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Chapter 5

Catalyst characterization: applications

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1. Introduction

While the most frequently used characterization techniques in catalysis have been described in the first part of this paper, in this part the application of the techniques to the solution of practical problems is described.

A lot of excellent reviews on the application of the characterization techniques in catalysis can be found in the literature. Usually the papers are centred on the use of a technique (i.e. NMR application on catalysts study) or on a class of catalysts (i.e. determination of metal dispersion in metal supported catalysts). Those reviews are widely reported in the references.

In this paper we shall try to do something different, possibly closer to the need of a catalysis school: we shall attempt to describe how characterization can operate in everyday practice following the catalyst during its 'life':

$$\begin{tikzcd} \text{preparation} \arrow[r] & \text{use in reaction} \arrow[r] & \text{regeneration} \arrow[l, bend left] \end{tikzcd}$$

To give a more systematic exposition the whole subject was divided in to five sections.

1. How to choose the methods.
2. Sample choice and treatment.
3. Preparation.
4. Characterization and catalytic activity.
5. Deactivation and regeneration.

Each section contains a few examples to underline its applicative character and to explain the general statements present in the text.

All the presented cases derive from the authors' experience. This choice could be considered somewhat subjective: however, in our opinion, this is the best way to transfer our experience derived from years of experimental work.

1.1. How to choose the right methods

1.1.1. Most important techniques

The techniques presented in the first part of the work have been chosen on the basis of their:

(i) applicability to real catalysts;

(ii) easy accessibility, in terms of facilities required and/or investment and management costs;

(iii) wide applicability, in terms of number of catalytic systems that they can study;

(iv) high informative contents, in terms of number of information about catalyst aspects.

All the techniques potentially usable have been chosen following these rules. However a characterization laboratory can have only a part of those techniques directly , while others are available in analytical services and in spe-

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cialised laboratories of industry, university or other public institutions.

The choice of the method to be run directly depends on the available funds and on the access to 'external' techniques. In Table 1 a possible division of the most important techniques derived from the authors' experience is reported. Except for monothematic laboratories, which take care of only one argument for years, normal catalyst characterization laboratories have to face a lot of different subjects, each of them requiring the use of a specific technique. So it must be taken into account that an excessive narrowing of the techniques managed directly can cause several problems in the characterization work.

Table 1 points out that fortunately this group is formed by techniques that require middle and low investments.

This is very important for the competence development of a characterization team, which must be constituted not by 'technique specialists', but by 'catalyst specialists' which use the techniques to make a model of the catalyst and its behaviour.

1.1.2. *Technique choice in relation to the case under study*

In the previous paragraph we have discussed about the techniques suitable for facing general characterization problems. If we are working on a specific case, we must choose which techniques, among all them, are the most useful. For example: what is the best method to determine the compounds present in the solid or to single out the surface active sites or to study the deactivation causes?

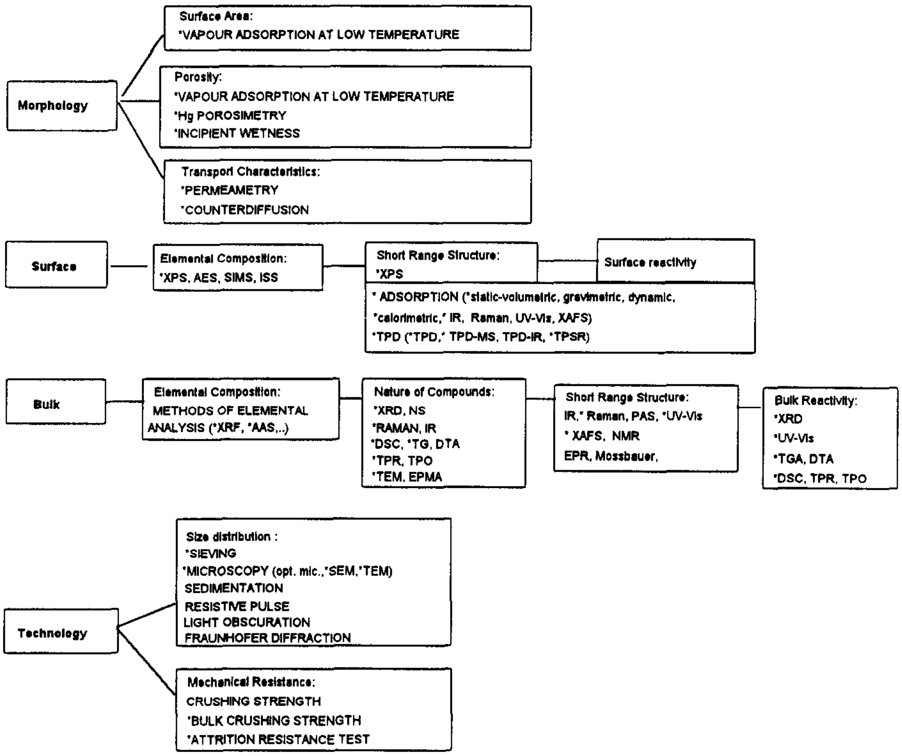
In Table 2 techniques suitable for the determination of specific characteristics are described.

The technique choice depends on the case under study, so it is better to examine a few examples frequently encountered in catalysis.

Table 1
Schematic grouping of characterization techniques on the basis of their relative importance

	Directly managed	Borderline	In collaboration with analytical services or specialized laboratories
Very important techniques	· Vapour adsorption at low temperature	SEM-TEM	Elemental Analysis
	· Hg-porosimetry	XRD	(XRF, AAS,....)
	· Incipient wetness		
	· Static volumetric adsorption		
	· IR		
	· UV-Vis		
	· TPD, TPD-MS, TPSR		
	· TG, TPR		
	· Sieving		
	· Bulk crush strength or crush strength		
Useful techniques	· Gravimetric adsorption	NMR	EXAFS, XANES
	· Calorimetric adsorption	XPS	Granulometry (for particle $< 50\ \mu m$)
	· Raman		
	· TPD-IR		
	· DSC, TPO		
	· Attrition resistance text		
Complementary techniques	· Permeametry		AES
	· Counterdiffusion		SIMS
	· Dynamic adsorption		ISS
	· PAS		EPMA (EDX)
	· DTA		Mossbauer
	· Crush strength or bulk crush strength		EPR

Table 2
Schematic grouping of characterization techniques on the basis of properties to be investigated (stars identify the most important techniques)



1.1.3. Crystallites dispersion and size of supported metals

The most important characteristics of supported metals are:

(i) crystallite size and dispersion (that is the fraction of exposed metal atoms), both characteristics being related to the active site number;

(ii) distribution in the support granules that determines the accessibility of active sites;

(iii) ratio between different crystallites faces that have a fundamental role in the 'structure sensitive' reactions.

Table 3
Methods for the determination of supported metal catalyst dispersion. It is noteworthy that every technique gives a different average size because each particle participates to the average with a weight proportional to its volume (XRD), to its surface (Chemisorption) or mass (SEM, TEM)

Techniques	Detected characteristics	Calculated characteristics	Applicability	Example of comparison (Pt/AL_2O_3) from ref.
SEM-TEM	·	· Mean size	$\phi > 2$ nm	$\phi = 2.79$
	· Particle size	· Distribution		$\phi_s = 3.07$
	· Distribution	· Surface average size (ϕ_s)		$\phi_v = 3.19$
		· Volume average size (ϕ_v)		
XRD	· Line width	· Volume average size (ϕ_v)	$\phi > 0.3$ nm content > 0.5%	$\phi_v = 3.29$
XPS	· Metal to carrier intensity ratio	· Surface average size (ϕ_s)	no limitations	n.d.
Chemisorption	· Adsorbed gas uptake	· Dispersion	no limitations	$\phi_s = 2.93$
		· Surface average size (ϕ_s)		

Table 4
Probe molecules for the determination of supported metal catalysts dispersion by chemisorption

Metal	Adsorbate	Temperature
Pt	H_2, O_2, CO, O_2+H_2	room temperature
Pd	H_2, CO, H_2+O_2	
Ir	H_2, O_2, CO	
Ru, Os	H_2, O_2	
Rh	H_2, CO	
Fe, Co, Ni	H_2, CO	77 K–room temperature
Ni	O_2	room temperature
Au	O_2	250–700 K
Ag	O_2	room temperature–450 K
	N_2O	room temperature
Cu	N_2O	

For the sake of brevity, only the first property will be examined in the following, while the other characteristics can be found in the references.

The techniques used are listed in Table 3: physical characterization supplies the average size, while the probe molecules chemisorption gives directly the exposed atoms number.

For this reason the last technique must be preferred. Nevertheless it should be recommended to use at least another technique as a comparison (Table 3). This recommendation is a good general rule, especially useful in this case, where the measurements are really very delicate. Unlike physical measurement, chemisorption is based on a chemical reaction of the probe molecules:

$$\mathrm{Me}_{(\mathrm{surface})} + \mathrm{Probe}_{(\mathrm{gas})} \rightarrow \mathrm{Me\text{-}Probe}_{(\mathrm{surface})}$$

so it requires a different approach. In Table 4 we have compiled a list of the molecules used with the most common metals.

To go deeper into the argument see [1–11] and references therein.

1.1.4. Acidity

Following the Brönsted and Lewis definition, a solid acid has the tendency to donate a proton or to accept an electron pair, so it is capable to transform an adsorbed base molecule into its conjugated acid.

The principal characteristics of a solid acid are:

1. acid site number (and density);
2. site strength;
3. site type (Brönsted or Lewis).

According to the given definition, all the methods for the acidity measurement are based on the interaction between the solid and basic molecules (except the ^{1}H NMR method proposed as an absolute method).

The most used methods are based on adsorption or on desorption of gaseous bases and, to a minor extent, on long and complicate titration methods (Table 5).

Table 5
Methods for acidity measurements. B = methods suitable for separate determination of Bronsted sites. L = methods suitable for separate determination of Lewis sites

Methods	Number	Strength	Quantitative analysis?
· **Direct titration in aqueous suspension**	B		Yes
· **Titration in aqueous solution after ion exchange**	B		Yes
· **Adsorption of coloured indicators**		B,L	Yes
· **Amine titration using indicators:**			
· visible method	B,L	B,L	Yes
· spectroscopic (UV-Vis) method	B,L	B,L	Yes
· **Adsorption of gaseous bases:**			
· static-volumetric method	B,L	B,L	Yes
· calorimetric method	B,L	B,L	Yes
· spectroscopic (IR) method		B,L	No
· **TPD of preadsorbed bases**	B,L	B,L	Possible
· **Adsorption of bases giving carbenium ions or radicals (UV-Vis)**	B,L		Possible
· **^{1}H NMR**		B	Yes
· **Test reaction**	B,L	B,L	Possible

It is advisable to use more than one method: for instance the adsorption calorimetry, which gives the acid sites distribution, can be coupled conveniently with IR spectroscopy, which gives information about acid sites nature.

Acidity measurements are treated with more details in [12–16].

1.1.5. Oxides

The oxides and the mixed oxides are widely used in catalysis both as supports or as real catalysts.

The most important class is that of transition metal oxides (directly used as catalysts), of the alkaline earth metal oxides (used both as catalysts and carrier) and that of a ill-defined group of oxides, including Al_2O_3, SiO_2, ZrO_2, widely used as carriers. The class of mixed metal oxides, comprising SiO_2-Al_2O_3, Al_2O_3-TiO_2, SiO_2-MgO and so on, finds its application mainly in acid catalyzed reactions. Oxides show a great variety of morphological characteristics, sometimes also inside the same chemical compound. For example there are microporous, mesoporous and non-porous silicas (aerosil); as well as silicas having very high porosity (more than 5 cm^3 g^{-1}).

The most important bulk properties are: the chemical composition (very important are the impurities), the framework that determines the surface characteristics and the thermal stability.

The oxides surface can contain:

(i) hydroxyl groups, or surface carbonates, allowing surface atoms to complete their coordination sphere;

(ii) acid and base Brönsted sites;

(iii) coordinatively unsaturated acid and base Lewis centres.

The nature of the sites (but also the morphology) depends not only on the type of oxide but also on the oxide precursor and on the preparation procedure, temperature and atmosphere of calcination and, finally, on the presence of impurities or intentionally added compounds.

In Table 6 there is a list of the principal characteristics and the best method for their determination.

The use of UV-Vis spectroscopy for bulk characterization of transition metal oxides and of IR spectroscopy of adsorbed molecules to study the surface sites of all oxides is especially recommended.

Much information on oxides can be found in [17–24].

1.1.6. Zeolites

The zeolites entered the catalysis scene in the 60s with Y and X types, and they play a role

Table 6
Main techniques for oxide characterization

Techniques	Information	Quantitative analysis
Elemental analysis techniques (XRF, AAS, etc.)	Atomic composition	Yes
XRD	Structure	Possible
Raman	Structure	Possible
Uv-Vis	Structure	Possible
N_2-adsorption at 77 K	Morphology	Yes
Hg porosimetry	Morphology	Yes
Incipient wetness method	Morphology	Yes
	Surface sites:	
IR	· Direct observation	No
NMR		Yes
Static-volumetric adsorption		Yes
Calorimetric adsorption	· Reactivity	Yes
IR spectroscopy of adsorbed molecules		No
TPD (TPD-MS, TPSR)		Possible

which is still increasing (ZSM-5, Ti-silicalite, MeAlPO$_4$, etc.), not only for the successes they allowed to obtain in this field, but also because they are at the same time real catalysts and model solids.

In fact:

(i) they have a microporous structure determined by the framework (whose pore structure is uniform) and their channels have molecular size;

(ii) all the atoms are on the surface, so the bulk techniques can be used to study the surface;

(iii) the guest atoms in the structure confer on the zeolite peculiar characteristics; they are all isolated, have the same coordination number and all are accessible.

Though they are 'perfect solids', their characterization is not so easy as it appears.

The most important morphologic characteristics are the crystallite external surface area, the channel volume and size.

About the first and the second characteristics see also example 7, about the third one it must be pointed out that a reliable measurement method, also capable of taking into account that the channel size can be changed by the presence of an adsorbate does not exist.

XRD is an established technique that gives excellent results in structural measurements. More difficult, owing to the spectra complexity, is the quantitative determination of the crystallites size and crystalline degree.

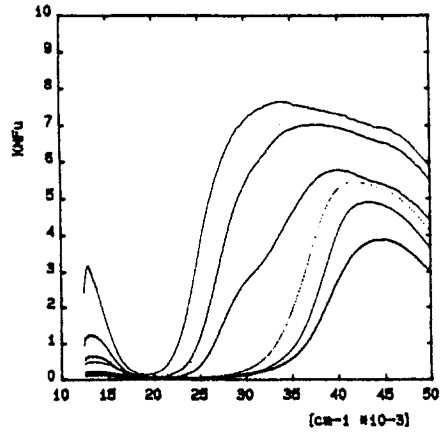


Fig. 1. UV-Vis spectra of Al_2O_3 impregnated with $CuCl_2 \cdot 2H_2O$ and dried at room temperature (the Cu concentration increases from the bottom to top).

For the latter parameters (when possible) the thermogravimetric method can be used, as illustrated in example 9.

It is hard to establish the occurred introduction of a guest element in the framework, because it requires the contemporary use of many techniques (often the quantitative aspects remain unsolved).

In Table 6 the most useful techniques to characterize zeolites are reported.

A lot of books and reviews on zeolites are available: [25–38] represent a basic choice.

1.1.7. Supported salts

It is not possible to give general rules for supported salts characterization because each salt has specific characteristics and requires a specific approach. For this reason the illustration of an example, concerning a real case, has been preferred.

Example 1: $CuCl_2/Al_2O_3$ (catalyst for the oxychlorination of ethylene; [39]).

Literature reports that impregnation of Al_2O_3 with $CuCl_2 \cdot 2H_2O$ and H_2O gives rise to paratacamite $Cu_2(OH)_3Cl$ formation, which is the catalytic active species. In Fig. 1 the UV-Vis spectra of samples at different Cu concentration are reported.

If the concentration is low, chlorine is absent from the Cu coordination sphere and the spectra do not change under heating at 900 K. A copper aluminate is formed in these conditions. In samples with high Cu concentration chlorine is in the metal coordination sphere as paratacamite (from XRD). The Cl/Cu ratio is 2 for all samples (from elemental analysis); the excess of chlorine is bonded to Al_2O_3 surface. By heating at the reaction temperature (500 K) the high concentration samples assume the brown colour of $CuCl_2$, formed by reaction between paratacamite and Cl fixed on alumina surface (as seen by heating a mechanical mixture of paratacamite and partially chlorinated alumina). In conclusion two Cu species are present on the 500 K treated samples: copper aluminate and $CuCl_2$ (Fig. 2).

The exposure at reaction temperature to C_2H_4 reduces the surface Cu as demonstrated by IR studies of NO adsorption (interacting only with Cu^{II}) and of CO (interacting with Cu^I and Cu^0 see Fig. 2). At high concentration surface is constituted of CuCl while, when the concentration is low, the Cu^0 form is also present.

The above example, as well as the other examples reported in the following paragraphs, well demonstrate the necessity to use always a wide set of techniques to obtain a complete picture of the catalyst under study.

1.2. Sample choice and treatment

Precision and repeatability of the measurements are very important in catalyst characterization, but they are of little utility if the properties of the analyzed sample do not well represent those of the solid under investigation. So the correctness of the second and third step of the following sequence must be always verified:

analyzing solid → sampling → pretreatment
→ analysis

1.2.1. Sampling: homogeneity and representativity problems

Sampling may be complicated by:

(i) inhomogeneity of the solid in relation to properties;

(ii) large amount of analyzing solid, size and manufacture;

(iii) small amount of sample required for the analysis;

(iv) solid stability towards the characteristics under determination.

Problems can be revealed analyzing either industrial stocks or laboratory samples, either fresh catalysts or used ones.

Example 2: sampling an industrial stock [40].

A Ni based hydrogenation catalyst supplied in the form of prereduced and stabilized extrudates in a 200 l drum (approximately 40 drums every supply) was sampled. Determining properties were: specific surface area, degree of Ni reduction, average crushing strength, fraction with crushing strength < 10 Kg.

Differences inside a drum are reported in Table 7. The most substantial variations are between the top and the bottom. Samples drawn from the bottom of the drum present better mechanical properties: in fact in this part the most fragile extrudates broke during the carriage of the drums, as testified by the amount of

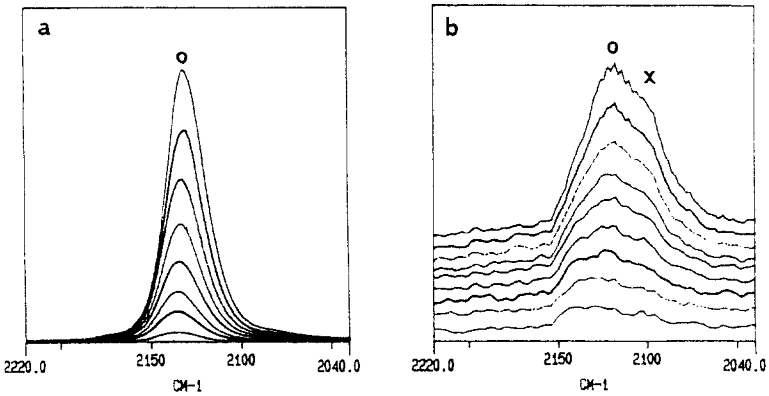


Fig. 2. IR spectra of CO adsorbed on $CuCl_2/Al_2O_3$ after reduction with C_2H_4 at 500 K: (a) high Cu content, (b) low Cu content; O = Cu(I)Cl-CO; × = Cu(0)-CO.

Table 7
Effect of sampling on characterization results of a Ni based hydrogenation catalysts

Characteristic	Sampled from a single drum				Sampled from all drums			
	Top centre	Top lateral	Centre	Bottom	Average value	Min.	Max.	Variation coefficient (%)
Specific surface area ($m^2\ g^{-1}$)	179	181	172	183	160.8	141	189	8.5
Reduction degree (%)	22.3	22.8	25.4	26.1	24.7	19.2	32.0	17.8
Average crushing strength (Kg)	13.2	15.5	19.1	20.7	17.0	10.5	26.5	17.8
Fraction with crushing strength < 10 Kg (%)	38.5	33.3	19.6	16.0	21.1	4.5	42.0	55.4

powder and crushed particles. Also chemical and morphological properties undergo little variations: samples drawn from the top present a lower degree of Ni reduction and a higher specific surface area (that so depends on reduction degree), probably caused by the exposure to external atmosphere infiltration. Samples drawn from different parts of the top are almost identical and the differences are in agreement with analytical methods reproducibility.

Differences among samples drawn from the top of different drums (reported in Table 7) are considerable especially as far as the mechanical properties are concerned and indicate the existence of reproducibility problems in preparation procedure.

Example 3: laboratory sampling [41].

This was apparently a simple case dealing with a UV-Vis-DRS analysis of a mechanical mixture of Ti-silicalite and SiO_2 powders. About 2.5 cm^3 of a 5 cm^3 sample were put in a cuvette 5 cm high. In spite of all precautions, different spectra were obtained not only at every loading but also analyzing the sample-holder at different height. To solve the problem it was found necessary to powder finely everything with a ball-mill.

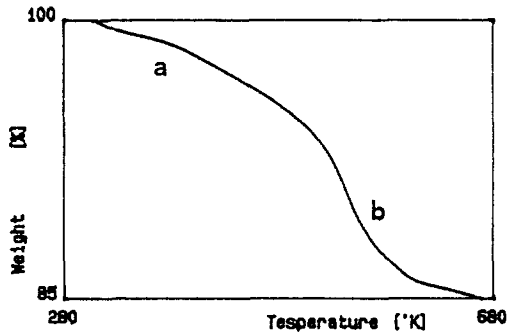


Fig. 3. TG curve of a Zn acetate catalyst showing the loss of adsorbed water (a) and of crystallization water (b).

Similar problems are very frequent in laboratory tests, especially for analyses (e.g. N_2 adsorption, TG, DSC, IR) requiring few mg of solid: checking the representativity of analyzed samples must be a part of normal analytical procedures.

1.2.2. *Samples pretreating and its influence on analytical results*

Aim of pretreatment is to produce a sample in a state suitable for the analysis without unintentional alteration. In most cases the treatment consists in drying sample to eliminate adsorbed water. Even in this case, it is indispensable to verify sample stability to treatment conditions.

Example 4: drying of vinyl-acetate catalyst.

The catalyst is active carbon impregnated with 30% of $Zn(CH_3COO)_2 \cdot 2H_2O$. As shown by thermogravimetric analysis (Fig. 3) adsorbed water cannot be completely eliminated without release of the crystallization water. Being surface area influenced by the acetate hydration degree (Fig. 4), to develop a method for determining this characteristic (in different laboratories) was needed. To do this, it was necessary to realize a treatment able to warrant a reproducible dehydration degree. This requires a rigorous and complicated procedure where every parameter has been established: sample weight, size, thickness, time and temperature of thermal treatment and so on.

Pretreatment becomes more complicated

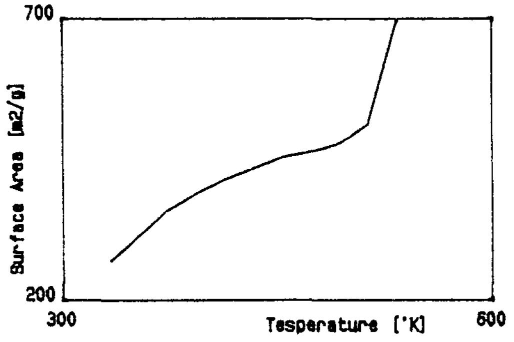


Fig. 4. Effect of pretreatment temperature on surface area of a Zn acetate catalyst.

when it is necessary to treat the sample 'in situ' to avoid damage caused by exposure to atmosphere. The determination of metal in prereduced samples preserved under H_2O (i.e. Ni-based catalysts) or of metal exposed surface area in noble metal based catalysts is a complex problem to solve.

Example 5: pretreatment reduction of a Pt/C hydrogenation catalyst [43].

To determine metal exposed surface area, it is necessary to reduce the sample without sintering the metal. For Pt supported on carbon, the following scheme of operations can be used:

$$\text{drying} \rightarrow \text{reduction with } H_2 \rightarrow \text{outgassing} \rightarrow \text{measurement} \; (\text{titration with } H_2 \text{ of preadsorbed } O_2)$$

To evaluate the effect of pretreatment on metal surface area, the temperature of the first three steps was varied alternately. As shown in Fig. 5a and Fig. 5c it was found that: (i) the drying temperature is uninfluential, (ii) too high reduction or outgassing temperature causes sintering of the metal.

It is impossible to always apply the same conditions on samples obtained with different procedure or on different carbons (as shown for instance in Fig. 6 where sample C needs a reduction temperature higher than the others).

Sometimes it is necessary to pretreat the sample in reaction-like conditions or to contact it with one or more compounds present in the reaction environment.

Example 6: treatment of $CuCl_2/Al_2O_3$ with C_2H_4.

Look over the second part of example 1 again.

As regard catalysts used in industrial reactors or in activity tests the problem is more complicated.

To analyze their characteristics, it is necessary to remove volatile or soluble substances present in the reaction medium, to distinguish from the irreversible fouling, with a procedure not affecting the properties to be analyzed. This problem will be more extensively discussed in the paragraph regarding catalyst deactivation and regenerability (see also example 20).

1.3. Preparation study

Catalyst preparation generally passes through three phases:

(i) obtainment of a precursor by wet procedure (precipitation, hydrothermal synthesis, impregnation, etc..)

(ii) activation (drying, calcination to eliminate organic compounds or to decompose inorganic substances, reducing atmosphere treatments, etc.)

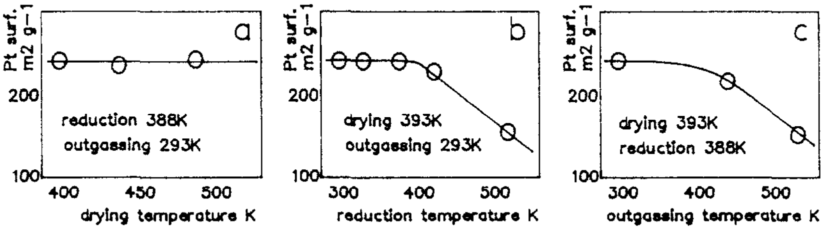


Fig. 5. Effect of pretreatments temperature on metal surface area of a Pt/C catalyst: (a) drying; (b) reduction; (c) outgassing.

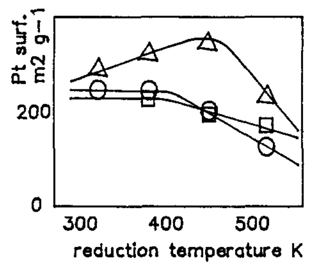


Fig. 6. Effect of reduction temperature on metal surface area of three different Pt/C catalysts.

(iii) shaping (tableting, pelletization, extrusion, spray-drying, etc.).

Sometimes, one step can be avoided (i.e. the shaping in the screening phase) and in some cases, not reported here for the sake of brevity, preparation can follow different paths.

General remarks on catalyst preparation and characterization can be found in [44–56].

1.3.1. Precursor preparation

Even if studies on wet phase of preparation are known, usually the characterization work begins on the dried solid, either because of the objective difficulty in studying the wet phase, or because laboratories are chiefly equipped for solid characterization. For these reasons the study on dried or even on calcined solids is used to obtain information on the process occurred in the previous step.

Example 7: defective silicalites [57].

As shown in Fig. 7 the adsorption isotherms of silicalite S_D, synthesized from Si-alcoholate, and silicalite S_T, synthesized by a traditional method, are different. The first has an external surface and a channel volume greater than the second one.

Sample S_D has an average crystallite size (determined by XRD) of 100 nm that corresponds to a calculated external surface area of 30 m^2 g^{-1}. The much higher value of 55 m^2 g^{-1} (determined by the *t*-plot method) can be explained with the presence of an amorphous fraction, confirmed by the crystallinity measurement (decomposition of TPA; see example 9) that gives a value of 90%. It is noteworthy that the amorphous surface is very high (500 m^2 g^{-1}).

The high channel volume value of sample S_D apparently disagrees with its low crystalline degree (90% vs. 98% of S_T). The IR (Fig. 8) spectroscopy and the thermogravimetric analysis show that S_D has an high number of OH groups (~ 15 OH/u.c.), most of them inside the channels, which are due to the vacancy of Si groups producing hydroxylated 'nests'.

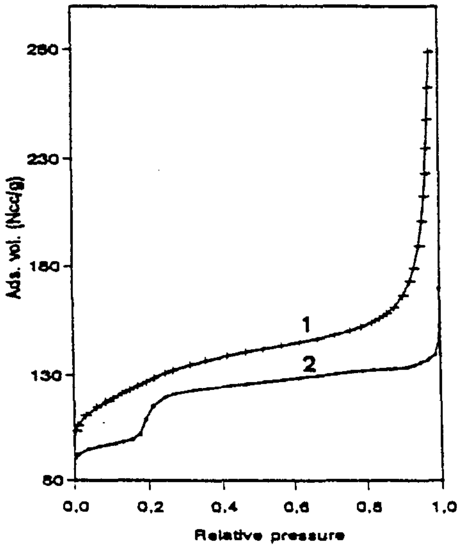


Fig. 7. N_2 adsorption at 77 K. Isotherms of (1) S_D sample and (2) S_T sample.

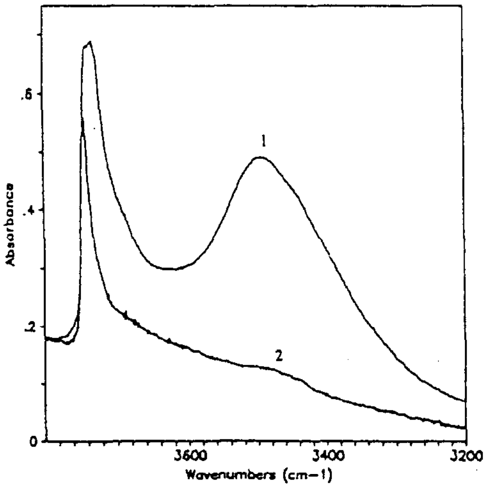


Fig. 8. IR spectra of (1) S_D sample and (2) S_T sample showing the OH stretching region.

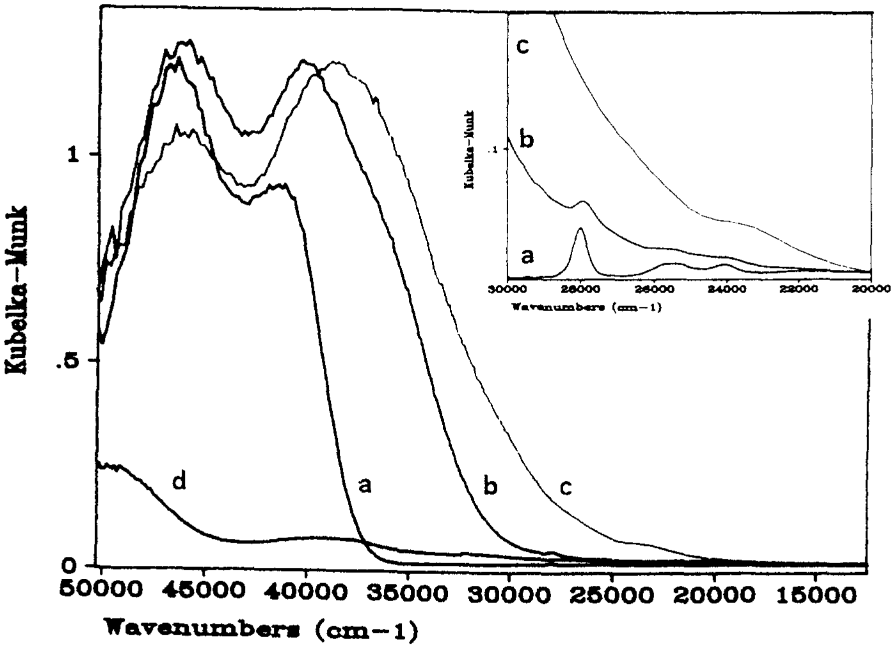


Fig. 9. UV-Vis spectra of different Fe-silicalite samples: (a) uncalcined; (b) calcined at 773 K in air; (c) calcined at 973 K N_2 + air and of silicalite as a reference (d).

ST sample has a more regular structure because, unlike S_D, it is synthesized in the presence of Na (that behaves as mineralizing agent). Adding a small quantity of NaOH during the S_D-type synthesis is enough to obtain a sample with characteristics closer to those of S_T.

It must be always borne in mind that high temperature treatments can cross out the information: so a good way of acting, is to extract all the possible data from the simply dried solid.

Example 8: evaluation of framework Fe in Fe-silicalite [58].

The UV-Vis spectrum of Fe-silicalite is characterized by a series of weak signals due to Fe included in the zeolite structure (Fig. 9). The maximum intensity is found in the dried sample: thermal treatments, besides removing template, produce Fe destructuration. Similar phenomena are observed on ZSM-5 and B-silicalite.

Example 9: determination of zeolite content in silicalite and Ti-silicalite by thermogravimetry.

Removal of organic template contained in the zeolite channels after synthesis can be followed by thermogravimetric analysis (Fig. 10). As the number of template molecules per unit cell is known, analysis enables us to determine the zeolite content in the solid, before any eventual collapse induced by thermal treatment.

Study on wet phase generally requires: (i) a wide set of analysis techniques, (ii) the examination of sample after different treatment steps and/or (iii) the variation of one or more preparation parameters.

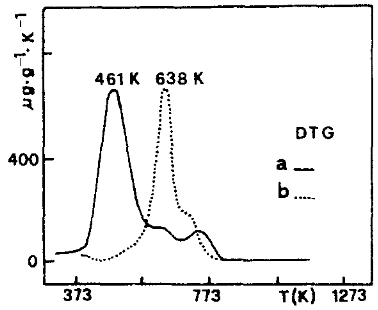


Fig. 10. DTG (derivative TG) showing the release of tetrapropylammonium hydroxide (via Hoffmann decomposition) from two silicalite samples: (a) crystalline degree ~ 10%; (b) crystalline degree 98%.

Example 10: preparation of $CuCl_2/AlO_3$.

As reported in example 1, we were able to define a complete picture only studying samples at different Cu concentration and treated in different ways.

Example 11: Ti-silicalite synthesis [59].

It was conclusive to have at our disposal samples at different synthesis time (1–20 h).

We have studied Ti-silicalite synthesis, starting from microspheroidal SiO_2 and Ti alcoholate at 448 K in relation to two aspects: (i) zeolite framework formation, (ii) Ti insertion into the zeolite framework.

As regard the first aspect (Fig. 11) the prevalent phenomenon, during the first 2 h, is SiO_2 dissolution, while zeolite formation is only beginning: solid yield lowers and crystallinity degree increases (as deduced from thermogravimetric analysis of template, IR band at 550 cm^{-1} and N_2 adsorption at 77 K). During the next 8 h, an increase in yield (till 95%), of crystallinity degree, of crystallite diameter (from XRD), while external surface (from N_2 adsorption at 77 K) diminishes. This means that crystallization proceeds via growth of formed crystallites rather than through formation of new crystals. No changes were observed during the next 10 h.

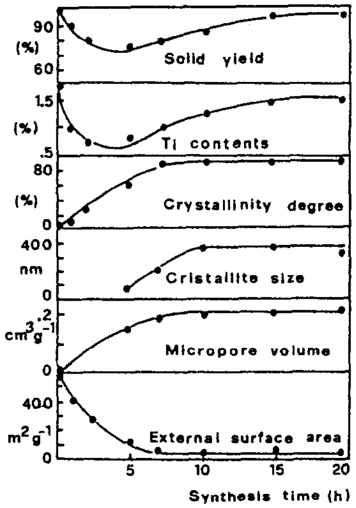


Fig. 11. Changes in main characteristics of samples vs. synthesis time.

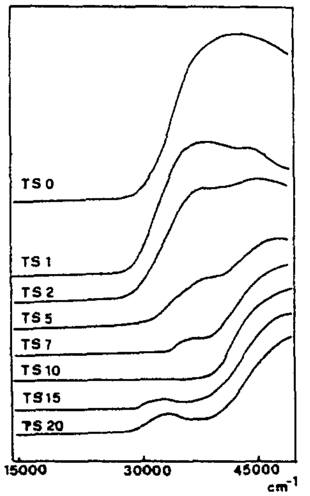


Fig. 12. UV-Vis spectra of sample at increasing synthesis time (for instance TS10 indicates the sample after 10 h synthesis time).

As regard the second aspect (Fig. 12), during the early hours, the solid contains TiO_2 (from UV-Vis) segregated into the amorphous part, because structural Ti (from IR band at 960 cm^{-1}) grows parallel to the crystalline degree. During the intermediate phase, the excess Ti goes into solution and the solid contains only structural Ti. Finally during the last 10 h, the excess Ti precipitates to form TiO_2 (from UV-Vis).

In conclusion the best results are obtained using the intermediate times.

1.3.2. Activation

The activation has the aim to obtain the catalyst in the desired state before its loading in the reactor. Generally the procedure consists of one or more thermal treatments in air or under controlled (i.e. inert, reducing, oxidizing) atmosphere. Less frequently mild treatment in liquid phase (i.e. reduction) are enough. More rarely, thermal treatments are not necessary and the activation takes place directly in the reaction environment.

Temperature programmed techniques (TG, DSC, DTA, TPR, TPO, TPD) are very useful to study this step as they allow to reveal changes in catalyst properties: decomposition, loss of volatile substances, melting, crystallization, etc.

The expected results are:

(i) help to identify the best operative conditions, i.e. temperature, heating rate, time, atmosphere, etc.;

(ii) help to face reproducibility problems due to incomplete or uncontrolled transformations (insufficient temperature or time treatment, too fast crossing of the transformation temperature).

Example 12: activation of $CrCl_3/Al_2O_3$ [60].

By heating samples of alumina impregnated with $CrCl_3$ at 700 K, the transformation of Cr to Cr_2O_3 both in air and in nitrogen atmosphere were obtained. Otherwise TPO analysis (Fig. 13) shows that air-treatment passes through an high oxidation state (Cr^{VI}, as demonstrated by next UV-Vis measurement) and that a further decomposition to Cr^{III} occurs. As a result the air treated samples contain Cr_2O_3 with crystallites having diameter larger than those treated under N_2 (from XRD and UV-Vis results).

Example 13: drying of vinyl-acetate catalyst.

The case has already been discussed in example 4. Here it can be noticed that the thermogravimetric analysis allowed us to define also the treatment conditions to be used in the reactor before the industrial run, removing some anomalies due to uncontrolled dehydration.

Temperature programmed techniques, though useful, are not able to clarify all the transformations of the solid. Typically, morphological characteristics are affected by thermal treatments and they can be verified only on the activated catalyst by proper measurements.

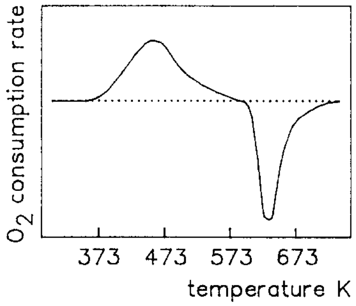


Fig. 13. TPO curve of Al_2O_3 impregnated with $CrCl_3$.

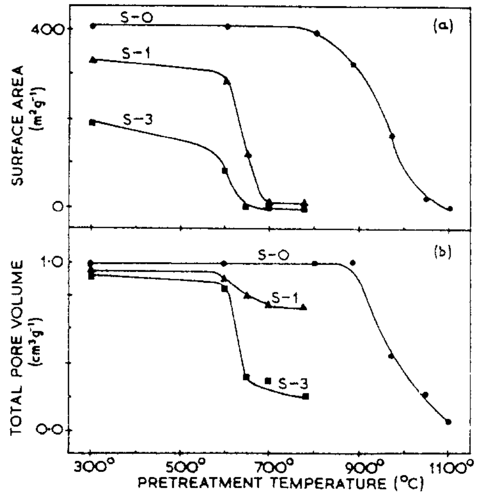


Fig. 14. Variation with the treatment temperature of: (a) surface area; (b) total pore volume.

Example 14: calcination of SiO_2 containing NaOH [61].

Pure and alkali containing silica samples showed different thermal behaviours (Fig. 14): the first is stable till 1000 K, while alkali impure silicas underwent a first loss of surface during impregnation and drying, and a second one (accompanied by crystallization as revealed by XRD) at about 900 K. Only specific surface area determination was able to underline the effect of NaOH at low temperature.

Another typical case is the activation of catalyst based on supported metal that requires delicate drying and reduction procedure.

Example 15: activation of Pt/C hydrogenation.

The case, illustrated in example 5, can be regarded also as a study for the optimization of catalyst activation.

1.3.3. Shaping

It has the aim to confer on the catalyst the size required for the use in the reactor.

Tableting, extrusion, pelletization are used for fixed bed catalysts; spray-drying for fluid bed ones. Tableting and extrusion require the compression of the solid. All the procedures require the use of volatile or non-volatile

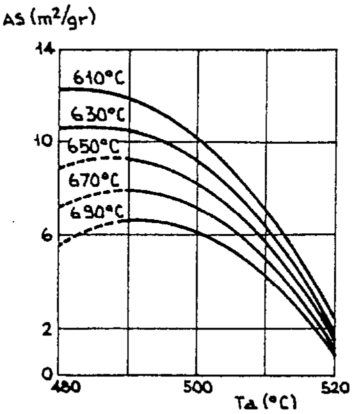


Fig. 15. Surface area vs. activation temperature at different T_c.

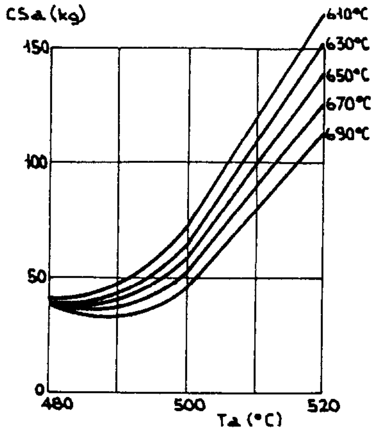


Fig. 16. Crushing strength vs. activation temperature at different T_c.

binders, the latter remaining in the shaped catalyst. Thermal treatments are needed to remove volatile binders, or to give consistency to the solid especially if non-volatile binders have been used.

All these operations modify the catalyst because:

(i) compression can alter the pore structure of the powder;

(ii) thermal treatments have the same effect of the previously described activation procedures;

(iii) the pore network, generated by aggregation of catalyst particles, affects both mass and heat transfer process inside the granule;

(iv) the surface of non-volatile binders can be catalytically active towards the reaction medium.

The effect of compression on pore structure can be determined by the same techniques used for the powder (N_2 adsorption at 77 K, Hg porosimetry, incipient wetness method). The techniques suitable for studying thermal treatment are described in the part concerning the activation of catalysts.

Hg porosimetry is the best technique to characterize the porous network of the shaped catalyst.

Finally the contribution of the binder surface to the total surface of the shaped catalyst can be determined quantitatively by N_2 adsorption at 77 K (by comparing the data of shaped and unshaped samples) and studied qualitatively by spectroscopic techniques (i.e. OH groups and probe molecules adsorption).

Example 16: shaping and activation of acrylic acid catalyst [62].

The binder (Klucel 250L) and a promoter (Te_2MoO_7) were mixed together with $NiMoO_4$ and calcined at 880–910 K (T_c). The mixture was tableted and activated at a temperature (T_a) of 750–790 K. Fig. 15 and Fig. 16 show that T_a and T_c affected both crushing strength and surface area (the latter because of the presence of an eutectic point at 800 K). The last parameter

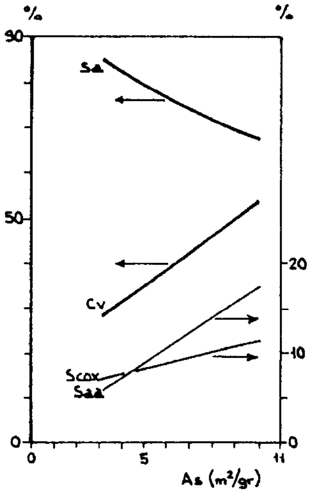


Fig. 17. Catalytic performances vs. specific surface area at 600 K.

is determinant for catalytic activity (Fig. 17) so the study enabled to optimize the catalyst, both in activity and in mechanical resistance, by selecting proper preparation conditions.

1.4. Characterization and performance of catalysts

The main purpose of the characterization work is to define the nature of the active centres suitable to catalyze a definite chemical reaction. The knowledge of these characteristics helps in projecting improved catalysts and in modifying the preparation method with the aim of optimizing the catalytic performances. The performances to be optimized are generally: (i) activity; (ii) selectivity to a desired product; (iii) selectivity to particularly undesired by-products (i.e. particularly difficult to separate, so limiting the use of the main product or decreasing its commercial value); (iv) the catalyst life; (v) the possibility of an easy recovery and/or reactivation of the catalyst. In the next paragraph we will discuss about the last two characteristics (because they require a specific treatment), while in this one we discuss the aspects related to the catalytic reaction.

It is easy to understand that a single characteristic taken alone cannot explain all the aspects of the catalyst behaviour during the catalytic reaction. Normally even a specific performance is influenced at the same time by several properties of the catalyst. That means that the object of the characterization work must be the acquisition of a complete knowledge of the catalyst and of the process.

Some general purpose book are quoted in [63–69]. See also references on surface characterization by probe molecules in the first part of the paper.

1.4.1. Identification of the characteristics determining the catalytic performance and of the reaction mechanism

There are conceptually two approaches:

(i) to determine the most relevant characteristics of the catalyst followed by an attempt to correlate them with the results of the catalytic tests;

(ii) to study the reaction mechanism, to single out adsorption sites, chemical intermediates and so on, that is to understand how the catalyst works.

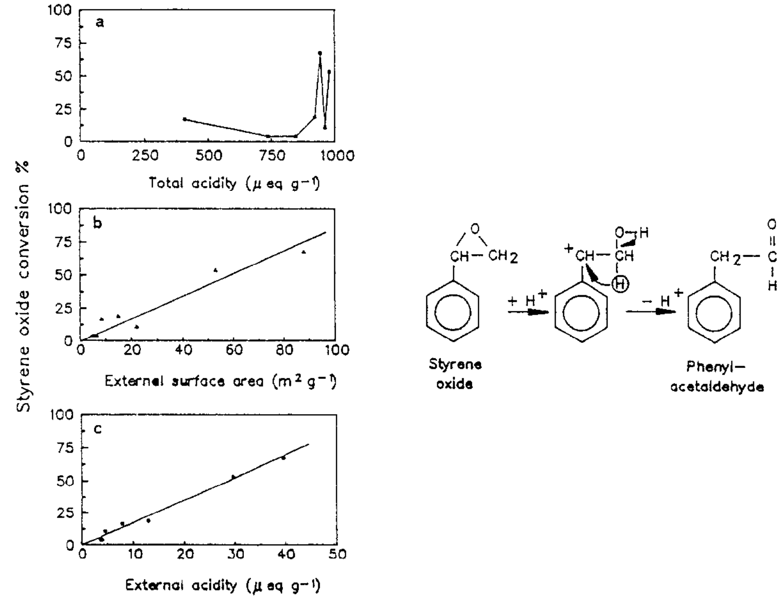


Fig. 18. Conversion in styrene oxide isomerization vs.: (a) total acidity; (b) external surface area; (c) external acidity.

In practice the two approaches are generally merged also if there are numerous exceptions. The first approach prevails generally at the beginning of the research work, while the second becomes more relevant in the following.

Generally there is no a prior criterion to direct the characterization work and the identification of the most relevant properties; tentatively it can be oriented by:

1. the literature;
2. the results of preliminary catalytic tests (catalyst screening);
3. personal experience.

Initially it is more convenient to characterize a small number of parameters and to increase progressively the knowledge of the catalyst, taking into account the analytical results. Moreover the work must be strictly related to the results of the catalytic tests that must be continuously used to verify the indications coming from the characterization, as shown in the following example.

Example 17: styrene oxide isomerization on ZSM-5 catalyst [70].

The reaction was performed at 320 K in the liquid phase, following scheme 1:

Although the isomerization requires an acid site, the activity do not correlate with the total acidity, determined with *n*-butylamine titration (Fig. 18a).

The catalyst samples were fully crystalline (from XRD) and the zeolite channels were fully accessible (from nitrogen adsorption at 77 K). The catalyst samples were characterized by different crystal size (from XRD) and then by different external surface area (from nitrogen adsorption at 77 K). The last characteristic correlated with the activity data much better than the total acidity (Fig. 18b). The obtained relationship suggested that the reaction is taking place on the external surface of the zeolite crystals, as confirmed by the excellent correlation between the activity and the external acidity, determined by titration with base molecules having a size too large to enter the zeolite channels (Fig. 18c). The results were confirmed by catalytic tests performed on a zeolite sample having the channels filled by the synthesis template molecule, and another one with the channels free but the surface hindered by large size basic molecule: the former sample resulted active, the latter inactive.

The above example shows a traditional approach, the next one, more recent, a more sophisticated approach. However we must point out that in this case the close interaction between the characterization study and the activity test runs was the key to understand the mechanism of catalytic process.

Example 18: ammoximation of cyclohexanone to cyclohexanoneoxime with ammonia and hydrogen peroxide on Ti silicalite catalyst [71–74].

Ti silicalite is a MFI type zeolite, containing Ti; its synthesis is described in the example.

The first step of the study was the characterization of the catalyst, mainly with the aim to identify the location and the structure of Ti centres. The study was made by means of several physical methods: UV-Vis, IR, Raman and XAFS spectroscopies. The most important spectroscopic features associated with Ti can be summarized as follows:

(i) IR and Raman bands at 960 cm^{-1} and a Raman band at 1127 cm^{-1} associated with Si–O stretching mode in $[SiO_4]$ units perturbed by adjacent $[TiO_4]$ units,

(ii) an optical transition at 48000 cm^{-1} with ligand to metal charge transfer (CT) character in tetracoordinated and isolated Ti (IV),

(iii) X-ray absorption in Ti k pre-edge region with peak position, full half width half maxi-

Table 8
Oxime yield in ammoximation of cyclohexanone on different catalysts

Catalyst	Ti content (%)	Oxime yield based on H_2O_2 (%)
		0.3
Silicalite		0.2
Amorphous TiO_2-SiO_2	1.5	4.3
Amorphous TiO_2-SiO_2	9.8	54.2
Ti-silicalite	1.5	93.5

mum and intensity indicating that Ti has a symmetry very closed to a perfect tetrahedron.

The whole results point out that in a well synthesized Ti silicalite: (i) Ti is contained inside the zeolite channels, (ii) Ti is inserted in the zeolitic framework as a vicariant of Si, (iii) Ti is tetracoordinated and isolated.

In the ammoximation of the cyclohexanone as reported in Table 8:

(i) Ti is the active site in the catalyst;

(ii) Ti in the zeolitic framework is much more active than Ti in other compounds.

Such extraordinary activity can be explained by the capability of Ti centres to form at the same time a complex containing both ammonia and an hydroperoxide group, increasing to a maximum the possibility of producing hydroxilamine, the key intermediate in the ammoximation reaction. In fact tetracoordinated Ti in the zeolite framework tends to assume the typical coordination value of 6 by the adsorption of extra ligands as demonstrated by;

(i) a shift of Ti(IV) CT band to lower frequency,

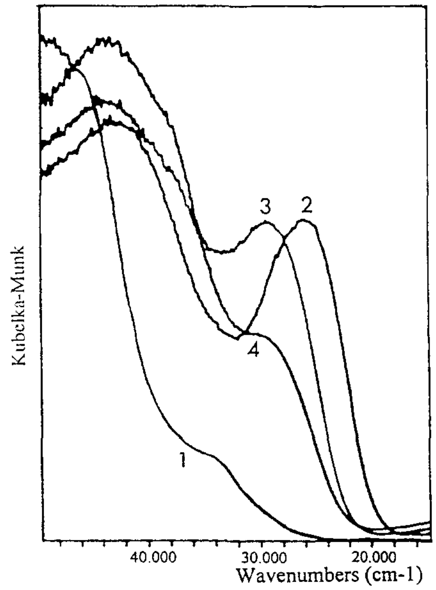


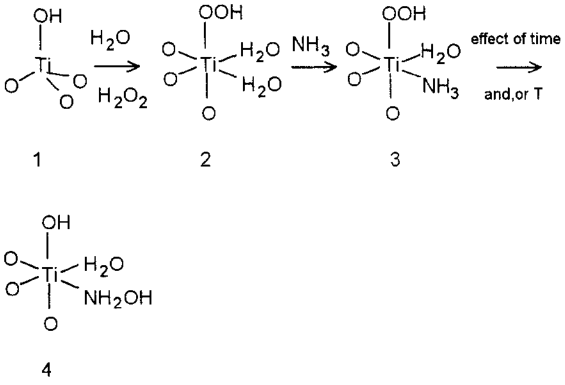
Fig. 19. UV-Vis spectra of Ti-silicalite: (1) in vacuum (reference spectrum); (2) in H_2O_2 solution; (3) the same after NH_3 addition; (4) after 30 min.

(ii) a shift in the IR and Raman bands to higher frequency,

(iii) a disappearance of the pre-edge peak.

The formation of hydroperoxo species is demonstrated by the appearance in the UV-Vis spectrum of a band at 26000 cm^{-1} associated with a CT from the hydroperoxo species to Ti(IV).

The above steps are visible in Fig. 19, where also the successive oxidation of coordinated ammonia with hydroperoxo Ti species is shown. In the last step hydroxilamine reacts with the ketone to give the oxime as in the next scheme (the numbers correspond to those of the spectra reported in Fig. 19):



In fact, according to the activity test results:

(i) a direct correlation between ammoximation yield and oximation yield with hydroxylamine base is well established,

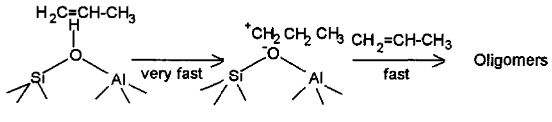
(ii) the hydroxylamine base formed inside the zeolite channels goes outside and oximate hindered ketone that can not enter the channels themselves.

It is interesting to note that these results allow to reject a supposed mechanism via oxidation of the cyclohexanoneimine (still present in the reaction medium), suggested by results obtained via IR spectra of adsorbed molecules only.

This example shows that, if used in a concerned way, the optical spectroscopies, together with TPSR, are powerful tools to study the reaction mechanism. A further confirmation is shown in the next example.

Example 19: propene oligomerization on ZSM-5 catalyst [75].

IR fast scanning spectroscopy (20 spectra s^{-1}, see Fig. 20) allowed to follow the reaction steps according to the mechanism:



The results (in difference towards the zeolite background) are shown in Fig. 20 where each spectrum is the average of ten interferograms. In this representation the band appearing as a negative peak belongs to species which are consumed (Brönsted acid sites at 3610 cm^{-1}), while those appearing as positive belong to species formed during the adsorption (hydrogen bonded species centred at 3070 cm^{-1}) and the oligomerization process (growing chains at 3080–2850 cm^{-1} and 1628–1338 cm^{-1}). The hydrogen bonded precursor disappears in few seconds both for its consumption and to displacement of propene molecules by the growing chain into the channels (growth of the band at 3740 cm^{-1}).

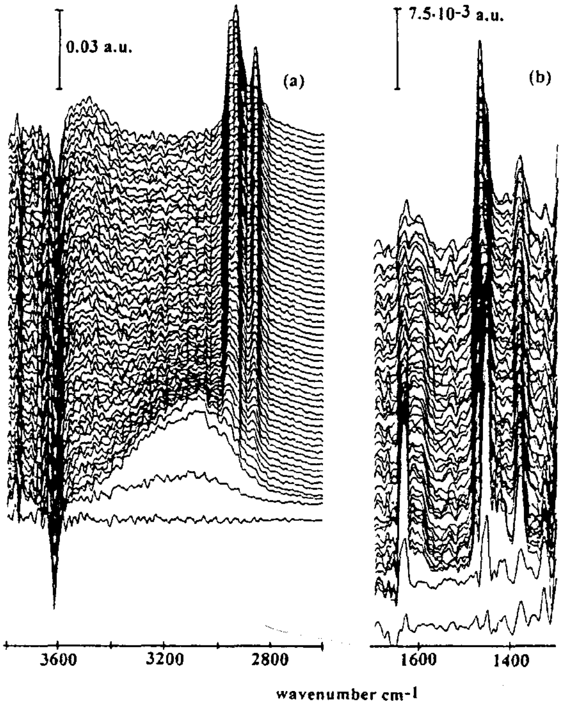


Fig. 20. IR spectra of HZSM-5 exposed to propene at room temperature.

The most important limitation of the described approaches is represented by the state of the catalyst under investigation: it is completely different from that can be found under reaction conditions. It is known that the catalytic reaction modifies the catalyst, sometimes very deeply; so it can be easily understood because difficulties to correlate activity and characterization data are often encountered and because the catalysis mechanism is not easy to elucidate.

More indirect but 'realistic' results can be obtained by studying catalysts recovered from catalytic runs at different working time, i.e. different aging degree. This will be the object of the next paragraph.

1.5. Study of deactivation and regeneration

The deactivation process, that is the decay of the catalyst performance during the reaction run, is much frequent and has important economic effects. Consequently many techniques for restoring the catalytic activity have been developed (regeneration techniques).

The causes of the catalyst deactivation can be grouped in two classes:

(i) coverage of the surface with heavy molecules (fouling);

(ii) physico-chemical changes in the solid, especially occurring at the catalytic surface.

The two classes are schematically shown in Table 9.

A wide choice of the literature on the argument is represented by [76–87].

A possible approach to the study of the decay and of the regeneration of an exhausted catalyst follows the following steps:

(i) quantitative determination of organic deposits and their identification;

(ii) determination of the main catalytic properties of the exhausted solid and comparison of the results with those obtained on the fresh catalyst;

(iii) development of a method (i.e. burning) suitable to remove the organic deposit and without effect on the solid (when applied to the fresh catalyst);

(iv) removal of deposits from the exhausted catalyst, followed by the determination of the main catalytic properties and comparison of the results with those obtained on the fresh catalyst (subjected to the same procedure);

(v) activity test on the regenerated catalyst and comparison of the results with those obtained on the fresh catalyst.

1.5.1. Analysis of organic deposit

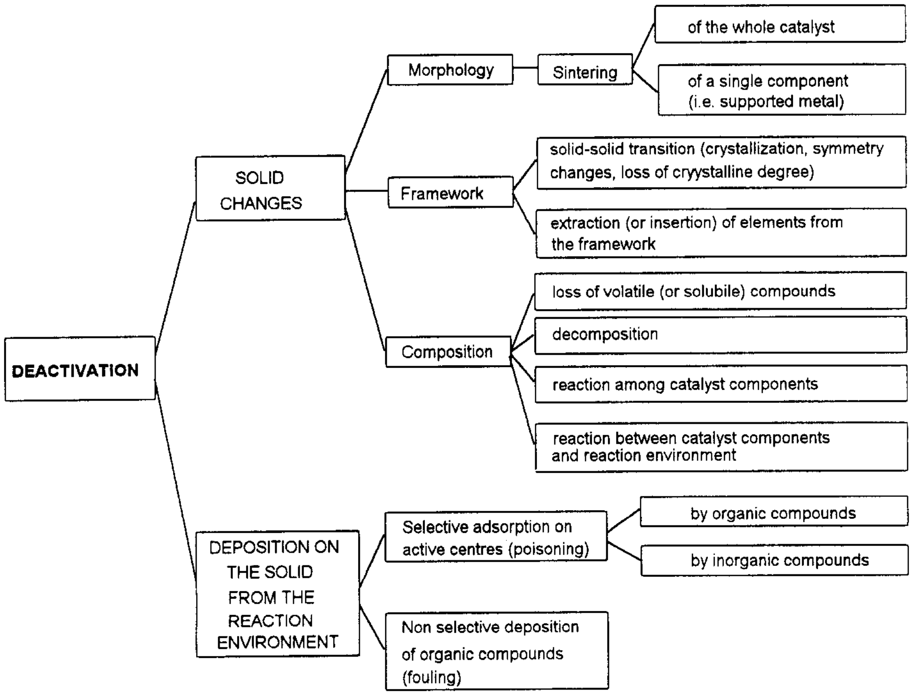
The quantitative analysis of the organic material deposited on an exhausted catalyst can be performed by C, H, N determination or, very rapidly, via TG or TPO (the last being more suitable for small fouling level).

Particular attention must be paid to discriminate among irreversibly adsorbed materials and easily removable materials remained on the catalyst because of an incorrect discharge operations. Experience is teaching that the above possibility is more frequent than people can imagine: so it is necessary, before any measurement, to carefully remove from the catalyst all volatile substance or solvent used in the catalytic reactor. The choice of the suitable procedure to remove the volatile substances can be made easier by TGA or TPD techniques.

Example 20: removal of volatile compounds from Ti-silicalite used in an ammoximation run [76].

TG analysis on a Ti-silicalite sample unloaded from an ammoximation reaction run performed at 350 K (see example 18) showed a content of organic compounds too high to be

Table 9
Causes of catalyst deactivation



contained in the zeolite channels (28 wt%). A comparison with reference sample (Fig. 21) allowed to identify the presence of cyclohexanoneoxime outside the zeolite channels (20 wt%): the unloaded sample was not washed to remove the reaction medium. Outgassing at 373 K under vacuum was enough to remove the extra-channel oxime (Fig. 21 curve c) and the preparation of the sample for characterization.

The nature of irreversibly adsorbed or nonvolatile organic materials is, generally speaking, difficult to determine. We can try to extract them with a solvent and to study the solution with the methods of traditional analysis (GC, GC-MS, HPLC, NMR, etc.), nevertheless the solubility of organic deposits is frequently very low or nil. Alternatively, we can study the IR spectrum of the solid to point out functional groups or coke precursor. Another group of useful techniques is based on the combination of temperature programmed desorption and analytical devices (TPD-IR, TPD-MS).

Another important useful information is the distribution of the deposit through and/or along the catalytic particle, especially when its concentration is very high. The morphological characterization (N_2 adsorption at 77 K, Hg porosimetry) is the most suitable technique because it allows to evaluate the variation of the size and volume of the pores compared to the fresh catalyst.

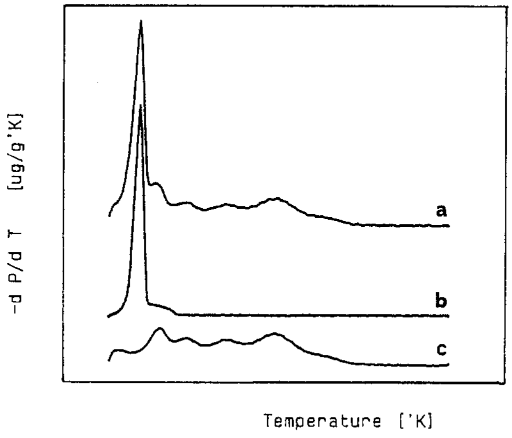


Fig. 21. DTG curves of: (a) Ti-silicalite sample unloaded from ammoximation reaction run; (b) pure cyclohexanoneoxime; (c) sample treated under vacuum at 373 K.

It is imperative, in this type of approach, to understand if the morphological modification is caused by the organic material deposit or by structural modification of the solid.

Example 21: fouling on zeolites [77].

The catalyst under study was a MFI-type zeolite used as aggregates of crystals without any binder and then containing two classes of pores: (i) zeolite channels ($V_z = 0.16$ cm^3 g^{-1}); (ii) intercrystalline voids ($V_m = 0.40$ cm^3 g^{-1}, average size $\phi_m = 50$ nm), both determined by N_2 adsorption at 77 K.

After reaction, the organic content was 2.2 wt% (TG), and a loss of pore volume was observed ($V_z = 0.12$ cm^3 g^{-1}, $V_m = 0.20$ cm^3 g^{-1}, $\phi_m = 25$ nm).

The data point out that the fouling took place substantially only outside the zeolite crystals, filling the intercrystalline voids. The loss of channel volume is probably due to the blockage of pore mouth.

The burning of organic compounds fully restores the original values of V_z and V_m suggesting that no structural modification of the solid happened.

1.5.2. Characteristics of the solid affected by the presence of organic deposits

All the techniques utilized for the characterisation of the fresh solid are suitable: sometimes particular pretreatment can be necessary to remove the reversibly adsorbed compounds. Typical cases are the poisoning of acid sites by base molecules and covering of dispersed metal crystallites by fouling. A comparison between the results of measurements (i.e. acidity or dispersion) on fresh and aged catalysts are necessary to solve the problem.

Example 22: Pd/Al_2O_3 for hydrogenation [78].

In this case the catalyst unloaded from industrial reactor contained about 8 wt% of heavy by-products. Nevertheless, the exposed surface area of the metal was no affected: the same

Table 10

Characteristics of aged samples. With exception of the weight loss by TG expressed as wt%, all the data are expressed as ratio between the values of the aged and the fresh sample, respectively

Sample		Catalyst recovered	Ti content	Weight loss of samples by TG	Crystalline degree by XRD	Micropore volume by N_2 adsorption	*m*-Xylene adsorption capacity by TG	Oxime yield
P_1	as unloaded			9.8		0.13		0.90
	calcined	> 0.95	1.0		1.00	0.97	0.95	1.00
P_2	as unloaded			10.0		n.d.		0.37
	calcined	0.90	1.1		1.02	0.93	0.65	0.74
P_3	as unloaded			12.5		n.d.		0.15
	calcined	0.35	4.4		0.91	0.73	0.10	0.40

value was obtained on both fresh and unloaded catalyst. Then the fouling happened only on the carrier surface.

1.5.3. Variation of solid characteristics non-attributable to organic deposit

The reaction conditions can affect bulk (composition, structure), surface and morphological characteristics of the catalyst, independently from the organic material deposition.

In most cases bulk properties can be determined applying the necessary corrections, also in presence of organic deposits. On the contrary the modification of surface and morphological properties can be measured only after the removal of organic deposit and so after the regeneration study. Rigorously, we can say that the two phases are strictly related each other, because the regeneration procedure can affect the catalyst characteristics. Therefore it is necessary to clarify if the differences between the fresh and the used catalyst are due to the reaction conditions or to the regeneration procedure.

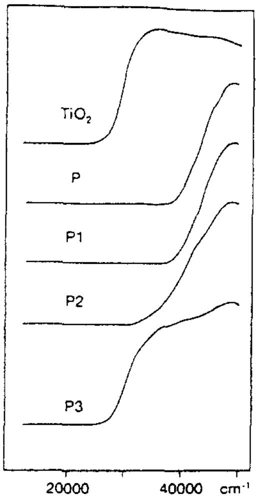


Fig. 22. UV-Vis spectra of fresh and aged samples: P fresh; P1, P2, P3 unloaded samples (see Table 10).

Of course all the techniques used for the characterization of the fresh catalyst are suitable also for the used ones.

These problems are illustrated in the next example that allows also an overview of the arguments discussed in the present paragraph.

Example 23: study on Ti-silicalite unloaded from an ammoximation reaction [79].

Catalyst deactivation during the catalytic run is due to many causes.

A first deactivation cause lies in the fact that the catalyst is slightly soluble in the reaction medium and some silica is lost (with the reactor effluent Table 10). As the titanium compound is not soluble, it accumulates as TiO_2 in the residual solid (UV-Vis spectrum, Fig. 22, P3 sample).

The final solid remains crystalline (as shown by XRD), but also after a short period of catalytic ageing some titanium is extracted from the structure (UV-Vis spectrum, Fig. 22, P2 sample) going into extraframework position.

The exhausted catalyst samples contain approximately 10% of organic material (from TG) that hinders the entrance to the channels (from N_2 adsorption at 77 K). The organic material is partially soluble in the reaction solvent, but a substantial part is completely insoluble (heavy molecules).

The catalyst is not regenerable because the volume of the channels decreases probably because of local structure collapse. Also the size of the channels decreases, as evidenced by the adsorption of a large size probe molecule (from TG of pre-adsorbed *m*-xylene).

The characterization results allow to explain the loss of the performance of the catalysts after use in pilot plant tests and the only partial recovery of the activity after the regeneration procedure (laboratory activity test, Table 10).

1.5.4. Study on the regenerability of the catalyst

The characterization work can contribute to point out the regeneration procedure of a catalyst in the following ways:

(i) by studying the removal of the deposits or by studying other regeneration treatments (i.e. reduction, oxidation) with the TG, TPO, TPD, TPR techniques;

(ii) by verifying the restoration of the original catalyst characteristics after the regeneration procedure (i.e. complete removal of organic material) without any additional undesired effect. Also in the present case the techniques used for the characterization of the fresh catalyst can be used [42].

Acknowledgements

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