ELECTRONIC SUPPLEMENTARY INFORMATION

Sustainable oxidation of methane into formic acid using a polarized bioceramic under mild reaction conditions

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METHODS

Ultraporous HAp

HAp was synthesized as follows. 15 mL of 0.5 M $(NH_4)_2HPO_4$ in de-ionized water were added at a rate of 2 mL/min to 25 mL of a 0.5 M of $Ca(NO_3)_2$ solution in ethanol with pH previously adjusted to 11 using NH_4OH solution. The mixture was left aging for 1 h under gentle agitation (150 rpm) at room temperature. Hydrothermal treatment at 150 ºC was applied using an autoclave Digestec DAB–2 for 24 h. The autoclave was allowed to cool down before opening. The precipitates were separated by centrifugation and washed with water and a 60/40 v/v mixture of ethanol/water (twice). After lyophilizing it for 3 days, a white powder was obtained. The HAp powder was extensively grinded to reduce aggregates and homogenize the grain size.

Pluronic® F-127 hydrogel was prepared by mixing 25 g of distilled water and 25 g of Pluronic® F-127 polymer using a FlackTek SpeedMixer at 3500 rpm for 5 minutes. After that, 50 g of Pluronic® polymer were added and vigorously stirred using the same conditions. The resultant hydrogel was stored at 4 ºC.

Ultraporous HAp was obtained by slowly adding 60% wt. of previously prepared Pluronic® F-127 hydrogel to grinded HAp powder in a cold room at 4 ºC. In order to achieve a homogeneous mixture, such addition process was periodically interrupted for stirring at 2500 rpm for a 2 min minutes using a Fisherbrand™ Digital Vortex Mixer. The resulting white paste was left aging at 4 ºC for 24 h to ensure the homogeneous distribution of the hydrogel. The resulting ink was modeled using a cold spatula (< 4 ºC) to obtain 3D ultraporous HAp scaffolds with the desired shape. Finally, the mixture was calcined at 1000 ºC using a muffle Carbolite ELF11/6B/301 for 2 h. In this step, the Pluronic® F-127 hydrogel was completely removed from the modeled structure.

p-HAp catalyst

Calcined porous structures were catalytically activated by placing the samples between two stainless steel plates (AISI 304), which acted as electrodes. The ultraporous HAp sample was left in contact with negative electrode, while the positive electrode was separated 4 cm from the calcined sample. A constant DC voltage of 500 V was applied for 1 h with a GAMMA power supply, while the temperature was kept at 1000 ºC. Samples were allowed to cool down maintaining the applied electric potential for 30 minutes, and finally, all the system was powered off and left to cool down overnight.

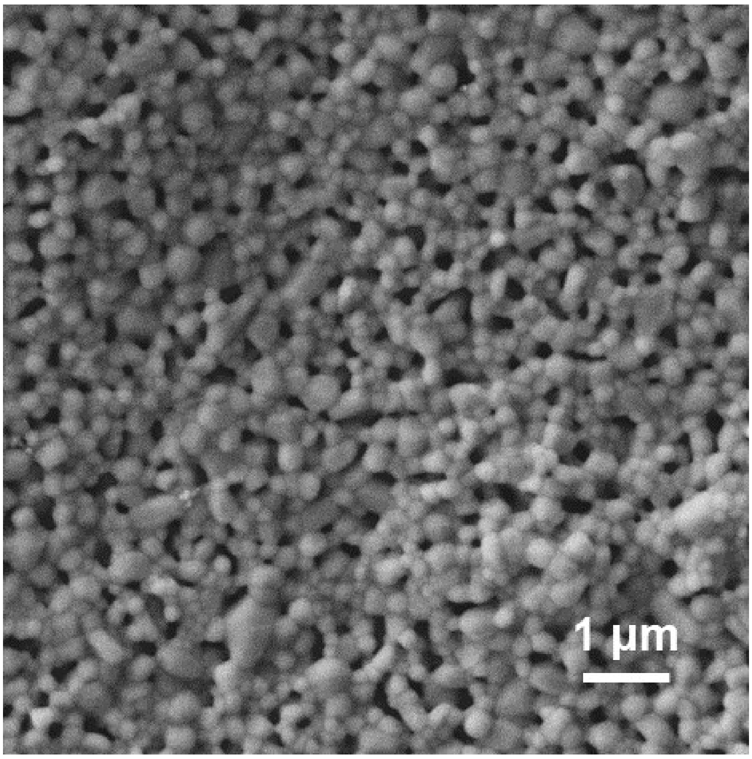
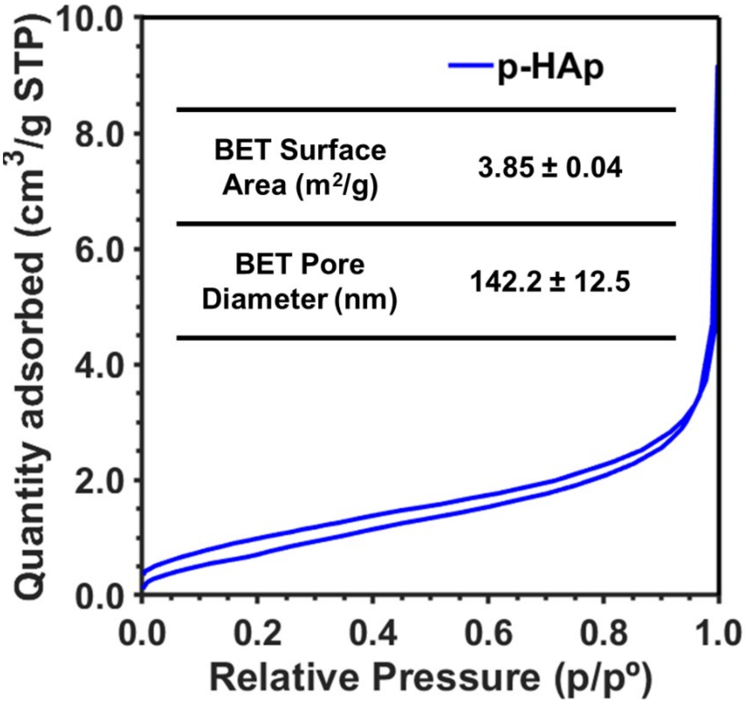


Figure S1. SEM micrograph of HAp.



BET Surface Area (m^2/g)	3.85 ± 0.04
BET Pore Diameter (nm)	142.2 ± 12.5

Figure S2. BET isotherm recorded at 300 ºC for catalytically active p-HAp.

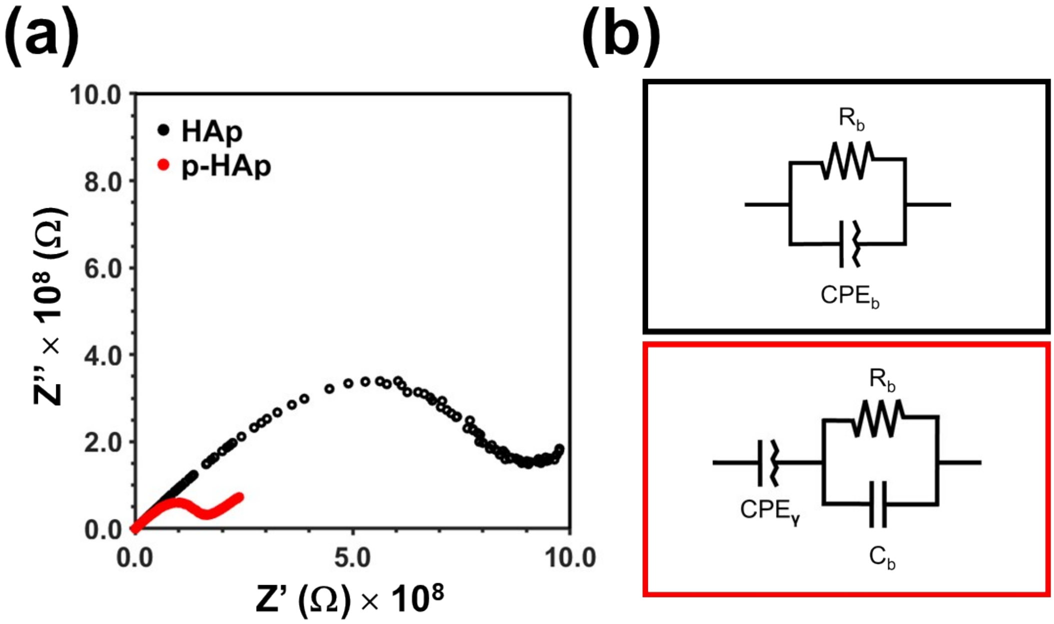


Figure S3. (a) Nyquist plots obtained from EIS measurements on p-HAp and calcined HAp. (b) Electric Equivalent Circuit (EEC) developed for calcined HAp (black box) and p-HAp (red box) to explain the electrical and capacitive properties of catalytically active p-HAp.

Table S1. Data derived from experimental EIS recorded for p-HAp and sintered HAp, considering the EEC models displayed in Figure S2b.

Element	**p-HAp**	**Calcined HAp**
R_b (MΩ/cm^2)	175.2	1109.1
(error, %)	(2.5)	(2.0)
CPE Y_b (nS×s^n/cm^2)	-	39.3
(error, %)		(3.4)
n_b	-	0.92
(error, %)		(0.3)
CPE Y_γ (nS×s^n/cm^2)	12.1	-
(error, %)	(8.4)	
n_γ	0.6	-
(error, %)	(1.5)	
C_b (pF/cm^2)	19.7	-
(error, %)	(2.1)	

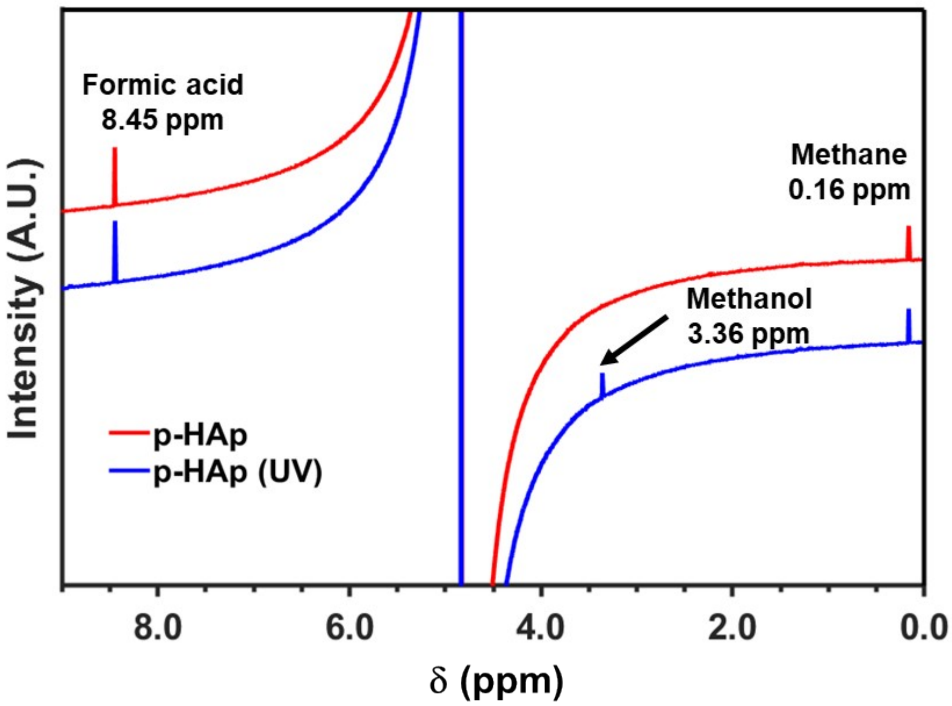


Figure S4. ^{1}H NMR spectra of the supernatant for the reactions performed without and with UV irradiation. The reactions catalyzed by p-HAp were conducted for 24 h using CH_4 (4 bar) and H_2O (20 mL) at 120 ºC.

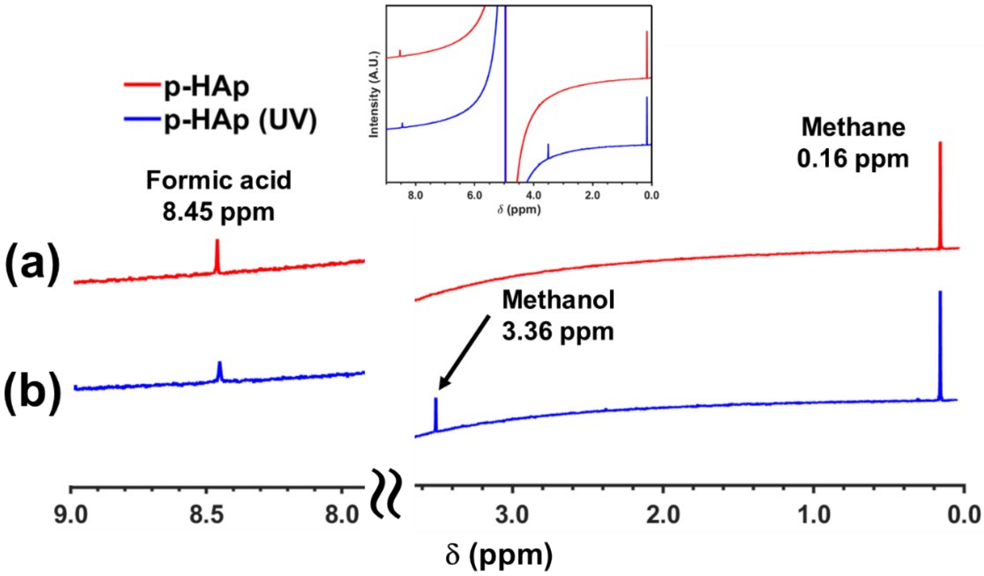


Figure S5. ^{1}H NMR spectra of the solutions obtained by dissolving the catalysts after the reaction (a) without and with UV irradiation. Complete spectra are shown in the inset at the top. The reactions were conducted for 24 h using CH_4 (4 bar) and H_2O (20 mL) at 120 ºC using p-HAp as catalyst.

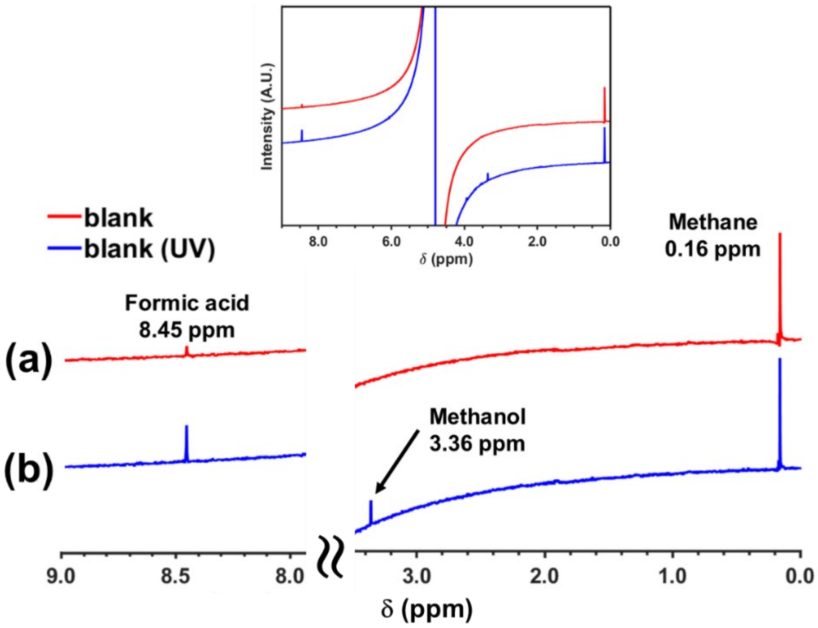


Figure S6. ^{1}H NMR spectra of the water after blank reactions with non-polarized HAp as catalyst: (a) without and (b) with UV irradiation. Complete spectra are shown in the inset at the top. The reactions were conducted for 24 h using CH_4 (4 bar) and H_2O (20 mL) at 120 ºC (without catalyst in both cases).

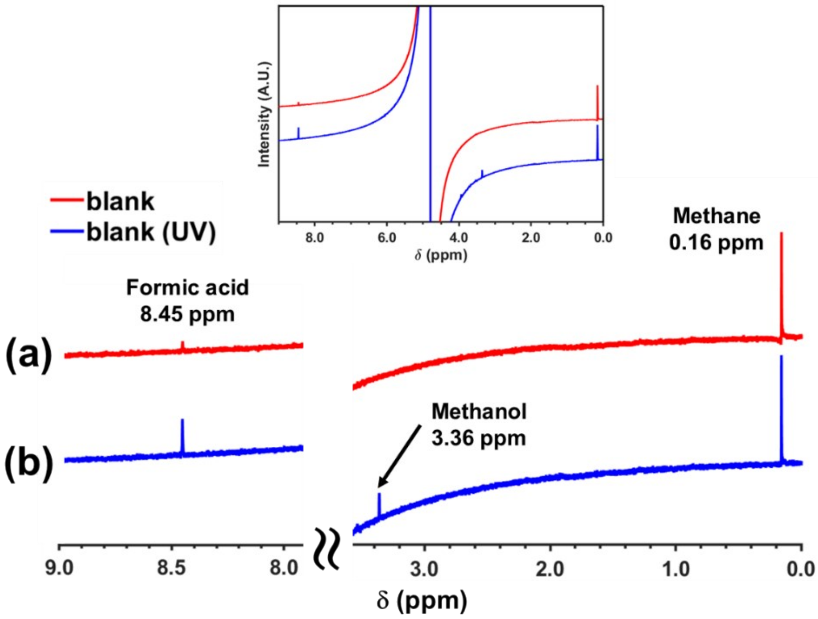


Figure S7. ^{1}H NMR spectra of the water after blank reactions without catalyst: (a) without and (b) with UV irradiation. Complete spectra are shown in the inset at the top. The reactions were conducted for 24 h using CH_4 (4 bar) and H_2O (20 mL) at 120 ºC (without catalyst in both cases).

Table S2. Yields (in µmol/g_c) of formic acid and methanol in the supernatant and the catalyst for the oxidation of CH_4 catalysed by p-HAp without and with UV irradiation The reaction was performed at 120 ºC for 24 h starting from 4 bar of CH_4 and 20 mL of de-ionized water in contact with the surface of the catalyst. The yields in the supernatant were corrected by subtracting the area of the formic acid and methanol peaks obtained in the corresponding blank reaction (Figure S4).

Reaction	Phase	Formic acid	Methanol
Without UV	Supernatant	131.3 ± 7.1	-
	Catalyst	5.6 ± 1.5	-
With UV	Supernatant	47.8 ± 7.9	27.9 ± 3.2
	Catalyst	4.1 ± 0.4	0.3 ± 0.1

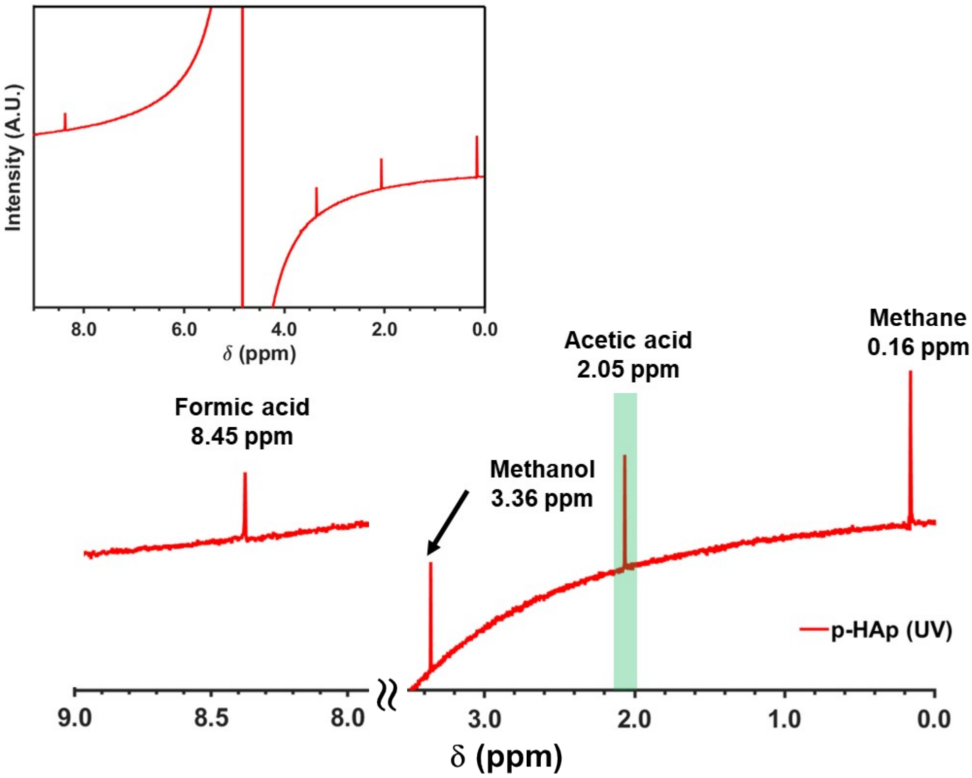


Figure S8. ^{1}H NMR spectra of the supernatant after the reaction with UV irradiation. Complete spectrum is shown in the inset at the top. The reaction was conducted for 48 h using CH_4 (4 bar) and H_2O (20 mL) at 120 ºC using p-HAp as catalyst.

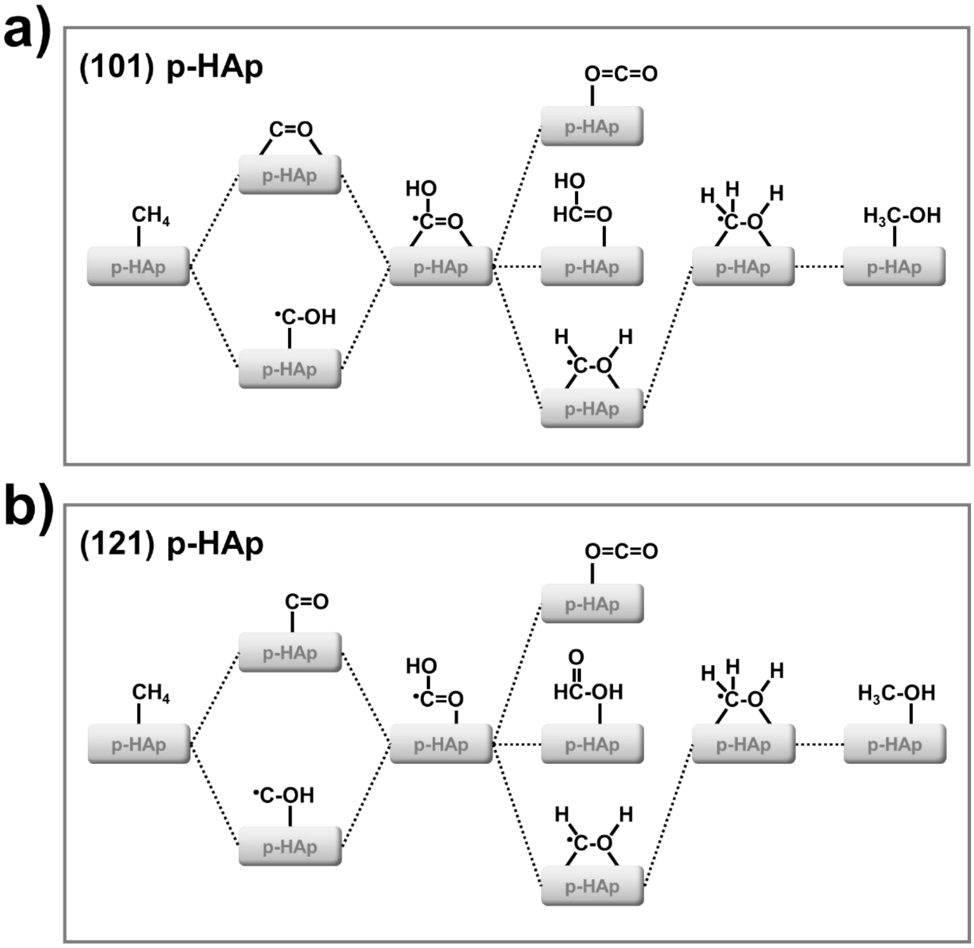


Figure S9. Scheme displaying the reaction pathways calculated considering the (a) (101) and (b) (121) crystallographic planes of p-HAp (see Figure 5b-c).

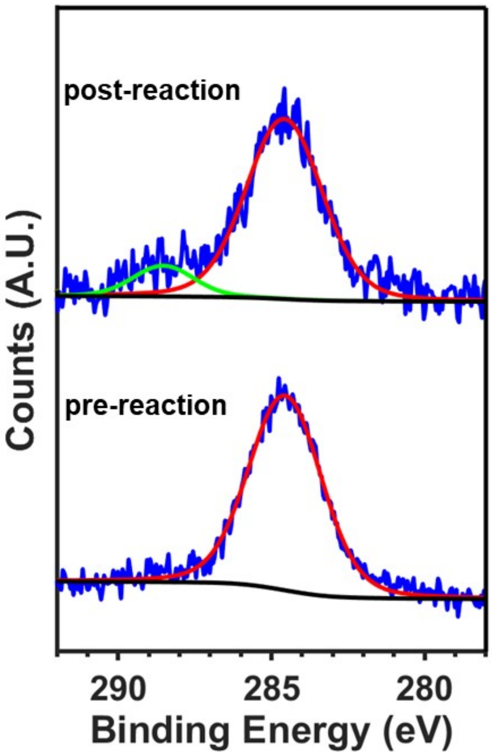


Figure S10. C 1s high resolution XPS spectra for the p-HAp catalyst before and after batch reaction at 120 ºC for 24 h with 4 bar of CH_4. The carbon-containing species detected after the reaction were attributed to adsorbed carboxylic groups from formic/acetic acid: C–H: 284.6 Ev and O–C=O: 288.6 Ev.

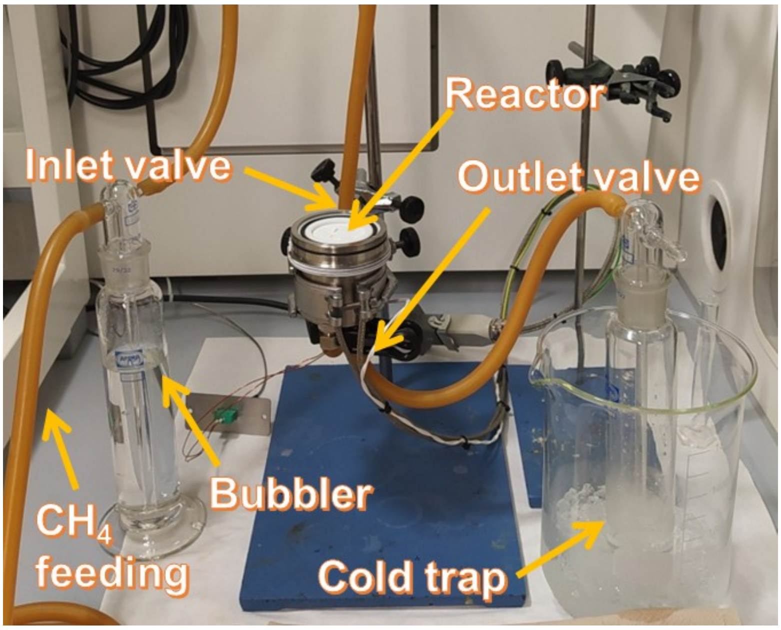


Figure S11. Set up used for the continuous-flow process. Photograph of the reactor, the connections to the inlet and outlet valves, the bubbler, and the cold trap.

Table S3. Comparison of batch and continuous methane oxidation reactions to produce formic acid. The catalyst, reaction conditions and yield of formic acid are displayed for each case.

Catalyst	**Reaction conditions**	**Yield**	**Ref.**
	Batch reactions		
p-HAp	4 bar CH_4 flow + 20 mL H_2O, 120 ºC without UV illumination	136 µmol/g_c·	This work
p-HAp	4 bar CH_4 flow + 20 mL H_2O, 120 ºC with UV illumination	55.7 µmol/g_c·	This work
GaN	0.3 bar CH_4 + 0.7 bar O_2 + 1 mL H_2O; 25 ºC with UV illumination	20.01 µmol/g_c·	11
ZIF-8	30 bar CH4 + 0.5 mol/L H_2O_2 (oxidant); 50 ºC, 30 min	110 µmol/g_c	16
Fe-ZIF-8-0.28	30 bar CH4 + 0.5 mol/L H_2O_2 (oxidant); 50 ºC, 30 min	1086 µmol/g_c	16
	Continuous reactions		
p-HAp	Constant CH_4 flow of 1.84 mmol/s (gas bubbled in liquid water), 120 ºC without UV illumination,	70 µmol/g_c·min	This work
CsPW-TiO_2	6 bar CH4 + 1 MPa air + 100 mL H_2O; 20º C with UV illumination	18 µmol/g_c·min	9
CsPW-TiO^2 + Ru/Al_2O_3	6 bar CH_4 + 1 bar air + 100 mL H_2O; 20º C with UV illumination	42µmol/g_c·min	9