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Mechanical strength and reliability of the porous materials used as adsorbents/ catalysts and the new development trends

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ABSTRACT

Purpose: This paper aims to provide an understanding on some aspects of the porous material strength and reliability and to present future trends of the research on the mechanical properties of this solid porous materials.

Design/methodology/approach: It shows that a multitest approach must be designed in order to measure the particle strength and then optimise the production process to enhance its strength. This approach combines measurements reproducing the different types of stress generated in the separation or catalytic process with an extensive characterisation of the physical and mechanical properties of the porous solid, such as hardness, fracture toughnes, brittle, crushing, attrition, etc. The methodology outlined here on alumina single particle or bulk goes beyond the common practice of evaluating mechanical strength based on a comparative study using a single-crushing test and a bulk-crushing test.

Findings: Some recent developments on the basic mechanics of solid porous materials are shown. The main concepts presented are the brittle fracture which leads to the mechanical failure of the porous materials, the measurement and statistical properties of the strength data, the mechanical reliability of the porous material pellets, the mechanical properties of the adsorbent or catalyst packed beds, etc. The use and use limitations of inorganic binders for increasing the mechanical strength is discussed and the most binder systems are presented.

Research limitations/implications: The scientific basis for the issues on the adsorbent/ catalyst mechanical properties calls yet for further elucidation and development.

Practical implications: It is pointed out that porous materials used as adsorbents/ catalysts, with a high and uniform distributed mechanical strength are beneficial to industrial, energetic and environmental applications.

Originality/value: A new route for improving mechanical strength of adsorbents/catalysts will become an unavoidable task not only for their manufacturing but also for to improve the efficiency of separation and catalysis processes

Keywords: Thermo-chemical treatment; Copper droplets coagulation; Solidification

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MATERIALS

1. Introduction

Porous materials play a significant role in our daily life. It can imagine these materials as being "solid sponges" which absorb and host molecular species and they take place in a large number of processes in both nature (*e.g., natural gas,* rocks storing water, petroleum, or biological tissues) and industrial, energy or environmental applications (*e.g.,* activated carbon, porous silica, zeolites for gas/water separation/purification processes, filters, porous supports for nanoparticles, catalysis, molecular sieves, etc.). Commercial sorbents used in cyclic adsorption processes should ideally meet the following requirements: large selectivity derived from equilibrium, kinetic, or steric effect; large activity or adsorption capacity; fast adsorption and catalytical kinetics; easily regenerable; a very good mechanical strength; low cost. The above performance requirements can simply transfer to characteristic requirements as follows: large internal pore volume; large internal surface area; controlled surface properties through selected functional groups; controlled pore size distribution; weak interactions between adsorbate and adsorbent (mostly on physical sorbents); inorganic or ceramic materials to enhance chemical and mechanical stability; low-cost raw materials. These basic requirements are usually proposed for porous materials used in cyclic adsorption processes that are based on physical adsorption.
Solid catalysts are normally composites or agglomerates of mixed metal oxides, or supported metal, metal oxide, on high resistant supports. Both the sorbents and catalysts are brittle porous materials made deliberately to have high porosity and optimal pore distribution. Commercial sorbents and catalysts have a variety of shapes, e.g., granules, spheres, rings, tablets, extrudates, etc. It is well known that a high efficiency both solid adsorbent and catalyst requires not only a good adsorption or catalytic properties such as selectivity and activity, but also good physical and mechanical properties [1,2]. Sorbent and catalyst pellets can present various damaging stresses, e.g. chemical, thermal and mechanical stresses, during transport and storage, or in the columns and reactors, as shown in Figure 1.

For example, mechanical failure of the porous materials pellets results in the formation of fragments and fine particles, which can cause various problems for the functioning of industrial units [3-6], such as blockage, unacceptably high pressure drop across the column or reactor, the formation of fragments and fine particles can lead to maldistribution of fluid flow, variations in heat and mass flux, downstream fouling, in many situations to environmental problems because of the release of fine particles into the atmosphere.

The mechanical strength of solid porous materials used as sorbents or catalysts is therefore one of the key parameters for the reliable and efficient performance of an industrial unit [7-10] However, the researchers are generally focused on the composition and chemistry rather than the mechanical properties of sorbents and catalysts. Few articles on the mechanical strength are therefore available in the literature. Because of an insufficient research in this field, in many industrial applications, the mechanical or physical failure of the sorbents and catalysts is more often the cause of process shutdowns and sorbent or catalyst replacements than their loss of adsorption or catalytic activity [3,4].

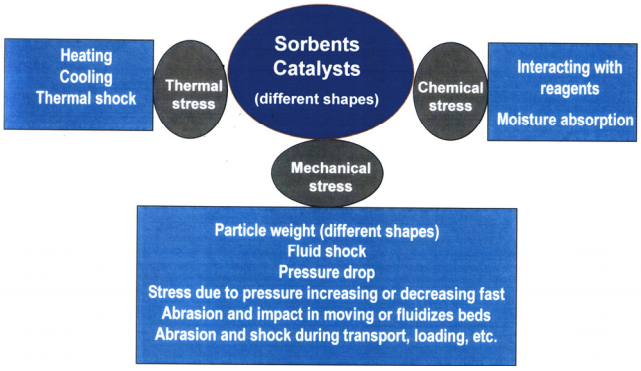

Fig. 1. Different types of stress to which the solid porous materials (sorbents, catalysts) can be exposed

A porous material is a solid that contains cavities, interstices or channels that liquid and gas molecules are able to enter through them. Figure 2. shows a schematic cross-section of a porous solid material.

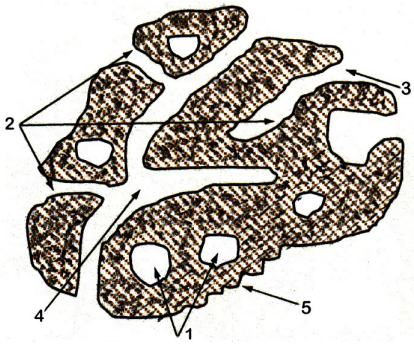

Fig. 2. A schematic cross-section of a porous solid material: 1 - closed pores; 2 - open pores; 3 - blind pores; 4 - through pores; 5 - roughness

Those pores that are totally isolated from their neighbours are called "closed" pores (1) and have an effect on some macroscopic properties of the material such as its mechanical strength, bulk density and thermal conductivity. On the other hand, "open" pores (2) have a continuous channel of communication with the external surface of the body, and they have great influence on the sorption processes. Open pores can also be "blind" (open only at one end 3) or "through" (open at two ends 4). A practical convention is used to make a distinction between porosity and roughness (5), which assumes that a rough surface is not porous unless it has irregularities that are deeper than they are wide [6]. Porous materials can be classified as cellular, fibrous or granular, this being based on their configuration alt microscopic level.

This paper aims to provide an understanding on some aspects of the porous material strength and to present future trends of the research on the mechanical properties of solid porous materials used as sorbents or catalysts. It will focus on porous material pellets used as sorbent or catalyst support (alumina) in a fixed bed reactor.

2. Mechanical failure of porous pellet materials

Porous materials such as carbons, zeolites, alumina, mixed oxides and metal oxide supported catalysts are usually brittle materials and their mechanical damage is due to brittle fracture under tensile stress induced in sorbent or catalyst bulk [6,7]. Variations of size, shape and orientation of the flaws, e.g. pores, defects, dislocations and discontinuations, result in a large scattering range of the single-pellet strength data. It has been well demonstrated that the mechanical strength of solid porous materials can be modeled well by Weibull distribution [8-10]. The correlation between single-pellet and packed bed behaviours, and that between activity, mechanical reliability, and mass or heat transport characteristics are of primary importance for the process catalyst design. The mechanical strength of solid porous material (sorbents, catalysts) is therefore one of the key parameters for the reliable and efficient performance of an industrial process and reactor [7-10].

Solid porous materials are fragile [1,12]. Literature on catalyst and sorbent engineering give guides with details for handling: must not fall; must not roll the drum which contains a sorbent or catalyst; the reactor must fill with a great care and do not drop the pellets into a reactor; must not heat a catalyst with a high heating rate; must keep the sorbent and catalyst in dried place without moisture. Porous sorbent, mixed oxides and oxide-supported metal catalysts are usually materials with a brittle failure mode and their mechanical failure is due to brittle fracture. [13-16]. The pellets have very little plastic deformation and a small elastic deformation before the fracture happens.

The mechanical strength characteristics of the alumina particles were determined according to ASTM D4179 &D6175 compliant for extruded pellet crushing strength and according to ASTM 7084-04 for bulk crushing strength and was used Crush-BKinstrument. Density was determined according to ASTM D2854-09.

2.1. Side crushing strength testing for a single particle

The side crushing strength test (SCS) is known as the Brazilean test, and is a test method to determine the strength of a particle when, at two diametrically opposed contact points this is compressively loaded [11,12]. Individual particle, in different forms (spheric, extrudate, tablet, etc., Fig. 3) is compressed between two rigid platens, using a mechanical testing device at a slow and constant crosshead speed, usually in the range 0.1-0.5 mm/min, producing strain rates usually below 5×10^{-3}/s, until its breakage is detected by a sudden drop in the load. The maximum force before breakage is noted as the SCS value. This test method is appropriate for situations where compression and slow shearing deformation predominate. Figure 4 presents the load displacement curve and the possible sudden drop in the load obtained for a model test porous material, such as alumina.

Fig. 3. Different forms of porous solid materials (sorbents, catalysts): spherical pellets; cylindrical pellets; tablets, tubes

This behaviour is a typical trend for the brittle failure mode. The repeating of such a test on a big number of particles shows that particles of a similar size and from the same batch, break under different loads. This characteristic, together with the brittle failure mode, shows that fracture

initiates small defects into the particles, such as microcracks, and these are distributed on the surface and into particles [12]. The image of pellets obtained by microscopy clearly shows the presence of these cracks. Therefore, a big number of pellets should be tested to obtain reliable information on the particle mechanical strength. This test is known as "indirect tensile test", a tensile failure is obtained from a compressive loading. An estimation of the tensile stresses can be calculated using Equation 1 [13-15]:

$$\sigma_f = 2.8P_f / \pi D^2 \quad (1)$$

where P_f is the load at the point of breakage and D is the particle diameter.

Prior to the testing of the pellet, the diameter of each particle is measured by, for example, optical microscopy. The crushing strength distribution obtained for the model sample is presented in Fig. 5a. The average SCS value is 40 kgf and the standard deviation 12.1 kgf. The results show that the strength of the spherical pellets is not uniform within the particle, this is due to the presence of defects.

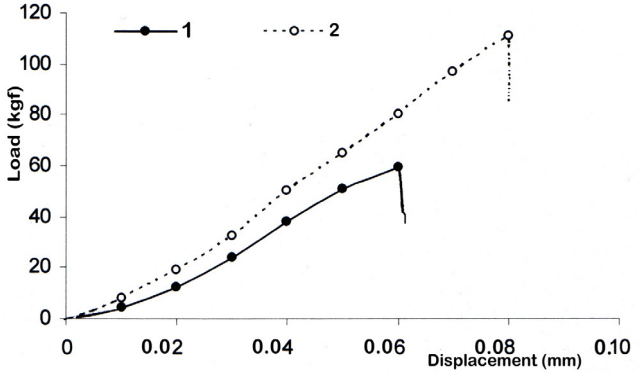

Fig. 4. The load-displacement curve during the crushing strength test of the alumina pellets: 1 - spherical pellet; 2 - a tablet

In contrast to an SCS test, where the pellets are individually compressed between two rigid platens, the particles in a bulk subjected to a compressive loading are loaded at more contact points, this is known as multiple particle crushing strength (MPCS). Figure 6 is shown a crushing strength test instrument.

Because of this the tensile stress and crushing strength distribution is different from that obtained in an SCS test (Fig. 5b).The average MPCS is 37.5 kgf and the standard deviation is 9.2 kgf, therefore the average is lower than the average SCS value. A comparison of the two distributions shows that the MPCS distribution is narrower and displaces towards higher loads, around 26% of the pellets have a crushing strength below 30 kgf for SCS test and this is decreased to 21% in a MPCS test. This highlights pellets loaded in a bed of particles will be more resistant to breakage under compressive loading than pallets loaded in a platen.

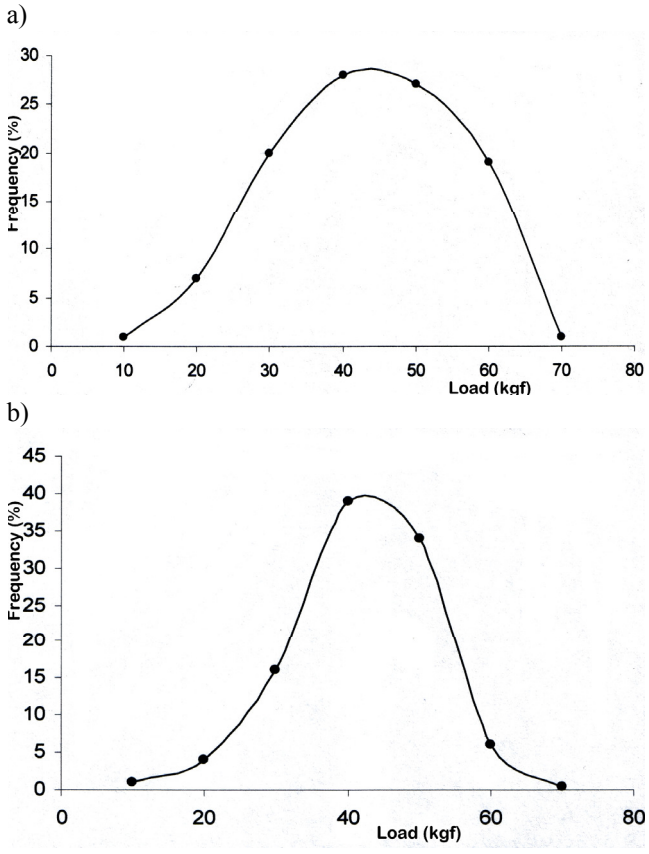

Fig. 5. Crushing strength distributions for alumina spherical pellet in the range 1.6-2.0 mm: a) side crushing strength distribution; b) multiple spherical pellet crushing strength distribution

The shape of the scraps resulted during a SCS test is shown in Figure 7a and after a MPCS test in Figure 7b. In majority of SCS tests the breakage occurs in form of some fragments and fines. The breakage pattern should result from the defects from which the cracks will preferably initiate and then propagate. The shape of the fragments after an MPCS test differs, the spherical pellets usually are braked into a central part of the particle that are bigger and other fragments are in the smaller different shapes. A slight flattening could be observed on the top of the particles.

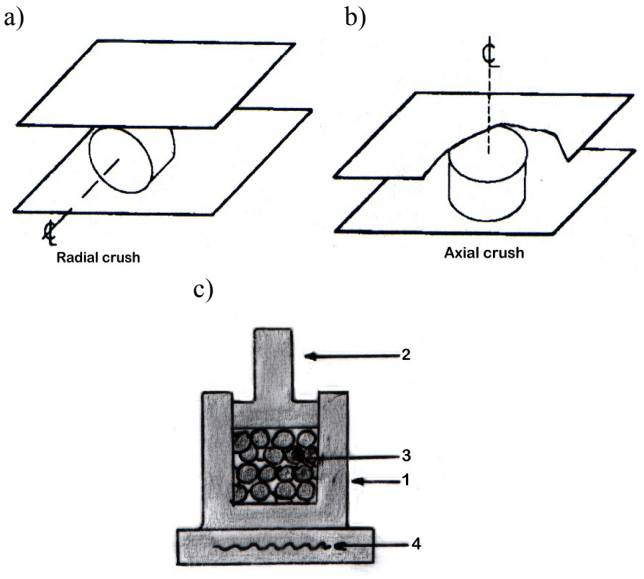

Fig. 6. Schematic representation of a crushing strength test: a) radial crushing for cylindrical pellet; b) Axial crushing for cylindrical pellet; c) instrument for bulk crushing test, where the numbers represents: 1 - steel cylinder; 2 - piston; 3 - bed of pellets; 4 - force sensor

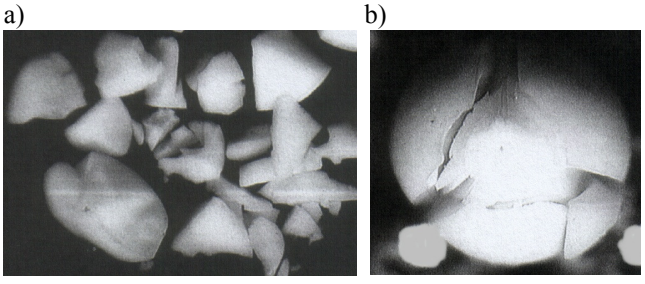

Fig. 7. Optical micrographs of the scraps of alumina spherical particles after an SCS test a) and after MPCS test b)

Extruded pellets of sorbent or catalyst are also made as cylinders, tubes, multilobes, tablets (Fig. 3). In industrial practice, materials are extruded as pastes of enough fluidity and plasticity [13,16]. Before heat treating, the extruding is followed by cutting and conveying. As the raw pellets are plastic and are often found formed pellets with deformations and curvature. For pellets with irregularities, a radial crushing measurement of strength is uncertain, because of the no repeatability of stress distribution for different specimens of the sample. During measurement test, the repeatability of stress distribution is one of the requirements to obtain correct and valid results. Therefore, can be used different test methods to determine the mechanical strength of differently shaped material pellets (used as sorbents or catalysts), as it is shown in Figure 8.

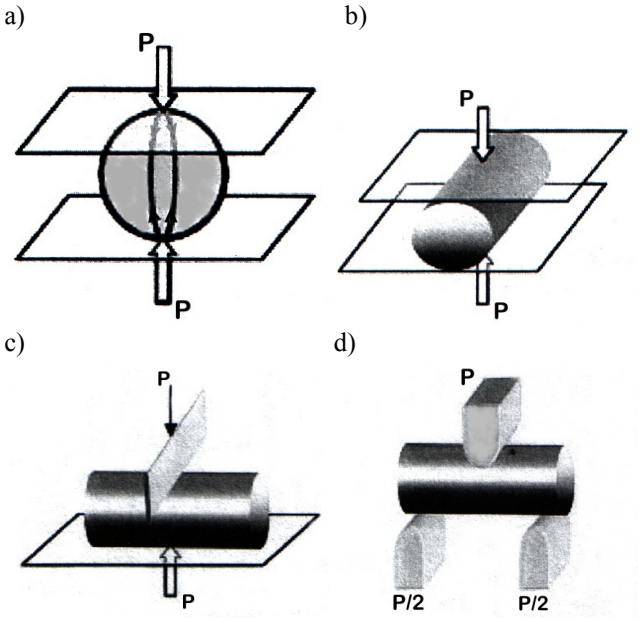

Fig. 8. Schematic representation of various indirect tensile strength tests: (a) crushing-spherical pellet; (b) crushing-cylindrical extrudate pellet; (c) cutting-cylindrical extrudate pellet; (d) bending-cylindrical extrudate pellet

For example, the crushing strength method is suitable one for spheres, short regular cylinders or tablets, while others methods such as the bending method is more suitable to extrudates with a big ratio of length to diameter. The cutting method is much more appropriate for extrudates and tablets with more irregularities [17]. The measurement and determination of a single pellet strength allows a comparison of the sorbent or catalyst mechanical characteristics among various samples. However, it should be highlighted that parameters such as the size of pellet, loading speed, loading way, the properties of the loading platens, humidity and temperature of sample may have direct influences on the measured strength data and therefore much caution should be taken when comparing samples tested with different device in different laboratories.

2.2. Bulk crushing strength testing

For industrial applications, the mechanical strength of bulk solid porous materials is commonly evaluated by bulk

crushing and bulk shearing and their relationship with single particle properties must be done. For studying the mechanical strength of a bed of particles under compressive loading, bulk crushing strength (BCS) tests must be performed. The BCS testing is defined as the pressure at which 0.5 or 1 wt. % of fines or broken particles is produced [18]. In a BCS test, a bed of particles, in different shapes, is quasi-statically compressed in a cylindrical form to a specified pressure(as it is shown in Fig. 6b). The cylinder has an internal diameter of 40 mm and the walls are lined with teflon to reduce the friction. Tests were carried out with about 2500 particles in a wide range of pressures, 4-35 bar. The bed of particles was compressed at a slow crosshead speed of usually around 0.5 mm/min. The particles were then carefully removed from the cylinder and were sieved, by using a sieve of 500 μm, to determine the amount of fines below 500 μm and broken particle fraction in the sample. The percentage of fines and broken particles was calculated for each loading. The BCS values are 9 bar, considering the amount of broken particles as the criterion, and 26 bar, considering the amount of fines. In Fig. 9 is shown the SEM images of the particles after a BCS test.

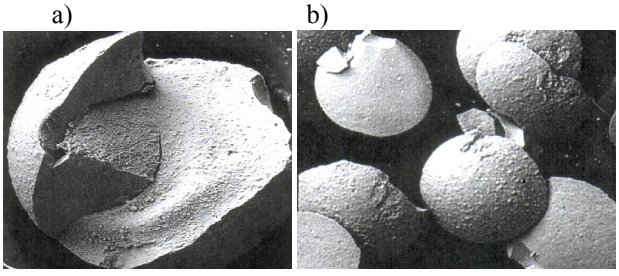

Fig. 9. SEM images of alumina spherical particle bead after crushing strength test, at room temperature: (a) - image for one particle separated from particle bed; (b) - image for an assembly of particles, a particle bed

It can be observed, the shape of the fragments is different of the shape observed after a SCS test (Fig. 7a), and is similarly as an assembly of particles (Fig. 7b) that have a bigger number of contact forces than in a SCS test. This leads to different compressive and tensile stresses and therefore different shapes of scraps.

The dependence of the bulk crushing strength on the property of single pellets and the relationship between the pressure drop across the sorbent or catalyst bed and pellet failure are of major importance to tailor the sorbent and catalyst, for the design of reactor and to establish optimal process parameters. For different sorbent or catalyst shapes, the measure of percentage of broken particles is impractical, but the percentage of fines passing a suitable sieve is a more practical and used.

2.3. Attrition testing

The drum attrition test simulates the shear stress inside moving bed, fluidized bed and silos. The standard ASTM [19] indicates the use of a drum that incorporates a baffle. The latter was withdrawn of device to reduce the impact stress brought and hence stimulates the contribution of shear stress. The drum attrition used is composed of a cylinder with an internal diameter of 80 mm and a height of 160 mm closed at its ends by two stoppers screwed over a Teflon shirt as in schematic represented in Figure 10.

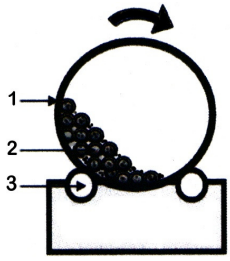

Fig. 10. Schematic representation of a drum used for attrition test: 1 - rotating cylinder; 2 - bed of porous pellet material; 3 - roller

This device makes it possible to limit the quantities of material introduced to 50 g of porous materials which corresponds to a ratio of the volume of solid introduced to the internal volume of the drum of 0.32. Two rollers a used to rotate the drum at 260 rpm, 280 rpm and 300 rpm. The follow-up of attrition rate during the tests needs at least a coarse separation of fines particles and initial spherical particles. This was done on a sieve shacked one manually. At the end of each test, the porous material was sieved with a weak intensity during 60 sec on a sieving machine Retsch AS-200. The oversize and undersize particles were called “parent particles” and “cutting particles”, respectively. It was found that the bed of porous material was in cascade state of flow for this angular velocity. The studied measurement parameters are the attrition rate λ and the normalized attrition rate E, which are defined as follow:

$$\xi = 1 - M_a / M_i \quad (2)$$

where M_a is the mass of parent particles, M_i is the initial mass of alumina porous material, ξ represents the attrition rate of alumina porous material. The attrition rate is useful

to compare the different tests and find the best operational parameters. The attrition rate of alumina spheres of 8 mm diameter exhibits a linear increase with a small inclination (slope). The damage remains insignificant even after two hours and half of rotation in the drum (Fig. 11).

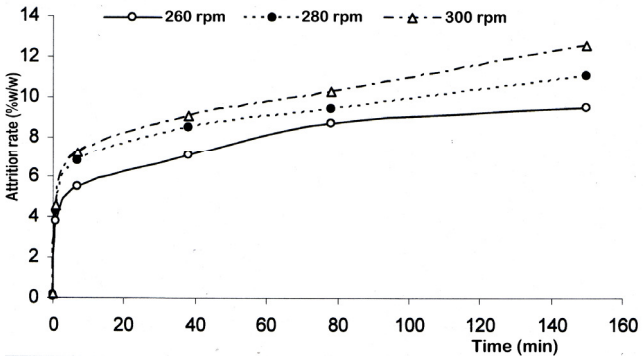

Fig. 11. Attrition rate during drum attrition test of alumina spherical pellets (8 mm diameter)

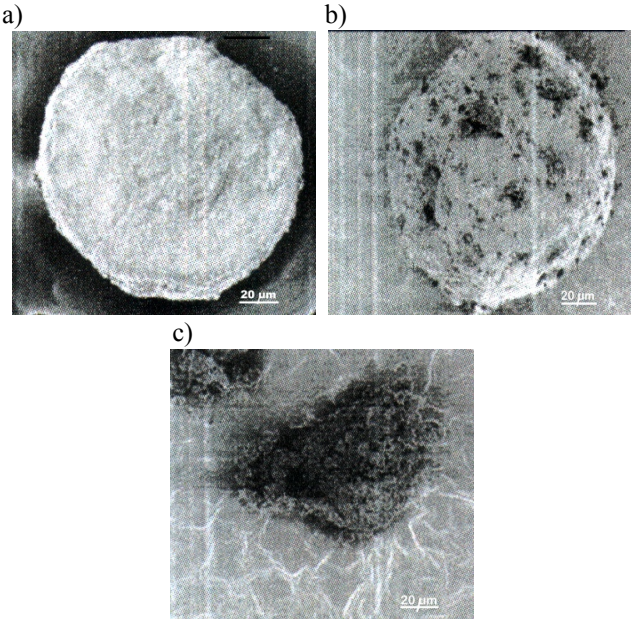

Fig. 12. SEM images of: a) - initial alumina spherical particle; b) - parent alumina spherical particle is partially damaged after 150 min at 260 rpm; c) - cutting generated after 150 min at 300 rpm

It was difficult to find a spherical pellet with a visible surface damage after 1-5 min of rotation, even at 300 rpm. The explications is that the generated cutting have a size under 10 µm which corresponds to the initial surface irregularities of spherical alumina pellets (Fig. 12a). After 20 min, the increase of becomes almost linear for all three speeds of rotation. The SEM images show that most the parent particles have lost from their initial mass (Fig. 12b). After 150 min, the debris come from the core and have an approximate size of 20 µm (Fig. 12c).

3. Mechanical reliability of sorbent/ catalyst pellets

In the column or reactor, the material used as sorbent or catalyst pellets pass through various damage stresses. In most industrial applications, if a small fraction of sorbent or catalyst pellets break or fracture, would take place serious process problems [4]. Thus it can be observed that the mechanical performance of sorbent or catalyst bed is rather mainly controlled by those pellets with lower strength and not of all particles forming the bed. This fact highlights that the low strength/probability fraction of the sorbent or catalyst strength distribution is the key part for the mechanical reliability, while the mean strength is of less importance. For any industrial application of solid sorbents or catalysts, there are a critical probability of failure of pellets, for example 5 to 10%, below which the solid material bed can be usually operated. A method to predict the fracture load with a probability of failure is provided by Weibull statistic. Consequently, the fracture load corresponding to the critical probability of failure can be established and used to indicate the mechanical reliability of the pellets and to assess and compare the mechanical characteristics between different sorbent or catalyst samples. A larger load predicted and a higher mechanical reliability will ensure a better industrial performance of the sorbent or catalyst materials. As an example, in Table 1 are given the data of several alumina extrudates used as support for high temperature catalysts.

It can be observed that the mechanical reliability of sample no 2 is lower than that of sample no 3, while it has the biggest mean strength of all five samples. For sorbent or catalyst pellets, low mechanical strength is due to increased risk of strength failure, and high strength is related of a high pellet density, low porosity and low efficiency, because the most of heterogeneous reactions are internal diffusion controlled. From this reasons, mechanical strength distributed in a narrow domain is therefore required for industrial applications of solid sorbents and catalysts (see Fig. 5b).

Table 1.
Crushing strength and fracture load for alumina pellet

No	D (mm)	H (mm)	R crushing strength (kg/pellet)			Fracture load (kg/pellet) (with failure spec. prob.)	
			min	mean	max	5%	10%
1	9.4	7.3	9.2	27.2	48.1	13.14	16.26
2	9.4	7.4	12.6	34.1	66.4	15.72	19.46
3	9.5	5.2	18.1	30.1	40.3	20.25	22.65
4	5.2	3.8	14.8	17.2	36.4	15.42	17.35
5	5.4	4.0	3.5	17.1	30.2	5.54	7.45

The mechanical strength of porous material is an important parameter that gives a measure of the mechanical reliability and this depends of material resistance to the bulk crushing and of pressure drop generated in column or reactor. From this point of view the measurements of the BCS and the pressure drop resulted can provide important information regarding to mechanical reliability. The measurements of the BCS were described in section 2.2. The measurements of the pressure drop were performed with using a special device [18,20,21]. A cylindrical sample recipient with a internal diameter of 55 mm, equipped with a movable disc, which was used to apply a uniform force on the top of the alumina packing material. The recipient, the disc and the support plate are of stainless steel. The disc and the support plate have holes with a diameter of 1.5 mm, which are uniformly distributed at a distance of 3 mm. The pressure drop across the alumina material bed was measured by a U-shaped tube using water as an indicator. The nitrogen flow was provided from a tank under pressure and was indicated by a rotary flow meter. A scale permitting to measure two decimals after millimetres was used to establish the bed displacement. The pressure applied by the disc on the top of the packing bed was indicated by a manometer. Three samples of alumina were used for measurements and they were differently shaped but with an identical chemical composition, γ-Al_2O_3, and are available in the market. Samples were in spherical, cylindrical and tubes pellets. A scale with an accuracy of 0.01 mm was used to measure the pellet size and a balance with a precision of 0.1 mg was used to determine the pellet weight. Before to all the laboratory experiments, the samples were heated in nitrogen at 150°C, for four hours and cooled at room temperature and then sieved to remove the fine particles by a sieve of 1.25 mm. Also, the broken and defected pellets were removed.

In Fig. 13, 14 and 15 are presented the results obtained in terms of influence of pressure applied on percentage of broken spheres and fines generated as well as the influence of the percentage of fine particles on the increase of the pressure drop.

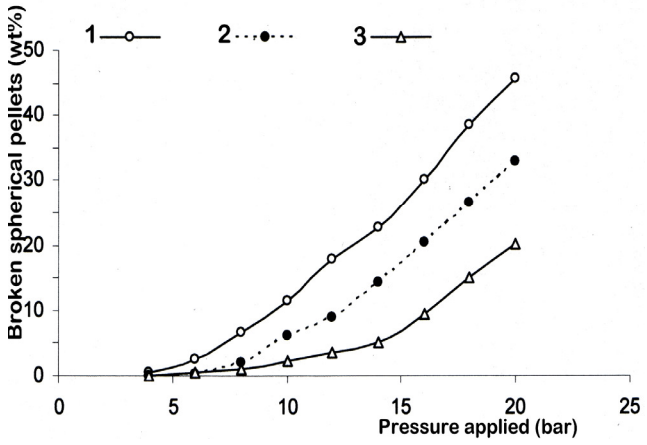

Fig. 13. Influence of pressure applied on percentage of broken spheres generated. Three spherical alumina samples: (1) 6 mm; (2) 8 mm; (3) 12 mm in diameter size

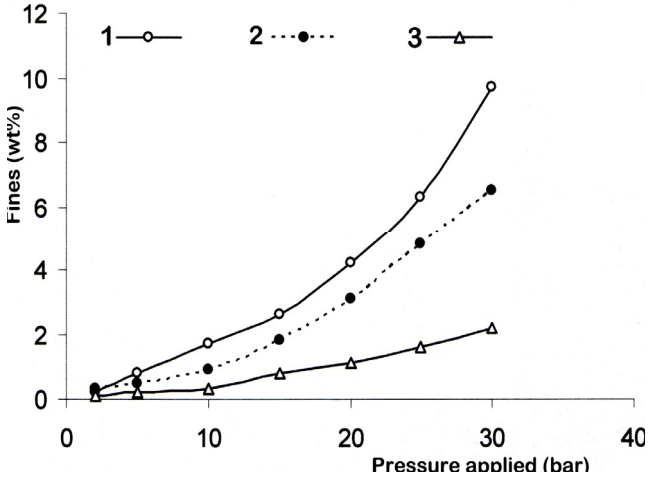

Fig. 14. Influence of pressure applied on percentage of fines generated. Extruded cylindrical sample (4 mm in diameter and a length of 8-12 mm) and fines generated below the sieves of 1.25 mm (1); 0.9 mm (2); and 0.5 mm (3) respectively

The mechanical failure of solid porous material in various forms result in the formation of fragments and

fines, that increases the pressure drops across the column or reactor. The data obtained after experimental tests show that together with the mechanical failure of the pellets in a sorbent or catalyst bed, there is a point of maximum curvature, after that the pressure drop begins to increase quickly (Fig. 15). The quick increase in the pressure drop did not result from the quick increase in the quantity of broken particles and fines, and especially because of the rearrangement in the packing structure, occurring as the quantity of failed pellets attains a certain critical value. It can be seen that a tubular extrudate is easier to result in the pressure drop increase than a cylindrical extrudate, and also that, a sorbent or catalyst with smaller pellet size is more susceptible to an increasing in the pressure drop. This is probably due to that more debris and fines are generated in the same load range for the sample which has smaller size. It can also be seen that the determination of pressure drop through a laboratory scale packed bed has a good reproducibility and provides relevant information to the mechanical reliability of a packed bed in a column or reactor. The knowledge of the influence of the mechanical failure on the pressure drop is useful in the estimation of power consumption and in the selection of compressor types in the step of engineering design. Also, the pressure drop across a packed bed filled with fresh sorbent or catalyst could be predicted approximately.

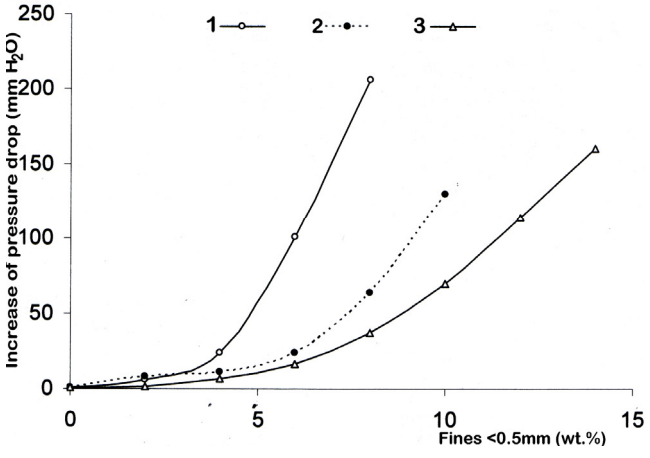

Fig. 15. Influence of the percentage of fine particles on the increase of the pressure drop at an nitrogen flow rate of 2.5 m^3/h. a spherical sample of 6 mm in diameter (1); an extruded cylindrical sample of 4 mm in diameter and a length of 8-12 mm (2); a tubular sample of 12 mm in outer diameter, 6 mm in internal diameter and a length of 12-16 mm (3)

4. New development trends

From production to industrial uses, the sorbents and catalysts pass through a lot of processes, such as pelletization, reduction, storage, transport, loading, start up, normal operation, regeneration, shutdown, discharge, etc. All these steps have a strong influence on the mechanical strength and reliability of the catalyst/sorbent materials. Figure 16 presents a typical scale framework for the mechanics research development of a fixed bed arrangement for catalyst/sorbent material.

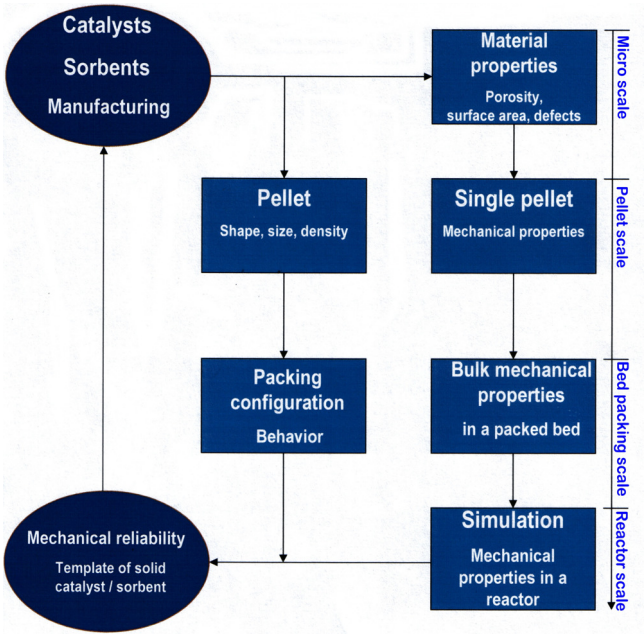

Fig. 16. Scale framework for the mechanics of solid catalyst/sorbent

For example, the manufacturing process determines the catalytic/sorbent characteristics, structure at microscopic level, pellet shape and size, and therefore influences the mechanical characteristics. In other processes, the catalyst/sorbent pellets are subjected to activation, structure reconstruction and subjected to external or internal chemical, thermal and mechanical stresses. Especially, in catalytical processes, the catalytic reaction is in most cases a complicated process and can affect the catalyst material strength. The mechanical reliability of porous materials used as catalysts/sorbents is directly related to the reactor type and its configuration, loading mode of material, reactor/column dimensions (diameter, height), reactant properties, conditions of reaction and process. All these show that an integrated research on solid porous material

mechanical characteristics should involve all the process aspects mentioned above, rather that only catalyst/sorbent pellets itself. The research on solid porous material mechanics must establish a model for mechanical reliability of solid catalyst/sorbent under specific operational parameters and conditions. The single pellet characteristics gives in most part the mechanical reliability of packed bed and the mechanical reliability of a reactor could be predicted and then the conditions and process parameters could be established. On the other hand, the conditions and process parameters could impose certain requirements for material properties and then material manufacturing could be conducted.

The mechanical characteristics of solid porous materials are usually related to the material characteristics (especially microstructure) of adsorbent/catalyst pellets. To obtain pellets material, the particles are subjected to processes of agglomeration and extrusion with or without a liant. Fracture strength depends on surface energy, elasticity modulus, and cracking size in the single material pellets or in the pellet bulk [11]. Weibull statistics shows that the Weibull modulus highlights only how the material defects are distributed and dispersed into material mass. On the other hand, it was considered [12] that the solid porous material (more evident for catalysts) the crushing strength depends of porosity and the size of the primary particles from which the material pellets are manufactured [13]. It is considered that a major role have also the binding forces inside agglomerated materials such as catalysts and sorbents. The forces like attraction, adhesion and cohesion between solid particles form close bonds because they are not freely movable binder bridges, and thus they help to keeping the particle agglomerate structure. In agglomerated material, there are developed pores and edges, which constitute defects. Based on these considerations, between tensile strength of the agglomerated material forms and the primary particle size, there is an inverse relationship. Regarding the manufacturing process, it determines the characteristics of the material, the microstructure and therefore, the mechanical properties. To develop and obtain **s**orbents and catalysts with improved mechanical characteristics it requires to study the process parameters and factors that can influence them to optimize the manufacturing process. A total quantitative correlation between the material characteristics, microstructure and the single pellet mechanical characteristics does not exist and must developed.

The analysis of bulk crushing strength emphasizes that there are many similar aspects between a practical fixed bed reactor and the small packed bed used in bulk crushing strength (BCS) test. For example, disordered packing of the pellets could have the same nature between large and small beds. In a practical reactor, the major force is usually also axial, which is formed of the weight of the pellets themselves and the pressure drop of the fluid phase. Actually, the BCS measurement test can be considered as a most simplified model for the operation of the practical reactor. If the correlation from the single pellet strength to the bulk crushing strength can be achieved, it is also expected that the bulk behaviour of the material pellet packing could be predicted in term of the single pellet characteristics. Or, more exactly, for a known system, the single pellet specifications can be defined precisely, and these refer to the pellet formation conditions which could be optimized for the final use of the material, and hence the pellet characteristics could be optimized. The correlation between the single pellet and bulk mechanical characteristics ensures an opportunity for the reliability prediction of a reactor and these benefits can lead to a important economical advance for any industrial process. The flow of fluid across the bed of material will have impact and will damage the material pellets. The adsorption of the molecules from fluid phase on the internal surfaces of the porous material reduces its surface energy, and thus reduces the fracture strength of the adsorbent and catalyst materials.

The simulation of the mechanical characteristics of the adsorbents or catalysts for real process conditions, e.g. temperature, pressure, flow velocity, reactant concentration, is required to establish the mechanical reliability model of solid material. Moreover, the evolution of the mechanical properties of the material with the varying of the process conditions is of real importance to efforts at increasing their mechanical reliability. Another important factor for the evolution of the mechanical properties in time, (adsorbent/catalyst lifetime) i.e. material fatigue strength, must also be studied and developed.

The applications of solid porous materials to catalysis, separation or capture processes are various and numerous, and the material either acts a support or it is functional itself. The applications range is from various applications in chemical and petrochemical fields till to exhaust gas control in cars, trucks, power plants. Industrially major separation processes refer to drying and purification of air, separation of oxygen /nitrogen from air, purification of gases such as, H_2, Ar, CH_4, aromatic separation, and recently a important attention has given to carbon dioxide separation and capture from flue gas and biogas. Effective use of microporous materials in applications mentioned above requires that the microporous particles are structured into a macroscopic shape. This shape must have sufficient mechanical, chemical and attrition resistance and

a structure that accepts high flows and rapid mass transfer. A new shape being, for example, honeycomb form. New trends to obtain materials in suitable shape and with improved characteristics are related of processing methods of the raw materials (initial porous powders). Versatile powder processing methods to process initial powders into different forms and porous structures such as extrusion, colloidal processing, coatings of pellet supports, use of new kinds of inorganic binders for increasing the mechanical strength are studied and developed.

The efficiency and performance of structured adsorbents or catalysts are based on the combined effect of a number of parameters such as mechanical strength, mass and heat transfer properties, pressure drop across the adsorbent /catalyst bed, gas diffusion kinetics, and also volumetric efficiency. All these are schematic illustrated in Figure 17.

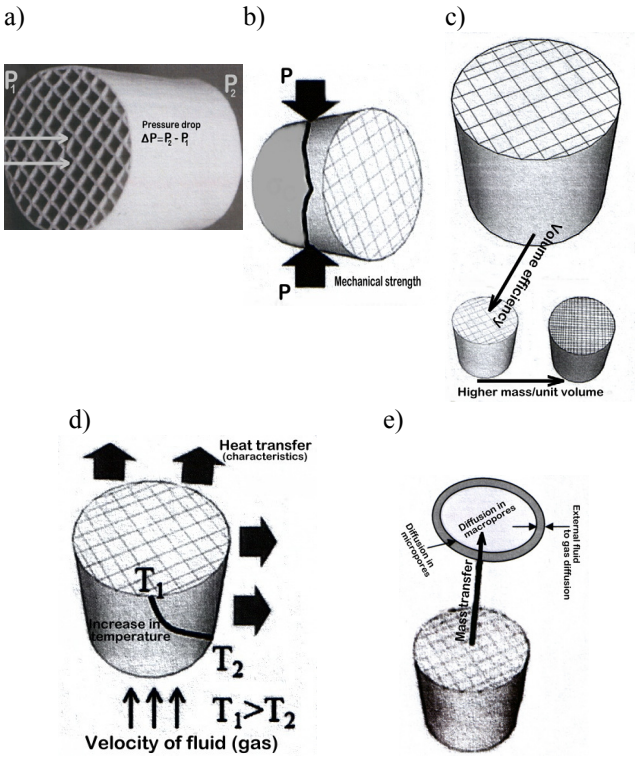

Fig. 17. Schematic illustration of the characteristics of structured porous adsorbents/catalysts: a) pressure drop; b) mechanical strength; c) volume efficiency; d) mass and heat transfer; e) gas diffusion kinetics

High mechanical stability of the structured porous materials is critical to the performance in processes where the pressure variations are rapid and large and also when thermal cycling determines damage and stress. The chemical durability of the adsorbents and catalysts is related to the corrosion or deterioration during use and this may determine the lifetime [22,23]. During gas separation, purification or catalytic processes, the heat waves appear in the beds and consequently a poor heat transfer flux from the porous material can adversely affect the process performance. The high pressure drop and a low mass transfer that are typical for a conventional bed of granulated or beaded adsorbents could be minimized for the ultra-rapid swing sorption processes that are needed for large scale applications such as CO_2 capture. These restrictions can be partially overcome by design and manufacturing structured porous materials (adsorbents and catalysts) with tailored porosity, shape, mass and heat transfer characteristics and high mechanical stability [23,24]. It is necessary to research the aspects related of mass and heat transfer, diffusion phenomenon, pressure drop and geometrical factors as guidelines for the design of high performance structured adsorbents and catalysts. On the other hand, the transport of molecules through a porous material depends on the pore volume, pore size, chemical composition and the interactions between the molecules (normally in gaseous state) and the material [25]. In a structured adsorbent or catalyst, the mass transfer depends on the characteristics and diffusion process length of the macropores, mesopores and/or micropores in the hierarchically porous structured material. All types of catalysts and adsorbents, irrespective of whether they are in the form of a packed bed of granules or consist of structured adsorbents and catalysts must be tested regarding to pressure drop which needs to be minimized.

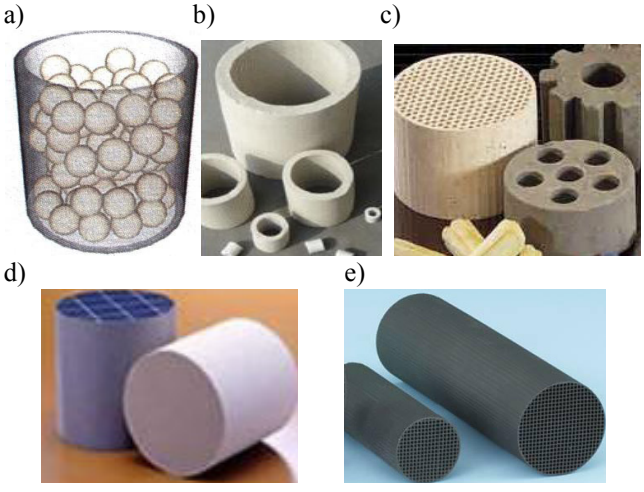

Fig. 18. Schematic representation of several examples of structured materials (adsorbent/catalyst): (a) spherical particles; (b) tube pellets; (c)-(e) monoliths with different size channels

The design of structured materials (adsorbents/catalysts) involves inevitably a compromise between some number of parameters, which determine their overall performance. For example, a rapid mass transfer is obtained with granules of small size, whereas this characteristic will determine a high pressure drop in a packed bed. A high porosity will enhance mass transfer and thus will decrease the cycle time for adsorption/catalyst process, whereas high loading of the adsorbent or catalyst per volume unit is required for a high mass transfer. From these reasons, in practice, the optimization depends on the requirements for the specific process and process conditions. Recently, studies [26-28] have shown that honeycomb, monoliths, and other hierarchical structures (Fig. 18) offer much more advantages compared to conventional pellets and granules, mainly in gas separation applications and catalysis.

5. Conclusions

Mechanical strength of solid porous materials used as adsorbents or catalysts is one of the most important factors for the reliable and efficient performance of a reactor and process. Some recent developments on the basic mechanics of solid porous materials are presented and discussed. The main concepts discussed are, the crushing, brittle fracture, attrition which lead to the mechanical failure of the porous material pellets, the measurement of porous material properties, strength data, the mechanical reliability of the adsorbent/catalyst pellets, the mechanical properties of the adsorbent/catalyst packed beds, etc. Furthermore, it is pointed out that an integrated research on mechanical properties should involve all the processes from manufacturing to industrial application, rather than only pellets itself. For this purpose, a scale framework for the mechanics of the fixed bed porous material is proposed. It is expected that a mechanical reliability model of solid porous material could be established under specific operational conditions. It is shown that the selection of a binder phase with relevant characteristics to the applications can enhance the mechanical properties of porous solid materials. It is also shown that porous structured adsorbents and catalysts have a important potential to overcome the deficiencies of conventional packed beds of pellets or granules. Poor mass and heat transfer, high pressure drop, low mechanical strength and attrition resistance are some of these deficiencies. The production of high performance porous solid materials that can be used as adsorbents and catalysts will require further development of efficient and easy ways to structure porous powders into complex shaped porous materials.

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Additional information

Selected issues related to this paper are planned to be presented at the 22nd Winter International Scientific Conference on Achievements in Mechanical and Materials Engineering Winter-AMME'2015 in the framework of the Bidisciplinary Occasional Scientific Session BOSS'2015 celebrating the 10th anniversary of the foundation of the Association of Computational Materials Science and Surface Engineering and the World Academy of Materials and Manufacturing Engineering and of the foundation of the Worldwide Journal of Achievements in Materials and Manufacturing Engineering.

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