Electronic Supplementary Information (ESI)

Active and durable copper phosphate catalysts dispersed with metal oxide additives for the methane oxidation with oxygen into formaldehyde

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Figure S1 Change of methane conversion, selectivity to HCHO, CO and CO_2 and yield of HCHO as a function of temperatures of the catalyst bed in the methane oxidation over CuPOx/SiO₂ catalysts.



Figure S2 Change of methane conversion, selectivity to HCHO, CO and CO_2 and yield of HCHO as a function of temperatures of the catalyst bed in the methane oxidation over CuPOx/SiO₂ catalysts.



Figure S3 Change of methane conversion, selectivity to HCHO, CO and CO_2 and yield of HCHO as a function of temperatures of the catalyst bed in the methane oxidation over AlO_x -CuPO_x catalysts.

Additive	Temp.	Conversion		Selectivity[%]		НСНО
	[K]	[%]	HCHO	0 CO	CO ₂	yield[%]
None	873	1.2	38	55	7	0.5
	923	4.1	19	68	13	0.8
MgOx	873	2.7	10	11	79	0.3
	923	2.2	27	46	27	0.6
AlOx	873	2.4	30	14	56	0.7
	923	6.6	16	19	65	1.0
CrOx	873	1.0	43	46	11	0.4
	923	2.6	28	67	5	0.7
MnOx	873	1.8	22	46	32	0.4
	923	3.2	20	32	43	0.6
SrOx	873	0.6	28	19	53	0.2
	923	2.3	17	20	63	0.4

Table S1 Methane oxidation over $CuPO_x$ catalysts modified with different metal oxides

	Temp.	Conversion	Se	electiv	ity	
Catalyst			[%]			HCHO yield[%]
	[K]	[%]	нсно	СО	CO2	_
$O_{\rm H}(10) D(4E) Al(4E)$	873	20.0	0	1	99	0.07
Cu(10)-P(45)-AI(45)	923	46.0	0	1	99	0.08
$O_{\rm H}(EQ) = D(2E) = AI(2E)$	873	4.1	2	1	97	0.08
Cu(50)-P(25)-AI(25)	923	12.3	1	3	96	0.2
$C_{\rm H}(80) = D(10) = AI(10)$	873	1.7	5	4	92	0.08
Cu(ou)-P(10)-AI(10)	923	5.6	3	4	94	0.1
$C_{\rm H}(25) = D(25) = AI(50)$	873	4.6	0	0	100	0.01
Cu(25)-F(25)-AI(50)	923	5.8	0	0	100	0.02
$C_{\rm H}(10) = B(10) = AI(90)$	873	2.4	2	5	93	0.02
Cu(10)-F(10)-AI(80)	923	4.4	2	7	91	0.04
Cu(45) - P(10) - Al(45)	873	10.6	1	0	99	0.06
Gu(45)-F(10)-Al(45)	923	20.5	0	0	99	0.06

Table S2 Methane oxidation over AlO_x-CuPO_x catalysts