Electronic Supporting Information

Efficient hydrogenation of 5-hydroxymethylfurfural using a synergistically bimetallic Ru-Ir/C catalyst

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1. Experimental details

Materials and reagents

All the chemicals were used as received without further purification or treatment. Iridium (III) chloride hydrate (99%) and ruthenium (III) chloride (37–40% on Ru basis) from Alfa Aesar, activated charcoal and polyvinyl pyrrolidone (PVP, > 98%, M.W. = 10,000) from Tokyo Chemical Industry Co. Ltd., were used for catalyst preparation. 5-Hydroxymethylfurfural (HMF, 99%), 5-methylfurfural (5-MF, 99%), 5-methylfurfuryl alcohol (MFA, 99%), dimethylfuran (DMF, 99%), and tetrahydrofuran (THF, 99%) from Acros Organics were used for catalytic reaction.

Catalyst preparation

All the catalysts were synthesized by adsorption method. Typically, with Ru-Ir/C catalyst as an example, 9 mg PVP was dissolved in 50 mL distilled water in a brown flask. And then 1 mL $IrCl_3$ precursor (Ir: 2.5 mg mL^{-1}) and 1 mL $RuCl_3$ (Ru: 2.5 mg mL^{-1}) precursor were added and the solution was stirred for 15 min at room temperature. The total loading of metals was of 1 wt%. After that 495 mg activated charcoal was dispersed in the solution and stirred for another 6 h (600 rpm). The black solids were then separated by filtration and washed repeatedly by excessive distilled water (90 °C and 25 °C, respectively) and adequate ethanol to completely remove PVP and Cl^- ions. Finally, the solids were oven-dried at 100 °C overnight and reduced in H_2 flow subsequently (10 mL min^{-1}) at 350 °C for 0.5 h. Preparation of Ru/C and Ir/C catalysts (1 wt%) used the same procedure.

Catalytic reaction

HMF (2 mmol), the catalyst (90 mg) and THF (10 mL) were mixed and sealed into a batch-type Teflon-lined stainless-steel autoclave (50 mL). After the purge and introduction of H_2 at a pressure of 1 MPa, the reactor was then placed in an oil bath pre-heated at 120 ± 1 °C with a magnetic stirring at 800 rpm. When the reaction was over, the reactor was rapidly placed in an ice-bath. And then the used catalyst was separated by magnet and completely washed by ethanol and water three times followed by drying at 80 °C under vacuum for 12 h and H_2 treatment at 350 °C for 0.5 h before the next use.

The reactant and products were analyzed on a Thermo Scientific TRACE 1310 gas chromatograph (GC) armed with a flame ionization detector (FID) and a TR-5 column (30 m × 0.32 mm × 0.25 μm). The quantification was based on an external standard method by calibrating the standard solution at different concentrations for HMF, 5-MF, BHMF, MFA and DMF. Conversion of reactant and selectivity of each product were defined as the molar percentage of reactant converted and the molar percentage of each product formed in reactant converted, respectively. Both conversion and selectivity were calculated on a carbon basis. Notably, the carbon balance was monitored for each reaction, and the obtained data were of 99−100% (not reported in figures and tables), which revealed that the reported catalytic performances are reliable. Each reaction was repeated at least twice to guarantee a reproducible result, and the error of the data must be no more than 2%. Conversion of reactant, selectivity of products and initial reaction rate (*r*) were calculated by the following equations.

$$Conv.\,(\%) = \frac{n_{reactant,initial} - n_{reactant,final}}{n_{reactant,initial}}$$

$$Select.\,(\%) = \frac{n_{product}}{n_{reactant,initial} - n_{reactant,final}}$$

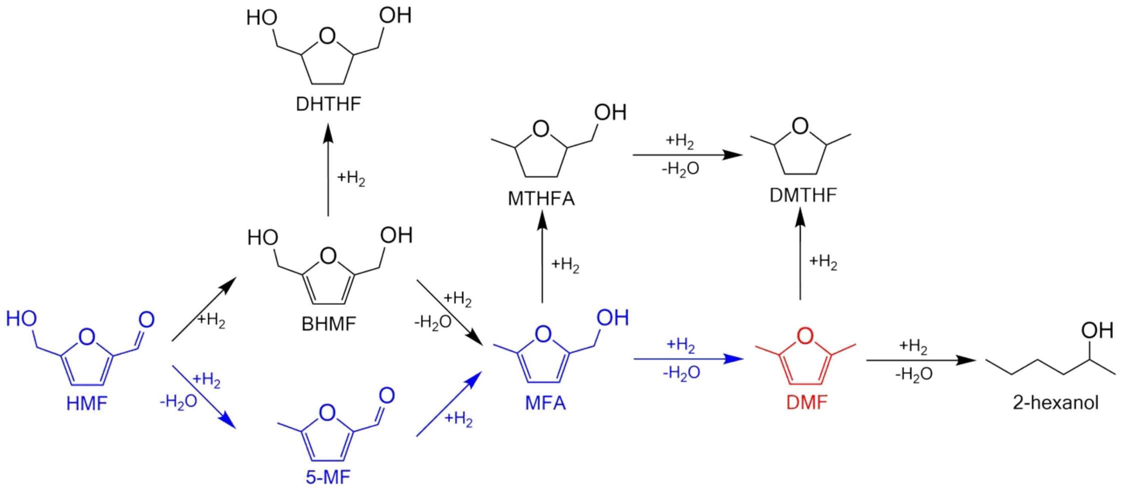
$$Initial\ reaction\ rate\ \left(\mu mol\ g_{metal}^{-1}\,s^{-1}\right) = \frac{n_{reactant,initial} - n_{reactant,final}}{W_{metal} \times time}$$

Characterization methods

The loadings of Ru and Ir were determined by Inductively Coupled Plasma Mass Spectrometry

(ICP-MS) using an Agilent 7500a apparatus. The solid sample was thoroughly dissolved by a mixed acid of HCl and HNO_3 and the obtained solution was placed at room temperature overnight. X-ray photoelectron spectroscopy (XPS) analysis was performed under ultra-high vacuum on a Thermo Scientifc Escalab 250Xi system equipped with Al Kα radiation. The binding energy (BE) shift due to the surface charging was adjusted based on a reference to the C 1s line at 284.5 eV. Transmission electron microscopy (TEM) measurement was conducted on a Philips-FEI TECNAI F30 field-emission electron microscope operated at an acceleration voltage of 300 kV. Samples were previously suspended in ethanol and dispersed ultrasonically. Drops of the suspension were applied on a lacey support film. Hydrogen temperature-programmed reduction (H_2-TPR) was carried out on a Micromeritics Autochem II Chemisorption analyzer. The sample was treated in a 5% H_2-Ar (in volume) mixed gas with a flow rate of 30 mL min^{-1}. The temperature was increased to 800 °C at a rate of 10 °C min^{-1}. The CO-adsorbed *in situ* diffuse reflectance Fourier transform infrared (DRIFT-IR) spectra were obtained on a Thermo Scientific Nicolet-iS50 FT-IR spectrometer with a MCT detector and 10-cm Demountable Gas Cell (resolution: 4 cm^{-1}, scan number: 64). The catalyst was pre-treated in H_2 flow (20 mL min^{-1}) at 350 °C (5 °C min^{-1}) for 30 min and then cooled down to 20 °C. Afterwards the solid was purged by He at 20 °C for 20 min and the DRIFT-IR background spectrum was recorded. The solid was further treated in pure CO flow (99.99%) at 25 °C for 60 min and subsequently purged by He to remove the free CO before the DRIFT-IR spectra were collected.

2. Complementary data



Scheme S1 The network of products derived from hydrogenation of HMF.

Table S1 Comparison of catalytic performances of the typical supported-Ru or Ir catalysts for hydrogenation of HMF to DMF

Catalyst	HMF (mmol)	Catalyst (mg)	Additive	*P* H_2 (MPa)	*T* (°C)	*t* (h)	Conv. HMF (%)	Select. DMF (%)	Reuse time	Ref.
Ru/Co_3O_4	2	100	none	0.7	130	24	99	93.4	6	1
Ru-NaY	1	25	*n*-decane	1.5	220	1	99	78	5	2
Ru-HT	1	50	none	1	220	4	99	58	5	3
Ru/C	7.9	200	H_2SO_4	1.5	200	12	99	93.9	3	4
RuCo/CoO_x	4	100	none	0.5	200	2	99	96.5	5	5
Ru/C	0.16	6	dodecane	1	140	2	91	98	1	6
Ir/SiO_2	HMF/Ir = 100/1, mole		H_2SO_4	1	60	5	74	24	3	7
Ru-Ir/C	2	90	none	1	120	18	99	99	5	our work

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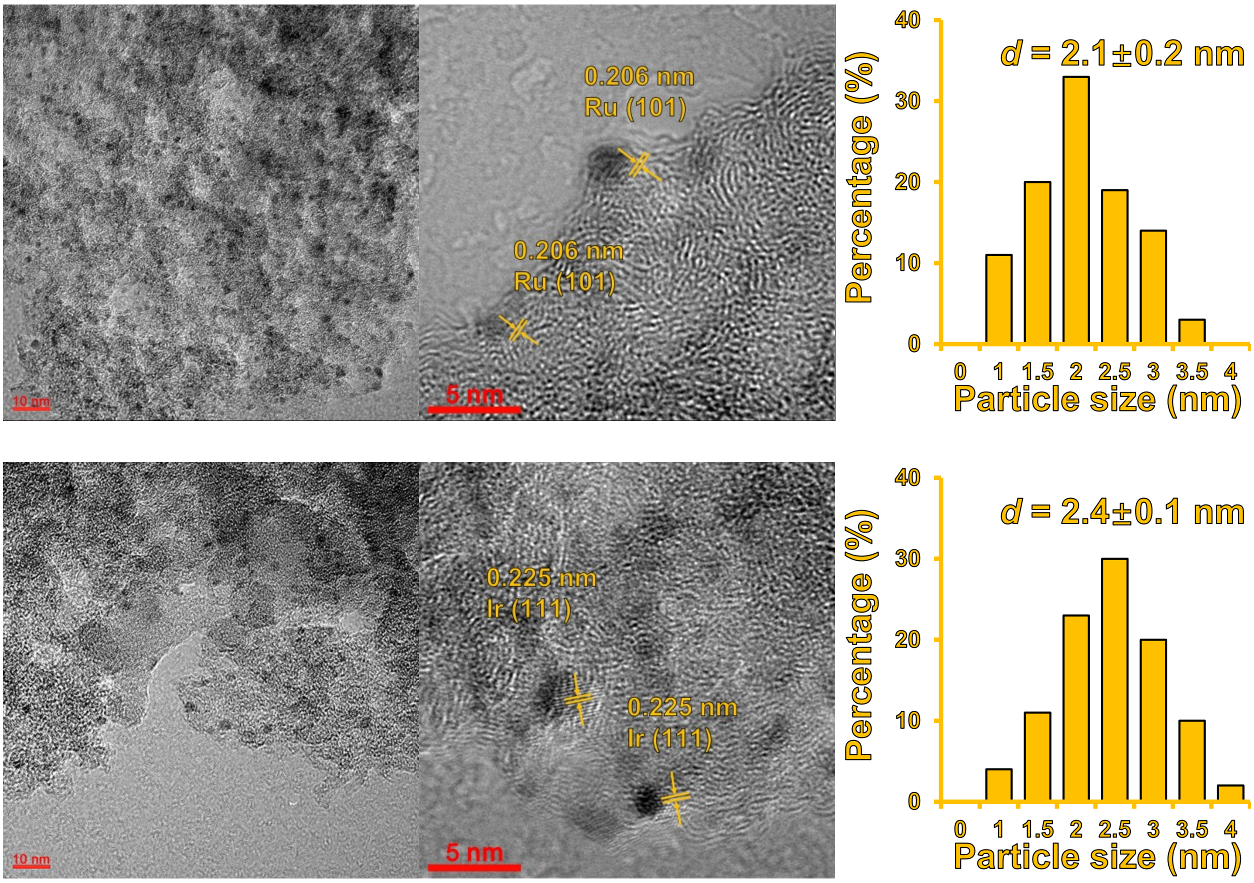

Fig. S1 TEM, HR-TEM images and the corresponding size distributions of supported nanoparticles for (top) Ru/C and (bottom) Ir/C catalysts.

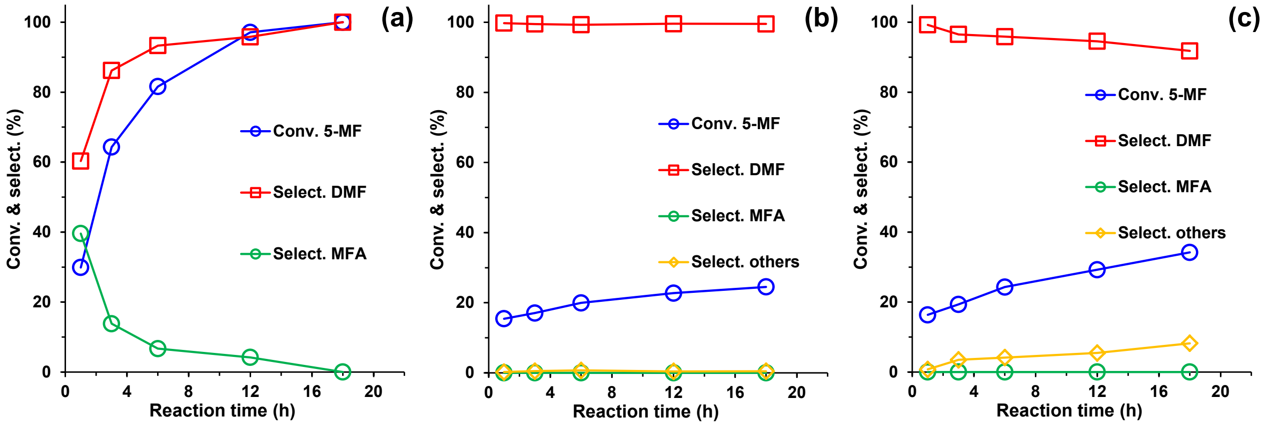

Fig. S2 Conversion of 5-MF and selectivity of products over (a) Ru-Ir/C, (b) Ru/C and (c) Ir/C catalysts during the time-course hydrogenation reaction. Reaction conditions: 5-MF, 2 mmol; catalyst, 90 mg; THF, 10 mL; H_2, 1 MPa; temperature, 120 °C.

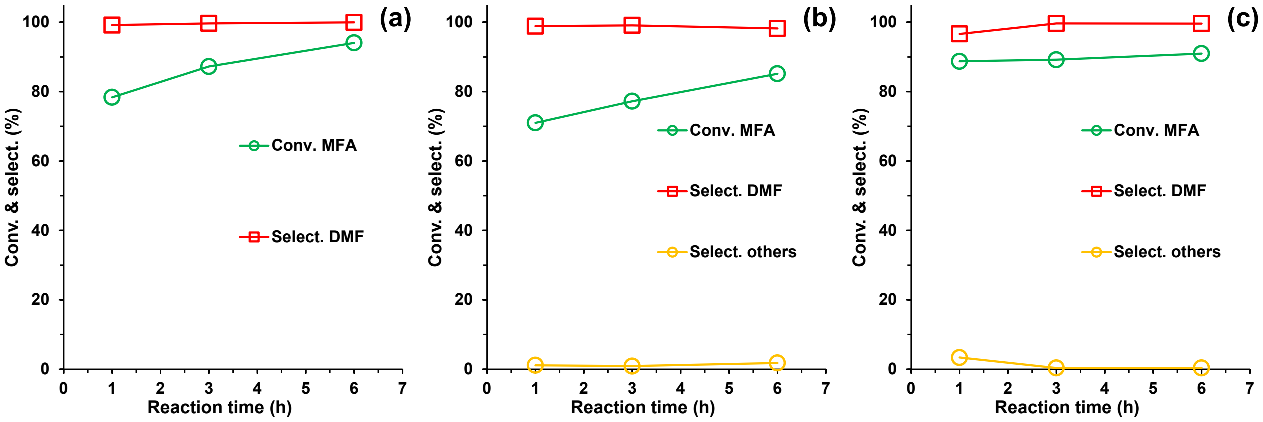

Fig. S3 Conversion of MFA and selectivity of products over (a) Ru-Ir/C, (b) Ru/C and (c) Ir/C catalysts during the time-course hydrogenation reaction. Reaction conditions: MFA, 2 mmol; catalyst, 90 mg; THF, 10 mL; H_2, 1 MPa; temperature, 120 °C.

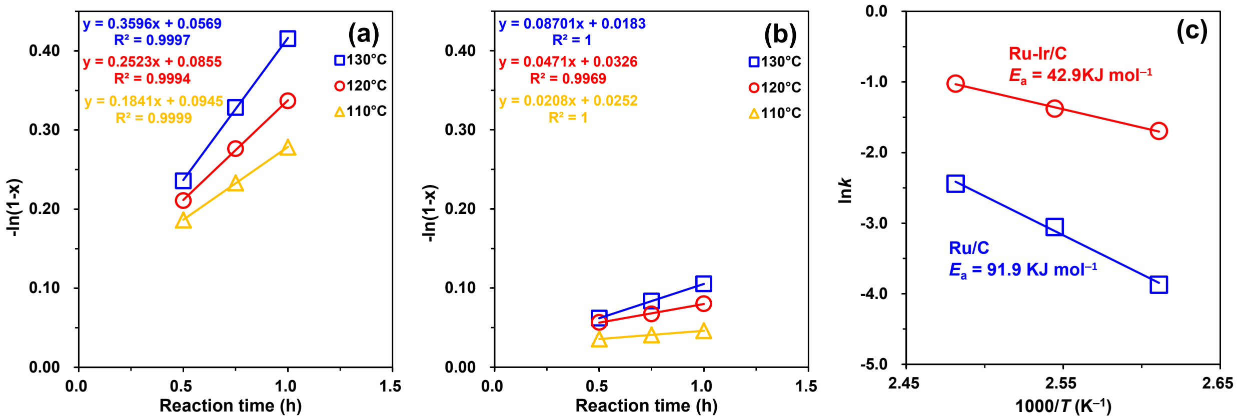

Fig. S4 Kinetic profiles for hydrogenation of HMF over the (a) Ru-Ir/C and (b) Ru/C catalysts. (c) Apparent activation energies (E_a) obtained on the Ru-Ir/C and Ru/C catalysts for hydrogenation of HMF. Reaction conditions: HMF, 2 mmol; catalyst, 90 mg; THF, 10 mL; H_2, 1 MPa; time, 0.5–1 h for (c); temperature, 110–130 °C.

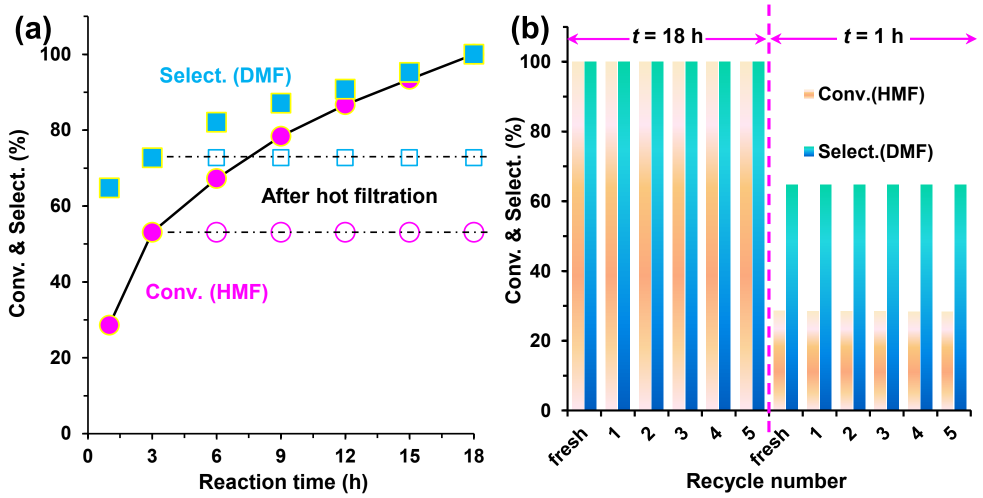

Fig. S5 (a) Leaching test after hot filtration for the Ru-Ir/C catalyst during hydrogenation of HMF. (b) Recycling test under the optimized conditions and within the kinetic-controlled region over the used Ru-Ir/C catalyst for hydrogenation of HMF. Reaction conditions: HMF, 2 mmol; catalyst, 90 mg; THF, 10 mL; H_2, 1 MPa, temperature, 120 °C.

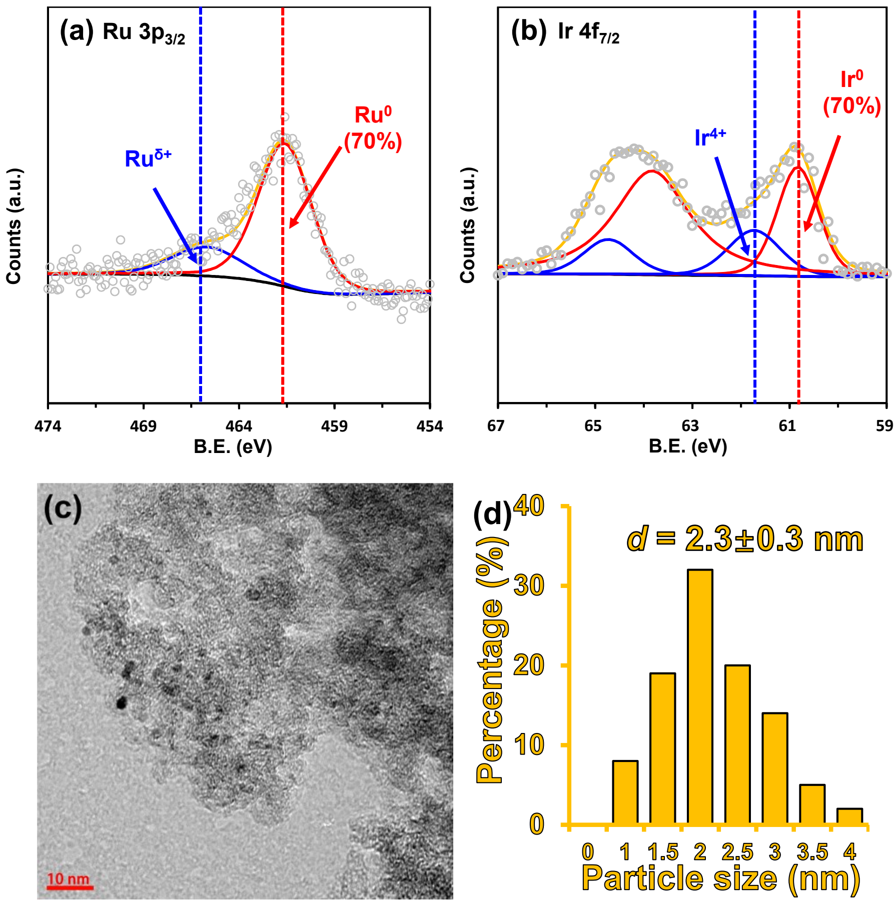

Fig. S6 (a, b) XPS spectra, (c) TEM image and (d) size distribution of the spent Ru-Ir/C catalyst.

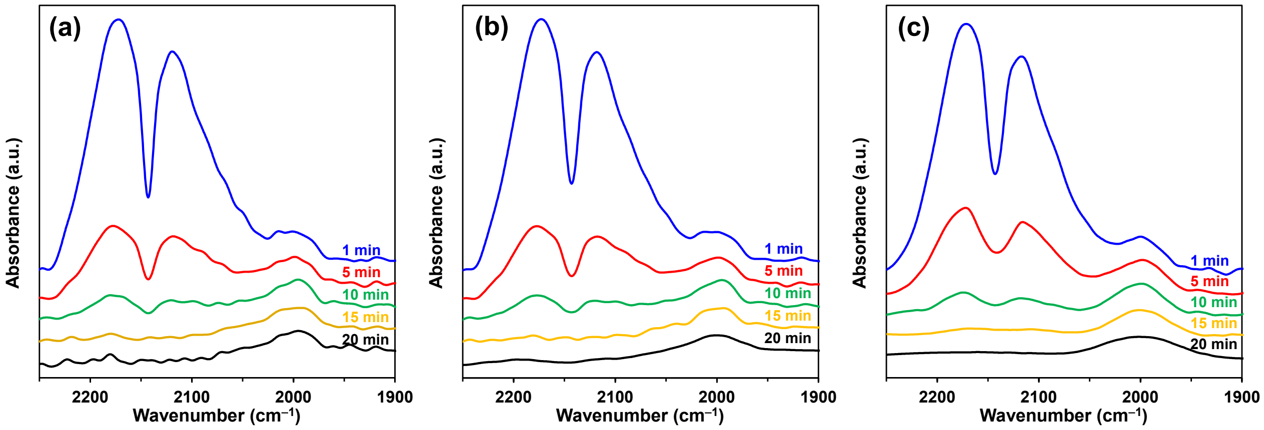

Fig. S7 Time resolved DRIFT-IR spectra of CO adsorption on (a) Ru-Ir/C, (b) Ru/C and (c) Ir/C catalysts. The spectra were recorded during the purge by He flow after CO adsorption at 25 °C for 60 min (see experimental details).