catalysts

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Supporting Information

Reaction Pathways of Gamma-Valerolactone Hydroconversion over Co/SiO_2 Catalyst

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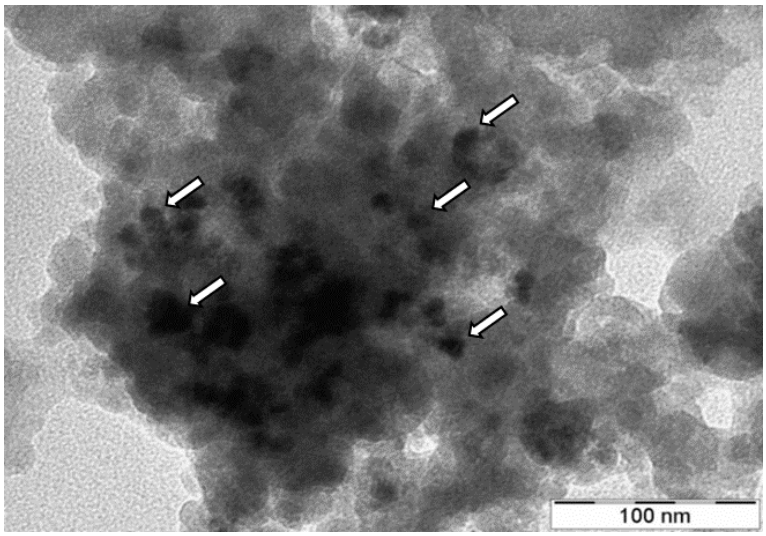

Figure S1. TEM image of the reduced Co/SiO_2 catalyst.

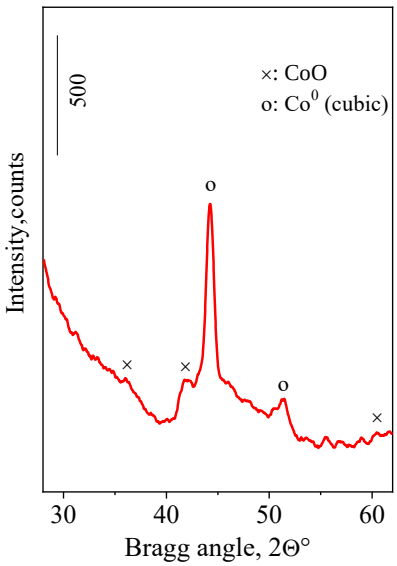

Figure S2. XRPD pattern of the used Co/SiO_2 catalyst. Sample was used in the hydroconversion of GVL to 2-MTHF for 58 h time-on-stream. Reaction conditions during the catalytic run were 225 °C, 30 bar, and space time of 1 $g_{cat.} \cdot g_{GVL}^{-1} \cdot h^{-1}$.

The TEM image of the Co/SiO_2 catalyst reduced in H_2 at 450 °C (Fig. S1) presents relatively homogeneously distributed spherical Co particles and agglomerates with a mean diameter of 20–30 nm.

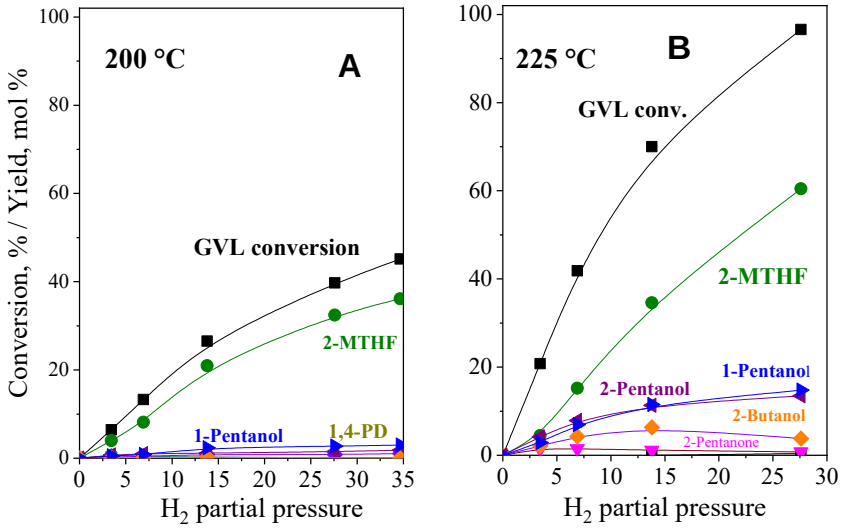

Figure S3. GVL hydroconversion and product yields over Co/SiO_2 catalysts as a function of H_2 partial pressure at 200 °C (A) and 225 °C (B) and 1 $g_{cat.} \cdot g_{GVL}^{-1} \cdot h$ space time. The partial pressure of GVL was kept constant at 2.3 bar. 2-MTHF: 2-methyltetrahydrofuran; 1,4-PD: 1,4-pentanediol.

To adjust the H_2 partial pressure (Fig. S3) the flow rate of H_2 was changed, whereas the partial pressure of the GVL reactant was kept at 2.3 bar by simultaneously adjusting the total pressure. The conversion of GVL and the yield of the main products seem to reach the highest level at an H_2 partial pressure of 27.7 bar and H_2/GVL molar ratio of 12. Under these reaction conditions the coverage of the catalyst surface by activated GVL and H_2 is considered to be well balanced for attaining the highest rate of the reaction.

Table S1. GVL conversion over SiO_2 support at different reaction temperatures.

Support	Temperature, °C	Conversion, %	Yield (mol %)		
			PE	PA	Others
SiO_2	225	-	-	-	-
	250	0.6	-	-	0.6
	275	1.4	0.7	-	0.7
	300	1.7	0.7	0.2	0.8

The support was activated at 450 °C in He flow for 2 hours. Reaction conditions: 1 $g_{cat.} \cdot g_{GVL}^{-1} \cdot h$ space time, 30 bar total pressure, H_2/GVL molar ratio of 12, time-on-stream 3 h. PE: pentenoic acid, PA: pentanoic acid.

The neat SiO_2 support material show negligible catalytic activity in the conversion of GVL.

Table S2. Weisz-Prater criterion and Thiele modulus [a] for the HDO reaction of GVL on Co/SiO_2 at 2.3 bar GVL partial pressure and 225 °C at increasing contact times.

Contact time, h	**$-r'_{GVL(obs.)}$ mol·g^{-1}·s^{-1}**	**C_{WP}**	**ϕ**
0.10	7.5E-8	8.0E-5	0.009
0.25	4.5E-7	4.8E-4	0.022
0.50	1.3E-6	1.4E-3	0.037
1.00	2.8E-6	2.9E-3	0.054

[a] See Ref. [40] and [41] in the main text.

The low C_{WP} values (<<0.3) and Thiele modulus values (ϕ<<3) clearly indicate the absence of diffusion limitations for the particle size range used in the present study (0.315-0.63 mm) under the applied reaction conditions.