Supporting information

Construction of Unique Structure of Ru Sites in RuP Structure for Propane Dehydrogenation

Tianxing Yang[a,b#], Yuan Zhong[a#], Jiale Li[a], Rui Ma[c], Hong Yan[a*], Yanan Liu[a,b], Yufei He[a,b*], Dianqing Li[a,b*]

[a]State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, China

[b]Beijing Engineering Center for Hierarchical Catalysts, Beijing University of Chemical Technology, Beijing 100029, China

[c]Chemistry and Chemical Engineering Guangdong Laboratory, Shantou, 515031, P.R. China

* Corresponding author

Address: Box 98, 15 Bei San Huan East Road, Beijing 100029, China

Tel: +86 10 64436992 Fax: +86 10 64436992

E-mail address: yanhong@mail.buct.edu.cn (Hong Yan); yfhe@mail.buct.edu.cn (Yufei He); lidq@mail.buct.edu.cn (Dianqing Li)

1. The calculation of the surface energy.

Surface energy (SE) is defined as the amount of energy required to cleave an infinite crystal into two parts, i.e. the energy required to form a new surface. It is calculated as shown in eqs1:

$$E_{\text{surf}} = \frac{1}{2A}(E_{\text{slab}} - E_{\text{bulk}})$$

Here, E_{slab} is the total energy of the slab, E_{bulk} is the energy in the bulk. In general, it is known that the smaller the surface energy is, the easier is to form a surface, i.e., the surface with smaller surface energy is easier to be exposed.

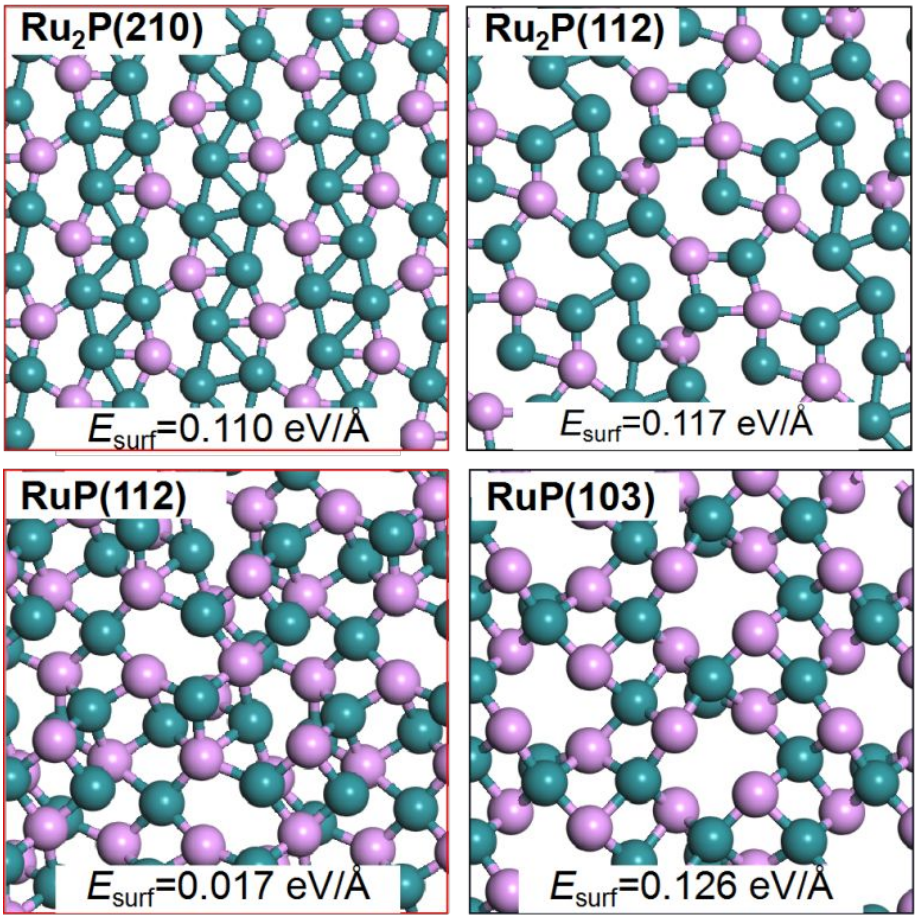

Figure S1. The top view of the optimized structures of Ru_2P(210), Ru_2P(112), RuP(112) and RuP(103). Ru:cyan; P:purple.

2. Energy test for K-point.

As shown in Table S1, when the K-point is set to 3×3×1, the adsorption energy is –0.565 eV, and when the K-point is increased to 5×5×1, the DFT calculation results show that the adsorption energy has only a small change (0.001 eV). Therefore, in order to save computing resources, the K-point of 3×3×1 is used to complete all calculations.

Table S1. Adsorption energy of methanol molecules on RuP(112) surface when K-point are 3×3×1 and 5×5×1(Unit: eV)

K-point	$E_{surface}$	$E_{adsorbate}$	$E_{adsorbate/surface}$	E_{ads}
3×3×1	–229.549	–57.012	–287.126	–0.565
5×5×1	–229.549	–57.012	–287.127	–0.566

3. Energy test for cut-off energy (ENCUT).

In order to make reasonable use of computing resources, we tested the cutoff energy (ENCUT) required for the calculation. If the ENCUT value is too small, the system will be difficult to converge, and if it is too large, it will take longer to waste computing resources. As shown in Figure S2, for the system we want to study, when the ENCUT value is 450 eV, it can not only ensure the convergence of the system, but also save computing resources.

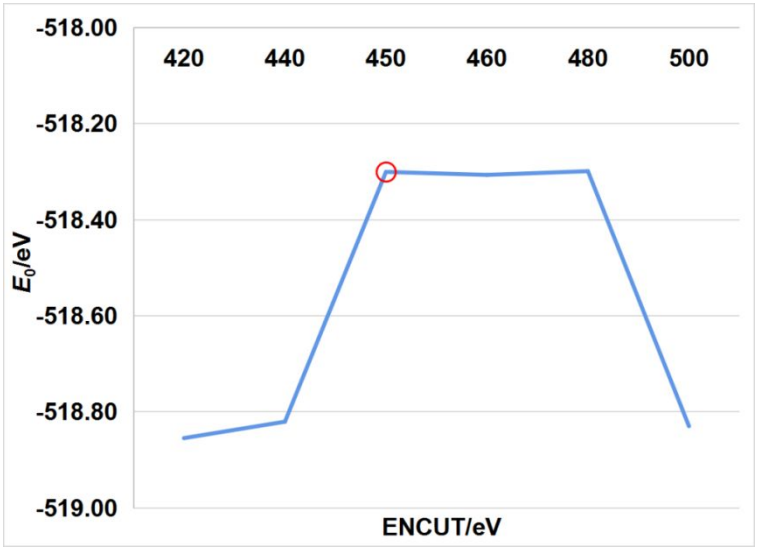

Figure S2. Take the energy E_0 of CH_3OH adsorbed on RuP(112) surface as an example for ENCUT test.

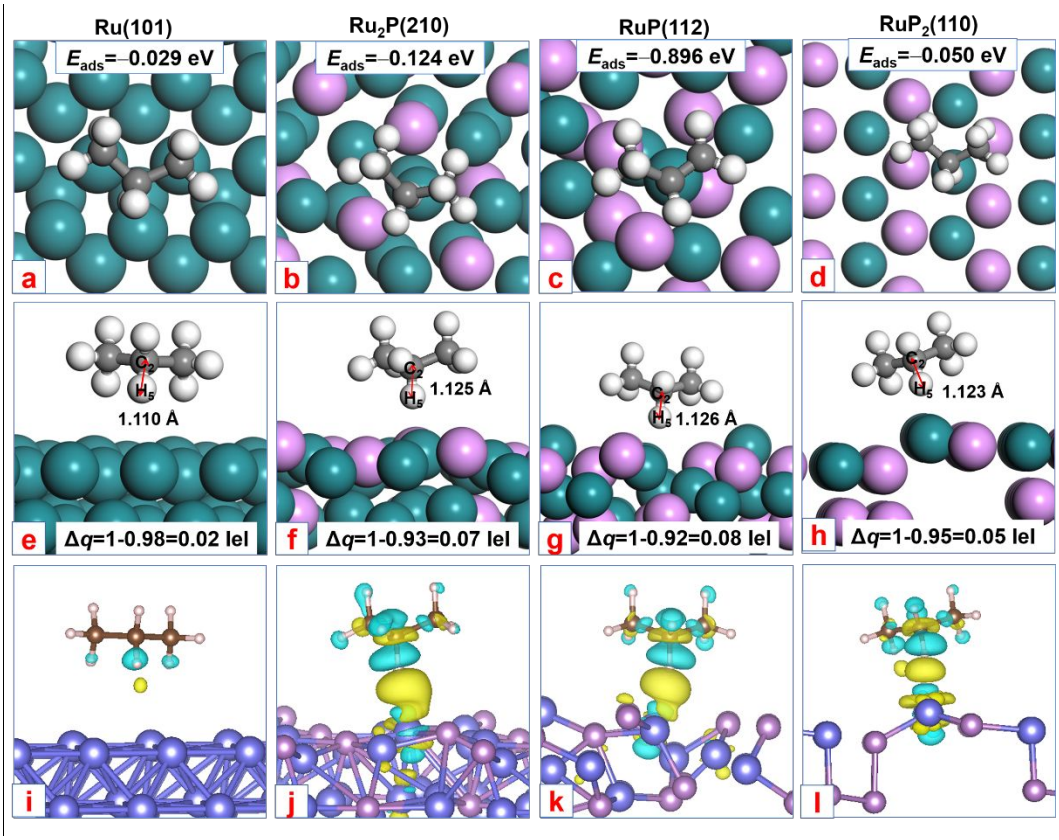

Figure S3. The top (a-d) and side (e-h) view of adsorption structures of propane on Ru and Ru_xP_y crystal surfaces, along with their adsorption energies (E_{ads}) and charge density difference analyses (i-l). The distance in the figure represents the C_2-H_5 bond length, and the Δq represents the charge transfer of the H_5 atom before and after adsorption, Ru: cyan; P: purple; C: black; H: white.

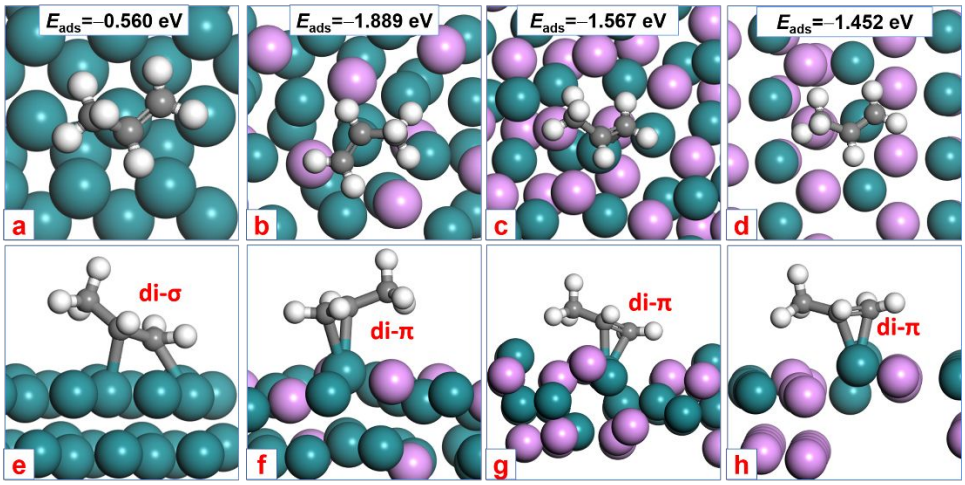

Figure S4. The top (a-d) and side (e-h) view of adsorption structures of propylene on Ru and Ru_xP_y crystal surfaces, Ru: cyan; P: purple; C: black; H: white.

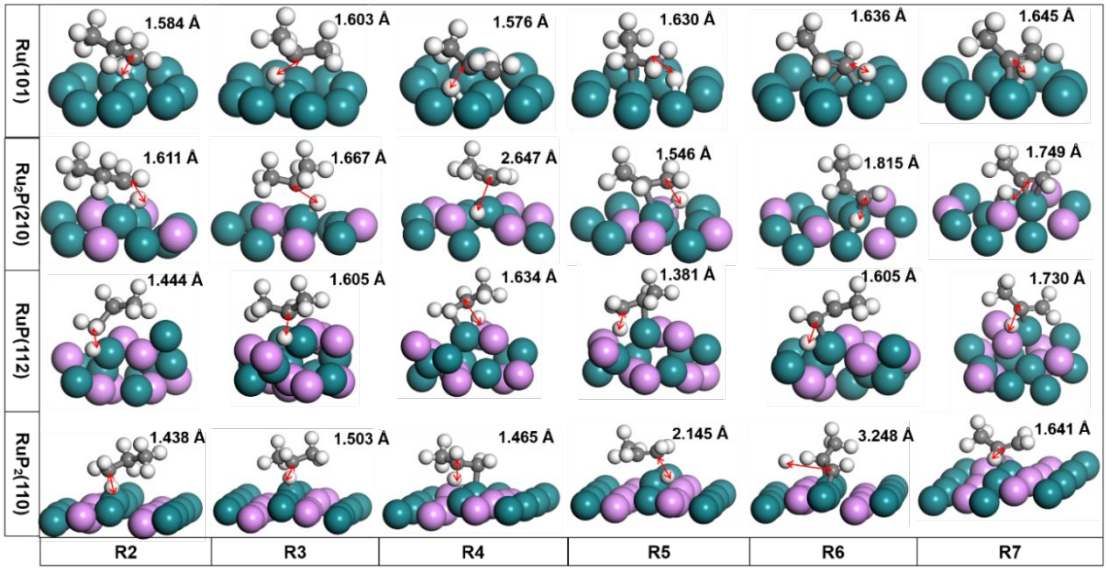

Figure S5. The side view of the transition state structure of propane dehydrogenation, where the lengths of the activated C−H bonds are also given, Ru:cyan; P:purple; C:black; H:white.

Table S2. Adsorption energies of propane and other reaction intermediates on Ru and Ru_xP_y surfaces (unit: eV)

	$CH_3CH_2CH_3$	CH_3CHCH_3	$CH_3CH_2CH_2$	CH_3CHCH_2	CH_3CHCH	CH_3CCH_2
Ru	–0.029	–1.005	–1.683	–0.560	–3.026	–2.617
Ru_2P	–0.124	–3.939	–2.506	–1.889	–3.229	–3.424
RuP	–0.896	–2.126	–2.614	–1.567	–2.803	–2.799
RuP_2	–0.050	–1.868	–2.476	–1.452	–3.648	–2.517

Table S3. The surface roughness (R) of Ru_xP_y surfaces

	Ru(101)	Ru_2P(210)	RuP(112)	RuP_2(110)
$R/10^{-3}$ Å	7.75	15.49	37.55	21.21

Table S4. Dehydrogenation reaction energy barriers of propane on Ru and Ru_xP_y surfaces (unit: eV)

	Reaction	Ru	Ru_2P	RuP	RuP_2
R1	$CH_3CH_2CH_3$ (g) → $CH_3CH_2CH_3$*	--	--	--	--
R2	$CH_3CH_2CH_3$* → $CH_3CH_2CH_2$* + H*	0.949	0.947	0.833	0.636
R3	$CH_3CH_2CH_3$*→ CH_3CHCH_3* + H*	1.156	0.934	0.714	0.790
R4	$CH_3CH_2CH_2$* → CH_3CHCH_2* + H*	0.373	0.811	0.870	0.414
R5	CH_3CHCH_3* → CH_3CHCH_2* + H*	0.645	0.866	0.649	0.910
R6	CH_3CHCH_2* → CH_3CHCH* + H*	0.320	1.913	1.796	2.820
R7	CH_3CHCH_2* → CH_3CCH_2* + H*	0.706	1.554	2.022	1.037

Table S5. Energy barrier difference between further dehydrogenation and desorption of propylene on Ru and Ru_xP_y surfaces (unit: eV)

		Ru (101)	Ru_2P(210)	RuP(112)	RuP_2(110)
R6	$E_{adesorption}$	0.560	1.889	1.567	1.452
$CH_3CHCH_2^* \rightarrow$	$E_{adehydrogenation}$	0.320	1.913	1.796	2.820
$CH_3CHCH^* + H^*$	E_{diff}	–0.240	0.024	0.229	1.368
R7	$E_{adesorption}$	0.560	1.889	1.567	1.452
$CH_3CHCH_2^* \rightarrow$	$E_{adehydrogenation}$	0.706	1.554	2.022	1.037
$CH_3CCH_2^* + H^*$	E_{diff}	0.147	–0.335	0.455	–0.414

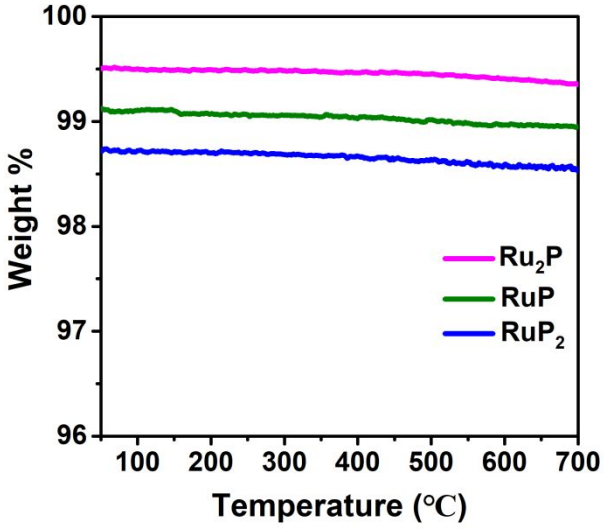

Figure S6. TG curves under N_2 atmosphere of fresh Ru_xP_y samples.

Table S6. BET data and atomic ratio of Ru_xP_y catalysts by EDX

Samples	**S_{BET} (m^2g^{-1})**	**Pore volume (cm^3g^{-1})**	**Average pore diameter (nm)**	**P/Ru atomic ratio**
Ru_2P	31	0.07	9.2	0.47
RuP	24	0.07	11.1	1.05
RuP_2	20	0.03	6.7	1.93

Table S7. PDH catalytic performance (180 min) of four samples

Catalyst	Conversion %		Propylene selectivity %		Carbon balance %	
	Initial	Steady-state	Initial	Steady-state	Initial	Steady-state
Ru/SiO_2	16.9	9.8	13.2	59.8	73±5	95±5
Ru_2P	19.8	11.4	55.3	72.2	80±5	97±5
RuP	18.8	12.7	87.2	90.5	90±5	98±5
RuP_2	19.1	11.2	42.3	67.7	83±5	97±5

.

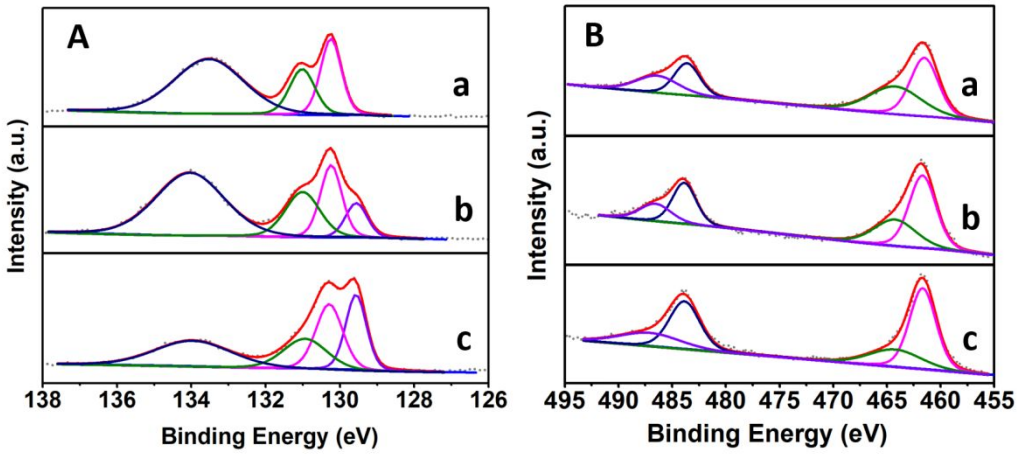

Figure S7. The XPS spectra of (A) P 2p, (B) Ru 3p for used catalysts. (a. Ru_2P, b. RuP, c. RuP_2)

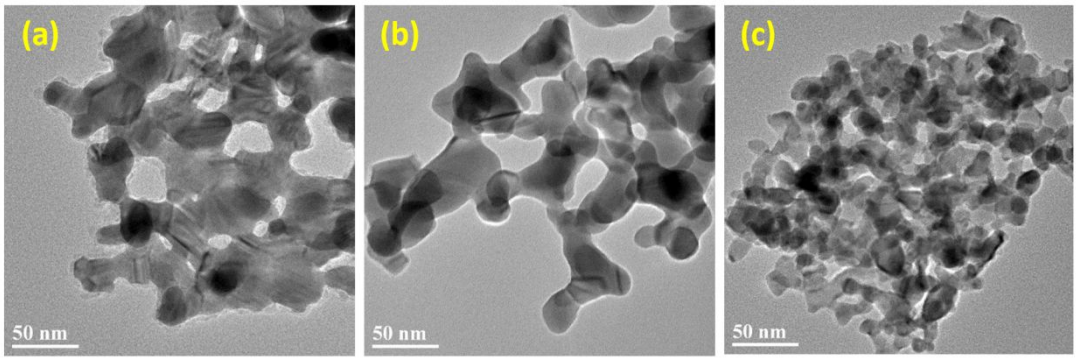

Figure S8. The HRTEM images used catalysts. (a. Ru_2P, b. RuP, c. RuP_2)

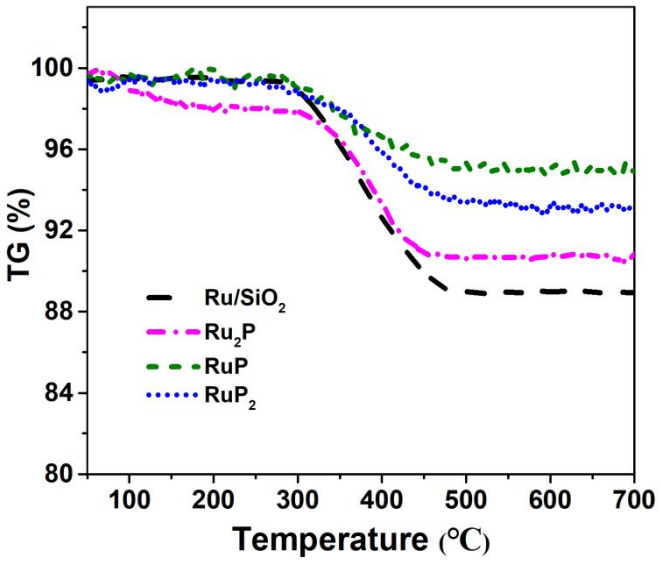

Figure S9. TG curves under air atmosphere of Ru, Ru_2P, RuP and RuP_2 catalyst