

Nanoparticles of Rh confined and tailored by LaFeO₃-La₂O₃ on SiO₂ for direct ethanol synthesis from syngas

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Fig. S1 Nitrogen adsorption and desorption isotherm curves (a) and BJH pore size distributions (b) of SiO₂ and LaFe_{1-x}Rh_xO₃/SiO₂ catalysts (x = 0.2 - 0.6, 1).

Table S1 Physical properties of SiO₂ and LaFe_{1-x}Rh_xO₃/SiO₂ catalysts (x = 0.2 - 0.6, 1).

Fig. S2 The EDS mapping images for LaFe_{0.5}Rh_{0.5}O₃/SiO₂ after reduction.

Fig. S3 XPS spectra (dotted lines) and the corresponding peak simulating (solid lines) of La 3d, Fe 2p and Rh 3d for LaFe_{0.5}Rh_{0.5}O₃/SiO₂ after reduction (a), reaction (b) and stability test (c).

Fig. S4 Catalytic performance for LaFe_{0.9}Rh_{0.1}O₃/SiO₂ catalysts with different rhodium content for DES from syngas.

Fig. S5 Catalytic performance for LaRhO₃/SiO₂ catalyst for DES from syngas.

Table S2 Catalytic performance of CO hydrogenation over LaFe_{1-x}Rh_xO₃/SiO₂ catalysts at 240 °C and LaRhO₃/SiO₂ catalyst at 280 °C.

Table S3 Apparent kinetic parameters of ethanol over LaFe_{1-x}Rh_xO₃/SiO₂ catalysts (x = 0.2 - 0.6, 1) at 230 - 245 °C and 3 MPa.

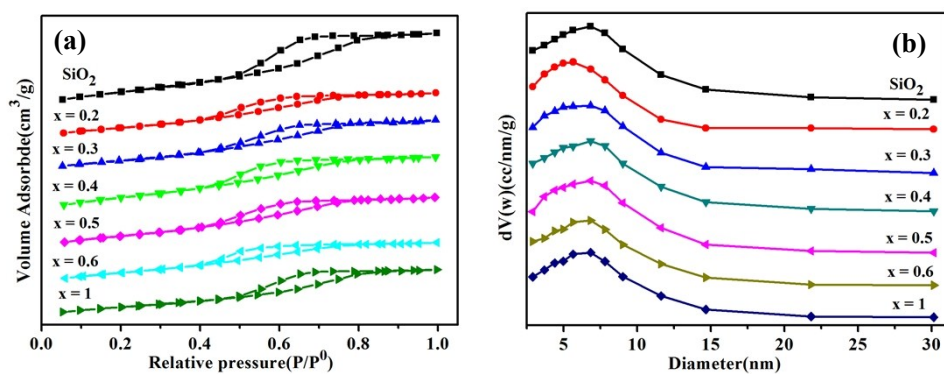


Fig. S1. Nitrogen adsorption and desorption isotherm curves (a) and BJH pore size distributions (b) of SiO₂ and LaFe_{1-x}Rh_xO₃/SiO₂ catalysts (x = 0.2 - 0.6, 1).

Table S1. Physical properties of SiO₂ and LaFe_{1-x}Rh_xO₃/SiO₂ catalysts (x = 0.2 - 0.6, 1)

Sample	S _{BET} (m ² ·g ⁻¹)	Pore size (nm)	V _{BJH} (cm ³ ·g ⁻¹)
SiO ₂	481	6.9	0.66
x = 0.2	410	5.3	0.38
x = 0.3	429	5.6	0.4
x = 0.4	435	5.8	0.44
x = 0.5	444	6.0	0.48
x = 0.6	450	6.3	0.53
x = 1	461	6.5	0.57

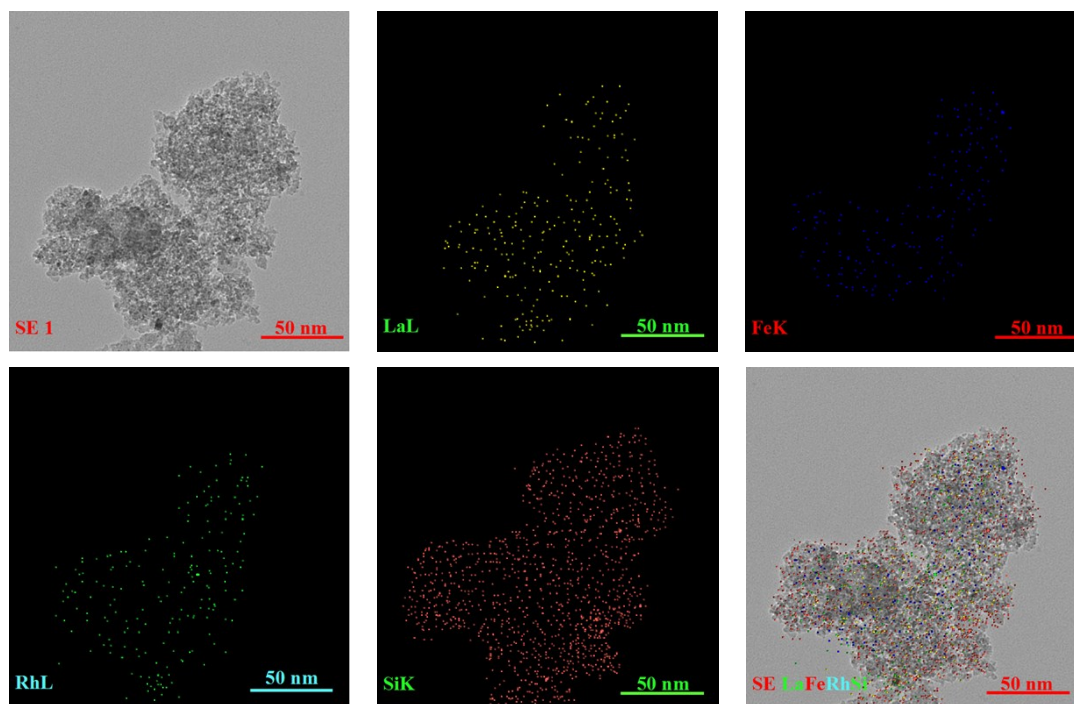


Fig. S2 The EDS mapping images for $\text{LaFe}_{0.5}\text{Rh}_{0.5}\text{O}_3/\text{SiO}_2$ after reduction.

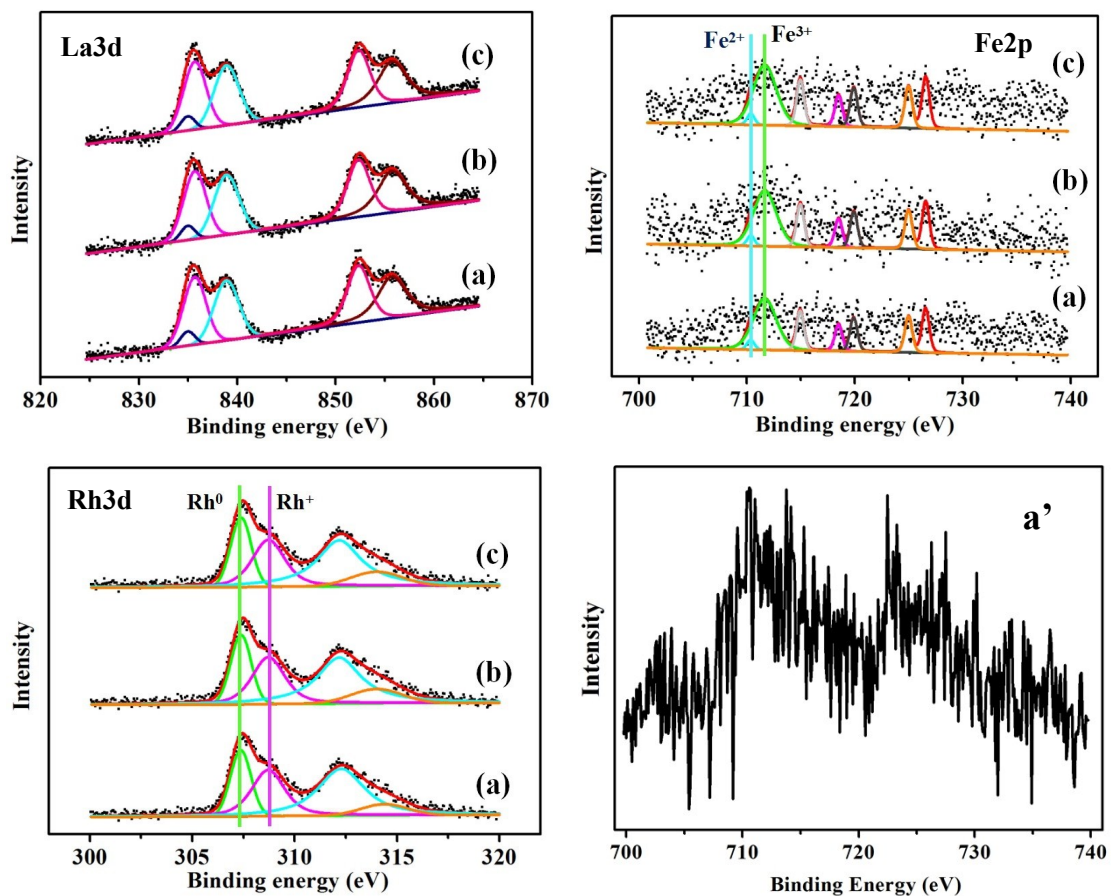


Fig. S3. XPS spectra and the corresponding peak simulating of La 3d, Fe 2p and Rh 3d for LaFe_{0.5}Rh_{0.5}O₃/SiO₂ after reduction (a), reaction (b) and stability test (c). The enlarge of XPS survey spectrum of Fe 2p for LaFe_{0.5}Rh_{0.5}O₃/SiO₂ after reduction (a').

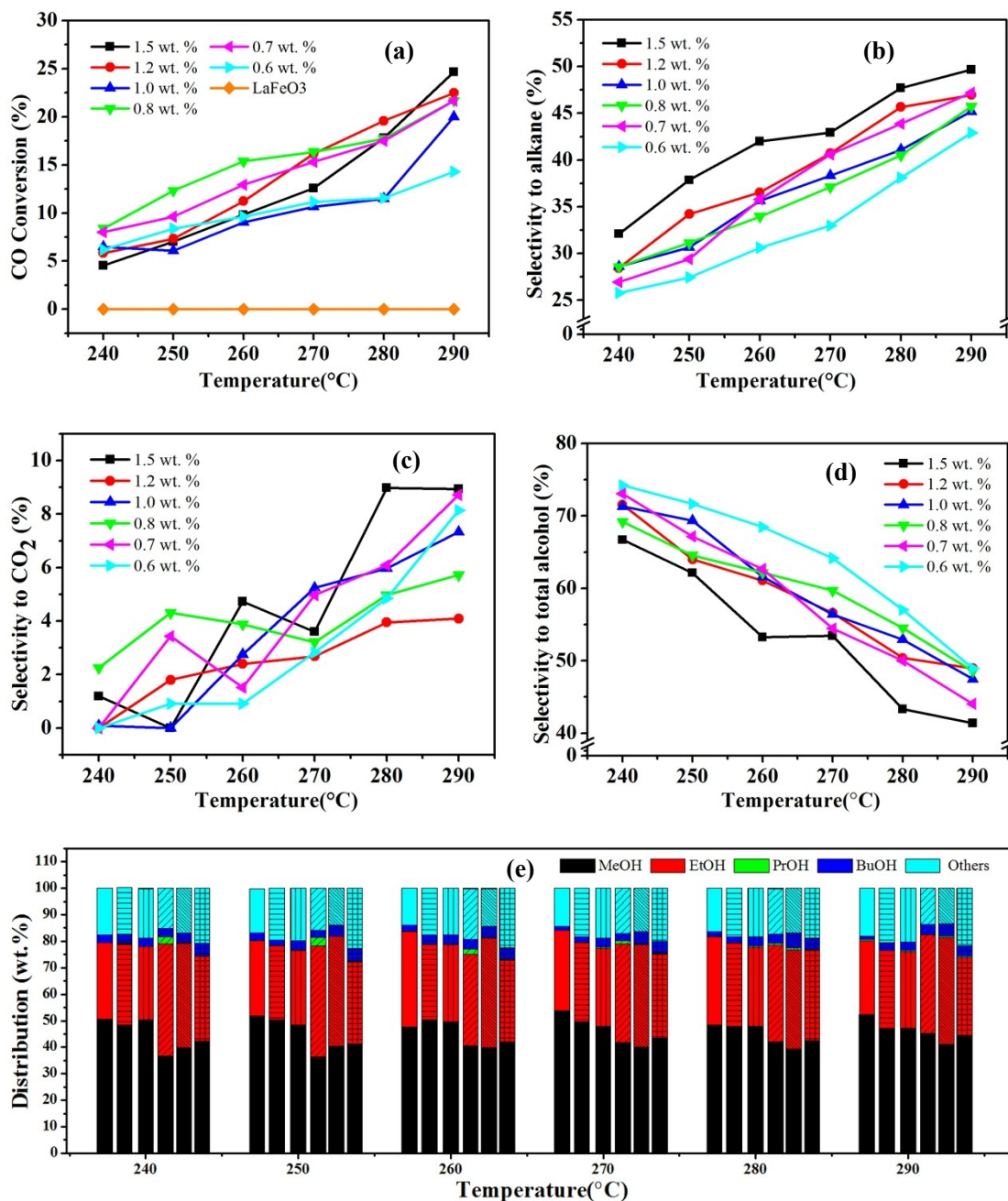


Fig. S4. The conversions of CO (a) and selectivities toward hydrocarbons (b), CO_2 (c) and alcohols (d) vs. reaction temperature over $y\text{Rh-LaFe}_{0.9}\text{Rh}_{0.1}\text{O}_3/\text{SiO}_2$ catalysts (y stands for weight ratio of rhodium in $\text{LaFe}_{0.9}\text{Rh}_{0.1}\text{O}_3/\text{SiO}_2$, $y = 1.5$ wt. %, 1.2 wt. %, 1.0 wt. %, 0.8 wt. %, 0.7 wt. % and 0.6 wt. %) and (\blacklozenge) 20 wt. % $\text{LaFeO}_3/\text{SiO}_2$. (\blacksquare) $y = 1.5$ wt. %, (\bullet) $y = 1.2$ wt. %, (\blacktriangle) $y = 1.0$ wt. %, (\blacktriangledown) $y = 0.8$ wt. %, (\blacklozenge) $y = 0.7$ wt. % and (\blacktriangleright) $y = 0.6$ wt. % at a GHSV of $3900 \text{ mL (g}_{\text{cat}} \text{ h)}^{-1}$ in the syngas mixture of $\text{H}_2/\text{CO}/\text{N}_2 = 8/4/1$ and at 3 MPa. The alcohol distributions (e) over $y\text{Rh-LaFe}_{0.9}\text{Rh}_{0.1}\text{O}_3/\text{SiO}_2$ catalysts, (\square) $y = 1.5$ wt. %, (\equiv) $y = 1.2$ wt. %, (\parallel) $y = 1.0$ wt. %, (▨) $y = 0.8$ wt. %, (▩) $y = 0.7$ wt. % and (▧) $y = 0.6$ wt. %.

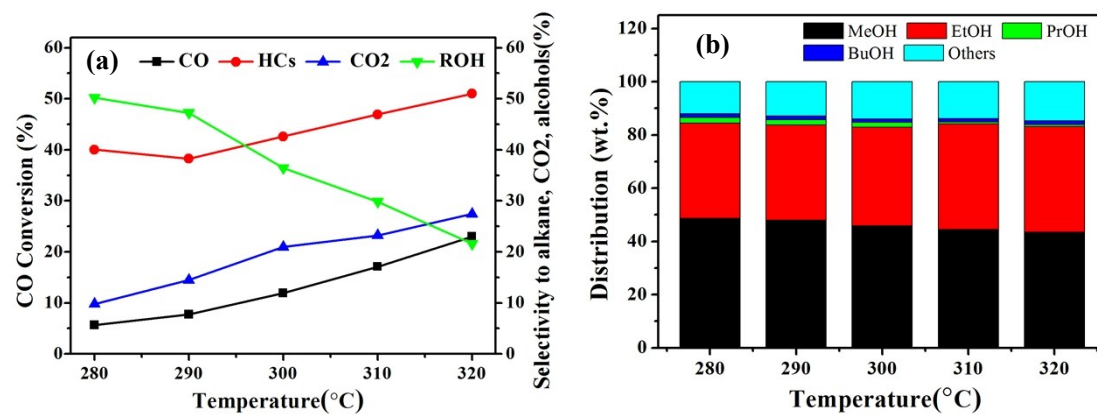


Fig. S5. The conversions of CO and selectivities toward hydrocarbons, CO₂, alcohols (a) and alcohol distributions (b) vs. reaction temperature over LaRhO₃/SiO₂ catalyst at a GHSV of 3900 mL (g_{cat} h)⁻¹ in the syngas mixture of H₂/CO/N₂ = 8/4/1 and at 3 MPa.

Table S2. Catalytic performance of CO hydrogenation over LaFe_{1-x}Rh_xO₃/SiO₂ catalysts at 240 °C and LaRhO₃/SiO₂ catalyst at 280 °C.

Catalysts ^c	Selectivity to hydrocarbons (%) ^b				Selectivity to alcohols (%) ^b			
	C1	C2	C3	C4+	C1	C2	C3	C4+
x = 0 ^a	34.95	0.94	2.17	1.98	48.7	35.8	2.0	1.4
x = 0.2	26.26	1.15	1.54	1.74	41.7	40.2	0.2	1.6
x = 0.3	25.47	1.20	1.61	1.63	37.1	43.8	1.5	1.9
x = 0.4	24.02	1.10	1.47	1.91	34.8	47.5	0.7	2.0
x = 0.5	20.96	1.20	1.61	1.80	30.8	51.2	1.9	1.7
x = 0.6	21.84	1.30	1.75	2.09	41.3	40.5	0.9	3.2

Reaction conditions: 240 °C, GHSV = 3900 mL (g_{cat} h)⁻¹, H₂/CO/N₂ = 8/4/1, 3 MPa.

^a the reaction temperature for reduced LaRhO₃/SiO₂ catalyst was 280 °C.

^b Selectivity = $n_i M_i / \sum n_i M_i$. Where n_i was the number of carbon atoms in product i (hydrocarbons, alcohols); M_i was the mole percent of product i measured.

Table S3. Apparent kinetic parameters^{a,b,c,d} of ethanol on LaFe_{1-x}Rh_xO₃/SiO₂ catalysts (x = 0.2 - 0.6, 1) at 230 - 245 °C and 3 MPa.

catalysts	x = 0.2	x = 0.3	x = 0.4	x = 0.5	x = 0.6	x = 1
E _a (kJ/mol)	85.0	87.1	88.2	88.1	79.1	77.1

^a The reaction orders of CO and H₂ were determined by fitting a power-law rate expression as equation $r_i = k \cdot p_{CO}^x \cdot p_{H_2}^y$.

^b Apparent activation energies (E_a) of products were determined by Arrhenius equation as equation $k = k_0 \cdot e^{-\frac{E_a}{RT}}$.

^c CO conversion was kept less than 10% to assure differential condition.

^d accuracy was ± 10%