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Gaining insight into structural changes with dynamic diffraction methods[☆,1]

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Abstract

Application fields of dynamic diffraction methods are highlighted. Dynamic X-ray or neutron diffractometry is a well-suited method for the study of structural changes in ordered materials, including crystalline solids, supported catalysts, liquid crystals, lipid structures and monolayers. The different forms of graphical representation of the extensive data are presented.

Keywords: Catalysis; Liquid crystal; Lipid; Neutron diffractometry; X-ray diffractometry

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1. Introduction

Dynamic processes are important in chemistry. With chemistry being the art of converting compounds in a controlled way into other compounds, it is clearly of interest to study the mechanisms of chemical reactions to better understand the basic underlying principles. This knowledge enables us to plan and design syntheses of new compounds or to improve existing syntheses. For the time-dependent study of the properties of chemical compounds, structural as well as energetic and electronic aspects have to be considered.

Thermal analysis and calorimetry cover energetic changes, and with spectroscopy, electronic properties can be investigated. The structure of reacting compounds is available through diffractometric experiments. When these are performed in a dynamic, i.e. time-dependent, way, they can ideally supplement thermoanalytical and spectroscopic techniques.

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[1] Dedicated to Professor Dr. W. Dannecker on the Occasion of his 60th Birthday.

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Diffraction methods are mostly non-destructive and can be applied on a sufficiently short time-scale. In principle, all ordered materials can be studied with these techniques. The applications are not limited to crystals, but include also liquid crystals, lipid structures, biomaterials, supported catalysts and monolayers. Here, only X-ray and neutron diffraction shall be considered. Electron diffraction methods, together with electron microscopy, are beyond the scope of this article.

Application fields of dynamic diffractometry are discussed below. The different methods of graphical representation of the obtained extensive data are demonstrated on the same data set.

2. Dynamic diffractometry

A comparatively easy method of initiating chemical reactions is to change the temperature. This led to the development of time- and temperature-resolved diffractometry, which was applied to solid state chemistry and metallurgy in the 1950s and 1960s (for an extensive literature survey see Ref. [1]). A reference from 1970 lists 99 different heating stages [2].

In those days, diffractograms were obtained as chart recorder output, making their evaluation both tedious and inexact. Only slow reactions of well crystallized (mostly inorganic) samples were investigated on a time-scale of minutes between the single diffractograms. Three developments spurred the expansion of dynamic diffraction methods into biological sciences, polymer science and catalysis: the development of fast position-sensitive detectors, the accessibility of synchrotron radiation, and, last but not least, the wide availability of fast computers.

Position-sensitive detectors are capable of recording a diffractogram in a few seconds or less, which is very fast compared to some minutes for conventional counters [3]. Synchrotron radiation is a much brighter light source than X-ray tubes, and therefore yields a substantial reduction in measuring time [4, 5]. Computers can be used for equipment control, fast data recording, data storing and data evaluation. Without their help it would be impossible to measure and evaluate the huge amounts of data recorded during a dynamic diffraction experiment. These tools now allow the study of fast processes (time-resolution in the order of ms and below) and poorly crystallized samples, like polymers or biomaterials. Consequently, the published literature on dynamic diffraction experiments is now rather extensive [1].

Neutron diffractometry can be better suited for the investigation of solids due to fundamental differences in the scattering behaviour of the elements in both methods. Hydrogen atoms can be localized, and neighbouring elements can be distinguished. This is important in mineralogy for the analysis of alumosilicates, where aluminium and silicon are almost indistinguishable with X-ray diffractometry. For a comparison of both techniques see Ref. [6]. Because of easier accessibility, X-rays are used more frequently for structural investigations, be it static or dynamic.

Because the crystal structure of every compound is unique, the diffractogram is characteristic for the compound, and can be used for identification. Fig. 1 shows which information can be extracted from a diffraction peak [7]. The peak positions allow the

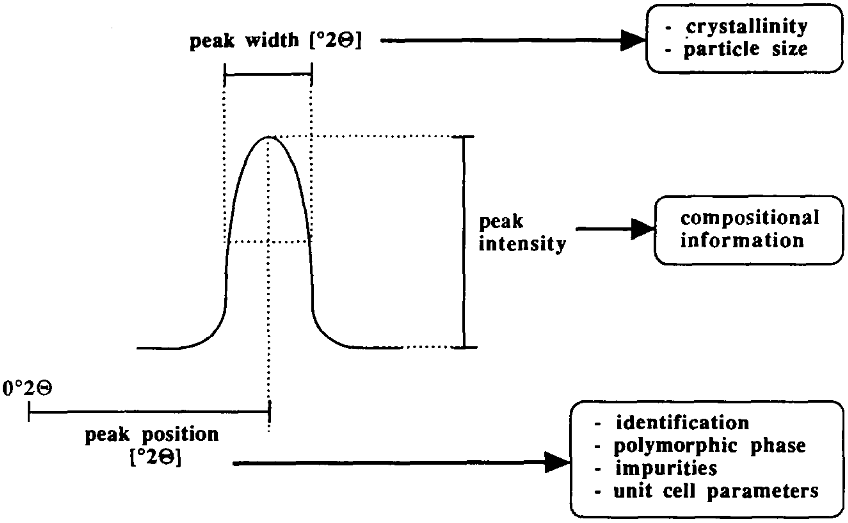

Fig. 1. Analysis of a diffraction peak. From the parameters width, intensity (height or area) and position, extensive structural and compositional information can be derived.

determination of the unit cell parameters $(a, b, c, \alpha, \beta, \gamma)$. The Rietveld method was derived to refine structural parameters, i.e. the positions of all atoms, from a powder diffractogram [8]. However, a structure model is necessary before the structure refinement can be started. The peak width is indicative of the crystallinity of the sample, and can also be used to determine the particle size.

Important for all studies related to quantification of the reactants are the peak intensities, measured either as peak height or peak integral. In mixtures, the intensity, after some usually minor corrections [9], is proportional to the mass fraction of the corresponding compound. Therefore, the composition of a reactive mixture can be determined by measuring the intensities of educt and product peaks. The evaluation yields all phases present in their relative amounts. Due to their different crystal structures, polymorphic phases can be distinguished, which makes it possible to study solid–solid phase transformations which can be associated with only small enthalpy changes.

There is a problem with amorphous phases, which cannot usually be detected or quantified by diffractometry, due to the absence of long-range order. In this case, other methods must be applied, or their relative proportion must be estimated indirectly.

The wealth of information which is accessible from a diffractogram leads to widespread application, especially in solid state chemistry. By introducing time and/or temperature as experimental variables, dynamic processes can be studied.

The basic idea is demonstrated for a solid state reaction in Fig. 2. During the course of the reaction, which may be initiated by temperature or irradiation, X-ray (or neutron) diffractograms are continuously recorded. The educt phase shows three peaks in the observed angle interval. As the reaction proceeds, the educt peaks shrink while

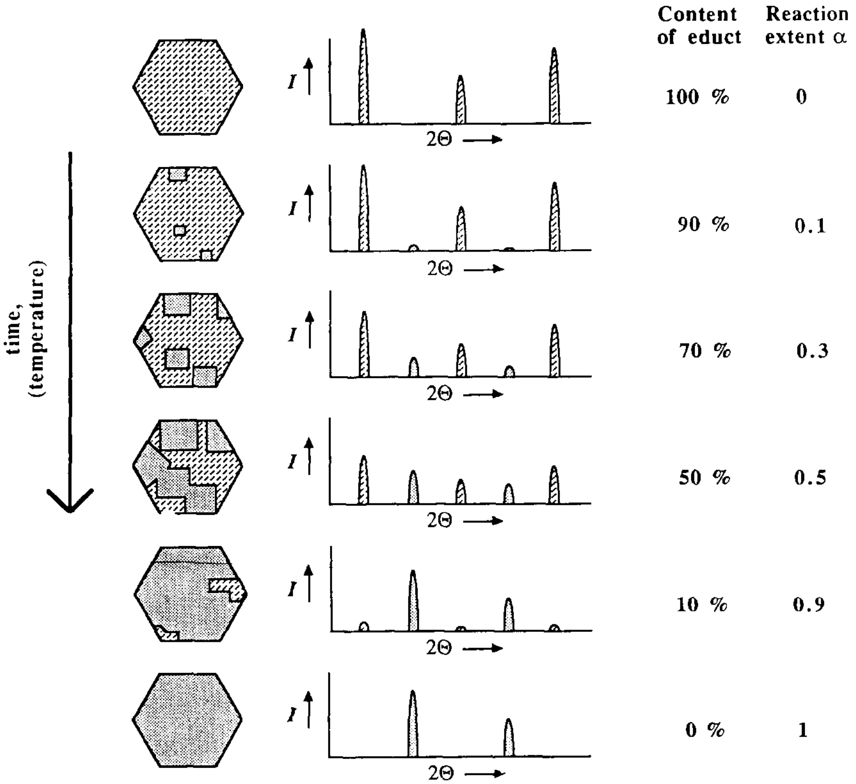

Fig. 2. Schematic picture of a dynamic X-ray experiment. A solid state reaction is monitored with time. The quantitative evaluation of the intensities of the three educt and two product peaks yields the sample composition, which can be converted into the reaction extent α.

two product peaks appear. The evaluation of the peak integrals allows the calculation of the contents of educt and product phases in the sample, displayed on the right of Fig. 2. This can be easily converted into the reaction extent α.

This information of sample composition during a reaction allows one to determine the reaction path and to draw conclusions about the possible mechanism. Intermediate phases can be quantitatively detected, and phase transformations before, during or after reactions can be followed. In principle, reaction kinetics can be calculated [9, 10].

3. Graphical representation of dynamic diffraction data

The data volume gathered in an experiment is large. A rough estimate shows that for a typical experiment with 1 min per diffractogram within an angular range of 10°2Θ (resolution 0.02°2Θ), 500 data points per minute are recorded. For a one-hour long experiment, 30000 data points must be stored, each of which consists of angle, intensity, time and temperature. This easily adds up to a 500 KByte data set. For high speed studies (1 diffractogram per second) or long-term experiments, an even larger data volume must be handled. This illustrates the requirement for computerized data recording and evaluation.

To present the extensive results of a dynamic experiment in an adequate form, different methods have been developed. Four methods described in the literature are reviewed in Figs. 3–6. A three-dimensional view of a set of diffractograms (Fig. 3) is often found in the literature. Many diffractograms can be conveniently displayed in a single graph. Single peaks can be followed to gain an impression of the processes taking place. Unfortunately, small peaks are frequently hidden behind larger ones, and changes in peak positions are difficult to detect.

In Fig. 4, a set of diffractograms is displayed as a sequence. For a temperature-dependent experiment, the reaction temperature can be followed for each diffractogram. This means, for example, that diffractogram 1 was recorded between $t = 0$ min and $t = 6$ min. The corresponding temperature range can then be read from the lower left scale. Changes in peak positions are easy to follow and no peaks are covered, but the number of diffractograms to be displayed is limited by the maximum size of the graph to approx. 20, even when very large peaks are cut off (scans 6 and 7).

Fig. 5 resembles an old-fashioned high-temperature X-ray experiment, where a film is moved through the camera while the temperature is raised. On an X-ray film, the peak intensity is characterized by the blackness and width of a line. Here, a computer evaluation of the single diffractograms can be used to extract all peaks. The line thickness is then selected to represent the peak intensity. The best representation is achieved with a line thickness proportional to the logarithm of the intensity, as with an X-ray film. Again, changes in peak positions can be followed, and overlapping peaks, which were separated by the computer, can be identified (note the peak splitting in the product phase). A drawback is the limited resolution of line thickness. Consequently, this representation is best suited for a quick overview to determine which phases are formed in which temperature interval, and whether intermediates are formed. Finally, an intensity contour plot is shown in Fig. 6. This is advantageous for large sets of scans.

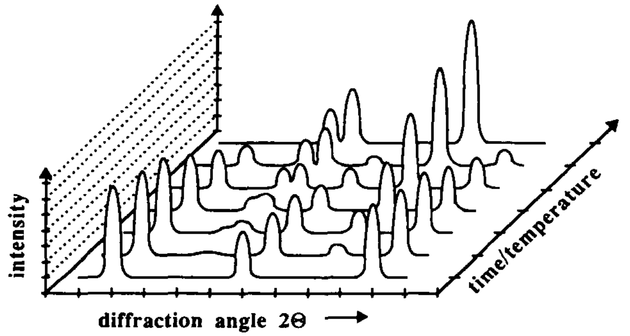

Fig. 3. A three-dimensional representation of dynamic X-ray data. Smaller peaks may be hidden behind larger ones. Changes in peak angles are not easily recognisable.

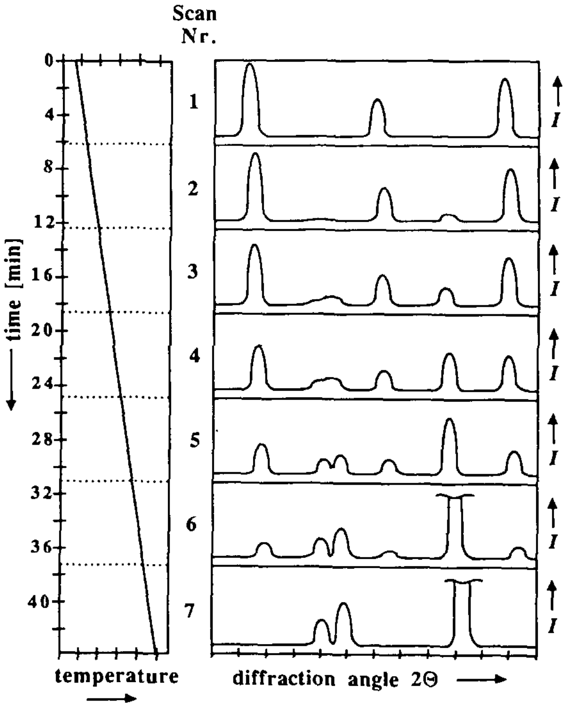

Fig. 4. X-ray diffractograms in a vertical array. The time and temperature for each scan can be derived from the graph on the left. This representation is limited to small numbers of scans.

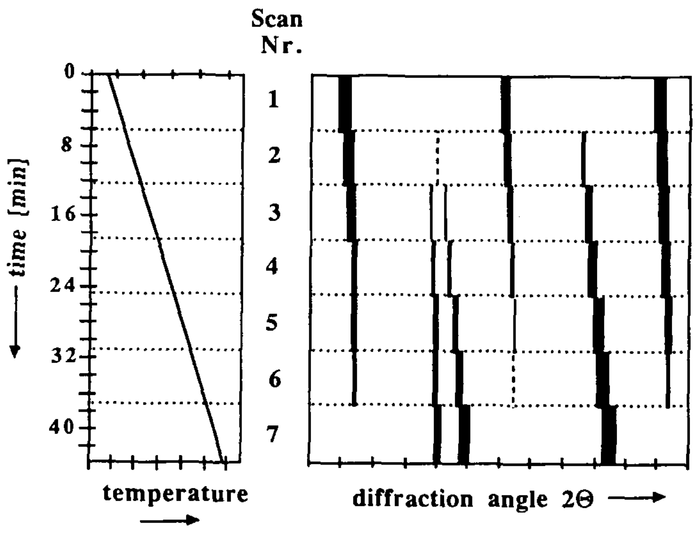

Fig. 5. Heating X-ray camera analogue plot. The computer evaluation of the raw data yields a number of peaks. With a width roughly proportional to the logarithm of the intensity, the lines represent the individual peaks.

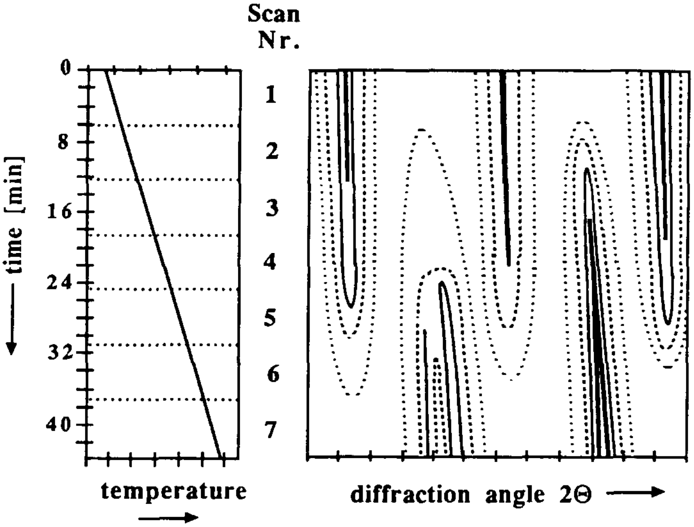

Fig. 6. Intensity contour plot of dynamic X-ray data. This representation is especially good if many scans were recorded.

4. Applications of dynamic diffraction methods

In principle, every reaction or transformation in which an ordered phase is involved can be examined by diffractometry. Thus, not only crystalline solids are suitable, but also liquid crystalline phases and structured biological material. Employing the very intense synchrotron radiation, it was even possible to follow structural changes in lipid monolayers on a water surface! In the following, we will consider some major fields of application [1].

Fig. 7 comprises some major applications of dynamic diffractometry. As outlined above, a solid state reaction can be conveniently followed. Applications are in materials science (preparation of ceramics, high-temperature superconductors), investigation of decomposition reactions, and in fundamental research studying reaction mechanisms of solid state reactions. A special case is the examination of processes on surfaces, important in corrosion and in the preparation of thin solid films. Polymorphic phase transitions can be important for judging the storage stability of pharmaceuticals (which are often desired in a specific polymorph). They are also important in polymer research (glass transitions) and research on liquid crystals. Because the reactivity depends strongly on the polymorphic phase present, it is generally necessary to identify the phases present in a solid reaction mixture.

Heterogeneous catalysis is still not very well understood, despite extensive research efforts [11, 12]. In recent years, some researchers started to use dynamic diffractometry to look at the changes in the catalyst during preparation and during the catalytic process [13–16]. In Fig. 7, a supported catalyst is displayed. The small precursor particles are reduced to yield the active catalyst, e.g. reduction of iron oxide to iron.

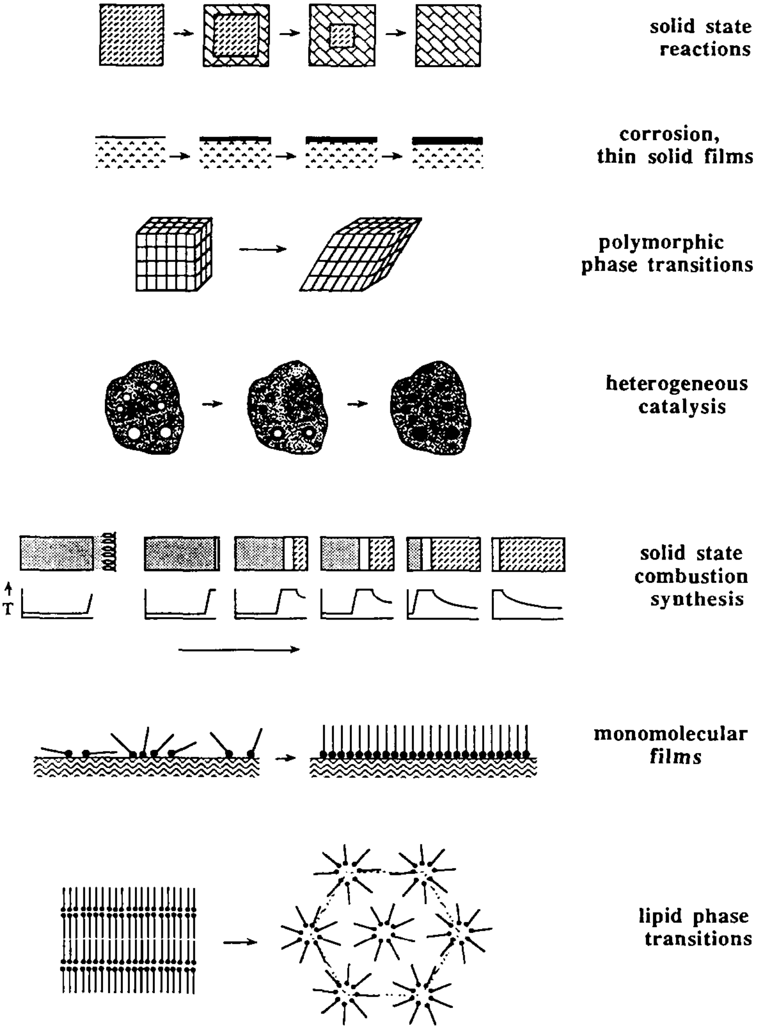

Fig. 7. Some major fields of application of dynamic diffraction methods. Applications can be found in solid state chemistry, catalysis, surface chemistry and biophysics/biology.

A novel application is the examination of solid state combustion synthesis. In this reaction type, a mixture of reactants is intimately mixed and pressed to a pellet. The reaction is started with a laser pulse or an electrically heated coil, as depicted in Fig. 7. The mixture begins to react, releasing so much energy that it becomes self-sustaining with a very hot reaction zone (1000–4000 K). The reaction zone moves through the pellet within seconds (approx. 1 $\mathrm{cm\,s^{-1}}$); leaving the reaction product behind. Synchrotron radiation was used to follow the reaction of titanium with carbon and nickel to form titanium carbide and a titanium–nickel alloy [17]. Because of the very fast reaction, one diffractogram was taken every 200 ms.

Biological materials are often poorly crystallized, and consequently are weak scatterers. This prevented the study of dynamic processes with conventional X-ray sources. After synchrotron radiation was applied to study these processes, the number of publications in this field has substantially increased [4]. Biophysical and biological investigators are now major users of synchrotron sources. The main research areas are the study of the physicochemical behavior of lipids (long-chain surfactants like phospholipids), which are the basic constituents of biological membranes [18, 19], the study of protein crystals and enzyme–substrate interactions [20], and research on biological materials like muscles and cell constituents (see Ref. [4]). In the following, the study of lipids is described.

A basic property of lipid molecules is the ability to form monomolecular films, “monolayers”, on liquid–gas surfaces. The adsorbed molecules behave like a two-dimensional gas, liquid or solid, depending on how much area per molecule is available. When changing from one state to the other, for example by compressing the film, a phase transition occurs. These films are subject to intensive research with many techniques. One problem is the small amount of substance encountered in a monolayer. By using the intense synchrotron radiation, it has been possible to obtain diffraction peaks from monolayers, and to draw conclusions on the molecular orientation [21].

Pure lipids often form liquid crystalline phases. The temperature-dependent phase relations are important for modelling biological membranes, which are lipid double-layers. Thermodynamic and kinetic aspects are of interest. Because lipids are capable of forming numerous different phases which are often metastable, a method like X-ray diffractometry has to be employed. In Fig. 7, a phase change from a lamellar to a hexagonal phase is shown. The kinetics of such transitions can now be studied on a time-scale of ms [22].

5. Conclusions

With dynamic diffraction methods, it is possible to study a wide variety of chemical processes. Possible applications can be found in any field of chemistry in which ordered phases are present. The development of fast detectors and the accessibility of synchrotron radiation has considerably enhanced the performance of this method. Because more and brighter synchrotrons are built, the possible time-resolution will further increase. This opens new prospects for the study of biological processes like enzyme–substrate interaction, which could be studied on a time-scale of ms or μs. For well-crystallized samples from organic and inorganic chemistry, better resolved and even faster processes will be studied. Sub-nanosecond diffraction on crystals has already been reported [23].

Without a synchrotron radiation source, interesting studies are possible nevertheless. Frequently, a time-resolution in the order of minutes is sufficient to study solid state reactions. This can be accomplished with a computer-controlled powder diffractometer and a heatable sample holder. As the fundamentals of dynamic X-ray diffractometry are now well known, and the basic applicability has been demonstrated numerous times, it is expected that the number of applications will continue to increase in the future.

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