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CNT supported Mo_xC catalysts: Impact of loading and carburization parameters

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$\text{Mo}_x\text{C}/\text{CNT}$ catalysts were prepared by carburization of an oxidic Mo precursor impregnated on multiwalled carbon nanotubes (CNTs). The effects of different carburization atmospheres, heating rates, and Mo loadings were tested. The catalysts were characterized by CO-TPD, XRD, N_2 physisorption, SEM, and TEM. The catalytic performance in the steam reforming of methanol (SRM) was used as a sensitive probe to indicate changes in the catalyst surface during catalytic action. Contrarily to the bulk Mo_xC catalysts the heating rate during carburization has practically no effect on the catalysts. Instead, Mo loading and carburization atmosphere are the key factors for catalyst

structure and performance. The Mo-based activity decreases at loadings >10 wt% at constant product selectivity. The CO_2/CH_4 product ratio sensitively indicates changes in the catalyst properties at the loadings <20 wt%, where the activity is practically constant. Carburization in 20% CH_4/H_2 yields 2 nm sized crystallites of cubic α - MoC . Carburization in pure H_2 and in He yields hexagonal β - Mo_2C with a larger particle size. This phase change is documented in a different catalytic performance in terms of activity and CO_2/CH_4 selectivity. Thus a multi-parameter toolbox for fine-tuning of catalyst properties is presented.

Introduction

Group VI transition metal carbides provide catalytic features similar to expensive noble metals,^[1] thus are permanently in the focus of intensive research. The high potential in reactions that involve the transfer of hydrogen, such as alkane (de)hydrogenations or isomerizations, ammonia decomposition, and Fischer-Tropsch synthesis has been documented.^[2]

As the conventional metallurgical route to metal carbides typically provides very low specific surface areas (SSA), the first successful synthesis of high-surface area carbides by carburization of an oxidic precursor^[3] was a break-through for catalytic application. However, the synthesis of porous carbides is demanding and it seems more appropriate to utilize a high surface area support such as alumina or carbon to stabilize highly dispersed carbide (nano)particles.^[4–6] Carbon-based support materials can also serve as the carbon source for carburization. This economic strategy furthermore avoids the formation of passivating carbon deposits on the catalytically active carbide surface at the end of the carburization process, which easily occurs when using a gaseous hydrocarbon as the carbon source.

Few $\text{Mo}_x\text{C}/\text{C}$ catalysts have been reported in literature.^[6–9] The carburization in CH_4/H_2 mixtures typically leads to well dispersed Mo_xC nanoparticles if the surface is sufficiently functionalized.^[6,7] The synthesis of multiwalled CNT-supported β - Mo_2C has been described by Bao *et al.*^[6] They also highlighted the positive impact of nitric acid treatment of the CNT support prior to its impregnation with the Mo precursor. The abundance of surface oxygen groups created here enables a sufficient metal-support interaction to avoid agglomeration. However, a more systematic study on the influences of, e. g. Mo loading, carburization conditions, or specific surface properties, is still lacking. The variation of loading in a series of activated carbon and CNT supported Mo_2C catalysts has been performed by

Solymsi *et al.*^[10] During ethanol decomposition at 723 K the catalysts initially deactivate within the first 7 h time-on-stream. Unfortunately, neither steady state data nor different space velocities are reported to compare the patterns of product selectivities at a similar level of ethanol conversion. Furthermore, the study misses substantial parts of physico-chemical characterization of the samples, thus published data are difficult to interpret and do not support a structure-reactivity-correlation with regard to a catalyst optimization. However, a Mo loading in the range up to 17 wt%, depending on SSA of the support, has been shown to yield finely dispersed β - Mo_2C nanoparticles. This is in good agreement with theoretical considerations: At optimum (maximum) loading the good wetting ability of MoO_3 ^[11] would ideally lead to a homogeneous monolayer coverage of ~ 5.0 atoms Mo per square nanometer^[12] as the prerequisite for finely dispersed carbide particles. Given a SSA of $300 \text{ m}^2 \text{ g}^{-1}$ of a carbon support material this corresponds to a Mo_xC loading of approx. 20 wt%.

The carburization conditions are predominantly discussed for bulk carbides.^[13] Here a comparison of CH_4/H_2 and $\text{C}_2\text{H}_6/\text{H}_2$ atmospheres shows that the formation of the carbide phase occurs slower in the presence of CH_4 ,^[14] which is the most stable alkane. On the other hand, the higher alkanes tend to easily decompose and favour coke deposition as an overlayer on the carbide particles. In the same study, the variation of the heating rate during carburization reveals that the lower rates enable the

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carbide formation process to occur at lower temperatures. It is discussed that soot deposit is the active form of carbon and that then an interfacial reaction sets in driving C into Mo, which could explain the kinetic control of carburization. For low-temperature carburization Mo bronzes are required as intermediates in the topotactic transformation. Such mechanism is of particular interest when using a carbon-based support material itself, such as CNTs. Unfortunately, Hanif *et al.* do not report surface areas in their study,^[14] however, according to the lower concentration of the carburization by-product H₂O, also a structural benefit is expected from low heating rates. The phenomenon of hydrothermal sintering is well known from the reduction process of Fe-based catalysts for ammonia synthesis.^[15] Both, the lower heating rate and a higher space velocity of the CH₄/H₂ flow effectively lower the H₂O concentration and at least for the bulk systems a strong structural impact is reported for Mo_xC and Mo_xN systems.^[16,17] However, also adverse effects are observed^[18] pointing at the high complexity of involved topotactical transformations, which are not fully understood.

Results and Discussion

Standard parameters and general observations

The standard MoC/oCNT system serving as the reference during all the catalyst modifications performed is the medium-loaded 20MoC/oCNT carburized in CH₄/H₂ at a heating rate of 5 K min⁻¹. As described in the introduction, a high concentration of well dispersed Mo species is expected here. Numerous reports confirm the complete carburization of oxidic Mo precursors in this atmosphere at 700°C,^[6,14,19] thus ramping has been stopped at this temperature.

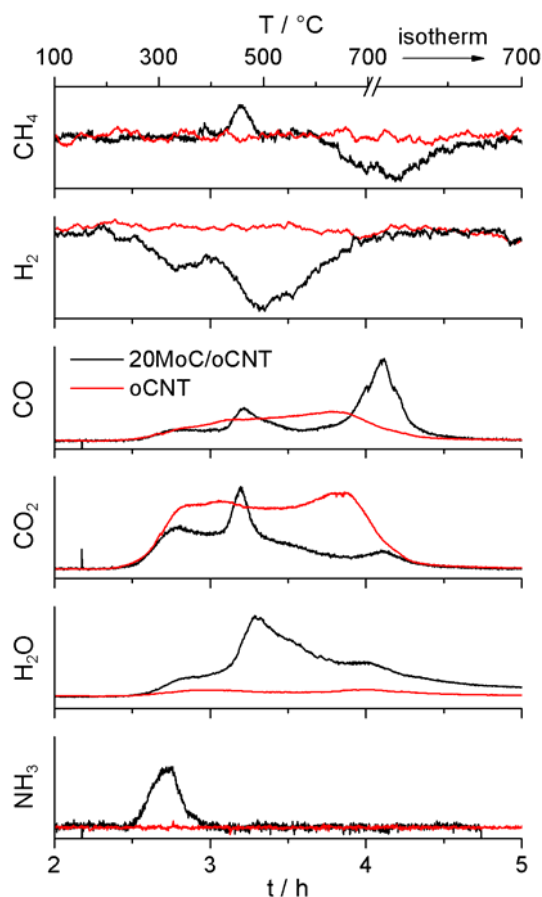


Figure 1. Profiles of CH₄ and H₂ consumption as well as of CO, CO₂, H₂O, and NH₃ formation during the carburization of 20MoC/oCNT and oCNT samples in 20% CH₄/H₂ at 5 K min⁻¹ (after drying in CH₄/H₂ at 100°C for 2 h). The profiles in arbitrary units are normalized with respect to the carbon mass of the sample.

The gases evolving during the carburization of 20MoC/oCNT are shown in Fig. 1. Due to the overlap with compounds being released from the metal-free oxidized carbon surface the blank oCNT is given as a reference. According to the traces of H₂ and CH₄ consumption as well as those of H₂O, CO, and CO₂ formation the following transformations can be assigned to the features observed: (i) decomposition of the ammonium heptamolybdate (AHM) precursor into MoO₃, (ii) reduction of MoO₃ to MoO₂, (iii) partial carburization of MoO₂ into a non-stoichiometric oxycarbide MoO_xC_y, and (iv) complete carburization of MoO_xC_y into Mo_xC. These steps are described extensively in literature,^[6,14,19] where intermediate phases are identified by X-ray diffraction (XRD). In Fig. 1 step (i) can be located in the temperature range of 250–400°C, where the formation of NH₃ and H₂O, respectively, is detected. H₂O also evolves from the blank oCNT surface, however, to a much lesser extent than over the AHM loaded sample. The (partial) instantaneous reduction of Mo⁶⁺ into Mo⁴⁺ by H₂ is suggested by a weak drop of the H₂ profile, which is not observed for the oCNT sample. CO₂ and CO are massively released from the oxidized carbon surface due to the thermal decomposition of carboxylic acid and anhydride groups in this temperature range.^[20] Step (ii) is the reduction of MoO₃ to MoO₂ at 400–500°C^[14] by both H₂ and carbon atoms from the CNT surface. The first is supported by an enhanced H₂ consumption under H₂O release; the latter is indicated by a sharp peak in both the CO and CO₂ profiles at 450°C, while no CH₄ is consumed here. Indeed, MoO₃ is well-known as a stoichiometric oxidant for elemental carbon.^[21] Surprisingly, instead of CH₄ consumption a small amount of additional CH₄ is generated in the temperature range of step (ii), which is most likely due to the high CO_x concentrations and the simultaneous presence of MoO₂ as a moderate CO_x hydrogenation catalyst.^[22] The intermediary formation of an orthorhombic Mo₄O₁₁ phase is also suggested to occur in this temperature range.^[13] The dissolution of support (CNT) carbon atoms into MoO_x clusters, which points at defective carbon sites as the oxycarbide nucleation points, should also be considered.^[23] Step (iii) covers the temperature range of 500–650°C and is indicated by still heavy, however, slowly declining consumption of H₂ under formation of H₂O. Also the CO and CO₂ concentrations are still high, however, this is most likely caused by the steady defunctionalisation oCNT support.^[20] The complete transformation into the oxycarbide MoO_xC_y is indicated by the finished H₂ consumption and the onset of CH₄ consumption. Finally, step (iv) is characterized by the heavy consumption of CH₄ under formation of CO, CO₂, and H₂O, which all slowly decay until the end of the carburization process after 1 h at 700°C.

It is noteworthy that the formation of CO and CO₂ from the blank oCNT sample temporarily exceeds their release from 20MoC/oCNT. This can be referred to the strong metal-support interaction between Mo species and the oxygen functionalities created on the carbon surface to anchor and disperse the AHM precursor as well as intermediate species. As suggested by Fig. 1, a substantial fraction of O atoms from the carbon surface are finally converted into H₂O.

Temperature-programmed desorption (TPD) of CO was directly performed on the freshly carburized catalysts without exposition to ambient O₂ and H₂O. Two main peaks at around 120 and a shoulder at 200°C are observed (Supporting Information, Fig. S1). The comparison with the blank oCNT material proves

that the CO profile exclusively originates from the interaction of CO with the Mo_xC particles. In particular Yang *et al.* in their FTIR supported study of CO adsorption on MoN assigned peaks at similar positions to the desorption of CO from Mo^{δ+} (0<δ<2) and N sites, respectively.^[24] Due to the structurally and catalytically similar properties between Mo carbides and nitrides this assignment is tentatively adapted to Mo_xC depending on the surface termination by Mo or by C (instead of N). Indeed, for β-Mo₂C(0001) theory predicts quite similar stabilities of CO adsorbed on the top positions (t1) on C- and on Mo-terminated surfaces, respectively.^[25] The total amount of CO desorbed up to 500°C is 332 μmol g(Mo_xC)⁻¹. This value appears rather low, however, it is reported that CO chemisorption on Mo_xC at ambient temperature only measures ~14% of total adsorption sites.^[26] Thus, the mean Mo_xC particle diameter can be estimated as ~5 nm.^[27]

Steam reforming of methanol (SRM) was chosen as a probe reaction due to a complex selectivity pattern, which is expected to sensitively indicate changes in the catalyst structure. In the reaction network of SRM, MeOH can react to CO₂ or CO,^[28] which in the presence of H₂ can further react to CH₄ and higher alkanes/alkenes via Fischer Tropsch synthesis over Mo-based catalysts.^[29]

The 20MoC/oCNT catalyst approaches a stable catalytic performance after 2 h time-on-stream at 250°C and only minor deactivation is observed in a 24 h test run. The conversion *X* of MeOH over this catalyst as a function of contact time is shown in the Supporting Information (Fig. S2a). The rapid increase in conversion is followed by a slow-down of the reaction rate after reaching approx. 50% conversion. This may be referred to inhibition by the main reaction products H₂ and CO₂ as observed over Cu-based catalysts,^[30] although the overall reactant concentration is relatively low. The main carbon-based products of the reaction are CO₂ and CH₄, whereas CO, C₂H₆, and C₂H₄ are formed only in trace amounts. The following reactions are expected to predominantly contribute to the product pattern observed:

- (1) methanol steam reforming
 $\text{CH}_3\text{OH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + 3 \text{H}_2$ ($\Delta H^0 = 49.6 \text{ kJ mol}^{-1}$)
- (2) methanol reduction
 $\text{CH}_3\text{OH} + \text{H}_2 \rightarrow \text{CH}_4 + \text{H}_2\text{O}$ ($\Delta H^0 = -115.4 \text{ kJ mol}^{-1}$)
- (3) methanol decomposition
 $\text{CH}_3\text{OH} \rightarrow \text{CO} + 2 \text{H}_2$ ($\Delta H^0 = 90.6 \text{ kJ mol}^{-1}$)
- (4) reverse water gas shift
 $\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O}$ ($\Delta H^0 = 41.1 \text{ kJ mol}^{-1}$)
- (5) CO_x hydrogenation
 $\text{CO}_x + \text{H}_2 \rightarrow \text{alkanes/alkenes} + \text{H}_2\text{O}$

In general, these observations agree with a previous report on supported Mo₂C catalysts.^[30,31] However, the detailed comparison of SRM activity fails due to different reaction conditions applied. The metal-free oCNT shows no catalytic activity under the reaction conditions applied.

Three parameters have been selected here to quantify changes in the catalytic performance of MoC/oCNT catalysts, namely the apparent activation energies of CO₂ and CH₄ formation, respectively, and the CO₂/CH₄ product ratio (see Tab. 2). For 20MoC/oCNT carburized in CH₄/H₂ at a heating rate of 5 K min⁻¹ the activation energies are 94 kJ mol⁻¹ and 108 kJ mol⁻¹, respectively, and a product ratio of 4.1. The CO₂/CH₄ ratio as a

function of MeOH conversion (see the Supporting Information, Fig. S2b) suggests that both CO₂ and CH₄ are primary products of the reaction; however, secondary methanation of CO₂ also occurs.

After SRM tests the catalyst samples were characterized by XRD, N₂-physisorption, and electron microscopy. Due to the contact with H₂O and CO₂ acting as mildly oxidizing agents^[33] during SRM no surface passivation by low-concentrated O₂ was needed prior to exposition to ambient conditions. XRD confirms the pervasive transformation of AHM into face-centered cubic (fcc) α-MoC (Supporting Information, Fig. S3a). Although the catalyst has been used in a catalytic reaction involving potential oxidants such as H₂O or CO₂ and even after long-term exposition to ambient conditions the patterns give no rise to oxidic bulk phases. As a reference, the pattern of molybdenum oxycarbide MoOC is characterized by a shift of the fcc pattern to higher angles,^[34] which is indicative for a lattice contraction as a result of partial C-O-substitution. This is not the case here, where the detected peaks fall in line with the reference pattern for α-MoC.^[35] Peak analysis reveals a crystallite size of approx. 2 nm. The reason for the formation of the metastable^[35,36] fcc α-MoC instead of hexagonal close packed (hcp) β-Mo₂C, which is predominantly reported to form under the synthesis conditions applied,^[3,4,6,13,14,32] is not fully understood. Initially formed nuclei of sub-carbides or α-MoC may be formed at low temperatures, where the thermodynamic equilibration of the phases is inhibited for diffusion limitation, and prevail during synthesis. This is evidenced by the pronounced polycrystallinity of the material as described later. Han *et al.* suggest that the Mo_xC phase can be controlled over the Mo loading on an ordered mesoporous carbon (OMC) support.^[8] However, presented XRD diffractograms are difficult to interpret. It is more likely that the controlled reduction of the Mo precursor is the key factor for α-MoC synthesis. This has been successfully managed by MoO₃ pre-reduction in a H₂/*n*-butane mixture,^[37] or by adding 0.5% Pt to the Mo precursor to facilitate H₂ activation.^[38] α-MoC proved a different performance than β-Mo₂C in some catalytic reactions^[9,36,38] and is traditionally prepared via nitridation of MoO₃ with NH₃ to fcc γ-Mo₂N followed by subsequent re-carburization with CH₄, which is a time- and resource-demanding process.^[38] In this context the one-step preparation of CNT-supported α-MoC is a valuable observation.

The specific surface area of the catalyst drops from 290 to 163 m² g⁻¹ if compared to the metal-free oCNT (Tab. 1). This is most likely caused by plugging of open CNT tips by agglomerates of α-MoC. The XRD observations are in good agreement with the α-MoC particle size that is estimated by CO TPD.

Impact of the heating rate during carburization

It is reported that the heating rate during the carburization of the metal carbide precursor can control the phase transformation temperatures and the pore structure of the resulting (bulk) carbide. Both effects are discussed for CNT supported systems at a nominal Mo_xC loading of 20 wt%. The heating rates were varied in the range of 0.2 to 10 K min⁻¹. For comparison the profiles of H₂O evolution are assembled in Fig. 2.

Fig. 2 reveals a dramatic impact of the heating rate on the carburization process. If referred to the temperature, peaks are sharp and well resolved at the lowest heating rate of 0.2 K min⁻¹. Here, the reaction is completed at approx. 600°C, however, on the cost of a reaction time of almost 50 h. Contrarily, at the highest heating rate of 10 K min⁻¹ peaks are broad and superimposed by each other. The release of H₂O approaches zero not before 1 h heat treatment in the CH₄/H₂ atmosphere. Nevertheless all the features observed at 0.2 K min⁻¹ can also be identified

here, indicating the successful carburization via the same intermediate phases in all the experiments.

The CO TPD (Supporting Information, Fig. S1) reveals no substantial differences between the 20MoC/oCNT samples carburized at different heating rates. The high-temperature shoulder is slightly more intense for the sample carburized at 1 K min⁻¹. The amount of CO desorbed up to 500°C varies in the range of 330–380 μmol g(Mo_xC)⁻¹ (Tab. 1) corresponding to a Mo_xC particle size of 4–5 nm. Also the specific surface areas of the samples are very similar with a very weak tendency to the higher values at the lower heating rates. Partial methanation of the carbon support^[40] to create a more defective surface or improved spreading of the Mo precursor during the protracted carburization process^[11] might be the reasons for this observation.

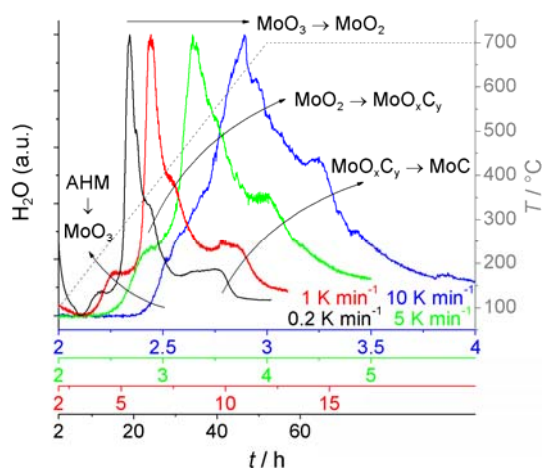


Figure 2. Profiles of H₂O desorption during carburization of 20MoC/oCNT at different heating rates (after drying in CH₄/H₂ at 100°C for 2 h). The m/e 18 traces are normalized for intensity and temperature

Table 1. Physico-chemical characterization of Mo _x C/CNT catalysts				
Sample	β ^[a] / K min ⁻¹	Atmosphere	SSA / m ² g ⁻¹	CO / μmol g(Mo _x C) ⁻¹
oCNT	5	CH ₄ /H ₂	290	0
20MoC/oCNT	0.2	CH ₄ /H ₂	172	332
20MoC/oCNT	1	CH ₄ /H ₂	169	379
20MoC/oCNT	5	CH ₄ /H ₂	163	332
20MoC/oCNT	10	CH ₄ /H ₂	163	346
5MoC/oCNT	5	CH ₄ /H ₂	245	509
10MoC/oCNT	5	CH ₄ /H ₂	197	391
30MoC/oCNT	5	CH ₄ /H ₂	128	229
20MoC/oCNT	5	H ₂	170	143
20MoC/oCNT	5	He	146	66

[a] heating rate during carburization.

The similar catalytic performance in the SRM reaction (Supporting information, Tab. S1) suggests only minor differences in the catalyst structure according to the variation of the heating rate during carburization. The activities for methanol conversion

at 250°C are almost identical (Supporting information, Fig. S2a). The apparent activation energies of CO₂ and CH₄ formation appear unaffected in the ranges of 91–95 and 108 kJ mol⁻¹, respectively. Accordingly, the CO₂/CH₄ product ratio is fixed at around 4–5. The catalyst carburized at the lowest heating rate of 0.2 K min⁻¹ shows a weakly enhanced ratio of 5.1 (Supporting information, Fig. S2b), which is in agreement with a somewhat lower apparent activation energy of CO₂ formation.

Post-catalytic sample analysis by XRD reveals the presence of α-MoC nanocrystallites (~2 nm). The diffractograms are almost congruent (Supporting information, Fig. S3b) and free of reflexes other than α-MoC and graphitic CNTs. This finally proves that the heating rate during carburization in CH₄/H₂ in the range of 0.2–10 K min⁻¹ has practically no effect on the structure and catalytic performance of 20MoC/oCNT catalysts. It is again worth mentioning that particles are polycrystals. These originate from frustrated growth at the mild conditions applied and this process is most likely induced by diffusion of defective carbon atoms from the support material into MoO_x nuclei.^[23] The formation of frustrated high-temperature metastable phases as active particles in turn might be the cause of activity and stability of the catalysts. Apparently, these can survive the redox stress during SRM much better than, e.g., single crystal surfaces or high-temperature phases converting into oxycarbides.

Variation of the metal loading of Mo_xC/CNT catalysts

The metal loading of MoC/oCNT catalysts was varied between nominal Mo_xC contents of 5–30 wt% to investigate the limits of surface coverage and agglomeration. AHM impregnated samples were carburized in CH₄/H₂ at a heating rate of 5 K min⁻¹.

The scanning electron microscopy (SEM) study reveals entangled CNTs without any agglomerates indicating the successful dispersion of metal species on the CNT surface. Even on the 30MoC/oCNT, which is the highest loading tested, bulky Mo_xC particles cannot be visualized by SEM (Fig. 3a). The energy-dispersive analysis of X-ray (EDX) quantification of Mo and O confirms the nominal metal content and also indicates the presence of residual O on the surface of all samples (Fig. 3b). However, the O content is similar on all the catalysts and as high as on the blank oCNT sample, which similarly has been subjected to the carburization treatment and CO TPD, respectively. Thus, the O can likely be assigned to the metal-free fractions of the carbon surface. Especially the C-OH, C=O, and C-O-C groups formed during initial HNO₃ treatment are very stable,^[20] thus can resist high temperatures in a reducing atmosphere.

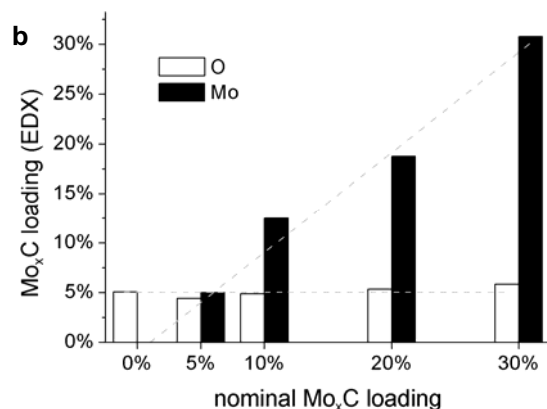
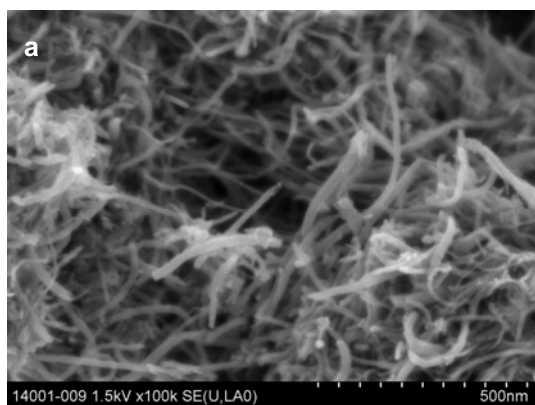


Figure 3. (a) Representative SEM image of 30MoC/oCNTs and (b) EDX analysis of MoC/oCNT catalysts. Dashed grey lines represent the parity line (Mo_xC) and the average (O), respectively.

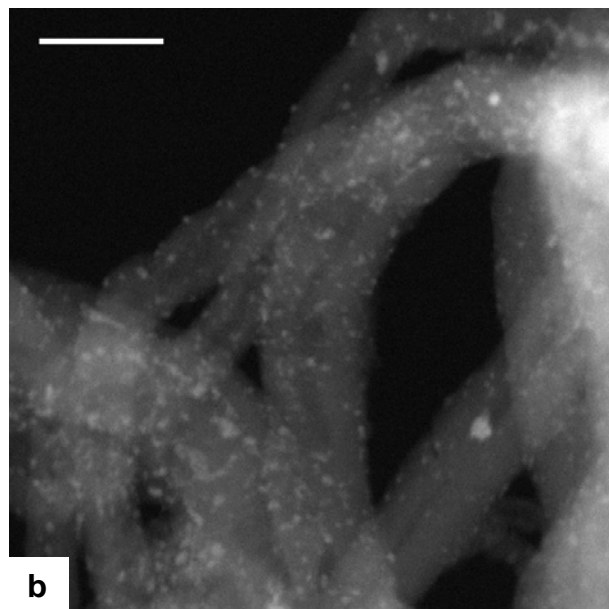
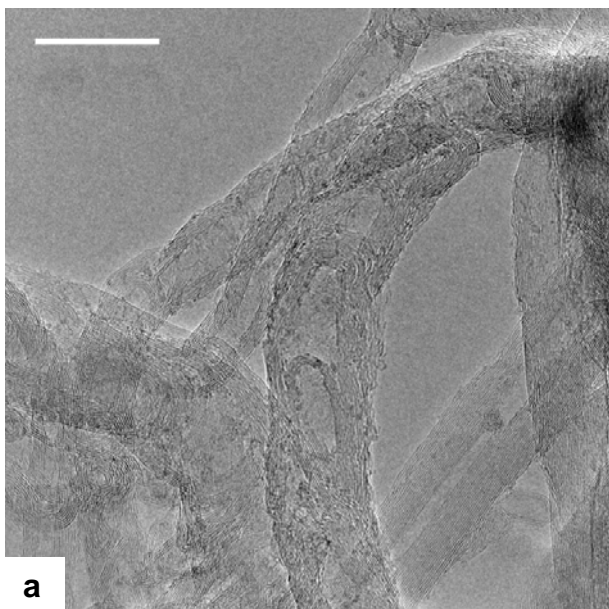


Figure 4. Representative (a) TEM and (b) corresponding HAADF images of the 5MoC/oCNT catalyst after reaction. Scalebar: 20 nm.

Transmission electron microscopy (TEM) gives an impression of the catalyst structure (Fig. 4a). The high dispersion of uniformly sized Mo_xC particles is best seen in the scanning mode (STEM) at the lowest loading of 5 wt%. A representative high angle annular dark field (HAADF) image is shown in Fig. 4b. The mean particle size as estimated from these figures is 1–2 nm. At the higher loadings agglomeration of crystallites occurs (see the Supporting Information, Fig. S4). However, the still finely structured agglomerates of small (< 5 nm) α -MoC crystallites are located preferably at the outer CNT surface and at their tips, which were previously opened by harsh HNO₃ treatment. They vary in size but rarely exceed a diameter of 10 nm. It is also visible that the CNT structure is intact after the carburization process, which indicates that CH₄ rather than the support serves as the main carbon source for α -MoC formation.

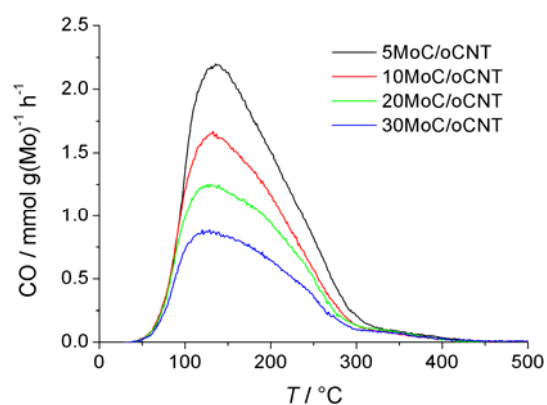


Figure 5. CO TPD profiles of differently loaded MoC/oCNT catalysts.

The quantitative analysis of CO TPD reveals a strong impact of the Mo_xC loading on the amount of CO desorbed at $<500^\circ\text{C}$ (Fig. 5). If referred to the mass of Mo_xC , the low loaded 5MoC/oCNT catalyst provides more than twice as much adsorption sites than the highly loaded 30MoC/oCNT catalyst (Tab. 1). It indicates that the mean Mo_xC particle diameter within the MoC/oCNT loading series varies in the range of 3–7 nm. The detailed analysis of curve shapes in Fig. 5 points at two contributions, as discussed above, for all catalysts. For the loading series the high-temperature shoulder, which is assigned to the CO adsorption on C-terminated surface sites, is more pronounced at the higher loadings. In particular, the two-component Gaussian fit proves that the fraction of CO desorbed at $\sim 200^\circ\text{C}$ steadily increases from 30 to 45% as the Mo_xC loading increases from 5 to 30 wt%. According to above assumptions this could be interpreted as an increased fraction of C-terminated Mo_xC surfaces with the increasing Mo_xC loading.

Regarding SRM catalysis two aspects have to be discussed. Firstly, the overall activity in terms of MeOH conversion (Fig. 6a) is similarly high for low loaded samples (≤ 10 wt% Mo_xC), if referred to the Mo content. The higher metal loadings decrease the effective reaction rate. Possible reasons are mass transport limitations in the high- Mo_xC catalyst particles being too rich in active sites or larger Mo_xC particles having a lower specific (active) surface area. The results obtained from CO TPD suggest the latter although even at the low loadings the amount of CO adsorbed remarkably differs. The second aspect is the CO_2/CH_4 product ratio (Fig. 6b). As listed in Tab. 2 the catalyst with the lowest Mo_xC loading of 5 wt% produces only half of the amount of CH_4 that is produced over the highly loaded catalysts. The catalysts approach similar selectivities at Mo_xC loadings ≥ 20 wt%. The opposite trend has been reported for SRM over Mo_2C supported on active carbon.^[31] Here, the CO_2/CH_4 product ratios of 2.5 and 4.1 were measured at 50% MeOH conversion over 5 wt% and 10 wt% loaded $\text{Mo}_2\text{C}/\text{C}$ catalysts, respectively. However, contrarily to the present study, high conversions have been achieved by temperature increase instead of GHSV variation. Thus, higher CH_4 selectivities can also be a result of the reaction temperature. For 20MoC/oCNT this assumption is exemplarily confirmed by plotting the CO_2/CH_4 ratio as a function of MeOH conversion during the step-wise temperature decrease from 250–200°C for determination of apparent activation energies (Supporting information, Fig. 2b). Indeed, the CO_2/CH_4 ratio increases from 4.6 to 6.6 when lowering the temperature in this range, where the impact of conversion on CO_2/CH_4 is rather low.

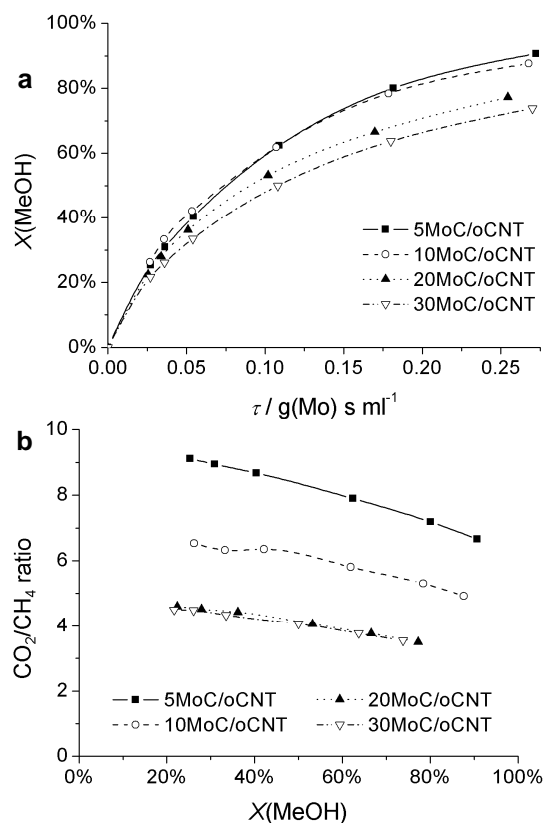


Figure 6. (a) Conversion of MeOH in the SRM reaction over MoC/oCNT catalysts as a function of the Mo-based contact time. (b) CO_2/CH_4 product ratio as a function of MeOH conversion. Reaction conditions: 167–1000 mg catalyst, 10–100 ml min^{-1} of 1% MeOH/1% $\text{H}_2\text{O}/\text{He}$, 250°C .

Table 2. SRM performance data of MoC/oCNT catalysts with different loadings carburized at 5 K min^{-1} in CH_4/H_2 .

Sample	$E_a(\text{CO}_2) / \text{kJ mol}^{-1}$	$E_a(\text{CH}_4) / \text{kJ mol}^{-1}$	$S(\text{CO}_2)/S(\text{CH}_4)^{[a]}$
oCNT	— ^[b]	— ^[b]	— ^[b]
5MoC/oCNT	95±1	111±1	8.4
10MoC/oCNT	93±2	111±1	6.1
15MoC/oCNT	91±1	108±1	4.0
20MoC/oCNT	94±2	108±2	4.1
30MoC/oCNT	92±2	108±1	4.1

[a] 250°C , $X(\text{MeOH})=50\%$. [b] no catalytic activity observed.

The specific surface areas of the differently loaded catalysts decrease with the increasing Mo loading and finally approach $128 \text{ m}^2 \text{ g}^{-1}$ (Tab. 1). It is well explained by the TEM observation of CNT open tips plugging with MoC. At the higher loadings also the mass fraction of MoC providing a lower SSA than the pure CNTs becomes a significant factor.

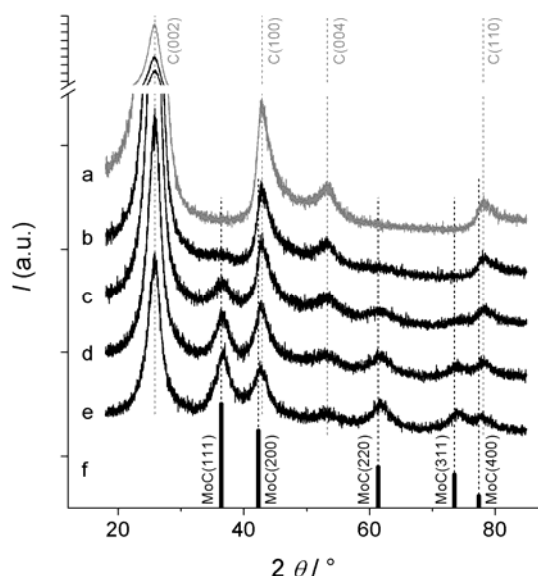


Figure 7. X-ray diffractograms of (a) oCNT and (b-e) Mo_xC-loaded oCNT catalysts after catalytic reaction (top down: oCNT, 5MoC/oCNT, 10MoC/oCNT, 20MoC/oCNT, and 30MoC/oCNT); f) Reference pattern of α -MoC.^[34,40]

The X-ray diffractograms for the loading series are depicted in Fig. 7. The metal-free oCNT identifies the graphitic reflections originating from the support material. With the increasing Mo loading the pattern is supplemented by adding the reflections of fcc α -MoC, which are clearly visible at a Mo_xC loading of ≥ 10 wt%. A superposition appears at around 42–43° and at 77–78° with the MoC(200)/C(100) and MoC(400)/C(110) reflections, respectively. For all the samples with Mo_xC ≥ 10 wt% the pattern analyses reveal an α -MoC crystallite diameter of ~ 2 nm.

Influence of the carburization atmosphere

The carburization atmosphere can have significant influence on the Mo_xC phase formed during carburization. Typically, in CH₄/H₂ the hcp β -Mo₂C is formed.^[6] However, Han *et al.* show that the use of pure H₂ at 700°C leads to the formation of both α -MoC and β -Mo₂C depending on the Mo concentration on the OMC support,^[6] which here serves as the carbon source. They also indicate that the carburization in inert N₂ at 700°C stops at the partially reduced MoO₂. Similar carburization conditions are applied for 20MoC/oCNT catalysts.

The carburization profiles monitored in H₂ and in inert He atmospheres, respectively, are shown in Fig. 8. Similar to CH₄/H₂ (Fig. 1), carburization starts with the decomposition of the AHM precursor under release of NH₃ and H₂O at 250–350°C. However, for unknown reason less H₂O is detected in H₂. Here, a subsequent drop of the H₂ profile is seen, which is accompanied by steadily increasing H₂O formation and indicates the reduction of MoO₃ into MoO₂ by H₂. Carbon oxides are formed only to a relatively low extend. At 700°C, the formation of CH₄ is detected, which can originate from both, the methanation of released CO_x and of the carbon support, respectively. Instead, when using He the formation of CH₄ is not observed and CO₂ and CO are the dominating gases produced, indicating that the reduction of Mo(VI) occurs via gasification of the carbon support.

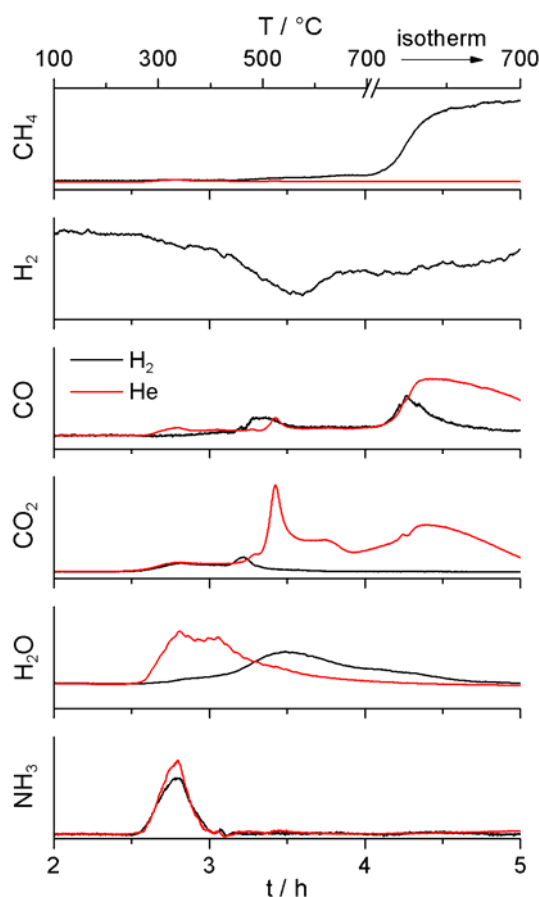


Figure 8. Profiles of H₂ consumption as well as of CH₄, CO, CO₂, H₂O, and NH₃ formation during the carburization of 20MoC/oCNT in H₂ and in He at 5 K min⁻¹, respectively.

The CO TPD experiments after carburization in H₂ and He show much less adsorption sites on the catalysts (Tab. 1, Fig. 9). This, however, originates from the mode of operation, i.e., the TPD starting at ambient temperature. Apparently, the profile is shifted to lower T upon alloying, making low-T desorption invisible in the set-up applied. Thus, the curves shown in Fig. 9 represent only the high-T shoulder of the whole profile. In particular, only 143 and 66 $\mu\text{mol g(Mo)}^{-1}$ can be detected, respectively, as compared to 332 $\mu\text{mol g(Mo)}^{-1}$ after carburization in CH₄/H₂. Again, two peaks are observed, however, the low-temperature contribution provides a much higher fraction of the overall profile. With regard to above assumptions it can be concluded that the only 25 and 20% of CO adsorption sites represent a C-termination of the Mo_xC surface. This is plausible if we consider the hydrocarbon-free carburization atmosphere.

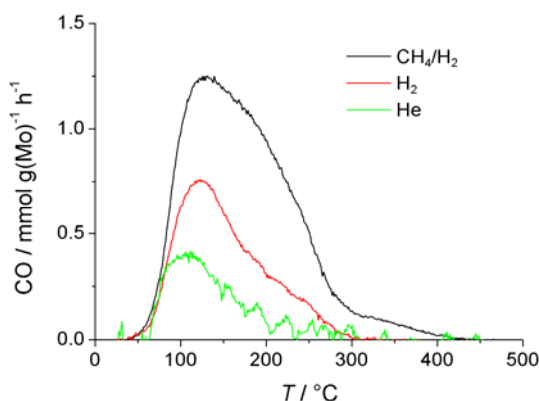


Figure 9. CO TPD profiles of 20 MoC/oCNT catalysts carburized in different atmospheres at 5 K min⁻¹.

The catalytic performances also strongly depend on the carburization atmosphere. The catalyst carburized in pure H₂ is slightly more active than those carburized in CH₄/H₂. Instead, the carburization in inert He yields a poorly active catalyst. The microstructural changes are also reflected in the CO₂/CH₄ product ratios. The catalytic data are assembled in Tab. 3 and in the Supporting Information, Fig. S5. The apparent activation energy of CO₂ formation drops to 87 and 88 kJ mol⁻¹ after carburization in H₂ and He, respectively, whereas the apparent activation energy of CH₄ formation changes to 105 and 128 kJ mol⁻¹, respectively. Consequently, for both alternative carburization atmospheres the CO₂/CH₄ product ratio remarkably increases and reaches a value as high as 9.2 after carburization in He.

Table 3. SRM performance data of 20MoC/oCNT catalysts carburized at 5 K min⁻¹ in different atmospheres.

Atmosphere	E_{a,CO_2} / kJ mol ⁻¹	E_{a,CH_4} / kJ mol ⁻¹	S(CO ₂)/S(CH ₄) ^[a]
20% CH ₄ /H ₂	94±2	108±2	4.1
H ₂	87±1	105±1	6.2
He	88±1	128±1	9.2

[a] 250°C, X(MeOH)=50%.

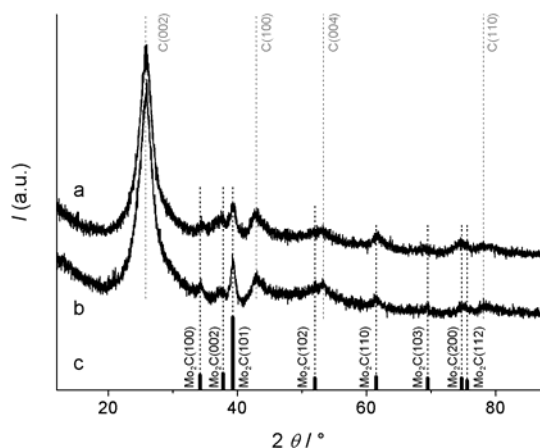


Figure 10. X-ray diffractograms of 20Mo/oCNT catalysts carburized (a) in H₂ and (b) in He after catalytic reaction; (c) Reference pattern of β-Mo₂C.^[40,41]

The reason for changes in the catalytic behaviour is poorly explained in the textural properties: catalysts carburized in H₂ and He provide specific surface areas of 170 and 146 m² g⁻¹, which are quite close to the reference value of 163 m² g⁻¹ obtained by carburization in CH₄/H₂ (Tab. 1). Besides CO TPD the most drastic change is seen in the XRD patterns of the catalysts (Fig. 10). Both the H₂ and He carburized samples show the typical bands of hcp β-Mo₂C in addition to the pattern of graphitic CNTs. Its mean crystallite sizes are 8 and 10 nm after carburization in H₂ and He, respectively, which confirm the larger particle sizes estimated by CO TPD. Moreover, the H₂ carburized sample shows a band at ~38°, which could tentatively be interpreted as α-MoC or oxycarbide with a crystallite diameter of ~3 nm. If we consider the gases evolved during carburization, the formation of α-MoC on this sample could possibly be related with the presence of CH₄ at the end of the carburization process. Instead, on the He carburized sample a considerable amount of ~20% MoO₂ is detected (Fig. 10). Metallic Mo is identified on none of the XRD patterns.

The (partial) carburization of AHM in inert He at 700°C is a surprising result, as the temperatures required for such solid state reactions are typically much higher.^[8,9] Taking the large crystallite size of remaining MoO₂ into account, the problem for incomplete reduction might be the Mo dispersion at elevated temperature. However, taking these differences in phase composition of the catalysts into account, the different catalytic performances (Tab. 3, Supporting information, Fig. S5) are not surprising. Results of the loading series and the variation of carburization atmosphere suggest that the formation of CO₂ and CH₄ could possibly be related with the Mo_xC surface terminations by Mo and C, respectively.

Conclusion

The preparation, characterization and catalytic testing of CNT-supported molybdenum carbide catalysts are presented. It is suggested that the nature of the Mo_xC crystal phase is a sensitive function of the highly defective state of the CNT support structure, which kinetically controls the formation of favorable crystallization nuclei leading to a stabilized polycrystalline catalyst. The pervasive carburization can be controlled by the carburization atmosphere. The carburization at 700°C in CH₄/H₂ yields α-MoC, whereas in pure H₂ a mixture of α-MoC and β-Mo₂C is formed. In inert He only the β-Mo₂C phase is formed, however, somewhat higher temperatures that 700°C are required according to the synthesis route applied in this study. The heating rate during carburization was found to be less important for the catalyst structure and reactivity. The Mo_xC particle size as estimated by CO TPD steadily increases with the Mo_xC loading from 5 to 30 wt%. Instead the crystallite size as given by XRD analysis remains constant at ~2 nm for α-MoC and <10 nm for β-Mo₂C (note: volume-average). The CO TPD reveals two contributions, which are tentatively assigned to Mo and C terminated surfaces. According to this the fraction of C termination increases with the increasing Mo_xC loading, however, sharply decreases when using a CH₄-free carburization atmosphere.

The materials synthesized are highly active and stable catalysts in the SRM reaction. Here, the activity and product selectivity sensitively depend on the Mo_xC loading and crystal phase. Probably also the surface termination by Mo or C plays an important role.

The experiments performed provide a versatile toolbox for the synthesis of differently performing catalysts, not only for SRM. It

is expected that trends and dependencies presented in this study to control the catalyst properties also provide important parameters to modify the activity and selectivity of CNT supported Mo_xC catalysts in other reactions, e.g., the Fischer Tropsch alcohol synthesis. In this way the SRM reaction was applied rather as a probe reaction than as the economically/industrially highly interesting pathway for H₂ generation from liquid fuels.

Experimental Section

Synthesis: Commercial MWCNTs (Baytubes C 150 HP) were pre-treated by refluxing in 65% HNO₃ (500 ml per 10 g) for 2 h. The product was washed with deionized water until neutral pH and dried in air at 110 °C for 1 day (oCNT). Aliquots of 1 g oCNT were impregnated with 3 ml of differently concentrated aqueous solutions of (NH₄)₆Mo₇O₂₄·4H₂O, respectively, to achieve final Mo_xC loadings between 5 and 30 wt%. Accordingly, samples are denoted as yMoC/oCNT, where y represents the nominal loading of Mo_xC in wt%.^[43] The resulting pastes were thoroughly kneaded in a mortar followed by drying in air at 110°C for 1 day. In a typical carburization procedure, a catalyst mass nominally containing 0.5 mmol Mo, e.g., 250 mg 20MoC/oCNT, was placed in a quartz tubular reactor (7 mm inner diameter) in a stream of 37 ml min⁻¹ of a 20 vol% CH₄/H₂ mixture. After elution of H₂O and O₂ (1 h at 100°C) the reactor temperature was linearly increased by 5 K min⁻¹ up to 700 °C and kept for 2 h, followed by cooling to ambient temperature in the reducing atmosphere.

Characterization: Temperature-programmed desorption (TPD) of CO was performed immediately after carburization without passivation or air contact of the catalyst. The reactor was flushed with 5 vol% CO/Ar for 10 min at ambient temperature and subsequently flushed with He until no CO was detectable by on-line mass spectrometry (MS, Pfeiffer GAM 200) and gas chromatography (GC, Varian xx Micro GC). In a He stream of 30 ml min⁻¹ the temperature was linearly increased by 10 K min⁻¹ up to 700 °C. Further characterization of the catalysts was performed after catalytic testing. Passivated samples were analyzed after exposition to ambient. TEM was performed on a FEI Cs-corrected Titan 80-300 microscope (300 kV) and SEM images were obtained on a Hitachi S-4800 FEG microscope (1.5 kV) equipped with an EDAX Genesis EDX detector (15 kV). The XRD measurements were performed on a Bruker AXS D8 Advance diffractometer equipped with a secondary graphite monochromator (Cu Kα₁₊₂ radiation) and scintillation detector. Crystallite size values were extracted by full pattern fitting and are reported as L_{Vol}-IB values (volume weighted mean column length based on integral breadth) without further assumptions concerning crystallite shape or size distribution. N₂ physisorption was performed at 77 K in the relative pressure range of $p/p_0 = 0.05-0.3$ after drying the sample in vacuum at 200°C for 2 h..

Catalytic testing: Catalysts were tested for their catalytic performance in the steam reforming of methanol (SRM) at 250 °C in 100 ml min⁻¹ of a 2 vol% CH₃OH/2 vol% H₂O/He mixture. After 2 h on stream, the flow rate was varied between 100 and 10 ml min⁻¹, followed by decreasing the temperature in 10 K steps to 200 °C at 100 ml min⁻¹. Reaction products were quantified by GC analysis. Contact of the catalyst with H₂O (reactant) and CO₂ (product) ensured the mild passivation of the Mo_xC surface, which is required prior to final exposure of the catalyst to ambient for its characterization.

Acknowledgements

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Keywords: molybdenum carbide • crystal phase • surface termination • steam reforming of methanol • CO TPD

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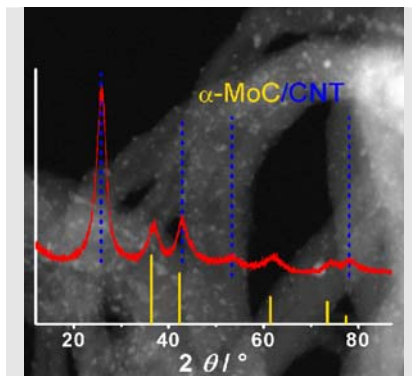
05MoC/oCNT (13894); 10MoC/oCNT (13896); 20MoC/oCNT (13898 and 13899); 30MoC/oCNT (13901).

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Entry for the Table of Contents

FULL PAPER

The synthesis of CNT-supported α -MoC and β -Mo₂C nanoparticles can be controlled by the carburization conditions applied. The impact of Mo loading, heating rate of carburization and carburization atmosphere as well as their impact on the catalytic performance of resulting Mo carbide catalysts in the steam reforming of methanol are discussed.



*Benjamin Frank, Klaus Friedel, Frank Girgsdies, Xing Huang, Robert Schlögl, and Annette Trunschke**

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**CNT supported Mo_xC catalysts:
Impact of loading and carburization
parameters**

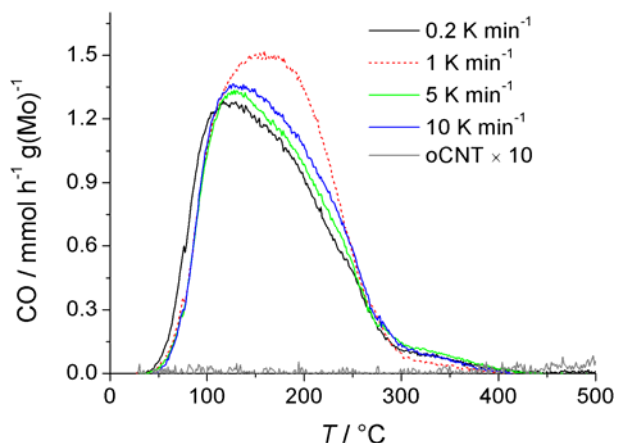


Figure S1. CO TPD profiles of 20MoC/oCNT catalysts (T ramping series). The increased intensity of the 1 K min^{-1} profile is most likely due to an experimental error.

β / K min^{-1}	$E_a(\text{CO}_2)$ / kJ mol^{-1}	$E_a(\text{CH}_4)$ / kJ mol^{-1}	$S(\text{CO}_2)/S(\text{CH}_4)^{[a]}$
0.2	91 ± 3	108 ± 1	5.1
1	95 ± 1	108 ± 1	4.2
5	94 ± 2	108 ± 2	4.1
10	92 ± 2	108 ± 1	4.2

[a] 250°C, $X(\text{MeOH})=50\%$.

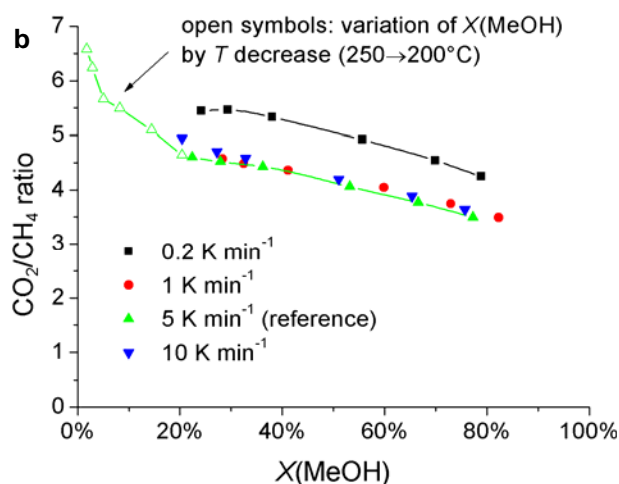
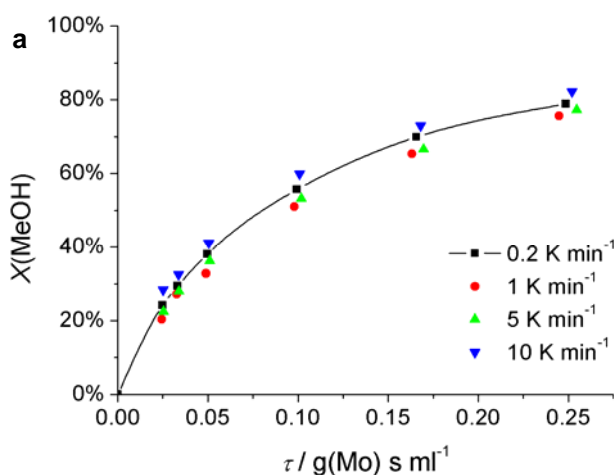


Figure S2. Catalytic performances of 20MoC/oCNT catalysts (T ramping series) in the SRM reaction. (a) MeOH conversion as a function of Mo-based contact time, (b) CO_2/CH_4 product ratio as a function of MeOH conversion. 10-100 ml min^{-1} 1% MeOH/1% $\text{H}_2\text{O}/\text{He}$, 250°C.

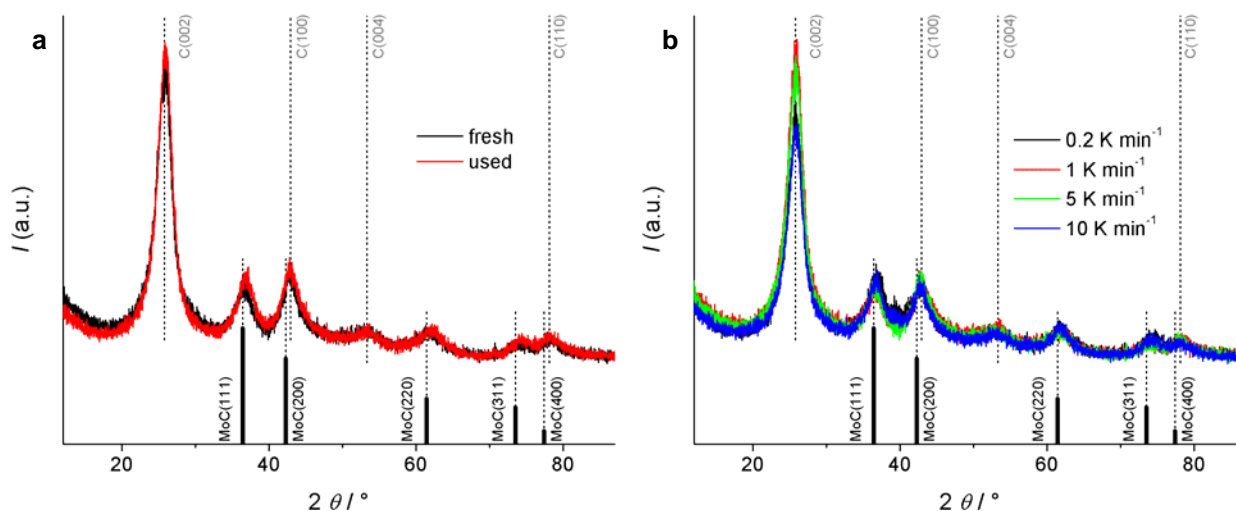


Figure S3. XRD patterns of 20MoC/oCNT catalysts (a) before and after catalytic reaction and (b) carburized at different heating rates in 20% CH_4/H_2 (the fresh 20MoC-oCNT sample has the FHI internal sample number 13942).

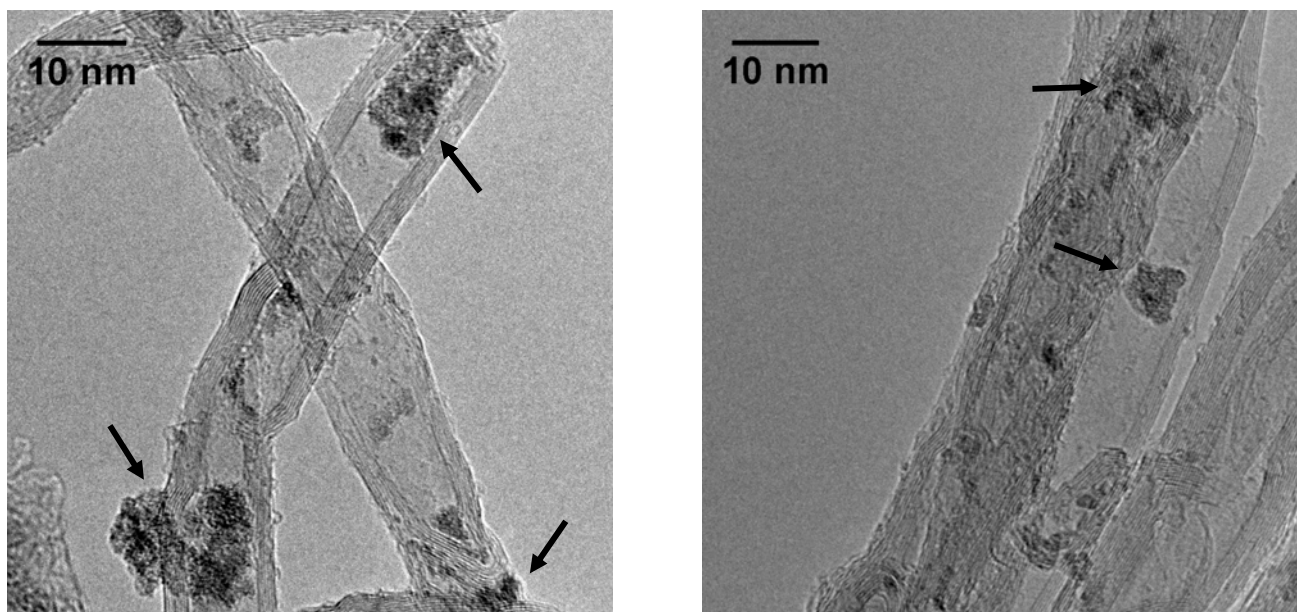


Figure S4. TEM images of high loaded 20MoC/oCNT catalyst showing agglomeration of Mo_xC crystallites (arrows).

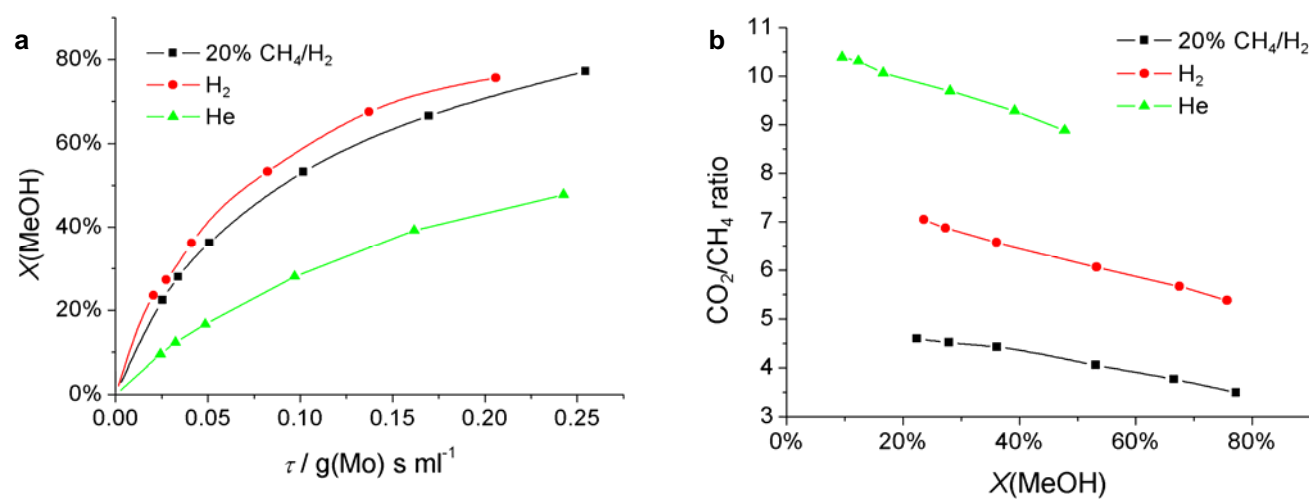


Figure S5 Catalytic performances of 20MoC/oCNT catalysts (atmosphere series) in the SRM reaction. (a) MeOH conversion as a function of Mo-based contact time, (b) CO_2/CH_4 product ratio as a function of MeOH conversion. 10-100 ml min^{-1} 1% MeOH/1% $\text{H}_2\text{O}/\text{He}$, 250°C.