

Supplemental information

“Cinnamaldehyde hydrogenation over carbon supported molybdenum and tungsten carbide catalysts”

M. Führer, T. van Haasterecht and J. H. Bitter

Biobased Chemistry and Technology, Wageningen University (The Netherlands)

Table of contents

Catalyst preparation.....	2
Catalyst characterization.....	2
Catalyst testing.....	3
Carbon Balance of W-carbide	4
Catalysts' selectivity at different pressures	6
COL/HCAL ratio as function of temperature	7
Evaluation of catalyst stability	7
References	10

Catalyst preparation

Carbon nanofibers (CNF) were grown from a mixture of hydrogen (102 ml/min), nitrogen (450 ml/min) and carbon monoxide (260 ml/min) at 550 °C and 3 barg for 24 h over a reduced 5 wt.% Ni/SiO₂ catalyst (3 g), as reported previously.¹ To remove SiO₂ after growth, the mixture (CNF+Ni+SiO₂) was three times refluxed in 1 M KOH for 1 h with intermediate decanting and washing with 1 M KOH. Next, the CNF was treated by refluxing in 65% concentrated nitric acid for 1.5 h, to remove the remaining nickel and to introduce surface oxygen groups on the CNF. Finally, the CNF were washed with demi water to neutral pH and ground to a 90-120 µm fraction.

All CNF supported catalysts were synthesized by Incipient Wetness Impregnation. Aqueous solutions of ammonium heptamolybdate (AHM; Sigma-Aldrich, 99.98% trace metals basis), ammonium metatungstate (AMT; Sigma-Aldrich, 99.98% trace metals basis) or Tetraammineplatinum(II) nitrate (Sigma-Aldrich, 99.995% trace metals basis) were used as precursor. After impregnation, the catalysts were dried overnight at 110 °C and stored for further use. The metal loadings of Pt, Mo and W were 5 wt%, 8.5 wt% and 15 wt%, respectively.

The carburization was performed at 650 °C (ramp of 5 °C/min) for the Mo-carbide and at 750 °C (ramp of 5 °C/min) for the W-carbide, for 2 h in flowing 20% CH₄/H₂ with 10 mL/min vertical furnace. This method is known as temperature-programmed reduction (TPR) method.

The reduction of 200 mg Pt/CNF was conducted in the same vertical furnace as mentioned above. The reduction temperature was ramped at 5 °C /min to 300 °C and held for 2 h in a flow of 30 ml/min H₂ and 60 ml/min N₂.

Catalyst characterization

XRD patterns were recorded on a Bruker D8 Advance equipped with a Lynxeye-XE-T PSD detector and a Cu-Kα_{1,2} tube generating X-rays with $\lambda = 1.542 \text{ \AA}$. The measurements were taken from $2\theta = 20^\circ$ to $2\theta = 80^\circ$ with a step size of 0.05°.

TEM images were taken with a JEOL JEM-1400 Plus microscope operated at 100 kV. For the sample preparation, 10 mg of the catalyst sample was added to 1 mL absolute ethanol and homogenized in an ultrasonic bath for 10 sec. Then 2 µL was dropped on a carbon-supported Cu grid (400 mesh) and dried at room temperature. The data were analysed with ImageJ and MS Excel to obtain the mean particle size and distribution of around 300 particles.

CO pulse chemisorption was performed on a Micromeritics AutoChem II 2920. Prior to the measurement, 200 mg of reduced Pt catalysts were activated at 300°C for 2 h before being evacuated for 2h at 300°C under Argon to remove any adsorbed H₂. Subsequently, the system was cooled down to 35°C and outgassed for 0.5h before the measurements. For the carbide samples, a similar CO

method was developed, however instead of the reduction, the dried carbide precursors were carburised at 600 °C for 1 h under a mixture of 20 % CH₄ in H₂.

The catalysts were analyzed by X-Ray Photoelectron Spectroscopy (XPS) using a JPS-9200 photoelectron spectrometer (JEOL). Spectra were obtained using monochromatic Al K α X-Ray radiation at 12 kV and 20 mA, with an analyzer energy pass of 10 eV for narrow scans and 50 eV for wide scans. The obtained spectra were processed using CASAXPS 2.3.22PR 1.0 peak fit program.

Metal leaching was assessed by Inductively Coupled Plasma (ICP-OES, Perkin Elmer AVIO 500) of the reaction mixture after filtering. 0.1 ml of the filtrate was added to 1 ml of 30% aqueous hydrogen peroxide and 9 ml of 65% nitric acid. The mixture was then digested with microwaves at 210 °C and 190 W for 40 mins.

Catalyst testing

The hydrogenation reaction was performed in a 100 mL stainless steel Parr autoclave, 4598 Micro batch reactor system. Typically, the reactor was filled with 250 mg or 100 mg catalyst, 50 ml toluene containing 1.36 g/l xylene and 13.6 g/l of cinnamaldehyde. Next, the loaded reactor was twice purged with 30 bar Ar and afterwards flushed with H₂. Subsequently, the reactor was pressurized to 20, 10 and 40 bar of H₂, heated up to either 140, 170 or 200 °C while stirring at 800 rpm. The reaction was performed for 3-7 h (depending on the catalyst). Liquid samples from the reactor were taken at regular time intervals to investigate the product distribution. The samples were analyzed using a GC-FID.

The following formulas were used to evaluate catalyst performance:

Conversion:

$$x_{CAL} = \frac{100}{[CAL]_{t,0}} * [CAL]_t \quad (1)$$

Normalized selectivity:

$$S_{N, Product x} = \frac{[Product X]_t}{\Sigma [Products]_t} * 100\% \quad (2)$$

With [CAL]_{t,0} the concentration of cinnamaldehyde at start of reaction, [CAL]_t concentration of cinnamaldehyde at time t, [Product X]_t concentration of product X at time t and Σ [Product]_t concentration of all products at time t.

The blank run (with no catalysts) for CAL hydrogenation was performed in the batch reactor at 200 °C and 20 bar, and only HCAL was produced as product. The conversion of CAL was less than 20 % after

5h and reached 50% after 24h under the reaction conditions used in this investigation; this value is much smaller in comparison to the reactivity of the catalysts.

Acidic properties of the catalyst

XPS measurements were done to further investigate the extent of oxidation of the carbide surface. The narrow scan of the Mo carbide and the W carbides samples was taken and shown in Figure S1. The W-4f region shows signals at 31.4 eV and 33.6 eV corresponding to tungsten carbide which is in agreement with literature data.^{2,3} The signals observed at 35.0 eV and 37.1 eV are related to tungsten oxide (W6+).

The Mo-3d region shows two signals (231.5 eV and the 228.3 eV) originating from the carbide. The signal at 234.7 eV has been assigned to Mo(VI) oxide species.^{2,4}

Since oxygen is visible on these samples it can be concluded that the carbidic surface gets partly oxidized during the brief exposure to air when transferring the catalyst from the carburization oven into the XPS analyzer (or the reaction vessel). The oxidation was less pronounced for the Mo-carbide than for the W-carbide, which is in accordance with the literature.² Since the oxides are expected to have acidic properties⁵, it can be concluded that some acidity will be introduced during the exposure of the sample to air. This, in turn, might change the selectivity of the catalysts since it has been shown before⁶ that oxides are active for decarboxylation/decarbonylation while carbides are active for hydrodeoxygenation.

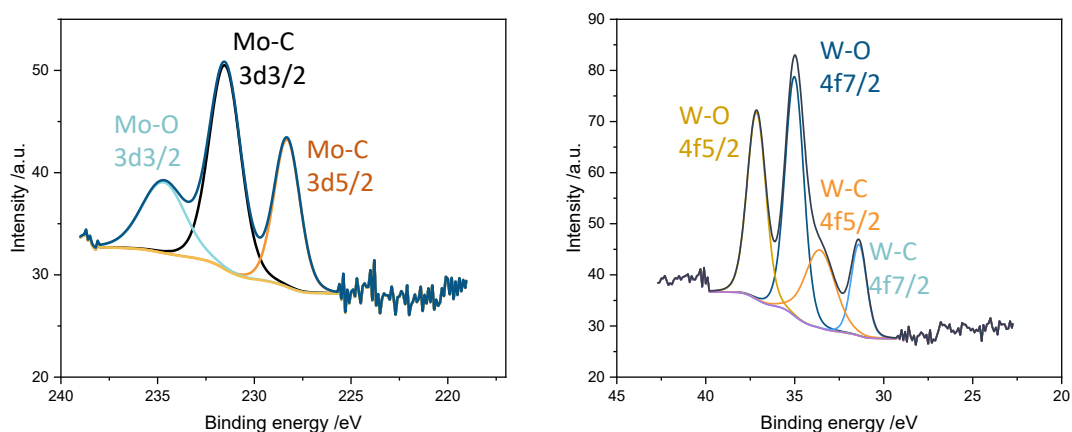


Figure S1. XPS spectra of W-carbide/CNF, W-4f (right) and Mo-carbide/CNF, Mo-3d (left).

Carbon Balance over W-carbide

As can be seen from Table S1, the carbon balance of W_2C during the hydrogenation of CAL decreases significantly. Figure S2 shows the GC-FID spectra of the three catalysts at a high conversion level (90-100%). Next to the known products (propylbenzene, methylstyrene, HCAL and HCOL), we observed peaks at the retention time of 29-35 min. From GC-MS analysis these peaks were identified to represent C18 compounds (such as 1,5-Diphenyl-3-pentanone, 2,5-Diphenyl-1,5-hexadiene, 1,5-Diphenyl-1,5-hexadiene and Benzene, 1,1'-(1,6-hexanediy)bis-). Remarkable is that W-carbide has more of these C18 compounds (33 % at 5h) in comparison to Mo-carbide (12 % at 5h) and the Pt (4 % at 1h).

Table S1. Carbon balance of W_2C over time

Catalyst	Reaction time	Carbon Balance (%)	Unidentified products (%)	Final Carbon Balance (%)
W	5h	36	33	69
Mo	5h	85	12	97
Pt	1h	95	4	99

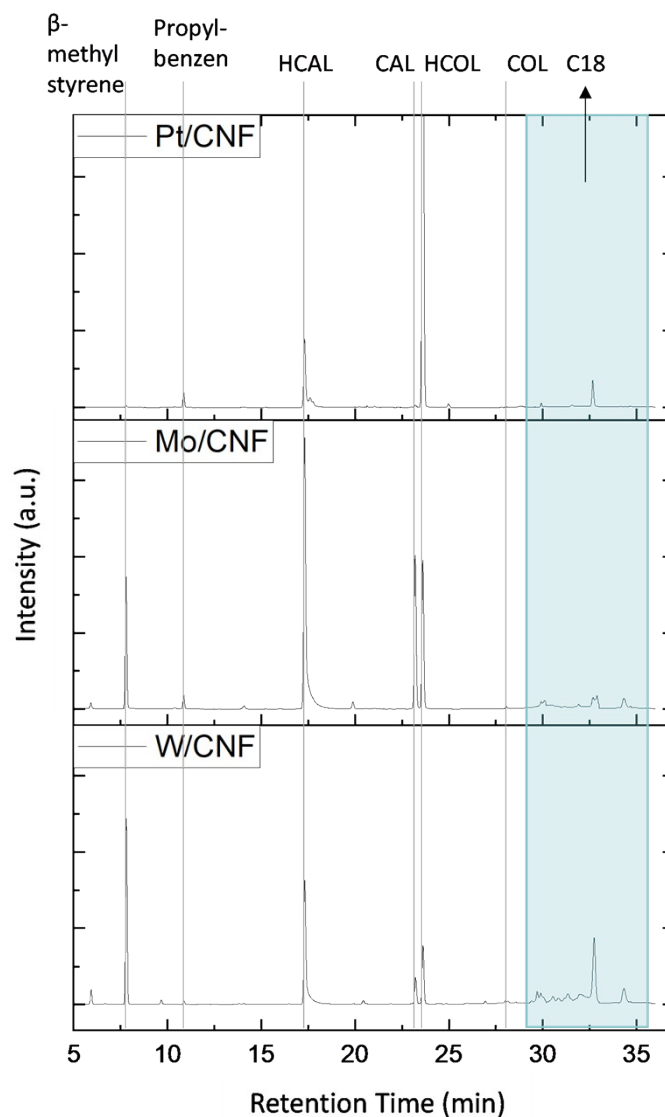


Figure S2. GC-FID of CAL hydrogenation over W-carbide

Catalysts' selectivity at different pressures

The hydrogenation was conducted at 200 °C with varying H₂ pressures (10-40 bar). The conversion and the selectivity of Mo-carbide catalyst at these different pressures are shown in Figure S33. When comparing the activities measured for 20 and 40 bar, it can be concluded that the CAL conversion is almost independent of the H₂ pressure. With both pressures, the CAL conversion reaches full conversion after 5h. However, at 10 bar the conversion significantly decreases to 40 % after 5 h. The selectivity of the Mo-carbide was not significantly influenced by the pressure and predominantly HCAL and β-methylstyrene were formed.

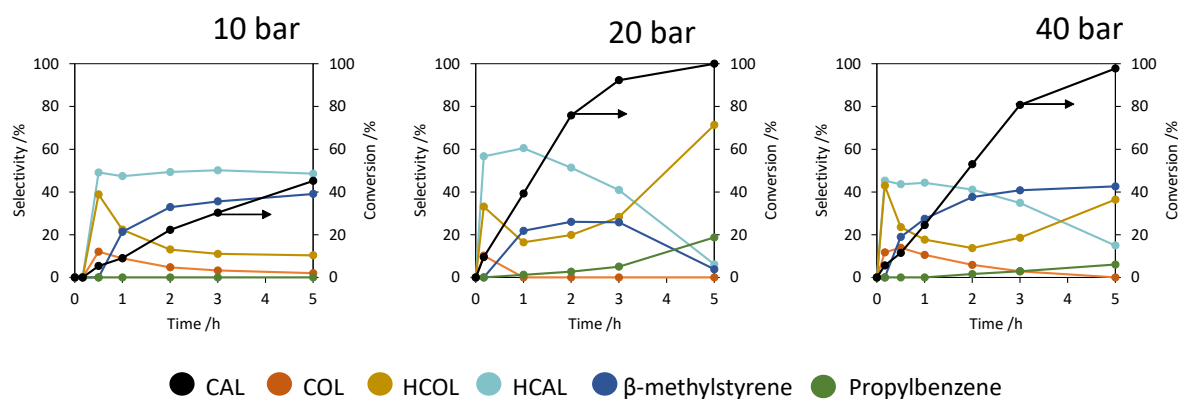


Figure S3. CAL Conversion and product yield of the Mo-carbide catalyst at 10 and 40 bar (50 ml toluene, 13.6 g/l CAL, $T = 200\text{ }^{\circ}\text{C}$, 800 rpm)

COL/HCAL ratio as function of temperature

Figure S44 shows the ratio between COL to HCAL at low conversion (5-40%). For the hydrogenation at $140\text{ }^{\circ}\text{C}$, the COL/HCAL ratio stays ~ 0.7 whereas at $170\text{ }^{\circ}\text{C}$ and $200\text{ }^{\circ}\text{C}$ the ratio decreases with increasing conversion rates from 0.3 to 0.2 and 0.1 to 0.0, respectively. This data shows that at lower temperatures the selectivity towards COL hydrogenation increases.

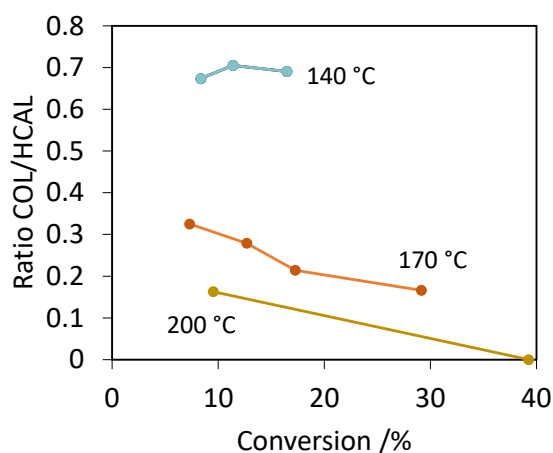


Figure S4. COL to HCAL ratio at CAL conversions from 5 to 40 %

Evaluation of catalyst stability

To investigate the deactivation of the catalyst, subsequent experiments with one batch of Mo-carbide catalyst were conducted. Between the runs, the remaining reaction medium was decanted, then the catalysts were washed/decanted repeatedly with toluene before adding the fresh reaction medium. As can be seen from Figure S5, the catalyst loses activity after the first run but is rather stable after the 2nd run.

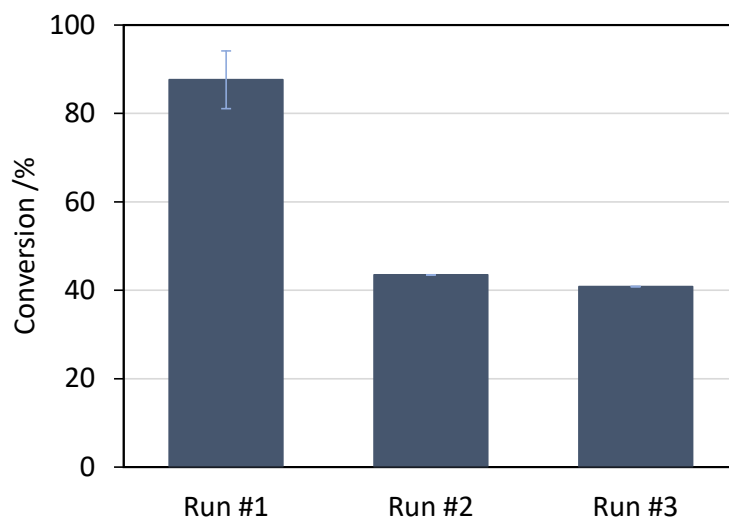


Figure S5. Multiple runs of cinnamaldehyde conversion (50 ml toluene, 13.6 g/l CAL, $T = 200\text{ }^{\circ}\text{C}$, 20 bar H_2 , 800 rpm) upon recycling Mo-carbide catalyst

In order to elucidate the cause of the catalyst deactivation, the spent Mo-carbide catalyst was characterised by XRD shown in Figure S6. The signals at $2\theta=28$ and $2\theta=43^{\circ}$ represent the (002) and (101) reflections of the CNF.⁷ The reflections marked with the green diamond indicate the presence of the hexagonal $\beta\text{-W}_2\text{C}$ phase (PDF 79-0743).⁸ The Mo carbide sample shows reflections representing the cubic $\alpha\text{-MoC}_{1-x}$ phase (PDF 65-0280), marked with yellow dots.⁹ The characteristic carbide reflections are observed for both fresh and spent catalysts. This result shows that no bulk oxidation of the carbide catalyst occurs during the reaction. When comparing the peak intensity of fresh with the spent catalysts a decrease in intensity can be observed. This indicates metal leaching during the reaction might have occurred. This argument is further supported by the amounts metal found in the liquid phase. ICP analysis shows that $\sim 0.1\%$ Mo of the 8.5 wt% was found in the reactant medium after the first run (with a duration of 4 h). It need to be mentioned that the obtained metal concentration was measured close to the detection limit of the analyzer. No other metals were found.

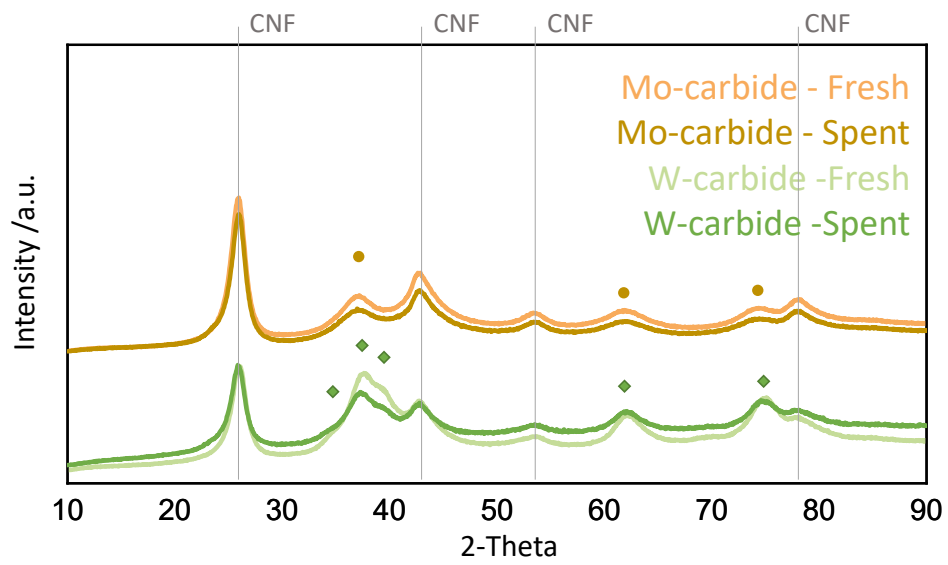


Figure S6. XRD of the spent and fresh Mo and W carbide

References

1. M. L. Toebes, E. M. P. van Heeswijk, J. H. Bitter, A. J. van Dillen and K. P. de Jong, *Carbon*, 2004, **42**, 307-315.
2. D. R. Stellwagen and J. H. Bitter, *Green Chemistry*, 2015, **17**, 582-593.
3. H. Guo, Z. Qi, Y. Liu, H. Xia, L. Li, Q. Huang, A. Wang and C. Li, *Catalysis Science & Technology*, 2019, **9**, 2144-2151.
4. M. Abou Hamdan, A. Lilic, M. Vecino-Mantilla, C. Nikitine, L. Vilcocq, M. Jahjah, C. Pinel and N. Perret, *Ind Eng Chem Res*, 2020.
5. S. A. W. Hollak, R. W. Gosselink, D. S. van Es and J. H. Bitter, *Acs Catalysis*, 2013, **3**, 2837-2844.
6. R. W. Gosselink, D. R. Stellwagen and J. H. Bitter, *Carbohydrate research*, 2013, **52**, 5089-5092.
7. A. L. Jongerius, R. W. Gosselink, J. Dijkstra, J. H. Bitter, P. C. A. Bruijninx and B. M. Weckhuysen, *ChemCatChem*, 2013, **5**, 2964-2972.
8. R. A. Mitran, M. C. Radulescu, L. Buhalteanu, L. C. Tanase, D. G. Dumitrescu and C. Matei, *Journal of Alloys and Compounds*, 2016, **682**, 679-685.
9. L. S. Macedo, D. R. Stellwagen, V. T. da Silva and J. H. Bitter, *Chemcatchem*, 2015, **7**, 2816-2823.