Supporting Information

Physical and Chemical Studies of Tungsten Carbide Catalysts: Effects of Ni Promotion and Sulphonated Carbon

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1. Experimental

N_2 Physisorption

Nitrogen adsorption-desorption isotherms were measured at -196 ^oC using a Quantachrome Autosorb-1C automatic analyzer. The wet samples were degassed at 120 ^oC for 12 h before the isotherms were measured. The specific surface area values were determined with the B.E.T. model using a multipoint method from the data collected at the relative pressures $P/P_0 < 0.1$ due to the presence of microporosity in the samples. The total pore volume was derived from the amount of gas absorbed at a relative pressure of $P/P_0 = 0.95$.

2. Results

2.1 Adsorption-Desorption Isotherms

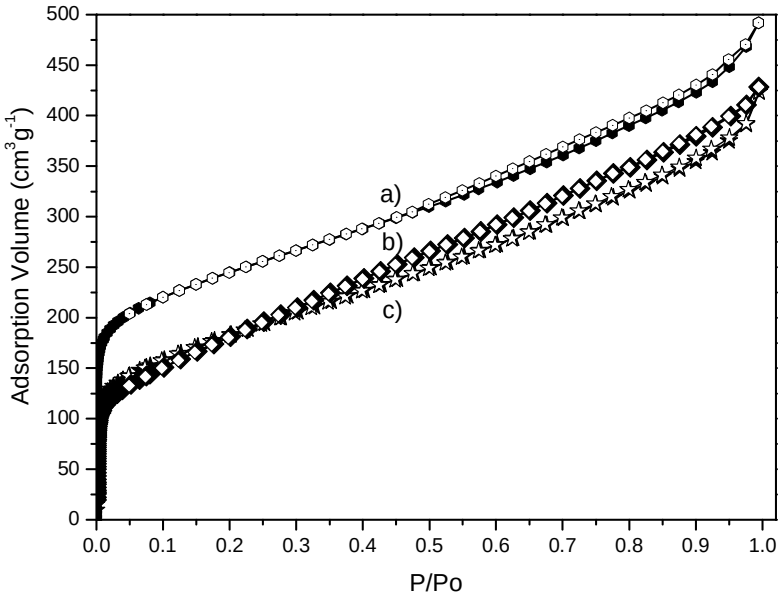

Figure S1. Adsorption-desorption isotherms of tungsten carbides catalysts supported on commercial carbon: a) C (commercial carbon); b) 2%Ni-W_xC/C and c) W_xC/C.

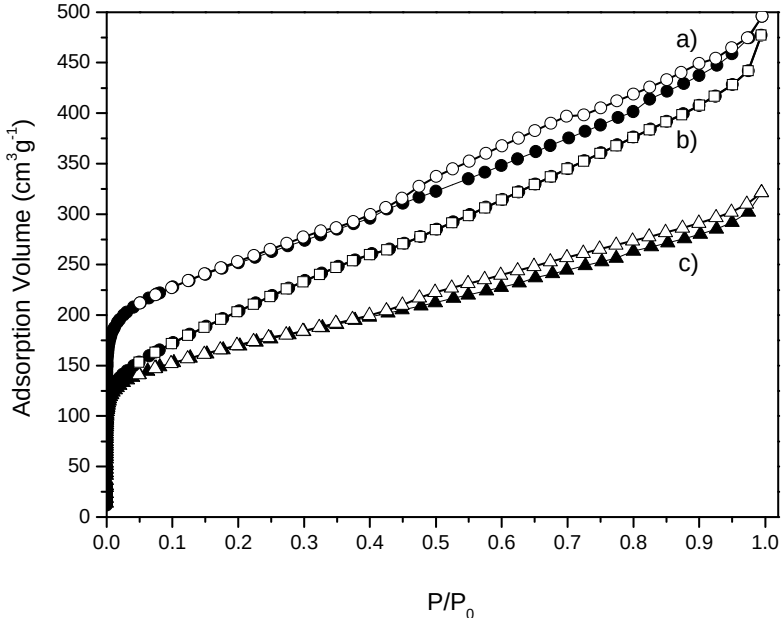

Figure S2. Adsorption-desorption isotherms of tungsten carbides catalysts supported on sulfonated carbon: a) C-SO_3H: b) W_xC-SO_3H and c) 2%Ni-W_xC-SO_3H.

In general, the isotherms are characteristic of materials comprising both micro and mesoporosity.

Table S1. Textural properties of the supports and synthesized tungsten carbide catalysts (±5% error).

Sample	S_{BET} (m^2g^{-1})	V_t (cm^3g^{-1})
C	891	0.700
W_xC/C	649	0.577
Ni-W_xC/C	620	0.614
C-SO_3H	906	0.705
W_xC/C-SO_3H	714	0.657
Ni-W_xC/C-SO_3H	609	0.449

The textural characteristics seem to not be affected by the functionalization of the carbon support, the surface area nor the total pore volume as they are similar for both activated and sulfonated carbon.

In general, the tungsten carbide catalysts have smaller surface areas and pore volumes compared with the support. This was to be expected due to pore blocking and syntherization effect provoked by the impregnation and carburization process at high temperatures. Ni-promoted samples exhibited smaller surface areas in comparison with non-promoted samples probably as a result of the higher carbon deposition on the surface of the catalyst.

2.2 *In situ* XRD

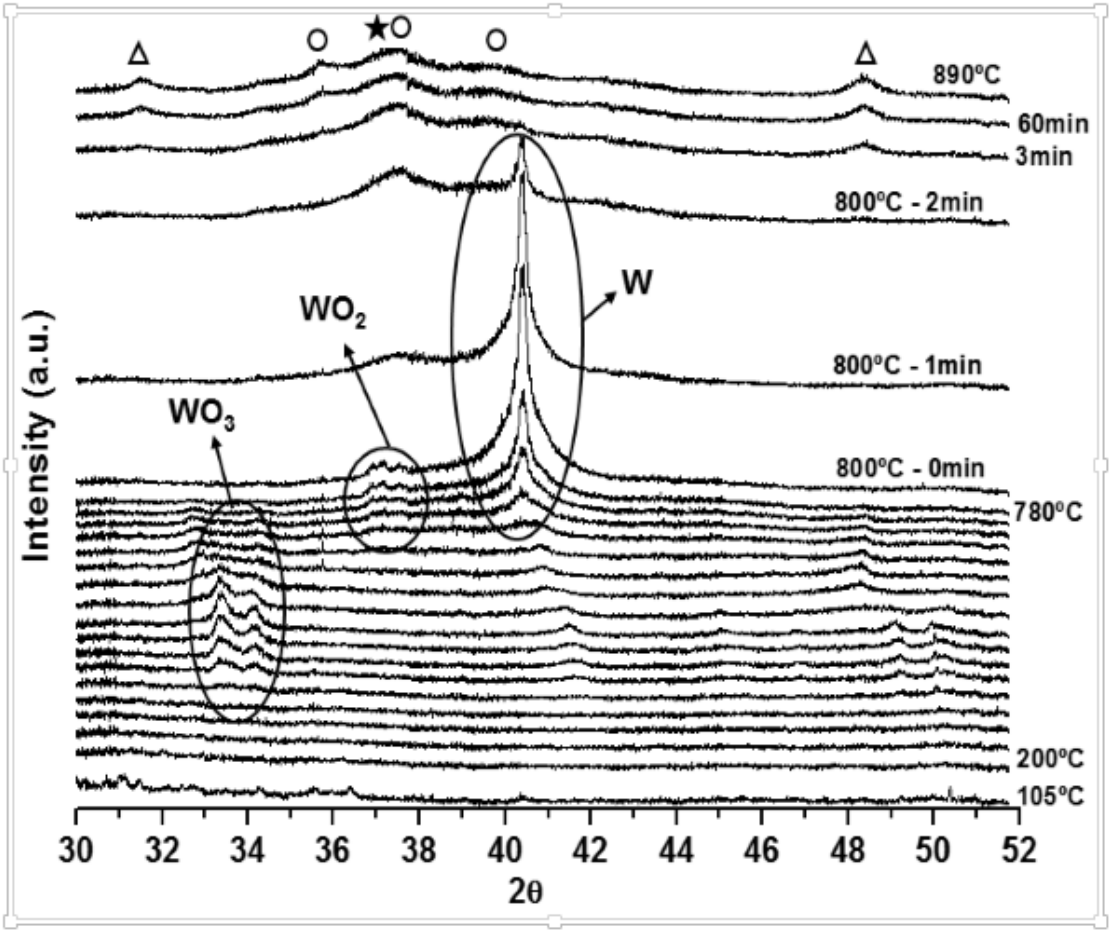

Figure S3. *In situ* X-ray diffraction patterns obtained during carburization process of W_XC/C sample:△ WC; ○ W_2C and ★WC_{1-x}.

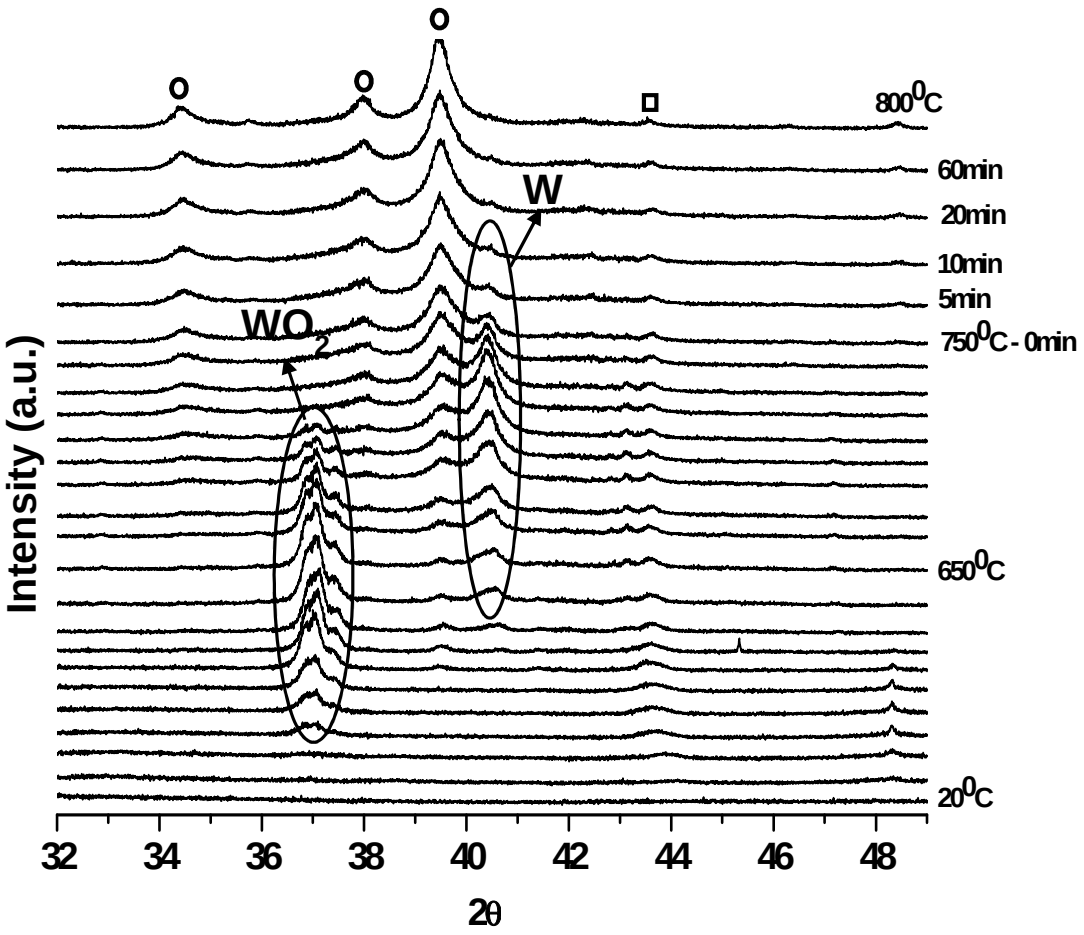

Figure S4. *In situ* X-ray diffraction patterns obtained during carburization process of Ni-W_XC/C sample: O W_2C and □ Ni_4W alloy.

2.3 XPS

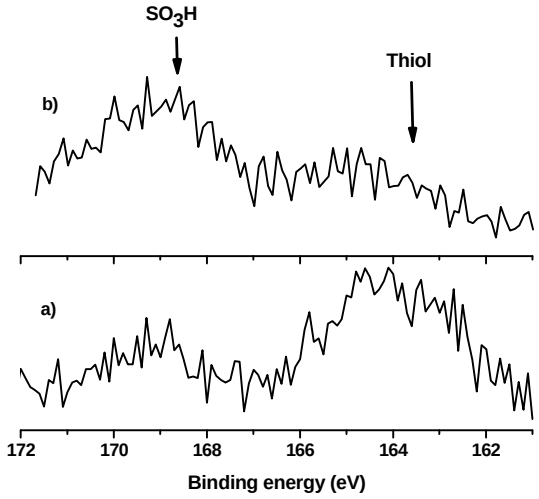

Figure S5. XPS graph of S 2P after catalytic reaction: a) and b WxC/C-SO_3H) Ni-WxC/C-SO_3H.

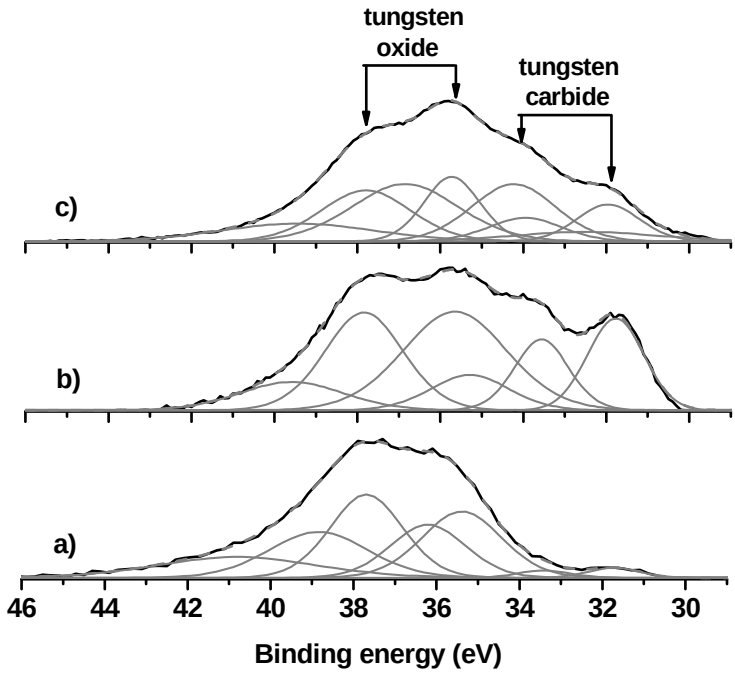

Figure S6. XPS graph of W 4f level after catalytic reaction: a) Ni-WxC/C; b) Ni-WxC/C-SO_3H and c) WxC/C

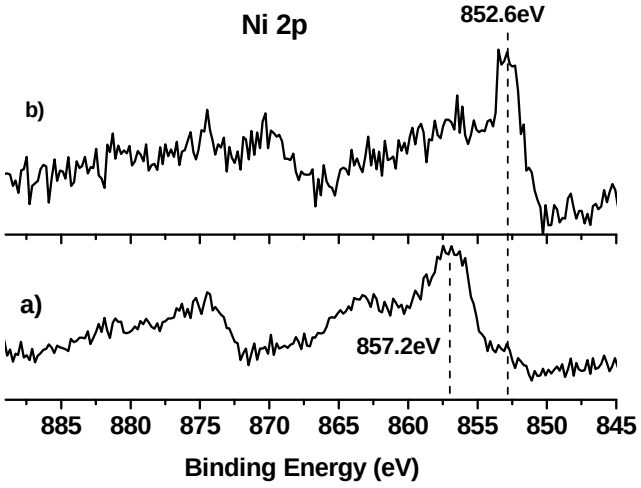

Figure S7. XPS Ni 2p after catalytic reaction: a) Ni-W_XC / C and b) Ni-WxC/C-SO_3H.

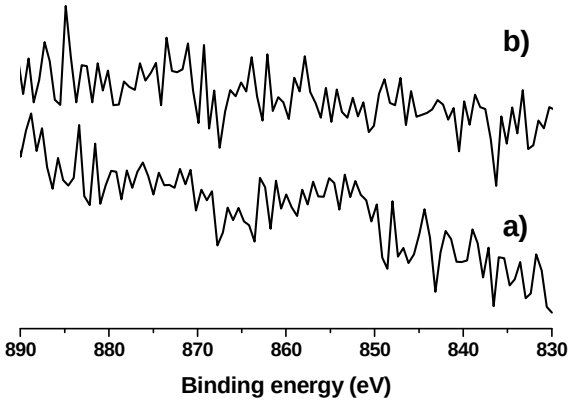

Figure S8: Ni 2p XPS spectra of tungsten carbides after carburization and passivation: a) Ni-W_xC/C-SO_3H and b) Ni-W_xC/C.

2.4 . Mass Spectrometry

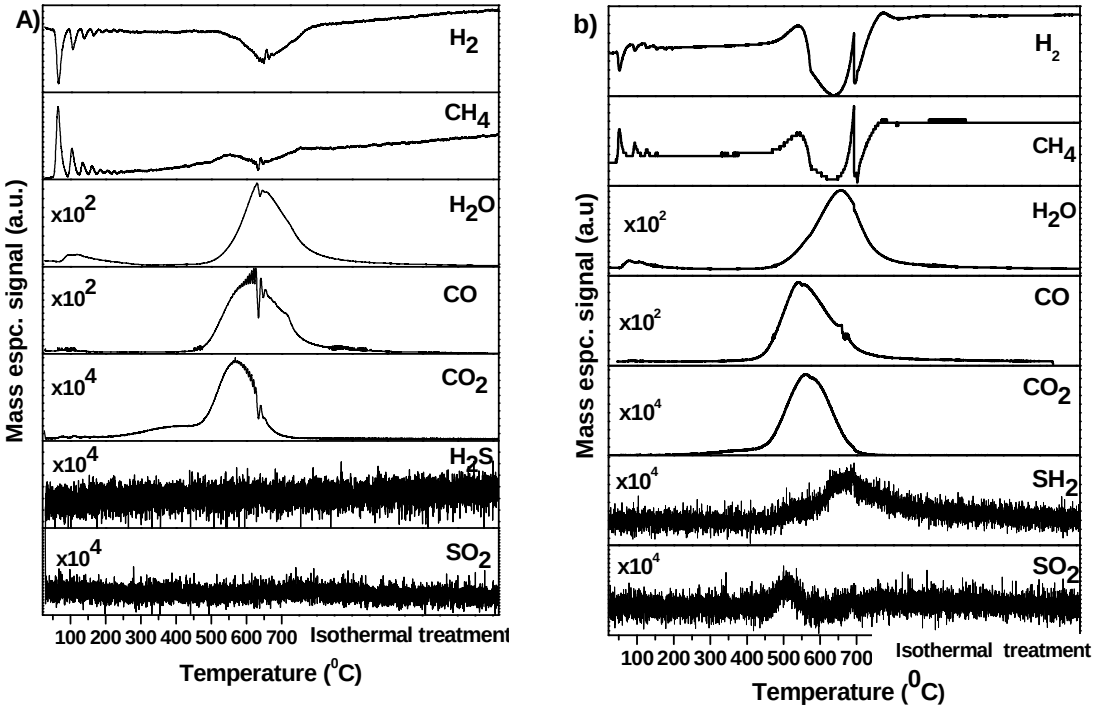

Figure S9. Water, carbon monoxide, carbon dioxide, methane and sulfur compounds formation profiles of the C (A) and C-SO_3H (B) samples under carburization conditions. Some of the mass spectrometer signals were multiplied by a factor, showed on the left side of each profile, to allow for a better visualization and comparison of the signals.

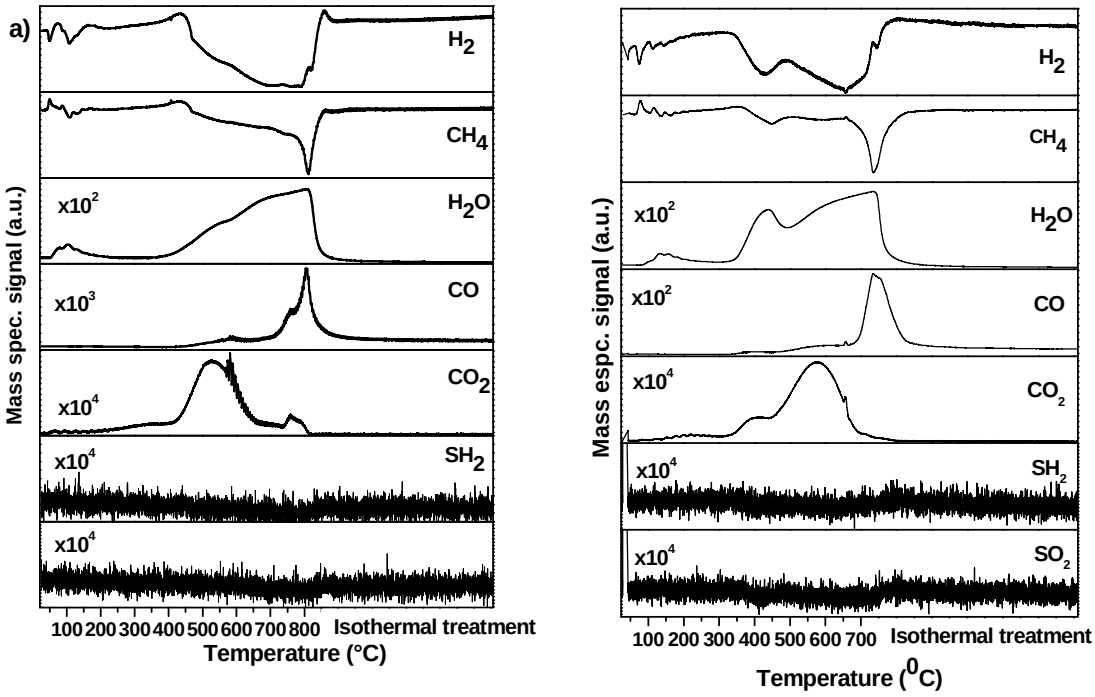

Figure S10. Water, carbon monoxide, carbon dioxide, methane and sulfur compounds formation profiles of the $W_xC/C\text{-}SO_3H$ (A) and $Ni\text{-}W_xC/C\text{-}SO_3H$ (B) samples under carburization conditions. Some of the mass spectrometer signals were multiplied by a factor, showed on the left side of each profile, to allow for a better visualization and comparison of the signals.

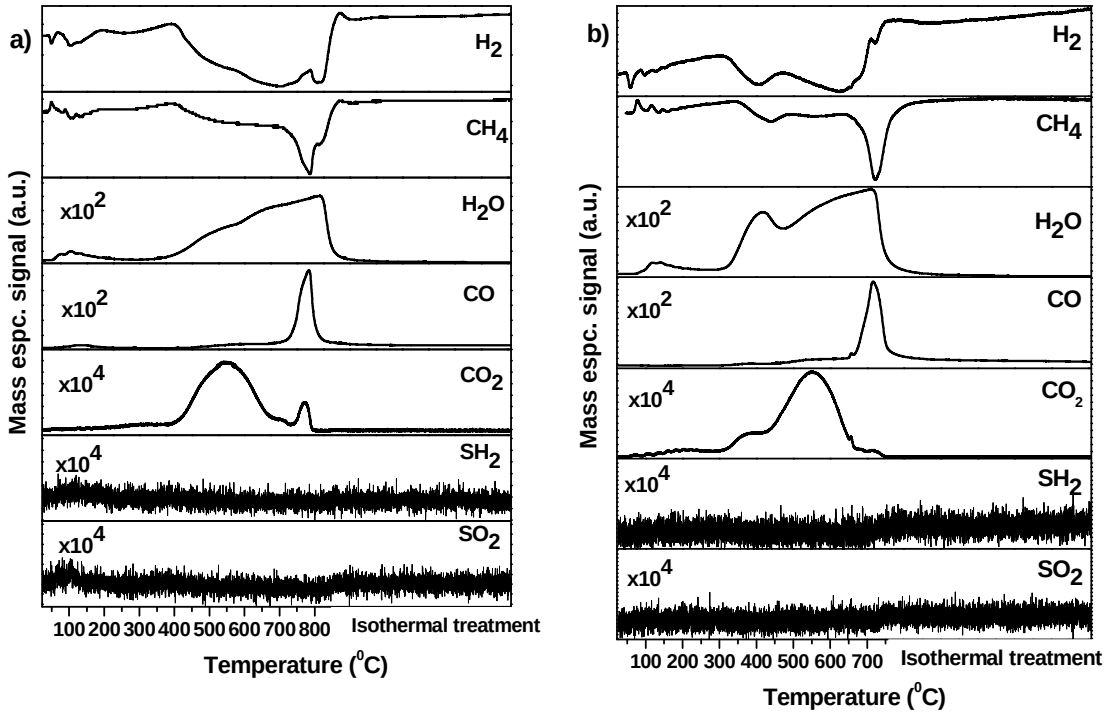

Figure S11. Water, carbon monoxide, carbon dioxide, methane and sulfur compounds formation profiles of the $W_xC/C\text{-}SO_3H$ (A) and $Ni\text{-}W_xC/C\text{-}SO_3H$ (B) samples under carburization conditions. Some of the mass spectrometer signals were multiplied by a factor, showed on the left side of each profile, to allow for a better visualization and comparison of the signals.