Supporting Information

Selective deoxygenation of polar polymers using metal supported on TiO_2 nanotubes

Dai-Phat Bui, Laura A. Gomez, Ismael Alaq, Luis Trevisi, Ana Carolina Jerdy, Han K. Chau, Lance L. Lobban, Steven P. Crossley*

[a] School of Chemical, Biological and Materials Engineering, University of Oklahoma, Norman, OK 73019, United States

*Corresponding author. Email: stevencrossley@ou.edu

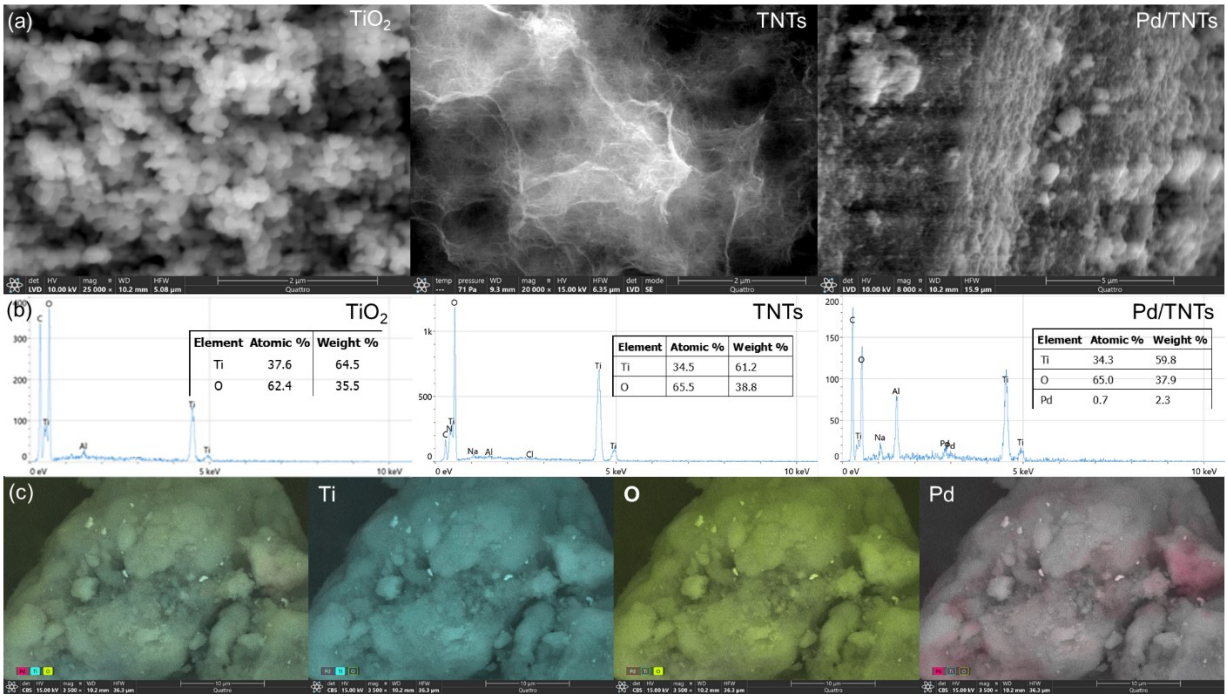


Figure S1. (a) SEM images and (b) EDX spectra of TiO_2, TNTs, and Pd/TNTs. (c) EDX mapping of Pd/TNTs. The SEM images show that the source TiO_2 is nanoparticles, while TNTs and Pd/TNTs have clusters of tubes. The EDX spectra determine that there is about 2 wt% of Pd in TNTs. The EDX mapping confirmed the good distribution of Pd over TNTs catalyst.

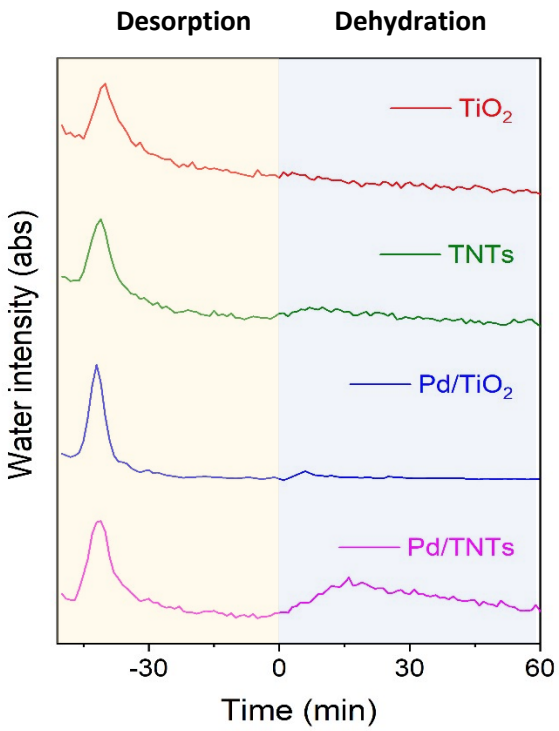


Figure S2. Mass spectrometry results for the dehydration and hydrogenation of EVOH over TiO_2, TNTs, Pd/TiO_2, and Pd/TNTs obtained during TGA analysis. Only water was released from the reactions. Reaction conditions: $W_{cat.}$ = 2 mg, W_{EVOH}= 20 mg, F_{H2} = 40 mL/min and $T_{reaction}$= 195°C.

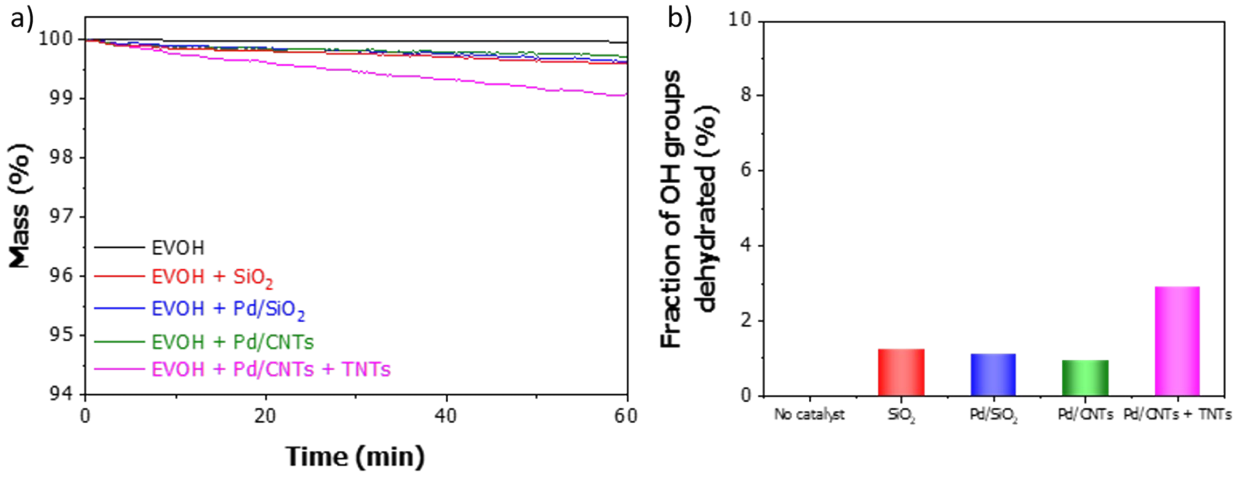


Figure S3. (a) TGA results of dehydration and hydrogenation of EVOH over SiO_2, Pd/SiO_2, Pd/CNTs, Pd/CNTs +TNTs, and without catalyst. (b) Dehydration percentage and rate of EVOH over SiO_2, Pd/SiO_2, Pd/CNTs, Pd/CNTs +TNTs and without catalyst. Reaction conditions: $T_{reaction}$ = 195ºC, $W_{cat.}$= 2 mg, W_{EVOH}= 20 mg and F_{H2}= 40 ml/min.

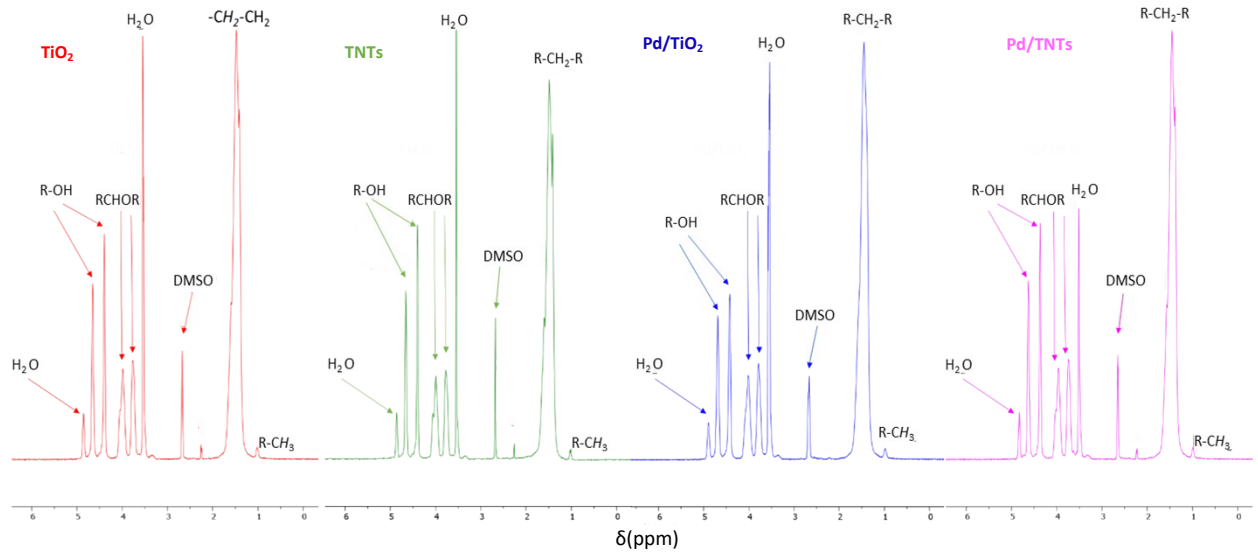


Figure S4. NMR results of the products from the EVOH conversion conducted in a TGA crucible. Reaction conditions: $W_{cat.}$ = 2 mg, W_{EVOH}= 20 mg, F_{H2} = 40 mL/min and $T_{reaction}$= 195°C.

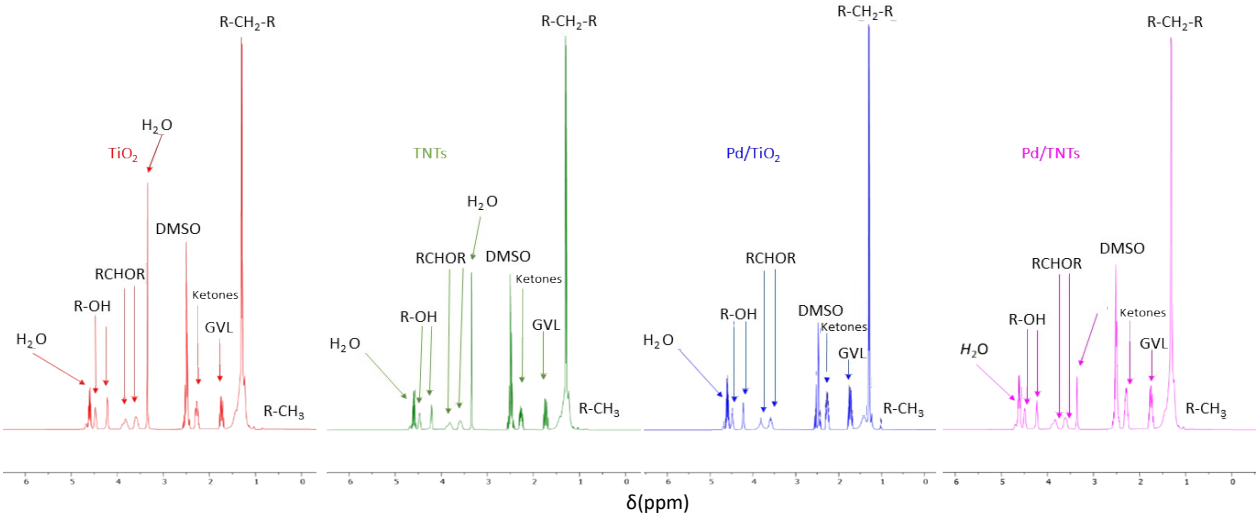


Figure S5. NMR results of the products from the EVOH conversion conducted in a semi-batch reactor. Reaction conditions: W_{cat}=10 mg, W_{EVOH}=100 mg, F_{H2}= 60 mL/min, $T_{reaction}$= 195 °C, TOS= 1 h. For all the cases, 2 mL of GVL was used as a solvent.

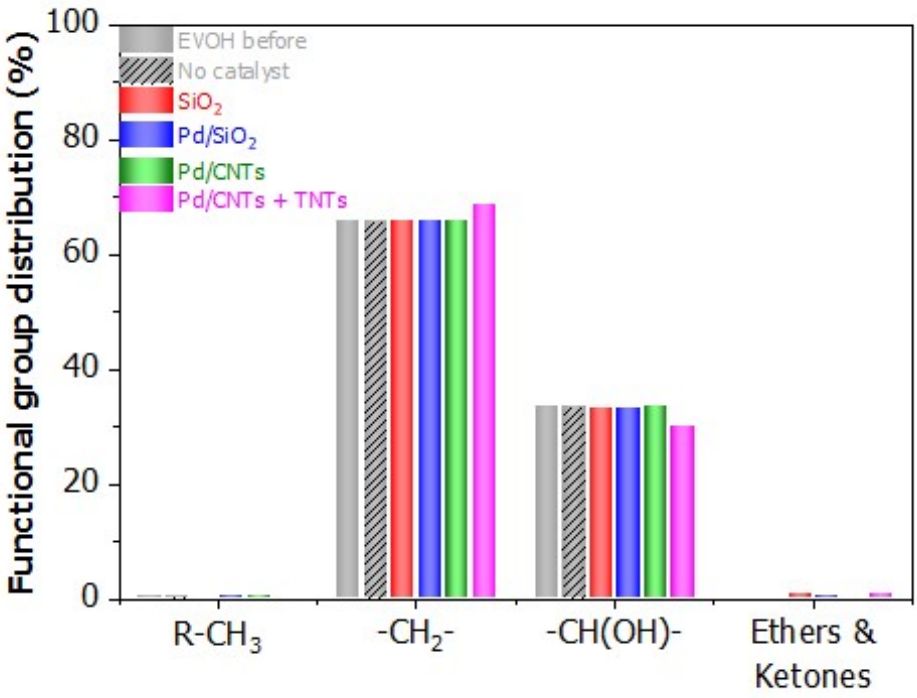


Figure S6. Dehydration of EVOH and product percentage over the catalysts without metal or acid sites in a semi-batch reactor. Reaction conditions: W_{cat}=10 mg, W_{EVOH}=100 mg, F_{H2}= 60 mL/min, $T_{reaction}$= 195°C, TOS= 1 h. 2 mL of GVL was used as a solvent for all the cases. For the physical mixture of Pd/CNT + TNTs, 20mg of Pd/CNT and 20mg TNTs were used. The quantities for the functional groups related to ether and ketones were added together.

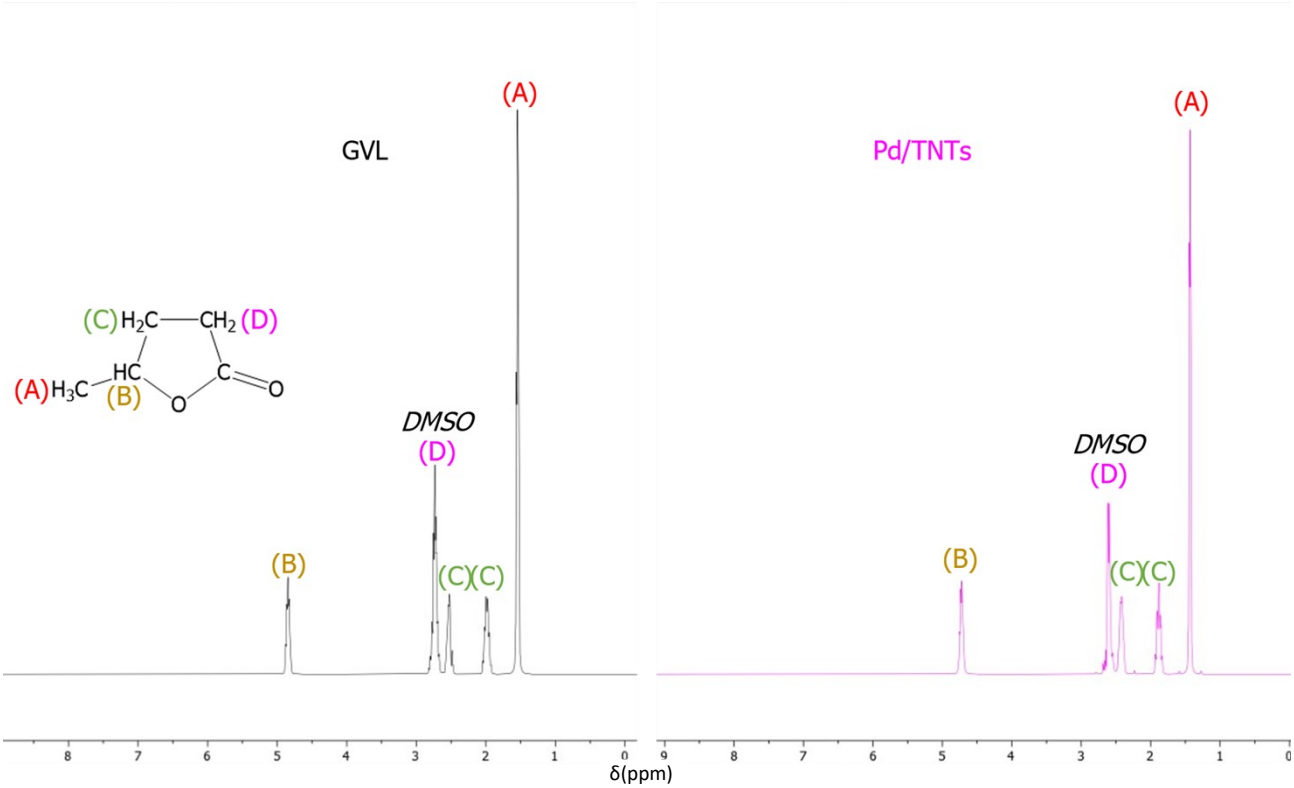


Figure S7. NMR results of the GVL solvent before the reaction and from the EVOH conversion conducted in a semi-batch reactor with W_{cat}=30 mg, W_{EVOH}=100 mg, F_{H2}= 60 mL/min, $T_{reaction}$= 195 °C, TOS= 12 h. For all the cases, 2 mL of GVL was used as a solvent. There is no new peak corresponding to the hydrogenation of GVL.

Pellets EVOH (EVOH before cryomilling)	**R-CH_3**	**R-CH_2-R**	**R-OH**	**RCHOR**	**Ethers**	**Ketones**
Area	722.8	66529.8	17295.7	16845.2	Area of R-OH minus Area of RCHOR	0
Number of protons	3	2	1	1	1	4
Normalized area (Area/Number of protons)	220.9	33264.9	17295.7	16845.2	112.6	0
Total area	220.9 + 33264.9 +16845.2 + 112.6 + 0 = 50443.7					
% (Normalized area/Total area)	0.4%	65.9%	33.4%	N/A	0.1%	0%
Estimated $M_W = M_{R\text{-}CH2\text{-}} \times \%_{R\text{-}CH2\text{-}}/(\%_{R\text{-}CH3}/2) + M_{R\text{-}OH} \times \%_{R\text{-}OH\text{-}}/(\%_{R\text{-}CH3}/2) + 2 \times M_{CH3}$ ≈ 9653 (g/mol)						
Cryomilled EVOH (EVOH in this work)	**R-CH_3**	**R-CH_2-R**	**R-OH**	**RCHOR**	**Ethers**	**Ketones**
Area	609.0	72131.0	18687.0	18406.2	Area of R-OH minus Area of RCHOR	0
Number of protons	3	2	1	1	1	4
Normalized area (Area/Number of protons)	203.0	36065.5	18687.0	18406.2	70.2	0
Total area	203.0 + 36065.5 + 18406.2 + 70.2 = 54744.9					
% (Normalized area/Total area)	0.4%	65.9%	33.6%	N/A	0.1%	0%
Estimated $M_W = M_{R\text{-}CH2\text{-}} \times \%_{R\text{-}CH2\text{-}}/(\%_{R\text{-}CH3}/2) + M_{R\text{-}OH} \times \%_{R\text{-}OH\text{-}}/(\%_{R\text{-}CH3}/2) + 2 \times M_{CH3}$ ≈ 9683 (g/mol)						

Table S1. NMR characterization of EVOH pellets and cryomilled EVOH.

Sample	**surface area (m^2/g)**	**Pore volume (cm^3/g)**
Pd/TNTs	180.99	0.37
Pd/CNTs	259.44	0.65
Pd/SiO_2	310.38	1.21

Table S2. Surface area and pore volume of Pd-supported catalysts.

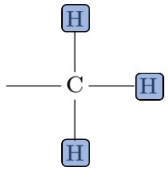
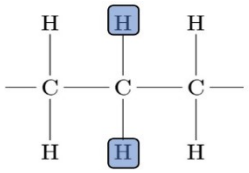
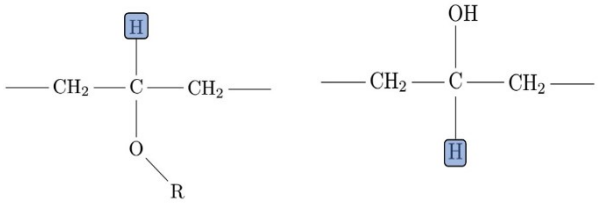
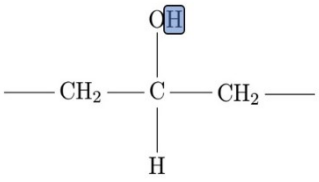
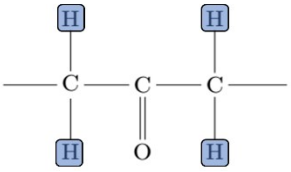
Functional groups	Structure	Shift (ppm)
R-CH_3		0.7-0.9
R-CH_2		1-1.66
RCHOR		3.4-4.0
R-OH		4.0-4.6
Ketones		1.8-2.3

Table S3. H NMR chemical shift ranges of the functional groups involved in the deoxygenation of EVOH