SUPPLEMENTARY INFORMATION

Evaluation of Au/ZrO_2 Catalysts Prepared via Postsynthesis Methods in CO_2 Hydrogenation to Methanol

Tatiparthi Vikram Sagar [1], Janez Zavašnik [2], Matjaž Finšgar [3], Nataša Novak Tušar [1] and Albin Pintar [1,*]

[1] Laboratory for Environmental Sciences and Engineering, Department of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1001 Ljubljana, Slovenia; tvikramsagar@gmail.com (T.V.S.); natasa.novak.tusar@ki.si (N.N.T.)

[2] Department of Gaseous Electronics, Jožef Stefan Institute, Jamova 39, SI-1000 Ljubljana, Slovenia; janez.zavasnik@ijs.si

[3] Faculty of Chemistry and Chemical Engineering, University of Maribor, SI-2000 Maribor, Slovenia; matjaz.finsgar@um.si

* Correspondence: albin.pintar@ki.si; Tel.: +38-6-1476-0237; Fax: +38-6-1476-0460

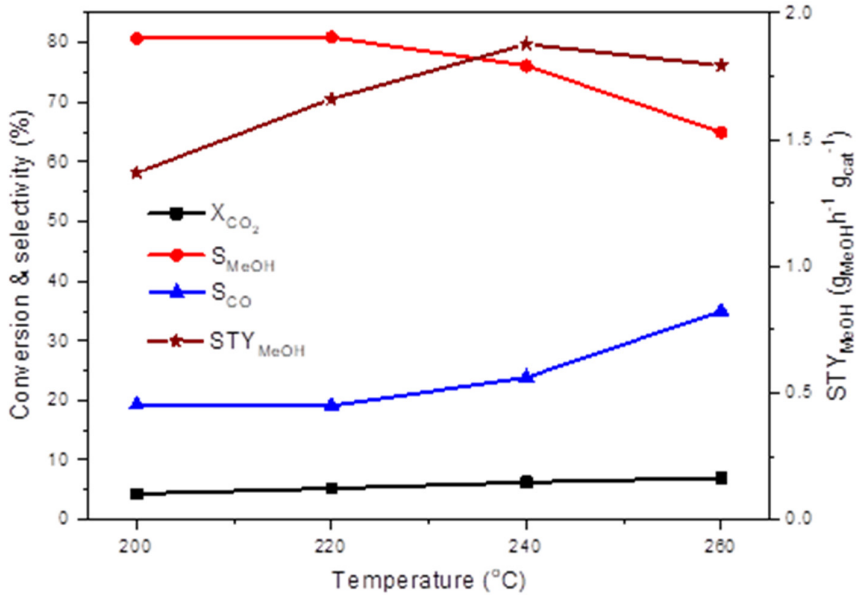
Table S1. Comparison of performance of Au/ZrO_2 solids examined in this study with the reported Au supported ZrO_2 and modified ZrO_2 catalysts for CO_2 hydrogenation to methanol.

Catalyst	Reaction Conditions	$x(CO_2)$ (%)	$s(CH_3OH)$ (%)	STY(CH_3OH) (g_{MeOH} h^{-1} g_{cat}^{-1})	Ref.
[a]Au(0.5 wt.%)/ZrO_2	240°C, 40 bar	6	72.5	1.6	This work
[a]Au(1 wt.%)/ZrO_2	240°C, 40 bar, WHSV=120000 cm^3 h^{-1} g_{cat}^{-1}	7	71.5	1.9	This work
Au(3 wt.%)/ZrO_2	220°C, 5 bar	5	5	-	[1]
Au(1 wt.%)/ZrO_2	180°C, 45 bar		73	-	[2]
Au(10 at.%)/3ZnO/ZrO_2	220°C, 80 bar, GHSV=10000 h^{-1}	2	100	0.01	[3]
Au/In_2O_3-ZrO_2	300°C, 50 bar, GHSV=21000 cm^3 h^{-1} g_{cat}^{-1}	14	70	0.5	[4]

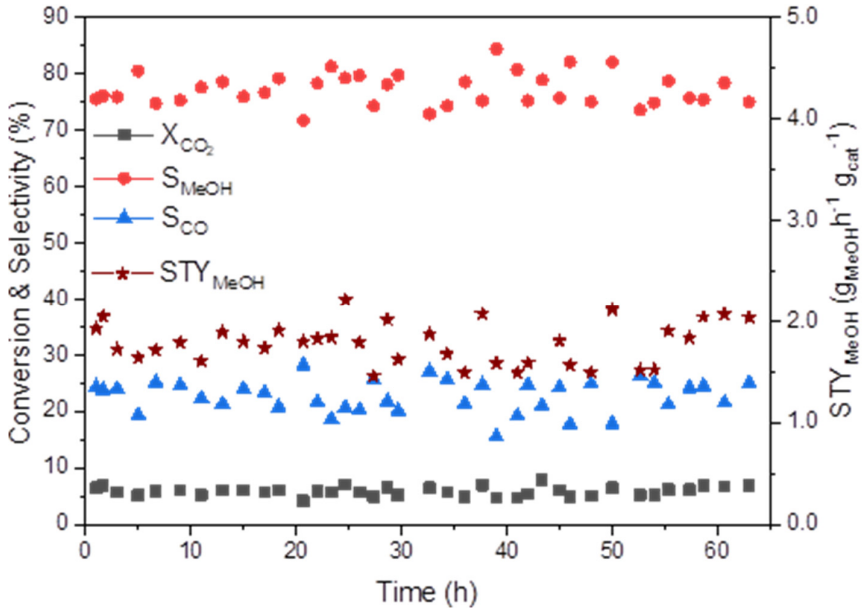
[a]These catalysts were prepared by means of the deposition precipitation method.

Table S2. Relative atomic and relative weight surface concentration for the ZrO_2 support and Au/ZrO_2 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_2	13.4	4.7	24.7	66.2	61.9	29.1	-	-
0.5Au/ZrO_2 DP	15.4	5.3	25.3	66.7	59.2	27.4	0.1	0.5
1Au/ZrO_2 DP	14.0	4.7	25.9	66.1	59.6	26.6	0.5	2.5
0.5Au/ZrO_2 IMP	12.6	4.2	26.5	67.8	60.8	27.3	0.1	0.6



(**a**)



(**b**)

Figure S1. a) Catalytic activity of 0.5Au/ZrO_2 DP catalyst obtained at different temperatures, and **b**) results of the stability test carried out at 240°C. Operating conditions: $P_{tot.}$=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_2, 72 vol.% H_2 (balanced with N_2).

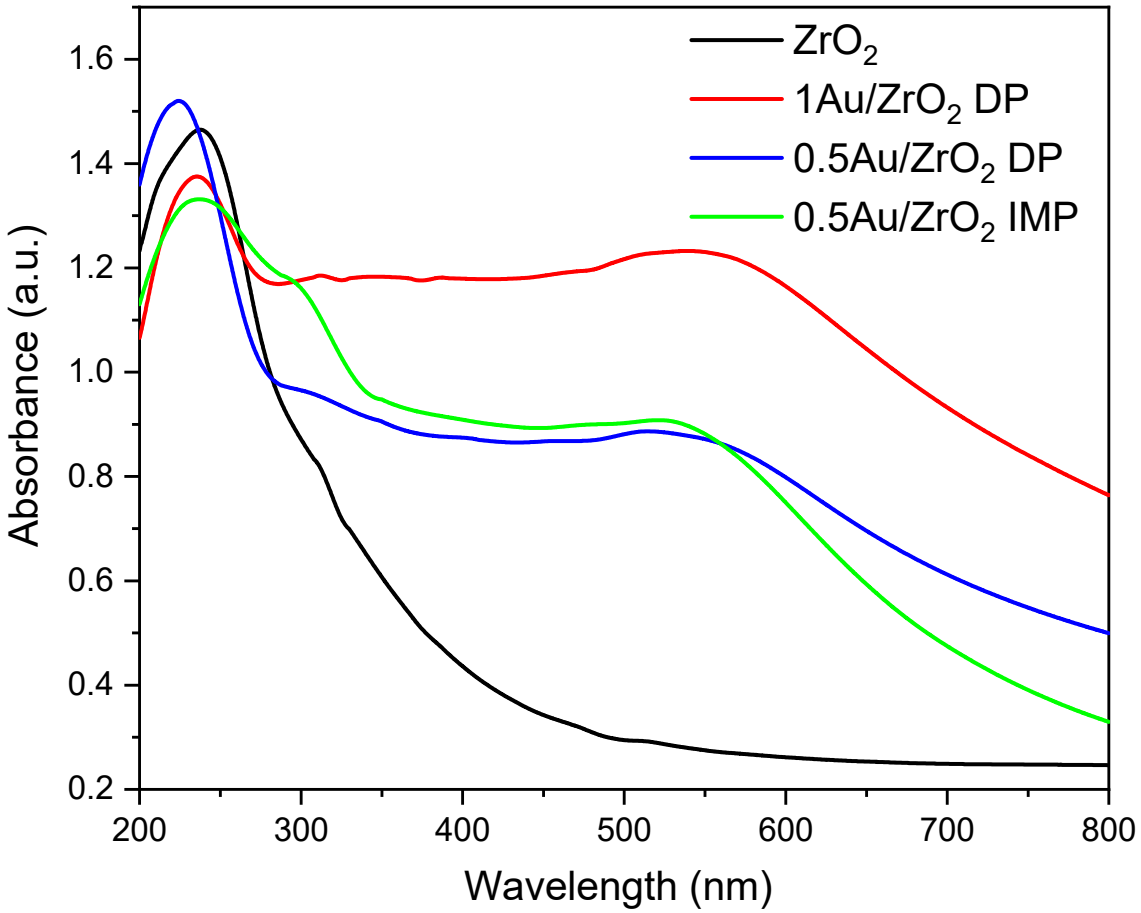


Figure S2. UV-Vis DR spectra of ZrO_2 support and Au/ZrO_2 deposition precipitation/impregnation catalysts after reduction.

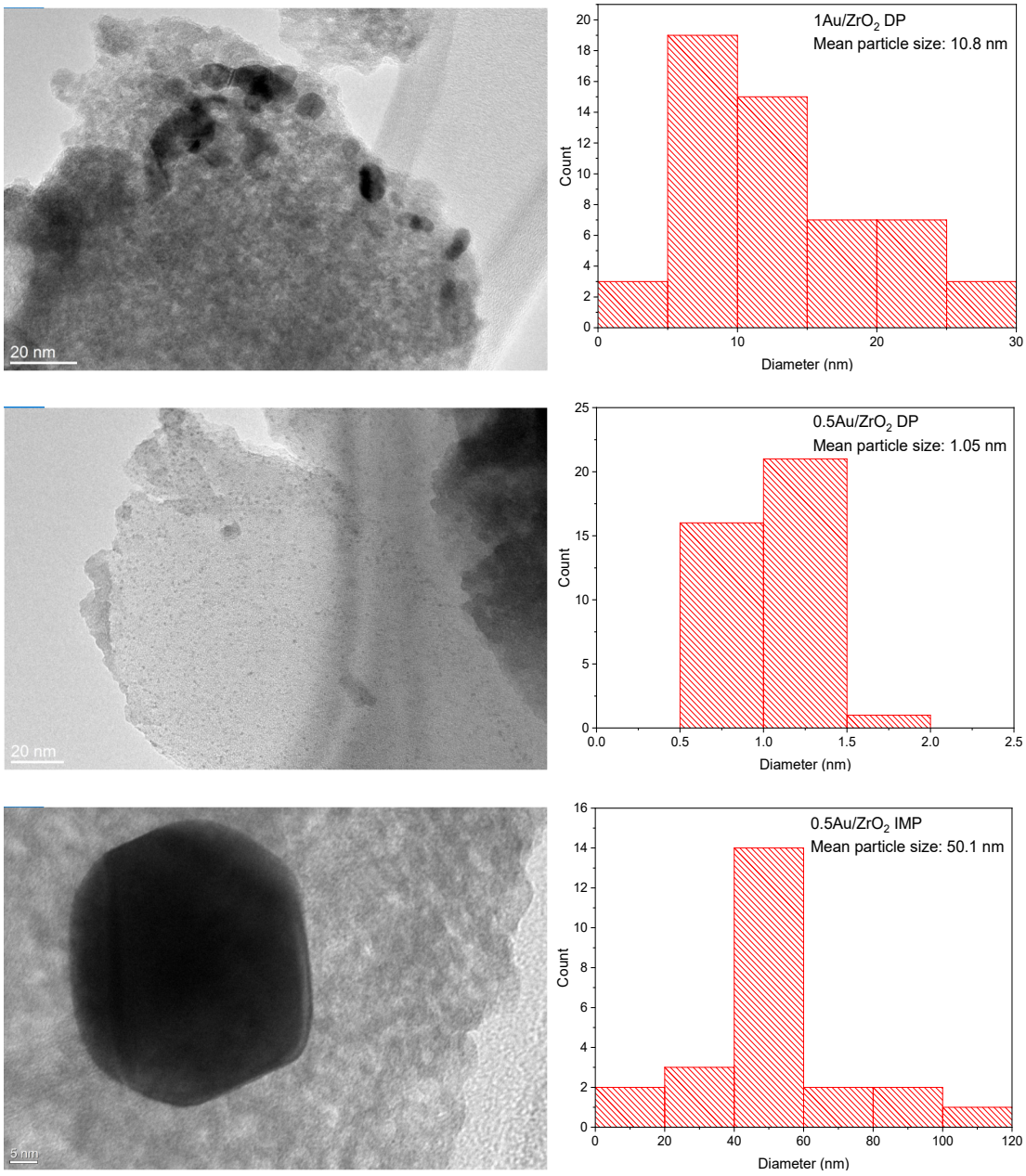


Figure S3. TEM images of Au/ZrO2 deposition precipitation/impregnation catalysts after reduction.

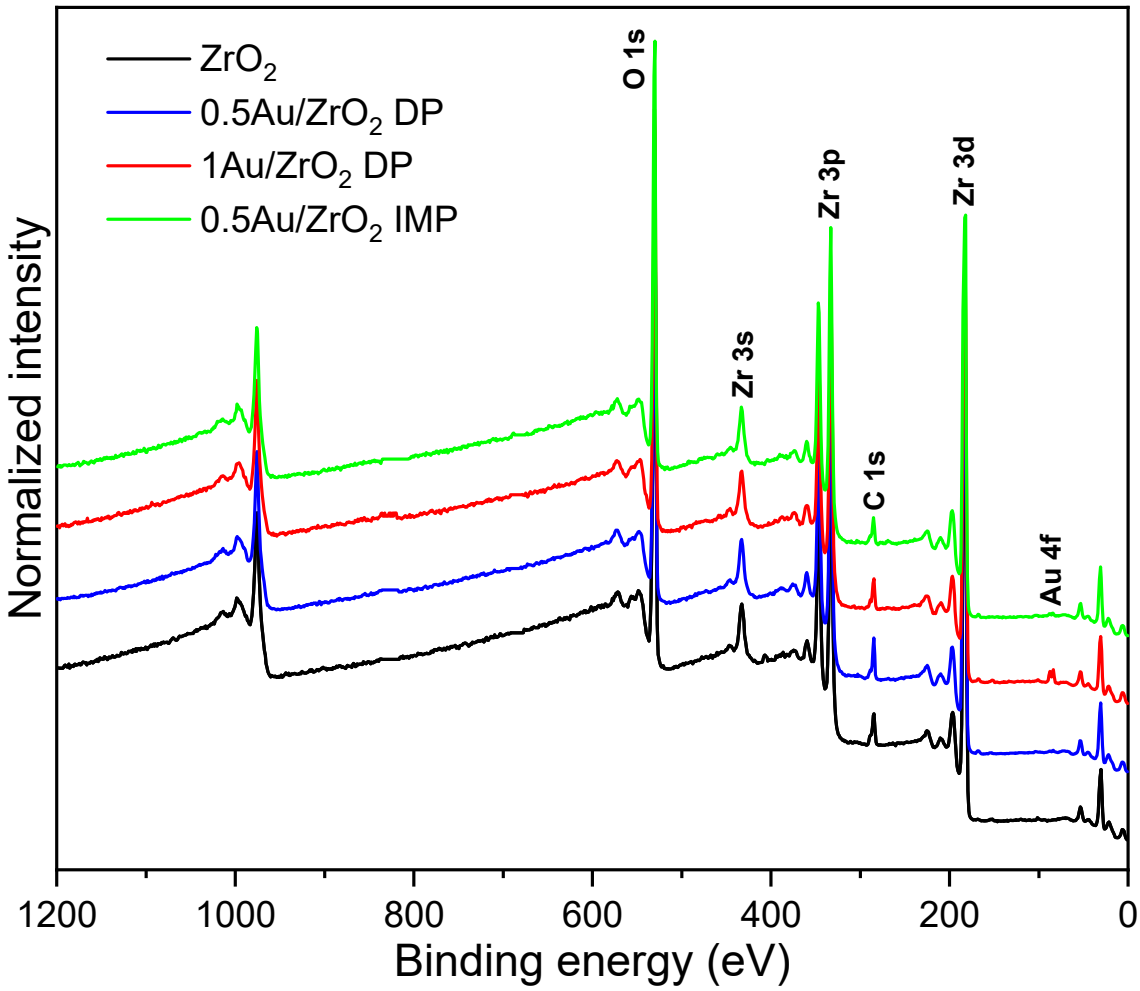


Figure S4. XPS survey spectra measured for the ZrO_2 support and Au/ZrO_2 catalyst samples.

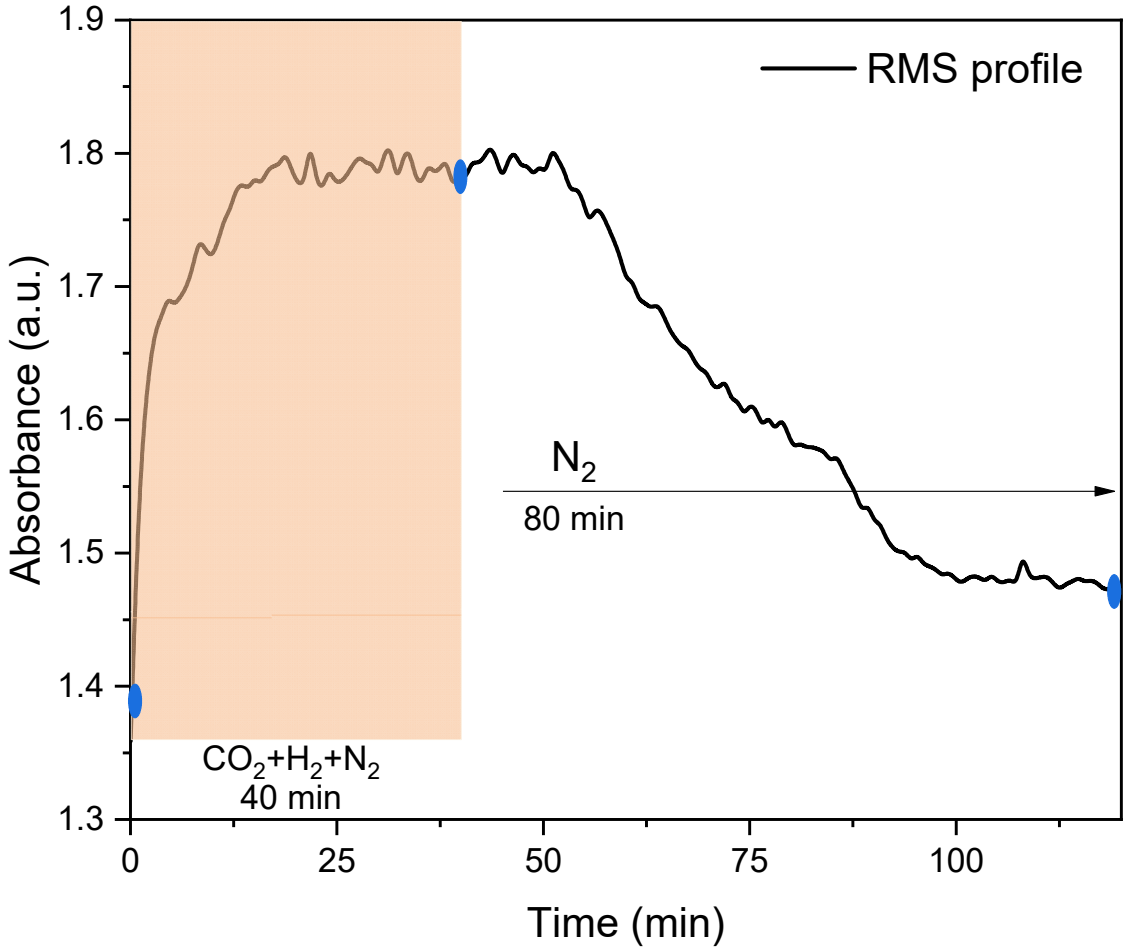
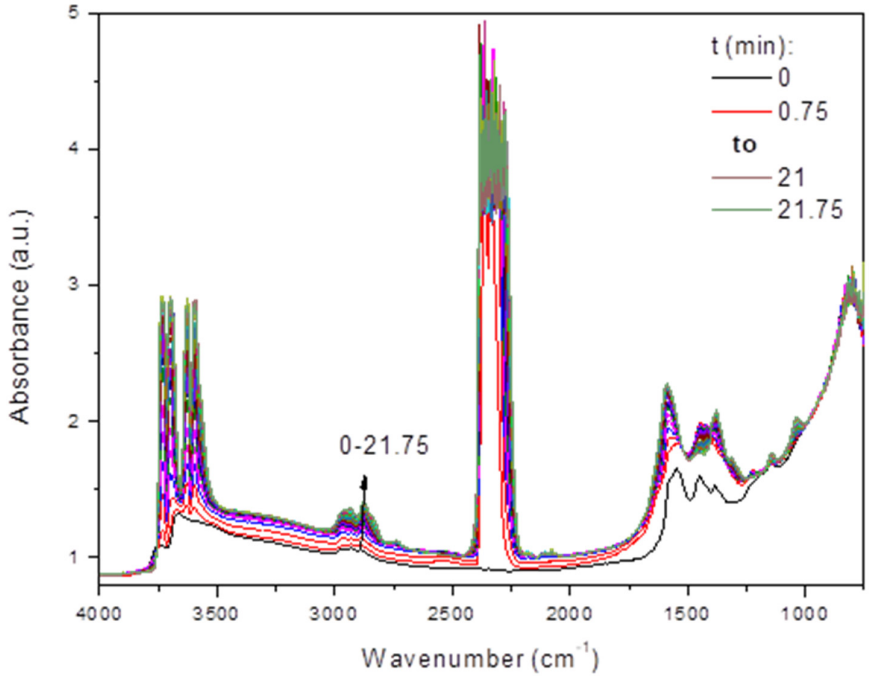


Figure S5. RMS profile of time resolved DRIFTS spectra for the whole steady-state experiment region conducted over 1Au/ZrO_2 DP catalyst under reaction mixture and N_2 gas switch after 40 min at 240°C and 40 bar total pressure.

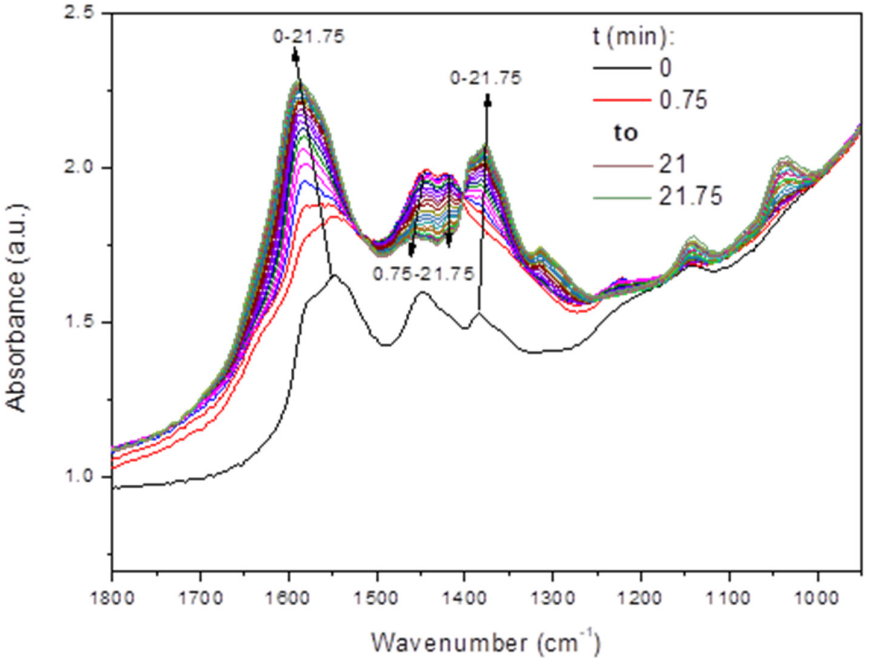
1. Reaction steps of CO_2 to methanol hydrogenation via CO route

Direct CO_2 to methanol hydrogenation via CO route starts with the reaction of adsorbed CO_2* 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_2 hydrogenation [5]. OCOH* is later decomposed by reacting with H* into *CO and H_2O. Further, *CO reacts with H* and forms HCO* which is continuously hydrogenated to CH_3OH.

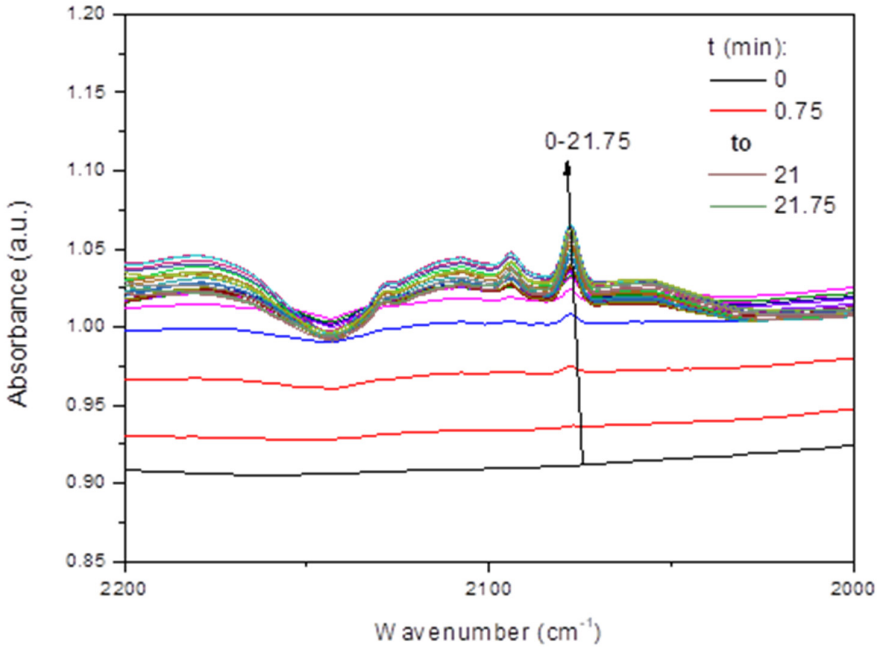
CO_2*+2H_2+*H_2 → OCOH*+H*+2H_2 (S1)
OCOH*+H*+2H_2 → CO*+H_2O*+2H_2 (S2)
CO*+H_2O*+2H_2 → CO*+2H*+H_2-H_2O (S3)
CO*+2H*+H_2 → HCO*+3H* (S4)
HCO*+3H* → H_2CO*+2H* (S5)
H_2CO*+2H* → H_3CO*+H* (S6)
H_3CO*+H* → H_3COH (S7)


t (min):
0
0.75
to
21
21.75
0-21.75
Absorbance (a.u.)
Wavenumber (cm-1)

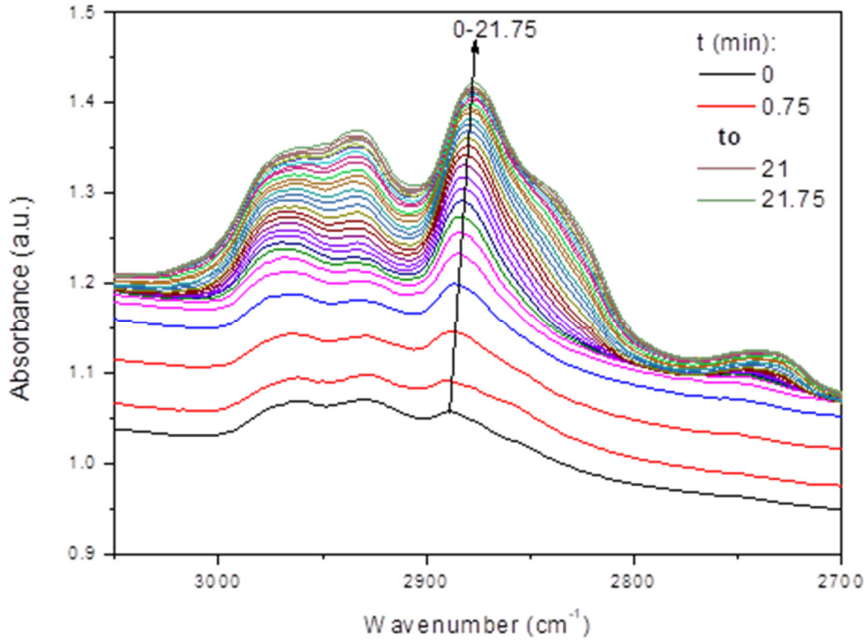
(**a**)


0-21.75
0-21.75
0.75-21.75
t (min):
0
0.75
to
21
21.75
Absorbance (a.u.)
Wavenumber (cm-1)

(**b**)

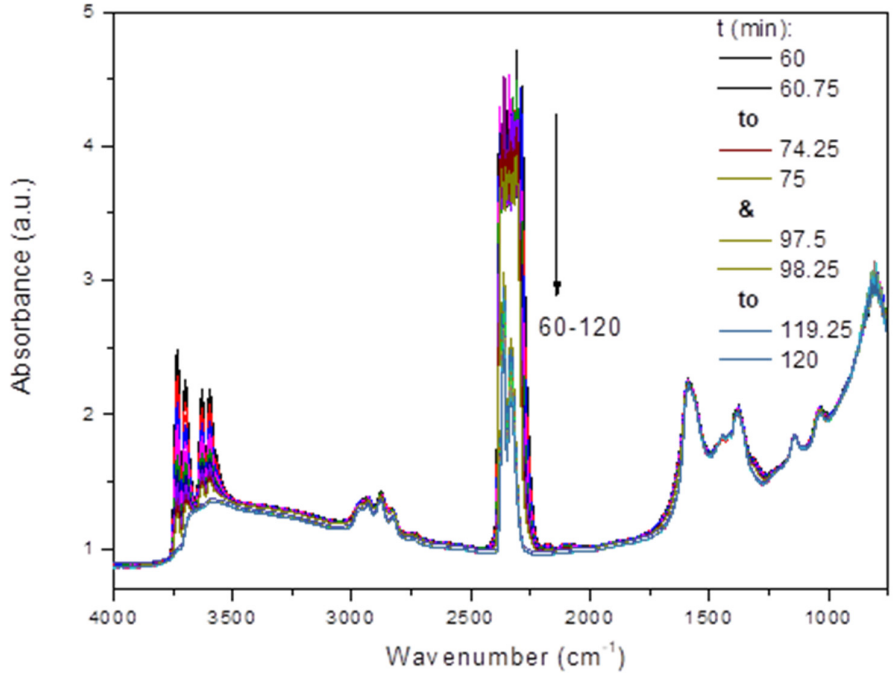


(**c**)

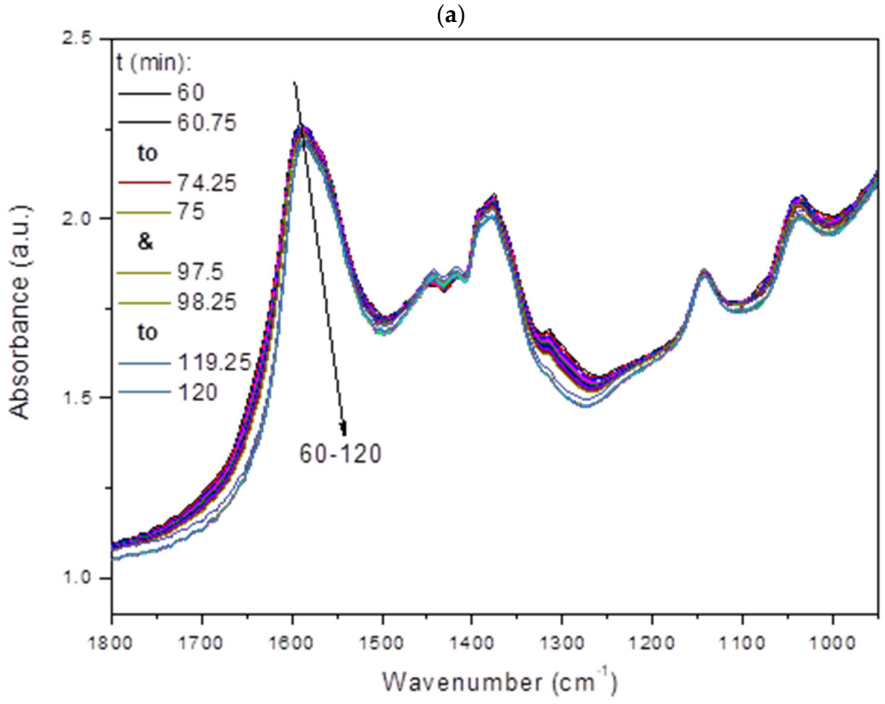


(**d**)

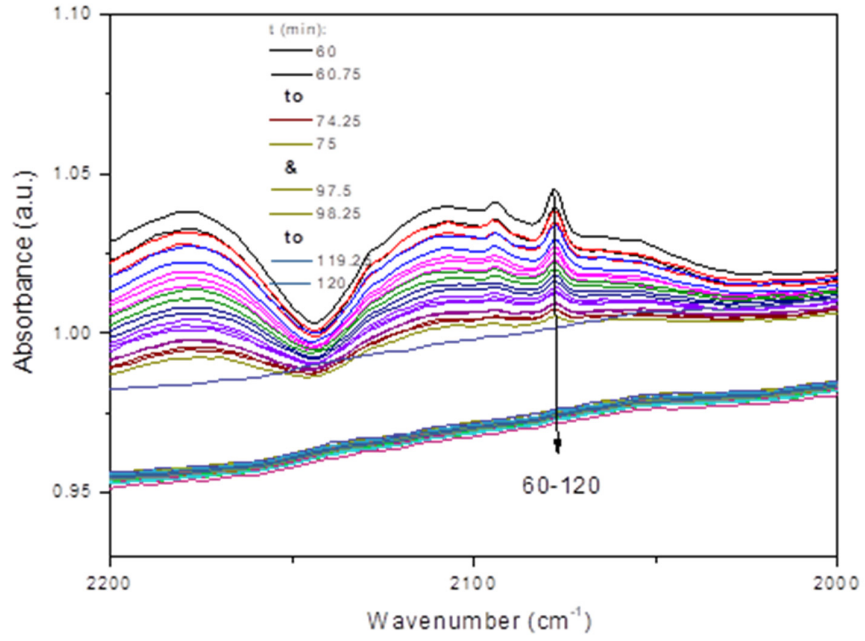
Figure S6. DRIFTS spectra recorded for 1Au/ZrO_2 DP catalyst under reaction gas mixture at T=240°C and $P_{tot.}$=40 bar: a) the overall spectra, b) the carbonate segment, c) CO vibration segment and d) CH vibration segment. The numbers 0 to 21.75 indicate time in minutes.


t (min):
60
60.75
to
74.25
75
&
97.5
98.25
to
119.25
120
60-120
Absorbance (a.u.)
Wavenumber (cm-1)

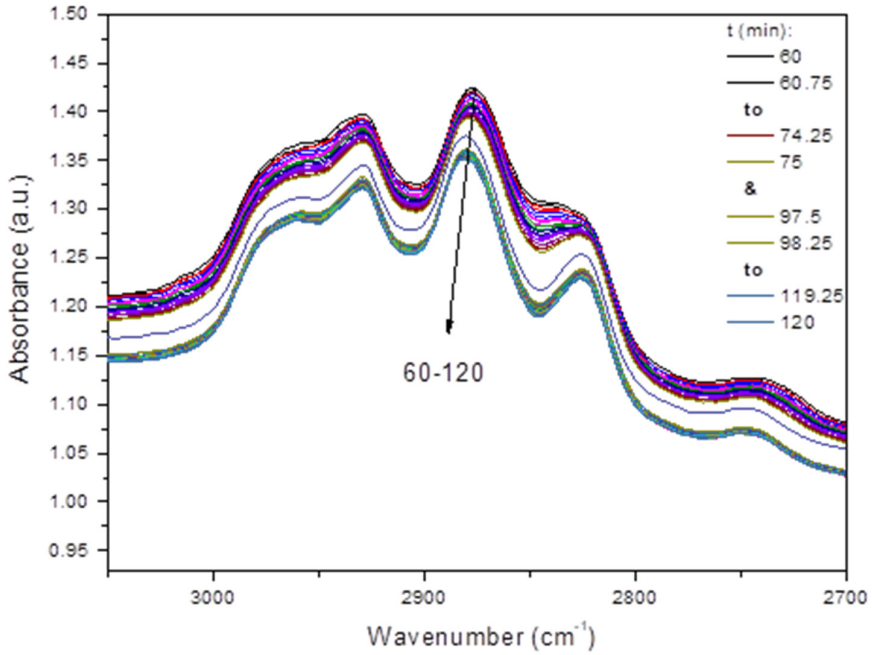
(**a**)


t (min):
60
60.75
to
74.25
75
&
97.5
98.25
to
119.25
120
60-120
Absorbance (a.u.)
Wavenumber (cm-1)

(**b**)



(**c**)



(**d**)

Figure S7. DRIFTS spectra recorded for 1Au/ZrO_2 DP catalyst under N_2 mixture at T=240°C and $P_{tot.}$=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.

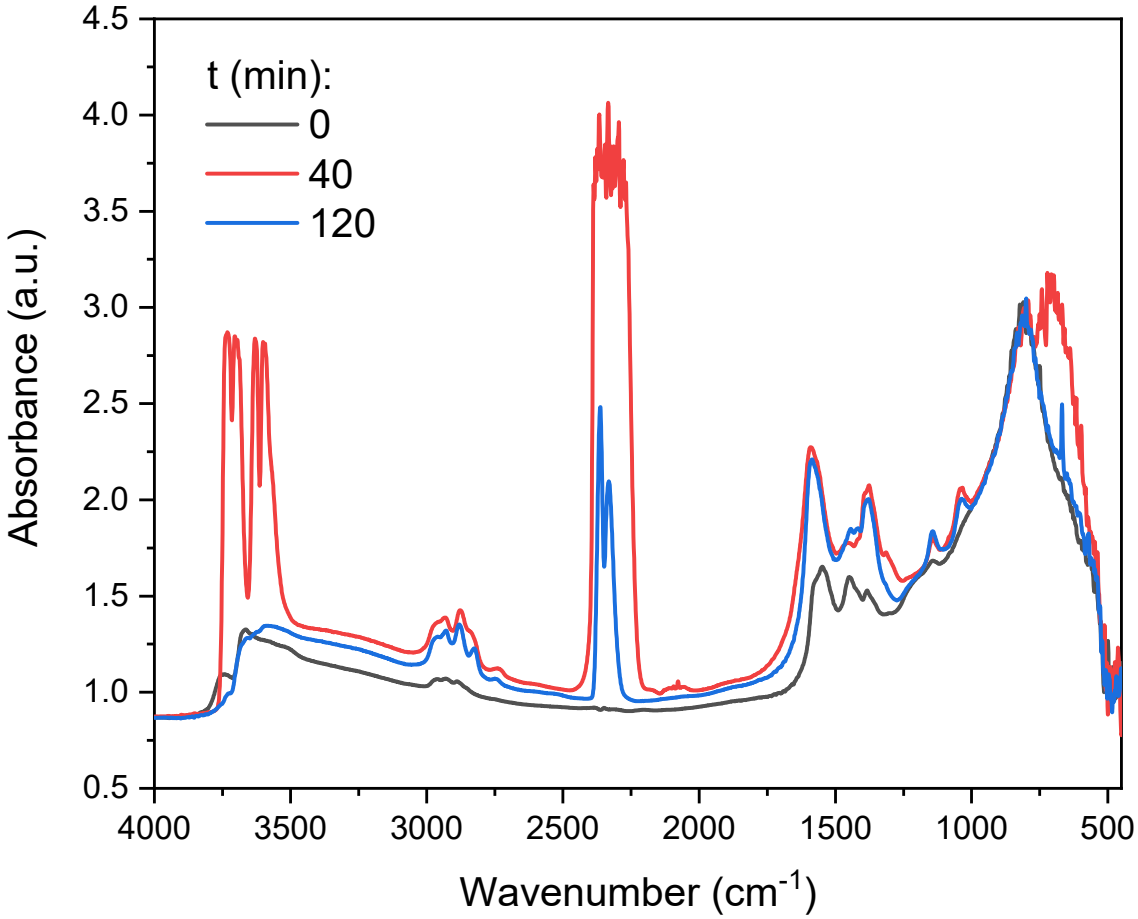


Figure S8. Selected DRIFTS spectra acquired at 0, 40 and 120 min by either using reaction gas mixture or N_2 gas, respectively, in the presence of 1Au/ZrO_2 DP catalyst. Operating conditions: T=240°C, $P_{tot.}$=40 bar.

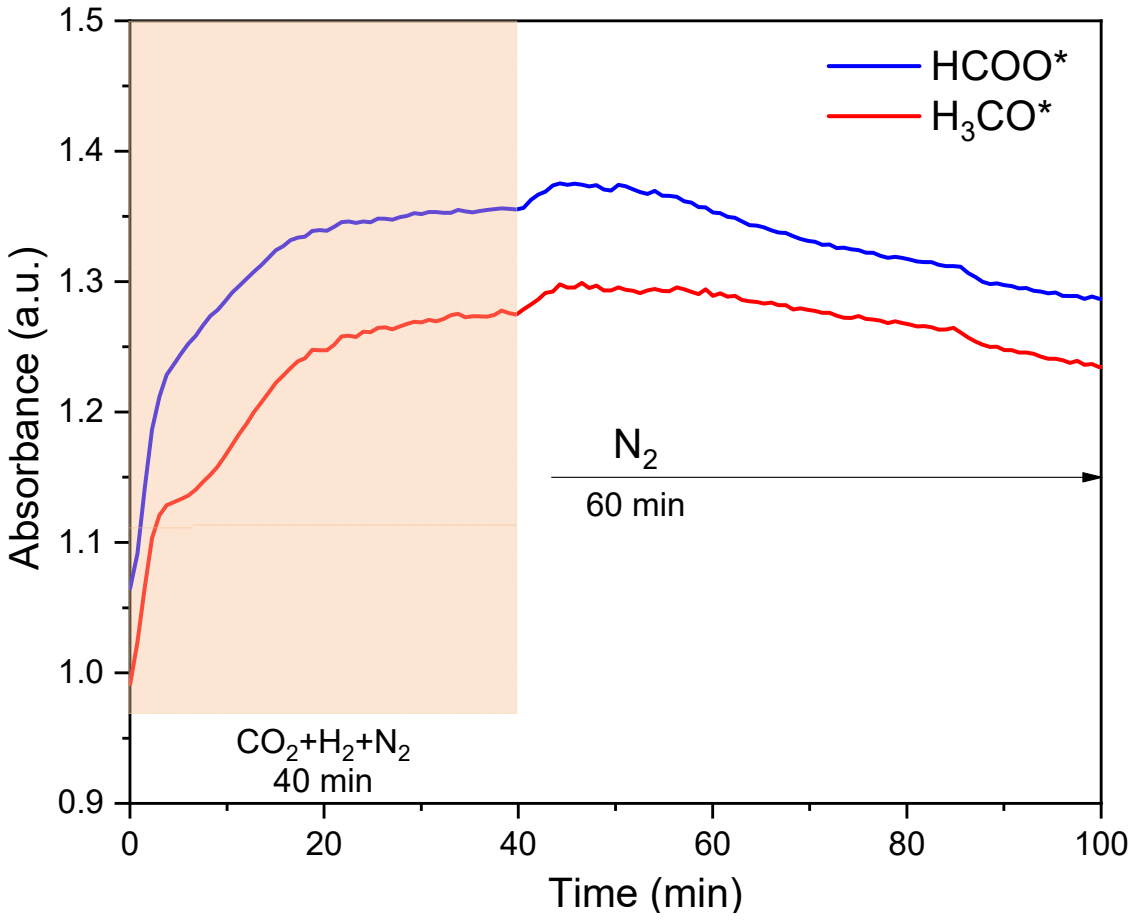


Figure S9. Temporal profiles for HCOO* and H_3CO* surface intermediates obtained during the *in-situ* DRIFTS measurements carried out in the presence of 1Au/ZrO_2 DP catalyst.

References

1. Hartadi, Y.; Widmann, D.; Behm, R.J. CO_2 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_2 to Methanol over Supported Subnanometer Gold Catalysts at Low Temperature. *ChemCatChem* **2017**, *9*, 3691–3696. https://doi.org/10.1002/cctc.201700872.
3. Słoczyński, J.; Grabowski, R.; Kozłowska, A.; Olszewski, P.; Stoch, J.; Skrzypek, J.; Lachowska, M. Catalytic activity of the M/(3ZnO·ZrO_2) system (M = Cu, Ag, Au) in the hydrogenation of CO_2 to methanol. *Appl. Catal. A: Gen.* **2004**, *278*, 11–23. https://doi.org/10.1016/j.apcata.2004.09.014.
4. Lu, Z.; Sun, K.; Wang, J.; Zhang, Z.; Liu, C. A Highly Active Au/In_2O_3-ZrO_2 Catalyst for Selective Hydrogenation of CO_2 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_2 solid solution catalyst for CO_2 hydrogenation to methanol. *Sci. Adv.* **2017**, *3*, e1701290. https://doi.org/10.1126/sciadv.1701290.