

Use of Pt/Ce_xZr_{1-x}Al₂O₃ as Advanced Catalyst for Hydrogen Peroxide Thrusters

L. Romeo¹, C. Genovese², L. Torre³, A. Pasini⁴, A. Cervone⁵, L. d'Agostino⁶, G. Centi⁷ and S. Perathoner⁸
ALTA S.p.A. - Via Gherardesca, 5 - 56121 Ospedaletto, Pisa, Italy

and

Dipartimento di Chimica Industriale ed Ingegneria dei Materiali – Salita Sperone, 31 – 98166, Messina, Italy

The capability of different Pt/Ce_{0.6}Zr_{0.4}/Al₂O₃ catalytic systems of effectively decomposing H₂O₂ has been studied in view of their application to monopropellant thrusters. BET surface area measurements, X-Ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM) have been used together with catalytic tests in order to evaluate the advantages of using CeO₂-ZrO₂ mixed oxide solid solution as an alternative to current three ways catalysts (TWCs). From the assessment of alternative solutions, a Pt/Ce_{0.6}Zr_{0.4}/Al₂O₃ catalyst suitable to effectively decompose H₂O₂ has been identified. SEM-EDX analyses ruled out the occurrence of phase segregation and selective deposition of Pt on Zr during the catalyst preparation. No changes in the crystalline arrangement of the catalyst samples after H₂O₂ decomposition have been detected by XRD measurements, except for a slight crystallization or grain size growth as a consequence of the high temperatures experienced during the reaction. The use of Pt/Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ catalysts for rocket-grade applications with much higher reaction rates than in automotive three-way converters has thus been successively demonstrated.

Nomenclature

t_{max} = time needed from the H₂O₂ decomposing solution to reach the peak temperature
 $s/t.n.$ = seconds for test number

I. Introduction

THE first applications of hydrogen peroxide as propellant dates from 1938, when it was used in the assisted take-off rocket system of the Heinkel He-176 aircraft and in the gas generator of the V2 rocket turbopump. Later H₂O₂ has been used in a number of applications culminating in the attitude control system of the manned Mercury spacecraft and in the primary propulsion of the Black Arrow launcher¹. In order to take advantage of the H₂O₂ decomposition reaction in rocket propulsion applications, an effective, reliable and durable catalytic bed is required. It should provide fast and reproducible performance, be insensitive to poisoning by stabilizers and impurities contained in the propellant², as well as capable to sustain the large number of thermal cycles imposed by typical mission profiles in small satellite applications. Traditionally pure silver and silver coated stainless steel grids^{3,4} have been the most used H₂O₂ catalysts in space propulsion applications, even if their use was associated with strong temperature limitations⁵. With the aim of developing more suitable substitutes, in recent years ceramic materials have been widely studied for the decomposition of hydrogen peroxide in gas generators or in monopropellant

¹ Ph.D. Student, Dipartimento di Ingegneria Aerospaziale, Università di Pisa, AIAA Member; l.romeo@alta-space.com

² Post-Doc Researcher, Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, Università di Messina; c.genovese@unime.it

³ Project Manager, ALTA S.p.A., AIAA Member; l.torre@alta-space.com

⁴ Ph.D. Student, Dipartimento di Ingegneria Aerospaziale, Università di Pisa, AIAA Member; a.pasini@alta-space.com

⁵ Project Manager, ALTA S.p.A., AIAA Member; a.cervone@alta-space.com

⁶ Professor, Dipartimento di Ingegneria Aerospaziale, Università di Pisa, AIAA Member; luca.dagostino@ing.unipi.it

⁷ Professor, Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, Università di Messina; centi@unime.it

⁸ Professor, Dipartimento di Chimica Industriale ed Ingegneria dei Materiali, Università di Messina; perathon@unime.it

thrusters. In particular, both conventional alumina-based supports (extrudates, pellets, spheres)^{6,7} and honeycomb monolith carriers⁸ have been used for the preparation of catalysts. Under suitable conditions, the former supports can be directly impregnated using an active phase precursor, while the latter require surface impregnation of a thin and porous wash-coat layer, which is necessary to increase the relatively surface area of typical support materials, such as cordierite and mullite. According to the experience gained at Alta S.p.A. with catalytic beds for small rocket applications, alumina pellets with a medium content of the alpha-phase represents an effective solution for successfully withstanding the thermal shocking induced by the H₂O₂ decomposition reaction⁹. In order to optimize the properties of the alumina substrate and at the same time stabilize the active metal phase, Alta S.p.A., in collaboration with the Department of Industrial Chemistry and Material Engineering of the University of Messina, Italy, has developed a catalyst based on alumina spheres coated with a thin film of Ce_xZr_{1-x}O₂, which is known to stabilize noble metal particles in oxidation reactions by strong metal-support interaction (SMSI)¹⁰. Platinum has been deposited on the mixed oxide support at concentrations of 6-10% by weight, in order to promote H₂O₂ decomposition. In this work we report the synthesis, morphological characterization and catalytic behavior of Pt/Ce_{0.6}Zr_{0.4}O₂ in controlled hydrogen peroxide decomposition experiments at conditions representative of typical small rocket applications, emphasizing the relationships between catalyst structure and reactivity. It is to be stressed that this catalytic system, originally developed for automotive three-way converters, has been applied for the first time to H₂O₂ decomposition in small rocket engines, demonstrating high performance stability under extremely severe operational conditions.

II. Description of the Experiment

A. Preparation of the Catalysts

After a careful screening of different commercial Al₂O₃ supports, SASOL's 0,6/170 spherical γ -Al₂O₃ (spheres of mean diameter of 0.6 mm with a surface area of 170 m²/g) has been chosen as the support for the Pt/Ce_{0.6}Zr_{0.4}O₂ phase. The first step of the catalyst preparation consisted in the thermal treatment in air at 1100°C for 1 hr of the Al₂O₃ substrate in order to obtain the desired crystal phase with a measured BET surface area of about 74 m²/g (see Section III). The second step consisted in the preparation of a sol containing Ce/Zr in a 60-to-40 atomic ratio, starting from the correspondent nitrates (Aldrich) in the presence of citric acid and following a procedure already described in the literature¹¹. The third step consisted in coating the Al₂O₃ spheres with the CeO₂/ZrO₂ sol precursor by wet impregnation and absorption. In particular, wet impregnation has been used for the CZ-4 sample to deposit the Ceria-Zirconia film on the alumina substrate, while the other catalyst samples have been coated by means of the absorption technique. After impregnation, the samples have been calcined at 550°C for 6 hr. The fourth step has consisted in the deposition of Pt by a modified ion exchange method using a Pt(NH₃)₄(NO₃)₂ water solution for the CZ-4-CZ-9 samples and a H₂PtCl₆ solution in acetone for the CZ10-CZ11 sample. For the CZ-7 and CZ-8 samples the platinum precursor solution has been directly added to the Ce/Zr sol prior to carrying out the absorption step on the alumina substrate. The final Pt loading was 10% by weight for the CZ-7 and CZ-11 samples and 6% by weight for the remaining ones. Finally, the samples have been calcined at 500°C for 4 hr and reduced in H₂ at 400°C for 4 hr. The main differences between samples CZ4 and CZ9 are mostly related to the increasing thickness of the CeO₂/ZrO₂ film.

B. Characterization of the Catalysts

1. Catalytic Activity Tests

A dedicated test bench has been realized by Alta for the comparative characterization of the activity and reaction rates of the catalyst formulations in controlled hydrogen peroxide decomposition experiments at atmospheric pressure. Figure 1 shows a schematic drawing of the test bench. It consists of a 250 ml reaction flask contained in a glass vessel with a volume of about 2 liters. The upper part of the vessel is closed by a sealing lid with the connection for the H₂O₂ supply funnel and the connection to the exhaust duct of the hot gas generated by the reaction. In the cover are also located two thermocouple taps, one for the measurement of the temperature of the liquid H₂O₂ and the other for measuring the temperature of the gas in the cylinder.

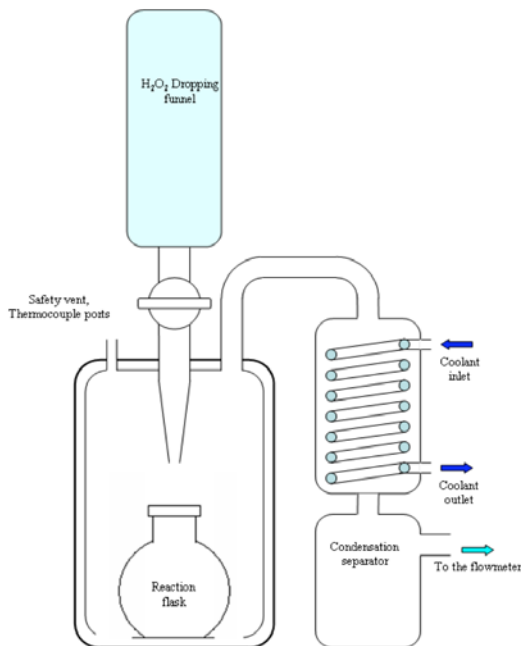


Figure 1. Scheme of the batch reactor

Before each test, a known mass of catalyst is put in the reaction flask. Next, a given quantity of hydrogen peroxide solution is added by opening the tap of the H_2O_2 tank. The decomposition reaction promoted by the catalyst generates a hot gas mixture at nearly atmospheric pressure, where molecular oxygen, steam and a small quantity of gaseous hydrogen peroxide are present. After leaving the vessel, these gases enter a heat exchanger, where their temperature is lowered by means of a cold coolant flow which passes through a coil pipe. The heat exchanger has been designed in order to condense most of water and hydrogen peroxide vapors in a liquid separator. As a consequence, the gas flow at the exit of the heat exchanger practically contains pure oxygen at known pressure and temperature conditions. In this way its flow rate, measured by means of a flowmeter, can be directly correlated to the rate of H_2O_2 decomposition. Temperature measurements are carried out by means of K-type thermocouples with a diameter of 1.5 mm and a length of 250 mm. The reduced order model used for the design of the test bench and the interpretation of the experimental results has been illustrated in a previous paper¹².

2. BET Measurements

The specific surface area (S_{BET}) of the original Al_2O_3 supports and of the final catalysts has been measured by the BET method using N_2 adsorption/desorption isotherms at 77 K using a Micromeritics ASAP 2010 apparatus. Pore size and pore volume distributions have been obtained using the BJH method.

3. X-ray Diffractometry (XRD)

X-ray diffraction measurements have been carried out using a Philips PW 1710 diffractometer with a $CuK\alpha$ radiation. The XRD data were collected at 0.02° per step between $2\theta = 5^\circ - 80^\circ$.

4. Scanning Electron Microscopy (SEM)

EDX-SEM characterization of the catalyst samples has been carried out by means of a scanning electron microscope Jeol 5600LV. Elemental analysis has been carried out via energy dispersion analysis using an X-Ray analysis system EDX OXFORD, coupled with a scanning electron microscope.

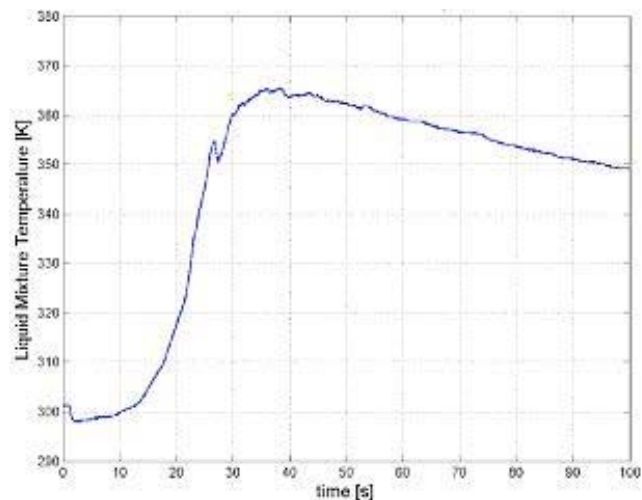


Figure 2. Time history of the decomposing mixture temperature during the 8th test on the CZ-9 catalyst.

III. Results

A. Activity Tests

For each prepared catalyst a sample of 0.85 gr, corresponding to a standard catalyst volume of 1 ml, has been selected. In order to measure the chemical activity, fifty consecutive drop tests have been carried out on each sample using the test bench previously described. In each test, the sample of catalyst spheres has been introduced in the reaction flask and 5 ml of 30% H_2O_2 hydrogen peroxide solution have been added. The temperature of the liquid mixture has then been continuously acquired until completion of the decomposition reaction. Finally, the initial conditions of the sample have been restored by removal of the decomposition products. The 30% H_2O_2 solution is produced by Riedel-de-Haen (Sigma-Aldrich) and exhibits a

particularly low content of impurities and stabilizers ($\text{PO}_4^{3-} < 1 \text{ ppm}$, $\text{SO}_4^{2-} < 1 \text{ ppm}$).

Figure 2 shows the time history of the decomposing mixture temperature during the 8th drop test on the CZ-9 catalyst sample. The temperature tends to increase rapidly up to about 380 K, corresponding to the boiling point of the decomposing hydrogen peroxide solution, followed by a slower decline as the reaction tends to completion. When the temperature of the decomposing liquid solution approaches its peak value, the reaction becomes very fast and the residual hydrogen peroxide decomposes in few seconds, even if its temperature declines more slowly. The time needed for the liquid to reach its peak temperature, hereafter indicated as t_{max} , has been used as quantitative indicator of the decomposition activity because of its strong relation to the rate of release of the heat of reaction. Figure 3 compares the t_{max} plots for the catalysts developed in the context of the present activity as functions of the consecutive test number on the same catalyst sample. In addition, a further sequence of fifty drop tests has been carried out on the same CZ-10 sample after it underwent a second reduction cycle in H_2 at 400 °C for 4 hours (5 °C/min). After this treatment the sample and the relative t_{max} plot have been indicated with CZ-10-UR. Except for the CZ-10, CZ-10-UR and CZ-11 catalyst samples, from the 2nd test on the experimental values of t_{max} tend to follow a linear trend, with different slopes depending on the catalyst sample. In particular, the CZ-7 catalyst exhibited the lowest increase of t_{max} with a slope of 0.66 s/t.n. (t.n. stands for test number), followed by CZ-5 and CZ-4 with 1.53 s/t.n. and 1.63 s/t.n. respectively, while the highest slope values (1.9 s/t.n and 2 s/t.n) have been displayed by the CZ-8 and CZ-9 catalyst samples. As a consequence of the excessively high values of t_{max} exhibited by those catalysts, unsuited for propulsive applications, it has been decided to stop the sequence of experiments before reaching the 50th drop test.

Conversely the CZ-10 and CZ-11 samples showed nearly constant values of t_{max} lower than 10 seconds over the

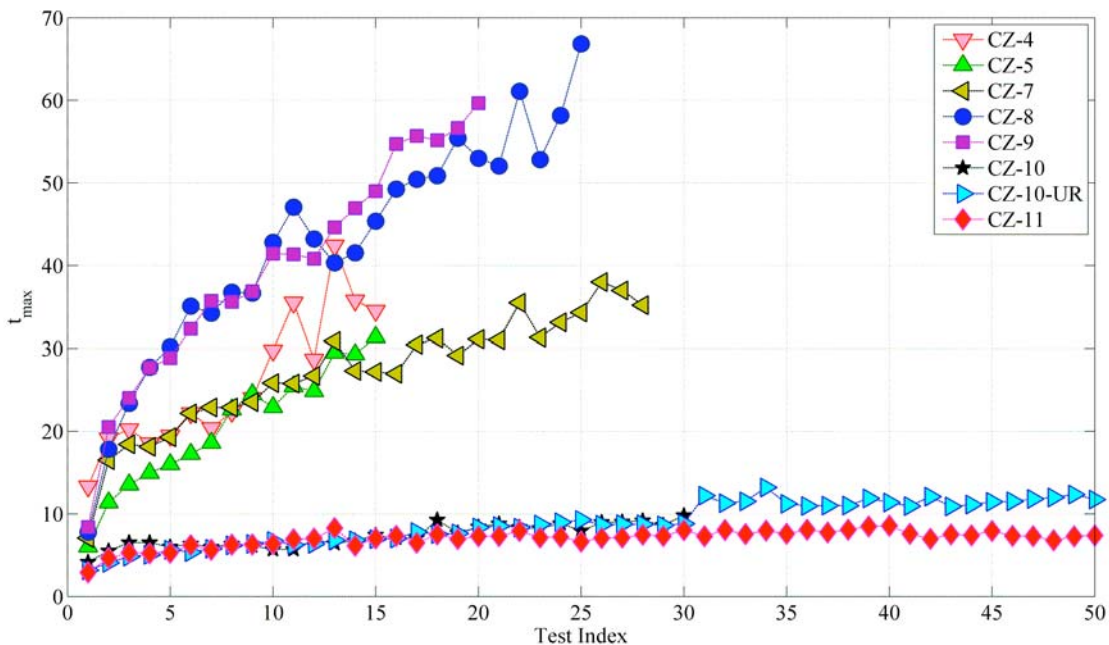


Figure 3. Time needed for the decomposing hydrogen peroxide solution to reach the peak temperature as a function of the test index for all the catalyst samples.

whole sequence of fifty tests. In order to better distinguish the test results of the CZ-10, CZ-10-UR and CZ-11 samples, Figure 4 illustrates an enlargement of the experimental values of t_{max} between 0 and 14 seconds. With reference to the CZ-10 catalyst, after the 5th test the t_{max} plot started to follow a nearly linear trend with a slope of 0.16 s/t.n., even though some oscillations of the experimental points have been detected. With reference to the understanding the reasons of this increase of t_{max} , the test sequence for the CZ-10 catalyst has been stopped after the 30th test and the spent sample has been reduced under H_2 in the attempt to regenerate it. The second sequence of drop tests on the regenerated CZ-10, hereafter indicated as CZ-10-UR, has been extended beyond the 30th test up to the test number 50. The values of t_{max} for the first 30 tests on CZ-10-UR resulted to be perfectly superposable to the ones of the CZ-10, and in later tests approached a constant value of about 12 s. The CZ-11 sample displayed a different decomposition activity with respect to the CZ-10 catalyst. In particular, the t_{max} value increased from 2 to 8 s over

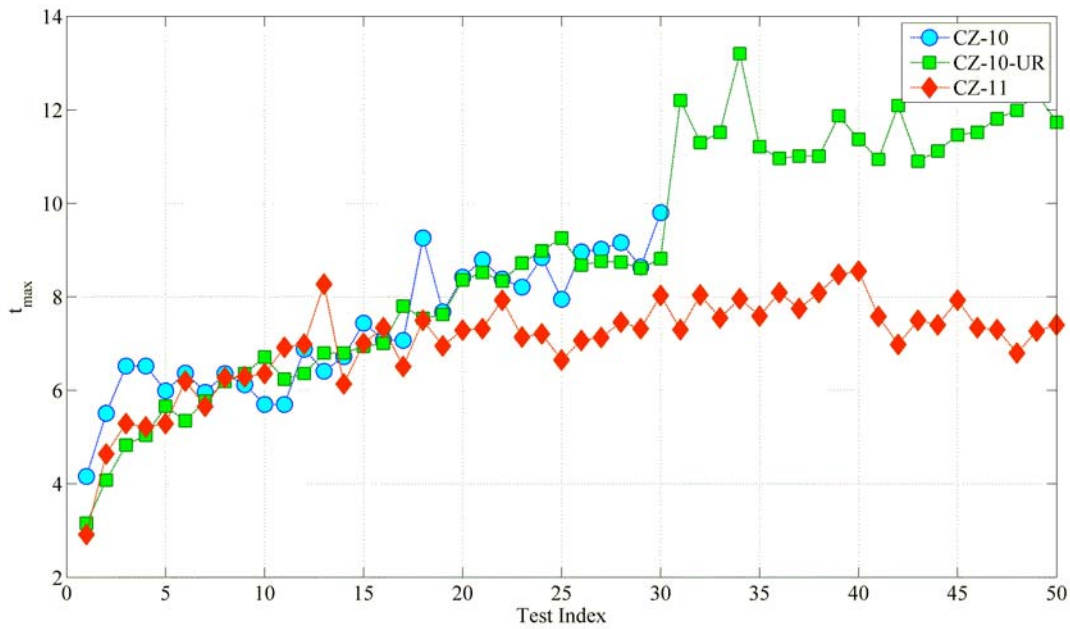


Figure 4. Plot of the t_{max} as a function of the test index for the CZ-10 and CZ-11 catalyst samples.

the first twenty tests, and later remained nearly constant until the end of the test sequence. In conclusion, in view of the development of a $\text{Pt/Ce}_{0.6}\text{Zr}_{0.4}/\text{Al}_2\text{O}_3$ catalyst able to fulfill the typical mission requirements of HTP thrusters, the results of decomposition tests have demonstrated that:

- Despite an initial slight degradation, the CZ-11 catalyst exhibited the highest catalytic activity and excellent performance in terms of repeatability and near absence of susceptibility to poisoning.
- The CZ-10-UR sample showed a decomposition performance similar to that of CZ-11 over the initial twenty tests, but its activity decreased continuously until the 30th test, reaching stable value lower than that of CZ-11.
- The increase of t_{max} (indicating the reduction of the decomposition activity) exhibited by the CZ-10 and CZ-11 samples during the initial 30 tests can presumably be related to the superficial oxidation reaction of the active phase. This finding is clearly consistent with the superposition between CZ-10 and CZ-10-UR experimental data, which demonstrates the successful regeneration of the H_2 reduction.
- All of the other catalyst samples showed considerable signs of catalytic activity decay after the decomposition of only 100 ml of H_2O_2 . The activity tests indicated that those samples as unsuitable for propulsive application as confirmed by the low values of t_{max} reached in correspondence of the 20th test. A slight better performance in terms of decomposition activity has been displayed by the CZ-7 sample, even though it also remains unsuitable for propulsive applications.

B. Characterization

1. BET Surface Area Measurements

In order to find the Al_2O_3 support with the highest hydrothermal and mechanical resistance for the severe conditions reached during activity tests, SASOL's 0,6/170 spherical $\gamma\text{-Al}_2\text{O}_3$ and ALCAN's $\gamma\text{-Al}_2\text{O}_3$ supports have been calcined at different temperatures for different times. The main results of the specific surface areas and mean pore diameters obtained with this procedure are summarized in Table 1.

Table 1. BET specific surface area and mean pore diameter of γ -Al₂O₃ samples treated at different temperatures

Sample	Initial S_{BET} m ² /g	Final calcination T °C	Heating rate, °C/min	Isothermal step duration, h	Final S_{BET} m ² /g	Mean Pore diameter, Å
Sasol 0,6/170	170	950	2	1	147	80
Sasol 0,6/170	170	1000	2	8	109	95
Sasol 0,6/170	170	1000	2	20	102	100
Sasol 0,6/170	170	1150	5	4	7	450
Sasol 0,6/170	170	1100	5	1	74	105
ALCAN	170	1100	5	4	25	290

The best compromise between specific surface area and mean pore diameter has been obtained for the SASOL's 0,6/170 γ -Al₂O₃ support calcined at 1100°C for 1 hr. Moreover, XRD pattern of this sample showed the coexistence of the α and θ phases and preliminary thermal shocking tests indicated good thermo-mechanical performance. Therefore all catalysts reported in this work were prepared using the 1100°C calcined Al₂O₃ from SASOL with a BET specific surface area of 74 m²/g.

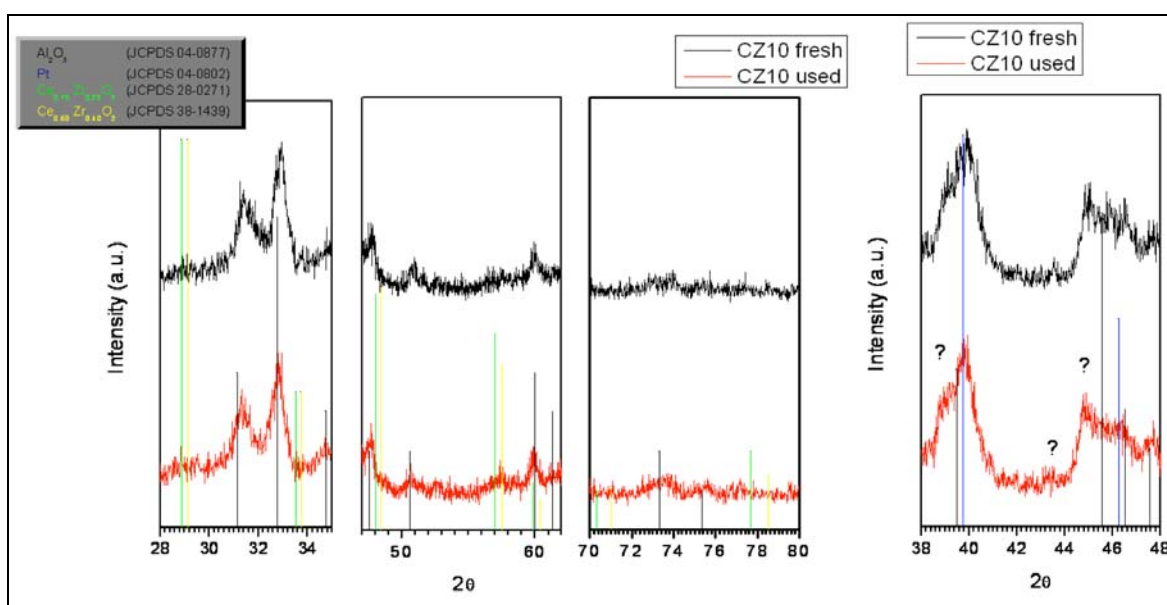


Figure 5. X-ray spectra of the CZ-10 catalyst before and after the sequence of fifty drop tests.

2. XRD Analysis

Figure 5 and Figure 6 report the XRD spectra of the CZ-10-UR and CZ-11 catalyst samples before and after the fifty consecutive activity tests. In order to better distinguish the samples before and after the catalytic reaction, the indications *fresh* and *used* have been added hereafter to the labels. No significant differences have been observed in the comparison the spectra of the *fresh* and *used* samples, except for the higher resolution of the XRD peaks of the *used* samples. This finding is most probably due to the crystallization or grain size growth of the catalyst as a consequence of the high temperature of the H₂O₂ decomposition reaction. Moreover, the XRD analysis allowed to detect a number of crystalline compounds, namely: alumina Al₂O₃ (JCPDS 04-0877), metal Platinum (JCPDS 04-0802), as well as a mixed oxide Ce_xZr_{1-x}O₂ with x ranging between 0.75 and 0.60. Enlargements of the spectra are shown on the right in Figure 5 and 6, showing the presence of other peaks labeled with the symbol “?”. From the comparison with the X-Pert library spectra, these peaks have been related to the presence of reduced Cerium or Zirconium, but it has not been possible to clearly distinguish these two metals because of their similar diffraction patterns. Their formation probably originates from the reduction process of platinum or the deposition of chlorine as

a consequence of the decomposition of hexachloroplatinic acid during catalyst impregnation. This finding is in accordance with the SEM-EDX analysis carried out on the 0.6/74, intermediate $Ce_xZr_{1-x}O_2/Al_2O_3$ and final catalyst samples. Unlike for the CZ-10 and CZ-11 samples where traces of chlorine have been found, only the presence of the nominal elements has been detected on the 0.6/74 and intermediate samples.

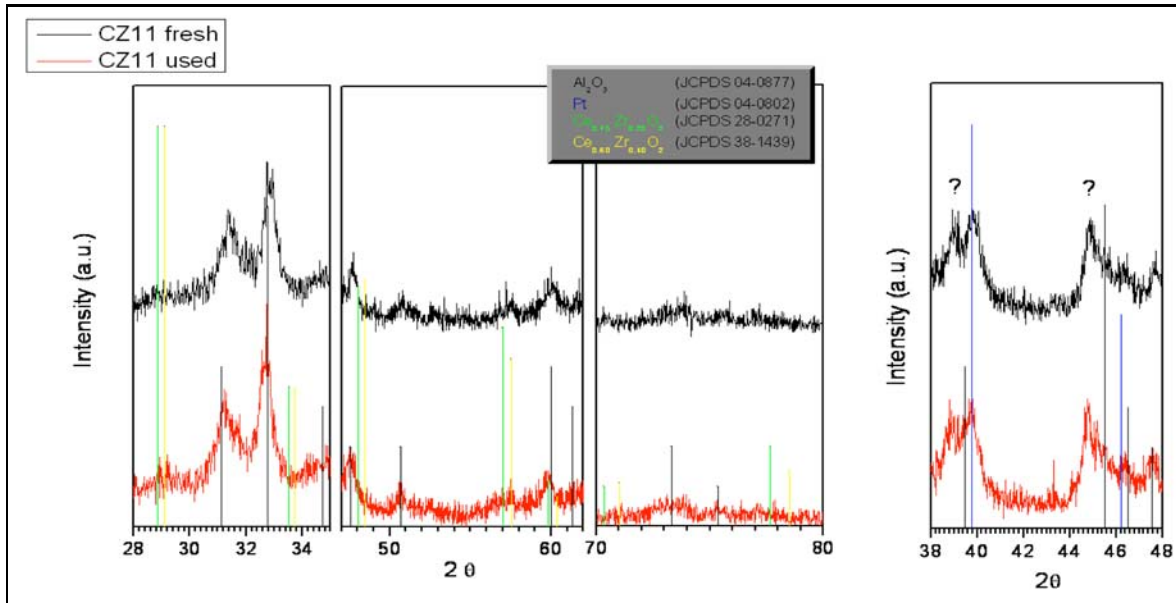


Figure 6. X-ray spectra of the CZ-11 catalyst before and after the sequence of fifty drop tests.

3. SEM Measurements

In order to assess the differences in morphology and structure between the CZ-10 and CZ-11 catalysts before and after H_2O_2 decomposition, SEM-EDX analyses have also been carried out on the intermediates of the catalyst preparation. They include the original 0.6/74 alumina support and the spheres coated with a Ceria-Zirconia film through the sol-gel technique. The latter compound has been labeled $Ce_xZr_{1-x}O_2/Al_2O_3$. Figure 7 reports the SEM picture of the analyzed area and the relevant EDX spectrum for the Al_2O_3 sample. The SEM analysis indicates the presence of closed macropores on the surface of the original alumina support, while according to the EDX spectrum the substrate is composed only by aluminum and oxygen. In Figure 8 are shown the SEM/EDX results on the $Ce_xZr_{1-x}O_2/Al_2O_3$ intermediate compound. Comparing Figure 7 and 8 the initial macropores of the substrate seem to be filled and the film of Ceria-Zirconia appears partly removed in some points. The filling of micropores with Ceria-

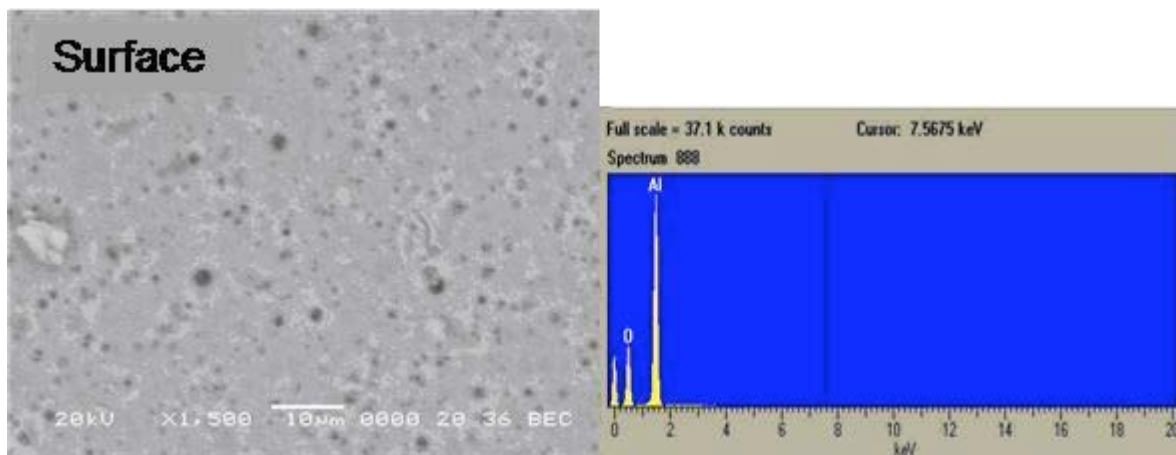


Figure 7. SASOL 0.6/74 alumina: SEM image (left) and EDX spectrum (right) of the surface.

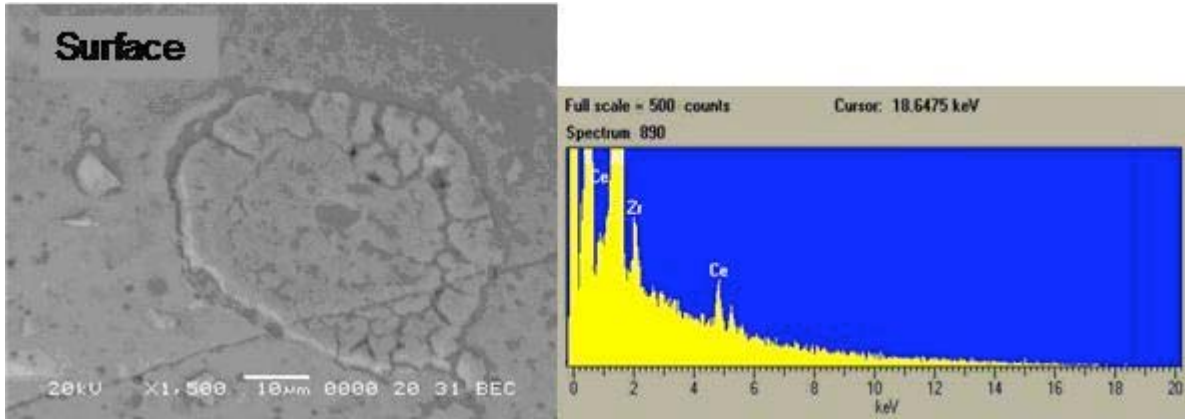


Figure 8. $Ce_xZr_{1-x}O_2/Al_2O_3$ intermediate: SEM picture (left) and the EDX spectrum (right) of the surface.

Zirconia is confirmed in Figure 12, where the coating elements are clearly penetrated inside an internal pore of a CZ-11 *used* pellet. In the presence of residual porosity of alumina, it is likely that the Ceria-Zirconia sol has first penetrated inside the carrier for capillarity and then gellation has occurred. For this reason the $Ce_xZr_{1-x}O_2/Al_2O_3$ interface is difficult to identify. The presence of the coating in the CZ-11 catalyst after H_2O_2 decomposition (see Figure 11) also provides convincing evidence of the stable and effective deposition of the Ceria-Zirconia coating on the alumina substrate obtained by means of the sol-gel technique.

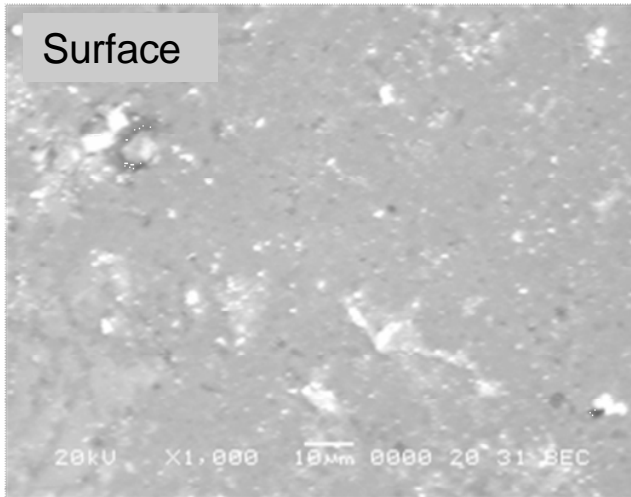


Figure 10. CZ-11 fresh: SEM picture of the surface SEM,

The EDX spectrum of the $Ce_xZr_{1-x}O_2/Al_2O_3$, reported in Figure 8 indicates that the peak intensities due to the presence of Ce and Zr are comparable. Hence, phase segregation and selective deposition of Pt on Zr have not occurred during the catalyst preparation. Figure 10 reports a SEM picture showing the surface of the CZ-11 *fresh* catalyst sample. It is possible to note the presence of a distribution formed by white agglomerates, which clearly identify the platinum deposited on the catalyst surface. After the H_2O_2 decomposition the CZ-11 catalyst morphology has remained essentially

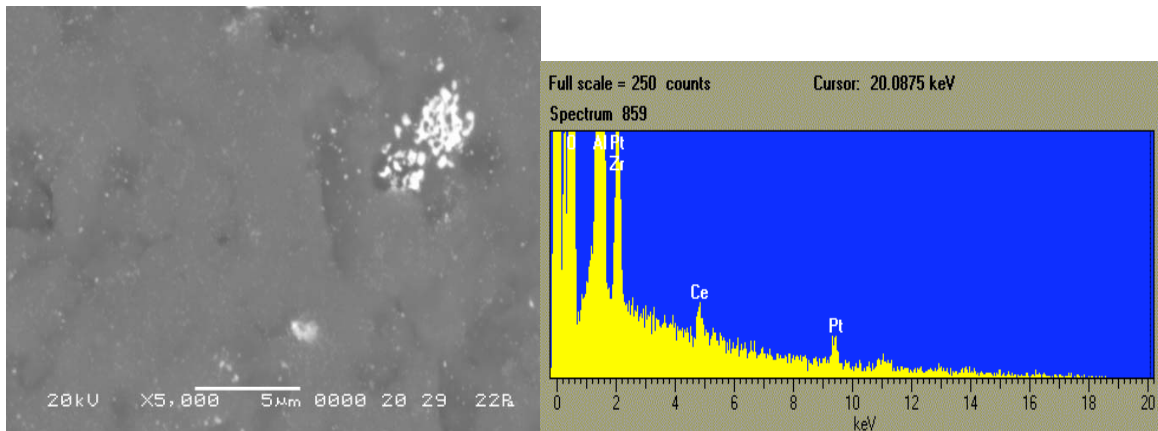


Figure 9. CZ-11 used catalyst : SEM picture (left) and relevant EDX spectrum (right) of the surface.

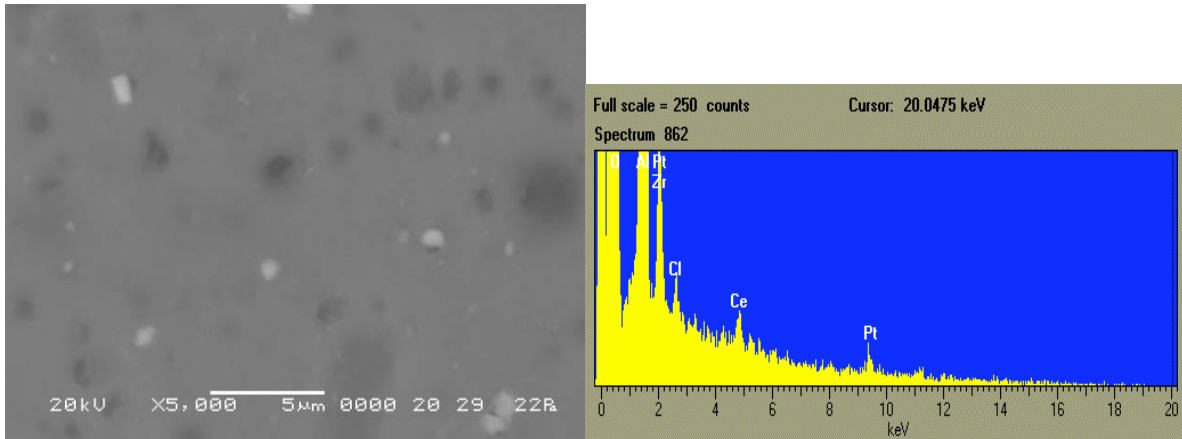


Figure 12. CZ-10 fresh sample: SEM image (left) and relevant EDX spectrum (right) of the surface.

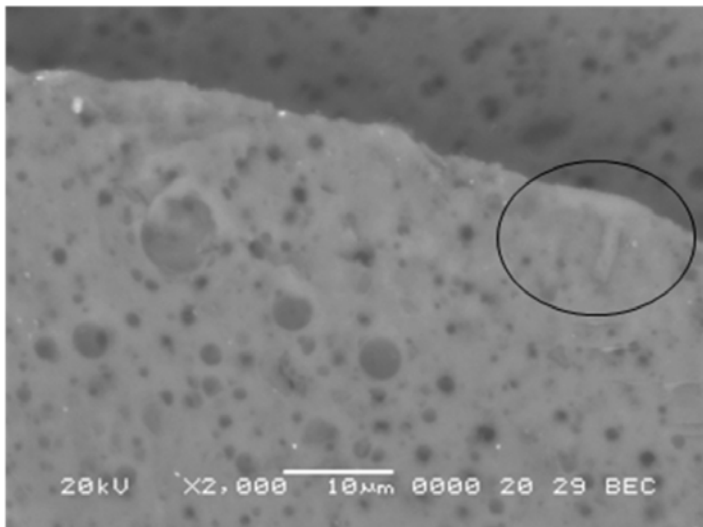


Figure 11. CZ-11 used catalyst: Enlargement of the Ceria-Zirconia film inside the alumina matrix.

unchanged, as shown in Figure 10, and the EDX analysis revealed a Zr peak more intense than the corresponding one of the $Ce_xZr_{1-x}O_2/Al_2O_3$ intermediate (see Figure 8). This peak is probably associated with the superposition of the emission bands of platinum and zirconium.

In order to determinate the thickness of the Ceria-Zirconia coating, a SEM linescan has been carried out from the outer surface down to 7 µm in depth on a catalyst sphere cross section (see Figure 14). As a consequence of the sample geometry, this scan could not be significant for the whole catalyst. To better characterize the surface of the CZ-11 catalyst after the H_2O_2 decomposition reaction, a SEM mapping of the surface has been carried out (see Figure 15). The results confirm that the white agglomerates showed in Figure 9 are formed by platinum and no morphology changes occurred after the catalytic reaction. In

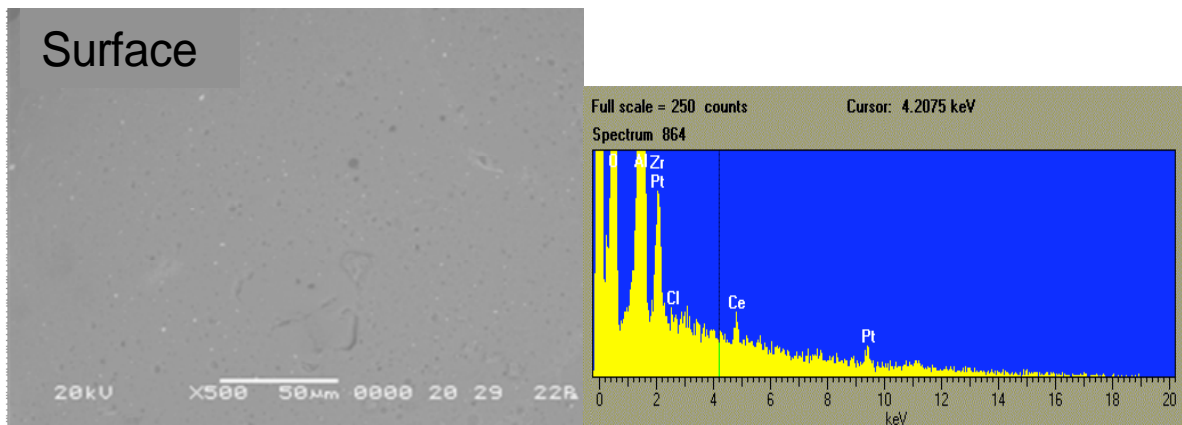


Figure 13. CZ-10 used sample: SEM image (left) and relevant EDX spectrum (right) of the surface.

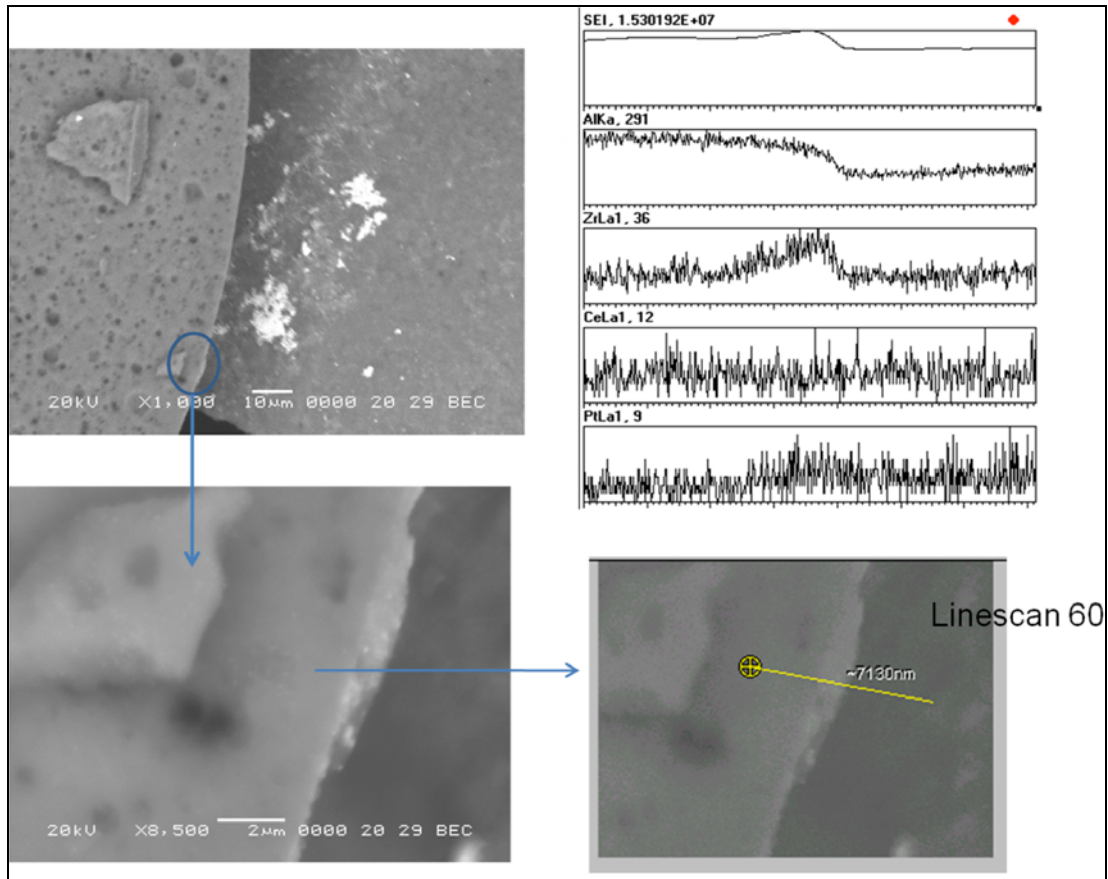


Figure 14. CZ-11 used catalyst: SEM linescan image and concentration profile across the Ceria Zirconia coating.

addition, the mapping data incorrectly show that platinum is preferentially bonded to zirconium. On the contrary, this results is due to the superposition of the platinum *La* and zirconium *Ma* emission bands around energy values close to 2 keV. Thereby, the white spots of zirconium are actually related to the presence of platinum. This finding is perfectly in agreement with the EDX results for the $Ce_xZr_{1-x}O_2/Al_2O_3$ intermediate and for the CZ-11 *used* sample discussed previously. The SEM pictures and the relevant EDX spectra for the CZ-10 *fresh* samples and the CZ-10 *used* samples are reported in Figures 11 and 13, respectively. The $Ce_xZr_{1-x}O_2$ film on the CZ-10 *fresh* sample appear to be discontinuous, as underlined by the presence of dark regions on the catalyst surface. These dark areas probably are the alumina macropores that have not been filled by the sol. The EDX analyses reveal a Ce/Zr ratio equal to 38/62, close to the nominal value, and traces of chlorines, probably introduced during the impregnation with the H_2PtCl_6 precursor solution. Furthermore, according to the microanalysis carried out on the core of the CZ-10 spheres (not reported), the $Ce_xZr_{1-x}O_2$ film penetrates inside the alumina substrate. Comparing the EDX spectra of the CZ-10 sample before and after the H_2O_2 decomposition reaction, virtually no changes in morphology and element concentration have occurred, except for a reduction in the chlorine concentration after the H_2O_2 catalysis.

IV. Discussion and Conclusions

As discussed in the Section III, in the catalytic characterization tests the CZ-11 sample exhibited the best performance in terms of chemical activity and repeatability with a nearly constant t_{max} value of 8 seconds, while for the other catalysts the t_{max} values progressively increased with different rates strongly dependent on the sample under investigation.

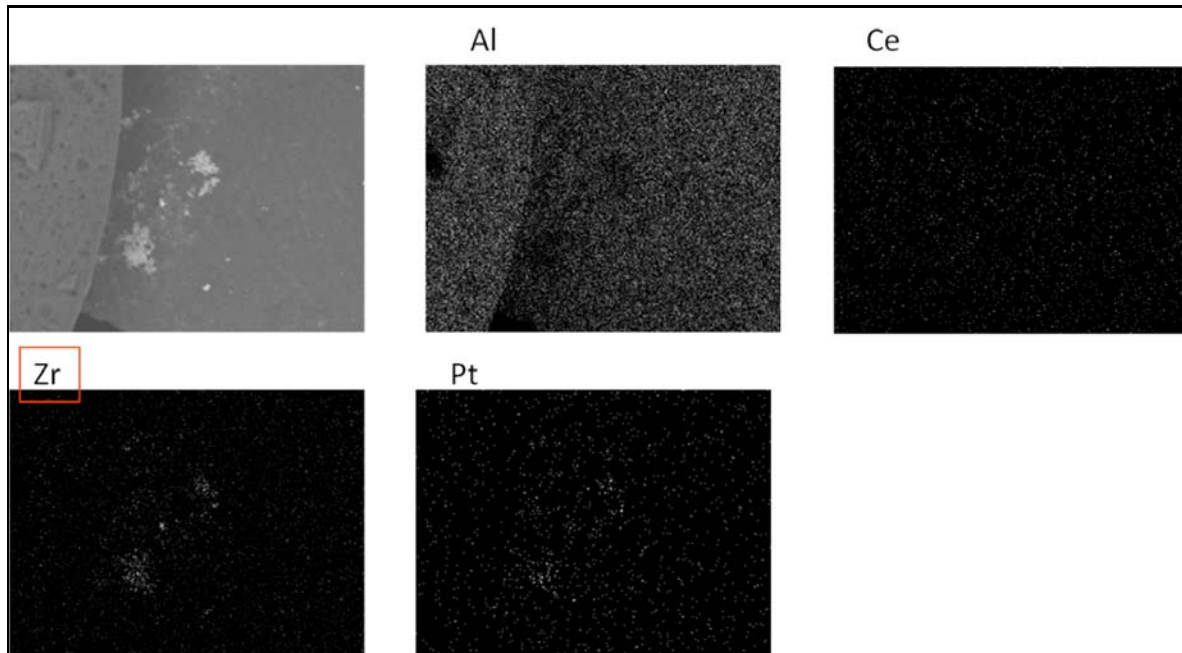


Figure 15. SEM mapping performed on the surface of the CZ-11 used catalyst.

From the comparison of the activity test results on the different catalyst samples several qualitative conclusions can be drawn:

- The similarity of the t_{max} plots for the CZ-4 and CZ-5 samples suggests that no improvement of catalytic activity has been gained by changing the deposition method of the Ce-Zr coating. As a matter of fact, wet impregnation and absorption of the Ce-Zr sol appeared to be essentially equivalent.
- The direct addition of the $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ water solution on the Ce-Zr sol before absorption on the alumina led to a deterioration of the catalytic activity, as indicated by the t_{max} plots for the CZ-7 and CZ-8 samples. The quantitative differences between the t_{max} values of the two samples are linked to the different nominal load of platinum, equal to 6% and the 10% by weight for the CZ-8 and CZ-7, respectively.
- An outstanding improvement of the activity of the CZ10-CZ11 sample has been obtained by using the solution of H_2PtCl_6 in acetone for the precursor impregnation instead of the solution of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ in water. In parallel, the enhancement of Ce-Zr load on the CZ-11 catalyst sample has helped in reducing significantly the deterioration of the chemical activity experienced by the CZ-10 sample. This finding has been confirmed by SEM-EDX analyses, where the CZ-11 sample exhibited a more uniform deposition of the $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ film than with respect to the CZ-10 catalyst. In addition, the Ce-Zr coating showed to be penetrated inside the alumina macropores, allowing for platinum to remain confined on the alumina surface.

The chemical composition of the CZ-10 and CZ-11 includes metallic platinum, a mixed $\text{Ce}_x\text{Zr}_{1-x}\text{O}_2$ oxide with x ranging from 0.6 to 0.75, a component attributable to either metallic Ce or Zr, as well as chlorine (SEM-EDX and XRD results). The presence of chlorine on the CZ-11 sample, as indicated by SEM-EDX analyses, is definitely linked with the use of the hexachloroplatinic acid as precursor, while the presence of metallic Ce or Zr could be due to the reduction step undergone by all catalyst during their preparation. Neither the structure nor the morphology of the catalysts have been modified by the H_2O_2 decomposition reaction, as indicated by the XRD analyses and further confirmed by SEM-EDX measurements. Therefore, the differences between the CZ-10 and CZ-11 samples are only attributable to the preparation method. The crystalline arrangement of the samples remained unchanged after the H_2O_2 catalysis decomposition, except for a higher amplitude of the peaks relating to the used samples. This finding can probably be mostly due to crystallization or grain size growth as a consequence of the high temperatures experienced during the H_2O_2 decomposition reaction. With reference to the arrangement of the chemical elements, SEM-EDX analyses excluded the occurrence of phase segregation and selective deposition of Pt on Zr during the preparation of the CZ-11 catalyst. In conclusion, XRD characterizations and SEM-EDX analyses, as well as the activity tests, confirmed for the CZ-11 catalyst the attainment of a $\text{Pt}/\text{Ce}_{0.6}\text{Zr}_{0.4}\text{O}_2/\text{Al}_2\text{O}_3$ suitable for effectively decomposing H_2O_2 without undergoing morphological and structural changes. In such way the use of a

Pt/Ce_{0.6}Zr_{0.4}O₂/Al₂O₃ catalyst for an application different from the automotive three-way converters has been successively demonstrated.

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