THE ROLE OF SURFACES IN THE REACTIVITY OF SOLIDS

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Abstract — The overall mechanism of a solid state reaction as well as texture and thus properties of the resulting product depend on the relative rates of the development of the reaction interface, whereat the reaction is localized, and the reaction flux per unit area of this interface. Variation of the reaction interface may be caused by rapid surface spreading under the influence of surface forces manifested in the phenomenon of wetting of one oxide by another oxide. This results in the formation of cherry-like grains, whose properties and reactivity are determined by the surface layer. The reaction flux is influenced by the presence of surface defects, which concentrate at the surface changing its composition. Surface segregation and formation of two dimensional phases may take place, modifying the properties and reactivity of the surface layer.

Reactions involving solids are localized at the interface between the solid substrate and other reactants, which may be gas, liquid or another solid. In contrast to homogeneous reactions which proceed in the whole volume occupied by the reacting phase, they are thus characterized by the existence of well localized reacting zones (Ref. 1-3). The reacting zone separates two domains filled by substances of different compositions and properties, one of them being in the case of solid-solid reactions the reaction product. These zones are called reaction interface. As the area of the reaction interface changes in the course of the reaction, it must be considered as additional variable in the kinetic equation, which may be expressed in the form:

\[ R_t (C_i, T, t) = r (T, C_i) \cdot S (t) \]  \hspace{1cm} (1)

where \( R_t \) is the total rate of the reaction, \( r \) is its specific rate i.e. the rate per unit surface of the reaction interface and \( S \) is the area of reaction interface. Both the specific rate and the area of reaction interface are functions of surface properties of the reacting system. Thus, by appropriate pretreatment of the surface the total rate of the solid state reaction may be modified and the texture of the resulting product designed in a controlled manner.
Let us first consider the variation of the reaction interface in the course of the reaction. The influence of this factor depends on the geometry of the reacting system: whether it is composed of pellets or whether it is a powder mixture.

As the majority of technological processes are based on reactions in powder mixtures, the mechanisms of reactions in such systems are of particular interest. In the first approximation they may be considered as composed of spherical crystallites, the reaction being localized at distinct sites on their surface. Such topochemical reactions are characterized by the fact that the initiation of the chemical process takes place at some defined sites at the surface, called potential nucleation centers. The reaction interface is visualized as the interface between crystallites of the less mobile reactant and nuclei of the product formed at their surface at the potential nucleation centers, to which the more mobile reactant has been transported either through the gas phase or by surface migration. The overall mechanism of the reaction as well as the texture and thus properties of the resulting product depend on the relative rates of the development of the reaction interface and those of nucleation and nuclei growth.

In the case of the powder mixture of two solid reactants, if the surface migration or gas phase transport is much slower than the rate of nucleation or nuclei growth, the reaction interface is formed only at the intergranular contacts, from which it moves towards the inside of the solid (Fig. 1a).

\[ a) \]

\[ b) \]

\[ t=0 \quad t=t_1 \quad t=t_2 \]

Fig. 1 Scheme of the structure of a reacting solid state system at three different periods of the reaction. Rate of nucleation and nuclei growth much higher (a) or much smaller (b) than the rate of transport of the reactant B to the reaction interface.
The kinetic curve expressed in terms of the degree of conversion \( \alpha \) as function of time has a sigmoidal shape (Fig. 2a), because at first the area of the reaction interface increases as it moves inwards the grains as the result of the growth of nuclei of the product until they begin to contact each other. From this moment on, the area of the reaction interface decreases and so does the reaction rate. If however, the transport of the more mobile reactant to the surface of the less mobile one is very fast, grains of the latter are rapidly enveloped by a thin layer of the former, their whole surface becoming the reaction interface (Fig. 1b). In such case the reaction interface is largest at the beginning of the reaction and decreases as the grains shrink due to the consumption of the substrate in the course of the reaction, what results in the monotonous diminution of the reaction rate with the time of the reaction (Fig. 2b).

![Fig. 2 Two types of kinetics observed for solid state reactions in powder mixtures.](image)

It is usually considered that migration of one solid over the surface of another solid results from surface diffusion of constituents of the lattice under the driving force of the concentration gradient. Taking into account the relatively high values of the lattice energy of oxides one can however expect surface diffusion to be slow in the temperature range often encountered in the solid state synthesis of oxide systems.

Some time ago we have advanced a hypothesis that a different mechanism may be responsible for the rapid surface migration of solids (Ref. 4), described as wetting of one oxide by another oxide and due to the operation of the forces of surface tension. Clear manifestation of this phenomenon is the behaviour of vanadium pentoxide at the surface of two polymorphic...
modifications of \( \text{TiO}_2 \); anatase and rutile (Ref. 5). Namely, when small pellets of \( \text{V}_2\text{O}_5 \) were placed on flat discs of compressed rutile and anatase, heated at 923 K for 48h, and separated, no changes were observed in the case of rutile, whereas in the case of anatase \( \text{V}_2\text{O}_5 \) penetrated along the grain boundaries into the disc of anatase to the depth of about 500 \( \mu \)m. Fig. 3 shows the photoelectron spectra of V2p, O1s and Ti2p electrons of the samples of anatase, taken from the region of \( \text{V}_2\text{O}_5 \) migration, and these spectra after computer deconvolution.

![Photoelectron spectrum](image)

Two doublets of V2p electrons are visible hinting to the presence of two types of vanadium ions: \( \text{V}^{+5} \) ions in the environment similar to that in \( \text{V}_2\text{O}_5 \) (form I) and \( \text{V}^{+3} \) ions in the environment strongly modified in comparison with pure vanadium compounds (form II). The Ti2p doublet and O1s peak are single. Fig. 4 illustrates the in-depth concentration profiles obtained by sputtering with argon ions for different periods of time. The intensity of Ti2p peak grows with sputtering time, whereas the total intensity of V2p peaks decreases practically to zero after 20 min. exposure to argon bombardment indicating that the thickness of vanadium oxide layer is of the order of several nm. Considerable increase of the ratio of intensities of the two forms of vanadium ions in the first period of sputtering is in line with the conclusion that the vanadium oxide layer enveloping the anatase grains is composed of two parts, form II of vanadium ions being in direct contact with \( \text{TiO}_2 \) and form I constituting the upper part. Following mechanism of the migration of vanadium ions over the surface of anatase...
Role of Surfaces in Reactivity of Solids

Concentration of vanadium and titanium as function of time of sputtering. The same sample as in Fig. 3. (Ref. 5)

Grains emerge from these experiments. At first a thin probably monomolecular layer is formed, its properties being strongly modified by the interaction with the anatase surface, what in higher temperatures results in the reduction of vanadium ions to a lower valence state. Further migration of vanadium ions on top of the first layer results in the formation of a multilayer structure, the outer part assuming the structure of V$_2$O$_5$. The fact that the XPS spectra reveal the presence of the Ti2p peak of considerable intensity leads to the conclusion that vanadium ions migrate not over the whole surface of anatase crystallites, but only over certain crystal planes characterized by appropriate values of surface free energy.

Migration of vanadium oxide over the surface of anatase cannot be due just to the spreading under the influence of the concentration gradient, as in identical experimental conditions no migration takes place over the surface of rutile. The only other driving force which may cause the migration of V$_2$O$_5$ over the surface of anatase is the change in surface free energy, the migration being the manifestation of a general phenomenon of wetting of one oxide by another oxide. Such migration will namely take place if the surface tension of anatase which is the measure of its cohesion energy is greater than the appropriate sum of the surface tension of V$_2$O$_5$ measuring its cohesion energy and the interfacial tension V$_2$O$_5$/anatase, related to the energy of adhesion of these two solids. Fig. (5) The migration of vanadium oxide will continue until the film attains such thickness, whereat its surface free energy does not depend any more on the presence of the TiO$_2$ support. As the values of cohesion energy vary with the type of crystal plane, it may be easily explained that wetting takes place only on certain crystal planes of anatase, other planes remaining exposed to the gas phase. Even greater differences in the cohesion energy may characterize various
polymorphic modifications, as illustrated by the case of anatase and rutile: vanadium oxide is wetting some crystal planes of anatase, but not those of rutile.

Table 1 summarizes the interfacial relations in different oxide systems, which have been studied recently (Ref. 6). It may be seen that V$_2$O$_5$ is wetting not only TiO$_2$ (anatase), but also ZrO$_2$ and both $\delta$ and $\alpha$-$\text{Al}_2\text{O}_3$ whereas no wetting is observed in the case of SiO$_2$. Similarly, SiO$_2$ is not wetted by MoO$_3$. It is interesting that at variance with the behaviour of V$_2$O$_5$, MoO$_3$ is wetting both anatase and rutile, what would imply a much lower surface energy of MoO$_3$ as compared to V$_2$O$_5$.

<table>
<thead>
<tr>
<th>Migrating oxide</th>
<th>Immobile oxide</th>
<th>Temperature K</th>
<th>Wetting</th>
</tr>
</thead>
<tbody>
<tr>
<td>V$_2$O$_5$</td>
<td>TiO$_2$ anatase</td>
<td>823-923</td>
<td>+</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>TiO$_2$ rutile</td>
<td>823-923</td>
<td>-</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>ZrO$_2$ monoclin.</td>
<td>823-923</td>
<td>+</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>SiO$_2$</td>
<td>923</td>
<td>-</td>
</tr>
<tr>
<td>V$_2$O$_5$</td>
<td>$\delta$-$\text{Al}_2\text{O}_3$</td>
<td>923</td>
<td>+</td>
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<tr>
<td>V$_2$O$_5$</td>
<td>$\alpha$-$\text{Al}_2\text{O}_3$</td>
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<td>+</td>
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<tr>
<td>MoO$_3$</td>
<td>TiO$_2$ anatase</td>
<td>923</td>
<td>+</td>
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<tr>
<td>MoO$_3$</td>
<td>TiO$_2$ rutile</td>
<td>923</td>
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<td>MoO$_3$</td>
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<tr>
<td>MoO$_3$</td>
<td>Co$_3$O$_4$</td>
<td>823</td>
<td>-</td>
</tr>
<tr>
<td>MoO$_3$</td>
<td>Mn$_2$O$_3$</td>
<td>823</td>
<td>+</td>
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It should be noted that because of the high value of the surface free energy of many solids the driving force of the surface migration may attain considerable value and spreading may take place already at relatively low
temperature. As an example Fig. 6 shows the changes of electrical conductivity on heating to different temperatures and cooling a powder mixture of MgO and Cr$_2$O$_3$ (Ref. 7). It may be seen that already on heating to 350°C irreversible changes of electrical conductivity are observed indicating that Cr$_2$O$_3$ was spread over the surface of MgO grains.

![Fig. 6 Changes of electrical conductivity observed on heating the mechanical mixture of MgO and Cr$_2$O$_3$ to different temperatures and subsequent cooling (Ref. 7).](image)

The phenomenon of wetting of oxides by other oxides is of paramount importance for the progress of solid state reactions in oxide systems. As an illustration we shall describe the solid state synthesis of some transition metal oxysalts. In the case of synthesis of isostructural CoMoO$_4$ and MnMoO$_3$ from MoO$_3$ and Co$_3$O$_4$ or Mn$_2$O$_3$ respectively the reactions begin to proceed at a measurable rate at about 500°C and the parabolic rate law is obeyed indicating that diffusion is the rate determining step of the reaction (Ref. 8,9), MoO$_3$ being the attacking reactant. At this point however, the difference in the behaviour of the two systems should be emphasized; in the case of the Co$_3$O$_4$+MoO$_3$ system the rate constant strongly depends on the composition of the reacting mixture, whereas in the Mn$_2$O$_3$-MoO$_3$ system it is independent of the composition. This difference is due to different rates of migration of MoO$_3$ over the surface of Co$_3$O$_4$ or Mn$_2$O$_3$ grains. In the powder mixture of Co$_3$O$_4$ and MoO$_3$ the latter is not wetting the former and the reaction starts only at the intergranular contacts, the reaction interface being a function of the number of intergranular contacts. The observed dependence of the rate constant on the composition can be well described by the equation taking into account the dependence of the number of contacts between the grains of the two reactants on the composition of the reacting mixture. On the other hand MoO$_3$ when mixed with Mn$_2$O$_3$, migrates rapidly over the surface of its grains, enveloping them in a thin overlayer and then diffusing inwards through the reaction product, formed at the interface. In these conditions the reaction interface is independent of the number of intergranular contacts.
Rapid surface migration of oxides over other oxides is in many cases responsible for the surface properties of oxide systems and is therefore of fundamental importance in the preparation of catalysts. As an example of the effect of surface migration on the catalytic properties of oxide systems Fig. 7 shows the temperature dependence of the catalytic activity of MgMoO₄-NiMoO₄ catalysts of different composition in the oxidation of propylene to acrolein (Ref. 10). The catalysts were obtained by prolonged heating of mixtures of MgMoO₄ and NiMoO₃, taken in appropriate proportions, at 700°C.

![Graph showing temperature dependence of rate constant of oxidation of propylene on mixtures of MgMoO₄-NiMoO₄ of different composition (Ref. 10).](image)

Activity of MgMoO₄ was very low, whereas the activity per BET unit surface area of all other samples, from those of composition 0.1 NiMoO₄ + 0.9 MgMoO₄ through Ni : Mg = 0.5 : 0.5 and Ni : Mg = 0.7 : 0.3 to pure NiMoO₃ was practically the same. This indicates that NiMoO₃ migrates over the surface of MgMoO₃ grains enveloping them with a thin layer so that the surface of the catalyst exposed to the interaction with the gas phase reactants, is composed only of NiMoO₄ irrespective of the composition of the catalyst. The resulting structure of these catalysts is schematically represented in the insert in Fig. 7. This type of structure is very often encountered in the case of oxide-on-carrier catalysts. One of the most spectacular examples is the industrially important V₂O₅-on-anatase catalyst for oxidation of o-xylene to phthalic anhydride. It is now established (Ref. 11) that the catalyst is composed of grains of TiO₂ covered by a monolayer of V₂O₅, which constitutes the active and highly selective catalyst. The rest of vanadium is present in form of V₂O₅ crystallites and serves as a reservoir of vanadium to replenish those parts of the overlayer, which could be worn off in the course of the catalytic reaction. Indeed, Fig. 8 shows the results of an experiment, in which a mechanical mixture of V₂O₅ and anatase was placed in a reactor and its catalytic activity (curve I) was determined as a function of the time-on-stream (Ref. 12). It may be seen that the activity of the catalyst increases gradually in the course of the reaction as a result of
Role of Surfaces in Reactivity of Solids

Fig. 8 Catalytic activity in oxidation of o-xylene for the V₂O₅-anatase (curve I) and V₂O₅-rutile (curve II) mechanical mixtures as function of the time-on-stream (Ref. 12).

spreading of V₂O₅ over the surface of anatase in the conditions of the reaction and formation of a monolayer of high activity and selectivity. It is noteworthy that no increase of the catalytic activity is observed in the course of the reaction when a mixture of V₂O₅ and rutile is used (curve II) in Fig. 8). This demonstrates that it is the difference in surface energy which is responsible for the rapid migration of V₂O₅.

Very often the rapid surface migration may explain the dramatic influence of very small amounts of foreign additives on the course of the solid state reactions. In this respect let us discuss the reduction of CuMoO₄ in hydrogen (Ref. 13). Fig. 9 shows the degree of conversion α as function of time of the reaction carried out at 420°C in 21.5 torr of hydrogen (curve I). The curve is composed of two parts, corresponding to two consecutive steps of reduction:

\[ \text{CuMoO}_4 + 5\text{H}_2 \rightarrow 2\text{Cu}_2\text{Mo}_3\text{O}_{10} + \text{Cu}_6\text{Mo}_4\text{O}_{15} + 5\text{H}_2\text{O} \]

\[ 2\text{Cu}_2\text{Mo}_3\text{O}_{10} + \text{Cu}_6\text{Mo}_4\text{O}_{15} + 11\text{H}_2 \rightarrow 10\text{Cu} + 10 \text{MoO}_2 + 15\text{H}_2\text{O} \]

It should be emphasized that this is an interesting example of a consecutive reaction, in which the second step is much faster than the first one. Namely metallic copper formed as the result of consecutive reduction of the intermediate products serves as sites responsible for a very rapid activation of molecular hydrogen. However no metallic copper can appear before the whole initial amount of CuMoO₄ becomes converted to the intermediate products, because it reacts with CuMoO₄. Once the latter disappears, metallic copper starts to be formed and accelerates the activation of hydrogen so that the second step of the reaction can proceed
much faster than the first one.

![Graph](image_url)

**Fig. 9** Degree of reduction in 21.5 Torr of hydrogen at 418°C as function of time for: 1 - pure CuMoO₄, 2 - CuMoO₄ + 1% MoO₃ (Ref. 13)

Completely different behaviour is observed when small amounts of different additives are mixed with CuMoO₄. Curve 2 in Fig. 9, shows the kinetics of the reduction of CuMoO₄ with 1% of MoO₃. It may be seen that addition of MoO₃ even in such small amount as 1% increases the rate of the first step of the reduction of CuMoO₄ by more than one order of magnitude. One of the hypothesis which may explain these observations is the assumption of a very rapid migration of MoO₃ which in the very initial stage of the reaction could spread uniformly over the surface of CuMoO₄, generating on reduction a large number of MoO₂ centers for activation of hydrogen and facilitating in this way the surface redox processes.

In many instances the two limiting cases of the kinetics of solid state reactions, shown in Fig. 1 and 2 are not due to transport phenomena but to chemical factors. As already mentioned, in the case of reactions, in which a solid reacts with another solid, liquid, or gas, nucleation takes place at the surface of the crystallites of the "attacked" solid, the nuclei being preferentially formed at certain surface sites called potential nucleation centers. Formation of a nucleus at such center may perturb the surface in its vicinity, increasing its reactivity. The zone of increased reactivity will thus move along with the growing nucleus. In such case a preferential growth of the nuclei will be observed, once they are formed. This phenomenon is called "autolocalization" and gives rise to the kinetics analogous to that illustrated in Fig. 1a and 2a. Conversely, when the nuclei do not exert any influence on their surrounding, the reactivity of the surface is uniform.
and the whole surface of the crystallites may become the reaction interface. The course of the reaction may be then represented by a model analogous to that shown in Fig. 1b and 2b.

The role of potential nucleation centers may be played by surface sites, whereat the strict periodicity of the lattice potential is perturbed. This may be caused by the presence of many various defects of the surface, such as:
- point defects (vacancies, interstitial ions, altervalent ions, foreign ions),
- extended defects (dislocations, shear planes),
- three dimensional defects (steps, kinks, etc.),
- adsorbed species.

All these defects may be generated or annihilated by an appropriate treatment of the surface such as outgassing or adsorption of different molecules, prereduction or preoxidation, irradiation, impregnation with foreign ions or their implantation, mechanical treatment, thermal processing etc. It should be emphasized that the pretreatment of the surface is one of the most powerful methods of controlling the rate of solid state reaction. It may be applied either to activate the solids and increase the rate of a solid state reaction in the case when synthesis of a given product is the objective, or to dezactivate the solid in order to stabilize the surface structure against such processes as ageing, wearing etc.

When discussing the influence of the pretreatment on surface properties it should be borne in mind that the surface layer of the crystallite may have different physical and chemical properties than its bulk. It is now well established that e.g. the surface composition of the solid is in general different from the composition of the bulk (Ref. 14-16) due to the important contribution from the surface free energy to the condition of the thermodynamic equilibrium. We are namely used to discuss the adsorption at the gas-solid or liquid-solid interface from the position of the gas or liquid phase and we are accustomed to treat this phenomenon as the increased concentration of one of the components of the gas or liquid solution at the interface. However, the interface has two sides and the same phenomenon of adsorption takes place at this interface from the side of the solid, if the solid is a solid solution. This results in the increased concentration of one of the components of the solid solution at the interface, its surface excess being described by the Gibbs adsorption equation. This phenomenon operates even in case of pure oxides, because they usually are nonstoichiometric compounds which may be considered as solid solutions of defects in the lattice. When the surface concentration of defects exceeds certain critical value, their ordering may take place at the surface, resulting in the formation of new surface phases. As shown by Nowotny (Ref. 17) the mobility of cations in the surface layer of oxides may be by orders of magnitude higher than their mobility in the bulk so that equilibration of the surface layer of an oxide with gas phase oxygen, and the resulting reconstruction of the surface layer or formation of new
surface phases may be very fast.

It should be remembered that due to the contribution from the surface free energy the values of the Gibbs free energy, where a given phase transformation occurs at the surface may be different from that required for this transformation to take place in the bulk of the crystal. When an oxide may form two different polymorphic modifications, the phase transformation on heating may take place at the surface long before the temperature is attained, whereas this transformation is observed in the bulk of the crystallites. The crystallites are then composed of the bulk having the structure of one polymorphic modification, enveloped by a surface layer of a structure characteristic for the other modification. As an example let us discuss the behaviour of cobalt molybdate CoMoO$_4$. Under normal pressure this compound forms two polymorphic modifications (Ref. 18): the low temperature green modification "b" in which molybdenum is in tetrahedral coordination and the high temperature violet modification "a" with molybdenum in octahedral sites. The transition takes place at 420°C. XPS studies of this system revealed however that on heating modification "b" its surface becomes reconstructed already at 250°C, the reconstruction being fully reversible (Ref. 19). This is illustrated in Fig. 10, in which the

![Fig. 10 Changes of the photoelectron spectra in the region of the Mo3d core level of the sample of CoMoO$_4$ on heating and subsequent cooling (Ref. 19)](image-url)

Fig. 10 Changes of the photoelectron spectra in the region of the Mo3d core level of the sample of CoMoO$_4$ on heating and subsequent cooling (Ref. 19)
photoelectron spectra of Mo3d electrons from modification "b" of CoMoO₄ are shown at different stages of heating and cooling the sample. At normal temperature the Mo3d doublet is visible at 234.2 and 237.2 eV. On heating the sample a shift of this doublet to lower values of binding energy started to be visible around 100°C, and at 200°C the doublet assumed a new position at 232.2 and 235.3 eV, which did not change on further heating to higher temperatures. When the sample was cooled again to room temperature, the shift of the Mo3d doublet was observed back to the initial value. It should be noted that on heating above 390°C reduction of the sample began to be perceptible. It may be assumed that the shift of Mo3d peak reflects the reversible polymorphic transformation, which at the surface takes place at the temperature 300°C lower than in the bulk. A general conclusion may be thus formulated that not only the chemical composition of the surface layer but also its structure is very often different from that of the bulk.

As the last important factor we would like to mention the effect of the interaction of solids with the gas phase. Experimental evidence accumulated in recent years indicates that composition of the gas phase may have a profound influence on the structure of the surface, and hence on the properties of the solid and its reactivity. It has been shown above that due to the contribution from the surface free energy the composition of the surface of the solid differs from that of the bulk. As however the surface free energy depends on the composition of the gas phase, it may be expected that changes of the latter will entail changes of the surface composition. This may be particularly pronounced in case of adsorption of molecules of surface active compounds. In the case of transition metal oxides changes of the defect equilibria will simultaneously take place, influencing also the surface composition. This may result in a number of different phenomena such as ordering of defects at the surface, transformations of surface structure and formation of new bidimensional surface phases. They may entail the appearance of new types of potential nucleation centers, considerable changes of the mobility of lattice elements at the surface, modification of the electrical surface double layer, shift of the chemical potential of electrons Fermi level and many other effects - all of them having a profound influence on the reactivity of solids.

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