

Characterization and industrial performance of a rhodium catalyst used in the production of an API

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ABSTRACT

This work aims to characterize a rhodium supported carbon catalyst used in the API production process. Several production parameters concerning the catalyst preparation and the first three steps of the production process were also evaluated. The results obtained were correlated with the catalyst performance in order to optimise the process. Regarding the results obtained, it was determined through XRD, TEM and AE that the rhodium catalyst supported onto activated carbon has metal particles of about 3 nm well dispersed in the support (about 6% Rh). By the BET method and H₂/O₂ titration, the differences between a fresh, reactivated, and exhausted catalyst in which both the texture properties and the metallic dispersion decrease between each type of sample are perceptible. By XPS analysis, was detected the presence of organic species entrapped in the catalyst, resulting from the industrial process, which can compromise the performance of the catalyst and are probably associated with the efficiency of catalyst cleaning.

Keywords: Rh/AC catalyst, life cycle, catalyst performance, hydrogenation, API production, catalyst properties

1. Introduction

Cipan – *Companhia Industrial Produtora de Antibióticos* – is a company that is dedicated to the production of active pharmaceuticals ingredients (API's) [1].

This work is focused on the production process of API where the rhodium catalyst (catalyst Rh/C) is used in the hydrogenation reaction to obtain an intermediate product called C. The rhodium supported on activated carbon catalyst has an important role in this process since it influences the yield of the product [2]. This way is important to characterize the catalyst in order to obtain his properties and correlate them with the results obtain industrially.

Through different characterization techniques, such as TEM, XPS, BET, H₂/O₂ titration, we obtain the textural and structural properties as well as the metallic dispersion and chemical analysis. These results were related with the analysis of the different production parameters with the aim of optimize the process.

2. State of Art

2.1. API production

The production process of API consists in some steps, having as a raw material called A. In this case, is important to know the steps that have a direct influence in the catalyst under study. To achieve the desired quality of the final product the process is monitored to check the presence of impurities and the efficiency of the catalyst. In fact, the catalyst can be deactivated due to four reasons: poisoning, deposition/ fouling, thermal degradation (sintering) and volatilization of active components. These factors lead to a decrease in activity and selectivity along the use of the catalyst [3].

2.2. Characterization techniques

The catalytic activity and the selectivity depend on the textural, structural and the chemical composition of the supported catalyst [3].

Taking into account the properties that we decided to analyse we can say that the catalyst support (activated carbon) was characterized by nitrogen adsorption (BET method), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) whereas the active phase was characterized by H₂/O₂ titration, transmission electron microscopy (TEM), elemental

analysis (AE) and XPS. Based on the literature and on the results from the different method it is possible to sum up some characteristics expected to obtain in the case of the catalyst under study.

In relation to the textural properties, it is expected that the activated carbon has a BET area between 680 and 1200 m²/g. From the adsorption-desorption isotherm, for low relative pressure, it was verified the rapid filling of the micropores while for higher pressures the adsorption curve reaches the equilibrium [4]. For the rhodium catalysts supported on activated carbon it was observed that the textural parameters are lower than those of activated carbon and decrease between a fresh and used catalyst [5].

The X-ray diffraction gives us information about the structure of the catalyst. This way, it is expected to obtain only peaks corresponding to the crystallographic planes of the carbon, which means a diffraction angle (2θ) between 23 e 25° and between 41 e 43° both in catalyst and activated carbon samples. In the catalyst samples, this fact is related with the high dispersion of the rhodium in the catalyst [4,6].

Based on the catalyst preparation and the quantities of reagents that are used [15,21], the rhodium percentage for the fresh and reactivated catalysts is about 6%. It should be noted that the catalyst has a high amount of humidity/ water (approximately, 53%) whereas the remaining percentage corresponds to the activated carbon.

From the HRTEM it is possible to obtain the size of the rhodium particles. So, considering the similarities between the catalysts in the literature and the catalyst under study, it is expected that the catalyst has metal particles with 3 to 4 nm of diameter [6].

To characterize the chemical nature of the samples, it was used the XPS technique. From the literature, it is possible to identify the characteristics peaks of rhodium: Rh 3d_{3/2} at 311.8 eV and Rh 3d_{5/2} at 306.9 eV which corresponds to the metallic rhodium and two peaks at 308.7 eV and 314.3 eV for rhodium oxidised species [7]. In relation to the carbon region (C 1s) it is expected the following peaks: 284.6 ± 0.2 eV for C-C and C=C bonds; 286 ± 0.2 eV corresponding to C-OH and C-O groups and 288.2 ± 0.2 eV which is related to C=O and O-C=O

groups [16]. Additionally, when it is compared a rhodium catalyst in different phases: used, reduced, and as prepared it is expected that the intensity of the peaks decreases from the fresh to the used catalyst. This can be justified by the decrease of the rhodium in the samples due to the use in the catalytic reaction [8].

Finally, in relation to the H₂/O₂ titration, we can obtain the percentage of dispersion of the metal on the support of the catalyst throughout the hydrogen that is adsorbed by the metal. For a catalyst with particles with a mean diameter of 5 nm, it is expected a dispersion of 22%. This value is valid to compare with fresh catalysts [9].

3. Experimental Part

3.1. Rhodium catalyst

The rhodium catalyst under study is supported on activated carbon and it is classified as a heterogeneous catalyst. The activated carbon was chosen due to his porous structure, high surface area and high stability where the active phase (rhodium) is adsorbed. Currently, the catalyst has two cycles of operation (designated as lifes) with four uses each one. Each batch of catalyst produced is divided into two parts (A and B).

The pre-reduction consists in the reduction of the catalyst and it occurs only before the first use. Then, the catalyst is used in the catalytic reaction and after the fourth use it is deactivated by washing the catalyst with water (after this step the catalyst is designated as exhausted catalyst). Finally, the catalyst is reactivated to perform the next reactions corresponding to the second life of the catalyst. The number of uses is influenced by the performance of the catalyst [10]. However, it is known that the activity of the catalyst is reduced from the first to the last use. This way is important to study the catalyst properties to discover what can be responsible for the reduction of the activity of the catalyst and the variability between different batches of catalyst.

3.2. Characterization techniques

The characterization techniques selected for the study of the properties of the catalyst were already mentioned. It should be noted that the HRTEM was

performed in the INL Braga, the AE (ICP-OES method) was carried out in the University of Aveiro (UA) and the remain methods were done at Instituto Superior Técnico. Each technique followed the respective procedure in order to obtain the results. The theory behind each method was considered to analyze the results shown in the following section.

4. Results and Discussion

4.1. Catalyst preparation parameters

In order to study the influence of some production parameters in the catalyst performance was elaborated some graphics. It should be noted that in this campaign were made some changes in the process that it is important to refer:

1. In the first step of the production process, there are the reuse of the catalyst P.
2. The use of FPH filter in the preparation of the Rh/C catalyst.
3. Some changes in the pre-reduction procedure of the Rh/C catalyst.

The performance of the catalyst can be evaluated by the % C. In the Figure 1, for the first life of the catalyst, we can see that the % C increases throughout the uses in the case of the pre-reduction change as well as with the change in the filter, except for the 5th use of the catalyst referring to the 00420 batch.

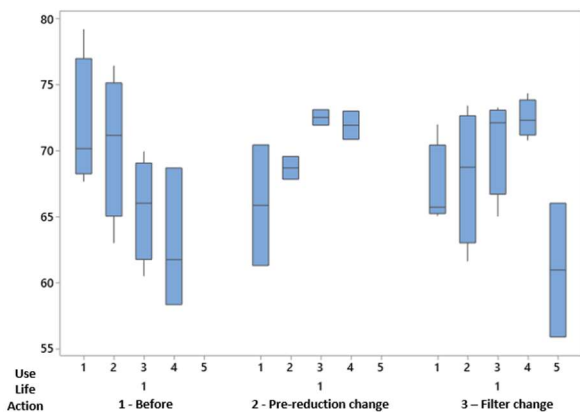


Figure 1 - Boxplot of %C as a function of the uses and actions

Another parameter studied was the hydrogenation time that with the changes made decreases between the uses. It was also observed the yield of each D batch according to the changes made in the process and

comparing the 2019 and 2020 results. For both situations, it was verified the increase in the yield.

In relation to the catalyst was elaborated the next graphic where we can see that the purity of the catalyst, obtained as the mean of the % C in each use, increase in relation to the last campaign of 2019.

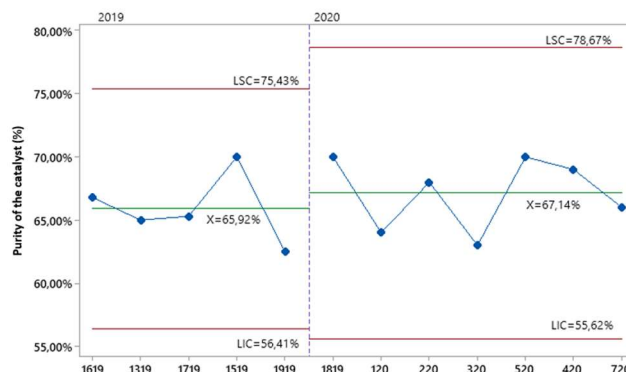


Figure 2 - Catalyst purity of each batch per year

In respect of the production parameters was studied the influence of temperatures, stirring speed and times that could affect the performance of the catalyst. As a result, it was found that a lower pre-reduction temperature is related with higher C percentage, which means that a temperature between 23°C and 26°C is preferred.

4.2. Catalyst characterization

4.2.1. Textural properties

These properties were obtained by the adsorption of nitrogen and the application of the BET method and t-method. The adsorption-desorption isotherm of the activated carbon is showed in the next figure.

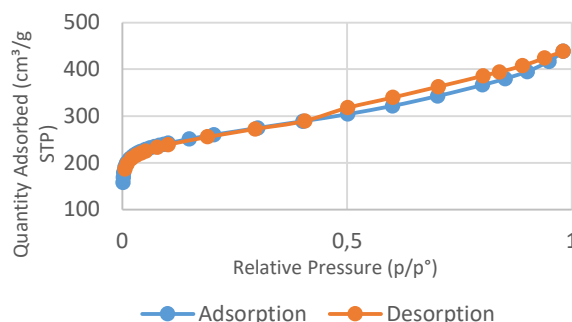


Figure 3 - Adsorption-desorption isotherm of the activated carbon

The Figure 3 shows that the activated carbon isotherm has hysteresis, since desorption does not coincide with adsorption for relative pressures above 0.4. For low relative pressures there is a rapid filling of the pores which is indicative of the presence of micropores. This is also true for the catalyst samples analysed. Considering the literature, these isotherms can be classified as Ib with a H4-type hysteresis [16,17]. The type of isotherm is characteristic of microporous materials but with some mesoporosity, so there is

hysteresis which indicate the occurrence of capillary condensation.

In the next table, there are represented the values of the different textural parameters for each sample. Similar to the isotherms, the parameters values decrease from the activated carbon to the exhausted catalyst, which corresponds to the observed in the literature and mentioned previously.

Table 1 - Textural parameters of the catalyst samples and activated carbon

Samples	Total volume (cm ³ /g)	Microporous volume (cm ³ /g)	Mesoporous volume (cm ³ /g)	BET area (m ² /g)	External area (m ² /g)	Microporous area (m ² /g)
Activated carbon	0.68	0.26	0.42	960	333	627
1819B fresh	0.63	0.24	0.38	908	316	592
120A fresh	0.62	0.24	0.38	886	313	573
420A fresh	0.61	0.24	0.38	881	310	571
420A pre-reduced	0.61	0.23	0.38	854	298	556
520A reactivated	0.41	0.12	0.30	529	251	278
1819B exhausted	0.30	0.08	0.22	366	182	184
120A exhausted	0.30	0.06	0.24	325	179	146

4.2.2. Structural properties

From the Figure 4, we can observe that the samples of catalyst, as well as the activated carbon only have the characteristic peaks of the support of the catalyst. In fact, we can identify two peaks for $\theta=23.8^\circ$ and $\theta=43.3^\circ$ related with the graphitic coal. These values agree with the ones provided by the literature. Moreover, it can also be concluded that the rhodium is well dispersed in the support of the catalyst [4,6]. Between different samples representing different phases of the life cycle of the catalyst there was not seen any difference by using this technique.

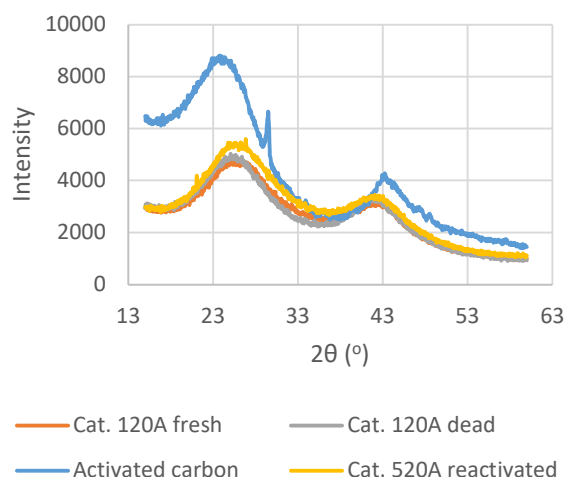


Figure 4 - X-ray diffraction pattern of activated carbon and the 120A new and exhausted (dead) catalyst and 520A reactivated catalyst

4.2.3. Elemental analysis

By the ICP-OES method, it was possible to perform the elementary chemical characterization of certain catalyst samples. Thus, all samples were found to contain approximately 3% of rhodium, i.e., about 6% on a dry basis. Considering the theoretical information, this observation is in line with the expected and allows us to

state that there is no leaching of the metal. The results obtained for each sample are presented in the following table.

Table 2 - Rhodium percentage of each catalyst sample

	% Rh
120A fresh	3.2
1819B fresh	3.2
520A reactivated	2.3
120A exhausted	3.0
1819B exhausted	2.7

It should be noted that the results obtained from this technique are also in accordance to the TG analysis that gave a mean percentage of about 50% of weight loss related to the humidity in catalyst.

4.2.4. TEM

This characterization technique allows us to have some pictures of the catalyst and determine the particle size. From the next figures it can be observed that the rhodium particles have a high dispersion in the activated carbon and the mean diameter of the particles is about 3 nm. These conclusions were observed for all the samples analyzed. For some samples, by electron diffraction it was observed some reflections of the rhodium for values between 1.9 Å and 2.2 Å, which are values associated to spacing of the cubic face structure (fcc) of some metals, as is the case of rhodium [11].

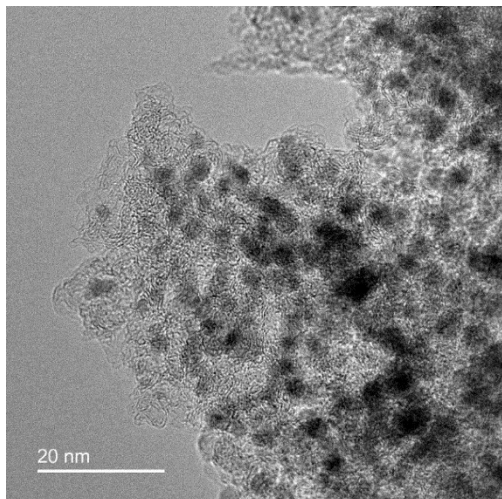


Figure 5 – TEM image of the 120A fresh catalyst

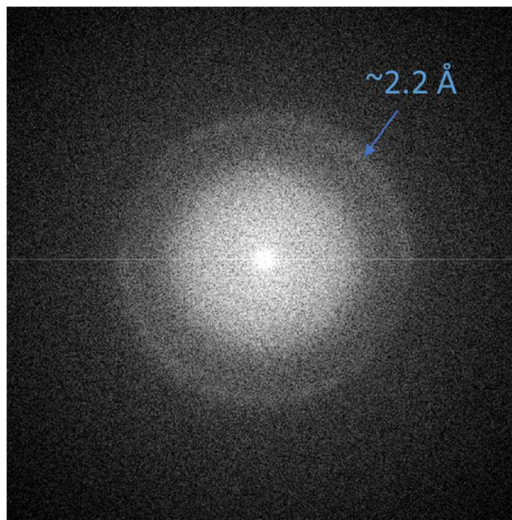


Figure 6 - Electron diffraction of the 120A fresh catalyst

4.2.5. XPS

For this technique was selected three samples that represented the life cycle of the catalyst: 00120A fresh, 00120A exhausted and 00520A reactivated, which is the reactivation of the 00120 catalyst.

This way, was obtained the complete spectrum for each sample and in detail the region of C 1s, O 1s and Rh 3d. From these graphics, the energy bonds and the respective attributions were determined as well as the global percentages of each element as shown in the next table.

Table 3 - Global concentrations (%) of the elements [12]

Elements	% global		
	120A Fresh	120A Exhausted	520A Reactivated
C	89.9	75.3	81.4
O	8.5	18.8	14.4
Rh	1.5	0.99	1.2
N	-	4.4	3.0
S	-	0.50	-
Rh/C	0.017	0.013	0.015
N/C	-	0.059	0.037
O/C	0.095	0.25	0.18
Rh(O)	1.19	0.73	0.84
Rh(III)	0.36	0.26	0.40
Coxide/Ctotal	0.20	0.32	0.31
Hydroxide or oxide/metal	0.31	0.35	0.47

From the results of this technique, we can conclude that the exhausted catalyst is richer in oxidated carbonic groups and in oxygen than the other samples. In the fresh catalyst, the presence of oxygen is associated to the rhodium oxide that is present in the sample. In relation to the rhodium the two components were detected which correspond to the Rh(0) and Rh(III). It was observed that the fresh catalyst has the higher amount of rhodium, followed by the reactivated and lastly, the exhausted catalyst. These conclusions are in accordance with the ones from the literature that were referred previously. Additionally, it was detected the presence of nitrogen and sulfur. Also, the energy bonds of the carbon and rhodium obtained were the expected, as well as the fact that the intensity of the peaks of the rhodium region decrease from the fresh catalyst to the used one. However, these values are not in line with the industrial performances of the catalyst, i.e., despite having higher amount of rhodium the 00120 catalyst was considered as a bad catalyst whereas the 00520 has a better performance. From this evidence, and together with the other conclusions, we can affirm that the preparation process is not affecting the performance of the catalyst. The Rh/C values at a general view have a similar quantity of rhodium which is in line with the observed by elemental analysis, indicating that throughout the process we don't have a significant loss of rhodium.

4.2.6. Metallic dispersion characterization

To obtain the values of the metallic dispersion, it was considered the 1st and 2nd cycles of hydrogen in order to have the integration area of the peaks. This method is based on the adsorption of hydrogen by the metal particles that are in the sample. This way, in relation to the activated carbon was obtained the graphic in the Figure 7 for the 2nd cycle of hydrogen. It is noted that the peaks have all the same signal which means that the activated carbon does not adsorb hydrogen and there are not metal particles in the sample.

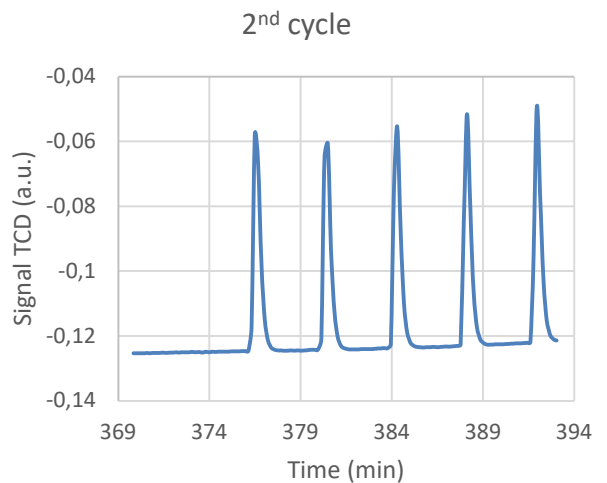


Figure 7 - H₂/O₂ titration (2nd cycle): activated carbon

In the catalyst samples, for example for the 00120A fresh catalyst (Figure 8), it was verified that the first peaks have small signal due to the adsorption of hydrogen. After these peaks, the surface becomes saturated and reaches a maximum signal close to the one registered in the activated carbon. It should be noted that the graphs for the 2nd cycle are shown as an example, but they are similar to those for the first cycle for both coal and samples.

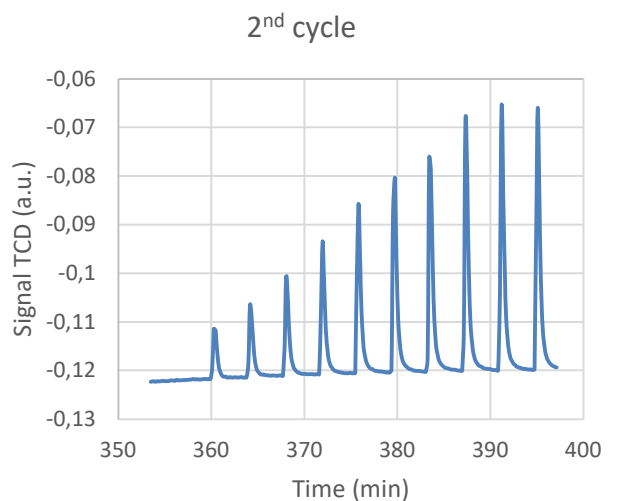


Figure 8 - H₂/O₂ titration (2nd cycle): 00120A fresh catalyst

The values of the metallic dispersion, metallic area and diameter are displayed in the next table.

Table 4 - Results obtained by the H₂/O₂ titration

	Mean dispersion (%)	Metallic area (m ² /g)	Diameter (nm)
1819B fresh	19	4.87	4.95
120A fresh	22	5.58	4.32
420A fresh	20	5.31	4.54
220B pre-reduced	3	0.71	34
520A reactivated	14	3.61	6.68
1819B exhausted	4	1.02	24
120A exhausted	4	1.13	21

From the table above, we can see that the fresh catalyst samples have higher dispersion values and smaller particle size which is in accordance with the TEM images of the respective samples. Then, we have the reactivated catalyst followed by the exhausted catalyst that has the smaller dispersion and higher diameter. These values are not in concordance with the results from TEM. However, these can be justified by the presence of organic molecules detected in the XPS analysis that prevents hydrogen from reaching the microporous. In fact, from the nitrogen adsorption, the exhausted catalyst has the smallest microporous area, reinforcing the fact that the micropores are contaminated with organic species other than rhodium. Comparing the values of the fresh catalyst with the literature (22%), the results are very similar.

5. Conclusion and Perspectives

Firstly, considering the main objectives of this work we can say that they were achieved since it was possible to characterize the catalyst by the different techniques and correlate these results with the industrial process in order to optimize the production process.

Based on the industrial results of the API production process, Cipan's optimization team implemented some actions that resulted from the analysis of graphs similar to those represented in section 4.1 - Catalyst preparation parameters that are already being monitored. Thus, it will be interesting to monitor the effect of these changes on the catalyst performance. As a suggestion, it is proposed to increase the pressure and time as well as to control the temperature of the Rh/C catalyst pre-reduction.

As far as the catalyst filtration is concerned, keeping the FPH filter, it is important to optimize the filtration time as well as the process itself (reduction of the amount of water) to obtain catalysts with an acceptable weight in the stipulated range in order to avoid drying in the oven. If this happens, it is proposed to follow the technique developed in order to standardize this stage of the process.

To sum up, through the various characterization techniques it was possible to conclude that the Rh/C catalyst is a mostly microporous catalyst with well dispersed rhodium particles (about 6%) whose diameter is about 3 nm.

Elemental analysis shows that there is no major change in the percentage of rhodium over the life cycle of the catalyst which is also in line with the expected and verified XPS. Thus, it is concluded that there is no great loss of metal during the process and no leaching of the metal. The absence of leaching of the metal can be confirmed by the supplier through the value of the recovered metal mass.

By XPS analysis, it was possible to verify that there is nitrogen in the exhausted (higher percentage) and reactivated catalyst samples, which is associated with the solvent used. The presence of this element may lead to catalyst poisoning due to the presence of nitrogen molecules in the active centres, so that they become less available for the catalytic reaction. In the exhausted catalyst the presence of sulphur, however, the absence of this element in the reactivated catalyst indicates that the catalyst cleaning procedure is efficient. To eliminate the presence of nitrogen in the reactivated catalyst it is suggested to optimise the catalyst cleaning process, namely the optimisation of the amount of solvent used.

In order to complement the study, another life cycle could be studied including a sample of pre-reduced catalyst and catalyst between 2nd and 3rd use, as well as catalyst samples for various oxidation times and wash waters. Another suggestion would be to evaluate the influence of catalyst storage time.

Finally, it can be concluded that the rhodium catalyst preparation process supported by activated carbon is somewhat robust and reproducible as different samples

of new catalysts have similar results. It has been found that a poorly performing catalyst at process level has properties similar to a good performing catalyst. Therefore, it can be said that the problem of this variability in catalyst performance is operational, so it is suggested to analyse several relevant points which may have an influence on the process. It should be noted that as analysed, the parameters of the API production process for the first three steps do not reveal any cause of catalyst performance variability either.

6. References

- VCH Verlag GmbH & Co. KGaA, 2008, pp. 738-765.
- [1] Cipan, fevereiro 2020. [Online]. Available: <https://cipan.suanfarma.com/>.
- [2] Cipan, "Preparação de DOT.B (1^o+2^o+3^o passo)," 2020.
- [3] O. Deutschmann, H. Knozinger, K. Kochloefl and T. Turek, *Heterogeneous Catalysis and Solid Catalysts*, Wiley-VCH Verlag GmbH & Co., 2009.
- [4] A. H. Wazir, I. u. Haq, A. Manan and A. Khan, "Preparation and characterization of activated carbon from coal by chemical activation with KOH," *International Journal of Coal Preparation and Utilization*, pp. 1939-2702, 2020.
- [5] E. Diaz, A. F. Mohedano, J. A. Casas, L. Calvo, M. A. Gilarranz and J. J. Rodriguez, "Comparison of activated carbon-supported Pd and Rh catalysts for aqueous-phase hydrodechlorination," *Applied Catalysis B: Environmental*, vol. 106, pp. 469-475, 2011.
- [6] Y. Suo and I.-M. Hsing, "Highly active rhodium/carbon nanocatalysts for ethanol oxidation in alkaline medium," *Journal of Power Sources*, vol. 196, pp. 7945-7950, 2011.
- [7] S. Akbayrak, Z. Ozçifçi and A. Tabak, "Noble metal nanoparticles supported on activated carbon: Highly recyclable catalysts in hydrogen generation from the hydrolysis of ammonia borane," *Journal of Colloid and Interface Science*, pp. 546, 324-332, 2019.
- [8] M. Álvarez-Montero, L. Gómez-Sainero, J. Juan-Juanb, A. Linares-Solanob and J. Rodriguez, "Gas-phase hydrodechlorination of dichloromethane with activated carbon-supported metallic catalysts," *Chemical Engineering Journal*, vol. 162, pp. 599-608, 2010.
- [9] G. Bergeret and P. Gallezot, "Physical Properties - Particle Size and Dispersion Measurements," in *Handbook of Heterogeneous Catalysis - Vol. 3: Characterization of Solid Catalysts*, Wiley-
- [10] Cipan, "Avaliação do impacto da 3^a vida do catalisador de ródio no processo de cloridrato de minociclina," 2019.
- [11] A. Lagrow, "Rh catalyst supported onto activated carbon matrix," Braga, 2020.
- [12] A. M. Rego and A. Ferraria, "Resultados XPS - Instituto Superior Técnico," 2020.
- [13] C. A. Wilde, Y. Ryabenkova, I. Firth, L. Pratt, J. Railton, M. Bravo-Sanchez, N. Sano, P. J. Cumpson, P. D. Coates, X. Liu and M. Conte, "Novel rhodium on carbon catalysts for the oxidation of benzyl alcohol to benzaldehyde: A study of the modification of metal/support interactions by acid pre-treatments," *Applied Catalysis A, General*, pp. 570, 271-282, 2019.
- [14] K. K. Dwivedi, P. Shrivastav, M. K. Karmakar, A. K. Pramanick and P. K. Chatterjee, "A comparative study on pyrolysis characteristics of bituminous coal and low-rank coal using thermogravimetric analysis (TGA)," *International Journal of Coal Preparation and Utilization*, 2019.
- [15] Cipan, "Preparação de Catalisador 2/C," 2020.
- [16] Cipan, "Plano de amostragem para a hidrogenação da DOT.T," 2020.
- [17] Cipan, "Utilização de catalisador 1/C e pré-redução de catalisador 2/C na DOT.B," 2020.
- [18] Cipan, "Instrução Técnica - Preparação de catalisador 2/C," 2020.
- [19] M. M. L. R. Carrott, "Physisorption of Gases By Solids: Fundamentals, Theories and Methods for the Textural Characterization of Catalysts," in *Catalysis from theory to application: an integrated course*, Coimbra, Imprensa da Universidade de Coimbra, 2008, pp. 83-105.
- [20] M. Thommes, "Physical Adsorption Characterization of Nanoporous Materials," *Chemie Ingenieur Technik*, pp. 1059-1073, 2010.
- [21] Cipan, "Preparação de Catalisador 2/C - Reativação," 2020.