

**Supplementary Material**

**Wool-supported Pd and Rh nanoparticles for selective hydrogenation of maleic acid to succinic acid in batch and flow systems**

Francesca Coccia,<sup>a,b</sup> Andrea Mascitti,<sup>c</sup> Stefano Caporali,<sup>d</sup> Laura Polito,<sup>e</sup> Andrea Porcheddu,<sup>f</sup> Corrado Di Nicola,<sup>g</sup> Lucia Tonucci,<sup>a,h\*</sup> and Nicola d'Alessandro<sup>b,h,i</sup>

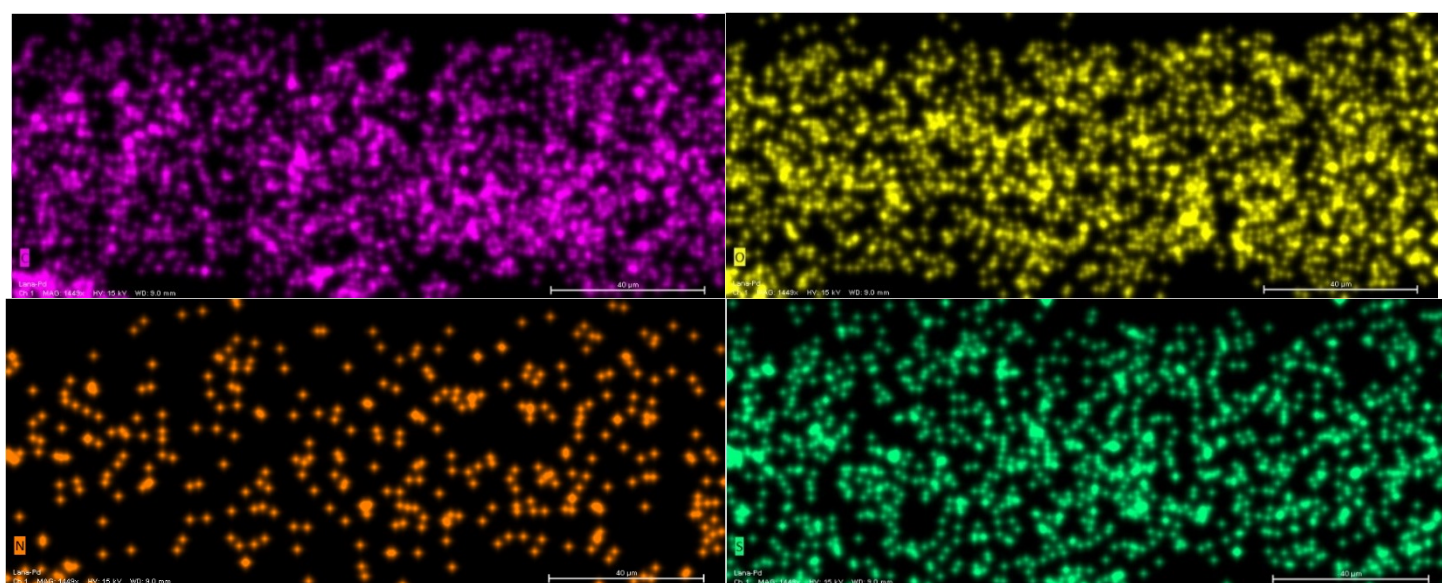


Figure S1: elemental mapping (C and O, above; N and S, below) of H-Pd/WF. The SEM image of this sample is in Figure 2. Scale bar: 40  $\mu\text{m}$

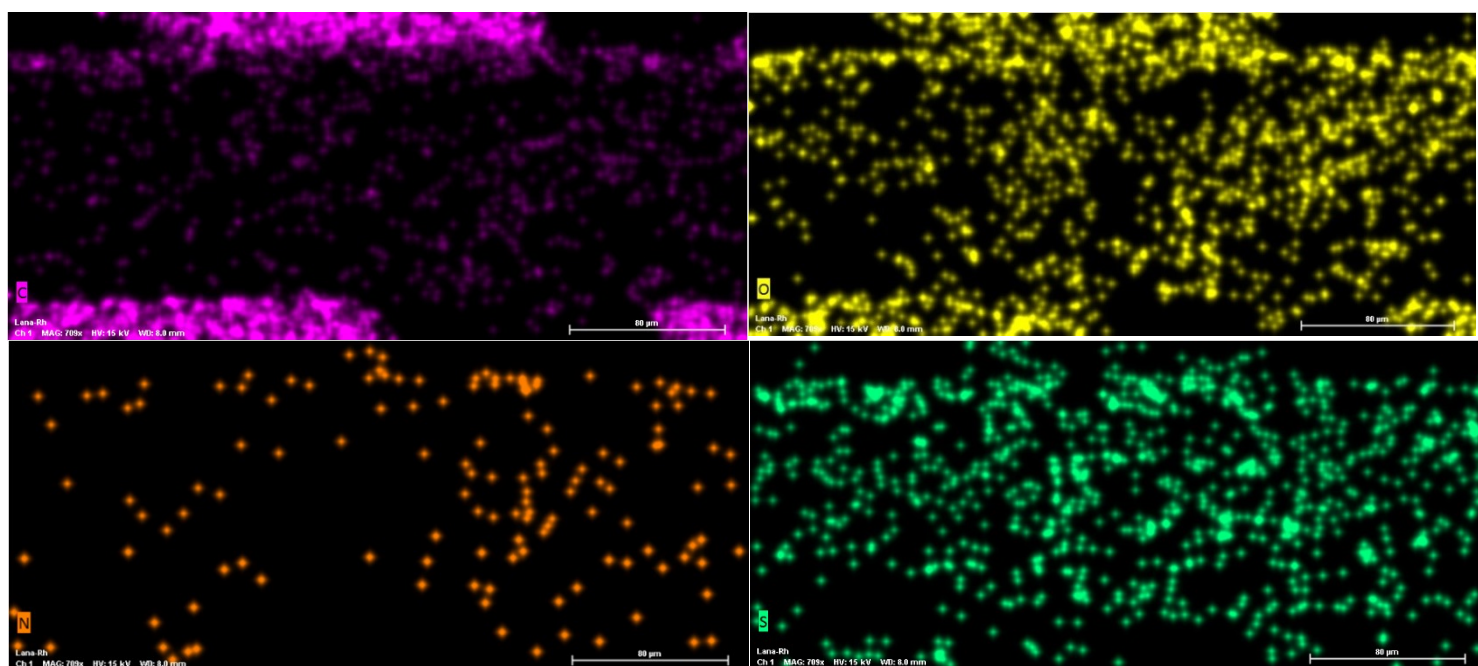


Figure S2: elemental mapping (C and O, above; N and S, below) of H-Rh/WF. The SEM image of this sample is in Figure 2. Scale bar: 80 μm

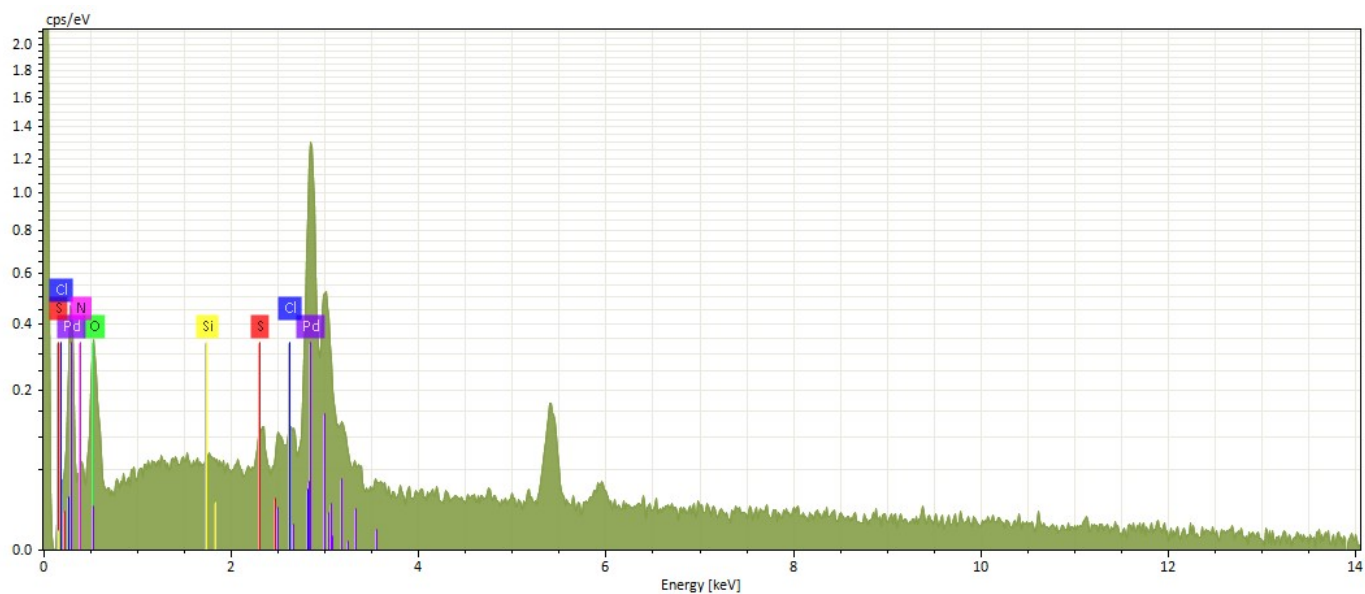


Figure S3: EDX spectrum of H-Pd/WF

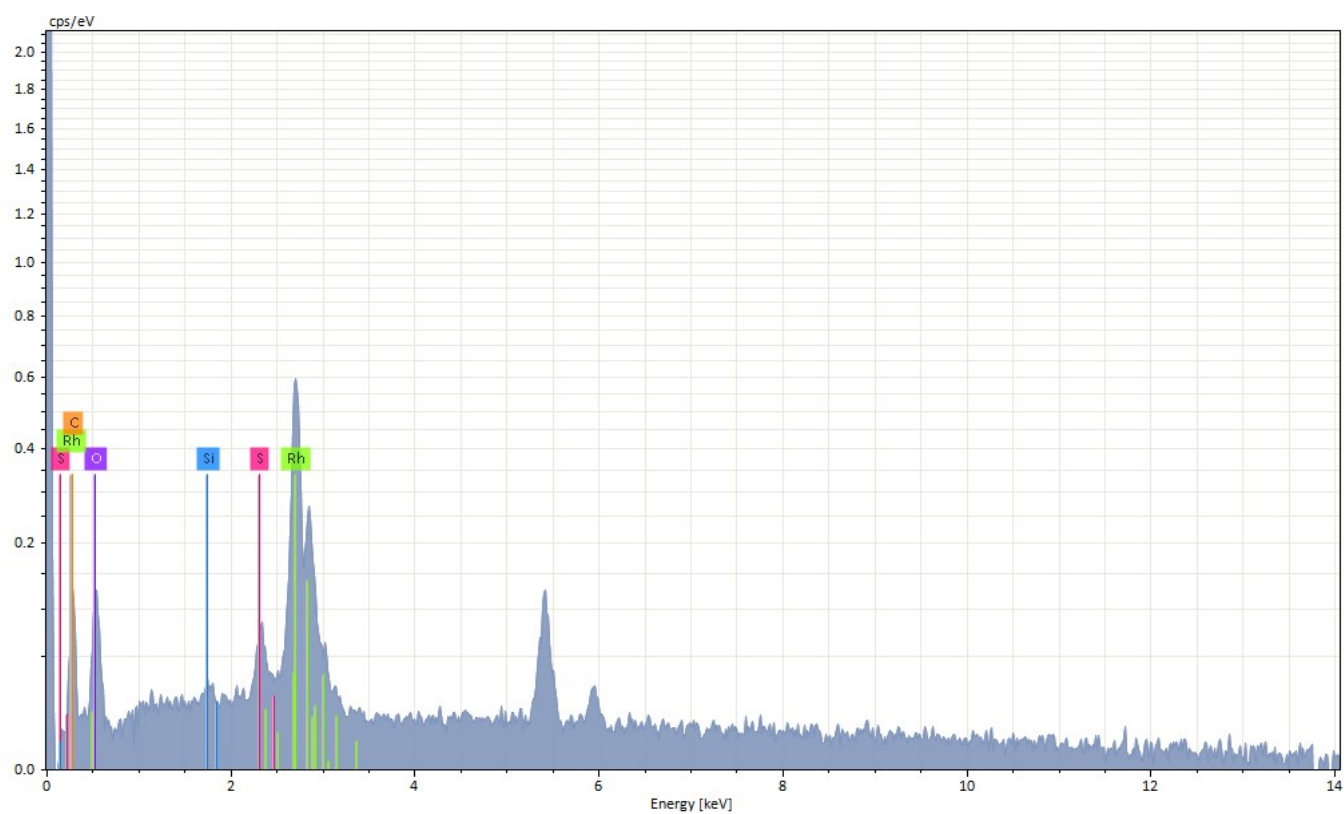


Figure S4: EDX spectrum of H-Rh/WF

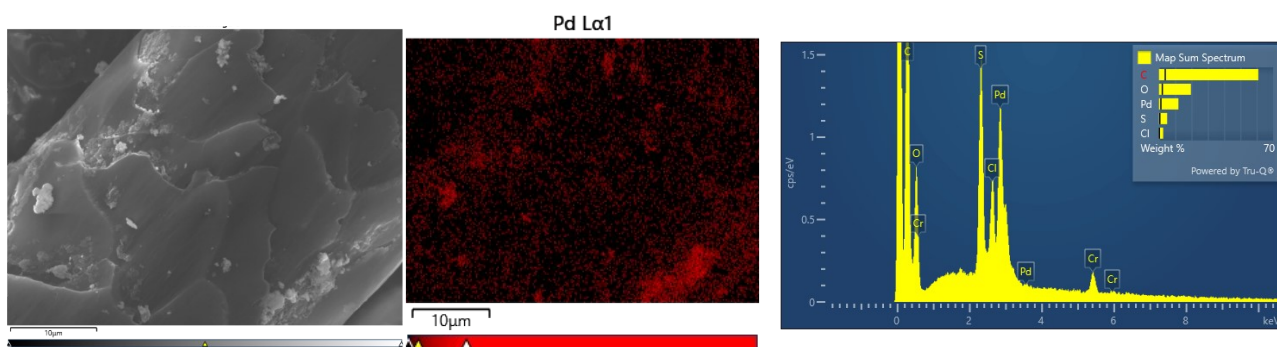


Figure S5: SEM image (left), palladium mapping (middle), EDX (right) of L-Pd/WF

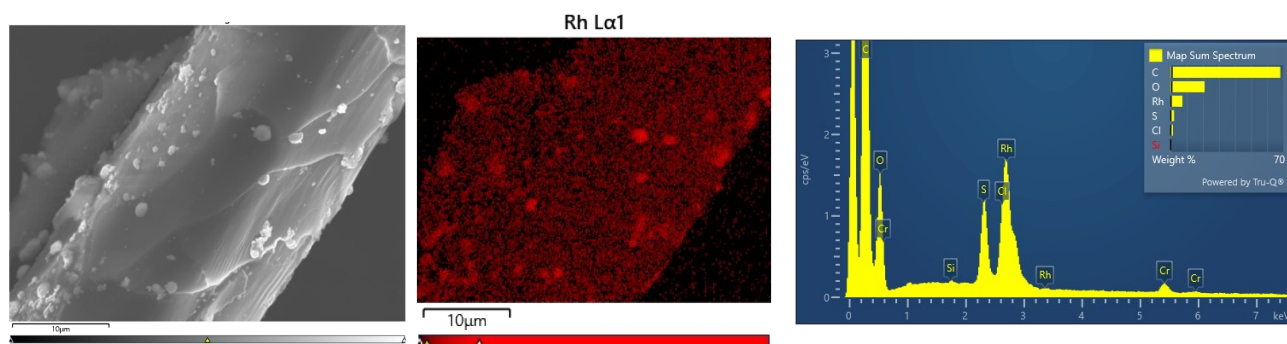


Figure S6: SEM image (left), rhodium mapping (middle), EDX (right) of L-Rh/WF

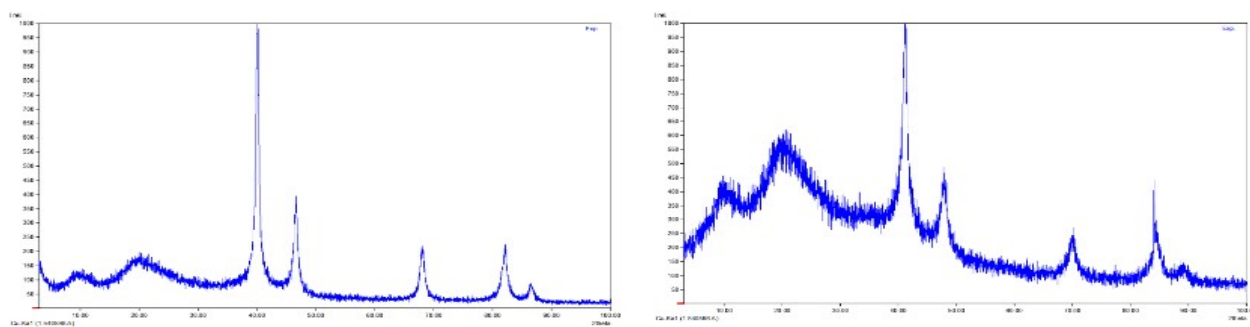


Figure S7: XRD pattern of H-Pd/WF (left) and H-Rh/WF (right)

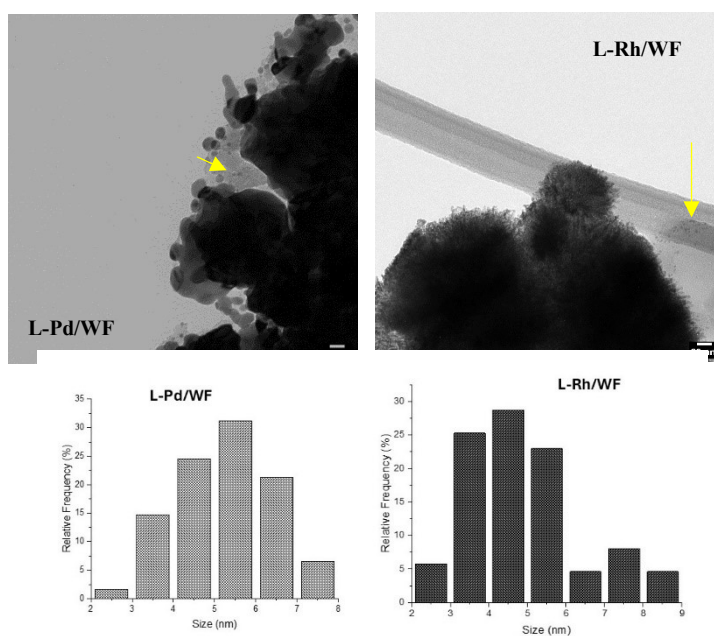


Figure S8: TEM micrographs (top) of L-Pd/WF (left) and L-Rh/WF (right) and diameter sizes (bottom) of L-Pd/WF (left) and H-Rh/WF (right)



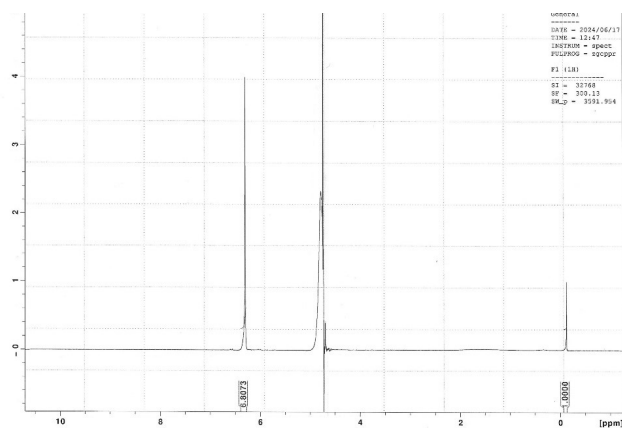


Figure S9:  $^1\text{H}$  NMR spectrum of commercial MA 30 mM ( $\delta = 6.3$  ppm) in water. All spectra at 0 h of the hydrogenation reactions were qualitatively the same. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt ( $\delta = -0.2$  ppm) was used as the reference

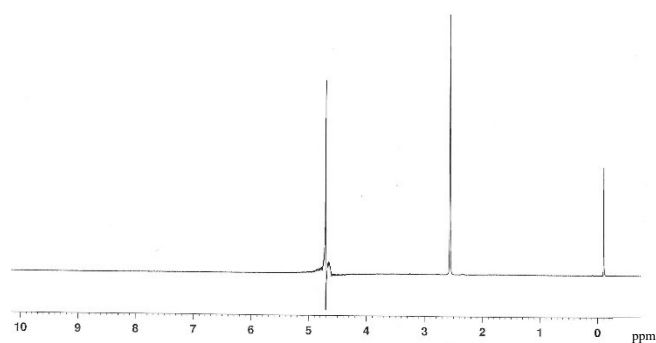


Figure S10:  $^1\text{H}$  NMR spectrum of commercial SA 30 mM ( $\delta = 2.6$  ppm) in water. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt ( $\delta = -0.2$  ppm) was used as the reference

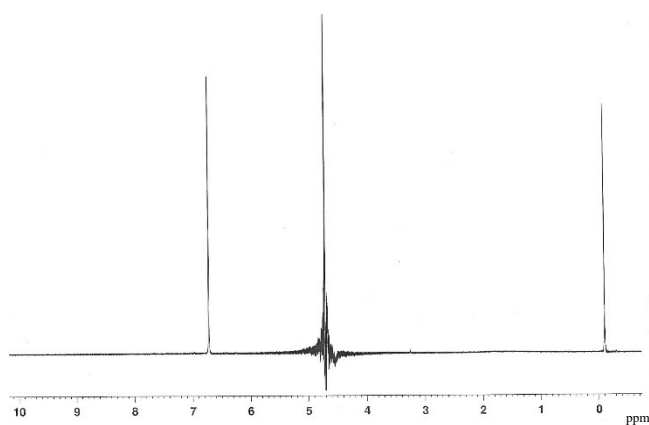


Figure S11:  $^1\text{H}$  NMR spectrum of commercial FA 30 mM ( $\delta = 6.8$  ppm) in water. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt ( $\delta = -0.2$  ppm) was used as the reference

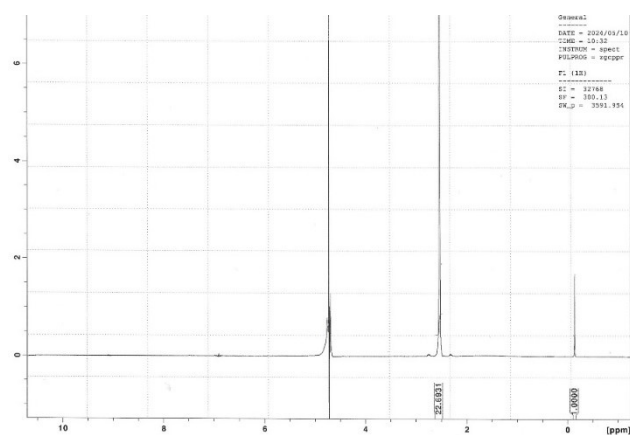


Figure S12:  $^1\text{H}$  NMR spectrum of the reaction solution of MA after 2 h in the presence of H-Pd/WF and under  $\text{H}_2$  flux in water. Only the peak of SA was present at 2.6 ppm, the peak of MA (6.3 ppm) disappeared, and the peak of FA (6.8 ppm) was not present. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt (at -0.2 ppm) was used as the reference

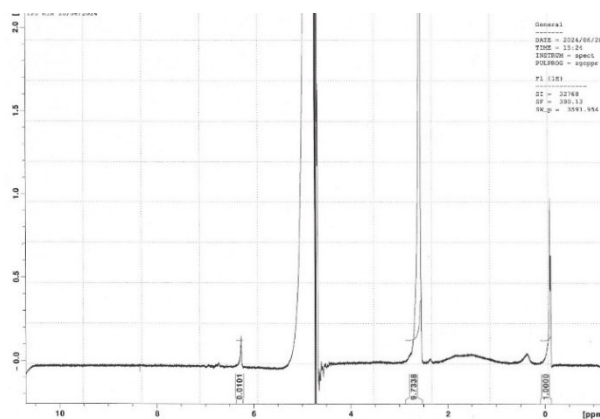


Figure S13:  $^1\text{H}$  NMR spectrum of the reaction solution of MA after 2 h in the presence of H-Rh/WF under  $\text{H}_2$  flux in water. The peak of SA was present at 2.6 ppm, the peak of MA (6.3 ppm) was reduced but still present, and the peak of FA (6.8 ppm) was not present. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt (at -0.2 ppm) was used as the reference

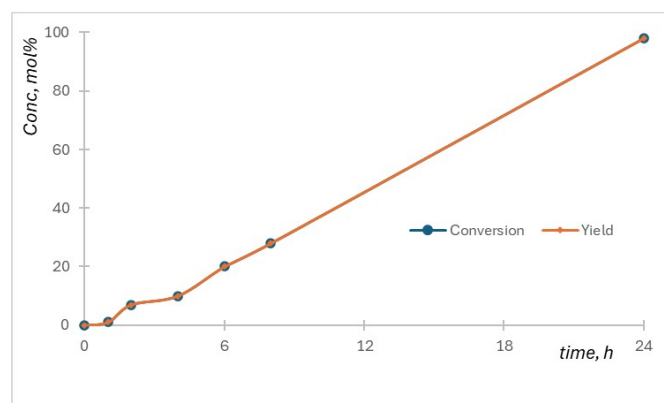


Figure S14: conversions of MA and yields of SA (mol %) in batch reactions, carried out in the presence of L-Pd/WF (3% mol of Pd/mol of MA) in water solution at room temperature and under H<sub>2</sub> flux

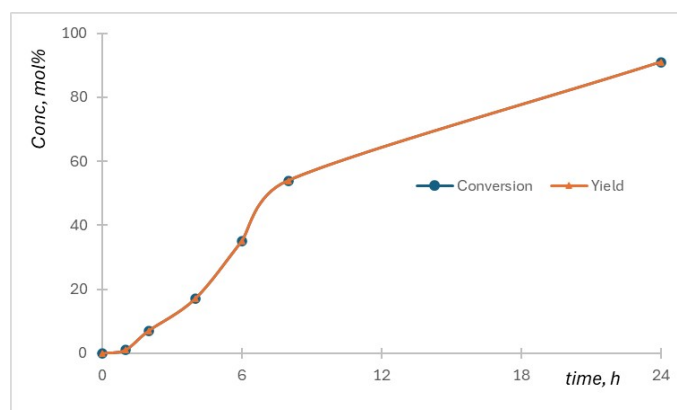


Figure S15: conversions of MA and yields of SA (mol %) in batch reactions, carried out in the presence of L-Rh/WF (3% mol of Rh/mol of MA) in water solution at room temperature and under H<sub>2</sub> flux



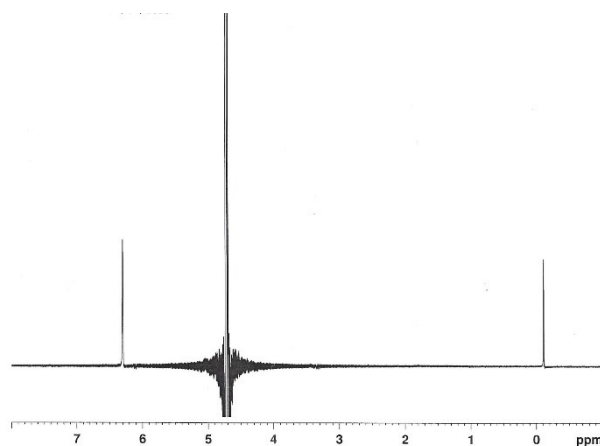


Figure S16:  $^1\text{H}$  NMR spectrum of the reaction solution of MA after 24 h in the presence of H-Pd/WF with hydrazine salt in water. Only the peak of MA (6.3 ppm) was present. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt (at -0.2 ppm) was used as the reference

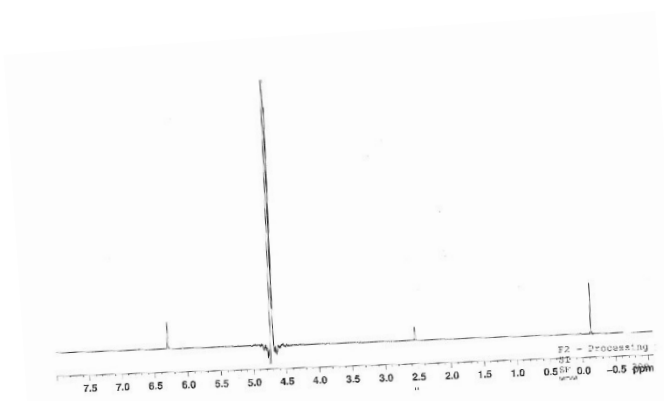


Figure S17:  $^1\text{H}$  NMR spectrum of the reaction solution of MA after 24 h in the presence of H-Rh/WF with hydrazine salt in water. The peak of MA (6.3 ppm) was reduced; the peak of SA (2.6 ppm) was present; FA (6.8 ppm) was not present. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt (at -0.2 ppm) was used as the reference

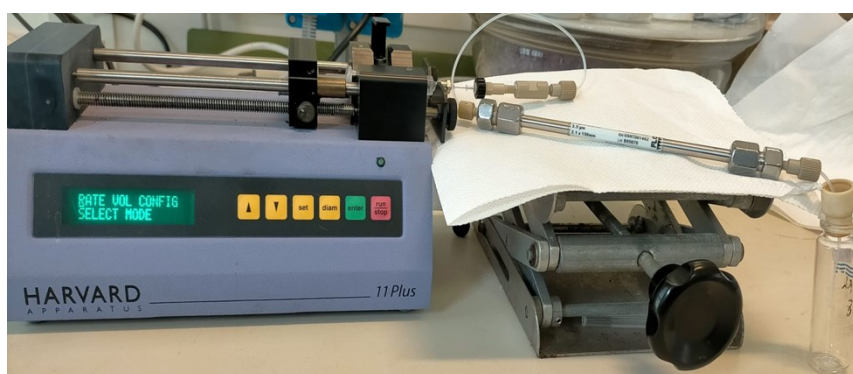


Figure S18: apparatus for MA hydrogenation reaction carried out in continuous flow mode

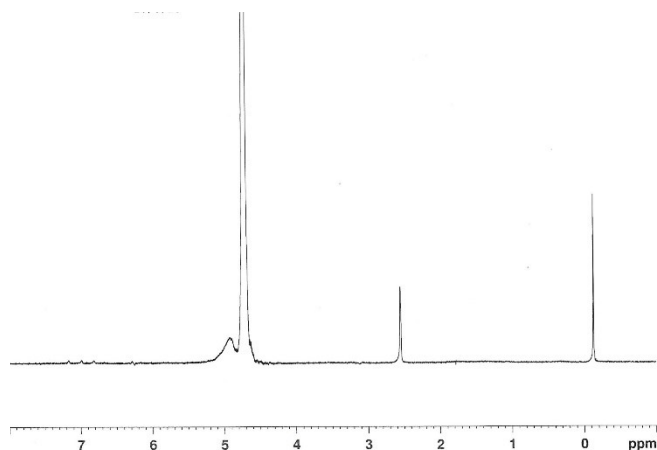


Figure S19:  $^1\text{H}$  NMR spectrum of the reaction solution of MA after 75 minutes, carried out in a fixed-bed reactor with L-Rh/WF and hydrazine salt in water. The peak of SA was present at 2.6 ppm, the peak of MA and the peak of FA were not present. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt (at -0.2 ppm) was used as the reference

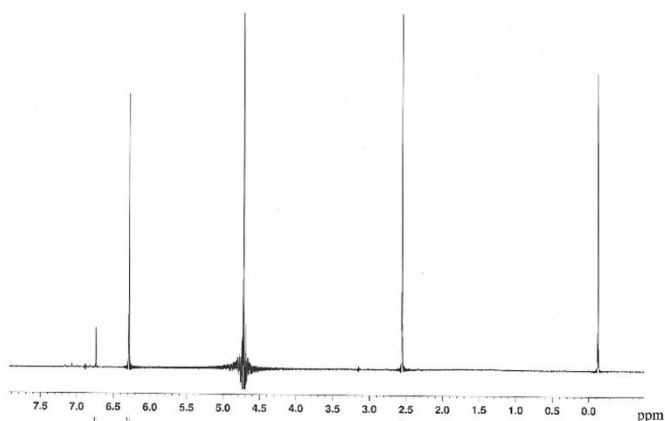


Figure S20:  $^1\text{H}$  NMR spectrum of the reaction solution of MA after 180 minutes, carried out in a fixed-bed reactor with L-Pd/WF and hydrazine salt in water. The peaks of SA and FA were present, the peak of MA decreased. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt (at -0.2 ppm) was used as the reference

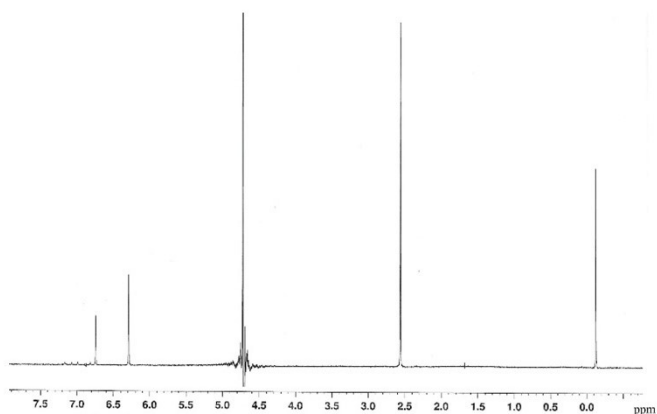


Figure S21:  $^1\text{H}$  NMR spectrum of the reaction solution of MA after 38 minutes, carried out in a fixed-bed reactor with L-Rh/WF and hydrazine salt in water. The peaks of SA and FA were present, the peak of MA decreased. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt (at -0.2 ppm) was used as the reference

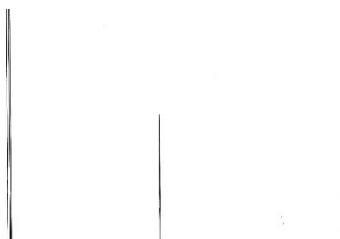


Figure S22:  $^1\text{H}$  NMR spectrum of the reaction solution of MA after 75 minutes, carried out in a fixed-bed reactor with L-Rh/WF and hydrazine salt in water. At 2.6 ppm there was the peak of SA, the peak of MA disappeared; the signals of ammonium (derived from hydrazine) were around 7 ppm. The peak of 3-(trimethylsilyl) propionic-2,2,3,3- $\text{d}_4$  acid, sodium salt (at -0.2 ppm) was used as the reference

Table S1: TON and TOF of the H-Pd/WF catalyst in the conversion of MA to SA in water solution under H<sub>2</sub> flux at room temperature

Catalyst	Reaction time ( <i>min</i> )	MA Conversion ( <i>mol</i> )	TON	TOF ( <i>h<sup>-1</sup></i> )
H-Pd/WF	5	0.018	1.1	13.20
	10	0.036	2.2	13.20
	15	0.055	3.3	13.20
	20	0.078	4.7	14.10
	25	0.106	6.4	15.24
	30	0.125	7.5	15.00
	60	0.700	42.0	42.00
	120	1.00	60.0	30.00

Table S2: TON and TOF of the H-Rh/WF catalyst in the conversion of MA to SA in water solution under H<sub>2</sub> flux at room temperature

Catalyst	Reaction time ( <i>min</i> )	MA Conversion ( <i>mol</i> )	TON	TOF ( <i>h<sup>-1</sup></i> )
H-Rh/WF	5	0.010	0.6	7.20
	10	0.045	2.7	15.00
	15	0.076	4.6	18.40
	20	0.100	6.0	18.00
	25	0.130	7.8	19.50
	30	0.160	9.6	19.20
	60	0.700	42.0	42.00
	120	0.970	58.2	29.10