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Controlling CO_2 hydrogenation selectivity by Rh-based catalysts with different crystal phase TiO_2

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Experimental section

Catalyst preparation

Materials

Rhodium chloride hydrate ($RhCl_3 \cdot 3H_2O$, Rh content 38.5 - 42.5%, Shanghai Macklin Biochemical Co., Ltd), p25 (Degussa), Titanium oxide (TiO_2, anatase, purity 99.8%, Shanghai Macklin Biochemical Co., Ltd), Titanium oxide (TiO_2, rutile, purity 99.8%, Shanghai Macklin Biochemical Co., Ltd) were used in the experiments without further purification.

Synthesis of catalysts

All samples were prepared via incipient-wetness impregnation method. Specifically, for synthesis of 1wt. % Rh/TiO_2 catalyst, a solution of 1wt. % Rhodium chloride was prepared as the precursor solution. The mentioned solution was slowly added into the prepared TiO_2 support (p25, rutile, and anatase) under stirring and ultrasonication at room temperature for 1 h. The aforementioned mixtures were dried in air at 80 °C for 10 h, and calcined at 450°C for 4 h. Here, the prepared Rh/TiO_2 catalysts of which support were p25, rutile, and anatase respectively were denoted as 1%Rh/p, 1%Rh/r, and 1%Rh/a.

Catalyst characterization

The powder X-ray diffraction patterns (XRD) was carried out on a Rigaku MiniFlex Ⅱ powder X-ray diffract meter at 40 mA and 40 kV using Cu Kα radiation(λ = 0.15418nm), between a scanning angle range of 10 - 90°. The crystallite size was estimated by Scherrer's equation.

H_2 temperature programmed reduction (H_2-TPR) measurements were performed using a chemisorption instrument (TP-5080). Typically, the catalyst (50mg) was preheated under a flow of N_2 (30 mL/min) from room temperature to 200°C for 30min, then cooled to 50°C, and maintained at that temperature for 15min to clean the catalyst surface. After cooling, the flow was switched to a H_2/N_2 (volume) = 0.09 mixture (30 mL/min). The TPR experiments were performed from 50°C to 700°C, at a ramp rate of 10°C/min.

CO temperature programmed desorption (CO-TPD) measurements were carried out on a chemisorption instrument (TP-5080) to monitor desorption of CO. In each experiment, the sample was reduced at 400 °C for 1 h with hydrogen. After cooling down to 50 °C, the catalyst was exposed on CO flow for 1 h, and then flushed with Ar until the baseline was stable. The CO desorption was performed from 50 °C to 600 °C with a heating rate of 10 °C/min and the signal was recorded by thermal conductivity detector (TCD).

CO_2-temperature-programmed desorption (CO_2–TPD) measurement was performed on a chemisorption instrument (TP-5080). In each experiment, the sample was reduced at 400 °C for 1 h with hydrogen. After cooling down to 50 °C, the catalyst was exposed on CO_2 flow for 1 h, and then flushed with Ar until the baseline was stable. The CO_2–TPD was started by raising the temperature from 50 to 700 °C at a rate of 10 °C/min.

The catalyst pore diameter and specific surface area (SA) were measured using a Micrometrics ASAP 2020 gas adsorption device at the temperature of liquid nitrogen (77K) after being degassed at 200°C. Specific surface areas were calculated according to BET (Brunauer-Emmett-Teller) method. The pore diameter was determined by BJH (Barrett-Joyner-Halenda) method.

X-ray photoelectron spectroscopy (XPS) data were performed on an AXIS ULTRA DLD spectrometer. In this case, the laser source was Al Kα (1486.6eV) X-ray source. The binding energies was calibrated by the C1s peak (284.6eV). All previously prepared samples were reduced in situ under a flow of pure H_2 at 400°C for 1 h, then, purged by Ar flow for cooling to room temperature.

In situ DRIFT spectra and CO-FTIR were measured using a TENSOR-27 spectrometer. Before measuring, all sample was in situ reduced under a flow of H_2 at 400°C for 1 h ,and thereafter, cooled to 200°C. After flushing with Ar for 15 min, the samples were purged with the feed gas (H_2/CO_2 (volume) = 3) for 30min, then, flushed with Ar for 30min.

H_2 chemisorption at 50°C was used to measure the amount of exposed Rh atoms. Experiments were performed with a BELCAT-B. The sample was loaded into a Pyrex tube and subsequently heated in He (20 ml/min) at 120 °C for 1 h. After evacuation, the sample was reduced at 400 °C during 1 h in pure H_2 (100 ml/ min) followed by purging with He at the same temperature for 30min and cooling in He to adsorption temperature. Two isotherms were measured in the range 0.07–90 kPa, the first corresponding to total (irreversible + reversible) adsorption and the second to reversible H_2 adsorption. The subtraction of the two isotherms gave the total amount of irreversibly adsorbed (chemisorbed) hydrogen. The amount of surface Rh atoms (mol/g) was calculated from the amount of chemisorbed hydrogen assuming that the chemisorption stoichiometry is H:Rh = 1. Dispersion is defined as surface Rh atoms divided by total Rh atoms in the catalyst.

High-resolution transmission electron microscopy (HRTEM), high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM), and element mapping were performed on TECNAI G2 F20 transmission electron microscope (TEM) under an acceleration voltage of 300 kV.

Catalytic tests

Catalytic performance tests were performed in a fixed bed reactor (stainless steel, 10mm inner diameter, 300mm length). In each run, 0.3 g catalyst mixed with 2.0 g quartz sands (20-40 mesh), and thereafter, placed into the constant-temperature place of reactor. The reaction was carried out at 200 °C, atmospheric pressure and pre-reduced at 400°C for 1h under H_2 atmosphere. The reaction’s space velocity is 12000 ml/g_{cat}/h. The composition of feed gas was 19% CO_2, 76% H_2, and 5% N_2. The products of after-reaction were analyzed by two online gas chromatographs (GC4000A) equipped with thermal conductivity detector (TCD) and a hydrogen flame ionization detector. The two gas chromatographs analytical results were connected with the CH_4 concentration. The CO_2 conversion (Conv.) and products selectivity (Sel.) were calculated based on

Eq. S1–S4

$$CO_2\,Conv.(\%) = \frac{n\left(CO_2{,}in\right) - n\left(CO_2{,}in\right)}{n\left(CO_2{,}in\right)} \times 100\%$$

Eq. S1

$$CO\,Sel.(\%) = \frac{n(CO{,}out)}{n(CO{,}out) + n\left(CH_{4,6,8}{,}out\right) + n(MeOH)} \times 100\%$$

Eq. S2

$$CH_4\,Sel.(\%) = \frac{n\left(CH_4{,}out\right)}{n(CO{,}out) + n\left(CH_{4,6,8}{,}out\right) + n(MeOH)} \times 100\%$$

Eq. S3

$$MeOH\,Sel.(\%) = \frac{n\left(CH_4{,}out\right)}{n(CO{,}out) + n\left(CH_{4,6,8}{,}out\right) + n(MeOH)} \times 100\%$$

Eq. S4

Where n (CO_2, in) and n (CO_2, out) were the molar quantity of CO_2 fed into the reactor and fed out the reactor. Where n (CH_4, out) and n (MeOH, out) were the molar quantity of CH_4 and MeOH fed out the reactor. Meanwhile n ($CH_{4,6,8}$, out) were the molar quantity of methane, ethane and propane. It was worth mentioning that the carbon balance was within 100% ± 3%.

The reaction activity was assessed via turnover frequency (TOF), which was normalized by the loading amount and the dispersion of Rh deposits on TiO_2 supports. The turn-over frequency (TOF) is calculated based on Eq. S5.

$$TOF = \frac{F_{CO_2}M}{WDx}$$

Eq. S5

Where F_{CO_2} denotes the converted molar number of CO_2 molecules at the reaction temperature per unit time (mol h^{-1}), M is the atomic mass of Rh (g mol^{-1}), W denotes the weight of the catalyst packed into the reactor (g), D denotes the dispersion of Rh deposits, and x denotes the loading amount of Rh deposits on the TiO_2 supports.

Supplementary Figures and Tables

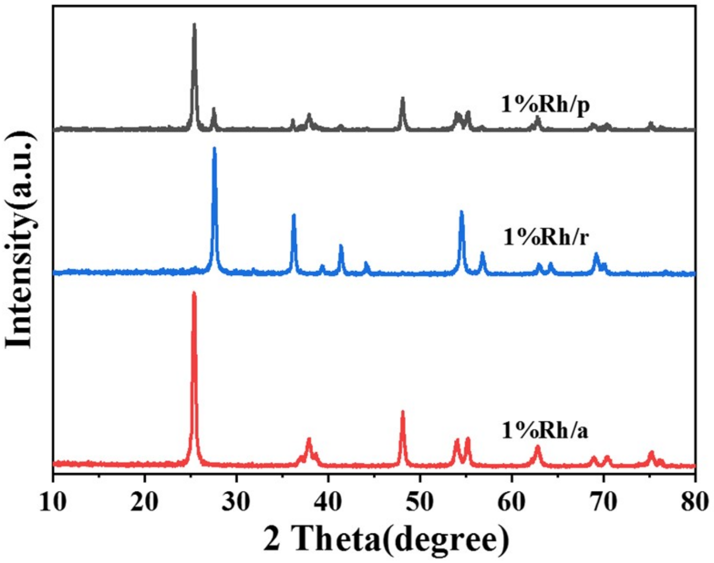

Fig.S1 XRD patterns of 1%Rh/p, 1%Rh/a, and 1%Rh/r catalysts

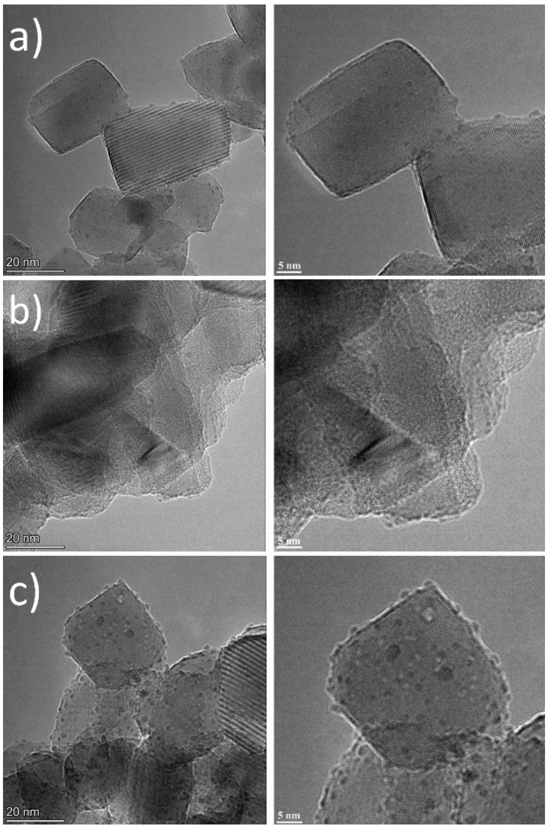

Fig. S2. TEM (left) and HRTEM (right) images of pre-reducted 1%Rh/TiO_2: (a) 1%Rh/p, (b) 1%Rh/r, and (c) 1%Rh/a.

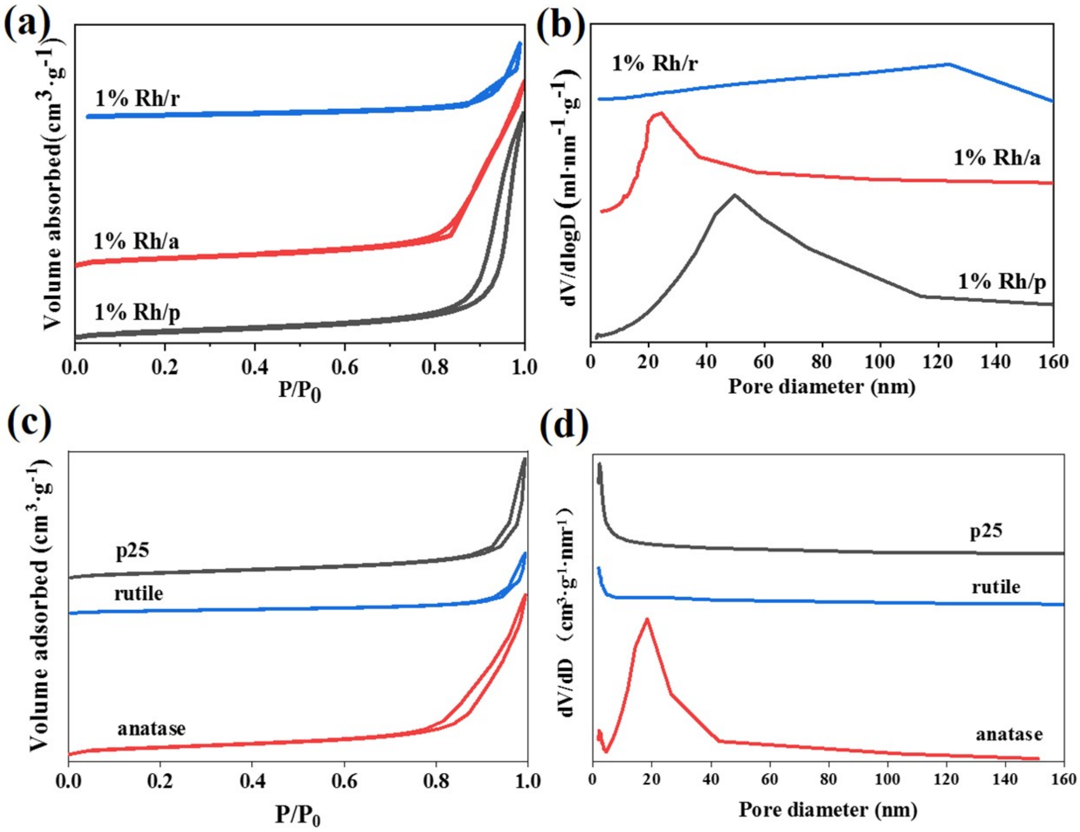

Fig.S3 Nitrogen adsorption and desorption isotherm (a) and pore size distribution (b) of 1%Rh/p, 1%Rh/a, and 1%Rh/r catalysts, nitrogen adsorption and desorption isotherm (c) and pore size distribution (d) of supports (p25, rutile, and anatase)

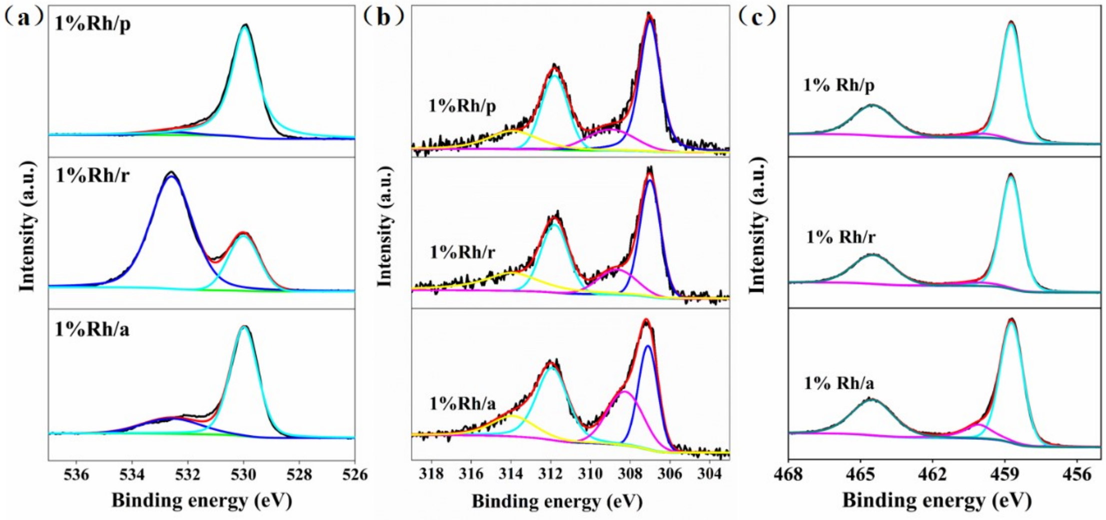

Fig.S4 XPS spectra of catalysts: (a) O 1s, (b) Rh 3d and (c) Ti 2p core level spectra of 1%Rh/p, 1%Rh/r, and 1%Rh/a catalysts.

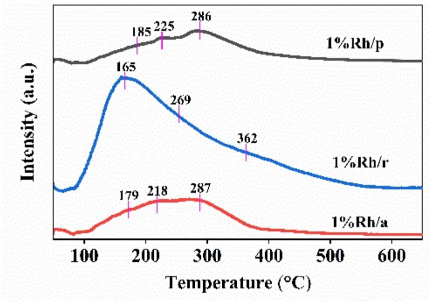

Fig. S5 CO_2–TPD profiles of 1%Rh/p, 1%Rh/r, and 1%Rh/a catalysts.

Table S1 The catalytic performance over 1%Rh/p, 1%Rh/a, and 1%Rh/r catalysts.

Sample	CO_2 conv. (%)	Production sel. (%)					
		CO	CH_4	C_2H_6	C_3H_8	CH_3OH	DME
1%Rh/p	1.26	0	91.32	0.97	0.84	2.92	3.93
1%Rh/r	0.40	0	11.71	0.23	0.14	80.43	7.49
1%Rh/a	2.27	81.27	2.21	0.03	0.02	15.15	1.31

Reaction conditions: atmospheric pressure, TR=200 °C, H_2:CO_2:N_2=76:19:5, GHSV=12000 ml g^{-1} h^{-1}

Table S2 Textural properties of catalysts.

Sample	Crystalline size [a] (Å)	BET surface area [b] ($m^2 \cdot g^{-1}$)	Pore volume [c] ($ml \cdot g^{-1}$)	Average pore Diameter [d] (nm)	Rh contents [e] (wt %)	Dispersion [f] %
1%Rh/p	214	50.94	0.4156	32.64	0.70	90
1%Rh/r	273	23.99	0.1495	24.93	0.80	52
1%Rh/a	229	59.00	0.3424	23.21	0.88	40
p25	235	53.22	0.2891	23.23	-	-
rutile	258	28.30	0.1438	23.40	-	-
anatase	221	70.30	0.3879	23.41	-	-

Note: [a] *Calculated from XRD results with Scherrer equation.*[b] *Calculated by the BET equation.* [c] *BJH desorption pore volume.* [d] *BJH desorption average pore size.* [e] *ICP - Rh contents.* [f] *Calculated by the* H_2 chemisorption.

Table S3 Summary of detailed XPS information from Fig. S4 (b).

Sample	Position (eV)	Chemical specie	Relative content （%）
1%Rh/p	307.00/311.80	Rh^0	63.59
	308.65/313.94	Rh^{v+}	36.41
1%Rh/r	307.01/311.92	Rh^0	60.84
	308.25/313.90	Rh^{v+}	39.16
1%Rh/a	307.01/311.80	Rh^0	70.63
	308.98/313.90	Rh^{v+}	29.37

Table S4 Summary of detailed XPS information from Fig. S4 (c).

Catalyst	Position (eV)	Chemical specie	Relative content （%）
1%Rh/p	457.30/460.08	Ti^{3+}	5.00
	458.74/464.46	Ti^{4+}	95.00
1%Rh/r	457.30/460.01	Ti^{3+}	11.53
	458.72/464.49	Ti^{4+}	88.47
1%Rh/a	457.43/459.91	Ti^{3+}	4.88
	458.74/464.46	Ti^{4+}	95.12