Supporting Information

Promotion effects of Pd on tungsten carbide catalysts: physiochemical properties and cellulose conversion performance

Glauco F. Leal\textsuperscript{a,b}, Silvia F. Moya\textsuperscript{a}, Debora M. Meira\textsuperscript{a,c}, Dean H. Barrett\textsuperscript{a},
Erico Teixeira-Neto\textsuperscript{d}, Antonio Aprigio S. Curvelo\textsuperscript{b,e}, Victor Teixeira da Silva\textsuperscript{f} and
Cristiane B. Rodella\textsuperscript{a}

\textsuperscript{a} Brazilian Center for Research in Energy and Materials (CNPEM) - Brazilian Synchrotron Light Laboratory (LNLS), C. P. 6192, 13083-970, Campinas, SP, Brazil
\textsuperscript{b} Institute of Chemistry of São Carlos (IQSC)/University of São Paulo (USP)/ C.P. 780, CEP 13560-970, São Carlos, SP, Brazil
\textsuperscript{c} European Synchrotron Radiation Facility (ESRF), 71 Avenue des Martyrs, 38000 Grenoble, France
\textsuperscript{d} CNPEM – Brazilian Nanotechnology National Laboratory (LNNano)-CNPEM, CP 6192, CEP 13083-970, Campinas, SP, Brasil
\textsuperscript{e} CNPEM - Brazilian Bioethanol Science and Technology Laboratory (CTBE), C. P. 6192, 13083-970, Campinas, SP, Brazil
\textsuperscript{f} Universidade Federal do Rio de Janeiro/COPPE/Chemical Engineering Program/NUCAT, P.O. Box 68502, Rio de Janeiro, RJ 21945-970, Brazil

*Corresponding author: cristiane.rodella@lnls.br
Phone: +55 19 3512 1040
FAX: +55 19 3512 1004

I. Adsorption-Desorption Isotherms

\begin{figure}
\centering
\includegraphics[width=\textwidth]{FigureS1.png}
\caption{Adsorption-desorption isotherms of tungsten carbide catalysts supported on commercial carbon: a) C (commercial carbon); b) W\textsubscript{X}C/C; c) 1Pd-W\textsubscript{2}C/C; d) 2Pd-W\textsubscript{2}C/C.}
\end{figure}

Figure S2: Pore size distribution determine by BJH method of the catalysts.

2. Mass Spectrometry

Water, carbon monoxide, carbon dioxide and methane formation profiles for the tungsten carbides catalysts obtained during the carburization process. Some of the mass spectrometer signals were multiplied by a factor, showed on the left side of each profile, to allow for better visualization and comparison of the signals.
Figure S3. Mass spectrometer profile of the carburization synthesis of the non-promoted tungsten carbide catalyst ($W_xC/C$).
Figure S4. Mass spectrometer profile of the carburization synthesis of the 1wt.% of Pd-promoted tungsten carbide catalyst (1Pd-W$_2$C/C).
Figure S5. Mass spectrometry profile of the carburization synthesis of the 2wt.% of Pd-promoted tungsten carbide catalyst (2Pd-W2C/C).
3. EXAFS

Figure S6. Phase uncorrected FT of the experimental EXAFS spectra of the 1Pd-W$_2$C/C and 2Pd-W$_2$C/C samples. Experimental data is in black, red solid lines are the corresponding best fits, calculated in the radial distance window colored in blue.

4. XPS

Figure S7. W 4f XPS spectra of the tungsten carbides catalysts: a) non-promoted sample W$_x$C/C; b) 1%Pd-W$_2$C/C and c) 2%Pd-W$_2$C/C. Experimental signal: solid curve; deconvoluted signal and fitting: dash curve.
Figure S8. Pd 3d XPS spectra of the Pd-promoted tungsten carbides catalysts: a) 1%Pd-W\textsubscript{2}C/C and b) 2%Pd-W\textsubscript{2}C/C. Experimental signal: solid curve; deconvoluted signal and fitting: dash curve.
5. TEM

Pd-promoted and non-promoted tungsten carbide catalyst present very similar particles morphology. Furthermore, particles are not recovered with graphitic or filamentous carbon.

Figure S9. TEM images of the tungsten carbides catalysts.
6. XEDS chemical maps

**Figure S10:** EDX analysis with W and Pd mapping of two catalyst particles.
7. Catalytic tests

Figure S11: Sequence of four runs of catalytic reactions over 2Pd-W₂C/C catalyst. Reaction conditions: 150mL of deionized water, 1.0g of Avicel microcrystalline cellulose Merck, 0.300g of catalyst, 220°C, 120 min, 5.8 MPa of H₂ and 1000 rpm, respectively.
Figure S12: XRD analysis of 1PdW₂C/C catalyst before and after the recycling reactions.