Bio Adipic Acid Production from Sodium Muconate and Muconic Acid: A Comparison of two Systems

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sodium muconate and *trans,trans*-muconic acid were heterogeneously hydrogenated to adipic acid, a strategic intermediate for the industry of polyamides and high performance polymers. Hydrogen pressure, metal to substrate ratio, substrate concentration and reaction temperature were varied to study the effect of these parameters on the reaction products. Commercial Pd/AC 5% was used as catalyst and characterized by TEM, BET and XPS analyses. The results revealed that temperature is the parameter which mainly affect the reaction. Moreover, hydrogenation of *trans,trans*-muconic acid is faster than sodium muconate reduction. Full conversion and full yield toward adipic acid was obtained using *trans,trans*-muconic acid as substrate after 60 min at the following operating conditions: temperature = 70 °C, metal/substrate = 1/200 (mol_{Pd}/mol_{sub}), *trans,trans*-muconic acid concentration = 1.42E-02M and hydrogen pressure = 1 bar. In all reactions (2E)hexenedioic acid was detected as main intermediate.

Introduction

Greenhouse gasses are causing several damages in terms of global warming, raising in temperature and unusual weather events.[1] Moreover, the wastes produced from industries and their disposal are one of many problems that the modern society has to deal with to not compromise the future of the new generations.[2]

Many companies are trying to convert their traditional production to a more environmental sustainable manufacture[3] following the recommendations of many European projects and regulations. In this sense one of the most important topic is the use of renewable resources to produce high added value chemicals.[4] Adipic acid (AdA) is drawing the attention of industry due to its versatility and its use in a lot of applications.[5,6] AdA is a dicarboxylic acid and one of the most required bulk chemicals. Its market size is evaluated at 5.56 billion of USD in 2016[7] and its global demand is continuously growing (4 %). AdA is mainly used for the production of polyamides such as nylon-6,6[8] in packaging[9] and automotive[10] industries. The traditional production of AdA involves the strong oxidation of a mixture composed by cyclohexanol and cyclohexanone derived from oil treatment. This mixture, called KA oil, is oxidized with concentrated nitric acid at 80–90 °C.[8] The conversion of KA oil is complete while the AdA yield (Y) is about 93–95 %. Upon reaction, nitric acid is reduced to nitrogen oxides: NO_2, NO, N_2O, and N_2.[11] These dissolved oxides are stripped from the reaction product using air in a bleaching column and subsequently recovered as nitric acid in an absorption tower.[12,13] Nitrous oxide is a well-known greenhouse gas due to its strong infrared absorption. Although it is non-toxic it seems to have a number of recognized ill effects on human health, whether through breathing it in or by contact of the liquid with skin or eyes.[14,15] In the troposphere it also acts as a catalyst in the cycles of ozone destruction, contributing to its decline. Before the introduction of the most recent N_2O abatement technology, AdA plants alone were the responsible of the 10% of anthropogenic nitrous pollution worldwide.[16] To overcome the problem of greenhouse gasses, researchers are trying new production strategies for the syn-thesis of AdA from renewable resources.

For example, it is possible to produce AdA from waste woods. In particular a two steps biological-chemical process was consid-ered worth of more detailed investigation for its good yields and sustainability potential.[17] This process consists in a first fermenta-tion step to produce muconic acid (MA), which is in its sodium muconate (Na-Muc) form due to the alkalinity of the fermentation broth, starting from either glucose (from cellulose)[18] or benzoic acid (from lignin).[19] The conversion of glucose or benzoic acid to Na-Muc occurs thank to modified bacteria strains of *Escherichia Coli* or *Saccharomyces Cerevisiae*.[20,21]

The so produced Na-Muc is purified to produce MA which is catalytically hydrogenated to AdA. The purification of Na-Muc involves the use of highly acidic environment that isomerizes the *cis,cis* substrate to the *trans,trans* MA compound, but it is necessary for the obtainment of a substrate with a purity

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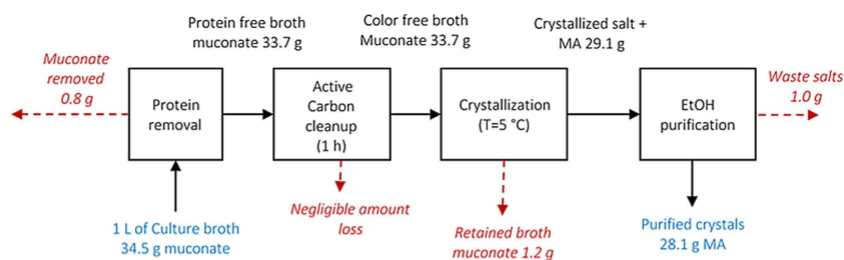
Scheme 1. Process for the recovery of t,t-MA from Na-Muc in the fermentation broth.

> 98 %.[22] Also, it has been extensively proven that both *cis,cis* and *cis,trans*-MA tend to isomerize to *trans,trans*-MA (t,t-MA) in the presence of metals that strongly bind hydrogen molecules.[23,24] On the other side MA has a low solubility in water respect to its salified form.

Both t,t-MA and Na-Muc have been used as substrate to study the hydrogenation reaction for bio-AdA production. In a recent paper Vardon et al. reported the steps for the recovery (Scheme 1) of MA achieving a purification yield of 81.4 % with a MA final purity of 99.8 %. The hydrogenation was performed using c,c-MA in ethanol and Pd/AC commercial catalyst at 24 bar, 24 °C .[17]

Previously, different supported Rh catalysts were tested for c,c-MA hydrogenation as well, obtaining a selectivity > 90% and conversion > 95 % in 5 h, but it required 69 bar of hydro-gen pressure, high temperature (210 °C), and a toxic solvent ie methanol.[25] In our previous work we tested the hydrogenation of sodium muconate using commercial Pt/AC 5 % at low temperature (50–70 °C) and hydrogen pressure (4 bar) using water as reaction medium. After 2 h full conversion and selectivity towards AdA were reached.[26] Pd/AC was identified from Vardon et al. as a highly active catalyst for AdA production from MA using ethanol as solvent.[27] The authors performed the reaction at 25 °C and 24 bar of hydrogen obtaining full conversion and AdA yield of 97% after 40 min.

In this work, we examine and compare the catalytic hydro-genation of Na-Muc and t,t-MA for the production of bio-AdA

under mild operating conditions, using commercial Pd/AC (5% wt/wt loading) as catalyst.

We decided to consider two substrates because several studies showed the possibility to produce AdA from both. In fact, after the fermentation step, the culture broth is deacti-vated and Na-Muc is obtained.[28] Performing the hydrogenation reaction on this substrate, sodium adipate is produced and can be further purified and transformed into AdA. On the other hand, Na-Muc produced in the fermenter can be firstly crystalized to t,t-MA, that can be directly hydrogenated to AdA. In both cases the crystallization step involves an acidic environ-ment (HCl in ethanol) as described by Vardon et al.[28] Since the same purification step is required for the two substrates, this study aims to establish which one is the most suitable for the bio production of AdA. Particular attention will be devoted on how the operating parameters (pH, hydrogen pressure, sub-strate concentration and temperature) can affect the behavior of the reaction which was performed at mild pressure and temperature. This choice allows to make the reaction safer for a future scale-up. Hydrogenation reaction of both Ma and Na-Muc occurs with the formation of two different monounsatu-rated intermediates (2E)hexenedioic acid ((2E)HxAc) and (3E) Hexenedioic acid ((3E)xAc) (Scheme 2). Substrate conversion and products selectivity were evaluated using UV-Vis and GC analysis, respectively.[29]
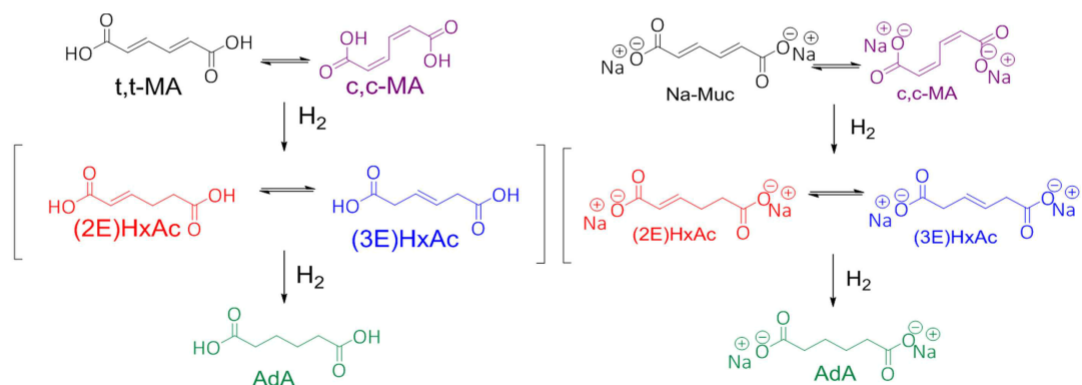
Scheme 2. Hydrogenation reaction of Na-Muc (left) and t,t-MA (right) to AdA.

Results and Discussion

Commercial Pd/AC 5% was characterized by BET, Transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). This catalyst was used for the hydrogenation of Na-Muc and t,t-MA varying hydrogen pressure, metal/substrate ratio, substrate concentration, and temperature.

Fresh Catalyst Characterization

Brunauer-Emmett-Teller (BET) method was utilized to measure the surface area of fresh Pd/AC 5 % commercial catalyst which is 812 m^2/g. The desorption pore diameter was evaluated using BJH method[30] and the result is 3.8 nm. The total pore volume for pores with diameter less than 147 nm (at P/P0 = 0.9868) is 0. 73 cm^3/g, while using the DR method[31] the cumulative desorption pore volume is 0.36 cm^3/g. TEM analysis was used to evaluate the particle size distribution and the metal dispersion. The results shows that metal Pd nanoparticles are well dispersed on the carbon support and counting 200 different particles their average size is 3.1 � 1.0 nm (Lognormal distribution) (Figure 1).[32]
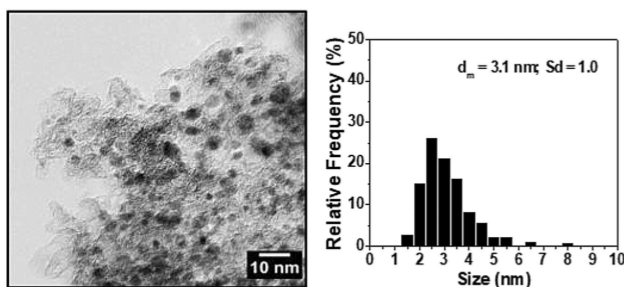

Figure 1. Representative TEM micrograph and particle size distribution of fresh Pd/AC 5 %.

The oxidation state of Pd and Pd surface exposure was studied by XPS analysis that revealed the presence of two Pd species (Figure 2). In particular Pd displays two peaks due to the Pd 3d$_{3/2}$ and Pd 3d$_{5/2}$ transition. Pd(0) 3d$_{5/2}$ core electron binding energy is at 335.6 eV, while the Pd(0) 3d$_{3/2}$ is at 340.54 eV. The Pd(II) peaks are at 343.46 and 338.18 eV, and they are identified as 3d$_{3/2}$ and 3d$_{5/2}$ transition, respectively. These binding energy values are in good agreement with that data reported in Chen et al.[32] and Sanchez et al.[33] Fresh Pd/AC 5% catalyst is equally composed by Pd oxide and Pd metal. The ratio between Pd and Pd(II) for the 3d$_{5/2}$ and 3d$_{3/2}$ configurations are 1.14 and 1.12, respectively while the Pd exposure at the surface is equal to 5.0%.

Hydrogenation of Sodium Muconate

Na-Muc was firstly hydrogenated because it is the first compound which is produced during the conversion of glucose
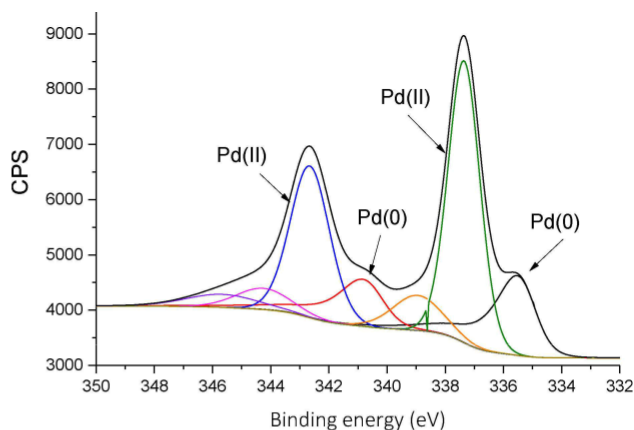

Figure 2. Fitted XPS spectra of Pd 3d core level for fresh catalyst.

to MA. In particular Na-Muc derives from the fermentation tank in which sodium hydroxide is used to control the pH of the broth culture.[27]

Hydrogen pressure was varied from 1 to 3 bar keeping constant the substrate concentration, the metal/substrate ratio, and temperature. The initial activity was calculated as mol of sodium muconate converted per mol of Pd per second as reported in Eq.4.

Increasing the pressure from 1 to 3 bar the initial activity is at similar range (0.26 0.3 s^{-1}) (Figure 3), while AdA yield
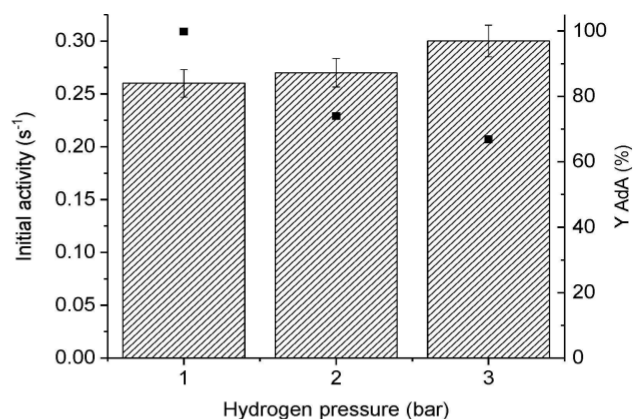

Figure 3. Initial activity (bar) and Y AdA (square) for Na-Muc hydrogenation calculated at 10 min and 120 min, respectively, for different pressures. T = 70 °C, stirring = 700 rpm, metal/sub = 1/200 (mol$_{Pd}$/mol$_{sub}$), and [Na-Muc] = 1.42E-02M.

strongly depends from this operating parameter. After 120 min of reaction all the substrate is converted, but only at 1 bar a full yield toward AdA is reached (Figure 3 and 1SI). This behavior might be explained considering that the higher the pressure, the higher solubility of hydrogen and thus the higher is the hydrogen adsorption on the active site that might interfere with the adsorption process of other species. The main intermediate produced during the reaction is the (2E)HxAc,

which is largely formed during the first 60 min of reaction (Figure 2SI). Considering these results, it is preferably to work at pressure as low as possible to increase AdA yield (Figure 3SI) and for safety and economic reasons.

In the second test, metal/substrate molar ratio was varied from 1/200 to 1/700 (mol_{Pd}/mol_{sub}). Initial activity is similar for all the considered metal/substrate ratio (0.28 s[1], 0.33 s[1], 0.32 s[1], for 1/200, 1/500 and 1/700, respectively) (Figure 4). The

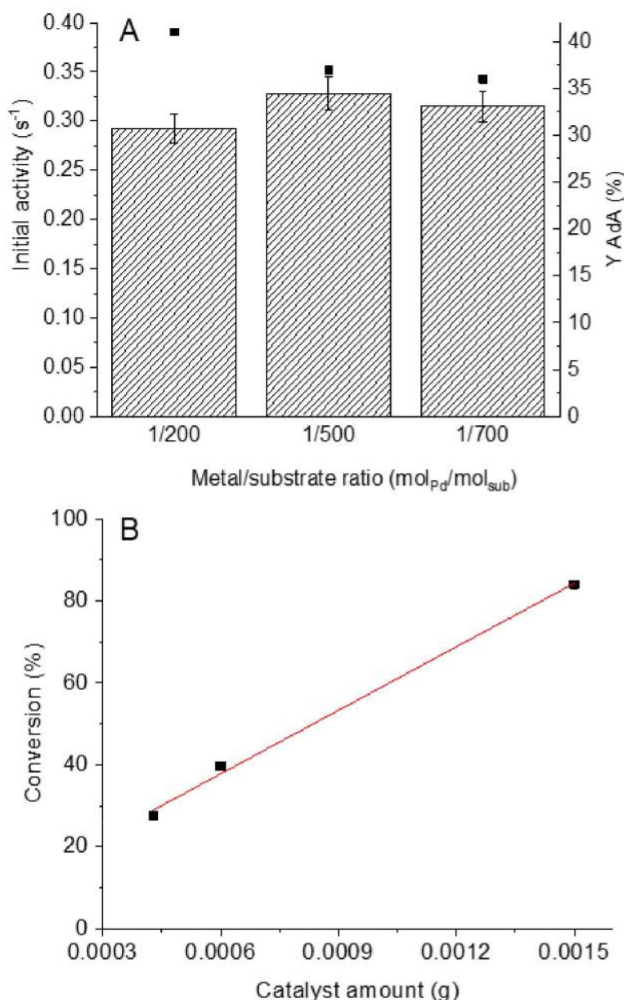**Figure 4.** A) Initial activity (bar) and Y AdA (square) for Na-Muc hydrogenation calculated at 10 min and 60 min, respectively, for different metal/substrate ratio. B) Na-Muc conversion at different amount of catalyst. T = 70 °C, stirring = 700 rpm, [Na-Muc] = 1.42E-02M, and P(H$_2$) = 1 bar.

reaction works under kinetic regime because the conversion linearly increases with the amount of catalyst (Figure 4B), and therefore the initial activity based on mole of Pd metal is constant.

Na-Muc conversion and AdA yield slightly depend on the metal/substrate molar ratio. The best results were obtained using a ratio of 1/200 by which 99 % of conversion and 41% of AdA yield are reached after 60 min of reaction (Figure 4SI).

Afterwards, the concentration of Na-Muc was varied from 1.01E-02M to 1.84E-02M keeping constant hydrogen pressure,

metal/substrate molar ratio, and temperature. Initial activity and AdA yield were evaluated after 10 min and 90 min, respectively.

The initial activity at 1.01E-02M is 0.074 s[1] which is lower than the one obtained at higher concentration (◆ 0.1 s[1]) (Figure 5). Maximum conversion (97 %) and AdA yield (31 %)
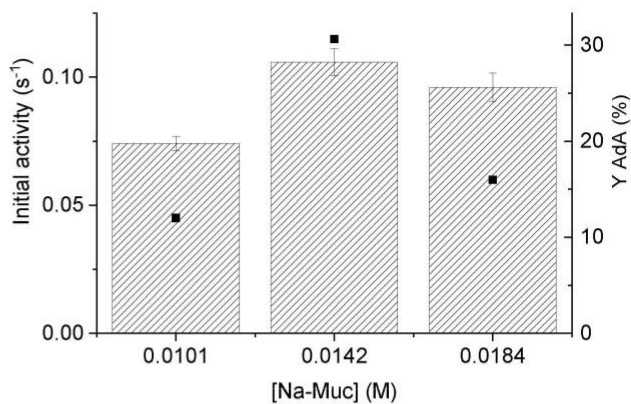
Figure 5. Initial activity (bar) and Y AdA (square) for Na-Muc hydrogenation calculated at 30 min and 90 min, respectively, for different Na-Muc concentration. T = 70 °C, stirring = 700 rpm, metal/sub = 1/200 (mol_{Pd}/mol_{sub}), and P(H$_2$) = 1 bar.

were obtained using Na-Muc 1.42E-02M (Figure 5SI). For all these reasons it is preferably to work with a Na-Muc concentration of 1.42E-02M to have the highest AdA yield.

Finally, the reaction temperature was varied from 30 °C to 70 °C using the previous optimized operating parameters. Temperature affects not only the reaction rate, but also hydro-gen solubility: the lower the temperature, the higher is the amount of hydrogen that can be solubilized in the reaction media.
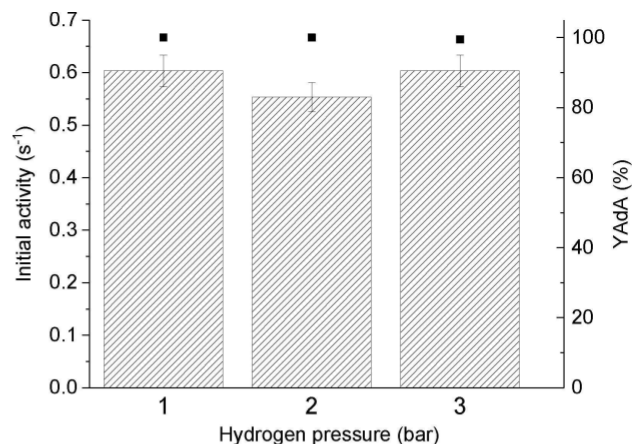
Hydrogenation at different reaction temperatures reveals that the higher the temperature, the higher is the initial activity and AdA yield (Figure 6). Hydrogen concentration in water was evaluated using Henry's law. From 30 to 70 °C hydrogen concentration decreases from 7.57E-04M to 6.17E-04M; but this difference does not influence the initial activity, as previously reported in Figure 3. Therefore, temperature is a discriminant operating parameter which helps the reaction rate. Although the hydrogen solubility at 70 °C is the lowest, the initial activity at this temperature is the highest (0.27 s[1]). After 90 min of reaction full conversion of Na-Muc is reached at 50 and 70 °C, while the highest AdA yield (91 %) is obtained at 70 °C after 90 min of reaction (Figure 6B and 6C). In all the reactions the main intermediate is the 2EHxAc (Figure 7SI).

## Hydrogenation of Trans,Trans Muconic Acid

In the downstream for the recovery of Na-Muc from the fermentation broth, crystallization step involving acidic environment and ethanol transforms Na-Muc to t,t-MA, increasing the
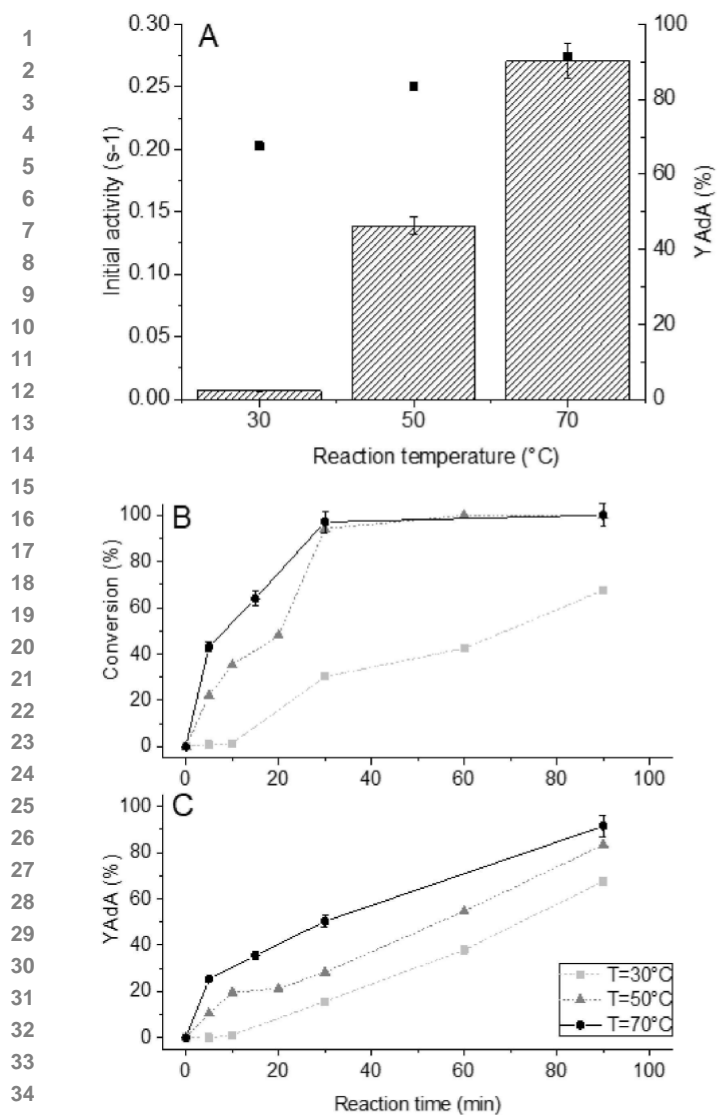
Figure 6. A) Initial activity (bar) and Y AdA (square) for Na-Muc hydrogenation calculated at 5 min and 90 min, respectively, for different reaction temperature. B) Na-Muc conversion and C) AdA yield at different reaction temperatures. Stirring = 700 rpm, metal/sub = 1/200 (mol$_{Pd}$/mol$_{sub}$), P(H$_2$) = 1 bar, and [Na-Muc] = 1.42E-02M.

purity of the final AdA.[17] Therefore, the previous study was also applied to t,t-MA hydrogenation to bio-AdA.

Firstly, hydrogen pressure was varied from 1 to 3 bar. The initial activity after 5 minutes does not strictly depend on the pressure used to perform the reaction (Figure 7). The calculated initial activity is about 0.6 s^{-1} and in full AdA yield is always obtained after 60 min of reaction (Figure 8SI).

In all the reactions (2E)HxAc was detected as the main intermediate with a maximum yield of 18 % at 15 min and 1 bar of hydrogen (Figure 9SI).

Then, the metal/substrate molar ratio (mol$_{Pd}$/mol$_{sub}$) was varied from 1/10 to 1/500 to see how this parameter affects the initial activity and AdA yield. The reactions were performed at 70 °C and 1 bar of hydrogen pressure with a starting concentration of t,t-MA of 1.42E-02M.

Figure 7. Initial activity (bar) and Y AdA (square) for t,t-MA hydrogenation calculated at 10 min and 60 min, respectively, for different hydrogen pressures. T = 70 °C, stirring = 700 rpm, metal/sub = 1/200 (mol$_{Pd}$/mol$_{sub}$), and [t,t-MA] = 1.42E-02M.
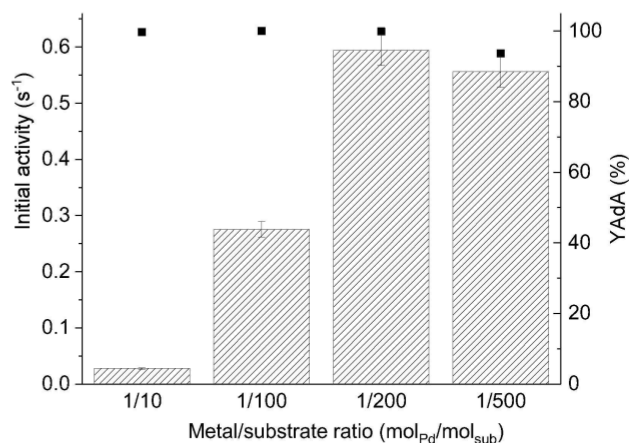
Figure 8. Initial activity (bar) and Y AdA (square) for t,t-MA hydrogenation calculated at 10 min and 60 min, respectively, for different metal/substrate ratio. T = 70 °C, stirring = 700 rpm, P(H$_2$) = 1 bar, and [t,t-MA] = 1.42E-02M.

Initial activity increases from 0.027 s^{-1} to 0.57 s^{-1} decreasing the metal/substrate molar ratio (hence decreasing the amount of catalyst) (Figure 8). After 60 min of reaction full conversion and AdA yield was obtained except for 1/500 molar ratio t,t-MA conversion and AdA yield are not influenced from metal/ substrate ratio and after 60 min of reaction total conversion of t,t-MA to AdA was obtained except for 1/500 ratio (Figure 10SI). For these reasons, 1/200 ratio was chosen as optimized parameter.

Subsequently, the concentration of t,t-MA was varied from 8.52E-03M to 1.42E-02M keeping constant all the previous optimized parameters.

Increasing the substrate concentration, higher values of initial activity were calculated (Figure 9). Only at 0.0142M full conversion of t,t-MA was achieved after 60 minutes with an AdA yield of 95.1 %; also in this case (2E)HxAc was detected as main intermediate (Figure 11SI).
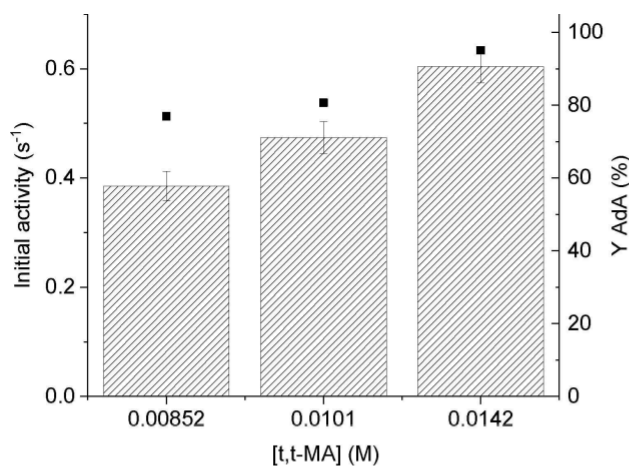
Figure 9. Initial activity (bar) and Y AdA (square) for t,t-MA hydrogenation calculated at 5 min and 60 min, respectively, for different t,t-MA concentration. $P(H_2)$ = 1 bar, T = 70 °C, stirring = 700 rpm, metal/sub = 1/200 (mol_{Pd}/mol_{sub}).

Finally, the temperature was decreased from 70 °C to 30 °C. Decreasing the temperature, the initial activity decreases from 0.28 s^{-1} to 0.52 s^{-1} (Figure 10). Full t,t-MA conversion and AdA yield are obtained at 50 °C and 70 °C after 60 min of reaction (Figure 1SI and 10B). At these temperatures, after 1 h, full t,t-MA conversion to AdA was achieved (Figure 10C). In these cases the main reaction product was always AdA, with a maximum yield of 48% of (2E)HxAc at 30 °C after 5 min of reaction (Figure 13SI). Since temperature is the discriminant operating parameter in both the considered cases, a comparison between the results obtained at different temperature allows to better understand the behavior of the substrates.

Temperature affects the intermediates behavior, during Na-Muc hydrogenation a larger amount of (2E)HxAc is produced at low reaction times while, for t,t-MA reduction, AdA is always the main product (Figure 11). From the reaction behavior we can hypothesized that the hydrogenation reaction is a two steps process where the substrate is firstly hydrogenated to (2E)HxAc intermediate and then further converted, in a second step, to AdA.

t,t-MA hydrogenation occurs faster than Na-Muc one, after 60 min t,t-MA hydrogenation leads to full conversion to AdA, while Na-Muc reduction, at the same reaction time, is able to convert 78% of substrate with an AdA yield of about 60 %. This behavior can be also explained considering the pH of the starting solution. Na-Muc and t,t-MA have a starting pH of 11.5 and 3.7, respectively. At low pH hydrogenation reaction occurs faster than at high pH. Singh et al. reported the same catalytic behavior during phenol hydrogenation. They found that the higher reaction rate is attributed to weakening of the hydrogen binding energy on the metal surface with decreasing pH.[34]

Comparing the catalytic results with the ones reported in literature (Table 1), commercial Pd/AC 5% in our operating conditions shows good catalytic performance during both Na-Muc and t,t-MA hydrogenation. Low pressure and temperature allowed to reach full conversion and high AdA yield avoiding the use of pressurized hydrogen, which is a matter of concern
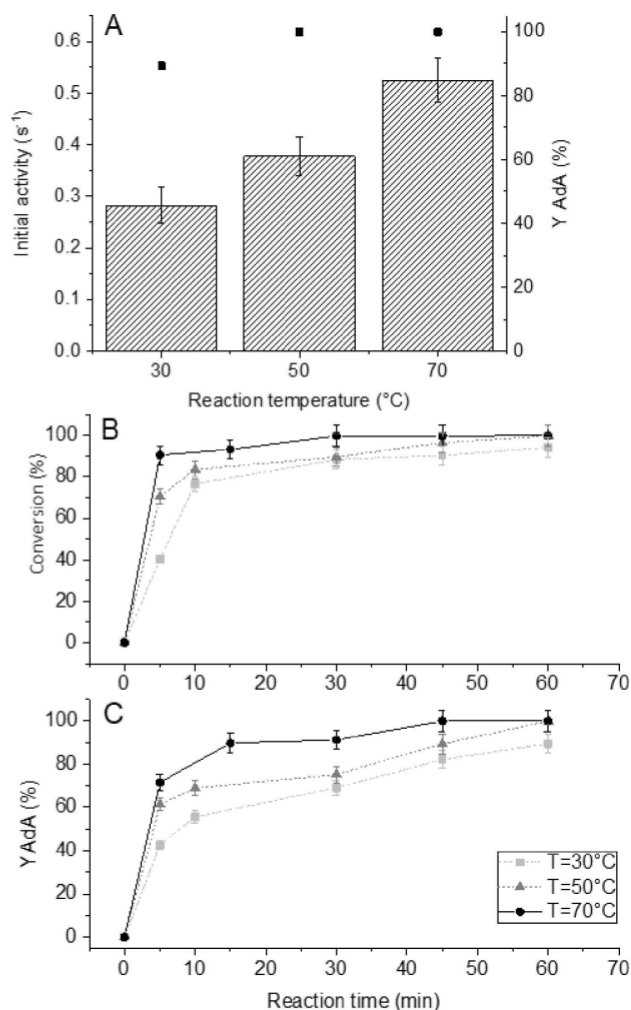

Figure 10. A) Initial activity (bar) and Y AdA (square) for t,t-MA hydrogenation calculated at 5 min and 60 min, respectively, for different reaction temperatures. B) t,t-MA conversion and C) AdA yield at different reaction temperatures. Stirring = 700 rpm, $P(H_2)$ = 1 bar, metal/substrate = 1/200 (mol_{Pd}/mol_{sub}), reaction time = 10 min, [t,t-MA] = 1.42E-02M.

for industrial safety reasons. Moreover, our mild operating conditions, let to use low amount of catalyst, which is one of the lowest values reported up to now.

Used Catalyst Characterization

Used catalyst recovered after the filtration was analyzed by XPS analysis and TEM microscopy to study possible modification of Pd oxidation state and particle size distribution during Na-Muc and t,t-MA hydrogenation reaction (temperature = 70 °C, pressure = 1 bar, catalyst/substrate molar ratio = 1/200 (mol_{Pd}/mol_{sub}), stir-ring = 700 rpm, and substrate concentration = 1.42E-02M).

XPS analyses were made on the used catalyst recovered from Na-Muc hydrogenation after 30 and 90 min of reaction. The oxidation state of the Pd varied during the reaction. Pd(II) present on the surface of the catalyst is reduced to metallic Pd due to the presence of hydrogen in the reaction media
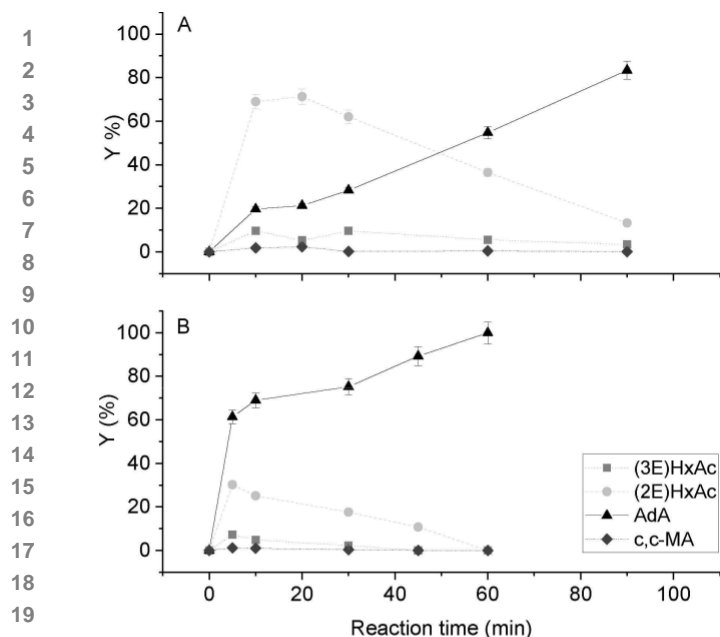
Figure 11. Yield of compounds during Na-Muc (A) and t,t-MA (B) hydrogenation at P(H$_2$) = 1 bar, [Na-Muc/t,t-MA] = 1.42E-02M, stirring = 700 rpm, metal/sub = 1/200 (mol$_{Pd}$/mol$_{sub}$), T = 50 °C.
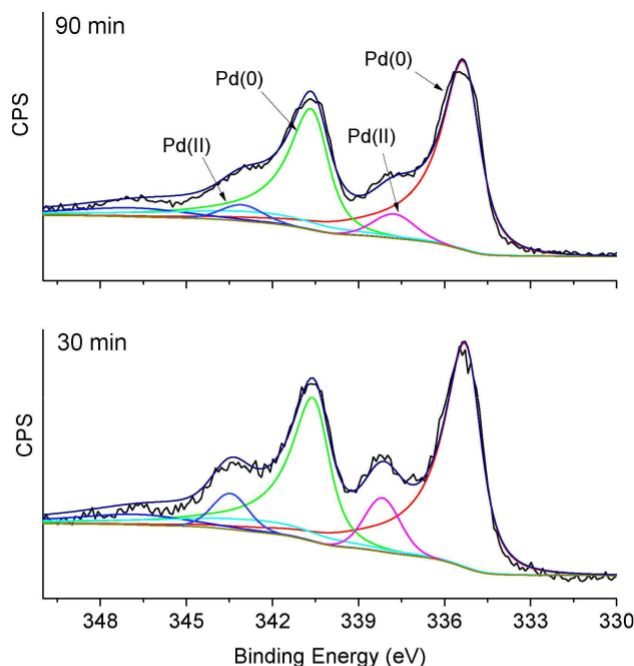
Figure 12. XPS of used catalyst recovered during Na-Muc hydrogenation.

(Figure 12). Metal Pd amount increases during the reaction from 50.1 % to 91.1 % after 90 min of reaction (Table 2).

TEM analysis on the used catalyst after 90 min of reaction revealed that no particle size change occurs during the hydrogenation of Na-Muc. Both fresh and used catalysts show a comparable mean particle size (3.1 nm) with particles mainly distributed in the 1.5–4.5 nm size range (Figure 13).

XPS analyses were also made on used catalyst recovered from t,t-MA hydrogenation at 15, 30 and 60 min of reaction.

Analyzing the area of the deconvolution peaks the evaluation of the percentage of the two species was calculated. The oxidation state of the Pd varied during the reaction: in reducing environment the Pd(II) present on the surface of the catalyst is reduced to metallic Pd, as mentioned for Na-Muc hydrogenation (Figure 14). Metal Pd amount increases during the reaction from 50.1 % to 94.7 % after 60 min of reaction (Table 3).

TEM analysis on the used catalyst after 60 min of reaction revealed that no particle size change occurs during the hydrogenation of t,t-MA. Both fresh and used catalyst show a mean

Table 2. Pd(II) and Pd(0) percentage during Na-Muc hydrogenation.

Sample	Pd 3d (II) [%]	Pd 3d (0) [%]
0 min	49.9	50.1
30 min	14.0	86.0
90 min	8.9	91.1

Table 3. Pd(II) and Pd(0) percentage during t,t-MA hydrogenation.

Sample	Pd 3d (II) [%]	Pd 3d (0) [%]
0 min	49.9	50.1
15 min	31.3	68.7
30 min	25.0	75.0
60 min	5.3	94.7

Table 1. Published results about t,t-MA and Na-Muc hydrogenation reactions.

| Ref	Catalyst	Metal loading [%]	Substrate	T [°C]	H$_2$ pressure [bar]	MA conversion (time) [%]	AdA yield [%]	Metal/substrate ratio [mol/mol]	Solvent
[35]	Pt/AC	10	MA	25	3.5	100 (3 h)	90	1/4	Water
[36]	Pt/AC	10	MA	25	34	100 (2.5 h)	97	1/20	Water
[37]	Ru$_{10}$Pt2/SiO$_2$	–	MA	80	30	91 (5 h)	96	–	Ethanol
[25]	Re/TiO$_2$	–	MA	210	–	100 (5 h)	88	1/33	Methanol
[38]	Pt/C	5	MA	160	–	100 (12 h)	99	–	Pentanol
[39]	Pd on PEI/SiO$_2$	2.44	MA	37	–	–	75	1/12	Water
[40]	Pd/AC	1	MA	25	24	100 (40 min)	97	1/1000	Ethanol
[41]	Ni/Al$_2$O$_3$	14.2	MA		10	100 (5 h)	98	1/5	Water
[26]	Pt/AC	5	Na-Muc	70	4	100 (2 h)	100	1/275	Water
Current work	Pd/AC	5	MA	70	1	100 (60 min)	100	1/200	Water
Current work	Pd/AC	5	Na-Muc	70	1	100 (90 min)	95	1/200	Water
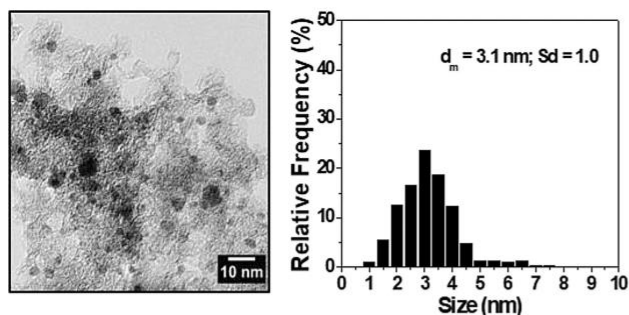
Figure 13. Representative TEM micrograph and particle size distribution of used catalyst recovered during Na-Muc hydrogenation.
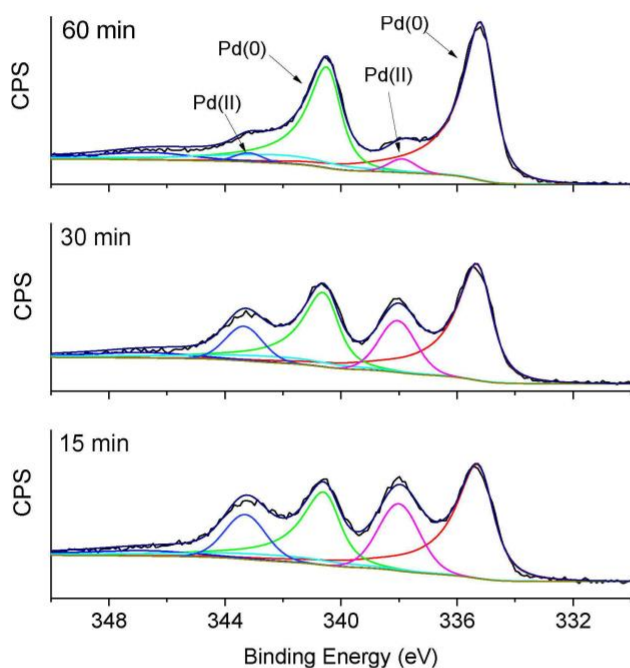
Figure 14. XPS of used catalyst recovered during t,t-MA hydrogenation.
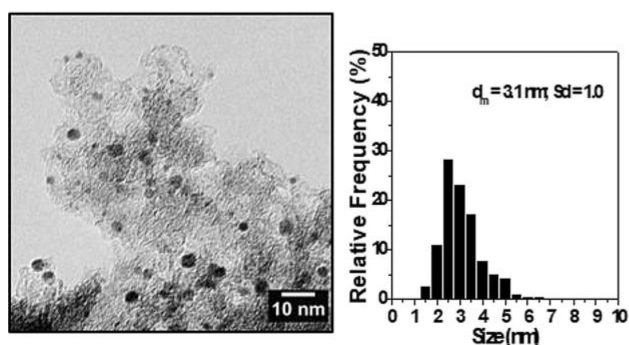
Figure 15. Representative TEM micrograph and particle size distribution of used catalyst recovered during t,t-MA hydrogenation.

particle size of 3.1 nm (Figure 15). Therefore, the catalyst is stable under the reaction conditions. In the literature reported in Table 1 only Scelfo et al.[41] and Capelli et al.[26] investigated the catalyst characterization after the reaction and the catalyst was stable in the two mentioned works.

Conclusions

The conversion of bio-chemical derived compounds into platform chemicals is an attractive goal in contemporary catalysis research. Commercial 5% Pd/AC was used for the catalytic hydrogenation of Na-Muc and t,t-MA at mild operating conditions. We varied the following operating parameters to study diffusion/kinetic regime, the effect of temperature, hydrogen pressure, substrate concentration and metal to substrate molar ratio. Hydrogen pressure did not affect the conversion while influenced AdA yield when Na-Muc was used as substrate. Temperature variation showed the most interesting results. In fact, this parameter largely has a great influence on the products yield and initial activity. Initial activity was 0.52 s^{-1} and 0.27 s^{-1}, for t,t-MA and Na-Muc hydrogenation, respectively (at T = 70 °C, metal/substrate = 1/200, P(H$_2$) = 1 bar, t,t-MA (or Na-Muc) concentration = 1.42E-02M, and reaction time of 5 min). t,t-MA hydrogenation reaction occurs faster than Na-Muc one and after 60 min t,t-MA was fully converted to AdA, while during Na-Muc hydrogenation after 90 min 95.1 % of AdA yield was obtained. In conclusion t,t-MA hydrogenation is preferably to Na-Muc one due to the higher reaction rate and AdA yield, but there is not the possibility to increase substrate concen-tration above 1.42E-02M due to solubility limitation. The possibility to increase Na-Muc concentration could be of interest despite high salt concentration might be harmful for the catalyst, that can be deactivate faster.[26]

Experimental Section

Hydrogenation Reaction

Low pressure glass reactor was designed to perform hydrogenation reaction up to 3 bar and at mild temperatures. The glass reactor was equipped with a pressure controller and an external jacket linked to a thermostatic water bath. The hydrogen was added using a proper line. The third neck of the glass cap was equipped with a silicon septum that allows to make a withdrawal at different reaction times without stopping the reaction or lose pressure. The glass reactor was placed on a hot plate for the magnetic stirring.

A known amount of reagent solution was placed in the reactor and it was thermostated at the desired temperature under magnetic stirring. Sodium muconate was prepared adding a stoichiometric amount of NaOH to t,t-MA (Sigma Aldrich, purity > 98 %). The reactant solutions were prepared at 0.0142 M and a volume of 10 ml were introduced in the reactor.

Then the commercial Pd/AC 5% catalyst (Sigma Aldrich) was added with a ratio 1/200 (mol$_{Pd}$/mol$_{substrate}$), and the reactor was pressur-ized at the desired pressure (1, 2 or 3 bar) after being purged with hydrogen 3 times. The zero time of the reaction was taken after the addition of hydrogen at the desired temperature (30, 50 or 70 °C). The sample was collected using a syringe equipped with a needle of the proper length. The sample was filtered using a filter paper to

remove the solid catalyst. Conversion and selectivity were evaluated as reported in Capelli et al.[26] Briefly, after the end of the reaction, 1 g of the reaction mixture was used for UV analysis sample preparation. Two or three dilutions were necessary to read an absorbance below 1. The analysis was performed from 500 to 190 nm using distilled water as blank. The value of absorbance was kept at 264 nm. The conversion was evaluated using Equation (1)

$$Conversion(\%) = \frac{mol_i^{IN} - mol_i^{OUT}}{mol_i^{IN}} \cdot 100 \tag{1}$$

Were mol_i^{IN} are the moles of the substrate used for the reaction while mol_i^{OUT} are the moles of the substrate that remain after the reaction.

Yield of AdA and the intermediates were evaluated by GC-FID analysis after products derivatization.

The remaining filtered sample was dried at rotavapor or placed in an oven at 70 °C to remove the reaction solvent; in this way a white/yellow solid product was obtained. The product was then subjected to an esterification reaction. 5 mL of methanol were added to a catalytic amount of sulfuric acid. The reaction was performed at 70 °C for 48 hours. The selectivity was evaluated analyzing the esterified products by gas chromatographic analysis using dimethyl glutarate as internal standard. SP-2380 capillary column (Sigma Aldrich) was used allowing the separation of the different stereoisomers in isothermal mode at 180 °C. The temperature of the injector and the detector was 220 °C. He, air and H_2 flows were 43, 310 and 38 mL/min, respectively. The injection volume was 1.5 %L and the analysis time 8 min. Selectivity and product yield were evaluated using Equation (2) and Equation (3), respectively.

$$Selectivity_n(\%) = \frac{mol_n}{mol_n + \Sigma mol_i} \cdot 100 \tag{2}$$

Where mol_n is the number of moles of the considered reaction product and Σmol_i is the sum of the moles of all the other reaction products.

$$Yield_n(\%) = \frac{Selectivity_n(\%)}{100} \cdot Conversion(\%) \tag{3}$$

The results are also expressed in term of initial activity [Eq. (4)] that was evaluated considering the amount of catalyst used for each test, the conversion and the time of the reaction.

$$Initial\,activity\,(s^{-1}) = \frac{Conversion(\%)=100 \cdot C_s^O \cdot V}{n_{Pd} reaction\ time\ 60\frac{s}{min}} \cdot 100 \tag{4}$$

Where C_s^0 (M) is the initial concentration of the substrate, V (L) is the liquid volume of the solution, n_{Pd} (mol) are the moles of Pd introduced in the reactor and reaction time (min) is the considered reaction time.

The reactions were performed three times to evaluate the relative error of the analyses stated with the error bars.

Catalyst Characterization

Fresh and used commercial Pd/AC 5 % catalysts were characterized using TEM and XPS analyses.

Transmission electron microscopy (TEM) were performed on a ZEISS LIBRA200FE microscope operating at 200 kV (FEG source). Samples were prepared by sonication in isopropanol and deposited on 300 mesh copper grids coated with lacey carbon film. Histograms of the particle size distribution were obtained by counting onto the micrographs at least 200 particles. The mean particle diameter (d_m) was calculated by using the formula $d_m = \Sigma d_i n_i / \Sigma n_i$ where n_i was the number of particles of diameter d_i.

X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-alpha + spectrometer. Samples were analyzed using a monochromatic Al x-ray source operating at 72 W (6 mA × 12 kV), with the signal averaged over an oval-shaped area of approximately 600× 400 microns. Data was recorded at pass energies of 150 eV for survey scans and 40 eV for high resolution scan with a 1 eV and 0.1 eV step size respectively.

Charge neutralization of the sample was achieved using a combination of both low energy electrons and argon ions (less than 1 eV) which gave a C(1 s) binding energy of 284.8 eV.

All data were analyzed using CASAXPS (v2.3.17 PR1.1) using Scofield sensitivity factors and an energy exponent of 0.6.

Conflict of Interest

The authors declare no conflict of interest.

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