Supplementary Information

Family Feature of Lanthanide Rare-earth (RE) Phosphate: Cooperative Activation of H_2 with H_2O or NH_3 Enables Efficient Furfural Upgradation over $Ni_2P/REPO_4$ Catalysts

Wen-yi Xu, Chao Cheng, Wei-ming Xiao, Sheng-jun Deng, Shun-li Shi, Dan Zhao*, Shu-hua Wang, Shun-min Ding, Chao Chen

Key Laboratory of Jiangxi Province for Environment and Energy Catalysis, School of Chemistry and Chemical Engineering, Nanchang University, Nanchang, Jiangxi, 330031, China

* Corresponding authors: Professor Dan Zhao;

E-mail: zhaodan@ncu.edu.cn (Dan Zhao);

Phone: +86-15879176996 (Dan Zhao);

Table S1. Comparison of catalytic performance for hydrogenation of **FAL** to **CPO** on different catalysts. "-" means the value is lower than margin of test error. Reaction conditions: 5 mg $_{Cat.}$ / mL $_{water}$, 0.1 mol/L FAL, 423 K, P-H_2: 0.5 MPa, 6h.

Entry	Catalyst	Conv. (%)	Selectivity (%)			CPO yield (%)
			FOL	CPO	CPL	
1	Ni_2P/SiO_2	8.7	51.7	48.3	-	4.2
2	Ni_2P/YPO_4	96.3	11.5	86.2	2.3	83.1
3	$Ni_2P/DyPO_4$	91.8	11.3	87.9	0.8	80.7
4	$Ni_2P/LaPO_4$	98.8	11.5	83.9	4.6	82.9
5	$Ni_2P/CePO_4$	97.1	5.5	92.9	1.6	90.2
6	$Ni_2P/PrPO_4$	89.5	8.4	89.6	2.0	80.2
7	$Ni_2P/NdPO_4$	94.2	8.2	91.4	0.4	86.1
8	$Ni_2P/SmPO_4$	98.3	10.9	85.8	3.3	84.3
9	$Ni_2P/EuPO_4$	78.2	2.9	96.4	0.7	75.4
10	$Ni_2P/GdPO_4$	90.9	13.7	86.1	0.2	78.3
11	YPO_4	-	-	-	-	-
12	$LaPO_4$	-	-	-	-	-
13	$SmPO_4$	-	-	-	-	-
14	$CePO_4$	-	-	-	-	-

Table S2. Comparison of catalytic performance for reductive amination of **FAL** to **FFA** on different catalysts. Reaction conditions: 5 mg $_{Cat.}$ / mL $_{isopropanol}$, 0.1 mol/L FAL, 393 K, P-(NH_3+H_2): 1.0 MPa, 5h.

Entry	Catalyst	Conv. (%)	Selectivity (%)			FFA yield (%)
			FFA	Schiff base	primary imine	
1	Ni_2P/SiO_2	>99	21.6	51.4	27	21.6
2	Ni_2P/YPO_4	>99	17.1	43.9	39	17.1
3	$Ni_2P/DyPO_4$	>99	9.7	90.3	-	9.7
4	$Ni_2P/LaPO_4$	>99	98.2	1.8	-	98.2
5	$Ni_2P/CePO_4$	>99	96.5	4.5	-	96.5
6	$Ni_2P/PrPO_4$	>99	66.9	33.1	-	66.9
7	$Ni_2P/NdPO_4$	>99	71.2	28.8	-	71.2
8	$Ni_2P/SmPO_4$	>99	98.9	1.1	-	98.9
9	$Ni_2P/EuPO_4$	>99	98.5	1.5	-	98.5
10	$Ni_2P/GdPO_4$	>99	87.9	12.1	-	87.9
11	YPO_4	80.6	5.7	84.8	9.5	4.6
12	$LaPO_4$	>99	13.0	76.8	10.2	13.0
13	$SmPO_4$	90.8	10.1	83.0	6.9	9.2
14	$CePO_4$	95.0	16.8	79.9	3.3	16.0

Fig. S1. XRD patterns of Ce-P, Pr-P and Gd-P samples.

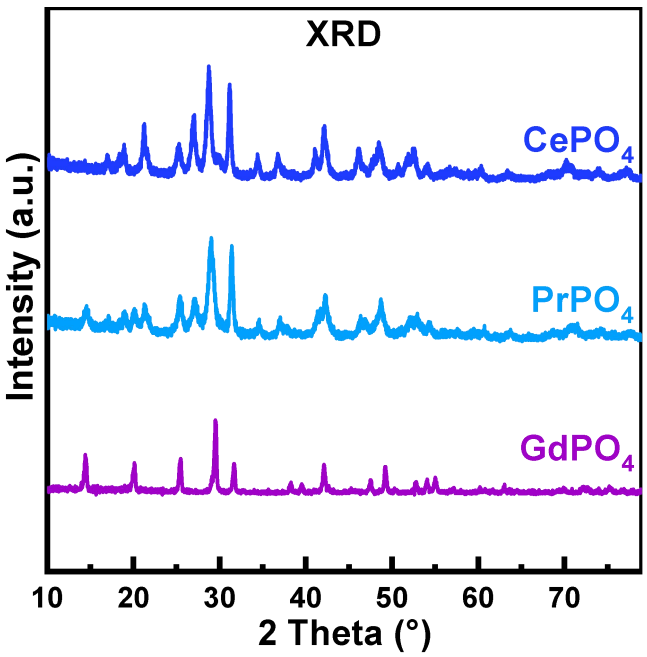


Fig. S2. The influence of catalyst ($Ni_2P/LaPO_4$) concentration on the yield of CPO or FFA from FAL conversion.

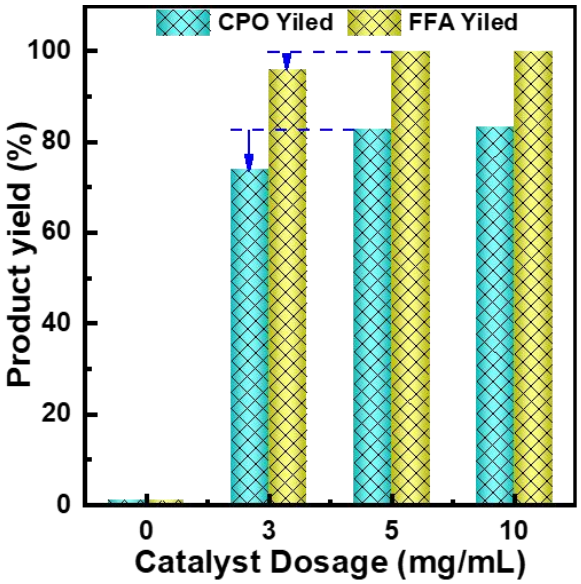
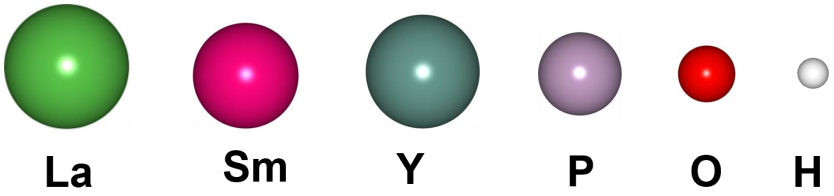
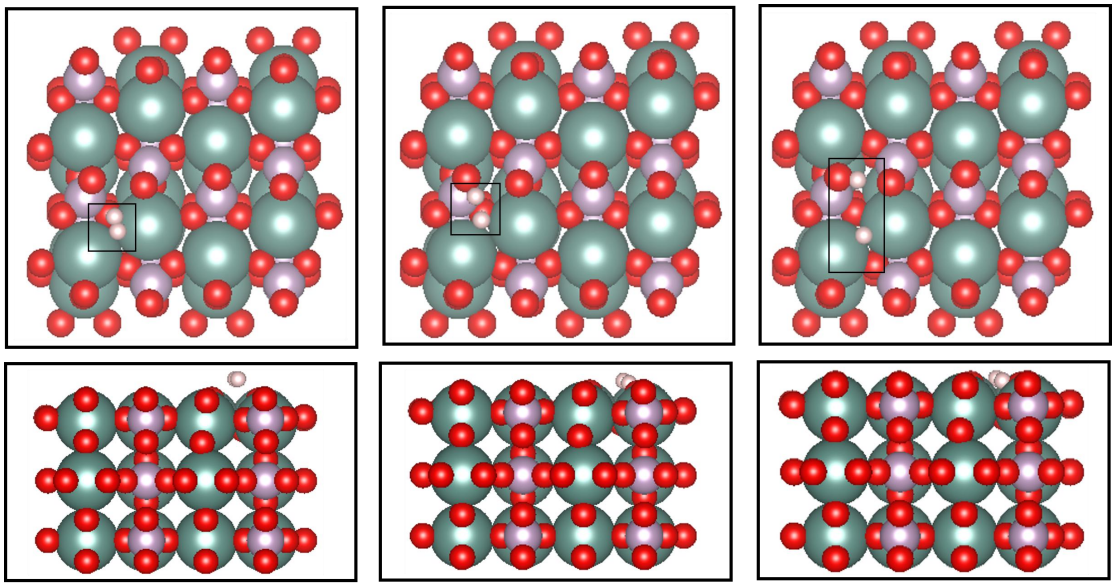


Fig. S3. Top and side views of DFT simulation of H_2 adsorption and dissociation pathway on the surface of $REPO_4$. H_2*: adsorbed H_2 on surface; H-H*: two adsorbed transition state atoms; 2H*: the adsorption of two isolated H on RE and O, respectively. (RE =Y, La, Sm)

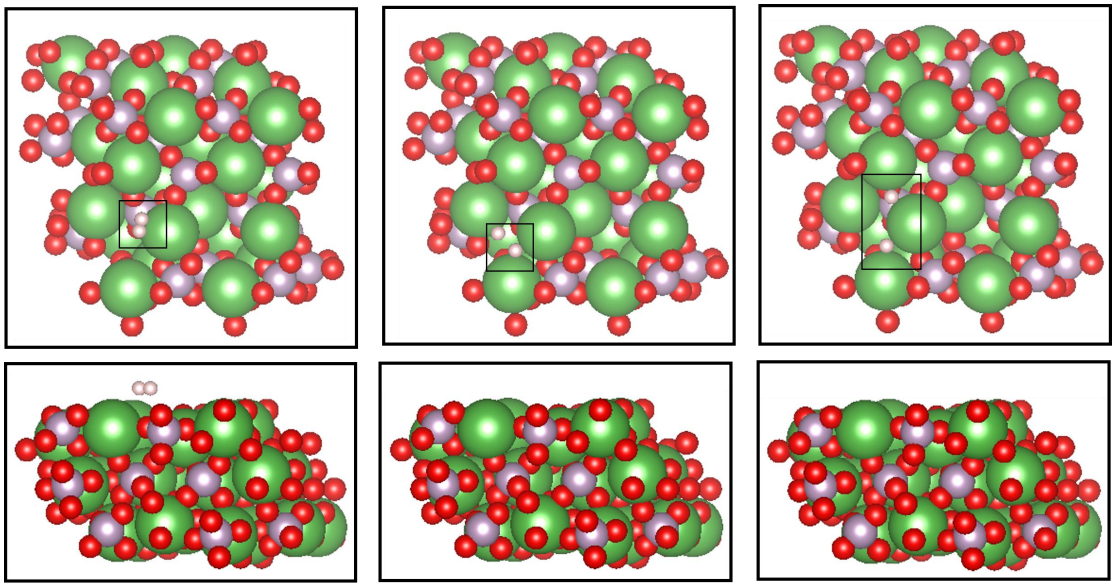


(a) YPO_4 (Tetragonal Crystal Form)



Characteristics: The c-axis is the short axis, while the b-axis is the long axis. The angles α and γ are both approximately 90°, and β is around 103°. Rare earth element atoms and oxygen atoms form a nine-coordinate structure.

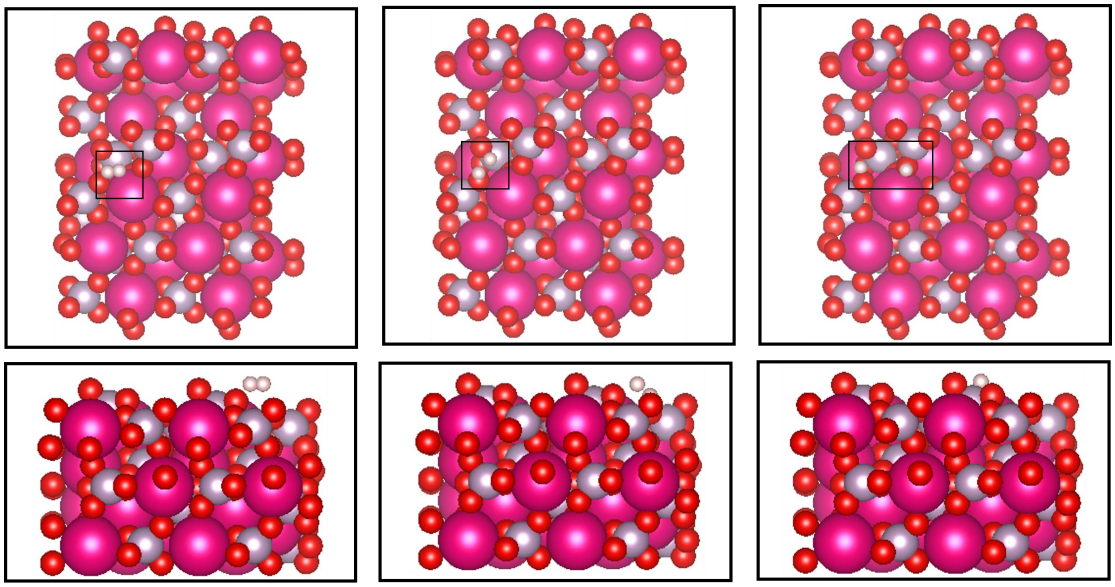
(b) $LaPO_4$ (Monoclinic Crystal Form)



(H_2*) (H-H*) (2H*)

Characteristics: The c-axis is the short axis, while the b-axis is the long axis. The angles α and γ are both approximately 90°, and β is around 103°. Rare earth element atoms and oxygen atoms form a nine-coordinate structure.

(c) $SmPO_4$ (Hexagonal Crystal Form)



(H_2*) (H-H*) (2H*)

Characteristics: The c-axis is the short axis, while the a and b axes are equal and serve as the long axes. The angles α and β are both 90°, and γ is 120°. Rare earth element atoms and oxygen atoms form an octahedral coordination.