Supporting information

Highly selective photocatalytic conversion of methane to liquid oxygenates over silicomolybdic-acid/TiO_2 in mild condition

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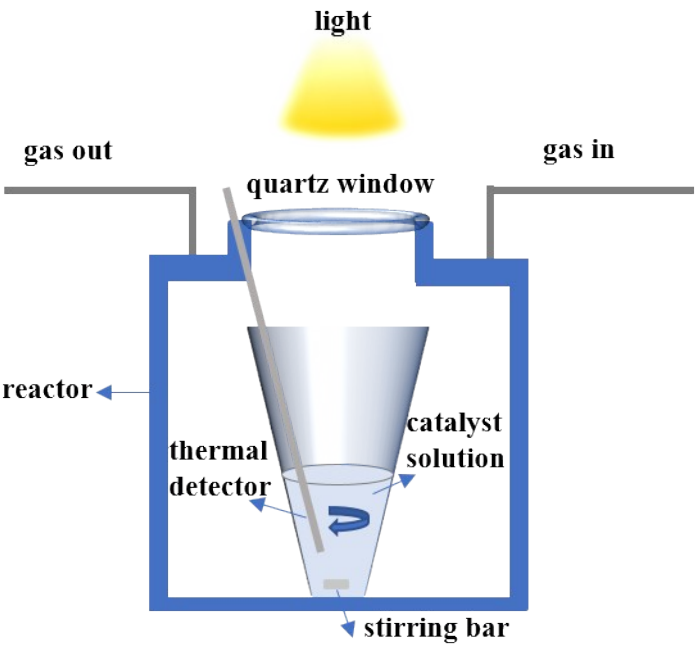

Fig. S1. Schematic diagram of reactor system.

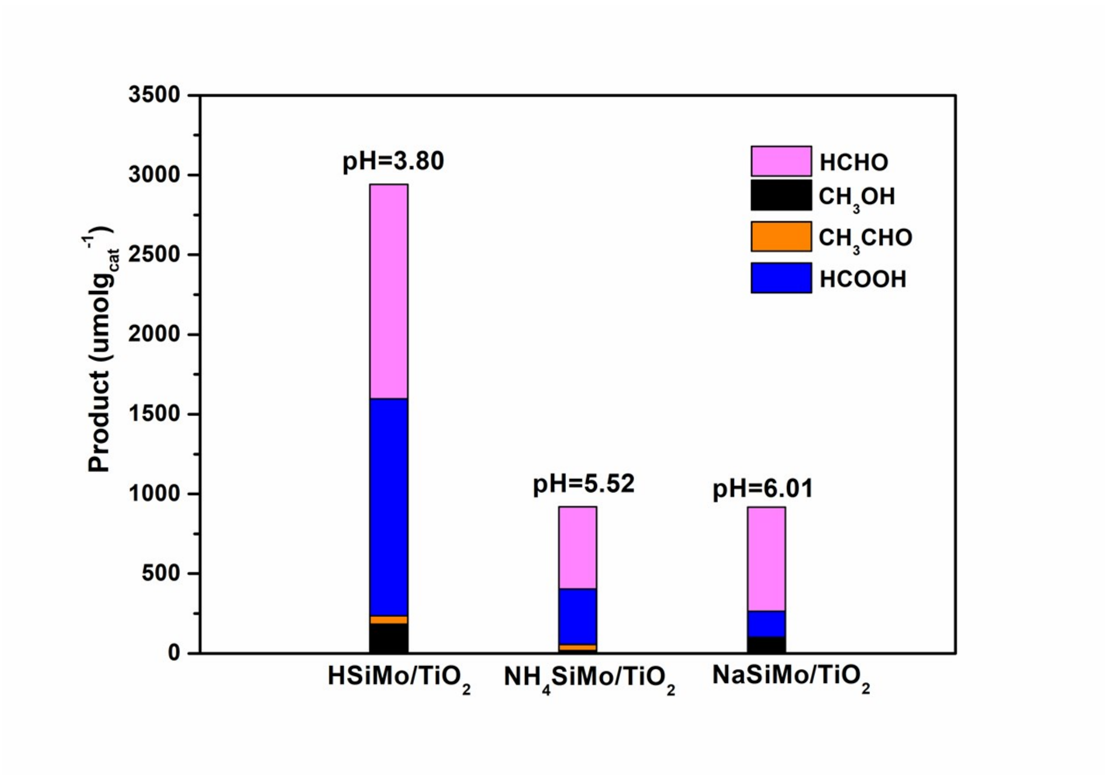

Fig. S2. Oxidation of CH_4 over different photocatalysts. Reaction conditions: 20 mg catalyst, 2 MPa O_2, 3 MPa CH_4, 20 ml water, 2 h reaction time, and 150 °C reaction temperature.

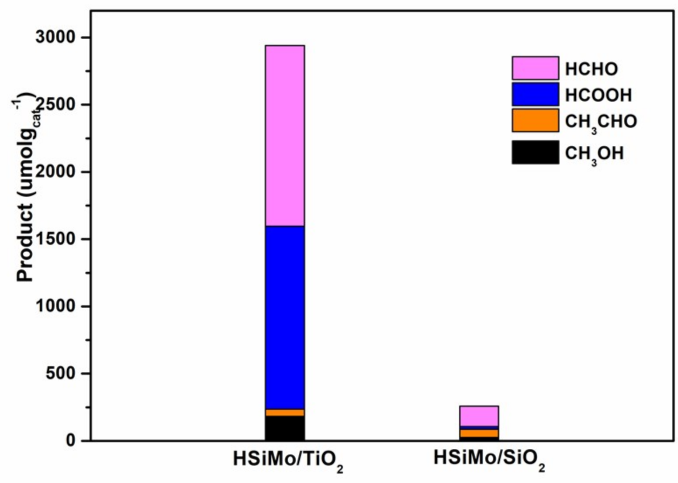

Fig. S3. The photocatalytic performances of 2.5% HSiMo/SiO_2 catalyst and 2.5% HSiMo/TiO_2 under light illumination. Reaction conditions: 20 mg catalyst, 2 MPa O_2, 3 MPa CH_4, 20 ml water, 2 h reaction time, and 150 °C reaction temperature.

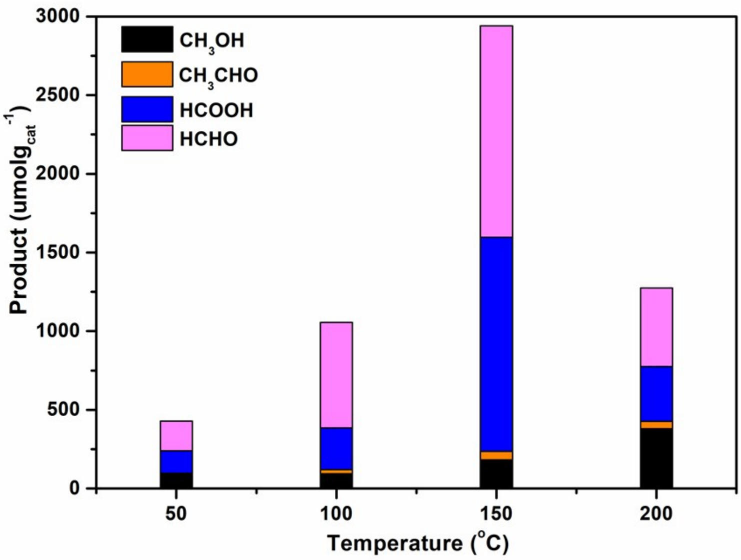

Fig.S4. Photo product yield vs. temperature over 2.5% HSiMo/TiO_2 catalyst under light irradiation. Reaction conditions: 20 mg catalyst, 2 MPa O_2, 3 MPa CH_4, 20 ml water, 2 h reaction time.

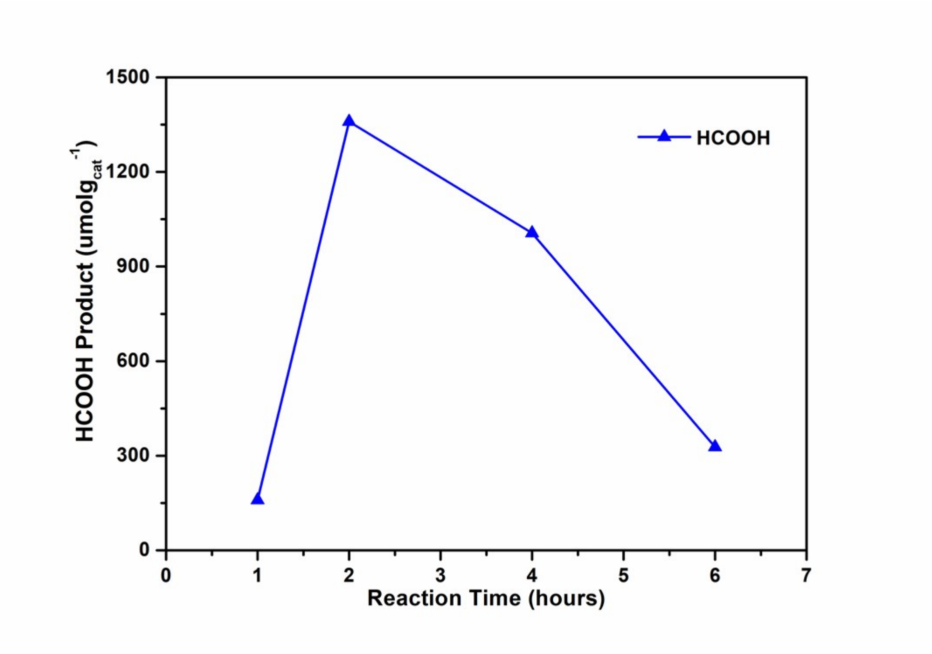

Fig. S5. Photo product HCOOH yield vs. reaction time over 2.5% HSiMo/TiO_2 under light irradiation. Reaction conditions: 20 mg catalyst, 2 MPa O_2, 3 MPa CH_4, 20 ml water, and 150 °C reaction temperature.

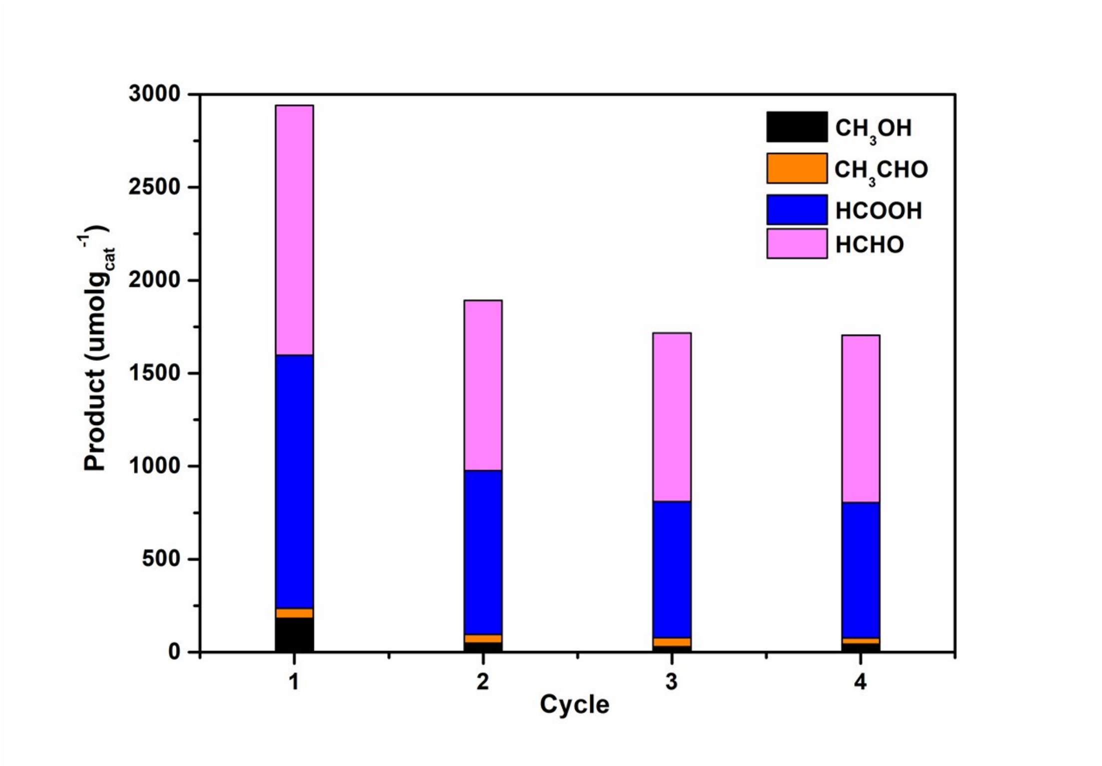

Fig. S6. Cycles of photocatalytic methane oxidation over 2.5% HSiMo/TiO_2 under light irradiation. Reaction conditions: 20 mg catalyst, 2 MPa O_2, 3 MPa CH_4, 20 ml water, 2 h reaction time, and 150 °C reaction temperature.

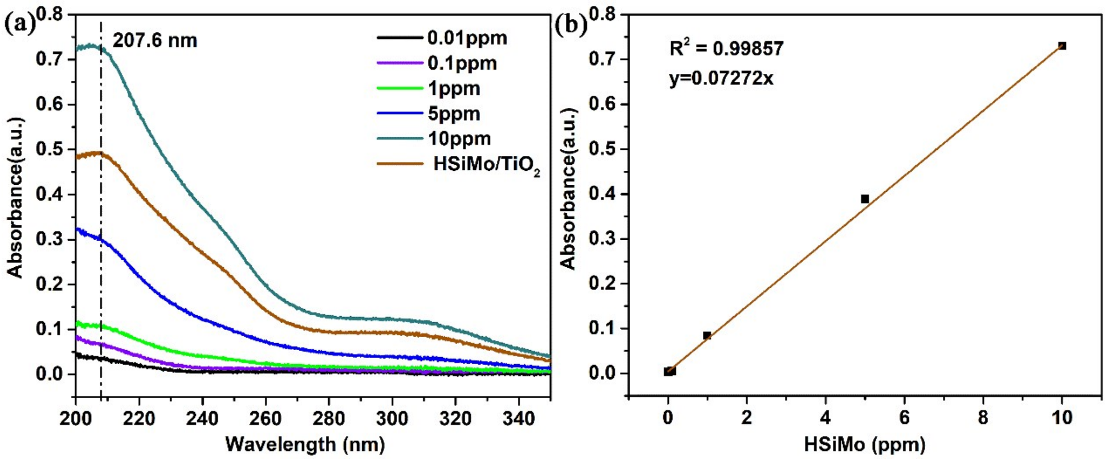

Fig. S7. (a) UV spectra of HSiMo with selected concentrations and (b) The standard line of HSiMo concentration vs. UV intensity at wavelength of 207.6nm, revealing the concentration of HSiMo dissolved in the reaction solution with HSiMo/TiO_2 catalyst.

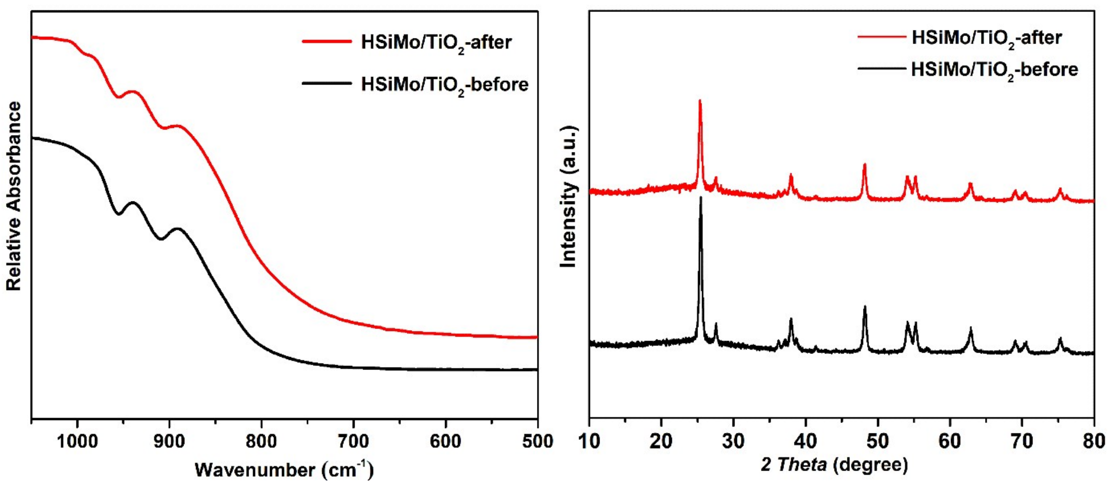

Fig. S8. (a) The IR spectra and (b) XRD pattern of HSiMo/TiO_2 catalyst before and after photo reaction. Reaction conditions: 20 mg catalyst, 2 MPa O_2, 3 MPa CH_4, 20 ml water, 2 h reaction time, and 150 °C reaction temperature.

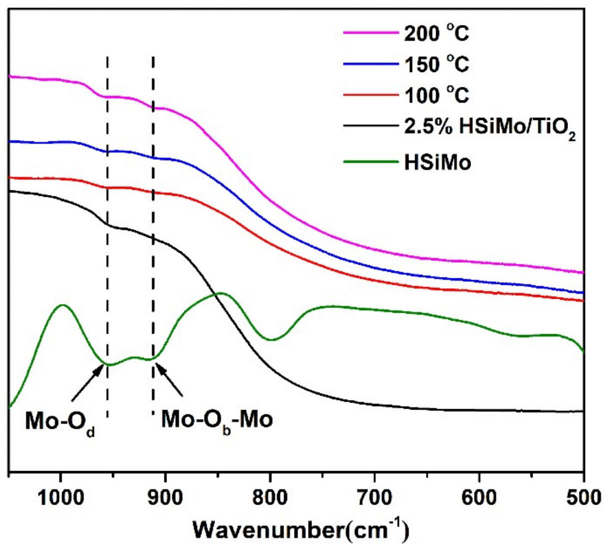

Fig. S9. The IR spectrum of HSiMo/TiO_2 at the temperature of 100°C, 150°C and 200°C

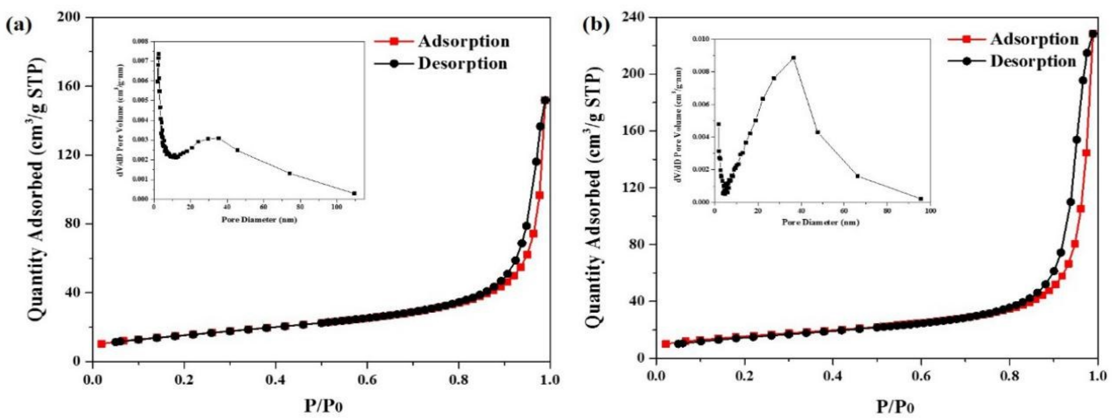

Fig. S10. N_2-sorption isotherms and corresponding pore-size distribution and total pore volume curves (inset) of (a) TiO_2 and (b) 2.5%HSiMo/TiO_2 composites.

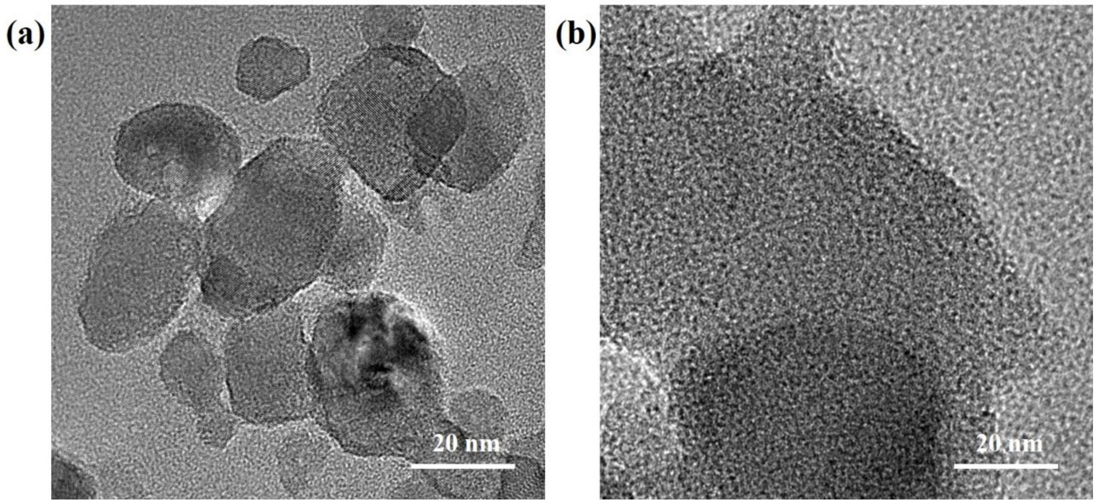

Fig. S11. HRTEM image of (a) TiO_2 and (b) HSiMo

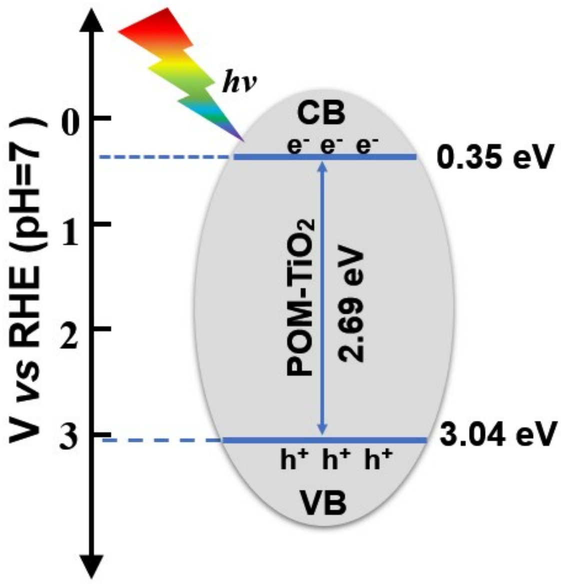

Fig. S12. Band structure of 2.5wt% HSiMo/TiO_2. Note: The band gap (BG) of 2.69 eV was obtained from UV-visible spectrum (Fig. 5b). The potential of the conduction band (CB) is -0.26 eV (vs. Ag/AgCl) from the Mott-Schottky plot (Fig. 5d). The CB vs. RHE is 0.35 eV, which was calculated using E(RHE) = E(VAg/AgCl) + 0.059 pH + 0.197. The potential of the valence band (VB) vs. RHE is equal to BG+CB=2.69eV+0.35eV=3.4eV.

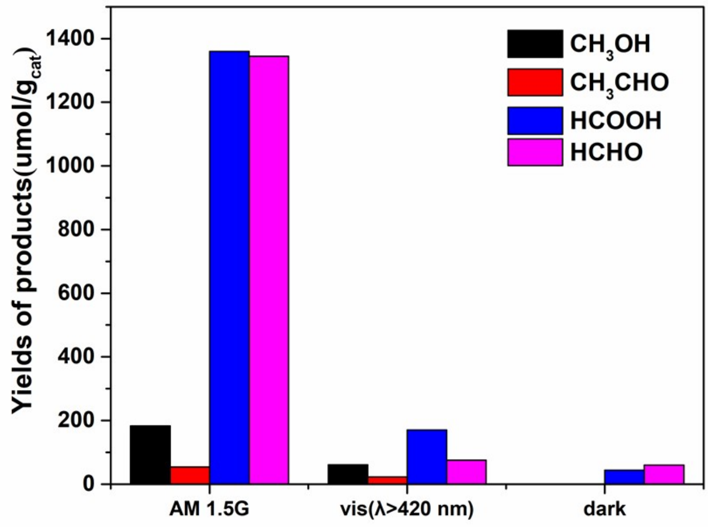

Fig. S13. Photo product yield over 2.5% HSiMo/TiO_2 catalyst under irradiation of 1.5G light and visible light and without light irradiation. Reaction conditions: 20 mg catalyst, 2 MPa O_2, 3 MPa CH_4, 20 ml water, 2 h reaction time, and 150 °C reaction temperature.

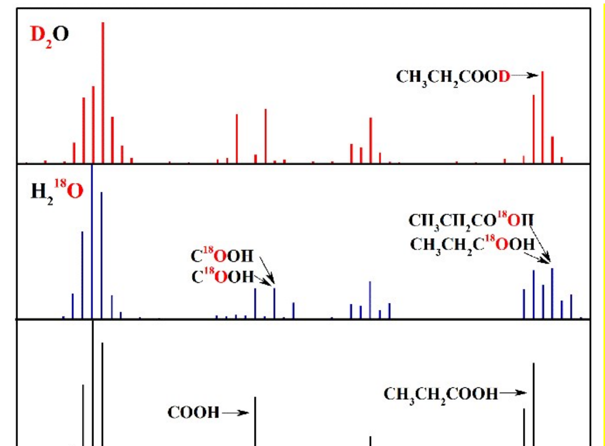

Fig. S14. GC-mass spectra of CH_3CH_2COOH generated from photocatalytic CH_4 oxidation with O_2 in D_2O or $H_2{}^{18}O$ over 2.5% HSiMo/TiO_2.

Table S1. Physicochemical properties of TiO_2 and $HSiMo/TiO_2$ catalysts.

Sample	HSiMo loading (wt%)
2.5% $HSiMo/TiO_2$	2.67
5% $HSiMo/TiO_2$	4.95
10% $HSiMo/TiO_2$	8.15

Table S2 Photocatalytic conversion of methane into oxygenates between this studies catalysts and other representative catalysts.

Catalyst	Oxidant	Photoproduct (umol/g_{cat})						Ref
		CH_3OH	CH_3OOH	HCHO	HCOOH	CH_3CHO	CO_2	
0.33 wt.% FeO_x/TiO_2	H_2O_2	900	-	-	-	-	-	[1]
0.1 wt % Au/ZnO	O_2	41.2	123.4	86.3	-	-	11.6	[2]
0.1 wt.% Ag/ZnO		7.3	19.3	112.1	-	-	7.1	
$Au_{0.75}/ZnO$	O_2	1082	951	-	-	-	-	[3]
$HSiMo/TiO_2$	O_2	183.2	-	1344.6	1359.8	53.7	300.9	This work

Table S3. Textural properties of TiO_2 and $HSiMo/TiO_2$ catalysts.

Sample	S_{BET} (m^2/g)	Average pore diameter (nm)	Pore volume (cm^3/g)
TiO_2	55.7647	18.1165	0.2349
2.5%$HSiMo/TiO_2$	55.8930	25.6163	0.3532
5%$HSiMo/TiO_2$	53.3726	27.2799	0.3603
10%$HSiMo/TiO_2$	37.0964	20.6932	0.2144

References:

[1] J. Xie, R. Jin, A. Li, Y. Bi, Q. Ruan, Y. Deng, Y. Zhang, S. Yao, G. Sankar, D. Ma, *Nat. Catal.*, 2018, **1**, 889–896.

[2] H. Song, X. Meng, S. Wang, W. Zhou, X. Wang, T. Kako, J. Ye, *J. Am. Chem. Soc.*, 2019, **141**, 20507-20515.

[3] W. Zhou, X. Qiu, Y. Jiang, Y. Fan, S. Wei, D. Han, L. Niu, Z. Tang, *J. Mater. Chem. A*, 2020, **8**, 13277-13284.