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Solid – gas reactions in synthetic chemistry: what can we learn from reaction pathways?

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The knowledge of reaction pathways in the preparation of solids is usually rather scarce, which hinders synthesis planning and process control. This is particularly true for metastable compounds, which are a challenge for chemical synthesis, especially in the solid state. *In situ* studies can help in exploring the energy landscape around their local minimum by investigating formation and decomposition. Screening the multi-parameter space in synthetic chemistry is much more efficient using *in* as compared to *ex situ* methods. Studying solid – gas reactions *in situ* is demanding due to the oftentimes harsh conditions as for temperature and gas pressure. Examples are given for a variety of solids and applications, *e.g.*, metal hydrides (hydrogen storage, hydrogenation – decomposition – desorption – recombination), intermetallics (heterogeneous catalysis), metal nitrides, nitride oxides and oxides (magnetic materials, photocatalysts). Many new metastable compounds with intriguing properties were discovered by such *in situ* studies in flowing or static gas atmosphere (H_2, Ar, NH_3, air) at elevated pressures and temperatures using a variety of *in situ* methods such as X-ray and neutron powder diffraction, thermal analysis, environmental scanning electron microscopy, Raman, NMR, UV-VIS and X-ray absorption fine structure spectroscopy. The potential of unravelling reaction pathways of solid – gas reactions for improving syntheses and controlling chemical processes is demonstrated.
The bibliography includes 48 references.

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Contents

1. Introduction 275
2. Formation and decomposition of metal hydrides 276
3. Synthesis of metastable metal nitrides, nitride oxides and oxides 278
4. Reactions on surfaces: oxidation of alloys and heterogeneous catalysis 279
5. Elements: black phosphorus as an example 279
6. Conclusion and outlook 279

1. Introduction

The synthesis of solids comes in many variants. Methods may include harsh reaction conditions such as high temperature and high pressure, or try to avoid them and work close to ambient conditions, which is often called soft chemistry or *chimie douce*. Chemists may choose from diverse synthesis techniques, *e.g.*, precipitation from solution, solid – gas and solid-state reactions, reactions in salt or metal melts, chemical vapour transport (CVT), chemical vapour deposition (CVD), solvothermal methods, topotactic reactions, self-propagating reactions or decomposition of precursor compounds, just to name a few. Most of them are used in an explorative way by cycling between synthesis attempt → characterization → change in parameters → new synthesis attempt, *etc*. Such a half-empiric evolutionary approach is often led by more or less educated guesses rather than sound knowledge and reason. This is in stark contrast to the well-developed theory and methodology of organic chemistry, as employed in chemical retrosynthesis.[1] Such a strict synthesis planning is hampered in the case of solid-state chemistry by the fact that, in general, little is known about the basic steps of the formation of solids. This problem of solid-state chemistry has been well known for many decades and it was argued that without the knowledge of reaction processes they cannot be controlled or utilized in an efficient way.[2] Therefore, *in situ* studies revealing reaction pathways are highly desirable and yield a wealth of information useful for planning and optimization of preparation procedures. They provide a feedback loop between synthesis and characterization and allow higher efficiency in

Prof. Dr. Holger Kohlmann. Research interests are solid-state chemistry and crystallography. The research group of Prof. Dr. Holger Kohlmann uses explorative approaches for the synthesis of new solids and functional materials with a focus on intermetallic compounds and metal hydrides. They also try to get a detailed understanding of reaction pathways at the level of the most basic steps of the formation of solids by *in situ* methods (X-ray and neutron diffraction, thermal analysis, Raman spectroscopy), in order to make synthesis planning more efficient. In situ methods are also applied for the improvement of common synthesis reactions and technical processes.
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exploring the multi-parameter space of synthesis conditions. Moreover, obviously, they also provide information about the properties of solids at non-ambient temperatures, which are often insufficiently studied. However, due to technical complications of investigating solid under sometimes extreme conditions, the number of such *in situ* studies is limited.

Solid–gas reactions play an important role in many areas of chemistry. They are at the heart of the synthesis of solids in chemical laboratories and the industry alike for a wide variety of compounds. Moreover, they govern many technically relevant processes, *e.g.*, ore smelting, gas storage, thermochemical energy storage, heterogeneous catalysis, and oftentimes the corrosion and degradation of functional materials. A deeper insight into the pathways of such reactions is, therefore, expected to contribute to many different areas of solid-state sciences.

This contribution is not meant to be a comprehensive review on solid–gas reactions, but will rather give only a few examples in which the knowledge of reaction pathways has helped to understand formation, use and wear of solid materials. They are chosen with individual bias and focus on real-time *in situ* studies. Instrumental aspects, however, are only briefly mentioned. They are to be found in recent reviews on *in situ* techniques, such as diffraction, thermal analysis and various spectroscopic methods.[3–9] Calculations based on quantum-chemical theories on the electronic structure and the thermodynamic stability of products and possible intermediates were not covered either in this mini-review for reasons of conciseness and focus, but of course they are often a very valuable complementary source of insight.

2. Formation and decomposition of metal hydrides

Metal hydrides are a class of compounds with great chemical and structural diversity, ranging from ionic to covalent and metallic compounds. Many of them may be prepared by solid–gas reaction between a metal or intermetallic compound and hydrogen gas, often under increased pressure and temperature in a high-pressure device such as an autoclave. The temperature–pressure–time protocol allows many variations, which are often chosen empirically rather than based on well-founded knowledge. *In situ* methods have been employed on such reactions as a function of temperature, gas pressure and flow by various methods, the most popular being thermal analysis, X-ray and neutron diffraction.[3–6] The latter is indispensable for the location of hydrogen atoms within the crystal structure of metal hydrides in most cases. This is because the atomic form factor of hydrogen atoms for X-rays is rather low and thus X-ray diffraction patterns carry little information on hydrogen atom positions and occupation in compounds with more electron-rich atoms. Metal hydrides are often investigated with regard to hydrogen storage materials or hydrogen embrittlement, and unravelling reaction pathways of hydrogen uptake and release can contribute considerably to the development of new materials and the improvement of their performance.[3–6] Moreover, they provide a fertile playground for studying basic element–hydrogen interactions and for tuning physical properties of intermetallics by incorporation of hydrogen.

For reversible hydrogen storage in a single-phase compound, all its requirements must be met in this one phase at the same time. More degrees of freedom for adjusting properties to desired values arise when mixtures are considered. So-called reactive hydride composites (usually nothing else but ordinary mixtures of two or more hydrogen-containing compounds) allow fine-tuning of thermodynamic and kinetic properties with respect to hydrogen uptake and release, because they increase the compositional degrees of freedom of the system. Reaction pathways can be quite complex and *in situ* studies are a great help in understanding basic steps of hydride formation and decomposition. *In situ* synchrotron diffraction of $LiAlH_4-LiNH_2$ mixtures, which have an excellent weight efficiency for hydrogen storage, for example, allowed the direct observation of a new intermediate solid solution $Li_{4-x}Al_x(NH)_{2-2x}N_{2x}$ upon hydrogen release from the mixture. It forms from Li_2NH and Al, which are intermediates of the hydrogen release reaction themselves. Its structure, composition and thermal stability could be inferred from the *in situ* diffraction data as well.[10] Further reaction with aluminium yields Li_3AlN_2, which takes up hydrogen to form $LiNH_2+2\,LiH+AlN$. The discovery of the hitherto unknown transient solid solution $Li_{4-x}Al_x(NH)_{2-2x}N_{2x}$ was thus important for the understanding of the occurrence of AlN in the dehydrogenation–hydrogenation cycle of $LiAlH_4-LiNH_2$ mixtures.[10] This example shows the benefits of *in situ* experiments quite impressively. 1) Transient phases, which cannot be quenched and examined *ex situ*, may be identified and characterized; 2) *in situ* experiments often deliver a massive amount of data, whose analysis can bring a plentitude of useful information on crystal structure, dynamics, composition and other physical properties as a function of one or more externally controlled condition parameters. Both advantages of *in situ* over *ex situ* approaches will be demonstrated by the following examples as well.

A relatively new class of compounds, which is interesting for both hydrogen storage and basic bonding properties, are hydrides of Zintl phases.[11] Zintl phases are composed of group 1 or 2 and group 14–16 elements and obey simple electron-counting rules, called Zintl–Klemm rules, which explain the connectivity within the characteristic polyanions.[12–15] CaSi may serve as an example, where according to the Zintl–Klemm concept we assume a complete electron transfer from calcium to silicon atoms. The Si^{2-} ion is isoelectronic to sulfur and expected to exhibit similar structural feature as that element, *i.e.*, form two covalent bonds to silicon atom neighbours. In fact, CaSi shows infinite silicon atom zigzag chains as polyanions $^1_\infty[Si]$. CaSi reversibly takes up hydrogen under mild conditions and is thus of interest as a potential hydrogen storage medium.[16–21] Hydrogen is being reduced and incorporated into the crystal structure in distorted Ca_4 tetrahedra as hydride ions, H^-. In turn, the polyanions are being oxidized, which, according to the Zintl–Klemm rules, (see above) should increase their connectivity. In CaSi this leads to a limiting ionic formula $Ca^{2+}(Si^-)_{2/3}(SiH^-)_{1/3}H^-$ ($=\gamma$-$CaSiH_{4/3}$) and a novel polyanion, where all silicon atoms are three-binding (formally Si^-, isoelectronic to phosphorus). Three chains are now interconnected by forming new Si–Si bonds and the outer chains are decorated with hydrogen (Fig. 1). The polyanion in the hydride has thus a ribbon-like structure and may be described as $^1_\infty[(HSi_6H)^{4-}]$. Covalently bound hydrogen atoms show some defects, such that the formula is actually γ-$CaSiH_{4/3-x}$.[19–21] A similar behaviour was found also for the hydrogenation of SrGe and BaSn, which form

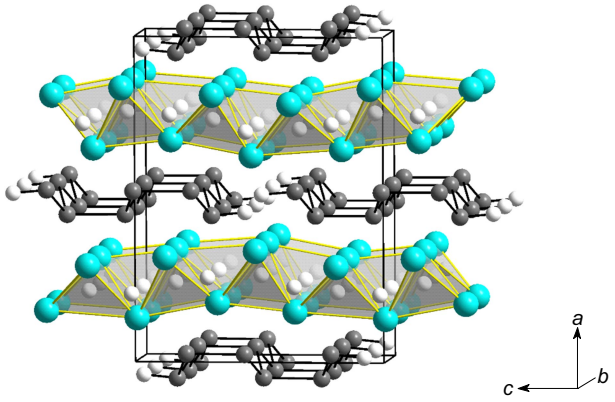


Figure 1. Crystal structure of γ-$AeTtH_{4/3}$ (Ae = Ca, Sr, Ba; Tt = Si, Ge, Sn); covalent bonds are marked by black lines between atoms, HCa_4 tetrahedra edges are marked by yellow lines; colour code: Ca (blue), Si (grey), H (white).

γ-$SrGeH_{4/3-x}$ and γ-$BaSnH_{4/3-x}$,[20] while other combinations of alkaline earth and tetrel atoms yield hydrides with different composition and polyanions like $SrSiH_{5/3}$, $BaGeH_{5/3}$ and $BaSiH_2$.[20–22]

The hydrogenation of $AeTt$ to γ-$AeTtH_{4/3}$ (Ae = Ca, Sr, Ba; Tt = Si, Ge, Sn) is reversible and involves hydrogen-poor α-$AeTtH_{<0.2}$ and β-$AeTtH_{\approx 0.5}$.[16–23] Interestingly, the different types of hydrogen atoms cannot be released independently from each other when decomposing γ-$AeTtH_{4/3}$. Hydrogenation–dehydrogenation cycles between α and β phases are very fast (80% yield in 1 min for 0.2 MPa pressure increase), which is of great importance for possible hydrogen storage applications. The hydrogen storage capacity of CaSi is moderate (1.9 wt.%), but the reversibility is very promising and it may serve as a model system for reversibly storing hydrogen in polyanions. The hitherto unknown hydrogen-poor phases α-$AeTtH_{<0.2}$ and β-$AeTtH_{\approx 0.5}$ (Ae = Ca, Sr, Ba; Tt = Si, Ge, Sn)[20,21,23] could not be quenched to ambient conditions and thus had to be investigated by *in situ* methods (Fig. 2). This example also nicely illustrates that the time resolution may be very important in such studies. The γ → β reaction from the hydrogen-rich to the hydrogen-poorer Zintl phase hydride could only be detected by *in situ* synchrotron diffraction, but was missed by *in situ* neutron diffraction (see Fig. 2).[23] This is due to the better time resolution of synchrotron as compared to neutron diffraction.[3,4]

Further examples where *in situ* diffraction revealed intermediates which could not be quenched and characterized *ex situ* are palladium-rich intermetallic hydrides[24] and Laves phases.[25–27] In these compounds, hydrogen atoms are usually distributed in octahedral or tetrahedral interstices in a statistical manner. Upon cooling, some show hydrogen ordering, which causes distortions of the Laves phase structures.[26–28] A very detailed study of different hydrogen species in the hydrogenation–dehydrogenation cycle of the hydrogen storage compound $ZrCr_2$, a cubic Laves phase, was possible by *in situ* NMR spectroscopy using a high pressure assembly. This allowed activation of the pristine intermetallic at 573 K under vacuum and subsequent reaction with hydrogen gas at room temperature while acquiring NMR signals.[29] Hydrogen gas, physisorbed hydrogen, and chemisorbed hydrogen could be distinguished, giving new insight into the reaction pathway of hydrogen uptake and also on the density of d states at the Fermi level of the metallic hydride, which were found to correlate with a change in NMR shift with progressing hydrogenation.[29]

Hydrogenation–dehydrogenation cycles play also a crucial role in the preparation of finely divided metal particles and the industrial fabrication of magnetic materials, as part of HIA (hydrogen induced amorphization) and HDDR (hydrogenation–decomposition–desorption–recombination) processes. The latter is used for improving the magnetic properties of permanent magnets like $SmCo_5$ or $Nd_2Fe_{14}B$. *In situ* investigations of the HDDR process, especially hydrogen uptake and release, helped adjusting the reaction for optimized phase purity and magnetic properties (coercivity).[30–32]

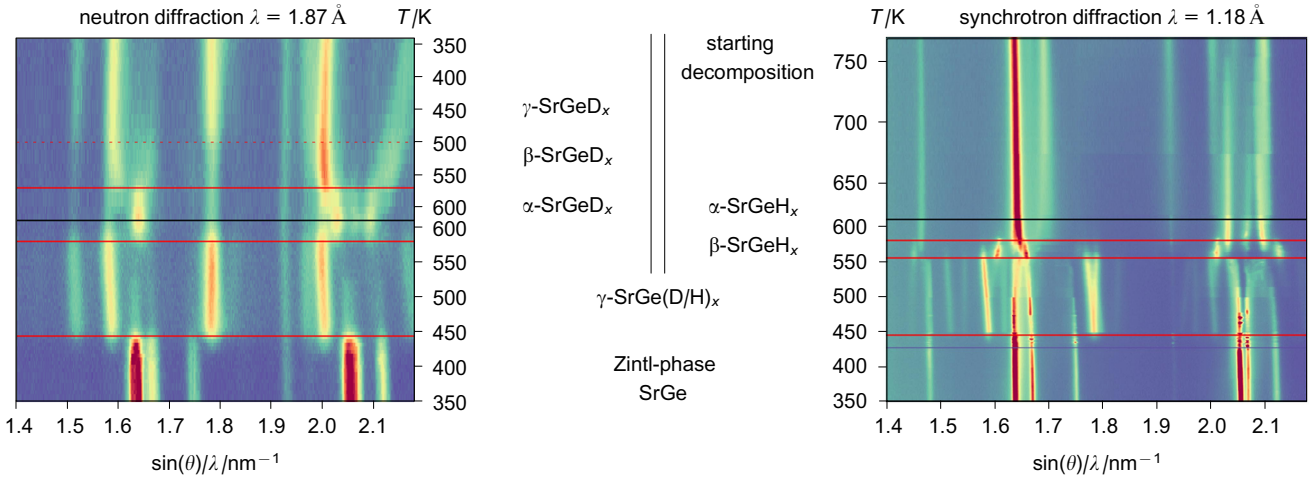


Figure 2. *In situ* neutron (left; time resolution 120 s) and synchrotron (right; time resolution 14 s) powder diffraction data of the reaction of the Zintl phase SrGe with 5.0(1) MPa of deuterium gas (left) and hydrogen gas (right), respectively.
Hydrogen content x = 0.2, 0.5, 1.2 for phases α, β, γ, respectively. Note the occurrence of β-$SrGeH_{0.5}$ is only recorded for the synchrotron experiment (right) due to better time resolution. Reprinted with permission from H.Auer, D.Wallacher, T.C.Hansen, H.Kohlmann. *Inorg. Chem.* **56**, 1072 (2017).[23] Copyright 2017 American Chemical Society.

3. Synthesis of metastable metal nitrides, nitride oxides and oxides

Many nitrides of the transition metals may be produced by solid–gas reaction between metals, metal halides or metal chalcogenides with gaseous flowing ammonia. Reaction pathways were revealed by *in situ* neutron powder diffraction and thermal analysis, which sometimes showed unexpected reaction sequences. The reduction of chromium(III) to chromium(II) and re-oxidation to chromium(III) in the formation of γ-CrN by ammonolysis of $CrCl_3$ or Cr_2S_3 is an example.[33] On the basis of these reaction pathways, synthesis procedures could be optimized in order to get single-phase materials. [33,34] By utilizing the knowledge of reaction pathways from similar experiments, an unprecedented phase purity was achieved for the metastable giant magnetic moment material α''-$Fe_{16}N_2$.[34]

Nitride oxides (also called oxynitrides) are currently being scrutinized for their potential applications as photocatalysts and anion conductors. The reaction of gallium oxide, Ga_2O_3, with flowing gaseous ammonia, NH_3, produces gallium nitride, GaN, which is of great interest for solid-state lighting, *i.e.*, for the use in blue light-emitting devices (LEDs).[35] Gallium nitride oxides have been proposed as intermediates; however, *in situ* EXAFS suggests a direct conversion of Ga_2O_3 with flowing gaseous ammonia, NH_3, to GaN.[36] For the production of thin films, *in situ* optical absorption edge measurements are very useful to govern and monitor the synthesis process, *e.g.*, for nitride oxide photocatalysts like TaNO (usually written TaON). A nice example is the controlled nitridation of Ta_2O_5 films by flowing ammonia gas, where process control was realized by *in situ* UV-VIS measurements (Fig. 3), and furthermore hints for a series of intermediate nitride oxide phases were found.[37]

Vanadium(III) oxide, V_2O_3, shows intriguing physical properties with a metal–insulator transition and an associated structural and magnetic transition. Upon cooling, the corundum-type paramagnetic metallic phase transforms to an antiferromagnetically ordered insulator with a monoclinic crystal structure.[38] V_2O_3 is used as a component in composite electrocatalysts for the hydrogen evolution reaction by alkaline water electrolysis.[39] A further polymorph in the cubic bixbyite type was found by heating vanadium trifluoride hydrate in a water-saturated gaseous mixture, for which canted antiferromagnetism was observed below 50 K.[40] Bixbyite type V_2O_3 is metastable and, therefore, it is a challenge to synthesize single phase. *In situ* neutron powder diffraction of the reaction of vanadium trifluoride hydrate with flowing $Ar/H_2/H_2O$ revealed an intermediate phase of vanadium fluoride with a lower water content around 700 K, which had to be heated slowly to around 900 K, in order to yield the desired metastable V_2O_3 in bixbyite type.[40,41] In this case, knowledge of the reaction pathway helped to avoid unwanted side reactions and to optimize the synthesis.

The uptake of hydrogen by chromium(IV) oxide, CrO_2, to form chromium(III) oxide hydroxide, CrOOH, is known to be reversible and to proceed topotactically.[42] In view of the numerous oxide hydroxides of other trivalent transition metals such as iron, one might expect intermediates of such a reaction. However, *in situ* diffraction did not show any signs for either non-stoichiometry or intermediates.[43]

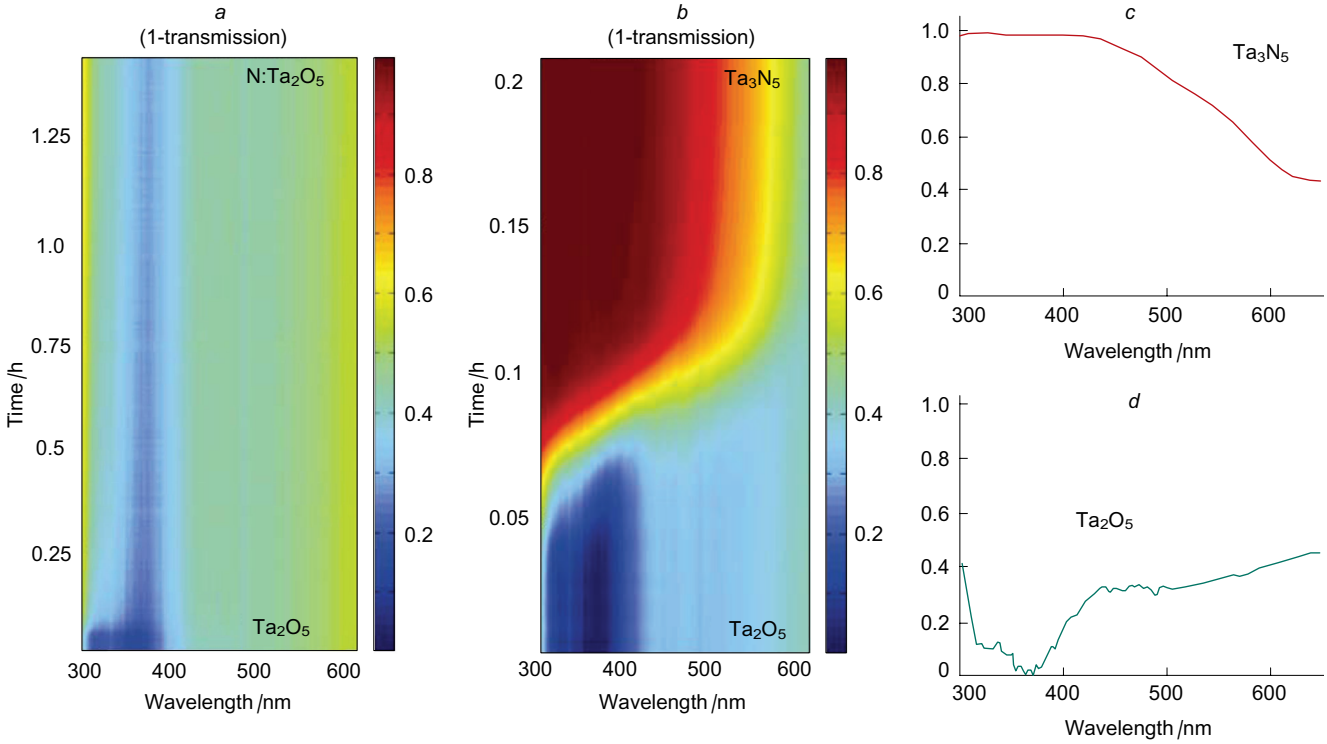


Figure 3. Monitoring the ammonolysis of tantalum oxide, Ta_2O_5, to tantalum nitride, Ta_3N_5.
Optical absorption edges of Ta_2O_5 thin film upon nitridation under flow of 100 mL min^{-1} argon in NH_4OH at 700 (*a*) and 800 °C (*b*); line-plot of Ta_3N_5 (*c*) and Ta_2O_5 (*d*) showing the starting and end points in (*b*). Reprinted with permission from A.Dabirian, H.van't Spijker, R.van de Krol. *Energy Procedia*, **22**, 15 (2012).[37] Copyright 2012 Elsevier Ltd.

4. Reactions on surfaces: oxidation of alloys and heterogeneous catalysis

In the preceding examples, bulk analysis of materials was in the focus of the investigations. Of course, for understanding synthesis, function and wear of materials, surface-sensitive studies are also of great importance. In this short review two areas of interest are briefly described: surface oxidation of alloys and tuning reactivity and sensitivity of heterogeneous catalysts.

Alloys used in industry are typically multi-phase components optimized for certain properties, *e.g.*, resistance to high temperatures or chemical inertness. Oxidation resistance is often a key issue, which may be influenced by minor alloying elements. Since the formation of thin oxide films is of interest, a combination of surface-sensitive methods is often applied for the *in situ* observation. The surface oxide growth characteristic of manganese containing nickel–chromium alloys for high-temperature applications in air were investigated *in situ* by thermal analysis and environmental scanning electron microscopy (ESEM). The formation of spinel-type $MnCr_2O_4$ crystallites on top of a chromium oxide layer could be observed from the beginning of the oxidation process and their size was found to depend on the initial manganese concentration. The formation of a triple-layer alloy$-Cr_2O_3-MnCr_2O_4$ is caused by the higher diffusion rate of manganese as compared to chromium both in the lattice and at the grain boundaries, which explains both the reaction pathway and the improved oxidation resistance at least for low partial pressures of oxygen.[44]

Another important area where surfaces are decisive is obviously heterogeneous catalysis. *In situ* infrared spectroscopy coupled with mass spectrometry (IR/MS setup) has been used to unravel reaction intermediates and pathways on catalyst surfaces for a number of catalytic reactions involving CO/H_2, $CO/H_2/C_2H_4$, NO/CO, CO_2/CH_3OH and photocatalytic reactions.[45] Such investigations give information on surface coverage, coordination modes, absorbed species, intermediate phases and reaction pathways, which might contribute to a rational design of new catalyst materials of high activity and selectivity.

Bimetallic CuZn catalysts were investigated *in situ* for their selectivity on electrochemical CO_2 reduction. *Operando* X-ray absorption fine structure (XAFS) spectroscopy measurements revealed that substitution of copper for zinc atoms occurs under reaction conditions. Copper particles close to ZnO lead to the production of CH_4 at the initial stages of the reaction. The progressive reduction of the ZnO species taking place under CO_2 reduction conditions and the subsequent formation of brass changed the selectivity to the generation of CO and H_2.[46] The nature of the active species and the relation of structure, reactivity and selectivity were accessible in depth only by these *in situ* investigations.

5. Elements: black phosphorus as an example

Although black phosphorus is the thermodynamically stable modification of phosphorus, its synthesis is not trivial and has been perfected only recently.[47] Several millimetre-long high-quality single crystals of orthorhombic black phosphorus can be grown by chemical vapour transport (CVT) reaction from red phosphorus and Sn/SnI_4 as transport agent. Question arose whether the crystallization yields black phosphorus directly or *via* intermediate compounds or other modifications.[48] An *in situ* neutron diffraction study made it possible to find the temperature window in which black phosphorus is crystallizing and to adjust conditions for perfect crystal growth, which is much more efficient by *in situ* as compared to *ex situ* experiments. Heating a $P_{red}/Sn/SnI_4$ to 800 K at a 4 K min^{-1} rate, followed by a holding period at this temperature leads to the formation of black phosphorus after an induction period at about 2 h. These experiments have also shown that black phosphorus forms directly *via* the gas phase without the occurrence of any other intermediate phase.[48] This is of interest not only for the synthesis of black phosphorus as a bulk, but also for the possibility to grow single- or multilayer phosphorene by CVT methods.

6. Conclusion and outlook

Real-time *in situ* investigations reveal details of reaction pathways, which often provide access to metastable compounds, reveal intermediate phases, give reaction control, or explain fatigue and ageing of materials. As compared to a series of *ex situ* studies, real-time *in situ* experiments with changing condition parameters monitoring a solid–gas reaction offer several advantages. Unravelling reaction pathways is, in general, more efficient, reaction intermediates may be readily identified, which is especially important, when they cannot be quenched to ambient conditions, and a wealth of data on compounds as a function of condition parameters (T, p, ...) are being provided. A key issue for choosing the best experimental setup in all the diverse applications is the time resolution of the *in situ* methods. Just as you may not get the message when hearing only every third word of a telephone conversation, reaction pathways may not make much sense when the time-grid of data points is too coarse and intermediates get undetected. There is of course a price one has to pay when employing *in situ* techniques, especially for time-resolved studies. This is first of all the oftentimes high technical demand on sample environment and measurement techniques, which may make the construction of optimized sample environment necessary.[3–9] *In situ* methods may require a higher effort than standard measurements under ambient conditions. The same concept applies of course to technical processes involving solids like in heterogeneous catalysis, ore smelting or the HDDR process for the production of permanent magnets. In industry, however, such rational approaches to solid-state syntheses are even rarer than in academia.

From the examples given above, it is obvious that *in situ* experiments may give deep insight in the synthesis, the function and the ageing of materials. The latter two are rather well-developed as demonstrated by a wealth of investigations, for example, on materials for gas storage or rechargeable batteries, where sometimes also whole devices may be tested (*operando*). The use of *in situ* experiments for the improvement of chemical synthesis is less well developed. The aim of this mini-review is to gather a few examples from different areas of solid-state sciences and involving different experimental techniques. It is meant to serve as an appetizer for those who want to learn more about the underlying basic steps of synthesis reactions in order to control them for their purpose and at their will. The great instrumental developments of the last decades (see Refs 3–9 and references therein) and the ones to be anticipated for the near future enable us to investigate many

known processes with the aim to better understand and control them and also to develop synthesis protocols for new materials. There is a lot of work to be done.

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References

1. E.J.Corey. *Angew. Chem., Int. Ed.*, **30**, 455 (1991)
2. H.Schäfer. *Angew. Chem.*, **83**, 35 (1971)
3. K.T.Møller, B.R.S.Hansen, A.-C.Dippel, J.-E.Jørgensen, T.R.Jensen. *Z. Anorg. Allg. Chem.*, **640**, 3029 (2014)
4. T.C.Hansen, H.Kohlmann. *Z. Anorg. Allg. Chem.*, **640**, 3044 (2014)
5. V.K.Peterson, J.E.Auckett, W.-K.Pang. *IUCr J.*, **4**, 540 (2017)
6. A.Götze, H.Auer, R.Finger, T.C.Hansen, H.Kohlmann. *Phys. B (Amsterdam, Neth.)*, **551**, 395 (2018)
7. J.Yang, S.Muhammad, M.R.Jo, H.Kim, K.Song, D.A.Agyeman, Y.-I.Kim, W.-S.Yoon, Y.-M.Kang. *Chem. Soc. Rev.*, **45**, 5717 (2016)
8. N.Pienack, W.Bensch. *Angew. Chem.*, **123**, 2062 (2011)
9. H.Terraschke, L.R.Arana, P.Lindenberg, W.Bensch. *Analyst*, **141**, 2588 (2016)
10. L.H.Jepsen, D.B.Ravnsbæk, C.Grundlach, F.Besenbacher, J.Skibsted, T.R.Jensen. *Dalton Trans.*, **43**, 3095 (2014)
11. U.Häußermann, V.F.Kranak, K.Puhakainen. *Struct. Bond.*, **139**, 143 (2011)
12. E.Zintl. *Angew. Chem.*, **52**, 1 (1939)
13. F.Laves. *Naturwissenschaften*, **29**, 244 (1941)
14. H.Schäfer. *Annu. Rev. Mater. Sci.*, **15**, 1 (1985)
15. *Structure and Bonding of Zintl Phases and Ions*. (Ed. S.M.Kauzlarich). (John Wiley and Sons, 1996)
16. M.Aoki, N.Ohba, T.Noritake, S.Towata. *Appl. Phys. Lett.*, **85**, 387 (2004)
17. N.Ohba, M.Aoki, T.Noritake, K.Miwa, S.Towata. *R. D. Rev. Toyota CRDL*, **39**, 40 (2004)
18. M.Aoki, N.Ohba, T.Noritake, S.Towata. *J. Alloys Compd.*, **404 – 406**, 402 (2005)
19. N.Ohba, M.Aoki, T.Noritake, K.Miwa, S.Towata. *Phys. Rev. B: Condens. Matter Mater. Phys.*, **72**, 075104 (2005)
20. H.Auer, F.Yang, H.Y.Playford, T.C.Hansen, A.Franz, H.Kohlmann. *Inorganics*, **7**, 106 (2019)
21. H.Auer, S.Weber, T.C.Hansen, D.M.Többens, H.Kohlmann. *Z. Kristallogr.*, **233**, 399 (2018)
22. H.Auer, R.Schlegel, O.Oeckler, H.Kohlmann. *Angew. Chem.*, **129**, 12515 (2017) [*Angew. Chem. Int. Ed.*, **56**, 12344 (2017)]
23. H.Auer, D.Wallacher, T.C.Hansen, H.Kohlmann. *Inorg. Chem.*, **56**, 1072 (2017)
24. A.Götze, H.Kohlmann. In *Elsevier Reference Module in Chemistry, Molecular Sciences and Chemical Engineering*. (Ed. J.Reedijk). (Waltham, MA: Elsevier, 2017). DOI:10.1016/B978-0-12-409547-2.12204-8
25. D.Shaltiel, I.Jacob, D.Davidov. *J. Less-Common Met.*, **53**, 117 (1977)
26. V.A.Somenkov, A.V.Irodova. *J. Less-Common Met.*, **101**, 481 (1984)
27. H.Kohlmann, F.Fauth, P.Fischer, A.V.Skripov, K.Yvon. *J. Alloys Compd.*, **327**, L4 (2001)
28. H.Kohlmann, K. Yvon. *J. Alloys Compd.*, **309**, 123 (2000)
29. J.Ahmad, H.Maekawa, H.Takamura, I.Oikawa, M.Ando, K.Takahashi. *J. Alloys Compd.*, **540**, 222 (2012)
30. T.Takeshita. *J. Alloys Compd.*, **231**, 51 (1995)
31. J.L.Soubeyroux, D.Fruchart, A.S.Biris. *J. Alloys Compd.*, **293 – 295**, 88 (1999)
32. I.I.Bulyk, V.V.Panasyuk, A.M.Trostianchyn. *J. Alloys Compd.*, **379**, 154 (2004)
33. M.Widenmeyer, E.Meissner, A.Senyshyn, R.Niewa. *Z. Anorg. Allg. Chem.*, **640**, 2801 (2014)
34. M.Widenmeyer, T.C.Hansen, R.Niewa. *Z. Anorg. Allg. Chem.*, **639**, 285 (2013)
35. I.Akasaki. *Ann. Phys.*, **527**, 311 (2015)
36. J.Brendt, D.Samuelis, T.E.Weirich, M. Martin. *Phys. Chem. Chem. Phys.*, **11**, 3127 (2009)
37. A.Dabirian, H.van't Spijker, R.van de Krol. *Energy Procedia* **22**, 15 (2012)
38. K.Held, G.Keller, V.Eyert, D.Vollhardt, V.I.Anisimov. *Phys.Rev. Lett.*, **86**, 5345 (2001)
39. X.Y.Zhang, H.Yuan, F.Mao, C.F.Wen, L.R.Zheng, P.F.Liu, H.G.Yang. *ChemSusChem*, **12**, 5063 (2019)
40. D.Weber, A.Stork, S.Nakhal, C.Wessel, C.Reimann, W.Hermes, A.Mäller, T.Ressler, R.Pöttgen, T.Bredow, R.Dronskowski, M.Lerch. *Inorg. Chem.*, **50**, 6762 (2011)
41. D.A.Weber. Ph.D. Thesis, TU Berlin, 2014
42. M.Maciejewski, K.Köhler, H.Schneider, A.Baiker. *J. Solid State Chem.*, **119**, 13 (1995)
43. F.Gehlhaar, S.Keilholz, H.Kohlmann. *Z. Anorg. Allg. Chem.*, **646** (2020) (in the press)
44. T.Perez, L.Latu-Romain, R.Podor, J.Lautru, Y.Parsa, S.Mathieu, M.Vilasi, Y.Wouters. *Oxid. Met.*, **89**, 781 (2018)
45. J.King, C.Liu, S.S.C.Chuang. *Res. Chem. Intermed.*, **45**, 5831 (2019)
46. H.S.Jeon, J.Timoshenko, F.Scholten, I.Sinev, A.Herzog, F.T.Haase, B.R.Cuenya. *J. Am. Chem. Soc.*, **141**, 50, 19879 (2019)
47. S.Lange, P.Schmidt, T.Nilges. *Inorg. Chem.*, **46**, 4028 (2007)
48. M.Köpf, N.Eckstein, D.Pfister, C.Grotz, I.Krüger, M.Greiwe, T.Hansen. H.Kohlmann, T.Nilges. *J. Cryst. Growth*, **405**, 6 (2014)