

# pH-dependent catalytic activity of Au and Pd-based hybrid cryogels by investigating the acid/base nature of the polymeric phase

Stefano Scurti<sup>1</sup>, Giuseppe Proietto Salanitri<sup>1,3</sup>, Tommaso Mecca<sup>4</sup>, Elena Rodríguez-Aguado<sup>5</sup>, Juan Antonio Cecilia<sup>5</sup>, Giusy Curcuruto<sup>3</sup>, Sabrina Carola Carroccio<sup>3</sup>, Daniele Caretti<sup>1</sup>, Nikolaos Dimitratos<sup>1,2\*</sup>

<sup>1</sup> Industrial Chemistry “Toso Montanari” Department, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

<sup>2</sup> Center for Chemical Catalysis-C3, Alma Mater Studiorum Università di Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

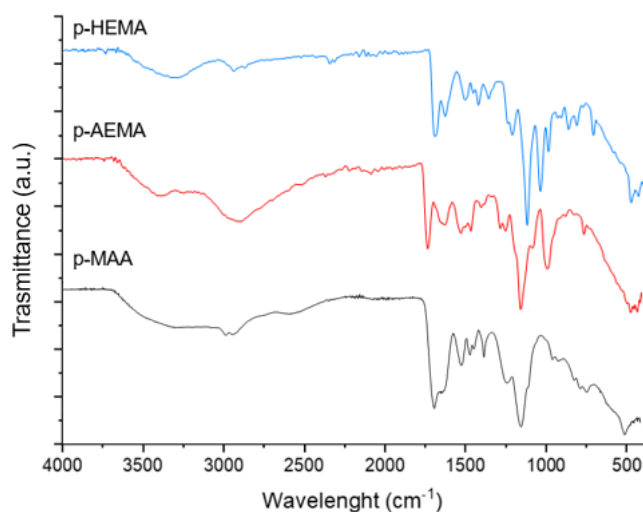
<sup>3</sup> Institute for Polymers, Composites and Biomaterials (IPCB) – CNR, Via Paolo Gaifami 18, 95126 Catania, Italy

<sup>4</sup> Institute for Biomolecular Chemistry (ICB) – CNR, Via Paolo Gaifami 18, 95126 Catania, Italy

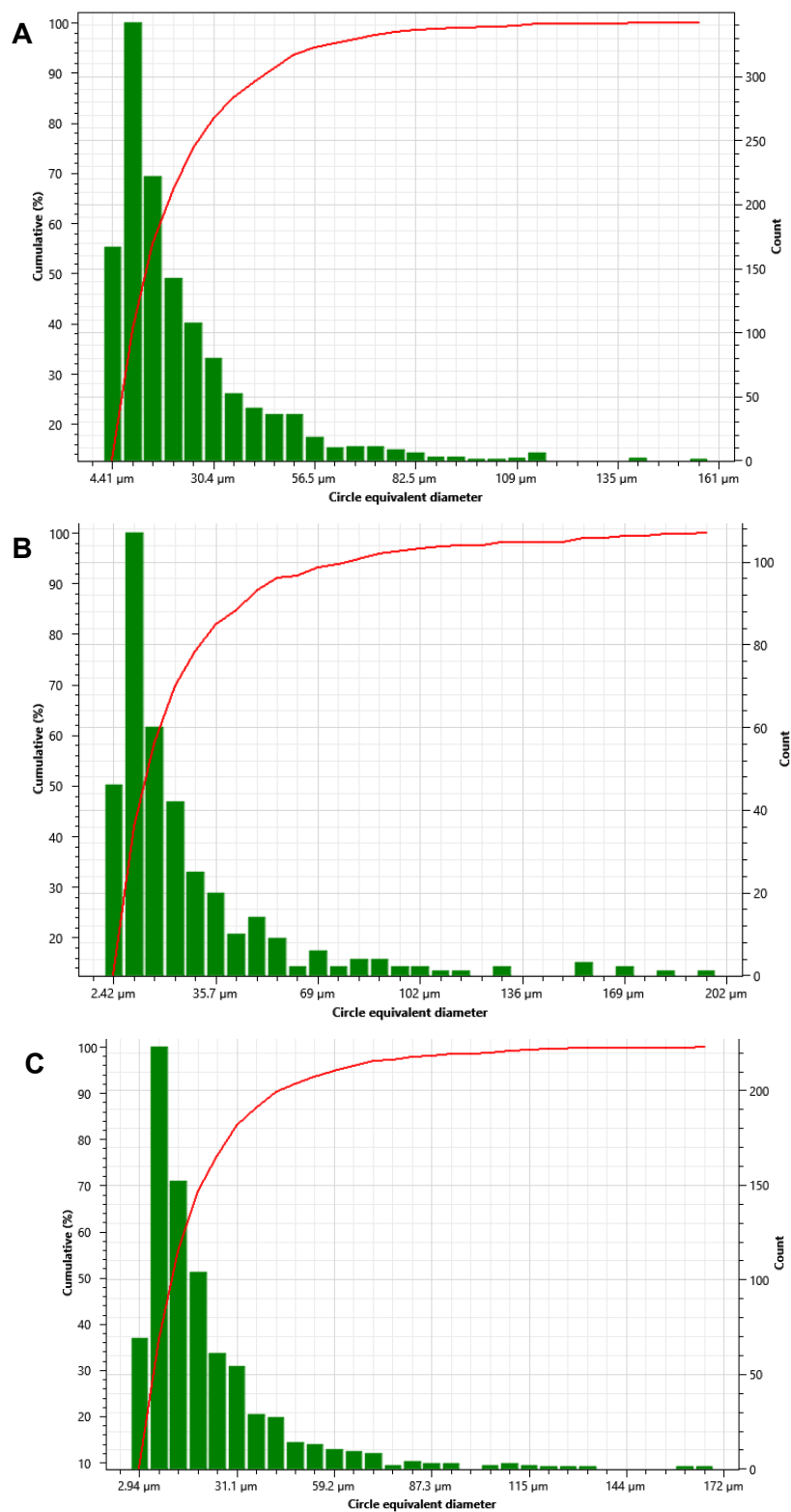
<sup>5</sup> Departamento de Química Inorgánica, Cristalografía y Mineralogía (Unidad Asociada al ICP-CSIC), Facultad de Ciencias, Universidad de Málaga, Campus de Teatinos, 29071 Málaga, Spain

\*[nikolaos.dimitratos@unibo.it](mailto:nikolaos.dimitratos@unibo.it); Industrial Chemistry “Toso Montanari” Department, University of Bologna, Viale Risorgimento 4, 40136 Bologna, Italy

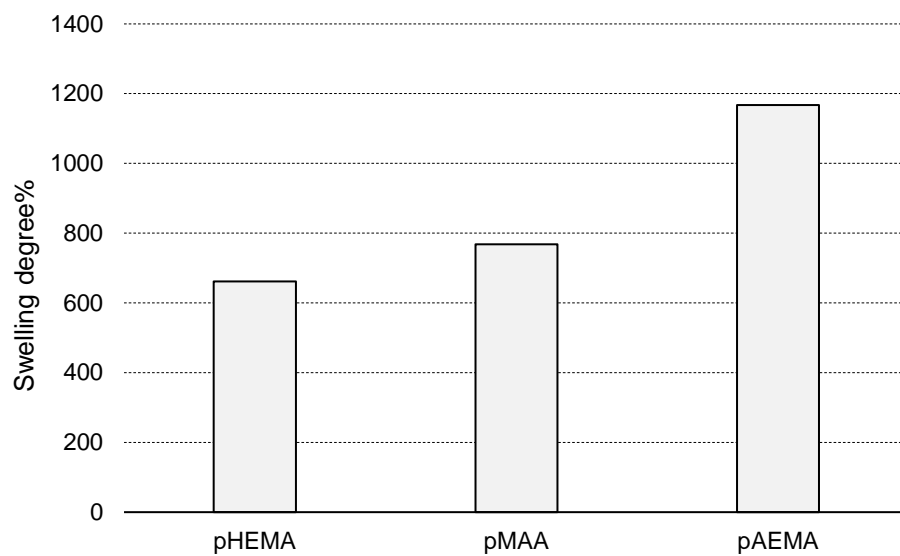
## Cryogels characterization



**Fig. S1.** ATR-IR spectra of synthesized polymeric cryogels.



**Fig. S2.** Circular equivalent diameter distribution for the bare cryogels: p-HEMA (A), p-MAA (B) and p-AEMA (C).

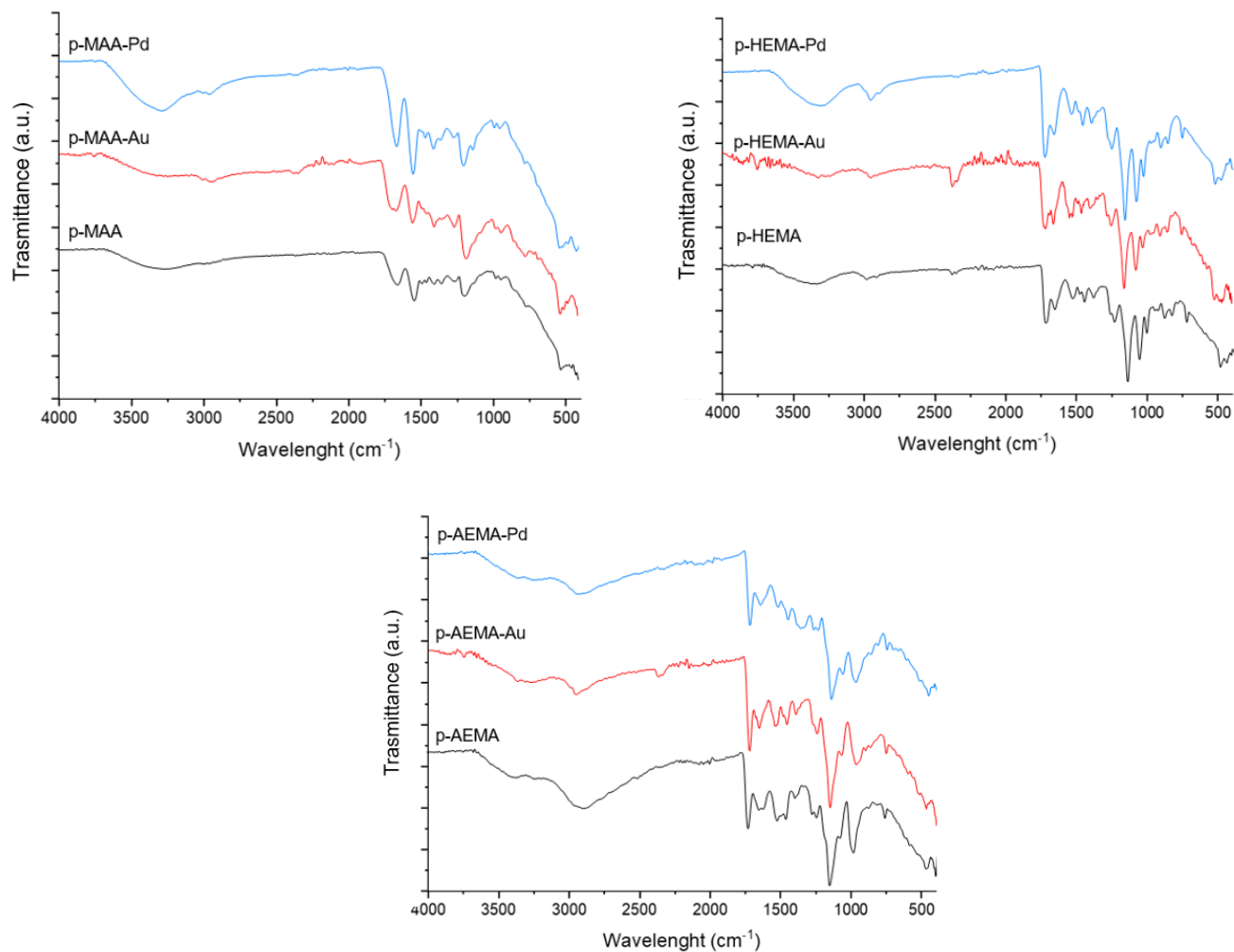


**Fig. S3.** Swelling degree % for the bare cryogels.

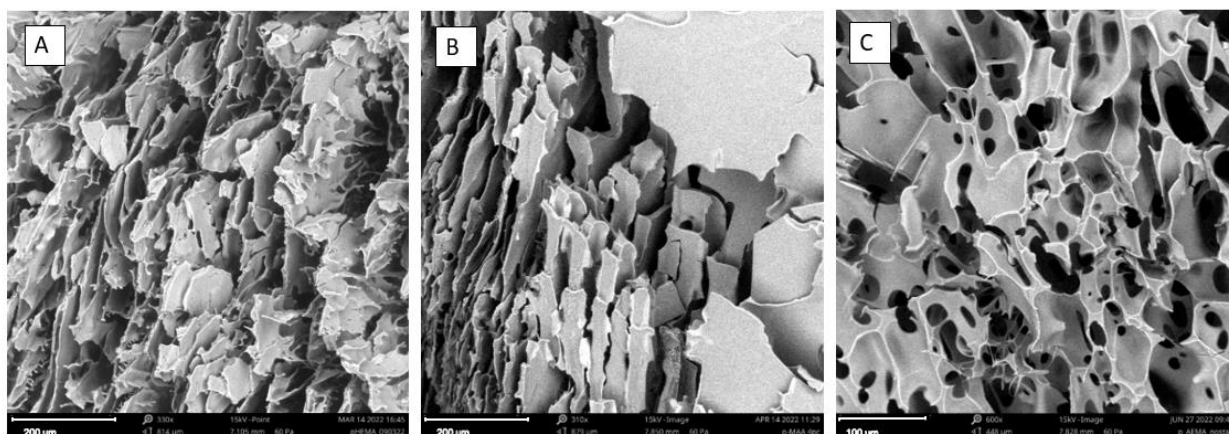
**Table S1.** Swelling test data.

<b>Sample</b>	<b>m<sub>w</sub> (g)</b>	<b>m<sub>d</sub> (g)</b>	<b>SD%</b>
p-HEMA	1.36	0.18	660
p-MAA	0.61	0.07	770
p-AEMA	1.52	0.12	1170

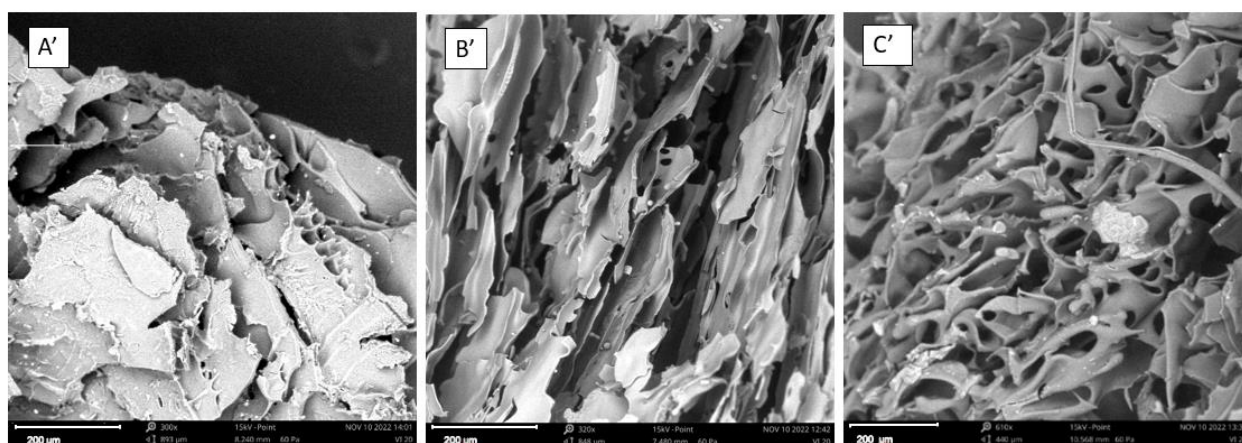
## Characterization of hybrid metal-polymer nanocatalysts



**Fig. S4.** Comparison between ATR-IR spectra of bare and functionalized cryogels with Au e Pd nanoparticles for each sample prepared.

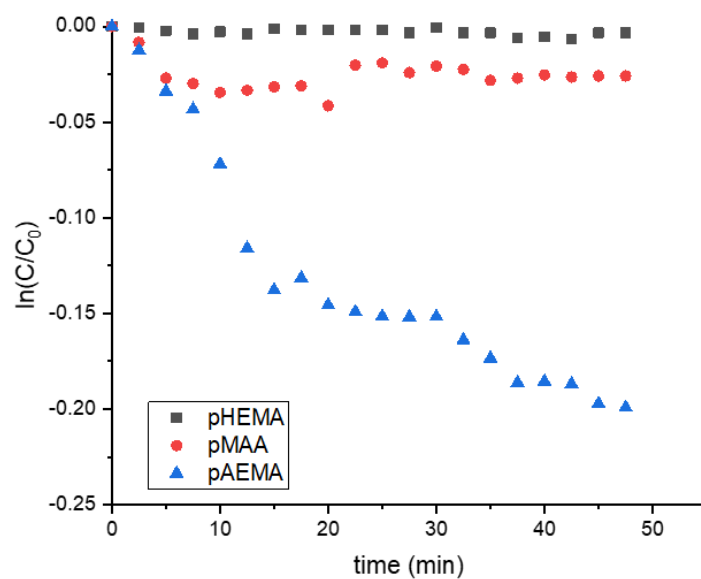


↓ After impregnation

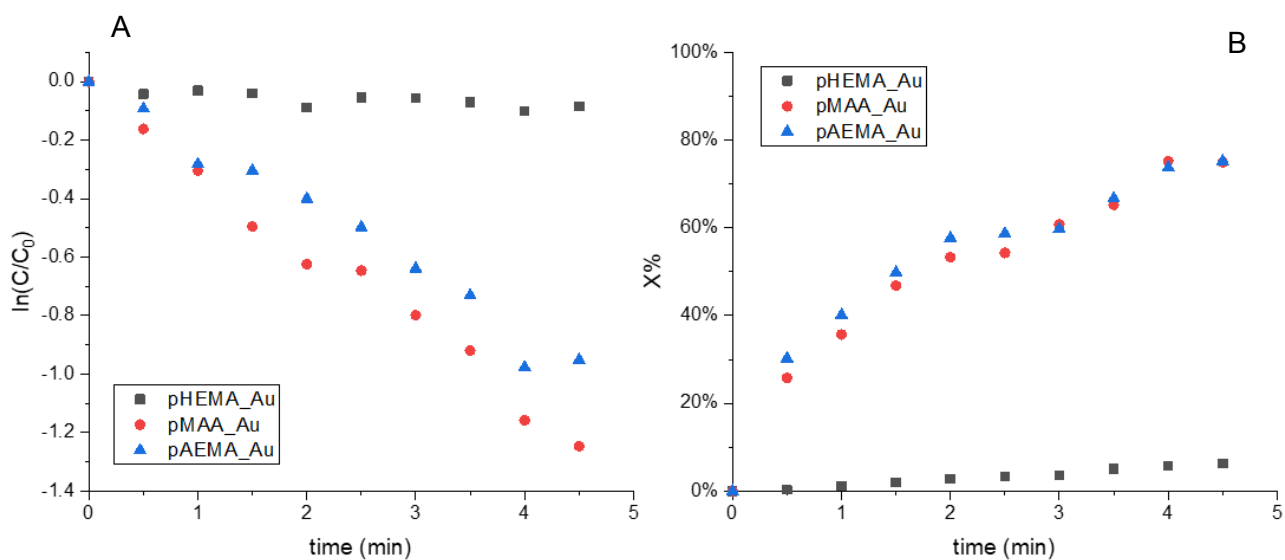


**Fig. S5.** SEM images before and after the impregnation phase (the images reported are related to the Au-based catalysts: (A-A') p-HEMA, (B-B') p-MAA, (C-C') p-AEMA).

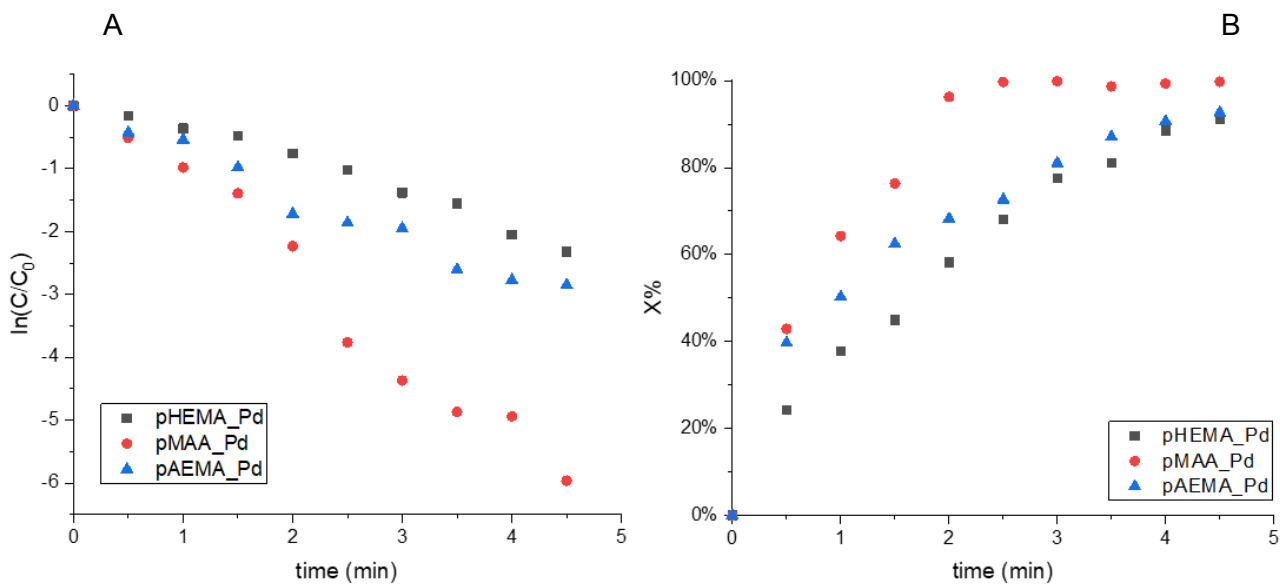
## Catalytic tests



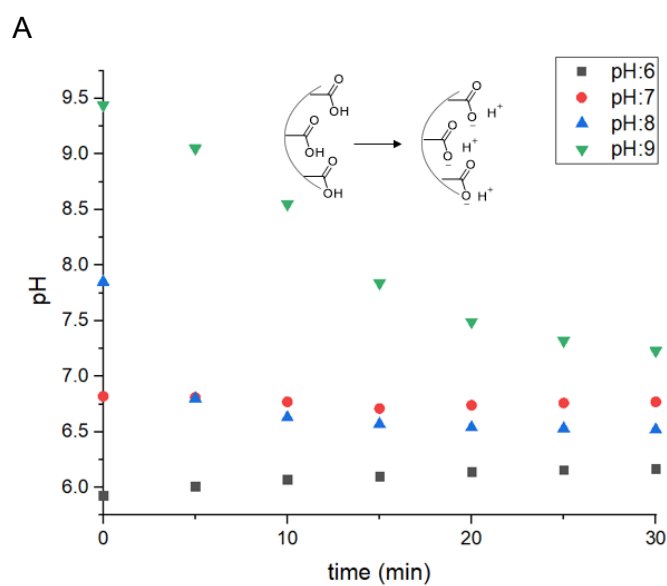
**Fig. S6.** Adsorption test for the bare cryogels: 25 mL of 4-NP ( $2 \cdot 10^{-4}$  M), 25 mL of  $\text{NaBH}_4$  ( $9.0 \cdot 10^{-3}$  M) at 25 °C and 500 rpm.

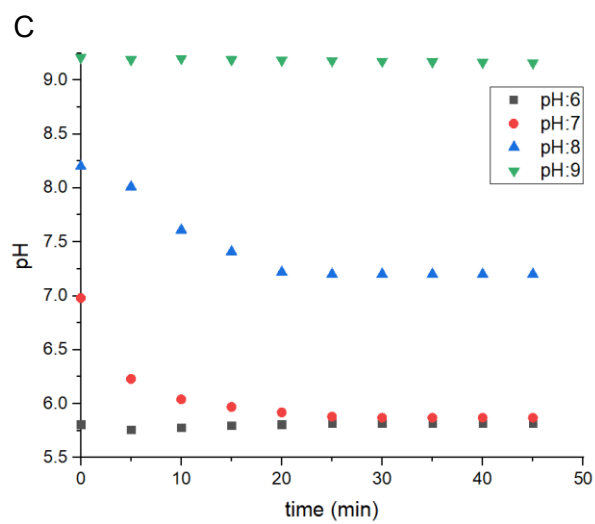
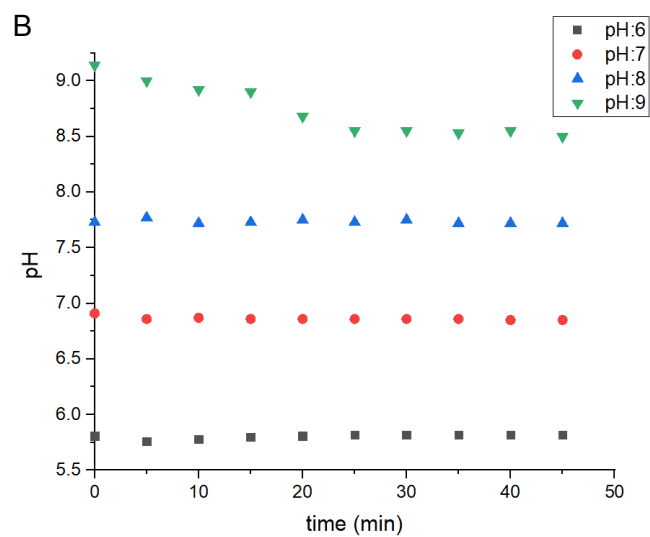


**Fig. S7.** Pseudo-first-order kinetic plot (A) and (B) conversion plot for Au-based hybrid catalysts. The reduction of 4-NP was carried out using 25 mL of 4-NP ( $2 \cdot 10^{-4}$  M), 25 mL of  $\text{NaBH}_4$  ( $9.0 \cdot 10^{-3}$  M), 4 mg of catalyst at 25 °C and 500 rpm.



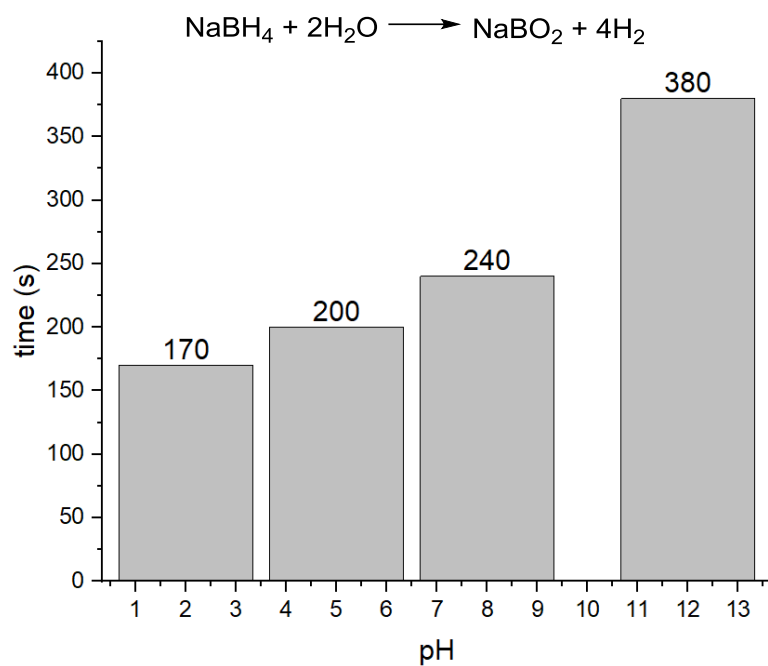
**Fig. S8.** Pseudo-first-order kinetic plot (A) and (B) conversion plot for Pd-based hybrid catalysts. The reduction of 4-NP was carried out using 25 mL of 4-NP ( $2 \cdot 10^{-4}$  M), 25 mL of  $\text{NaBH}_4$  ( $9.0 \cdot 10^{-3}$  M), 4 mg of catalyst at 25 °C and 500 rpm.



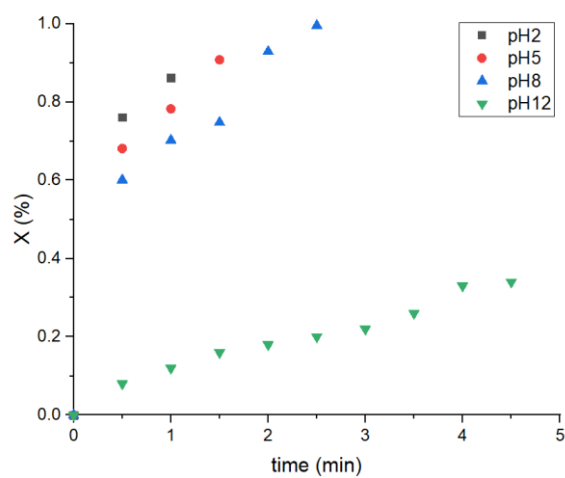


**Fig. S9.** pH measures as a function of time starting from values in the range of the reaction pH for bare cryogels: p-MAA (A), p-HEMA (B) and p-AEMA (C).





**Fig. S10.** Evaluation of  $\text{NaBH}_4$  decomposition time as a function of pH.



**Fig. S11.** Conversion plot related to p-MAA\_Pd for the 4-NP reduction carried out using 25 mL of 4-NP ( $2 \cdot 10^{-4}$  M), 25 mL of  $\text{NaBH}_4$  ( $9.0 \cdot 10^{-3}$  M), 4 mg of catalyst at different pH.