Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supporting Information

Phosphorous oxide clusters stabilized by carbon nanotubes for selective isomerization and dehydrogenation of *β*-isopentene

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Experimental Section

Preparation of catalysts. The heat-treated carbon nanotubes (A1500) annealed at 1500 °C in argon (Ar) for 5 h, which were used as an inert carbon carrier for supporting the active ingredients. The supported VOx-A1500 and PO*x*-A1500 catalysts were prepared by incipient wetness impregnation combined with ultrasonic dispersion. The aqueous solutions of NH_4VO_3 (>99%, Aldrich, Inc.) or $(NH_4)_2HPO_4$ (>99%, Aldrich, Inc.) was added oxalic acid (>99%, Aldrich, Inc.) in a 1:3 molar ratio in order to ensure dissolution of ammonium salt precursors. The supports were soaked in the above aqueous solution and stirred ultrasonically until all the water to be evaporated. The impregnated samples were dried in air at 80 °C for 12 h and crushed, followed by heat-treated at 500 °C in Ar for 3 h. The TPP-A1500 catalyst was prepared by chemical vapor deposition using triphenylphosphine (TPP, >99%, Aldrich, Inc.) as phosphorous source in two continuous furnaces, shown in Figure S1. TPP was vaporized (Furnace I, 380 °C for 2 h) and carried to the preheated supports (Furnace II, 500 °C for 3 h) by an Ar flow of 50 ml/min.

Characterization. Surface chemistry properties of the samples were conducted by using an ESCALAB 250 instrument with Al K a radiation (1486.6 eV, 15 kV, 10 mA, 150 W). X-ray diffraction (XRD) patterns were recorded by a D/max 2400 diffractometer (JEOL Ltd., Japan) with Cu Kα (40 kV, 40 mA) radiation. The acidity of catalysts was measured by ammonia temperature-programmed desorption (NH_3-TPD). 0.05 g of sample was used in each test and was placed in a vertically positioned quartz tubular reactor. It was firstly adsorbed to balance under 5% NH_3/He at 25°C and then desorbed from 25 to 900 °C with a ramp rate of 5°C/min. The released NH_3 (m/z=17) was monitored by an in-situ quadrupole mass spectrometer (MS, Pfeiffer-Balzer Omnistar). Transmission electron microscopy (TEM) and high-angle annular dark field scanning TEM (HAADF-STEM) images were acquired by using an FEI Tecnai G2 F20 microscope equipped with HAADF-STEM detector and operated at 200 kV.

Catalytic reactions. Each catalyst (0.1 g, 100×400 μm) mixed with quartz sand (1 g) was placed in a quartz tubular reactor for the reaction test. It was then kept at 400°C in a 20 ml/min flow with fixed ratio of 2M2B/O_2/He (1:1:18) until constant conversion was achieved. The different conversions were obtained by variation of reaction temperature at the range of 400-450 °C. The reactants and products were analysed by using an on-line gas chromatography system (Agilent 7890A) with two Hayesep Q columns, a HP-PLOT/Al_2O_3 column (50 m 0.32 mm 8 mm) and a molecular sieve column. CO and CO_2 were detected with TCD detector, and hydrocarbons were detected with FID detector.

Calculation methods. The conversion (X_{2M2B}), product selectivity (S_p), yield (Y_p) and reaction rate (R_i) is calculated by formula (1), (2), (3) and (4), respectively. Among them, "*F*, *C*, *w*" denotes flow rate (mL min^{-1}), concentration (v.v %) and catalyst weight (g), respectively. "i" means any product from the reaction system and "p" only represents one specific product, whereas "j" denotes any specific

component including reactant or product. For consumption rate of reactant, the formula (4) is calculated by "X_{2M2B}", whereas the formation rate of product is obtained by "Y_p". "Σ" means summation.

Conversion: $$X_{2M2B} = \frac{F_{2M2B} \times (C_{2M2B,inlet} - C_{2M2B,outlet})}{F_{2M2B} \times C_{2M2B,\ inlet}} \times 100\% \quad (1)$$

Selectivity: $$S_p = \frac{C_{p,outlet}}{\sum C_{i,outlet}} \times 100\% \quad (2)$$

Yield: $$Y_p = X_{2M2B} \times S_p \times 100\% \quad (3)$$

Reaction rate: $$R_j = \frac{F_{2M2B} \times C_{2M2B,inlet} \times X_{2M2B}\ (\text{or } Y_p)}{22.4 \times w_{cat.} \times t} \quad (4)$$

Table S1. Blank test for the homogeneous conversion of 2M2B at different reaction temperature.

Temperature (°C)	X_{2M2B} (%)	Y_{iso}(%)	Y_{deh} (%)	Y_{com} (%)
350	0.14	0	0.14	0
450	0.71	0	0.71	0

Table S2. Typical XPS fitting data of different samples from Figure 3.

Sample	A1500		TPP-A1500		POx-A1500		K-POx-A1500		P_2O_5	
Component	BE[a] (eV)	PA[b] (%)	BE (eV)	PA (%)	BE (eV)	PA (%)	BE (eV)	PA (%)	BE (eV)	PA (%)
C_C (at %)[c]	98.03		89.25		83.07		95.04		50.07	
C_O (at %)	1.97		9.63		15.37		4.45		39.94	
C_P (at %)	0.00		1.12		1.56		0.51		9.99	
=O[d]	531.4	4.36	531.4	21.99	531.4	27.84	531.4	2.64	531.2	14.24
-O-	533.1	95.64	533.3	78.01	533.2	69.34	533.1	97.35	532.7	85.76
H_2O/O_2	535.7	0.00	535.7	0.00	536.1	2.82	535.7	0.00	535.7	0.00
C-P[e]			132.5	38.75						
PP			133.5	61.25	133.7	56.59	133.7	85.75	133.7	32.13
MP					134.6	43.41	134.6	14.25	134.5	51.91
P_2O_5									135.4	15.96

[a] binding energy; [b] percentage of peak area of each component from XPS fitting results in Figure 3; [c] "C_C, C_O, C_P" represents the content of carbon, oxygen and phosphorus atom in each sample. [d] "=O, -O-, H_2O/O_2" denotes the three components (double bonded oxygen, single bonded oxygen and adsorbed H_2O/O_2) from the fitting O1s spectra (Figure 3b). [e] "C-P, PP, MP and P_2O_5" is the four components (C-P bond, polyphosphate, monophosphate and phosphorus pentoxide structure) from the fitting P2p spectra (Figure 3c).

Table S3. XPS fitting data of different TPP- and POx-A1500 samples from Figure 3 and Figure 4.

	A1500	1POx[a]	3POx	5POx	10POx	TPP	K-POx
C_C(at%) [b]	98.03	97.63	94.47	91.37	83.07 (80.19)[c]	89.25	95.04
C_P(at%)	0.00	0.12	0.31	0.59	1.56 (1.29)	1.12	0.51
C_{PP} (at%)	0.00	0.04	0.19	0.44	0.88	0.69	0.44
C_{MP}(at%)	0.00	0.08	0.12	0.15	0.68	0.00	0.07
$\%_{PP}$[d]	0.00	0.30	0.62	0.75	0.57	0.61	0.86
$\%_{MP}$	0.00	0.70	0.38	0.25	0.43	0.00	0.14
C_O(at%)	1.97	2.25	5.22	8.04	15.37 (18.52)	9.63	4.45
$C_{=O}$(at%)	0.09	0.18	0.86	1.85	4.28	2.12	0.12
C_{-O-}(at%)	1.88	1.17	4.01	5.49	10.66	7.51	4.33
$\%_{=O}$	0.04	0.08	0.17	0.23	0.28	0.22	0.03
$\%_{-O-}$	0.96	0.52	0.77	0.68	0.69	0.78	0.97
R_{total} (mmol g^{-1} h^{-1})[e]	2.43	4.25	4.70	4.85	5.26	4.16	1.81
R_{ISO} (mmol g^{-1} h^{-1})	2.05	3.88	3.94	3.86	3.98	3.28	0.54
R_{DEH} (mmol g^{-1} h^{-1})	0.31	0.33	0.67	0.79	1.04	0.64	0.07
R_{COM} (mmol g^{-1} h^{-1})	0.07	0.04	0.09	0.19	0.24	0.24	1.19
S_{ISO} (%)[f]	84.35	91.27	83.87	79.71	75.63	78.82	30.15
S_{DEH} (%)	12.89	7.84	14.20	16.30	19.85	15.37	3.87
S_{COM} (%)	2.76	0.89	1.93	3.99	4.52	5.81	65.98

[a] "1POx" represents the 1POx-A1500 sample with 1% phosphorus content in theory; [b] "C_C, C_P, C_{PP}, C_{MP}, C_O, $C_{=O}$, C_{-O-} "corresponds to the content of carbon atom, phosphorus atom, polyphosphate structure, monophosphate structure, oxygen atom, double bonded oxygen linkage and oxygen single bond in each sample from XPS fitting data in Figure 3 and Figure 4; [c] the value of spent sample; [d] "$\%_{PP}$, $\%_{MP}$" denotes the proportion of polyphosphate structure and monophosphate structure to all P atoms in each sample, and also "$\%_{=O}$, $\%_{-O-}$" means the proportion of double bonded oxygen and single bonded oxygen to all O atoms in each sample; [e] "R_{total}, R_{ISO}, R_{DEH}, R_{COM}" indicates the reaction rate of all products(total), isomerized products (iso, 2M1B and 3M1B), dehydrogenated products (deh, 2M-1, 3-Butadiene) and combusted products (com, CO and CO_2), and it was acquired from the data at 400 °C in Figure 2 and Figure S2; [f] "S_{ISO}, S_{DEH}, S_{COM}" is the selectivity for isomerization, dehydrogenation and combustion.

Table S4. The structure-activity relations based on the linear and non-linear analysis from Figure S5.

Entry	Linear regression of $y=kx+b$				Non-linear shift from exceptional samples				
	y	x	R^2	k	Downward shift			Upward Shift	
1	R_{total}	$C_{=O}$	0.90	0.22	A1500	TPP	K-POx		
2		C_{-O-}	0.96	0.10	A1500	TPP	K-POx		
3		C_O	0.93	0.07	A1500	TPP	K-POx		
4		C_{PP}	0.92	1.08	A1500	TPP	K-POx		
5		C_P	0.86	0.60	A1500	TPP	K-POx		
6		C_{MP}	0.71	1.24	A1500	TPP	K-POx		
7	R_{ISO}	C_{MP}	0.56	0.14	A1500	TPP	K-POx		
8		C_P	0.45	0.05	A1500	TPP	K-POx		
9		C_{PP}	0.03	0.08	A1500	TPP	K-POx		
10		$C_{=O}$	0.40	0.02	A1500	TPP	K-POx		
11		C_{-O-}	0.46	0.01	A1500	TPP	K-POx		
12		C_O	0.41	0.01	A1500	TPP	K-POx		
13	R_{DEH}	$C_{=O}$	0.86	0.16			K-POx		
14		C_{-O-}	0.83	0.07			K-POx		
15		C_O	0.87	0.05			K-POx		
16		C_{PP}	0.76	0.67			K-POx		
17		C_P	0.72	0.39			K-POx		
18		C_{MP}	0.63	0.86			K-POx		
19	R_{COM}	C_{PP}	0.92	0.24					K-POx
20		C_P	0.84	0.14					K-POx
21		C_{MP}	0.22	0.17					K-POx
22		C_{-O-}	0.86	0.02					K-POx
23		$C_{=O}$	0.76	0.05					K-POx
24		C_O	0.82	0.02					K-POx
25	S_{ISO}	$\%_{=O}$	0.99	-79.40	A1500		K-POx		
26		$\%_{-O-}$	0.47	-39.90			K-POx	A1500	
27		$\%_{MP}$	0.44	15.59			K-POx		
28		$\%_{PP}$	0.30	-10.79			K-POx		
29	S_{DEH}	$\%_{=O}$	0.98	60.85				A1500	
30		$\%_{-O-}$	0.60	-18.61	1POx		K-POx		
31		$\%_{PP}$	0.30	7.85			K-POx		
32		$\%_{MP}$	0.28	-9.05			K-POx		
33	S_{COM}	$\%_{MP}$	0.71	-6.55					K-POx
34		$\%_{=O}$	0.51	14.10					K-POx
35		$\%_{PP}$	0.20	2.95					K-POx
36		$\%_{-O-}$	0.08	3.67					K-POx

All the parameters originated from Figure S5. The explanatory variables (x) of each dependent variable (y) are sorted by the correlation coefficient (R^2) and the slope (k) of lines. The PO_x-A1500 samples without potassium addition nearly meet the linear relationship. "Downward shift"/"Upward shift" indicating the value of dependent variable is less /more than the value on the line regression, in which the corresponding structure variable of special sample is un/favorable for that catalytic function.

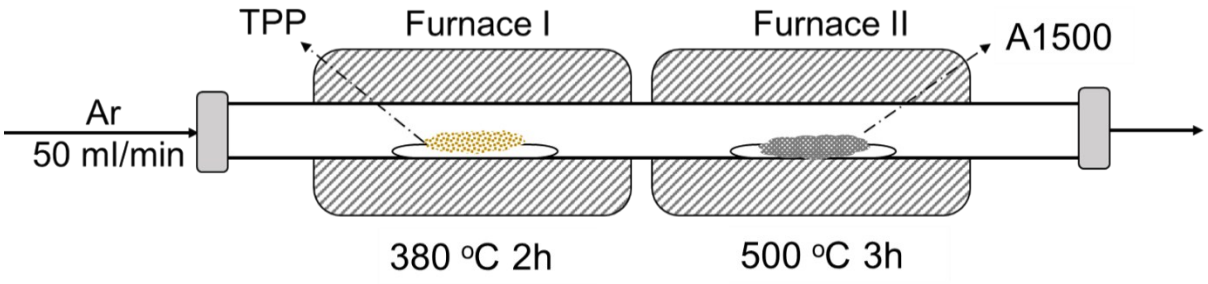

Figure S1 Schematic diagram for the preparation of TPP-A1500 via chemical vapour desorption.

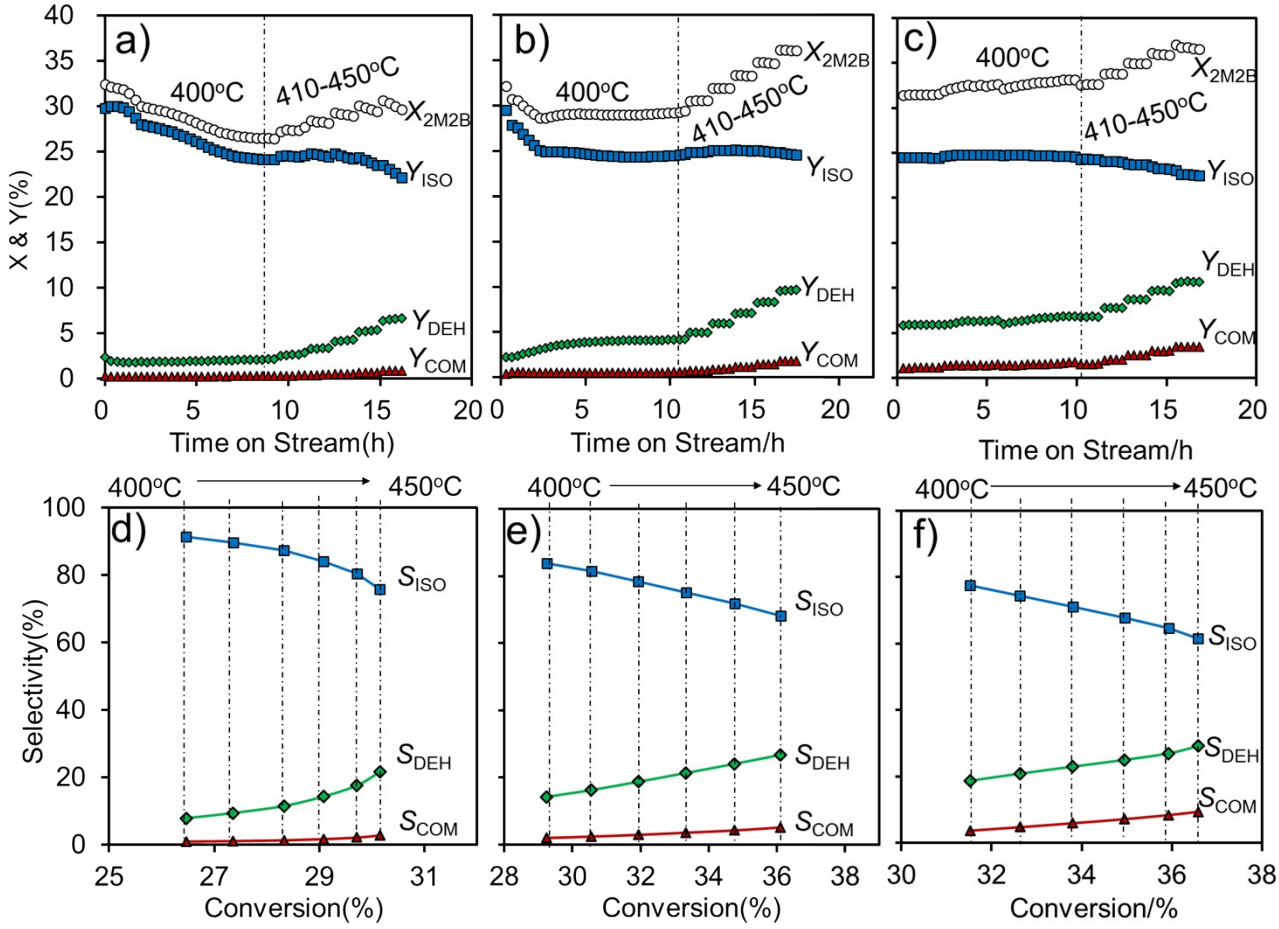

Figure S2 Catalytic performance for oxidative conversion of *β*-isopentene (2M2B) over different catalysts. (a-c) Conversion of 2M2B (○: X_{2M2B}) and yield of products as a function of time on stream over 1POx-A1500 (a), 3POx-A1500 (b) and 5PO$_x$-A1500 (c) at isoweight of catalyst (0.1 g, 12 L g^{-1}h^{-1}, 2M2B:O_2:He=1:1:18). ■: Y_{iso}, the yield of isomerized products containing 2-methyl-1-butene (2M1B) and less 3-methyl-1-butene (3M1B) ; ◆: Y_{deh}, the yield of dehydrogenated product containing 2-methyl-1, 3-butadiene (2M-1,3-Butadiene); ▲: Y_{com}, the yield of combusted products containing CO and CO_2.

(d-f) The product selectivity as a function of 2M2B conversion over 1POx-A1500 (d), 3PO$_x$-A1500 (e) and 5PO$_x$-A1500 (f).

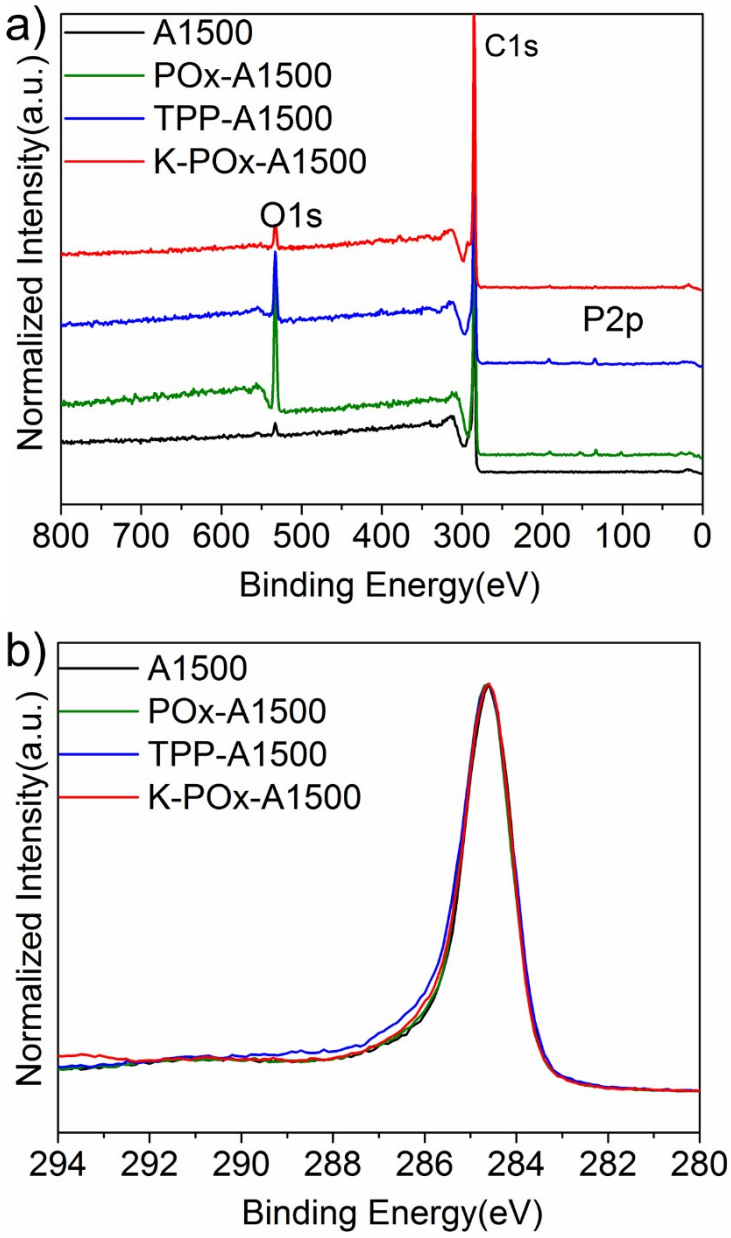

Figure S3 XPS survey spectra (a) and C1s spectra (b) of different samples. The survey spectra (Figure S3a) of PO$_x$-A1500 confirm the neat presence of carbon, oxygen and phosphorus elements. In the C *1s* spectra (Figure S3b), no change in the binding energy (BE) could be identified before and after P-modification in the C *1s* spectra.

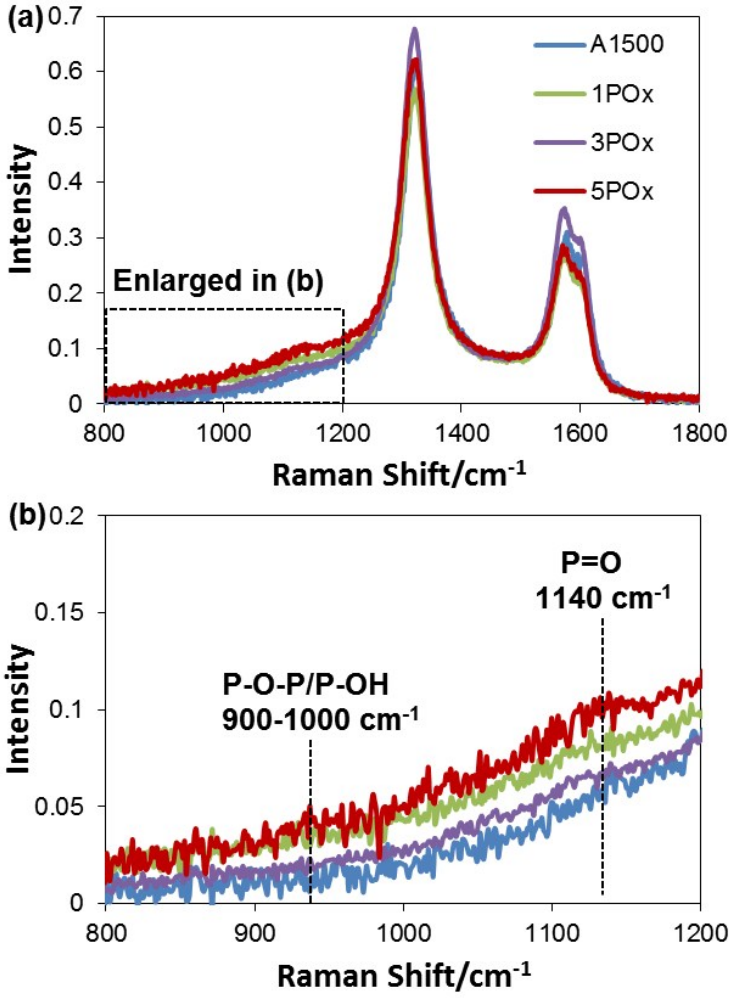

Figure S4 Overlay of Raman spectra for phosphate modified carbon nanotubes.

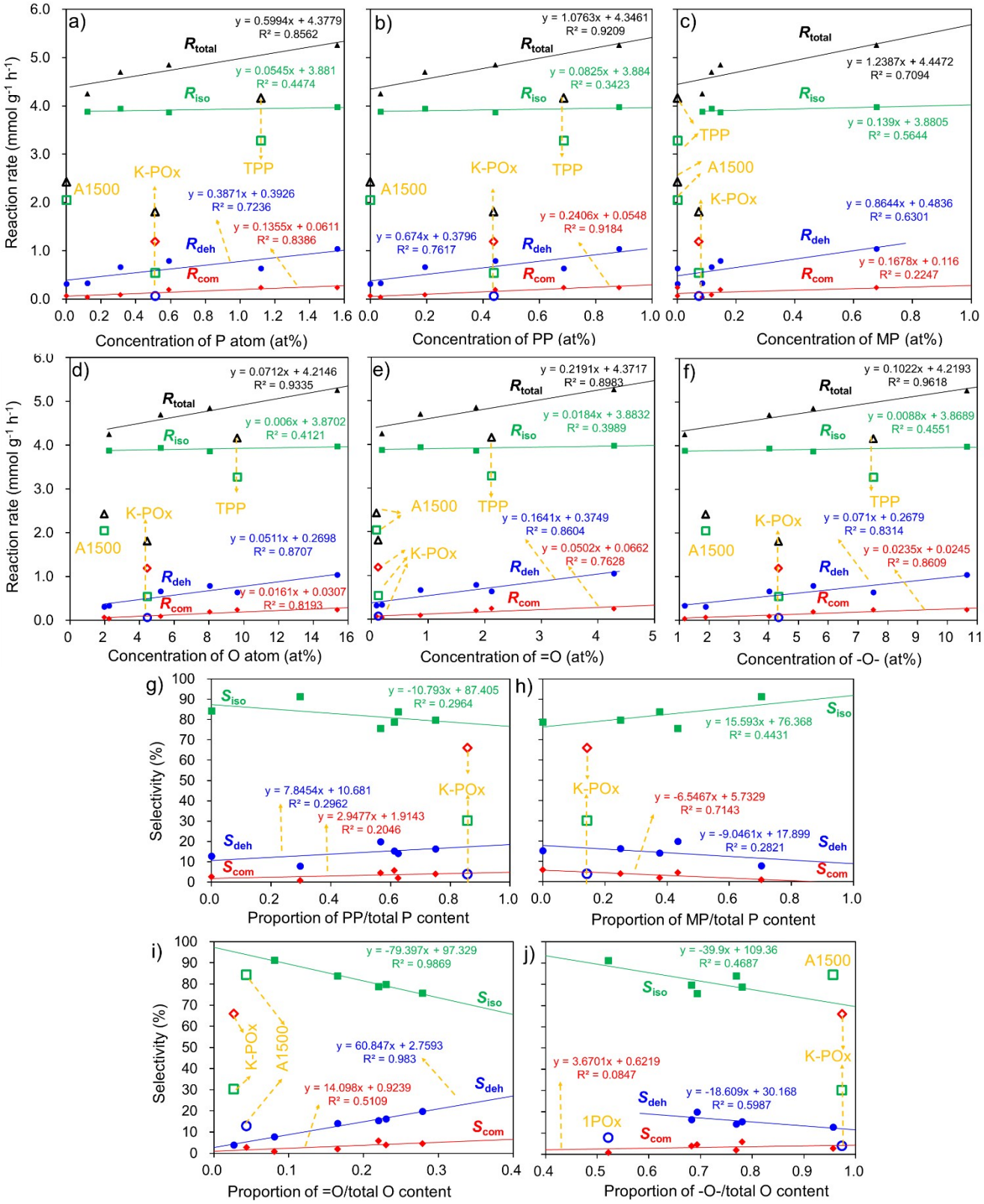

Figure S5 Linear and non-linear correlation between the catalytic function and the structure properties of samples.

Linear regression (Figure S5) was used to model the relationship between the catalytic function (dependent vabriable, y) and the structure variables (exlpantoatory variable, x) by fitting a linear equation ($y=kx+b$) to the obtained data of 7 samples (A1500, TPP-A1500, 1POx-A1500, 3POx-A1500, 5POx-A1500, 10POx-A1500, K-10POx-A1500) in Table S3. The correlation coefficient (R^2) is a value between 0 and 1 indicating the strength of the association of the two variables. The slope of the line is k and b is the intercept. Most points meet the linear relationship between two variable pairs while a few outliers deviate from the line indicating the presence of exceptional samples (labelled in Figure). All these parameters and the direction of outliers deviating from the line have been summarized in Table S4. (a) y: total reaction rate (R_{total}), isomerization rate (R_{iso}), dehydrogenation rate (R_{deh}), combustion rate (R_{com}), x: the content of P atom in each sample (C_P, at %); (b) y: R_{total}, R_{iso}, R_{deh}, R_{com}, x: the content of polyphosphate strcuture in each sample (C_{PP}); (c) y: R_{total}, R_{iso}, R_{deh}, R_{com}, x: the content of monophosphate strcuture in each sample (C_{MP}); (d) y: R_{total}, R_{iso}, R_{deh}, R_{com}, x: the content of O atom in each sample (C_O); (e) y: R_{total}, R_{iso}, R_{deh}, R_{com}, x: the content of oxygen double bonds in each sample ($C_{=O}$); (f) y: R_{total}, R_{iso}, R_{deh}, R_{com}, x: the content of oxygen single bonds in each sample (C_{-O-}); (g) y: isomerized selectivity (S_{iso}), dehydrogenated selectivity (S_{deh}), combusted selectivity (S_{com}), x: the proportion of polyphosphate/total P atom ($\%_{PP}$); (h) y: S_{iso}, S_{deh}, S_{com}, x: the proportion of monophosphate/total P atom ($\%_{MP}$); (i) y: S_{iso}, S_{deh}, S_{com}, x: the proportion of oxygen double bonds/total O atom ($\%_{=O}$); (j) y: S_{iso}, S_{deh}, S_{com}, x: the proportion of oxygen single bonds/total O atom ($\%_{-O-}$).