



PHOTOCATALYTIC REDUCTION OF CARBON DIOXIDE IN CONTINUOUS FLOW PHOTOREACTOR USING TiO₂-BASED MATERIALS

T. Maniecki^{1,2}, O. Shtyka^{1,2}, V. Shatila¹, R. Ciesielski^{1,2}, A.
Kedziora^{1,2}, S. Dubov², D. Gromov²,

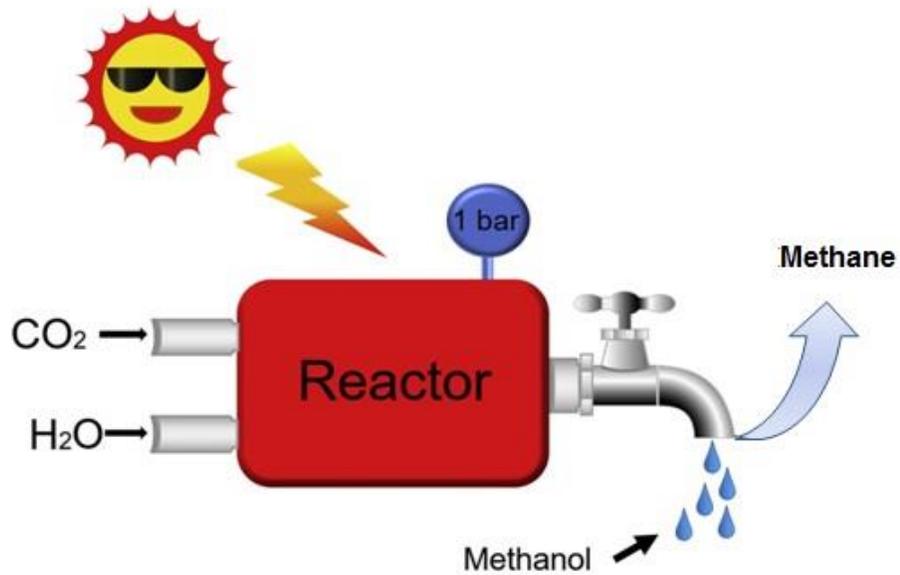
¹Institute of General and Ecological Chemistry, Lodz University of Technology, Zeromskiego 116,
90-924 Lodz, Poland

²National Research University of Electronic Technology, Institute of Advanced Materials and
Technologies, Shokin Square 1, 124498, Zelenograd, Moscow, Russia

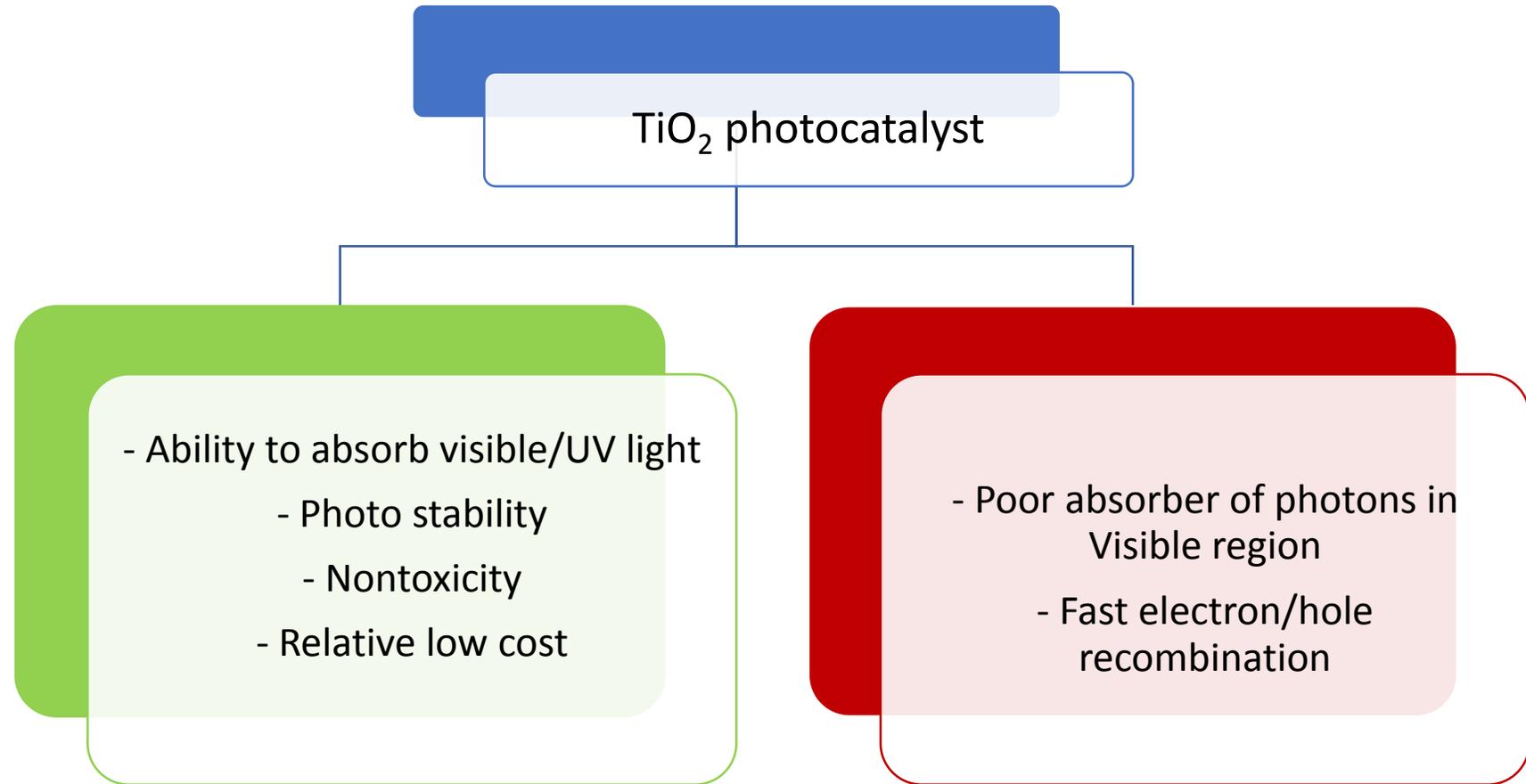
XXIV International Conference on Chemical Reactors CHEMREACTOR-24
September 12 - 17, 2021



Photocatalytic reduction of CO₂



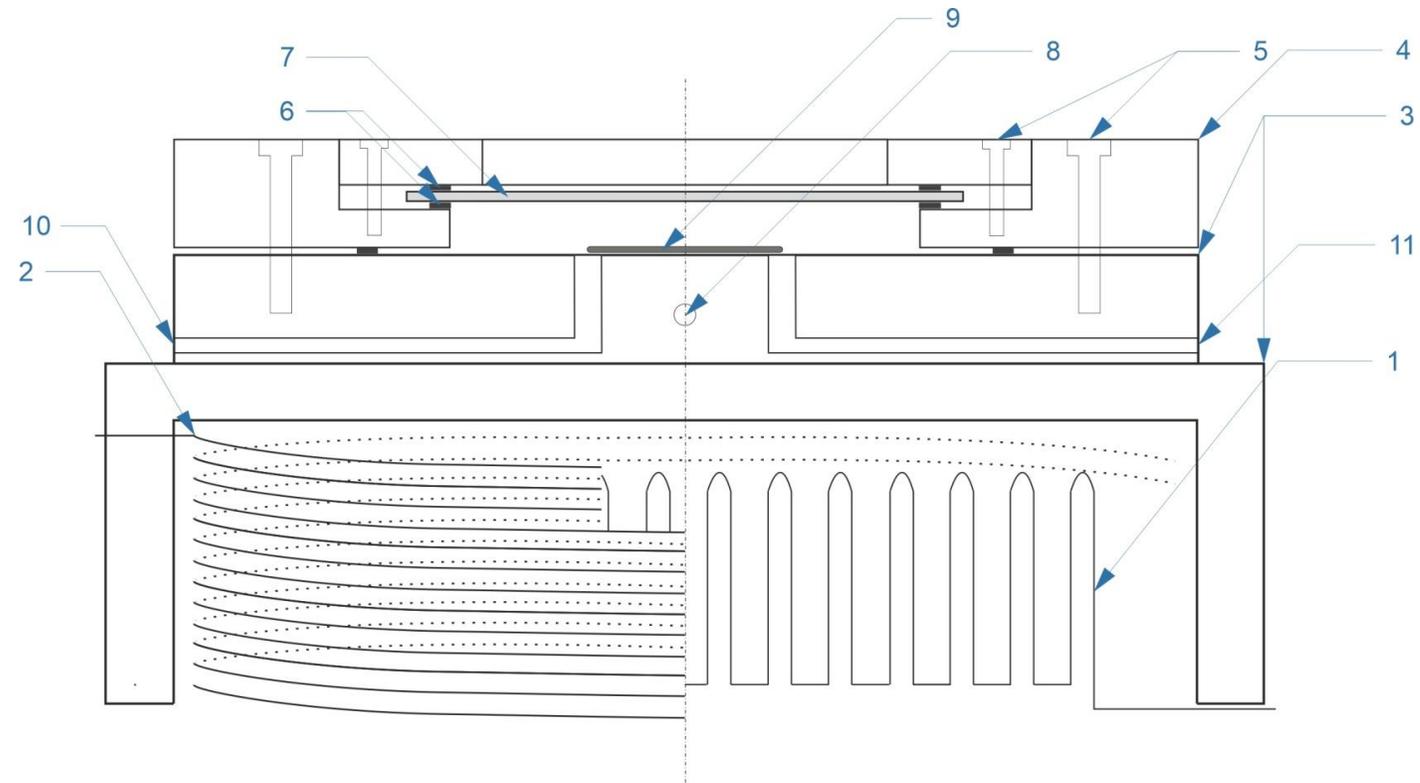
	Reactions	ΔG° (kJ·mol ⁻¹)
1	$H_2O (l) \rightarrow H_2 (g) + 1/2O_2 (g)$	237
2	$CO_2 (g) \rightarrow CO (g) + 1/2O_2 (g)$	257
3	$CO_2 (g) + H_2O (l) \rightarrow HCOOH (l) + 1/2O_2 (g)$	286
4	$CO_2 (g) + H_2O (l) \rightarrow HCHO (l) + O_2 (g)$	522
5	$CO_2 (g) + 2H_2O (l) \rightarrow CH_3OH (l) + 3/2O_2 (g)$	703
6	$CO_2 (g) + 2H_2O (l) \rightarrow CH_4 (g) + 2O_2 (g)$	818





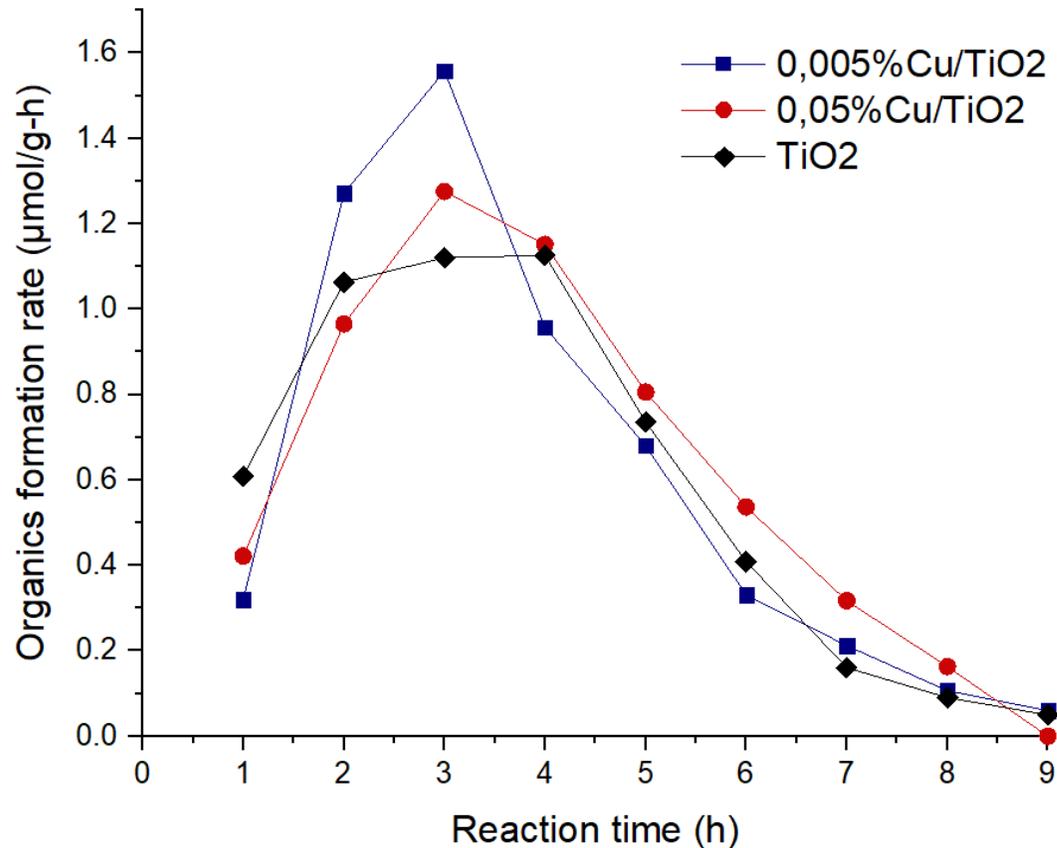
Scheme of the continuous flow photoreactor

- 1 – heater
- 2 – cooling
- 3 – main reactor body
- 4 – top cover
- 5 – bolts
- 6 – seals
- 7 – quartz glass
- 8 – thermocouple
- 9 – photocatalyst
- 10 – gas inlet
- 11 – gas outlet





Photocatalytic activity of TiO₂ and Cu/TiO₂ samples under UV irradiation

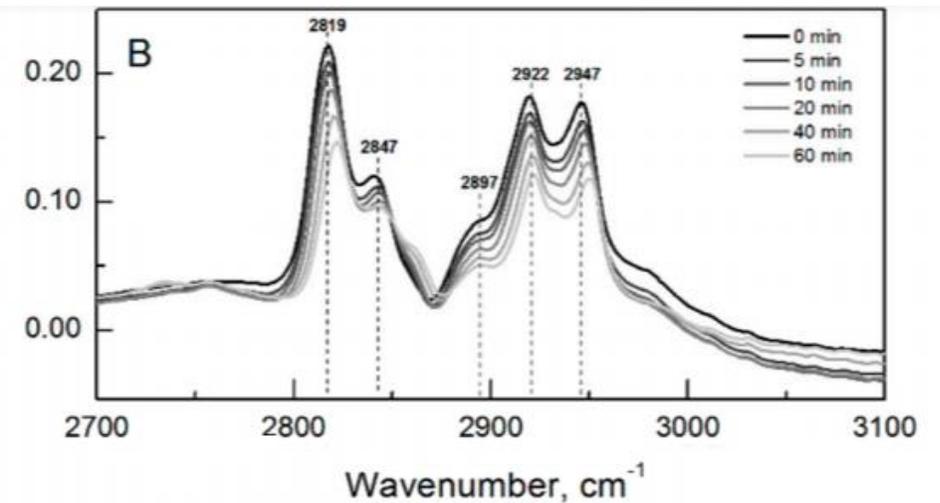
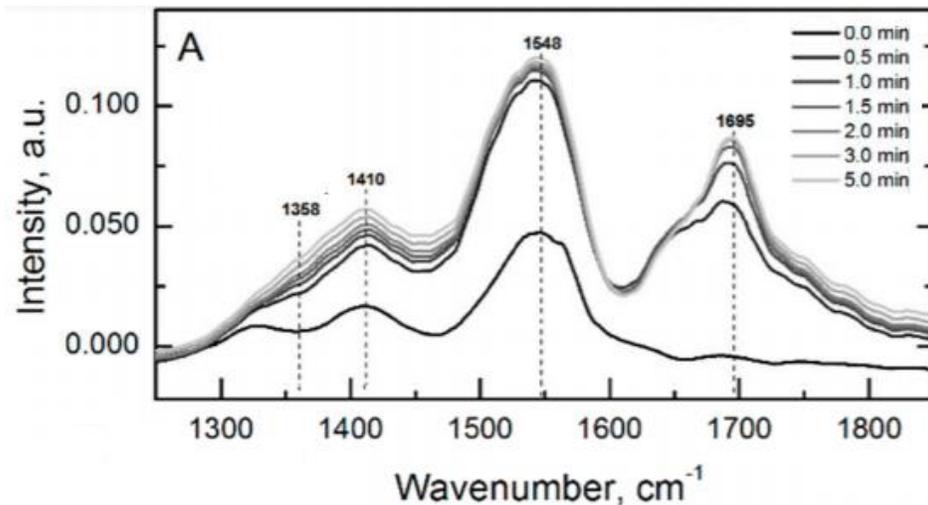


- the deposition of metal on the surface of TiO₂ enhance the photocatalytic reduction of CO₂ to some extent. However, high concentration of metal led to decreased activity.
- the photocatalysts undergo deactivation, as can be seen by the sharp decrease of formation rate of organics with time on stream.



Why photocatalysts deactivate: fast adsorption of reactants and slow desorption of products

Adsorption of CO₂ **(A)** and desorption of methanol **(B)** on/from the surface of TiO₂



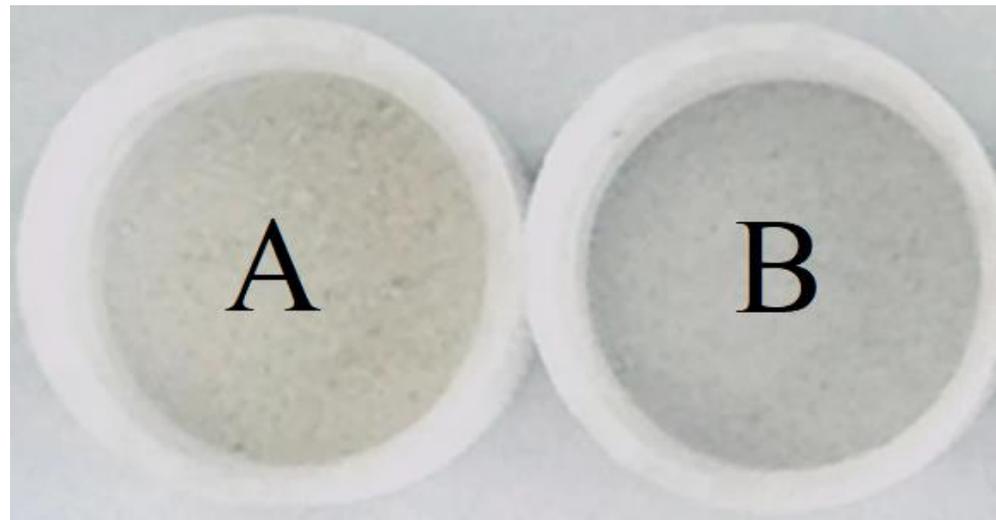
- the surface properties are needed to be adjusted to find the optimal trade-off between adsorption and desorption rate



Why photocatalysts deactivate: reduction of TiO₂ surface

Ratio of positive secondary ions from the surface of TiO₂ samples

Sample	Ti ₂ O ₃ /Ti	Ti ₂ O ₃ /Total counts of ions
(A) Cu/TiO ₂ (fresh)	18,94%	6,6%
(B) Cu/TiO ₂ (after reaction)	13,43%	5,6%





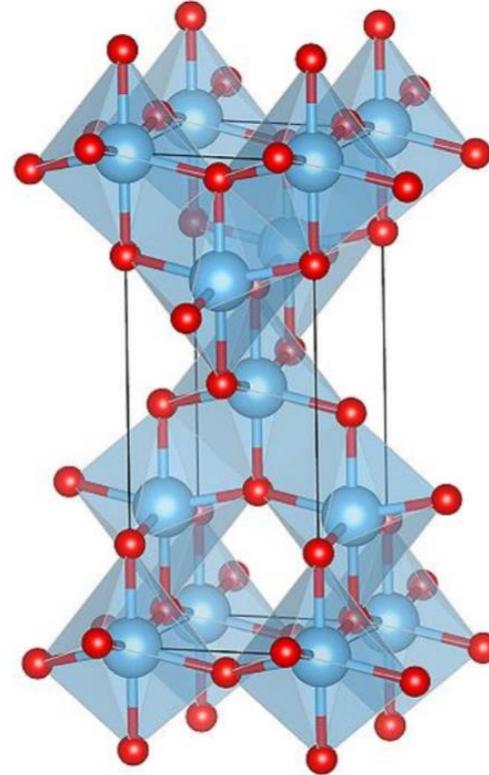
Intercalation of metals (Na and Li) into titanium dioxide

Na+



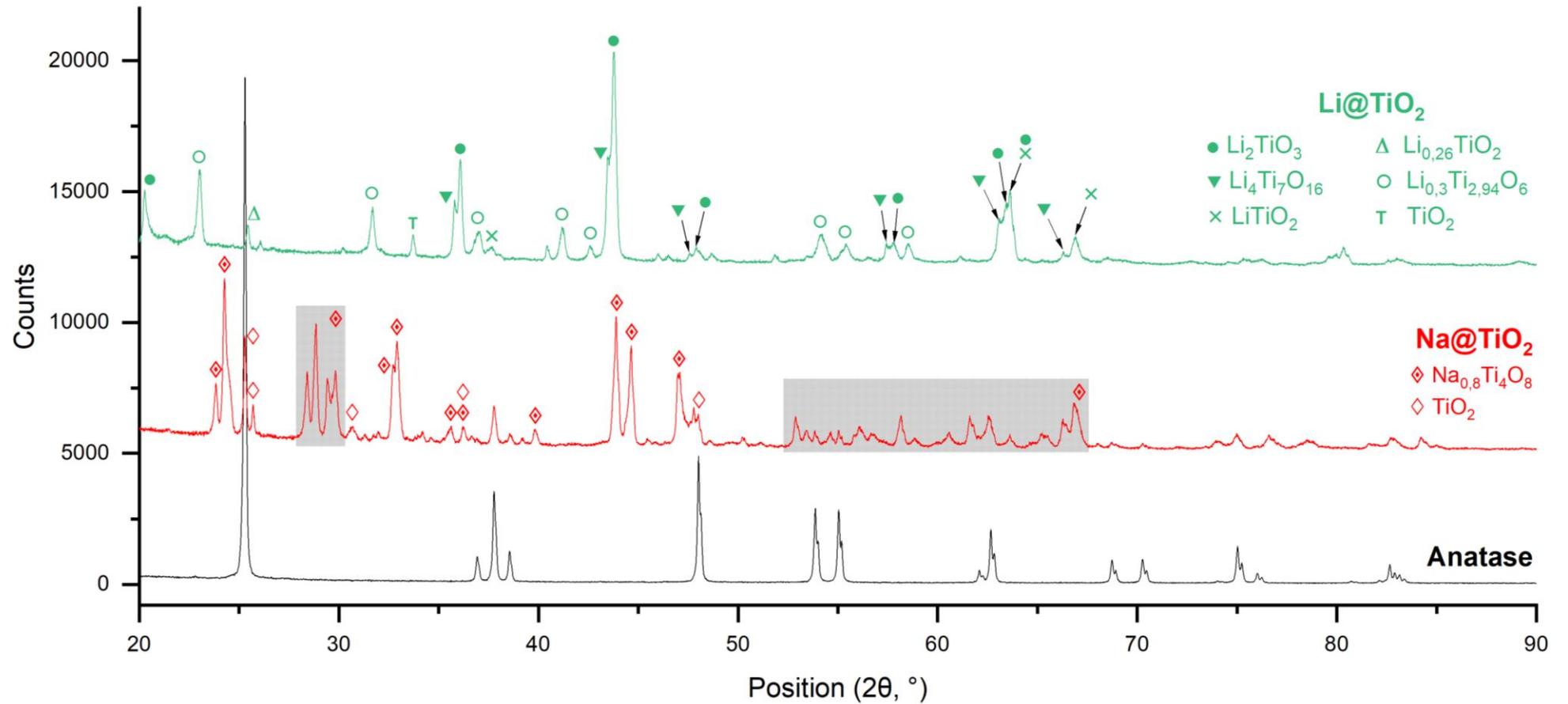
or

Li+



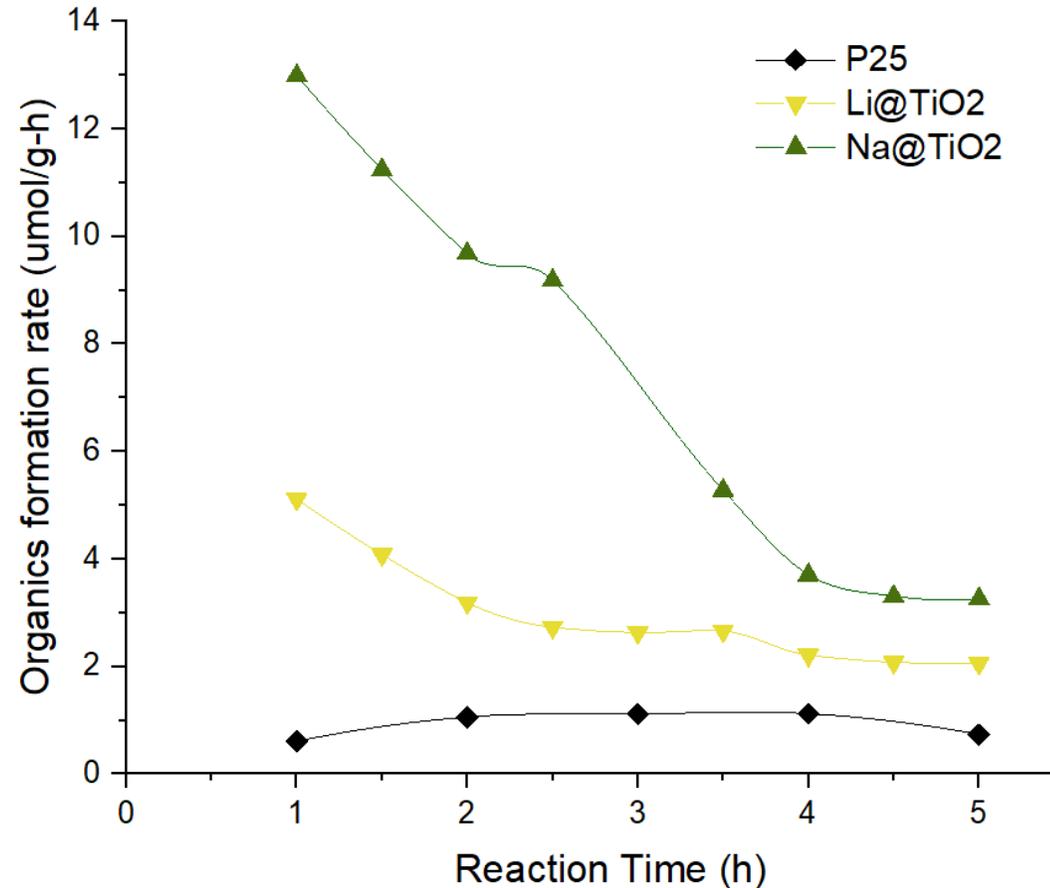


Intercalation of metals (Na and Li) into titanium dioxide





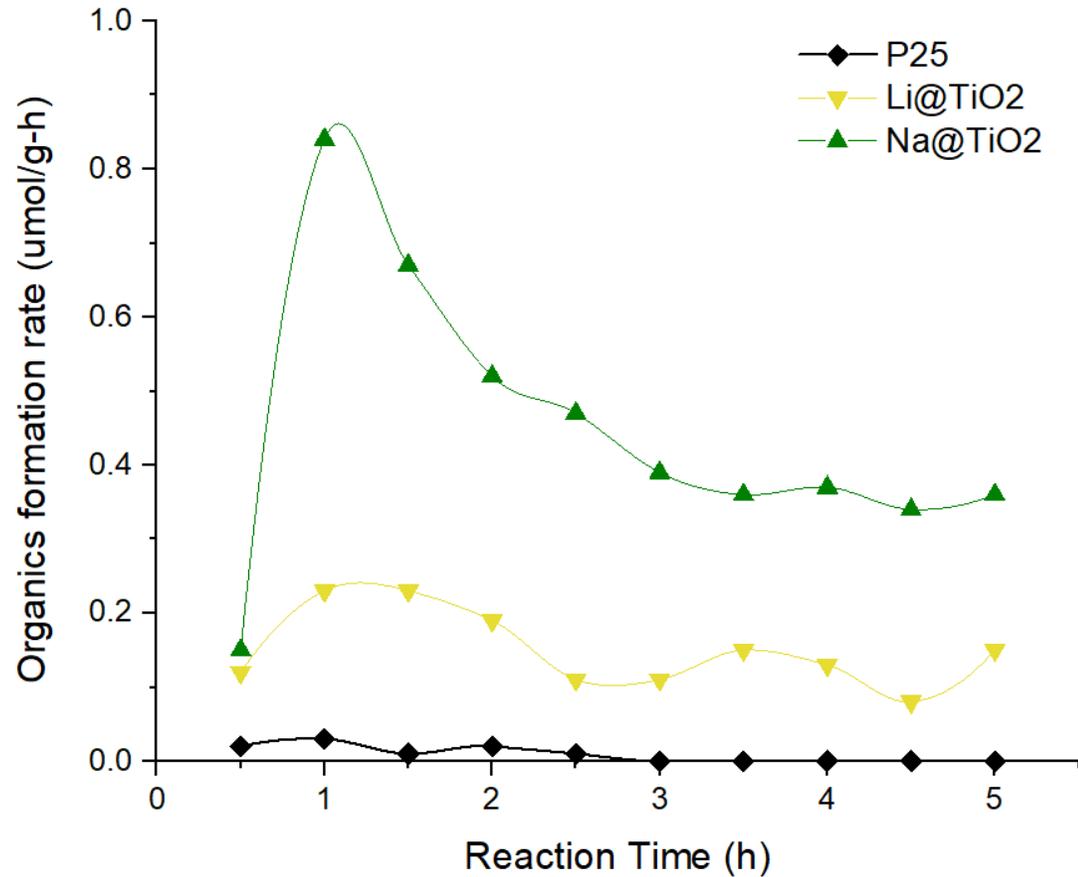
Photocatalytic activity of modified samples under UV irradiation



- intercalation of metal ions provides better mean of modification of TiO₂ than deposition.
- the Ni and Li – modified samples exhibit significantly higher activity under both UV and sun light irradiation
- the stability of modified samples are still need to be improved



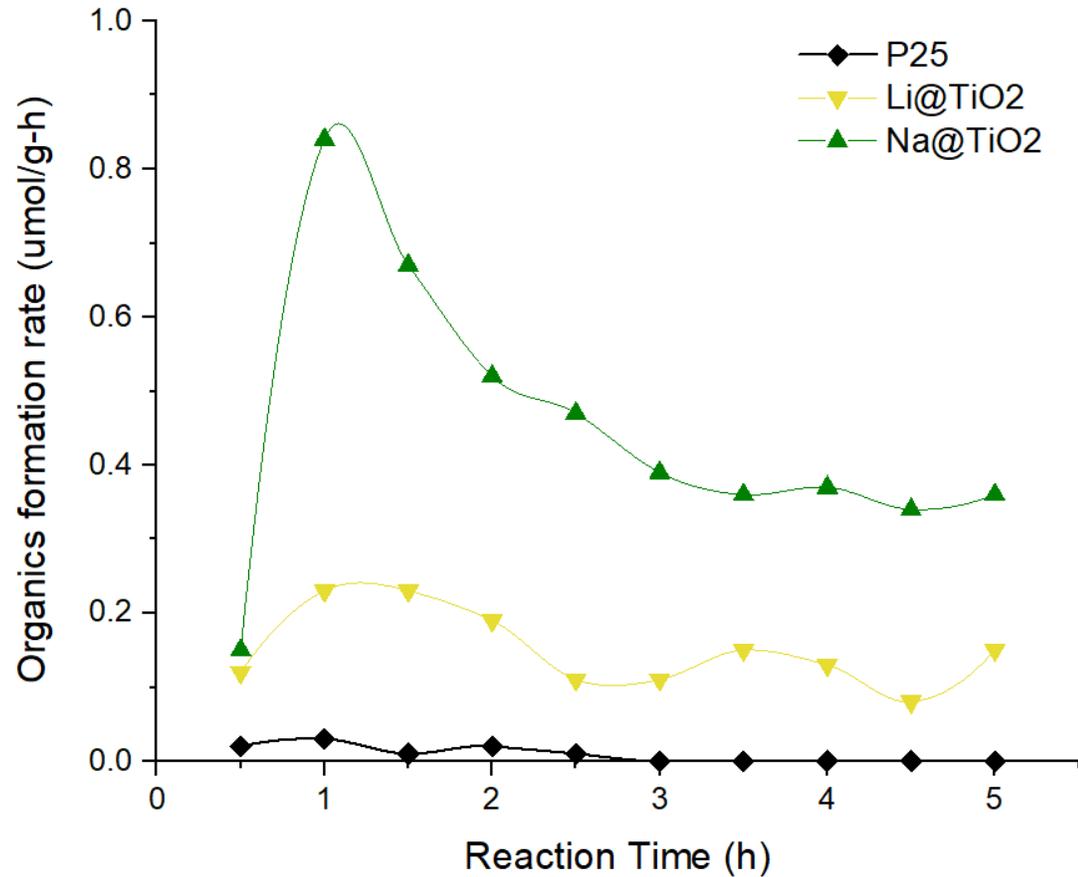
Photocatalytic activity of modified samples under sun light irradiation



- intercalation of metal ions provides better mean of modification of TiO₂ than deposition.
- the Ni and Li – modified samples exhibit significantly higher activity under both UV and sun light irradiation
- the stability of modified samples are still need to be improved



Photocatalytic activity of modified samples under sun light irradiation



- intercalation of metal ions provides better mean of modification of TiO₂ than deposition.
- the Ni and Li – modified samples exhibit significantly higher activity under both UV and sun light irradiation
- the stability of modified samples are still need to be improved



Conclusions

- the photocatalysts during the reduction of CO₂ undergo deactivation during the accumulation of reaction products.
- when metal particles were deposited on the surface of TiO₂, the reduction of its surface during the reaction was observed which also inhibited the conversion of carbon dioxide.
- high concentration of metal also negatively effected the photocatalytic activity of modified samples (probably due to enhanced recombination of charge carriers).
- intercalation of metal ions provides better mean of modification of TiO₂ than deposition technique: the intercalated samples exhibited high photocatalytic activity under both UV and sun light irradiation.