Supporting Information

Probing the morphological effects of ReO_x/CeO_2 catalysts on CO_2 hydrogenation reaction

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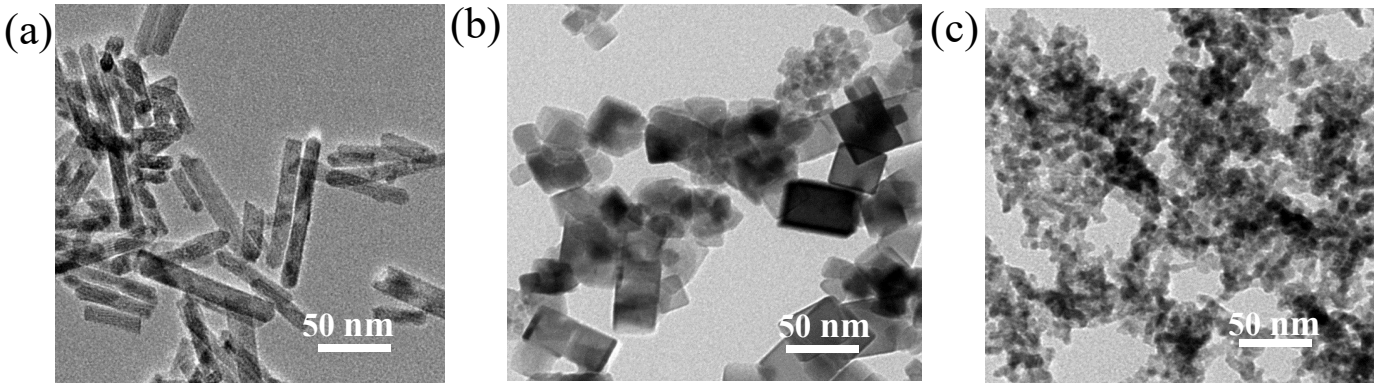

Fig. S1. HRTEM images of (a) CeO_2-R, (b) CeO_2-C and (c) CeO_2-P supports.

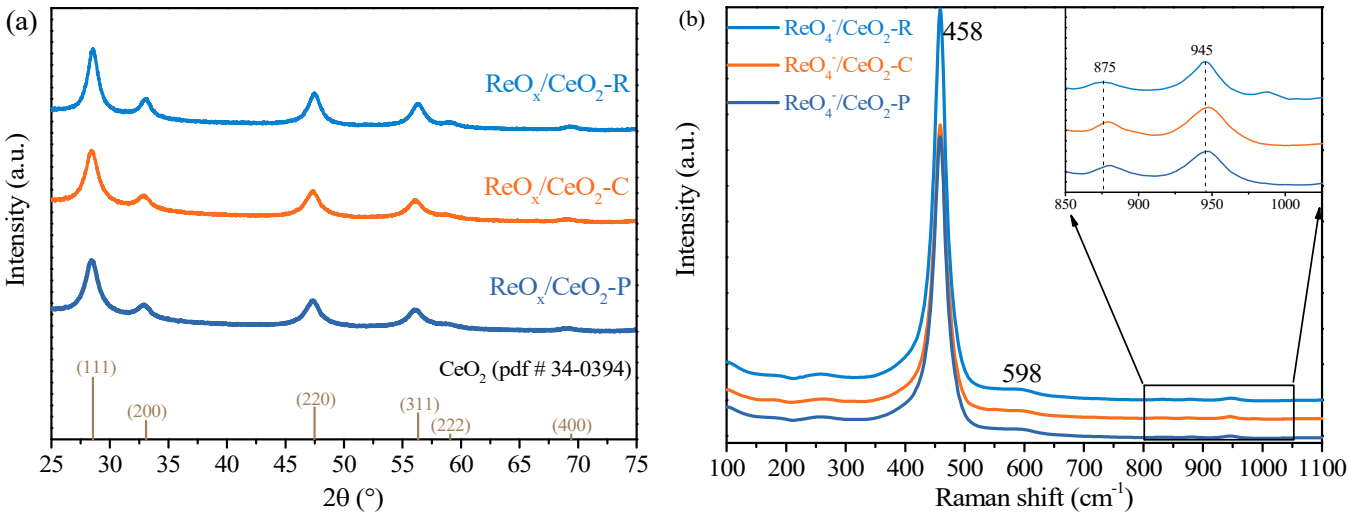

Fig. S2. (a) XRD patterns of ReO_x/CeO_2-R, ReO_x/CeO_2-C and ReO_x/CeO_2-P. (b) Raman spectra of ReO_4^-/CeO_2-R, ReO_4^-/CeO_2-C and ReO_4^-/CeO_2-P.

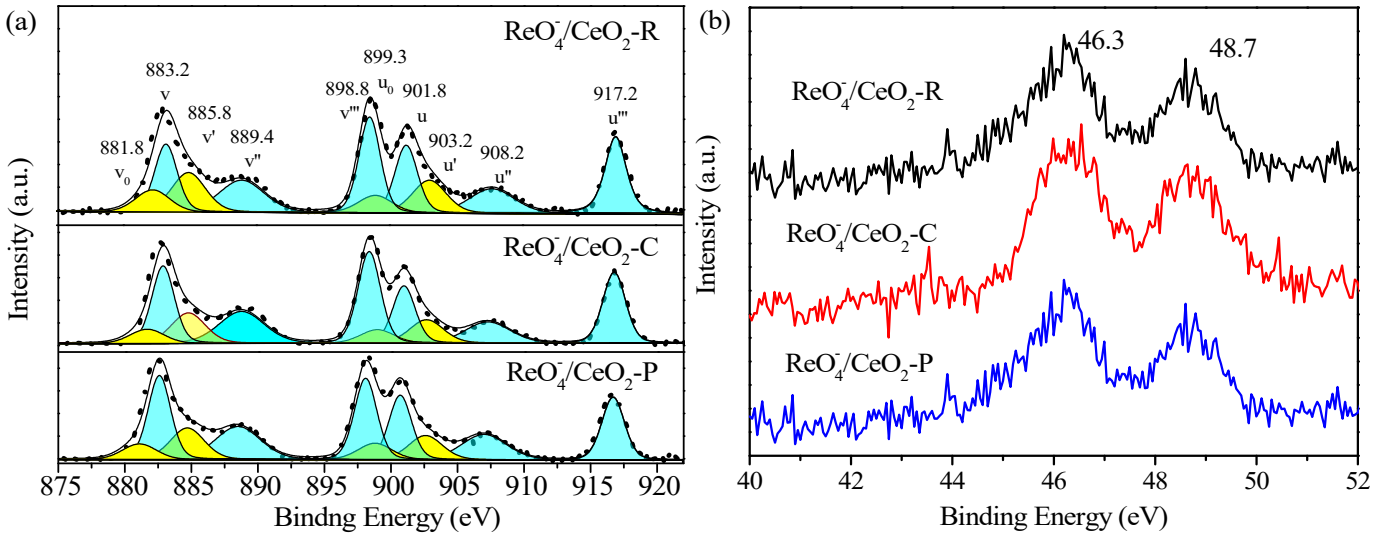

Fig. S3. Deconvolution of XPS spectra of (a) Ce 3d and (b) Re 4f of ReO_4^-/CeO_2-R, ReO_4^-/CeO_2-C and ReO_4^-/CeO_2-P.

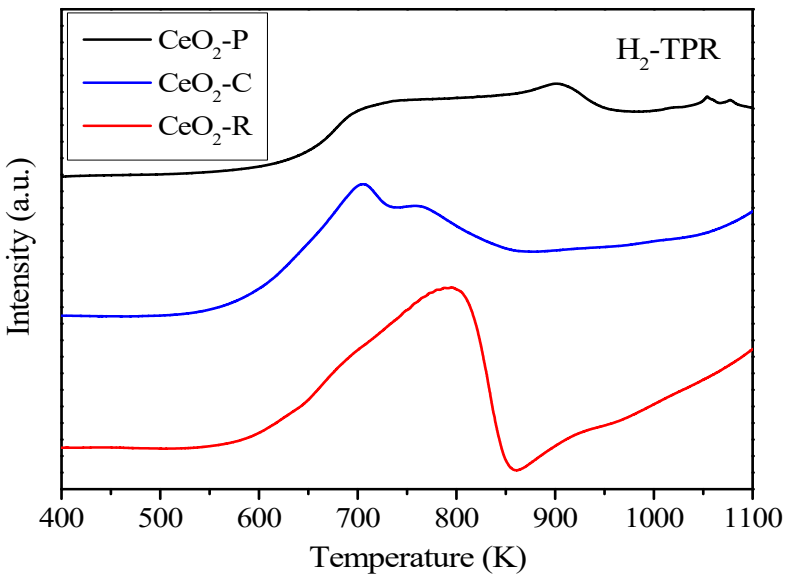

Fig. S4.H_2-TPR of CeO_2-R, CeO_2-P and CeO_2-C.

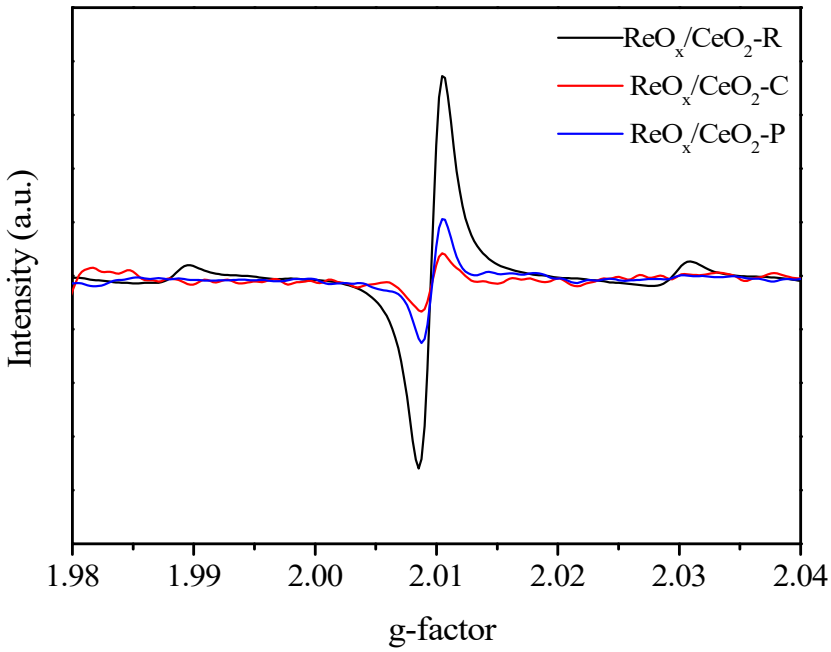

Fig. S5. EPR spectra of the catalysts.

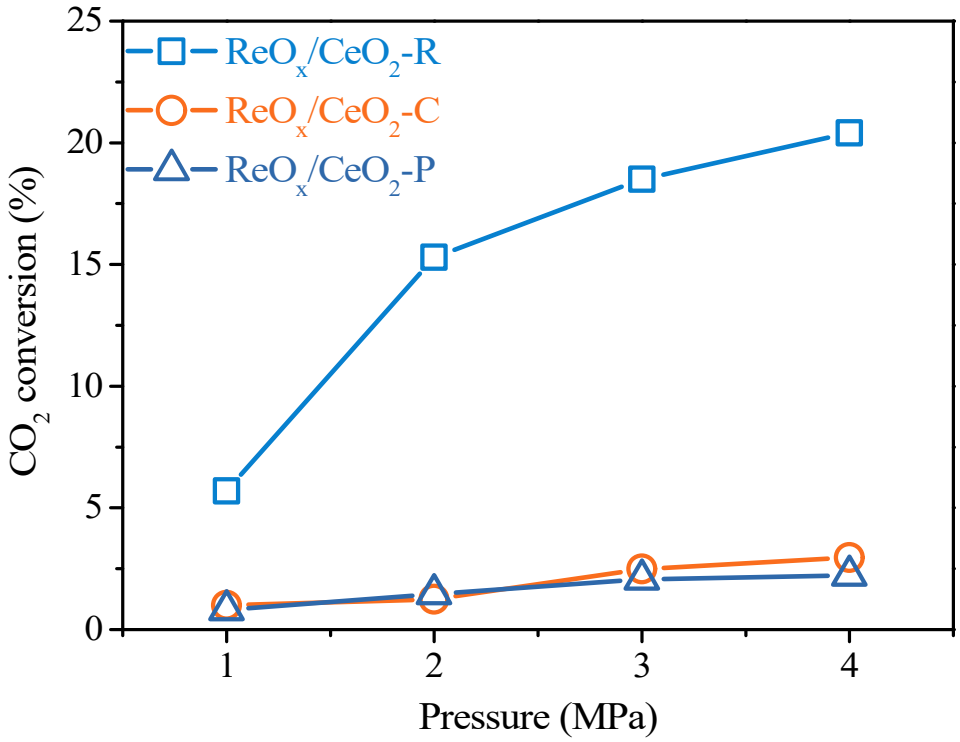

Fig. S6. The effect of pressure on CO_2 conversion on ReO_x/CeO_2-R, ReO_x/CeO_2-C and ReO_x/CeO_2-P at 613 K, CO_2/H_2=1/3 and GHSV=12000 mL/g h.

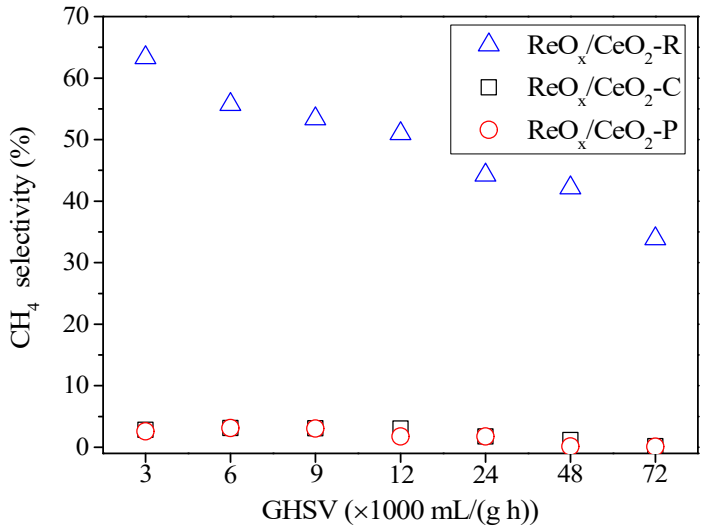

Fig. S7. The effect of GHSV on CH_4 selectivity on ReO_x/CeO_2-R, ReO_x/CeO_2-C and ReO_x/CeO_2-P at 613 K, $CO_2/H_2 = 1/3$ and 2 MPa.

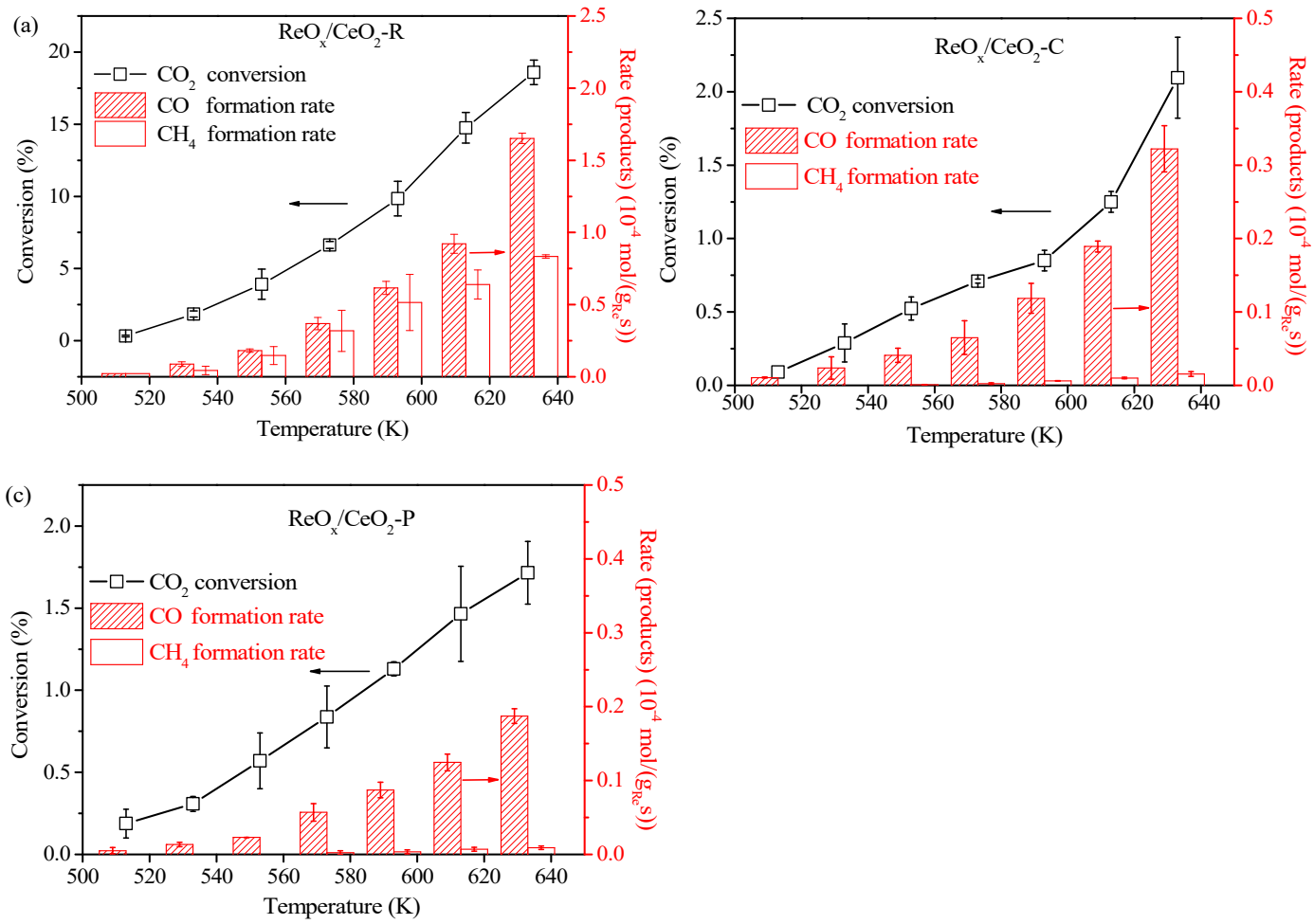

Fig. S8. Temperature-dependent performance of (a)ReO_x/CeO_2-R, (b)ReO_x/CeO_2-C and (c)ReO_x/CeO_2-P. The left vertical axis is CO_2 conversion and the right is the formation rate of products.

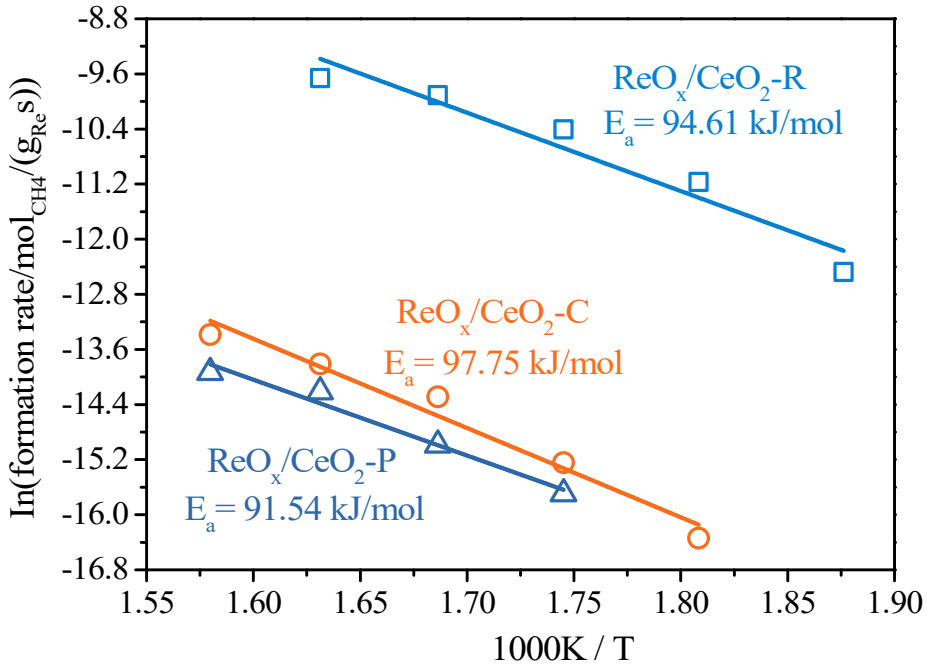

Fig. S9. Arrhenius plots for CH_4 generation on ReO_x/CeO_2-R, ReO_x/CeO_2-C and ReO_x/CeO_2-P.

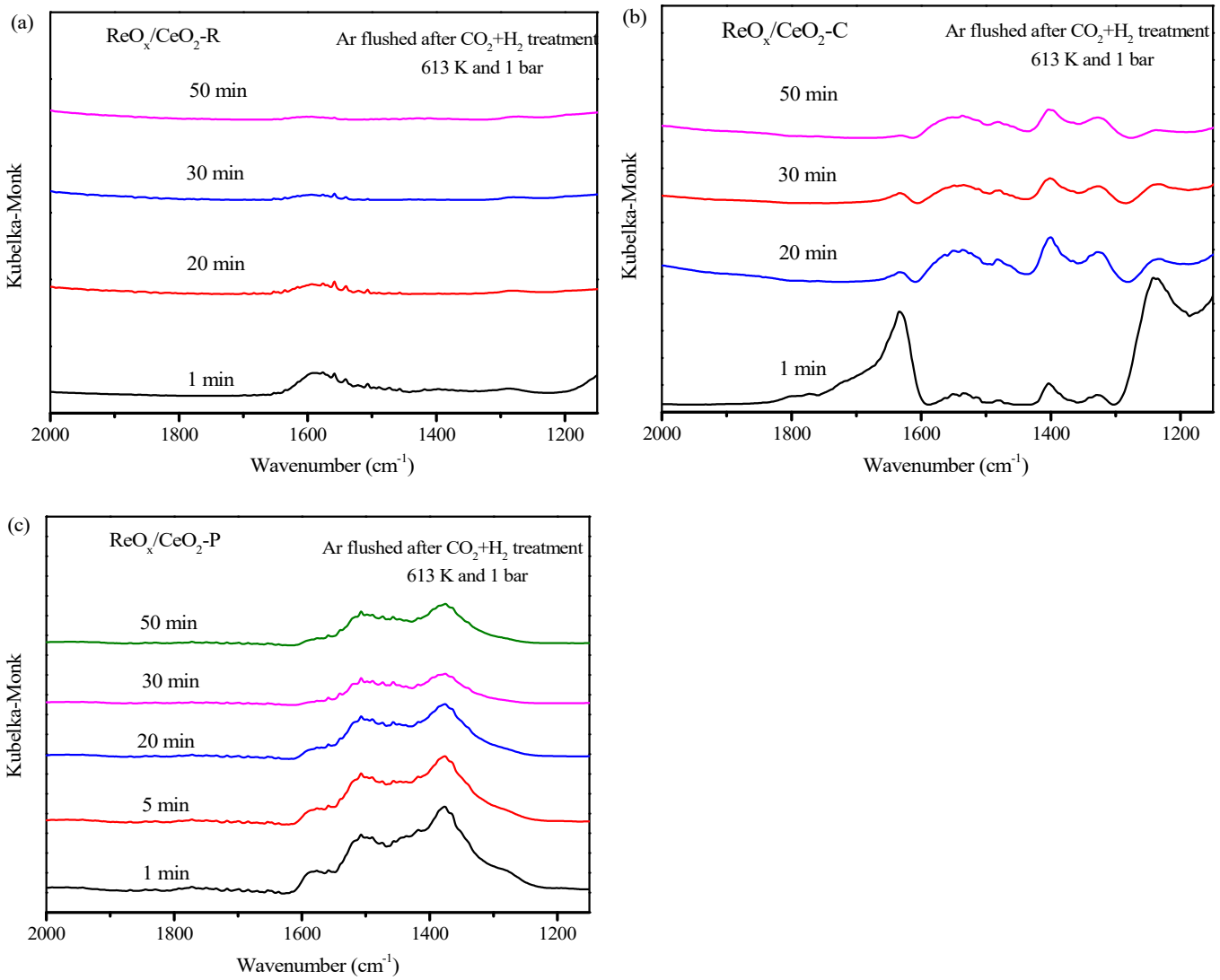

Fig. S10. Infrared spectra recorded under Ar flushing after CO_2+H_2 reaction at 633 K and 0.1 MPa. (a) ReO_x/CeO_2-R, (b) ReO_x/CeO_2-C and (c) ReO_x/CeO_2-P.

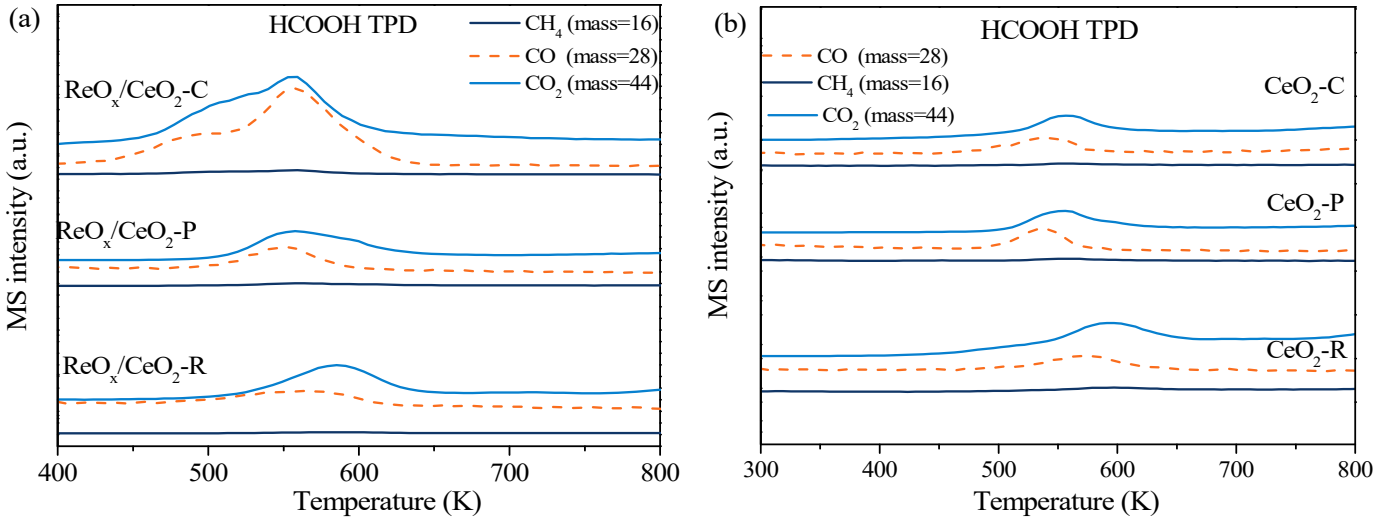

Fig. S11. TPD of HCOOH over (a) ReO_x/CeO_2-C, ReO_x/CeO_2-P and ReO_x/CeO_2-R, (b) CeO_2-C, CeO_2-P and CeO_2-R.

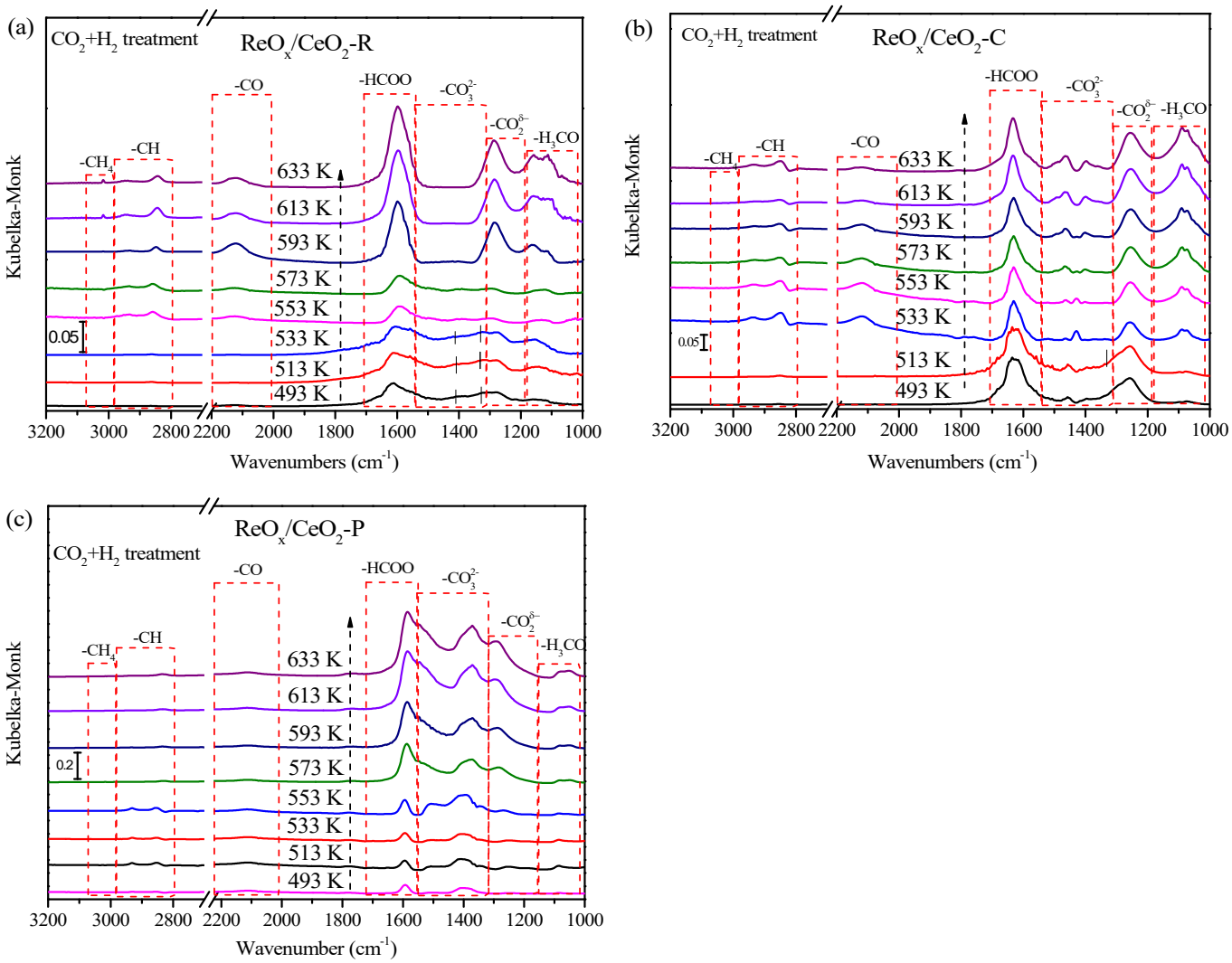

Fig. S12. Temperature-dependent infrared analysis of CO_2 hydrogenation after exposing the catalysts to CO_2+H_2 at 493 K and subsequently heating to 633 K. (a) ReO_x/CeO_2-R, (b) ReO_x/CeO_2-C and (c) ReO_x/CeO_2-P.

Table S1. Assessment of extraparticle mass transfer limitations in CO_2 hydrogenation over catalysts.

Parameter	ReO_x/CeO_2-R			ReO_x/CeO_2-C.			ReO_x/CeO_2-P		
P(MPa)	2	2	2	2	2	2	2	2	2
T(K)	613	613	613	613	613	613	613	613	613
Particle size (μm)	25-45	25-45	25-45	25-45	25-45	25-45	25-45	25-45	25-45
W_{cat} (g)	0.05	0.1	0.2	0.05	0.1	0.2	0.05	0.1	0.2
H_2: CO_2 : Ar (cm^3/min)	36:12:2	72:24:4	144:48:8	36:12:2	72:24:4	144:48:8	36:12:2	72:24:4	144:48:8
CO_2(10^{-5} mol/g_{Re} s)	14.95	15.60	15.82	1.94	1.90	2.01	1.25	1.31	1.41

Table S2. Assessment of intraparticle mass transfer limitations in CO_2 hydrogenation over catalysts.

Parameter	ReO_x/CeO_2-R			ReO_x/CeO_2-C.			ReO_x/CeO_2-P		
P(MPa)	2	2	2	2	2	2	2	2	2
T(K)	613	613	613	613	613	613	613	613	613
Particle size (μm)	≤25	25-45	125-300	≤25	25-45	125-300	≤25	25-45	125-300
W_{cat} (g)	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
H_2: CO_2 : Ar (cm^3 min^{-1})	72:24:4	72:24:4	72:24:4	72:24:4	72:24:4	72:24:4	72:24:4	72:24:4	72:24:4
CO_2(10^{-5} mol/g_{Re} s)	15.94	15.60	15.13	1.96	1.90	1.86	1.39	1.31	1.32

Table S3. Structural parameters of the samples

	Re (wt%)-XRF	Re (wt%)-XPS	$S_{BET}(m^2/g)$	Pore volume (cm^3/g)
ReO_x/CeO_2-R	1.97	2.21	109.06	0.32
ReO_x/CeO_2-C	1.98	2.02	38.24	0.16
ReO_x/CeO_2-P	1.98	2.31	34.39	0.19

Table S4. (1) Infrared band assignments of the surface species on ReO_x/CeO_2-C.

Surface species	Wavenumber (cm^{-1})	assignment
Carbonate	1398	ν_s(O-C-O)
	1512	ν_{as}(O-C-O)
Carboxylate	1289	ν_s(O-C-O)
CO bond	2007	linearly bound
	1892	bridge bound
Formate	2948, 2853	ν(CH)
	1631	ν_{as} (O-C-O)
Methoxyl	1096	$\nu_{(CO)}$ of terminal of bridged-OCH_3
Methane	3019	ν(CH)

(2) Infrared band assignments of the surface species on ReO_x/CeO_2-R.

Surface species	Wavenumber (cm^{-1})	assignment
Carboxylate	1289	ν_s(O-C-O)
CO bond	2007, 1912	linearly bound
	1892	bridge bound
Formate	2948, 2853	ν(CH)
	1594	ν_{as} (O-C-O)
Methoxyl	1096,1157	$\nu_{(CO)}$ of terminal of bridged-OCH_3
Methane	3019	ν(CH)

(3) Infrared band assignments of the surface species on ReO_x/CeO_2-P.

Surface species	Wavenumber (cm^{-1})	assignment
Carbonate	1398	ν_s(O-C-O)
	1512	ν_{as}(O-C-O)
Carboxylate	1289	ν_s(O-C-O)
CO bond	2007	linearly bound
	1892	bridge bound
Formate	2948, 2853	ν(CH)
	1617,1594	ν_{as} (O-C-O)
Methoxyl	1096	$\nu_{(CO)}$ of terminal of bridged-OCH_3
Methane	3019	ν(CH)