

Supporting information

Physico-chemical characterization of catalysts

To check the integrity of mesoporous structure, low angle X-ray diffraction pattern (XRD) pattern of individual Ru/MCM-41 and Ir/MCM-41 catalysts are shown in Fig. S1. A typical hexagonal structure characteristic of MCM-41¹ was confirmed in each case. Focusing on the catalysts after mixing by different processes (mechanical, chemical and physical) are presented in Fig. S2a-c. In addition, Fig. S2d also presents the XRD pattern of Ru-Ir-PM after reaction. The low angle (1 0 0) reflection at $2\theta=2.400$ ($d_{100}=3.7$ nm) of fresh catalyst was also maintained even after the reaction with a nominal change of $2\theta=2.420$ ($d_{100}=3.6$ nm) suggested the retention of mesoporous structure. Moreover, in the wide-angle region of parent catalyst (Fig. S2; inset) peaks correspond to Ru and Ir oxides at $2\theta=27.8$ (1 1 0), 35.0 (1 0 1), 40.2 (2 0 0) (Ir oxide) and 54.3 (2 1 1) (Ir oxide)² are attributed to the dispersed crystalline particles. In the spectra of spent catalysts, although peaks of Ru oxide ($2\theta=34.9$, 52.0) and Ir⁰ ($2\theta=40.9$)³ were visible no characteristic diffraction of Ru⁰ being detected (Fig. S2; inset). The textural properties of Ru/MCM-41 and Ir/MCM-41 analysed by N₂-adsorption-desorption isotherm shows Type IV isotherm typical of a mesoporous material (not shown). Both the catalysts (Ru/MCM-41 and Ir/MCM-41) possesses relatively large BET surface areas of ~ 815 m²/g and ~ 787 m²/g, respectively. The mean pore size varies from 3.8 to 4.2 nm.

XP spectroscopy studies were conducted to understand the surface oxidation states of Ru and Ir in Ru-Ir-PM before and after the reaction (Fig. S13a-d). It has to be mentioned that Ru

containing catalysts exhibited complex spectra. For the Ru 3d core level spectra of fresh catalyst, peaks located at 280.9 eV is attributed to the primary 5/2 spin-orbit components of RuO₂⁴ (Fig. S13a). However, in the used catalyst another new peak appears at 280.2 eV (3d_{5/2}) along with the peak at 281.0 eV, which suggested the partial reduction of RuO₂ (Fig. S13b). It has to be mentioned that the formation of oxide species from metallic Ru under ambient condition depend on length of exposure in air and calcination-reduction processes as well as particle size.⁵⁻⁸ On the other hand, corresponding Ir 4f spectra are depicted in Fig. S13c, which appears as a doublet and the observed binding energy of 62.2 eV (4f_{7/2}) and 65.2 eV (4f_{5/2}) fits well with the earlier reports on IrO₂ (Fig. S13d).⁴ In contrast, after reaction new doublets assigned to Ir⁰ was detected at 61.03 eV (4f_{7/2}) and 64.01 eV (4f_{5/2})^{9, 10}. Taking into the account of C peak as contamination from sticky tape, all the spectra were de-convoluted using a peak fitting program (Gaussian-Lorentzian), because of the overlapping of C1s peak with Ru 3d peak.

References

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10. Pfeifer *et al.* *Surf. Interface Anal.* **2016**, 48, 261.

Fig. S1: Low angle XRD pattern of (a) Ru/MCM-41 and Ir/MCM-41 catalysts.

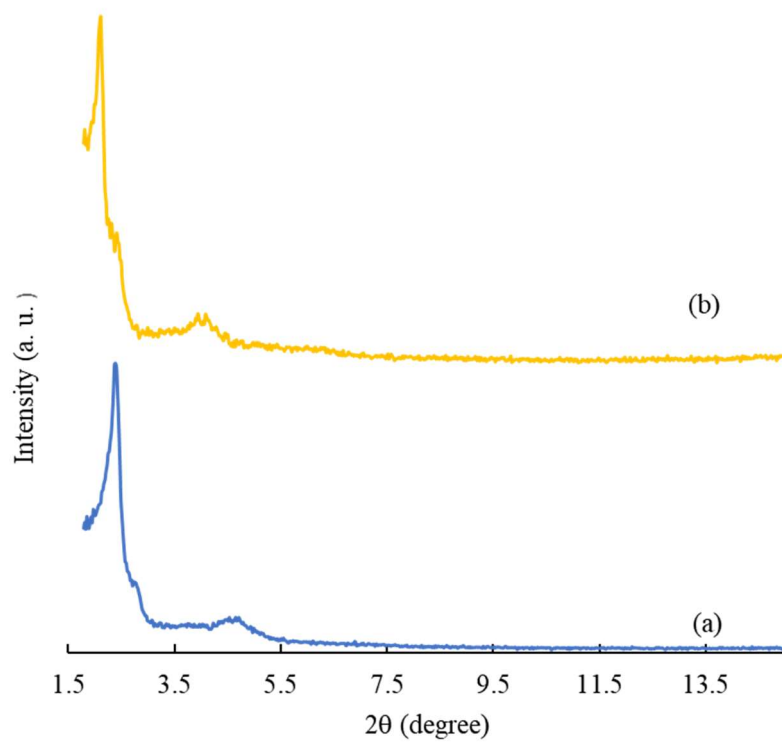


Fig. S2: Low angle XRD pattern of mechanically (a), chemically (b) and Ru-Ir-PM catalysts; (c) before and (d) after reaction. Inset shows wide angle spectra of Ru-Ir-PM catalysts.

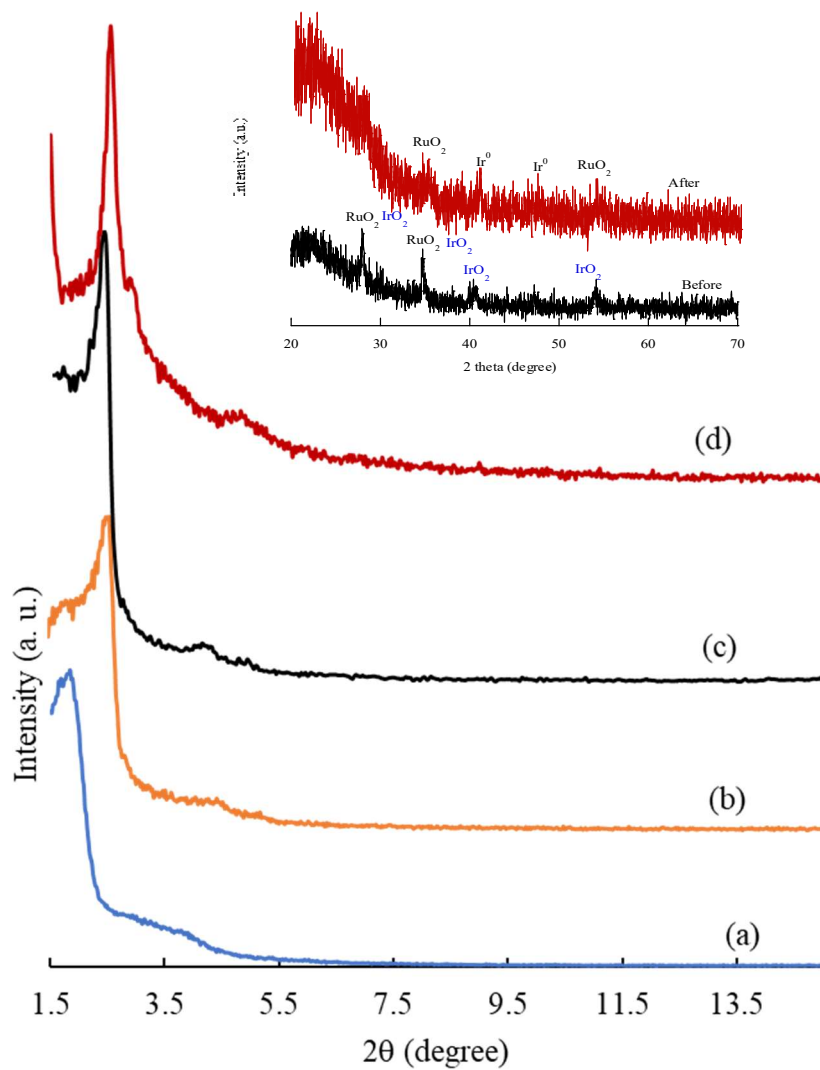


Fig. S3: HAADF-STEM images of individual catalysts (a) Ru/MCM-41, (b) Ir/MCM-41 and their corresponding particle size distributions.

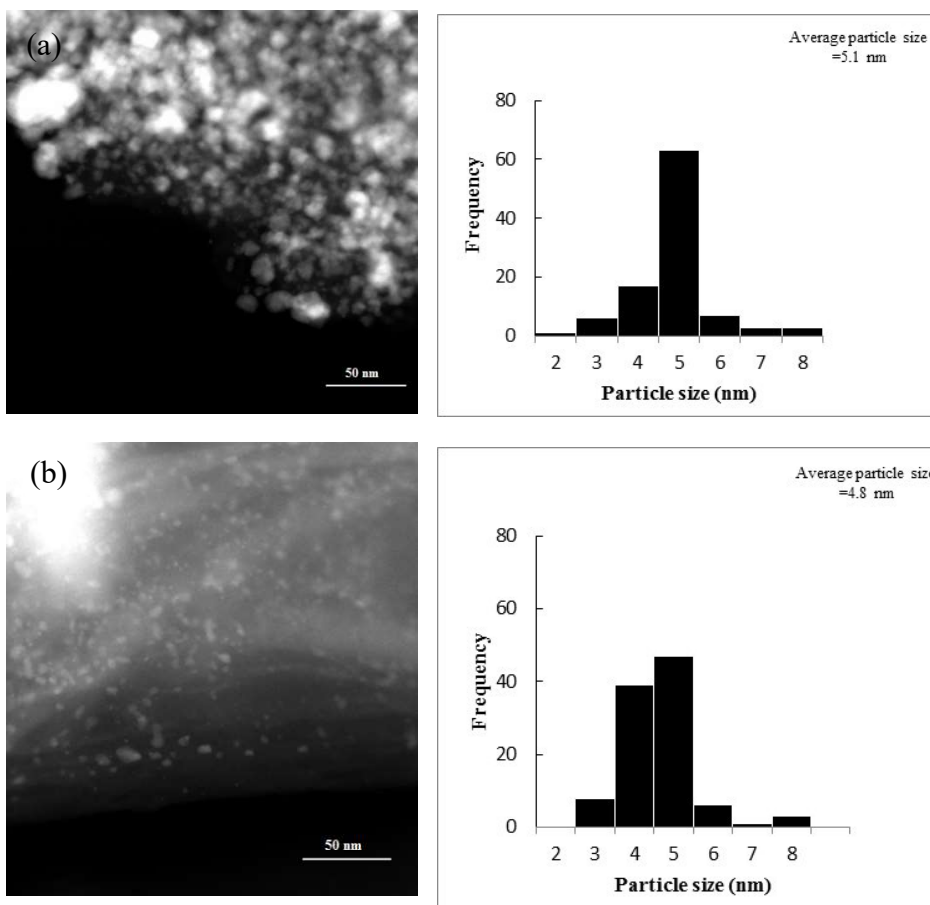


Fig. S4: HAADF-STEM images, electron mapping and the corresponding EDS spectra of **mechanically mixed** catalyst. (a) HAADF images in black and white alongside with corresponding particle size distributions. Elemental mapping of (b) Ru (red), (c) Ir (turquoise), (d) Si (green) and (e) Ir-Ru. (f) EDS of two different regions of Ir-Ru.

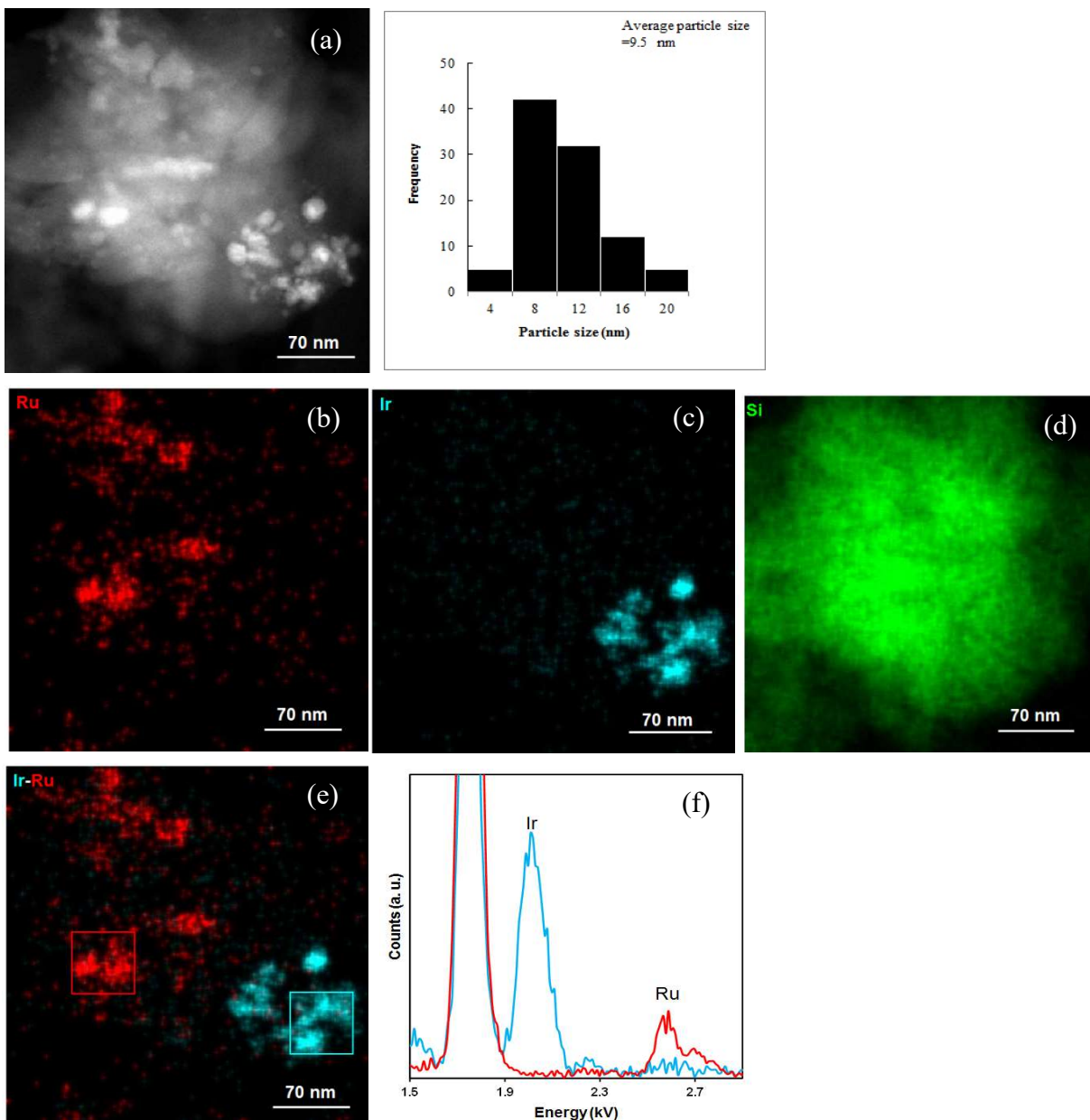


Fig. S5: HAADF-STEM images, electron mapping and the corresponding EDS spectra of **chemically mixed** catalyst. HAADF image in black and white alongside with corresponding particle size distributions Elemental mapping of (b) Ru (red), (c) Ir (turquoise), (d) Si (green) and (e) Ir-Ru. (f) EDS of specified regions of Ir-Ru.

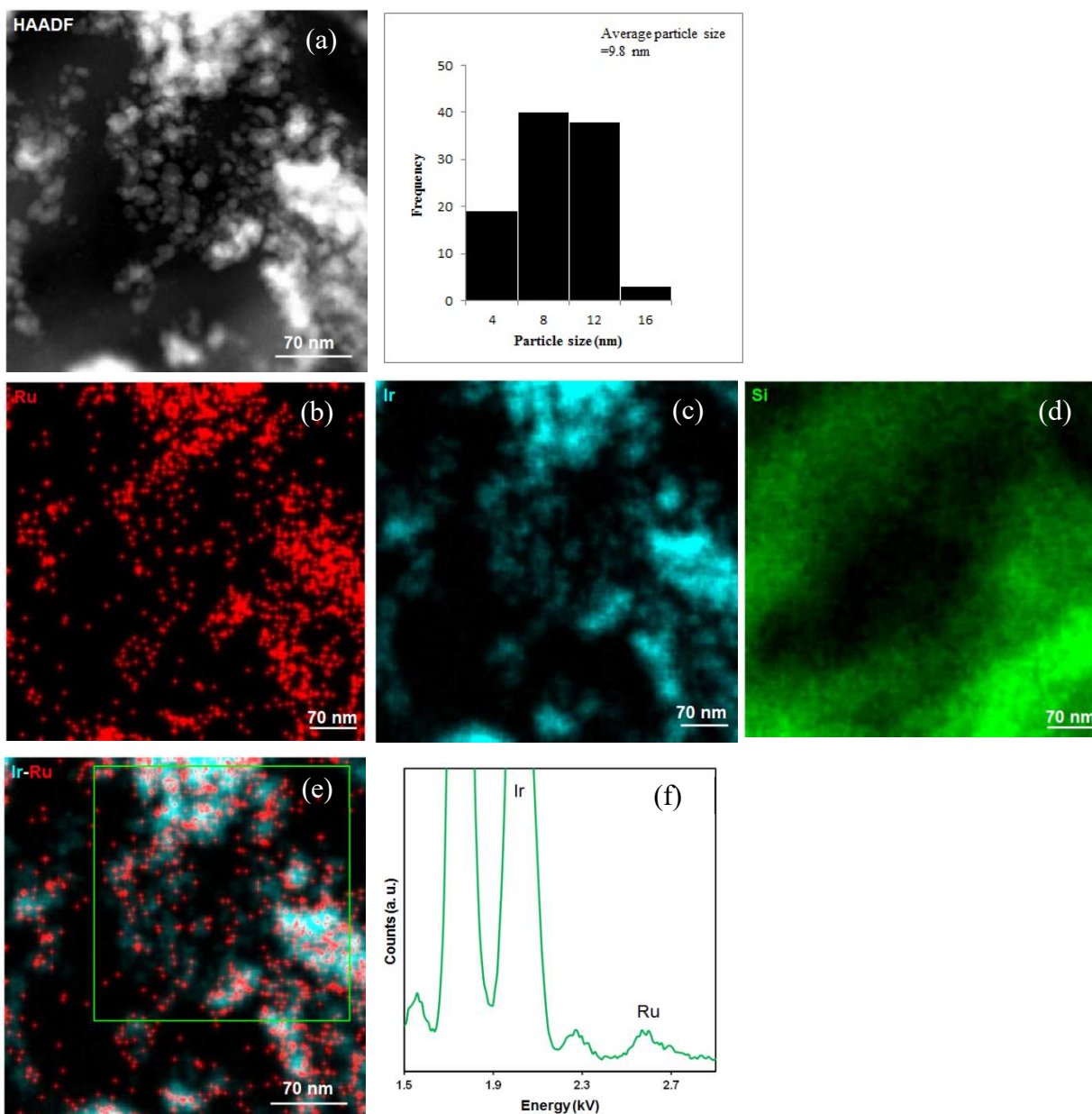


Fig. S6: Mass spectra of (a) condensable liquid products collected after reaching the steady state of the reaction on Ru-Ir-PM and validation with (b) standard.

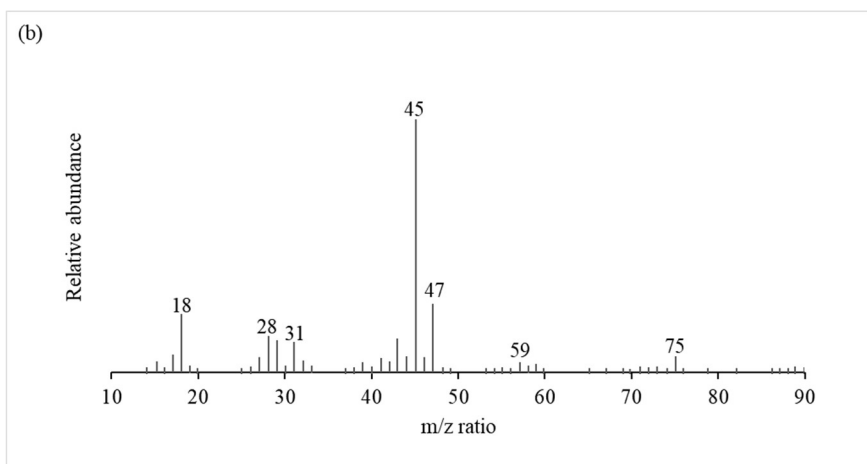
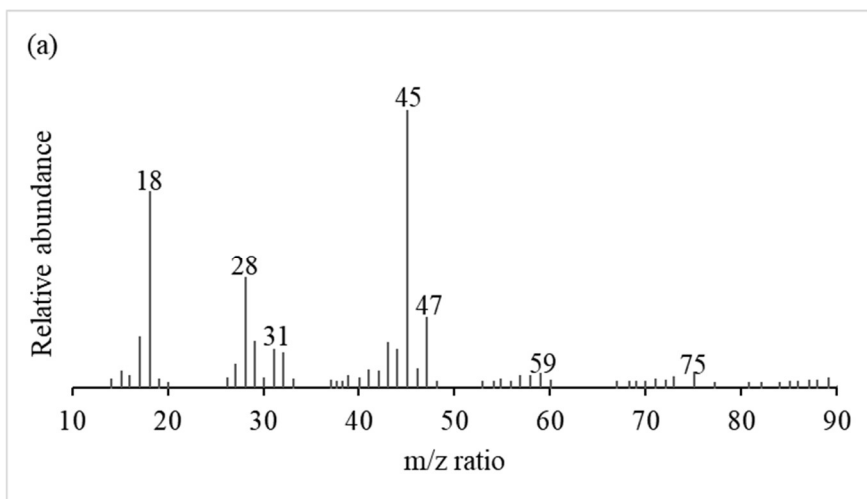


Fig. S7: ^1H NMR spectra of condensable liquid product in D_2O . Spectra were referenced to the solvent peak of an internal capillary reference solution. Resonances are assigned and labelled according to the numbered positions in the drawing of PGME as shown in the inset.

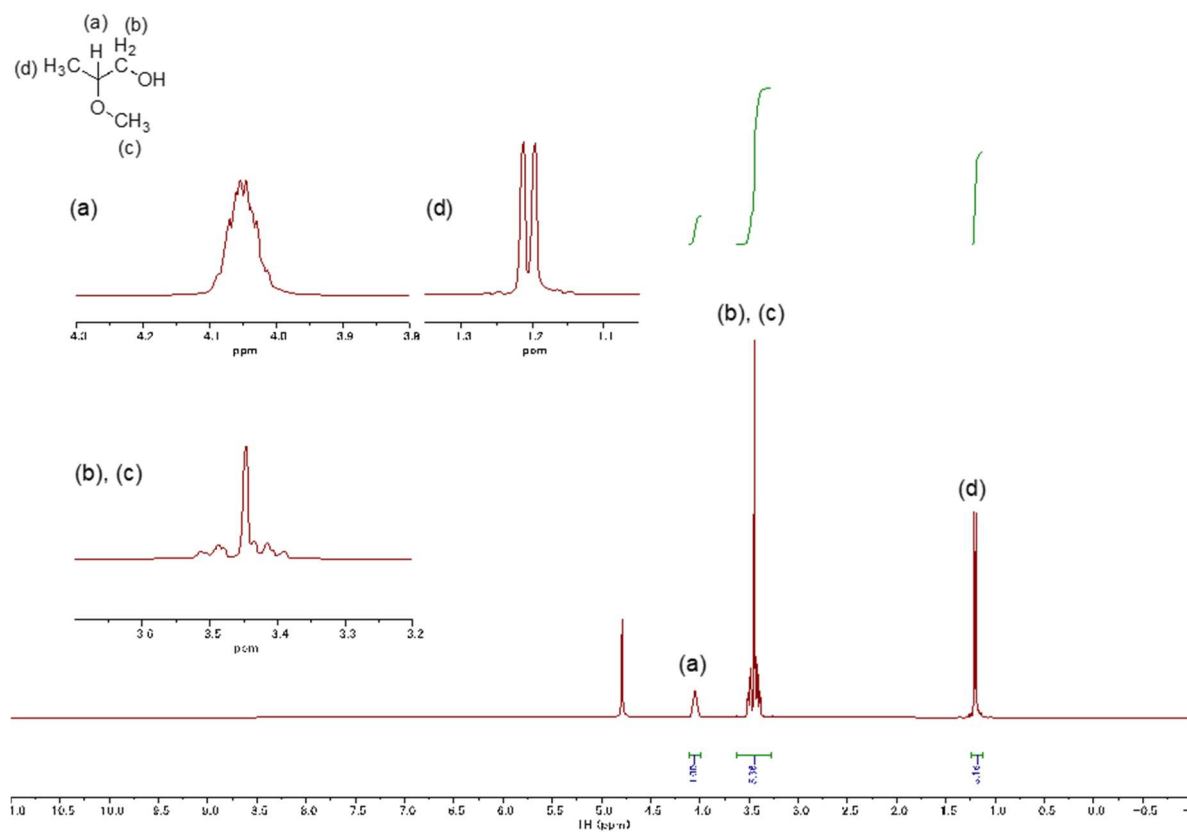


Fig. S8: ^{13}C NMR spectra of condensable liquid product in D_2O . Spectra were referenced to the solvent peak. Resonances are assigned and labelled according to the numbered positions in the drawing of PGME as shown in the inset.

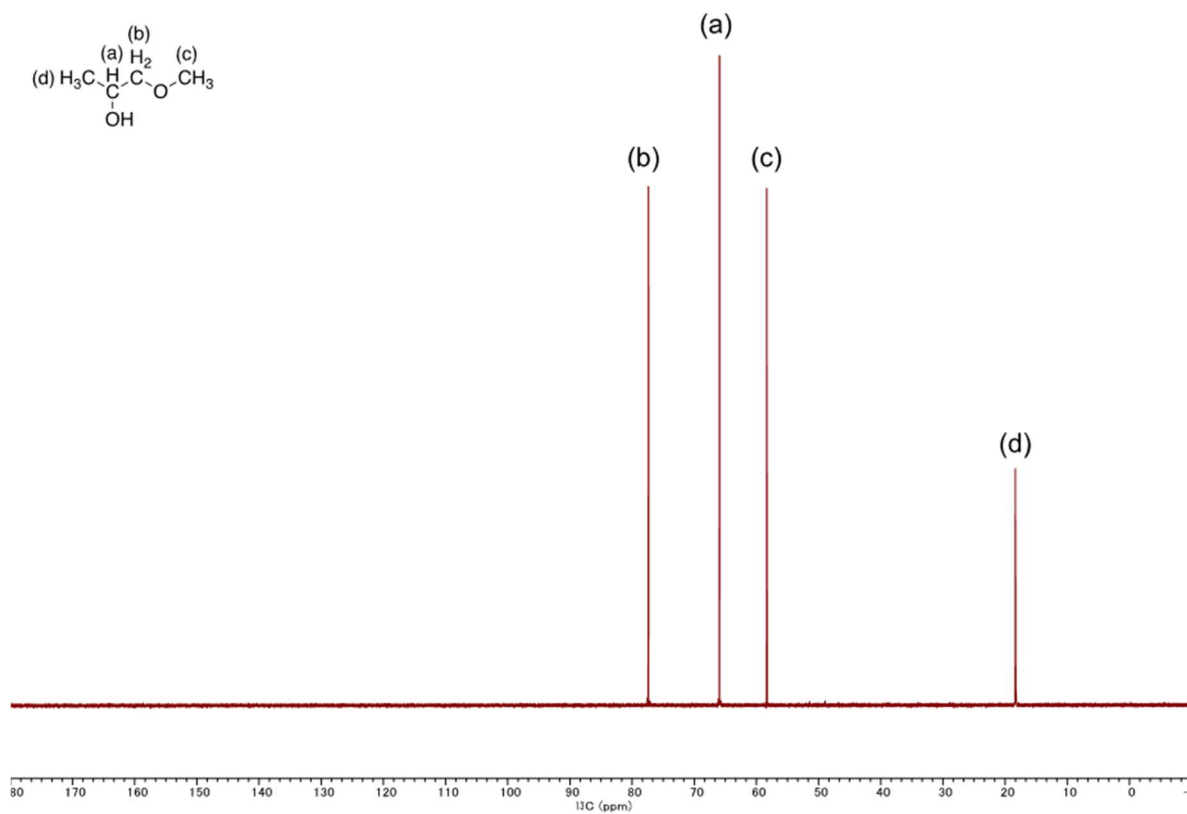


Fig. S9: Different phases of CO₂ in presence of hydrogen at 150 °C depending on total pressure (a) 8 MPa; (b) 12 MPa; (c) 14 MPa; (d) 16 MPa and (e) 20 MPa. The cell was pressurized with hydrogen (4 MPa) and completed with CO₂ to the desired pressure.

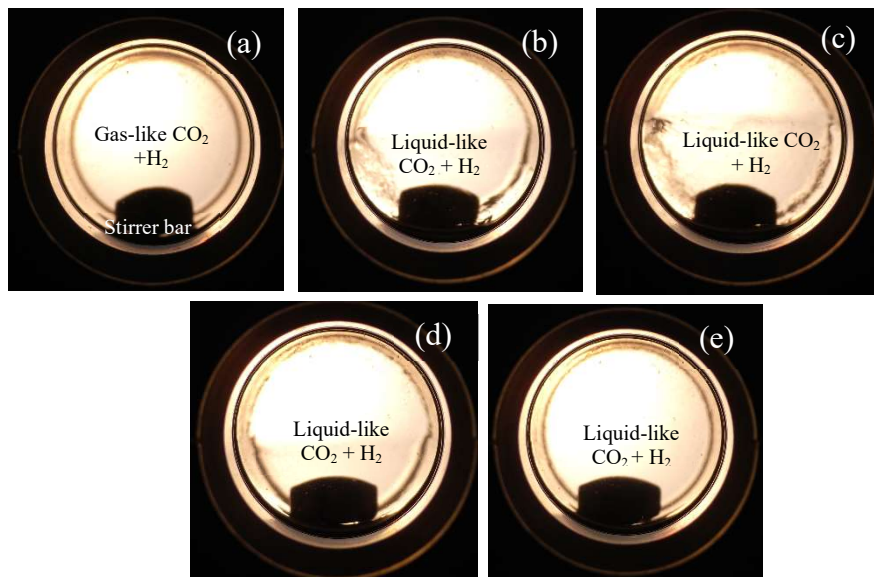


Fig. S10: Gas analysis spectra obtained with different P_{H_2}/P_{CO_2} ratios (a) 0.33 and (b) 0.6 shows methane (CH_4) as confirmed with standard. N_2 and O_2 are from air. In each case large CO_2 peak has been omitted for clarity.

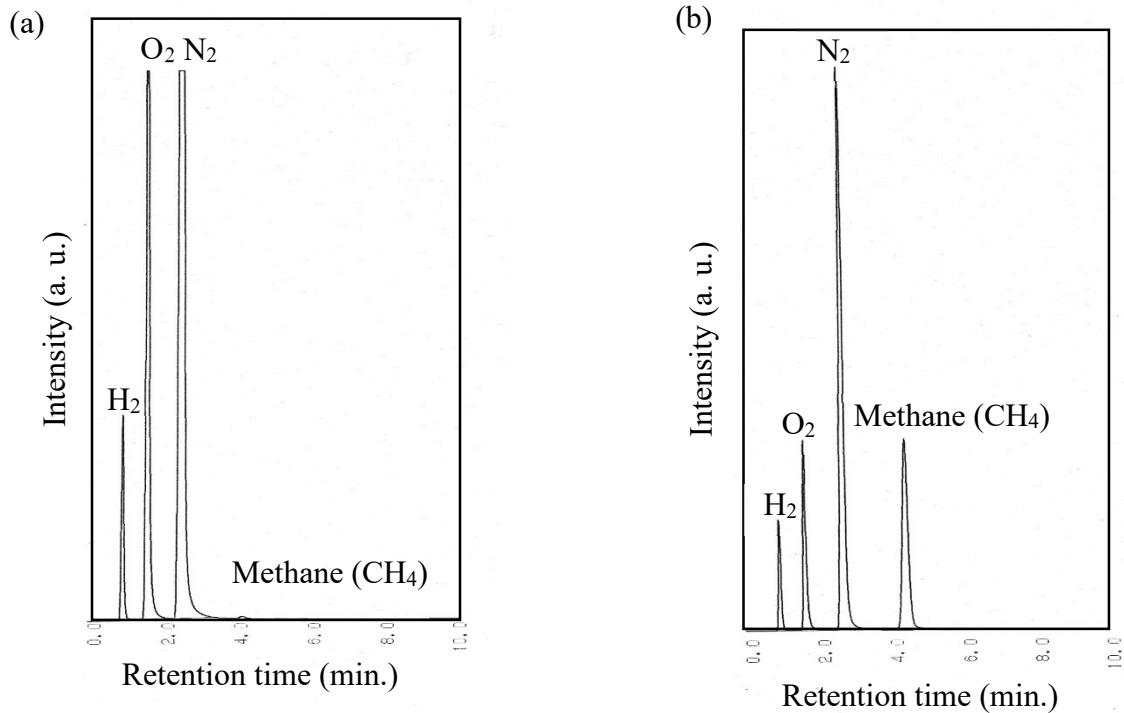


Fig. S11: Plot of methane concentration obtained from the analysis of gaseous product as a function of reaction time.

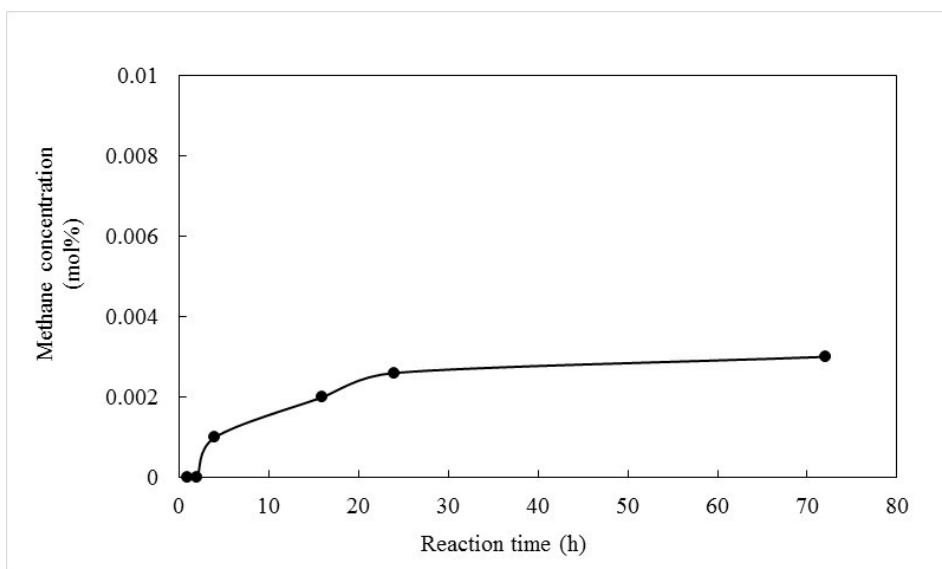


Fig. S12: Time profile of CO₂ transformation on (a) mechanically and (b) chemically mixed catalysts. Reaction conditions: catalysts=0.1g, temperature=150 °C and total pressure=16 MPa (P_{H₂}= 4 MPa rest is CO₂). Each experimental result are average values from three measurements with a reproducibility of ± 10 %

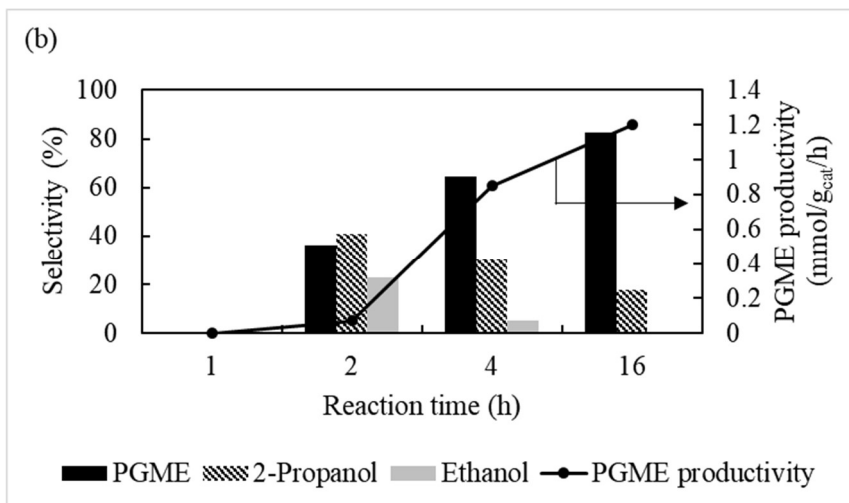
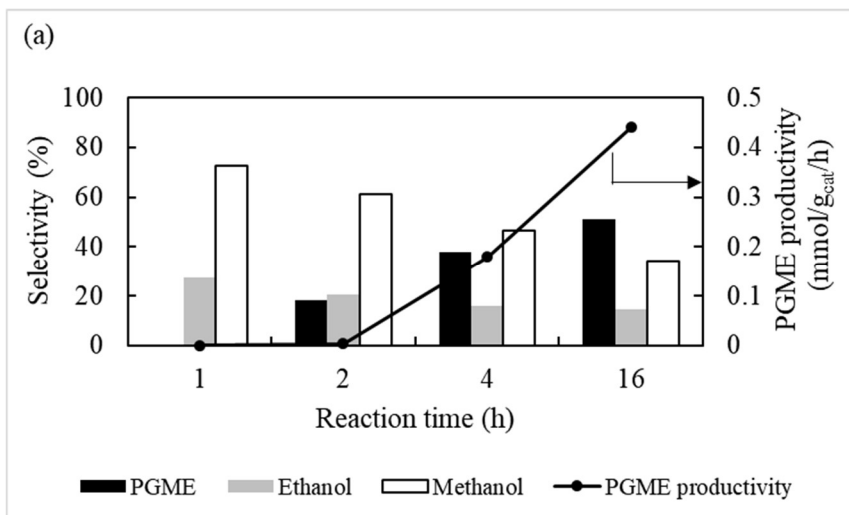


Fig. S13: XPS spectra of Ru-Ir-PM before and after CO₂ hydrogenation. Spectra of Ru 3d and Ir 4f are represented by (a, b) and (c, d), respectively.

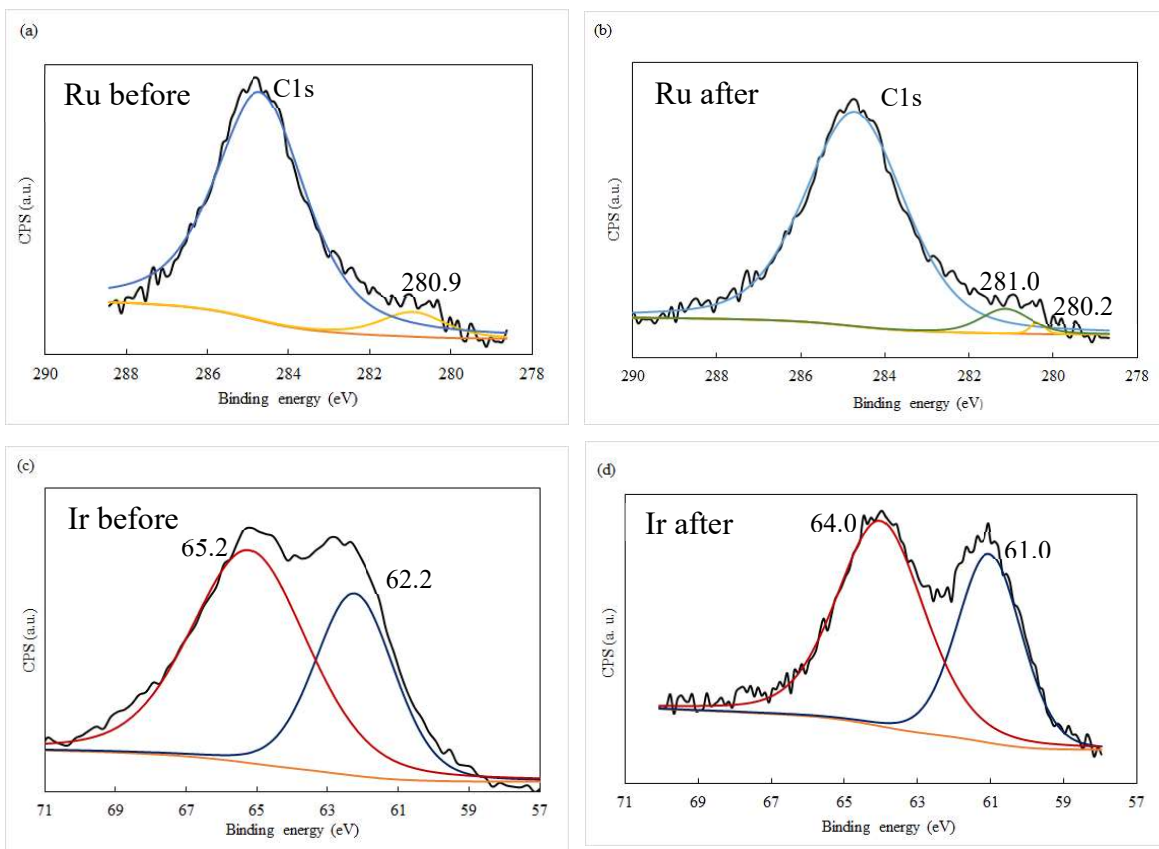


Fig. S14: Optimized structures of final states in each reaction steps on RuO₂ (left), IrO₂ (2nd), Ru⁰ (3rd) and Ir⁰ (right) of each column, where, oxygen= red, carbon= gray, hydrogen= white, Ru= teal and Ir= blue.

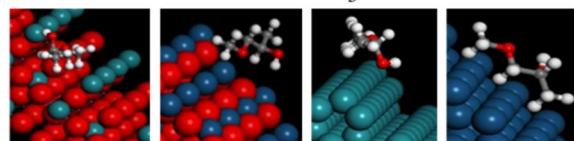
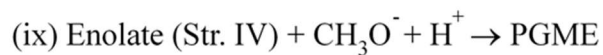
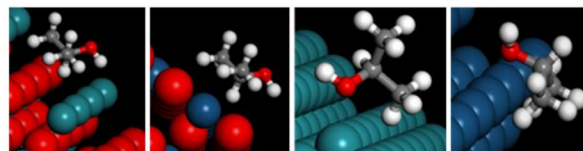
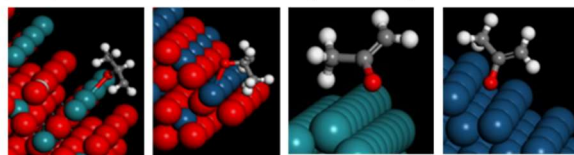
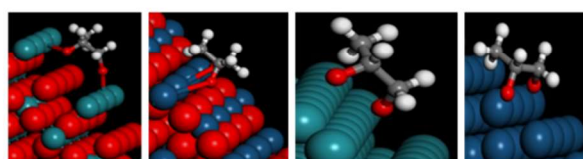
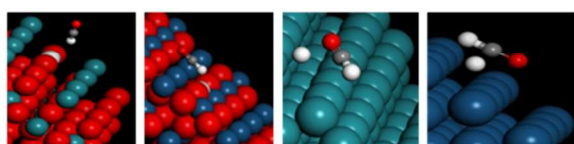
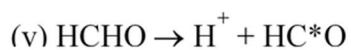
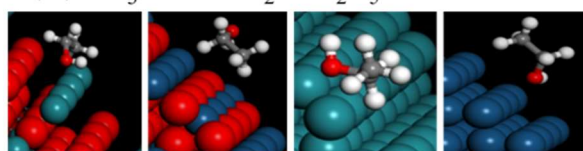
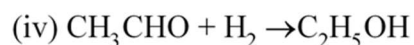
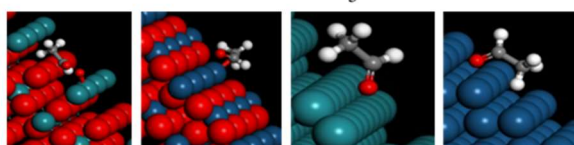
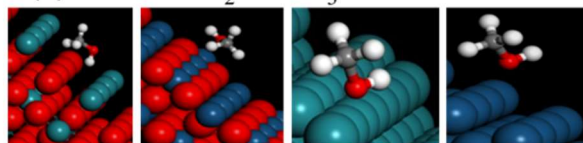
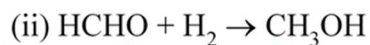
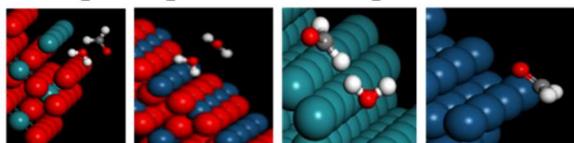


Fig. S15: Transition state of each reaction steps presented in Table S2. From the left RuO₂ (left), Ru⁰ (2nd) IrO₂ (3rd), and Ir⁰ (right), where, oxygen= red, carbon= gray, hydrogen= white, Ru= teal and Ir= blue.

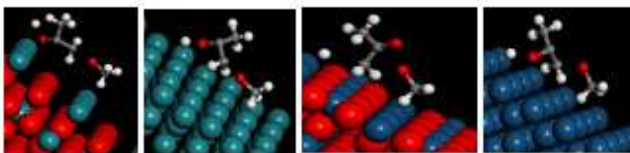
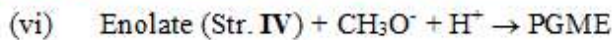
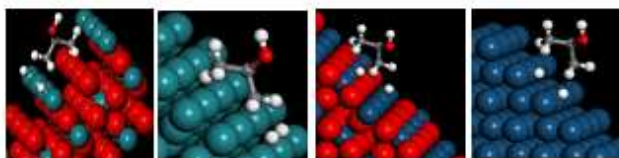
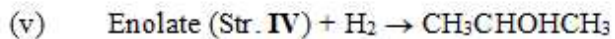
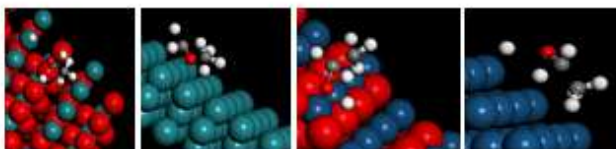
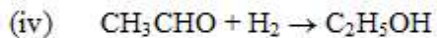
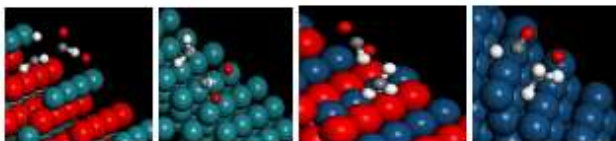
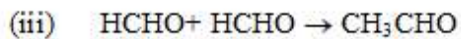
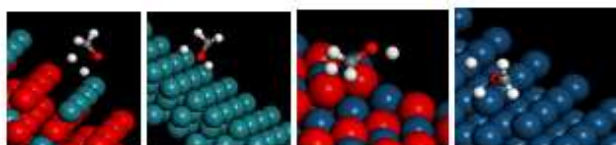
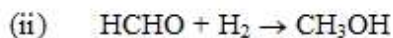
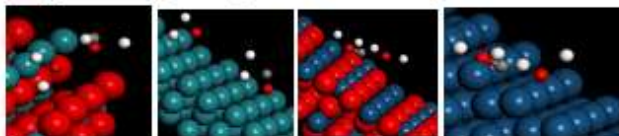
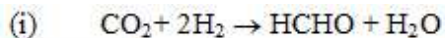


Fig. S16: Experimental setup used for CO₂ hydrogenation. (a) Reactor and view cell, (b) inside the oven, where autoclave was placed on a magnetic stirrer for continuous stirring the content during the reaction, (c) details of autoclave and (d) view cell detail. BPR=back pressure regulator.

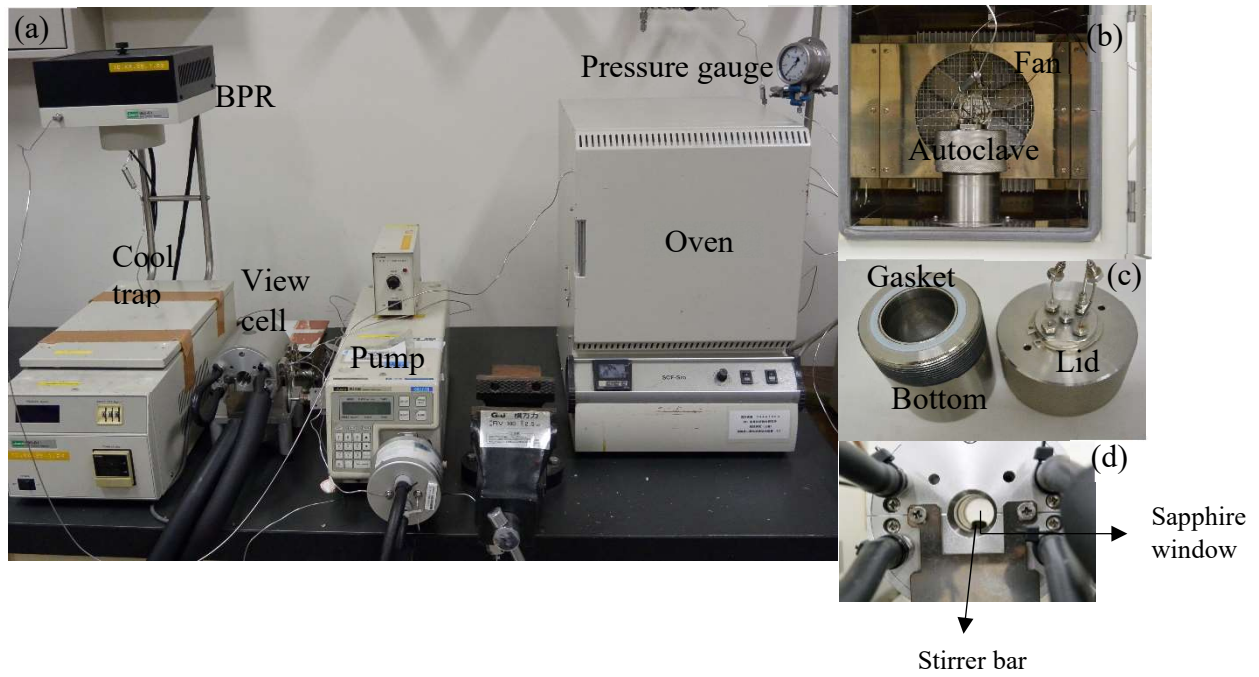


Table S1: Control experiments with different probe compounds under the present reaction conditions.

Entry	Probe	Product selectivity (%)						
		Methanol	Ethanol	IPA	PGME	EtOAc	PrOAc	Other
1	Methanol	-	-	-	100	-	-	-
2	Ethanol	-	-	-	20.6	-	-	79.4 ^a
3	2-Propanol	-	-	-	-	-	100.0	-
4	HCHO	97.5	2.5	-	-	-	-	-
5 ^b	CO	-	-	-	-	-	-	-
6	CH ₃ CHO	-	59.3	21.3	-	10.0	-	9.4 ^a

Reaction conditions: Ru-Ir-PM=0.1g, total pressure =16 MPa (The cell was pressurized with 4 MPa H₂ and completed with CO₂ to the desired pressure); temperature=150 °C, reaction time=16h, probe compounds=10 mmol.

IPA= 2-Propanol; PGME= Propylene glycol methyl ether; EtOAc= ethyl acetate; PrOAc=2-propyl acetate.

^adiethoxy ethane ^bP_{CO}=0.2 MPa

Table S2: Calculated activation energies of the experimentally derived compounds.

Reaction	Activation energy (eV)			
	RuO ₂	Ru ⁰	IrO ₂	Ir ⁰
(i) CO ₂ + 2H ₂ → HCHO + H ₂ O	0.39	0.46	0.59	0.57
(ii) HCHO + H ₂ → CH ₃ OH	0.8	0.68	1.1	1.0
(iii) HCHO+ HCHO→ CH ₃ CHO	0.49	0.51	0.33	0.38
(iv) CH ₃ CHO + H ₂ →C ₂ H ₅ OH	0.46	0.68	0.80	0.92
(v) Enolate (Str. IV) → CH ₃ CHOHCH ₃	0.71	0.53	0.48	0.44
(vi)Enolate (Str. IV) + CH ₃ O ⁻ + H ⁺ →PGME	0.39	0.57	0.79	0.70