

SUPPLEMENTARY INFORMATION

# Evaluation of Au/ZrO<sub>2</sub> Catalysts Prepared via Postsynthesis Methods in CO<sub>2</sub> Hydrogenation to Methanol

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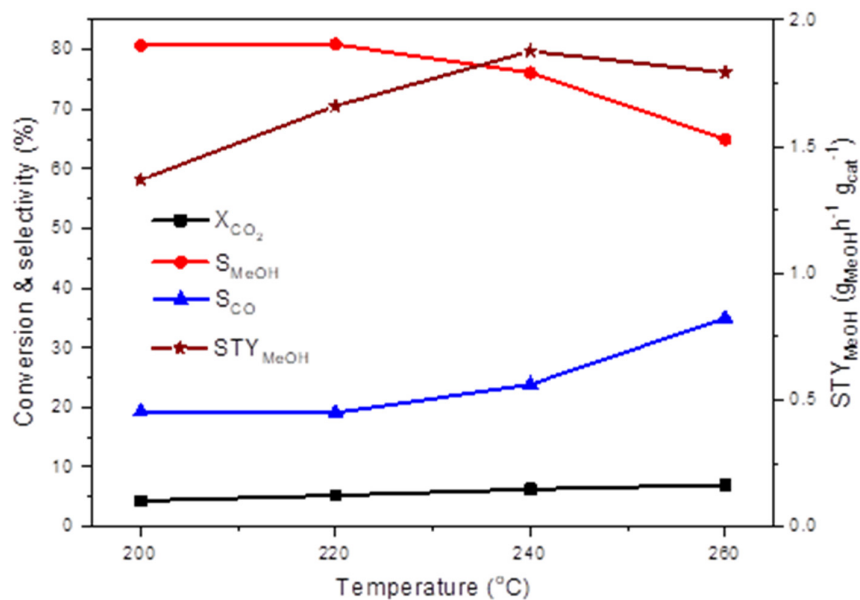
**Table S1.** Comparison of performance of Au/ZrO<sub>2</sub> solids examined in this study with the reported Au supported ZrO<sub>2</sub> and modified ZrO<sub>2</sub> catalysts for CO<sub>2</sub> hydrogenation to methanol.

Catalyst	Reaction Conditions	$x(\text{CO}_2)$ (%)	$s(\text{CH}_3\text{OH})$ (%)	STY( $\text{CH}_3\text{OH}$ ) ( $\text{g}_{\text{MeOH}} \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$ )	Ref.
<sup>a</sup> Au(0.5 wt.%)/ZrO <sub>2</sub>	240°C, 40 bar	6	72.5	1.6	This work
<sup>a</sup> Au(1 wt.%)/ZrO <sub>2</sub>	240°C, 40 bar, WHSV=120000 $\text{cm}^3 \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$	7	71.5	1.9	This work
Au(3 wt.%)/ZrO <sub>2</sub>	220°C, 5 bar	5	5	-	[1]
Au(1 wt.%)/ZrO <sub>2</sub>	180°C, 45 bar		73	-	[2]
Au(10 at.%)/3ZnO/ZrO <sub>2</sub>	220°C, 80 bar, GHSV=10000 $\text{h}^{-1}$	2	100	0.01	[3]
Au/In <sub>2</sub> O <sub>3</sub> -ZrO <sub>2</sub>	300°C, 50 bar, GHSV=21000 $\text{cm}^3 \text{h}^{-1} \text{g}_{\text{cat}}^{-1}$	14	70	0.5	[4]

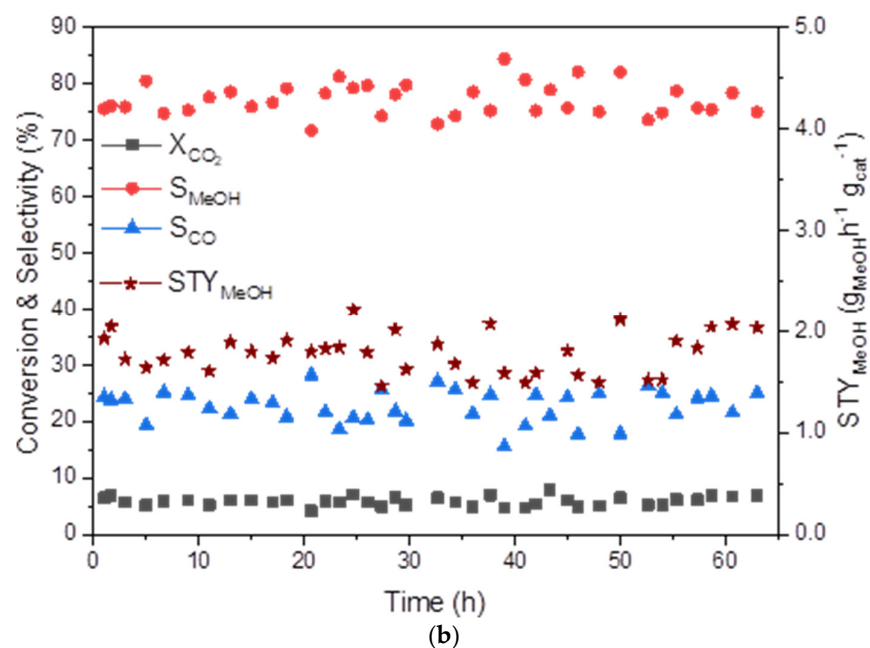
<sup>a</sup>These catalysts were prepared by means of the deposition precipitation method.

**Table S2.** Relative atomic and relative weight surface concentration for the ZrO<sub>2</sub> support and Au/ZrO<sub>2</sub> catalysts calculated based on the measured high-resolution XPS spectra.

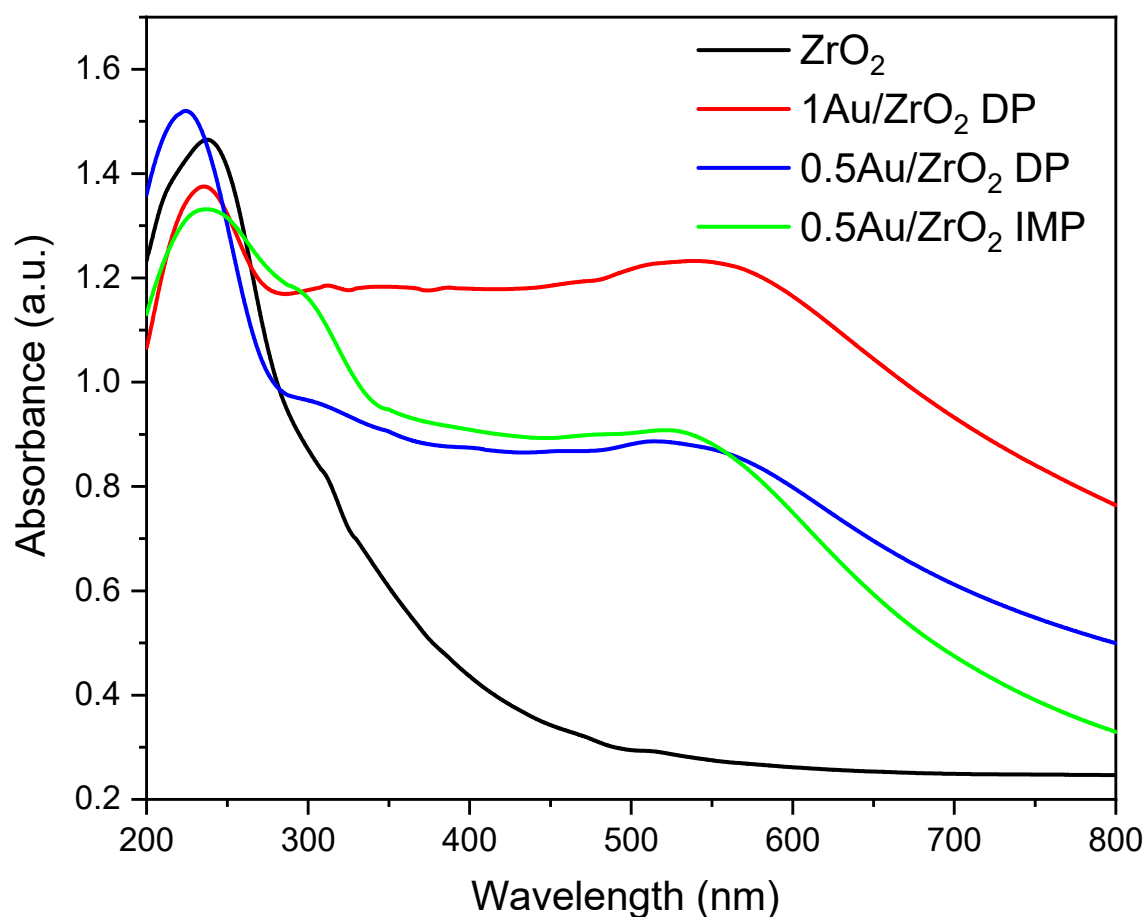
Sample	C		Zr		O		Au	
	Rel. at. conc. (%)	Rel. wt. conc. (%)	Rel. at. conc. (%)	Rel. wt. conc. (%)	Rel. at. conc. (%)	Rel. wt. conc. (%)	Rel. at. conc. (%)	Rel. wt. conc. (%)
ZrO <sub>2</sub>	13.4	4.7	24.7	66.2	61.9	29.1	-	-
0.5Au/ZrO <sub>2</sub> DP	15.4	5.3	25.3	66.7	59.2	27.4	0.1	0.5
1Au/ZrO <sub>2</sub> DP	14.0	4.7	25.9	66.1	59.6	26.6	0.5	2.5
0.5Au/ZrO <sub>2</sub> IMP	12.6	4.2	26.5	67.8	60.8	27.3	0.1	0.6



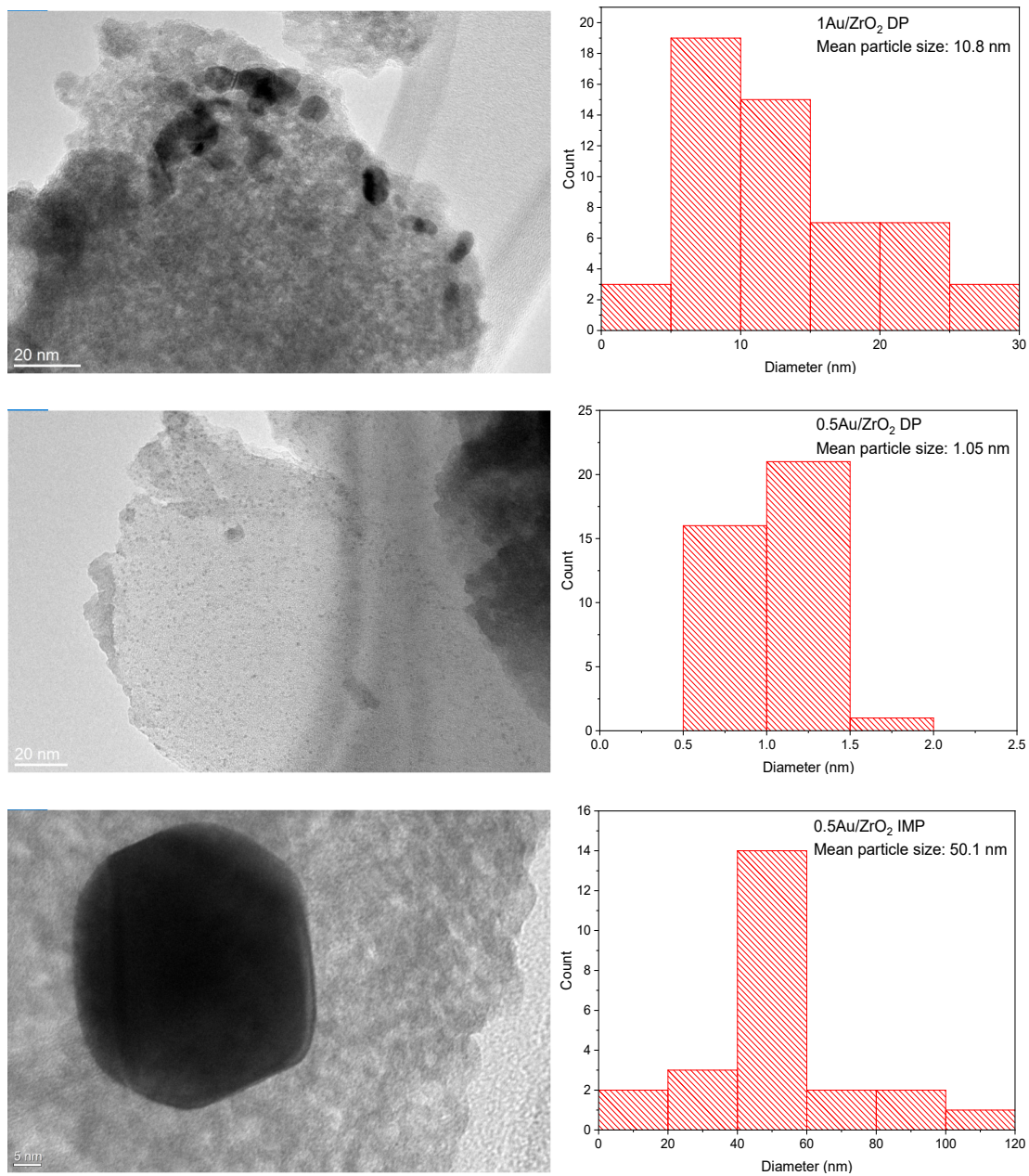
(a)



**Figure S1.** a) Catalytic activity of 0.5Au/ZrO<sub>2</sub> DP catalyst obtained at different temperatures, and b) results of the stability test carried out at 240°C. Operating conditions: P<sub>tot</sub>=50 bar, catalyst weight: 50 mg (homogeneously mixed with 200 mg of SiC), gas flow rate: 100 ml/min, composition of the feed gas stream: 24 vol.% CO<sub>2</sub>, 72 vol.% H<sub>2</sub> (balanced with N<sub>2</sub>).



**Figure S2.** UV-Vis DR spectra of ZrO<sub>2</sub> support and Au/ZrO<sub>2</sub> deposition precipitation/impregnation catalysts after reduction.



**Figure S3.** TEM images of Au/ZrO<sub>2</sub> deposition precipitation/impregnation catalysts after reduction.

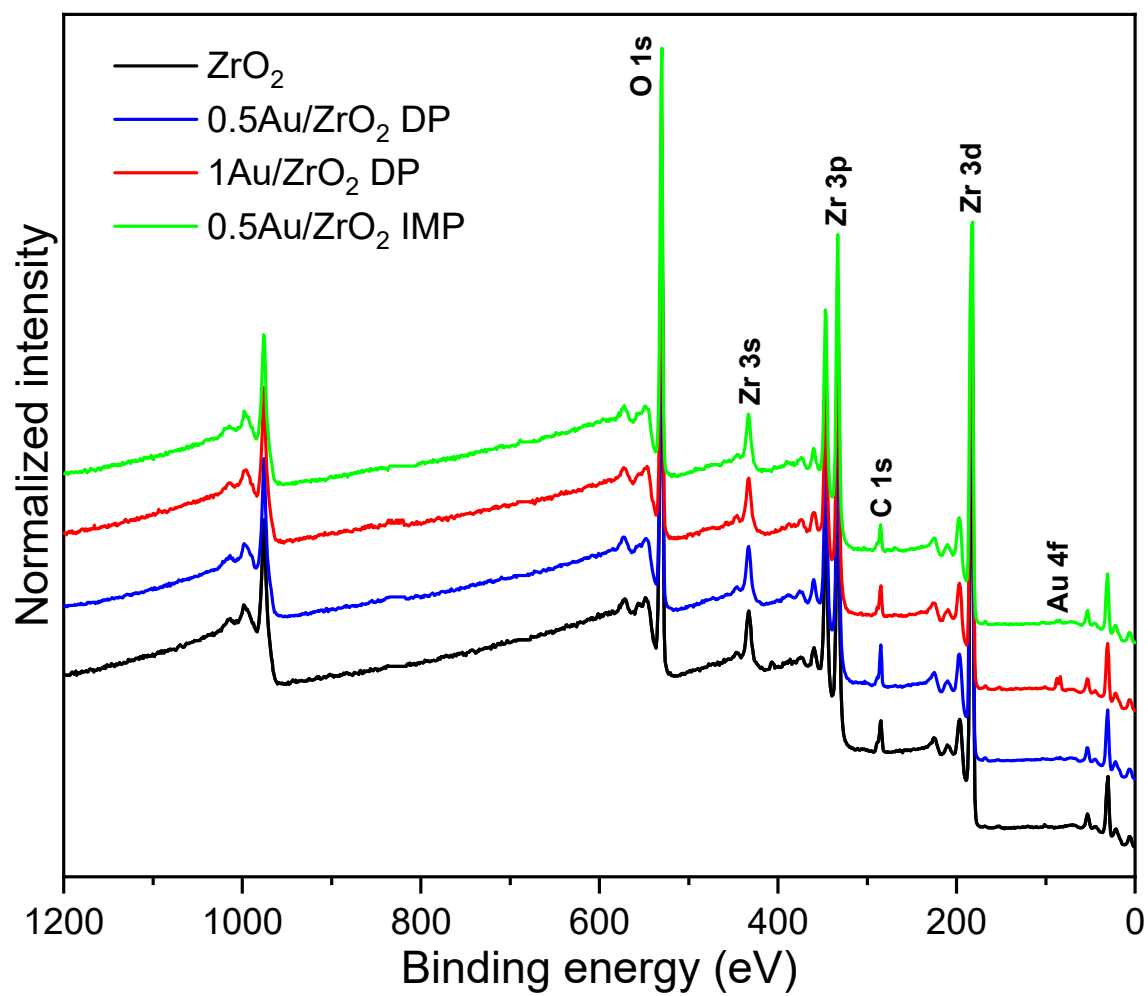
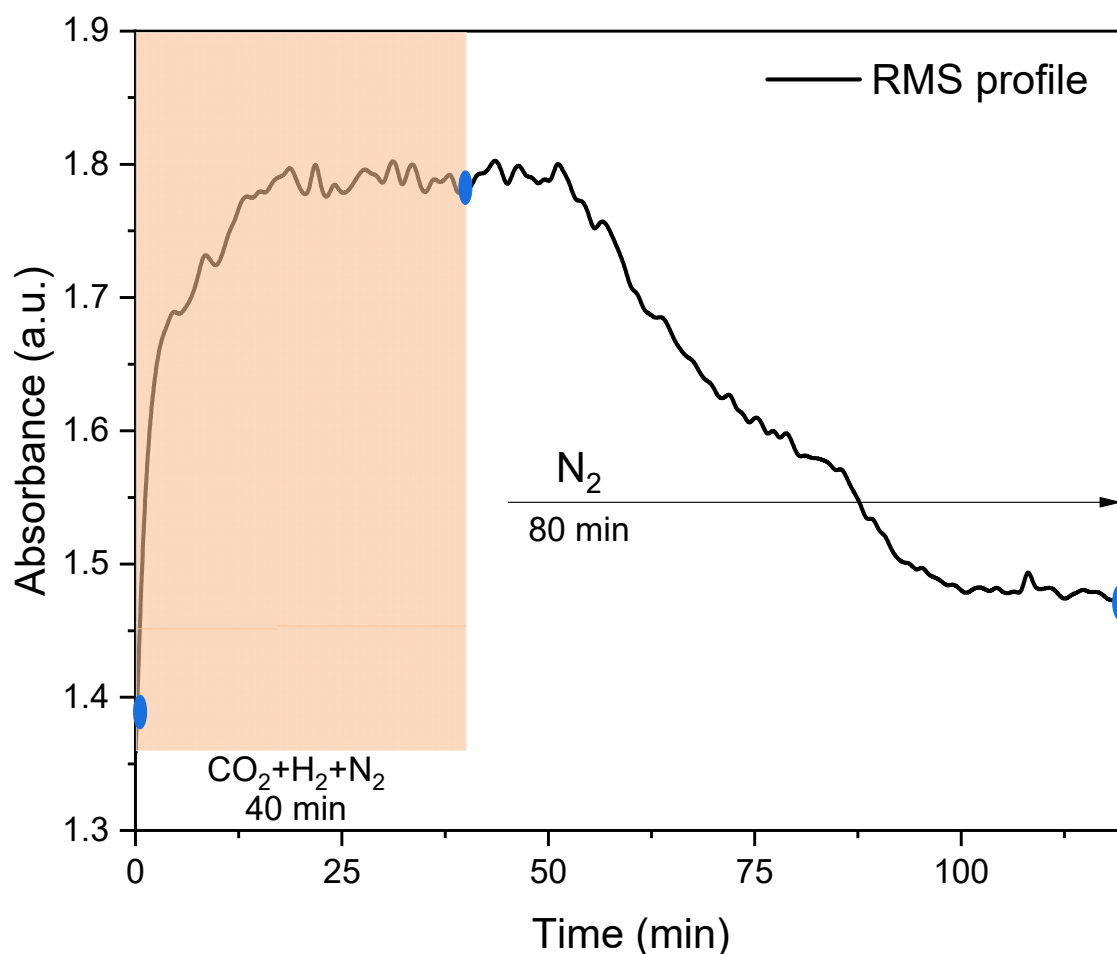


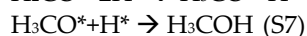
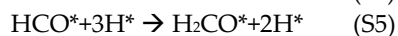
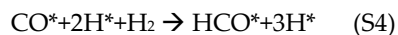
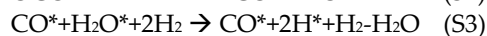
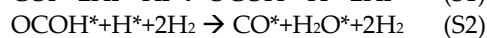
Figure S4. XPS survey spectra measured for the  $\text{ZrO}_2$  support and  $\text{Au/ZrO}_2$  catalyst samples.

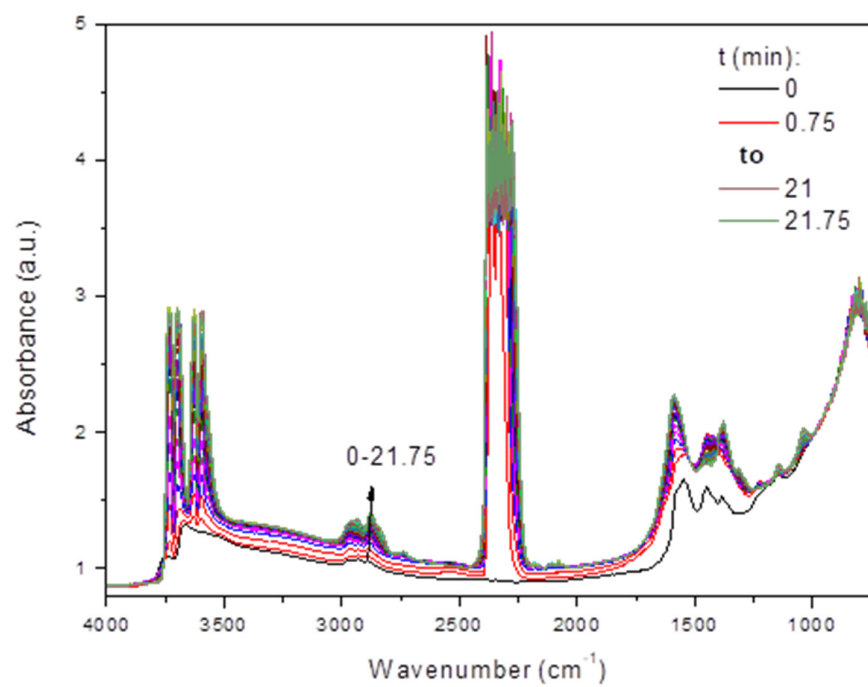


**Figure S5.** RMS profile of time resolved DRIFTS spectra for the whole steady-state experiment region conducted over 1Au/ZrO<sub>2</sub> DP catalyst under reaction mixture and N<sub>2</sub> gas switch after 40 min at 240°C and 40 bar total pressure.

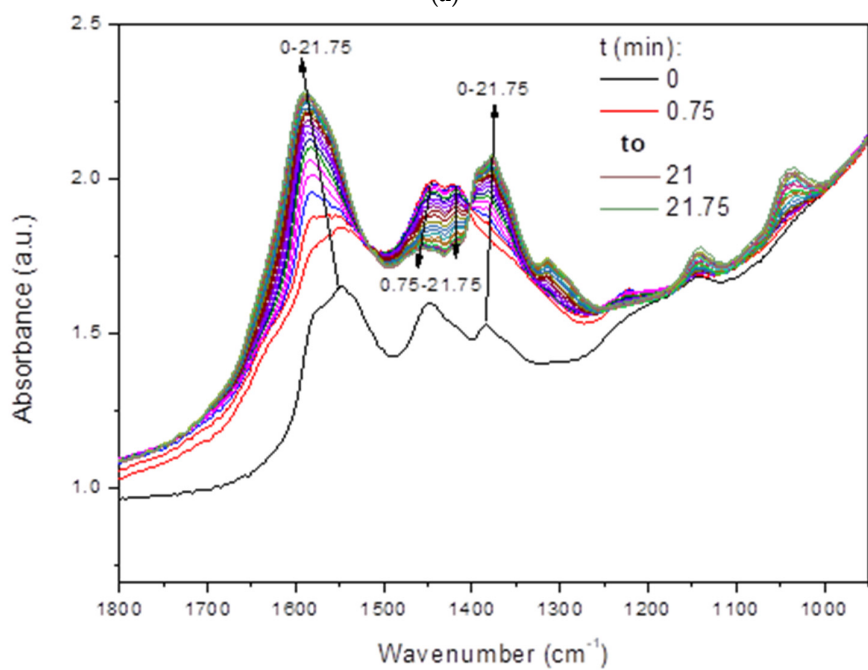
### 1. Reaction steps of CO<sub>2</sub> to methanol hydrogenation via CO route

Direct CO<sub>2</sub> to methanol hydrogenation via CO route starts with the reaction of adsorbed CO<sub>2</sub>\* with adsorbed H\* and forms an intermediate OCOH\*. This intermediate is highly active when compared to the formate intermediate that is formed via the formate route (Eq. 7). High energy is required for the reaction in Eq. S1 that makes it an unfavorable route for methanol production from CO<sub>2</sub> hydrogenation [5]. OCOH\* is later decomposed by reacting with H\* into \*CO and H<sub>2</sub>O. Further, \*CO reacts with H\* and forms HCO\* which is continuously hydrogenated to CH<sub>3</sub>OH.

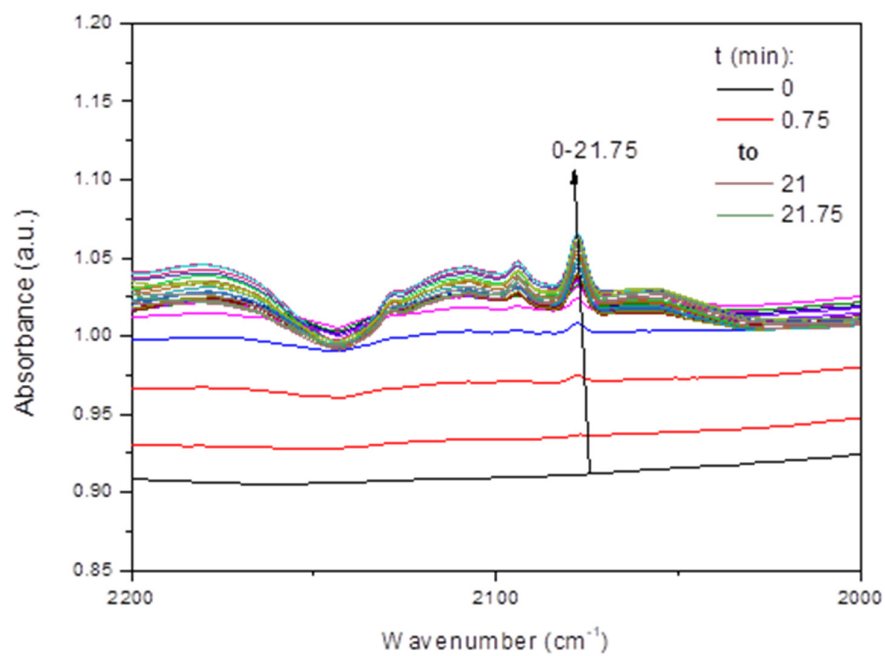




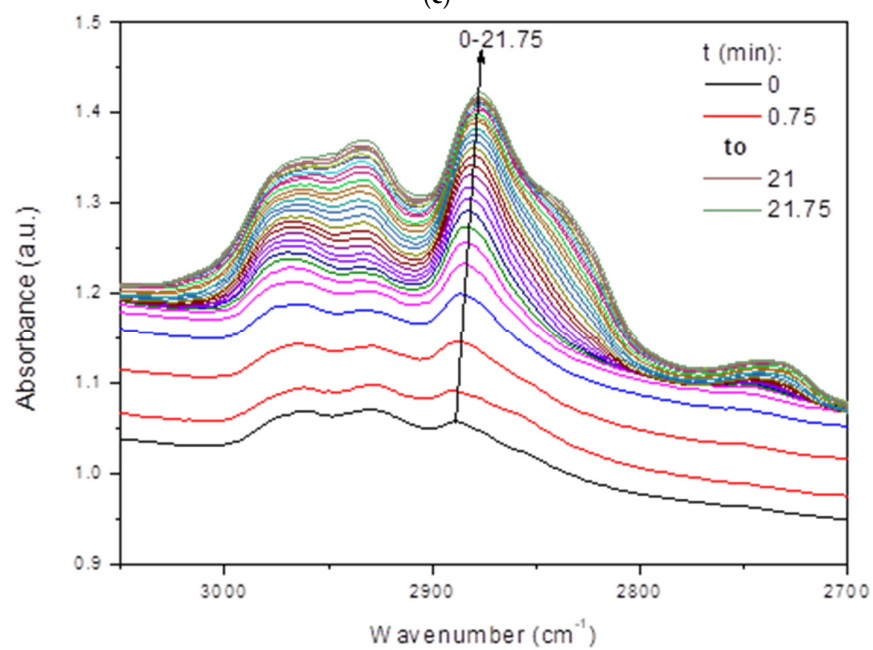
(a)



(b)

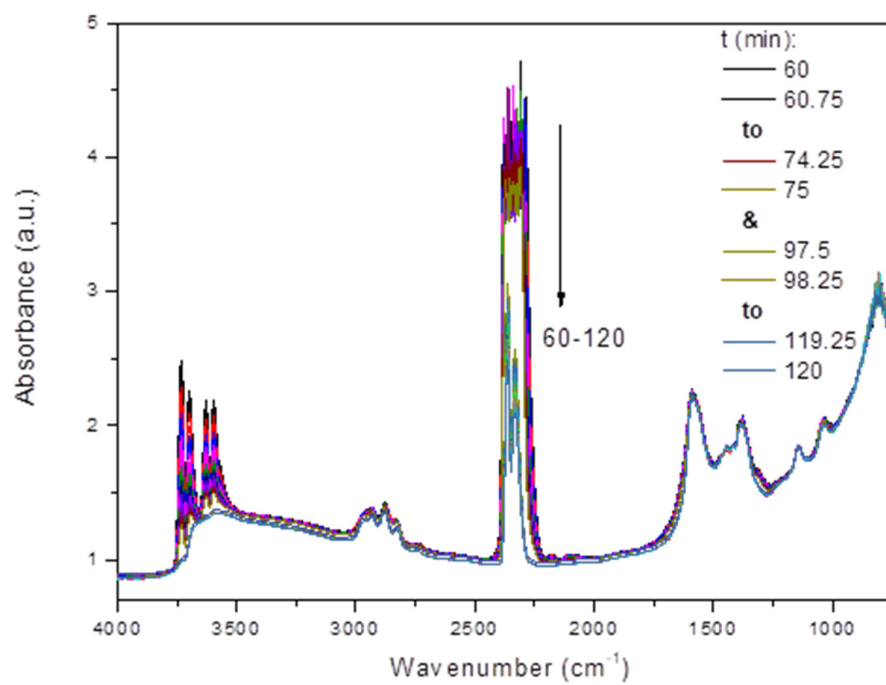


(c)

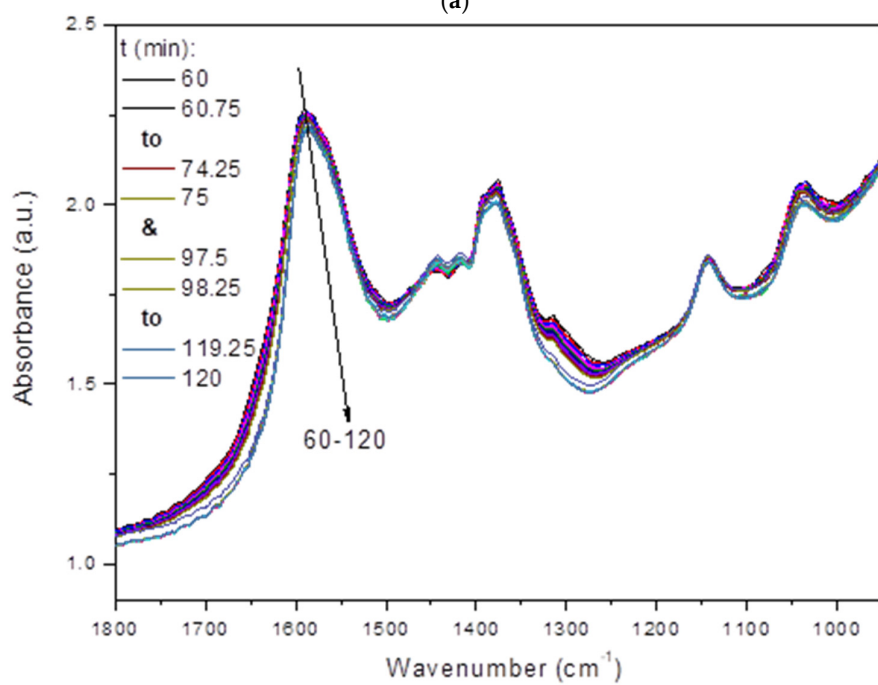


(d)

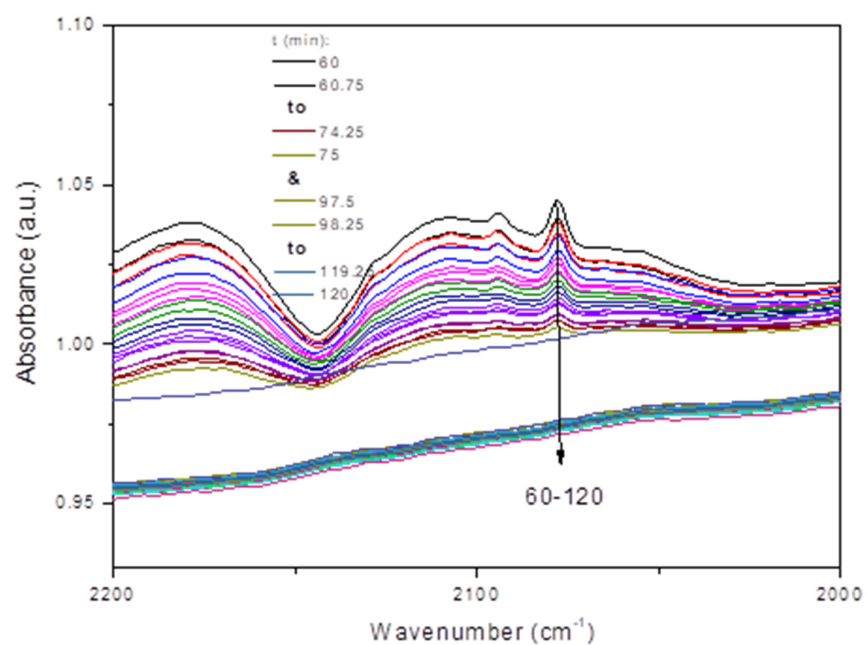
**Figure S6.** DRIFTS spectra recorded for 1Au/ZrO<sub>2</sub> DP catalyst under reaction gas mixture at T=240°C and P<sub>tot</sub>=40 bar: a) the overall spectra, b) the carbonate segment, c) CO vibration segment and d) CH vibration segment. The numbers 0 to 21.75 indicate time in minutes.



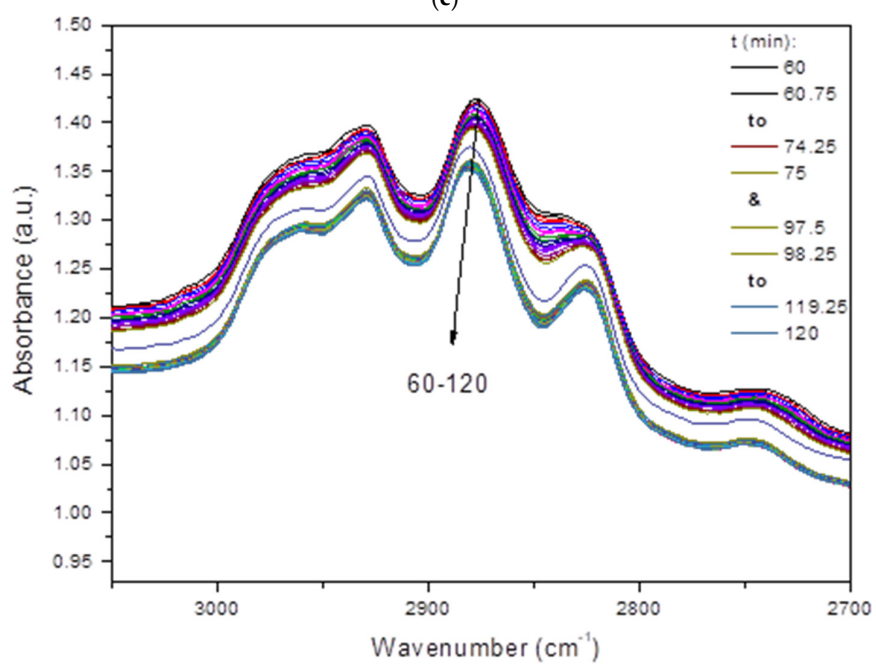
(a)



(b)

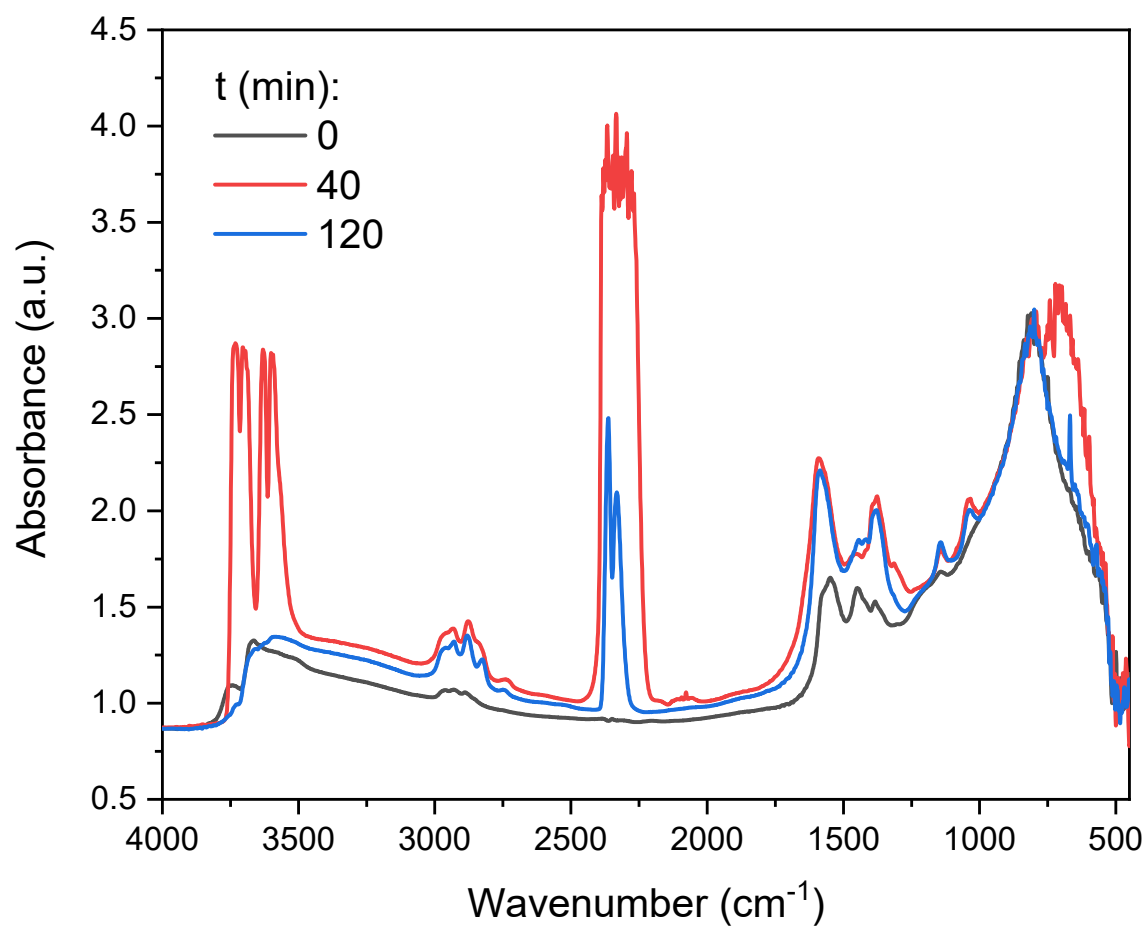


(c)

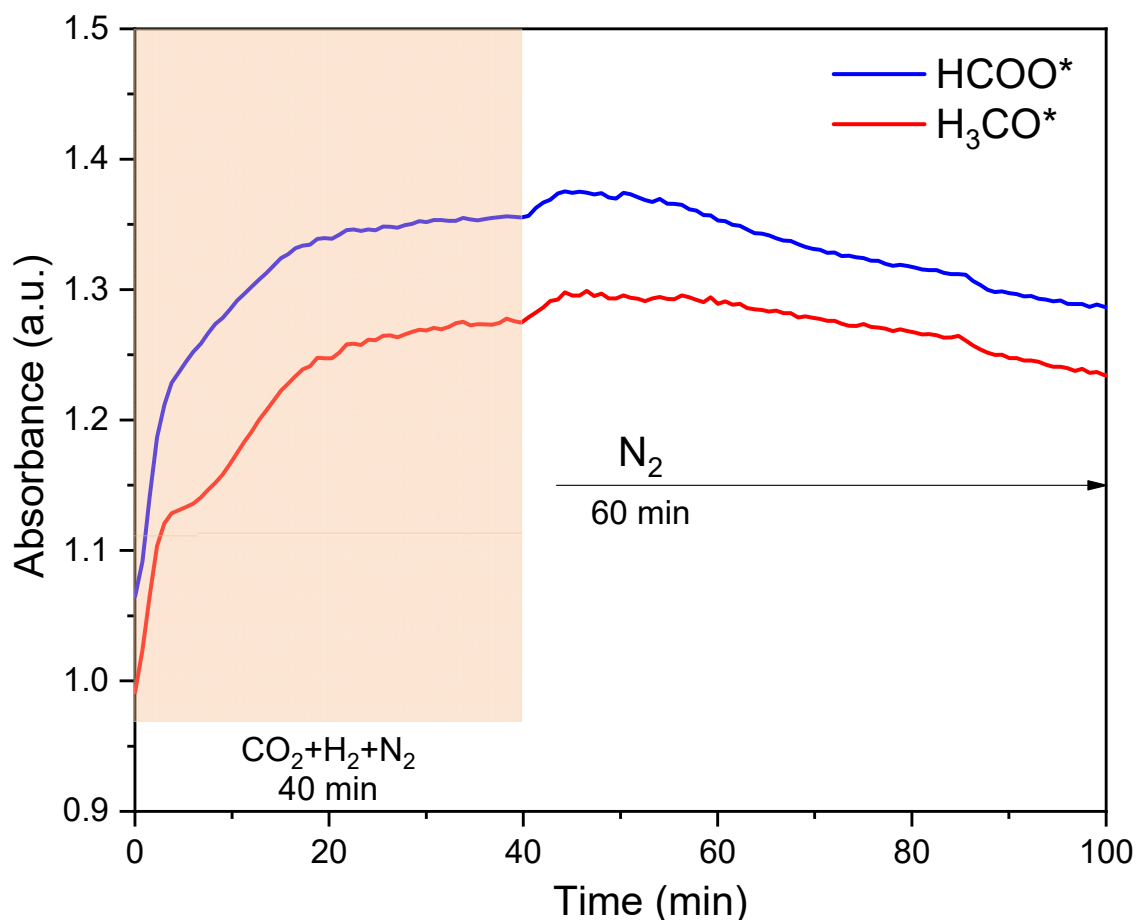


(d)

**Figure S7.** DRIFTS spectra recorded for 1Au/ZrO<sub>2</sub> DP catalyst under N<sub>2</sub> mixture at T=240°C and P<sub>tot</sub>=40 bar: a) the overall spectra, b) the carbonate segment, c) CO vibration segment and d) CH vibration segment. The numbers 60 to 120 indicate time in minutes.



**Figure S8.** Selected DRIFTS spectra acquired at 0, 40 and 120 min by either using reaction gas mixture or N<sub>2</sub> gas, respectively, in the presence of 1Au/ZrO<sub>2</sub> DP catalyst. Operating conditions: T=240°C, P<sub>tot</sub>=40 bar.



**Figure S9.** Temporal profiles for HCOO\* and H<sub>3</sub>CO\* surface intermediates obtained during the *in-situ* DRIFTS measurements carried out in the presence of 1Au/ZrO<sub>2</sub> DP catalyst.

## References

1. Hartadi, Y.; Widmann, D.; Behm, R.J. CO<sub>2</sub> Hydrogenation to Methanol on Supported Au Catalysts under Moderate Reaction Conditions: Support and Particle Size Effects. *ChemSusChem* **2015**, *8*, 456–465. <https://doi.org/10.1002/cssc.201402645>.
2. Wu, C.; Zhang, P.; Zhang, Z.; Zhang, L.; Yang, G.; Han, B. Efficient Hydrogenation of CO<sub>2</sub> to Methanol over Supported Subnanometer Gold Catalysts at Low Temperature. *ChemCatChem* **2017**, *9*, 3691–3696. <https://doi.org/10.1002/cctc.201700872>.
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4. Lu, Z.; Sun, K.; Wang, J.; Zhang, Z.; Liu, C. A Highly Active Au/In<sub>2</sub>O<sub>3</sub>-ZrO<sub>2</sub> Catalyst for Selective Hydrogenation of CO<sub>2</sub> to Methanol. *Catalysts* **2020**, *10*, 1360. <https://doi.org/10.3390/catal10111360>.
5. Wang, J.; Li, G.; Li, Z.; Tang, C.; Feng, Z.; An, H.; Liu, H.; Liu, T.; Li, C. A highly selective and stable ZnO-ZrO<sub>2</sub> solid solution catalyst for CO<sub>2</sub> hydrogenation to methanol. *Sci. Adv.* **2017**, *3*, e1701290. <https://doi.org/10.1126/sciadv.1701290>.