Enhanced hydrogenation catalytic activity with polydopamine as interfacial glue between Pd NPs and porous UVM-7 silica supports

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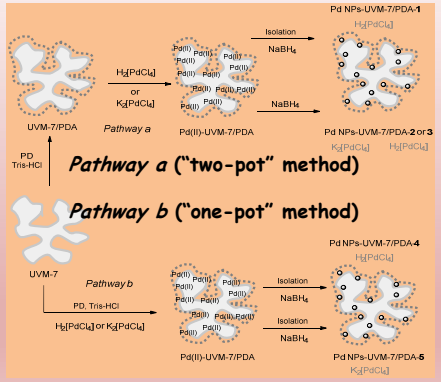
ABSTRACT: The immobilization of metal nanoparticles (NPs) on supports has attracted a considerable attention by their potential applications as efficient heterogeneous catalysts. In order to improve the dispersion and avoid the Pd NPs aggregation on the UVM-7, we have decorated the silica with PDA which will allow the interfacial assembly of the Pd NPs stabilizing them on the support [1]. We have used two preparative strategies to incorporate both Pd and PDA on the UVM-7 silica: sequential or joint incorporation of Pd and PDA. Different Pd NPs-UVM-7/PDA catalysts have been synthesized and their activity has been studied using the model reaction of 4-nitrophenol reduction with NEt_4BH_4. The most active Pd (0) centres seem to be Pd NPs of less than 1 nm on the PDA surface.

Synthesis design

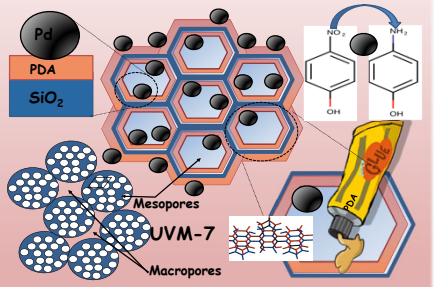


Synthesis scheme showing the two strategies or preparatory paths used

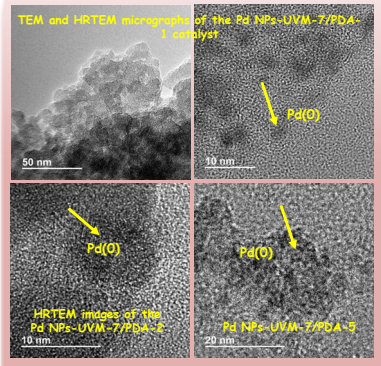
Compositional data of the Pd NPs-UVM-7/PDA-n catalyst.

Catalyst n	Si/Pd[1] Molar ratio	PDA content[2] % (wt.)	Water content[2] % (wt.)
1	768	10	2
2	92	13	3
3	383	7	2
4	44	21	3
5	41	9	2

[1] Values determined by EDX. [2] Values determined through the TGA curves.

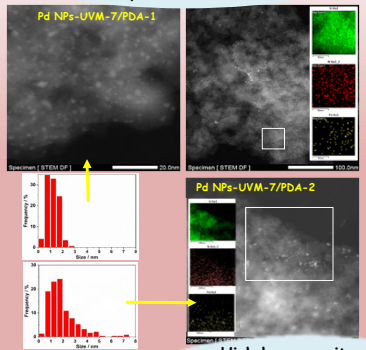


Characterization



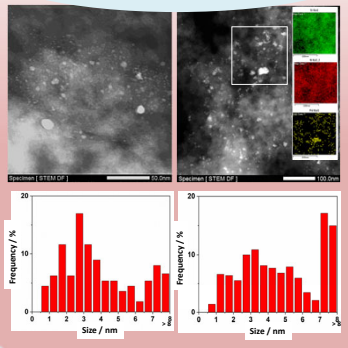
TEM and HRTEM images of selected catalysts

Pathway a, High homogeneity and distribution particles sizes



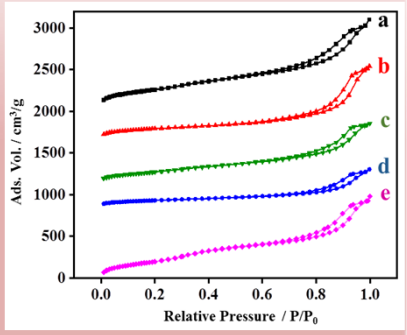
High homogeneity and POOR distribution particles sizes

Pathway b, large heterogeneity, HIGH dispersion and especially in particle size distribution



HAADF-STEM image, Histograms and mapping of catalysts isolated by the PATHWAY a and PATHWAY b (Right)

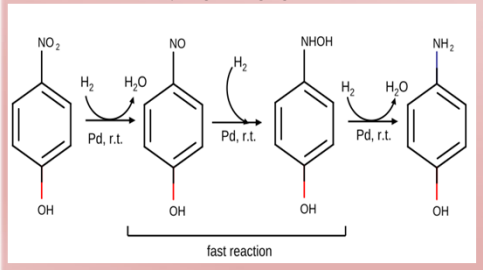
All catalysts preserve the bimodal pore system



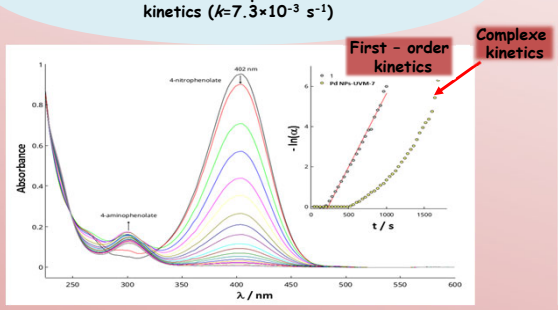
N_2 adsorption-desorption isotherms of the Pd NPs-UVM-7/PDA-n catalysts. (a) n= 1, (b) n= 2, (c) n= 3, (d) n= 4 and (e) n= 5

Catalyst activity

The catalytic activity of materials was tested against the hydrogenation of 4-nitrophenol using $(NEt_4)BH_4$ as the hydrogenating agent

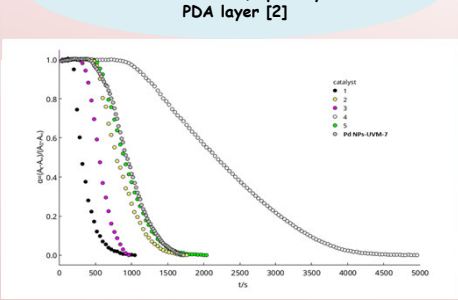


Plot of -ln(a) *vs.* time for materials Pd NPs-UVM-7/PDA-1 and Pd NPs-UVM-7. Pd NPs-UVM-7/PDA-1 shows pseudo-first-order kinetics (k=7.3×10^{-3} s^{-1})



Variation of absorbance during the reduction at room temperature of 4-nitrophenolate with $(Et_4N)BH_4$ catalyzed by material Pd NPs-UVM-7/PDA-1

The induction period is due to the oxidation of 4-aminophenol by the O_2 dissolved in medium, specially in the PDA layer [2]



a(t) values calculated from absorbance at 402 nm during the reduction at room temperature of 4-nitrophenolate with $(Et_4N)BH_4$ catalyzed by materials Pd NPs-UVM-7/PDA-n (n=1 to 5) and Pd NPs-UVM-7

Conclusions

We have synthesized a highly efficient catalyst that has been tested for the "model reaction" of hydrogenation of 4-nitrophenol using $(NEt_4)BH_4$ as the hydrogenating agent. The best catalyst is a composite based on isolated Pd NPs decorating the PDA/UVM-7 surface. Regardless the support nature, the TOF values achieved are among the best described in the bibliography. These excellent results open up the possibility of using these catalysts for other related reactions of industrial interest such as the reduction of nitroarenes.

References

[1] Alfonso Albiñana, P.; El Haskuri, J.; Marcos, M.D.; Estevan, F.; Amorós, P.; Úbeda, M.A.; Pérez-Plá, F. A new efficient, highly dispersed, Pd nanoparticulate silica supported catalyst synthesized from an organometallic precursor. Study of the homogeneous vs. heterogeneous activity in the Susuky-Miyaura reaction. *J. Catal.* 2018, *367*, 283-295.
[2] Lara, L. R. S.; Zottis, A. D.; Elias, W. C.; Faggion, D.; Maduro de Campos, C. E.; Acuña, J. J. S., Domingos, J. B. The catalytic evaluation of in situ grown Pd nanoparticles on the surface of Fe_3O_4@dextran particles in the p-nitrophenol reduction reaction. RSC Adv. 2015, *5*, 8289-8296.