

Solvent Effect in Hydrogenolysis of Xylitol over Bifunctional Ru/MnO/C Catalysts under Alkaline-Free Conditions

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Table S1. Metal loading, BET surface area, MnO crystallite size, total amount of basic sites of Ru/C and Ru/MnO/C catalysts.

Catalyst	Metal loading ^a (wt%)		Mn/Ru (wt. ratio)	S _{BET} ^b (m ² g ⁻¹)	MnO crystallite size ^[c] (nm)	Total basic sites ^d (μmol g ⁻¹)
	Ru	M ^[b]				
Active carbon	-	-	-	1095	-	n.d
2.9%Ru/C	2.85	-	-	1087	-	237
3.1%Ru/MnO(4.5%)/C	3.13	4.48	1.4	1120	14	355

^a Determined by ICP-OES, ^b relative error: ±5%, ^c Debye-Scherrer equation, ^d Determined by CO₂-TPD, n.d: not-detectable.

Table S2. Physicochemical properties data of solvents used in the study and H₂ solubility in mixtures.

Solvent	Type	Molar Volume at 20°C (mL/mol)	Dielectric constant at 20°C / dipolar momentum (D)	Boiling point (°C)	Surface tension (mN/m)	Vapor pressure at 25°C (kPa)	Solubility of H ₂ in H ₂ O:solvent (90:10) at 60 bar and 200°C ¹ (mmol/L)
H ₂ O	protic	18.1	80.1 / 1.85	100	72.0	3.2	94
MeOH	protic	40.5	33.0 / 1.70	64.5	22.1	16.0	103
EtOH	protic	58.4	25.3 / 1.69	78.2	22.0	7.9	97
1-PrOH	protic	74.7	20.8 / 1.55	97.0	23.3	2.8	94
2-PrOH	protic	76.5	20.2 / 1.58	82.2	21.0	6.0	-
1-BuOH	protic	91.0	17.8 / 1.66	117.6	25.0	0.8	93
1,4-dioxane	aprotic	85.2	2.2 / 0	101.2	32.7	5.0	-

¹ from data of T. K. H. Trinh et al. *J. Chem. Eng. Data* **2016**, *61*, 19-34 and the approximation equation: $\ln H(H_2O:ROH(90:10)) = x_{H_2O} \ln H_{H_2O} + x_{ROH} \ln H_{ROH}$ (J.-M. Prausnitz et al., *Molecular Thermodynamics of Fluid Phase Equilibria*, 2nd Ed., **1986**, Prentice-Hall, Inc. Englewood Cliffs, p399.)

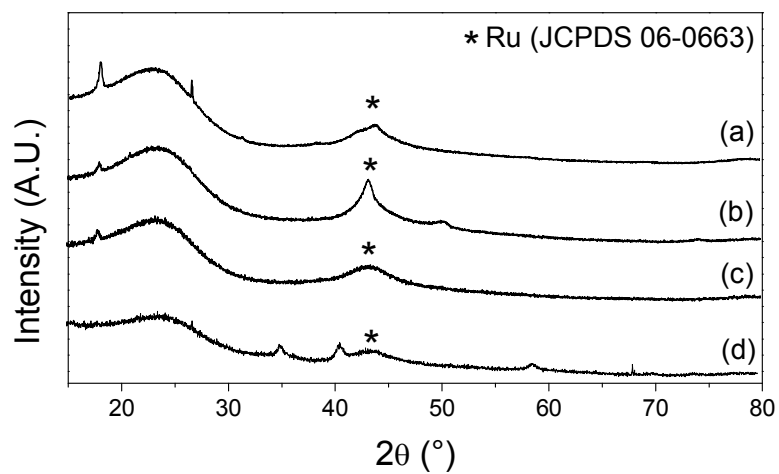


Figure S1. XRD patterns of used 3.1%Ru/MnO(4.5%)/C catalysts after reaction in (a) pure water, (b) 90:10 vol.% H₂O:MeOH, (c) 90:10 vol.% H₂O:EtOH in comparison with (d) the fresh catalyst.

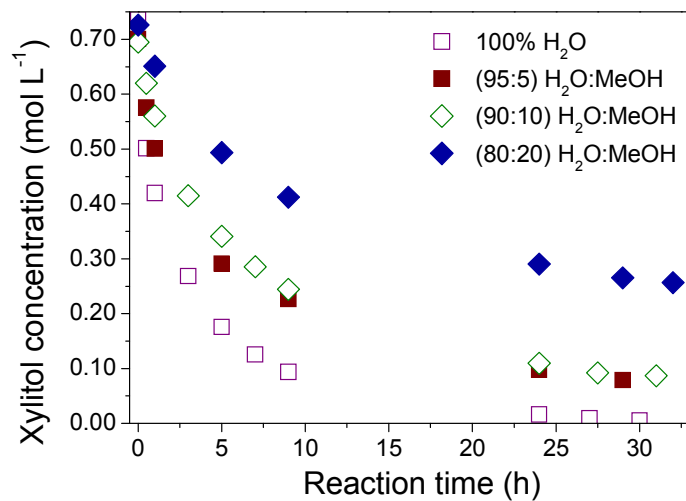


Figure S2. Evolution of xylytol concentration as a function of time over 3.1%Ru/MnO(4.5%)/C in H₂O:MeOH solvent with different compositions.
 Reaction conditions: xylytol 0.7 mol.L⁻¹ (10 wt.%), 135 mL H₂O:MeOH solvent, 0.5 g 3.1%Ru/MnO(4.5%)/C catalyst, 60 bar H₂, 200°C.

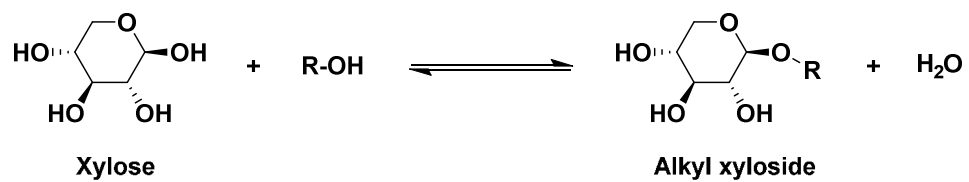


Figure S3. Possible by-product formation from xylose intermediate (pyranose form) in H₂O:ROH solvent.

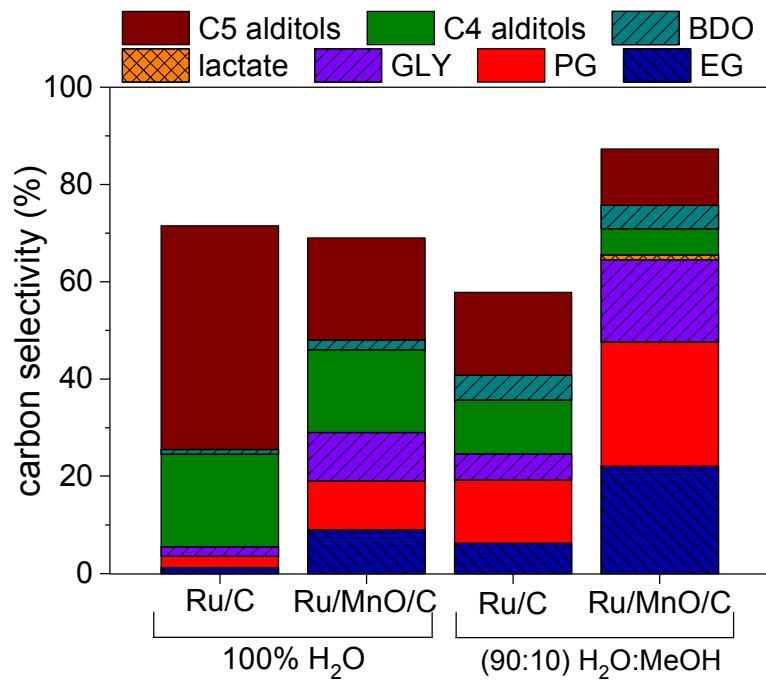


Figure S4. Selectivity to the products at 60% conversion over 2.9%Ru/C and 3.1%Ru/MnO(3.5%)/C in water and 90:10 vol.% H₂O:MeOH.

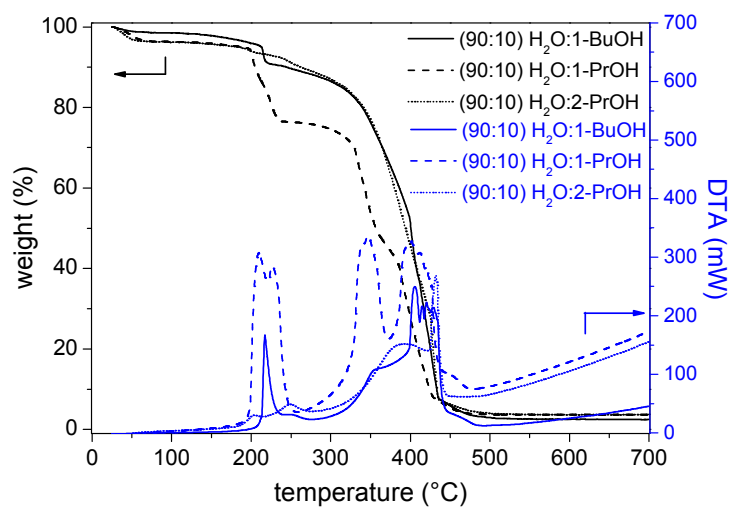


Figure S5. TGA-DTA curves under air flow of used 3.1%Ru/MnO(4.5%)/C after xylitol hydrogenolysis in different solvents.
 Reaction conditions: xylitol 0.7 mol.L^{-1} (10 wt.%), 135 mL solvent, 0.5 g 3.1%Ru/MnO(4.5%)/C catalyst, 60 bar H_2 , 200°C.

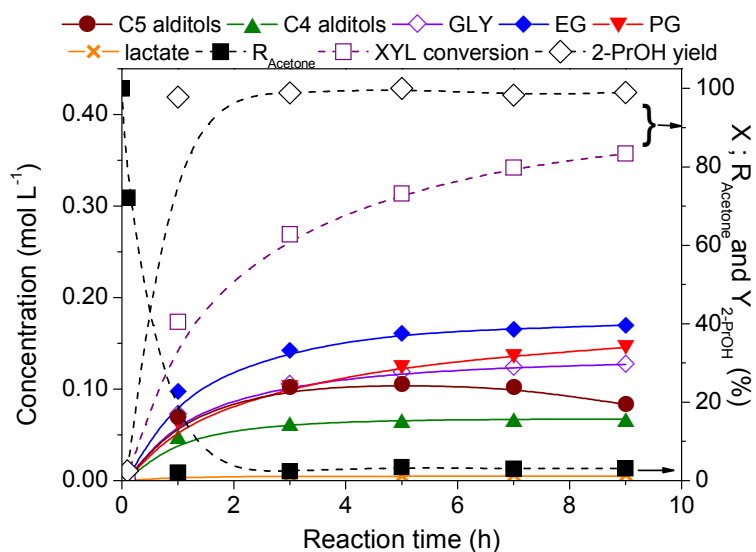


Figure S6. Concentration time profiles during xylitol hydrogenolysis over 3.1%Ru/MnO(4.5%)/C in 90:10 vol.% H₂O:Acetone.

X: xylitol conversion, R_{acetone}: ratio of recovered acetone concentration to the initial concentration, Y_{2-PrOH}: yield of 2-PrOH. Reaction conditions: xylitol 0.7 mol.L⁻¹ (10 wt.%), 135 mL solvent, 0.5 g 3.1%Ru/MnO(4.5%)/C, 60 bar H₂, 200°C