Support Effect on Hydrogenation Reaction - Understanding the high activity of Pd supported on Graphene

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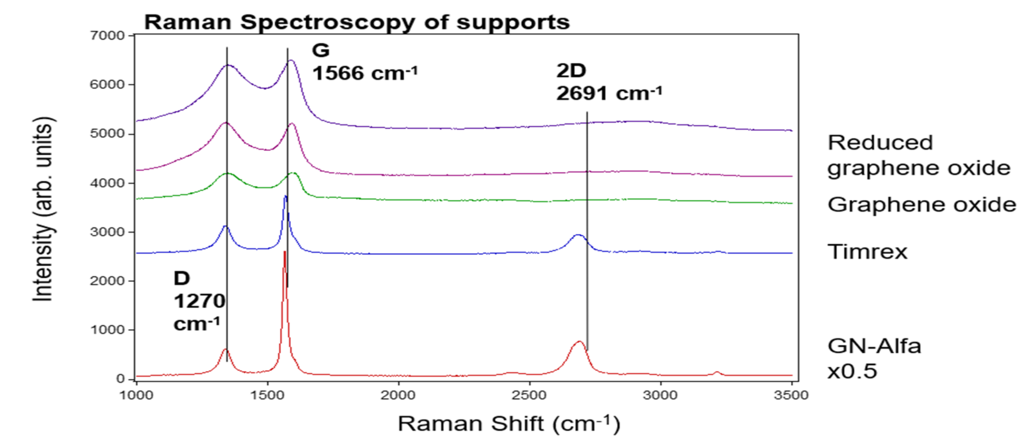
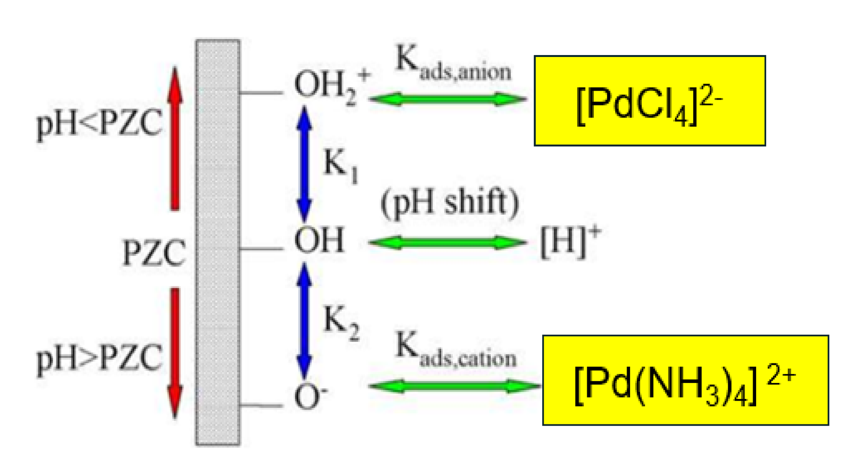
Introduction

- Pd supported on graphene has been explored in literature as catalyst for several reactions, including Suzuki coupling reaction where high TOF was observed using Pd on Graphene nanoplatelets (GN-Alfa) support.
- Our goal is to use strong electrostatic adsorption (SEA) method to synthesize well dispersed Pd catalysts on different supports (graphene and timrex which are highly graphitic, VXC-72 carbon, silica, and graphene coated silica).
- The catalyst were evaluated for toluene hydrogenation to methylcyclohexane (MCH) and Pd/GN-Alfa was found to give the highest activity.
- We have explored different sources of graphene while also coating graphene layers on silica to improve the activity of the silica. Raman spectroscopy was used to investigate the graphitic structure of the materials.
- We have also studied the effect of oxygen groups and the thickness of carbon layer on activity. We have also investigated metal precursor-chloride participation in the reaction.
- Overall, we hypothesize that the observed high activity of graphitic samples is due to their ability to intercalate hydrogen and make it available for hydrogenation.



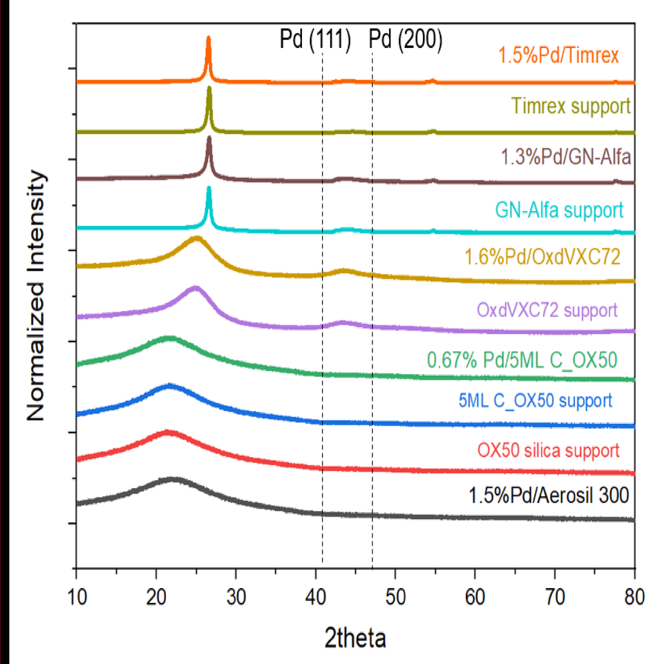
Catalyst Synthesis by Strong Electrostatic Adsorption

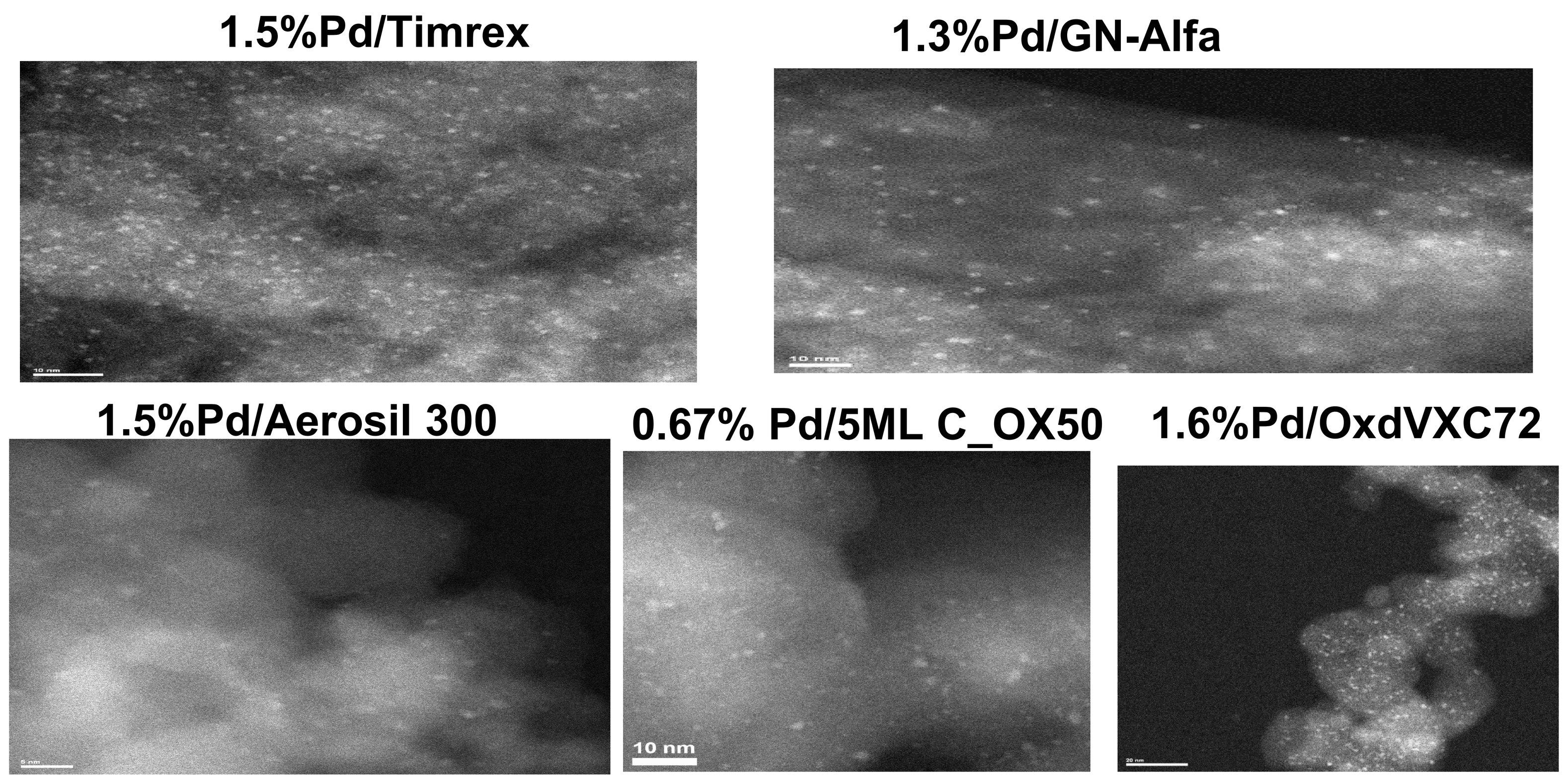


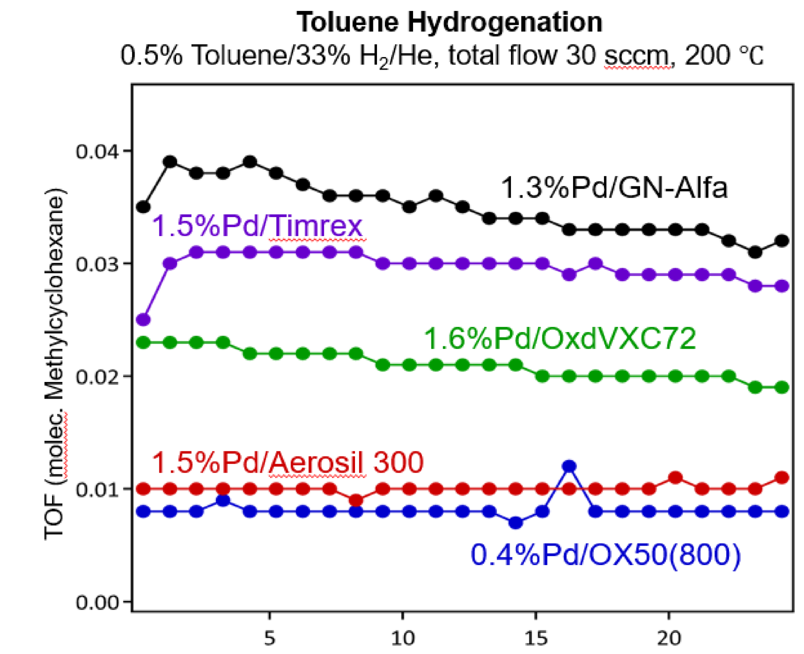
- Unless otherwise stated, cationic chloride-free palladium precursor (palladium tetraamine nitrate) was used for all synthesis, at pH 10.5-12

Results

- XRD and STEM showing well dispersed particles synthesized by SEA method.
- The most active catalysts for toluene hydrogenation are those on graphitic supports such as GN-Alfa and Timrex

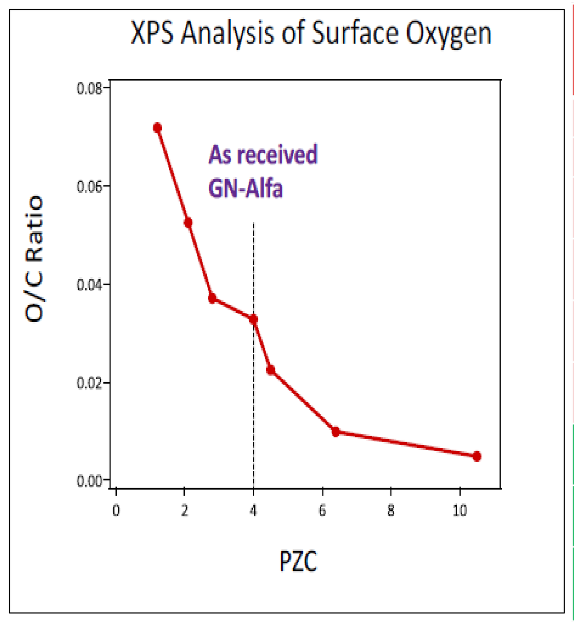




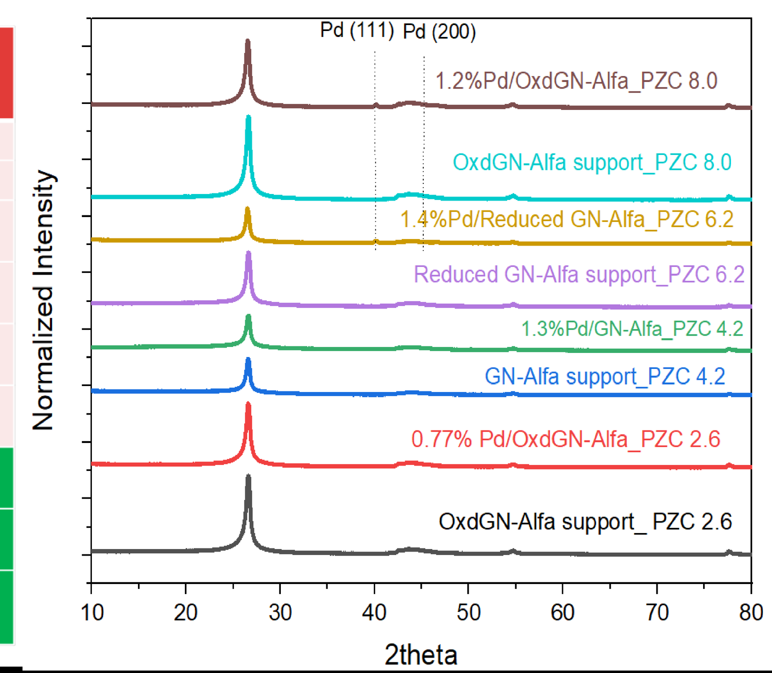


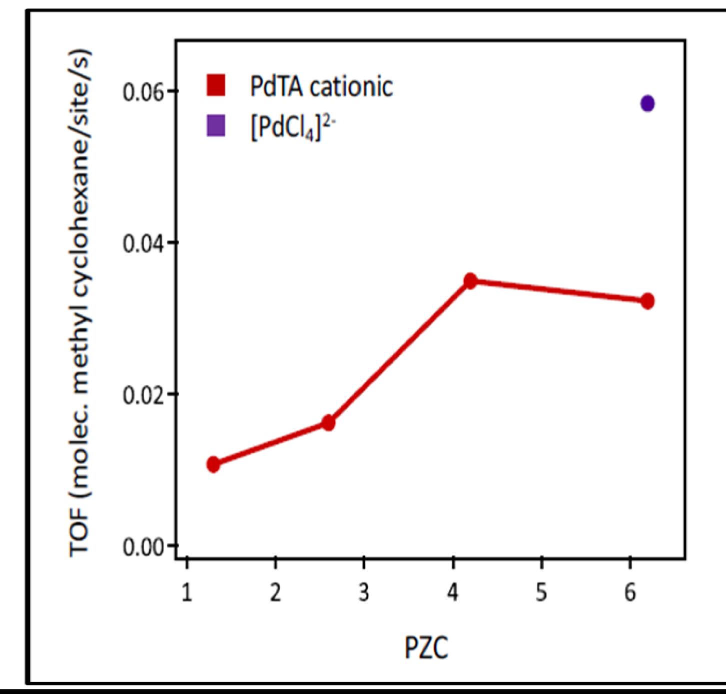
Effect of Functional Groups on Activity:

- From XPS, the amount of oxygen groups on GN-Alfa support has been shown to correlate directly with the point of zero charge of the support.
- The PZC of GN-Alfa support can be modified by oxidizing in nitric acid at 90^{0}C to get low PZC or by thermal reduction to take out oxygen groups and achieve high PZC.
- Palladium chloride stabilized in hydrochloric acid(5.6:1 molar ratio) was used to synthesize catalysts on the relatively high PZC supports (PZC 6.2 and 8.0). These high PZC catalysts showed obvious Pd peaks in XRD corresponding to larger sized particles.
- For the same PZC support (PZC 6.2) using Cl and Cl-free precursor, the TOF was higher showing evidence of chloride participation

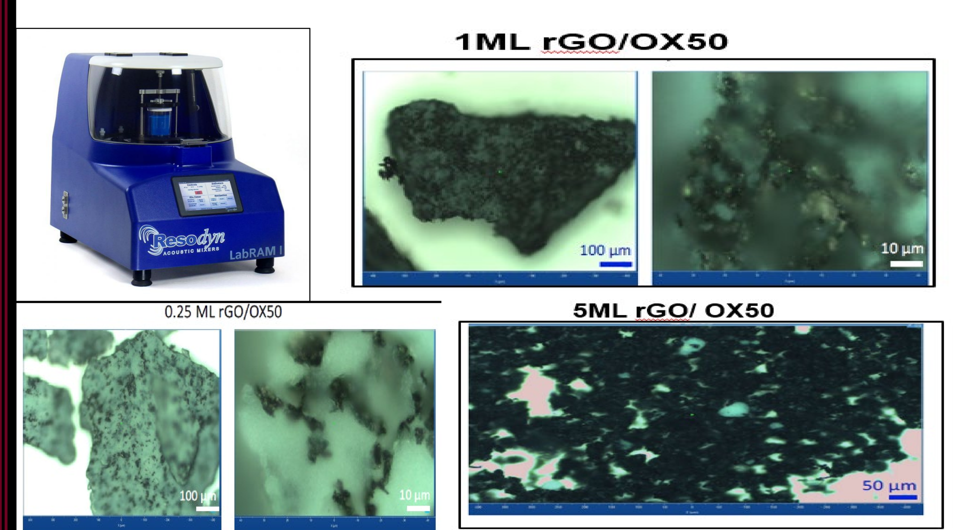


GN-Alfa Support Treatment Condition	Annealing Temperature	PZC	Surface Area (m^2/g)	Precursor Used	Metal weight loading
GN Alfa_as received	NA	4.2	496	$Pd(NH_4)_3(NO_3)_2$	1.3
GN Alfa + 15M HNO_3	NA	1.3	112	$Pd(NH_4)_3(NO_3)_2$	1.2
GN Alfa + 15M HNO_3 + 1hr 10%H_2/N_2	300	1.6	134	$Pd(NH_4)_3(NO_3)_2$	-
GN Alfa + 15M HNO_3 + 2hrs 20% H_2/N_2	400	2.6	-	$Pd(NH_4)_3(NO_3)_2$	0.8
GN Alfa + 15M HNO_3 + 2hrs 20% H_2/N_2	450	4.6	-	-	-
GN Alfa + 15M HNO_3 + 2hrs 20% H_2/N_2	500	8.0	-	H_2PdCl_4	1.2
GN Alfa + 2hrs 20% H_2/N_2	400	6.2	466	H_2PdCl_4	1.4
GN Alfa + 2hrs 20% H_2/N_2	500	9.0	-	-	-
GN Alfa 2hrs Argon	400	5.2	-	-	-

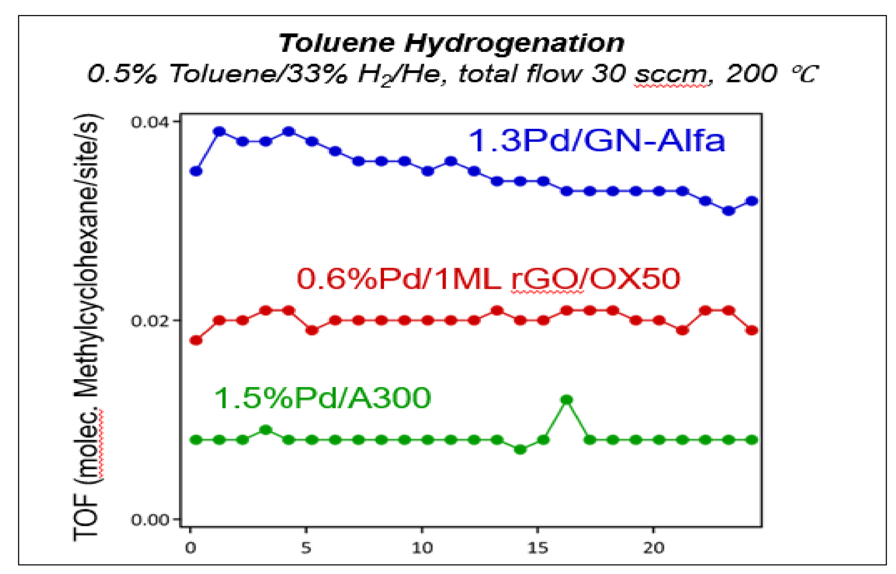




Coating Reduced Graphene Oxide (rGO) on OX50 silica by Resodyne Mixing-Improving the Activity of Pd/Silica

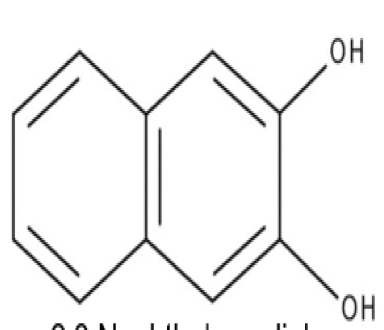


- The most uniform coverage was achieved at 1ML rGO coating.
- The 5ML rGO coating has the graphene layers sticking together and leaves large areas of silica uncovered.
- Catalyst was synthesized on the 1ML rGO support. The presence of the graphene improved TOF.
- Indeed, graphitic supports contributes to improved toluene hydrogenation activity

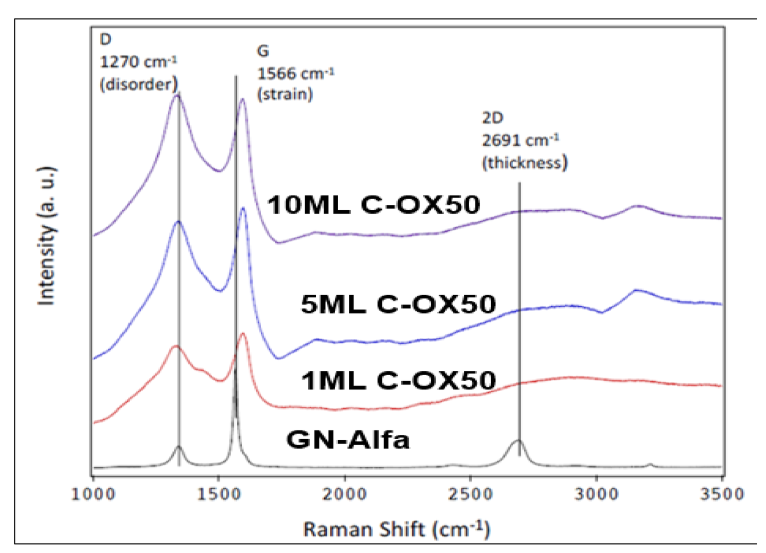


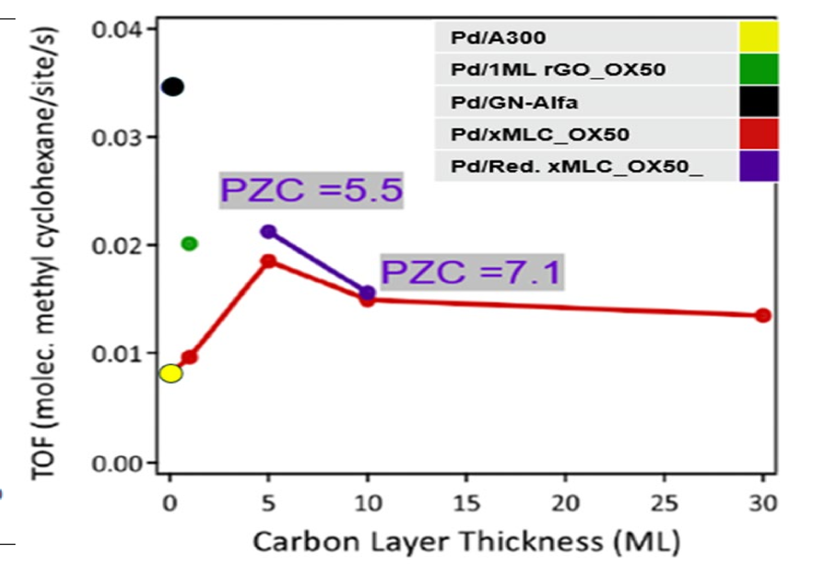
Coating of Graphene Layers on OX50 silica by Pyrolysis of 2,3 naphthalene diol

- So far, we have seen that the catalysts with the highest activity are those coated with graphene or are graphitic themselves.
- We have furthermore explored a cheaper source of graphene by dissolving 2,3 naphthalene diol in acetone, mixing with OX50 silica and pyrolyzing at 800C for 4hrs in inert. Raman spectroscopy confirms the presence of graphitic modes.
- We observed maximum activity was at 5ML coverage, with 2.3times higher TOF than OX50 silica but only 50% of the TOF of Pd/GN-Alfa was achieved.


2,3 Naphthalene diol

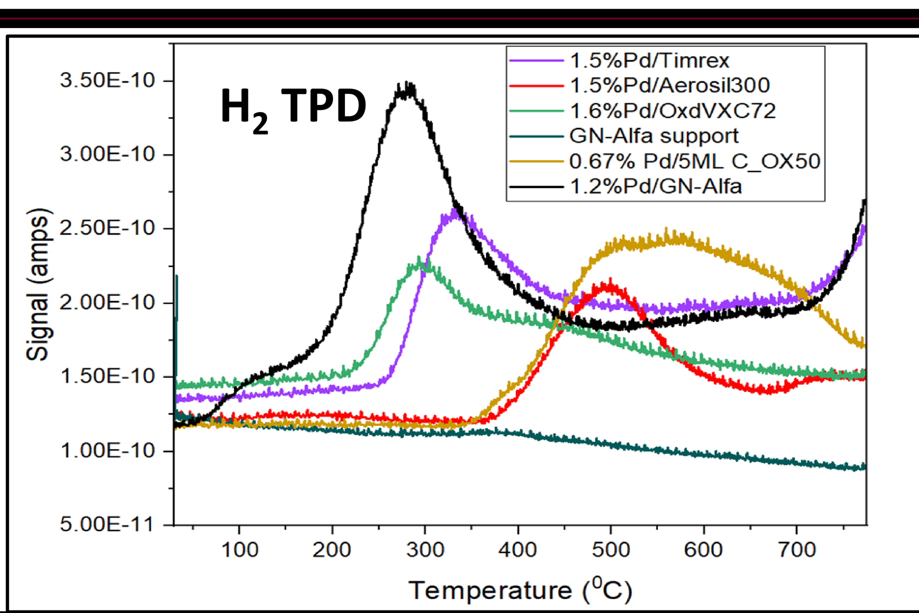
Support Treatment	Estimated Wt% Carbon prior to pyrolysis	Temp. (^{0}C)	PZC	Surface area B.E.T(m^2/g)
OX50	0%	NA	3.2	42.9
1ML C- OX50	2.5%	NA	3.8	41.4
5ML C-OX50	7.6%	NA	4.2	42.6
10ML C-OX50	13.8%	NA	4.3	41.5
30ML C-OX50	30.3%	NA	6.1	41.1
5ML C-OX50 + 20% H2/N2	7.6%	500	4.8	-
5ML C-OX50 + 20% H_2/N_2	7.6%	1000	5.5	16.4
10ML C-OX50	13.8%	1000	7.1	25.6
30ML C-OX50 + 20% H_2/He	30.3%	300	6.1	20.8
30ML C-OX50 + 20% H_2/He	30.3%	500	7.7	

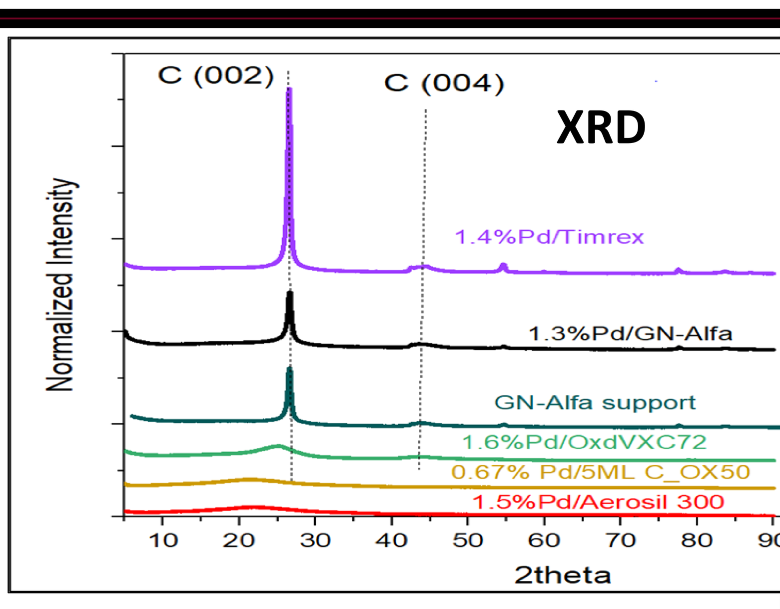




Summary of the Activity of all Catalysts Evaluated

- Pd/GN-Alfa > Pd/Timrex > Pd/OxdVXC72 >5ML C_OX50 > Pd/1ML rGO/OX50 >Pd/Silica.
- Interestingly, the three most active catalysts exhibited low temperature hydrogen desorption (below 350^{0}C) confirming that the ease of desorption of hydrogen improves TOF.
- The XRD of these three catalysts (VXC72 inclusive) also showed 2 peaks peculiar to graphitic materials. Our final goal is to confirm the extent of graphitization of VXC72 using Raman spectroscopy





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