Supporting Information

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

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1. Experimental

N2 Physisorption
Nitrogen adsorption-desorption isotherms were measured at -196 °C using a Quantachrome Autosorb-1C automatic analyzer. The wet samples were degassed at 120 °C 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/P0 < 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/P0 = 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\(_x\)C/C and c) W\(_x\)C/C.

Figure S2. Adsorption-desorption isotherms of tungsten carbides catalysts supported on sulfonated carbon: a) C-SO\(_3\)H; b) W\(_x\)C-SO\(_3\)H and c) 2%Ni-W\(_x\)C-SO\(_3\)H.
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).

<table>
<thead>
<tr>
<th>Sample</th>
<th>( S_{\text{BET}} ) (m(^2)g(^{-1}))</th>
<th>( V_t ) (cm(^3)g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>891</td>
<td>0.700</td>
</tr>
<tr>
<td>( \text{W}_x\text{C/C} )</td>
<td>649</td>
<td>0.577</td>
</tr>
<tr>
<td>( \text{Ni-W}_x\text{C/C} )</td>
<td>620</td>
<td>0.614</td>
</tr>
<tr>
<td>C-SO(_3)H</td>
<td>906</td>
<td>0.705</td>
</tr>
<tr>
<td>( \text{W}_x\text{C/C-SO}_3\text{H} )</td>
<td>714</td>
<td>0.657</td>
</tr>
<tr>
<td>( \text{Ni-W}_x\text{C/C-SO}_3\text{H} )</td>
<td>609</td>
<td>0.449</td>
</tr>
</tbody>
</table>

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\textsubscript{x}C/C sample: \(\triangle WC\); \(\circ W_2C\) and \(\star WC_{1-x}\).
Figure S4. *In situ* X-ray diffraction patterns obtained during carburization process of Ni-W\textsubscript{x}C/C sample: ♦ W\textsubscript{2}C and □ Ni\textsubscript{4}W alloy.

2.3 XPS

Figure S5. XPS graph of S 2P after catalytic reaction: a) and b W\textsubscript{x}C/C-SO\textsubscript{3}H) Ni-W\textsubscript{x}C/C-SO\textsubscript{3}H.
Figure S6. XPS graph of W 4f level after catalytic reaction: a) Ni-WxC/C; b) Ni-WxC/C-SO$_3$H and c) WxC/C

Figure S7. XPS Ni 2p after catalytic reaction: a) Ni-W$_x$C/C and b) Ni-WxC/C-SO$_3$H.
Figure S8: Ni 2p XPS spectra of tungsten carbides after carburization and passivation: a) Ni-W$_x$C/C-SO$_3$H and b) Ni-W$_x$C/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$_3$H (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 WxC/C-SO3H (A) and Ni-WxC/C-SO3H (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 W₅C/C-SO₃H (A) and Ni-W₅C/C-SO₃H (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.