Supplementary Information

Correlation of the Catalytic Performance with Ru $^{\delta+}$ Species on Ru/Nb_2O_5 in Furfural Aqueous Reductive Conversion

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Materials and Methods

Materials

$RuCl_3 \cdot xH_2O$ (metal content ≥ 37%), niobium pentaoxide (Nb_2O_5, AR, 99.9%), furfural (FFR, AR, 99%), furfuryl alcohol (FAOL, AR, 98%), 2-cyclopenten-1-one (2-CPEO, AR, 98%), cyclopentanone (CPO, AR, 99.5%), cyclopentanol (CPOL, AR, 99.5%), 2-methyltetrahydrofuran (2-MTHF, AR, 99.5%), tetrahydrofurfuryl alcohol (THFAOL, AR, 99%), activated carbon (AC, 200 mesh), silicon dioxide (SiO_2, 200 mesh), alumina (Al_2O_3, AR), molybdenum trioxide (MoO_3, AR), zirconia (ZrO_2, AR), titanium dioxide (TiO_2 (anatase), AR) were purchased from the commercial reagent companies. All chemicals were used as received without further purification.

Preparation of Ru-based catalysts

A series of Ru/Nb_2O_5 precursors were synthesized following the classic wetness impregnation method. Specifically, 10 g of Nb_2O_5 support powder and 50 mL ultrapure water were mixed and stirred sufficiently at 70℃. And then 50 mL $RuCl_3$ aqueous solution at a varied concentration was added into the slurry dropwise, and the precursor solution was heated at 70℃ till water was fully evaporated. The as-prepared Ru/Nb_2O_5 precursors were dried at 110℃ overnight. After cooling under ambient condition, Ru/Nb_2O_5 precursors were calcinated at 500℃ for 3 h at continuous air flow of 50 mL min^{-1} with a heating ramp of 5℃ min^{-1}. After cooling down, 2 g of calcinated samples were submitted to reduction at a varied of temperatures, for 3 h under 10% H_2/Ar mixed gas flow (80 mL min^{-1}). The prepared catalyst was denoted as *x*%Ru/Nb_2O_5-H(y), where x indicates metal loading and y represents reduction temperature. Other catalysts using different supports, like Al_2O_3, MoO_3, ZrO_2 and TiO_2, were also prepared in a similar production protocol.

Characterizations

Hitachi SU-70 Field Emission Scanning Electron Microscope (SEM) was used to characterize the microscopic surface topography of the sample with an operating voltage of 5.0 kV. The sample was placed on a conductive adhesive and the height of the stent was adjusted. A high-resolution transmission electron microscope (TEM, JEM-2100F) was used to record the microscopic morphology of the catalyst under the condition of an accelerating voltage of 200 kV. Typically, the samples were firstly dispersed in methanol to form supernatant, which was further added drop wisely on a copper mesh for the analysis. The porous structure of catalysts was characterized by N_2 adsorption-desorption analysis at 77 K with the instrument of iPore 400 Automated Surface Area and Pore Size Analyzer using the Brunauer-Emmet-Teller (BET) method. The catalysts were degassed at 200 ℃ for 180 min to remove the physically adsorbed moisture before the analysis. The metal loading in the samples was determined using an inductively coupled plasma–atomic emission spectrometer (Perkin-Elmer OPTIMA 8000). Generally, weigh a certain amount of catalyst and stir it in Aqua Regia solution to completely dissolve the metallic particles, filter out the insoluble substance, and take the filtrate for measurement.

X-ray diffraction (XRD) patterns from an X' Pert Pro MPD desktop X-ray diffractometer equipped with CuKα radiation were analyzed to determine the crystal structure of samples. The patterns were recorded in the 2θ range from 5° to 80° at a wavelength of 0.154 nm and a scanning speed of 1 °/min. The elemental composition and element valence state of the catalyst were found by X-ray photoelectron spectral analysis using a Thermo Fisher Scientific Escalab 250 Ⅺ instrument with Mg Kα (1235.6 eV) as the radiation source. The spectra were based on C 1s (284.8 eV) as the standard for charge shift calibration.

The reduction behavior of catalysts was tested using temperature programmed reduction in hydrogen (H_2-TPR) was carried out using a Micromeritics (Auto Chem II 2920) instrument. Generally, 100 mg of the sample was used, and a 10% H_2/Ar mixed gas with a flow rate of 30 mL/min was employed as the carrier gas. The samples were heated from room temperature to 900℃ with a ramping rate of 10 ℃/min, and the signal was recorded by using a TCD. Pyridine adsorption infrared (Py-FTIR) was detected on a Fourier transform infrared spectrometer with the instrument (Thermo Scientific Nicolet 6700-Q50). This characterizations method is used to measure the amount of Lewis and Brønsted acids on the surface of the catalyst. The samples were first conditioned at 10^{-4} Pa vacuum, 300℃ for 30 min. After the activation was completed and the temperature was reduced to 30℃, pyridine vapor was introduced. After adsorption of pyridine vapor for 0.5 h, the reaction cell was again evacuated to 10^{-4} Pa to remove the physically adsorbed pyridine molecules, and then the FTIR cell was heated, using a ramping rate of 10 ℃/min, from 30℃ to 150/300℃ for 1h. Finally infrared data were collected by the detector.

Raman spectroscopy is a type of scattering spectroscopy. Raman spectroscopic analysis is based on the Raman scattering effect, which obtains information on molecular vibration and rotation, and this information is used to reflect the bulk structure of catalysts such as metal oxides. This characterization was performed on a HORIBA Scientific LabRAM HR800 instrument, in which the excitation wavelength of the laser is 532 nm,

and the screening range is from 80 cm^{-1} to 1800 cm^{-1}.

Hydrogen pulse chemisorption characterizations were carried out on a Micromeritics (Auto Chem II 2920) instrument. For testing the dispersion and particle diameters of different Ru/Nb_2O_5 catalysts, the precursor sample was pre-reduced with 10% H_2/Ar mixed gas flow of 80 mL/min for 3 hours under its corresponding temperature following a temperature program of 5 ℃/min, which is as the same as the preparation of Ru-based catalysts. After the pre-reducing process above, the catalyst was under desorbing at 300℃ for 1 hours under Ar gas flow.

The hydrogen pulse chemisorption was then carried out at 200℃ for 2.5 hours before determining the dispersion and particle diameter of catalyst. The number of surface Ru metal atoms was determined using the total amount of hydrogen atoms chemisorbed and assuming a stoichiometry of $H/Ru_S = 1$.[1, 2] The average Ru particle diameter was estimated using the equation $d_{avg} = 5/(S_{Ru} \times \rho_{Ru})$, where ρ_{Ru} is the density of Ru (12.3 g/cm), S_{Ru} is the surface area of Ru per gram of Ru determined from Htotal × (8.17 $Å^2$/Ru surface atom) × (100/wt% Ru).[3]

Catalytic evaluation for the hydrodeoxygenation reaction of furfural

The catalysts were evaluated for the hydrogenation of furfural in an autoclave reactor with a volume of 50 mL (or 300 mL). Generally, solvent and reactant were mixed, and then the mixture and catalysts were loaded to the reactor vessel at room temperature. The reactor was purged initially with 99.9% H_2 gas for five times, and then further charged with 99.9% H_2 gas to specific pressure. The reactor was heated to the reaction temperature within ca. 30 min, and a stirring rate of 800 rpm was used. The reactor was maintained at the required temperature for a specified reaction time. After that, the liquid products were collected for the further quantitative analysis. The spent catalyst was collected and washed with ethanol, and then dried at 223 K in a vacuum drying oven for 10 h for the reusability experiment or the further characterization.

For the reaction kinetic evaluation of furfural hydrodeoxygenation, the catalysts were evaluated in an autoclave reactor through a sampling valve device and with a volume of 300 mL. Generally, solvent and reactant were mixed, and then the mixture and catalysts were loaded to the reactor vessel at room temperature. The reactor was purged initially with 99.9% H_2 gas for five times, and then further charged with 99.9% H_2 gas to specific pressure. The reactor was heated to the reaction temperature within ca. 30 min, and a stirring rate of 800 rpm was used. The reactor was maintained at the required temperature for a specified reaction time. Specifically, for each sampling operation, the procedure commences at predetermined reaction time points with an initial flushing step. This involves the release of three aliquots of the reaction fluid, totaling approximately 1 mL in volume. The primary purpose of this step is to displace any residual reaction fluid from the previous sampling that may still be present in the tubing. Following this preparatory step, a sampling tube is employed to collect the requisite volume of reaction fluid, approximately 0.5 mL, which is then earmarked for subsequent quantitative analysis.

Products analysis

The liquid products were determined qualitatively by Thermo Fisher TRACE 1300 ISQ gas chromatography and electrospray ionization mass spectrometry (GC-ESI-MS). Besides, the liquid products were analyzed quantitatively by a Shimadzu 2014C gas chromatography, which is equipped with an Agilent HP-INNOWax column. According to the standard calibration curves, the components of liquid products were determined. The conversion of the substrate (Conv., or C), yield (Y), selectivity (S) and content of the products were calculated by **Equations (1-4)**:

$$\text{Conv.}(\%) = C = \frac{n_{initial} - n_{final}}{n_{initial}} \times 100\% \quad (1)$$

$$Y(\text{C-mol}\%) = \frac{n_{product} \times k_{product}/M_{product}}{n_{initial} \times k_{substrate}/M_{substrate}} \times 100\% \quad (2)$$

$$S(\text{C-mol}\%) = \frac{n_{product} \times k_{product}/M_{product}}{(n_{initial} - n_{final}) \times k_{substrate}/M_{substrate}} \times 100\% \quad (3)$$

$$\text{Content}(\text{C-mol}\%) = \frac{n_{product} \times k_{product}/M_{product}}{\frac{n_{final} \times k_{substrate}}{M_{substrate}} + \sum n_{product} \times k_{product}/M_{product}} \times 100\% \quad (4)$$

In **Equations (1-4)**, $n_{initial}$ is the moles of the added substrate, n_{final} accounts for the moles of the remained substrate in the post-treated liquid, and $n_{product}$ is the moles of each product in the post-treated liquid, $M_{product}$ is the molar mass of each product in post-treated liquid, $k_{product}$ is the number of carbon atoms of one molecule of each product in post-treated liquid, $M_{substrate}$ is the molar mass of the added substrate, $k_{substrate}$ is the number of carbon atoms of one molecule of the added substrate.

***In-situ* analysis of adsorptive behavior of varied probing molecules**

In-situ Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFTS) was used to investigate the reaction process and adsorption mode of the hydrogenation of probe molecules, including FFR, FAOL, CPEO, and CPO, over the catalysts. The characterization was performed on a Nicolet iS50 spectrometer equipped with a modified Harrick Praying Mantis DRIFT cell. The catalyst surface was saturated with a stream of N_2 that passed through a FFR bubbler. After that, the catalysts were heated from room temperature to 160℃ at a

ramping rate of 10℃/min and maintained at this temperature for 20 min in a constant gas flow. The spectra were recorded simultaneously by the detector.

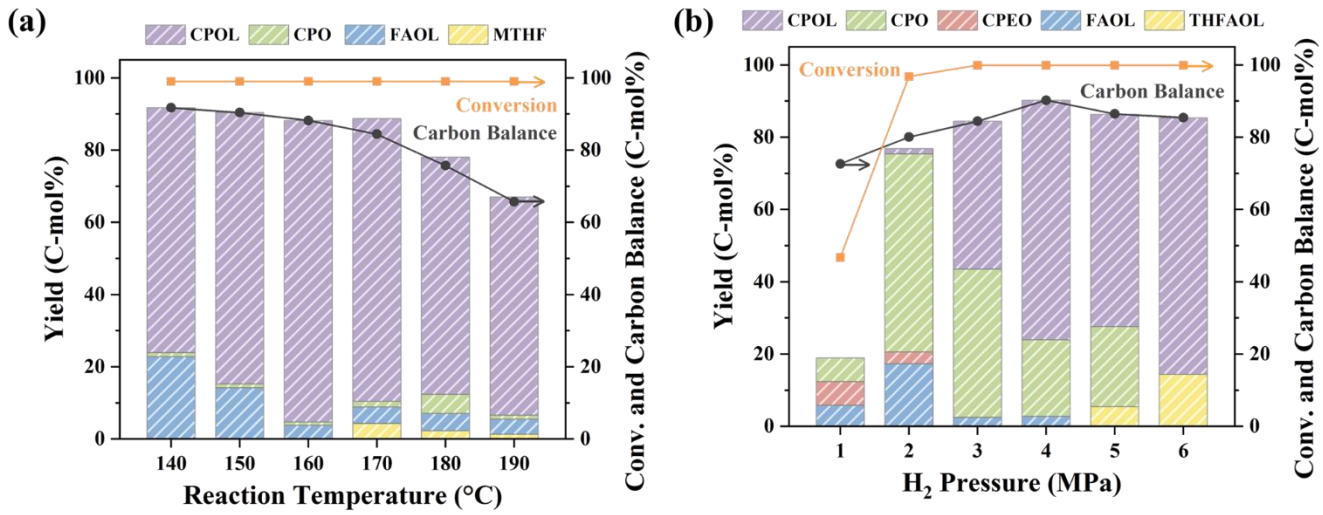

Figure S1. (a) Influence of reaction temperature on furfural conversion. Reaction conditions: 0.20 g furfural, 0.04 g catalyst 5% Ru/Nb_2O_5-H(450), 20 mL of H_2O, p (initial H_2) = 4.0 MPa, stirring speed = 800 rpm, reaction time = 9h. (b) The hydrodeoxygenation of furfural over 5% Ru/Nb_2O_5-H(450) catalyst under different initial H_2 pressure. Reaction conditions: 0.20 g furfural, 0.04 g catalyst, 20 mL of H_2O, reaction temperature T = 160 °C, heating rate = 4.5 °C/min, stirring speed = 800 rpm, reaction time = 6h.

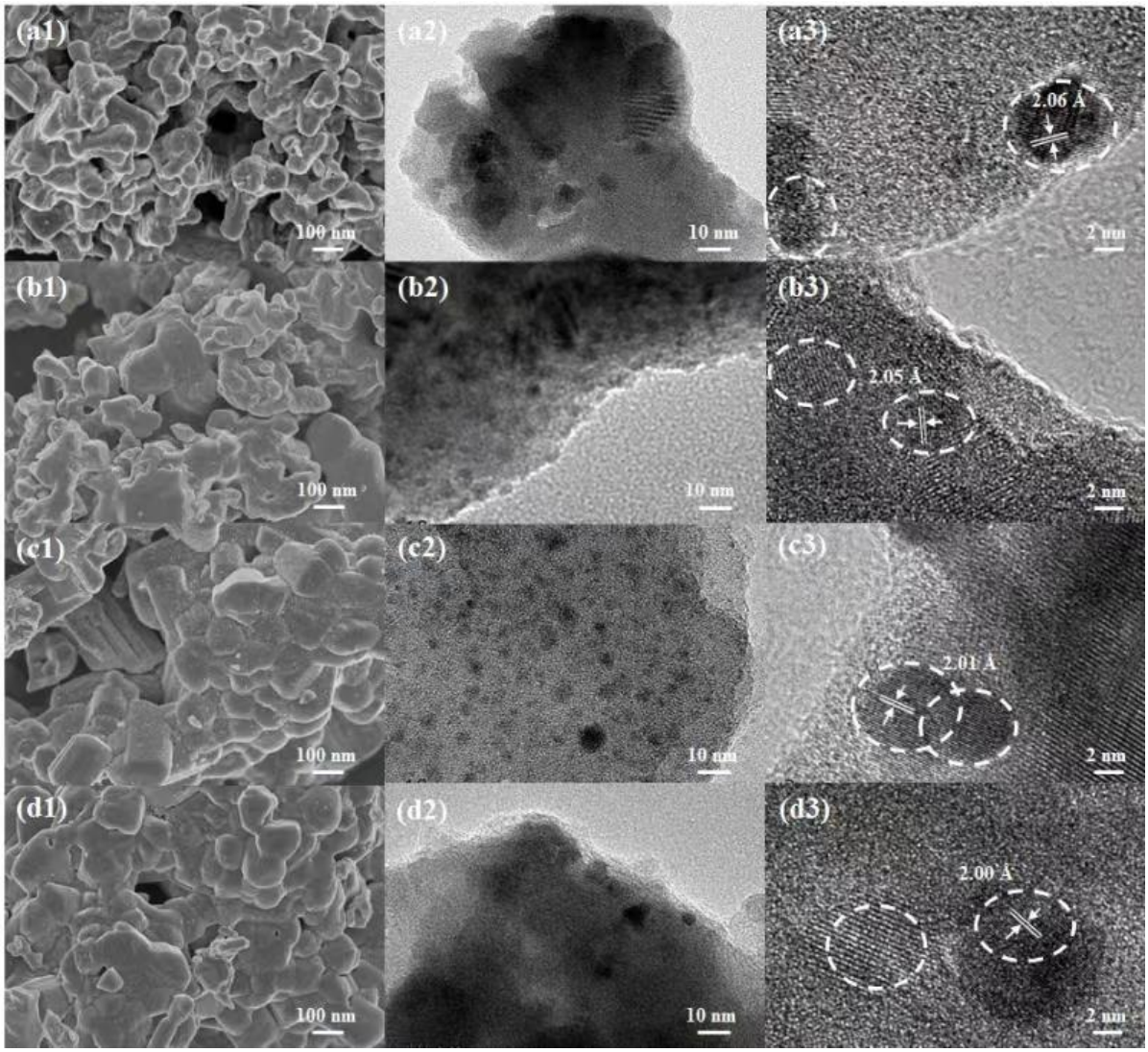

Figure S2. SEM and TEM images over various Ru/Nb_2O_5 catalysts of (a1-a3) 1% Ru/Nb_2O_5-H(250), (b1-b3) 1% Ru/Nb_2O_5-H(450), (c1-c3) 1% Ru/Nb_2O_5-H(650), and (d1-d3) 1% Ru/Nb_2O_5-H(850).

Table S1. The Ru content of various fresh Ru/Nb_2O_5 catalysts for hydrodeoxygenation of furfural.

Catalysts	Total H_2 uptake at 200 ℃ (μmol H_2/g cat.)	Dispersion%[a] (H/Ru_S)	Active hemisphere particle diameter[b] (nm)	*Ru content (wt%)
1% Ru/Nb_2O_5-H(250)	10.6	20.4	4.7	0.97
1% Ru/Nb_2O_5-H(450)	10.5	21.3	4.7	0.99
1% Ru/Nb_2O_5-H(650)	9.8	19.7	5.1	1.00
1% Ru/Nb_2O_5-H(850)	9.9	20.1	5.0	0.92

[a] Dispersion of Ru—number of hydrogen atoms chemisorbed to the total number of Ru atoms.

[b] Average Ru particle size calculated from irreversible H_2 pulse-chemisorption.

*These results were determined by ICP-OES.

Table S2. Physical properties of various Ru/Nb_2O_5 catalysts.

Catalysts	S_{BET} (m^2 g^{-1})	Pore volume (cm^3 g^{-1})
Nb_2O_5 with no treatment	0.49	0.0016
Calcinated Nb_2O_5	0.52	0.0014
0% Ru/Nb_2O_5-H(450)	0.51	0.0014
1% Ru/Nb_2O_5-H(450)	0.56	0.0046
5% Ru/Nb_2O_5-H(450)	1.67	0.0130

Table S3. Surface elemental concentration of various catalysts derived from deconvolution results of XPS.

Catalysts	$Ru3d_{5/2}$	$Nb3d_{5/2}$	
	$Ru^{\delta+}/(Ru^0 + Ru^{\delta+})$	$Nb^{5+}/(Nb^{5+} + Nb^{4+})$	$Nb^{4+}/(Nb^{5+} + Nb^{4+})$
1% Ru/Nb_2O_5-H(250)	0.41	0.89	0.11
1% Ru/Nb_2O_5-H(450)	0.34	0.74	0.26
1% Ru/Nb_2O_5-H(650)	0.19	0.65	0.35
1% Ru/Nb_2O_5-H(850)	0.08	0.54	0.46

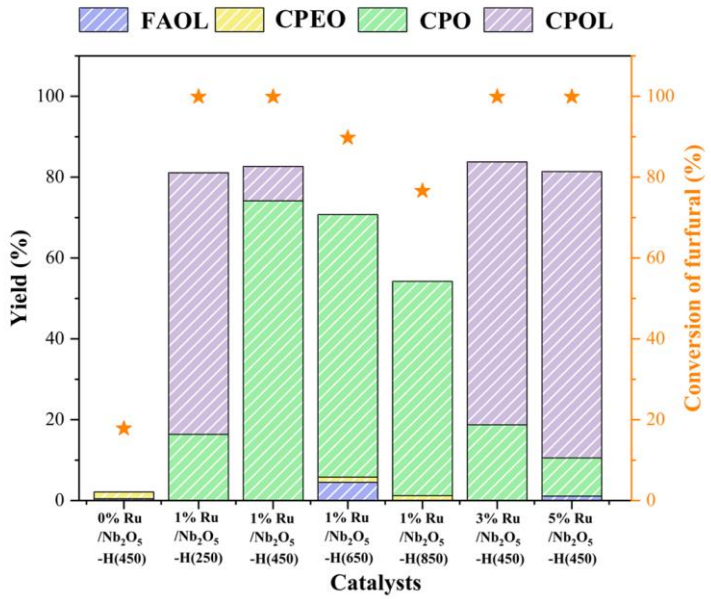

Figure S3. The product distribution of Ru/Nb_2O_5 catalysts with different metal loading and different reduced temperature. Reaction conditions: 2.0 g furfural, 0.40 g catalyst, 200 mL of H_2O, reaction temperature T = 160 °C, heating rate = 4.5°C/min, stirring speed = 800 rpm, reaction time = 12 h.

Table S4. Catalytic kinetic apparent rate constant of conversion of FFR hydrodeoxygenation over various prepared Ru/Nb_2O_5 catalysts.

Catalysts	k [a] (h^{-1})	R^2 [b]
1% Ru/Nb_2O_5-H(250)	0.4991	0.9813
1% Ru/Nb_2O_5-H(450)	0.2793	0.9509
1% Ru/Nb_2O_5-H(650)	0.1234	0.9104
1% Ru/Nb_2O_5-H(850)	0.1081	0.9568

[a] Series of rection apparent rate constants, k, are obtained from **Figure 3.**

[b] Series of R^2 are obtained from **Figure 3**.

Reaction conditions: 2.00 g furfural, 0.40 g catalyst, 200 mL of H_2O, p (initial, H_2) = 5.0 MPa, the initial reaction temperature is 25 °C, heating rate is 4.5 °C/min, T = 160 °C, stirring speed = 800 rpm, reaction time = 720 min.

Table S5. H_2 uptake and corresponding reduction peak of various Ru/Nb_2O_5 catalysts.

Uptake [a](μmol/g)	**Reduction Peak**	**Catalyst**
364.34	β	Calcinated 1%Ru/Nb_2O_5
1135.21	β	Calcinated 3%Ru/Nb_2O_5
1938.92	β	Calcinated 5%Ru/Nb_2O_5
157.08	α	1%Ru/Nb_2O_5-H(250)

64.22	α	1%Ru/Nb_2O_5-H(450)
33.06	α	1%Ru/Nb_2O_5-H(650)
19.75	α	1%Ru/Nb_2O_5-H(850)

[a] The amounts of H_2 uptake were obtained from **Figure 1d** and **Figure 3b**.

Table S6. Comparison of functional groups collected over various Ru/Nb_2O_5 catalysts.[a]

Entry	Catalyst	Groups	Wavenumber (cm-1)	Intensity (a.u.)
1	1% Ru/Nb_2O_5-H(250)	C═O	1673	1.3602
2	1% Ru/Nb_2O_5-H(450)	C═O	1673	1.0414
3	1% Ru/Nb_2O_5-H(650)	C═O	1673	0.9113
4	1% Ru/Nb_2O_5-H(850)	C═O	1673	0.7536

[a]The groups were determined by time-resolved *in-situ* DRIFTS spectra as shown in **Figure 4**. Also, the intensity of C═O group is determined during the same testing situation, i.e., sampling time is 13 min.

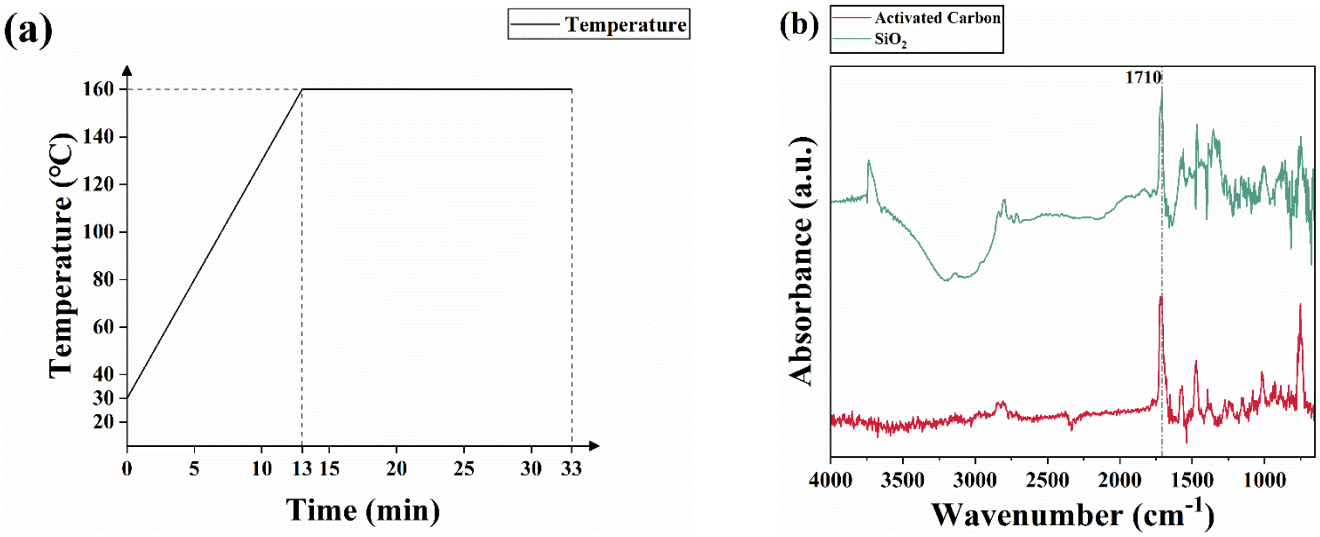

Figure S4. The temperature programming process of time-resolved *in-situ* DRIFT spectra of (a) furfural adsorption experiments, (b) FT-IR spectra for furfural physical adsorption over SiO_2 and AC.

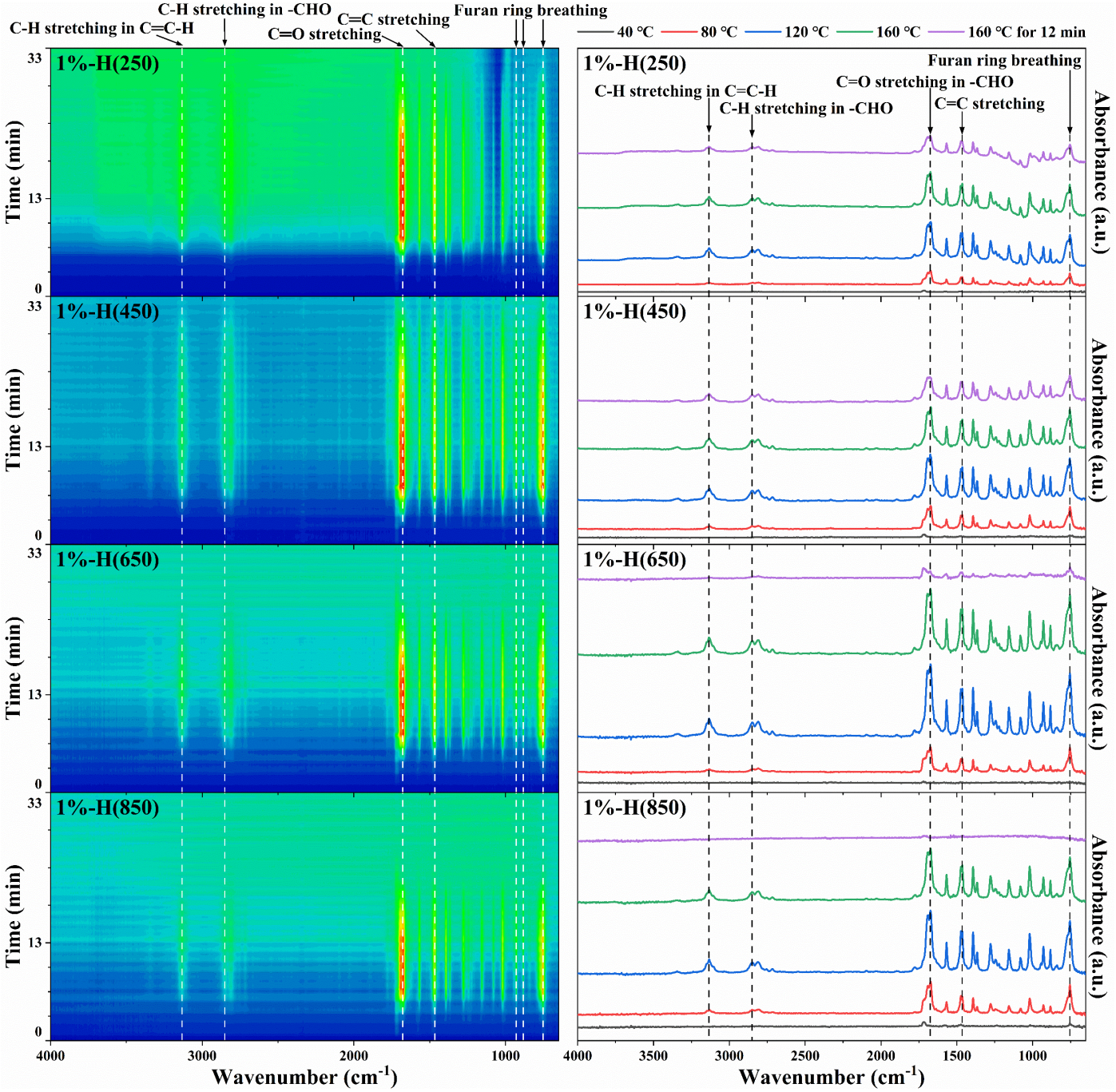

Figure S5. Time-resolved *in-situ* DRIFT spectra for FFR adsorption over 1% Ru/Nb_2O_5-H(250), 1% Ru/Nb_2O_5- H(450), 1% Ru/Nb_2O_5-H(650) and 1% Ru/Nb_2O_5-H(850) catalysts.

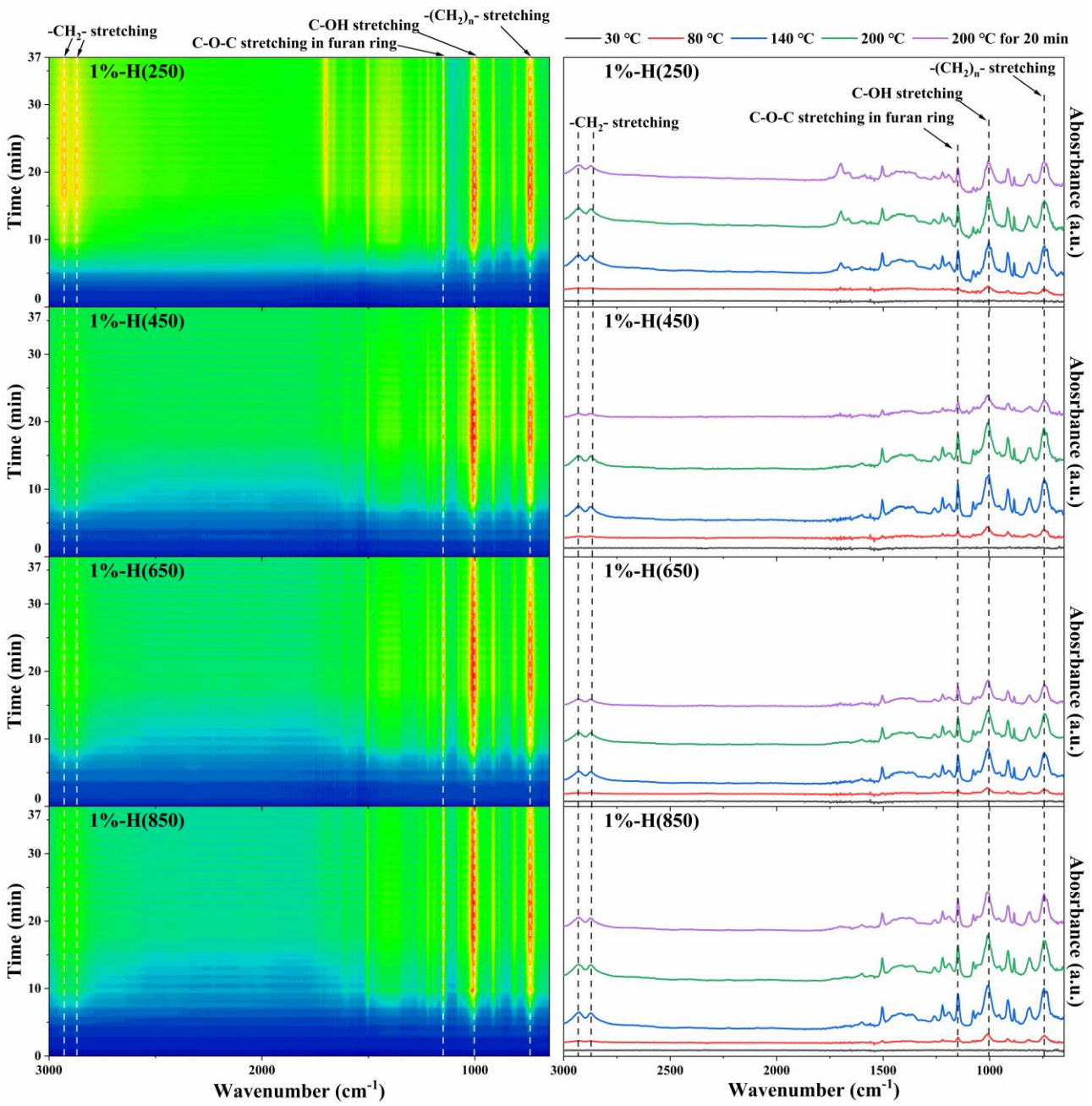

Figure S6. Time-resolved *in-situ* DRIFT spectra for FAOL adsorption over 1% Ru/Nb_2O_5-H(250), 1% Ru/Nb_2O_5- H(450), 1% Ru/Nb_2O_5-H(650) and 1% Ru/Nb_2O_5-H(850) catalysts.

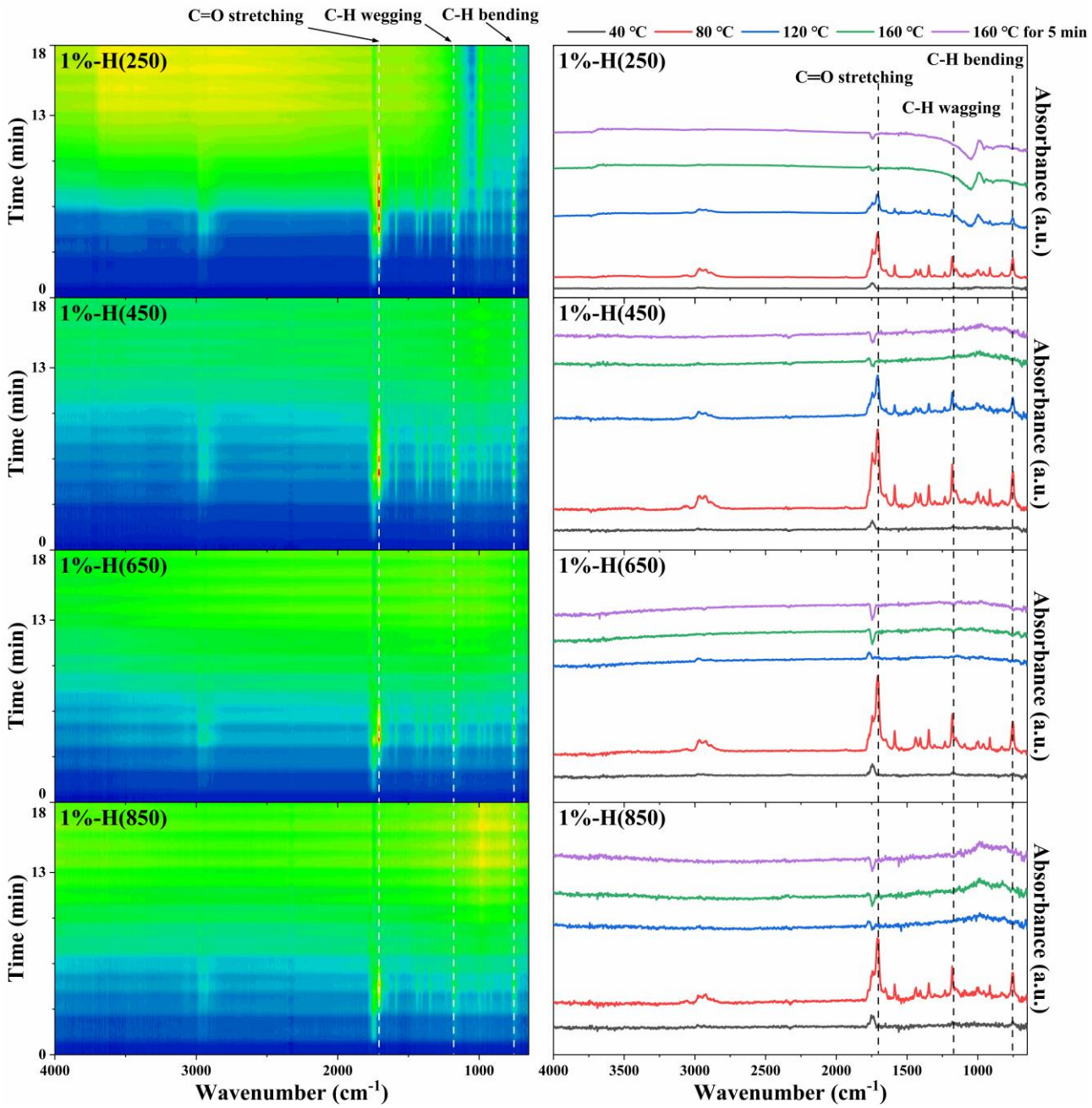

Figure S7. Time-resolved *in-situ* DRIFT spectra for CPEO adsorption over 1% Ru/Nb_2O_5-H(250), 1% Ru/Nb_2O_5- H(450), 1% Ru/Nb_2O_5-H(650) and 1% Ru/Nb_2O_5-H(850) catalysts.

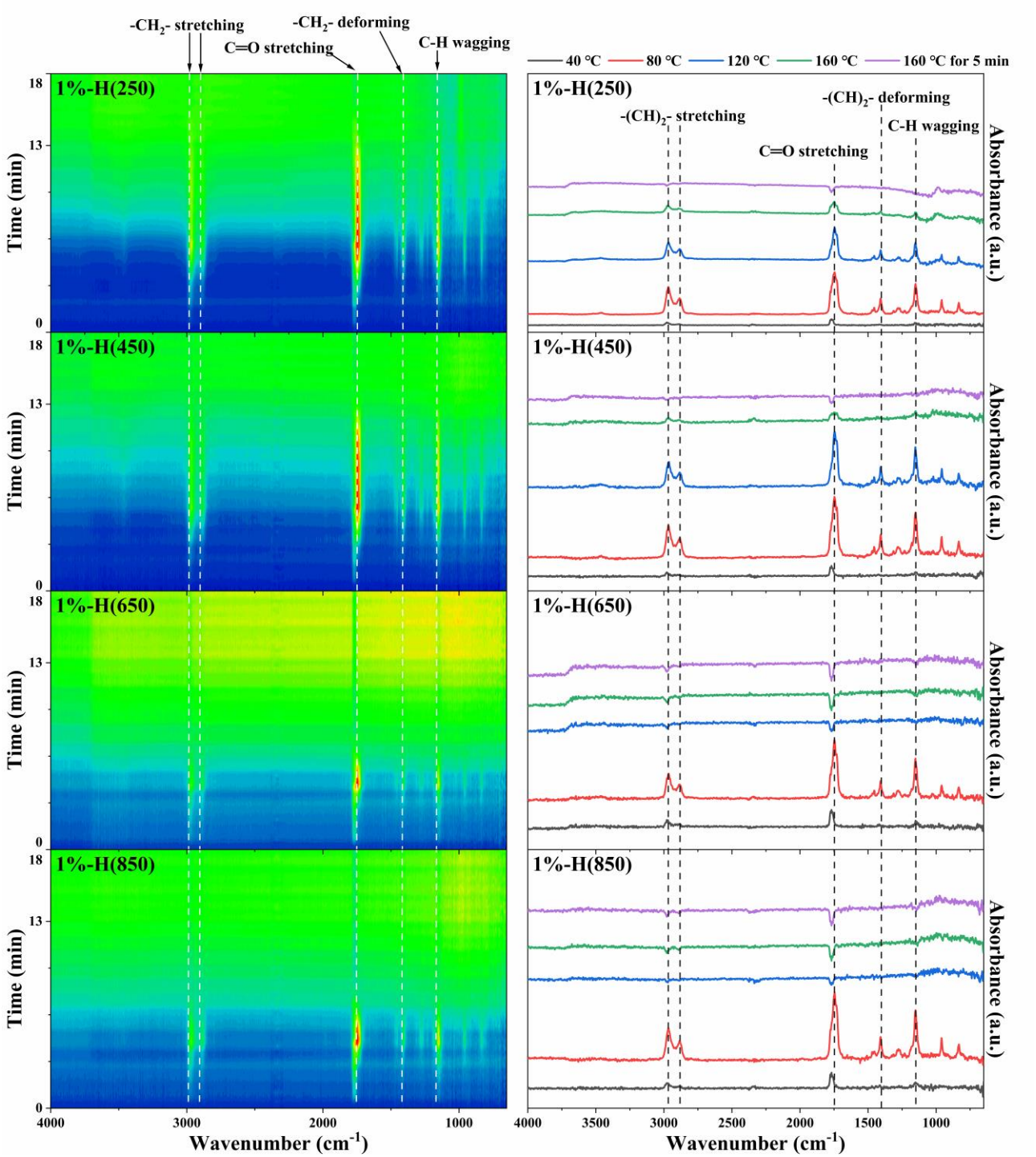

Figure S8. Time-resolved *in-situ* DRIFT spectra for CPO adsorption over 1% Ru/Nb_2O_5-H(250), 1% Ru/Nb_2O_5- H(450), 1% Ru/Nb_2O_5-H(650) and 1% Ru/Nb_2O_5-H(850) catalysts.

References

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