Electronic Supplementary Information

Modification of the carbide microstructure by N- and S-functionalization of the support in Mo$_x$C/CNT catalysts

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Sample information

The catalysts have the following identification numbers (required to clearly identify the batch of reproductions in catalyst synthesis):

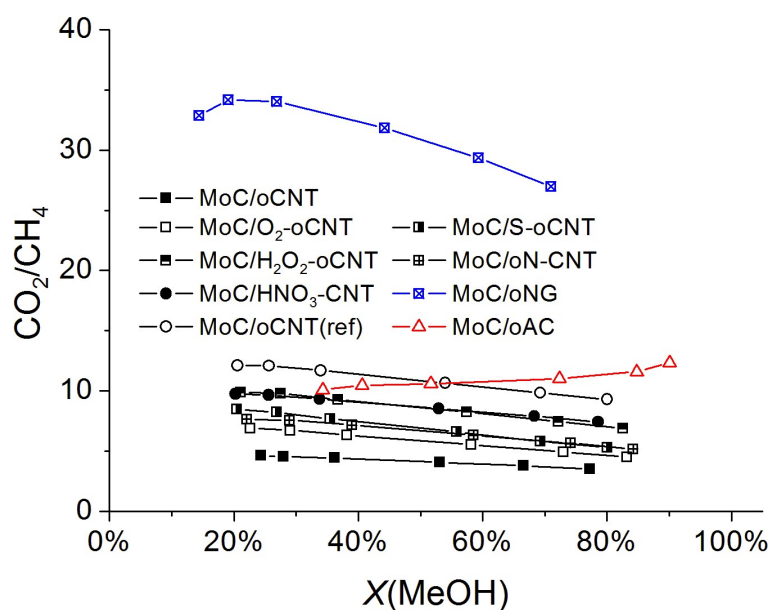|	
MoC/oCNT	13898 and 13899
MoC/O$_2$-oCNT	14169
MoC/H$_2$O$_2$-oCNT	14170
MoC/HNO$_3$-CNT	16193
MoC/oCNT(ref)	16194
MoC/oN-CNT	14172
MoC/S-oCNT	16195
MoC/oNG	14173
MoC/oAC	14174

Fig. S1 CO_2/CH_4 product ratio as a function of MeOH conversion. Reaction conditions: 250 mg catalyst, 10-100 ml min^{-1} of 1% MeOH/1%H_2O/He, 250°C.
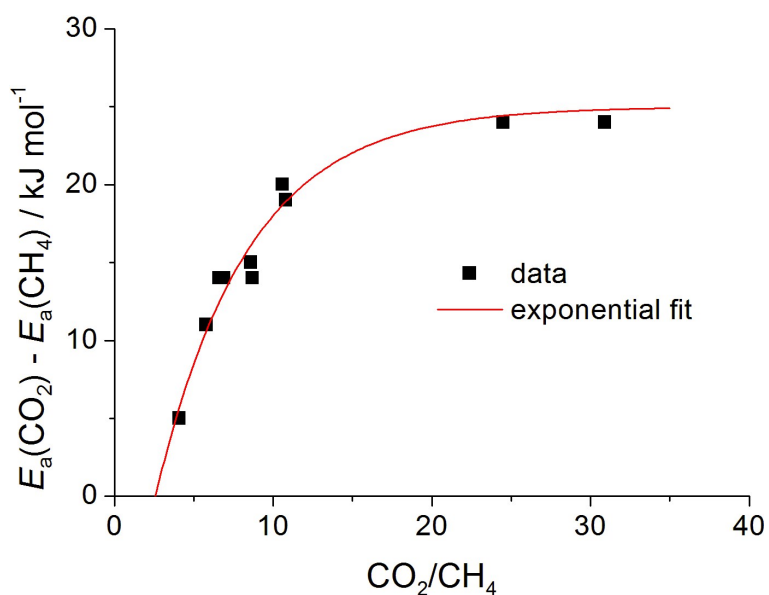

Fig. S2 Dependency of CO_2/CH_4 product ratio at 50% MeOH conversion on the difference of apparent activation energies of their formation.
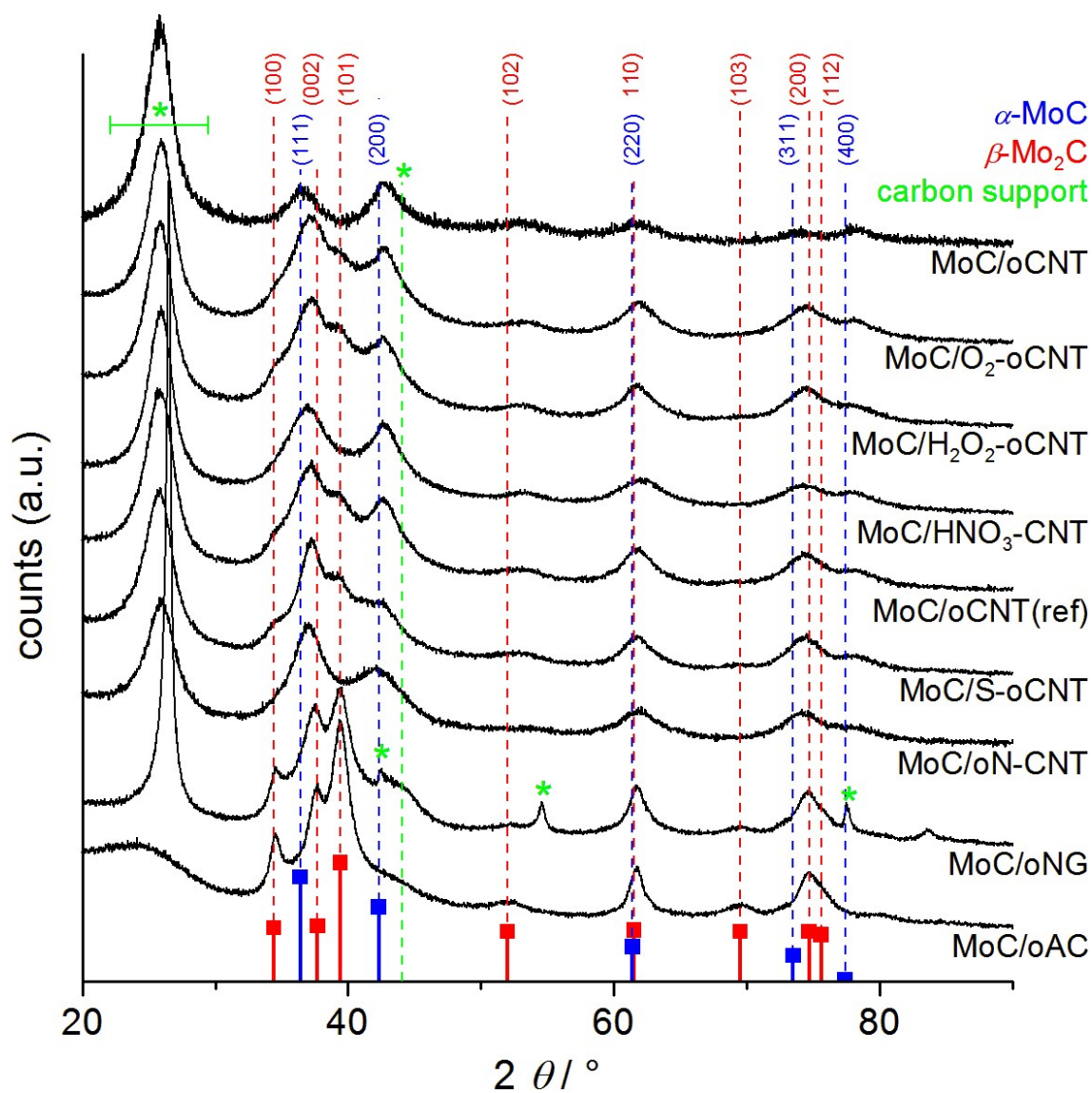
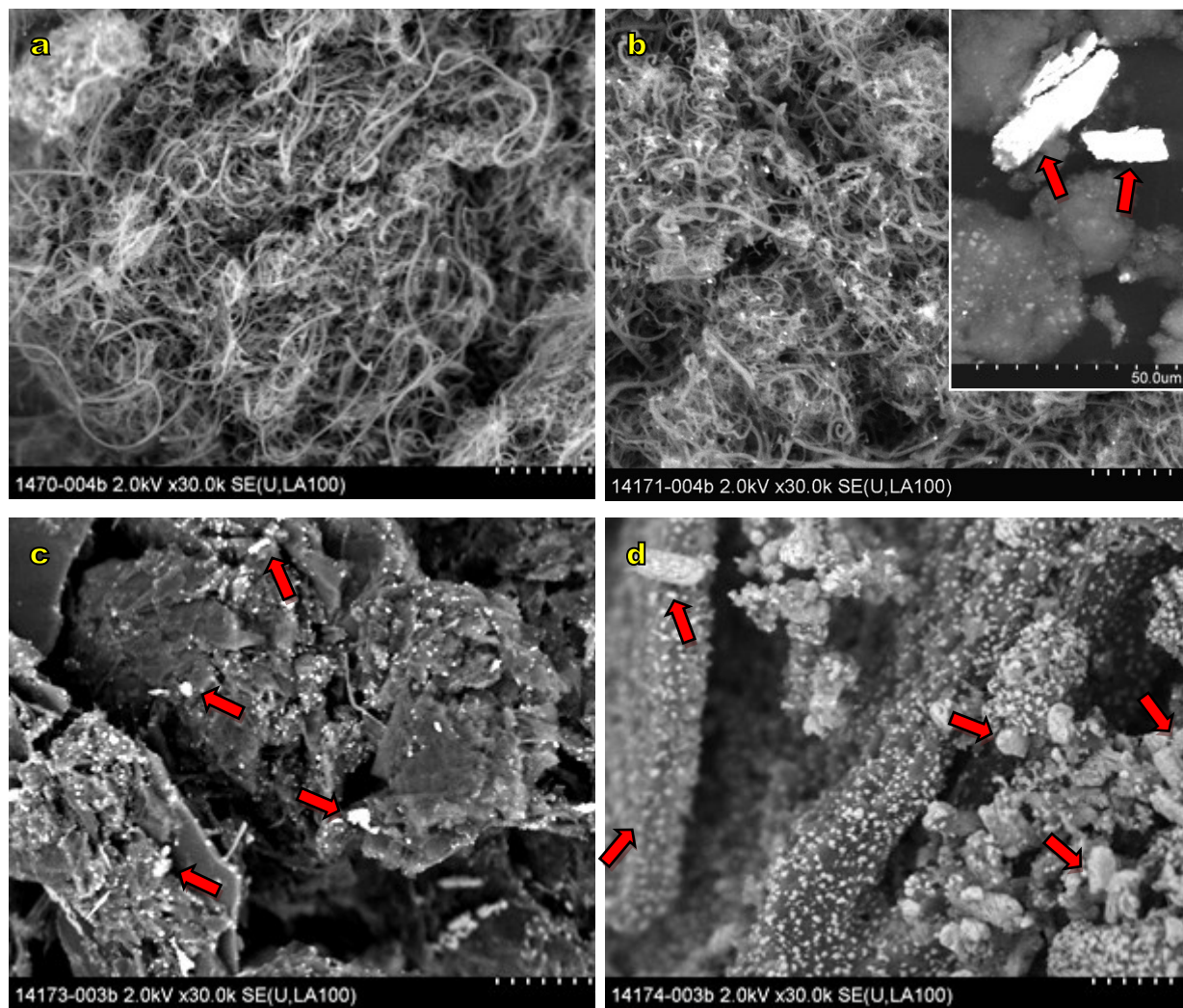**Fig. S3** Full XRD patterns of carbon supported MoC catalysts.

Fig. S4 SEM micrographs (BSE mode) of carbon supported Mo$_x$C catalysts. The active phase is supported on (a) oxidized CNTs, (b) N-doped CNTs, (c) oxidized graphite, and (d) oxidized activated carbon. The inset in (b) shows a large MoC particle in MoC/N-CNT. Red arrows point at larger Mo$_x$C particles.
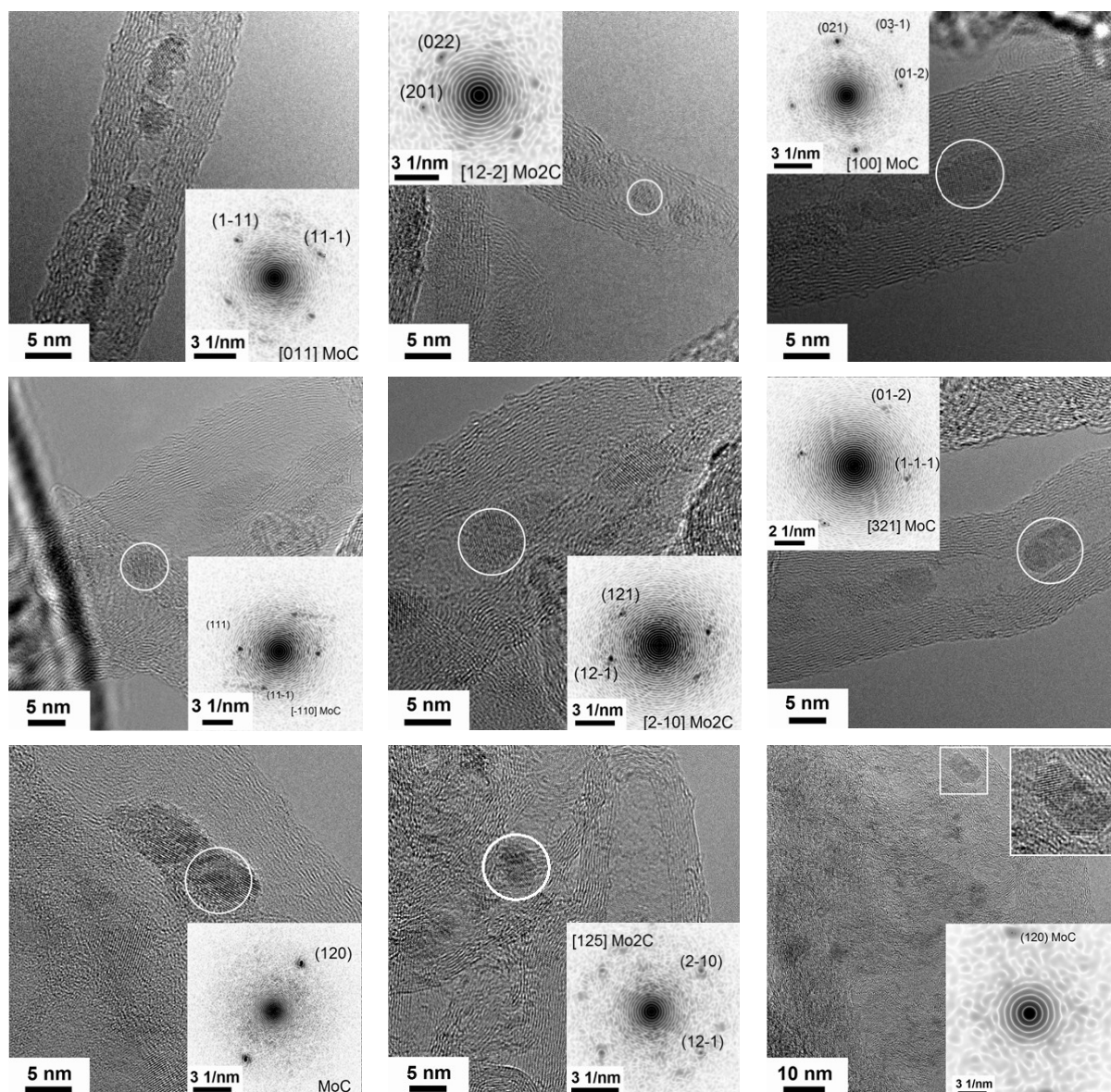
Fig. S5 HRTEM analysis of lattice spacings within MoC/O$_2$-CNT (top), MoC/oN-CNT (middle), and MoC/S-CNT (bottom).

Table S1 Evaluation of lattice spacings in Fig. S6

Sample	Reflex	Phase	$d_{theor.}$ / Å	$d_{exp.}$ / Å	Δ / %
O_2-CNT	(111)	α-MoC	2.47	2.486	+0.6
	(111)	α-MoC	2.47	2.559	+3.5
	(022)	β-Mo$_2$C	1.97	1.96	-0.5
	(201)	β-Mo$_2$C	2.15	2.12	-1.4
	(012)	α-MoC	1.91	1.93	+1.0
	(021)	α-MoC	1.91	1.914	+0.2
	(031)	α-MoC	1.35	1.35	±0.0
oN-CNT	(111)	α-MoC	2.47	2.692	+9.0
	(111)	α-MoC	2.47	2.766	+12.0
	(121)	β-Mo$_2$C	2.68	2.602	-2.9
	(121)	β-Mo$_2$C	2.68	2.634	-1.7
	(111)	α-MoC	2.47	2.45	-0.8
	(012)	α-MoC	1.91	2.07	+8.5
S-CNT	(120)	α-MoC	1.91	1.917	+0.3
	(200)	α-MoC	2.14	1.917	-10.4
	(210)	β-Mo$_2$C	2.20	2.313	+5.1
	(121)	β-Mo$_2$C	2.29	2.29	±0.0
	(120)	α-MoC	1.91	1.99	+4.1
	(200)	α-MoC	2.14	1.99	-6.9