

Coke characterization for an industrial Pt–Sn/ γ -Al₂O₃ reforming catalyst

Nancy Martín^{a,*}, Margarita Viniegra^a, René Zarate^b,
Gabriela Espinosa^c, Nikola Batina^d

^a *Area de Catálisis, Departamento de Química, CBI, Universidad A. Metropolitana-Iztapalapa (UAM-I),
Av. San Rafael Atlixco 186, 09340 México D.F., Mexico*

^b *Subdirección de Transformación Industrial, Gerencia de Catalizadores, Instituto Mexicano del Petróleo (IMP) and
GIDT-PEMEX-Refinación, México D.F., Mexico*

^c *Programa de Ingeniería Molecular, Instituto Mexicano del Petróleo (IMP), Eje Central 156, 07730 México D.F., Mexico*

^d *Laboratorio de Nanotecnología e Ingeniería Molecular, Area de Electroquímica, Departamento de Química,
CBI, UAM-I, Av. San Rafael Atlixco 186, 09340 México D.F., Mexico*

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Abstract

This work presents the characterization of carbon on deactivated Pt–Sn/Al₂O₃ industrial catalysts, with Pt–Sn (0.3–0.3 wt.%) and γ -Al₂O₃ (with 0.9 wt.% Cl). The samples were deactivated in different cycles of industrial operation and compared with a catalyst deactivated in methylcyclopentane (MCP) reaction under laboratory conditions. Different sets of samples were used: (a) PS0 (deactivation under laboratory conditions); (b) PS1, with one cycle of industrial operation; and (c) PS2, with 106 cycles of industrial operation. Deactivated catalysts were analyzed and characterized using a combination of different techniques: elemental analysis, atomic force microscopy (AFM), temperature-programmed oxidation (TPO) and ¹³C nuclear magnetic resonance spectroscopy for solids (NMR). The ¹³C-CP/MAS NMR spectra were very similar, indicating the presence of aromatic carbons. TPO profiles showed differences between the samples deactivated during industrial operation and that deactivated in the MCP reaction. In the case of industrial catalysts, one type of carbon was detected. In contrast, the catalyst deactivated under laboratory conditions showed two types of carbon or two types of adsorption sites. AFM images revealed two types of coke morphology, granulate and laminate, which were characterized at the nanometer scale. Our results show that the characteristics of the coke depend on the deactivation process, and that coke on the industrial catalyst could be successfully described and defined. However, to correlate all the data obtained from different techniques and to understand the complete mechanism of coke formation, more detailed analysis should be performed.

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1. Introduction

Deactivation of naphtha reforming catalysts by coke deposition has been extensively studied during the last decade, due to its important impact on production yields

[1–4]. It is well established that coke formation depends on the operating conditions, the type of catalyst and the reactor feed composition. Catalytic reforming involves isomerization and dehydrogenation. Catalysts used in such processes are bifunctional, with the acidic function represented by chlorinated alumina and the metal function represented by Pt, with or without an alloying component. The acidic function promotes cracking and isomerization, and the metallic function promotes hydrogenation, dehydrogenation and hydrogenolysis. Both functions are required for

* Corresponding author. Fax: +52 55 58044666.

E-mail addresses: mgnc@xanum.uam.mx (N. Martín),
mgnc@xanum.uam.mx (M. Viniegra), gaespino@imp.mx (G. Espinosa),
bani@xanum.uam.mx (N. Batina).

bifunctional isomerization, ring enlargement and dehydrocyclization. The catalyst used in our study (Pt–Sn/ γ -Al₂O₃ with 0.3–0.3 wt.% Pt–Sn and 0.9 wt.% Cl) is one of the most frequently used industrial catalysts for reforming processes. Concurrently with these reactions, coke is deposited over the catalyst, decreasing its activity and modifying the selectivity [5–9]. Therefore, it is very important to understand the characteristics of coke and the mechanism of its formation, as well as the process for regeneration of industrial catalysts. For more data on the mechanisms involved in the deactivation process of such catalysts, see the recent paper of Sahoo et al. [10] and references therein.

For the deactivation and regeneration of reforming catalysts, it has been reported [11,12] that metallic sites with low coke concentrations lose their activity very quickly towards isomerization reactions and hydrogenolysis, while isomerization reactions controlled by the acidic function diminish linearly with increasing coke quantity. This opposed behavior was observed when the catalyst was regenerated. The metallic function is re-established more quickly after removing a small quantity of coke, but the acidic function recovers slowly [11,12].

At the industrial level, typical naphtha reforming catalysts such as Pt–Sn/Al₂O₃–Cl and Pt–Re/Al₂O₃–Cl are used with complex feeds during hundred of cycles, with operating cycles and regeneration treatments alternated. The latter consist of exposing the spent catalyst to oxygen or air at high temperature to burn off carbon produced during the reforming process, followed by a reduction step that returns the catalyst to the active (metallic) form. This decoking process normally involves the combustion of coke with a low concentration of oxygen in the first stage, with the oxygen content increased as coke is gradually gasified. This regular interval of operation is called a cycle, which has to be extended as much as possible to increase catalyst efficiency. However, the regeneration process has some impact on the physical and chemical properties of the treated catalyst (both metal and support). It slowly leads to global deterioration and low efficiency of industrial catalysts [13–15]. Whatever the industrial process, finding ways to limit or prevent deactivation by carbonaceous deposits and to regenerate the activity are important objectives. To this end, a great number of techniques have been used for locating and identifying carbonaceous deposits [16]. However, these deposits generally consist of a large number of compounds, which makes their identification difficult. Therefore, carbonaceous deposits responsible for deactivation are still often characterized in a simple manner, by their amount and their bulk elemental composition. More recently, examples using more sophisticated techniques for coke characterization have been reported. Transmission electron microscopy (TEM) coupled with electron energy loss spectroscopy (EELS) showed that on HSZM-5 and H-offretite, the coke structure was similar to that of coronene (pregraphitic), while on USHY it was more similar to pentacene (linear polyaromatic) [17]. X-ray diffraction (XRD) [18] and

Raman spectroscopy [19] analysis revealed features characteristic of graphitic carbon. Scanning probe microscopy (SPM), in particular atomic force microscopy (AFM), provides the opportunity to extend this surface science protocol to particles of carbon with nanometer scale resolution.

The aim of this paper was to study coke deposited on a Pt–Sn/ γ -Al₂O₃ catalyst after industrial operation in several cycles to analyze the changes suffered by the catalyst under different reaction conditions. As a reference, Pt–Sn/ γ -Al₂O₃ deactivated in the laboratory in the methylcyclopentane reaction was used. The catalysts were characterized by temperature-programmed oxidation (TPO), elemental analysis, nuclear magnetic resonance of ¹³C (¹³C-CP/MAS NMR) and AFM. Our particular focus was on AFM results. Although AFM is an established technique in materials and surface science [20–24] as a powerful tool for nanometer scale characterization, so far it has not been used as frequently in the field of catalysis, especially for industrial sample characterization. Among the many different and possible reasons, visualization of the surface of the industrial catalysts is undoubtedly a difficult process and interpretation of such multi-composite and multi-crystalline or even amorphous surfaces is still a very difficult task. The major goal in our study was to find an easy and secure methodology to identify coke in the AFM images and characterize it in terms of the shape and the size of surface features. Further intentions are to locate the exact position as the preferential site for coke formation on the catalyst surface, and to compare and support the visualization findings with data obtained from the other techniques used in our study.

2. Experimental

2.1. Materials

The samples of industrial catalysts used, PS1 and PS2, are commercially available Pt–Sn/ γ -Al₂O₃-based catalysts (IMP, Mexico) used in the PEMEX industrial plant for naphtha reforming (UOP) in the continuous catalyst regeneration mode. The PS1 sample went through a single operation cycle, whereas PS2 endured 106 cycles at the industrial level. The reaction conditions in these cycles for both samples were: pressure, 10.5 kg/cm²; LHSV, 2.2 h⁻¹; H₂/Hc molar ratio, 3.7. The laboratory reference catalyst (Pt–Sn/ γ -Al₂O₃-Cl; PS0), was prepared by coimpregnation of the Al₂O₃ support with H₂PtCl₆·6H₂O (Aldrich, 99%) and SnCl₄·5H₂O (Aldrich, 99%). The impregnated sample was dried at 393 K and calcined in air at 673 K for 3 h. It was then reduced under H₂ flow for 4 h at 673 K. The hydrogenolysis of methylcyclopentane (MCP) (Aldrich, 99.7%) was conducted in a conventional flow-differential reactor under the following conditions: reaction temperature, 500 °C; WHSV, 4.5 h⁻¹; H₂/MCP molar ratio, 2; atmospheric pressure. The run length was typically 8 h.

Table 1
The elemental analysis and general properties of the tested catalysts

Samples	Pt (wt.%)	Sn (wt.%)	Cl (wt.%)	BET surface area (m ² /g)	Pore volume (cm ³ /g)	Carbon (wt.%)
PS0	0.37	0.37	0.93	212	0.50	5.9
PS1	0.27	0.26	1.12	182	0.78	5.4
PS2	0.32	0.30	0.86	133	0.82	6.0

2.2. Catalyst characterization

The BET specific area of the catalysts was determined by nitrogen adsorption using a Micromeritics ASAP 2000 instrument. Samples were reactivated in vacuum ($<10^{-2}$ Pa) at 300 °C for 2 h. The main textural characteristics of the catalysts are shown in Table 1.

Elemental analysis was performed on a Perkin-Elmer CHNS/O PE-600 instrument to determine the amount of carbon deposited.

TPO analysis of the deactivated samples was carried out in an ISRI-RIG automatic reactor with a thermal conductivity detector using a mixture of 5 mol% O₂ in Ar, with a heating rate of 5 °C/min from room temperature to 900 °C and a flow rate of 60 cm³/min.

¹³C-CP/MAS NMR spectra were recorded on an ASX 300 Bruker spectrometer at 75.47 MHz with a contact time of 1 ms at a spinning rate of 5 kHz and 90° pulses of 4 μs.

The surface morphology of the catalyst samples was probed using a Nanoscope III AFM (Digital Instruments, Santa Barbara, CA, USA). Imaging was performed *ex situ* under laboratory atmosphere conditions. AFM was operated in the so-called tapping mode (Digital Instruments, manual for Nanoscope III-SPM) [22], which is less invasive and recommended for surfaces with “soft” adsorbed material. Commercial Si cantilevers (NanoSensors TESP, DI), were used. An optical stereovideo-microscope was used to select up to five different points for AFM probing on each sample to allow for the statistical nature of AFM analysis. Images presented in this paper are plotted as a combination of the height and amplitude modes, which increases resolution, but only partially represents the surface topography. All quantitative evaluations, as measurement of the lateral dimensions (size) and height of the observed surface features, were based on the interpretation of AFM images recorded in the pure height topographic mode.

3. Results and discussion

According to the main objectives of this study, samples were characterized with a variety of different techniques to obtain information about the chemical composition (primarily quantity) and physico-chemical characteristics of carbon deposits. To obtain this basic information, we first used measurement of the standard BET specific area and standard elemental analysis. Results presented in Table 1 show interesting but more or less expected findings. First of

all, the chemical composition of all investigated samples is the same with respect to Pt and Sn content. Indeed, the amount of carbon present in the industrial catalyst after different cycles (PS1 and PS2) is very similar to that obtained in the sample deactivated in the MCP reaction (PS0). Note that PS0 was deactivated in a laboratory process and serves as a model (reference) system in this study. The BET surface area for the industrial catalyst after 106 cycles decreases by 27%, which clearly shows that extended use leads to a decrease in catalyst area and to deactivation. As concluded in previous work based on a similar concept as used here, results from elemental analysis and BET surface area determination cannot alone explain the complex process involved in coke formation [10].

Furthermore, our samples were characterized using the sophisticated ¹³C-CP/MAS NMR technique. Fig. 1 shows the ¹³C-CP/MAS NMR spectrum for sample PS0, with a sharp and dominant peak in the region of 120–130 ppm. According to the literature [10,25] this can be assigned to the presence of aromatic carbon. The existence of a signal attributable to the presence of aliphatic carbon was hard to confirm (see the almost undetectable shoulders at 20 ppm). To improve the resolution and quality of our spectra, we optimized our analysis by changing the contact time and the recycle delay; however, this did not give the expected result. More interestingly, we found similar spectra for all three samples, which clearly indicates the highly aromatic nature of the coke deposit in all cases. Similar types of spectra with the same conclusions have been reported [10,25] for Pt–Sn/Al₂O₃ industrial catalysts. However, in those cases the catalysts underwent different treatments than our samples,

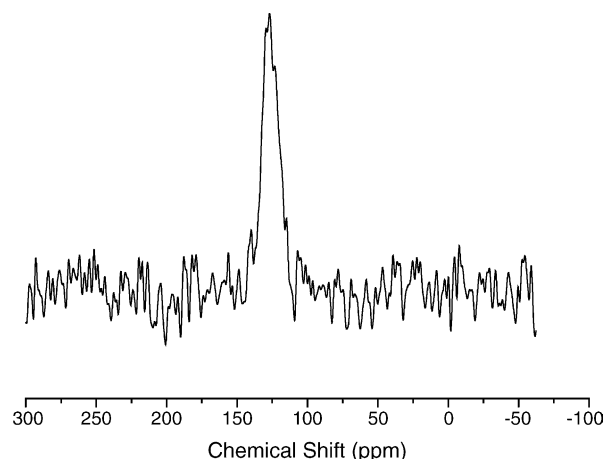


Fig. 1. ¹³C (CP/MAS) NMR spectra of the PS0 sample.

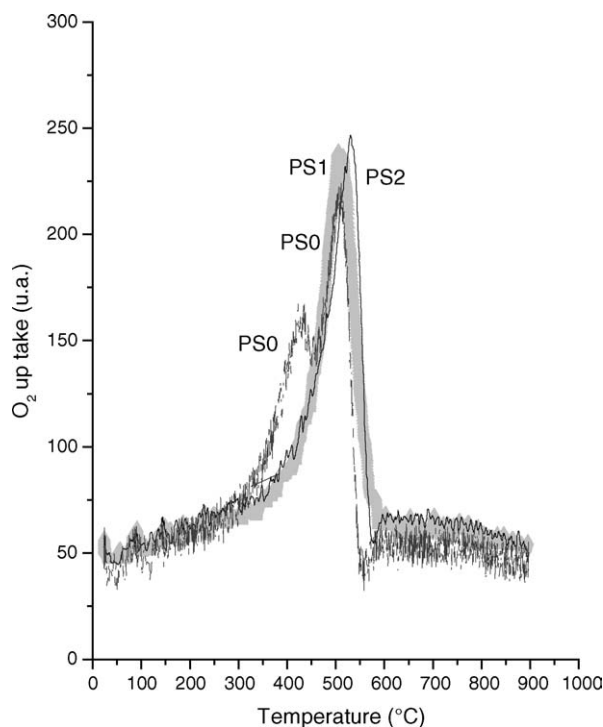


Fig. 2. TPO profiles of deactivated samples: (---) PS0, (····) PS1 and (—) PS2.

which we expect would lead to the development of a different type of coke.

In terms of location of coke deposits on the catalyst surface, results of the TPO analysis seem to be of special interest. The TPO profiles for all three samples, shown in Fig. 2, exhibit some differences in the number and shape of peaks. TPO peaks for industrial samples PS1 and PS2 show only one peak for coke oxidation at approximately 520 °C. It has been shown that this type of coke is less reactive to oxygen [8,25,26] and corresponds to coke deposited in particular on γ -Al₂O₃ supports, far from the metallic centers that catalyze the gasification of carbon [29]. In line with this, it could be concluded in the case of PS1 and PS2 (samples with industrial treatment) that either one type of coke forms on the substrate, or all types of coke formed occupy the same type of site.

Indeed, we demonstrated in a separate experiment that coke oxidation on pure γ -Al₂O₃ takes place at the same temperature. On the other hand, the reference sample, PS0, showed two TPO peaks, one at 523 °C assigned to carbon deposited on the support and an additional peak at 440 °C, attributed to coke deposited on the metal–support interface [8]. The fact that the nature of the coke could be different on metal and support sites in bifunctional catalyst systems should be considered, as reported in the literature [7,27,29]. In addition, the TPO results clearly show differences between catalysts treated in industrial processes (PS1 and PS2) and the laboratory catalyst (PS0). Using the nature of the coke formed as a basis, differences between the

deactivated samples can be attributed to different coke characteristics. In the industrial samples, the coke formed should be more polymerized, burn at higher temperature, and be deposited on the support. The coke formed during the MCP reaction readily spreads to cover a larger surface and is deposited in both catalytic phases, the metallic and acidic sites of the support. However, it is important to remark that NMR provides no evidence for any different coke nature in the three catalysts.

Sárkány et al. [28] proposed two possible pathways for the formation of coke on metal sites, one involving adsorbed single C-atom entities, and the other occurring by polymerization of polyolefins. The first mainly occurs on metallic sites and the second pathway corresponds to the metallic-support interface. These carbonaceous residues are more or less mobile carbon islands. It has been reported [29] that the time on-stream significantly affected the mechanisms of coke formation, mainly by decreasing the formation of coke on metallic particles and increasing the coke deposited on acidic sites of the support by forming graphite-like 3D structures. In principle, this is in agreement with our observations, since more coke was found on the support for the industrially treated PS1 sample.

It is also interesting to note that our findings of two types of coke or two types of sites on the Pt–Sn/ γ -Al₂O₃ samples are very close to the data reported by Sahoo et al. [10]. However, in this particular work, the analysis was carried out separately for soluble and insoluble coke, which apparently makes comparison more difficult. As reported by Afonso et al. [30], the structure of insoluble coke contains more polyaromatic structures and is quite different from that of soluble coke, with dominant proportions of aliphatic groups. They also showed that the elimination of soluble coke caused the disappearance of the low-temperature oxidation peak in TPO spectra.

In general, AFM analysis of the deactivated catalyst samples revealed two types of surface morphology, consisting of large laminate-type features (ellipsoid or disc-like features with diameter of 1.5–2.5 μ m) and small granulate features (spheres of diameter 50–250 nm). Fig. 3 shows AFM images for (a) PS0, (b) PS1 and (c) PS2 samples. Since all samples were black in color, visual inspection led us to believe that they were completely covered by coke, and it is easy to suppose that all features observed in the AFM images are related to the carbon deposit. Furthermore, both types of visualized features should be related to two different forms of coke. More detailed analysis of the images obtained leads to further conclusions. First, it was apparent that PS0 and PS1 samples had a similar ratio of large disc-like and small spherical features. On both samples, small spherical coke clusters were aggregated around the edges of the large discs. More structural details of the aggregated coke clusters were clearly resolved in the high-resolution AFM image of the surface of the PS1 sample (Fig. 4). A large aggregate of almost 1800 nm in diameter was formed from

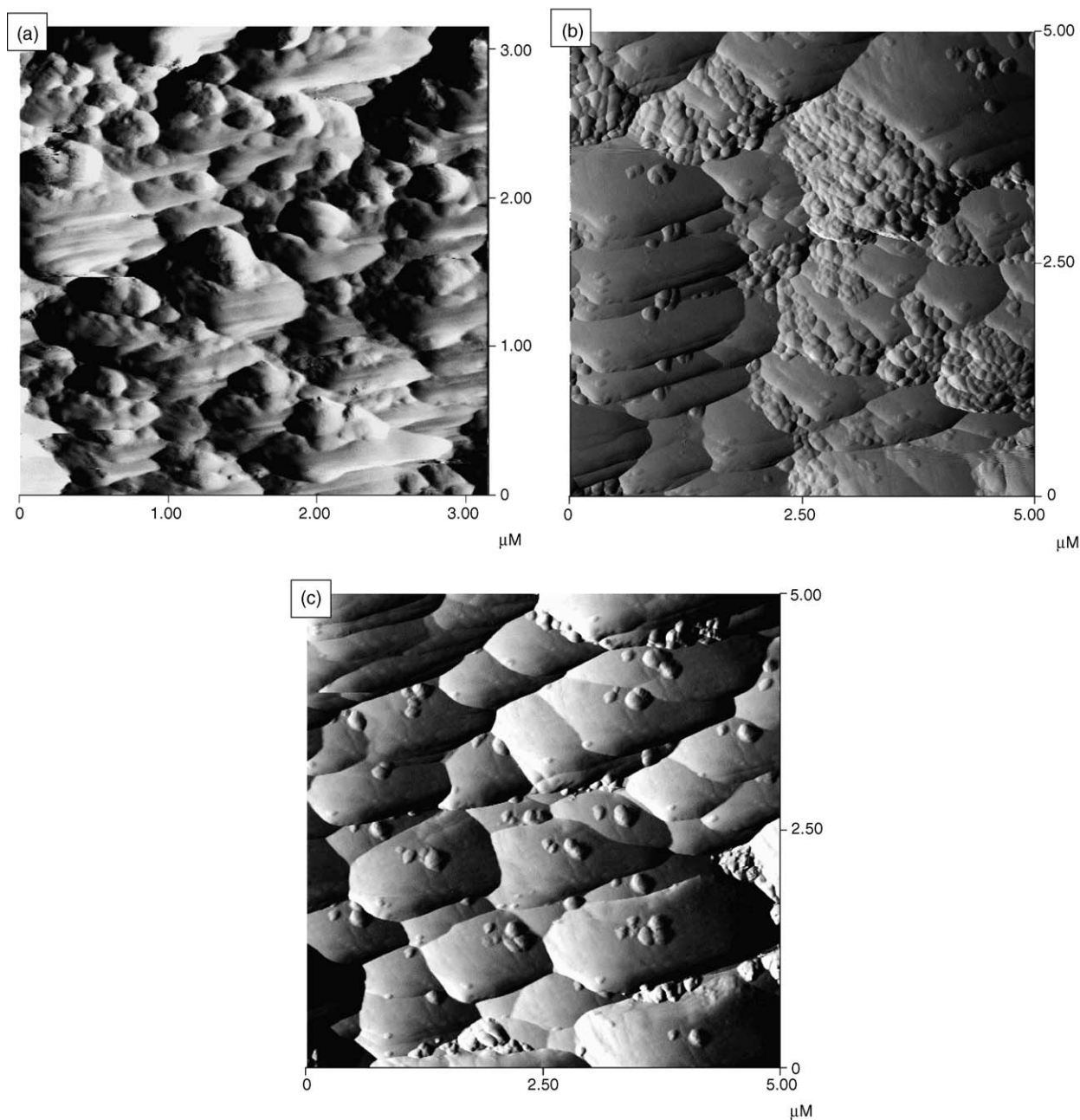


Fig. 3. AFM images of deactivated samples: PS0 (a), PS1 (b) and PS2 (c). Z-scale range in the images (a and c): 0–0.70 μm and in the image (b): between 0 and 1.50 μm .

approximately 220 much smaller spherical coke particles of 55–59 nm in diameter. As seen in Fig. 3a and b, coke aggregated preferentially around the edges of the large discs. The reason for this could be a property of the surface, e.g. the influence of surface roughness, or related to the non-homogeneous distribution of metal particles on the catalyst surface. We could not speculate further, since our results do not show a level of detail sufficient to see where the metallic centers are located on the catalyst surface. However, we noted that images recorded in the amplitude mode do not show great differences in contrast

between the small spherical and large disc-like features, which means that images show a surface with similar mechanical properties (hardness or elasticity of a single type of material, i.e. carbon).

In contrast, from the image presented in Fig. 3c for the PS2 sample, which passed through 106 cycles, it is evident that prolonged use resulted in a decrease in the proportion of small spherical coke particles, with carbon mainly present in the form of large, smooth disc-like grains. According to the elemental analysis results, all three samples have a very similar carbon content (Table 1), which means that in the

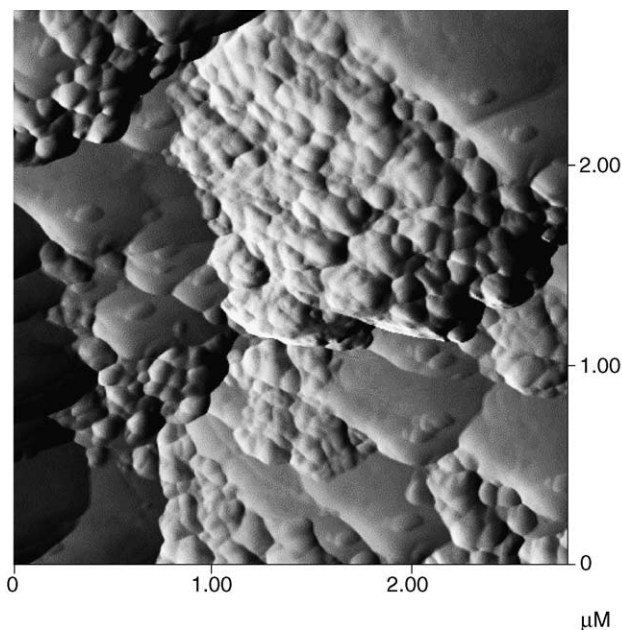


Fig. 4. Detailed structure of the coke aggregate located at the edge of the PS1 catalyst grain. Z-scale range between 0 and 0.50 μm .

case of PS2, coke is mostly in the form of large disc-like grains (laminated phase). Small spherical coke clusters were also apparent on the PS2 sample, growing more independently and showing no tendency for preferential aggregation and accumulation (Fig. 5). These results are interesting, since very few detailed visualizations of coke on industrial catalysts have been reported so far. Differences observed in the growth behavior led to conclusions on the type of carbon on the catalyst surface, with granular aggregated carbon deposited on the support (PS0 and PS1) while laminated carbon was deposited on the metal–support interface (PS2). In line with this, it could be supposed that the formation of laminated coke is a favorable process after an extended number of cycles.

Finally, TPO experiments showed that these two types of coke were oxidized at different temperatures. However, this does not entirely agree with the TPO data, which indicated a major difference between PS0 and the industrial catalysts (PS1 and PS2). Therefore, it should be noted that the different coke features visualized by AFM are not directly related to the TPO behavior observed. In other words, the TPO behavior observed is not related to the selective oxidation of coke in granulated and laminated phases. An explanation for the TPO behavior observed is rather related to a different level, which requires visualization of catalyst surfaces at atomic resolution. At this point, it is worthwhile mentioning that the quantity of metal in the catalyst is very small (0.3 wt.%) and that so far we have no reliable data on what proportion is on the surface (accessible to AFM analysis) and what is in the bulk. Further experiments using more model systems are in progress to resolve this crucial issue.

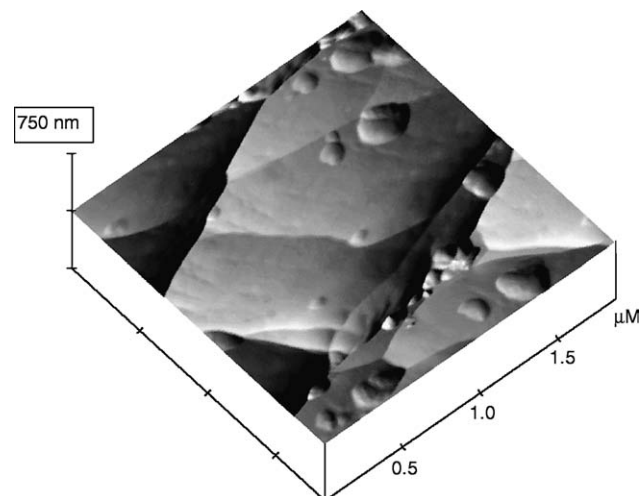


Fig. 5. High resolution AFM image of the surface of PS2 catalyst covered by small clusters of coke, presented in 3D view mode.

4. Conclusions

Carbon deposits on Pt–Sn/ γ - Al_2O_3 industrial catalysts were characterized by a combination of different techniques, including elemental analysis, AFM, TPO and ^{13}C -CP/MAS NMR spectroscopy. Besides the detailed qualitative and quantitative evaluation, which showed the same quantity of carbon on all samples, we found that coke on the industrial catalysts was of aromatic type, independent of the number of use cycles. TPO analysis pointed to a difference between the industrial catalysts and the catalyst treated in the laboratory as a model system, clearly showing that either two types of coke or two types of sites (substrate versus metal–substrate interface) for the formation of coke are indicated by interpretation of these data. AFM analysis revealed characteristics of two types of coke morphology, described as laminated (elliptic disc-like structure) and granular (spherical) coke phases. Large coke aggregates were observed at surface defects, such as grain edges. In general, our results show that the nature of the coke depends on the deactivation process, and that the coke on the industrial catalyst could be successfully described and defined. However, to correlate all the data obtained from the different techniques and to understand the mechanism of coke formation, more detailed analysis is required.

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