

## Chapter 4

# Catalyst characterization: characterization techniques

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### 1. Characterization techniques

#### 1.1. Introduction

The most remarkable difference between catalysis during the 50s and 60s and nowadays is the remarkable development of characterization techniques.

Various factors contributed to that growth:

(i) need of having a better control on the catalyst in order to meet the requirements for further optimization of processes already in operation and/or for realization of new processes;

(ii) appearance of new classes of solids with catalytic properties and peculiar characteristics (zeolites, zeolite-like materials, oxides with controlled porosity, very high pore volume silica, superacids, etc.);

(iii) technology and computer development have placed on the market more powerful and friendly to use versions of known techniques (FT-IR, FT-Raman, calorimeter, etc.) or new techniques, often initially developed for other sectors use (XPS, EXAFS, SIMS, ISS, EPMA, etc.).

To realize how large is the growth of the characterization influence in the development of catalysts it is enough to look at scientific magazines and catalysis congresses proceedings.

Because of the tremendous variety of dispos-

able techniques it is impossible to review all of them in few pages. So we have to decide what techniques to describe and what to treat deeply.

The choice has been done on the basis of:

(i) applicability to real catalysts (so spectroscopies on single crystals like LEED, UPS, etc. were rejected);

(ii) easy access, either in cost and/or in necessary facilities (however also techniques both expensive like XPS, NMR, TEM and of difficult access like EXAFS, requiring synchrotron radiation, will be reported because of their importance);

(iii) applicability to many different systems (then little space will be devoted to Mössbauer and PAS, much more to N<sub>2</sub> adsorption, IR spectroscopy and temperature programmed techniques, etc.);

(iv) informative content, or capacity to give a manifold information (multipurpose techniques like IR spectroscopy are preferred).

On the whole 35 techniques, i.e. a number enough to face adequately nearly all the problems of daily practice, are described; on a few other (about 20) a short description is given. For all of them an adequate bibliography useful for a first deepening will be given.

Techniques have been grouped on the basis of:

1. morphology and physical characteristics,
2. surface characteristics,

3. bulk characteristics,

4. technological properties (granulometric distribution and mechanical properties).

Specific arguments are discussed by choosing information difficult to find in literature, consequently:

(i) the space dedicated to theory has been reduced to the minimum indispensable level;

(ii) instrumentation is described only in case of laboratory-made apparatus;

(iii) the problems usually encountered in the practice, the obtainable information and the limits of the different methods are the most closely examined topics;

(iv) when different approaches to determine the same properties can be used, the preferable techniques, on the basis of our experience, are indicated.

This choice, aiming to underline the practical application of characterization, is strengthened in the second part of this work, where the approach to specific problems will be examined.

## 1.2. Morphology and physical properties

Most heterogeneous catalysts are porous solids. The porosity arises from the preparation methods of the solids. For example the precipitation from a solution originates precursor particles that agglomerate and form a porous structure. Crystallization in hydrothermal conditions can produce zeolites, in which the peculiar disposition of the 'building units' generates intracrystalline cavities of molecular size. As mentioned above, during the thermal treatment the elimination of the volatile material (burning, evaporation) produces cavities that represent both the result of the solid rearrangement and the exit way of the removed material. Different shaping procedures, employed to obtain the catalysts suitable for industrial reactors (tableting, extrusion, spray drying, etc.), give rise to stable aggregates of particles that contain a porous structure. Then a typical catalyst contains one or more group of pores whose size and volume depend on preparation method.

The pores are classified in different classes depending on their size:

1. micropores ( $\phi < 2$  nm),

2. mesopores ( $2 < \phi < 50$  nm),

3. macropores ( $\phi > 50$  nm).

The porous structure enables the solid to have a total surface much higher than that corresponding to the external one. Most common catalysts have a specific surface area between 1 and 1000 m<sup>2</sup> g<sup>-1</sup>, while their external specific surface area is in the range 0.01–10 m<sup>2</sup> g<sup>-1</sup>. The knowledge of the morphological parameters is very important to understand the catalyst evolution during the preparation procedure and to give a feedback useful for modifying the method and to obtain the desired results. It is a matter of fact that a better comprehension of the catalytic behaviour requires the knowledge of the morphological characteristics. In fact the catalytic process takes place at the surface.

To reach the surface sites the molecules of the reagents must diffuse through the porous system, while the reaction products follow the opposite path. Mass transfer process inside the granules depends on pore size (bulk diffusion in macropores, Knudsen diffusion in mesopores and molecular diffusion in micropores). Also deactivation phenomena (i.e. organic material deposition) are greatly influenced by pore size; deposition of carbonaceous material with blockage of micropore mouth and coverage of the whole wall in meso and macropores are typical examples. The morphological characteristics of interest are the specific surface area, the specific pore volume, and the distribution of the area and of the pore size.

The methods for pore determination are numerous; the right choice depends on type of pore and, as will be clarified later, on the use we want to do of such data. The most utilized techniques are schematically reported in Table 1.

### 1.2.1. Vapour adsorption at low temperature

Nitrogen adsorption at boiling temperature (77 K) represents the most used technique to

Table 1  
Techniques and methods for the determination of morphological characteristics

Techniques	Evaluation method	Information	Micropores	Mesopores	Macropores
N <sub>2</sub> adsorption at 77 K	BET <sup>a</sup>	Surface	yes	yes	yes
	<i>t</i> -plot			yes	yes
	$\alpha$ -plot				yes
N <sub>2</sub> adsorption at 77 K	BJH	Surface area = (pore size)		yes	
	modelless				yes
N <sub>2</sub> adsorption at 77 K	<i>t</i> -plot	Pore volume	yes		
	$\alpha$ -plot		yes		
	DRK		yes		
	MP		yes		
	Horvath–Kavazoe		yes		
	Oliver–Conklin		yes	yes	
	BJH			yes	
	Gurvitsch		yes	yes	
Hg porosimetry			yes	yes	
Incipient wetness			yes	yes	yes
From chemical and particles density			yes	yes	yes
N <sub>2</sub> adsorption at 77 K	Horvath–Kavazoe	Pore volume = (pore size)	yes		
	Oliver–Conklin		yes	yes	
	BJH			yes	
Hg porosimetry				yes	yes
All techniques	Calculated from $\phi = KV_p/S$	Average pore size	yes	yes	yes
Permeametry			yes	yes	yes
Counterdiffusion			yes	yes	yes

<sup>a</sup> The value of the surface area in the presence of micropores is questionable (see [1]).

determine catalyst morphology. The starting point of that technique is the determination of the adsorption isotherm, i.e. of the nitrogen volume adsorbed vs. its relative pressure.

By analyzing the data with suitable models (reported in Table 1) the nitrogen adsorption at 77 K allows the determination of:

- (i) total surface of the solid (BET method);
- (ii) total surface, external to micropores (*t*-plot or  $\alpha_s$  plot method);
- (iii) mesopore surface distribution vs. their size (BJH method);
- (iv) micropore volume (*t*-plot or  $\alpha_s$  plot method);
- (v) mesopore volume and volume distribution vs. their size (Gurvitsch and BJH methods).

On the basis of our experience the methods that give the best results are reported inside the brackets. Additionally we put remark that the H-K and the Oliver–Conklin methods (although needing further verification) represent the only tools to obtain data on the size and size distribution of micropores.

Some valid alternatives to nitrogen adsorption at 77 K exist in special cases. We remember argon and krypton adsorption at 77 K (to determine surface area  $< 1 \text{ m}^2 \text{ g}^{-1}$ ) and argon adsorption at 87 K to study micropores in which it is less interactive than nitrogen.

All these techniques utilize automatic commercial apparatuses giving good performances.

For further details on the arguments see [1–7].

### 1.2.2. Mercury porosimetry

Mercury enters the pores whose size is inversely proportional to the applied pressure. Usually mercury porosimetry based on that principle allows to study pores in the range  $7.5\text{--}1.5 \times 10^4 \text{ nm}$  (2000 atm). The technique utilizes only commercial apparatuses. Working under pressure requires some care because it can cause compression of the solid or breakage of the pore walls (this occurs in very highly porous silica with  $V_p > 3 \text{ cm}^3 \text{ g}^{-1}$  obtained by sol–gel method).

Mercury porosimetry, carefully utilized, is

the sole technique capable to determine the size distribution of macropores. In the mesopore range both porosimetry and nitrogen adsorption techniques can be used and the results are, generally, in good agreement. If different results are obtained, the following parameters can be wrong:

- (i) the geometric model of pores;
- (ii) the value of the contact angle between mercury and the solid surface;
- (iii) the equation that defines the thickness of adsorbed nitrogen vs applied pressure.

More details can be found in [8,9].

### 1.2.3. Incipient wetness method

Following this method [10] the solid is impregnated with a non solvent liquid, usually water or hydrocarbons, just to fill the pores, without any meaningful excess. Addition of liquid must be stopped when the solid starts to be sticky or, if a large excess has been used, the liquid can be removed by centrifugation. In that condition the pore volume is equal to the volume of the liquid adsorbed by the solid.

That is a good, precise method, very useful to control values obtained with other ones and it is the only one that can be applied on high porous silica where the other methods fail.

### 1.2.4. Permeametry and counterdiffusion

Up to now all the efforts to utilize pore size distribution to interpret mass transfer processes inside the pores failed.

Permeametry and counterdiffusion [11,12] allow to obtain the values of the 'average diffusive diameter' and the 'tortuosity factor' that are of direct use in the equations describing mass transfer in catalyst pores.

Both techniques require that the gas can flow only through the pores of a shaped catalyst fixed to a non porous support. In permeametry a slight pressure difference between the two faces of catalyst particles is established and the equilibration pressure rate is recorded. Counterdiffusion measures the diffusional counterflux of two gases of different molecular weight through cat-

alyst particles. Suitable models allow to calculate the desired parameters. All apparatus are laboratory-made.

### 1.2.5. Microscopy

By microscopy we intend both the conventional optical and the modern electron microscopies: i.e. SEM (scanning electron microscopy) and TEM (transmission electron microscopy), with increasing resolution power up to few Angstroms.

They are substantially qualitative techniques. However they have, in respect of the above described quantitative techniques, the advantage to give a direct view of the solid under study. So microscopy and quantitative morphological techniques can be considered as complementary.

SEM and TEM are quite expensive and they usually are not directly available in characterization laboratories. Nevertheless this electron microscopy is frequently used to study catalysts, particularly to obtain data about shape, size, crystalline habit, homogeneity, contemporary presence of amorphous and crystalline (or different crystalline) compounds and their distribution, relative surface of different crystalline faces.

Most interesting results have been obtained on zeolites or zeolite-like solids, on which even the pore mouth can be visible, and on supported metals, on which data about distribution and preferentially exposed faces (affecting the structure sensitive reactions) can be obtained.

Electron microscopy is reviewed in [13–15].

## 1.3. Surface properties

The importance of the total surface area measurement has been pointed out in the previous paragraph. However, although the surface is the place of catalytic activity, only a part is utilized in the catalytic reaction. In catalysts based on supported metals only a little fraction of the solid total surface is occupied by the active centre (that is the metal particle). In acid cata-

Table 2  
Main techniques for surface characterization of catalyst using probe molecules

Techniques	Information	Quantitative analysis
Volumetric adsorption	Amount of adsorbate as a function of pressure	Yes (high precision)
Gravimetric adsorption	Amount of adsorbate as a function of pressure	Yes (high precision)
Dynamic adsorption	Amount of irreversible adsorbate	Yes
Calorimetry	Heat of adsorption as a function of coverage	Yes (high precision)
IR-spectroscopy	Surface functional groups	Possible
	Functional groups of adsorbates	
Raman spectroscopy	Surface functional groups	Possible
	Functional groups of adsorbates	
UV-Vis spectroscopy	Local environment of surface groups perturbed by adsorption	Possible
TPD (temperature programmed desorption)	Amount of desorbed species as a function of temperature	Yes
TPD-MS (TPD coupled with Mass spectrometry)	Amount and composition of desorbed species as a function of temperature	Yes
TPD-IR (TPD coupled with IR spectroscopy)	Composition of desorbed species as a function of temperature	No
TPSR (MS)	Competitive interaction of different probe molecules—Reactivity of surfaces	Possible

**Table 3**  
Main spectroscopies and related techniques for surface characterization of catalysis. Other techniques: LEED (low energy electron diffraction), HREELS (high resolution electron energy loss spectroscopy), ellipsometry, SEXAFS (surface extended X-ray absorption fine structure)

Techniques	Excitations	Response	Information	Monolayers sampled	Quantitative analysis	Gaseous atmosphere
XPS (X-ray photoelectron spectroscopy)	Photons	Electrons	Surface atomic composition Nature and binding of the atoms	2–20	Yes	Difficult
AES (Auger electron spectroscopy)	Electrons	Electrons	Surface atomic composition	2–20	Possible	Difficult
SIMS (secondary ions mass spectrometry)	Ions	Ions	Surface atomic composition Short distance order	1–3	Possible	No
ISS (ion scattering spectroscopy)	Ions	Ions	Surface atomic composition	1	No	No

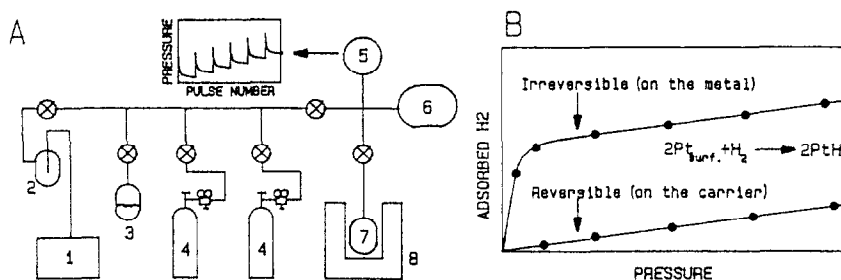


Fig. 1. Schematic diagram of a static-volumetric apparatus for adsorption measurements (A) and typical representation of the results (B): 1, vacuum pump; 2, cold trap; 3, liquid reservoir; 4, gas reservoir; 5, high precision pressure transducer; 6, calibrated volume; 7, sample holder; 8, furnace.

lysts the acid sites not only occupy a little fraction of the surface, but also differ in acid strength and sometimes in nature. To understand how a catalyst works, why a sample gives better performance than others or why activity decays by time, the knowledge on the number and on the nature of active sites is indispensable. So it is easy to understand why researchers are so interested in surface methods giving data on atomic and molecular levels.

Techniques actually available can be divided in two groups:

1. techniques using probe molecules;
2. techniques enabling the direct study of the catalyst surface.

Volumetric and gravimetric static chemisorption, adsorption calorimetry, spectroscopies of adsorbed molecules and temperature programmed desorption methods belong to the first

group (Table 2). They are very versatile techniques allowing to operate practically on all the type of catalysts and in conditions (temperature, pressure) not too far from the reaction ones. Moreover they can be used to study many different characteristics and to choose from them those relevant for the case under investigation. These advantages, joined to the low and medium cost of the instruments required, explain the wide diffusion of these techniques. So nowadays they are part of the standard equipment of catalysis laboratories.

The techniques belonging to the second group (Table 3), being more expensive and less available, are usually administrated by specialists which operate in big research centres or in universities. Moreover they are techniques which can be used only under vacuum or under limited gas pressure. For these reasons their use is more

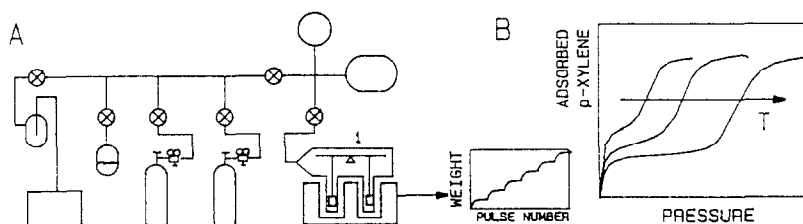


Fig. 2. Schematic diagram of a static-gravimetric apparatus for adsorption measurements (A) and typical representation of the results (B): 1, vacuum balance; for other components see Fig. 1.

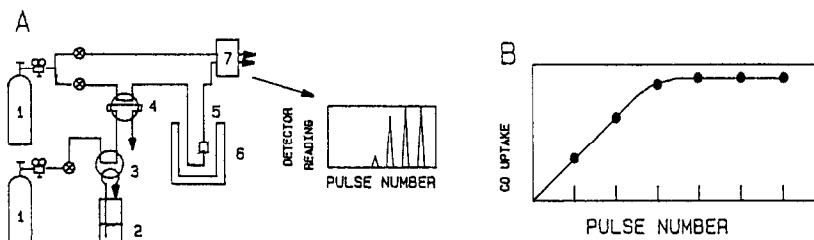


Fig. 3. Schematic diagram of a dynamic pulse apparatus for adsorption measurements (A) and typical representation of the results (B): 1, gas reservoir; 2, liquid reservoir; 3, four way valve; 4, sampling valve; 5, sample holder; 6, furnace; 7, katharometer.

limited than those of first group. XPS is an exception because of its surface sensitivity to atomic chemical environment.

### 1.3.1. Volumetric, gravimetric and dynamic adsorption methods

All the techniques for the quantitative determination of the adsorbed molecules are grouped into:

(i) static-volumetric techniques in which the outgassed solid is contacted with a known volume of gas and the adsorbed quantity is measured through the pressure decrease (Fig. 1);

(ii) static-gravimetric techniques similar to the previous ones, except the quantity of adsorbed gas is determined by the weight increase of the solid (Fig. 2);

(iii) dynamic techniques in which the probe gas is fed continuously or by pulse on the solid and the update is followed by gaschromatography (Fig. 3).

The laboratory-made instruments predominate in this field, even if some commercial

devices with good performance are now available.

Static techniques give more precise data than dynamic ones, being the last preferentially used for routine measurements (for example for production control). The static-volumetric techniques are preferred in gas adsorption; while the gravimetric ones give better performances in vapour adsorption and particularly in the case of organic vapours.

Static methods are slow and delicate because of the difficulty of recognizing the reaching of the equilibrium conditions and of distinguishing between the chemisorbed and the physisorbed fraction (a further measure after an intermediate outgassing is necessary). However the results can at last greatly depend on the measurement of the temperature: a preliminary investigation with TPD is suggested.

Typical applications are the determination of exposed surface of dispersed metals and the measurement of acidity as discussed in the second part of this paper. It is also possible to

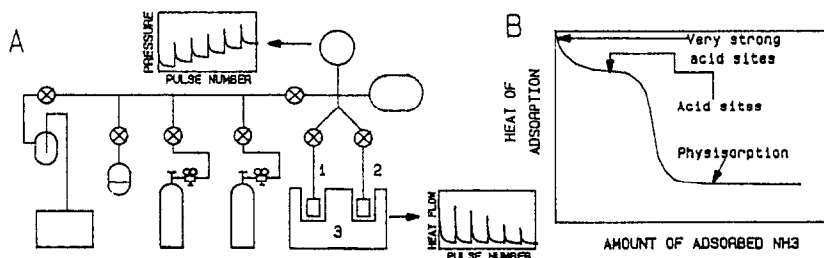


Fig. 4. Schematic diagram of an apparatus for calorimetric measurements (A) and typical representation of the results (B): 1, sample holder; 2, reference holder; 3, isothermal calorimeter. For other components see Fig. 1.



follow the adsorption of reagents and products of reaction, obviously in non-reactive conditions.

More details are available in [16–18].

### 1.3.2. Adsorption calorimetry

Equipment and methodology are in large part identical to those used in volumetric methods (Fig. 4).

The sample holder is positioned in a calorimeter that enables the measure of the developed heat and of the adsorbed volume. So it is possible to obtain data on the nature of the interactions between adsorbate and adsorbent and on the heterogeneity of the surface sites. For example, by using a base as probe molecule, this technique allows to determine the number of surface acid sites and their distribution vs. acid strength.

The limits of this technique are the length of the measurements and a great fan of execution difficulties. Anyway this is the only technique giving both quantitative and qualitative data on the energy distribution of sites.

Some examples of its employment are reported in the second part of this paper and in [19].

### 1.3.3. Spectroscopy of adsorbed molecules

The best techniques to obtain a qualitative information on the structure and reactivity of adsorbed molecules are the spectroscopic ones. Equipment and methodology are in large part identical to those of volumetric methods except

for the sample holder which is inserted in the spectrophotometer to allow the acquisition of spectra upon dosage of probe molecules (Fig. 5).

**1.3.3.1. IR spectroscopy.** IR spectroscopy is the most diffuse technique. It is possible to operate both in transmittance (sample is a thin tablet crossed by the beam) and in reflectance (sample is placed in a horizontal holder on which a mirrors system conveys the beam: a parabolic mirror collects all the scattered and reflected light and send it to the detector). The first method is preferred, because it allows to work with cheaper laboratory-made cells and to obtain spectra without artefacts due to reflected light.

The most used probe molecules are CO, NO, NH<sub>3</sub>, C<sub>2</sub>H<sub>4</sub>, CH<sub>3</sub>OH, H<sub>2</sub>O and pyridine because:

(i) they are simple, and have spectra easy to interpret

(ii) they have vibrations significantly affected by adsorption located in the spectral range 1200–4000 cm<sup>-1</sup> (MID-IR) where skeleton vibrations of solid do not interfere.

There are no limitations to the use of more complex compounds: of course the spectroscopic response becomes increasingly more complex. It is possible in this way to study interactions of molecules present in the reaction environment and to obtain more direct pieces of information on surface reactivity and reaction mechanism (see for example the paragraph in the second part of this paper).

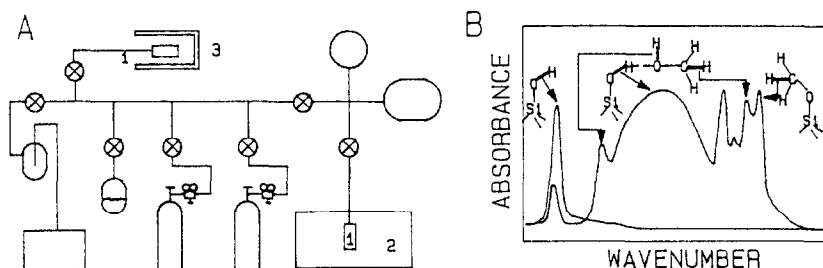


Fig. 5. Schematic diagram of an apparatus for spectroscopic measurements of adsorption of probe molecules on catalysts (A) and typical representation of the results (B): 1, sample holder; 2, spectrophotometer; 3, furnace for thermal treatment of the sample. For other components see Fig. 1.

IR spectroscopy can give also a direct information on the surface; particularly in the case of oxides: in fact the surface atoms tend to complete their coordination sphere using mainly OH groups, whose stretching vibrations fall in the 3000–4000  $\text{cm}^{-1}$  range. Position of bands gives pieces of information on the nature (i.e. the acid strength) of hydroxyl group that are often the catalytic active sites. Moreover it is possible to verify the influence on surface sites of probe molecules (see Fig. 5).

IR spectroscopy has two main limitations:

- (i) the low frequency region can not be used because of skeleton vibrations of the solid;
- (ii) most IR transparent materials (NaCl, KBr,  $\text{CaCl}_2$ , and so on) are not resistant to water or other liquids.

**1.3.3.2. Raman spectroscopy.** Raman spectroscopy allows to overcome these limitations because:

- (i) structural bands are often sharp and weak;
- (ii) even water (which is strongly absorbing in IR) gives rise to weak bands;
- (iii) inert and resistant materials, for instance quartz, can be used.

Weak Raman bands usually correspond to strong IR bands and vice versa: in most cases the same bands are detectable in both spectra.

This spectroscopy, whose use was once limited to expert spectroscopist, is in the last years become available for industrial applications due to significative improvements in the commercial instrumentation.

Traditional application fields are the study of heteropolyacids and of molybdates. Very interesting results have been recently obtained on zeolites, in both structural and adsorption studies.

Most limitations arise from luminescence phenomena due to organic contaminants of the sample.

**1.3.3.3. UV-Vis spectroscopy.** UV-Vis spectroscopy is less used in surface studies, sometimes wrongly, because it supplies a direct in-

formation on the adsorption centre. The best results are reached when all the optically active compounds under investigation are on the surface (because there is no need to separate surface and bulk contributions). The study of supported metal precursors and of zeolites containing optically active elements like transitions elements, Ti, Zn, etc. have received a great help by this technique.

Among the numerous papers on the argument we recommend [20–30].

#### 1.3.4. Temperature programmed desorption

The sample is placed in a tube fluxed by an inert gas. The substance to be adsorbed is fed by pulses or continuously till the equilibrium is reached. After outgassing the physisorbed fraction, the temperature is raised at constant rate: so the adsorbate undergoes a progressive release at temperature as higher as stronger is its interaction with the solid surface. A detector system placed beyond the sample-holder allows the monitoring of the process (Fig. 6). The most used analytical systems are:

- (i) a katharometer when the adsorbate is released unchanged;
- (ii) an IR spectrophotometer equipped with a gas cell or a mass spectrometer when more than one probe molecules are used together or when the adsorbate released is modified by interaction with the solid surface. The techniques are named respectively TPD-IR and TPD-MS.

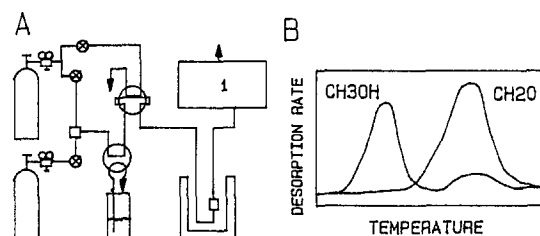


Fig. 6. Schematic diagram of a TPD apparatus (A) and typical representation of the results (B): 1, katharometer (TPD) or mass spectrometer (TPD-MS) or gas cell for IR spectroscopy. For other components see Fig. 3.

The technique, especially in the simplest form, is widely diffuse because:

(i) it is possible to build up a cheap laboratory-made instrument even if good commercial devices are available;

(ii) the use is simple;

(iii) the qualitative interpretation of results is also simple.

For a deeper understanding of the results we have to consider that:

(i) the release of adsorbed substances is a complex process, with contributions due to diffusion and readsorption: consequently without an adequate model the interpretation can be misleading;

(ii) during the experiment, the exposure to increasing temperatures can modify the solid as well as the adsorbate–adsorbent interaction.

An advantageous variation of TPD is often the so called TPSR (temperature programmed surface reaction) in which mixed probe molecules are fed during all the experiment. Important data can be obtained on the catalyst functionality and on reaction mechanism, as pointed out in the second part of this paper, using molecules present in the reaction environment.

Among the numerous papers on the argument we recommend [31–36]

#### 1.3.5. *Techniques for direct characterization of surface*

All the techniques presented in the previous paragraphs use probe molecule to investigate the solid surface. The techniques allowing the direct characterization of surface are here briefly discussed. Among those reported in Table 1 only XPS and, to a little extent, AES are widely used in catalyst characterization.

Both the techniques reported give pieces of information on the composition and chemical status of the elements on the solid surface before and after reaction test. Both the techniques provide data, via expulsion and analysis of the related energies, of electrons from the solid.

XPS is exciting ‘core’ electrons by means of a soft X-ray beam (i.e.  $Mg K_{\alpha}$ ); while Auger spectroscopy utilizes electrons to bombard the surface. The emitted electrons bring to us an information coming from a depth of 1–4 nm, so providing a good surface picture.

XPS provides more useful data than AES since the exciting beam does not usually damage the surface. On the contrary Auger spectroscopy possesses a higher sensitivity and can discover contaminants better than XPS (at least in traditional commercial instruments). Nevertheless the use of XPS in catalyst investigation is increasing and nowadays the availability of synchrotron light instrumentation (super ESCA) is favouring the XPS investigations because they are of great help in surmounting also the sensitivity problem.

More details on XPS and other surface techniques can be found in [37–45].

#### 1.4. *Bulk properties*

Even if the main effort in catalysts characterization is devoted to the surface knowledge, bulk properties maintain their importance being the nature of surface sites determined by those properties.

There is a large number of techniques available for analyzing bulk characteristics but most of them are expensive and not specific being their main application in material science. So they are usually placed in general analytical services or in specialistic groups, while catalysis laboratories are more frequently equipped with less expensive traditional spectroscopic and thermal analysis.

In spite of the large number of those techniques, only a few are frequently used in studying catalysts.

(i) elemental analysis techniques;

(ii) spectroscopic and diffraction (XRD, IR, Raman, UV-Vis, NMR) techniques;

(iii) thermal analysis (TG, DTA, DSC, TPR, TPO) techniques.

Table 4  
Main spectroscopies and related techniques for bulk characterization:  $\blacklozenge$  = molecular spectroscopy;  $\bullet$  = X-ray spectroscopy;  $\square$  = resonance

Techniques	Excitation	Response	Information	Quantitative analysis	Gaseous atmosphere	Applicability
$\blacklozenge$ IR (infrared spectroscopy)	Photons	Photons	Local environment Functional groups Structure	Possible	Yes	Quite all solids except C and few others
$\blacklozenge$ Raman	Photons	Photons	Local environment Functional groups Structure	Possible	Yes	Quite all solids, fluorescence can give problems
$\blacklozenge$ PAS (photoacoustic spectroscopy)	Photons	Photons	Local environment Functional groups Structure	Possible	Yes	Like IR (in particular for solids opaque to usual IR)
$\blacklozenge$ UV-Vis (ultraviolet-visible spectroscopy)	Photons	Photons	Chemical bonds Coordination Oxidation degree	Possible	Yes	Solids containing transition metal ions and few others
$\bullet$ XRD (X-ray diffraction)	Photons	Photons	Crystalline species Crystalline degree Crystal size	Yes	Yes	All crystalline solids
$\bullet$ EXAFS (extended X-ray absorption fine structure)	Photons	Photons	Local structure (coordination number, inter- atomic distances)	Yes	Yes	Quite all metal compounds
$\bullet$ XANES (X-ray absorption near edge structure)	Photons	Photons	Local structure	Possible	Yes	Like XAFS
$\square$ NMR (nuclear magnetic resonance)	Photons	Photons	Local environment Functional groups Molecular diffusion	Yes	Yes	Quite all solids
$\square$ EPR (ESR) (electron paramagnetic spin resonance)	Photons	Photons	Oxidation degree  Symmetry	Yes	Yes	Paramagnetic species (transition metal ions).
$\square$ Mössbauer	Photons	Photons	Nature of ligands Local environment Oxidation degree (few elements)	Yes	Yes	Few elements, in particular Fe, Sn
TEM (transmission electron microscopy)	Electrons	Electrons	Structure Crystal shape	No	No	Quite all, in particular zeolites, supported metals
EPMA (electron probe microanalysis)	Electrons	Electrons	Atomic composition (resolution 1 $\mu\text{m}$ )	Yes	No	
XRF (X-ray fluorescence)	Photons	Photons	Atomic composition	Yes	Yes	Elements with $Z > 5$
NS (neutron scattering)	Neutrons	Neutrons	Crystal structure Molecular diffusion	Yes	Yes	Quite all solids

### 1.4.1. Elemental analysis techniques

The description of elemental analysis techniques is out of the scope of this paper: usually researchers working in catalysts characterization are discussing problems with analysts which choose the most suitable method.

The knowledge of solid chemical composition must be the starting point of every investigation. This statement is not so obvious as it could seem. A lot of literature results cannot be evaluated because of lack of composition data.

It is noteworthy to remember that:

(i) catalyst composition at the end of preparation can be different from that calculated from the weight of reagents; this is frequently observed in coprecipitation, hydrothermal synthesis, calcination of solids containing volatile compounds;

(ii) composition reproducibility is a very common problem in catalyst preparation, so frequent experimental checks are necessary;

(iii) impurities can always be present; their origin is extremely variable as they can come from polluted reagents, previous preparation residues, release of substances from vessels, etc.;

(iv) exposure to the reaction atmosphere changes almost every time the catalyst composition: because of loss of volatile compounds, deposition of organic substances, reactions between solid and environment.

Further details are available in [46] and references therein.

### 1.4.2. Spectroscopic techniques

The spectroscopic techniques are widely used for bulk characterization and this is not a surprise. On the whole they allow to determine both local (oxidation state, ligands nature and number, symmetry) and structural (framework, crystalline degree, crystal size) characteristics. Unfortunately a single spectroscopic method able to supply all these pieces of information does not exist. Many different techniques must be chosen from time to time to obtain the desired information. In Table 4 the informative

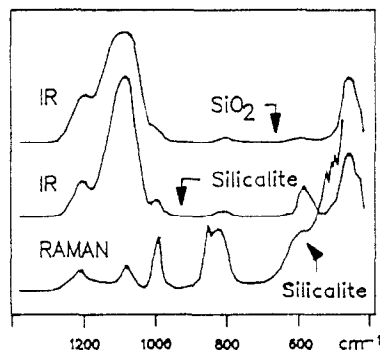


Fig. 7. Example of information obtainable by IR and Raman spectroscopy.

potential of the most diffuse techniques is schematically reported.

**1.4.2.1. Molecular spectroscopies.** IR spectroscopy allows us to obtain spectra of solids, working both in transmission and reflectance; sample dilution must be generally used because of the high intensity of the IR bands of the skeleton vibration. In reflectance mode phenomena such as specular reflection can deeply affect the spectra.

IR spectroscopy does not find much applications in structural characterization of solids because most of the inorganic supports, particularly oxides, give rise to broad bands of difficult interpretation, with the exception of few compounds, like molybdates, vanadates and zeolites. The last give rise to well defined bands due to secondary building units vibrations then characteristic of each framework (Fig. 7).

Raman spectroscopy suffers by different problems: it is difficult to obtain good spectra, particularly of some oxide species, due to luminescence phenomena. Alike IR techniques the application of this spectroscopy is limited to Mo, V, W, Ti compounds and few other substances. Anyway the possibilities of this technique has not already been investigated deeply: recently we have obtained important information on zeolites (Fig. 7).

UV-Vis spectroscopy is certainly the most interesting molecular spectroscopic technique to

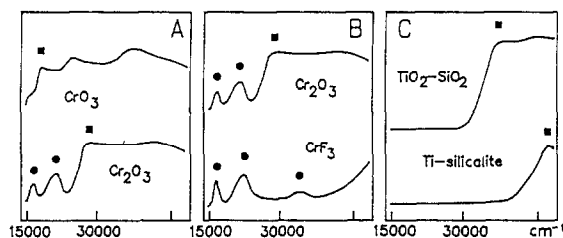


Fig. 8. Example of information obtainable by UV-Vis spectroscopy: (A) change in oxidation state; (B) change in ligands type; (C) change in coordination number (●, d-d transition; ■, charge transfer transition).

study bulk characteristics. In fact in the spectral range usually available (10000–50000 cm<sup>-1</sup>) it is possible to investigate d–d transitions, which are characteristic of transition elements, and other transitions due to charge transfer from ligand to metal or vice versa (Ti, Zn, Ce, Zr, Mo, Sn, rare earths, alkaline earths metal oxides, and many transition metal oxides). With UV-Vis spectroscopy a direct information on electronic structure and on the first coordination sphere of the examined ions can be obtained. In particular oxidation state, type of ligands, ligands number and coordination can be studied.

Changes in oxidation state involve a variation of electronic configuration and this in turn usually greatly influences the spectra. See for example in Fig. 8A Cr<sub>2</sub>O<sub>3</sub> (d<sub>3</sub>) and CrO<sub>3</sub> (d<sub>0</sub>) spectra.

Electronic transitions are also influenced by ligand nature, as foreseen by ligand field theory, and the series of ‘optical electronegative’ was proposed, parallel to Pauling’s series to qualify this influence:

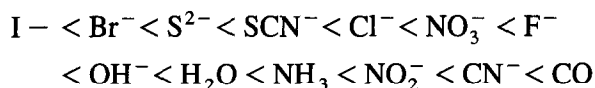


Fig. 8B presents as an example Cr<sub>2</sub>O<sub>3</sub> and CrF<sub>3</sub>.

Likewise the influence of coordination type on both d–d transition and charge transfer is of interest. Fig. 8 shows spectra of titanium having oxygen in the coordination sphere respectively in tetrahedral (Ti-silicalite) and octahedral (amorphous TiO<sub>2</sub>-SiO<sub>2</sub>) coordination.

Most problems derive from difficulty in interpretation of spectra, particularly for charge transfer transitions, characterized by broad bands covering large spectra region. From a practical point of view it must be pointed out that:

- (i) it is necessary to use reflectance technique;
- (ii) easy to use materials, like quartz, are UV transparent, so there are not limitations as in IR spectroscopy;
- (iii) commercial instruments are reliable and relatively cheap.

On the whole the UV-Vis spectroscopy is a technique relatively easy to use and reliable, also if non exhaustively used.

It is not possible to summarize all the UV-Vis spectroscopy applications in the study of solids. A few examples are reported in the second part of this paper.

To go deeper into molecular spectroscopy techniques see [22,27–30,47–55].

*1.4.2.2. X-ray diffraction and X-ray absorption spectroscopies.* Most catalysts are crystalline solids such as zeolites, many oxides, supported metals, salts and so on. So X-ray powder diffraction becomes a fundamental technique enabling us to evaluate:

1. nature of crystalline phases;
2. their concentration in the solid;
3. crystallite size.

The last two characteristics can be determined only in simple spectra. In the case of solids with low symmetry (i.e. zeolites), the calculation of crystallinity degree is very difficult.

During the last ten years these difficulties have been partially overcome by the help of new methods of structural refinement, like the Rietveld one, which permits the reproduction of the whole diffractogram, through the optimization of both structural (peak position and intensity) and non-structural (peaks shape) data. For instance this method enables an accurate determination of cell parameters of MFI zeolites and then makes possible to evaluate the volume

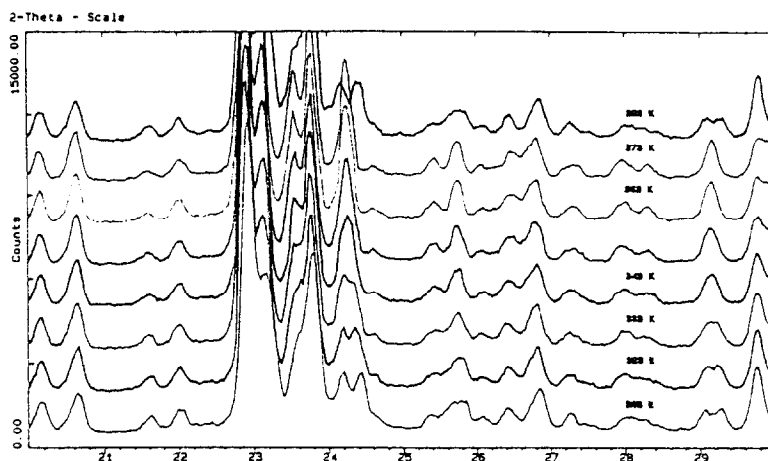


Fig. 9. Example of information obtainable by XRD spectroscopy on solid–solid transition induced by thermal treatments in silicalite; the transition from monoclinic to orthorhombic symmetry is revealed by the substitution of the two doublets at about 24 and 29° ( $2\theta$ ) with two singlets.

increase due to the insertion of guest atoms in the framework.

An interesting possibility offered by XRD is to follow solids evolution during thermal treatment or exposure to gases or vapours. An example is presented in Fig. 9, where spectra of silicalite at different temperatures, showing the transition from orthorhombic to monoclinic symmetry, are reported.

XRD technique can be applied without particular limitations, although it requires a not negligible quantity of samples. However the instrumentation is expensive: so usually it is managed in specialized laboratories rather than in characterization groups.

A great number of applications are possible. Some examples are reported in the second part of this paper.

EXAFS (extended X-ray absorption fine structure) technique deserves a mention because it is extremely interesting in catalysis even if not easily available, as it is requiring the availability of synchrotron radiation.

The technique allows the determination of:

- (i) average coordination number of investigated element;
- (ii) interatomic distances of the first (sometimes also of the second) shell.

In the region before the adsorption edge

XANES (X-ray absorption near edge structure) gives indications on the coordination symmetry.

These techniques can be used even at high temperature and under controlled atmosphere, so it is possible to work in reaction conditions. Some studies on XAFS reactors are known. An example is reported in the second part of the paper, where the technique has been used to demonstrate the tetrahedral coordination of Ti in Ti-silicalite, (and then its insertion in the framework), and also the change in coordination following the exposure to different molecules (Ti is a reactive centre).

The techniques are illustrated in detail in [46,56–63].

#### 1.4.2.3. Nuclear magnetic resonance (NMR).

The application of NMR on solids is now possible because of improvement in instrumentation and of introduction of new techniques, such as MAS (magic angle spinning).

The technique is useful in zeolite study of Al distribution ( $^{29}\text{Si}$ ,  $^{27}\text{Al}$ ), silanols number ( $^{29}\text{Si}$ ), acidity ( $^1\text{H}$ ), porosity ( $^{129}\text{Xe}$ ). Surely its importance is destined to increase in spite of the required investment as shown in Refs. [64–67].

1.4.2.4. Other spectroscopies. The number of available spectroscopic techniques is larger than

that described before. Most of them have a limited use because they require expensive investment or must be used under vacuum conditions or they are applicable to a limited number of elements. Some of them would deserve a mention (EPR, Mössbauer) but they are not described for sake of brevity. See Refs. [46,68–78] to examine closely the argument.

#### 1.4.3. Temperature programmed techniques

Under this denomination are grouped all the techniques where the variation of a physical parameter as a function of temperature (when it is varied with constant rate) is measured.

We can distinguish:

1. TG (thermal gravimetry);
2. DTA (differential thermal analysis);
3. DSC (differential scanning calorimetry);
4. TPR (temperature programmed reduction);
5. TPO (temperature programmed oxidation);

The techniques are generally reliable and well tested. TG, DTA, and DSC are executed only on commercial instruments, while the laboratory-made instruments for TPO and TPR are progressively substituted by commercial devices. Usually the selected parameter variation vs. temperature is reported, obtaining a plot like that showed in Fig. 10.

Analyzing the results it must be considered that peaks are representative of several kinetic phenomena happening on solids changes altered by readsorption, diffusion into the sample, heat transport to the detector, etc. Even scanning rate

has a great influence: low rate guarantees a better peak resolution, but gives broad signals and vice-versa. Experiments at different scanning rate are used for kinetic analysis with alternate results.

As regard the study of the solid, each technique can reveal:

- (i) loss of volatile components and reactions involving mass change such as decomposition (TG);
- (ii) reduction (TPR) or oxidation reactions (TPO);
- (iii) solid–solid, solid–gas or liquid–gas transitions (DSC and DTA).

Examples concerning TPR, TG, TPO and DSC are reported in the second part of this paper.

The ability of TPR to identify different species of the same element is particularly noticeable. For instance in the Fe-silicalite case Fe in the zeolite framework and Fe in extraframework position are reduced at different temperature, so allowing the quantitative determination of the two species. But not always two signals mean two different species. That is the case of chlorinated Cu compounds that are reduced in two steps with the formation of  $\text{Cu}^{\text{I}}$  compound as intermediate. Another application of TPR is the quantitative determination of oxidized species, for example  $\text{Cr}^{\text{VI}}$ , in the presence of the species in lower oxidation state.

TG, TPO and DSC find their main applications in studies of activation of the fresh catalysts and regeneration of exhausted ones or to evaluate the thermal stability (see paragraph 6 in the second part of the paper).

Useful data are reported in [19,33,35,79–81].

#### 1.5. Particle size distribution and mechanical properties

This part is devoted to properties of apparently low scientific interest, but surely of great importance in practical use: granulometric distribution and mechanical properties.

As regard the importance of particle size

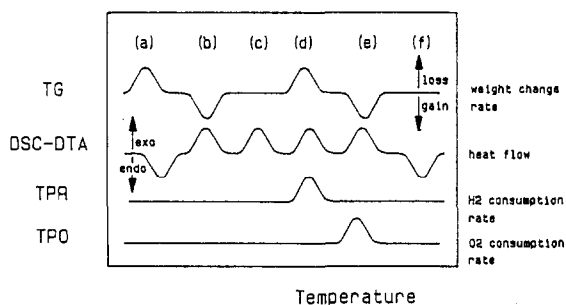


Fig. 10. Typical representation of temperature programmed technique results: (a) loss of volatile compounds; (b) adsorption; (c) crystallization; (d) reduction; (e) oxidation; (f) melting.



distribution it must be taken into account its effect on:

1. mass transport processes (i.e. interparticle diffusion);
2. heat transport processes;
3. pressure drop through catalytic beds;
4. catalyst deactivation by fouling.

As for as the mechanical strength, we have to distinguish between fixed bed and fluid bed catalysts.

In fixed bed catalysts problems arise from the presence of powder or fragments generated during the transport, from the reactor charge and the industrial run. The results are:

- (i) change in particle size distribution with the consequence above illustrated;
- (ii) irregular distribution of the pressure drop (then of the fluxes, in tubular reactors);
- (iii) local accumulation of powder (then possibility of too high activity and heat transfer problem).

In fluid bed catalysts, low resistance of the solid, produces a great amount of small particles which are eliminated from the reactor. So it becomes necessary to reintegrate frequently the catalyst: consequently problems of catalyst consumption and disposal arise.

In conclusion the working capacity of a catalyst depends on particle size distribution and mechanical resistance as well as on its chemical, structural and morphological characteristics.

### 1.5.1. Particles size analysis

A large number of techniques, based on many different principles, are nowadays available, most of them were developed and offered by commercial producers. In Table 5 a choice of suitable techniques, divided on the basis of size of analyzing particles, are reported.

The most diffuse technique for particle size analysis is sieving. Most catalysts can be analyzed with this technique. The limits of the technique are:

- (i) difficulty to complete the sieving with particles smaller than 40  $\mu\text{m}$ ;

Table 5  
Main techniques for particle size analysis

Techniques	Detectable size ( $\mu\text{m}$ )
Sieving	20–10 <sup>4</sup>
Optical microscopy	0.1–10 <sup>4</sup>
SEM (scanning electron microscopy)	0.003–10 <sup>4</sup>
TEM (transmission electron microscopy)	0.0005–10 <sup>4</sup>
Gravitational sedimentation	1–100
Resistive pulsed (Coulter effect)	0.5–200
Light obscuration	(1) 10–9000
Fraunhofer diffraction	(1) 10–2000
Centrifugal sedimentation	0.05–5
PCS (photon correlation spectroscopy)	0.01–1
HCD (hydrodynamic chromatography)	0.01–1
FFF (field flow fractionation)	0.01–100

(ii) crushing and abrasion of the most particles;

(iii) agglomeration of electrostatically charged particles.

With an adequate procedure it is possible to overcome points (ii) and (iii) in most cases.

Besides sieving it is possible to use other instruments, based on different principles, whose (on the whole) are applicable for particle ranges between 10 nm and 1 cm. The best use of them is in the range where sieving is not applicable (1 and 50  $\mu\text{m}$ ). The most used instruments are those based on sedimentation (the size is determined via XRD), on resistive pulse, on the light obscuration, and on the Fraunhofer diffraction.

Techniques working even under 1  $\mu\text{m}$  are used only in particular cases and are not reported here for sake of brevity (see references).

Techniques based on microscopy usually are used as reference in catalysis, however it is difficult to obtain quantitative results (even if more sophisticated instruments of automatic image counting are now available).

It is noteworthy that this method gives a size distribution based on particles number and not on their mass (like sieving).

Refs. [82–84] allow deepening in particle size analysis.

### 1.5.2. Crushing strength measurements

They are applied to catalysts shaped for fixed bed (tablets, extrudates, granulates).

Two different type of measurements have been developed (Table 6):

1. crushing strength of the single granule,
2. bulk crushing strength.

The measurement of crushing strength is made by gradually compressing a single catalyst granule and by continuously registering the value of the applied force until the crush happens. The measurement is repeated on a significant number of granules (at least 50): the mean value of crushing strength and its distribution is so obtained. Generally, the distribution is narrow for tablets, broad for pellets, and very broad for extrudates.

Crushing strength depends not only on the material intrinsic resistance, but also on several factors, such as shape, size, wetness degree: consequently the comparison is realistic only among homogeneous series of catalysts (i.e. different supplies of the same batch). For the same reasons it is difficult to predict the behaviour of a single sample only on the bases of the results of these techniques.


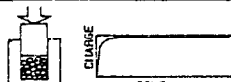

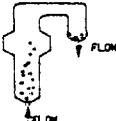
The main utility of the method consists on the capacity of underlining the presence of fractions with particularly low resistance.

The bulk crushing strength technique measures the mean value of the mechanical resistance subjecting to a predetermined pressure a catalyst volume enclosed in a cylinder and by determining, through granulometric analysis, the powder formed by granule crushing.

Since the granules in contact with walls are preferentially crushed we must work with a large cylinder ( $\phi_{\text{cylinder}}/\phi_{\text{granule}} > 10$ ) to minimize this effect. For the same reason the force applied must be enough to induce the formation of a significant amount of powder. On the other hand too high pressure must be avoided otherwise the difference among samples will not be appreciable. Meaningful measurements are possible with powder fraction between 1 and 10%. Really it would be more correct to determine the pressure necessary to obtain a given powder fraction, but as in this way several measures would be indispensable, this method is seldom used.

Based on our experience, the determination of bulk crushing strength supplies results able to predict the catalyst resistance during its practical application. Anyway when problems in catalyst charging of industrial reactors are found,

Table 6  
Main techniques for mechanical properties determination

TECHNIQUES	DETECTED CHARACTERISTIC	APPLICATIONS
	Crushing strength C.S. distribution	Tablets, Extrudates, Pellets
	Bulk crushing strength	Tablets, Extrudates, Pellets
	Attrition resistance for fixed bed catalysts (fines %)	Tablets, Extrudates, Pellets
	Attrition resistance for fluid bed catalysts (fines %)	Spray dried catalyst

the best test is a simulation of that operation, for example by filling a tube having the same height and diameter of one of the tubular reactors, and by measuring the amount of formed powders.

See for more details [85–89].

### 1.5.3. Attrition resistance measurements

They are applied, in different versions, either on fixed bed or on fluid bed catalysts (Table 6).

For fixed bed catalysts the granules are placed in a turning drum or in a horizontal cylinder swinging along its axis and, after a prefixed time, the formed powder is determined by sieving.

In most cases the measurement gives results comparable to those obtained by bulk crushing strength test, so meaning that a catalyst gives good or bad results with both measurements.

For fluid bed catalysts the powder is fluidized under controlled conditions in a tube collecting the fines formed in a fixed time. The collection begins after a time long enough to warrant the elimination of the fines previously present in the catalyst.

The measurement is delicate and often presents reproducibility problems due, for example, to adhesion of a part of the sample to the tube surface and wear of the nozzle from which the flux exits. It is noteworthy that, as the fluid bed catalyst is subjected to mechanic solicitations during all the run, it can happen that its mechanical properties are modified by exposure to the reaction environment.

Notwithstanding these limitations, the attrition resistance measurements are in some case the only available technique to control the results of catalyst shaping. Recommended references are [87,90].

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