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amateur experimentalism

Replacement of Palladium on carbon by powdered catalytic converter for hydrogenation reactions.

Chemistry Science

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INTRODUCTION

Catalytic hydrogenation is a useful and relatively common chemical reaction in organic synthesis, usually used to hydrogenate alkenes. The catalyst of excellence for these reactions is 5% palladium on carbon. These catalysts are usually not difficult to buy or make, and it's reasonable amateur accessible, however in some cases palladium on carbon can be hard to obtain. Personally, in Argentina is not something easy to obtain. The goal of these report is to report on the efficacy on the replacement of palladium on carbon by powdered catalytic converters from cars for 3 reactions.

EXPERIMENTAL PART

Reagents

- _ Methylene Blue [Cicarelli]
- _ Nitrobenzene [Lab grade, distilled]
- _ Aniline [Synthesized]
- _ Hydrogen Peroxide 250v [Tech. Grade]
- _ Sodium Hydroxide 98% [Tech. Grade]
- _ Ethanol 96% [Pharmacological]
- _ Isopropanol [Todo Droga Lot: 2020081701] (density: 0.783 g/mL)
- _ Hydrochloric acid (10.0 ± 0.1) M [Tech. Grade, colorless]
- _ Beta-Naphthol [Sigma Lot: 80H3402]
- _ Sodium Nitrite [Pura Química lot: 89163824uo]
- _ Double-Distilled Water [Pura Química Lot:18-12]
- _ Methanol [Tech. Grade]

_Cinnamyl Alcohol [Lab. Grade]

_Petroleum Ether [Cicarelli Lot:73314] (Recycled)

_Elemental Bromine [Synthesized]

Apparatus and procedures

Photo colorimeter [Crudo Caamaño]

Photo colorimeter Crudo Caamaño



Methods

Catalyst Activation

Catalytic converters from cars are in charge of destruction of nitrogen oxides and left gasoline from the motor exhaust, so they become contaminated with gasoline, oil, and some iron. These contaminants can slow the catalyst action, and or contaminate the reaction, so a couple of washings were made to remove as much as these contaminants as possible.





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To an arbitrary amount of powdered catalyst in an Erlenmeyer flask, methanol was added to completely cover the catalyst and have an excess of methanol, these was left to sit for 12hs. After 12hs the catalyst was filtered, and washed with a little methanol. These operations were repeated for 6hs instead of 12, and the catalyst dried on a hotplate.

Methanol Washes [Fist on left, last on right]



The methanol washed catalyst was covered with an excess of approx. 8M hydrochloric acid, and left to sit for 12hs, after which it was filtered and washed with Double-distilled water. [Filtered acid was yellow]

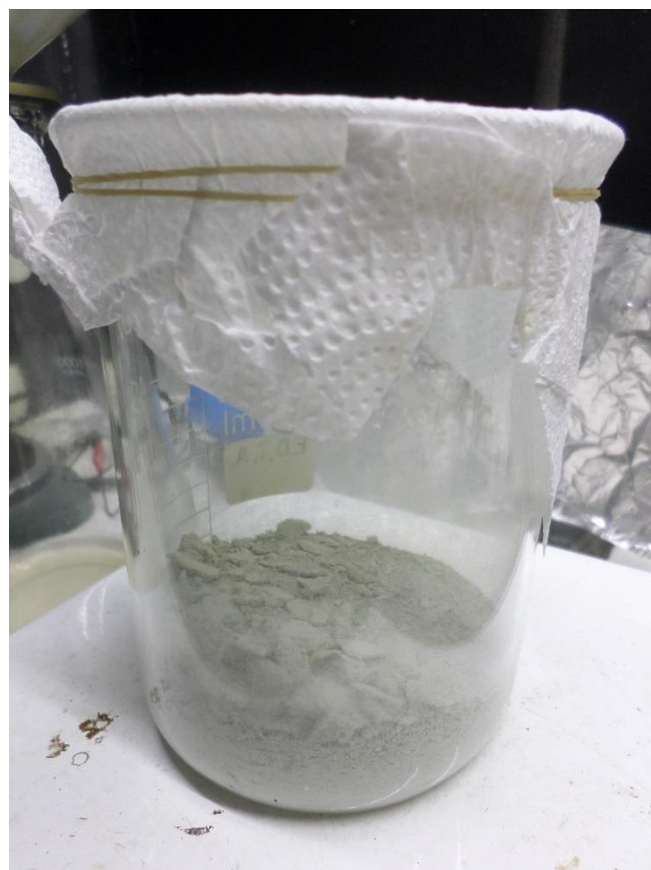
The damp catalysts was mixed with 500mL of double-distilled water and 10ml of 10M HCl, and was boiled until 200mL of volume were lost, after which it was filtered and washed with double-distilled water and ethanol.

Filtered solution from boiling.



The catalyst was heated in a beaker over a hotplate to 120°C overnight.

Catalyst drying on hotplate.



After these procedures the catalyst was saved and labeled as “Activated Catalyst”





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Activated Catalyst [left] Vs Crude Catalyst [right]



Hydrogen generator apparatus.

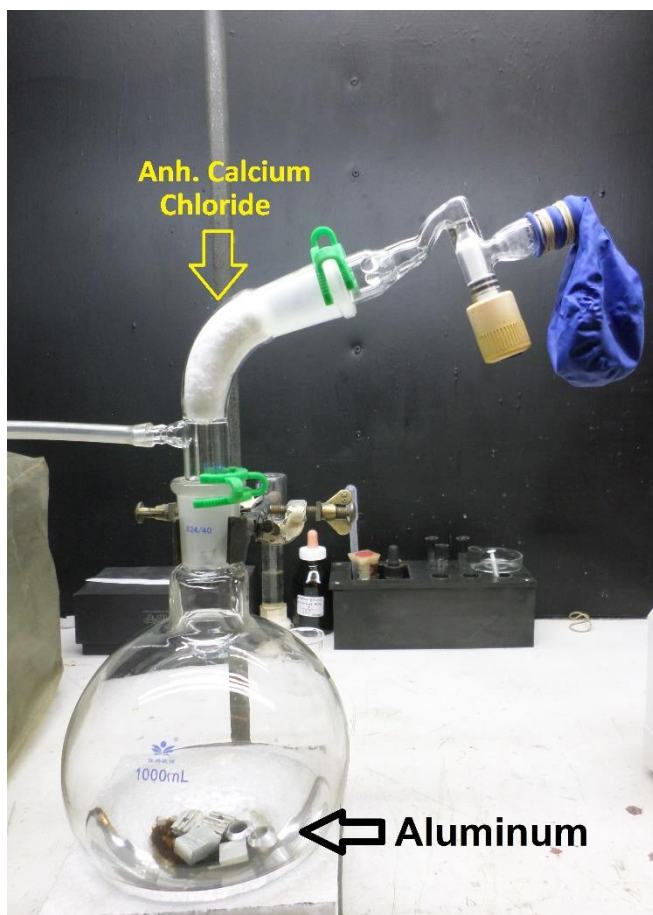


After NaOH is added to the RBF, vacuum is applied, and then the apparatus isolated, and hydrogen is collected in the balloon, until approx. 1L of hydrogen is collected.

Hydrogen Generator

Hydrogen was generated by the reaction of aluminum with aqueous sodium hydroxide, in a 1L RBF connected to vacuum and a balloon, as shown in the following image.

Hydrogen generator apparatus.



Hydrogenation-Reduction reactions.

Methylene blue Reduction.

First, 2 solutions of Methylene blue (MB) were prepared.

Solution 1: Consisting of (11 ± 2) mg of MB in $(250,0 \pm 0,2)$ mL of double-distilled water.

Solution 2: Consisting of $(25,00 \pm 0,06)$ mL of Solution 1 in $(250,0 \pm 0,2)$ mL of double distilled water.

In a 250mL Schlenk RBF, (100 ± 1) mL of Solution 2 were mixed with $(2,5 \pm 0,2)$ g of inactivated catalyst, a stir bar and connected to the hydrogen balloon and vacuum.

A control reaction was made with (50 ± 1) mL of solution 2 and $(1,2 \pm 0,2)$ g of inactivated catalyst.





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Apparatus for Methylene Blue reduction.



The RBF was connected to vacuum for 2 min, filled with hydrogen, pull vacuum again and finally left with hydrogen and stirring.

The reaction only took 10 minutes to go colorless. After these the absorbance was measured.

Reaction[left] and control [Right]



Nitrobenzene to aniline

In a 250mL Schlenk RBF (50±1) mL of isopropanol were mixed with (1,5±0,4) mL of nitrobenzene and (4,0±0,2) g of inactivated catalyst along with a stir bar.

The RBF was connected to vacuum and a hydrogen balloon.

A control reaction consisting of (50±1) mL of isopropanol, (1,5±0,4) mL of nitrobenzene and (4,0±0,2) g of inactivated catalyst in a Erlenmeyer flask.

Reaction [left] and Control [Right]



The reaction flask was connected to vacuum for 2-3 min, filled with hydrogen, set to vacuum and finally let with hydrogen and stirring.

The reaction started 02/02 at 18:40hs., and stopped 06/06 at 10:30hs.





Both reaction and control were filtered and tested for the presence of Aniline.

Cinnamyl alcohol hydrogenation

Inactivated Catalyst:

In a 250mL Schlenk RBF, (5,0 \pm 0,2) g of cinnamyl alcohol were mixed with (2,5 \pm 0,2) g of inactivated catalyst, and 50 mL of ethanol as solvent.

The RBF was connected to vacuum and hydrogen as in previous examples.

The reaction flask was connected to vacuum for 2-3 min, filed with hydrogen, set to vacuum and finally let with hydrogen and stirring.

The reaction was started on 08/06 at 23:30hs and stopped on 09/06 at 21:20 hs

After which the mixture was filtered, and diluted with ethanol to a final volume of (100,0 \pm 0,2) mL. These was analyzed by TLC and titrated with aqueous bromine.

Activated Catalyst:

In a 250mL Schlenk RBF, (2,5,0 \pm 0,2) g of cinnamyl alcohol were mixed with (2,5 \pm 0,2) g of inactivated catalyst, and 50 mL of ethanol as solvent.

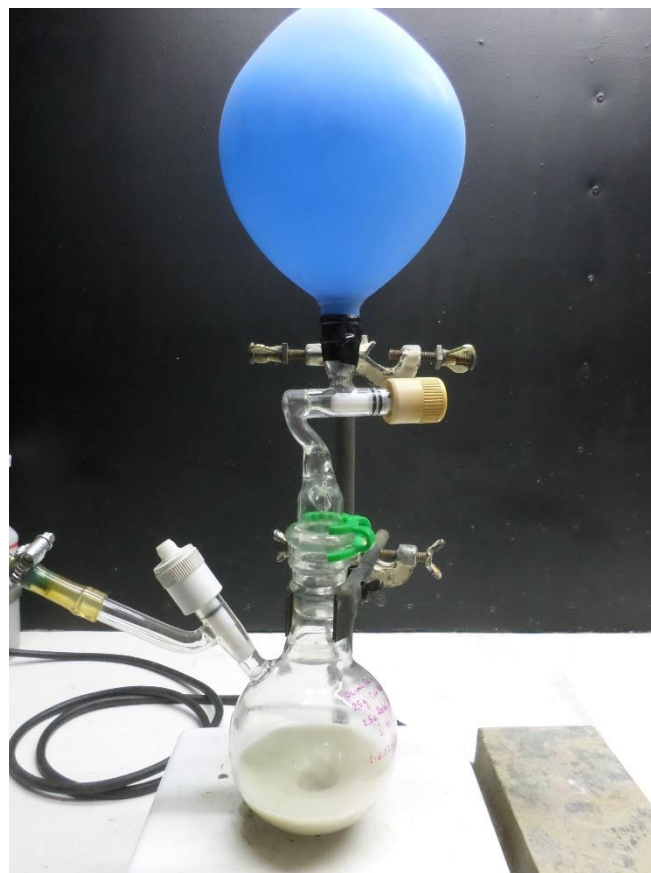
The RBF was connected to vacuum and hydrogen as in previous examples.

The reaction flask was connected to vacuum for 2-3 min, filed with hydrogen, set to vacuum and finally let with hydrogen and stirring.

Total reaction time was 31hs 30min.

After which the mixture was filtered, and diluted with ethanol to a final volume of (100,0 \pm 0,2) mL. These was analyzed by TLC and titrated with aqueous bromine.

Cinnamyl alcohol hydrogenation with activated catalyst.



RESULTS AND DISCUSSION

Methylene Blue Reduction

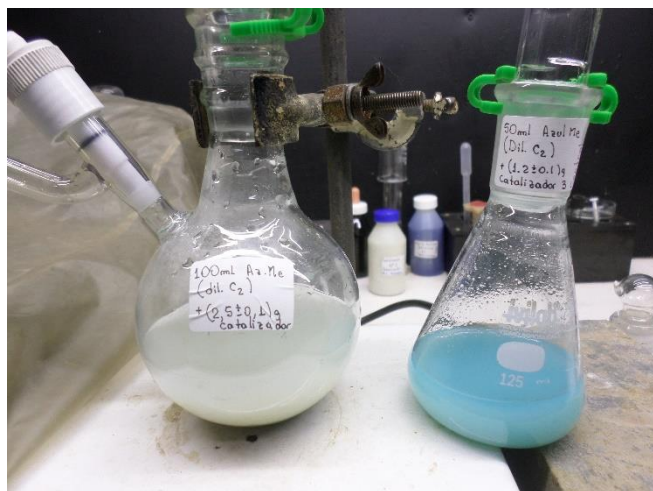
The idea of using methylene blue, was to test if the catalytic converter was useful as a Hydrogenation Catalyst, since methylene blue is a blue color in the oxidized form, and colorless in the leuco reduced form. The idea was inspired from the paper "Hydrogenation/Oxidation induced efficient reversible color switching between methylene blue and leuco-methylene blue." [1].

On the example of these report, methylene blue was reduced to colorless in less than 10 minutes.





Reduced Methylene blue [left] and control [Right]



Addition of hydrogen peroxide to the reduced methylene blue gave back the blue color.

Given the low concentration of Palladium on the catalyst (From other work with these catalyst) , the reaction was expected to be slow, and hence the set of the photo colorimeter.

It was quite the surprise when the reaction went colorless in just less than 10 minutes. Non the less the absorbance was measured at $\lambda=670\text{nm}$, after filtering the reaction and control.

Reaction: Abs= 0,07

Control: Abs= 0,11

Solution 2: Abs=0,24

The set of a control reaction was made to discard effect's like, contaminant's, adsorption on the catalyst, and unexpected interferences. The difference in absorbance between the Control and Solution 2 seems to confirm these was a good thing to have.

Nitrobenzene

The reduction of nitrobenzene to aniline with the use of palladium catalyst is mentioned in "Palladium nano-catalysts encapsulated on porous

silica @ magnetic carbon-coated cobalt nanoparticles for sustainable

hydrogenations of nitroarenes, alkenes and alkynes" [2].

After the 87hs of reaction, hydrogen adsorption was not observed, and the reaction was stopped and filtered.

To test the presence of aniline a Azo-coupling reaction was done with beta-naphthol in the following manner.

Solution A: HCl [$0,50\pm0.01\text{M}$]

Solution B: Beta-naphthol: approx. 100mg.

Sodium Hydroxide: 2,1g

Double-Distilled water: 100mL (Final Volume)

Solution C: Sodium Nitrite: approx. 100mg

Double-distilled water: 100mL (Final Volume)

Test step's:

1] 3 mL of solution A is mixed with 1 mL of solution C, and 1 or 2 drops of the substance under test on a test tube at 0°C and left it for 2-3 min.

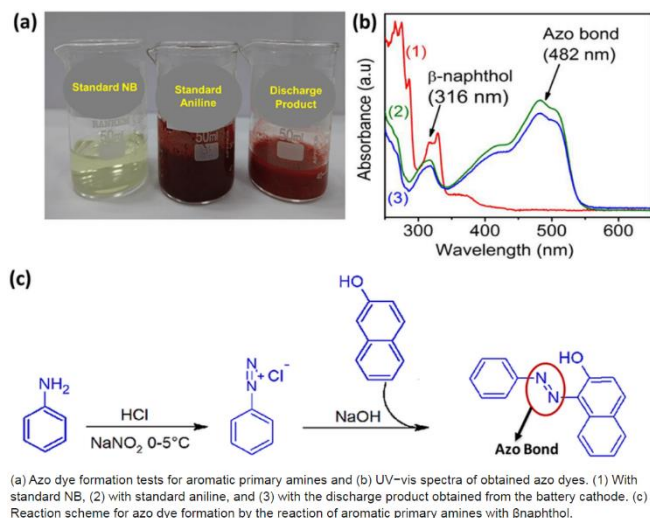
2] To the previous cold mixture, 2mL of solution B is added





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Aniline-beta naphthol azo dye reaction scheme. Doi:
[10.1021/acssuschemeng.8b03486]



Results:

If aniline is present a vivid orange precipitate is observed.

Results of Aniline test.



Unfortunately, TLC plates were not available when these reactions were done. However, this reaction was not expected to work on the first place, and this analysis was enough to not pursue this reaction anymore.

A consequence of the hardness of the catalyst and the long reaction time was the loss of the stir bar.

Worn stir bar.

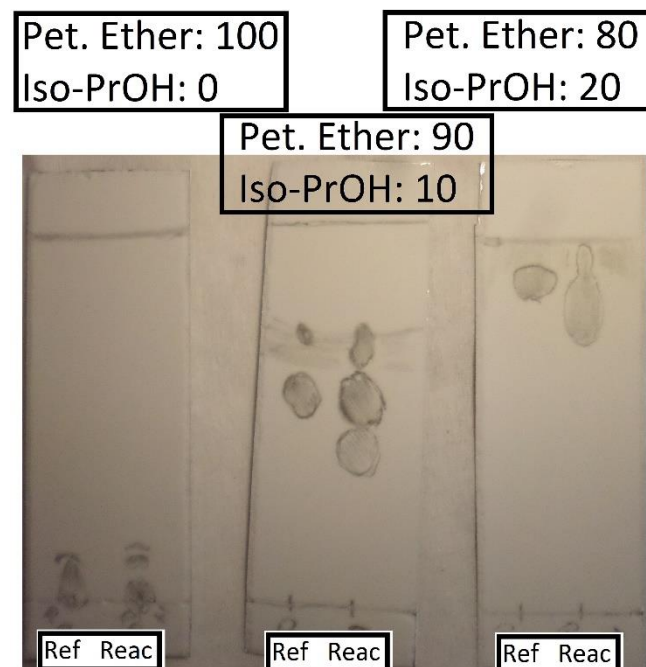


Cinnamyl Alcohol

To check the progress of the cinnamyl alcohol hydrogenation TLC was performed.

The Solvent system was a mixture of petroleum ether and isopropanol. The first 3 TLC runs were used to find the best eluent mixture.

TLC test to find the best eluent mixture.



The eluent mixture of choice was Pet.Ether/IPR (90:10).

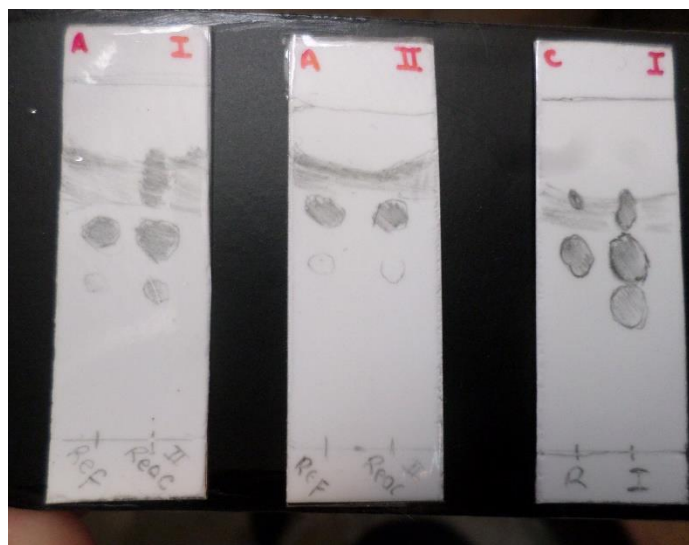
The TLC for both reactions are shown below.





TLC of Reactions.

A: Activated Catalyst.; C: Crude Catalyst.



The TLC shows a new product forming, but it's not conclusive. The eluent seems to have some impurity, and the cinnamyl alcohol is not pure.

A crude Bromine titration was performed to compare results.

Bromine Titration:

A solution of $(3,0 \pm 0,2)$ g of elemental bromine, with some Sodium Bromide was dissolved in $(100,0 \pm 0,1)$ mL of double-distilled water (Bromine Water Solution)

A Reference solution was made by dissolving (262 ± 2) mg of cinnamyl alcohol in $(25,00 \pm 0,06)$ mL of ethanol. (Reference Solution)

Results:

$(5,00 \pm 0,04)$ mL of reference solution reacts with $(1,9 \pm 0,2)$ mL of Bromine water solution.

$(2,00 \pm 0,02)$ mL of Crude catalyst reaction reacts with $(2,7 \pm 0,2)$ mL of bromine water solution.

$(2,00 \pm 0,02)$ mL of Activated catalyst reaction reacts with $(1,2 \pm 0,2)$ mL of bromine water solution.

Reference solution [Left] Bromine Water [Right]



Using these results, it's possible to extrapolate the cinnamyl alcohol content in the reactions, for the Crude catalyst reaction the content of cinnamyl alcohol is $(3,7 \pm 0,4)$ g which represents a conversion of 1,3g of the 5g.

The Activated catalyst contains $(1,6 \pm 0,5)$ g of cinnamyl alcohol, which represents a conversion of only 0,4g.

These results suggest that in these cases, catalyst activation was not beneficial, the palladium content was probably reduced and therefore the reaction speed reduced to.

The particular catalytic converters used were known to have small palladium content, and the activation procedure while it did get rid of





contaminants, it also reduced the palladium content on the particularly bad catalyst I had access to.

CONCLUSIONS [≤10 Lines]

The use of Powdered catalytic converter as a substituent of palladium on carbon seems to be possible in some cases, however the palladium content of the catalyst should be check.

Also, the wear on the glassware and stir bar should be taken to account.

BIBLIOGRAPHY

[1] "Hydrogenation/Oxidation induced efficient reversible color switching between methylene blue and leuco-methylene blue"

[doi: 10.1039/c7ra04498d]

[2] "Palladium nanocatalysts encapsulated on porous silica @ magnetic carbon-coated cobalt nanoparticles for sustainable

hydrogenations of nitroarenes, alkenes and alkynes"

[doi: 10.1002/cctc.201901371]

