

Variation in Structural Characteristics of a Hydrotreatment Catalyst with Deactivation/Regeneration Cycles

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The effect of reaction/regeneration cycles on some structural characteristics of a NiMo/Al₂O₃ hydrotreatment catalyst has been studied. The first regeneration produces increases in pore volume, porosity, and specific area. Above 5% coke deposit, various changes in such properties appear. Mo and Ni relative XPS intensities depend on the reaction/regeneration cycles Ni exposure decreases with them, whereas Mo exposure follows the opposite trend. The effect of coke on metal dispersion seems to be almost negligible. Coke concentration proved to be the variable which really influenced coke composition (H/C), independently of the history of the catalyst. The equation relating both variables is $H/C = 0.4378 + 1.342 \exp[(-C_c/S_e)/0.059]$ where C_c is the percentage coke concentration and S_e the specific surface area.

Introduction

Hydrotreatment catalysts are used in several refinery processes to eliminate sulfur and other contaminants present in petroleum. Their industrial and environmental applications and intrinsic nature have led to this type of catalyst being widely studied.

The activity of hydrotreatment catalysts decreases during the reactions they catalyze. This fact predetermines both the technology and economy of the processes they are applied in.

Carbon deposition plays an important role in their deactivation, being a function of feed and reaction conditions. It is the consequence of a polymerization/dehydrogenation reaction which generates coke structures capable of physically impeding the access of reagents to active centers and progressively blocking the porous structure of the catalyst.

Ocampo et al. (1978) and Beuther et al. (1980) have demonstrated that deactivation by coking is dominant under certain conditions.

In hydrotreatment catalysts, the characteristics, composition, and formation process of coke deposits in a fixed-bed reactor follow the general tendencies of all catalysts. Chang et al. (1986), Thakur and Thomas (1985), and Wukasz and Rase (1982) studied deactivation by coke deposition in this type of catalyst, finding that maximum deposition occurs on the outer edge of the catalyst and coke formation considerably reduces catalyst pore size and efficiency.

This loss in activity due to the blocking of active centers or pores by carbonaceous deposits is partially reversible. Regeneration is carried out by burning off the deposits in an oxygen-rich stream. Logically, regenerant composition is related to the necessity of avoiding excessive temperature rises that may damage the catalyst. The temperature needed for regeneration must be carefully controlled to avoid catalyst sintering, altered component distribution, or phase transformations as pointed out by Delmon and Grange (1980).

The importance of studying the regeneration of these catalysts became obvious from the work of Bogdanor and Rase (1986) and Teixeira da Silva et al. (1994). Additionally, in the study of their structural characteristic variations with each operation cycle, Ramaswamy et al. (1985) and Arteaga et al. (1986, 1987), for CoMo/Al₂O₃ catalysts, and Jiménez-Mateos et al. (1993) and García-Ochoa and Santos (1996), for NiMo/Al₂O₃ catalysts, found that changes occur in both the support and the active agent of the catalyst during the reaction/regeneration cycles and in some cases considerable reductions in diffusivity appear.

In order to study the effect of coke deposits and their later regeneration on the structural characteristics of the catalyst, sulfur was eliminated by an oxidative regeneration and the material obtained ("fresh catalyst") was subjected to the cumene cracking reaction. This causes deactivation in the bed due exclusively to coke deposits and is generally used as a test reaction in the study of catalyst deactivation in different reactors; since its kinetics, coke formation reactions and reaction products have been extensively studied by Wojciechowski and Corma (1986). The beds thus deactivated were later subjected to various reaction/regeneration cycles, allowing the effects of the coke deposit to be studied independently.

The aim of this work is to study the changes in a commercial Mo–Ni/Al₂O₃ catalyst as a result of different amounts of activity-reducing deposits, on being used industrially.

Coke composition must also be determined along with its possible variations with reaction conditions, these being important parameters in the exothermicity of the bed regeneration reaction. Knowledge of the structural changes in the catalyst, including metal dispersion and deposited coke composition, will allow better regeneration programming and catalyst life.

Method/Experimental Section

An industrial hydrotreatment MoNi/Al₂O₃ catalyst was used whose characteristics are given in Table 1.

The presulfured catalyst was provided from a kerosene hydrosulfurization process unit in a refinery.

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Table 1. Catalyst Characteristics

Chemical			
Al ₂ O ₃	73.8	Na ₂ O	0.07
MoO ₃	19.5	Fe	0.02
NiO	4.0	SO ₄	1.1
Physical			
nominal size (mm)	1.30/1.10	length (mm)	3.5
shape	extruded	average pore diameter (Å)	70
surface area (m ² /g)	122	quadrulobe	apparent
pore volume (total) (mL/g)	0.234	density (g/mL)	1.62

Sulfur deposits on this catalyst are due to the normal operation of the commercial unit using sulfured kerosene feedstocks.

Before the study, sulfur was eliminated by an oxidative regeneration, and these samples, called "fresh catalyst" were subjected to deactivation/regeneration cycles in order to study the effect of the carbonaceous deposits and its regeneration in the structural characteristics of the catalyst.

The catalyst deactivation and regeneration experiments were carried out in an installation made up principally of a fixed-tubular stainless steel reactor, 114 cm length $\times$ 3.5 cm internal diameter, offering the possibility of controlling the temperature gradient in the bed. The gas flows utilized were controlled by mass flowmeters. Temperature measurement was by a mobile probe with a chromel–alumel thermocouple 1.5 mm in diameter, which slides concentrically to the reactor.

For the cumene cracking experiments the reactor was heated to the appropriate temperature in a preheated stream of nitrogen. When the correct temperature had been attained, the nitrogen stream was switched to a mixture of cumene in nitrogen. The cumene was vaporized prior to being carried into the reactor by the nitrogen stream. The mixture was passed through the catalytic bed, with the cumene cracking reaction and coke deposition taking place with a possible catalyst deactivation. Outlet gases were analyzed by gas chromatography.

The deactivated bed was regenerated by burning off coke deposits in an O₂/N₂ stream at high temperature, analyzing the outlet gases with a CO₂ detector. During the regeneration reaction, nitrogen was passed through the catalytic bed until steady state was reached, and then the O₂/N₂ mixture was introduced to the desired concentration, measuring the temperature along the bed at several intervals.

Once the reaction and regeneration operations were over, catalyst samples were taken at different lengths of the bed and analyzed by thermogravimetry to obtain their carbon concentration, by mercury porosimetry and X-ray photoelectronic spectroscopy (XPS) to measure their structural characteristics, and by elemental analysis to measure coke composition.

The reaction conditions used in the cumene cracking reaction were as follows: temperatures ranging from 548 to 713 K, gas stream at values between 5×10^{-5} and 12.5×10^{-5} m³ s⁻¹, inlet gas composition for cumene concentrations in the interval 11.67×10^{-3} – 35.01×10^{-3} kmol m⁻³, and reaction times between 1800 and 5400 s. Meanwhile, the regeneration of beds with between 0.9 and 8% carbon was done in the range 668–786 K, at oxygen concentrations from 5 to 12% O₂ in N₂, and with gas flows at the inlet of 3–8 NL min⁻¹.

Photoelectron spectra were acquired with a Fisons ESCALAB 200R electron spectrometer equipped with

a hemispherical electron analyzer and a Mg K α X-ray source ($h\nu = 1253.6$ eV) powered at 120 W. A PDP 11/05 computer from DEC was used for collecting and analyzing the spectra. The samples were placed in small copper cylinders and mounted in a transfer rod placed in the pretreated chamber of the instrument. The base pressure in the ion-pumped analysis chamber was maintained below 5×10^{-9} Torr during data acquisition. The intensities were estimated by calculating the integral of each peak after smoothing and subtracting the "S-shaped" background and fitting the experimental curve to a combination of Gaussian and Lorentzian distributions, whose G/L proportion varied in the range 5–27%. All binding energies (BE) were referred to the Al 2p peak at 74.7 eV, giving values with an accuracy of ± 0.2 eV.

Results

The differences in characteristics of the presulfured, fresh, and coked catalyst have been studied, to see how the presence of carbon affects its structural parameters. In the same way, the catalyst can be tested for any physical effects of the total reaction/regeneration cycle by analyzing samples of the catalyst after the first regeneration. Even though this catalyst material contains no appreciable carbon and is operative, its physical structure might vary with coke deposition and its combustion during the regeneration reaction.

Structural Characteristics of the Catalyst. In order to study and compare the variations in the structural characteristics of the catalyst support with the reaction/regeneration cycles, mercury porosimetry were carried out on presulfured, fresh, coked, and regenerated samples. The catalyst shows a practically unimodal distribution for all samples, having a small percentage of macropores. However, most of the extrudate is formed by meso- and micropores of less than 90 Å as observed in Figure 1 for presulfured, fresh, and regenerated catalyst. The dip observed in all the curves for pores between 50 and 60 Å is due to the intrinsic pore structure of this commercial catalyst. In this figure the influence of reaction/regeneration cycles on pore diameter distribution can also be seen.

The presulfured catalyst presents a greater number of macropores and a more irregular distribution, caused almost certainly by deposits in the catalyst, while fresh and regenerated catalysts have a much more uniform macropore zone.

In addition, from the first regeneration the pore structure appears to alter, with the average diameter increasing considerably. This phenomenon grows along with the reaction/regeneration cycles, as seen in Table 2, where results are shown for the structural characteristics of fresh, presulfured, and regenerated catalyst for different reaction/regeneration cycles. The pore intrusion volume increases by 18% when the catalyst is regenerated the first time but decreases in successive regenerations, so the initial intrusion pore volume for cracking reactions is gradually less.

The sample regenerated for the first time presented a higher porosity than fresh catalyst, as found by Jiménez-Mateos et al. (1993) for this catalyst, furthermore increasing with successive reaction/regeneration cycles, which explains why beds with the same carbon deposits may present higher porosities than fresh catalyst. Specific area increases with the first regeneration and slightly decreases with time of catalyst use.

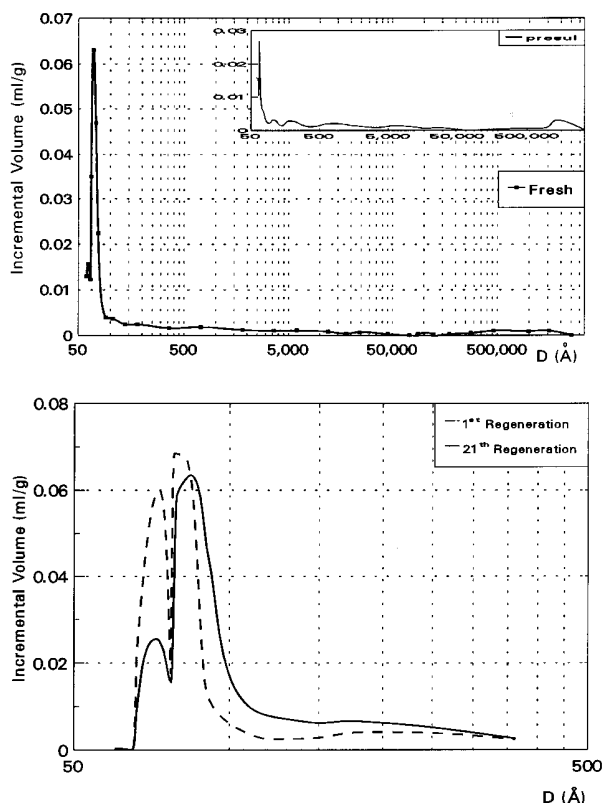


Figure 1. Incremental volume vs pore diameter for presulfured, fresh, and regenerated catalysts.

Table 2. Structural Characteristics

catalyst	D (Å)	ρ_{ap}	Vol_{Intr} (mL/g)	S_e (m ² /g)	ϵ
presulfured	66	1.69	0.106	51	0.18
fresh	70	1.62	0.234	122	0.38
1st regeneration	79	1.47	0.277	127	0.41
21st regeneration	84	1.64	0.251	110	0.43

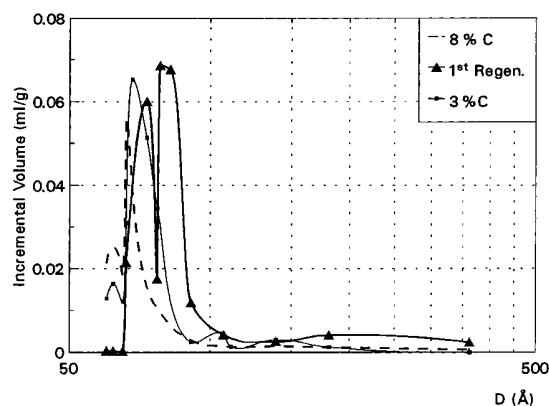


Figure 2. Incremental volume vs pore diameter for deactivated catalyst with different carbon percentages.

Figure 2 shows the pore distribution curves for the catalyst with coke deposits obtained after the first regeneration. It is seen that mean pore diameter decreases slightly as deposits increase.

The results coincide with those of García-Ochoa and Santos (1996) with regard to reduction in pore volume for C percentages higher than 3% but not in their distribution, since for these authors the change occur-

Table 3. Structural Characteristics Variations with Coke Content

catalyst	% C	D (Å)	ρ_{ap}	Vol_{Intr} (mL/g)	S_e (m ² /g)	ϵ
after 1st regeneration	8.5	67	1.61	0.168	89	0.27
	3.7	72	1.55	0.230	115	0.36
	3.0	71	1.52	0.249	129	0.38
after 3rd regeneration	1.0	72	1.68	0.243	121	0.41

ring with use is simply a reduction in pore volume, following the same distribution as fresh catalyst.

In Figures 1 and 2, changes are also observed in the pore diameter at which maximum intrusion occurs, due to the thermal effect of coke oxidation. The catalysts with a low C content show an even greater total pore volume than when fresh, due to increase of the intrusion volume observed after the first regeneration. However, at 8.5% C there was found to be a 39.2% reduction in the accumulative pore volume.

In Table 3 the structural variables for a catalyst with different coke deposits in material regenerated only once are shown, so that they are comparable without showing the influence of reaction/regeneration cycles. The decrease in the average pore diameter and intrusion volume when the coke deposit increases can also be seen from the Table 3. The same phenomenon is observed for the specific area, as expected. Similar results have been obtained by Wukasz and Rase (1982) and Díez et al. (1980). In any case, the changes only begin to be significant for deposit concentrations above 3%, in accordance with the results of García-Ochoa and Santos (1996), who record changes for carbon deposits of 5% and over.

As already commented, after each regeneration a slight rise in the average pore diameter and a similarly slight drop in the specific area and intrusion volume were seen. This explains the structural characteristics shown as examples in Table 3 for a material with 1% coke utilized after the 3rd regeneration, with specific area data lower than those for a 3% coke deposit in the catalyst only regenerated once. The behavior with the variation in coke percentage is analogous in all the cycles, so only one is shown as an example.

Coke Composition. This coke composition (CH_n) is to be taken into account during catalyst regeneration, since several researchers [Brito et al. (1990); Royo (1994)] have found it affects the maximum temperature developed during combustion.

The hydrogen content was measured in different beds and points in the reactor so as to determine how it is affected by the reaction variables and the coke profile along the bed. The H/C values were within the range reported in the literature, 0.4–1.8, varying inversely with coke content along the reactor.

Thus, when coke concentration increases, its hydrogen content decreases, as found by Hashimoto et al. (1983), Díez et al. (1980), García-Ochoa and Santos (1996), and Brito et al. (1996). However, this reduction is not as pronounced above 5% coke concentrations.

To see the influence of coke deposited on its composition, the H/C values obtained for different experiments are found in Figure 3, along with those at different points in the bed, independent of reaction conditions used, expressed against coke concentration. The values obtained by García-Ochoa and Santos (1996) for the same catalyst have also been included, finding that all the points fit the same curve, independently of the

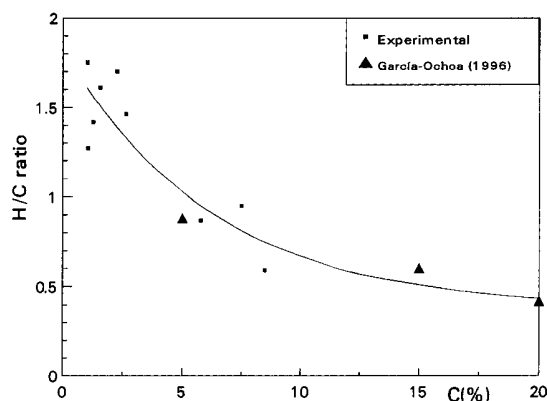


Figure 3. Catalyst coke composition vs carbon deposition.

catalyst's history. For low coke concentrations, the hydrogen content is high, and when it increases, the ratio H/C falls, tending toward a value of 0.42 for high coke contents.

These results may be normalized to the specific surface area when results from both parameters are available, continuing to give the independence of H/C from the experimental conditions. However, this result will be easier to compare with other catalysts than when only H/C and coke are related. An empirical correlation of these data produces

$$H/C = 0.4378 + 1.342 \exp[(-C/S_e)/0.059]$$

This equation may be used to obtain the coke composition once the concentration and specific surface area of the sample are known.

This correlation also fits the data of García-Ochoa and Santos (1996) but cannot be totally generalized since a lower density of active centers may be reflected in a lower coke concentration under the same reaction conditions.

These results are comparable with those of Brito et al. (1996), who also find for Cr_2O_3/Al_2O_3 catalysts that the only factor which really influences coke composition at any point in the bed is the coke concentration there and not the reaction history. This result allows coke composition in the bed to be found simply by measuring its concentration without the need to determine the hydrogen concentration, independently of conditions previously used in that reactor. Optimum regeneration conditions are thus able to be established.

Changes in Metal Dispersion. The changes in the metal exposure at the catalyst surface brought about by reaction/regeneration cycles have been evaluated by photoelectron spectroscopy (XPS).

The Mo 3d and Ni 2p_{3/2} core-level spectra of fresh, coked, regenerated, and presulfured catalyst are shown in Figures 4 and 5, respectively. The binding energy of the Mo 3d_{5/2} peak for oxidic catalyst (Figure 4, spectra a–c) at 232.7–232.8 eV is typical of Mo⁶⁺ ions, in agreement with that reported for MoO₃ or Al₂(MoO₄)₃ by Patterson et al. (1976), Okamoto et al. (1977), López Cordero et al. (1988), and Ramaswamy et al. (1985). For the presulfured catalyst (Figure 4, spectrum d), the Mo 3d_{5/2} peak is shifted to 229.4 eV, which is characteristic of Mo⁴⁺ ions in compounds of the type MoS₂ or MoO₂ according to Patterson et al. (1976), Okamoto et al. (1977), and Moulder et al. (1992). This catalyst also displays an additional S 2p line at 162.9 eV (Table 4), assigned to sulfide (S²⁻) ions. Elemental or oxidic sulfur

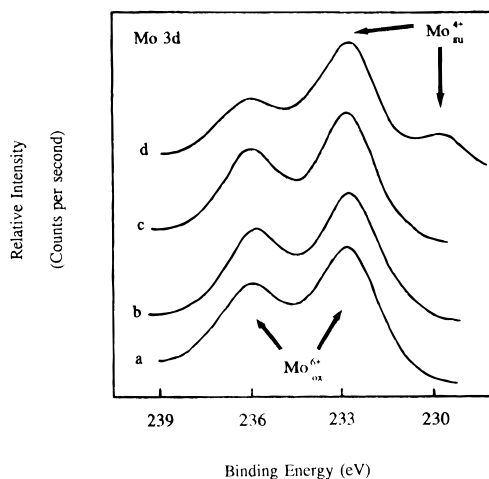


Figure 4. Mo 3d core level for fresh, coked, regenerated, and presulfured catalysts.

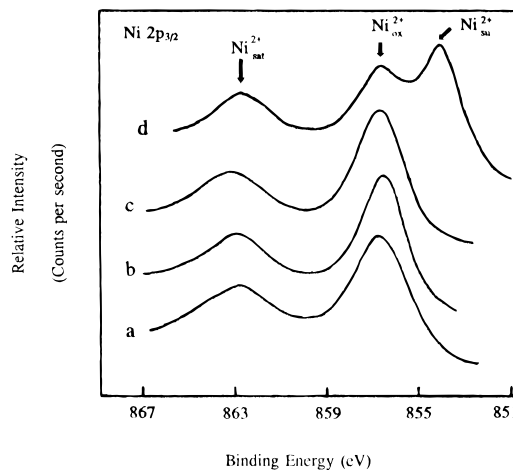


Figure 5. Ni 2p core level for fresh, coked, regenerated, and presulfured catalysts.

species like SO₃²⁻ or SO₄²⁻ must be ruled out as they appear at substantially higher binding energies [Moulder et al. (1992); Jiménez-Mateos et al. (1993)].

The binding energy of the Ni 2p_{3/2} peak at 856.6–856.7 eV for the oxidic samples is typical of Ni²⁺ ions tetrahedrally coordinated with oxygen ions (O²⁻) and approximately 1 eV higher than that expected for NiO (octahedral) species. As the peak is rather broad, octahedral Ni species might well be present although their proportion with respect to tetrahedral species seems to be rather low. Moreover, the Ni 2p_{3/2} peak of the presulfured catalyst (Figure 5, spectrum d) exhibits a major component at 853.9 eV attributed to nickel sulfide species, with a remaining component at 856.4 eV associated with unsulfided Ni²⁺ species. This conclusion is also supported by the observation of the satellite line at ca. 863 eV arising from shake-up processes in Ni–O species by Jiménez-Mateos et al. (1993). Table 4 also compiles the integrated intensities of Mo 3d and Ni 2p peaks relative to the Al 2p peak, which could be used as a measure of the dispersion of molybdenum and nickel oxides (or sulfide) as in Blasco et al. (1991). The results indicate that Mo and Ni relative XPS intensities depend on the reaction/regeneration cycles in agreement with Bogdanor and Rase (1986). The general observation is that Ni exposure

Table 4. Binding Energy (eV) of Core Electrons and XPS Intensity Ratios of the Mo 3d/Al 2p and Ni 2p/Al 2p

catalyst	% C	Mo 3d _{5/2}	Ni 2p _{3/2} ^o	S 2p	ξ	I _{Mo} /I _{Al}	I _{Ni} /I _{Al}	I _S /I _{Al}
presulfured		232.7	856.4			1.344	0.554	0.565
		229.4	853.9	162.9				
fresh		232.8	856.7			1.441	0.618	
1st deactivation	1.8	232.7	856.7		0.5	1.580	0.656	
1st regeneration		232.8	856.7			1.5697	0.656	
4th deactivation	1.0	232.7	856.6		0.5	1.69	0.562	
14th deactivation	6.1	232.8	856.6		0.16	2.043	0.569	
14th deactivation	3.5	232.8	856.6		0.5	2.063	0.575	
20th regeneration		232.8	856.6			1.819	0.541	

decreases with regeneration cycles whereas Mo exposure follows the opposite trend. This effect has already been observed by other authors [Jiménez Mateos et al. (1993)], and confirmed by the absorbances of the NO molecule chemisorbed on oxidic and sulfided catalysts. This phenomenon has been reported for CoMo/Al₂O₃ catalysts, becoming clearer as the number of regeneration cycles increased.

The increase in Mo exposure has been explained on the basis of a redistribution of MoO₃ species generated during the oxidation of sulfided or coked catalysts, with this redistribution being concentrated mainly at the outer surface of the carrier particle. The MoO₃ redistribution has been explained by assuming a very simple evaporation–condensation mechanism as in Arteaga et al. (1986), Prada et al. (1987), and Fierro et al. (1987). Although the MoO₃ vapor pressure at temperatures around 670 K is on the order of 10⁻⁵ Torr, exposure of the catalyst bed to the O₂:N₂ mixture for long periods of time or increasing the number of regeneration cycles favors migration of MoO₃ toward the close molybdena-free alumina surface. Such a mechanism would imply a change in the coordination of MoO₃ structures with the carrier surface, which becomes altered by the severity of the regeneration and the number of cycles. The effect of coke on metal dispersion seems to be almost irrelevant because, for two samples subjected to the same number of regeneration cycles but with different coke levels, the Mo/Al XPS intensity ratio remains quite similar, suggesting that molybdenum dispersion is mainly governed by temperature.

Finally, important changes in nickel exposure occur during catalyst regeneration. Table 4 shows that the Ni/Al XPS ratio decreases slightly in regenerated samples, in complete agreement with literature findings. Nickel losses are expected by solid-state reactions of the surface NiO phase over the free alumina interface during regeneration, whose extent depends on the temperature and duration of the regeneration process.

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Nomenclature

C:	carbon deposition degree (%)
D:	average pore diameter (Å)
S _e :	specific area (m ² /g)
V _{intr} :	mercury volume intrusion (mL/g)
ε:	porosity

ξ: adimensionless position in the catalytic bed

ρ_{ap}: apparent density (g/mL)

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