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Supplementary Information

Catalytic Conversion of Ferrous Carbonate to Higher Hydrocarbons under Mild Conditions and Its Application in Transformation of CO_2 to Liquid Fuels

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Experimental section

Materials

Hydrogen (99.999%) and carbon dioxide (99.999%) were supplied by Beijing Haikeyuanchang Utility Gas Co., Ltd. $RuCl_3·nH_2O$, $H_2PtCl_6·6H_2O$ and $FeCl_3·6H_2O$ were purchased from Sinopharm Chemical Reagent Co., Ltd. TiO_2 (AR) was purchased from Xilong Scientific Co., Ltd. ^{13}C labeled carbon dioxide (purity: 99%) was purchased from Sigma-Aldrich Corporation. Cyclohexane of GC grade was purchased from ANPEL Laboratory Technologies (Shanghai) Incorporation. Other reagents used in this work were of analytical grade.

Preparation of catalysts.

A glycol solution of NaOH (50 ml, 0.26 M) was added dropwise into a glycol solution of $H_2PtCl_6·6H_2O$ (50 ml, 20 g/L) under stirring. The mixture was stirred for 30 minutes and subsequently heated at 160 °C by microwave for 5 minutes under nitrogen atmosphere. A colloidal solution of Pt nanoclusters with an average diameter of 1.3 nm (Pt: 3.7 g/L) was obtained [1]. A colloidal solution of Ru nanoclusters (Ru: 3.8 g/L) was prepared using a similar method.

$FeCl_3·6H_2O$ (50g) and urea (50g) were dissolved in 300 ml of glycol. The obtained solution was heated till an orange precipitate was generated. After being washed with water and ethanol, the precipitate was dried by an infrared lamp. The resulting yellow powder was calcined at 400 °C under nitrogen atmosphere for 3 hours to generate a Fe_3O_4 support as a black powder [2].

20 ml of hydrochloric acid (8 M) was added into 5.5 ml of the prepared colloid solution of Pt nanoclusters to get a precipitate of Pt nanoclusters that was separated by centrifugation. The obtained Pt nanoclusters were dispersed in 10 ml of acetone to obtain a stable colloidal solution, which was then added dropwise into a suspension of the Fe_3O_4 support (1.0 g) in 100 ml of acetone. The mixture was stirred for 24 hours, then the solid product in the mixture was filtered, washed

with acetone three times, and dried in an oven under vacuum at 60 °C for 3 hours to get a Fe_3O_4 supported Pt nanoclusters (Pt/Fe_3O_4) precursor. The obtained Pt/Fe_3O_4 precursor was dispersed in an aqueous solution of $NaHCO_3$ (100 ml, 0.1 M), and 5.2 ml of aqueous solution of $RuCl_3 \cdot xH_2O$ (20 g/L) was added dropwise into the suspension. After the mixture was stirred for 24 hours, the solid product in the mixture was filtered, washed with water three times, and then dried at 60 °C for 3 hours to get a precursor composed of nanoparticles of Pt and $RuO_x \cdot nH_2O$ on the Fe_3O_4 support. The obtained precursor was reduced with 2.8 MPa of hydrogen in water under stirring at 150 °C for 2 hours, and then the solid was separated by centrifugation and dried at 60 °C for 3 hours to obtain the Fe_3O_4 supported Pt and Ru nanoparticles ($Ru\text{-}Pt/Fe_3O_4$). A catalyst composed of Ru and Pt nanoparticles ($Ru\text{-}Pt/TiO_2$) on TiO_2 was prepared using a similar method.

$Ru\text{-}Pt/Fe_3O_4$ was treated with a 4.3 MPa of gas mixture of CO_2 and H_2 with a molar ratio of 1:3 at 160 °C in a mixture of cyclohexane and water for 24 hours to obtain $Ru\text{-}Pt/FeCO_3$. The obtained solid was washed with cyclohexane and water three times, respectively, and separated from liquid by centrifugation. No hydrocarbon except cyclohexane was detected in the supernatant of the third separation. $Ru\text{-}Pt/Fe^{13}CO_3$ was prepared by treating $Ru\text{-}Pt/Fe_3O_4$ with $^{13}CO_2$ and H_2 using the same method.

A colloidal solution of PtRu alloy (Ru/Pt=2.5) nanoclusters was prepared using previously reported method [3].18 ml of glycol solution of NaOH (0.26 M) was added into 7.8 ml of glycol solution of $H_2PtCl_6 \cdot 6H_2O$ (20g/L) and 10 ml of glycol solution of $RuCl_3 \cdot nH_2O$ (20g/L) under stirring. The mixture was stirred for 30 minutes and subsequently heated at 160 °C by microwave for 5 minutes under nitrogen atmosphere. PtRu alloy nanoclusters were deposited on Fe_3O_4 by treating 8 ml of PtRu alloy colloidal and 0.5 g of Fe_3O_4 under hydrogen (3.0 MPa) in 20 ml of water at 150 °C for 2 h, and the obtained solid was washed with 150 ml of water and dried at 60

°C in a vacuum oven. $PtRu/Fe_3O_4$ was subsequently converted to $PtRu/FeCO_3$ using the method for the preparation of Ru-Pt/$FeCO_3$

Catalyst characterizations.

Transmission electron microscope (TEM) images were taken on an FEI Titan Cubed Themis G2 300 transmission electron microscope with an acceleration voltage of 200 kV. High-angle annular dark filed (HAADF) and elemental distribution images were obtained using scanning transmission electron microscope (STEM) mode. To prepare the TEM samples, the catalysts were dispersed ultrasonically in ethanol for 30 minutes, and then a drop of suspension was placed and dried on a copper grid covered with a carbon film.

X-ray diffraction (XRD) patterns of the samples were measured on a Rigaku D/MAX-PC 2500 diffractometer with monochromatic Cu Kα radiation (λ = 1.5406 Å) at an accelerating potential of 40 kV and a tube current of 100 mA.

X-ray photoelectron spectroscopy (XPS) measurements of the samples were carried out with an Axis Ultra photoelectron spectrometer using an Al Kα (1486.7 eV) X-ray source, with the pressure of the measuring chamber of 5×10^{-9} Torr. For the XPS measurement of Ru-Pt/$FeCO_3$, the sample was reduced with a gas mixture of H_2 and He (H_2/He=1/4) at 373 K for 1 hour in the sample treatment chamber, and then directly transferred to the measuring chamber. After reaction of H_2 with Ru-Pt/$FeCO_3$, the solid was separated, washed with cyclohexane and water three times, and dried at 60 °C in a vacuum oven for XPS measurement. The obtained solid was subsequently treated with a mixture of CO_2 (1.25 MPa, 298 K) and H_2 (3.75 MPa, 298K) at 130 °C in a mixture of water (15 ml) and cyclohexane (15 ml) for 48 h, and the sample was collected for XPS measurement in the same way.

The Pt and Ru contents of catalysts were analyzed by an inductively coupled plasma atomic emission spectrometer (Leeman Corp.).

Catalytic properties evaluation.

In CTHC, 0.30 g of Ru-Pt/$FeCO_3$ or Ru-Pt/$Fe^{13}CO_3$, and 15 ml of water and 15 ml of cyclohexane were charged in a 50-ml autoclave. The autoclave was sealed and flushed with hydrogen three times to remove the air. Subsequently, 3.75 MPa of H_2 was introduced into the autoclave. The autoclave was heated to the reaction temperature, and the reaction was carried out under magnetic stirring (1200 rpm). After the reactions, the autoclave was cooled to room temperature with water, and the products were collected for analysis.

To measure the carbon balance of CTHC, the solid residue after reaction was recovered, washed and dried at 60 °C in a vacuum oven. The mass of carbon in the solid residue was measured by elemental analyzer (vario EL). The carbon consumed in CTHC could be obtained by the mass difference of carbon between catalyst and the solid residue, and mass of carbon in the products was measured by gas-chromatography (GC) (see below). Carbon balance was calculated based on the following equation:

$$carbon\ balance = \frac{Mass\ of\ carbon\ in\ the\ products}{Mass\ of\ consumed\ carbon\ in\ CTHC}$$

C-CTHC was conducted under the conditions applied in CTHC, expect for the introduction of 1.25 MPa of CO_2 to the reaction system. C-CTHC was also conducted under H_2 pressure of 2.50 and 1.25 MPa, respectively.

C-CTHC was conducted in water (30 ml) without addition of cyclohexane under the same conditions as a comparison experiment.

In the experiments for testing the stability of Ru-Pt/$FeCO_3$ in C-CTHC at 130 °C, the catalyst was recovered by centrifugation, washed with water and cyclohexane three times, and used for a new recycling test.

In the ^{13}C isotope tracing experiments, 0.75 MPa of ^{13}C labeled carbon dioxide (purity: 99%), 2.25 MPa of hydrogen, Ru-Pt/$FeCO_3$, and 15 ml of cyclohexane (or 15 ml of water and 15 ml of cyclohexane) were charged in a 50-ml autoclave, and C-CTHC were conducted at 130 °C.

In the control experiments, Ru/$FeCO_3$, Pt/$FeCO_3$, Ru-Pt/$FeCO_3$, PtRu/$FeCO_3$, Ru-Pt/TiO_2, or Ru-Pt/Fe_3O_4, CO_2 and H_2 were charged in a 50-ml autoclave, and the reactions were conducted in a mixture of water (15 ml) and cyclohexane (15 ml) over the five catalysts at 130 °C for 8 hours, respectively.

Products were identified using gas chromatography (GC) by comparison with authentic samples and gas chromatography-mass spectrometer (GC-MS). The gas mixture was collected with a gas container and analyzed by a GC (Shimadzu GC-2010). The analysis of hydrocarbons in gas mixture was conducted with an HP-PLOT Q capillary column (ϕ 0.53 mm × 30 m) and a flame-ionization (FID) detector. The concentration of CH_4 was analyzed using external normalization method. Each concentration of C_2^+ hydrocarbons was quantified by comparing with the CH_4 peak area using response factor. CO was analyzed by a CarboPLOT P7 capillary column (ϕ 0.53 mm × 25 m) and a thermal conductivity detector (TCD).

The analysis of hydrocarbons in cyclohexane was conducted with an Rtx-5MS capillary column (ϕ 0.25 mm × 60 m) and a FID detector. The concentration of decane was quantified using external normalization method. Each concentration of hydrocarbons in cyclohexane was quantified by comparing with the peak area of decane using response factor as followed:

$$m_{decane} = CVM$$

$$\frac{m_x}{m_{decane}} = \frac{A_x f_x}{A_{decane} f_{decane}}$$

$$n_x = \frac{m_x}{M_X}$$

where C is the measured concentration of decane; V is the volume of cyclohexane; M is the molar mass of decane; f_x is the response factor of hydrocarbon; A_x is the measured peak area of hydrocarbon; and n_x is the mole of hydrocarbon.

The alcohols in water were analyzed using an HP-INNOWAX capillary column (ϕ 0.32 mm × 30 m) and an FID detector. The concentration of ethanol in water was quantified using external normalization method, and other alcohols were quantified using the methods applied in hydrocarbon quantification.

The amount of CO_2 charged in the autoclave was calculated according to the actual gas equation of state using compressibility factor. The conversions of carbon in the substrates (including CO_2 and $FeCO_3$) in reactions were calculated based on the following equation:

$$Conversion = \frac{\sum_{i=1}^{n} i \times mole\ of\ Ci\ hydrocarbon + \sum_{i=1}^{n} i \times mole\ of\ Ci\ alcohol}{mole\ of\ carbon\ in\ the\ substrates} \times 100\%$$

The selectivity for hydrocarbons and alcohols was calculated according to the following equation:

$$Sel(Ci) = \frac{i \times mole\ of\ Ci\ hydrocarbon\ (or\ alcohol)}{\sum_{i=1}^{n} i \times mole\ of\ Ci\ hydrocarbon + \sum_{i=1}^{n} i \times mole\ of\ Ci\ alcohol} \times 100\%$$

The mass spectra of produced hydrocarbons in isotope tracer experiments were measured by GC-MS coupling (Shimadzu GCMS-QP2010).

Fig.S1 X-ray diffraction patterns of Ru-Pt/$FeCO_3$ and $FeCO_3$ (PDF # 29-0696).

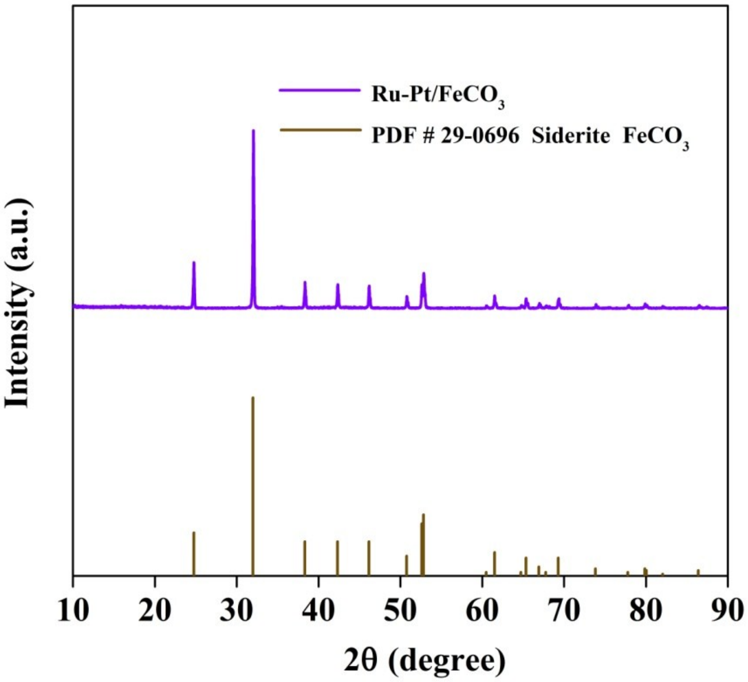


Fig. S2 High resolution transmission electron microscope (HRTEM) image of Ru-Pt/$FeCO_3$ (A) and metal particle size distribution (B).

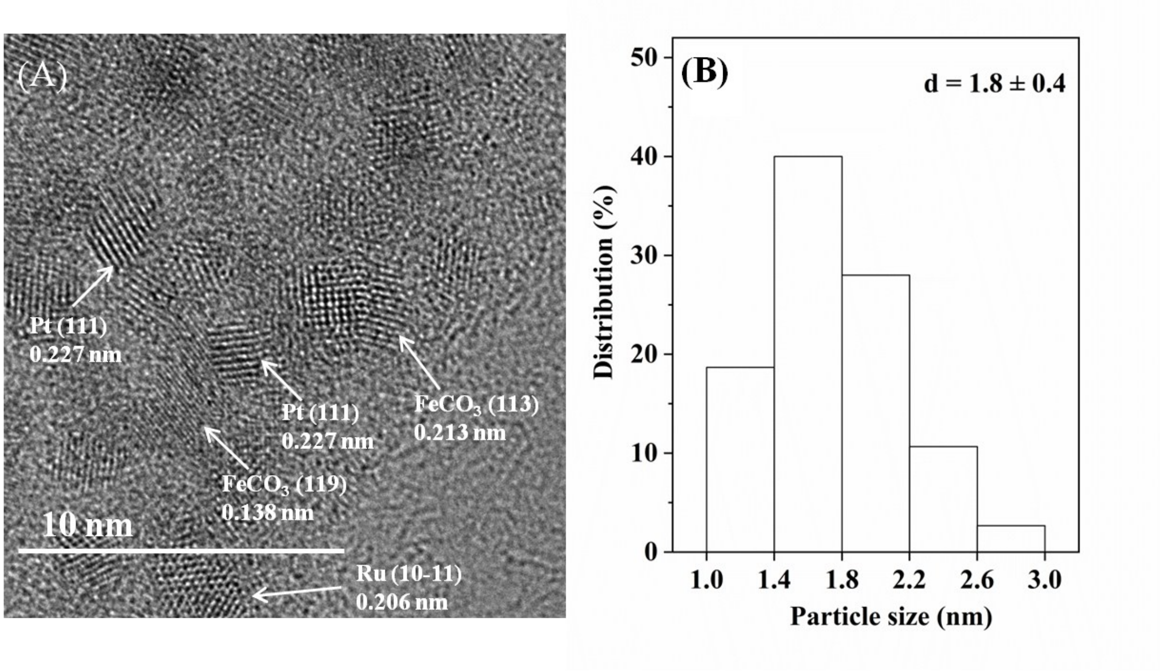


Fig. S3 X-ray photoelectron spectroscopy (XPS) spectra of Ru (A), Pt (B), O (C), and Fe (D) in Ru-Pt/$FeCO_3$. The binding energy scales for the samples were referenced by setting the C 1s binding energy of contamination carbon to 284.8 eV.

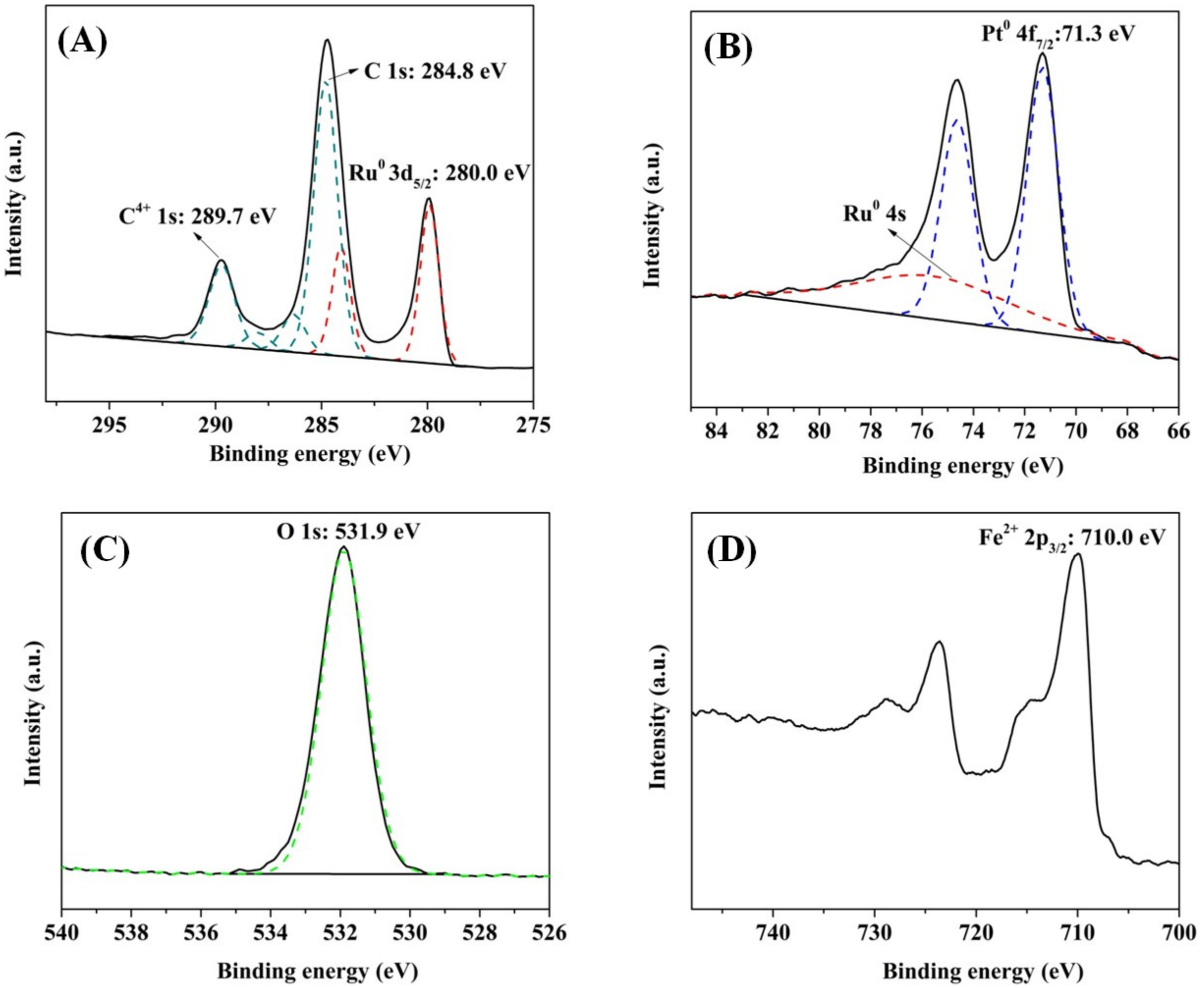


Fig. S4 Mass spectrum of pentane produced in the reaction of H_2 with Ru-Pt/Fe$^{12}CO_3$ (A), and in the reaction of Ru-Pt/Fe$^{12}CO_3$ with H_2 under an atmosphere of $^{13}CO_2$ (B) at 130 °C in cyclohexane, respectively.

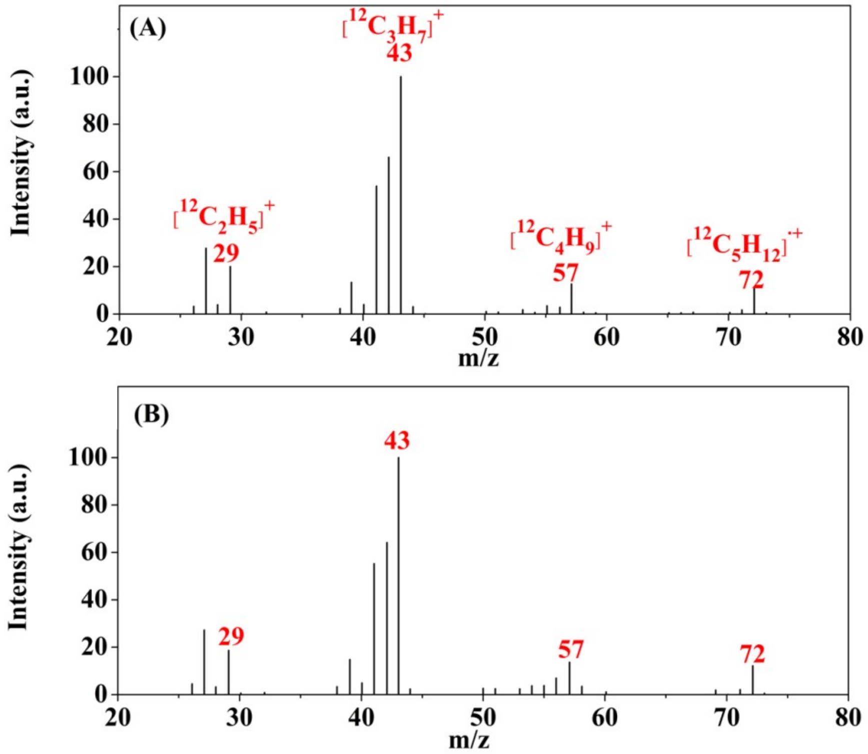


Fig. S5 XPS spectra of Fe 2p in Ru-Pt/$FeCO_3$ (A), the recovered sample after treating Ru-Pt/$FeCO_3$ with H_2 (B), and the sample obtained by treating the recovered sample with H_2 and CO_2 (C).

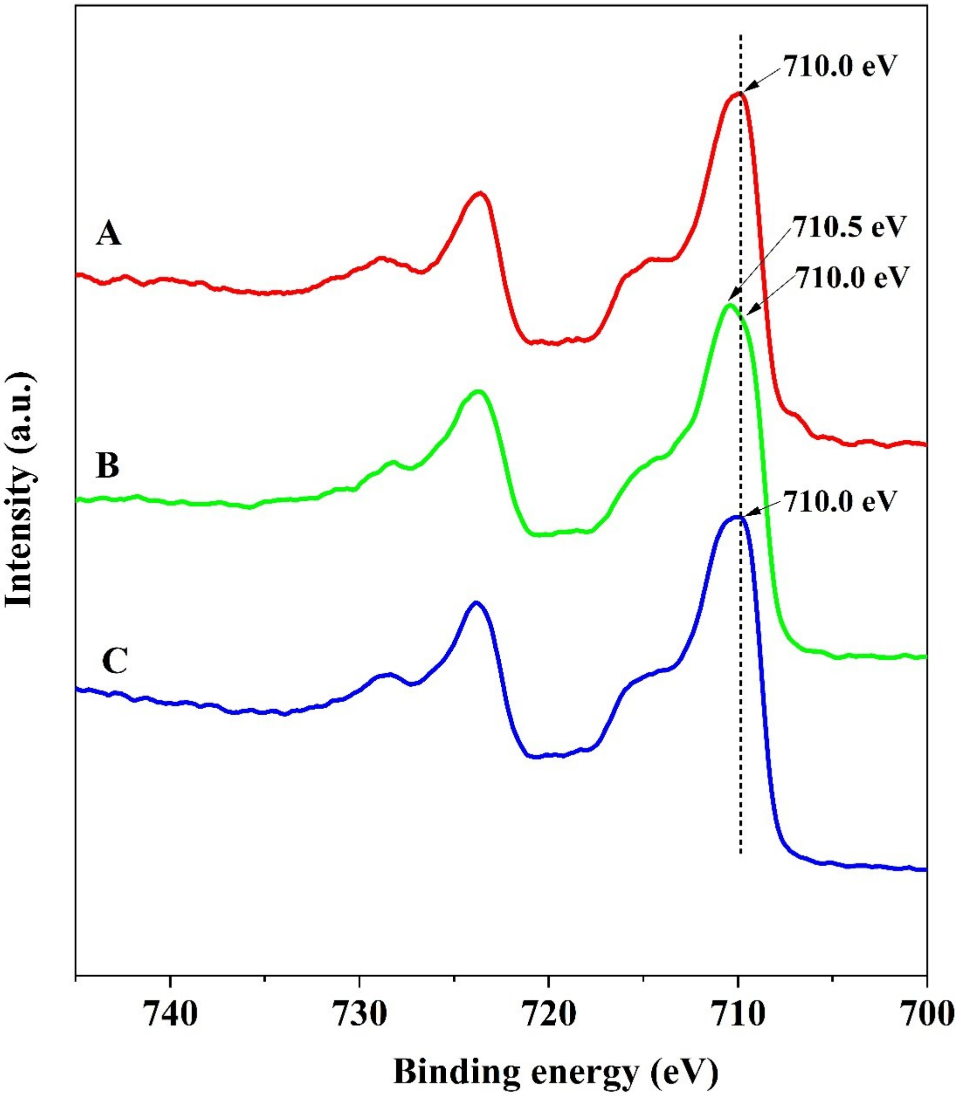


Fig. S6 GC spectra of C_3^+ hydrocarbons produced in CTHC (A) and C-CTHC (B) at 130 °C.

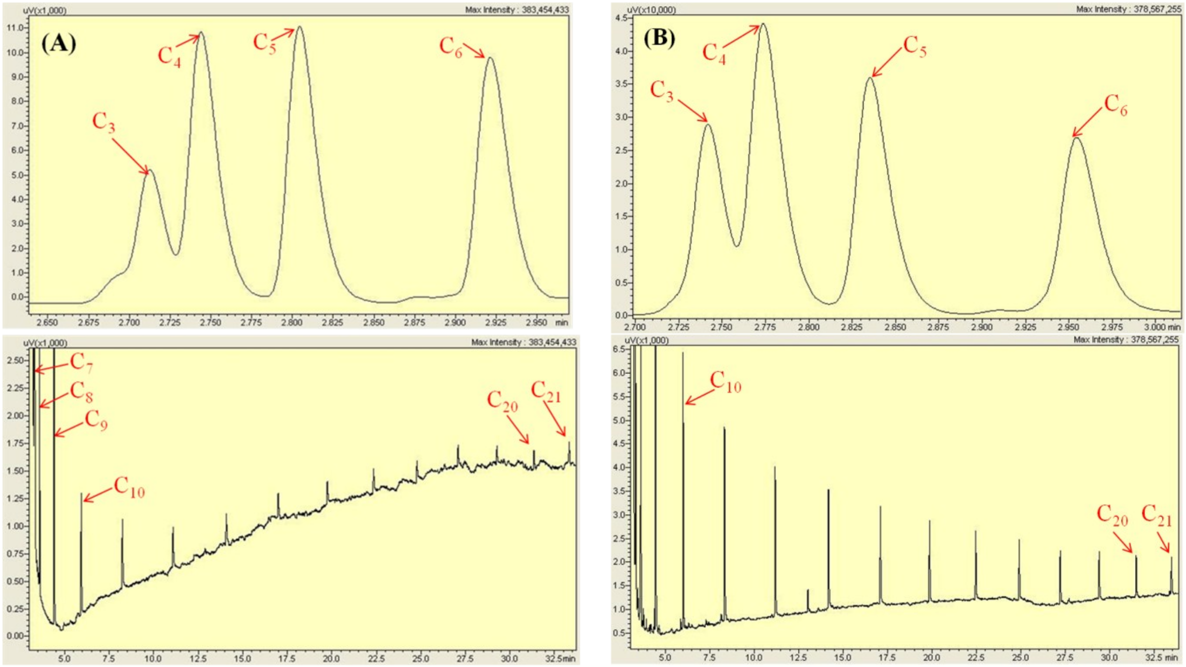
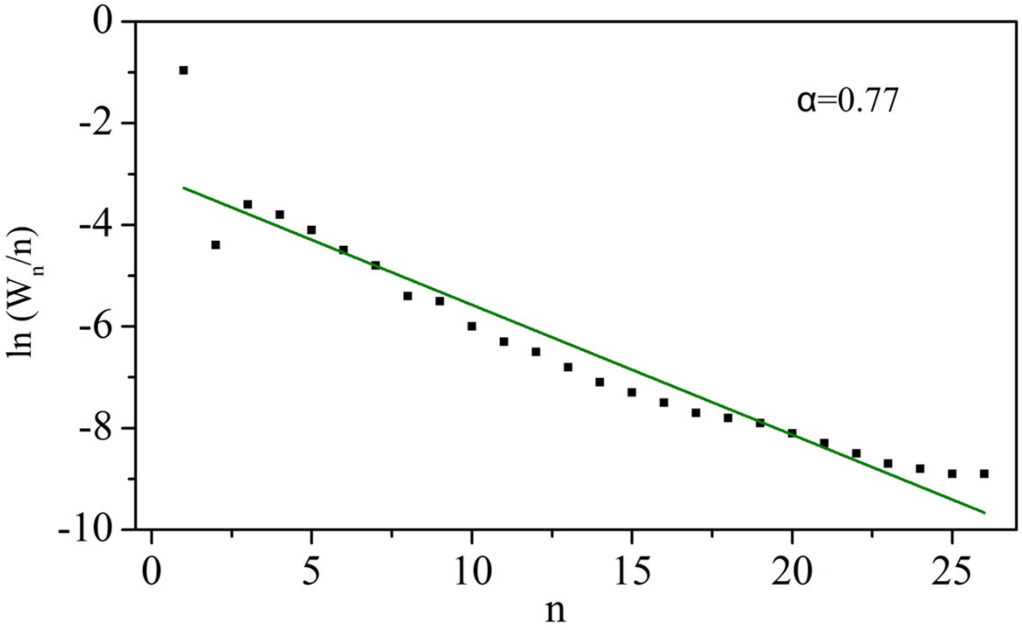

(A)
uV(x1,000)
Max Intensity : 383,454,433
11.0
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
2.650
2.675
2.700
2.725
2.750
2.775
2.800
2.825
2.850
2.875
2.900
2.925
2.950
min
C_3
C_4
C_5
C_6
uV(x1,000)
Max Intensity : 383,454,433
2.50
2.25
2.00
1.75
1.50
1.25
1.00
0.75
0.50
0.25
0.00
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
min
C_7
C_8
C_9
C_{10}
C_{20}
C_{21}
(B)
uV(x10,000)
Max Intensity : 378,567,255
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
2.700
2.725
2.750
2.775
2.800
2.825
2.850
2.875
2.900
2.925
2.950
2.975
3.000
min
C_3
C_4
C_5
C_6
uV(x1,000)
Max Intensity : 378,567,255
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
5.0
7.5
10.0
12.5
15.0
17.5
20.0
22.5
25.0
27.5
30.0
32.5
min
C_{10}
C_{20}
C_{21}

Fig. S7 Distribution of the formed hydrocarbons in C-CTHC at 130 °C.



N

Fig. S8 X-ray diffraction (XRD) patterns of Ru/$FeCO_3$ and Pt/$FeCO_3$.

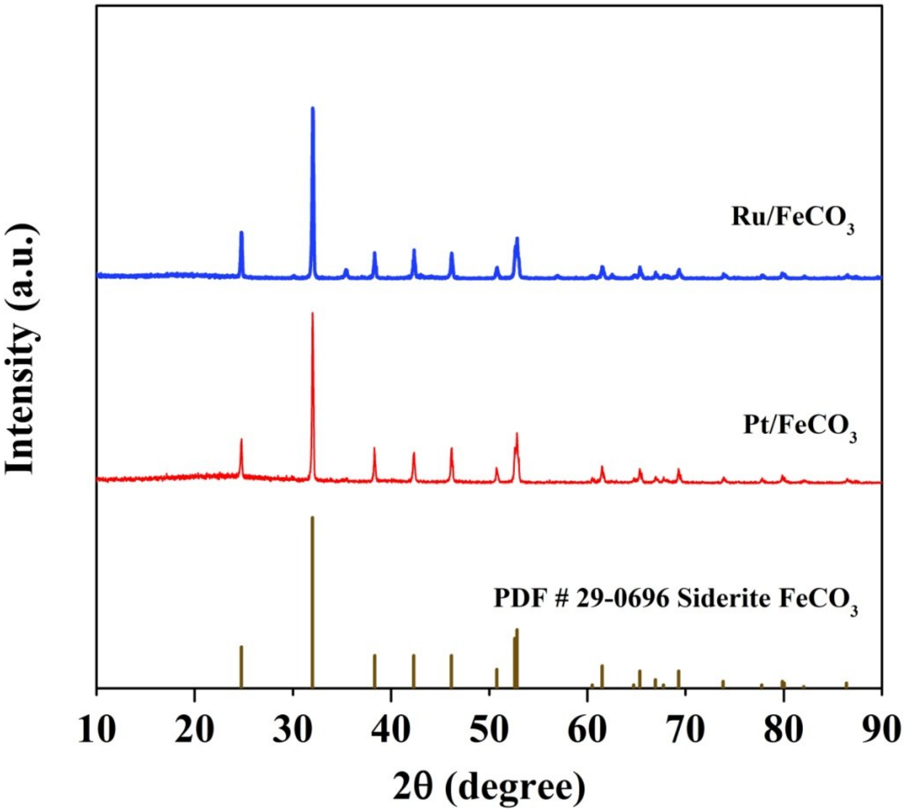


Fig. S9 The stability of Ru-Pt/$FeCO_3$ in catalyzing C-CTHC. Reaction conditions: Ru-Pt/$FeCO_3$, 0.3 g; water, 15 ml; cyclohexane, 15 ml; CO_2, 1.25 MPa; H_2, 3.75 MPa; time, 8 h. The triangle in the graph denotes the conversion of carbon in the substrates (including $FeCO_3$ and CO_2).

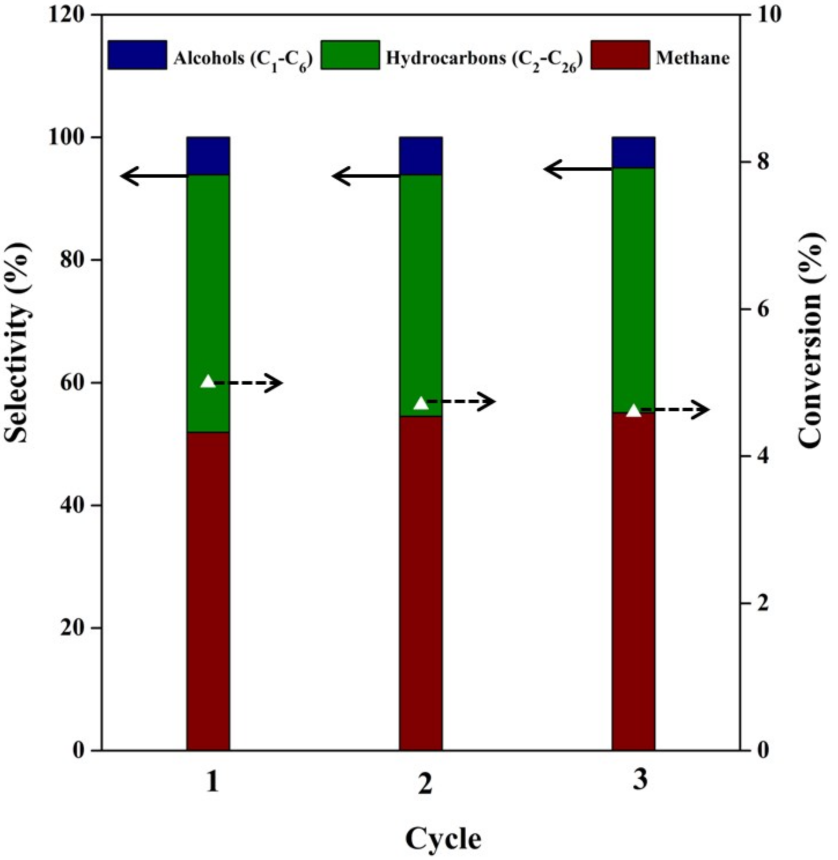


Table S1 Catalytic properties for C-CTHC over Ru-Pt/$FeCO_3$ under different H_2 pressures.

P_{H2} (MPa)	Selectivity[a]				Time-yield for C_2^+ hydrocarbons[a]
	CH_4	C_2^+[b]	C_5^+[b]	ROH[b]	
1.25	25.1	68.1	51.3	6.8	109.2
2.50	38.2	55.6	41.0	6.2	292.6
3.75	51.8	42.1	26.1	6.1	387.1

Reaction conditions: Pt-Ru/$FeCO_3$, 0.30 g; water, 15 ml; cyclohexane, 15 ml; CO_2, 1.25 MPa; time, 8 h. [a] Selectivity (%) and time-yield ($mmol\cdot mol_{metal}^{-1}\cdot h^{-1}$) were calculated based on moles of carbon. [b] C_2^+ and C_5^+ denote hydrocarbons with carbon number larger than 2 and 5. ROH denotes multi-carbon alcohols.

Table S2 Catalytic properties for C-CTHC over Ru/$FeCO_3$, Pt/$FeCO_3$, Ru-Pt/$FeCO_3$, and PtRu/$FeCO_3$, respectively.

Cat	Selectivity [a]			Time-yield of hydrocarbons[a]
	Hydrocarbon		Alcohol	
	C_1	$C_2^{+[c]}$		
Ru/$FeCO_3$	91.6	4.5	3.9	766
Pt/$FeCO_3$	26.1	49.6	24.3	175
Ru-Pt/$FeCO_3$[b]	51.8	42.1	6.1	863
PtRu/$FeCO_3$[b]	34.1	36.2	29.7	80

Reaction conditions: temperature, 130 °C; CO_2, 1.25 MPa; H_2, 3.75 MPa; reaction time, 8 h; cyclohexane, 15 ml; water, 15 ml; catalyst, 0.3 g. [a]Selectivity (%) and time-yield of hydrocarbons ($mmol_{CH2}/mol_{metal}/h$) were calculated based on moles of carbon. [b]Ru-Pt/$FeCO_3$ denotes $FeCO_3$ supported Ru and Pt nanoclusters, and PtRu/$FeCO_3$ denotes $FeCO_3$ supported PtRu alloy nanoclusters. [c] Hydrocarbons produced over Ru/$FeCO_3$, Pt/$FeCO_3$, and PtRu/$FeCO_3$ were C_1-C_{10}, C_1-C_{14}, and C_1-C_{11} hydrocarbons, respectively, while those produced over Ru-Pt/$FeCO_3$ were C_1-C_{26} hydrocarbons.

Table S3 Catalytic property for reaction of CO_2 with H_2 over Ru-Pt/TiO_2.

Temperature	Selectivity [a]	Conversion (%)

(°C)				
	Hydrocarbon		Alcohol	
	C_1	C_2-C_4	C_1-C_2	
130	97.9	1.2	0.9	29.5

Reaction conditions: CO_2, 1.25 MPa; H_2, 3.75 MPa; time, 8 h; cyclohexane, 15 ml; water, 15 ml; catalyst, 0.2 g.

Table S4 Catalytic property for C-CTHC over Ru-Pt/$FeCO_3$ in water.

Temperature (°C)	Selectivity [a]			Conversion (%)
	Hydrocarbon		Alcohol	
	C_1	C_2-C_7	C_1-C_7	
130	63.7	30.4	5.9	4.9

Reaction conditions: CO_2, 1.25 MPa; H_2, 3.75 MPa; time, 8 h; water, 30 ml; catalyst, 0.3 g.

References

[1] Y. Wang, J. W. Ren, K. Deng, L. L. Gui, Y. Q. Tang, *Chem. Mater.* 2000, **12,** 1622-1627.

[2] L. S. Zhong, J. S. Hu, H. P. Liang, A. M. Cao, W. G. Song, L. J. Wan, *Adv. Mater.* 2006, **18,** 2426-2431.

[3] L. W. Zhang, A. Gao, Y. Liu, Y. Wang, J. T. Ma*, Elctrochim. Acta* 2014, **132,** 416-422.