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Characterization of heterogeneous catalysts by X-ray diffraction techniques

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Abstract

Application of X-ray powder diffraction (XRPD) in heterogeneous catalysis is described. Some general aspects of the background of the technique are briefly mentioned, together with the recent advances regarding Rietveld analysis. Examples of application of XRPD are reported, concerning solid materials frequently used in heterogeneous catalysis (metal oxides and zeolites). © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Knowledge of catalyst structure is essential to the understanding of the chemistry actually occurring in catalysis. This makes structure characterization crucial throughout the life cycle of the catalyst, from the preparation step to the use in reaction conditions.

Though in heterogeneous catalysis the active sites are usually located on the solid surface, the bulk structure plays an important role, because many of the catalyst characteristics depend on it.

X-ray diffraction is the main technique for the investigation of bulk structure. Other techniques, such as solid state NMR, EPR and EXAFS, can probe the local environment of a particular element in the structure, while X-ray Photoelectron Spectroscopy can study the surface structure. Moreover, electron microscopy can supply information including lattice defects (High Resolution Electron Microscopy) and crystallite morphology. The synergism produced by information coming from all the above techniques is often crucial for identifying the structural features which really govern the catalyst behavior.

Till the end of 1970s, single crystal X-ray diffraction has been mainly used for structure analysis, while X-ray powder diffraction (XRPD) has been regarded to be inferior, particularly for structure refinement.

In the last two decades, the significant improvement of instrumentation and computer power, the easier access to synchrotron radiation sources and the development of powerful methods for structure refinement (Rietveld Analysis [1]) have made it possible to use XRPD for structure analysis. This evolution is of paramount importance because, practically, a solid used for a catalytic reaction is never in the form of single crystal. On the other hand, single crystals are obtained with difficulty for most of heterogeneous catalyst types.

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The paper will concentrate mainly on the recent advances on XRPD methods, with particular emphasis on application to catalyst characterization.

2. General aspects of X-ray diffraction methods

In a diffraction pattern from a crystal lattice, a number of reflections are generated, each one being associated to a lattice plane (identified by the Miller indices h,k,l) and occurring at an angular position (2θ) depending on the related interplanar spacing ($d(hkl)$) and on the X-ray wavelength (λ), as defined by the well-known Bragg's law.

A diffraction pattern contains a lot of structural information: the angular position of the reflections is related to the size and shape of the unit cell (the repeating unit of the crystal) while the intensities reflect the lattice symmetry and the electron density (practically the positions and types of atoms) within the unit cell.

In the case of a single crystal, a 3D pattern is obtained without any overlap among different reflections. On the contrary, in a powder diffraction experiment, a very large number of crystallites in all possible orientations are irradiated simultaneously. As a consequence, the 3D pattern typical of the single crystal becomes a 1D pattern with inevitable line overlaps, the severity of which depends on unit cell size and lattice symmetry.

The intensity of a Bragg reflection is proportional to $F(hkl)$ (the so called "structure factor", practically the Fourier transform of the electron density in the unit cell, evaluated at a point in the reciprocal lattice related to the (hkl) plane). Therefore, the distribution of scattering matter may be determined by means of the inverse Fourier transform, provided the "phase" of the complex number $F(hkl)$ is known (no information in this regard is derivable directly from the diffraction data). Computational methods are available for the "phase" determination, which take advantage of the presence of an atom much heavier than the others (Patterson method) or make use of iterative, trial and error procedures. Nowadays, starting from single crystal data, the crystal structure can be determined practically in almost all the cases.

Table 1
Typical applications of X-ray diffraction methods

Determination of crystallographic parameters
Unit cell dimensions and lattice symmetry
Atomic coordinates and thermal parameters
Isomorphous substitution in lattice sites
Intra-lattice porosity (zeolites, microporous materials)
Determination of physical/morphological features
Crystallite size
Crystallinity
Lattice strain (stacking faults, dislocations, microtwinning)
Preferred orientation of the crystallites (texture)
Identification and quantitation of crystalline phases

Due to the recent advances (see Section 3), XRPD data may be used more efficiently for quantitative analysis of the crystalline phases in a mixture and also for the determination of the structural parameters listed in Table 1. In the case of solid catalysts, crystallite size, lattice strain, and intracrystalline porosity (in the case of microporous materials such as zeolites) constitute important parameters. Information on the first two of the above parameters may be extracted from the analysis of line broadening in the diffraction pattern; the geometrical description of intracrystalline porosity comes directly from the knowledge of the crystal structure itself.

For a more detailed treatment of the topics mentioned above concerning polycrystalline materials, see [2].

3. Advances in powder diffraction methods

Traditionally, the information contained in a powder diffraction pattern has been used essentially as a fingerprint, for crystal phase identification purposes.

At the end of 1960s, a new method for crystal structure refinement was proposed by Rietveld, based on full-profile fitting of neutron powder diffraction data [3]. In the late 1970s the method was adapted for powder X-ray data to be used [4,5], becoming generally accepted for both X-ray and neutron powder diffraction while being usually referred to as "Rietveld analysis".

The method makes use of the full content of powder diffraction pattern, which can be considered as a collection of individual hkl reflection profiles (each one characterized by a peak height, a peak position, a peak broadening and an integrated area proportional to the Bragg intensity, *I(hkl))* not all resolved but partially (or totally) overlapped one another.

Starting from a diffraction pattern calculated on the basis of a postulated structural model, a least-squares refinement is performed, by minimizing the residual, S_y:

$$S_y = w_i(y_i - y_{ci})^2,$$

where $w_i = 1/y_i$, y_i is the observed intensity at the *i*th step, y_{ci} is the calculated intensity at the *i*th step and the sum represents overall data points.

The method has been proved to be efficient in many cases but it needs a reasonably good starting model. The same method can be applied to quantitative phase analysis in a mixture.

Many parameters are refinable, including atomic coordinates, thermal parameters, unit cell parameters, crystallite size and lattice strain (through profile parameters), preferred orientation. Nowadays, several computer programs are available for application of Rietveld analysis [1].

Recently, more and more attention is being paid to the so called ab initio structure determination with powder data. Practically, the approach is based on a first step which tries to use the experimental data as in a single crystal study, for arriving at a model refinable by the Rietveld method.

For increasing the chances of successful application of the above methods, it is very important to improve as much as possible the resolution in the powder pattern. In this regard, the use of synchrotron X-rays is of paramount importance.

The readers interested in the topics discussed in this section are addressed to [1].

4. Application of X-ray diffraction in heterogeneous catalysis

In this section examples will be illustrated in which XRPD investigation has played an important role, concerning types of solids frequently used in heterogeneous catalysis (metal oxides and microporous materials).

4.1. Metal oxides

Zn/Cr mixed oxides constitute a well-known class of catalysts for the synthesis of methanol from syngas at high temperature and pressure [6]. For a long time the active component of the catalyst was considered to be ZnO with very small crystal size, but a very careful X-ray investigation has demonstrated the active species to be really a non-stoichiometric spinel-like phase [7]. It is interesting to examine how this conclusion has been arrived at.

In the system Zn/Cr/O the existence of the spinel-type $ZnCr_2O_4$ phase is known, in which Zn^{2+} ions occupy tetrahedral sites (as in ZnO) while Cr^{3+} ions are placed in octahedral sites (Fig. 1(A)). This phase has been proved to be practically inactive in the catalyzed synthesis of methanol [6]. The XRPD pattern of $ZnCr_2O_4$ is shown in Fig. 2(A).

Very active catalysts are obtained when the Zn/Cr ratio is above 0.5. In this case, residual ZnO is expected, related to the excess of Zn with respect to the $ZnCr_2O_4$ stoichiometry. On the contrary, XRPD analysis has demonstrated that a pure spinel-type phase can be obtained, at least for Zn/Cr ratio up to 1 (see XRPD pattern of Fig. 2(B)); only exceeding this value, crystalline ZnO is detected. This result has been interpreted as occurring due to the formation of a non-stoichiometric spinel-like phase of the general formula $Zn_xCr_{2/3(1-x)}O$, containing an excess of Zn with respect to the stoichiometric $ZnCr_2O_4$ [7,8]. In the proposed structure of this phase, Zn^{2+} ions are located not only in tetrahedral sites (as in $ZnCr_2O_4$) but also in octahedral sites, randomly distributed with Cr^{3+} ions (Fig. 1(B)).

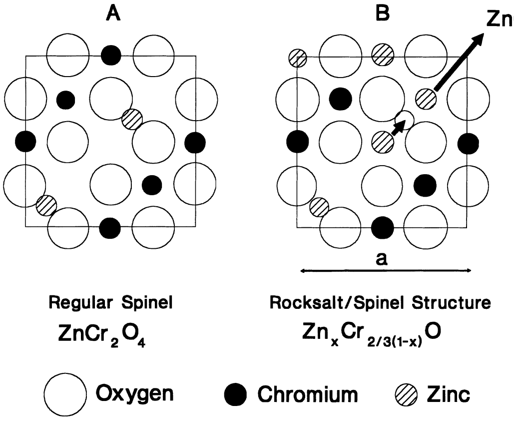

Fig. 1. Schematic representations of the regular spinel (A) and non-stoichiometric spinel-like (B)structures.

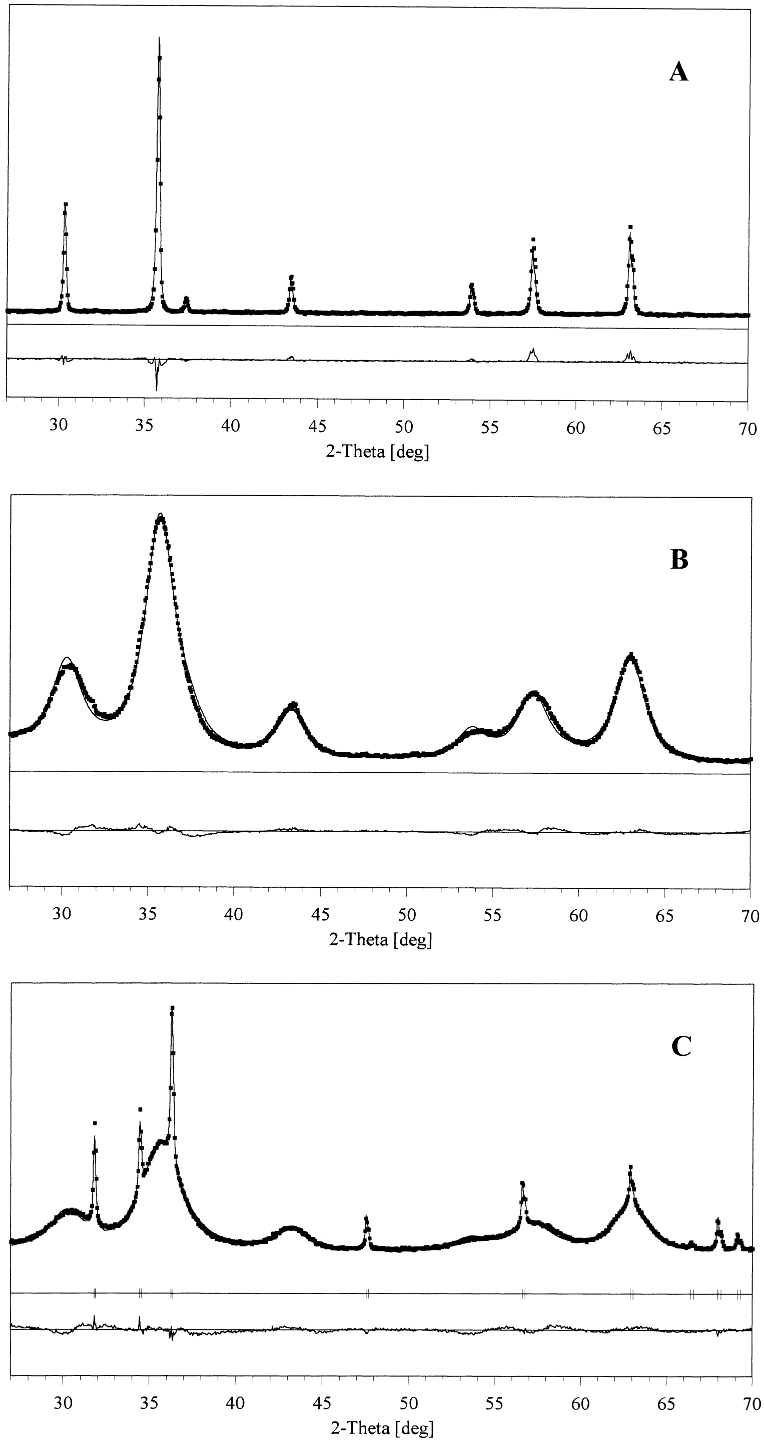

Fig. 2. Rietveld refinements of $ZnCr_2O_4$ (A), $Zn_{0.34}Cr_{0.44}O$ calcined at 623 K (B) and at 803 K (C). Experimental (■), calculated (———) and difference (lower) profiles.

Calcination temperature must not exceed 650°C for obtaining a pure spinel phase; overcoming this temperature results in a tendency to approach the stoichiometric spinel phase with consequent formation of residual ZnO [7] (see XRPD pattern of Fig. 2(C)). The migration of Zn from octahedral to tetrahedral sites and the consequent segregation of ZnO is the probable mechanism of evolution towards the regular spinel structure (Fig. 1(B)).

The XRPD pattern of Zn/Cr/O catalysts contains structural information (lattice parameters, occupancy of tetrahedral and octahedral sites and average crystallite size of the spinel phase, amount of crystalline ZnO) which can be extracted by applying Rietveld analysis. Examples of the results obtainable are reported in Table 2, while the fit obtained for the corresponding XRPD patterns by applying Rietveld refinement is shown in Fig. 2.

In the case of Zn/Cr/O system the contribution of XRPD has revealed to be crucial for better understanding of structure/catalytic properties relationships (role of octahedral Zn^{2+}, which can be formed only in the non-stoichiometric spinel-type phase), while giving clear indications about the characteristics of the catalyst required for optimizing the performance in methanol synthesis from syngas.

Table 2
Information obtained from the application of Rietveld analysis on XRPD patterns of Zn/Cr/O catalysts

	$ZnCr_2O_4$	Calcined at 623 K	Calcined at 803 K
Zn/Cr (nominal)	0.5	0.78	0.78
a (Å)	8.3264 (4)	8.36 (1)	8.35 (1)
Crystal size (Å)[a]	—	30	50
ZnO (wt%)	—	—	9.2
$ZnxCr_{2/3(1-x)}O$ phase			
x	0.25	0.34	0.29
Zn_{tet}	0.25	0.23	0.22
Zn_{oct}	—	0.11	0.07
Cr_{oct}	0.5	0.44	0.47

[a] From Scherre equation.

4.2. Zeolites and microporous materials

As is known well, zeolites constitute a class of crystalline aluminosilicates with intra-lattice porosity in the range 0.5–1 nm. The possibility to get zeolites in acid form, together with the high thermal stability and the shape-selective properties (related to the microporous structure) of these materials, renders them particularly suitable for being used in many of the catalytic processes typical of refinery and petrochemical industry. After the discovery of routes of synthesis which allow to partly replace framework Si(Al) atoms with transition elements (Ti) or to create new types of frameworks (e.g. aluminophosphates), interesting opportunities exist also for the application of microporous materials in catalytic reactions involving fine chemicals.

X-ray diffraction is widely used for characterizing this type of materials; especially in the patent literature, the XRPD pattern constitutes the main fingerprint for material identification. The framework structure of a large part of the microporous materials synthesized up to now has been determined by applying X-ray diffraction techniques. In the more recent years, parallel to the development of Rietveld analysis, the structure determination has been attempted successfully using XRPD data.

The XRPD pattern of a given crystalline phase is sensitive to framework composition (abundance of Si, Al or other elements in the tetrahedral sites), type of cations counterbalancing the framework charge, possible pore filling (organic or metallorganic molecules, metal clusters) and lattice disorder (stacking faults, intergrowth).

An example of wide application of XRPD is illustrated in the following, which concerns a family of porotectosilicates known as ‘pentasils’.

The framework structure of the members of this family, based on five-membered rings of $[(Si,Al)O_4]$ tetrahedra, can be described in terms of two different stackings of layer pairs related by an inversion center and mirror symmetry, respectively [9]; they are usually referred to with MFI and MEL acronyms, respectively [10]. The MFI framework structure was determined by single crystal X-ray analysis [11]; the structure of MEL was determined subsequently from XRPD data [12].

The high interest for the application of this class of materials in heterogeneous catalysis is related to the high selectivity expected, due to the peculiar pore structure (two intersecting channels with ca. 5.5 Å aperture).

ZSM-5 aluminosilicate [11] and TS-1 titanosilicate [13] are the most popular MFI-type analogs, together with the borosilicate (BOR-C [14]), gallosilicate [15] and pure silica (Silicalite-1 [16]) analogs. The synthesis of pure MEL-type structures is much more difficult, MFI/MEL intergrowth being obtained in most cases.

Pentasils are high silica materials (accordingly, the pure silica MFI [16] and MFI/MEL [17] analogs can be synthesized) with only few percent framework Si replaceable by other elements. This makes it difficult to assess real framework composition, because the minor element could be present, totally or partly, as oxide or silicate impurity, not always easily detectable.

The main proof assessing framework incorporation comes from the evaluation of lattice parameters. In fact, when a given element, T, is present in the silica framework, a lattice expansion is expected with respect to the pure silica parent structure if the T–O distance (d_T) is larger than Si–O distance (d_{Si}); accordingly, lattice contraction is expected in the opposite case. By admitting that no variation of bond angles on oxygen atoms occurs (which sound to be reasonable for low content of T element), the volume, V_x, of a unit cell containing an x molar fraction of T element can be related to the unit cell volume of the pure silica parent structure, V_{Si}, through the equation [14]:

$$V_x = V_{Si}[1 - (d_T/d_{Si})^3]x.$$

Accurate measurements of unit cell parameters from XRPD data have clearly shown small but significant lattice expansion (for Al-, Ti- and Ga-MFI analogs) or lattice contraction (for B-analogs). Moreover, a linear dependence of unit cell volume on the extent of framework incorporation of T element was observed, as predicted by the above equation.

Some experimental data were obtained by applying the conventional procedure based on a least-squares fit to the *d* values of *hkl* reflections selected in the XRPD pattern. Other data come from the application of Rietveld analysis. In the latter case, standard deviations 2–3 times lower were obtained with respect to the former procedure [18]. A Rietveld plot typical of a MFI-type material is reported in Fig. 3. It is evident from Fig. 3 the very good fit with experimental XRPD profile, which accounts for the high accuracy reached in evaluating unit cell parameters.

Starting from the slope of unit cell volume variation experimentally observed for a given element T and attributing to d_{Si} the value typically found in several crystal structure determinations of zeolites (1.61 Å), the value of d_T was derived by applying the above equation. The results obtained for some MFI analogs are summarized in Table 3. It must be remarked that the values of d_T agree very well with those found in oxides with tetrahedral coordination of the corresponding T element. These data constitute a strong evidence for framework incorporation of Ti, B, Al and Ga. Reasonable evidence exist also for Fe. Incorpora-

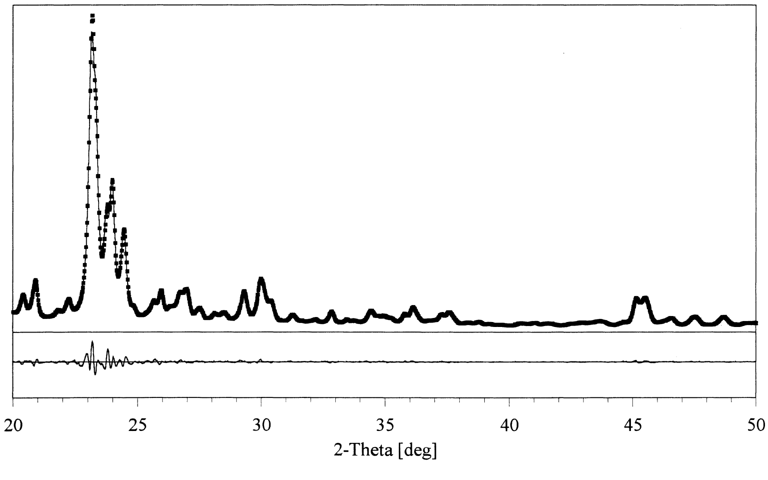

Fig. 3. Rietveld refinement plot for orthorhombic MFI zeolite. Experimental (■), calculated (———) and difference (lower) profiles.

Table 3
Evaluation of T–O distance (d_T) in substituted MFI-analogs from variation of lattice parameters

T	dT(Å)	Reference	Typical tetrahedral T–O distance (Å)
Ti	1.80	[18]	1.77–1.82
Ga	1.83	Unpublished results	1.80–1.83
Al	1.70	Unpublished results	1.71–1.75
B	1.46	[14]	1.43

tion of many other elements is claimed, especially in the patent literature, but not supported by adequate experimental evidence.

XRPD analysis remains the most powerful tool for characterizing the Ti-MFI analog, TS-1. This material possesses unique catalytic properties in many reactions involving hydrogen peroxide, which include the hydroxylation of phenol [19], the epoxidation of olefins [20], the oxidation of saturated hydrocarbons [21,22] and the synthesis of cyclohexanone oxime [23]. The catalytic properties depend on the peculiar structure of Ti sites, which can vary their coordination numbers from 4 (anhydrous state) to 6 (in the presence of adsorbed polar molecules [24]).

The presence of extra framework Ti, even in small amount, is generally detrimental, because it may promote the decomposition of hydrogen peroxide, change the distribution of isomer products and increase byproducts (tar) production [25]. Therefore, the knowledge of the amount of framework and non-framework Ti is crucial for catalyst characterization. Taking advantage of a well-assessed correlation between unit cell volume and Ti content [18], the amount of framework Ti can be actually evaluated routinely by applying Rietveld analysis to XRPD data. Extra framework Ti is detectable in the XRPD pattern as crystalline TiO_2 even in a very small amount (0.3–0.5%). Much more complicated is the case of possible presence of amorphous titanosilicate species, especially if they contain tetrahedrally coordinated Ti, because spectroscopic techniques, such as DRS-UV–vis can easily detect extra framework octahedral Ti species but can distinguish between framework and non-framework tetrahedral species with more difficulty. However, by combining the results of XRPD (amount of framework Ti) and chemical analysis (overall Ti content), the presence of extra framework Ti can be established by difference with adequate reliability.

4.3. *In situ X-ray powder diffraction*

Most investigations on catalyst structure are carried out at room temperature and pressure, far from the conditions generally present in a catalytic reactor. On the other hand, the phase composition and the texture of the catalyst may change in the reaction condition, especially when the reaction temperature is very high.

For the above reasons there is much interest for application of XRPD by approaching as much as possible the real reaction condition. The increasing availability of intense X-ray sources (rotating anode and synchrotron radiation) and position sensitive detectors (linear and area detectors) are currently adding much impetus to the use of X-ray diffraction at elevated temperatures [26]. In the last years home-made special cells suitable for in situ XRPD investigations have been described in the literature. The cell hosting the catalyst sample generally allows to work at atmospheric pressure and is provided with a system for controlling the internal temperature and the flow rate of reactant gases; observation temperature as high as 800°C is reported. The cell is generally connected on-line to a gas chromatograph and a mass spectrometer for monitoring the product gases [27–29].

In situ XRPD was applied for understanding the behavior of some oxides as catalysts in the oxidative coupling reaction of methane [28–30]. In the case of conversion reaction of methane to synthesis gas catalyzed by $Eu_2Ir_2O_7$, in situ XRPD data have demonstrated that europium iridate itself is inactive, the active phase being constituted by nanoparticles of iridium metal supported on Eu_2O_3, resulting from decomposition of $Eu_2Ir_2O_7$ occurring at the reaction temperature [27]. Another interesting application of the technique concerns the study of iron catalyst in Fischer–Tropsch synthesis [28].

Restrictions exist which make it very difficult to realize a cell for working at a pressure significantly higher than that of the atmospheric pressure. Another critical problem concerns the quality of experimental data. In fact, thermal expansion phenomena, possible melting and/or phase transformations, affect to some extent the geometry of the sample under examination with resulting lower accuracy of collected data (in terms of angular position and relative intensity of the peaks in the XRPD pattern).This makes it hazardous to compare quantitatively spectra collected at different temperatures and/or different times. Finally, a limitation can concern the timescale of the experiment, when the kinetic of the structure evolution of the catalyst under examination is fast, compared to the time required for XRPD data collection. In some cases, the latter problem can be overcome by using high energy sources, in such a way to reduce the required observation time. In this direction, more and more opportunities should come from the use of synchrotron radiation.

5. Future prospects

X-ray diffraction is a well-consolidated technique which should maintain its relevance in the catalyst characterization also in a long-term perspective. A growth of applications is expected in the near future concerning Rietveld analysis, which is demonstrated to be a powerful tool for structure characterization of polycrystalline materials. Actually, many efforts are being carried out for implementing computer programs, especially in the direction of ab initio structure determination. In some cases, the additional use of advanced tools for structure modeling (e.g. "Catalysis" package, from MSI) can be very useful for a successful approach to structure determination. As shown by the examples described above, the improvement of the information obtainable by taking advantage of the full profile of XRPD pattern is enormous.

The interest for in situ XRPD is expected to grow, especially if the features of apparatus (high temperature cell) will be improved allowing to approach real reaction conditions.

References

[1] R.A. Young (Ed.), The Rietveld Method, Oxford University Press, Oxford, 1993.

[2] H.P. Klug, L.E. Alexander, X-ray Diffraction Procedures for Polycrystalline Materials, Wiley, New York.

[3] H.M. Rietveld, J. Appl. Crystallogr. 2 (1969) 65.

[4] G. Malmros, J.O. Thomas, J. Appl. Crystallogr. 10 (1977) 7.

[5] R.A. Young, P.E. Mackie, R.B. Von Dreele, J. Appl. Crystallogr. 10 (1977) 262.

[6] G. Natta, in: P.H. Emmet (Ed.), Catalysis, vol. III, ch. 8, Reinhold, New York, 1953.

[7] G.D. Piero, F. Trifirò, A. Vaccari, Chem. Soc. Chem. Commun. (1984) 656.

[8] E. Errani, F. Trifirò, A. Vaccari, M. Richter, G. Del Piero, Catal. Lett. 3 (1989) 65.

[9] G.T. Kokotailo, W.M. Meier, in: R.P. Townsend (Ed.), Properties and Applications of Zeolites, Spec. Publ. No 33, vol. 133, The Chemical Society, London, 1980.

[10] W.M. Meier, D.H. Olson, Atlas of Zeolite Structure Types, Butterworths, London, 1987.

[11] D.H. Olson, G.T. Kokotailo, S.L. Lawton, W.M. Meier, J. Phys. Chem. 85 (1981) 2238.

[12] B.H. Toby, M.M. Eddy, C.A. Fyfe, G.T. Kokotailo, H. Strobl, D.E. Cox, J. Mater. Res. 3 (1988) 563.

[13] G. Perego, G. Bellussi, C. Corno, M. Taramasso, F. Buonomo, A. Esposito, in: Y. Murakami, A. Iijima, J.W. Ward (Eds.), Proceedings of the Seventh International Conference on Zeolites, Tokyo, 1986, Elsevier, Amsterdam, 1987, p. 129.

[14] M. Taramasso, G. Perego, B. Notari, in: L.V.C. Rees (Ed.), Proceedings of the Fifth International Conference on Zeolites, Naples, Heyden, London, 1980, p. 40.

[15] S. Hayashi, K. Suzuki, S. Shin, K. Hayamizu, O. Yamamoto, Bull. Chem. Soc., Japan 59 (1985) 52.

[16] E.M. Flanigen, J.M. Bennett, R.W. Grose, J.P. Cohen, R.L. Patton, R.M. Kirchner, J.V. Smith, Nature (London) 271 (1978) 512.

[17] D.M. Bibby, N.B. Milestone, L.P. Aldridge, Nature (London) 280 (1979) 664.

[18] R. Millini, E.P. Massara, G. Perego, G. Bellussi, J. Catal. 137 (1992) 497.

[19] A. Esposito, M. Taramasso, C. Neri, F. Buonomo, UK Patent 2 116 974 (1985).

[20] M.G. Clerici, G. Bellussi, U. Romano, J. Catal. 129 (1991) 159.

[21] D.R.C. Huybrechts, L. De Bruycker, P.A. Jacobs, Nature 345 (1990) 240.

[22] M.G. Clerici, Appl. Catal. 68 (1991) 249.

[23] P. Roffia, G. Leofanti, A. Cesana, M. Mantegazza, M. Padovan, G. Petrini, S. Tonti, V. Gervasutti, R. Varagnolo, Chim. Ind. (Milan) 72 (1990) 598.

[24] M.R. Boccuti, K.M. Rao, A. Zecchina, G. Leofanti, G. Petrini, in: C. Morterra, A. Zecchina, G. Costa (Eds.), Structure and Reactivity of Surface, Elsevier, Amsterdam, 1989, p. 133; A. Zecchina, G. Spoto, S. Bordiga, A. Ferrero, G. Petrini, G. Leofanti, M. Padovan, in: P.A. Jacobs, N.I. Jaeger, L. Kubelkova, B. Wichterlova (Eds.), Zeolite Chemistry and Catalysis, Elsevier, Amsterdam, 1991, p. 251; F. Geobaldo, S. Bordiga, A. Zecchina, E. Giamello, G. Leofanti, G. Petrini, Catal. Lett. 16 (1992) 109.

[25] U. Romano, A. Esposito, F. Maspero, C. Neri, M.G. Clerici, Chim. Ind. (Milan) 72 (1990) 610.

[26] D.D.L. Chung, P.W. DeHaven, H. Arnold, D. Ghosh, X-ray Diffraction at Elevated Temperatures. A Method for in situ Process Analysis, VCH Publishers, New York, 1992.
[27] R.H. Jones, A.T. Ashcroft, D. Waller, A.K. Cheetham, J.M. Thomas, Catal. Lett. 8 (1991) 169.
[28] G.D. Moggridge, T. Rayment, R.M. Lambert, J. Catal. 134 (1992) 242.
[29] H. Jung, W.J. Thompson, J. Catal. 134 (1992) 654.
[30] G.D. Squire, H. Luc, D.C. Puxley, Appl. Catal. A 108 (1994) 261.