

Supporting information: Influence of Water-Miscible Organic Solvent on the Activity and Stability of Silica-Coated Ru Catalysts in the Selective Hydrolytic Hydrogenation of Cellobiose into Sorbitol

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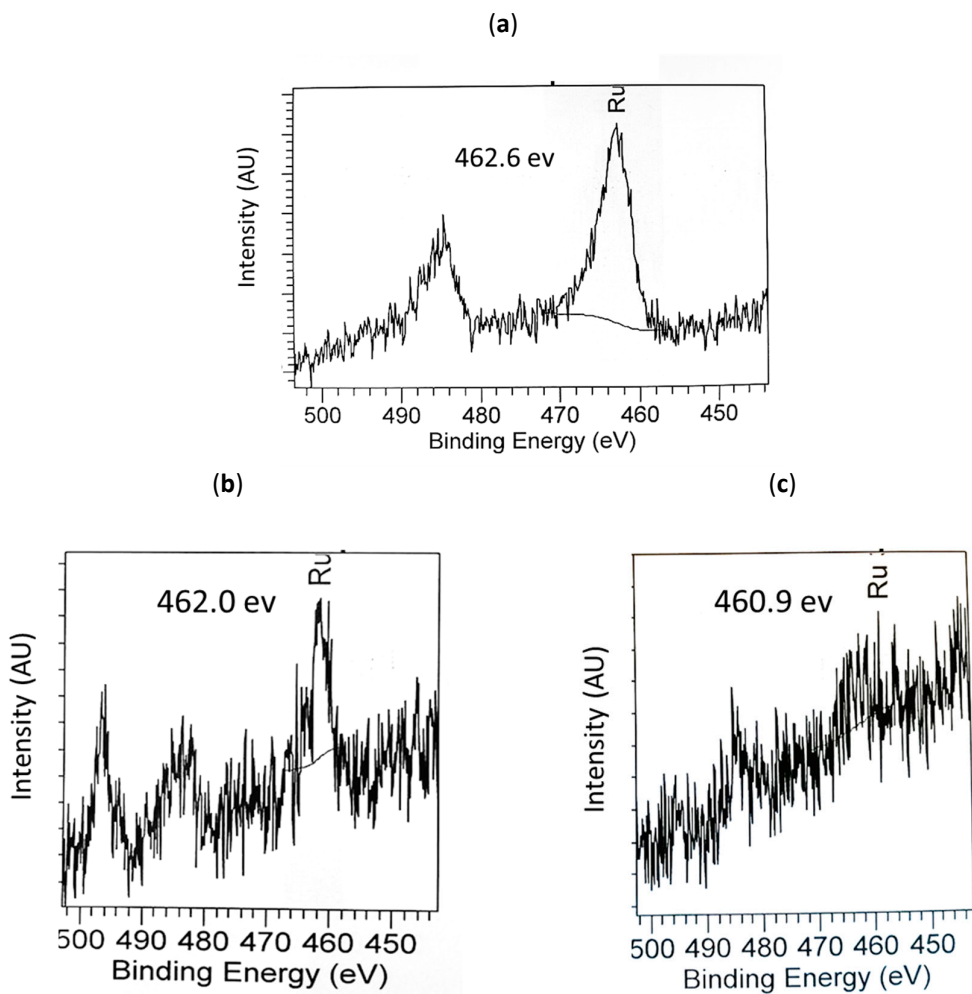
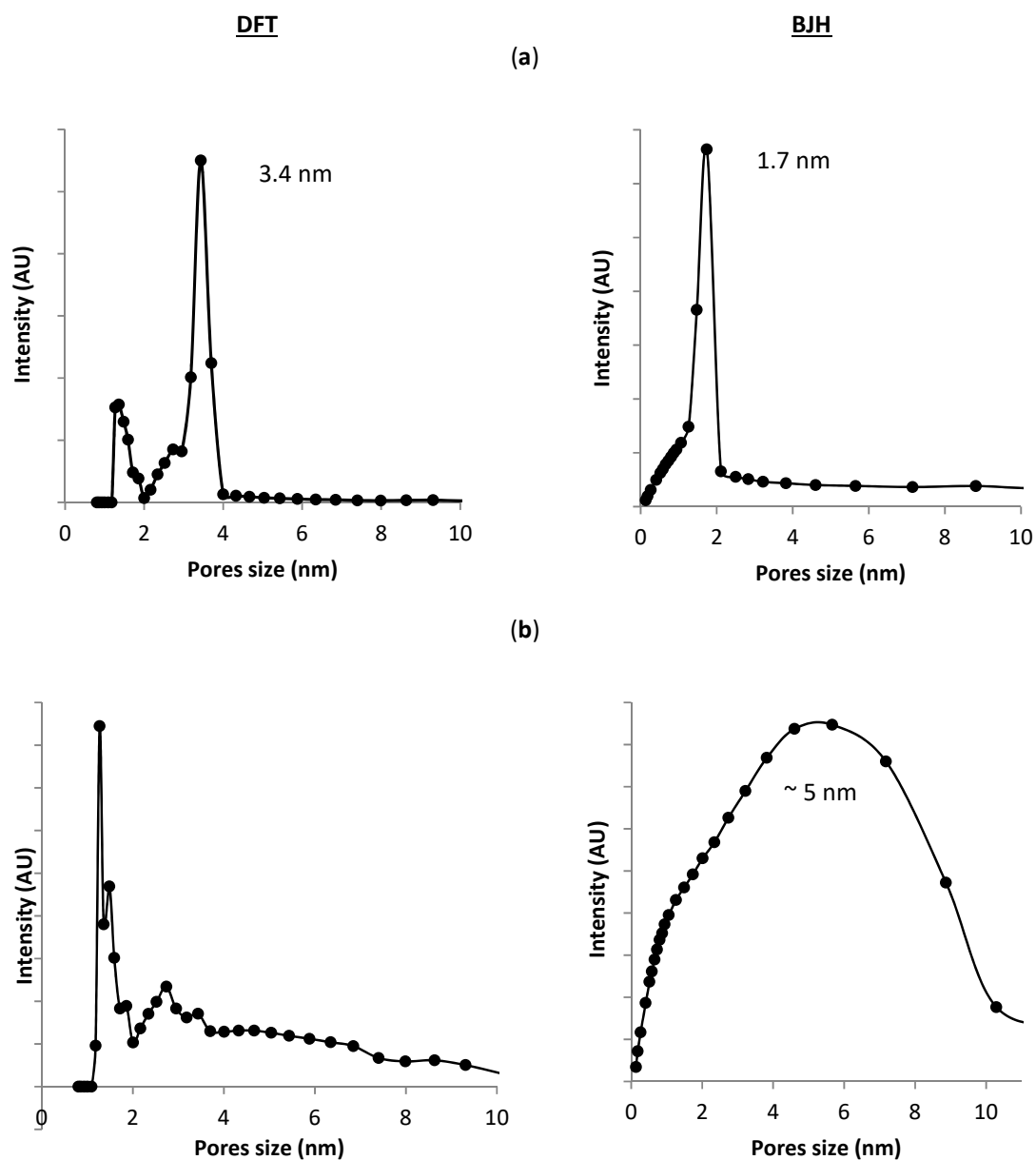


Figure S1. XPS Ru3p spectra for (a) Ru/CB (b) Ru/CB@SiO₂(C) and (c) Ru/CB@SiO₂(P) catalysts.



	V_{DUB} (cm ³ /g)	V_{cum} (cm ³ /g)	V_v (cm ³ /g) ^a	V_P (cm ³ /g)
Ru/CB@SiO ₂ (C)	0.16	0.21	0.37	0.36
Ru/CB@SiO ₂ (P)	0.09	0.19	0.28	0.25

$$^a V_v = V_{DUB} + V_{cum}$$

Figure S2. Pores size distribution obtained by DFT and BJH methods for (a) Ru/CB@SiO₂(C) and (b) Ru/CB@SiO₂(P) materials.

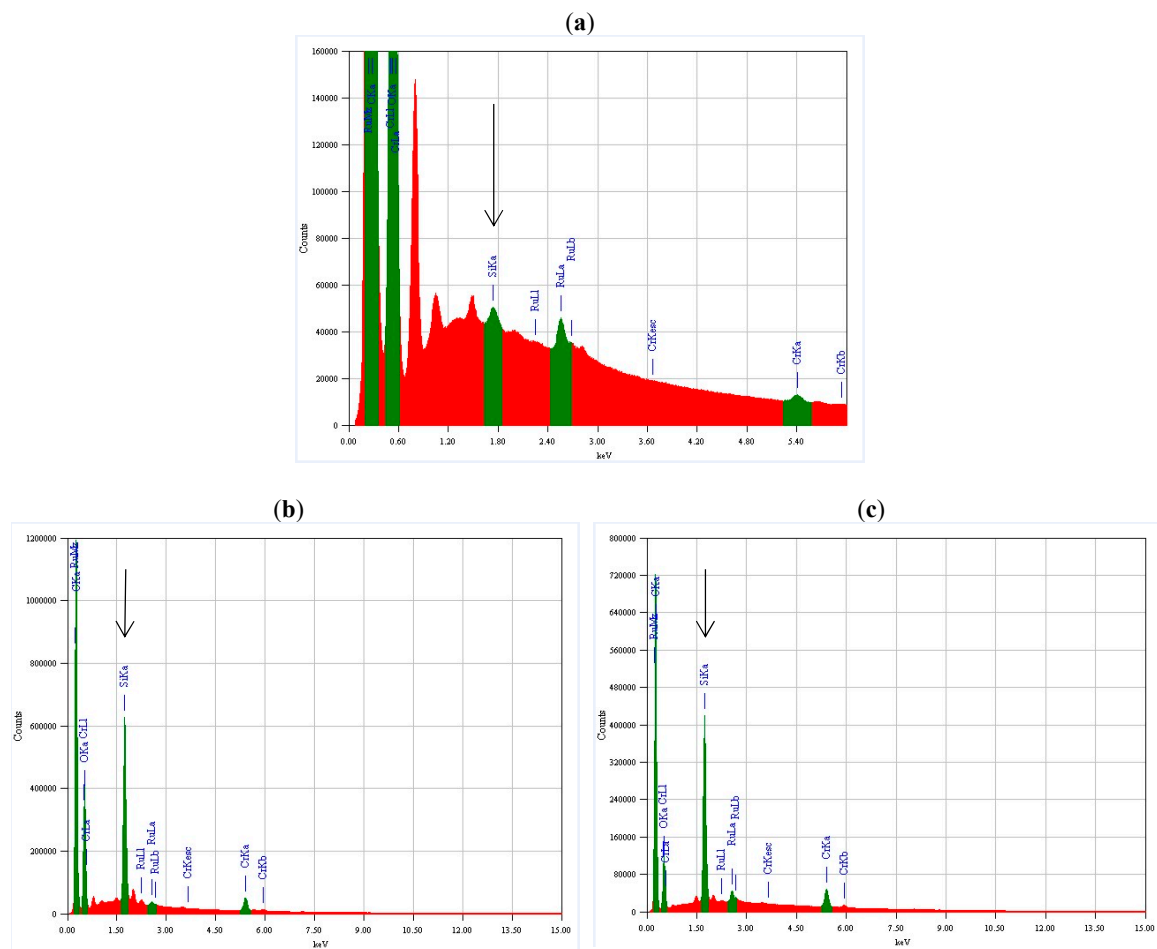


Figure S3. SEM-EDX analyses of (a) Ru/CB, (b) Ru/CB@SiO₂(C) and (c) Ru/CB@SiO₂(P) catalysts.

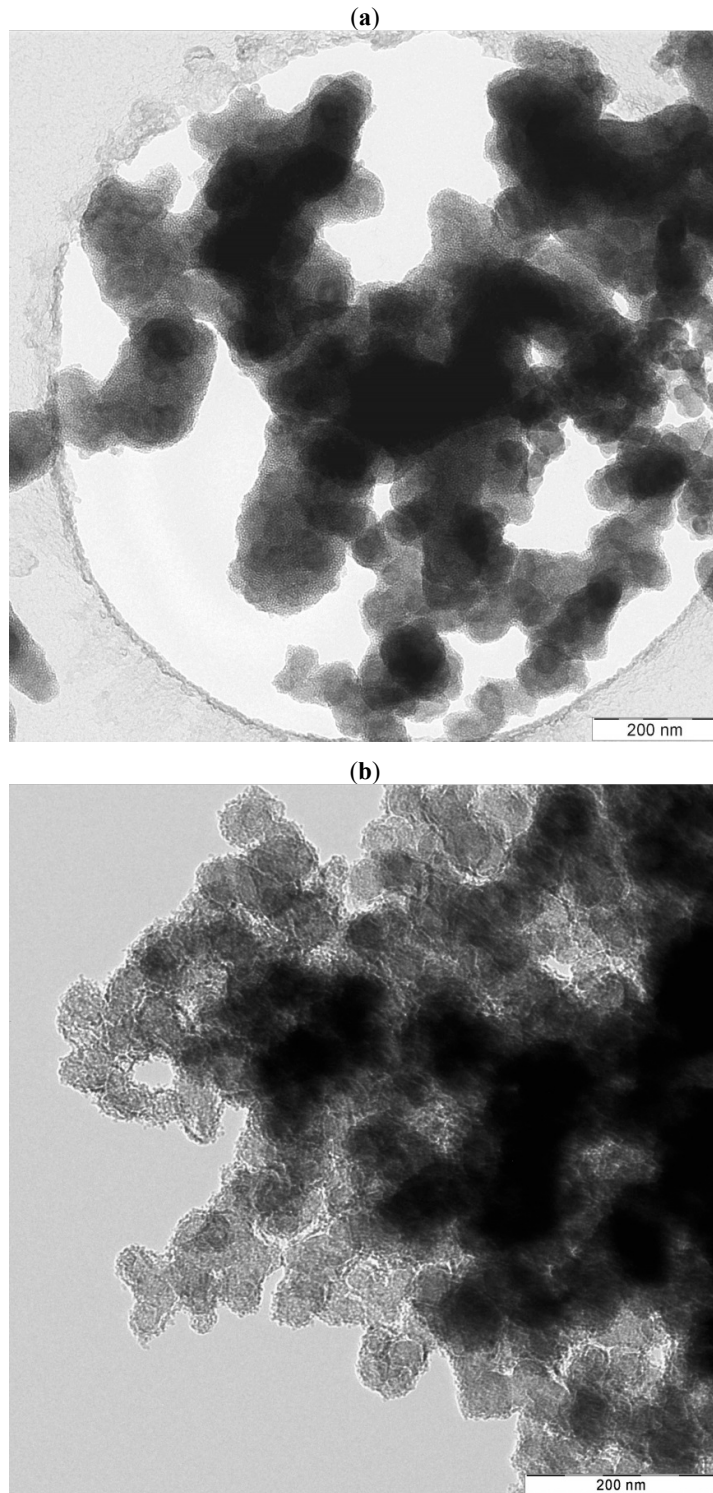


Figure S4. TEM images of (a) CB@SiO₂(C) and (b) CB@SiO₂(P) covered materials.

Table S1. Elemental analysis by ICP of Ru/CB@SiO₂(C) and Ru/CB@SiO₂(P) catalysts (wt.%).

	C	H	N	Si	Ru
Ru/CB	nd*	nd	nd	<0.05	2.3
Ru/CB@SiO ₂ (C)	71.78	3.36	1.14	10.19	1.84
Ru/CB@SiO ₂ (P)	65.89	0.79	/	11.00	1.31

*not determined

Table S2. XPS analyses (at. %) of covered catalysts before and after catalytic tests in pure water (W) or ethanol-water mixture (W/E).

Sample	C1s	O1s	Si2p	N1s	Ru3p
Ru/CB@SiO ₂ (C)	47.2	35.6	15.2	1.0	0.09
Ru/CB@SiO ₂ (C)-W	95.0	4.1	0.4	0.1	0.31
Ru/CB@SiO ₂ (C)-W/E	61.3	26.80	11.4	0.3	0.13
Ru/CB@SiO ₂ (P)	34.3	46.2	19.3	0.1	0.07
Ru/CB@SiO ₂ (P)-W/E	36.4	46.7	16.7	0.1	0.08

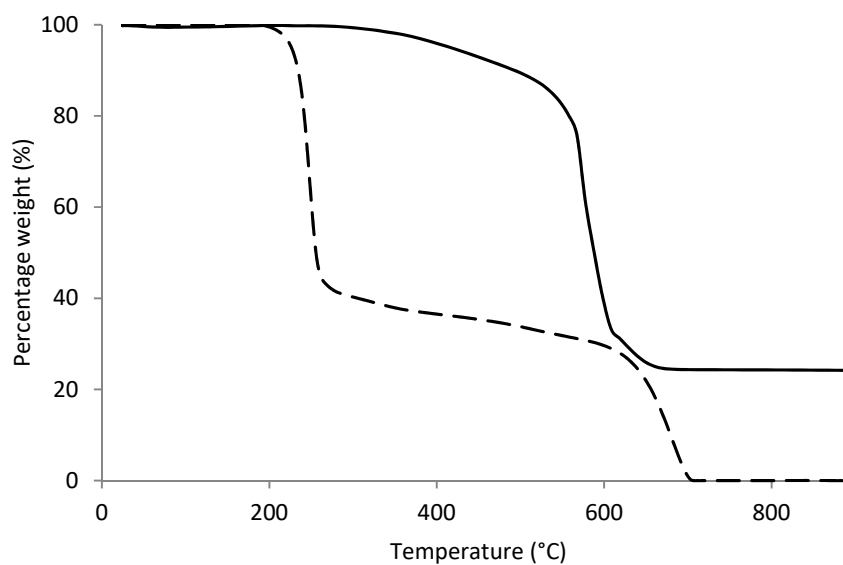
**Figure S5.** TGA measurement of CTAB deposited on CB (dashed line) and Ru/CB@SiO₂(C) after the catalytic test in ethanol/water media (solid line) showing no remaining CTAB.

Table S3. Comparison of normalized activity values with catalysts from literature.

Support	Metal	Metallic Weight (%)	Reaction Time (h)	Normalized Activity ^a	Reference
Carbon Black	Ru	3.5	2	136	This work
Silica (MCM-41)	Ru	5.0	2	26	[1]
Carbon	Ru	5.0	2	86	[2]
Carbon	Pt	3.0	2	71	
Alumina	Ru	2.8	5	313	[3]
Silica	Ni	68	5	4	

$$^a \text{ normalized activity} = \frac{\text{mmol sorbitol produced}}{(\text{mmol metal} \cdot \text{time})} \text{ (in h}^{-1}\text{)}$$

1. Zhang, J.; Lin, L.; Zhang, J.; Shi, J.; Efficient conversion of d-glucose into d-sorbitol over MCM-41 supported Ru catalyst prepared by a formaldehyde reduction process, *Carbohydr. Res.* **2011**, *346*, 1327–1332. doi:10.1016/j.carres.2011.04.037.
2. Tronci, S.; Pittau, B.; Conversion of glucose and sorbitol in the presence of Ru/C and Pt/C catalysts, *RSC Adv.* **2015**, *5*, 23086–23093. doi:10.1039/C4RA14073G.
3. Romero, A.; Nieto-Márquez, A.; Alonso, E.; Bimetallic Ru:Ni/MCM-48 catalysts for the effective hydrogenation of d-glucose into sorbitol, *Appl. Catal. A Gen.* **2017**, *529*, 49–59. doi:10.1016/j.apcata.2016.10.018.

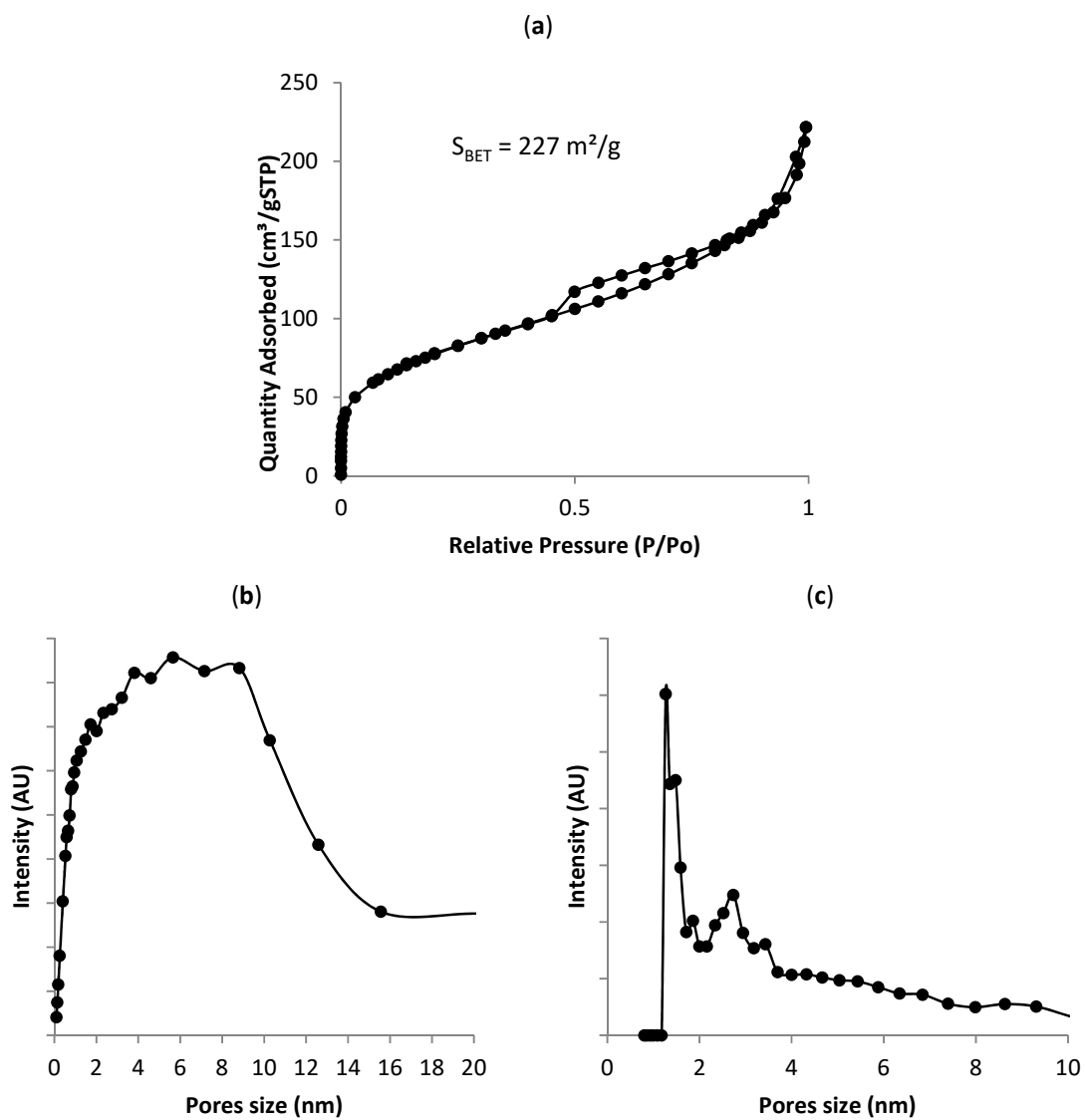


Figure S6. (a) Nitrogen adsorption-desorption isotherms at 77K and pores size distributions from (b) BJH and (c) DFT for Ru/CB@SiO₂(P) catalyst after a catalytic test.