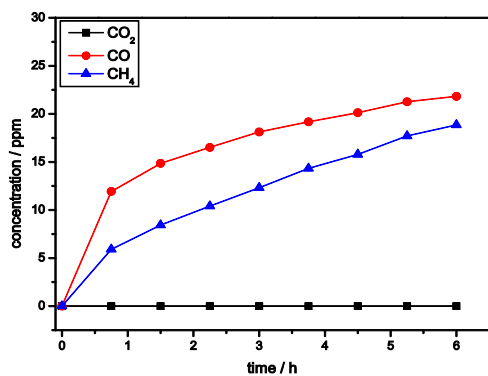
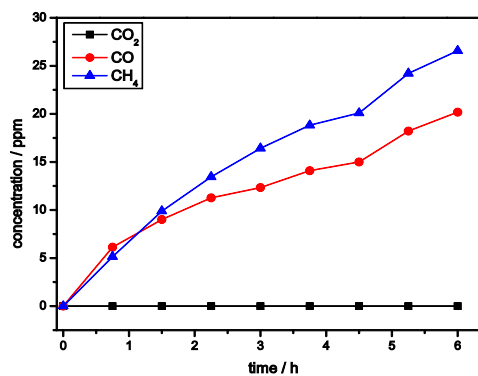


Identification and Exclusion of Intermediates of Photocatalytic CO₂ Reduction on TiO₂ under Conditions of Highest Purity

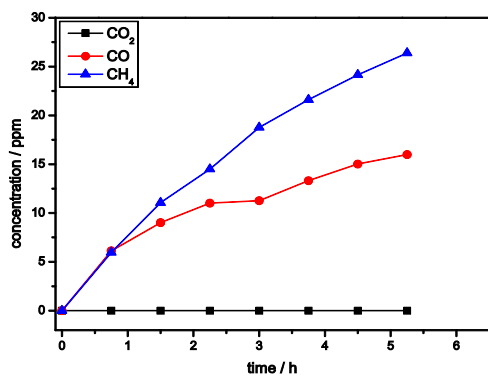
Anna Pougin, Martin Dilla, and Jennifer Strunk



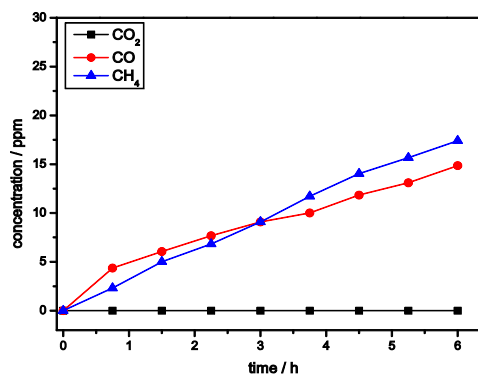
A) 1st day



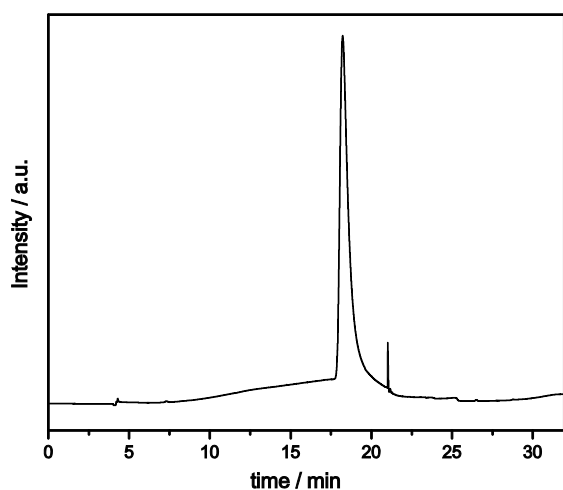
B) 2nd day



C) 3rd day



D) 4th day



E) Chromatogram after flow cleaning, desorbing molecules accumulated over 1h

Figure SI 1. A)-D) Example of the time profile of a typical batch cleaning for NaP25_NaNO₃ in 4 steps; cleaning procedure was concluded by a cleaning step in flow mode to complete cleaning fully. E) Chromatogram of NaP25_NaNO₃ after 4 batch cleaning steps (1st-4th day) and a cleaning in the flow mode for 15 h. The large peak at 18 min is representing H₂O and the slim peak at about 21 min is due to a valve switch.

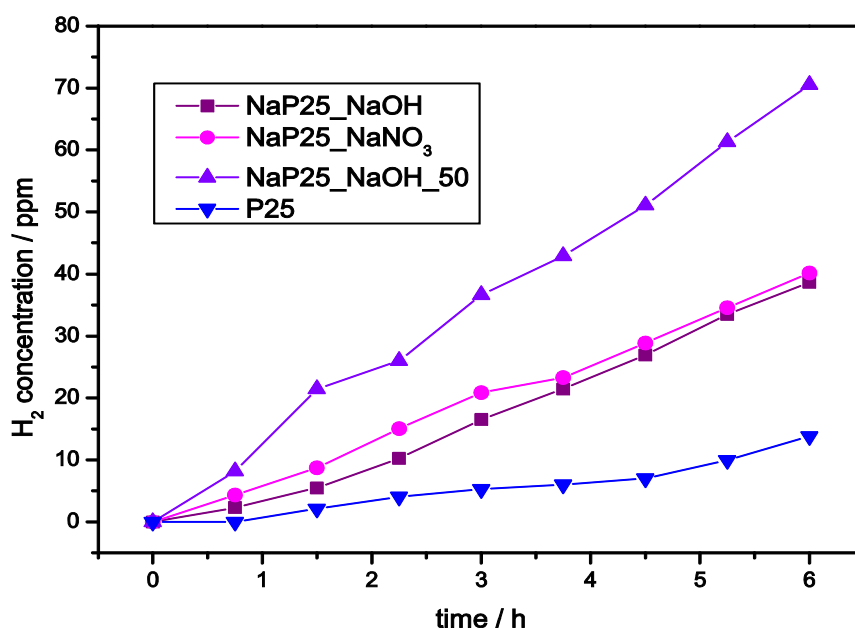
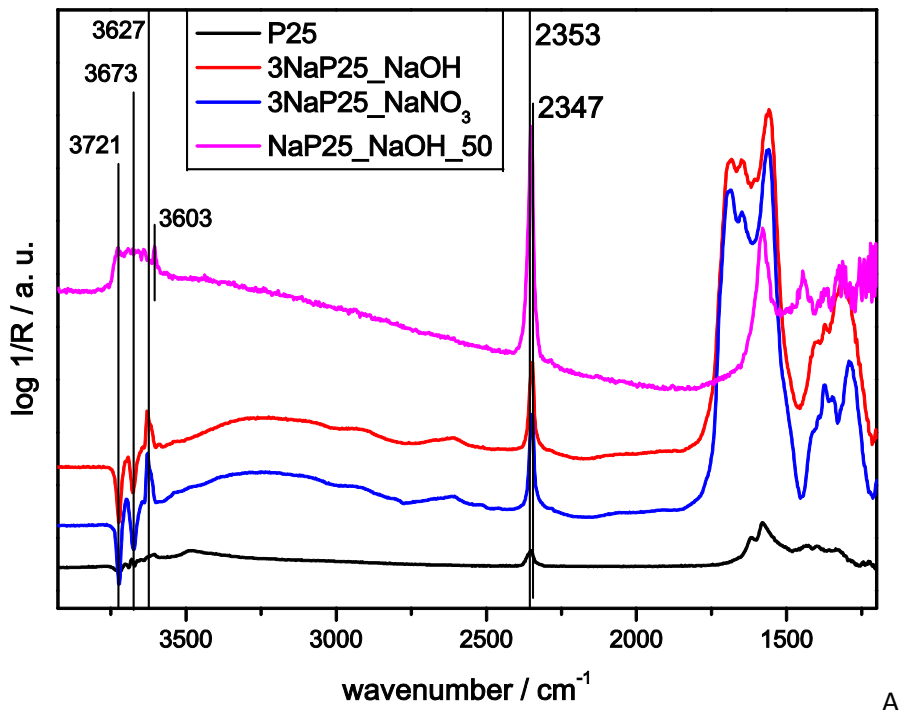


Figure SI 2. Hydrogen production for activity tests in photocatalytic CO₂ reduction for sample P25 and Na_P25 samples under standard conditions with 6,000 ppm H₂O and 1.5 % of CO₂; Na-modified samples: NaP25_NaOH (0.63 wt% of Na), NaP25_NaNO₃ (0.63 wt% of Na), Na_P25_NaOH_50 (0.013 wt% of Na).

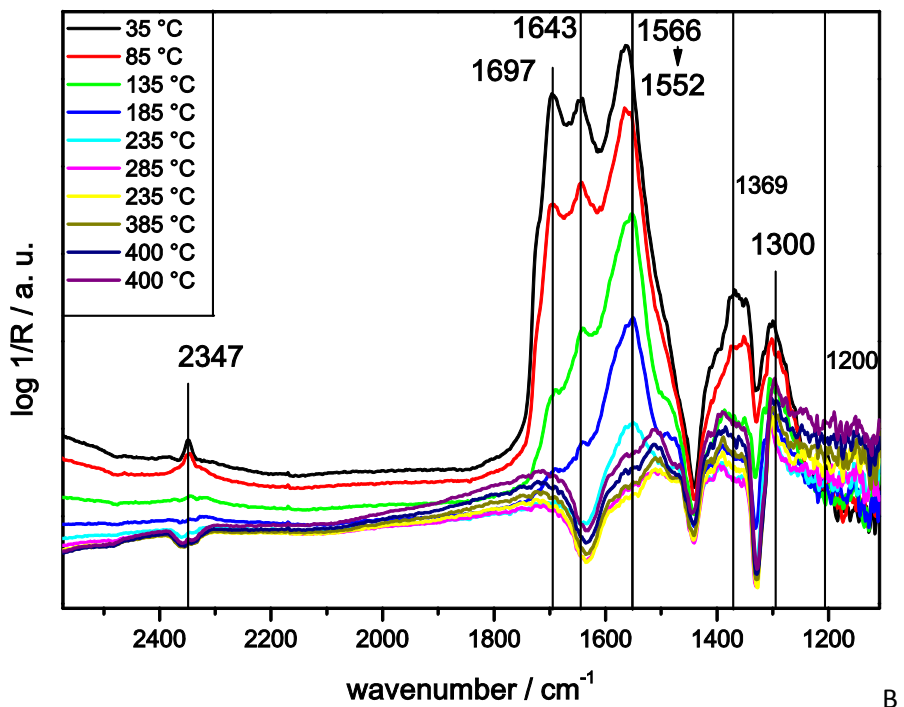
Table SI1. Assignment of IR bands for TiO₂ and the Na-modified P25 (denoted as Na-P25) during CO₂ adsorption.

IR band [cm ⁻¹]	Assignment	Ref.
2347	Linearly adsorbed CO ₂	[1], [2], [3]
Na-P25 1693-1695	Acetic acid, acetone $\nu(\text{C}=\text{O})$	[4]
	$\nu_{\text{AS}}(\text{CO})$ for HCO ₃ ⁻ in KBr matrix	[5], [6]
1675	Side on bonded O-C-O	[3]
	Carboxylate $\nu_{\text{AS}}(\text{COO})$ /bicarbonate	[7], [8]
	Carboxylate $\nu_{\text{AS}}(\text{O-C-O})$	[6], [9]
	Bidentate carbonate	[4]

Na-P25 1643	Bidentate carbonate u_{AS} (O-C-O)	[9]
1619	Adsorbed H ₂ O δ_{HOH}	[10]
1585-1579	Monodentate carbonate u_{AS} (CO)	[2], [4], [9]
	Bicarbonate	[7], [11]
	Bidentate carbonate u_{AS} (CO)	[8], [12]
1434	Bidentate bicarbonate u_{AS} (CO in COH)	[2], [5]
	Bicarbonate u_S (COO)	[4], [7]
	Monodentate carbonate u_S (CO ₃)	[8]
Na-P25 1424	Bicarbonate	[11]
1377	Monodentate carbonate u_S (CO)	[2], [7], [8], [9]
	Bicarbonate u_S (COO)	[11], [12]
1330	Bidentate carbonate u_S (COO)	[7], [12]
Na-P25 1313	Bidentate carbonate u_S (CO ₃)	[8], [9]
1245	Carboxylate u_{AS} (O-C-O)	[8], [9]
1222	Bidentate bicarbonate u_B (CO in COH)	[2], [4], [9]
	Bicarbonate δ_{OH}	[13], [14]
Na-P25 1200	Bicarbonate δ_{OH}	[5]

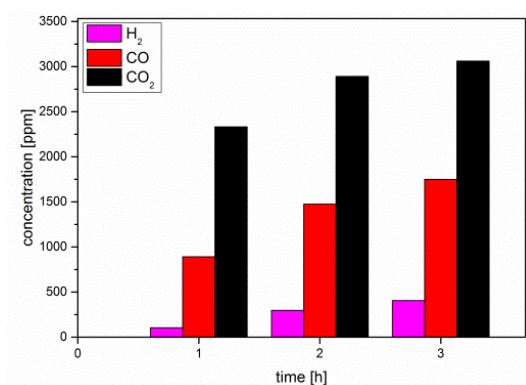


A

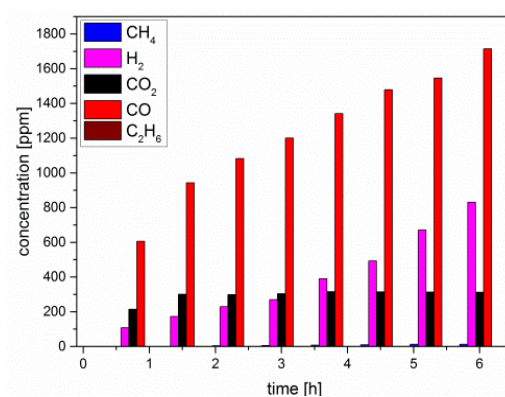


B

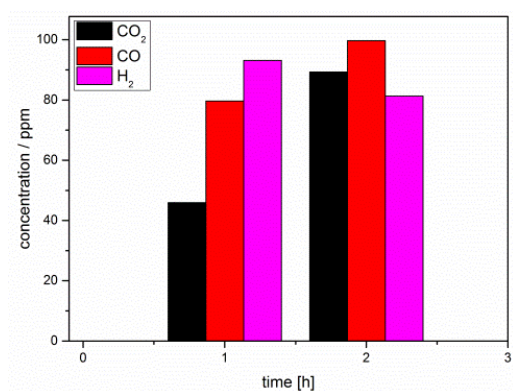
Figure SI 3. A) Overview difference spectra at minute 30 after CO₂ has been adsorbed and purged out of the gas phase. B) Temperature programmed desorption experiment inside the DRIFTS cell on NaP25_NaNO₃, involving heating of the sample after adsorption of CO₂ to 400 °C in Ar.



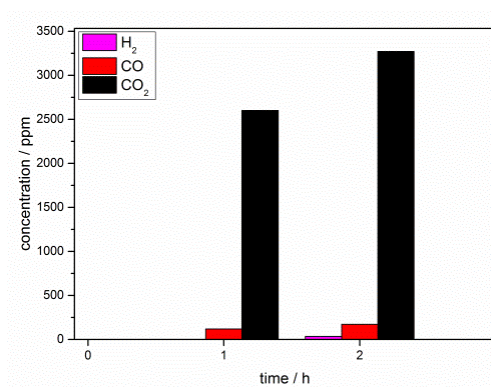
A



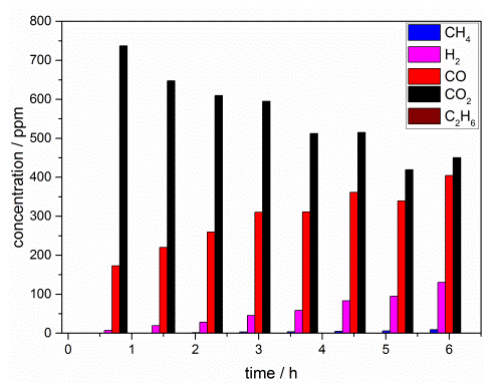
B



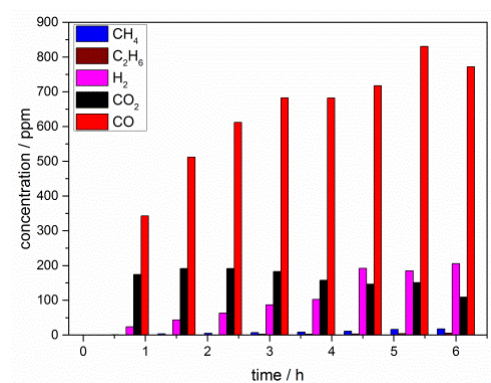
C



D



E



F

Figure SI 4: Decomposition of A: formic acid, B: formaldehyde, C: methanol, D: oxalic acid, E: glyoxylic acid, F: glyoxal.

References

- [1] G. Ramis, G. Busca, V. Lorenzelli, *Materials Chemistry and Physics* **1991**, 29, 425–435.
- [2] L. Mino, G. Spoto, A. M. Ferrari, *J. Phys. Chem. C* **2014**, 118, 25016–25026.
- [3] J. Rasko, F. Solymosi, *J. Phys. Chem* **1994**, 98, 7147–7152.
- [4] G. Martra, *Applied Catalysis A: General* **2000**, 200, 275–285.
- [5] D. L. Bernitt, K. O. Hartman, I. C. Hisatsune, *J. Chem. Phys* **1965**, 42, 3553.
- [6] K. O. Hartman, *J. Chem. Phys* **1966**, 44, 1913.
- [7] C.-C. Yang, Y.-H. Yu, B. van der Linden, J. C. S. Wu, G. Mul, *J. Am. Chem. Soc* **2010**, 132, 8398–8406.
- [8] W. Wu, K. Bhattacharyya, K. Gray, E. Weitz, *J. Phys. Chem. C* **2013**, 117, 20643–20655.
- [9] J. Baltrusaitis, J. Schuttlefield, E. Zeitler, V. H. Grassian, *Chemical Engineering Journal* **2011**, 170, 471–481.
- [10] C. Morterra, *J. Chem. Soc., Faraday Trans. 1* **1988**, 84, 1617.
- [11] K. Bhattacharyya, A. Danon, B. K. Vijayan, K. A. Gray, P. C. Stair, E. Weitz, *J. Phys. Chem. C* **2013**, 117, 12661–12678.
- [12] L.-F. Liao, C.-F. Lien, D.-L. Shieh, M.-T. Chen, J.-L. Lin, *J. Phys. Chem. B* **2002**, 106, 11240–11245.
- [13] C. J. Keturakis, F. Ni, M. Spicer, M. G. Beaver, H. S. Caram, I. E. Wachs, *ChemSusChem* **2014**, 7, 3459–3466.
- [14] S. J. Hug, D. Bahnemann, *Journal of Electron Spectroscopy and Related Phenomena* **2006**, 150, 208–219.