

Supplementary Information

Enhanced thermal stability of the palladium oxidation catalysts using phosphate-modified alumina supports

Jinshi Dong,^a Jun Wang,^a Jianqiang Wang,^a Ming Yang,^d Wei Li ^{*d} and
Meiqing Shen ^{*a, b, c}

^a Key Laboratory for Green Chemical Technology of State Education Ministry, School of Chemical Engineering & Technology, Tianjin University, Tianjin 300072, P.R. China.
Email: mqshen@tju.edu.cn (Prof. Shen)

^b State Key Laboratory of Engines, Tianjin University, Tianjin 300072, P.R. China.

^c Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300072, P.R. China.

^d Chemical and Materials Systems Laboratory, General Motors Global Research and Development, 30500 Mound Road, Warren, MI 48090, USA.
Email: wei.1.li@gm.com (Dr. Li)

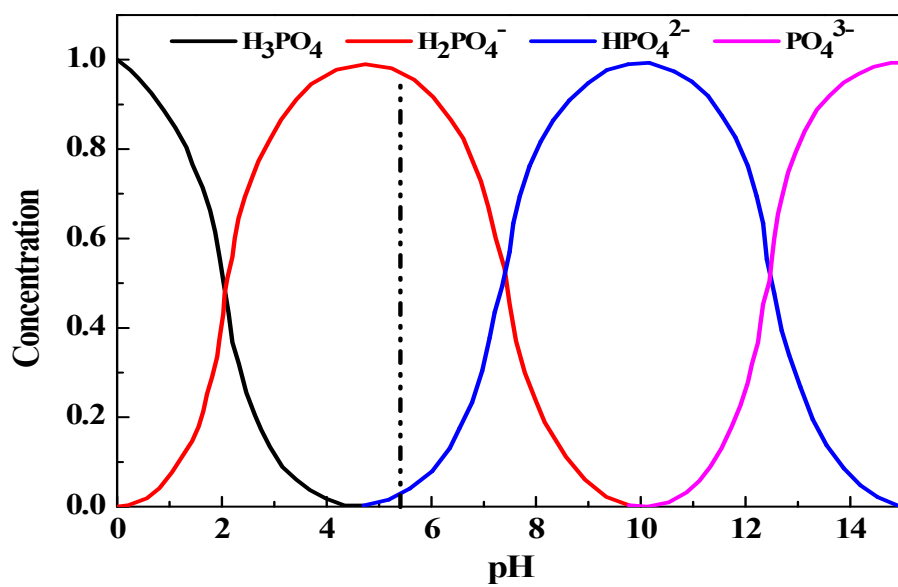


Fig. S1 The predicted concentration profiles of various phosphates species with the changing pH values.

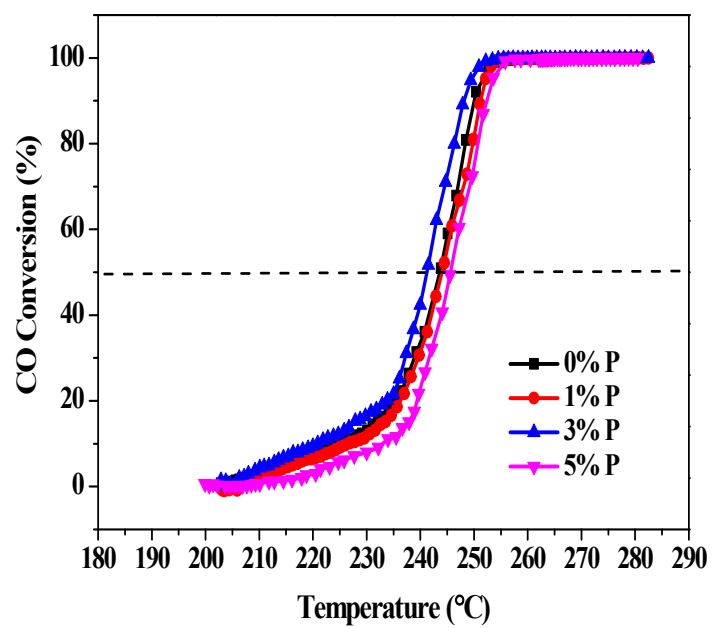


Fig. S2 The light-off curves of the fresh Pd/Al₂O₃ catalysts. The feed gas stream contains 2 % CO and 2 % O₂ balanced with N₂ at a flow rate of 1 L/min, 200 mg catalyst.

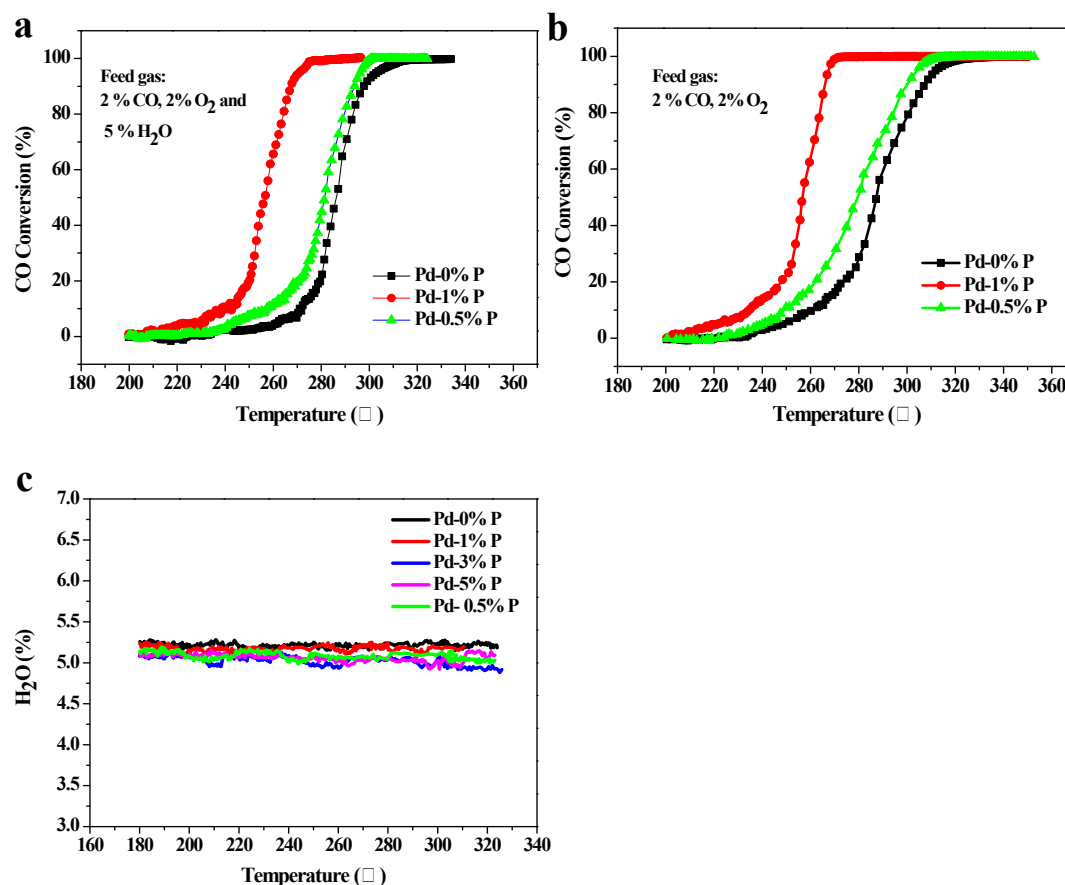


Fig. S3 (a) The light-off curves of the aged 0 %, 0.5 % (0.6% by ICP) and 1 % P-containing catalysts. Feed gas stream contains 2 % CO, 2 % O₂ and ~5 % H₂O balanced with N₂ at a flow rate of 1 L/min, 200 mg catalyst. (b) The light-off curves of the aged 0 %, 0.5 % and 1 % P-containing catalysts. Feed gas stream contains 2 % CO and 2 % O₂ balanced with N₂ at a flow rate of 1 L/min, 200 mg catalyst. (c) The changes of the contents of H₂O with elevated temperatures during the CO oxidation reactions.

Little improvement in catalytic activity was found for the Pd-0.5 % P sample, maybe due to a relative lower specific surface area— 56 m²/g (47 m²/g for the Pd-0% P sample). With or without H₂O in the feeds of CO oxidation reactions, the trends for light-off activities did not change obviously (Fig. 4c). The consumes of H₂O were all within 0.1% (Fig. S4c), illustrating very small portion of water-gas shift reactions were involved in the processes.

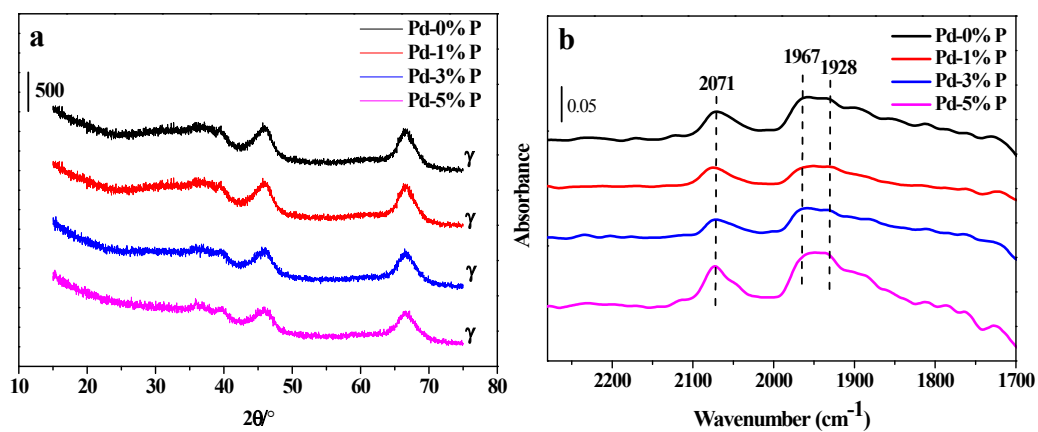


Fig. S4 (a) XRD patterns of the fresh catalysts after H₂ reduction. (b) CO DRIFTS of the fresh catalysts after H₂ reduction. The wavenumber 2071, 1967 and 1928 cm^{-1} corresponded to linear, bridge and hollow-bonded CO adsorbed on Pd surface, respectively.¹

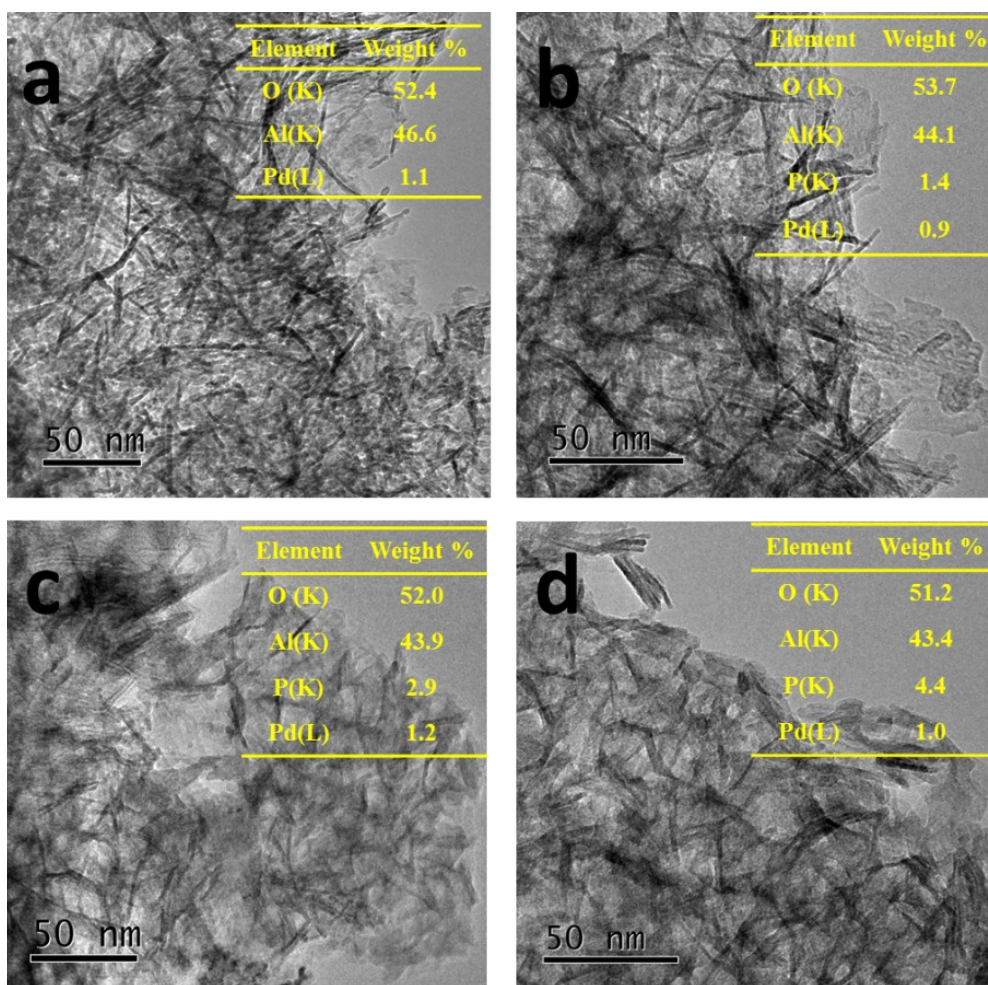


Fig. S5 TEM images of the fresh Pd catalysts after H₂ reduction. (a) Pd- 0% P sample; (b) Pd- 1% P sample; (c) Pd- 3% P sample; and (d) Pd- 5% P sample. Limited by the resolution of the TEM and relative “disordered” morphology of the support γ -Al₂O₃, we could not clearly observe the discrete Pd nanoparticle, but the EDS data (the inset table) showed that the Pd (in the form of sub-nm clusters and single atoms) indeed existed in these corresponding display areas.

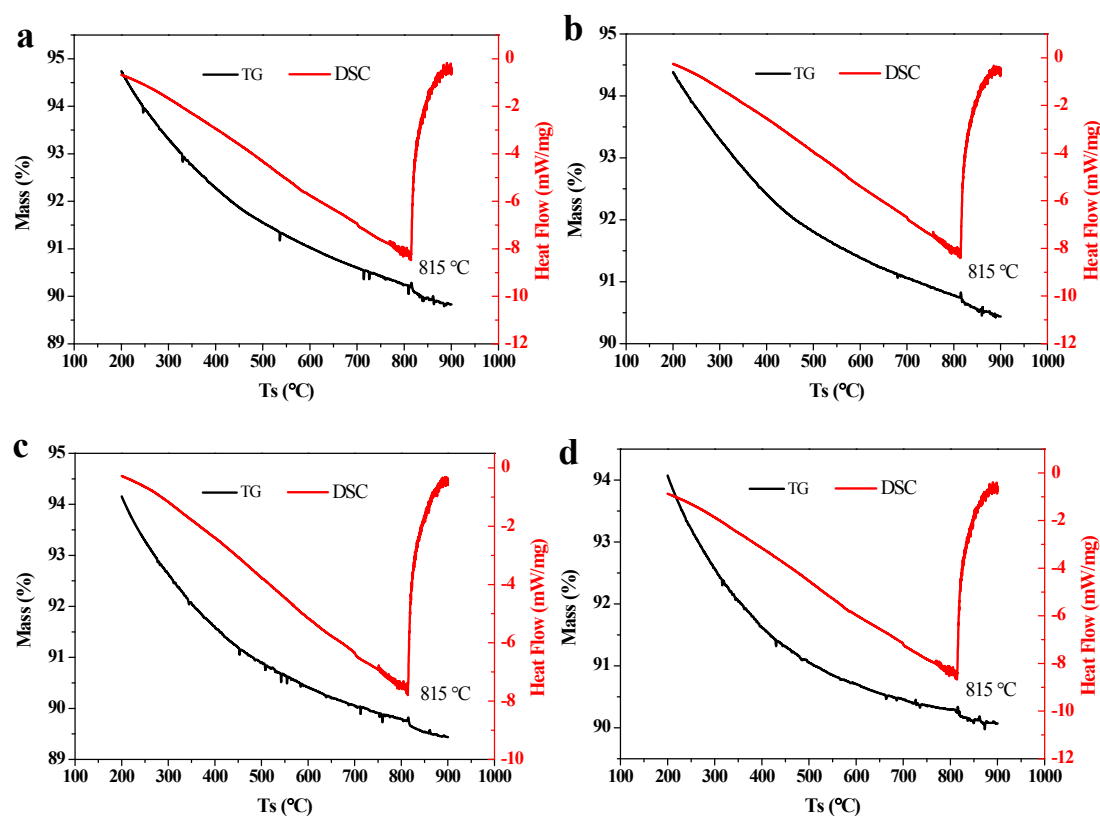


Fig. S6 TG and DSC profiles of the fresh catalysts. (a) Pd- 0% P sample; (b) Pd- 1% P sample; (c) Pd- 3% P sample; and (d) Pd- 5% P sample. The heating rate was 10 °C/min in ambient atmosphere.

4.1%- 4.8% weight losses were found for the four samples from 200 °C to 900 °C, which were mainly caused by dehydroxylation.² A endothermic reaction took place all at 815 °C based on the analyses of DSC profiles, it corresponded to the decomposition of PdO to Pd.³ Accordingly, no obvious differences were observed from the TGA-DSC profiles, illustrating that phosphate did not obviously affect the catalysts' surface dehydroxylation behaviors neither had chemistry with surface Pd species.

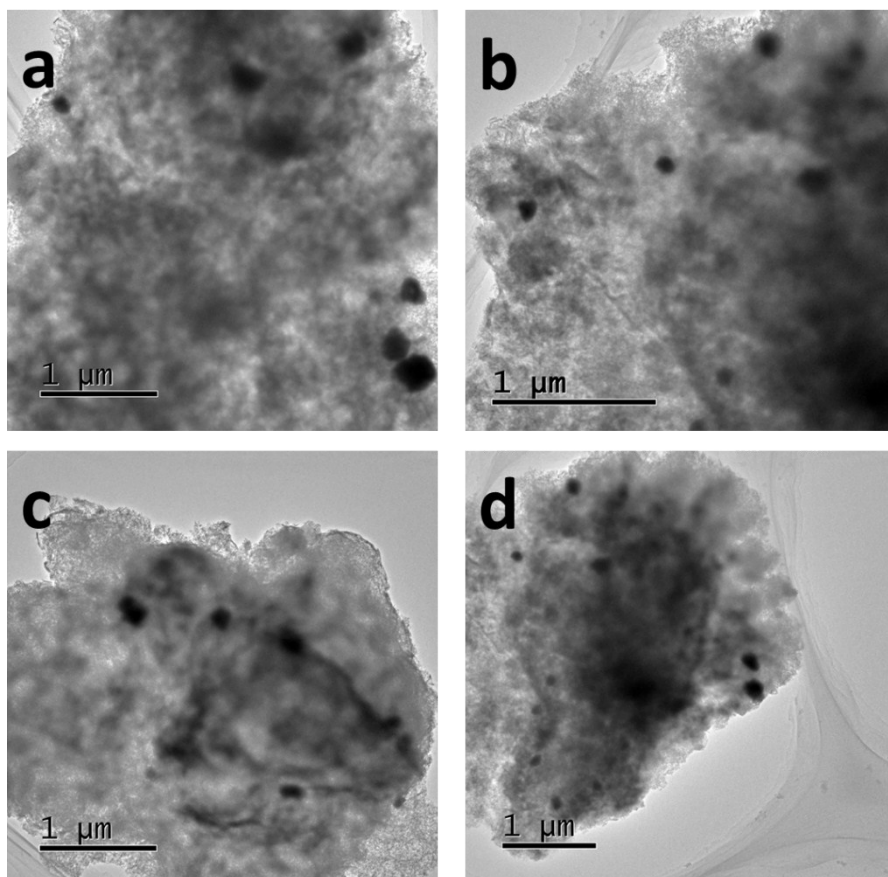


Fig. S7 TEM images of the aged catalysts after H₂ reduction (with large Pd particles (100- 250 nm) shown, not to exclude the presence of sub-nm Pd clusters). (a) Pd-0% P sample; (b) Pd-1% P sample; (c) Pd-3% P sample; and (d) Pd- 5% P sample.

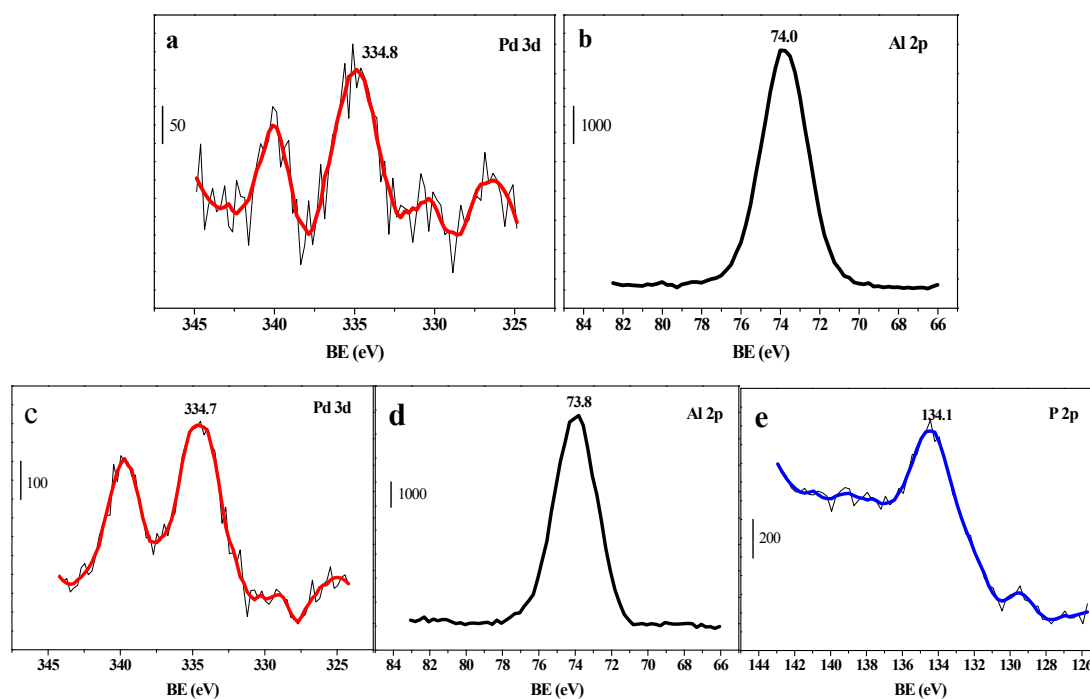


Fig. S8 XPS surface analyses of Pd, Al, P. (a) and (b) Aged Pd-0% P catalyst after H₂ reduction; (c), (d) and (e) Aged Pd-1% P catalyst after H₂ reduction.

The binding energy of 134.1 eV is P 2p in phosphate,⁴ 74.0/ 73.8 eV corresponds to Al 2p in Al₂O₃,⁵ A little shift in binding energy for Pd-1% P sample can be owed to surface CUS Al interacting with phosphate. The binding energy of 334.8/ 334.7 eV corresponds to Pd 3d_{5/2}.^{6, 7} No obvious differences were found in the Pd 3d spectra for the two samples, illustrating that the doping of phosphate did not change the state of Pd species, namely no chemistry was formed between phosphate and supported Pd species.

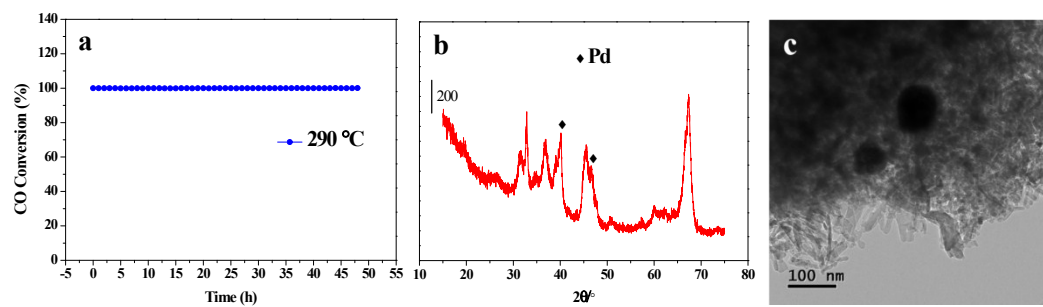


Fig. S9 (a) Long-term (48 h) CO oxidation reaction test of the aged Pd-1% P catalyst after H₂ reduction. Feed gas stream: 2 % CO and 2 % O₂ balanced with N₂ (flow rate: 1 L/min, 200 mg catalyst). (b) XRD pattern of the aged Pd-1% P catalyst after long-term reaction test. (c) TEM image of the aged Pd-1% P catalyst after long-term reaction test.

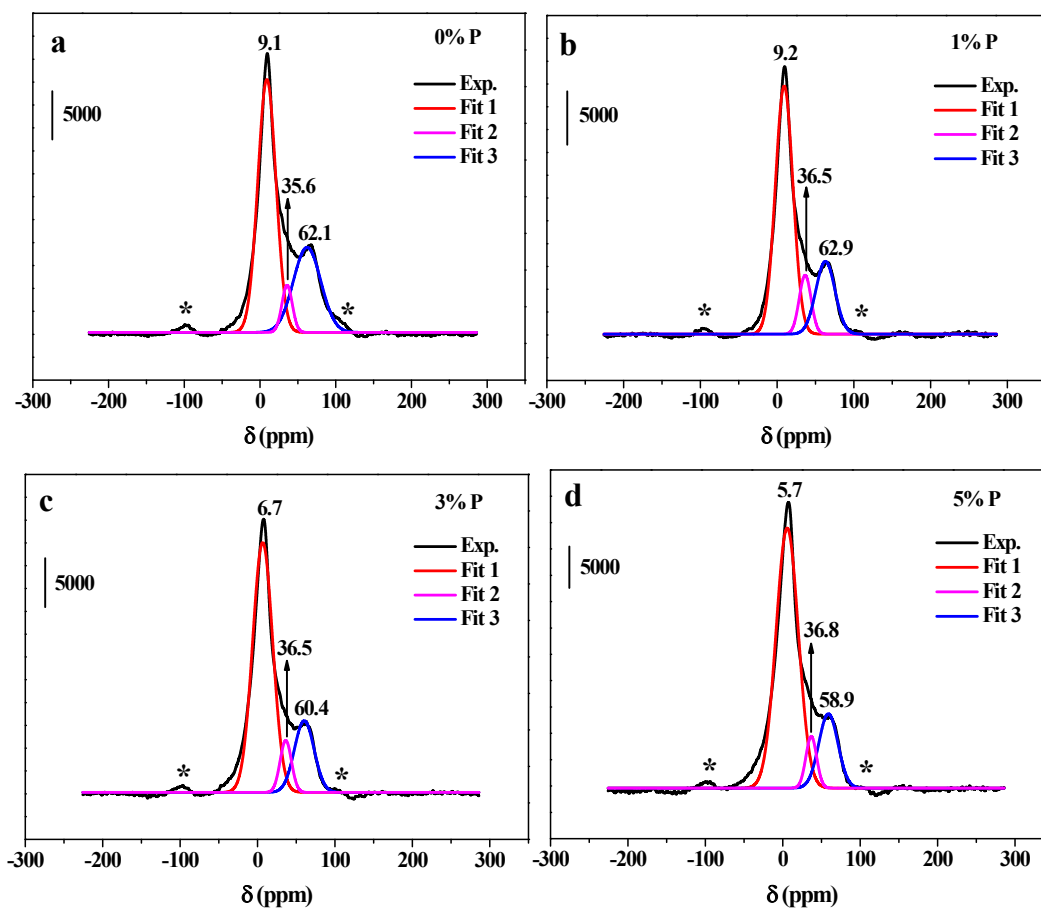


Fig. S10 The ^{27}Al NMR spectra of the as-prepared phosphate-stabilized alumina samples. All the samples were purged at 350 °C for 10 h prior to tests. Spinning sidebands were marked with asterisks.

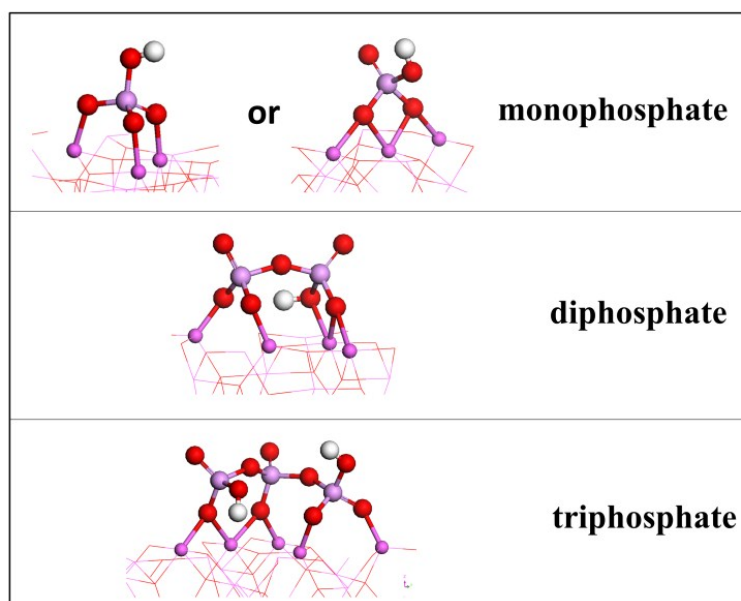
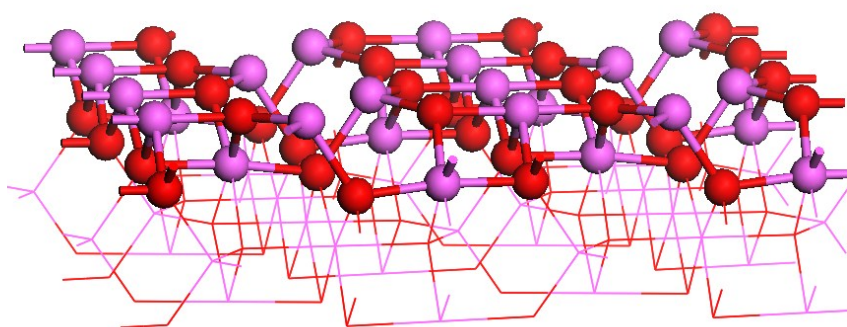
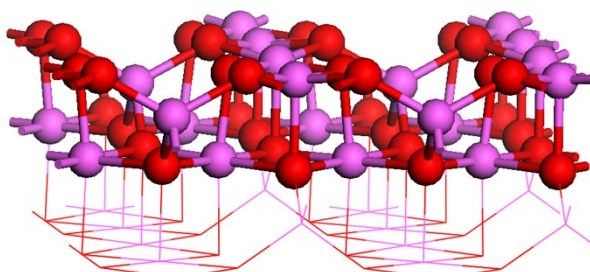


Fig. S11 Possible monophosphate and short-chain polyphosphate (diphosphate and triphosphate) structures based on DFT adsorption energy calculations shown in Table S1.



Relaxed Al_2O_3 (110C) surface

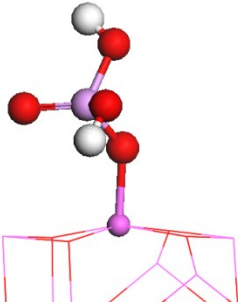
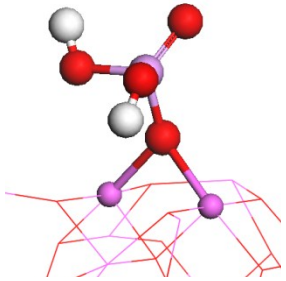
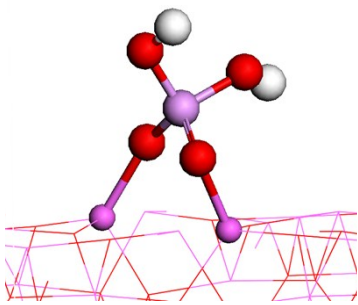


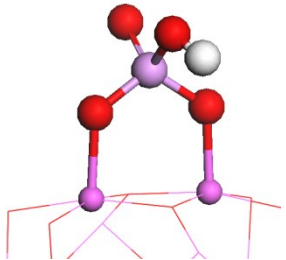
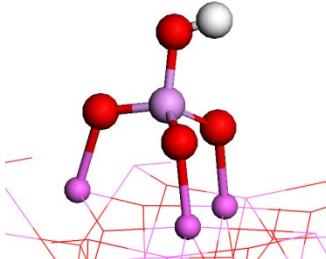
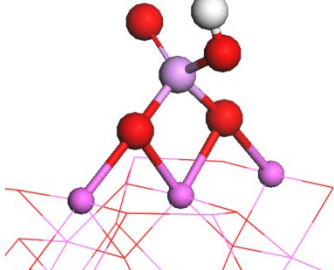
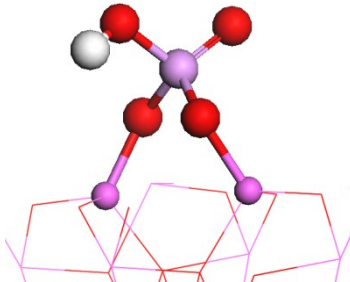
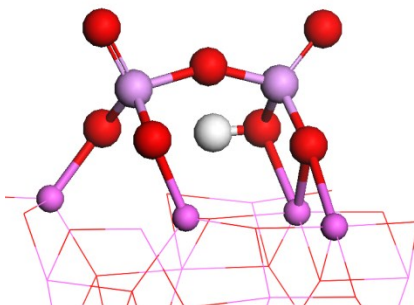
Relaxed Al_2O_3 (100) surface

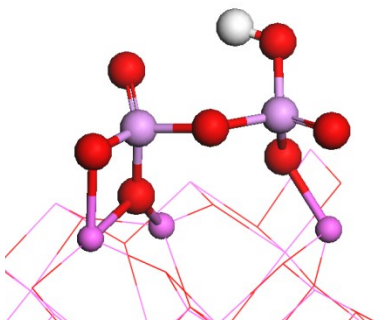
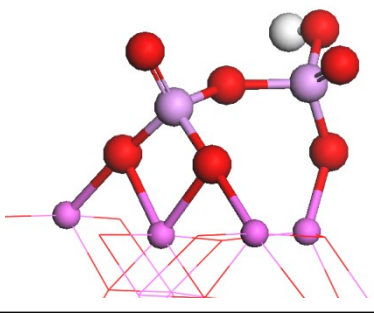
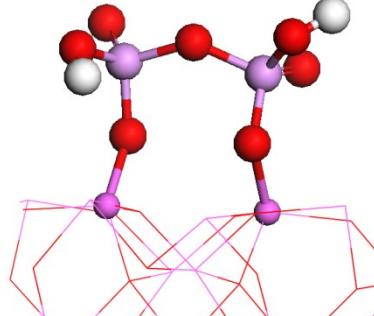
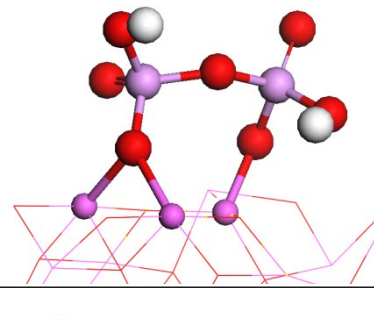
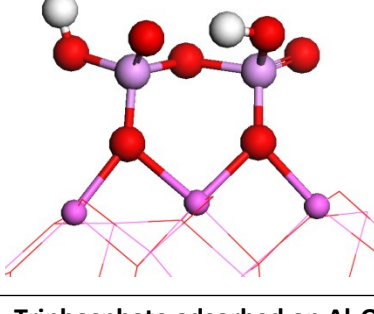
Fig. S12 The relaxed Al_2O_3 (110C) and (100) surfaces. Red and purple balls represent O and Al atoms, respectively.

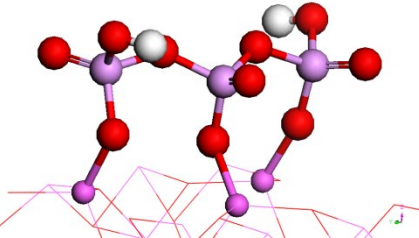
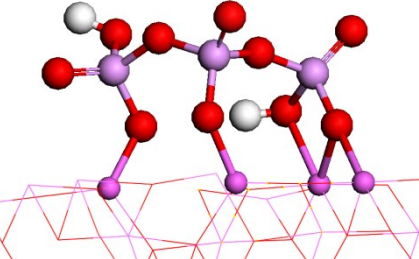
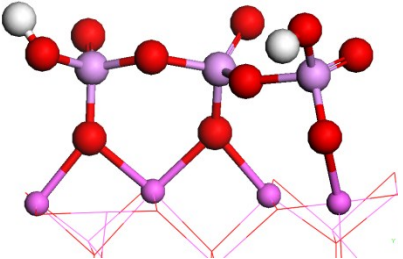
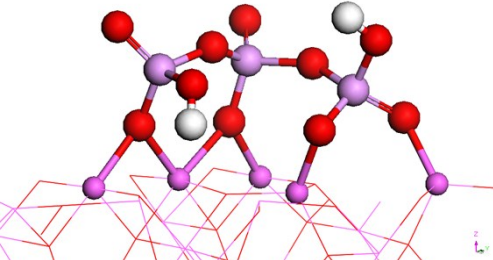
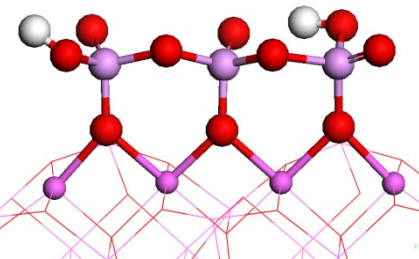
Table S1 The relaxed structures and corresponding adsorption energies of monophosphate, diphosphate and triphosphate adsorbed on Al_2O_3 surfaces. Gray, red, purple and pink balls represent H, O, P and Al atoms, respectively.

By comparing the adsorption energies of the various monophosphate configurations, we found that the PO_x (phosphate) prefer to adsorb on the Al_2O_3 (110) surface than (100) surface. Based on this point, the diphosphate and triphosphate were only set to adsorbed on (110) surface. The adsorption energies of PO_x were calculated as $E(\text{Al}_2\text{O}_3 \text{ surface} + \text{PO}_x) - E(\text{Al}_2\text{O}_3 \text{ surface}) - E(\text{PO}_x)$, the relaxed Al_2O_3 (110) and (100) surfaces are shown in Fig. S12, here (110C) was taken as (110) surface in that Al_{III} and Al_{IV} are both exposed on it.

Type	Structure	Adsorption energy/ eV
Monophosphate adsorbed on Al_2O_3 surface		
H_2PO_4 bonded with Al_{V} on (100) surface		-6.65
H_2PO_4 bonded with 2Al_{IV} on (110) surface		-6.79
H_2PO_4 bonded with 2Al_{III} on (110) surface		-6.96

HPO ₄ bonded with 2Al _{IV} on (100) surface		-2.80
HPO ₄ bonded with 2Al _{IV} and Al _{III} on (110) surface		-11.48
HPO ₄ bonded with 3Al _{IV} on (110) surface		-11.49
HPO ₄ bonded with 2Al _{III} on (110) surface		-11.09
Diphosphate adsorbed on Al₂O₃ surface		
H ₂ PO ₄ + HPO ₄ (-H ₂ O) bonded with 2Al _{III} and 2Al _{IV} on (110) surface		-16.56

$\text{H}_2\text{PO}_4 + \text{HPO}_4 (-\text{H}_2\text{O})$ bonded with 3Al_{III} on (110) surface		-14.88
$\text{H}_2\text{PO}_4 + \text{HPO}_4 (-\text{H}_2\text{O})$ bonded with Al_{III} and 3Al_{IV} on (110) surface		-15.89
$2\text{H}_2\text{PO}_4 (-\text{H}_2\text{O})$ bonded with Al_{III} and 3Al_{IV} on (110) surface		-11.39
$2\text{H}_2\text{PO}_4 (-\text{H}_2\text{O})$ bonded with Al_{III} and 2Al_{IV} on (110) surface		-12.04
$2\text{H}_2\text{PO}_4 (-\text{H}_2\text{O})$ bonded with 3Al_{IV} on (110) surface		-12.58
Triphosphate adsorbed on Al_2O_3 surface		

3H ₂ PO ₄ (-2H ₂ O) bonded with 3Al _{III} on (110) surface		-16.18
3H ₂ PO ₄ (-2H ₂ O) bonded with 2Al _{III} and 2Al _{IV} on (110) surface		-17.17
3H ₂ PO ₄ (-2H ₂ O) bonded with Al _{III} and 3Al _{IV} on (110) surface		-16.74
3H ₂ PO ₄ (-2H ₂ O) bonded with 2Al _{III} and 3Al _{IV} on (110) surface		-18.74
3H ₂ PO ₄ (-2H ₂ O) bonded with 4Al _{IV} on (110) surface		-17.83

Reference

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