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In situ electrochemical regeneration of deactivated coated foam catalysts in a Robinson-Mahoney basket reactor: Example of Pd/C for nitrobenzene hydrogenation

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Abstract

The electrochemical in situ regeneration of spent Pd/C/foam catalysts was investigated using a modified Mahoney-Robinson reactor (RM). The same reactor was used for reaction and regeneration experiments with and without removal/weighing of the catalyst between each measurement. The feasibility of the electrochemical regeneration was assessed by monitoring the catalyst activity versus cumulative turnover number (TON). The results showed that the catalyst activity was fully recovered after regeneration and that the catalyst had the same deactivation rate after several reaction/regeneration cycles. The influence of the foam pretreatment step and of the pH electrolyte solution on the catalyst loss was also studied. A basic pretreatment of the foam before the catalyst coating led to a significant improvement of the catalyst adherence on the foam.

Key words: Carbon washcoating, Nitrobenzene hydrogenation, Palladium, Electrochemical regeneration, Basket reactor

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1. Introduction

In most industrial catalytic processes with fixed-bed operations, the catalyst regeneration is nowadays performed *ex situ* [1], with periodic maintenance of the production unit and catalyst removal from the reactor. The increasing interest for structured monolithic reactors with wall-coated catalysts [2] is however not compatible with such operations. The future of such catalytic reactor technology thus depends on advances to changing or regenerating the supported catalyst without major impact on the production unit, i.e. without reactor dismantling. The most applied *in-situ* catalyst reactivation methods is the injection of gas (air, steam, nitrogen...) at controlled temperatures [3–5]. However, these methods are either too expensive or have low efficiency. Electrochemical regeneration methods are alternative strategies that have attracted less attention in the past decades. This technique presents some advantages compared to the conventional methods. Essentially, it can be conveniently operated *in situ*, at ambient temperature and pressure, with low energy consumption and with short time requirements [6, 7]. Previous experiments performed on Pd/C/substrate [8] have shown that an electrochemical regeneration was the most adapted amongst three regeneration methods (plasma, thermal oxidation and electrochemical treatment) and was the only one to allow the complete recovery of the textural properties of the fresh catalyst. In the present work, for the first time, the electrochemical regeneration was carried out in the same reactor than the catalytic experiments to demonstrate the feasibility of the *in situ* electrochemical regeneration for the structured catalysts. The influence of the foam pretreatment step and of the pH electrolyte solution was also evaluated. The obtained results during *in situ* deactivation/regeneration tests with removal/weighing of the foam between each experiment have been compared to those carried out without removal of the sample.

2. Experimental part

2.1. Chemicals

Vulcan XC72 powder (Cabot Corp.) was used for the carbon suspension preparation. Triton X-100 (polyethylene glycol octylphenyl ether) was Acros product. Dextrine was supplied by SigmaAldrich. The palladium precursor was palladium chloride (SigmaAldrich). Ethanol (96%) and nitrobenzene (99%, Sigma Aldrich) were used for catalytic tests. H₂SO₄ (98%, Sigma

Aldrich), phosphate Buffer solution at pH 7 (Sigma Aldrich) and KOH (99%, Sigma Aldrich) were used for the electrochemical tests.

2.2. Coated foams

2.2.1. Preparation of washcoated basket foam catalyst

Substrates and cleaning protocol. Plates of AISI 316L stainless steel (ThyssenKrupp), 80 mm long, 30 mm wide and 2 mm thick, about 20 g, were used as non structured supports for home made catalyst preparation. Stainless steel foams were purchased from Porvair Advanced Materials (40PPI, specific surface area of $1500\text{ m}^2/\text{m}^3$, estimated by X-ray tomography). They were cut into hollow cylindrical pieces of 46 mm external diameter, 30 mm internal diameter and various thickness (2-11 mm) by electric discharge method (EDM). The stainless steel (SS) substrates (plates and foams) were cleaned and pretreated at $500\text{ }^\circ\text{C}$ in air as detailed previously [8]. Then, the samples were chemically treated at ambient temperature, during 3 h, in: (1) 30 wt% H_2SO_4 or (2) 30 wt% KOH solution.

Preparation of catalyst. The Vulcan XC72 powder was contacted during 12 h with the acid solution (pH 3) of palladium chloride. Then, the excess solvent was evaporated and the powder was dried at $120\text{ }^\circ\text{C}$ for 24 h. The amount of Pd salt was calculated to obtain a reference carbon sample with a known Pd loading (ca. 3 wt% Pd). In this method, all the Pd salt was deposited on the carbon (chemisorbed and physisorbed). The Pd loading has been verified by ICP-AES analysis of the reduced Pd/C powder. A Pd loading of 2.7 wt% was found. The catalyst suspension was prepared according to the following procedure (from [8, 9]). First, 36 cm^3 of distilled water were mixed with 1 mL Triton X-100 and 0.8 g Dextrine (as dispersant). The dispersions were agitated by magnetic stirring for 30 min at room temperature and gradually mixed with 5.4 g Pd/Vulcan XC72 powder. Finally, the catalyst suspension was sonicated during 50 min. The substrates (plates and slices of cylindrical foams) were weighed, then immersed in the catalyst suspension for 30 min and dried in air at $120\text{ }^\circ\text{C}$ for 12 h. The samples were calcined under nitrogen flow (0.6 L/min) during 5 h at $550\text{ }^\circ\text{C}$ for dispersant and Pd precursor decomposition. After calcination, the plates were scratched and the Pd/C powder was recovered and reduced under hydrogen flow by two methods. In the first method, the Pd/C powder was reduced in the oven (0.6 L/min hydrogen) at $200\text{ }^\circ\text{C}$ during 2 h. These samples were called sample 1. For other samples (Pd/C powder, sample 2 and Pd/C/foams catalyst, samples

3-5), the Pd was reduced under 3 bars of hydrogen, in the reactor, at 40 ° C during 1 h. The catalytic activity of the home made Pd/C powder catalyst (sample 2) was considered as reference.

2.2.2. Characterization methods

For all the samples, the amount of Pd/C catalyst was obtained by weighing the object before and after coating and calcination. The morphology of the samples was examined using a Hitachi TM-1000 Tabletop Scanning Electron Microscope (SEM) coupled to a PGT Instruments energy dispersive spectrometer (EDS). The adherence of the catalytic layer was checked by ultra-sonic treatment in heptane (1 min) and water (1 min).

The chemical valences of Pd in Pd/C/foam catalyst were analysed by X-ray photoelectron spectroscopy (XPS, KRATOS Axis Ultra DLD) using an Al K X-ray source of 1486.6 eV. Each high-resolution spectrum was decomposed into a combination of Voigt functions, each with an overall full-width at half maximum (FWHM) of approximately 1.4 eV. Prior to analysis, the samples were outgassed during 24 h in a preparation chamber at a base pressure of 6×10^{-8} mbar. The analysed surface was of 0.21 mm². The average depth of XPS analysis was 5 nm. The carbon C 1s line at 284.4 eV was used as reference for correcting surface-charging effects. XPS measurements were carried out for the following states of the sample: (1) the Pd/C/foam catalyst was reduced under H₂ (3 bars pressure), in the batch reactor (ethanol/water mixture), at 40 ° C, during 30 min; (2) in addition to this step, the same sample was reduced “quasi in situ” under H₂ (3 bar) flow at 37 ° C, during 1 h, in a cell coupled with the characterization instrument, then transferred to the XPS analysis without any contact with air. The first test was called in the text ”before quasi in situ“ H₂ reduction and the second “after quasi in situ” H₂ reduction.

2.3. Set-up for catalytic tests and electrochemical regeneration

The deactivation and regeneration experiments were performed in a modified Mahoney-Robinson reactor (RM) of 300 mL from Top Industrie. The modifications include:

- the replacement of the catalytic basket by a cylindrical foam composed of several slices, catalytic or not,
- the insertion of electrodes through the autoclave cover.

The reactor was operated in semi-batch mode for the hydrogen, at a constant pressure of 3 bars, thanks to a pressure regulator. A picture of a slice of cylindrical catalytic foam is shown in Figure 1. For all the experiments, an impeller provided by Top Industrie has been used. The impeller was a gas-inducing turbine with three curved blades and a hollow shaft. The gas-inducing turbine at a stirring rate of 1800 rpm allowed to force the liquid and gas bubbles to flow through the catalytic foam. The complete set-up, including the electrodes and the turbine are shown in Figure 2.



Figure 1: 11 mm thick slice of Pd/C/foam

2.4. Catalytic runs

A weighed Pd/C/substrate catalyst (ca. 2 to 4.5 g) and 170 mL of ethanol/water (9:1 volume) were charged into the reactor. The catalytic foam was pre-activated with hydrogen during 1 h at the same temperature and pressure than the catalytic test. The temperature was 40 °C and the hydrogen pressure 3 bars for all the experiments. Nitrobenzene (3 mL) was then added to the mixture through a pressurised addition funnel. Hydrogen was supplied from an upstream-calibrated reservoir and was fed to the reactor at constant pressure via a pressure regulator. The pressure decrease in this reservoir was recorded. Initial catalytic activities were obtained from the slope of hydrogen consumption with time profile. Chromatographic analyses by GC/MS (DB1 column) were punctually carried out to check the nitrobenzene conversion and the product selectivity. Two procedures were followed. In procedure A, after a significant conversion of nitrobenzene (50 to 100%),

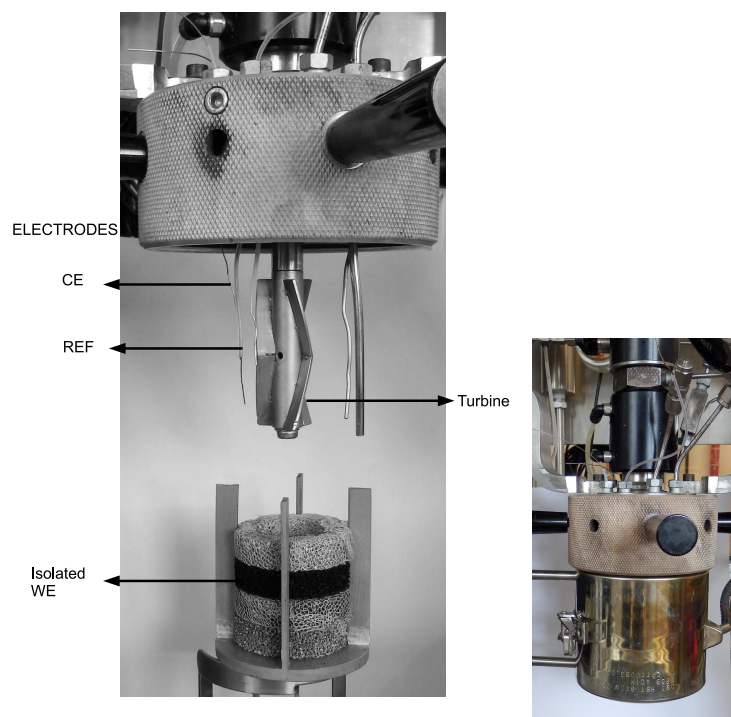


Figure 2: Set-up used for hydrogenation and regeneration. Left: inside the reactor, right: outside. (CE: counter electrode, WE: working electrode, REF: reference electrode)

the autoclave was emptied and rinsed, the Pd/C/ foam catalyst was removed, dried at 120 °C under air flow, during 2 h, then weighed. The foam was then reintroduced in the autoclave for a second run. The procedure was repeated until a significant deactivation of the catalyst could be observed, corresponding to 4 to 6 successive runs, reaching a TON of 2000 to 3000 mol of nitrobenzene transformed per mol of palladium . The initial activity observed at the last run was then significantly lower than that of the first run (70 to 80% decrease). In procedure B, after each run reaching 50 to 100% conversion, the liquid was removed with a syringe, the catalyst was washed by ethanol (with a syringe) and kept in the reactor under nitrogen, at ambient temperature, until the next run. Fresh solvent and nitrobenzene were introduced with a syringe for the next hydrogenation run. In that procedure, the foam was not removed and not weighed between each run.

2.5. Electrochemical regenerations

When the initial activity of catalyst was significantly reduced, the reaction mixture was removed. The autoclave was rinsed with ethanol and several times with the electrolytic solution. A schematic representation of the modified RM reactor used in this work has been presented in Figure 2. In this system, the deactivated Pd/C/foam catalyst, used as working electrode (WE), was electrically isolated from the other foam slices, by using a plastic grid. The sample used as WE was 2 to 11 mm thick. The other slices of foam, inert, were 11 mm thick. The electrochemical measurements were performed with a RADIOMETER potentiostat/galvanostat using the VOLTALAB version 3.10 software. The counter electrode (CE) and the reference electrode (REF) were two platinum (Pt) wires. During cyclic voltammetry (CV), the potential was swept between -800 and 450 mV/Pt, at $5 \text{ mV}\cdot\text{s}^{-1}$, 4 scans. Electrochemical regenerations were conducted at room temperature, with continuous nitrogen (N_2) flowing, in three different electrolyte solutions: (1) 0.1 M KOH (pH 12) ([10–12]); (2) Phosphate Buffer solution at pH 7 (Sigma Aldrich) ([12]); (3) 0.1 M H_2SO_4 (pH 1).

3. Results

3.1. Hydrogenation

In order to verify the morphology of the Pd/C/foam catalysts, the samples were examined by SEM before the hydrogenation test. The SEM picture 3 is similar to those obtained in our previous work [8]. In the cited paper, Pd was deposited by impregnation of carbon coated substrate. It seems that the method of Pd deposition did not influence the catalyst morphology. The performances of the prepared Pd/C/support catalysts were evaluated during the catalytic hydrogenation of nitrobenzene. Whatever the catalyst used, the selectivity to aniline was always higher than 95% and is not further discussed. All the initial activities of the first hydrogenation run have been collected in Table 1. Reference tests were performed with Pd/C powder obtained after the scratching of the plates. The first one (sample 1) is Pd/C powder activated at 200°C under H_2 in the oven, then reduced in the reactor at 40°C and 3 bars of H_2 before reaction. The second one (sample 2) is only activated in the reactor. We note that sample 1 presents a catalytic activity slightly superior but in the same order of magnitude than sample 2. This is probably due to the reduction step of Pd before hydrogenation. The sizes of Pd/C/foam samples did not allow the reduction step of Pd in the usual oven.

For this reason, in the following experiments all the samples were prepared with the same protocol as the reference (sample 2) (reduced in the reactor). One Pd/C/foam sample was reduced during 1h, in the reactor at 40 ° C and 3 bars of H₂, for XPS analysis purposes of the fresh catalyst. The results are showed in the next paragraph. A blank test was also performed after insertion of Pt electrodes through the RM autoclave cover without Pd/C/foams catalyst. The hydrogen consumption was zero. The product identified by GC/MS analyses was nitrobenzene. During hydrogenation, it was checked by GC/MS that the presence of the electrodes did not affect the selectivity to aniline. Thus, the modified RM reactor can be used for the catalytic and for in situ regeneration tests.

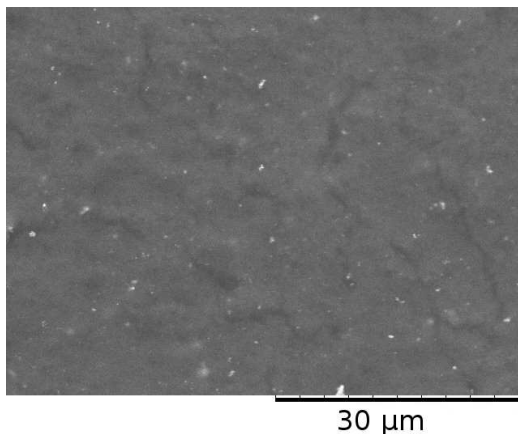


Figure 3: SEM picture of a Pd/C/foam catalyst

Sample number	Substrate	Chemical pretreatment	H ₂ reduction of Pd before reaction	Ini. H ₂ cons. (mmol.s ⁻¹ g _{Pd} ⁻¹)
1	powder*	acid	oven + reactor	7.9
2	powder*	acid	reactor	5.8
3	foam	acid	reactor	3.7
4	foam	basic	reactor	3.3
5	foam	basic	reactor	2.9

Table 1: Initial activity of all the samples in nitrobenzene hydrogenation. *The powder was scrapped from a coated stainless steel plate.

3.2. XPS surface analysis

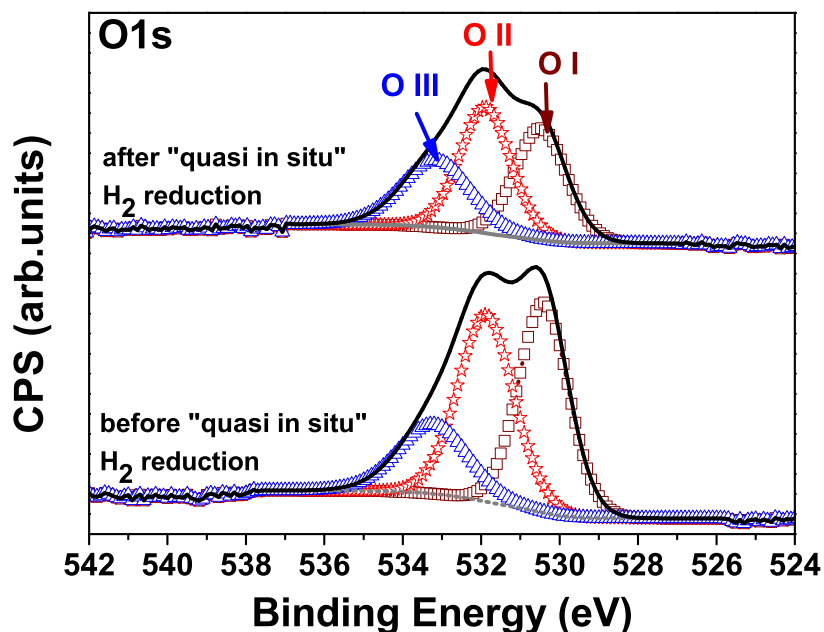


Figure 4: XPS spectra of the catalyst in the O 1s region

XPS analysis was used to study the effect of the H_2 treatment conditions on the degree of Pd reduction, by detecting the composition of catalyst surface coating. Figures 4, 5, and 6 exhibit the XPS spectra for major elements (Pd $3d_{5/2}$, O 1s, and C 1s) before and after "quasi in situ" H_2 reduction. The binding energy of Pd $3d_{5/2}$, O 1s, and C 1s peaks was represented in Table 2. The results obtained for this sample confirm the existence of various chemical states of palladium on the surface of the analyzed system. The analyses of XPS results are based on the literature data ([13–15]). The O 1s spectra of the catalyst were decomposed into three components (Figure 4). The dominating O-I component at 530.4 eV could be related to Pd O_{ads} . The O-II component located at 531.9 eV can be attributed to PdO. The peak at 533.2 eV may include contribution of OH^- bonds and of supersaturated O_{ads} layer ([16, 17]). Typical XPS spectra of the catalyst in Pd 3d region are shown in Figure 5. As can be seen in this picture, Pd/C/foam catalyst

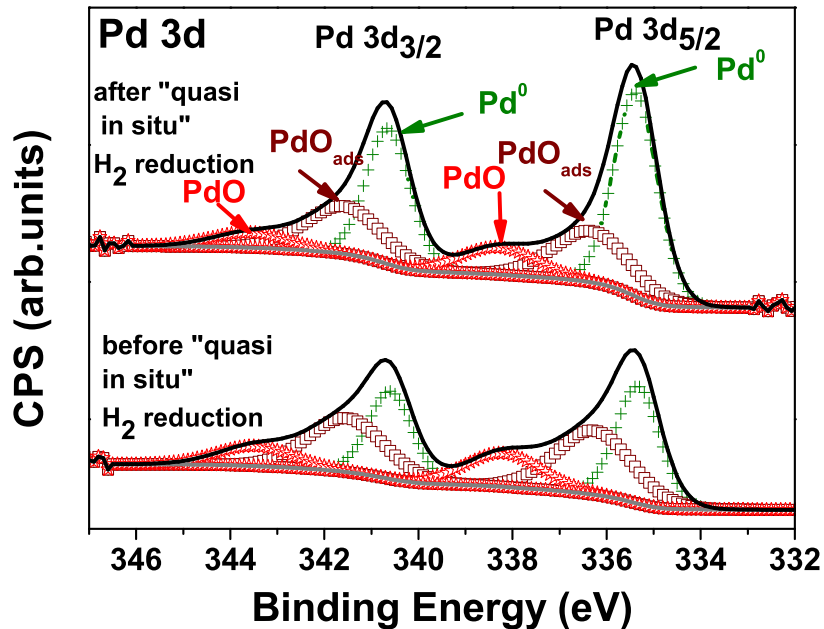


Figure 5: XPS spectra of the catalyst in the Pd 3d region

shows two asymmetrical peaks with high energy band at 335.3 and 344 eV in Pd 3d signal region. The different Pd chemical states can be analyzed by deconvolution of Pd 3d spectra. On the fitting curves, the Pd 3d signal consists of three doublets, which can be assigned to metallic Pd, PdO_{ads} and PdO, respectively ([18, 19]). According to the literature data, the electron binding energy of Pd 3d_{5/2} for metallic palladium is in the range 334.6-335.6 eV, whereas the energy for Pd²⁺ is 337.5-338.5 eV [7]. The relative content of Pd, PdO_{ads} and PdO 40.9%, 40.6% and 18.5% respectively and it is 58.2%, 29.3% and 12.5%, respectively, after "quasi in situ" H₂ reduction. Figure 6 shows the XPS spectrum of catalyst in C 1s region. The doublet consisting of C 1s at 284.4 eV corresponds to C-(C,H) or C-C bonds. Another peak has been identified at 285.8 eV and assigned with the presence of C-O and C-OH bonds. After a "quasi in situ" H₂ treatment during 1 h, the O 1s, Pd 3d and C 1s spectra appear changed. We note that the ratio of the PdO_{ads}/PdO peak intensities for O 1s decreases after treatment from 1.1 to 0.9. Moreover, the intensity of Pd peak increases after H₂ treatment and the ratio of

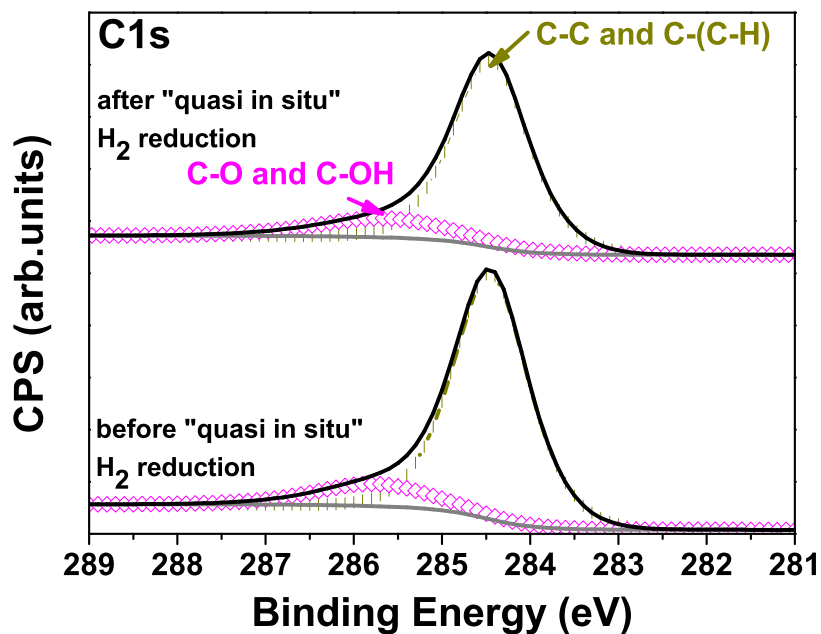


Figure 6: XPS spectra of catalyst in the C 1s region

$\text{PdO}_{ads}/\text{PdO}$ intensities decreases from 1.9 to 1.7. After H_2 reduction in the reactor, most of the palladium is in the zero oxidation state. The possible leaching of simply adsorbed species seems to be unlikely. An ICP analysis was performed for a liquid sample collected after Pd/C/ foam catalyst reduction in the reactor. The Pd concentration was <0.1 mg/L (detection limit), confirming a Pd leaching of less than 0.14 wt-% during one test.

Catalyst	Element	Binding energy (eV)	Chemical state on the surface (Assignment)	Relative content of chemical state on the surface (%)
Before “quasi in situ” H ₂ reduction	O 1s	530.4	PdO _{ads}	40.5
		531.9	PdO	40.8
		533.2	OH ⁻ /O _{ads}	18.8
	Pd 3d _{5/2}	335.3	Pd	40.9
		336.3	PdO _{ads}	40.6
	C 1s	338.2	PdO	18.5
		284.4	C-(C-H)/C-C	87.4
After “quasi in situ” H ₂ reduction	O 1s	285.8	C-O/C-OH	12.6
		530.5	PdO _{ads}	34.1
		531.9	PdO	38.5
	Pd 3d _{5/2}	533.1	OH ⁻ /O _{ads}	27.4
		335.4	Pd	58.2
	C 1s	336.3	PdO _{ads}	29.3
		338.3	PdO	12.5
C 1s	284.4	C-(C-H)/C-C	84.5	
	285.7	C-O/C-OH	15.5	

Table 2: XPS characteristic of the elements. Photon energy Al K.

3.3. *In situ deactivation/regeneration tests with weighing of the foam between each experiment*

The first in situ deactivation/regeneration measurements was conducted in the RM reactor with removal/weighing of the Pd/C/foam catalyst between each deactivation/regeneration cycle. All these reactivation experiments were performed in acid solution (0.1 M H₂SO₄). Two pretreatment methods of the foam (in (1) 30 wt% H₂SO₄ and (2) 30 wt% KOH solution) were used for the preparation of samples (see Substrates and cleaning protocol).

3.3.1. *Effect of the pH of the regeneration solution*

In order to study the influence of pH on the catalyst stability and activity after regeneration, experiments was carried out in three electrolyte solutions (pH 1-12). For these tests, the samples were removed, drained, dried and weighed before and after each measurement. The spent catalysts were regenerated in electrolyte solution with the same electrochemical parameters. Table 3 shows the mass loss of Pd/C/foam catalyst during the first in situ regeneration test in the RM reactor at different pH solutions.

pH solution	Catalyst activity after regeneration	Catalyst loss (wt-%)
1	recovered	2
7	non recovered	1
12	-	20

Table 3: Effect of pH solution on the mass loss and catalytic activity of the Pd/C/foam catalyst after the first regeneration.

We note that the mass loss is around 2% at pH 1 (0.1 M H₂SO₄) and that the catalytic activity was recovered in acidic solution. The mass loss was the lowest (1%) at pH 7 but the sample was not regenerated. In the alkaline solution (pH 12) the mass loss increased to 20% and the adhesion of the Pd/C catalyst on the foam support was strongly affected. For this reason the alkaline solution was abandoned. Thereafter, all the in situ regeneration tests were performed in acid solution (0.1 M H₂SO₄) which was considered to be the optimum condition for Pd/C/foam catalyst regeneration.

3.3.2. *Acid pretreatment of the foam before catalyst coating*

Figure 7 shows the profiles of Pd/C/catalyst (sample 3) activity during the deactivation/regeneration cycles versus the cumulative turnover number

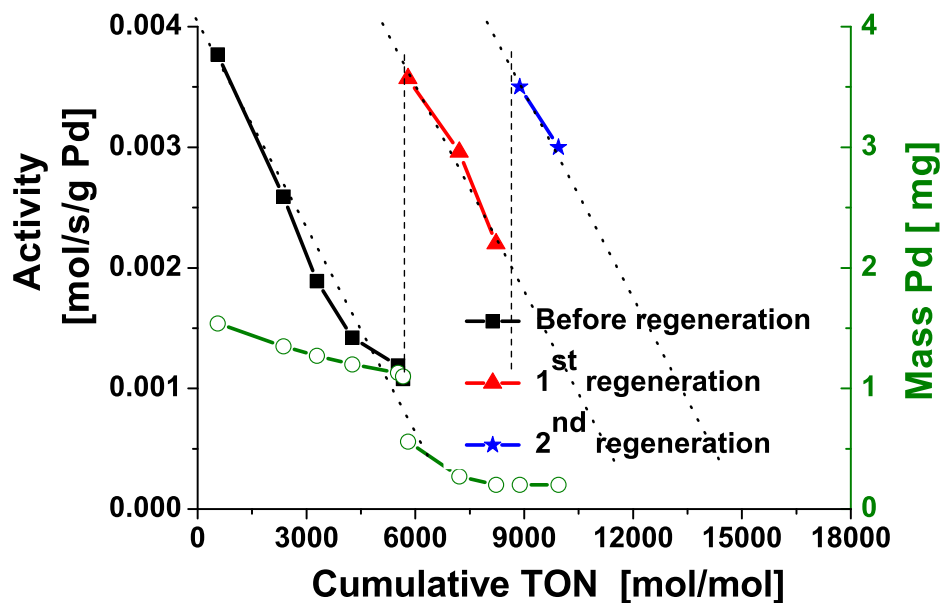


Figure 7: Catalytic activity variation versus cumulative TON during different deactivation/regeneration cycles in 0.1 M H_2SO_4 solution with removal and weighing of the sample between each experiment (circle symbols (\circ) represent the Pd mass). Acid pretreatment of the foam before catalyst coating.

(TON). Procedure A was applied between each batch experiment (each point corresponds to one batch experiment). The TON was expressed in mol of nitrobenzene transformed per mol of palladium. During the successive tests, the catalytic performance of the system strongly decreased due to the previously mentioned coke deposition on Pd active sites. These results are in good agreement with those obtained in [8, 9] with Pd/C/monolith. In the present experiments, after deactivation, the regeneration allowed to recover the initial activity of the catalyst, expressed per gram of palladium. However, it was observed that the weight of the sample strongly decreased during the experiments, especially after each regeneration step. The weight loss of the coating for a TON of 10000 mol/mol was 87%. We explained this result by the fact that the acid pretreatment of the stainless steel foam supports was not adapted to the reaction media of our experiments.

3.3.3. Basic pretreatment of the foam before catalyst coating

In order to select the most suitable preparation protocol for the Pd/C/foam catalyst, another sample (sample 4) was prepared after basic treatment of the foam. It was tested during the catalytic hydrogenation of nitrobenzene (Figure 8).

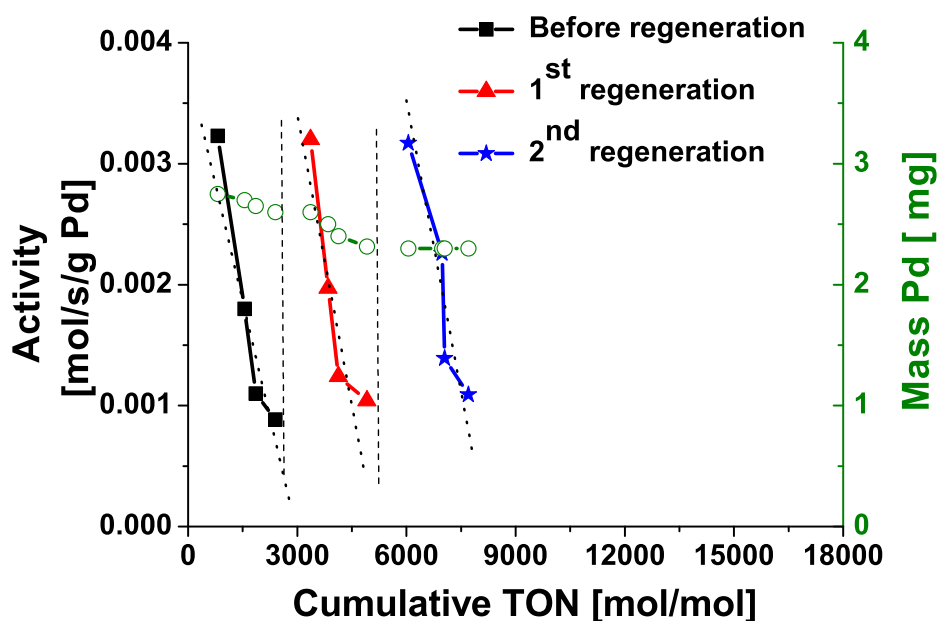


Figure 8: Catalytic activity variation versus cumulative TON during different deactivation/regeneration cycles in 0.1 M H_2SO_4 solution with weighing of the sample between each experiment (circle symbols (o) represent the Pd mass). Basic pretreatment of the foam before catalyst coating.

The initial mass of catalyst (and thus of Pd) is approximately two times higher for the catalyst prepared by alkaline treatment of the foam, due to a better adhesion of the coating. The catalyst showed the same deactivation curves than in Figure 7 (acid treatment of the foam) after several reaction/regeneration cycles (procedure A). However, it can be observed that the catalyst loss was much less than for the acid pretreatment of the foam (13%). The basic pretreatment of the foam before catalyst coating was able to passivate the stainless steel foam and to increase the coating adherence on

the support. Thereafter, all the samples were prepared with a basic pretreatment step. The remaining catalyst loss was expected to be due to the several handlings of the foam (removal from the reactor, weighing, reintegration into the reactor between each point of the figure).

3.4. *In situ deactivation/regeneration tests without weighing of the foam between each experiment*

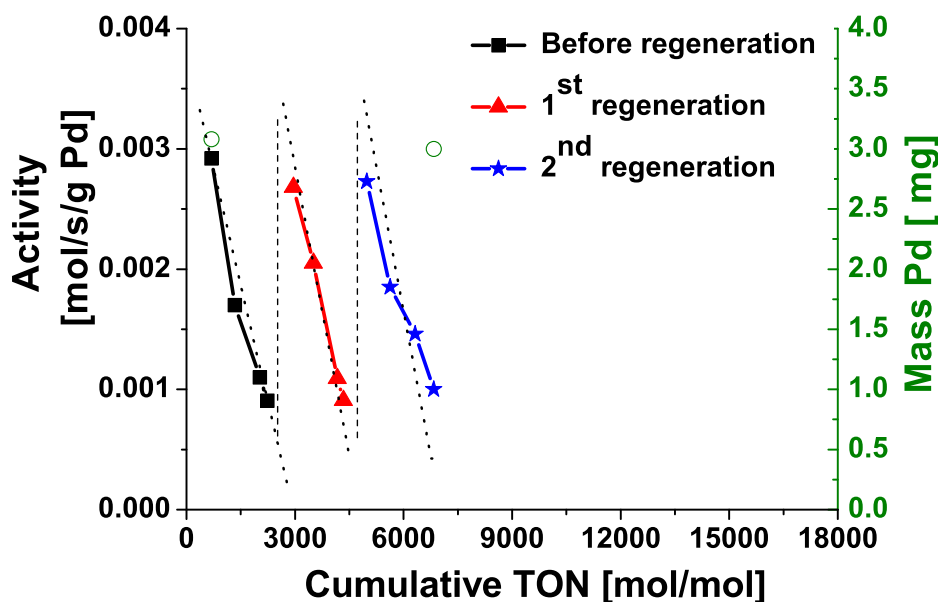


Figure 9: Catalytic activity variation versus cumulative TON during different deactivation/regeneration cycles in 0.1 M H_2SO_4 solution without weighing of the sample between each experiment (circle symbols (\circ) represent the Pd mass). Basic pretreatment of the foam before catalyst coating.

Finally, to avoid the weight loss due to the handling of the catalytic foam between each experiment, successive tests were run without removing the foam from the reactor (procedure B), thus simulating what could happen in a continuous set-up. As the catalyst (sample 5) was not removed from the reactor, several washings were performed to change the liquid solution from one batch operation to another. Figure 9 shows the variation of Pd/C/foam catalyst activity with cumulative TON during three cycles of

deactivation/regeneration. In agreement with the previous figure (Figure 8), it can be observed that the system can be electrochemically regenerated during in situ experiments. The deactivation rates were similar from one cycle to another. At the end of the three cycles, the foam was removed from the reactor; its weight decrease was only 0.06wt-%. This loss can be either due to the erosion of the entire object (foam + catalyst) or of its catalytic layer, thus corresponding to a loss of catalyst of 2wt-%. In both cases, the loss was considered as negligible and the in situ regeneration was validated.

4. Conclusion

The in situ regeneration of a Pd/C/foam catalyst by electrochemical method using a modified Mahoney-Robinson reactor was studied. It was found that a basic pretreatment of the foam before catalyst deposition strongly increased the Pd/C catalyst adherence on the foam substrates. Several deactivation/regeneration cycles were performed with and without removal/weighing of the catalyst between each measurement. Three kinds of electrolytes (pH 1, 7 and 12) were tested. The results demonstrated that the acid solution (0.1 M H₂SO₄) was the best electrolyte in that the catalytic activity of Pd catalyst could be recovered, at ambient temperature with low catalyst loss. The results of catalytic activity vs. cumulative TON curves suggested that the poisoning intermediate species were absorbed on the Pd surface and completely desorbed or transformed during in situ electrochemical regeneration. A new protocol for in situ regeneration of Pd/C/foam catalysts, by electrochemical treatment, was validated. The protocol developed during this study can be applied to structured catalysts that can not be removed from their hosting reactor. In this work, the electrochemical regeneration tests were performed in the same reactor than the catalytic experiments to demonstrate the feasibility of the in situ electrochemical regeneration for the structured catalysts. In future work, a study of the catalytic activity versus the applied potential for other reactions with other metal/carbon coated support catalysts (with possible other deactivation mechanisms) will be carried out.

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