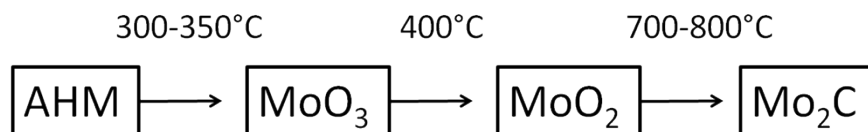**Supporting information**

<u>Carbothermal reduction pathways of CNF supported molybdenum- and tungsten carbides</u>

Preparation of metal carbides from metal oxides can proceed via many different processes. Most of these involve flowing carbon containing gasses such as CO or CH_4 that function as both a reducing agent and a carbon source for the carbide formation. Often H_2 is added to the gas mixture to facilitate the initial reduction of the metal oxide. These methods have the advantage that carbide formation proceeds at relatively low temperature, typically between 500-700°C for molybdenum- and tungsten carbides. However, when using carburizing gasses in the carbide synthesis, excess carbon is inevitably deposited on the surface of the material, leading to a contamination of the carbide surface sites. For this reason metal carbides are usually prepared via carbothermal (hydrogen) reduction if possible, in which a carbon support functions as both the reducing and carburizing agent. Like with the other processes, a flow of H_2 gas can also be added here to facilitate the initial reduction of the metal oxide. Since the carbothermal reduction process is a solid-solid reaction, carbide formation occurs at a higher temperature, typically between 700-1000°C for molybdenum and tungsten carbides, compared to gas-solid carburization processes. Details on the preparation of CNF supported molybdenum- and tungsten carbides by the carbothermal reduction process are described below.

1. Molybdenum

Molybdenum is introduced by impregnation of the CNF bodies with an aqueous solution of ammonium heptamolybdate, $(NH_4)_6Mo_7O_{24}$, AHM. Upon heating under inert gas flow (N_2, 50 ml/min), the AHM precursor decomposes between 200-300°C, releasing large amounts of ammonia. However, full decomposition of the precursor, meaning complete removal of all the nitrogen containing species, does not happen until temperatures of 500°C or higher, as previously shown by Ciembroniewicz and coworkers for the decomposition of ammonium paramolybdate in N_2 atmosphere. [26] Small MoO_3 crystallites are observed in XRD (not shown) at 350°C, which are reduced to MoO_2 at temperatures of 400°C or higher. The MoO_2 crystallites remain stable up to 700°C, at which temperature they are carburized to Mo_2C via a solid-solid reaction with the CNF support. Oxygen is removed as CO, while CO_2 is only formed in trace amounts. It should be noted that a metallic Mo^0 phase is not observed as an intermediate during the carbothermal reduction of the molybdenum oxide phases. [27] The diagram of the carbothermal reduction to Mo_2C is shown in scheme S1.

$$300\text{-}350°C \qquad 400°C \qquad 700\text{-}800°C$$

$$\boxed{AHM} \longrightarrow \boxed{MoO_3} \longrightarrow \boxed{MoO_2} \longrightarrow \boxed{Mo_2C}$$
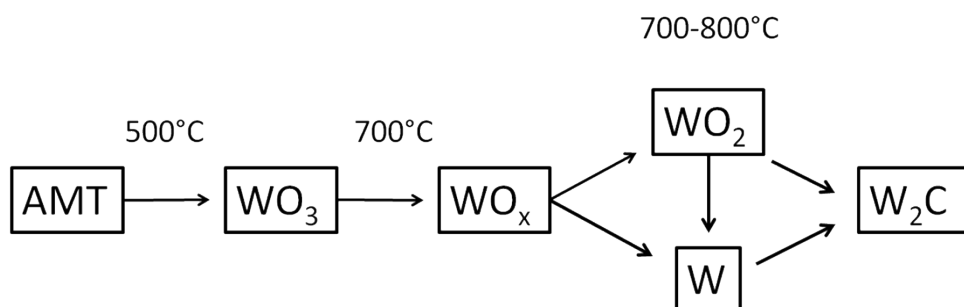
Scheme S1. Carbothermal reduction of ammonium heptamolybdate (AHM) on carbon nanofibers.

Molybdenum monocarbide (MoC) has been reported for materials prepared using CO as a carburizing gas, [27] or for carbothermal reduction of Mo-OMC composite materials. [28] However, in this work the Mo_2C phase was the only carbide that was obtained in the temperature range of 700-1000°C.

2. Tungsten

Tungsten is introduced by impregnation of the CNF bodies with an aqueous solution of ammonium metatungstate, $(NH_4)_6H_2W_{12}O_{40}$, AMT. The precursor decomposition is similar to the ammonium heptamolybdate described above. Upon decomposition of the precursor, crystalline WO_3 forms at temperatures around 500°C. Contrary to MoO_3, the WO_3 phase is relatively resistant against reduction, thus no low temperature WO_2 phase is observed. At 700°C reduction of the WO_3 crystallites by the CNF support starts. Initially oxygen removal results in shear plane defects, leading to WO_x (2< x< 3) phases that still have the WO_3 crystal structure. Between 750 and 800°C, rapid phase transitions occur, leading to a mixture of WO_x, WO_2, W_2C and metallic W phases. At temperatures above 800°C, the tungsten carbide W_2C becomes the dominant phase. Carburization is completed after 3 hours at temperatures of 900°C or higher. The diagram of carbothermal reduction to W_2C is shown in scheme S2.

Scheme S2. Carbothermal reduction of ammonium metatungstate (AMT) on carbon nanofibers.

Tungsten mono-carbide (WC) is often reported to be the final product in carburization of tungsten oxides. [14] Both in processes using carburizing gasses such as CO or CH_4 and in carbothermal reduction processes WC is typically the main product, while the W_2C phase is rarely reported. The reason for the preferential formation of W_2C on carbon nanofiber supports is still unclear at this moment.

Representative TGA plots for the weight loss during carburization of the various molybdenum- and tungsten carbide catalysts are shown in figure S1. The isothermal region (3h at 900°C) is not shown.
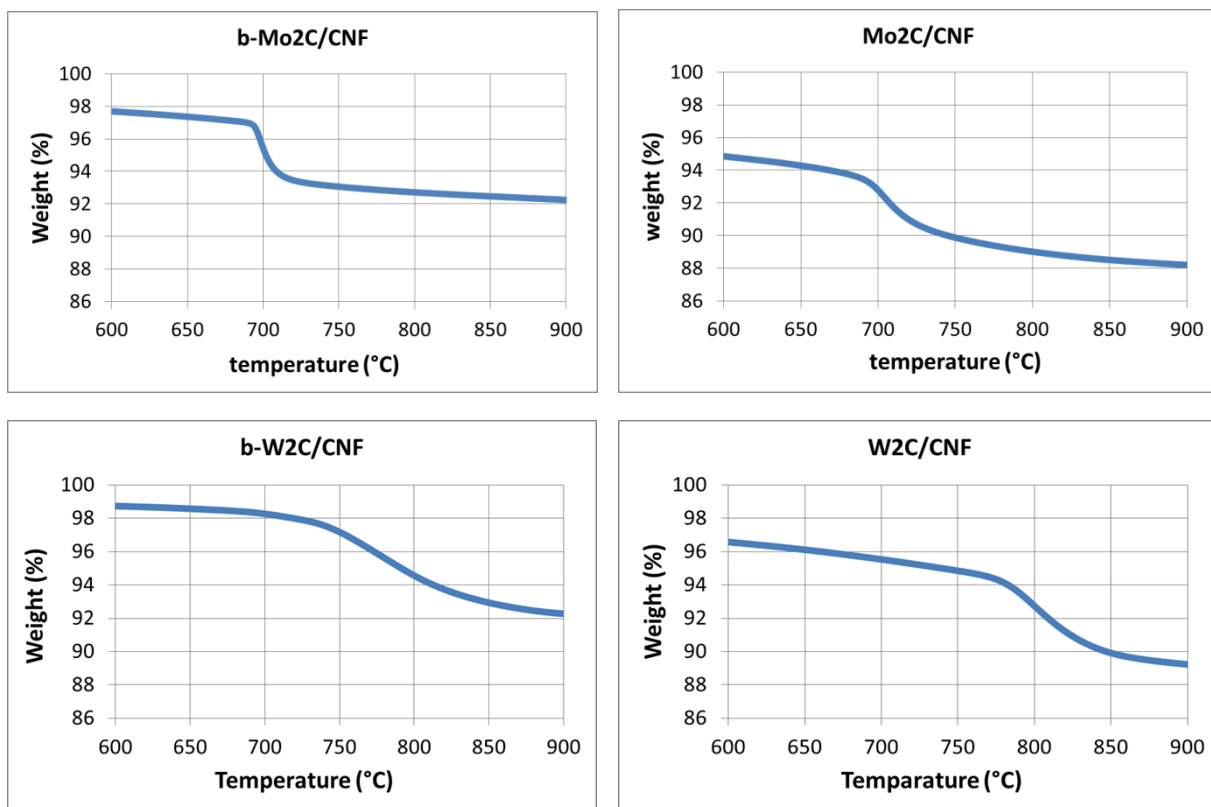
Figure S1. TGA of molybdenum- and tungsten oxides supported on carbon nanofibers. Measured in N_2 flow (50 ml/min), heating rate: 5°C/min.

The TGA data of the b-Mo2C/CNF and b-W2C/CNF catalysts clearly shows that carburization of the molybdenum oxide starts at 700°C, while that of tungsten oxide starts at 750°C. This is in accordance with thermodynamic data (equation S1) [29] for the solid state carburization of respectively MoO_2 and WO_2 with carbon. Below these threshold temperatures the carburization to an X_2C-phase (X= Mo,W) is calculated to be unfavorable. Since the carburization process is a solid-solid reaction, higher temperatures and longer reaction times are required to allow the carbon the diffuse through the metal oxide particles and achieve full carburization.

(eq. S1.1) $2WO_2 + 5C = 2W_2C + 4CO$ dG(750°C) = -5.4 kJ/mol

(eq. S1.2) $2MoO_2 + 5C = 2Mo_2C + 4CO$ dG(700°C) = -6.1 kJ/mol

When using pre-oxidized carbon nanofibers additional weight loss occurs due to decomposition of the surface oxygen groups on the support, releasing CO and CO_2. However, this does not appear to influence the starting temperature of the metal oxide carburization, which can still be seen to start at 700 and 750°C for Mo2C/CNF and W2C/CNF respectively.

Influence of drying step during impregnation of CNF support

The drying step used in the impregnation of the carbon nanofiber (CNF) bodies with an aqueous ammonium tungstate solution has a significant effect on the final distribution of the metal precursor on the CNF bodies. Examples are shown below for W2C/CNF samples. The CNF (90-212 um sieve fraction) were pre-treated with concentrated nitric acid to ensure good dispersion of the impregnation solution. The CNF were impregnated with an aqueous ammonium meta-tungstate solution and dried. The drying step involved either the use of a rotary evaporator (40°C, <20 mbar, 30 minutes), or placing the samples in an oven at 120°C for 16h. After the drying step, both samples were transferred to a tubular oven and heated to 900°C (5°C/min) under N_2 flow (50 ml/min) and kept at 900°C for 360 minutes.

- Drying using rotary evaporator (40°C, < 20 mbar, 30 minutes)
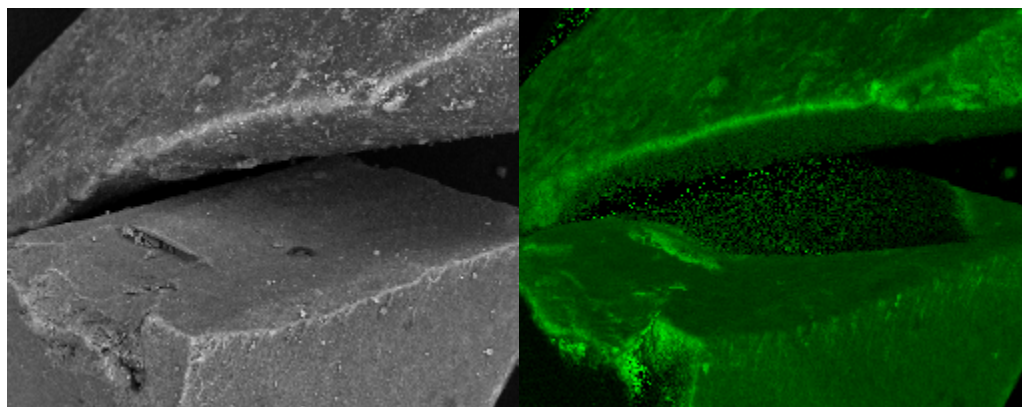

Figure S2. Elemental mapping using SEM-EDX. Left: SEM-image of W2C/CNF. Right: EDX-map of tungsten of the same region. Green "dotted" areas are due to low signal to noise ratio.

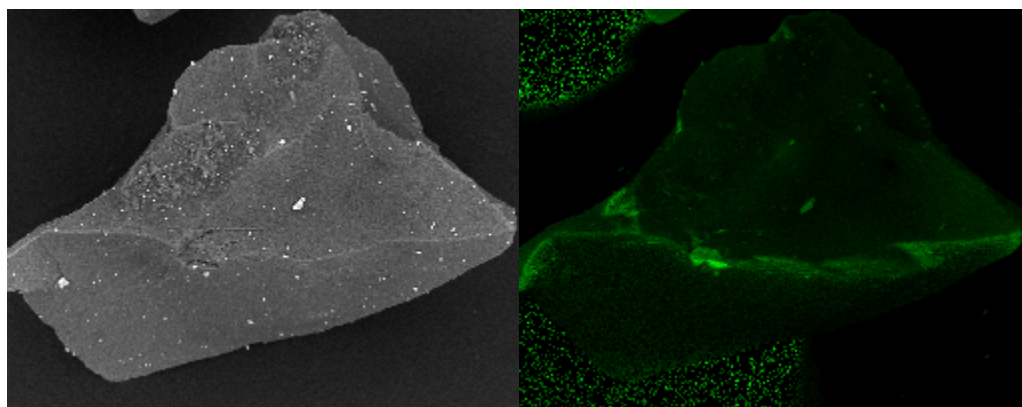- Drying in static air (120°C, atm. pressure, 16 h.)

Figure S3. Elemental mapping using SEM-EDX. Left: SEM-image of W2C/CNF. Right: EDX-map of tungsten of the same region. Green "dotted" areas are due to low signal to noise ratio.

Elemental mapping of the tungsten-precursor after drying and carburization indicates a difference in distribution over the CNF bodies. Drying in the rotary evaporator leads to tungsten being preferentially

located on the outside of the CNF bodies (figure S3), while conventional air drying leads to particles that are located inside the CNF structures (figure S2). This is in agreement with previously reported findings by Qin et al. for molybdenum carbides on CNF. [7] XRD patterns are identical for both the air-dried and the samples dried using the rotary evaporator (the latter shown in figure 1 of the main text). Catalyst activity is improved considerably for the W2C/CNF catalyst dried using the rotary evaporator. Initial rate of stearic acid hydrogenation at a reaction temperature of 350°C increased from 9.4 mmol g^{-1} h^{-1} in the first 60 minutes of reaction for the conventional air dried samples to 14.6 mmol g^{-1} h^{-1} for the new catalysts used in this work. [5]

Reference oxidation test

To verify the oxidative stability of the b-Mo2C/CNF catalyst that has been suggested by its stability in recycle tests (see for instance figure 6 in the main text), an additional experiment has been performed in which the b-Mo2C/CNF catalyst is exposed to ambient air for an additional 6 hours after the initial carburization and passivation steps.

The product compositions of the oxidized b-Mo2C/CNF (b-Mo2C/CNF-O) and the fresh b-Mo2C/CNF are shown in table S1 below. It can be seen that the difference in product composition between both catalysts is very small. This indicates that prolonged exposure to ambient conditions after the initial passivation procedure (see experimental section) does not have a significant impact on the catalyst surface structure under reaction conditions.

Table S1. Product compositions of oxidized and fresh b-Mo2C/CNF catalysts (see text for details).

Catalyst [a]	SA [b]	C18 [c]	C17 [c]	C18-OL [d]	C18-AL [e]	C36-oxy [f]
b-Mo2C/CNF-O (120 min)	4.1	6.7	5.5	60.1	12.8	10.5
b-Mo2C/CNF-O (300 min)	-	40.4	29.3	14.2	11.3	4.4
b-Mo2C/CNF (120 min) [g]	3.5	9.5	9.4	56.3	11.2	9.5
b-Mo2C/CNF (300 min) [g]	-	43.1	34.3	9.6	9.2	1.9

[a] reaction conditions: 300°C, 30 bar H$_2$. [b] stearic acid [c] sum of C18 or C17 hydrocarbons. [d] octadecanol [e] octadecanal [f] stearyl-stearate. [g] See also Table 4 (main text).

References

[25] G. Ciembroniewicz, R. Dziembai and R. Kalicki, *J. Therm. Anal.*, 1983, **27**, 125.

[26] E. L. Kugler, C. H. Clark, J. H. Wright, D. B. Dadyburjor, J. C. Hanson, Z. Song, T. Cai and J. Hrbek, *Top. Catal.*, 2006, **39**, 257.

[27] H. Wang, A. Wang, X. Wang and T. Zhang, *Chem. Commun.*, 2008, 2565.

[28] Calculated using HSC chemistry for windows, version 7.1.