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Methodology of mechanical characterization of coated spherical materials

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A B S T R A C T

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The aim of this work was to develop a methodology for the mechanical characterization of catalyst beads with a core-shell structure and more especially for coated spherical granules. Supports composed of an alpha alumina core coated by gamma alumina shell were shaped by pan coating to this purpose. The proposed methodology started with the characterization of the microstructure of the coating and the highlight of potential macro defects within. Thereafter three tests simulating mechanical stress, such as impact, compression (bulk crushing test), and shear (drum attrition test) are used. The operational parameters of these tests were also optimised in order to stress preferentially the shell of the coated materials. Among the evaluated tests, drum attrition seems to be most efficient for characterizing coated spherical granules.

1. Introduction

Attrition of granular materials is a wide spread phenomena during their life cycle within a large panel of industrial processes. Most of the time, attrition is determined specifically for a type of stress representative of a process step, storage conditions, transport, or handling. Mechanical characterization of the materials allowing to evaluate their strength towards these miscellaneous stresses is then critical. Associated tests should fit the following criteria: simulation of stresses during life cycle of catalyst (shear, impact, and compression), and ability to characterize a significant number of particles of millimeter scale. Drum attrition test, impact test, and bulk crushing test (BCS) are the usual tests being used at IFP that meet criteria for mechanical characterization of spherical or cylindrical catalyst beads.

Last advances in conception of catalyst beads have seen the emergence of core-shell catalysts possessing two catalytic functions [1]. These supports are obtained most of the time by coating a spherical oxide core by another oxide presenting other textural properties. If the tests quoted above are well suited for characterization of classical beads, we wish to check their relevancy for mechanical characterization of coated materials. Furthermore, it should be useful to have a methodology of mechanical characterization in order to study in a systematic way the influence of the coating formulation on attrition strength. The following study is about the optimisation of the mechanical characterization tests for coated materials composed of an alpha alumina core coated with a gamma alumina shell. After achievement of the coating thanks to the use of a

granulator pan, the mechanical behaviour of the coated materials has been studied and compared to the initial non-coated core.

2. Experimental section

2.1. Raw materials

Alpha alumina beads (Sphéralite 512 - Axens), sieved between 2.5 and 2.8 mm, were used as a core. The major constituent of the coating is a gamma alumina powder (Puralox - Sasol) with a mass median diameter of 40 μm ($dv_{10}=10 \mu\text{m}$, $dv_{90}=90 \mu\text{m}$) and a specific surface area of 210 $\text{m}^2 \text{g}^{-1}$. The binder used is a boehmite sol (Pural SB3 - Sasol). The device for coating is a pan granulator GRELBEX P30 equipped with a cylindrical conical bowl. First, 100 g of beads that corresponds approximatively to the use of 8000 beads, are placed in cascade state of flow at rotary speed of 40 rpm and 30° angle. Once the porous volume of Sphéralite 512 is filled with the boehmite sol by pulverisation, 10 g of gamma alumina powder is continuously added under sol pulverisation. After adding the precursors, the coated core are dried in a ventilated drying oven at 30 °C during two days, then calcined in a muffle furnace at 600 °C for 2 h in air with a heating rate of 3 °C/min.

2.2. Characterization

The first step of our methodology is to establish the structure of coated materials (textural properties, microstructure, presence of macro defects). All of the characterizations are performed on calcinated materials. The textural properties are determined by nitrogen physisorption (ASAP 2420 - Micromeretics) and mercury porosimetry (Autopore 4 - Micromeretics). The specific surface area is obtained by B.E.T mathematical treatment. The microstructure of coated materials and particles generated after mechanical tests are

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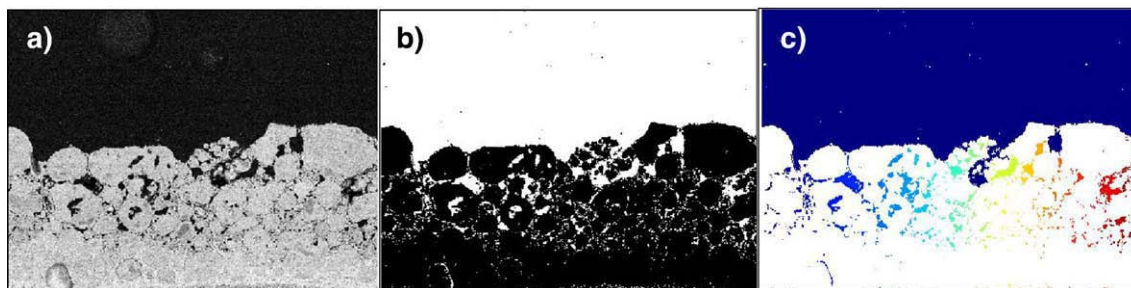


Fig. 1. Steps for image analysis a) initial image, b) binarised image (cracks are in white), c) detection of cracks (each crack is in different colour). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

analyzed by SEM (6300 and 6340F-JEOL). The occurrence of macro-defects inside the coating are also important for understanding the mechanical behaviour of a material. A software for image analysis called LoCaFi has been coded for this purpose (automatic determination of number, area, and circularity ($\phi=4\times\pi\times \text{area}/\text{perimeter}$) of cracks). The method of defect detection uses an image binarisation (Fig. 1), an assembly of connected zones, then an accounting of cracks with determination of their area and their circularity. This treatment is performed about on average of sixty micrographs of coating in order to get statistically significant data.

Then, it is wished to develop a mechanical characterization procedure for coated spherical material. Generally, catalyst beads received a pre-sieving to eliminate fine particles on their surface before mechanical characterization. It has been observed that sieving constitutes already a mechanical test as the latter leads, according to its intensity and duration, to an important generation of fine particles for our materials. Therefore this step has been withdrawn for a better qualification of mechanical tests' contribution to attrition. Also, the follow-up of attrition rate during the tests needs at least a coarse separation of fines particles and initial beads. This is done on a sieve shaken twice manually. At the end of each test, the coated material is sieved with a weak intensity during 1 min on a sieving machine Retsch AS-200. The oversize and undersize particles will be called respectively "mother particles" and "cuttings". The studied measurement parameters are the attrition rate ξ and the normalized attrition rate E , defined as follow:

$$\xi = 1 - \frac{M_a}{M_i} \quad (1)$$

$$E = \frac{\xi_e}{\xi_s} \quad (2)$$

With M_a the mass of mother particles, M_i the initial mass of coated material, ξ_e and ξ_s the attrition rate of coated materials and cores respectively. The normalized attrition rate will be useful to compare relatively the different tests and find the best operational parameters. Indeed an increase of value of E means an increase of the component of the stress applied to the coating compared to the component applied to the core.

The impact test has the advantage of characterizing a great number of particles with strain velocity similar to those met into industrial unit during loading of reactors, unloading of silos, pneumatic transport, and this, in a lapse of time relatively short compared to the standard method using a compression test. The impact tests are performed on a device elaborated by university of Surrey comparable to that used by Yuregir [2] (Fig. 2). Particles are introduced individually thanks to a vibratory distributor inside a tube. The particles are accelerated by a flow of air to undergo an impact against a target constituted of Duplex steel. The angle of the target can be oriented between 0° and 60° . The velocity of particles is determined just before the impact by measuring the time of flight between two photodiodes. Cuttings and mother particles are collected inside a chamber maintained under vacuum. The intensity of the vacuum inside the

collection chamber allows to control the flow of air needed to accelerate the particles. Each test is performed using a single impact with a given velocity and angle. A mass of 30 g corresponding to the use of 2500 coated beads used for each test. The impact angle of 0° , 30° , 45° and 60° have been studied, and for each angle, the coated materials have undergone an impact velocity of 3, 5, 8, 11, 14, and 21 m s^{-1} . The attrition rate is evaluated at the end of each test with a 2 mm sieve.

The drum attrition test simulates the shear stress inside silos, moving bed, and flourishing bed. The standard ASTM [3] recommends

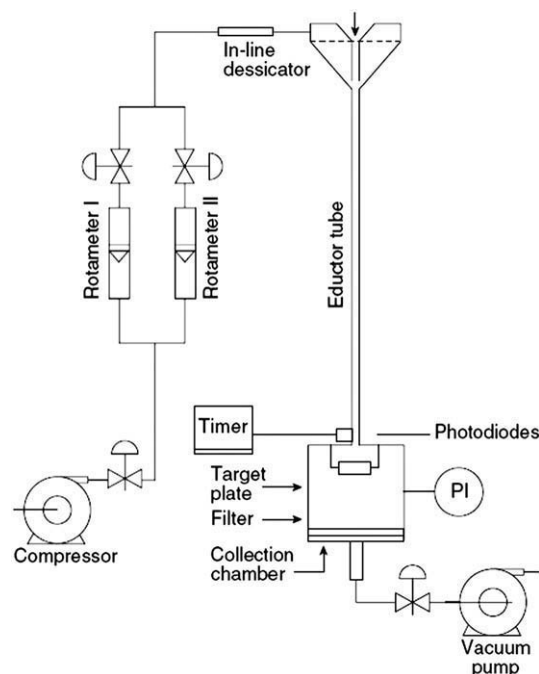


Fig. 2. Diagram of the impact test.

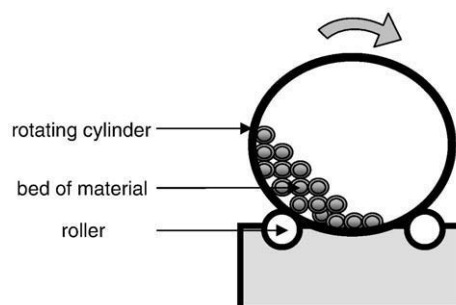


Fig. 3. Diagram of the drum attrition test.

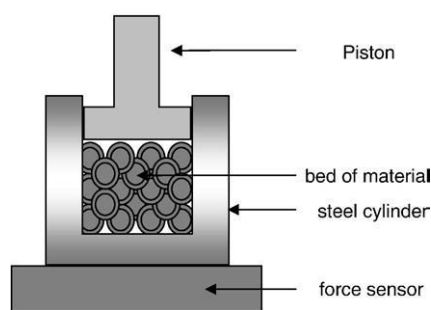


Fig. 4. Diagram of the bulk crushing strength test.

the use of a drum incorporating a baffle. The latter was withdrawn of our device to reduce the impact stress brought and hence stimulate the contribution of shear stress. Our drum attrition is composed of a cylinder with an internal diameter of 40 mm and a height of 80 mm closed at its ends by two stoppers screwed over a Teflon shirt (Fig. 3). This device makes it possible to limit the quantities of material introduced to 25 g of coated materials which corresponds to a ratio of the volume of solid introduced to the internal volume of the drum of 0.32. Two rollers with a rubber coating are used to rotate the drum at 268 rpm. We found that the bed of coated material was in cascade state of flow for this angular velocity.

Bulk crushing test is known to be the most representative test to simulate the stress faced by fixed bed catalysts. Compression tests are carried out by a bulk crushing test marketed by Vinci Technologies. A bed of 25 ml of particles is introduced into a metal cylinder closed at

the base surmounted by a piston. The cylinder is deposited on a force sensor (Fig. 4). The higher part of the bed is supplemented with 5 ml of steel balls to facilitate the transmission of the forces of the piston inside the bed. Then the latter undergoes cycles of loading and unloading with increasing forces (10 to 100 daN) according to the Shell 1471-74 standard. For each unloading, a measurement of the attrition rate is performed by using a sieve of 420 μm .

3. Results and discussion

3.1. Structure of materials

The nitrogen adsorption-desorption isotherm of Sphéralite 512 (Fig. 5a) is a type II according to the IUPAC classification. This type of isotherm is characteristic of nonporous or macroporous solids. Sphéralite 512 has a specific surface area of $8 \text{ m}^2 \text{ g}^{-1}$. The pore size distribution of Sphéralite 512 shows that the average diameter of pores is approximately 230 nm (Fig. 5b). Porous volume is 0.46 ml g^{-1} .

Characterizations of twelve batches of coated materials by nitrogen physisorption and mercury porosimetry show some dispersion of the results. Samples exhibiting similar textural properties have been preserved and then mixed gently with a cloth to avoid damaging the coating. The deposited layer mass as measured by weighing represents approximately 10% w/w of the coated beads. This value corresponds to the maximum theoretical attrition rate that should be reached if only the coating is damaged during a mechanical test. The pore size distribution of the mixture of coated materials highlights the macroporosity of the core at 230 nm and the mesoporosity at 8 nm brought by the coating (Fig. 5b). The nitrogen adsorption-desorption

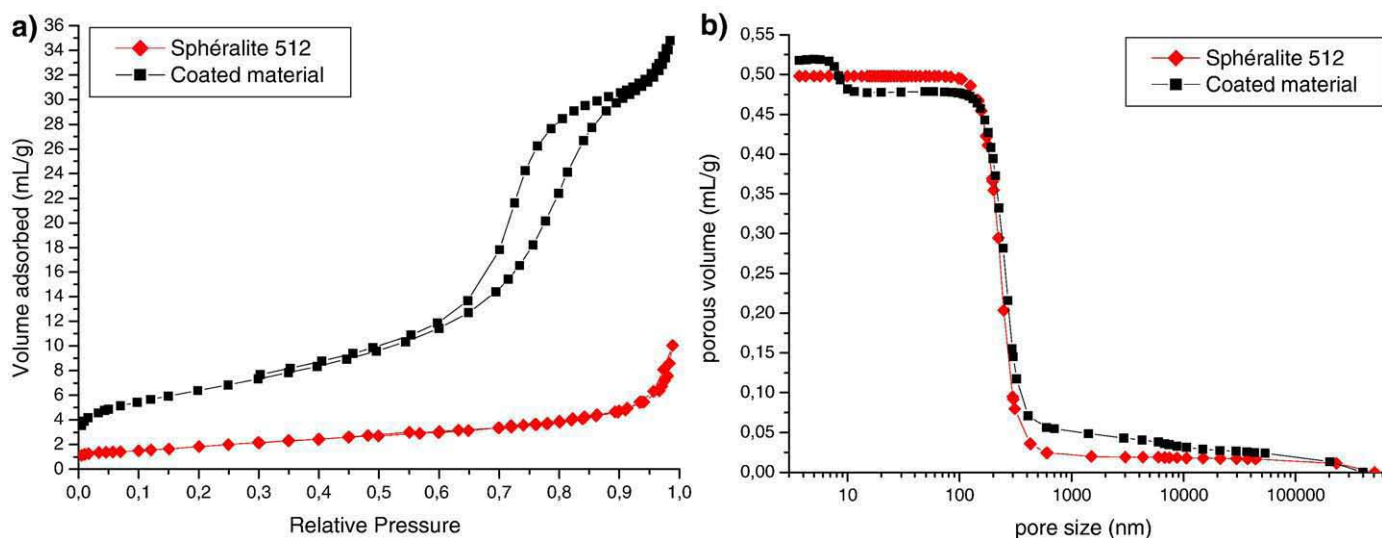


Fig. 5. Textural properties of Sphéralite 512 and coated material a) N_2 adsorption-desorption isotherm b) Hg-porosimetry.

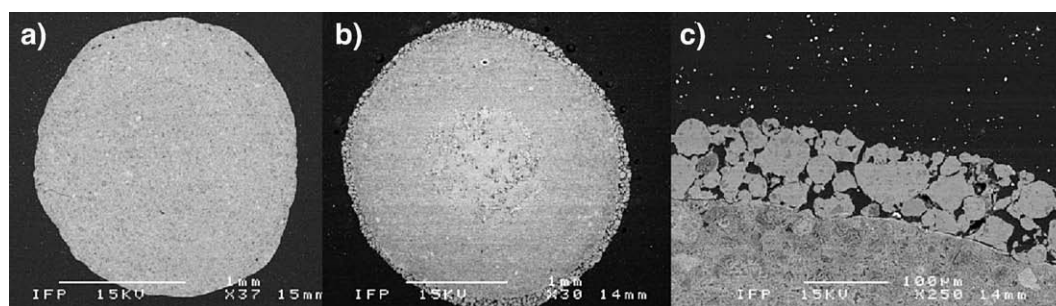


Fig. 6. SEM observations in polished section of a) Sphéralite 512 b) coated material, and c) coating deposited.

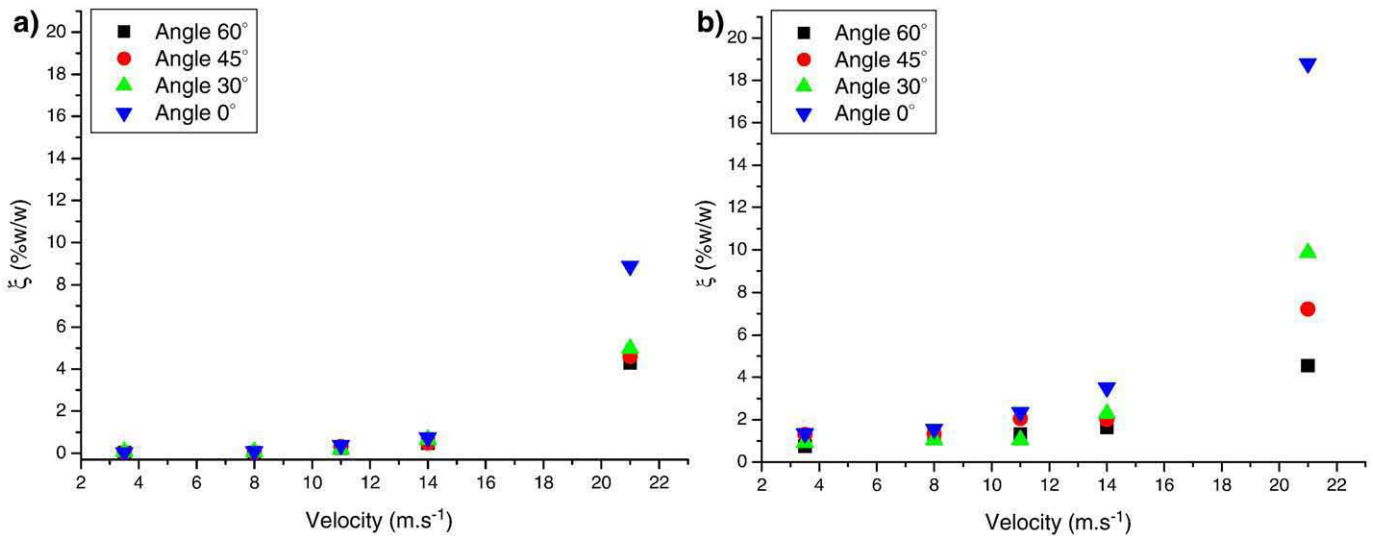


Fig. 7. Results of impact tests attrition rate of a) Sphéralite 512 and, b) coated material versus velocity and impact angle.

isotherm of coated materials is a type II with an H3 hysteresis (Fig. 5a) and the specific surface area is $23 \text{ m}^2 \text{ g}^{-1}$.

The Sphéralite 512 beads are relatively spherical (Fig. 6a). The observations in polished section showed a great heterogeneity of the batch due to the presence of initial agglomeration defects. The coated materials comprise a continuous layer of gamma alumina grains (Fig. 6b). The use of LoCaFi showed that this layer has an average thickness of $80 \mu\text{m}$ with a standard deviation of $33 \mu\text{m}$. 7340 cracks were counted among the sixty micrographs with an average surface of $20 \mu\text{m}^2$ and an average circularity of 0.6. The structure of the coating is comparable to an agglomerate comprising little binder between the grains (Fig. 6c), explaining why the coated materials were so sensitive to sieving.

3.2. Impact test

The attrition rate of coated materials and Sphéralite 512 increases regularly with the impact velocity for all angles. Between 14 and 21 m s^{-1} , an abrupt increase in attrition rate is observed for Sphéralite 512 and coated material (Fig. 7). It should be highlighted that this increase is greater with smaller impact angle for coated material. The effect of impact angle for Sphéralite 512 is almost negligible for 30° , 45° , 60° for every velocity (scheme of attrition: abrasion and chipping). An increase of attrition rate has been noticed only for normal impact at 21 m s^{-1} which correspond to the upcoming of a new scheme of attrition: transversal fragmentation.

The evolution of the normalized attrition rate for various angles and impact speeds shows that the coating is stressed stronger than the core essentially for impact velocity lower than 11 m s^{-1} (Fig. 8). For higher velocities, impact angle doesn't have a significant influence on normalized attrition rate. On the other hand, the results for lower velocities show great differences between impact angles. A maximum is observed for impact at 8 m s^{-1} and 60° . Under these conditions, the attrition rate of coated material is $1.3\% \text{ w/w}$. For the coated materials, the simple evaluation of the attrition rate does not make it possible to determine if the generated cuttings come from the core or the coating. This information is obtained by the visual observation of the morphology and hence the source of the cutting. We noted that the quantity of cutting coming from the core decreases with increasing impact angle and decreasing velocity.

SEM analyses of the cuttings and mother particles of coated material confirm the visual observations. At low speed and for all impact angles, the coated materials undergo some surface damages (Fig. 9a). Almost the totality of the cuttings are disjoined gamma

alumina grains. It is a singular attrition scheme that Subero [4,5] has already observed for impact tests on agglomerates. The latter will be called "local disintegration" of the coating. Very little cuttings coming from the core were observed (white circle on Fig. 9b). For higher impact velocity, the impact angle has an influence on attrition scheme. The mother particles observed for an angle of impact of 0° are often chipped (Fig. 9c), or fragmented particles (Fig. 9e). The morphology of the cuttings is varied. Particles of approximately $40 \mu\text{m}$ which correspond to gamma alumina grains (Fig. 9d), and chips (Fig. 9f) were observed. For impact angle of 60° , the same observations were made but in this case the fragmentation scheme has disappeared.

Therefore, the protocol retained for the mechanical characterization towards impact for future coated materials involves the use of an impact velocity and impact angle respectively of 8 m s^{-1} and 60° respectively.

3.3. Bulk crushing strength test

Sphéralite 512 shows a small attrition rate for the range of force used (Fig. 10a). SEM observations show that Sphéralite 512 is damaged

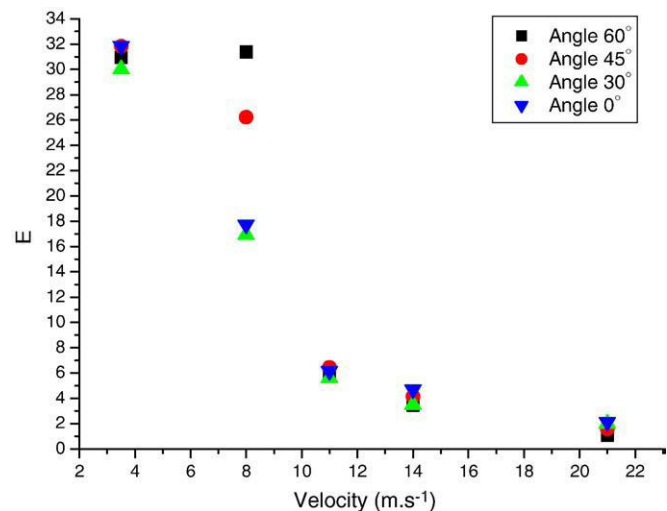


Fig. 8. Normalized attrition rate against velocity and impact angle.

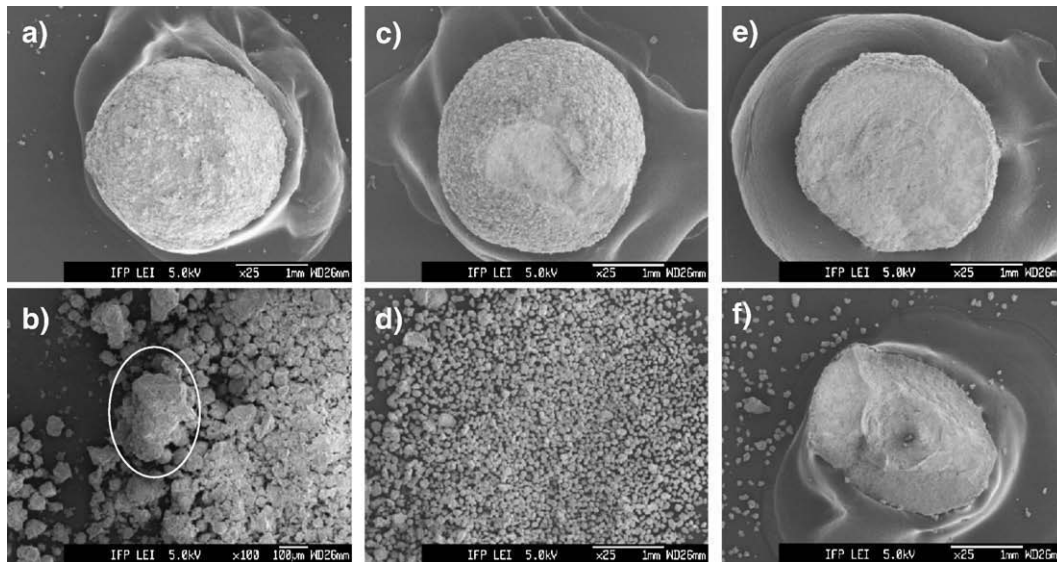


Fig. 9. SEM micrographs of particles after an impact test: a) mother particles (60° , 8 m s^{-1}), b) cuttings (60° , 8 m s^{-1}), c) and e) mother particles (0° , 21 m s^{-1}), d) and f) cuttings (0° , 21 m s^{-1}).

superficially by compression (circle on Fig. 10b). The cuttings are alumina chips with variable morphology and size, most of the time higher than $100 \mu\text{m}$ (Fig. 10c). The coated materials show an attrition rate much higher than Sphéralite 512 (Fig. 10a). Nevertheless, the attrition rate remains quite lower than the mass value of 10% w/w of deposited coating. It is deduced that the coating is damaged only partially. SEM observations confirm this assumption. The mother particles exhibit a specific damage which corresponds to the points of contact between the coated materials (Fig. 10d). The cuttings primarily consist of grains of gamma alumina (Fig. 10e). It is noted that these grains are coated with a calcinated boehmite gangue. Among the cuttings, the sporadic presence of some small particles coming from the core has been observed.

The curve for the normalized attrition rate presents a maximum near 6.5 for a force level of 80 daN (Fig. 10a). Hence, it corresponds to the optimum that should not be exceeded to maximize the mechanical response of the coating. The attrition of coated material is 1.4% w/w at this force level which is comparable with the value obtained for the impact test under its optimum conditions for characterization.

3.4. Drum attrition test

The attrition rate of Sphéralite 512 exhibits a linear increase with a small slope. The damage remains minor even after 2 h of rotation in the drum (Fig. 11a). It was difficult to find a bead with a visible surface damage (Fig. 11b). The reason is that the generated cuttings have a size of approximately $10 \mu\text{m}$ which corresponds to the initial surface irregularities of Sphéralite 512.

The attrition rate of the coated materials presents a particular evolution compared to Sphéralite 512 (Fig. 11a). An abrupt growth of attrition rate is observed in the beginning of the test. In the first 5 min, the attrition rate is significantly higher than the values obtained with the previous tests. Attrition drum seems to be the most adapted device for characterizing coated materials as the surface sollicitations are prevalent in this type of test. After 40 min, the increase of attrition rate becomes linear. The final attrition rate is far higher than Sphéralite 512, suggesting that generated cuttings come primarily from the coating.

The observations by scanning electron microscopy indicate that most the mother particles have completely lost their coating (Fig. 11c).

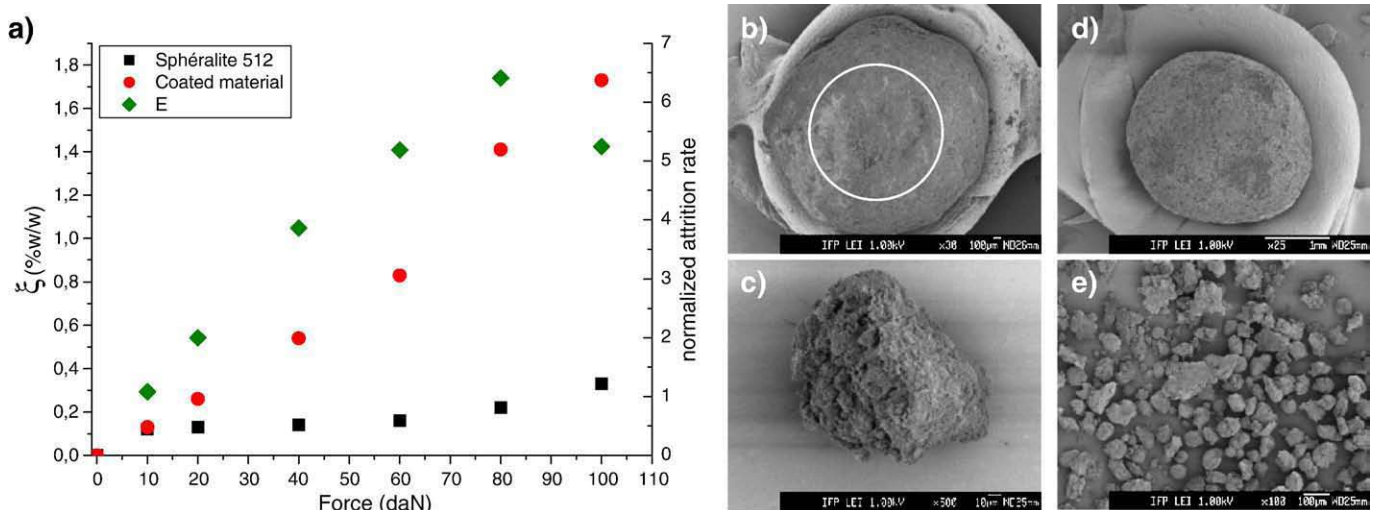


Fig. 10. a) Attrition rate and normalized attrition rate during BCS test of Sphéralite 512 and coated material. SEM micrographs of mother particles and cuttings after a force's level of 100 daN, b) mother particles of Sphéralite 512, c) cuttings of Sphéralite 512, d) mother particles of coated materials, e) cuttings of coated materials.

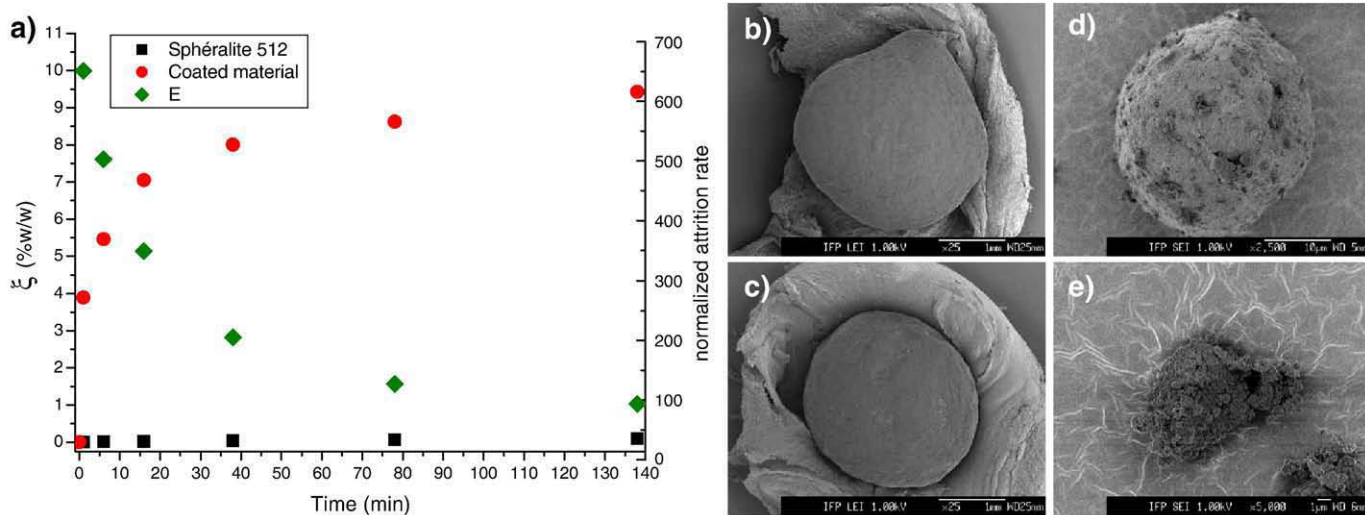


Fig. 11. a) Attrition rate and normalized attrition rate during a drum attrition test of Spheralite 512 and coated material. SEM observations of mother particles and cuttings after a drum attrition test (268 rpm - 140 min), b) coated material whose coating is completely removed, c) coated material whose coating is partially damaged, d) cutting generated after 1 min, e) cuttings generated after 140 min.

The cuttings observed after 1 min of attrition are grains of gamma alumina coated with a gangue of calcined boehmite (Fig. 11d). After 140 min, the debris come from the core and have an approximate size of 10 μm (Fig. 11e). It would seem, based on these observations, that it is possible to limit attrition time to 40 min since the attrition rate exhibits a stage corresponding to the stressing of the core. But subsequent work on materials with much more resistant coating showed that a limitation to 40 min of stressing is insufficient to pull apart the entire coating. The normalized attrition rate presents an exponential decay function of time (Fig. 11a). After 140 min, the value of 100 is reached. As normalized attrition rates, even after 140 min, remains well above the values obtained for bulk crushing test and impact test, materials coated will be characterized mainly by drum attrition test during 140 min at 268 rpm.

4. Conclusions

Fig. 12 shows the value of normalized attrition rates of tests in the selected operating conditions. The research of operating conditions for impact testing device has helped to optimize the amount of stress applied to the coating compared to the core with a normalized attrition rate of 32. The bulk crushing test remains satisfactory with a

normalized attrition rate of 6.5. This test is best suited to characterize the mechanical behaviour of coated material by compression compared to a standard Brazilian test. Most of the energy used for this test is spread within the core of the coated material. The coating is only stressed by the relative displacement of the particles and their friction at points of contact. Among all the tests used, attrition drum exhibits the most efficiency to characterize the mechanical behaviour of coated materials with its normalized attrition rate of 100. This is consistent with the nature of the forces involved in this test which are essentially surface shear forces. The combination of a rigorous characterization of the structure of coated materials and use of these tests with the usual protocols defined above is the key to optimize future formulations of coated materials towards attrition resistance.

If the tests used simulate stresses encountered during life cycle of a catalyst, however, they do not completely characterize the materials. This methodology will be extended in the near future through the evaluation of the fundamental mechanical properties like hardness, Young modulus, toughness of the coating and toughness of the interface. The indentation techniques seem to be the methods most suited to the size and geometry of the system under study.

Notation

ϕ	circularity of cracks
ξ	attrition rate
E	normalized attrition rate
dv_{10}	size of particle below which 10% vol of the sample lies
dv_{90}	size of particle below which 90% vol of the sample lies.

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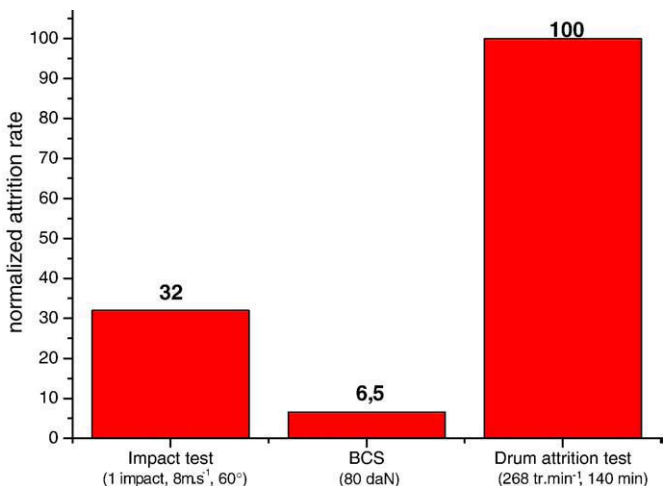


Fig. 12. Normalized attrition rate of tests in selected operating conditions.