Supplementary Information

Interfacial compatibility critically controls Ru/TiO_2 metal-support interaction modes in CO_2 hydrogenation

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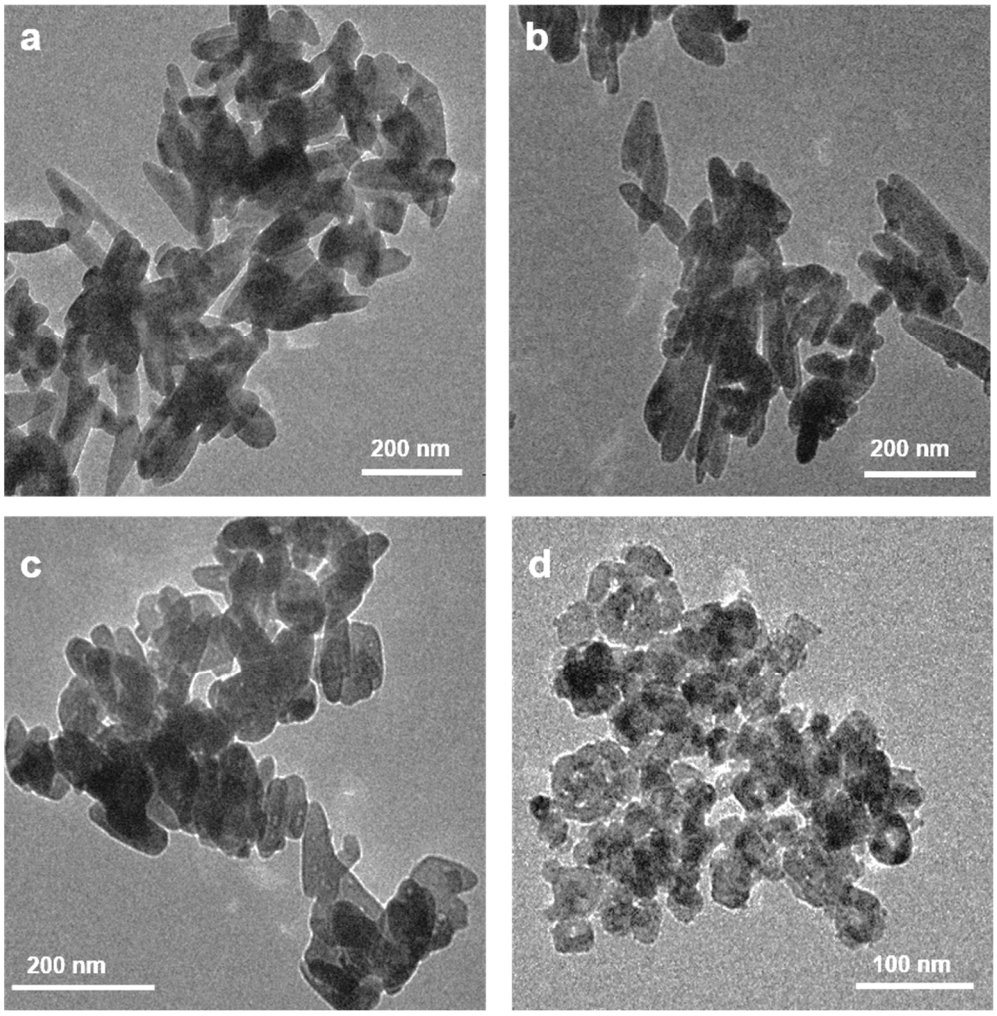
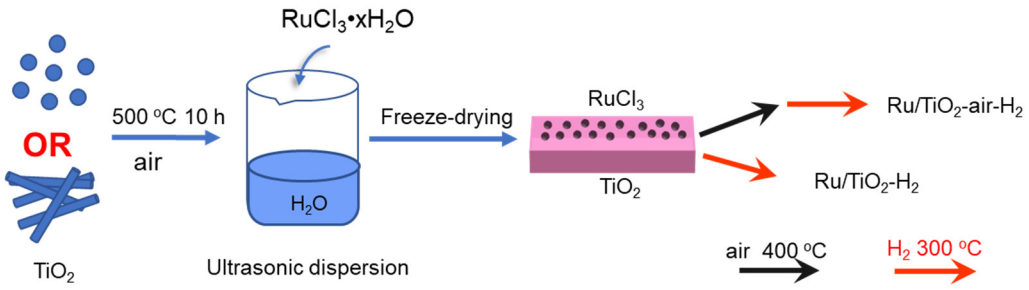
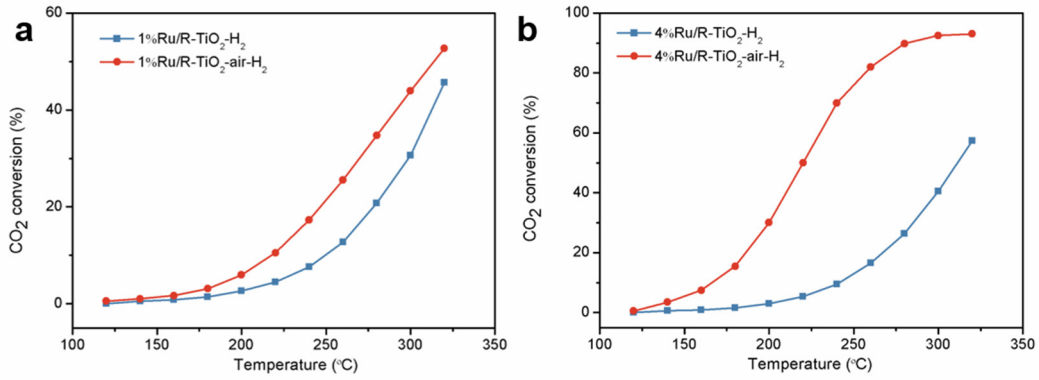


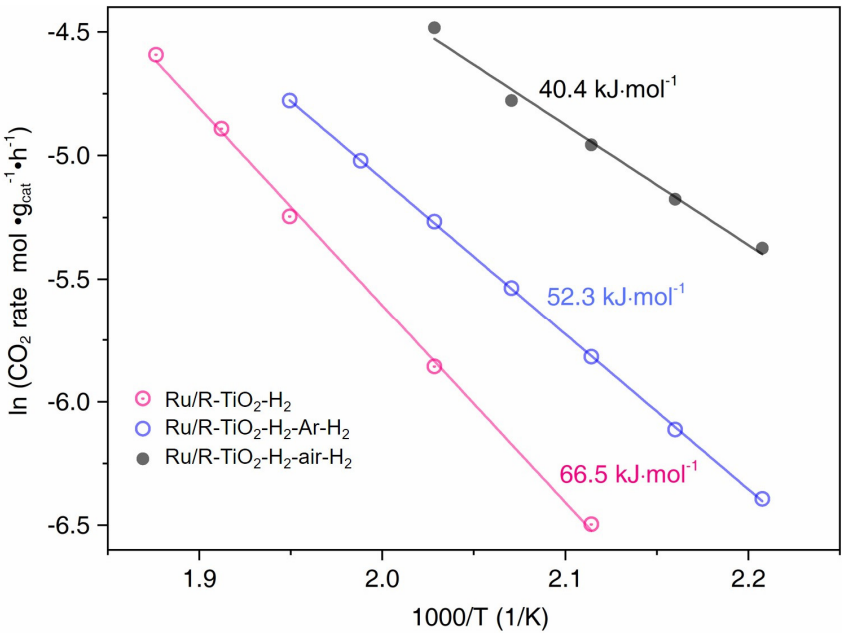
Supplementary Figure 1. TEM images of rutile-$TiCl_4$ (a), rutile-$TiCl_3$ (b), rutile-TiN (c) and anatase (d) after being annealed at 500 ^{o}C for 10 h.



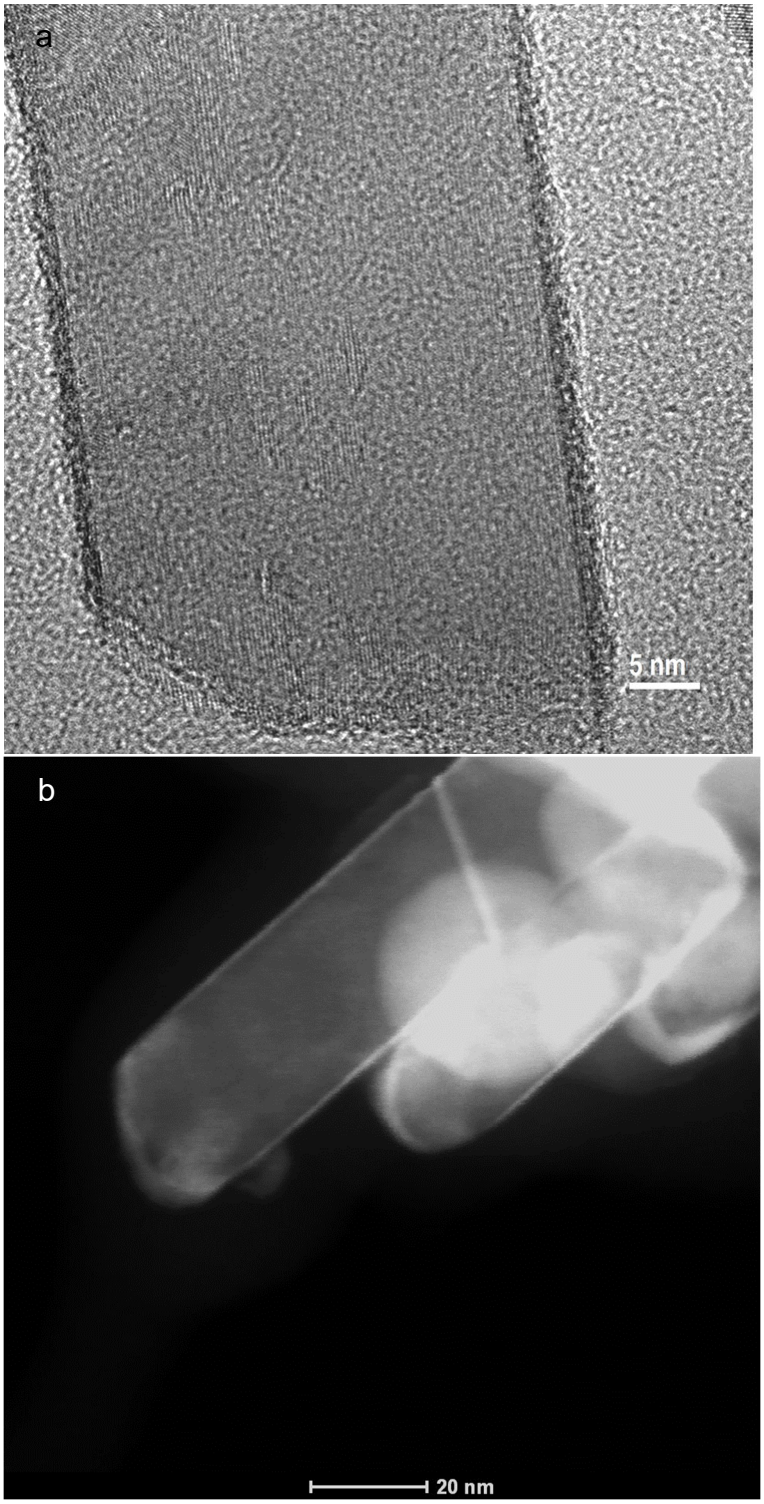
Supplementary Figure 2. Scheme of the synthetic procedures of Ru/TiO_2 catalysts.



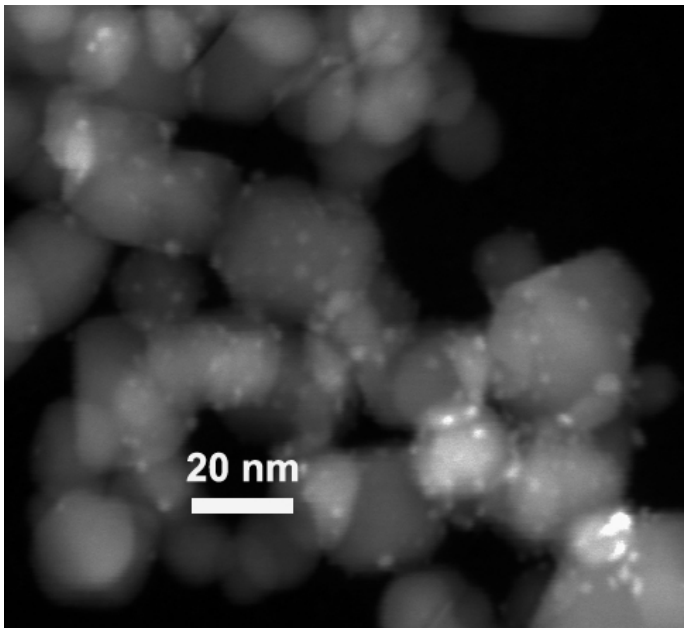
Supplementary Figure 3. Temperature-dependent CO_2 conversions of (a) 1%Ru/R-$TiO_2$and (b) 4%Ru/R-TiO_2.



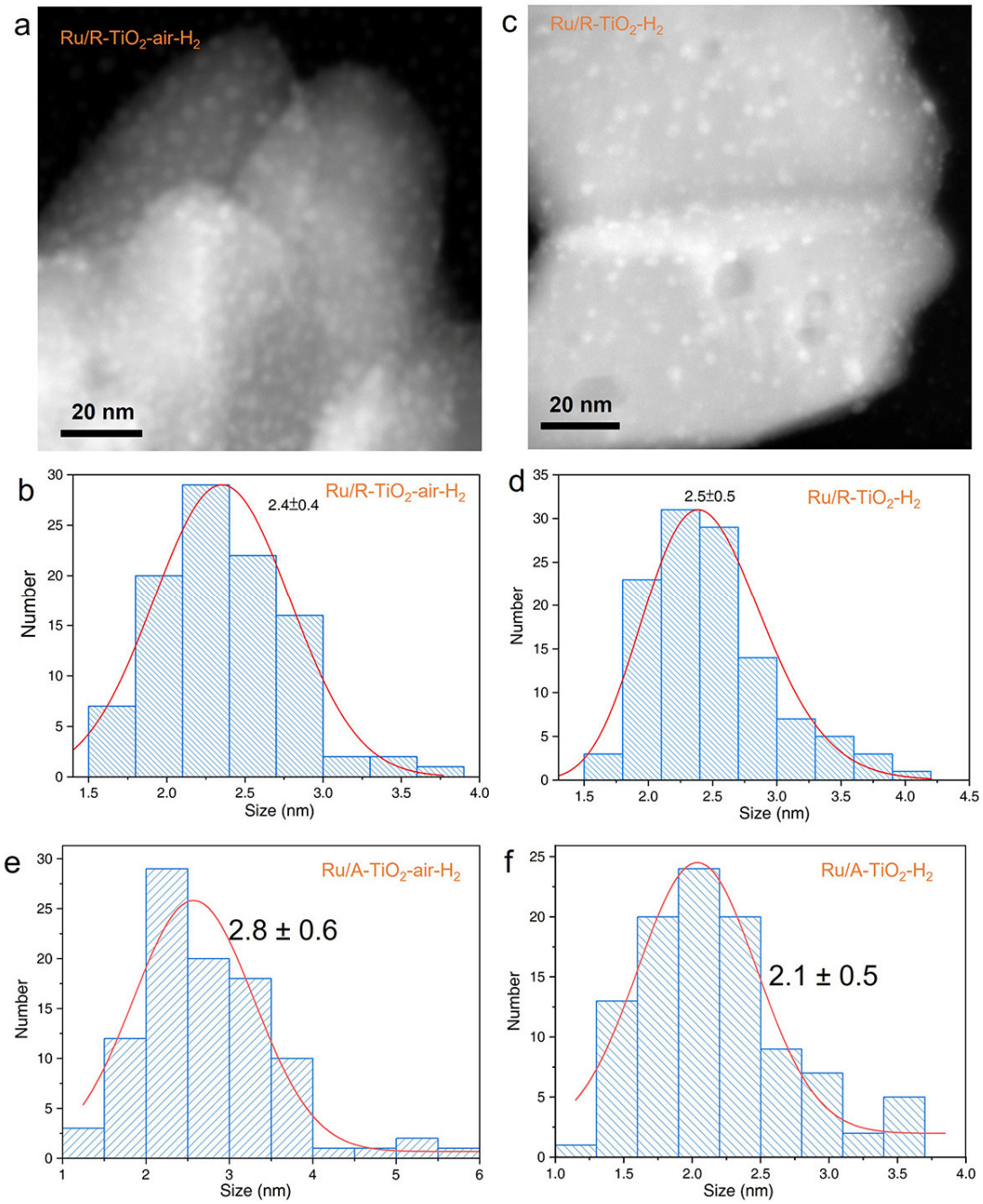
Supplementary Figure 4. Arrhenius plots of 2%Ru/R-TiO_2 catalysts treated in different procedures.



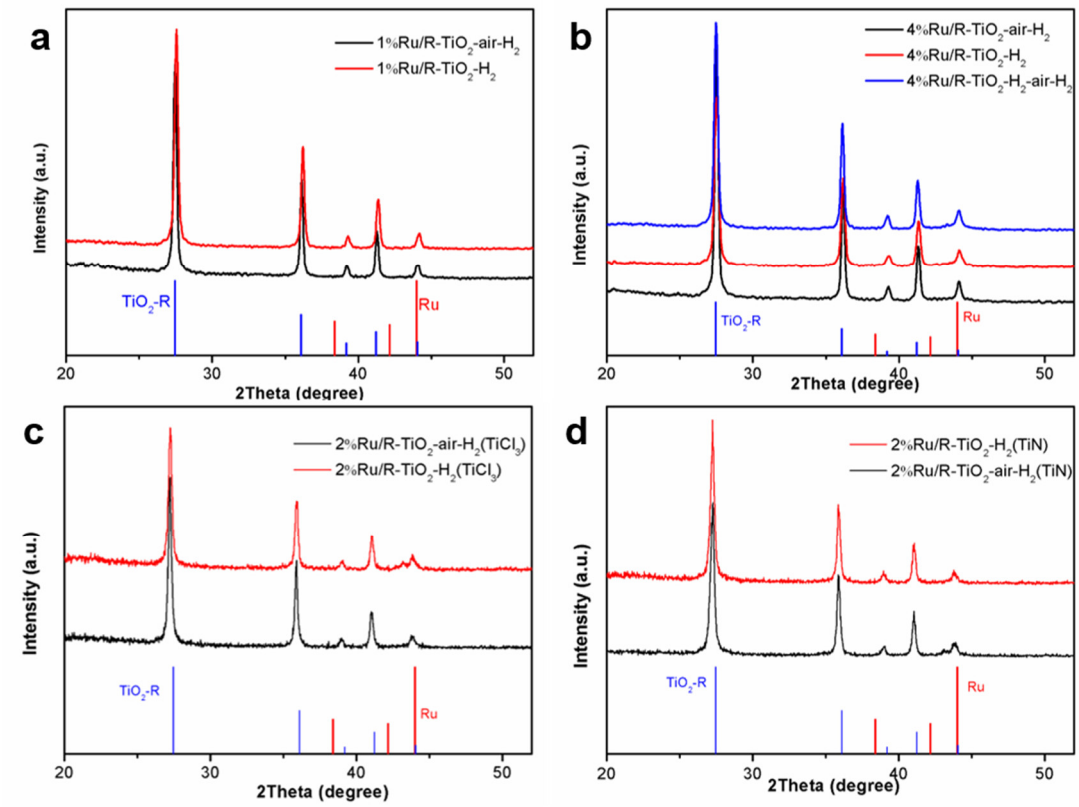
Supplementary Figure 5. TEM (a) and STEM (b) images of RuO_2 epitaxial layers on R-TiO_2 nanorod.



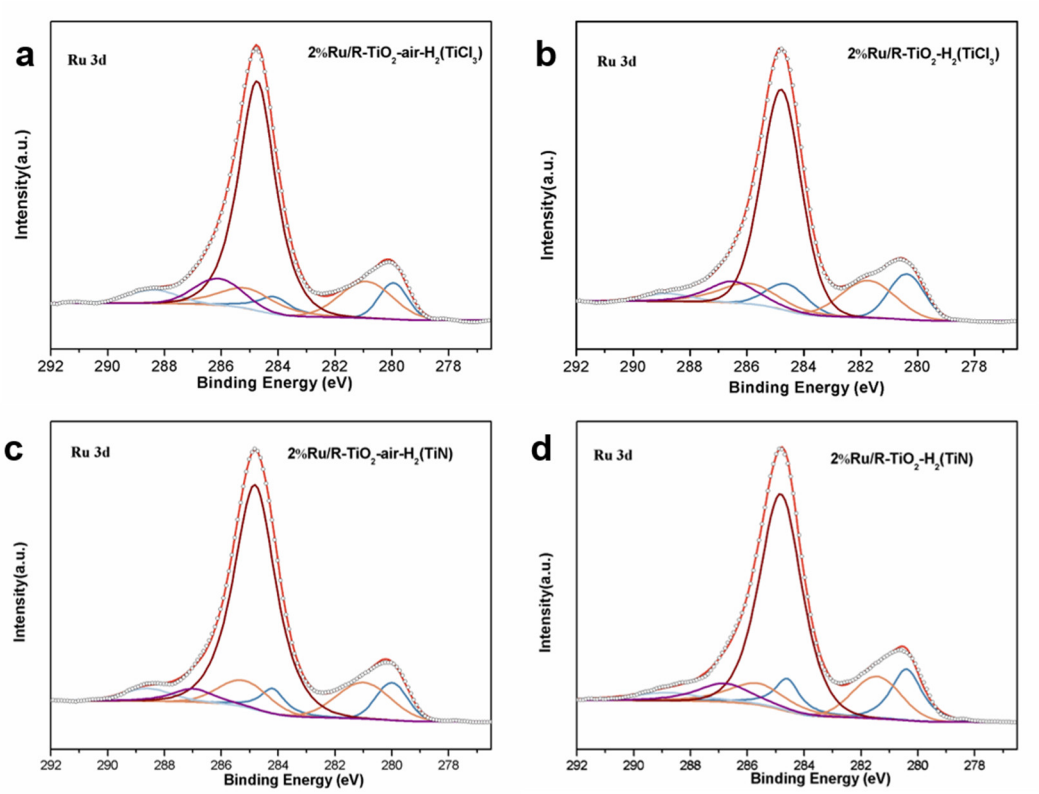
Supplementary Figure 6. STEM of RuO_2 on A-TiO_2.



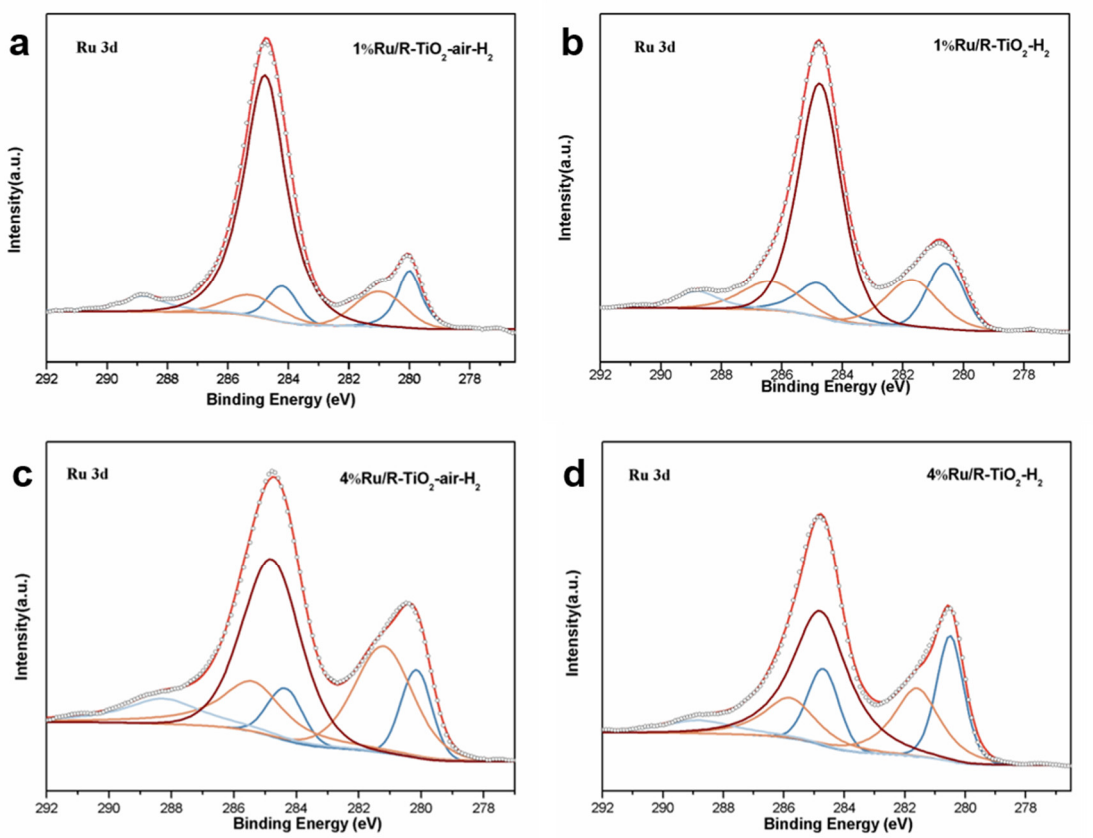
Supplementary Figure 7. Size distributions of 2%-Ru/TiO_2-H_2 catalysts. STEM images of (a) Ru/R-TiO_2-air-H_2 and (b) Ru/R-TiO_2-H_2 catalysts. Size distributions of Ru nanoparticles of (c) Ru/R-TiO_2-air-H_2, (d) Ru/R-TiO_2-H_2, (e) Ru/A-TiO_2-air-H_2, and (f) Ru/A-TiO_2-H_2 catalysts.



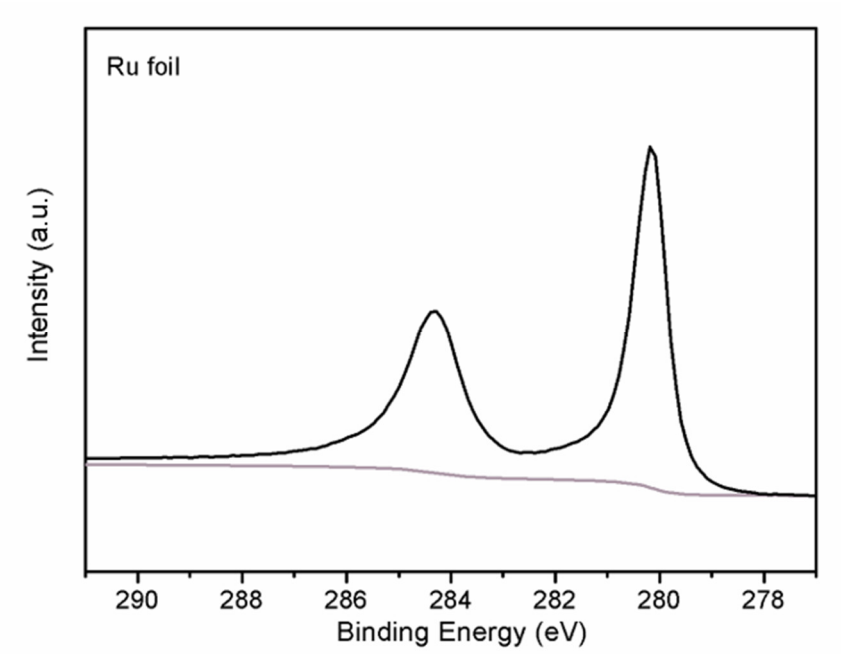
Supplementary Figure 8. XRD of 1%Ru/R-TiO_2 (a), 4%Ru/R-TiO_2(b), 2%Ru/R-TiO_2($TiCl_3$) (c) and 2%Ru/R-TiO_2(TiN) (d) after reaction



Supplementary Figure 9. XPS of 2%Ru/R-TiO_2-air-H2($TiCl_3$) (a), 2%Ru/R-TiO_2-H_2($TiCl_3$) (b), 2%Ru/R-TiO_2 -air-H_2(TiN) (c) and 2%Ru/R-TiO_2-H_2(TiN) (d) after reaction.



Supplementary Figure 10. XPS of 1%Ru/R-TiO_2-air-H_2(a), 1%Ru/R-TiO_2-H_2(b), 4%Ru/R-TiO_2-air-H_2(c) and 4%Ru/R-TiO_2-H_2(d) after reaction.



Supplementary Figure 11. XPS of Ru foil.

Supplementary Table 1. XPS fitting results of other catalysts.

Sample	Binding Energy [eV]		The radio of $Ru^{\delta+}/Ru^0$
	$Ru^{\delta+}$	Ru^0	
1%Ru/R-TiO_2-air-H_2	281.1	280.0	1.1
1%Ru/R-TiO_2-H_2	281.7	280.6	1.1
4%Ru/R-TiO_2-air-H_2	281.2	280.1	2.3
4%Ru/R-TiO_2-H_2	281.6	280.5	1.0
2%Ru/R-TiO_2-air-H_2($TiCl_3$)	281.1	280.0	1.8
2%Ru/R-TiO_2-H_2($TiCl_3$)	281.7	280.4	1.2
2%Ru/R-TiO_2-air-H_2(TiN)	280.9	279.9	1.9
2%Ru/R-TiO_2-H_2(TiN)	281.4	280.4	1.1

Supplementary Table 2. Metal dispersion of Ru on rutile calculated by CO pulse adsorption

Sample	Ru/R-TiO_2-air-H_2	Ru/R-TiO_2-H_2
D_{CO}(%)	33.64	31.1