Supporting Information

Highly Efficient Ru/CeO₂ Catalyst for Formaldehyde Oxidation at Low Temperature and Mechanistic Study

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Experimental

Catalyst Characterization

The CO pulse experiments were carried out on Chemisorption Analyzer (AutoChem 2920) equipped with a TCD detector to identify real active reaction surface area of Ru/CeO_2 or Ru/Al_2O_3. The catalysts were pretreated in the H_2 flow at 300 °C for 1 h. Pulse chemisorption was next carried out at 50 °C. Several pulses of CO were injected at regular intervals, until the area of the recorded peaks became constant. Active reaction surface area (S) was calculated from the amount of adsorbed CO based on the assumption that the stoichiometry factor of chemisorbed CO to surface Ru equals 1:1.[1, 2]

$$S = \frac{1}{2}abN_AM_a \qquad (3)$$

Where a and b are the lattice distance of RuO_2 (110), a = 3.12 Å, b = 6.43 Å.[4] N_A is Avogadro's number, $N_A = 6.02 \times 10^{23}$. M_a is the adsorbed quantity of CO.

List of Table Captions

Table S1. Active reaction surface area of Ru/CeO_2 and Ru/Al_2O_3 samples

List of Figure Captions

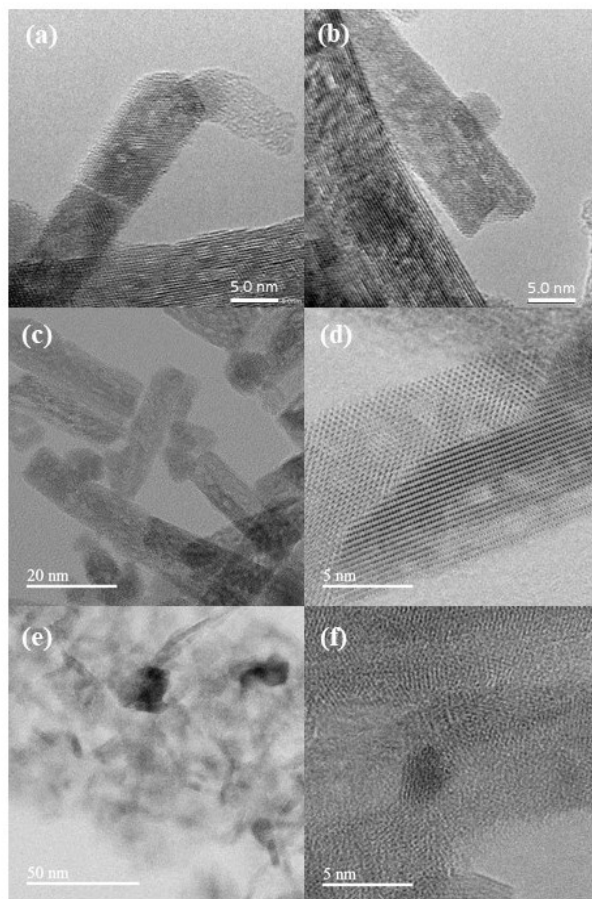**Figure S1**. HRTEM images of CeO_2 (a) and Ru/CeO_2-F (b) and HAADF/STEM images of Ru/CeO_2-F (c, d, bright field) and Ru/Al_2O_3-F (e, f, bright field)
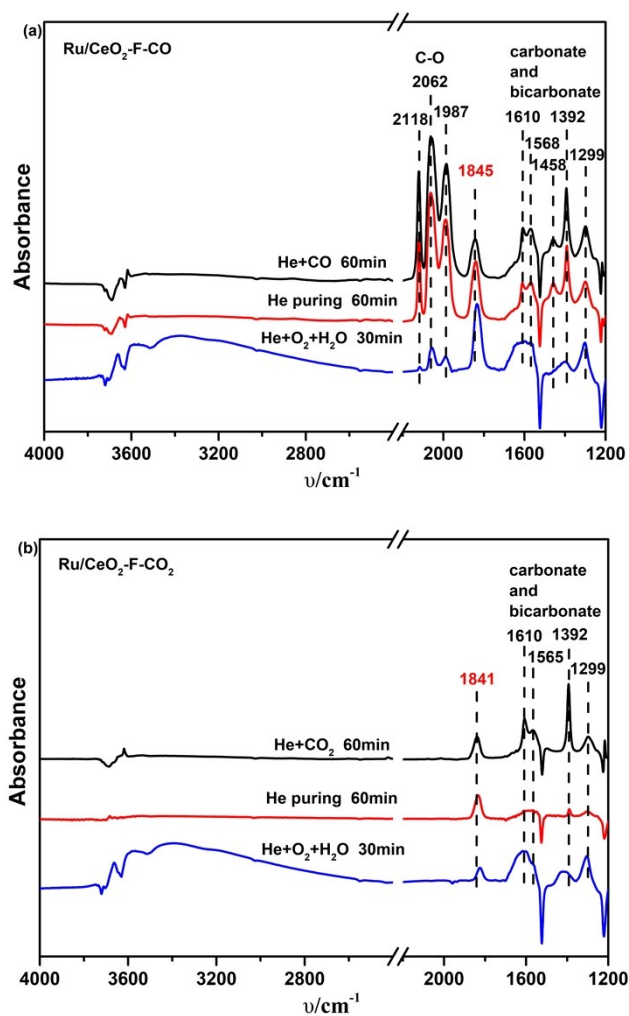
Figure S2. In situ DRIFTS over Ru/CeO_2-F after 1) a flow of He + CO (a) or He + CO_2 (b) for 60 min followed by 2) He purging for 60 min and finally 3) He + O_2 + H_2O for 30 min at 85 °C. For the dynamic time sequence of the DRIFTS spectra, see the Supporting Information, Figure S6 and S7. Reaction conditions: CO 300 ppm (a) or CO_2 300 ppm (b), He balance, total flow rate of 100 cm^3 min^{-1}

Figure S3. Results of stability testing performed at 85 °C under conditions with 300 ppm of CO_2, 130 ppm of HCHO and GHSV 100000 mL/(g_{cat} h)

Figure S4. Dynamic changes of in situ DRIFTS for the Ru/CeO_2-F catalyst as a function of time in a flow of (a) He + HCHO + O_2 + H_2O, (b) He purging, (c) O_2 purging and (d) He + O_2 + H_2O at 85 °C. Reaction conditions: HCHO 130 ppm, O_2 20%, RH 35%, He balance, total flow rate of 100 cm^3 min^{-1}

Figure S5. Dynamic changes of in situ DRIFTS for the Ru/Al_2O_3-F catalyst as a function of time in a flow of (a) He + HCHO + O_2 + H_2O, (b) He purging, (c) O_2 purging and (d) He + O_2 + H_2O at 160 °C. Reaction conditions: HCHO 130 ppm, O_2 20%, RH 35%, He balance, total flow rate of 100 cm^3 min^{-1}

Figure S6. Dynamic changes of in situ DRIFTS for the Ru/CeO_2-F catalyst as a function of time in a flow of (a) He + CO, (b) He purging and (c) He + O_2 + H_2O at 85 °C. Reaction conditions: CO 300 ppm, He balance, total flow rate of 100 cm^3 min^{-1}

Figure S7. Dynamic changes of in situ DRIFTS for the Ru/CeO_2-F catalyst as a function of time in a flow of (a) He + CO_2, (b) He purging and (c) He + O_2 + H_2O at 85 °C. Reaction conditions: CO_2 300 ppm, He balance, total flow rate of 100 cm^3 min^{-1}

Table S1. Active reaction surface area of Ru/CeO_2 and Ru/Al_2O_3 samples

Samples	Adsorbed quantity (mmol/g)	Reaction surface area (m^2/g)
Ru/CeO_2	0.020437	1.04*
Ru/Al_2O_3	0.006222	0.38
CeO_2	0.003160	-

* calculated by the difference of CO adsorbed quantities between Ru/CeO_2 and pure CeO_2.

Figure S1. HRTEM images of CeO$_2$ (a) and Ru/CeO$_2$-F (b) and HAADF/STEM images of Ru/CeO$_2$-F (c, d, bright field) and Ru/Al$_2$O$_3$-F (e, f, bright field).

Figure S2. In situ DRIFTS over Ru/CeO_2-F after 1) a flow of He + CO (a) or He + CO_2 (b) for 60 min followed by 2) He purging for 60 min and finally 3) He + O_2 + H_2O for 30 min at 85 °C. For the dynamic time sequence of the DRIFTS spectra, see the Supporting Information, Figure S6 and S7. Reaction conditions: CO 300 ppm (a) or CO_2 300 ppm (b), He balance, total flow rate of 100 cm^3 min^{-1}.
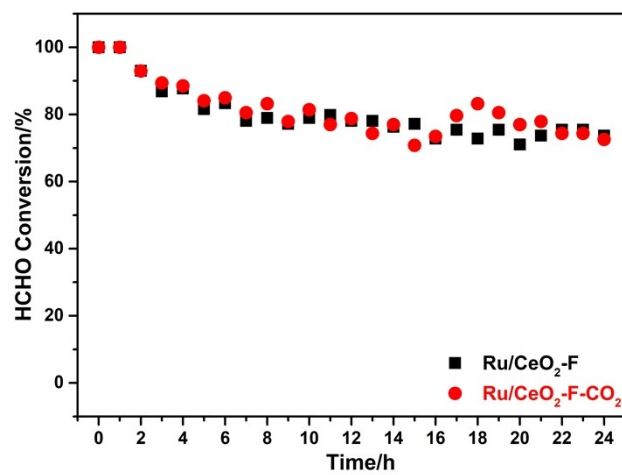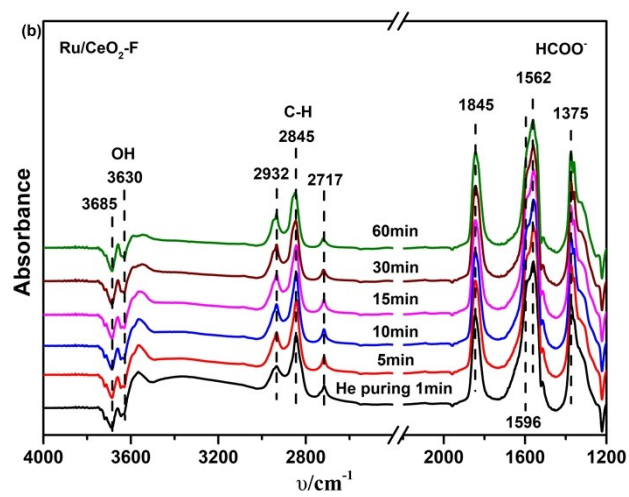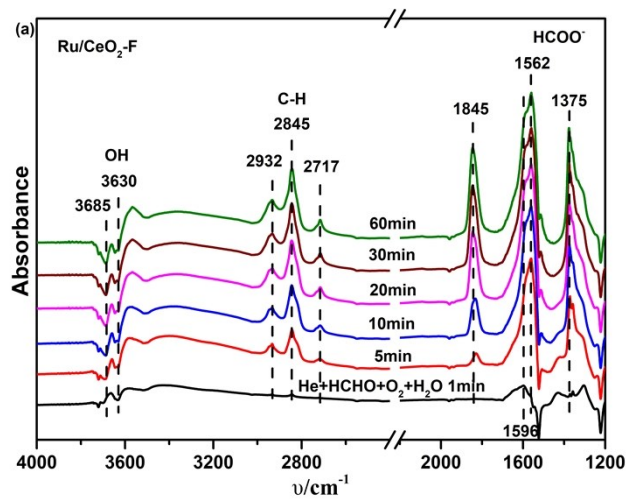
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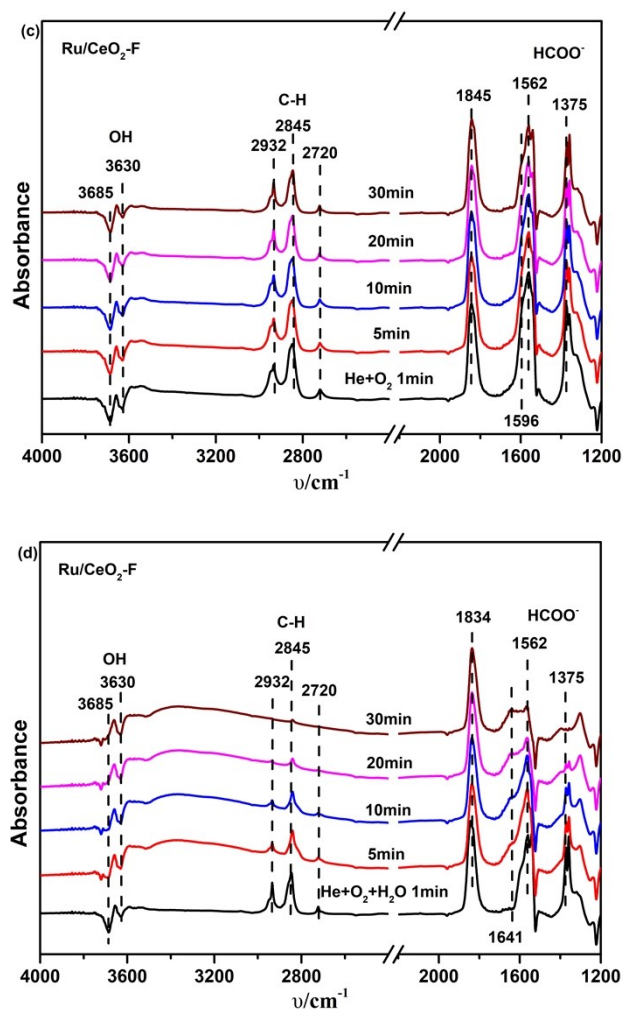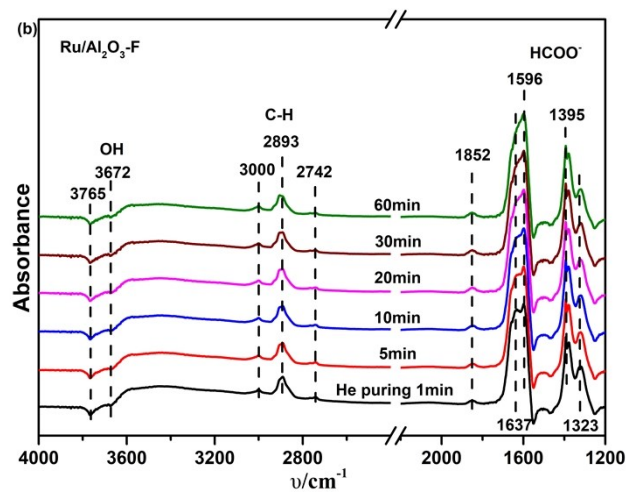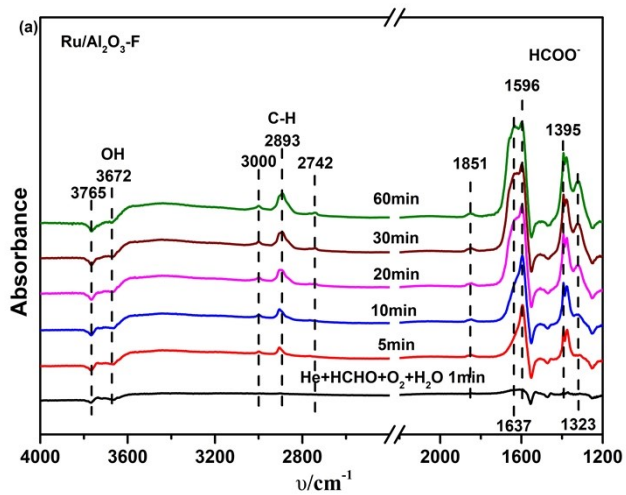
(a) Ru/CeO$_2$-F

OH
3685
3630
2932
C-H
2845
2717
HCOO$^-$
1562
1845
1375
60min
30min
20min
10min
5min
He+HCHO+O$_2$+H$_2$O 1min
1596

(b) Ru/CeO$_2$-F

OH
3685
3630
2932
C-H
2845
2717
HCOO$^-$
1562
1845
1375
60min
30min
15min
10min
5min
He puring 1min
1596

υ/cm^{-1}

Absorbance

Figure S4. Dynamic changes of in situ DRIFTS for the Ru/CeO$_2$-F catalyst as a function of time in a flow of (a) He + HCHO + O$_2$ + H$_2$O, (b) He purging, (c) O$_2$ purging and (d) He + O$_2$ + H$_2$O at 85 °C. Reaction conditions: HCHO 130 ppm, O$_2$ 20%, RH 35%, He balance, total flow rate of 100 cm^3 min^{-1}.
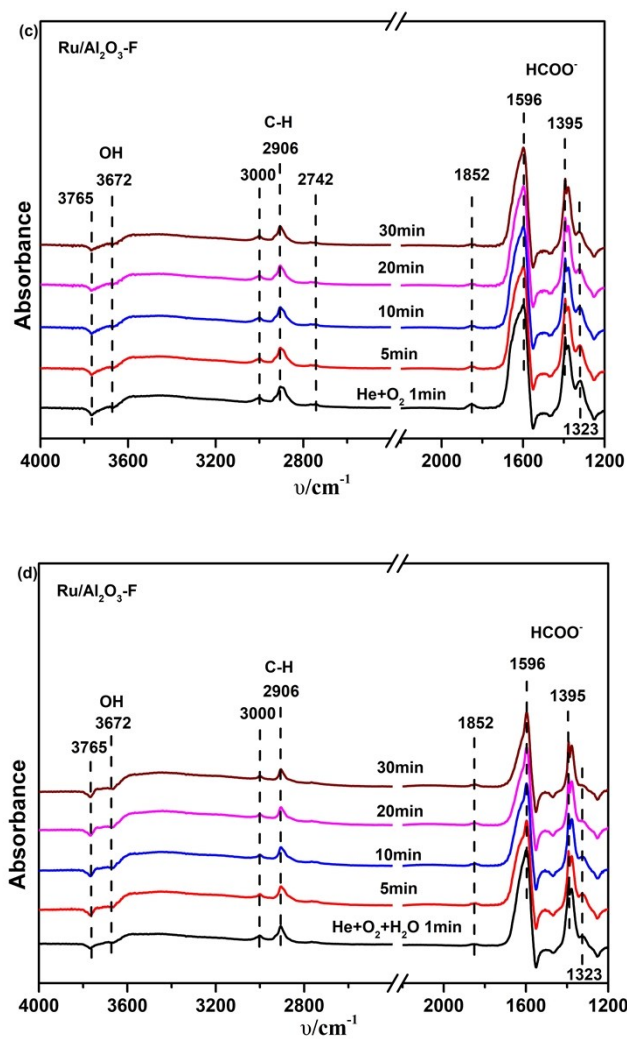
(a) Ru/Al₂O₃-F

HCOO⁻

OH
3672
3765

C-H
2893
3000   2742

1596
1395
1851

60min
30min
20min
10min
5min
He+HCHO+O₂+H₂O 1min

1637   1323

Absorbance

υ/cm⁻¹

(b) Ru/Al₂O₃-F

HCOO⁻

OH
3672
3765

C-H
2893
3000   2742

1596
1395
1852

60min
30min
20min
10min
5min
He puring 1min

1637   1323

Absorbance

υ/cm⁻¹

Figure S5. Dynamic changes of in situ DRIFTS for the Ru/Al$_2$O$_3$-F catalyst as a function of time in a flow of (a) He + HCHO + O$_2$ + H$_2$O, (b) He purging, (c) O$_2$ purging and (d) He + O$_2$ + H$_2$O at 160 °C. Reaction conditions: HCHO 130 ppm, O$_2$ 20%, RH 35%, He balance, total flow rate of 100 cm^3 min^{-1}.
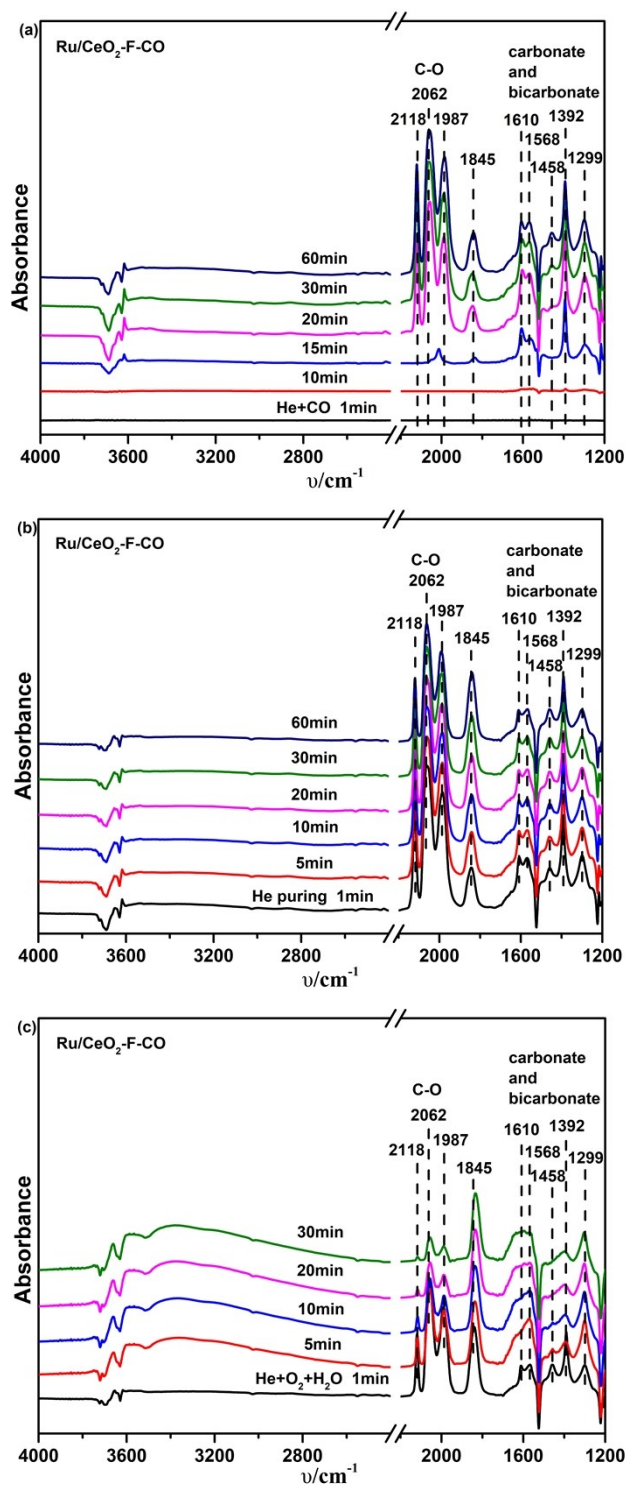
Figure S6. Dynamic changes of in situ DRIFTS for the Ru/CeO$_2$-F catalyst as a function of time in a flow of (a) He + CO, (b) He purging and (c) He + O$_2$ + H$_2$O at 85 °C. Reaction conditions: CO 300 ppm, He balance, total flow rate of 100 cm^3 min^{-1}.
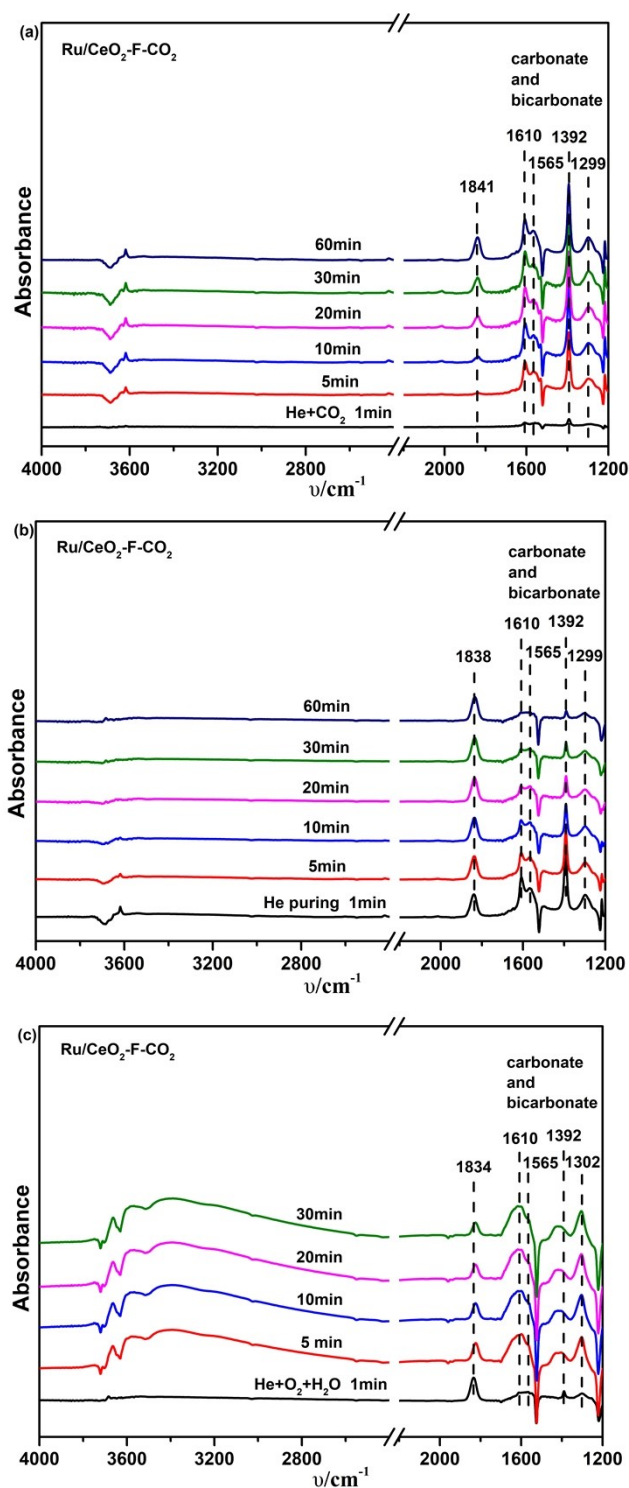
Figure S7. Dynamic changes of in situ DRIFTS for the Ru/CeO$_2$-F catalyst as a function of time in a flow of (a) He + CO$_2$, (b) He purging and (c) He + O$_2$ + H$_2$O at 85 °C. Reaction conditions: CO$_2$ 300 ppm, He balance, total flow rate of 100 cm^3 min^{-1}.

Reference

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