Electronic Supplementary Information

Modification of the carbide microstructure by N- and S-functionalization of the support in Mo_xC/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_2O_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

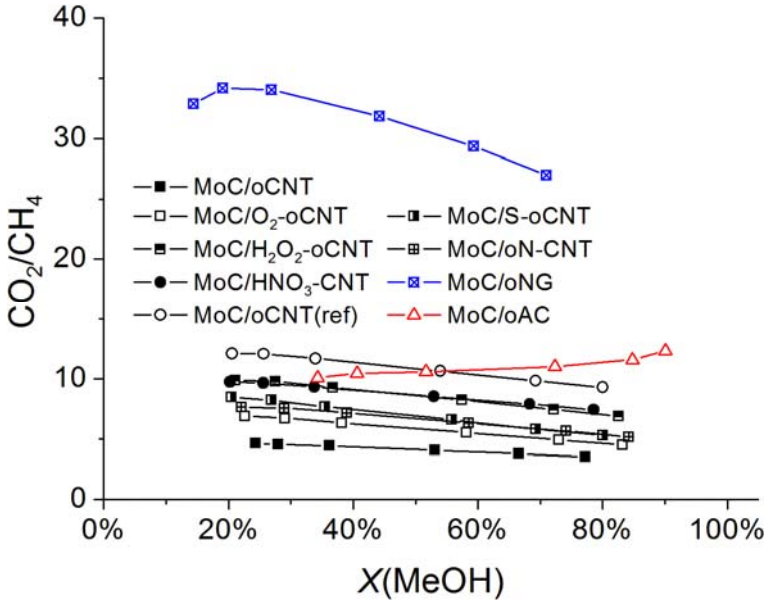

Fig. S1 CO_2/CH_4 product ratio as a function of MeOH conversion. Reaction conditions: 250 mg catalyst, 10-100 ml min^{-1} of 1% MeOH/1%H_2O/He, 250°C.

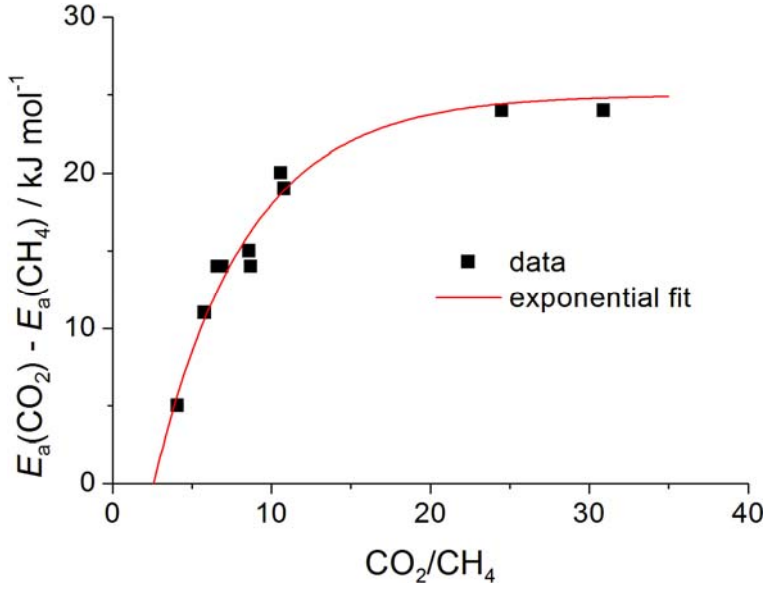

Fig. S2 Dependency of CO_2/CH_4 product ratio at 50% MeOH conversion on the difference of apparent activation energies of their formation.

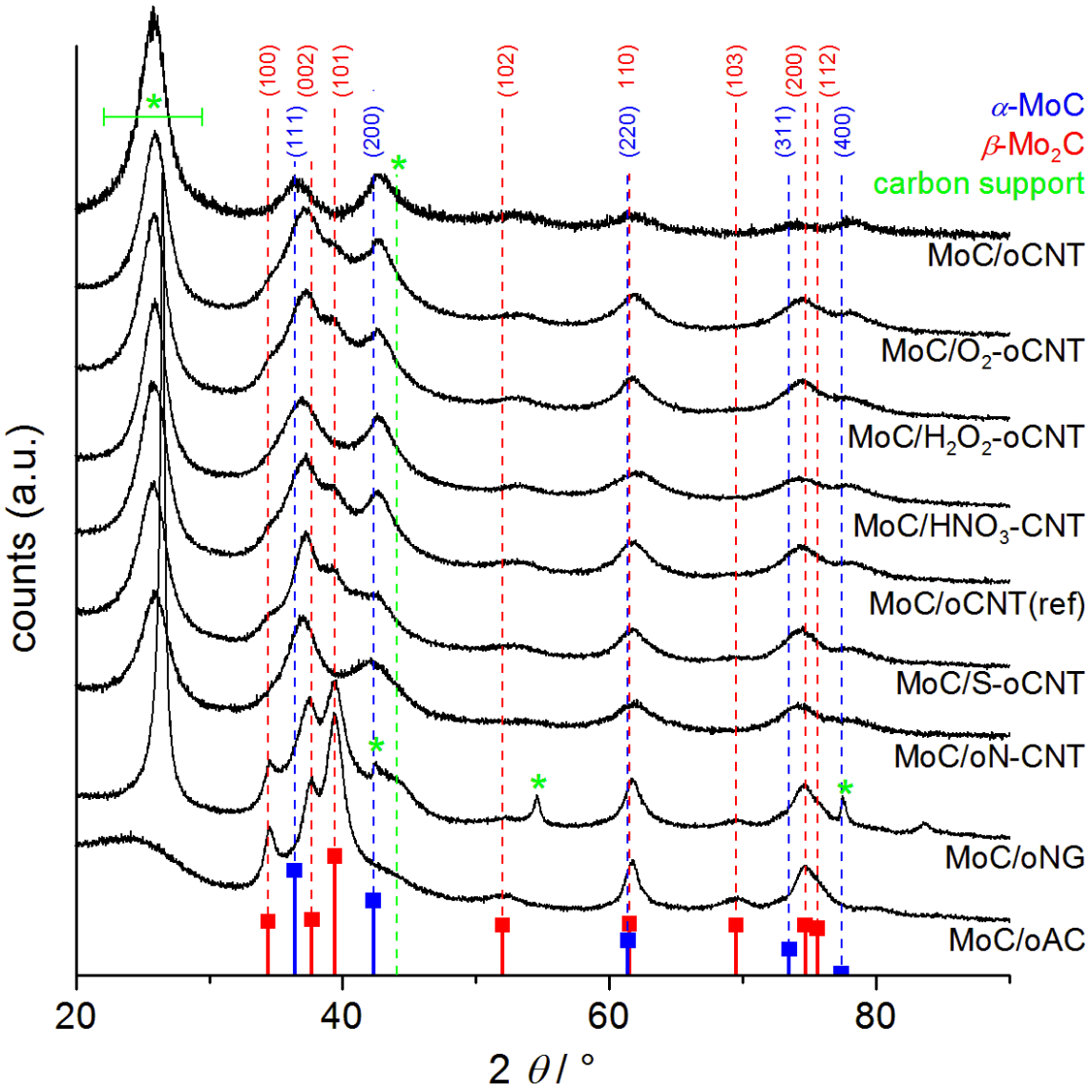

Fig. S3 Full XRD patterns of carbon supported MoC catalysts.

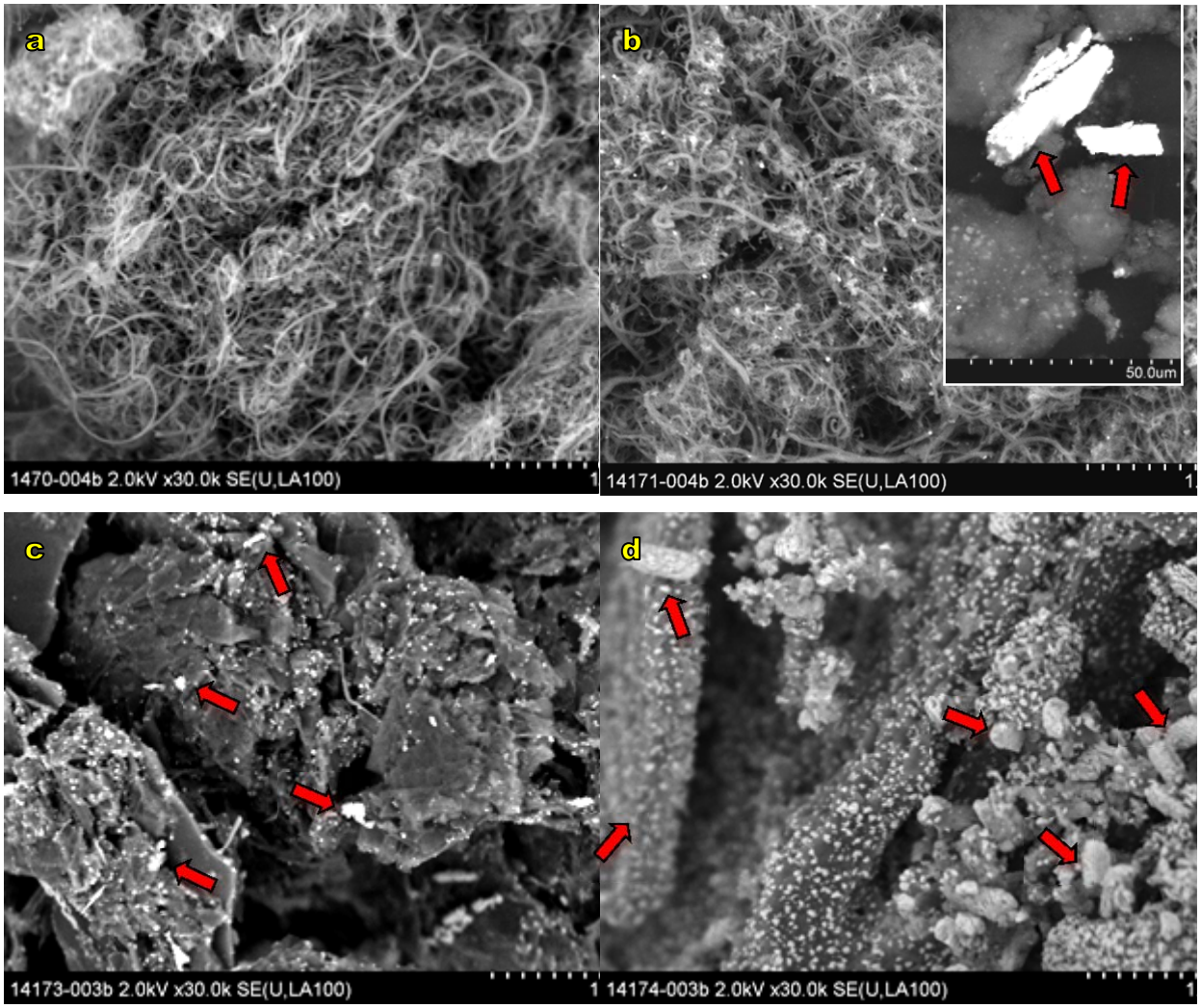

Fig. S4 SEM micrographs (BSE mode) of carbon supported Mo_xC catalysts. The active phase is supported on (a) oxidized CNTs, (b) N-doped CNTs, (c) oxidized graphite, and (d) oxidized activated carbon. The inset in (b) shows a large MoC particle in MoC/N-CNT. Red arrows point at larger Mo_xC particles.

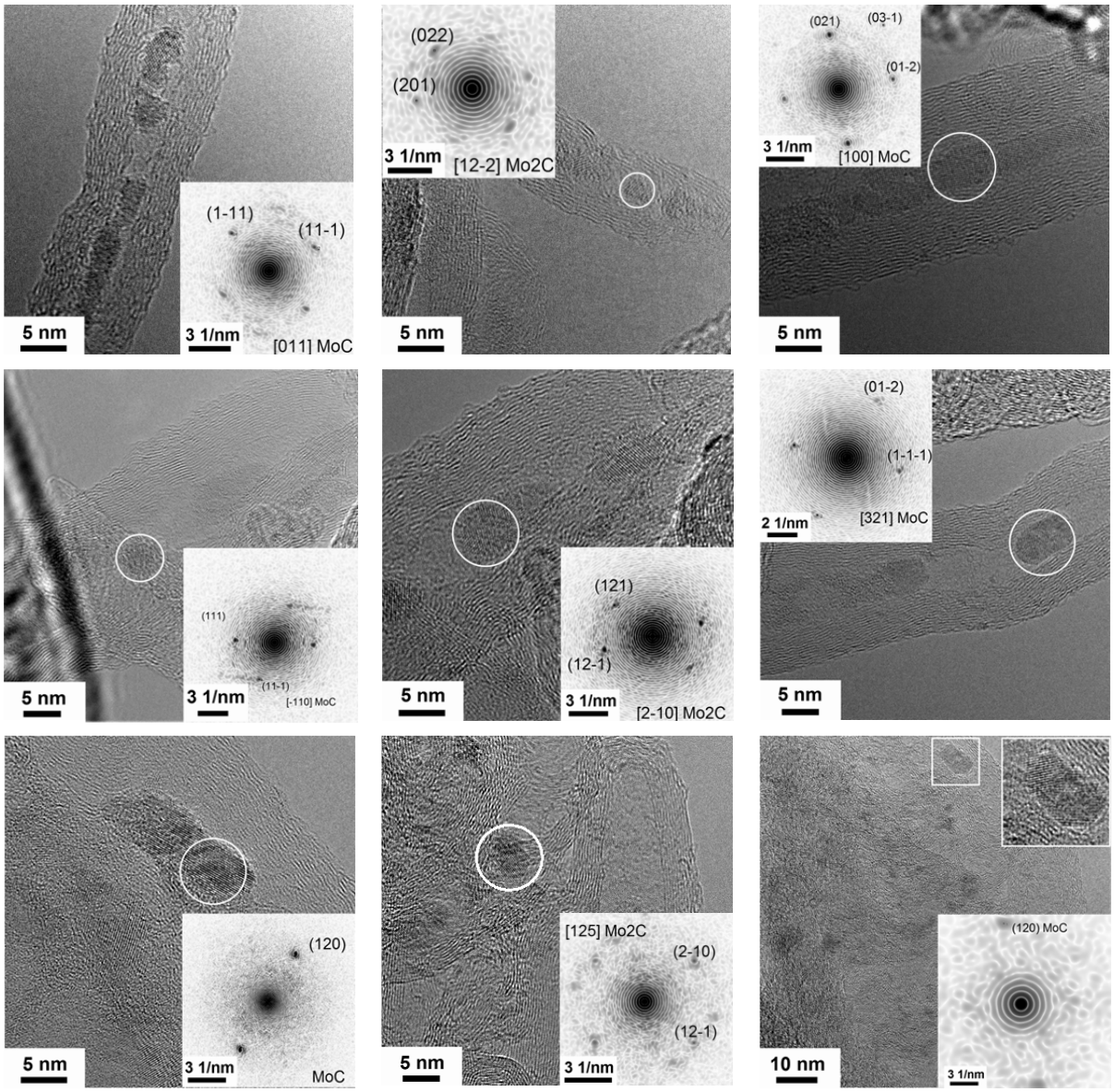

Fig. S5 HRTEM analysis of lattice spacings within MoC/O_2-CNT (top), MoC/oN-CNT (middle), and MoC/S-CNT (bottom).

Table S1 Evaluation of lattice spacings in Fig. S6

Sample	Reflex	Phase	$d_{\text{theor.}}$ / Å	$d_{\text{exp.}}$ / 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_2C	1.97	1.96	-0.5
	(201)	β-Mo_2C	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_2C	2.68	2.602	-2.9
	(121)	β-Mo_2C	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_2C	2.20	2.313	+5.1
	(121)	β-Mo_2C	2.29	2.29	±0.0
	(120)	α-MoC	1.91	1.99	+4.1
	(200)	α-MoC	2.14	1.99	-6.9