

Supporting Information

Catalyst preparation. Mo₂C/C and Pt-Mo₂C/C samples were prepared using a modification of Zhang's carbothermal hydrogen reduction method.¹ Pt/Mo₂C was synthesized by Schweitzer's temperature programmed reaction method.² Pt/C was obtained through temperature programmed reduction procedures. In detail, the commercial activated carbon supports were treated with a 33 wt% nitric acid solution at 5 80 °C for 24 h prior to the deposition of active metal components. To synthesize passivated Pt-Mo₂C/C catalysts, processed activated carbon was impregnated with an aqueous solution, which contained an appropriate amount of ammonium paramolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) and chloroplatinic acid (H₂PtCl₆·6H₂O), followed by stirring for 10 h at room temperature. Water was removed by infrared lamp, and the solid was dried at 120 °C. The resulting precursor was exposed to hydrogen, and it was heated to 400 °C at 10 °C/min, holding at this temperature for 1 h, then to 700 °C at 1 °C/min and holding it for 3 h. Prior to exposure to air, the catalysts 10 were further treated in a flow of 0.5 % O₂/N₂ for 10 h at room temperature, and these were denoted as "passivated catalysts". The "unpassivated catalysts" were used directly for reactions without passivation. The nominal weight loadings of molybdenum and platinum were 20% and 4%, respectively. Mo₂C/C catalysts were prepared using the same procedures as described above, except that the incipient impregnation solution contained only ammonium paramolybdate. Pt/C was prepared by impregnating processed carbon with H₂PtCl₆·6H₂O solution, subsequent drying at 120 °C, and then reduction at 500 °C in a H₂ flow for 60 min.

15 **Catalyst activity measurements.** Cellulose (Acros Organics, microcrystalline) with average size of 50 μm was used without pretreatment. The reactions were carried out in a stainless steel autoclave (120 ml) typically at 250 °C and 4.5 MPa CO for 15 min. The catalysts were used without pretreatment. For each reaction, 0.5 g cellulose, 0.15 g catalyst and 60 ml water were put into the reactor, and stirred at 800 rotations/min. After each reaction, the gas phase products were analyzed by infrared (IR) spectroscopy, and the liquid phase products were qualitatively analyzed by GC-MS and quantified by GC with benzyl alcohol used as an internal standard. Polyols were quantified 20 on an Agilent HPLC 1200 using a Prevail carbohydrate ES 5u column. Cellulose conversions were determined by the change in cellulose weight before and after the reaction. The yields of the products were calculated on a carbon basis using the following equation:
Yield (%) = carbon mole numbers of the product/carbon mole numbers of cellulose put into the reactor
The activity in the WGS reaction was measured in the same apparatus in which 0.15 g catalyst and 60 ml water were placed and then pressurized to 4.5 MPa CO at room temperature. The reaction temperature was 250 °C. After each reaction, the gas products were 25 quantified by GC with a TCD detector.

Catalyst characterization methods. Powder X-ray diffraction (XRD) patterns were collected on a Rigaku X-ray diffractometer operated at 40 kV and 100 mA, using Cu-Kα radiation. Scanning Transmission electron microscope (STEM) images were collected by a FEI Titan ST electron microscope (Cs = 1.2 mm, Cc = 1.5 mm and 300 kV). An inner detector angle of 76 mrad was used for the HAADF-STEM imaging. TEM simulation was carried out using multi-slice method with qSTEM code (by Christoph Koch). XPS was performed on an 30 Axis Ultra imaging photoelectron spectrometer. The metal loadings of the catalysts were tested on an inductively coupled plasma-atomic emission spectrometer. Surface areas of the samples were analyzed on a Micromeritics ASAP2020 instrument and calculated using the BET equation. CO desorption behaviors on the catalysts were examined by the temperature-programmed desorption-mass spectroscopy technique. In a typical procedure, about 0.100 g of the sample was reduced in a quartz tube and then cooled to room temperature in a H₂ flow. Then the gas was changed to He, and the temperature raised to 400 °C by 10 °C/min for H₂ desorption. Subsequently, the gas flow 35 was changed into CO at room temperature, and the samples were treated for 20 min. Then the gas flow was changed into He to blow off the physically adsorbed CO. Finally, the temperature was raised to 500 °C at 10 °C/min in a He flow. The signals of m/e=2, 4, 17, 18, 28, 32, and 44 were recorded by an OMNI Star Mass Spectrometer.

Table S1. Cellulose conversion on a physical mixture of the passivated Pt-Mo₂C/C and Pt/C^a.

catalysts	atmosphere	Yield/%			
		Polyols	Acetol	2, 5-HD/3-MCP	2-MCP
Pt-Mo ₂ C/C + Pt/C	CO	2.7	8.1	4.9	9.9

40 ^a. Reaction conditions: 60 ml water, 0.5 g cellulose, 4.5 MPa CO, 0.15 g of passivated Pt-Mo₂C/C and 0.15 g of Pt/C, 250 °C, 15 min.

Table S2. Cellulose conversion on unpassivated Pt-Mo₂C/C catalysts under CO^a

P ^b /MPa	Conv. /%	Yield/%					
		1, 2-Alkanediols ^c	glycerol	erythritol	sorbitol	mannitol	total
4.4	63.6	13.7	<1	3.2	21.7	3.5	42.1
3.5	55.4	8.9	1.5	1.6	21.9	3.0	36.9
2.5	55.8	11.0	<1	0	17.8	2.8	31.6
1.5	62.6	9.5	0	0	9.4	1.3	20.2

^a. Reaction conditions: 60 ml water, 0.500 g cellulose, 0.150 g unpassivated Pt-Mo₂C/C catalyst, 240 °C, 30 min. ^b. Pressure at room temperature. ^c. 1, 2-alkanediols include ethylene glycol, 1, 2-propanediol, 1, 2-butanediol, and 1, 2-hexanediol.

45 The conversion of glucose and treated cellulose under CO/water at different reaction were also studied. As glucose tends to coke at relatively higher temperature, the reactions were conducted at temperatures lower than 200 °C. However, at the relatively low reaction temperature, Pt-Mo₂C/C catalyst is not very efficient for the water-gas shift (WGS) reaction. As the result, although glucose is much easy to be converted as compared with cellulose, the less efficient WGS activity make the overall enhancement less pronounced as

expected. The data were listed in Table S3. The effect of pressure was also investigated which suggest that different with hydrogen-assisted biomass hydrogenation reaction, CO-mediated reaction is relatively independent of pressure.

Table S3. Glucose conversion on unpassivated Pt-Mo₂C/C under CO.^a Effect of reaction temperature

Entry	Temperature/ °C	Yield/ %		Selectivity in polyols/ %		
		polyols	others ^b	1,2-Alkanediols	glycerol	hexitols ^c
1	150	-	-	-	-	-
2	180	27	18	47	39	14
3	200	41	0	69	20	11

5 ^a. Reaction conditions: 60 ml water, 0.5 g glucose, 0.15 g unpassivated Pt-Mo₂C/C catalyst, 4 MPa CO at room temperature, 2 h reaction time. ^b. Including acetol, 2, 5-HD, 3-MCP and 2-MCP. ^c. Including sorbitol and mannitol.

Table S4. Glucose conversion on unpassivated Pt-Mo₂C/C under CO.^a Effect of reaction pressure

Entry	Pressure/ MPa	Yield/ %		Selectivity in polyols/ %		
		polyols	others ^b	1,2-Alkanediols	glycerol	hexitols ^c
1	4	41	0	69	20	11
2	2	44	0	77	10	13
3	1	39.5	0	75	11	14

10 ^a. Reaction conditions: 60 ml water, 0.5 g glucose, 0.15 g unpassivated Pt-Mo₂C/C catalyst, 200 °C, 2 h reaction time. ^b. Including acetol, 2, 5-HD, 3-MCP and 2-MCP. ^c. Including sorbitol and mannitol.

Table S5. Treated cellulose conversion on unpassivated Pt-Mo₂C/C under CO^a

Entry	Reaction conditions	Yield/ %		Selectivity in polyols/ %		
		polyols	others ^b	1,2-Alkanediols	glycerol	hexitols ^c
1	200 °C, 30min	8.8	10	0	34	66
2	200 °C, 120min	20	4.8	22	23	55

15 ^a. The cellulose was treated with sulfuric acid with 10 wt% loading before reaction. Reaction conditions: 60 ml water, 0.5 g substrate, 0.15 g unpassivated Pt-Mo₂C/C catalyst, 4 MPa CO at room temperature. ^b. Including acetol, 2, 5-HD, 3-MCP and 2-MCP. ^c. Including sorbitol and mannitol.

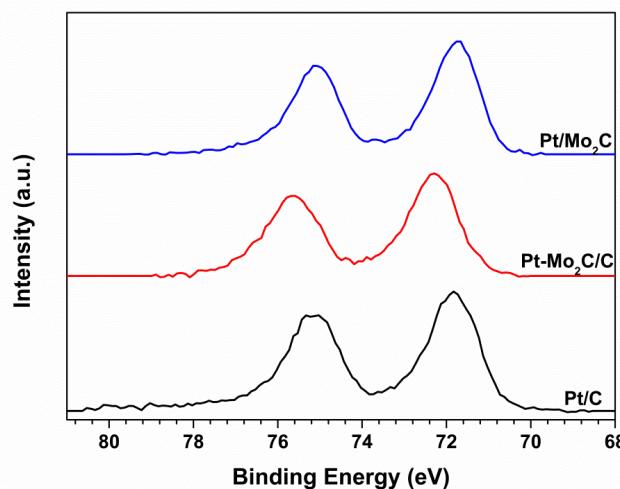


Fig. S1. Pt 4f XPS spectra of the passivated catalysts. On the passivated Pt-Mo₂C/C, the Pt 4f_{7/2} peak shifted to higher binding energy (0.520 eV) as compared to metallic Pt. This is normally assigned to Pt bonded to chemisorbed oxygen atoms.

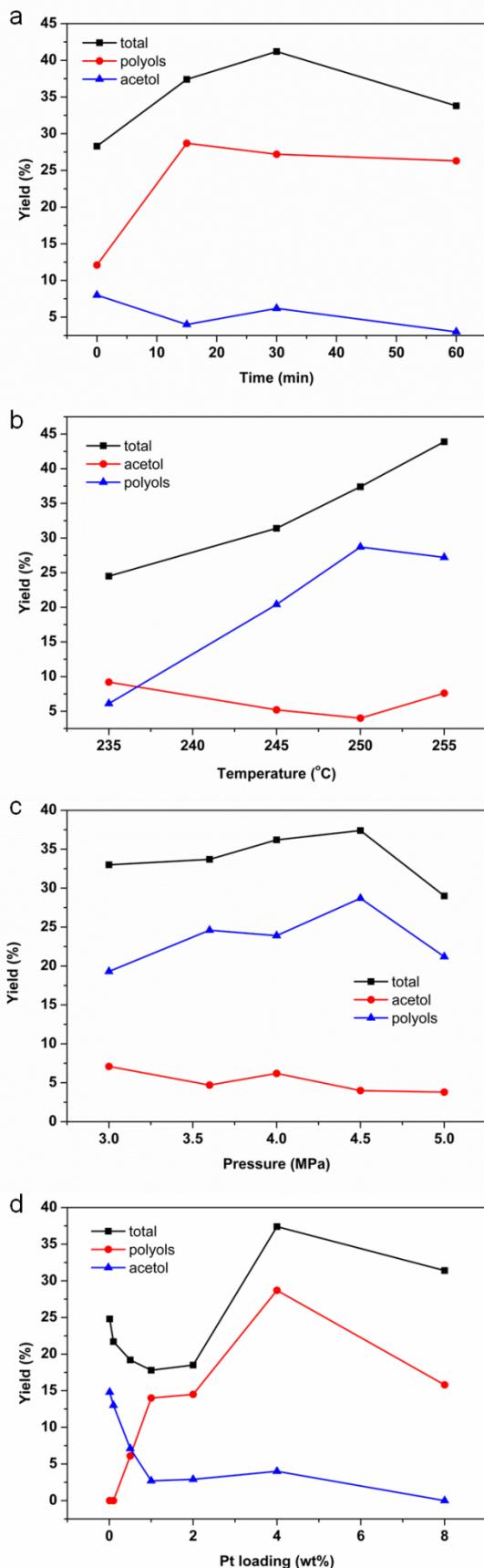
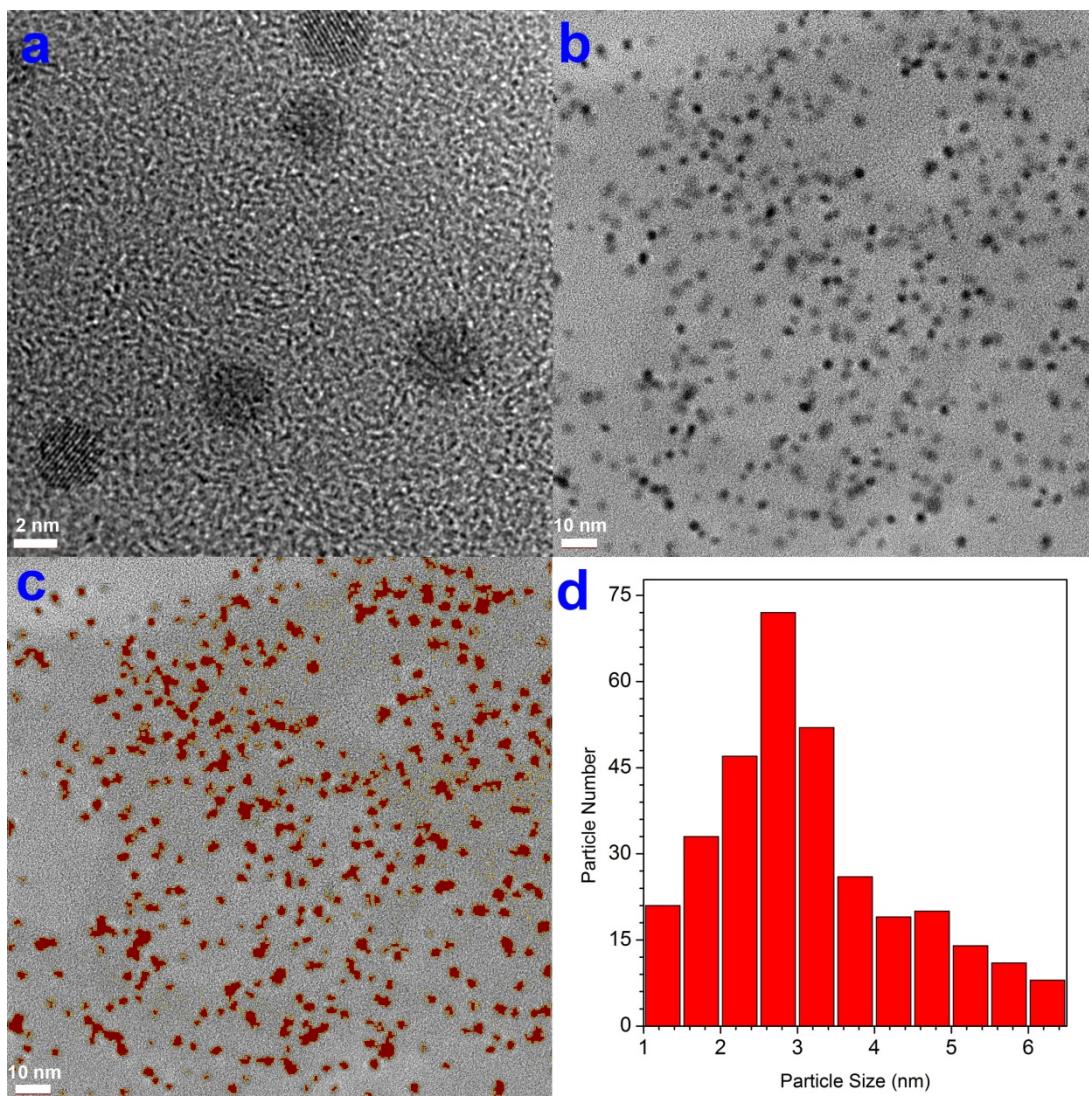


Fig. S2. Effects of the reaction time (a); temperature (b); CO pressure (c); and the nominal Pt loadings of the catalysts (d) on the main product yields on passivated Pt-Mo₂C/C catalyst.



5 Fig. S3. (a) HRTEM images of fcc-structured Pt NPs on carbon in the Pt/C catalyst. (b) Low-magnification TEM image of Pt NPs on the carbon support. (c and d) Statistical analysis of the particle size distribution of the Pt nanoparticles.

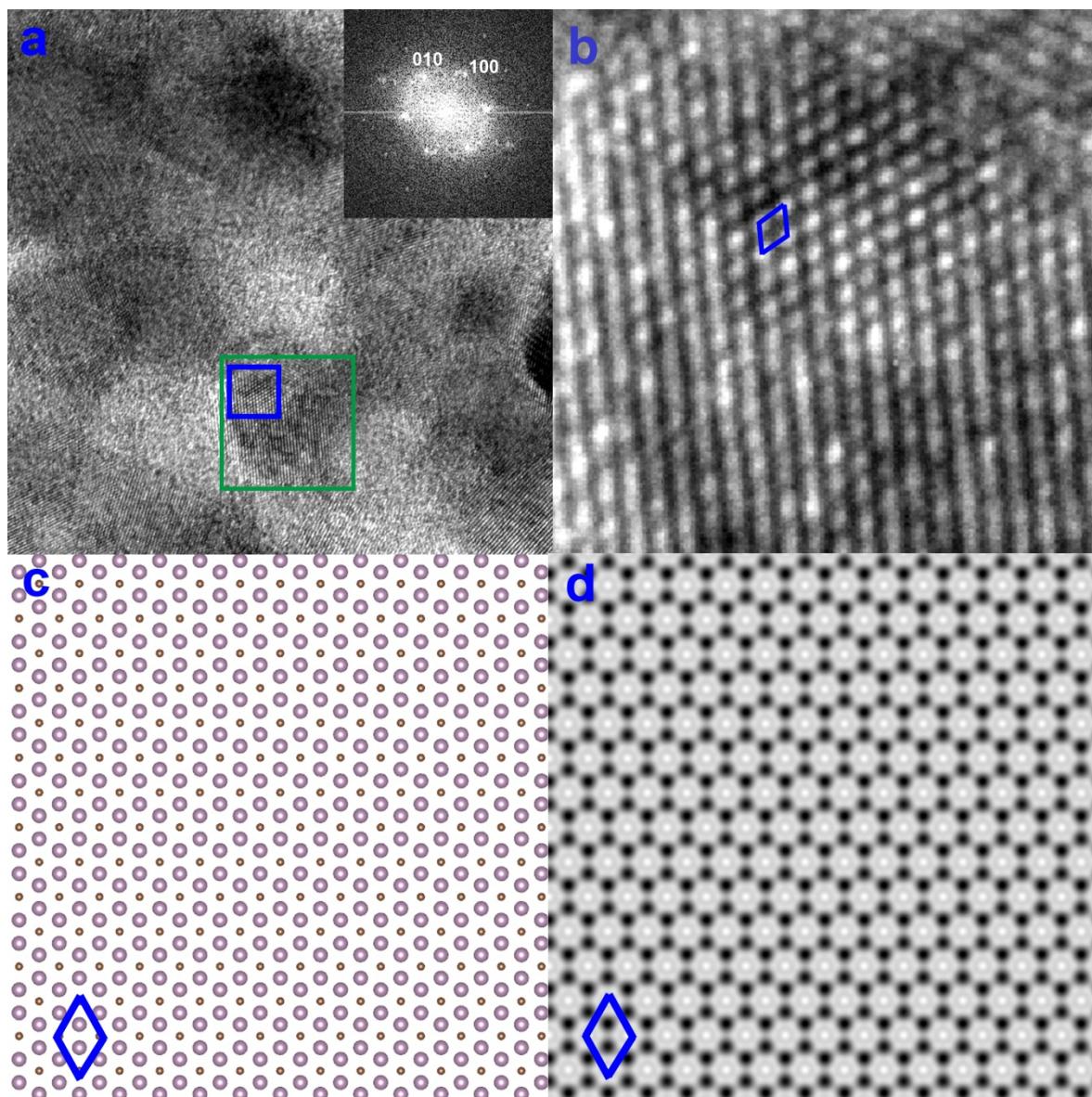
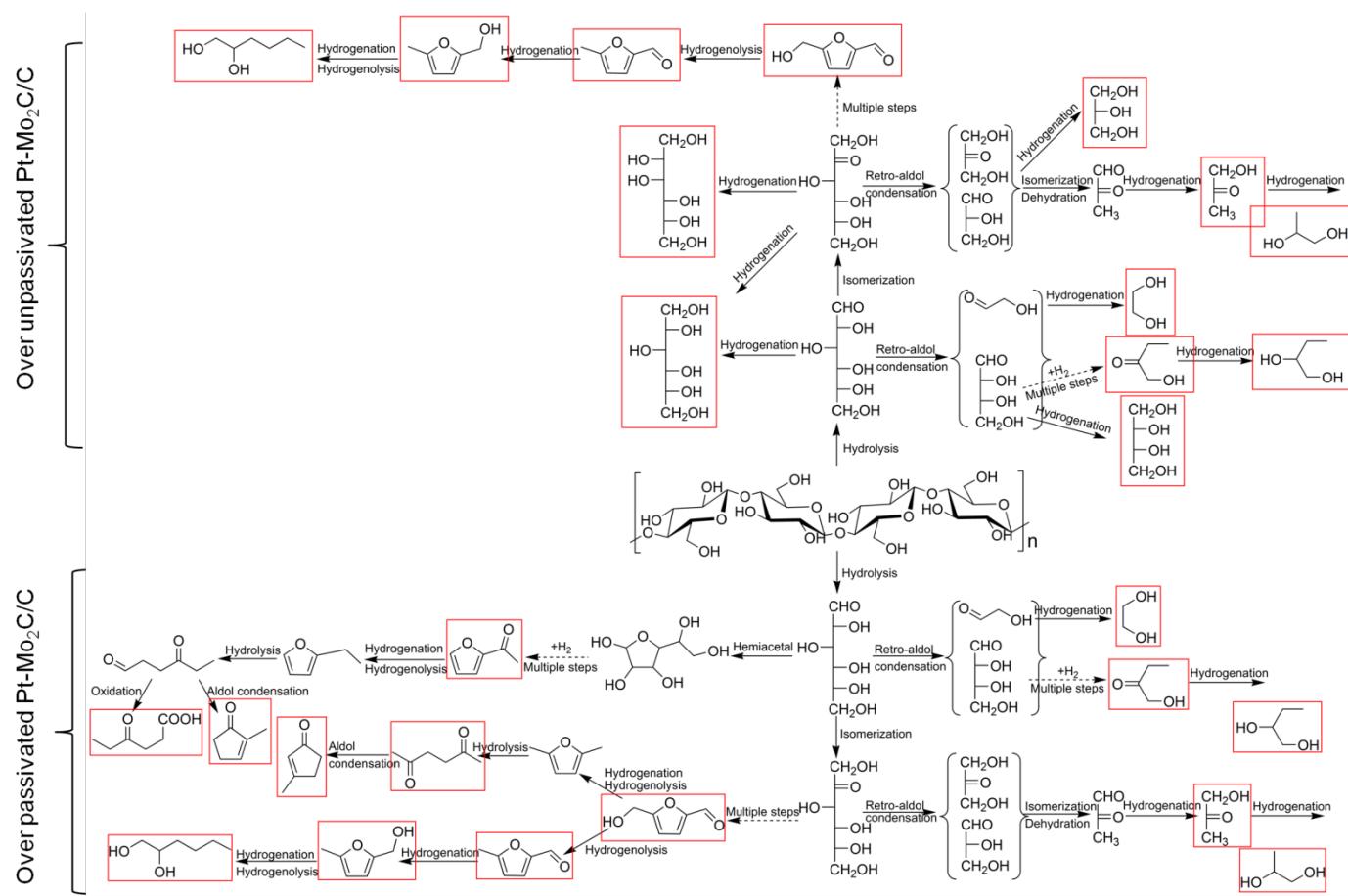


Fig. S4. (a) HRTEM image of crystalline Mo_2C nanoparticles in $\text{Mo}_2\text{C}/\text{C}$ catalysts. The inset shows the FFT diffractogram of the area in the green rectangle in the HRTEM image. (b) An enlarged HRTEM image of the area in the blue rectangle in (a). The blue cell defines a unit cell of the Mo_2C crystal. (c and d) A model of the crystal structure and a simulated HRTEM image of an [001] oriented Mo_2C crystal.



Scheme S1. Cellulose conversions over passivated and unpassivated Pt-Mo₂C/C. Red frames indicate the products that were detected after the reactions. Multiple steps may include dehydration, hydrogenation, isomerization and hydrogenolysis, etc.

- 5 1 N. Ji, T. Zhang, M. Zheng, A. Wang, H. Wang, X. Wang and J.G. Chen, *Angew. Chem. Int. Ed.*, 2008, **47**, 8510.
 2 N.M. Schweitzer, J.A. Schaidle, O.K. Ezekoye, X. Pan, S. Linic and L.T. Thompson, *J. Am. Chem. Soc.*, 2011, **133**, 2378.