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Manh Ha Le

University of Wollongong, mhl980@uowmail.edu.au

Anh Kiet Tieu

University of Wollongong, ktieu@uow.edu.au

Hongtao Zhu

University of Wollongong, hongtao@uow.edu.au

Thi D. Ta

University of Wollongong, thi@uow.edu.au

Haibo Yu

University of Wollongong, hyu@uow.edu.au

See next page for additional authors

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Abstract

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Authors

Manh Ha Le, Anh Kiet Tieu, Hongtao Zhu, Thi D. Ta, Haibo Yu, Thi Thuy Huong Ta, Nam Van Tran, and Shanhong Wan

Depolymerization of sodium polyphosphates on iron oxide surface at high temperature

M. H. Le,^a A. K. Tieu,^a H. Zhu,^{*a} D. T. Ta,^a H. Yu,^b T. T. H. Ta,^a V. N. Tran^a and S. Wan^a

a. School of Mechanical, Materials, Mechatronic and Biomedical Engineering, University of Wollongong, Northfield Avenue, Wollongong, NSW, 2522, Australia. Email: hongtao@uow.edu.au

b. School of Chemistry, University of Wollongong, Northfield Avenue, Wollongong, NSW, 2522, Australia.

Abstract

Density functional theory (DFT) and first principle molecular dynamics (FPMD) studies of pyrophosphate cluster $\text{Na}_4\text{P}_2\text{O}_7$ and triphosphate cluster $\text{Na}_5\text{P}_3\text{O}_{10}$ absorbed and decomposed on Fe_2O_3 (0001) surface have been conducted. Comparative analyses of structure properties and adsorption processes during the simulation at elevated temperature have been carried out. The results depict the key interactions including the covalent P-O bonds, pure ionic Na-O or Fe-O interactions. Iron oxide surface plays an important role in the bridging bond decomposition scheme which can both promote and suppress the phosphate depolymerization. It is found that chain length of polyphosphates do not have considerable effects on the decomposition of phosphate clusters. This study provides detailed insights into the interaction of phosphate cluster on iron oxide surface at high temperature, and in particular the depolymerization/polymerization of inorganic phosphate glass lubricant, which is an important behavior under hot metal forming conditions.

Introduction

An effective lubricant is essential in a hot metal manufacturing process due to vast of adverse effects at elevated temperatures such as high friction, considerable wear and severe oxidation. Phosphate glass lubricants have received more attention recently due to the excellent tribological behavior of zinc dialkyldithiophosphate (ZDDP) at the temperature below 250°C and also its environmentally friendly and thermal stability nature. In the harsh working condition of hot rolling of steel, alkaline polyphosphates can provide the good antiwear property, friction reduction and oxidation inhibition.¹⁻³ In previous studies on tribological tests,^{4, 5} a polyphosphate film has been observed to have layered structure and gradient composition which makes it a very effective lubricant.^{6, 7} However, the working mechanism of inorganic phosphate glasses as a promising lubricant at elevated temperature needs more in depth understanding. Besides the potential lubricant functionality, the glassy compounds contained polyphosphate are also well-known for their bioactivity,⁸ optical technology application,⁹ and radioactive waste immobilization.¹⁰

For the well-known ZDDP, Ito et al.¹¹ proposed the mechanism of physical adsorption on iron oxide surface and the dissociation of lubricant molecules at ambient temperature. The phosphate adsorption on the oxide surface at ambient temperature has been investigated in soil mechanics from both

experiments¹²⁻¹⁶ and simulations.¹⁷⁻²¹ The phosphate anion $H_nPO_4^{3-n}$ has been usually used as an adsorbate on metal hydr(oxide) surface. However, the complex formation and lubricant-oxide interaction in these studies are still controversial. Either monodentate or bidentate have been generated during the adsorption under different pH conditions.^{21, 22} The iron-phosphate interaction has been considered as both ionic bonding²³ and covalent nature.²⁴ Recently, we have examined the adsorption of sodium ortho- and pyrophosphate clusters on iron and iron oxide surface.²⁵ The initial phase of tribochemical reaction of phosphate glass lubricant has been investigated with in-depth analysis in electronic structures.

Besides, the depolymerization of polyphosphate lubricant during the tribological process has been widely reported and it plays a crucial role in the molten phosphate lubricity. At ambient temperature, Martin et al.⁷ showed that the long-chain zinc polyphosphate glass enhanced the antiwear property by digesting abrasive iron oxide and formed the short-chain iron/zinc phosphate glasses. Nicholls et al.²⁶ proposed the antiwear pad structure in the ZDDP tribofilm which composed of long-chain polyphosphate and was stiffer to withstand intense loads than nearby short-chain areas. Crobu et al.²⁷ mentioned that the initial short-chain phosphates exposed the lower wear and friction compared to long-chain polyphosphate case. For tribological behavior of phosphate at elevated temperature, Tieu et al.^{2, 4} employed alkaline phosphate glasses and noted the reduction of phosphate chain length with increasing temperature. Short-chain length orthophosphate structures were observed in the whole tribofilm. The digestion of iron oxide into polyphosphate film which shortens the polyphosphate chain was observed. Cui et al.²⁸ conducted works on different chain length phosphates such as ortho- (Na_3PO_4), pyro- ($Na_4P_2O_7$) and long chain meta-phosphate ($NaPO_3$)_n. The short chain tribofilm obtained from the depolymerization of metaphosphate produced a better tribological performance compared to the anti-oxidation orthophosphate case. Even though the experimental studies have shown the effect of depolymerization of polyphosphate lubricant on tribological properties, there is still limited understanding on the detailed mechanism and the influence of the oxide surface on this process.

In recent years, the theoretical methods have a remarkable growth and considerable impact on the academic and application field. These computational approaches have been used for exploiting the potential materials as well as studying the unexplored properties, especially in nanotribology.²⁹ Among all, quantum mechanics (QM) is a suitable tool to describe bond breaking and formation in a chemical reaction at atomic scale and the tribochemical reaction of phosphate gets no exception. Mosey et al.³⁰ conducted density functional theory (DFT) calculation for the unimolecular decomposition of ZDDP. Righi et al.³¹ proposed the mechanism of the dissociative adsorption of phosphite additive on Fe(110) surface. Ta et al.²⁵ discussed the sodium phosphate clusters adsorbed on iron-based substrates. Recently, the development of advanced computational resources allows more realistic tribological conditions to be considered by the first principle molecular dynamics (FPMD).³²⁻³⁴ Compared to the productive applications, limited number of theoretical studies using phosphate is available due to its complex structure and various behavior involvements inside the glassy system.

In this study, both DFT and FPMD calculations have been carried out to understand the depolymerization of sodium polyphosphates on iron oxide surface at high temperatures which is an important phenomena observed in experimental work.²⁸ The bridging bond dissociations of $Na_4P_2O_7$ and $Na_5P_3O_{10}$ cluster with and without iron oxide surface have been conducted. The detailed results about

the bond nature of the system, effect of surface, chain length and temperature on depolymerization reaction will be presented.

Computational methods

Static DFT calculation

DFT calculations have been conducted in order to investigate the structure optimization of phosphate clusters and their decomposed products on iron oxide surface. All spin-polarized calculations have been performed with Vienna Ab-initio Simulation Package (VASP).³⁵ The Projector Augmented Wave (PAW) method³⁶ has been chosen with the Generalized Gradient Approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) exchange and correlation functional³⁷ as it has been acknowledged as a reasonable compromise among other functionals when representing dynamic decomposition on a metallic surface.³⁸ The energy cutoff of 400 eV has been applied for all calculations to truncate the expansion of plane wave basis set. Fe_2O_3 (0001) facet has been chosen as the adsorption surface with the dimension of $a = b = 10.07 \text{ \AA}$, $c = 23.98 \text{ \AA}$ for $\text{Na}_4\text{P}_2\text{O}_7$ adsorption and $a = 15.11 \text{ \AA}$, $b = 10.07 \text{ \AA}$, $c = 23.98 \text{ \AA}$ for $\text{Na}_5\text{P}_3\text{O}_{10}$ adsorption in order to minimize lubricant periodic image interaction. A vacuum region of $20 \text{ \AA}$ is included in the system to avoid the effect of nearby Fe_2O_3 layers in the z-direction. For static calculations, a Γ -point only sampling has been used for super-cell geometry optimization and a denser Monkhorst-Pack mesh³⁹ of $9 \times 9 \times 1$ has been employed for total energy calculations of slab models. The geometry optimizations are conducted using the conjugate gradient algorithm along with a first order Methfessel-Paxton scheme⁴⁰ until the energy convergence criterion of 10^{-4} eV has been reached. For more accurate energetic properties, the single point calculation use tetrahedron smearing technique with Blöchl corrections and the energy converged within 10^{-4} eV .

The adsorption energy is defined as:

where, E_{ads} , E_{bare} , and E_{gas} are the total energy of the adsorbed molecules on substrate, bare Fe_2O_3 substrate and isolated gas-phase lubricant, respectively. Hence, the negative value of E_{ads} indicates a thermodynamically favorable adsorption. Besides, the dissociation of separated molecule in the gas phase has also been considered in order to investigate the effect of the iron oxide surface on phosphate decomposition process. This process focuses mainly on depolymerization of linear polyphosphate chain.

The dissociation pathway of P-O bond on Fe_2O_3 surface was investigated with constrained minimization approach.⁴¹⁻⁴³ P-O distance has been fixed and all remaining degrees of freedom have been optimized to minimize the Hellmann-Feynman forces.⁴⁴ The P-O distance is then varied to monitor the energy profile of the reaction with these conditions: (a) all forces on atoms vanish and (b) the energy is a maximum along the reaction coordinate (P-O distance) but it is a minimum for all other degrees of freedom. The geometry relaxation of the constrained systems has been performed with external optimizer GADGET,⁴⁵ which uses the VASP output, computes the optimal steps of internal coordinates and starts the new

VASP run. The relaxation stopped when the variation of the energy is less than 10^{-4} eV and the force less than 10^{-2} eV/Å.

To investigate the bonding characteristic, both Electron Localization Function (ELF) and Bond Overlap Population (BOP) have been employed in the high-accuracy single point calculations. The ELF (η) evaluates the probability of finding the same spin electron in the surrounded area of reference electron.^{46, 47} The maxima $\eta = 1$ has been found in C-C covalent single bond of diamond crystal while $\eta = 0.5$ shows the homogeneous electron gas in some metal structure.⁴⁸ The BOP has been computed by the integration of crystal orbital overlap population (COOP) using the Local-Orbital Basis Suite Towards Electronic-Structure Reconstruction (LOBSTER) package.⁴⁹ The BOP, which represents the shared electron density between two atoms, can measure the covalency of the system. It provides the information about bonding, antibonding and non-bonding nature of a covalent interaction when the BOP is over zero, below zero or close to zero, respectively.⁵⁰

FPMD simulation procedure

FPMD simulations have been implemented for dynamics depolymerization process of sodium polyphosphates on iron oxide surface at elevated temperature. Due to the high computational expense, only the Γ -point sampling is applied in these simulations. Based on the compromise between computational efficiency and integration error, 0.5 fs time step has been chosen. With this time step, the total energy deviation of less than 0.02 eV has been observed during a 500-step MD run which has assured the stability of the system.³⁸ Three bottom layers of iron oxide have been fixed while the top three and lubricant coordinates have been optimized. Three preliminary FPMD simulations at 300 K include one $\text{Na}_4\text{P}_2\text{O}_7$ cluster on Fe_2O_3 surface; one $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster on Fe_2O_3 surface; one Na_3PO_4 unit and one NaPO_3 unit on Fe_2O_3 surface. The main simulations use the same structures and have been heated to 1100 K. These simulations run for 20 ps which suggested stable ground-state or intermediate configurations for static calculation. The snapshots will be captured in the Supporting Materials (SM). Then, seven structures of each system have been chosen and subjected to energy minimizations. The lowest energy conformer of each case has been reported here as ground-state structures. Next, each decomposed unit, Na_3PO_4 and NaPO_3 have been optimized separately on the Fe_2O_3 surface in order to capture stable adsorption configurations. The active adsorption sites of the surface are Fe atoms which strongly link to oxygen atoms of the lubricant compound. On top of the Fe-terminated oxide surface, iron atoms form equilateral triangles with 5.04 Å side. The stable adsorption sites of decomposed products are usually inside these triangles. Finally, both decomposed units have been relaxed on top of the surface with different relative positions of triangles (shown in Fig. S2 in SM). In order to distinguish the different types of non-bridging oxygen (O_{nb}), we denoted the ionic-bonding Na-O as terminal oxygen (O_{t}), and the Fe-O-P as linkage oxygen (O_{l}). Thus, the oxygen types in the system include (1) bridging oxygen (O_{b}) in P-O-P, (2) terminal oxygen (O_{t}) in P-O-Na, (3) linking oxygen (O_{l}) in P-O-Fe linkage between lubricant and surface, and (4) surface oxygen (O_{s}) on Fe_2O_3 surface.

Results

Structure of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters

For lubricant compounds, tetrasodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$ has been chosen as a model for polyphosphate $(\text{NaPO}_3)_n$ according to Ref.⁵¹ Pyrophosphate is also one of the most stable structures of condensed phosphates which has been reported by Van Wazer.⁵² Another linear phosphate compound sodium triphosphate $\text{Na}_5\text{P}_3\text{O}_{10}$ has been included to investigate the chain length effect. Triphosphate is a main product of thermal decomposition phosphate glass up to 828 K.⁵³ These substances contain the oxygen sites of the same properties as in polyphosphate which are bridging oxygen (O_b) and non-bridging oxygen (O_{nb}). O_{nb} will be categorized into O_t and O_i as the oxide surface included in the system. In order to validate the geometry optimization of the sodium phosphates by DFT, we analyzed the structure of both $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters. Calculated bonding and angular properties were compared with the experimental data of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ (Table 1). The geometric properties of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster agree very well with crystalline structures reported by Larsen et al.⁵⁴, MacArthur and Beevers⁵⁵ and Cruickshank.⁵⁶ The distance difference of ~ 0.1 Å between P-O_b and P-O_{nb} has been observed in previous experimental work⁵⁷ which is consistent with our results (Table 1).

Table 1 The geometrical parameters of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters

	$\text{Na}_4\text{P}_2\text{O}_7$		$\text{Na}_5\text{P}_3\text{O}_{10}$	
	Current DFT	Expt. ^a	Current DFT	Expt. ^b
P-O_b (Å)	1.66	1.63	1.63 (inner)	1.61 (inner)
			1.72 (outer)	1.67 (outer)
P-O_{nb} (Å)	1.54	1.45 - 1.52	1.53	1.49 – 1.51
Na-O_{nb} (Å)	2.15	2.47 - 2.63	2.20	2.25 – 2.76
$\text{P-O}_b\text{-P}$ (degree)	139.5	128.7 - 133.5	132.5	122.2
$\text{O}_b\text{-P-O}_b$ (degree)	-	-	99.1	98.7
$\text{O}_b\text{-P-O}_{nb}$ (degree)	106.3	99.0 – 109.6	105.7	100.1 – 110.1
$\text{O}_{nb}\text{-P-O}_{nb}$ (degree)	112.4	113.0 – 116.0	115.4	113.4 – 116.4

^a Data obtained by Larsen et al.⁵⁴ and MacArthur and Beevers⁵⁵

^b Data obtained by Cruickshank⁵⁶

Moreover, we calculated the bond overlap population (BOP) and electron functional localization (ELF) to provide detailed information of chemical bonding in our system. The optimized structures of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters with BOP and ELF data have been presented in Fig. 1 and Fig. 2. Besides the consistent geometric properties of phosphate cluster, the BOP ratio P-O bridging bond/non-bridging

bond of 0.16-0.22 |e| / 0.33-0.35 |e| agrees well with the COOP curve of $P_2O_7^{4-}$ by Le Beuze et al.⁵⁸ The P-O non-bridging bonds are twice stronger than bridging ones. In Fig. 1 and Fig. 2, the maximal ELF value is 0.75 which represents a moderate degree of electron pairing and covalent bonding. Most of electron pairs are localized around oxygen atoms as electron receivers with different shapes and concentration. For bridging oxygen atom, three explicit regions have been observed in Fig. 1b and Fig. 2b. Two lumps appear in the middle of phosphorus and oxygen which indicates the modest covalent interaction of P-O_b. Another region on the bridging oxygens depicts the lone pair area which avoids the phosphorus-oxygen bond direction. In terms of non-bridging oxygen atoms, a P-O electron-pair lump for each O_{nb} is also spotted in the middle of the bond in Fig. 1d and Fig. 2d. Thus, the P-O interaction in general is the strongest covalent bond among all. The mushroom-like localized shape of lone pair electron gets no deformation toward sodium and is located in the opposite of covalent P-O area as seen in Fig. 1b and Fig. 2b. Besides, the BOP for Na-O bond is 0.01 to 0.02 |e|, which indicates no overlap area between sodium and oxygen. Thus, the interaction between sodium and non-bridging oxygen is purely ionic interaction. For Na₅P₃O₁₀ cluster, the non-bridging P-O_{nb} bonds have the average BOP of 0.35 |e| which is nearly identical to this bond type in Na₄P₂O₇ (BOP = 0.33 |e|). We show two bridging P-O_b bonds as inner and outer of the Na₅P₃O₁₀ cluster in the Fig. 2. The BOPs for these bonds are 0.22 |e| and 0.16 |e|, respectively. The bond distances are also matching with the BOPs: 1.63 Å for inner bond, and 1.72 Å for outer bond. With the difference of the BOP values and the distances of P-O_b inner and P-O_b outer bonds in Na₅P₃O₁₀ cluster, the ELF also shows that the electron localized area between P₁-O_b (inner) and P₂-O_b (outer) has a slightly distinct shape. P₁-O_b has a larger and more intense area of electron pair possibility which indicates that the covalent bond of inner P-O_b bond is stronger than the outer bridging bond. In conclusion, the bridging P-O bond is the most fragile site in the phosphate chain and has the topmost possibility to be detached in the working environment of hot metal forming process.

Dissociation of Na₄P₂O₇ and Na₅P₃O₁₀ clusters

Isolated phosphate clusters

In Fig. 3a of small Na₄P₂O₇ cluster, the number of oxygen atoms around sodium cation is two so the position between two PO₄ tetrahedra includes two sodium atoms. For alkali polyphosphates, there are some discrepancies in the reported oxygen coordination around Na atom in the literature, i.e. 5 by Hoppe et al.^{59, 60}, 2 by Uchino and Ogata⁶¹ and 2.4 by Musinu et al.⁶² This variation comes from different experimental and theoretical structures of alkali phosphate glass. Thus, the two-oxygen coordination around sodium ions in our study is feasible.

In Fig. 3, the Na-O bonds have been visualized with the cutoff distance of 2.4 Å during P-O bridging bond dissociation. Non-directional ionic Na-O interaction allows sodium atoms to move freely toward PO₃ unit or PO₄. Three different structures generated by three schemes with different sodium complexation have been optimized without constraints (shown in Fig. 3d, 3e and 3f). Along these schemes, P-O_b distance has been elongated from 1.66 Å to ~7.0 Å. Seven converged configurations have been depicted in Fig. 3. At the initial phase of the dissociation, PO₃ and PO₄ units have two shared sodium ions at the distance of ~2.72 Å (Fig. 3b) or have one shared sodium ion at the distance of ~4.25 Å (Fig. 3c). These structures

indicate that sodium ions can be distributed between two different phosphate chains. This means that sodium ions also have a weak network forming role besides the dominant modifier function as proposed by Uchino and Ogata.⁶³ The relative stabilities of three decomposed configurations are shown in Fig. 3d, 3e, and 3f. In these configurations, two phosphate units are separated by a distance about 7 Å. The optimized results show that the structure in Fig. 3f reaches the lowest total energy among the three configurations; therefore it has been used for the optimization of decomposed products on the Fe₂O₃ surface in the following steps. Remarkably, the relative energies yield positive values which mean the decomposition of P-O_b bridging bond in the isolated Na₄P₂O₇ cluster is not thermodynamically preferable. The energy of +2.74 eV is taken into account for the dissociation energy of P-O bridging bond in the isolated cluster as it follows the minimum energy path of the decomposition.

The ground-state structure and energy differences of Na₄P₂O₇, Na₅P₃O₁₀ and their decomposition products from isolated cluster and on iron oxide surface have been presented in the upper part of Fig. 4a and Fig. 4b. Besides, geometric parameters and bond overlap population (BOP) between them have been listed in Table 2.

Table 2 Geometric parameters and BOP of phosphate clusters and their decomposition products. Values of BOP ($|e|$) from integrated crystal orbital overlap population (COOP) are shown in parenthesis.

	Isolated Na ₄ P ₂ O ₇ cluster	Decomposed isolated Na ₄ P ₂ O ₇	Isolated Na ₅ P ₃ O ₁₀ cluster	Decomposed isolated Na ₅ P ₃ O ₁₀
P-O _b (Å) (outer)	1.66 (0.19)	1.60 (0.26) 7.02 (0.00)	1.72 (0.16)	1.85 (0.10) 7.41 (0.00)
P-O _b (Å) (inner)			1.63 (0.22)	1.60 (0.27) 1.61 (0.23)
P-O _{nb} (Å)	1.54 (0.33)	1.53 (0.33)	1.53 (0.35)	1.52 (0.35)
Relative energy (eV)	0.00	+2.74	0.00	+2.66

Firstly, different complexation forms of sodium ions have been considered for the ground state of Na₄P₂O₇ decomposition. As a result, the structure including one Na₃PO₄ cluster and one NaPO₃ unit has reached the lowest total energy as shown at Fig. 3f. Correspondingly, the products of Na₅P₃O₁₀ decomposition are optimized as NaPO₃ unit and Na₄P₂O₇ cluster. In Table 2, P-O_b bridging bond becomes P-O_{nb} non-bridging bond after decomposition. For Na₄P₂O₇ cluster, the P-O_b distance varies from 1.66 Å to 1.60 Å and the BOP increases from 0.19 $|e|$ to 0.26 $|e|$. Another P-O_b distance is elongated up to 7.02 Å and the BOP becomes 0.00 $|e|$, indicating that this P-O_b bond is completely broken. One covalent sharing area of O_b atom in Fig. 1b merges with the lone pair area of that bridging atom and is located

opposite to the remaining covalent localized area during the decomposition. At the end, the PO_4 unit contains four non-bridging oxygens with four P-O covalent lumps and four mushroom-like shapes of oxygen lone pair which interact ionically with sodium.

In terms of longer chain length cluster, one outer P-O_b bond has increased to 7.41 Å and BOP reduces to 0.00 |e| in the decomposition process of $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster (Fig. 4b). The inner bridging bond connects to the broken outer bridging has shortened from 1.63 Å to 1.60 Å and the BOP has risen from 0.22 |e| to 0.27 |e|, which is close to that of a typical non-bridging bond. Another inner bond slightly reorganizes the bond distance and BOP due to the alteration of outer bridging bond nearby. This outer bond is extended to 1.85 Å and reduces the BOP to 0.10 |e|. The decomposed-like variation is caused by an imbalanced distribution of sodium atoms around P_2O_7 unit as seen in the top structure of Fig. 4b. In particular, the bridging oxygen of P_2O_7 unit is surrounded by three sodium ions with the distances of 3.26 Å, 2.50 Å and 2.42 Å and the corresponding BOP values of -0.01 |e|, 0.02 |e|, and 0.01 |e|, respectively. In comparison with $\text{Na}_4\text{P}_2\text{O}_7$ cluster in the left structure in Fig. 4a which has the typical bridging P-O bond of 1.66 Å (BOP 0.19 |e|), two Na-O_b interactions produced an identical distance (BOP) of 2.98 Å (-0.01 |e|). The negative value of BOP represents the antibonding interaction. Thus, the bridging oxygen of P_2O_7 unit from $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster decomposition has been attacked by nearby sodium atoms and causes the elongation of outer bridging P-O bond. This phenomenon confirms the network modifier function and induced-depolymerizing effect of alkali metal on phosphate glass.⁶⁴

Both $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ dissociation are not thermodynamically favourable in the gas due to the positive energy difference up to 2.74 eV for $\text{Na}_4\text{P}_2\text{O}_7$ and 2.66 eV for $\text{Na}_5\text{P}_3\text{O}_{10}$. There is a difference between two P-O breakage energies but it is not considerable. The difference is mainly based on the sodium distribution around breakage bond. Moreover, the P-O_b split energy of P_2O_7 unit in Fig. 4b is 2.87 eV while this energy of outermost P-O_b on $\text{Na}_6\text{P}_4\text{O}_{13}$ is 2.78 eV. Hence, the P-O_b bond dissociation energy of sodium phosphate is about 2.6 – 2.9 eV and is affected to a minor degree by the chain length.

The energy profiles of P-O bridging bond dissociation for the isolated $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters have been showed in Fig. 5. The result of $\text{H}_4\text{P}_2\text{O}_7$ cluster has also included in the figure in order to investigate the effect of cations on bridging bond dissociation. The energy at the equilibrium P-O distance of the three clusters has been chosen as the reference energy. For $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster, the P-O outer bond is selected. In the figure, 3.5 Å is the cut off of the bond dissociation process, and the stable dissociation energy appeared after this distance. Compared among three clusters, the dissociation energies of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ are steady around 2.7 eV while much higher dissociation energy of 4.0 eV from $\text{H}_4\text{P}_2\text{O}_7$ result has been observed. Four hydrogen atoms of $\text{H}_4\text{P}_2\text{O}_7$ can play a role as dangling bonds in the network,^{61, 63} thus the dissociation energy of $\text{H}_4\text{P}_2\text{O}_7$ can represent the dissociation of 3-D network of polyphosphate without cation, i.e. P_2O_5 glass structure. Hence the modifier cation like sodium helps reduce the P-O bridging dissociation energy.

Sodium phosphates dissociation on Fe_2O_3 surface

For the oxide substrate, we conduct the study on the iron termination of Fe_2O_3 (0001) surface which has been reported as the most stable facet in many experimental and theoretical studies.^{65, 66} Six atomic

layers of Fe_2O_3 (0001) surface have been used and the number of atoms in the surface is up to 60 atoms. Three bottom atomic layers of the surface have been fixed in order to represent the bulk behavior of iron oxide while all above layers have gone through relaxation. For the iron oxide surface, the obtained charge of Fe_2O_3 (0001) is in agreement with the model by Ta et al.⁶⁷ The results have been provided in SM.

The most stable configurations of $\text{Na}_4\text{P}_2\text{O}_7$ cluster adsorption and $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster adsorption have been described in the bottom structures of Fig. 4a and 4b, respectively. $\text{Na}_4\text{P}_2\text{O}_7$ adsorption structure has been obtained from the study by Ta et al.²⁵ A variety of oxygen types have been noted in Fig. 5a. The geometry parameters and bond overlap population (BOP) in those configurations have been listed in Table 3.

Table 3 Geometric parameters and BOP of phosphate clusters and their decomposition products adsorbed on Fe_2O_3 surface. The BOP values ($|e|$) from integrated crystal orbital overlap population (COOP) are shown in parenthesis.

	Absorbed $\text{Na}_4\text{P}_2\text{O}_7^a$	Decomposed $\text{Na}_4\text{P}_2\text{O}_7$	Absorbed $\text{Na}_5\text{P}_3\text{O}_{10}$	Decomposed $\text{Na}_5\text{P}_3\text{O}_{10}$
P-O _b (Å) (outer)	1.66 (0.21)	1.57 (0.30) 4.04 (0.00)	1.71 (0.17)	1.65 (0.22) 4.40 (0.00)
P-O _b (Å) (inner)			1.61 (0.24)	1.58 (0.26) 1.66 (0.21)
P-O _t (Å)	1.52 (0.36)	1.51 (0.39)	1.51 (0.38)	1.51 (0.37)
P-O _i (Å)	1.59 (0.27)	1.58 (0.29)	1.55 (0.31)	1.58 (0.27)
P-O _s (Å)		1.70 (0.18)		1.78 (0.15)
O _i -Fe (Å)	1.91 (0.24)	2.09 (0.18)	1.98 (0.22)	1.91 (0.24)
Fe-O _s near P-O-Fe linkage (Å)	1.89 (0.21)	1.89 (0.21)	1.90 (0.21)	1.91 (0.20)
Fe-O _s on surface (Å) ^b	1.86 (0.23)	1.89 (0.20)	1.88 (0.21)	1.90 (0.20)
Relative energy (eV)	0.00	0.03	0.00	-0.22

^a Data obtained by Ta et al.²⁵

^b The Fe atoms on the top layer of the surface only

In terms of the phosphate – iron oxide adsorption, Atkinson et al.¹² proposed P-O-Fe monodentate structure of iron phosphate complex as one of the most stable linkages observed during the adsorption

of phosphate on goethite interface which is observed in Fig. 4a and b. The adsorbed structure of $\text{Na}_5\text{P}_3\text{O}_{10}$ is also in line with Kubicki et al.¹⁹ which mentioned P- O_i bond 1.56 Å and P-Fe distance 3.42 Å. In addition, these values are also observed in the studies of Belelli et al.¹⁷ and Acelas et al.¹⁸. When $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters adsorb on the Fe_2O_3 surface, some P- O_t bonds change into P- O_i interaction. The bond distance and bond overlap population change from 1.53 Å, 0.35 |e| into 1.55 Å, 0.31 |e|. The Fe_2O_3 surface will reduce the strength of P-O terminal bond if the terminal oxygen atom contributes to P-O-Fe linkage which is consistent with Ta et al.²⁵ for short chain length sodium phosphate cluster $\text{Na}_4\text{P}_2\text{O}_7$. In the case of adsorbed cluster structures, one oxygen atom of each PO_4 tetrahedron forms an interaction with one iron atom on the substrate. These O_i -Fe bonds are 1.91 – 1.98 Å long and have the BOP of 0.22 - 0.24 |e|, which are similar to the distance and BOP of Fe- O_s on the surface in both clusters. Thus, we categorize the bond type into three strength levels and their order based on BOP after adsorption is as follow:

$$\text{P-O}_b \approx \text{Fe-O}_s \approx \text{Fe-O}_s \text{ near linkage} \approx \text{Fe-O}_i < \text{P-O}_i < \text{P-O}_t$$

For iron-oxygen interaction, Fe- O_i bond is as strong as Fe- O_s next to linkage and the normal Fe- O_s on top of the surface which have BOP of 0.21 – 0.24 |e|. With the system contained phosphate clusters and iron oxide surface, P- O_b is still one of the most feeble bond and has a strong chance for dissociation. The finding is supported by the study of $\text{Na}_4\text{P}_2\text{O}_7$ adsorption on Fe_2O_3 .²⁵ In additional, the ELF value of cluster adsorption has been displayed in Fig. 6 for more information about Fe-O-P linkage interactions.

When the $\text{Na}_5\text{P}_3\text{O}_{10}$ adsorption occurs, terminal oxygens link with iron atom on the surface and create linkage oxygens as mentioned in Fig. 6a. There are three electron pair regions observed from linkage oxygen atoms: one medium covalent bond between P-O, one partial mushroom-like region for ionic interaction with sodium, and one small deformed area in the direction towards Fe surface atom which can be observed in Fig. 6c. The third has a similar contour to the Fe-O bond on the top of the oxide surface in Fig. 6d, hence this Fe-O bond has been considered to be a mixed ionic/covalent bond with the same nature as the iron oxide interconnection. The adsorption energy of isolated $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters on Fe_2O_3 surface is -5.51 eV for $\text{Na}_5\text{P}_3\text{O}_{10}$, which is thermodynamically favorable and is as strong as the chemical adsorption. The adsorption of short chain length sodium phosphate cluster on iron oxide substrate also has the same trend.²⁵ It is worth noting that most references data on the adsorption energies were from the study of phosphate adsorption in the soil industry. Thus, the models from these references will be more complicated than this work because of the contribution of proton, the dissociation of OH⁻ group or H₂O molecules from mineral surface. And the adsorbates are usually $\text{H}_n\text{PO}_4^{3-n}$ with one or two bridges with metal atoms on the surface. However, the adsorption energy per PO_4 tetrahedron about -1.83 eV for $\text{Na}_5\text{P}_3\text{O}_{10}$ is still comparable to previous studies of phosphate adsorption on goethite $\alpha\text{-FeO(OH)}$ or gibbsite Al(OH)_3 which have the listed energy from -3.44 to -0.66 eV^{17, 68}.

With the forming of strong chemical adsorption linkage, the alkali phosphate network can create a durable layer which provides a lower friction, significant wear reduction and significant oxidation prevention for steel/steel contact in metal forming process^{1, 2}. The adsorption energy of the system goes down from -4.51 eV of $\text{Na}_4\text{P}_2\text{O}_7/\text{Fe}_2\text{O}_3$ to -5.51 eV of $\text{Na}_5\text{P}_3\text{O}_{10}/\text{Fe}_2\text{O}_3$ (Fig. 4). Thus, for longer chain length of phosphate cluster, the absorbed structure is more stable. However, the absorbed energy per PO_4

tetrahedron or per Fe-O-P bond has a reverse trend. The absolute value rises from -2.25 eV of $\text{Na}_4\text{P}_2\text{O}_7$ cluster to -1.83 eV of $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster. Additionally, the average Fe-O_l bond distance stretches by 0.07 Å and the mean BOP slightly lessens by 0.02 |e|. Although the variation of linkage bond strength is minute, the small phosphate chain is preferable if the full coverage monodentate complex of phosphate spreads over iron oxide surface.

The ground-state structures of decomposed products adsorption are shown in the bottom right of Fig. 4a and 4b. Due to previous energy minimizations of NaPO_3 and Na_3PO_4 on the surface, the most stable configurations have been chosen. The PO_3 unit in both decomposition cases forms one or two P-O-Fe linkages and one P-O_s bond. This adsorption contains a FeO_4 tetrahedron and a PO_4 tetrahedron which share one edge. The P-O_s distances are 1.70 Å for $\text{Na}_4\text{P}_2\text{O}_7$ and 1.78 Å for $\text{Na}_5\text{P}_3\text{O}_{10}$ which are the longest P-O interaction and the BOP is 0.18 |e| and 0.15 |e| respectively which are the weakest bond type of the system. Meanwhile, the PO_4 unit in the $\text{Na}_4\text{P}_2\text{O}_7$ decomposition creates three linkages with the Fe atoms on the surface through three oxygen vertices of tetrahedron. And P_2O_7 unit in $\text{Na}_5\text{P}_3\text{O}_{10}$ breakage generates the monodentate complex as a full $\text{Na}_4\text{P}_2\text{O}_7$ cluster.

During the P-O-P cleavage, P-O_b bridging bond can become P-O_t terminal or P-O_l linkage bond depended on the relative position of O_b on the surface. The ELF of decomposed products of $\text{Na}_4\text{P}_2\text{O}_7$ cluster on the Fe_2O_3 surface has been depicted in Fig. 7. The ELF of $\text{Na}_5\text{P}_3\text{O}_{10}$ degradation is very similar (data not shown). As no bridging oxygen exists, all oxygens have mushroom-like shape of terminal atoms for isolated molecule decomposition. When these products are absorbed on oxide substrate, the P-O_s bond formed and PO_3 unit becomes a PO_4 tetrahedron with the help of one surface oxygen atom. The localized electron regions have been found along the P-O_s direction in Fig. 6b. These regions have the same shapes to other covalent P-O bridging, terminal or linkage bonds but have smaller bond overlap population values. This bond is a weak covalent bond and is the weakest P-O interaction in the system. This phenomenon is also observed in the $\text{Na}_5\text{P}_3\text{O}_{10}$ case and can be explained by an abundance of O_s coordination up to three before the P-O_s bond initiation. The maximum P-O coordination of four has been maintained in the phosphate glass network as reported by Hoppe et al.⁶⁹

The energy profiles of P-O bond dissociation of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters on Fe_2O_3 surface have been displayed in Fig. 8 and Fig. 9, respectively. The origins at 0 eV have been set for the adsorption of two clusters on iron oxide surface. The relative energies of structures which have different P-O bridging distances are related to the origins. In Fig. 8 and Fig. 9, there are some maxima and minima due to the simultaneous contribution of P-O bond stretch and mobile movement of sodium which can stabilize and destabilize our system. The energy barriers for the dissociation on the surface are 3.75 eV for $\text{Na}_4\text{P}_2\text{O}_7$ and 3.24 eV for $\text{Na}_5\text{P}_3\text{O}_{10}$ which are spotted from the highest relative energies. The beginning, the highest maximum and the end of Fig. 8 and Fig. 9 have been simplified and displayed in Fig. 4. As can be seen in Fig. 4, Fe_2O_3 surface can reduce the bridging bond dissociation reaction energy from +2.74 eV to +0.03 eV for $\text{Na}_4\text{P}_2\text{O}_7$ and from +2.66 eV to -0.22 eV for $\text{Na}_5\text{P}_3\text{O}_{10}$. Even though the energy barriers are quite high, around 3.3 – 3.8 eV, the structures at the top of the hill still have negative energy values compared to the total energy of isolated clusters, -0.76 eV in Fig. 4a and -2.27 eV in Fig. 4b. Thus, the decomposition reaction is more feasible on the iron oxide surface. The lower schemes in Fig. 4a and 4b are preferable in both cases. Phosphate chains will adsorb on the surface and then undergo the bridging

bond dissociation. This mechanism has been proposed before by Zhang et al.⁷⁰ when studying the tribofilm formation of ZDDP. The iron oxide surface plays a crucial role to help the system to achieve the lower energy states for cluster and decomposed products. However, when comparing the bridging bond dissociation reaction of the isolated clusters and the adsorbed clusters on surface, the barrier energies for the latter case are higher (~3.5 eV compared to ~2.7 eV). The barrier energy around 3.5 eV is also comparable with the bond dissociation energy of $\text{H}_4\text{P}_2\text{O}_7$. Hence, the Fe_2O_3 surface also has both positive and negative effects on the P-O bridging dissociation process. For the chain length effect, the higher chain length cluster $\text{Na}_5\text{P}_3\text{O}_{10}$ formed a more stable adsorbed complex with Fe_2O_3 surface and had a lower energy barrier for bond dissociation as shown in Fig. 4. However, this effect will not be much significant in the real polyphosphate system because of the extreme mobility of modifier metal like sodium. Besides, with a harsh environment of the metal forming process, all barriers in our system will be overtaken. The energy difference between adsorbed clusters and their decomposition is rather small which infers that there is a co-existence of breaking and non-breaking chains during the process. The chain and the decomposed products can be observed simultaneously due to the reciprocity of polymerization and depolymerization. In the following section, first principle molecular dynamics simulations were undertaken in order to investigate the nature of lubricant depolymerization/polymerization at elevated temperatures.

First principle molecular dynamics simulations at high temperatures

This section will discuss the behavior of $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ phosphate cluster during interaction of iron oxide surface at 1100 K which is the working temperature of the hot rolling process.⁷¹

Na₄P₂O₇ cluster on iron oxide surface

Fig. 10 exhibits the trajectory of sodium pyrophosphate cluster on iron (III) oxide surface at 1100K. Sodium atoms have been hidden for clarity. Iron sites on top of the surface have been introduced by gold spheres. The bridging oxygen has been noted as O_b , while the non-bridging oxygens which have interacted with surface have been marked from O_1 to O_4 . In the starting configuration, P_2O_7 cluster was placed randomly at 3 Å above the iron oxide substrate (Fig. 10a). As the cluster gradually moved closer to the surface to explore the favorable adsorption site, it rotated and formed the first linkage between Fe_1 and O_1 at 0.35 ps (Fig. 10b). The dangling part of cluster quickly went down and created the second linkage $\text{Fe}_2\text{-O}_3$ at 0.5 ps (Fig. 10c). After that, the cluster anchored stably on the surface through two linkages with Fe_1 and Fe_2 . During 20 ps of the simulation time, no bridging bond dissociation or depolymerization was observed. The evolution of the two bridging P-O bonds as a function of simulation time is shown in Fig. 11. Under the impact of elevated temperature, both bridging bonds fluctuated around an average value of 1.69 Å, which was 0.02 Å longer than the equilibrium bridging P-O bond in the isolated $\text{Na}_4\text{P}_2\text{O}_7$ and the adsorbed one on the surface. At ~1.0 ps, $\text{P}_1\text{-O}_b$ distance extended up to 2.6 Å then quickly got back to the average value. At 1100K, the thermodynamic movement of atoms increased and weakened the bridging bond to a slight degree. The thermal effect is expected to be more intense at a higher temperature. In fact, an additional simulation of $\text{Na}_4\text{P}_2\text{O}_7$ cluster on oxide surface at 1500 K produced the dissociation of P-O bridging bond. The snapshots have been shown in Fig. S6 in SM. Although there was no breakage occurred, the linkages Fe-O-P evolved over the simulation time.

The interatomic distances between different O_{nb} with Fe_1 and Fe_2 have been presented in Fig. 12. As shown in Fig. 10 and 12, the Fe adsorption sites had been competed by various non-bridging oxygens from one PO_4 tetrahedron. In particular, O_1 and O_2 interacted with Fe_1 (Fig. 12a), O_3 and O_4 connected to Fe_2 (Fig. 12b). From 0 ps to 0.5 ps, the adsorption of P_2O_7 cluster has been observed with a decrease of Fe-O distances in both PO_3 groups. After that, the linkage distances remain steady at 1.95 Å in Fig. 12a and 12b which is the equilibrium distance of Fe- O_i or Fe- O_s obtained from static DFT calculation in the previous section. Despite the fact that O_1 and O_2 , O_3 and O_4 replaced each other to form linkage with Fe, monodentate configurations between the $Na_4P_2O_7$ cluster and oxide surface were always maintained. This indicates that one Fe-O-P linkage per PO_4 unit is the most stable structure for the interaction between phosphate and iron oxide substrate, which has an agreement to the previous conclusion in previous section and the study of Atkinson et al.¹² Fe atoms at the adsorption site usually created a deformed FeO_4 tetrahedron which connected to a PO_4 tetrahedron through the linkage oxygen which has been mentioned in the structure of the iron phosphate crystal.⁷² This was different from the rigid FeO_6 octahedra in the bulk of Fe(III) oxide crystal. The deformed FeO_4 tetrahedra allowed the phosphate chain to be mobile but still strongly adhere to the surface. The oxygen atom at the bridging state did not form any stable bonds with iron from surface but being attacked by the floating sodium. The sodium atoms, which were not represented in the snapshots, were moving and terminated the non-bridging oxygen atoms or three oxygens on the oxide surface.⁷³

$Na_5P_3O_{10}$ cluster on iron oxide surface

The snapshots of $Na_5P_3O_{10}$ cluster on the iron oxide surface during FPMD simulation at 1100 K are shown in Fig. 13. Sodium, lower layer of irons and surface oxygens were also removed for better visualization. The bridging oxygens were noted as O_i and O_{ib} , the important non-bridging oxygens were counted from O_1 to O_5 , and three phosphorus atoms were P_1 to P_3 . The trajectory of P_3O_{10} cluster is more complicated than the P_2O_7 due to the occurrence of the bridging bond dissociation between $P_1-O_i-P_2$. Thus, the P_3O_{10} cluster could be divided into PO_3^1 which contained P_1 and three O_{nb} ; PO_4 which contained P_2 , two O_b and two O_{nb} ; and PO_3^2 for the rest (Fig. 13b). At the beginning, the cluster also stayed above the surface 3 Å. The first linkage between O_1 from PO_4 with Fe_1 of surface appeared at 0.5 ps (Fig. 13c). The second linkage from PO_4 continuously generated between O_2 and Fe_2 at 0.9 ps. Following the connection of the middle unit of P_3O_{10} cluster, the P_1-O_i bridging bond was broken at 1.5 ps and PO_3^1 unit moved far away from adsorbed phosphate chain. These steps can be observed in Fig. 14a and Fig. 15a. The snapshot at 3 ps showed the stable adsorption with two linkages from PO_4 unit and also the dissociation of P_1-O_i bond. The distance of P_1-O_i was about 4 Å at 3 ps (Fig. 13d). The linkage between PO_3^2 and Fe_3 was observed at 3.5 ps until the end of the simulation.

After moving above adsorbed P_2O_7 unit, P_2O_7 and PO_3^1 reunited to form the initial P_3O_{10} cluster at 7 ps (Fig. 13e). Firstly, P_1 approached O_1 atom, which was already bonded with Fe_1 . Then the O_5 from PO_3^1 competed with O_1 in order to connect with Fe_1 and interrupted the Fe_1-O_1 linkage. This process finished at 7.5 ps. The stable P_3O_{10} cluster reformed and attached itself to the oxide substrate through three monodentate linkages. No significant changes were observed after 10 ps. The detailed bond evolution during the adsorption and dissociation process has been illustrated in Fig. 14 and Fig. 15. The bridging

bonds related to P_1 were described in Fig. 14a while others bridging P-O were shown in Fig. 14b. P_1-O_1 bridging bond started to increase at 1.5 ps and confirmed the bond dissociation. Besides, the P_1-O_1 varied from 3 – 6 Å at the beginning because two atoms belonged to two groups, O_1 is the member of PO_4 unit which has center P_2 . After 7.5 ps, O_1 became a bridging oxygen between P_1 and P_2 with the average distance of 1.7 Å. All other bridging bonds such as P_2-O_I , P_2-O_{II} , and P_3-O_{II} showed no significant variations and maintained at a distance of 1.71 Å. With the bridging bond breaking and forming during the simulation run, the adsorbed cluster and decomposed products can coexist in the system as mentioned in the static DFT calculation. Therefore, the depolymerization and polymerization of phosphate chain can occur simultaneously in the hot rolling process. Moreover, the Fe-O linkages had some interesting rearrangements which were shown in Fig. 15. Fig. 15a showed two linkages of PO_4 unit formed after the adsorption at 0.5 and 0.9 ps with the average distance of 2.05 Å. The first linkage Fe_1-O_1 was then broken at 7.5 ps due to the competition of O_5 atom in Fig. 15b during the bridging bond forming process. Besides, the linkage between PO_3^{2-} with Fe was stable after 7.5 ps with some exchanged interactions between $Fe-O_3$ and $Fe-O_4$ in Fig. 15c. In conclusion, one monodentate linkage per PO_4 tetrahedron is the most observed structure in the FPMD simulations of $Na_5P_3O_{10}$ cluster on the Fe_2O_3 surface at 1100K.

In general, both sodium phosphates $Na_4P_2O_7$ and $Na_5P_3O_{10}$ tend to adsorbed on the surface regardless bond dissociation. In the comparison between different phosphate chains, at 1100 K bond dissociation has been recorded in $Na_5P_3O_{10}$ by cleaving $P-O_b$ bonds while $Na_4P_2O_7$ remains as a stable chain. A higher temperature is needed to break $P-O_b$ bonds of $Na_4P_2O_7$. This observation agreed with the study by Cui et al.²⁸ that the tribofilm observed after the pin-on-disk test with sodium pyrophosphate lubricant which showed a slight degree of polymerization and the depolymerization for longer phosphate chains.

Discussion

Polyphosphate glass has been built up from a network of PO_4 tetrahedra linked through P-O-P bridging bonds. With the metal addition which is a network modifier such as alkali or alkali earth metal, three-dimensional structures of polyphosphate can degrade into polymer-like metaphosphate chains, rings, short-chain pyrophosphate glass or isolated orthophosphate molecules. These structures are related to the ratio of bridging and non-bridging oxygen in the glass.⁷⁴ In P-O interactions of PO_4 tetrahedron, phosphorus atom promotes its fifth valence electron into its 3d orbital which creates a π -bond with a 2p orbital of oxygen. This π -bond has been shared equally to all $P-O_{nb}$ through resonance effect.⁷⁵ In comparison between bridging and non-bridging P-O bond overlap populations, the interaction of $P-O_b$ is weaker than $P-O_{nb}$ which has been studied by Boyd.⁷⁶ The electrons of non-bridging oxygens are more likely to fill the molecular orbital $P\ 3d_{\pi} + O\ 2p_{\pi}$ than do the bridging oxygens. Because of the electron sharing with two nearby phosphorus atoms, the bridging bond cannot be strengthened by “back-bonding” effect from 3d orbital as strong as the non-bridging bond. According to the bond overlap population in Table 3, one of the non-bridging P-O bonds is weakened by Fe atoms from surface and becomes $P-O_l$ link. The $P-O_l$ bond is weaker than normal $P-O_t$ terminal bond because the oxygen atom in the $P-O_l$ -Fe linkage has to share 2p orbital to both P and Fe, which reduces the effect of back-bond d-p orbital from terminal oxygens to phosphorus atoms. However, $P-O_b$ is still the weakest bond in both the

isolated cluster and the adsorbed phase. This conclusion has been supported by our FPMD simulations which observed no P-O_{nb} dissociation either at ambient temperature or elevated temperature but the bridging bond cleavage of phosphate cluster has been spotted at extremely high temperatures.

For iron-oxygen interactions, Fe-O_l bond is as strong as Fe-O_s next to linkage and the normal Fe-O_s on the top of the surface as indicated by similar bond overlap population and electron localization function. The iron-oxygen bond in iron oxide structure is well-known for its strong ionic nature and decent covalent property. The 2p orbitals of oxygen can hybridize with $3d_{\text{eg}}$ orbitals of iron to form σ -bonds, with $3d_{\text{t2g}}$ orbitals of iron to form π -bonds, and can weakly hybridize with 4sp orbitals of iron atom also.⁷⁷ As Fe(III) octahedral structure has been considered in Table 3 with an Fe(III)-O distance of 1.86 – 2.09 Å, the covalent nature of this bond is considerable when comparing a pure ionic Fe(II)-O bond distance of 2.16 Å and a covalent-metallic Fe(II)-O 2.01 Å.⁷⁸ Hence, the Fe-O_l bond is an ionic/covalent resonance bond which has a similar strength as Fe-O_s on the surface.⁷⁹ However, the BOP difference of four weakest bonds P-O_b , Fe-O_s , Fe-O_s near linkage, and Fe-O_l is rather minor, being 0.03 |e|. Comparing P-O_b bonds with Fe-O interactions, the bridging oxygen bond has the same covalent strength but less ionic nature than Fe-O. Therefore, the P-O bridging bond has the highest tendency to break during the tribological shearing test. The O_s -Fe bond can also be cleaved and form iron oxide nanoparticles which will be digested by phosphate lubricant. The digestion of iron oxide by polyphosphate tribofilm at 800°C has been proposed by Cui et al.⁸⁰ As the structure of iron/iron oxide nanoparticle is different from standard crystalline oxide⁸¹, the interactions of alkali phosphates and iron-based nanoparticles are worth further investigation, particularly the competition between alkali and iron ions inside phosphate tribofilm.

Generally, the alkali metal plays a role as a network modifier which reduces the P-O-P bridging bonds and ionically interacts with terminal oxygen atoms. Thus, the metaphosphate long chain structure has been commonly mentioned in alkali phosphate glass studies instead of 3D-network of vitreous P_2O_5 .⁸² The energy profile in Fig. 5 also supported this point. When adding iron oxide into alkali phosphate glass, the P-O-P chain will be substituted by durable Fe-O-P bonds.⁸³ The introduction of transition metal oxide intensifies the depolymerization degree of phosphate chain in condensed glass.⁸⁴ The mixed alkali iron phosphate glass gets high durability due to the rigid octahedral sites of Fe(III) which reinforce the cross-linking between short phosphate chains.⁸⁵ The Fe-O coordination value in iron phosphate glass is mixed from four to six.^{69, 86, 87} The abovementioned studies indicate the effect of iron/iron oxide to alkali phosphate in the bulk phase. In our study, the iron oxide plays quite a different role for the depolymerization as an adsorption surface. Firstly, the surface helps phosphate chain achieve low energy status through chemical adsorptions. The chemical bonds between non-bridging oxygens and iron atoms on top of surface contribute to the favorable adhesion of phosphate glass lubricant during the tribological process. Secondly, the dissociation scheme will attach with the surface adsorption then conducted the depolymerization. Last but not least, we propose that the oxide surface does not contribute directly to P-O_b dissociation but indirectly through partially immobilize the phosphate chain. In that way, the non-adsorbed units under harsh environment will get intense fluctuation and suffer the bridging bond decomposition. Besides the indirect P-O_b dissociation induction of the surface, it also has an inverse impact. As mentioned in previous section, the attacking of sodium or any cations on bridging oxygen will result in bridging bond dissociation. Iron oxide surface easily attracts flexible sodium atoms

through the most top oxygen, which retards the approaching of sodium to the oxygen from phosphate chain then lessens the decomposition.⁷³ It is noted from our static result that the barrier energy for bond dissociation reaction by iron oxide increases up to the value of $\text{H}_4\text{P}_2\text{O}_7$ which is related to non-modifier metal phosphate system. The sodium attraction by oxide surface has been also observed in all FPMD simulations. The snapshots with sodium atoms can be reached at Fig. S3 to Fig. S5 in SM. Even though iron oxide substrate reduces the appearance of sodium, the introduction of iron into phosphate glass induces the depolymerization because the higher field strength and a larger coordination number of Fe compared to Na which help iron approach oxygen better, especially bridging oxygen atoms.⁷⁴ Therefore, the diffusion of iron from oxide substrate into the phosphate layer plays an important role on reducing the chain length of phosphate structure.

According to P-O bridging bond dissociation energy, the chain length has a minor effect on the P-O_b decomposition. The static calculations of $\text{Na}_5\text{P}_3\text{O}_{10}$ barrier energy showed a lower value of 0.5 eV than that of the shorter $\text{Na}_4\text{P}_2\text{O}_7$ cluster. At 1100 K of FPMD run, $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster decomposed while the $\text{Na}_4\text{P}_2\text{O}_7$ did not. This result compares well with the study by Cui et al.²⁸, which found that the pyrophosphate lubricant slightly polymerized whilst polyphosphate experienced depolymerization. We suggest the steric effect has a contribution to the surface interaction of phosphate chain. Longer chain length $\text{Na}_5\text{P}_3\text{O}_{10}$ cannot fully adsorb on the surface when thermal movement of other free atoms are more intense at 1100 K. As partial cluster anchored on the surface, the free atoms experienced large movement which can terminate the weakest bond – bridging P-O.

It is worth noting that our study has some limitations which make it not fully comparable to experimental study of hot rolling lubricant. The important effect of pressure and shear rate haven't been included in the current study. Besides, the lubricant coverage should be higher to mimic the higher chain length and the behavior of lubricant at bulk stage. Finally, the interactions between iron oxide nanoparticles with condensed phosphate cluster should be considered. These shortcomings will be the foci in a subsequent work.

Conclusions

DFT calculations and FPMD simulations at 1100 K have been performed with the $\text{Na}_4\text{P}_2\text{O}_7$ and $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster on iron oxide surface. The BOP and ELF analyses as well as FPMD simulations provided detailed insights into the bond nature of the system, effect of surface and effect of chain length on depolymerization of phosphate-based lubricant. The conclusions have been summarized below:

- The system contains medium covalent P-O bond, pure ionic Na-O interaction and moderate Fe-O ionic/covalent bond. The bridging P-O_b is the weakest bond which can be targeted for the depolymerization. The interactions of sodium or any modifier metal with bridging oxygens induces the P-O_b separation. Elevated temperature is also a trigger factor for this process.
- Iron oxide surface supports phosphate clusters and their dissociation products to achieve more stable configurations. We propose that the adsorption then depolymerization phosphate on the surface is the most thermodynamically favorable pathway. Deformed FeO_4 tetrahedra observed

in the phosphate-iron oxide linkage allows the mobility of phosphate but still maintains the strong adherence. Due to the equivalent ground states, structures of phosphate cluster and the decomposed products coexist in the theoretical system. Moreover, the authors suggest that the substrate not only promotes the P-O_b breakage through partially immobilizing phosphate chain but also obstructs the depolymerization due to the interaction between modifier alkali metal and surface oxygen.

- The monodentate complex structures have been observed in all phosphate clusters adsorption regardless to the chain length. The chain length of phosphate clusters has little effect on the P-O bridging dissociation. However, the small chain will be preferable when the surface gets full phosphate coverage and all linkages are monodentate.

Conflicts of interest

There are no conflicts to declare.

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References

1. A. K. Tieu, S. Wan, N. Kong, Q. Zhu and H. Zhu, *RSC Advances*, 2015, **5**, 1796-1800.
2. A. K. Tieu, N. Kong, S. Wan, H. Zhu, Q. Zhu, D. R. G. Mitchell and C. Kong, *Advanced Materials Interfaces*, 2015, **2**, 1500032.
3. N. Kong, A. K. Tieu, Q. Zhu, H. Zhu, S. Wan and C. Kong, *Wear*, 2015, **330–331**, 230-238.
4. S. Wan, A. K. Tieu, Q. Zhu, H. Zhu, S. Cui, D. R. G. Mitchell, C. Kong, B. Cowie, J. A. Denman and R. Liu, *Scientific Reports*, 2016, **6**, 26008.
5. S. Wan, A. K. Tieu, Y. Xia, H. Zhu, B. H. Tran and S. Cui, *Tribology International*, 2016, **102**, 620-635.
6. H. Spikes, *Tribol Lett*, 2004, **17**, 469-489.
7. J. Martin, *Tribol Lett*, 1999, **6**, 1-8.
8. A. R. Boccaccini, D. S. Brauer and L. Hupa, *Bioactive Glasses: Fundamentals, Technology and Applications*, Royal Society of Chemistry, 2016.
9. M. Seshadri, K. V. Rao, J. L. Rao and Y. C. Ratnakaram, *Journal of Alloys and Compounds*, 2009, **476**, 263-270.
10. P. Sengupta, *Journal of Hazardous Materials*, 2012, **235-236**, 17-28.
11. K. Ito, J. M. Martin, C. Minfray and K. Kato, *Tribology Transactions*, 2007, **50**, 211-216.
12. R. J. Atkinson, A. M. Posner and J. P. Quirk, *Journal of Inorganic and Nuclear Chemistry*, 1972, **34**, 2201-2211.
13. D. B. Abdala, P. A. Northrup, F. C. Vicentin and D. L. Sparks, *Journal of Colloid and Interface Science*, 2015, **442**, 15-21.

14. D. B. Abdala, P. A. Northrup, Y. Arai and D. L. Sparks, *Journal of Colloid and Interface Science*, 2015, **437**, 297-303.
15. O. R. Harvey and R. D. Rhue, *Journal of Colloid and Interface Science*, 2008, **322**, 384-393.
16. E. J. Elzinga and D. L. Sparks, *Journal of Colloid and Interface Science*, 2007, **308**, 53-70.
17. P. G. Belelli, S. A. Fuente and N. J. Castellani, *Computational Materials Science*, 2014, **85**, 59-66.
18. N. Y. Acelas, S. M. Mejia, F. Mondragón and E. Flórez, *Computational and Theoretical Chemistry*, 2013, **1005**, 16-24.
19. J. D. Kubicki, K. W. Paul, L. Kabalan, Q. Zhu, M. K. Mroziak, M. Aryanpour, A.-M. Pierre-Louis and D. R. Strongin, *Langmuir*, 2012, **28**, 14573-14587.
20. J. D. Kubicki, K. D. Kwon, K. W. Paul and D. L. Sparks, *European Journal of Soil Science*, 2007, **58**, 932-944.
21. K. D. Kwon and J. D. Kubicki, *Langmuir*, 2004, **20**, 9249-9254.
22. Y. Arai and D. L. Sparks, *Journal of Colloid and Interface Science*, 2001, **241**, 317-326.
23. K. Hoang and M. D. Johannes, *Journal of Power Sources*, 2012, **206**, 274-281.
24. M. Koyama, J. Hayakawa, T. Onodera, K. Ito, H. Tsuboi, A. Endou, M. Kubo, C. A. Del Carpio and A. Miyamoto, *The Journal of Physical Chemistry B*, 2006, **110**, 17507-17511.
25. H. T. T. Ta, A. K. Tieu, H. Zhu, H. Yu, T. D. Ta, S. Wan, N. V. Tran and H. M. Le, *The Journal of Physical Chemistry C*, 2018, **122**, 635-647.
26. M. A. Nicholls, T. Do, P. R. Norton, M. Kasrai and G. M. Bancroft, *Tribology International*, 2005, **38**, 15-39.
27. M. Crobu, A. Rossi and N. D. Spencer, *Tribol Lett*, 2012, **48**, 393-406.
28. S. Cui, S. Wan, Q. Zhu, A. K. Tieu, H. Zhu, L. Wang and B. Cowie, *The Journal of Physical Chemistry C*, 2016, **120**, 25742-25751.
29. P. Selvam, H. Tsuboi, M. Koyama, M. Kubo and A. Miyamoto, *Catalysis Today*, 2005, **100**, 11-25.
30. N. J. Mosey and T. K. Woo, *The Journal of Physical Chemistry A*, 2004, **108**, 6001-6016.
31. M. C. Righi, S. Loehle, M. I. de Barros Bouchet, D. Philippon and J. M. Martin, *RSC Advances*, 2015, **5**, 101162-101168.
32. N. J. Mosey and T. K. Woo, *Tribology International*, 2006, **39**, 979-993.
33. N. J. Mosey, T. K. Woo and M. H. Müser, *Physical Review B*, 2005, **72**, 054124.
34. S. M. Haw and N. J. Mosey, *The Journal of Physical Chemistry C*, 2012, **116**, 2132-2145.
35. G. Kresse and J. Furthmüller, *Physical Review B*, 1996, **54**, 11169-11186.
36. P. E. Blöchl, *Physical Review B*, 1994, **50**, 17953-17979.
37. J. P. Perdew, K. Burke and M. Ernzerhof, *Physical Review Letters*, 1996, **77**, 3865-3868.
38. J. Zhong, L. G. Hector and J. B. Adams, *Physical Review B*, 2009, **79**, 125419.
39. H. J. Monkhorst and J. D. Pack, *Physical Review B*, 1976, **13**, 5188-5192.
40. M. Methfessel and A. T. Paxton, *Physical Review B*, 1989, **40**, 3616-3621.
41. A. Alavi, P. Hu, T. Deutsch, P. L. Silvestrelli and J. Hutter, *Physical Review Letters*, 1998, **80**, 3650-3653.
42. C. J. Zhang and P. Hu, *Journal of the American Chemical Society*, 2001, **123**, 1166-1172.
43. A. Michaelides and P. Hu, *Journal of the American Chemical Society*, 2001, **123**, 4235-4242.
44. R. P. Feynman, *Physical Review*, 1939, **56**, 340-343.
45. T. Bučko, J. Hafner and J. G. Ángyán, *The Journal of Chemical Physics*, 2005, **122**, 124508.
46. B. Silvi and A. Savin, *Nature*, 1994, **371**, 683-686.
47. A. D. Becke and K. E. Edgecombe, *The Journal of Chemical Physics*, 1990, **92**, 5397-5403.
48. A. Savin, R. Nesper, S. Wengert and T. F. Fässler, *Angewandte Chemie International Edition in English*, 1997, **36**, 1808-1832.
49. S. Maintz, V. L. Deringer, A. L. Tchougréeff and R. Dronskowski, *Journal of Computational Chemistry*, 2016, **37**, 1030-1035.

50. M. D. Segall, R. Shah, C. J. Pickard and M. C. Payne, *Physical Review B*, 1996, **54**, 16317-16320.
51. L. Delle Site, C. F. Abrams, A. Alavi and K. Kremer, *Physical Review Letters*, 2002, **89**, 156103.
52. J. R. Van Wazer, *Phosphorus and Its Compounds*, Interscience Pubs., 1958.
53. M. Banach and A. Makara, *Journal of Chemical & Engineering Data*, 2011, **56**, 3095-3099.
54. M. Larsen, R. Willett and R. G. Yount, *Science (New York, N.Y.)*, 1969, **166**, 1510-1511.
55. D. M. MacArthur and C. A. Beevers, *Acta Crystallographica*, 1957, **10**, 428-432.
56. D. Cruickshank, *Acta Crystallographica*, 1964, **17**, 674-675.
57. U. Hoppe, G. Walter, D. Stachel, A. Barz and C. Hannon Alex, *Zeitschrift für Naturforschung A*, 1997, **52**, 259.
58. A. Le Beuze, R. Lissillour, A. Quemerais, D. Agliz, R. Marchand and H. Chermette, *Physical Review B*, 1989, **39**, 11055-11065.
59. U. Hoppe, G. Walter, R. Kranold and D. Stachel, *Journal of Non-Crystalline Solids*, 2000, **263-264**, 29-47.
60. U. Hoppe, R. Kranold, D. Stachel, A. Barz and A. C. Hannon, *Zeitschrift für Naturforschung - Section A Journal of Physical Sciences*, 2000, **55**, 369-380.
61. T. Uchino and Y. Ogata, *Journal of Non-Crystalline Solids*, 1995, **191**, 56-70.
62. A. Musinu, G. Piccaluga and G. Pinna, *The Journal of Physical Chemistry*, 1996, **100**, 12462-12466.
63. T. Uchino and Y. Ogata, *Journal of Non-Crystalline Solids*, 1995, **181**, 175-188.
64. P. A. Bingham and E. R. Barney, *Journal of Physics: Condensed Matter*, 2012, **24**, 175403.
65. T. P. Trainor, A. M. Chaka, P. J. Eng, M. Newville, G. A. Waychunas, J. G. Catalano and G. E. Brown Jr, *Surface Science*, 2004, **573**, 204-224.
66. J.-J. Tang and B. Liu, *The Journal of Physical Chemistry C*, 2016, **120**, 6642-6650.
67. T. D. Ta, A. K. Tieu, H. Zhu and B. Kosasih, *The Journal of Physical Chemistry C*, 2015, **119**, 12999-13010.
68. C. V. Luengo, N. J. Castellani and R. M. Ferullo, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2015, **147**, 193-199.
69. U. Hoppe, M. Karabulut, E. Metwalli, R. K. Brow and P. Jónvári, *Journal of Physics: Condensed Matter*, 2003, **15**, 6143.
70. Z. Zhang, E. S. Yamaguchi, M. Kasrai, G. M. Bancroft, X. Liu and M. E. Fleet, *Tribol Lett*, 2005, **19**, 221-229.
71. N. Bay, A. Azushima, P. Groche, I. Ishibashi, M. Merklein, M. Morishita, T. Nakamura, S. Schmid and M. Yoshida, *CIRP Annals*, 2010, **59**, 760-780.
72. P. Stoch, W. Szczerba, W. Bodnar, M. Ciecinska, A. Stoch and E. Burkel, *Physical Chemistry Chemical Physics*, 2014, **16**, 19917-19927.
73. T. Yang, X.-D. Wen, Y.-W. Li, J. Wang and H. Jiao, *Surface Science*, 2009, **603**, 78-83.
74. G. N. Greaves and S. Sen, *Advances in Physics*, 2007, **56**, 1-166.
75. R. K. Brow, *Journal of Non-Crystalline Solids*, 2000, **263-264**, 1-28.
76. D. B. Boyd, *Theoretica chimica acta*, 1970, **18**, 184-192.
77. F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky and H. Petersen, *Physical Review B*, 1989, **40**, 5715-5723.
78. A. E. Ringwood, *GEOCHEMICAL JOURNAL*, 1977, **11**, 111-135.
79. R. C. Evans, *An Introduction to Crystal Chemistry*, Cambridge University Press, 1964.
80. S. Cui, H. Zhu, S. Wan, K. Tieu, B. H. Tran, L. Wang and Q. Zhu, *Tribology International*, 2017, **116**, 180-191.
81. C. Wang, D. R. Baer, J. E. Amonette, M. H. Engelhard, J. Antony and Y. Qiang, *Journal of the American Chemical Society*, 2009, **131**, 8824-8832.
82. J. J. Hudgens and S. W. Martin, *Journal of the American Ceramic Society*, 1993, **76**, 1691-1696.

83. B. Al-Hasni and G. Mountjoy, *Journal of Non-Crystalline Solids*, 2011, **357**, 2775-2779.
84. J. C. Knowles, *Journal of Materials Chemistry*, 2003, **13**, 2395-2401.
85. A. Musinu, G. Piccaluga and G. Pinna, *Journal of Non-Crystalline Solids*, 1990, **122**, 52-58.
86. D. Yu, C. Wu, Y. Kong, N. Xue, X. Guo and W. Ding, *The Journal of Physical Chemistry C*, 2007, **111**, 14394-14399.
87. Y. Song, P. Y. Zavalij, M. Suzuki and M. S. Whittingham, *Inorganic Chemistry*, 2002, **41**, 5778-5786.

Figures

Fig. 1 Optimized structure of $\text{Na}_4\text{P}_2\text{O}_7$ cluster with (a) average BOP of P-O_b and P-O_{nb} bond; (b) ELF isosurface (yellow regions) at $\eta = 0.62$; ELF contours of (c) $\text{P-O}_b\text{-P}$ slice, (d) $\text{O}_b\text{-P-O}_{nb}$ slice. Red, purple and yellow spheres represent oxygen, phosphorus and sodium atoms, respectively.

Fig. 2 Optimized structure of $\text{Na}_3\text{P}_3\text{O}_{10}$ cluster with (a) average BOP of P-O_b inner, P-O_b outer and P-O_{nb} bond; (b) ELF isosurface (yellow regions) at $\eta = 0.62$; ELF contours of (c) $\text{P}_1\text{-O}_b\text{-P}_2$ slice, (d) $\text{O}_{nb}\text{-Na-O}_{nb}$ slice. Red, purple and yellow spheres represent oxygen, phosphorus and sodium atoms, respectively.

Fig. 3 Structure evolution of sodium atoms during P-O-P bridging bond dissociation: (a) $\text{Na}_4\text{P}_2\text{O}_7$ cluster, (b) PO_3 and PO_4 units sharing two Na ions, (c, d) PO_3 and PO_4 units sharing one Na ion, (e) Na_3PO_3 and NaPO_4 structures, (f) Na_2PO_3 and Na_2PO_4 structures, (g) NaPO_3 and Na_3PO_4 structures. Red, purple and yellow spheres represent oxygen, phosphorus and sodium atoms, respectively. The energies are in eV.

Fig. 4 The bridging bond dissociation of (a) isolated $\text{Na}_2\text{P}_2\text{O}_7$ cluster and its interactions with Fe_2O_3 (0001) surface, (b) isolated $\text{Na}_3\text{P}_3\text{O}_{10}$ cluster and its interactions with Fe_2O_3 (0001) surface. Red, gold, purple and yellow spheres represent oxygen, iron, phosphorus and sodium atoms, respectively. The energies are in eV.

Fig. 5 Relative energies of P-O bond dissociation of isolated $\text{H}_4\text{P}_2\text{O}_7$, $\text{Na}_4\text{P}_2\text{O}_7$, and $\text{Na}_5\text{P}_3\text{O}_{10}$ clusters.

Fig. 6 Electron localization function (ELF) isosurfaces (yellow regions) at $\eta = 0.62$ of (a) adsorbed $\text{Na}_4\text{P}_2\text{O}_7$ cluster on Fe_2O_3 surface, (b) adsorbed $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster on Fe_2O_3 surface. Red, gold, purple and yellow spheres represent oxygen, iron, phosphorus and sodium atoms, respectively; ELF contour of (c) P-O-Fe slice (d) O-Fe-O slice in adsorbed $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster on Fe_2O_3 surface. The Fe_2O_3 surface is below the horizontal white lines.

Fig. 7 (a) Electron localization function (ELF) isosurfaces (yellow regions) at $\eta = 0.62$ of decomposed products of $\text{Na}_4\text{P}_2\text{O}_7$ cluster on Fe_2O_3 surface. Red, gold, purple and yellow spheres represent oxygen, iron, phosphorus and sodium atoms, respectively; (b) ELF contour of $\text{O}_i\text{-P-O}_i$ plane in NaPO_3 unit adsorbed on Fe_2O_3 surface. The Fe_2O_3 surface is below the horizontal white lines.

Fig. 8 Energy profile of P-O bridging dissociation of $\text{Na}_4\text{P}_2\text{O}_7$ cluster on Fe_2O_3 (0001) surface.

Fig. 9 Energy profile of P-O bridging dissociation of $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster on Fe_2O_3 (0001) surface.

Fig. 10 Snapshots of FPMD at 1100 K of $\text{Na}_4\text{P}_2\text{O}_7$ cluster on Fe_2O_3 surface at 0 ps (a), 0.35 ps (b), 0.5 ps (c), and 20 ps (d). Structures have been displayed in side view (upper) and top view (lower). Red, gold, and purple spheres represent oxygen, iron, and phosphorus atoms, respectively. Sodium, surface oxygen and lower-layered iron atoms have been removed for apparent visualization.

Fig. 12 Distances of Fe-O linkage bonds in the FPMD of $\text{Na}_2\text{P}_2\text{O}_7$ cluster on Fe_2O_3 surface at 1100 K.

Fig. 13 Snapshots of FPMD at 1100 K of $\text{Na}_2\text{P}_3\text{O}_{10}$ cluster on Fe_2O_3 surface at 0 ps (a), 0.35 ps (b), 0.5 ps (c), 3 ps (d), 7 ps (e), and 10 ps (f). Structures have been displayed in side view (upper) and top view (lower). Red, gold, and purple spheres represent oxygen, iron, and phosphorus atoms, respectively. Sodium, surface oxygen and lower-layered iron atoms have been removed for apparent visualization

Fig. 14 Distances of P-O bridging bonds in the FPMD of $\text{Na}_3\text{P}_3\text{O}_{10}$ cluster on Fe_2O_3 surface at 1100 K.

Fig. 15 Distances of Fe-O linkage bonds in the FPMD of $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster on Fe_2O_3 surface at 1100 K.

DEPOLYMERIZATION OF SODIUM POLYPHOSPHATES ON IRON OXIDE SURFACE AT HIGH TEMPERATURE

M. H. Le,^a A. K. Tieu,^a H. Zhu,^{*a} D. T. Ta,^a H. Yu,^b T. T. H. Ta,^a V. N. Tran^a and S. Wan^a

^a School of Mechanical, Materials, Mechatronic and Biomedical Engineering, University of Wollongong, Northfield Avenue, Wollongong, NSW, 2522, Australia

^b School of Chemistry, University of Wollongong, Northfield Avenue, Wollongong, NSW, 2522, Australia

* Corresponding author: hongtao@uow.edu.au

Fig. S1: Partial charges of nine top layers of Fe₂O₃ (0001) surface of (a) current work and (b) Ta *et al.*¹

Fig. S2: Different relative position of Fe adsorption sites triangles for PO₄ or PO₃ units. The triangles can share one edge (left), be separate (middle) and share one vertex (right). Red, gold, purple and yellow spheres represent oxygen, iron, phosphorus and sodium atoms, respectively.

Fig. S3: Snapshots of FPMD at 300K of $\text{Na}_4\text{P}_2\text{O}_7$ cluster on Fe_2O_3 surface for 0 ps (a), 0.5 ps (b), 0.7 ps (c), and 10 ps (d). Structures have been displayed in side view (upper) and top view (lower). Red, gold, purple and yellow spheres represent oxygen, iron on top surface, phosphorus and sodium atoms, respectively. Surface oxygen and lower-layered iron atoms have been removed for apparent visualization.

Fig. S4: Snapshots of FPMD at 300K of $\text{Na}_5\text{P}_3\text{O}_{10}$ cluster on Fe_2O_3 surface for 0 ps (a), 3.2 ps (b), 4.4 ps (c), and 10 ps (d). Structures have been displayed in side view (upper) and top view (lower). Red, gold, purple and yellow spheres represent oxygen, iron on top surface, phosphorus and sodium atoms, respectively. Surface oxygen and lower-layered iron atoms have been removed for apparent visualization.

Fig. S5: Snapshots of FPMD at 300K of PO_3 and PO_4 units on Fe_2O_3 surface for 0 ps (a), 0.2 ps (b), 2.1 ps (c), and 10 ps (d). Structures have been displayed in side view (upper) and top view (lower). Red, gold, purple and yellow spheres represent oxygen, iron on top surface, phosphorus and sodium atoms, respectively. Surface oxygen and lower-layered iron atoms have been removed for apparent visualization.

Fig. S6: Snapshots of FPMD at 1500K of $\text{Na}_2\text{P}_2\text{O}_7$ cluster on Fe_2O_3 surface for 0 ps (a), 1 ps (b), 4.3 ps (c), and 7.4 ps (d). Structures have been displayed in side view (upper) and top view (lower). Red, gold, purple and yellow spheres represent oxygen, iron on top surface, phosphorus and sodium atoms, respectively. Surface oxygen and lower-layered iron atoms have been removed for apparent visualization.

REFERENCE

1. T. D. Ta, A. K. Tieu, H. Zhu and B. Kosasih, *The Journal of Physical Chemistry C*, 2015, **119**, 12999-13010.