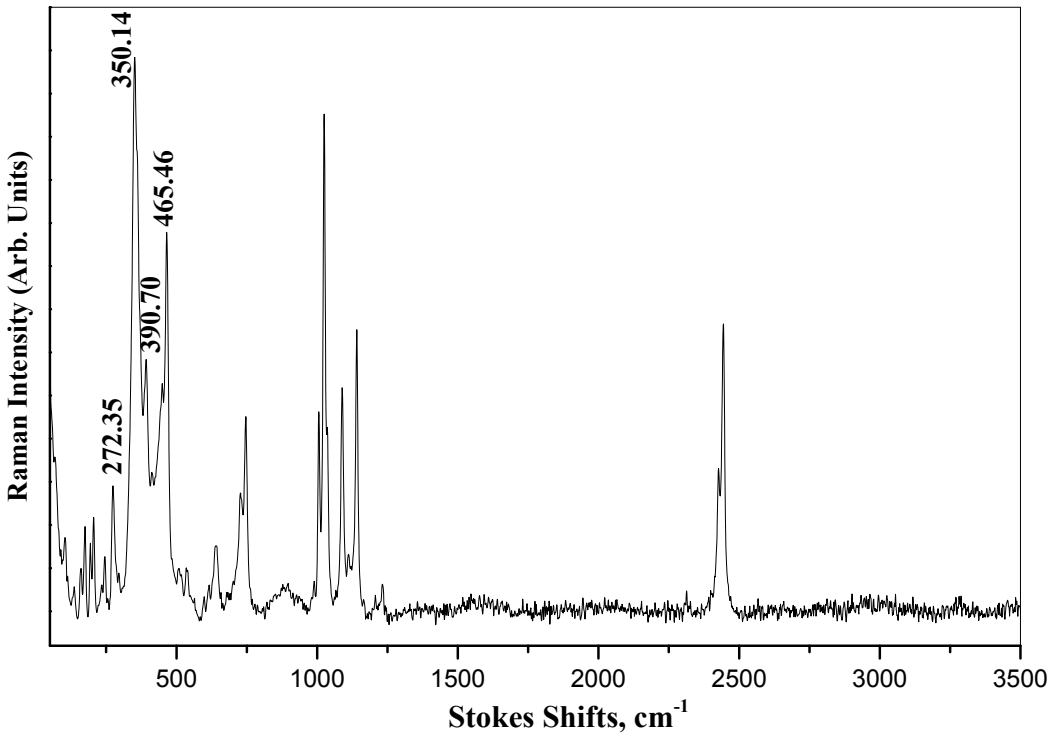

Fig. S18 Raman spectrum of the product of heating Na_2HPO_3+NaH_2PO_3 (1:1) in N_2 to 360 °C.

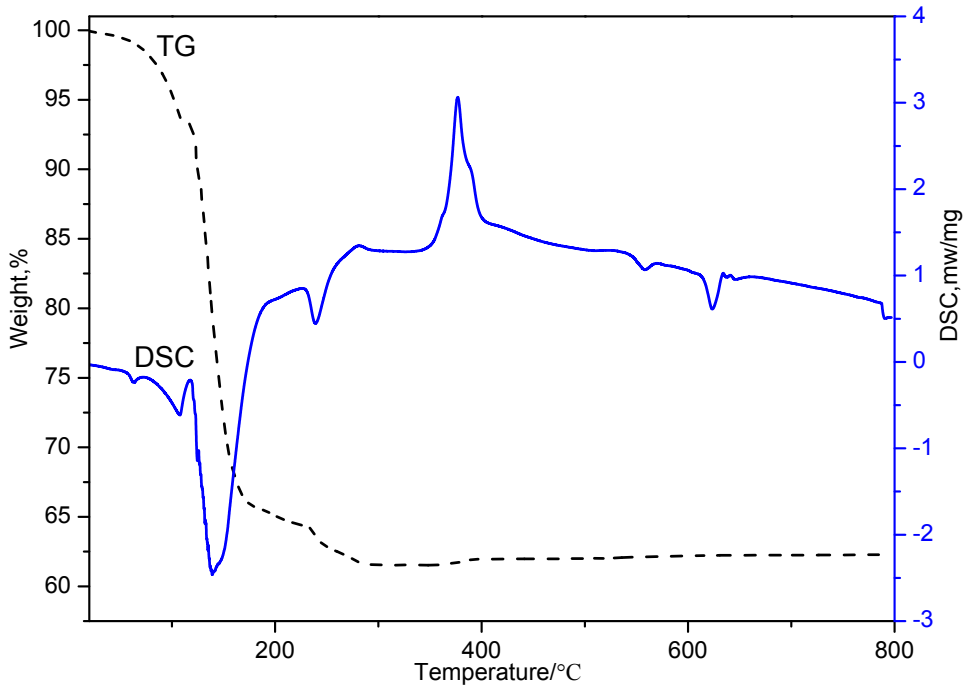

Fig. S19 TG-DSC curves of $Na_2HPO_3 \cdot 5H_2O$ +$NaH_2PO_4 \cdot 2H_2O$ (1:1) in N_2.

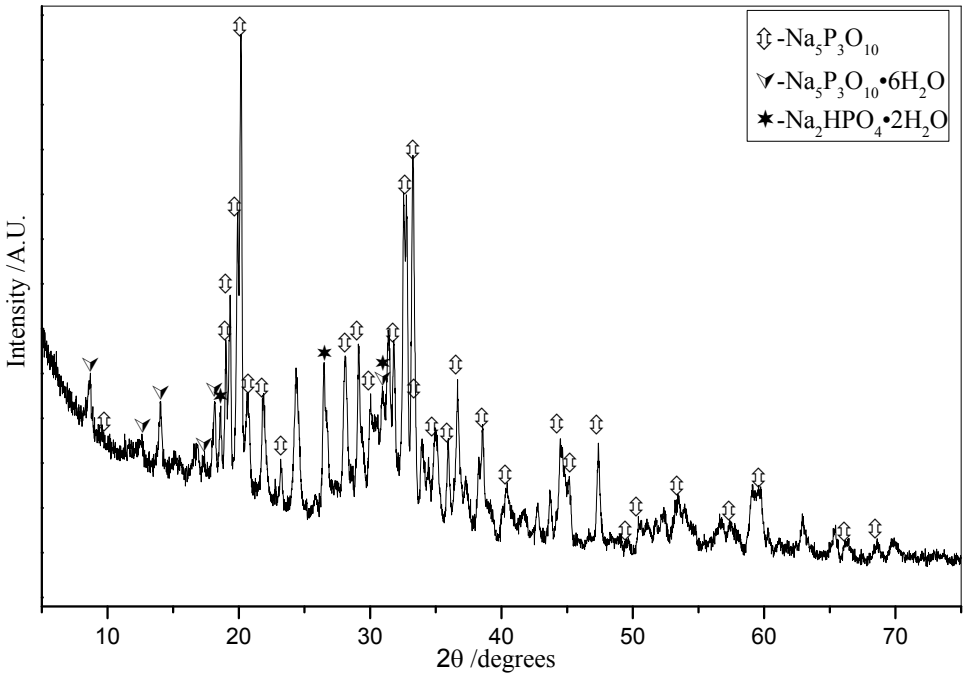

Fig. S20 XRD pattern of the products of heating Na_2HPO_3 + NaH_2PO_4 (1:1) in N_2 to 360 °C.

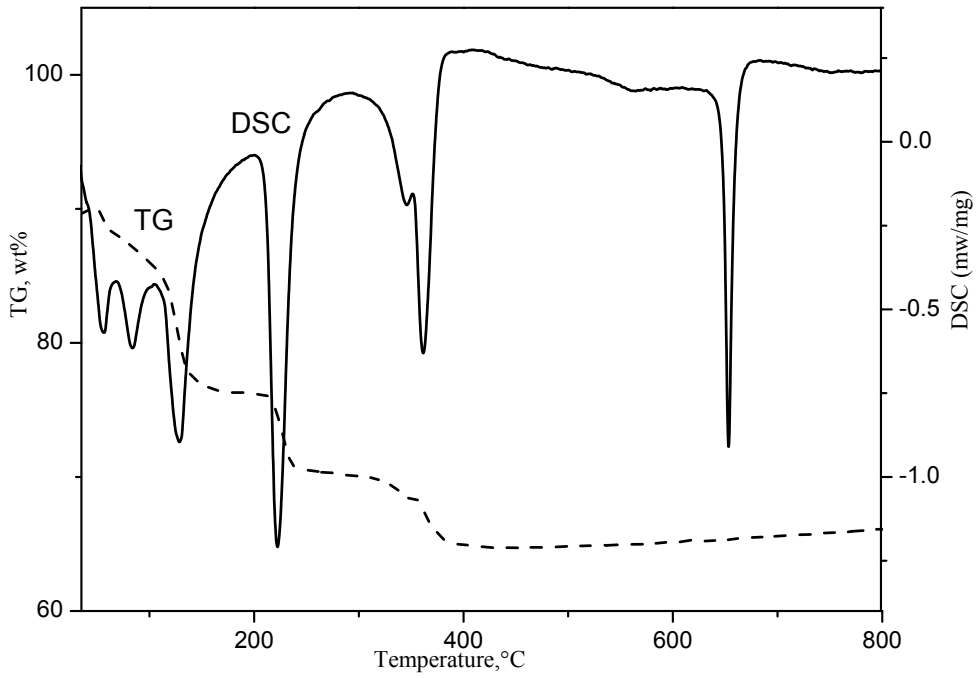

Fig. S21 TG-DSC curves of $NaH_2PO_4 \cdot 2H_2O$ in N_2.

The predicted reactions and weight changes are

at 150 °C: $NaH_2PO_4 \cdot 2H_2O \rightarrow NaH_2PO_4 + 2H_2O$ $\Delta = 100 \times 36/156 = 23.1\%$

at 220 °C: $2NaH_2PO_4 \xrightarrow{} Na_2H_2P_2O_7 + H_2O$ $\Delta = 100\times18/2\times156 = 5.8\%$

at 320 °C: $3Na_2H_2P_2O_7 \xrightarrow{} 2Na_3H_2P_3O_{10} + H_2O$ $\Delta = 100\times18/6\times156 = 1.9\%$

at 360 °C: $2Na_3H_2P_3O_{10} \xrightarrow{} 2Na_3P_3O_9 + 2H_2O$ $\Delta = 100\times36/6\times156 = 3.8\%$

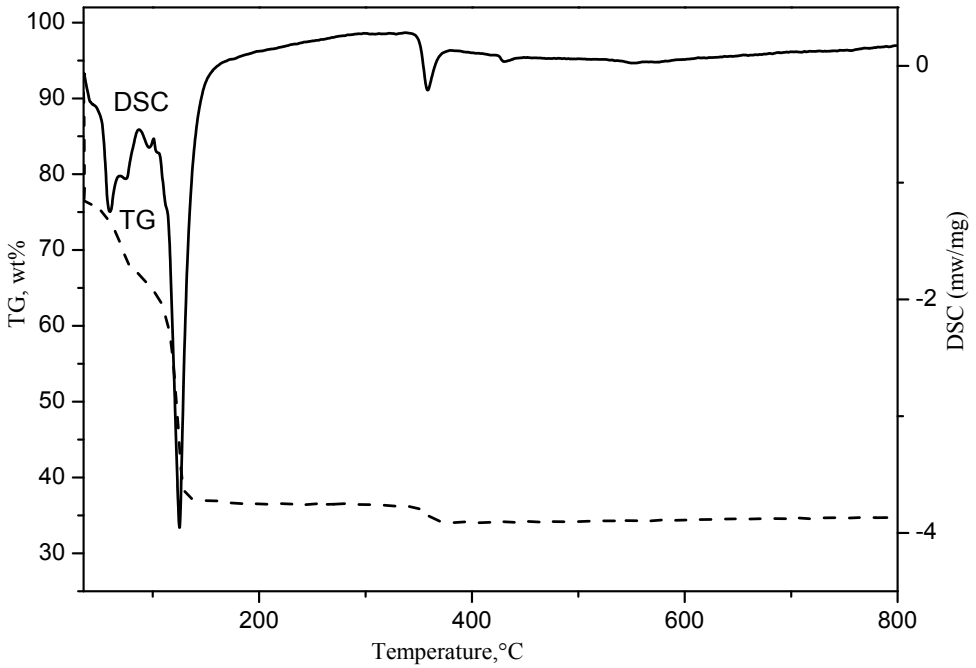

Fig. S22 TG-DSC curves of $Na_2HPO_4\cdot12H_2O$ in N_2.

The predicted reactions and weight changes are

at 120 °C: $Na_2HPO_4\cdot12H_2O \xrightarrow{} Na_2HPO_4 + 12H_2O$ $\Delta = 100\times216/358 = 60.3\%$

at 350 °C: $2Na_2HPO_4 \xrightarrow{} Na_4P_2O_7 + H_2O$ $\Delta = 100\times18/2\times358 = 2.5\%$