Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Adamantane-based covalent–organic framework: stability, adsorption capability, and behaviour as catalyst and support for palladium and gold for the hydrogenation of nitrostyrene

Mihaela M. Trandafir,[a] Lidia Pop,[b] Niculina D. Hădade,[b] Mihaela Florea,[a] Florentina Neațu,[a] Cristian M. Teodorescu,[c] Bahir Duraki,[d] Jeroen A. van Bokhoven,[d] Ion Grosu,[b*] Vasile I. Pârvulescu,[a*] Hermenegildo Garcia[e*]

Dependence of time-conversion and time selectivity

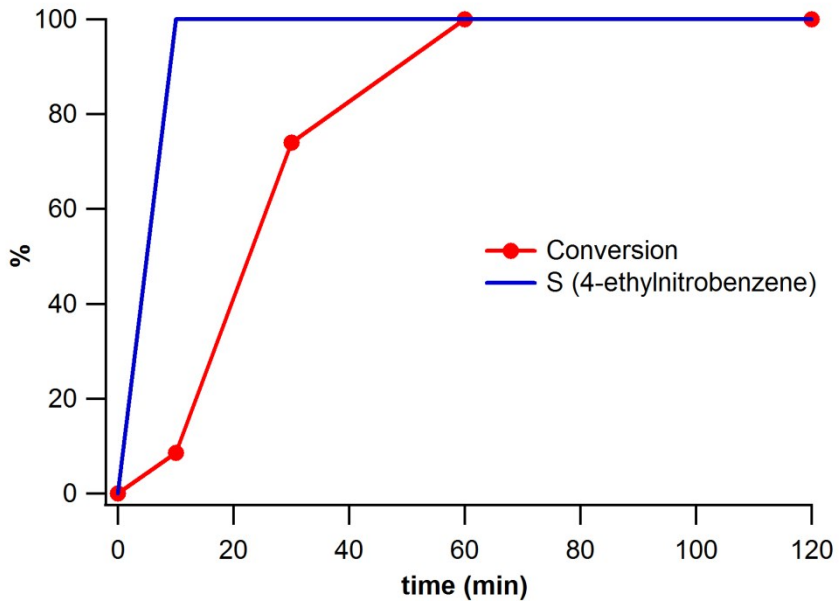


Figure S1. Evolution of conversion ad selectivity in time for the hydrogenation of 4-nitrostyrene (0.067 mmoles) in the presence of 0.5%Pd/COF (10 mg), heptane (5 cm^3) and 30 bars H_2.

Influence of solvent and CO_2 pressurization

The hydrogenation of 4-nitrostyrene was performed also in a polar solvent such as ethanol. The conversion in ethanol is higher than heptane, but the product distribution is similar (Table S1, entry 2). Pressurization with CO_2 did not change the product distribution, ethyl-nitrobenzene being the main product formed, irrespective of the nature of solvent or pressure. These results are in agreement with the results reported in similar conditions[1], where is emphasised that the nitro group interacts with CO_2 dissolved in the solvent, slowing down hydrogenation of the nitro group and decreasing the selectivity to aminostyrene **2**.

Table S1. Hydrogenation of 4-nitrostyrene in different solvents and CO_2 pressure.

Entry	Catalyst	Solvent	P_{CO2} (bar)	Conversion (%)	Selectivity (%) to		
					1	**2**	**3**

1	Pd/COF	heptane	-	8.6	100	-	-
2	Pd/COF	ethanol	-	27	100	-	-
3	Pd/COF	heptane	1	7	100	-	-
4	Pd/COF	heptane	30	5	100		
5	Pd/COF	ethanol	1	21	100		
6	Pd/COF	ethanol	30	18	100		

Reaction conditions : 0.067 mmols of 4-nitrostyrene, 5 cm^3 of heptane, 10 mg of catalyst, 30 atm hydrogen, 10 min.

Textural characterization of the fresh and spent catalysts

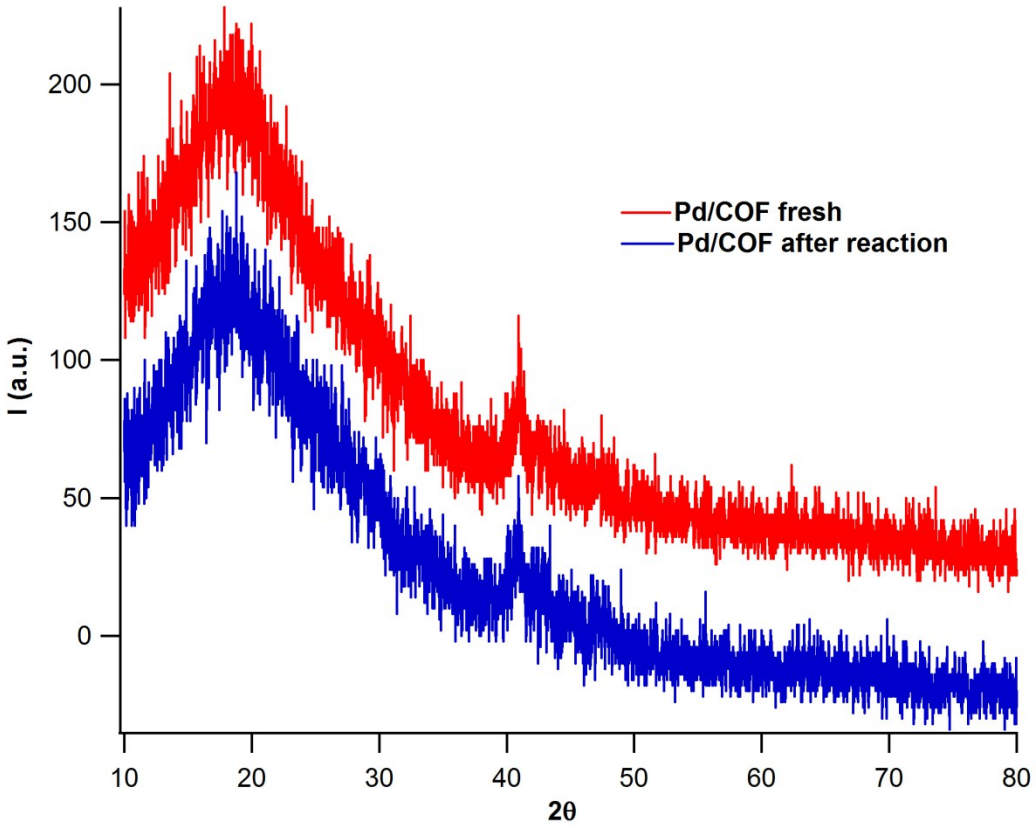


Figure S2. X-ray diffraction for Pd/COF fresh and spent catalysts

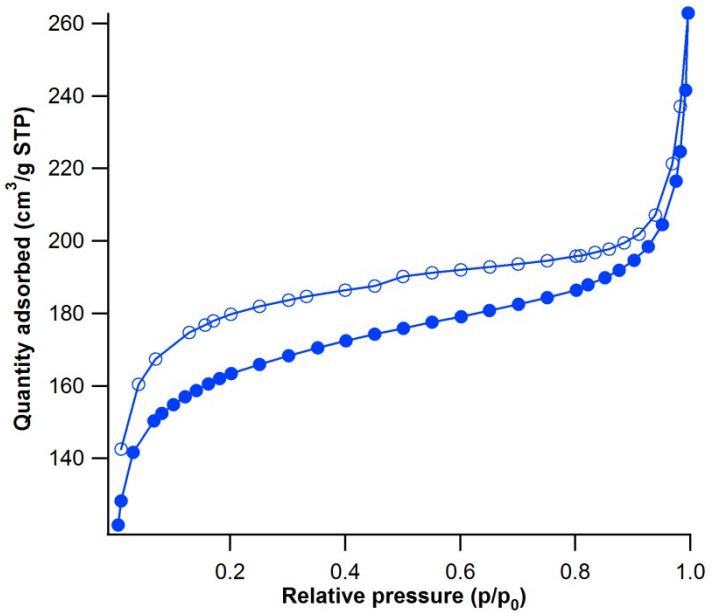
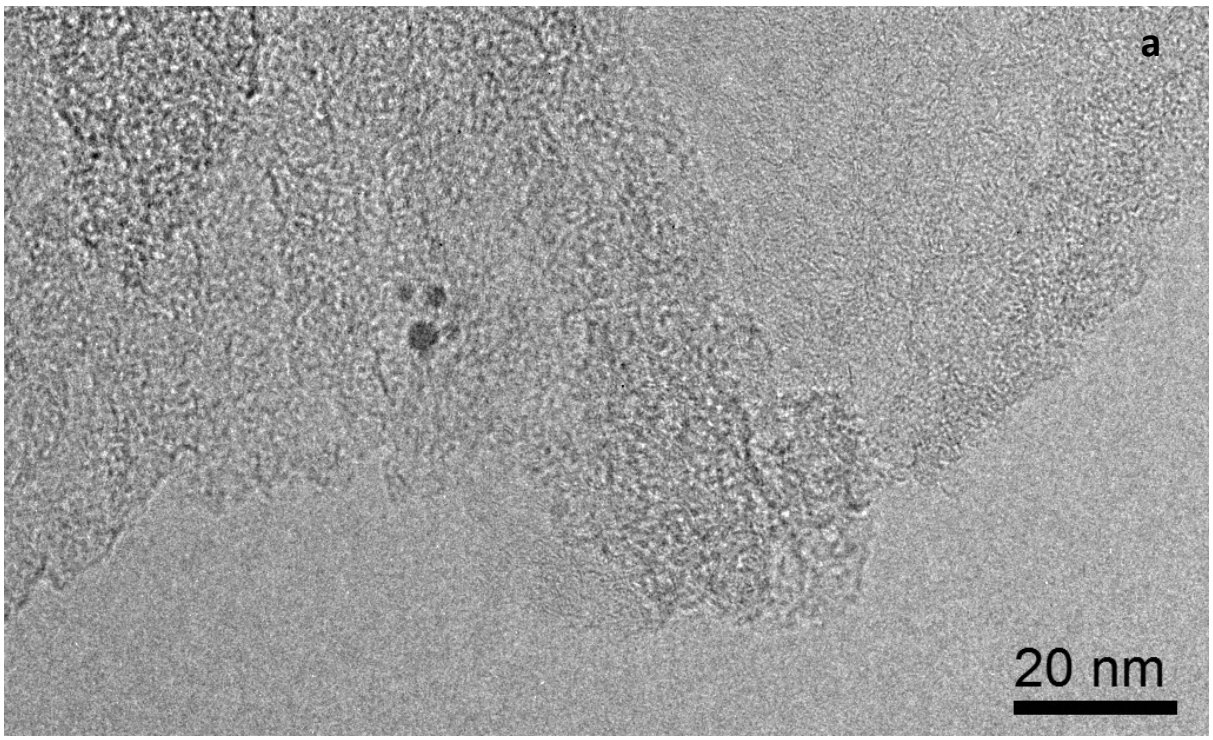


Figure S3. Nitrogen adsorption-desorption isotherms at -196 °C of spent Pd/COF.



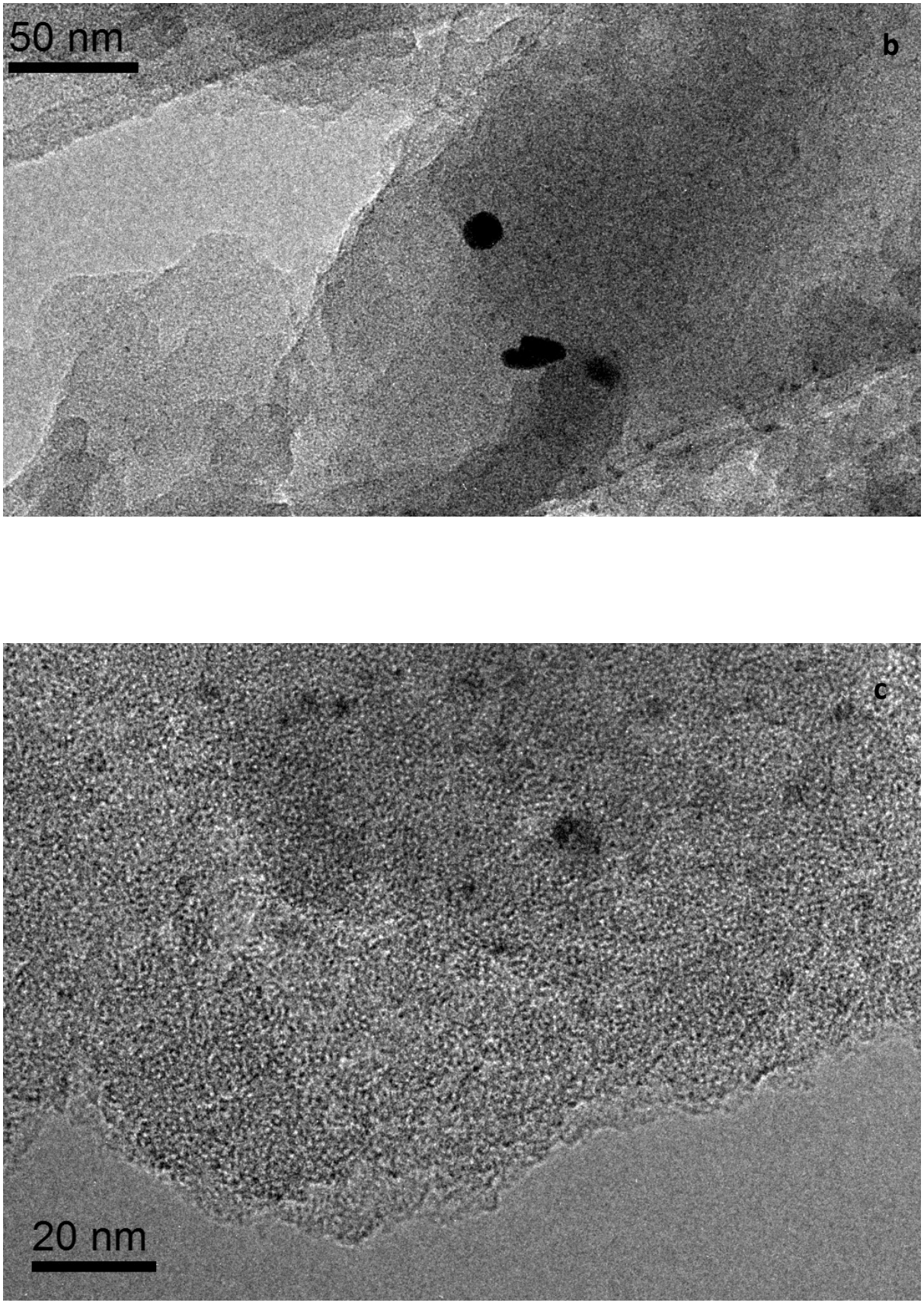


Figure S4. TEM of Au/C (a) Au/COF (b) and Pd/COF (c) of spent catalysts.

References:

1. H.Yoshida, K. Kato, J. Wang, X. Meng, S. Narisawa, S.Fujita, Z. Wu, F. Zhao and M. Arai, *J. Phys. Chem. C,* 2011, **115**, 2257-2267.