

Supporting Information

Switchable tuning selectivity of CO₂ hydrogenation via anions modification over Ru/TiO₂ catalyst

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Experimental

Materials

TiO₂ (anatase, 99.8%, 10–20 nm), decalin (AR) and RuCl₃·xH₂O (Ru content 45%–55%) were purchased from Aladdin Chemical Reagent Network. NaOH (AR) was purchased from Tianjin Kermel Chemical Reagent Network. Na₂CO₃ (AR) was purchased from Tianjin Tianli Chemical Reagent Network. Na₂SO₄ (AR), NaNO₃ (AR) and NaCl (AR) were purchased from Sinopharm Chemical Reagent Network.

Catalyst preparation

Firstly, 0.5 g of TiO₂ was added into a flask containing 100 mL ultrapure water. The flask was put in an oil bath and set at 50 °C. Then, 1.6 mL of RuCl₃ solution (0.03 mol L⁻¹) and 0.003 mol of sodium salt containing different anions (NaOH, Na₂CO₃, Na₂SO₄, NaNO₃ and NaCl) were added to the flask and stirred continuously for 12 h. The mixture was further centrifuged and washed to neutrality with ultrapure water. Next, the collected solid was dried overnight in an oven at 60 °C. Finally, the sample was reduced in H₂ atmosphere at 300 °C for 2 h to obtain Ru/TiO₂ catalysts. Ru/TiO₂-OH, Ru/TiO₂-CO₃, Ru/TiO₂-Cl, Ru/TiO₂-NO₃ and Ru/TiO₂-SO₄ correspond to the catalysts modified by different anions with NaOH, Na₂CO₃, NaCl, NaNO₃ and Na₂SO₄. Ru/TiO₂ catalyst was prepared by the same procedure without anions modification.

Characterization

X-ray diffraction (XRD) pattern was obtained by using Cu K α radiation on the miniflex II diffractometer. XPS spectrum was analyzed by thermal ESCALAB 250 spectrometer and the binding energy was calibrated according to the peak of C 1s (284.6 eV). Transmission electron microscope (TEM) and high resolution TEM (HRTEM) images were characterized by JEM-2010F instrument. The actual loading of Ru on the Ru/TiO₂ catalyst surface was detected by inductively coupled plasma optical emission spectrometry (ICP-OES) using a thermosensitive iCAP6300 spectrometer. The temperature programmed desorption of CO (CO-TPD) was performed by TP-5080 instrument. 100 mg of catalyst was pretreated in N₂ at 300 °C for 1 h, and then cooled to 50 °C before CO adsorption. After CO adsorption for 20 min, the catalyst was washed with N₂ at 50 °C for 30 min to remove the physically absorbed CO. Then the desorption mode was recorded from 50 to 500°C with a heating rate of 10 °C min⁻¹. The specific surface area of catalysts were

calculated by the Brunauer–Emmett–Teller (BET) method from the data in a P/P_0 range between 0.05 and 0.2.

In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) spectra were recorded by the Bruker tensor II spectrometer equipped with liquid nitrogen cooling. The test was proceeded as follows: the catalyst was added into the in situ cell, and the reaction cell was heated to 200 °C and maintained for 2 h under the Ar flow (30 mL min⁻¹) to remove the moisture on the catalyst surface, and then the background spectrum was recorded. Next, the mixed gas of CO₂/H₂ was introduced into the reaction cell, and the scanning spectrum were recorded. The spectrum of CO was obtained by introducing CO gas into the reaction cell with the same operation.

Catalytic performance evaluation

The catalytic performance of the catalyst for CO₂ hydrogenation was tested in a 100 mL stainless steel autoclave. Generally, 10 mL of decalin and 100 mg of catalyst were added into the autoclave, and purged with feed gas for 2 min. Next, the mixture of CO₂/H₂ (CO₂/H₂=1:3) was introduced into the autoclave, and set the pressure as 1.0 MPa. Then the autoclave was heated to 200 or 300 °C under magnetic stirring (500 rpm). Finally, the autoclave was put into a water bath for cooling. The reaction products were analyzed by Shimadzu GC-2014 gas chromatography. In the catalyst cyclic experiment, the catalyst was recovered by filtration and washed with ultrapure water, and then dried at 60 °C overnight.

Table S1 Comparison between anion modification strategy used in this work and other strategy previously reported in selective hydrogenation of CO₂.

Entry	Catalyst	Conversion (%) ^a /Reaction rate (mol _{CO2} g ⁻¹ h ⁻¹) ^b	Product	Selectivity (%)	Reference
1	Ru/TiO ₂ .OH	25.2 ^a	CH ₄	97.1	This work
2	Cl-TiO ₂	6.6 ^b	CH ₄	56	[1]
3	NaOH-TiO ₂	0.052 ^b	CH ₄	-	[2]
4	Ru/ZrO ₂	1.2 ^a	CH ₄	99	[3]
5	Rh/TiO ₂	0.15 ^b	CO	99	[4]
6	Rh/TiO ₂	2.9 ^b	CH ₄	91.3	[5]
7	FeP	-	CO	92% (Faradaic efficiency)	[6]
8	Ag electrode	-	CO	45.4% (Current efficiency)	[7]

^a The catalytic performance was evaluated in batch reactor.

^b The catalytic performance was evaluated in fixed bed reactor.

Table S2 Physical parameters of various catalysts. ^a

Entry	Catalyst	Surface area (m ² g ⁻¹)	Pore size (nm)
1	Ru/TiO ₂	67.50	19.13
2	Ru/TiO ₂ -CO ₃	71.13	18.89
3	Ru/TiO ₂ -Cl	70.71	18.72
4	Ru/TiO ₂ -NO ₃	72.90	18.79
5	Ru/TiO ₂ -OH	66.57	17.97
6	Ru/TiO ₂ -SO ₄	73.18	18.41

^a The specific surface area and pore size were measured by N₂ adsorption.

Table S3 The loading amount of Ru of various Ru/TiO₂ catalysts. ^a

	Ru/TiO ₂	Ru/TiO ₂ - CO ₃	Ru/TiO ₂ - Cl	Ru/TiO ₂ - NO ₃	Ru/TiO ₂ - SO ₄	Ru/TiO ₂ - OH
Ru Content (wt%)	0.92	0.94	0.92	0.95	0.89	0.91

^a Data were determined by ICP-OES.

Table S4 Analysis of different anions content.

	Ru-TiO ₂ -OH	Ru-TiO ₂ -CO ₃	Ru-TiO ₂ -Cl	Ru-TiO ₂ -NO ₃	Ru-TiO ₂ -SO ₄
The total amount of Cl ⁻ added during catalyst preparation (mg)	4.93	4.93	111.43	4.93	4.93
Cl ⁻ content in filtrate (mg)	4.41	4.14	102.7	4.07	3.95
Cl ⁻ content in catalysts (mg)	0.52	0.79	9.73	0.86	0.98
The total amount of OH ⁻ added during catalyst preparation (mg)	51.7	-	-	-	-
OH ⁻ content in filtrate (mg)	42.8	-	-	-	-
OH ⁻ content in catalysts (mg)	8.9	-	-	-	-
The total amount of CO ₃ ²⁻ added during catalyst preparation (mg)	-	176.4	-	-	-
CO ₃ ²⁻ content in filtrate (mg)	-	146.9	-	-	-
CO ₃ ²⁻ content in catalysts (mg)	-	29.5	-	-	-
The total amount of Cl ⁻ added during catalyst preparation (mg)	-	-	111.43	-	-
Cl ⁻ content in filtrate (mg)	-	-	102.7	-	-
Cl ⁻ content in catalysts (mg)	-	-	9.73	-	-
The total amount of NO ₃ ⁻ added during catalyst preparation (mg)	-	-	-	184.4	-
NO ₃ ⁻ content in filtrate (mg)	-	-	-	174.6	-
NO ₃ ⁻ content in catalysts (mg)	-	-	-	9.8	-
The total amount of SO ₄ ²⁻ added during catalyst preparation (mg)	-	-	-	-	286.2
SO ₄ ²⁻ content in filtrate (mg)	-	-	-	-	267.3
SO ₄ ²⁻ content in catalysts (mg)	-	-	-	-	18.9

Table S5 The average particle size of Ru nanoparticles of various Ru/TiO₂ catalysts.

	Ru/TiO ₂	Ru/TiO ₂ -SO ₄	Ru/TiO ₂ -NO ₃	Ru/TiO ₂ -OH	Ru/TiO ₂ -Cl	Ru/TiO ₂ -CO ₃
Particle size of Ru (nm)	1.50	1.52	1.68	1.62	1.36	1.43

Table S6 The effect of OH⁻ concentration on the catalytic performance of CO₂ over Ru/TiO₂-OH catalysts.

Entry	Molar amount of NaOH added (mol)	Catalysts	CO ₂ conversion	CH ₄ selectivity
1	0.0000	Ru/TiO ₂	11.3	4.6
2	0.0005	Ru/TiO ₂ -OH-0.5	12.1	5.9
3	0.0010	Ru/TiO ₂ -OH-1	19.4	54.2
4	0.0020	Ru/TiO ₂ -OH-2	23.7	86.5
5	0.0030	Ru/TiO ₂ -OH-3	25.2	97.1

Ru/TiO₂-OH-3 catalyst represents Ru/TiO₂-OH catalyst in the manuscript.

Table S7 The effect of NO_3^- concentration on the catalytic performance of CO_2 over Ru/TiO₂-
NO₃ catalysts.

Entry	Molar amount of NaNO ₃ added (mol)	Catalysts	CO ₂ conversion	CO selectivity
1	0.0000	Ru/TiO ₂	11.3	95.4
2	0.0005	Ru/TiO ₂ -NO ₃ -0.5	10.4	94.7
3	0.0010	Ru/TiO ₂ - NO ₃ -1	9.2	93.2
4	0.0020	Ru/TiO ₂ - NO ₃ -2	8.6	91.7
5	0.0030	Ru/TiO ₂ - NO ₃ -3	8.2	91.1

Ru/TiO₂-NO₃-3 catalyst represents Ru/TiO₂-NO₃ catalyst in the manuscript.

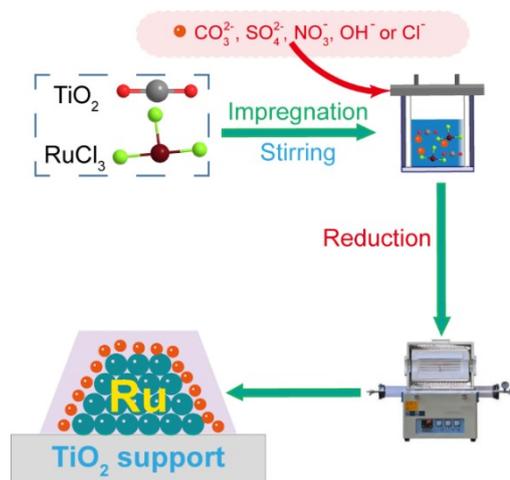


Fig. S1 Preparation process of Ru/TiO₂ catalysts modified by different anions.

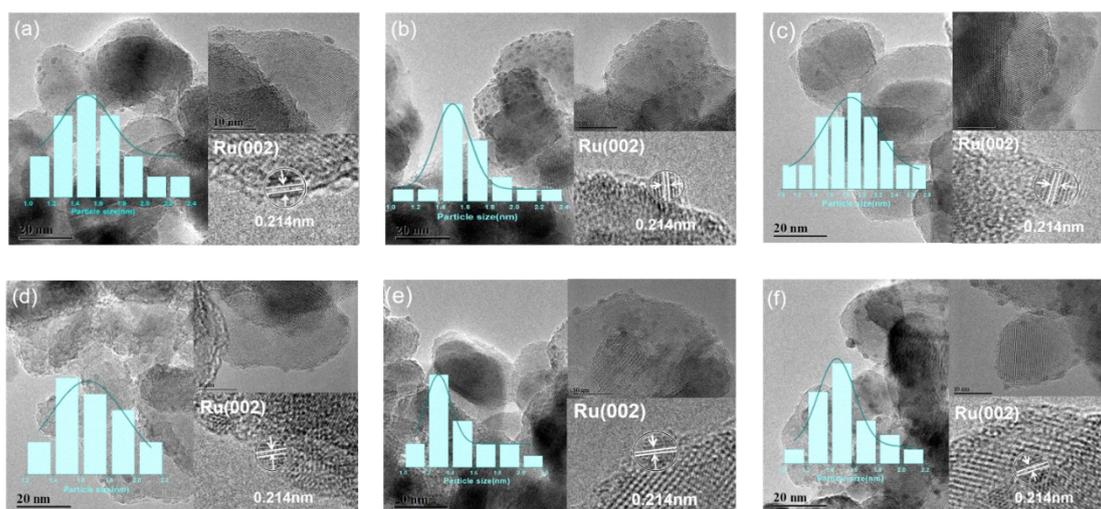


Fig. S2 TEM images of (a) Ru/TiO₂, (b) Ru/TiO₂-SO₄, (c) Ru/TiO₂-NO₃, (d) Ru/TiO₂-OH, (e) Ru/TiO₂-Cl and (f) Ru/TiO₂-CO₃ catalysts.

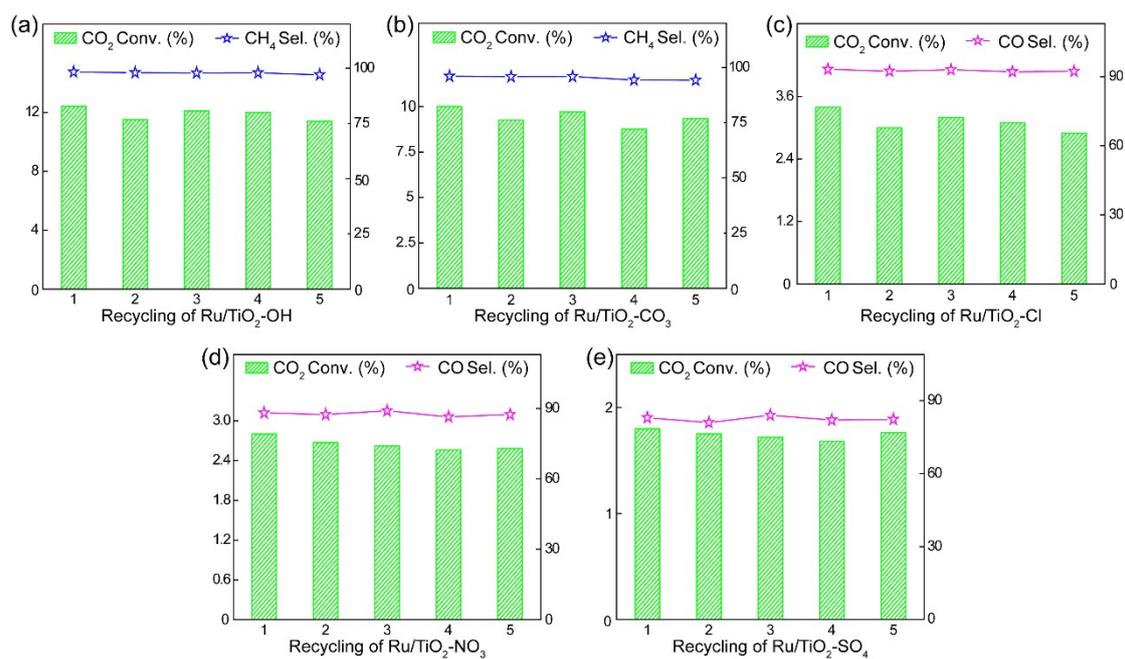


Fig. S3 Recycling test of (a) Ru/TiO₂-OH, (b) Ru/TiO₂-CO₃, (c) Ru/TiO₂-Cl, (d) Ru/TiO₂-NO₃ and (e) Ru/TiO₂-SO₄ catalysts.

Reaction conditions: 100 mg of catalysts, 10 mL decalin, CO₂/H₂ (CO₂/H₂=1:3, 1MPa), 4 h, 200 °C.

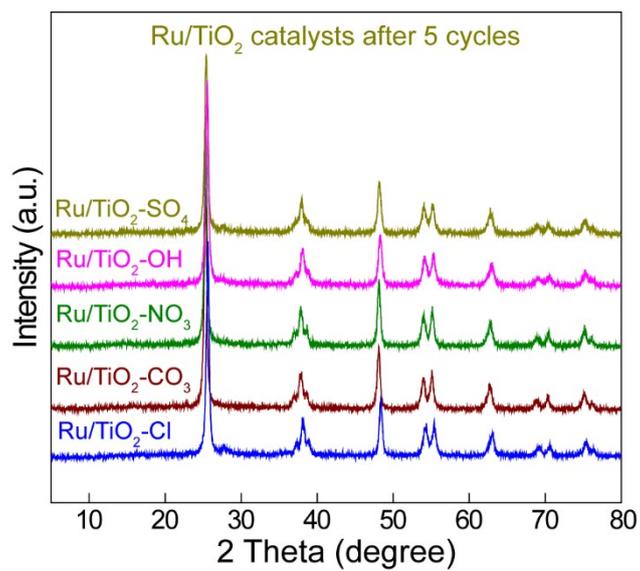


Fig. S4 XRD patterns of recycled Ru/TiO₂-OH, Ru/TiO₂-CO₃, Ru/TiO₂-Cl, Ru/TiO₂-NO₃ and Ru/TiO₂-SO₄ catalysts.

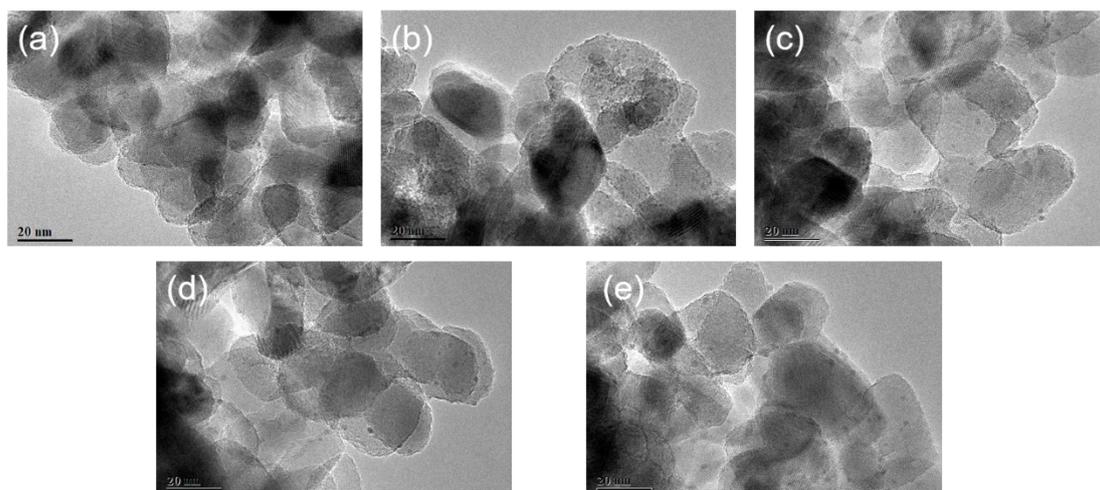


Fig. S5 TEM images of recycled (a) Ru/TiO₂-SO₄, (b) Ru/TiO₂-NO₃, (c) Ru/TiO₂-OH, (d) Ru/TiO₂-Cl and (e) Ru/TiO₂-CO₃ catalysts.

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