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Original scientific paper

MICROSCALE FEATURES OF Pd-Pt AGGREGATES RESULTED FROM ANILINE HYDROGENATION TAR INCINERATING PROCESS

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Abstract
The Ca-carbonate carbon capture filter product of a tar incineration plant captures the degraded and discharged catalyst metals also, which are Pd and Pt. The electron microscopy investigations have revealed a wide range of sizes and morphologies existent for the metal rich particles. Detailed investigations after different disaggregation procedures show the size scale dependent differentiation of metals and oxidic components. The smaller, submicrometric particles tend to be Pt-rich, while with increasing particle sizes aggregates are developed, with increasing Pd and possibly PdO content. The role Fe-oxide is the cementing phase of the Pd-rich larges aggregates.

***Keywords**: recovery, PGE, nanoscale*

1. INTRODUCTION

As a most suitable elimination process of the tar (non-utilizable byproduct) generated in an aniline plant is incineration, with flue gas neutralization system. In the generated ash fraction, removed by the flue gas filter system, the escaping catalyst residue is also captured, mostly as Fe-oxide cemented aggregates but also individual Pd +/- Pt grains. From the viewpoint of metal recovery and recycling, the morphological and aggregation state of catalyst metal components is of primary importance [1]. In order to draw a detailed picture about this issue, scanning electron microscopy and energy dispersive X-ray spectrometry (SEM+EDX) investigations have been carried out beyond bulk compositional analysis. The target of present study is on the microscale characterization of Pd and Pt distribution in the Ca-carbonate and hydroxide matrix, developed by the flue gas treatment process.

2. EXPERIMENTAL

Analytical sample preparation methods were adjusted to the scope of the investigations, the main focus being put on scanning electron microscopy with energy dispersive X-ray spectrometry (SEM+EDX) on samples prepared by water-based separation, magnetic separation and hydrochloric acid dissolution. Each treatment procedure revealed new and useful insights into the micro- and nanostructure of the oxide matrix – metallic particles relations and additional low amount components.

3. RESULTS AND DISCUSSION

XRD analysis (Figure 1) showed calcite (trigonal $CaCO_3$) as the matrix material, with significant amount of residual $Ca(OH)_2$, Ca-sulfates (as anhydrite, bassanite and gypsum) and Ca-Na sulfate as cesanite. Minor components are more numerous, including the Pd, Pt, PtO, maghemite,

aragonite, quartz and sylvine. The residual portlandite was also confirmed by the pH swift to 11 upon distilled water immersion, while the high Ca-carbonate content was supported by the weight loss upon HCl treatment.

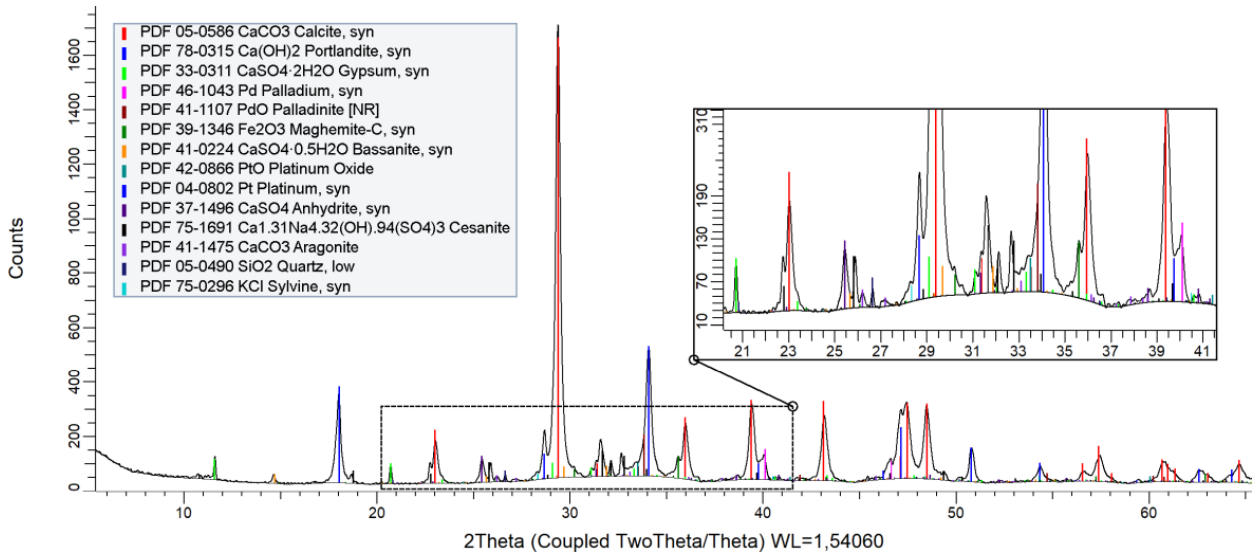

Figure 1. XRD pattern with database entries for the identified crystalline phases.

The relation between maghemite and Pd was clearly defined by X-ray mapping (Figure 2), with the intensity distributions suggesting that higher Pd and Pt concentrations are strongly related to the increase of Fe presence. While only maghemite (γ-Fe_2O_3) was identified as Fe-oxide by XRD, due to the large number of crystalline minor phases we cannot exclude the existence of wuestite (FeO), magnetite (Fe_3O_4) or even hematite (α-Fe_2O_3) – at an insignificant level due to their trace amounts, if present.

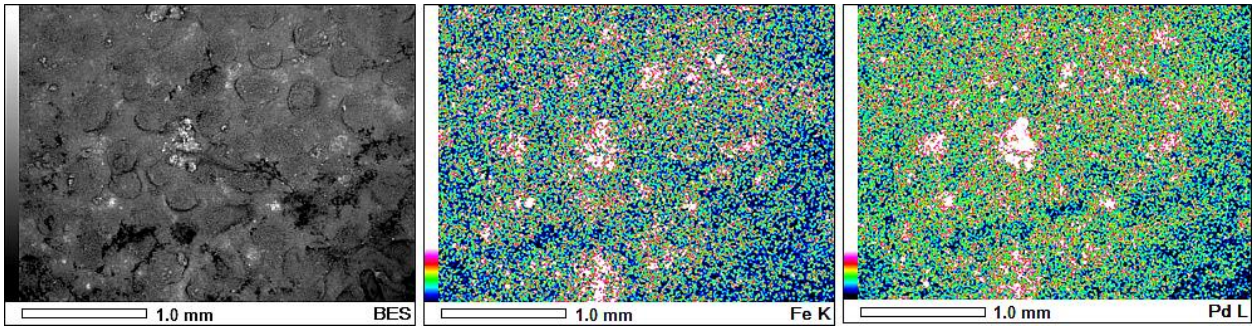

Figure 2. Relation of Fe and Pd agglomerations in the carbonate matrix (colors mark concentration increase towards white)

Microchemical measurements confirm the presence of Pd and Pt enrichment and its relation to Fe-oxide(s), also showing the chemical elements (Table 1) expected upon the XRD results. Distribution of S is mostly homogeneous in the Ca-carbonate matrix, returning weight percentages in the 0.2-0.8 range, thus a finely dispersed submicrometric presence of sulphate phases can be expected. A similar situation is observed for Mg, as a substituting cation for Ca in the crystal lattice of calcite, while Na, Al and Si is in the composition of ceramic or glass trace material, insignificant at these percentages.

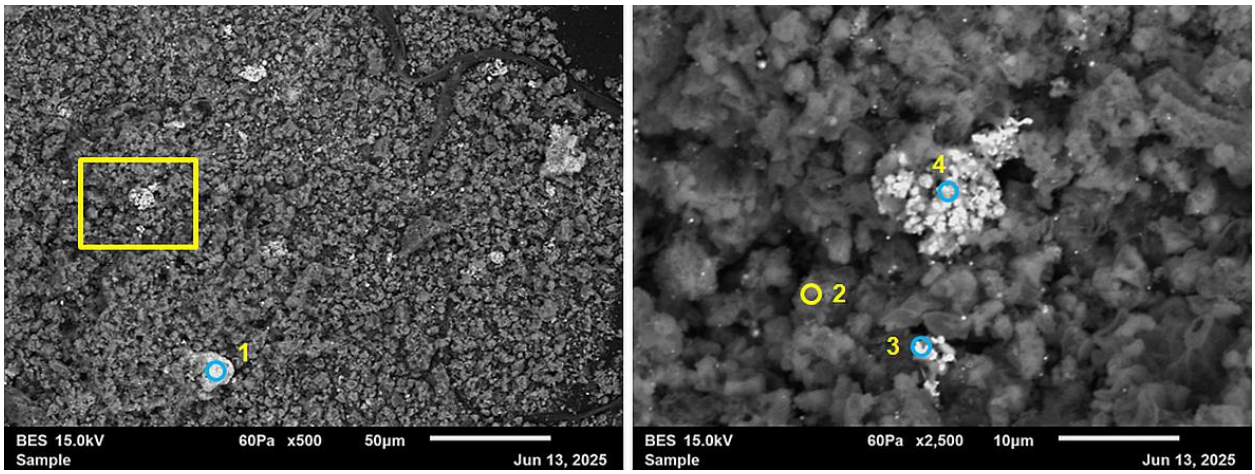

Figure 3. Distribution of Fe-rich grains and spherules in the carbonate matrix, back-scattered electron images, circles mark EDX analysis spots.

The size distribution of Pd and Pt bearing particles has a large range, from submicrometric single particles to different levels of aggregation and agglomeration. The smallest particles are spherical formations, with lower associated Fe-content, although due to the small sizes their precise chemical composition cannot be measured by SEM+EDX. With the increase of aggregate sizes, the Fe and Pd percentage is also increasing (Table 1), indicating the role of Fe-oxide(s) as cementing/binding phase(s).

Table 1. EDX measurements marked on the BES images in Fig 1 (non-standardized weight percents)

	Fe	O	C	Na	Mg	Al	Si	S	Ca	Mn	Zn	Pd	Pt
1	13.47	34.70	22.38	0.20	0.50	0.20	1.04	0.45	13.33			12.13	1.59
2	2.65	48.88	19.08	0.21	0.45	0.10	0.33	0.48	25.70			1.96	0.15
3	19.45	38.79	15.87	0.17	0.34	0.15	0.28	0.28	10.14	0.20		13.16	1.17
4	23.08	32.09	15.19	0.14	0.34	0.16	0.46		9.7	0.37	0.88	15.28	2.30

Examined at higher magnification, two types of Pd-Pt formations can be distinguished: nanoscale spherical particles dispersed individually of aggregated to a scale of several micrometers, and Fe-oxide cemented aggregates (Figure 4). Also in the Fe-oxide matrix nanoscale spherules can be observed, while some part of at least Pd is chemically dispersed, possibly as oxide phase

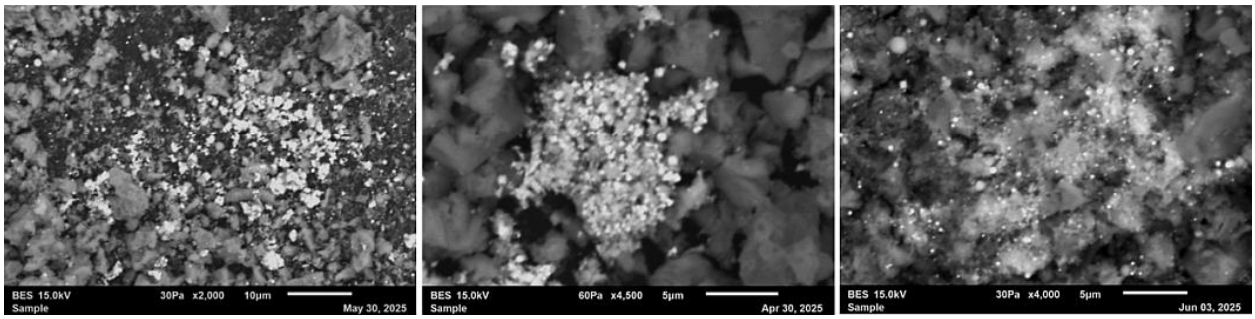

Figure 4. Distribution of Fe-rich grains and spherules in the carbonate matrix, back-scattered electron images

Due to the size of these phases their metallic, oxide or mixed nature cannot be determined, thus an assumption is made that PdO observed by XRD coexists with Pd and is a host for Pt.

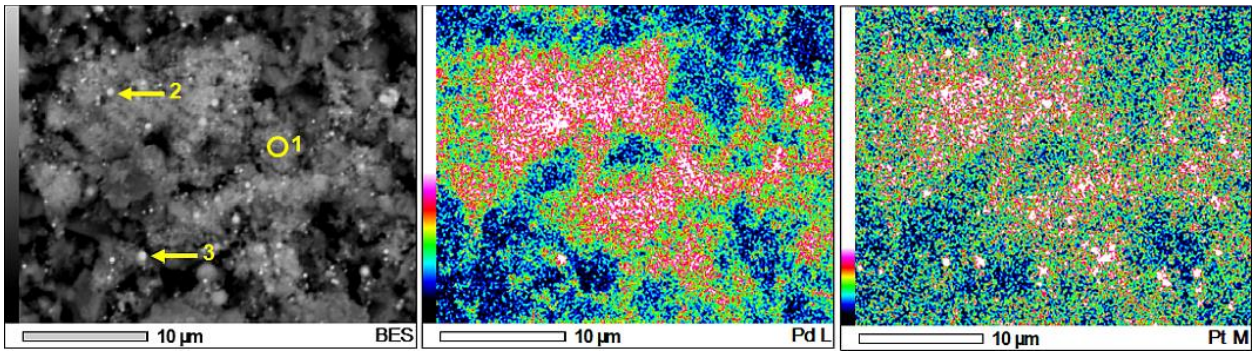

Figure 5. Submicrometric Pt-rich spherules in the Pd-rich Fe-oxide cement (colors mark concentration increase towards white)

High magnification X-ray mapping (Figure 5) brings evidence for the existence of Pt-enriched spherical single particles, supported by EDX analysis also (Table 2), although with limited accuracy since the particles are smaller than the excitation volume of the focused electron beam (cca. 2 µm for the given matrix).

Table 2. EDX measurements marked on the BES images in Fig 5 (non-standardized weight percents)

	P	Fe	K	O	C	Na	Mg	Al	Si	S	Cl	Ca	Pd	Pt
1	0,15	10,52	0,16	42,97	13,39	1,68	0,38	0,07	0,42	3,01	0,43	16,66	8,62	1,55
2	0,14	21,74	0,08	33,38	9,69	2,05	0,3	0,1	0,63	1,67	0,25	6,08	16,05	7,82
3	0,19	26,23	0,07	24,89	6,56	0,55	0,13	0,08	0,24	1,42	0,23	10,51	20,51	8,4

4. CONCLUSIONS

The capture of CO_2 generates a mineralized system in which colloidal and ash-type fragments from the decomposed catalyst are concentrated and captured. The deposition of Fe happens as oxide instead of carbonate, strongly linked to Pd and Pt, suggesting a pre-incineration history of these phases. Nanoscale spherical particles tend to be Pt-rich, while the larger Fe-oxide cemented aggregates accumulate Pd.

Recovery is expected to be complicated in the case of submicrometric particles, probably requiring a precisely adjusted multi-step chemical process [2], since physical concentration and extraction methods are not performing well in the observed particle size range.

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