Part A

2.1.1. Fused Catalysts

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2.1.1.1. Introduction

A small number of heterogeneous catalysts is prepared by fusion of various precursors. The obvious group of compounds are metal alloy catalysts which are applied in unsupported form like noble metal gauze for the ammonia oxidation to nitric oxide. Melting of the elements in the appropriate composition is the only way to produce bulk amounts of a chemical mixture of the constituent atoms. The process is well-described by thermodynamics and a large data base of phase diagrams and detailed structural studies is available. Metallurgy provides the technologies for preparation and characterisation of the products[1]. This allows to synthesise a large number of bulk alloys with well-defined properties. An interesting variety to such bulk-phase metallic alloy catalysts is the beginning application of bulk metallic glasses in form of ribbons with macroscopic dimensions[2,3,4,5]. In this class of materials the atomic dispersion in the liquid alloy is preserved in the solid state although the material may be metastable in its composition. This allows to prepare unique alloy compositions which are inaccessible by equilibrium synthesis. The solidification process by rapid cooling (cooling rates above $10^4$ K/s) creates a material with well-defined short range order but non-existing long range order designated as “glass”. The difference in free energy towards compositional equilibration and crystallisation is stored in the metallic glass and can be used to transform the material in an initial activation step from a glassy state into a nanocrystalline agglomerate with a large interface internal surface between crystallites. This still metastable state is the active phase in catalysis and the final transformation into the stable solid phase mix with equilibrium composition terminates the life of such a catalyst.

In oxide materials [2] which are fused for catalytic applications two additional factors contribute to the unique features of this preparation route. Many oxides are in their liquid states thermodynamically unstable with respect to the oxygen partial pressure present in ambient air i.e. they decompose into lower-valent oxides and release molecular oxygen into the gas phase. This process can be fast on the time scale of the fusion process as e.g. for vanadium pentoxide or manganese oxides or may be slow as with iron oxides. The existence of such decomposition reactions and the control of their kinetics [6] can create a unique quenched solid which is thermodynamically metastable at ambient conditions with respect to its oxygen content. In addition, by controlling the phase nucleation, a local anisotropy of phases i.e. a mixture of particles of different oxide forms interdispersed with each other can be obtained. Such oxides exhibit a complex and reactive internal interface structure which may be desired either for direct catalytic application in oxidation reactions or in predetermining the micromorphology of resulting catalytic material when the fused oxide is used as precursor.

The application of the fusion process can lead to a control over structure-sensitive reactions for unsupported catalysts. The prototype example for such a catalyst is the multiply-promoted iron oxide precursor used for ammonia synthesis. In the respective section (B 2.1.1) a detailed description is given of the necessity for oxide fusion and the consequences of the metastable oxide mixture for the catalytic action of the final metal catalyst.
Another feature of fused catalytic compounds can be the generation of a melt during catalytic action. Such “supported liquid phase” catalysts (SLP) consist of an inert solid support on which a mixture of oxides is precipitated which transform into a homogeneous melt at reaction conditions. These systems provide, in contrast to the case described before, a chemically and structurally homogeneous reaction environment. The standard example for this type of catalyst is the vanadium oxide contact used for oxidation of SO\textsubscript{2} to SO\textsubscript{3}.

### 2.1.1.2. The Concept of Fused Catalysts

The preparation of non-supported catalysts by fusion is an expensive and very energy-consuming high-temperature process. It has to compete with the concept of wet chemical preparation by the mixing-precipitating-calcimining process which can be used in oxidative and reductive modes to obtain oxides and metals. Sol-gel preparation or flame hydrolysis are derivatives of the general approach. Another unconventional alternative to this by far most important route of catalyst preparation is offered by tribochemical procedures which lack at present still much the general understanding and are hence in an early stadium of research.

This enumeration shows that the term “fused catalyst” is not synonymous to “unsupported catalyst” but designates a small sub-group of unsupported catalytic materials. Fused catalyst went in their history of generation at least once through a molten state. In this respect fused catalyst are fundamentally different from other catalysts prepared at high temperatures such as e. g. carbons which are produced in gas-solid reaction processes with substantially kinetic differences compared to melt-solidification reactions. Scheme 1 summarises the main differences and objectives between the major preparation strategies. A collection of the major individual reaction steps for the synthesis of unsupported catalysts can be found in table 1. One fundamental insight from this rather schematic comparison is that differences in the reaction kinetics of the synthesis of a given material will lead to different mesoscopic and macroscopic structures which severely affect the catalytic performance. It is necessary to control these analytically difficult-to-describe parameters in much the same precision as the atomic arrangement or the local electronic structure. Whereas these latter parameters influence the nature of the active site, it is the meso/macrostructure which controls the distribution and abundance of active sites on a given material. It is necessary in certain cases to apply the costly method of fusion as there is no other way to obtain the desired (and in most cases unknown) optimal meso/macrostructure of the final catalyst.

Details of the chemistry in the precipitation process can be found in other sections of the handbook. The present text focuses onto the situation with fused catalysts. The reader may contrast the following discussion with the contents of Table 1.

Fused catalysts allow to combine compounds and elements in atomic dispersion which do not mix either in solution (e. g. oxides) or in the solid state. Melting provides the necessary activation energy to generate an intimate, eventually atomically disperse distribution, a carefully controlled solidification can preserve the metastable situation in the melt down to operation temperature. In the melt the pre-formation of “molecules” like oxo-complexes or alloy clusters can occur. The final short-range order of environment of the melting furnace and the liquid oxide. For compounds in high formal oxidation states this can lead to thermochemical reduction as e. g. in iron oxide (reduction of hematite to magnetite and wustite) or with silver oxide which reduces to the blank metal. Compounds in low oxidation states like MnO, Sb\textsubscript{2}O\textsubscript{3}, VO\textsubscript{2} will oxidise to higher oxidation states and thus also change the chemical structure.

The kinetics to reach the equilibrium situation can be quite slow so that the holding time and mechanical mixing of the melt will crucially affect the extent of the chemical conversion. Early termination of the holding time will lead

<table>
<thead>
<tr>
<th>Step</th>
<th>wet chemical</th>
<th>fusion</th>
</tr>
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<tbody>
<tr>
<td>mixing of atoms</td>
<td>in solution</td>
<td>in melt</td>
</tr>
<tr>
<td>pre-formation of compounds</td>
<td>frequent, with solvent ligands</td>
<td>possible for alloys (E-L- TM), always for compounds (oxides)</td>
</tr>
<tr>
<td>compositional modification</td>
<td>frequent by ligand exchange and incorporation of solvent</td>
<td>possible with volatiles, frequent with compounds by thermochemical reduction</td>
</tr>
<tr>
<td>solidification</td>
<td>precipitation, difficult to control, very fine particles with molecular homogeneity</td>
<td>cooling, very important to control, affects chemical structure (exsolution) and long-range ordering</td>
</tr>
<tr>
<td>calcination</td>
<td>required for ligand removal, complex reaction, difficult to control</td>
<td>not required</td>
</tr>
<tr>
<td>formulation</td>
<td>pressing, extrudation precipitation onto supports</td>
<td>crushing, sieving, production of wires and gauze</td>
</tr>
</tbody>
</table>
to metastable situations for the melt with local heterogeneity in chemical composition of the final product. This can be desired as in the case of the iron oxide precursor for ammonia synthesis or it can be undesired as e.g. in most intermetallic compounds. Also the dissolution of e.g. one oxide into another one can take prolonged times and early cooling will lead to a complex situation of disperse binary compounds coexisting with ternary phases. Such an example are alumina and calcium oxide promoters in iron oxide melts where ternary spinell compounds can be formed provided that sufficient trivalent iron ions remain which requires the addition of activated forms of the binary oxides in order to dissolve some of the ions before the thermochemical reduction has removed the trivalent iron in excess of that required for the formation of the matrix spinell of magnetite. These examples illustrate that both the starting compounds, their purity and physical form, and the heating program will severely affect the composition and heterogeneity of the resulting material. Scaling-up of such fusion processes is a major problem as heat and ion transport determine to a significant extent the properties of the material. Also the gas phase over the melt and its control are of high importance as its chemical potential will determine the phase inventory of the resulting compound. Besides the complex cases of mixed oxides the more simple problems of oxide and scale formation in alloy production are mentioned. The detrimental effect of oxide scales around metal particles preventing intermixing is well known. The compositional change resulting from preferential oxidation of one component further have to be taken into account. Instability of the product and/or drastic changes in the thermochemical properties of the material after scale formation (e.g. massive increase in the required fusion temperature in noble metal eutectic mixtures) are common in particular in small scale preparations. These effects still set limits to the availability of catalytically desired alloys for practical purposes (e.g. for compounds with Zr, Si, alkali, Mg).

Besides these more practical problems of catalyst preparation, there are also severe theoretical problems associated with the prediction of the chemistry in the fluid state of a compound. The motion of all structural elements (atoms, ions, molecules) is controlled by a statistical contribution from Brownian motion, by gradients of the respective chemical potentials (those of the structural elements and those of all species such as oxygen or water in the gas phase which can react with the structural elements and thus modify the local concentration) and by external mechanical forces of e.g. stirring, gas evolution etc. In electric fields (e.g. from an arc melting furnace) field effects will further contribute to non-isotropic motion and thus to the creation of concentration gradients. An exhaustive treatment of these problems can be found in a textbook [6] and in the references therein.

The second step in the process is the cooling of the melt. Slow cooling (order of several K/min) will result in equilibration of the mix according to the thermodynamic situation. Only in simple cases this is the desired compound. In most cases the mixture of structural elements stable in the melt will be metastable at ambient conditions. Techniques of supercooling are applied to maintain the desired composition [7]. Rapid solidification with temperature gradients up to about 100 K/s are required to generate metastable crystalline solids. Local heterogeneity (e.g. concentration gradients or undissolved particles will disturb the equilibrium formation [8] of crystals and lead to unusual geometries of the grain structure. The crystallite size is also under control of the cooling rate, in particular close to the solidus point where the abundance of (homogeneous) nuclei is determined. Rapid cooling limits the growth of large crystals as the activation energies for diffusion and dissolution of smaller crystallites is only available for a short time. Tempering of the solid after initial solidification can be used to modify the crystallite size provided that no unwanted phase transition occurs in the phase diagram at or below the tempering temperature. Knowledge of the complete phase diagram for the possible multi-component reaction mixture is mandatory to design a temperature-time profile for a catalyst fusion experiment. As in many cases these phase diagrams are not available or not known with sufficient accuracy, series of experiments are required to adjust this most critical step in the whole process. Frequently, empirical relations between characteristic temperatures in the phase diagram and the critical temperatures for stable-to-metastable phase transformations (e.g. the ratio between an eutectic temperature and the crystallisation temperature of a binary system) are used to predict compositions of stable amorphous compounds of metals and metalloids [9,8].

Cooling rates between 100 and 10,000 K/s can lead to a modification of the long-range order of the material. At such rapid solidification conditions the time at which the activation energy for motion of structural elements is so short that the mean free pathlength reaches the dimension of the structural unit. Then the statistical orientation of the units in the melt is preserved and the glassy state is obtained. Such solids are X-ray amorphous and contain no grain boundary network and exhibit no exsolution phenomena. They are chemically and structurally isotropic [6]. These solids contain, however, the energy of crystallisation as potential energy preserved in the solid state. It is possible to transform these glasses into cascades of crystalline states some of which may be also metastable at the crystallisation condition as the activation energy for falling into the state of equilibrium is not high enough. Glassy materials are thus interesting precursors for the formation of metastable compositions and/or metastable grain boundary structures which are inaccessible by precipitation and calcination. The critical glass forming temperatures are widely different for various materials with alkali silicates requiring low cooling rates of several 100 K/s and transition metal oxides and E-L TM alloys higher rates above 1000 K/s. Pure elements cannot be transformed at all into the glassy state. By utilising these differences composite materials with a glassy phase coexisting with a crystalline phase can be obtained. An example are amorphous oxide promoter species dispersed in-between the iron oxides of the ammonia synthesis catalyst precursor.
The third step in the catalyst preparation process is a thermal treatment called “caltzination” which is essential in all wet chemical processes. It leads to solvent-free materials and causes chemical reactions between components with the oxidation states of all elements reaching their desired values. All this is already accomplished during preparation of the fluid phase and during precipitation of the fused catalyst and hence such a step is rarely required for these catalysts. This fact reduces the difference in energy input for the final catalyst between fusion and precipitation significantly. The fact that the conditioning of the catalytic material occurs in the fluid state for a fused catalyst and in the solid state for the precipitated catalyst has two important consequences. First, the temperature levels of conditioning are different and so is the composition of the resulting material in particular with respect to volatile components. Secondly, the calcination reaction occurs as solid-solid state reaction with diffusion limitations and eventual topocochemical reaction control both giving rise to spatial heterogeneity in large dimensions relative to the particle size. In fused systems the fluid state allows very intimate mixing and hence isotropic chemical reactivity provided that the composition is either stable during cooling or quenched so rapidly that no demixing occurs. Chemical heterogeneity at any dimensional level can be created or occurs unintentionally with no gradients between particle boundaries if the cooling process is suitably adjusted to allow partial equilibration of the system.

The last step of catalyst preparation is the activation which is required for both types of materials. In this step which often occurs in the initial stages of catalytic service (in-situ, “conditioning”) the catalyst is transformed into the working state which is frequently chemically and/or structurally different from the as-synthesised state. It is desirable to store free energy in the catalyst precursor which can be used to overcome the activation barriers into the active state and in order to initiate the solid state transformations required for a rapid and facile activation. These barriers can be quite high for solid-solid reactions and can thus inhibit the activation of a catalyst.

A special case are catalysts which are metastable in their active state with respect to the catalytic reaction conditions. In this case a suitable lifetime is only reached if the active phase is regenerated by solid state reaction occurring in parallel to the substrate-to-product conversion. In this case it is of special relevance to store free energy in the catalyst precursor as insufficient solid state reaction rates will interfere with the substrate-to-product reaction cycle. A class of catalyst in which this effect is of relevance are oxide materials used for selective oxidation reactions.

2.1.1.3. Thermodynamic and kinetic considerations

The following general considerations are intended to illustrate the potential and complications when a fused catalyst material is prepared. The necessary pre-condition is that the starting state is a homogeneous phase (the fluid).

Figure 1 shows a general free energy vs. composition diagram [10] for a fused catalyst system. The composition co-ordinate may be a projection [11] through a multinary phase diagram.

The melt will solidify in the phase (1) with little compositional variation, if the melt is cooled slowly. This path leads to a stable solid with little problems in its preparation and identification. If the melt is cooled suitably to follow the solides curve further down in free energy it reaches the eutectic point (2) and can then be rapidly quenched without any compositional variation. This creates a metastable solid with a large amount of free energy stored in the solid state. The resulting material is a characteristic fused catalyst (or precursor). If the cooling is slowed down, the composition will split in a primary crystallisation [11] of the supersaturated solution. The melt is then enriched in one component according to the tangent line (2) and the solid is depleted until it reaches the composition of the metastable solid (3). The enriched melt can either crystallise in (1) or react along pathway 3 provided that enough energy of crystallisation is released and the cooling conditions [12] are still adequate. The metastable solid (3) may either be quenched and form a further metastable component of the phase mix or it can undergo equilibration in the same way as system (2) along the tangent line (3). The cooling conditions and eventual tempering intervals will decide over the branching ratio. A further possibility is the formation (4) of a supersaturated solid solution (the “metastable solid” in Figure 1) directly from the melt followed by either quench cooling to ambient temperature leading to another metastable phase in the mix or by equilibration according pathway (3).

The solidification kinetics and compositional fluctuations in the melt will decide over the crystallisation pathway which can be followed by all of the melt. If local gradients in temperature or composition exit in the system the crystallisation pathway can be locally inhomogeneous and create different metastable solids at different locations in the macroscopic solidified blocks. This simple consideration shows that a wide variety of stable and metastable solids can be produced from a homogeneous melt if the solidification conditions are suitable chosen. In this way a complex solid phase mix can be obtained which is inaccessible by the wet chemical preparation route. The phase mix may either contain an active phase or may be used to generate by a suitable activation procedure at relatively low temperatures an active phase. A stable phase which is catalytically useful should be accessible by other less complex and costly ways and is thus not be considered here.

The kinetic situation is generalised in Figure 2. For a fused catalyst system a liquid phase is assumed to co-exist with a metastable solid solution. Additional solid phases crystallise with retarded kinetics and form “lenses” in the time-temperature diagram of Figure 2. Three characteristic cooling profiles are sketched. Rapid quenching (1) leads to
only the solid solution without compositional changes and without mesoscopic heterogeneity. Intermediate quenching (2) passes through the “solid 1” area and leads to a branching of the solid products between solid 1 and the solid solution with a modified composition (primary crystallisation, path 2 in Figure 1). Cooling with a holding sequence (3) allows pre-formation of structural units in the melt and leads to the formation of three solids with different compositions. Moving the holding temperature further down into the existence ranges of the solid phases allows to exert control over the branching of the solid products. It can be seen that rapid cooling of the fused melt leads to a clear situation with respect to the solid as all free energy is transferred into the solid phase and liberated only in solid-solid reactions. If the cooling rate is intermediate or if the cooling rate is not isokinetic in the whole melt, then we obtain complex situations with wide variations in chemical and local compositions of the final solids.

The reduced fused iron oxide for ammonia synthesis is a perfect example illustrating in its textural and structural complexity the merit of this preparation strategy which allows to create a metastable porous form of the element iron. The necessary kinetic stabilisation of the metastable solid is achieved by the ex-solution of irreducible oxide phases of “structural promoters”. Some of them are already precipitated during solidification, some others are liberated from the matrix during activation. Pre-requisite for the very important secondary ex-solution is the intimate phase mixture of ternary iron earth alkali oxides which cannot be achieved by wet chemical precipitation techniques due to the extremely different co-ordination chemistry of the various cations in solvent media.

2.1.1.4. The sulphuric acid catalyst

The reaction of gaseous SO\(_2\) with molecular oxygen in the contact process seems to proceed over two independent mechanisms [13] one of which is the direct oxidation of a vanadium pentoxide- SO\(_2\) adduct by oxygen and the other proceedings via a redox cycle involving V\(^{4+}\) and V\(^{3+}\) intermediate species.[13,14,15].

The technical catalyst is a supported liquid phase system of vanadium pentoxide in potassium pyrosulfate[16,17]. Other alkali ions influence the activity[18] at the low-temperature end of the operation range with Cs exhibiting a particular beneficial effect [13].

It is relevant to work at the lowest possible temperature in order to achieve complete conversion. Only at temperatures below 573 K the equilibrium conversion of SO\(_2\) is complete with about 99.5% conversion. The binary phase diagram vanadium-oxygen shows the lowest eutectic for a mixture of pentoxide and a phase V\(_2\)O\(_5\) at 910 K. All binary oxides are stable phases from their crystallisation down to ambient temperature. The pyrosulfate promoter is thus an essential ingredient rather than a beneficial additive to the system. Compositions of 33% alkali (equals to 16.5% pyrosulfate) solidify at around 590 K. This temperature is still too high as at around 595 K the activation energy increases sharply although the system is still liquid. The liquid state is thought to be essential for the facile diffusion [13,19] of oxygen to the active sites [13].

The small mismatch between required and achieved minimum operation temperature has the severe consequence that a special pre-absorption stage has to be included in the reactor set-up in order to achieve the essential complete conversion. By this arrangement the partial pressure of the SO\(_2\) product is lowered before the last stage of conversion allowing to live with the incomplete conversion of the “overheated” catalyst. Could the reason be cured why the catalyst does not operate efficiently down to its solidification point, one may circumvent the intermediate absorption stage and thus facilitate the reactor design considerably.

The catalyst fusion is essential to bring and keep the pyrosulfate-vanadium oxide system into a homogeneous stage which is the basis for operating the system at the eutectic in the ternary phase diagram. The reaction mechanism and the fact that the operation point of the catalyst is at the absolute minimum in the V\(^{5+}\)-oxygen section of the phase diagram point to the existence of a supersaturated solution of partly reduced vanadium oxides in the melt. The point at which the activation energy for SO\(_2\) oxidation changes over to a lower (transport-controlled) value marks thus the point at which crystallisation of the supersaturated solution begins under catalytic conditions. This hypothesis could be verified in pioneering studies by Fehrmann and co-workers using electric conductivity measurements and preparative isolation techniques[17,16]. They isolated indeed crystals of a variety of V\(^{4+}\) and V\(^{3+}\) ternary alkali sulphates. These precipitates can be re-dissolved in a regeneration procedure of the catalyst involving a heat treatment to 800 K under oxidising conditions[17]. In a rather elegant in-situ EPR study the deactivation mechanism was experimentally confirmed on an industrial supported catalyst in which the phase K\(_2\)V\(_2\)O\(_7\) was identified as V\(^{4+}\) deactivating species which could also be re-dissolved by a high temperature treatment. [20]

The accurate analysis of the problem is complicated as under reaction conditions (presence of oxygen) all redox equilibria between V\(^{5+}\) and the lower oxidation states are shifted towards the pentavalent state. The generation of realistic model systems in which e. g. conductivity experiments can be performed requires thus the exact control of the gas phase in contact with the melt.

The real pseudo-binary phase diagram [16] of V\(_2\)O\(_5\)/SO\(_2\)O\(_5\)M\(_2\) with M= K, Na is rather complex in the interesting range around the eutectic which is displayed in Figure 3. The formation of a complex salt with the composition 3M\(_2\)SO\(_5\)-xV\(_2\)O\(_5\) interferes with the eutectic and gives rise to two eutectic points with fusion temperatures of 587 K and of 599 K. It is interesting to note that the chemistry of vanadium pentoxide in molten alkali sulphates is different from the present case with pyrosulfates where no vanadium-oxo-oligomers are formed. This is an indication of a complex formation.
between pyrosulfate and vanadium oxide in the sense of pre-formed molecules in the fused melt. The dashed lines in Figure 3 indicate the estimated continuation of the phase boundaries which are inaccessible experimentally as in this regime glassy oxides with unknown compositions are formed.

These observations on the sulphuric acid catalyst are full in line with the general thermodynamic behaviour of fused catalyst systems. The “metastable solid” in Figure 1 has to replaced in this case by a cascade of the partly reduced vanadium ternary sulphates. The processes sketched above occur under thermodynamic control in a quaternary phase diagram vanadium-oxygen-sulphur-alkali as illustrated by the reversibility of the ex-solution of the partly reduced vanadium compounds under suitable partial pressures of oxygen within the melt. This partial pressure is adjusted by the operating temperature. The desired low operation temperature increases the viscosity of the melt and hence increases the diffusion barrier for the gas in the liquid. This in turn facilitates the exsolution of reduced vanadium sulfates which further hinder the oxygen diffusion.

2.1.1.5. Metallic glasses

Amorphous metals can be prepared in a wide variety of stable and metastable compositions with all catalytically relevant elements. This synthetic flexibility and the isotropic nature of the amorphous state with no defined surface orientations and no defect structure (as no long-range ordering does exists) provoked the search for their application in catalysis [21]. The drastic effect of an average statistical mixture of a second metal component to a catalytically active base metal was illustrated in a model experiment of CO chemisorption on polycrystalline Ni which was alloyed by Zr as a crystalline phase and in the amorphous state. As CO chemisorbs as a molecule on Ni and dissociatives on Zr it was observed that on the crystalline alloy a combination of molecular and dissociative chemisorption in the ratio of the surface abundance occurred. This additive behaviour was replaced by a synergistic effect of the Zr in the amorphous state where molecular adsorption with a modified electronic structure of the adsorbate was observed [22]. This experiment allowed to conclude that with amorphous metals a novel class of catalytic materials with tuneable electronic properties might be at our disposal.

First attempts to check this hypothesis [23] revealed a superior catalytic activity of iron in amorphous iron-zirconium alloys in ammonia synthesis to the same iron surface exposed of iron in crystalline conventional catalysts. A detailed analysis of the effect revealed later that the alloy was under catalytic conditions not amorphous but crystallised into platelets of metastable epsilon-iron supported on Zr-oxide[24,25].

This was the first proven example of the operation of the principle that free energy stored in the metastable amorphous alloy can be used to create a catalytically active species which is still metastable against phase separation and re-crystallisation but which is low enough in residual free energy to maintain the catalytically active state with useful lifetimes.

In Pd-Zr alloys a different principle of the usage of the excess free energy can be found. Amorphous alloys of the composition PdZr2 were activated in several procedures and compared to a Pd on ZrO2 supported catalyst for the activity in CO oxidation applications [26,27]. In-situ activation of the amorphous alloy caused crystallisation into small nanocrystalline Pd+O solid solution particles and larger pure Pd particles which are both embedded into a high interface area of zirconia being present as poorly crystalline phase mix of monoclinic and tetragonal polymorphs. This phase mix is still metastable against formation of large particles of pure Pd and well crystallised large particles of zirconia with little common interface area as it is obtained from conventional impregnation techniques. A detailed analysis of the surface chemistry of the in-situ activated amorphous alloy which is metastable against segregation of a thick layer of zirconia in air revealed that only under crystallisation in the reaction mixture the intimate phase mix between zirconia and Pd is present at the outer surface of the material. It was concluded from kinetic data [26] that the intimate contact between zirconia and Pd should facilitate the spillover of oxygen from the oxide to the metal.

Figure 4 illustrates schematically the advantages of the metastable structure of the active surface. It remains speculative, if the beneficial effect is really spillover of oxygen from the oxide through surface and/or bulk diffusion[26] or if the structural stabilisation of the proven to exist [27] oxygen storage phase in the Pd (the solid solution) by the defective zirconia matrix is the reason for the superior catalytic performance.

Most relevant for the oxygen transport should be the defective crystal structure of both catalyst components. The defective structure and the intimate contact of crystallites of the various phases are direct consequences of the fusion of the catalyst precursor and are features which are inaccessible by conventional wet chemical methods of preparation. Possible alternative strategies for the controlled synthesis of such designed interfaces may be provided by modern CVD methods with, however, considerably more chemical efforts as required for the fusion of an amorphous alloy.

The metastable character of amorphous alloys under catalytic conditions is illustrated in Figure 5. TG/DTA responses are shown for the treatment of a Pd-Zr alloy in reducing and oxidising atmosphere. In pure hydrogen the formation of hydride intercalation compounds are revealed by the small reversible weight changes in the temperature range between 300 K and 600 K. It is interesting to note that the low-temperature intercalation is an endothermal process (formation of a palladium hydride), whereas the high-temperature intercalation causes no thermal response (formation of a zirconium hydrogen solid solution). All this does not affect the amorphous character of the alloy which crystallises in a single exothermic step at 663 K. The
concomitant weight gain indicates the extreme reactivity of the fresh zirconium metal surface forming by the segregation and crystal growth leading to a gettering effect of impurities present in the hydrogen gas stream. Their transportation into the bulk of the alloy can be seen by the increasing weight above 680 K. In oxygen the crystallisation temperature is the same as in hydrogen indicating the absence of drastic chemically induced segregation phenomena as cause for the bulk crystallisation. The oxidation of Zr metal is a highly exothermic process occurring after the alloy has transformed into a crystalline phase mix. This stepped conversion with surface and bulk reactivity is reflected in the stepped weight increase. The thermal signal is overloaded by the heat evolution caused by the Zr oxidation so that little structure is seen in the DTA signals. The data show that the amorphous alloy is passivated at room temperature and can be used in oxygen up to the crystallisation temperature which breaks the passivation layer due to formation of a new mesostructure causing mechanical stress and strain on the protective coating. Hydrogen, on the other hand, can penetrate the passivation layer and form hydrides in the amorphous metallic subsurface regions. The shape of the TG signals indicates transport limitations arising from the non-isothermal experiment. The interaction of the hydrogen with the alloy was not strong enough to overcome the activation barrier for crystallisation. Such a diluted palladium catalyst may thus be used up to temperatures of 623 K. The lifetime, of the system is not determined by this type of experiment which is too insensitive to detect surface crystallisation which would induce slow bulk reactions at lower temperatures than seen in the TG/DTA experiments.

In a study of the application of Pd-Si amorphous alloys as selective hydrogenation catalysts[3] it was found that in-situ activation provides a means to obtain active and selective catalysts whereas ex-situ activation caused the crystallisation of the system into the thermodynamically stable Pd + SiO₂ system which is indistinguishable in its activity and poor selectivity from conventional catalysts of the same composition. In this study it was possible to show conclusively that all amorphous alloys are not amorphous on their surfaces as they undergo in reaction gas atmospheres chemically-induced phase segregation which starts the crystallisation process according to Figure 1 (pathway 2).

The function of the fused amorphous alloys is thus to serve as a precursor material for the formation of a metastable active phase characterised by an intimate mixture of phases with different functions. This mixture is pre-formed during preparation of the metallic melt and preserved by rapid solidification. The micromorphology consists of quenched droplets allowing to segregate later into platelets. The in-situ activation is the method to prevent crystallisation into the structure with the global free energy minimum. This activation allows the transformation of the supersaturated solution from the fusion process to only crystallise until the metastable state of the tangent line (2) in Figure 1 is reached. At this stage of transformation the catalytically active state is present. This principle of application of amorphous alloys is also highlighted in review articles[3,4,5] on the subject which describe a variety of other catalytic applications of this class of fused materials.

2.1.1.6. Mesostructure of fused catalyst materials

The aim of fusion and controlled solidification of a catalytic material is the generation of a metastable catalytic material. The thermodynamic instability can either be caused by a non-equilibrium composition or by a non-equilibrium morphology and of course by a combination of both. In the case of the SLP catalysts the desired effect is to avoid the formation of solidification in order to maintain a structureless state of the active material.

The detection of metastable phases by spectroscopic and local structure-sensitive methods has been described in case studies[3,28,29,30,31]. The detection of non-equilibrium mesostructure is rather difficult and less frequently carried out due to the fact that the relevant size range is in-between local atomic microstructural motives and macroscopic crystal morphologies. For this reason conventional scanning electron microscopy as well as transmission electron microscopy (which reveals only two-dimensional projections) are not ideally suited to study such mesostructures. High-resolution scanning electron microscopy with high-voltage probes and field emission instruments or scanning probe microscopies[25] are suitable techniques to retrieve the information about the metastable mesostructure. This information is of significant catalytic relevance as many reactions are structure-sensitive and thus exhibit different kinetics on different surface orientations. The generation of non-isotropic particles with the consequence of preferred abundancies of selected orientations (i. e. basal planes of platelets) or with large interfaces between different phases in the catalysts are key issues in the process of improving or even “tailoring” catalytic performance.

Fused materials provide a viable route to bulk amounts of non-isotropic particles prepared in a controlled yet complex preparation procedure. This is illustrated in the micrographs of Figures 6 and 7 which show metallic iron in non-equilibrium mesostructures generated by fusion processes. Figure 6 shows sections of the activated technical ammonia synthesis catalyst. In the top image the perimeter of an isotropic iron crystalite (a cube) can be seen. The high resolution image reveals, however, that the iron cube is of a spongy structure. The close-up images reveal stacks of platelets with a quite irregular basal plane shape. This irregular shape provides the opportunity to form stacks with irregular edges forming a pore system with a size range of about 10 nm. This pore system is suitable to bring gaseous reactants in the interior of the iron crystal. Only the fusion process of the oxide precursor is responsible for this clearly non-equilibrium mesostructure of a bcc metallic element (see also section B 2.1.1.).
In Figure 7 typical perspectives of an activated iron zirconium metallic glass (Fe$_{91}$Zr$_9$) also used for ammonia synthesis [24,32] can be seen. The top view in the large image shows the formation of a large-area interface between the metallic iron islands and the meandering system of ex-soluted zirconium oxide. The shape of the pattern is reminiscent of a spilled liquid and is the consequence of the supercooled liquid state of the amorphous precursor. The side views on the two components reveals clearly the different organisation of the crystallites in the metallic part with regular steps of prism faces from platelets for the iron metal and the spongy porous structure of the zirconia which is imaged here in a location with a large oxide patch allowing to orient the specimen suitably for the side view. A similar organisation was also shown to be characteristic for the Pd-Zr system used for CO oxidation [27]. The images of Figure 7 illustrate one realisation of the schematic structure given in Figure 4 for partly crystallised amorphous metals.

References