SUPPLEMENTARY INFORMATION

Influence of carburization time on the activity of Mo_2C/CNF catalysts for the HDO of guaiacol

E. Ochoa, D. Torres, J.L. Pinilla[1], I. Suelves

Instituto de Carboquímica, CSIC, C/ Miguel Luesma Castán 4, Zaragoza 50018, Spain

[1] Corresponding author: José Luis Pinilla (jlpinilla@icb.csic.es)

EXPERIMENTAL

Formulas used for the calculation of specific surface area of Mo_2C, guaiacol conversion, yield and specific yield to a product i, HDO ratio and carbon balance.

- Surface area-weighted diameter of Mo_2C ($d_{\bar{s}}$):

$$d_{\bar{s}}(cm) = \frac{\sum_i N_i \cdot d_i^3}{\sum_i N_i \cdot d_i^2}$$

Where, d_i is the diameter of Mo_2C nanoparticles and N_i is the number of those Mo_2C measured from STEM images.

- Specific surface area of Mo_2C on the catalyst (S_{Mo_2C}):

$$S_{Mo_2C}\left(\frac{cm^2}{g}\right) = \frac{6}{8.9 \cdot d_{\bar{s}}} \cdot \frac{g_{Mo_2C}}{g_{cat}}$$

Where, *8.9* is the Mo_2C density (g/cm^3), $d_{\bar{s}}$ is the surface area-weighted diameter calculated as described above and g_{Mo_2C}/g_{cat} is the mass of Mo_2C per gram of catalyst.

- Guaiacol conversion (X_{Gua}):

$$X_{Gua}\ (\%) = \frac{n_{0,Gua} - n_{f,Gua}}{n_{0,Gua}}\ x\ 100$$

Where, $n_{0,Gua}$ and $n_{f,Gua}$ are the initial and final moles of guaiacol in the feedstock and in the liquid product, respectively.

- Yield to a product *i* (Y_i; where *i* represents any of the products obtained from the guaiacol):

$$Y_i\ (wt.\%) = \left(\frac{m_i}{m_{0,Gua}}\right) x\ 100$$

Where, m_i is the final weight of a product *i* in the reaction liquid and $m_{0,Gua}$ is the initial weight of guaiacol in the feedstock.

- Specific product yield (SPY_i; where i represents any of the products obtained from the guaiacol):

$$SPY_i\left(\frac{mol_i}{mol_{Mo}}\right) = \frac{n_i}{n_{Mo}}$$

Where, n_i and n_{Mo} are the final moles of a product i in the reaction liquid and the moles of Mo in the catalyst, respectively.

- *HDO ratio* as the amount of oxygen removed from guaiacol:

$$HDO\ ratio\ (\%) = \left(\frac{n_{0,Ox} - n_{f,Ox}}{n_{0,Ox}}\right) x\ 100$$

Where, $n_{0,Ox}$ are the initial moles of oxygen in the feedstock and $n_{f,Ox}$ are the moles of oxygen in the product.

- Carbon balance of all products, including the non-reacted guaiacol:

$$C\ (\%) = \frac{n_{f,C}}{n_{0,C}} x100$$

Where $n_{f,C}$ are the moles of carbon in the product and $n_{0,C}$ are the moles of carbon in the guaiacol in the feedstock.

Table S1. Product yield (wt. %) of the products measured in the liquid phase by GC after the HDO of guaiacol (conditions: 300 ºC, 20 bar of H_2 and 2 h).

Yield (wt. %)	**Carburization time** (h)				
	1	**2**	**4**	**6**	**18**
Cyclohex.+Benzene	3.95	15.18	8.53	10.83	24.52
Anisole	3.14	11.23	5.22	2.41	1.98
Phenol	12.65	12.13	11.23	18.24	4.43
Methylcyclohexanol	1.59	1.79	1.45	2.68	12.47
Cresol	1.86	0.61	1.12	0.77	2.95
Xylenol	1.13	0.00	0.00	0.00	0.00
Catechol	3.04	3.27	0.54	0.44	2.76
Others	10.92	28.55	26.61	37.73	31.12

Figure S1. XPS spectra of the catalyst carburized at 1, 2, 4, 6 and 18 h.

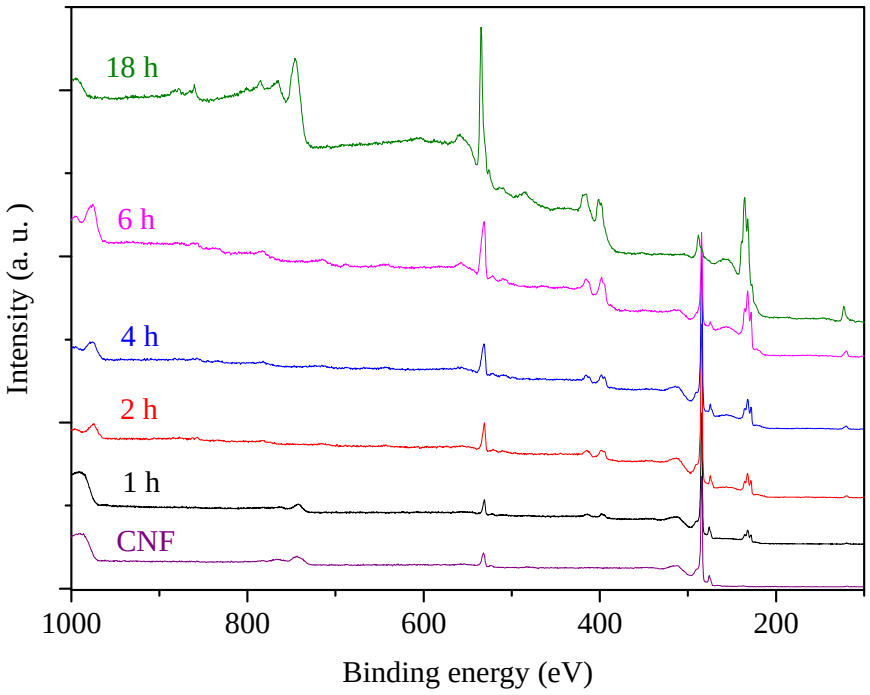
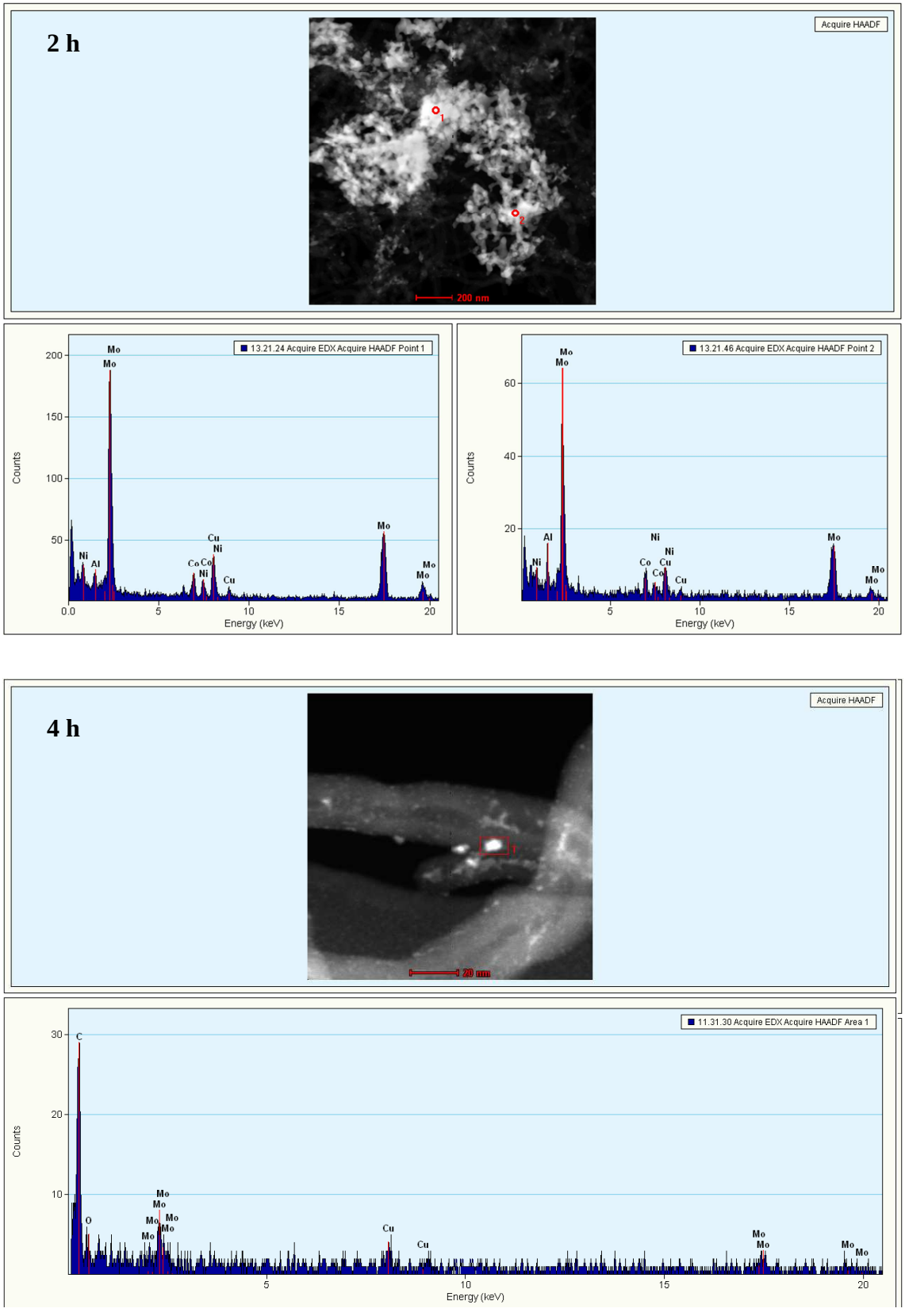
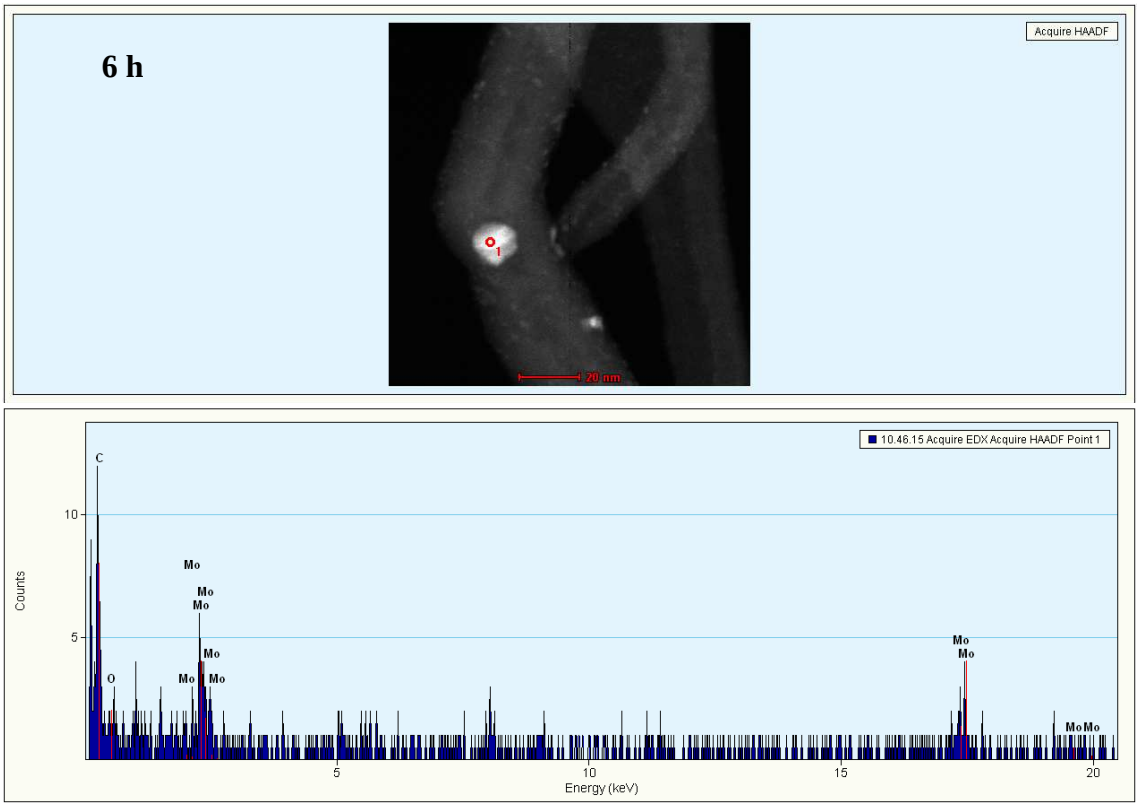


Figure S2. EDX performed to catalyst carburized at different times.




6 h
Acquire HAADF
1
20 nm
10.46.15 Acquire EDX Acquire HAADF Point 1
C
O
Mo
Counts
Energy (keV)

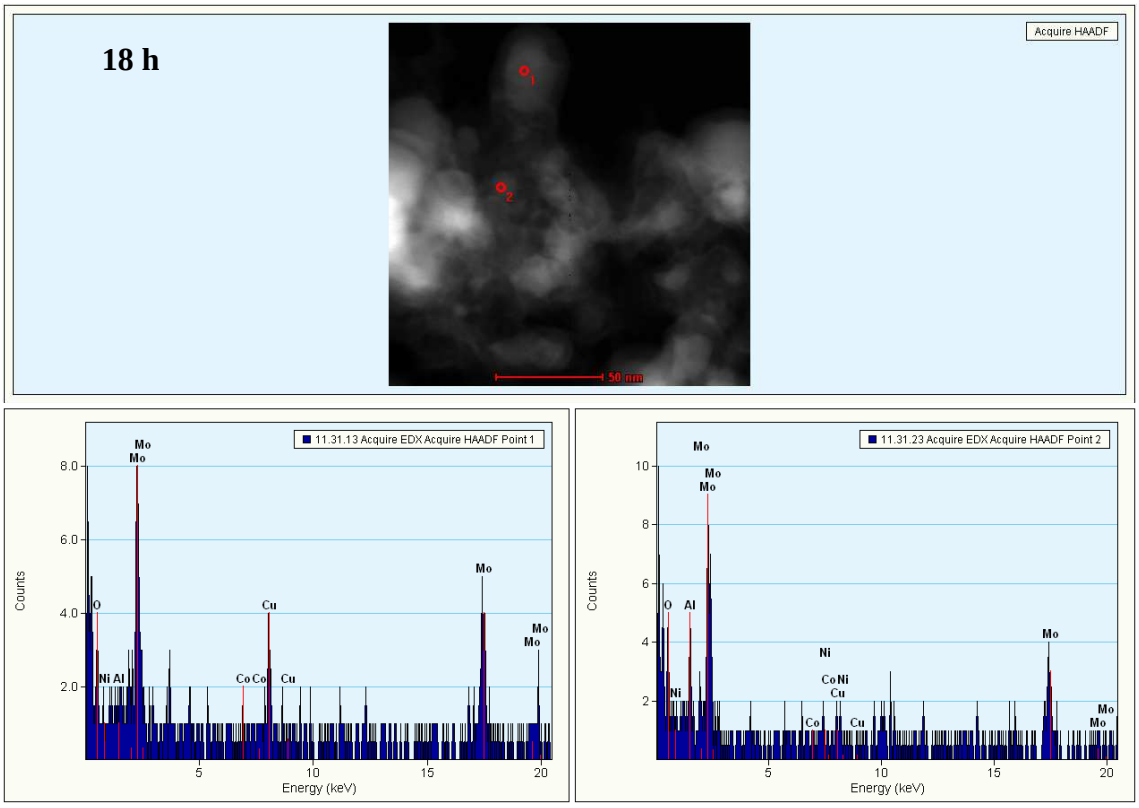

18 h
Acquire HAADF
1
2
50 nm
11.31.13 Acquire EDX Acquire HAADF Point 1
11.31.23 Acquire EDX Acquire HAADF Point 2
Mo
O
Al
Ni
Co
Cu
Counts
Energy (keV)

Figure S3. Mo_2C crystallite size distribution of the catalysts carburized at 1, 2, 4, 6, and 18h.