FUNCTIONAL COATINGS AS AN INTERESTING TOOL FOR INDUSTRIAL OPPORTUNITIES: DEVELOPMENT AND COMMERCIALIZATION

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1. INTRODUCTION

After almost 50 years of sol-gel chemistry, the questions arise about the state of commercialization of sol-gel materials. As investigated by many authors [1-4] sol-gel materials show very interesting properties as well as processing advantages. The intriguing idea was to fabricate glasses and ceramics through a liquid route [5]. This idea was first patented by Geffcken and Berger [6] and commercialized by Schott glass works in the 70's. It could be shown that the densification of thin sol-gel films, even in high Tg systems as SiO_2/TiO_2 could be achieved at temperatures below the softening point of the coated glass panes. This technology was commercialized for architectural glazing and gave a strong input into the material science community, and many investigations have been carried out for the further development and exploitation of these basic findings.

This example of commercialization, however, already pointed out one way how sol-gel technologies can be successfully commercialized, namely by rising the value of a product for an already existing market. This value increase is substantial and actually also may open up new markets, as shown in the case of architectural glazing from Schott. For a successful introduction into the market, one has to combine chemistry, chemical processing, coating technology, application or production technology, marketing and sales. The involvement of several disciplines is an indispensible requirement for the commercialization, and a company has to have access to all these disciplines. This requires a reasonable company size including a profound chemical knowledge. This is one of the basic

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aspects of sol-gel commercialization, but the majority of material users, unfortunately, do not have these skills.

In this paper, the question how to utilize sol-gel chemistry in a broader way will be discussed and examples for successful utilization, especially involving academia, are presented. It has to be said that in most areas where sol-gel technologies are successfully used, large companies which already have chemical departments or have built up chemical departments are involved. It is also true that most of these companies use the sol-gel process as an in-house high performance tool for developing high-tech products. There are only a few examples in which chemical industry is producing materials to be used in down-stream processes. Examples are TiO_2 as a pigment, wash coats for automotive catalysts or sol-gel coated mica pigments with interference layers, especially as additives for automotive lacquers, or more recently, ITO slurries for the fabrication of conductive coatings for displays. In most cases, however, the in-house route is preferred, since the added value can be „harvested" through the final product.

2. BASIC MARKET CONSIDERATIONS

It is well known that the time to development and time to market of materials has become rather long. In the opinion of experts, these times are 10 years or more. This means that the development costs of materials are rather high and the risk is fully covered by the material developers. On the other hand, if one considers the added value from the material to the system, the material always covers the first or lowest step of the added value chain only.

This leads to a situation that for a successful marketing of sol-gel materials by selling these materials directly, relatively large market volumes have to be obtained, otherwise the development costs will not be paid back. This leads to the situation that the vast majority of interesting materials never has been commercialized due to market restrictions. If one now takes into consideration that for the commercialization of the „sol-gel raw materials" only the chemical industry can be considered, it becomes clear that only a few mass commodities have been successfully commercialized. Second, the number of companies who are equipped with chemical development facilities plus the down-stream processing to high-added value material is also very restricted. Typical examples are the electronic industry, sometimes the sensor industry, and, in a few cases, also the automotive industry and large suppliers. On the other hand, the structures in academia only allow the generation of knowledge in the specific field of the scientists in charge. The required, well-managed „vertical" interdisciplinarity is

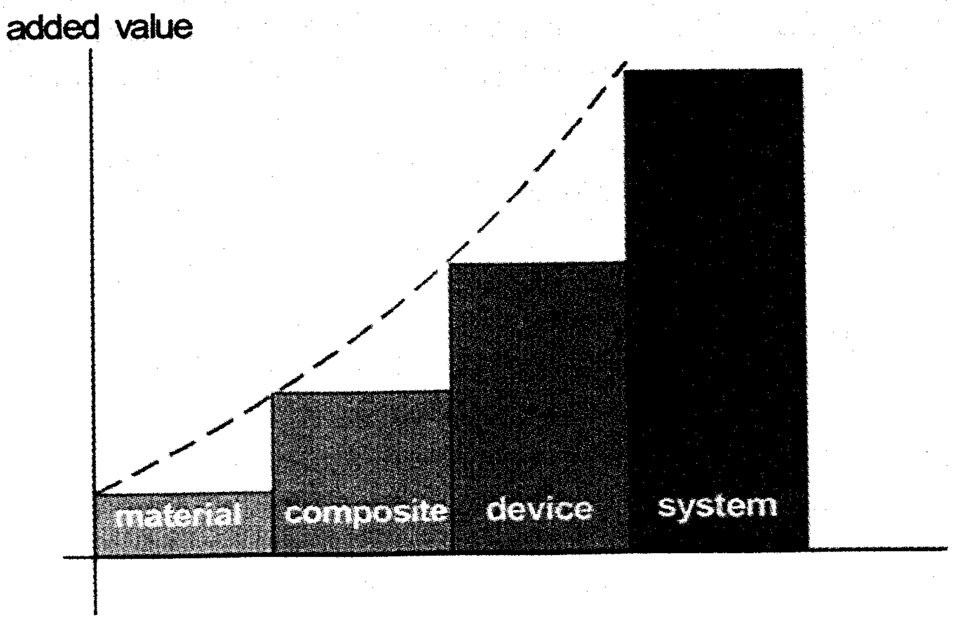


Fig. 1: Increase of added value from the material to the system

not organized in academia and one has to think about how to establish these structures. In the following, some technology platforms for sol-gel and related processes are given and it is shown, how they have been exploited for commercial use.

3. TECHNOLOGY BASIS

3.1. Fabrication of Nanoparticles

For the fabrication of nanoparticles, the sol-gel process has been choosen, since sols typically represents colloidal solutions with particle sizes in the nanometer range. The sol-gel process or the colloidal route to material is a route used by nature to form minerals like chalcedony or agate and known in industry for the fabrication of water glass since over 150 years. Many publications have been produced in the past [7-16]. Due to the large surface area and the strong particle to particle interaction, the sols have to be stabilized in order to prevent aggregation. Stern has shown that with electrostatically stabilized sol particles, stable and unstable regimes exist, depending on the particle to particle distance [17]. Other possibilities of stabilizing sols is the surface modification of sol particles during or after the sol formation, which can take place by the hydrolysis and condensation of alkoxides outside of the point of zero charge of the zeta potential curve, or by simple precipitation under similar conditions. Using surface modifiers, which bind to the colloidal particle surface by chemical bonds, results in several interesting options, which is schematically shown in figure 2. The stabilisation of the nanoparticles by electrostatic means only restricts the further use, since „leaving“ Stern’s stabilisation regime leads to uncontrolled aggregation (gel formation takes place). Gels, however, are rather difficult to process to compact materials, especially if no viscous flow sintering mechanisms can be employed for densification as it is the case for non-glassy systems. Silica is one of the exceptions and able to form large bodies as it has been shown for preforms by Lucent Technology.

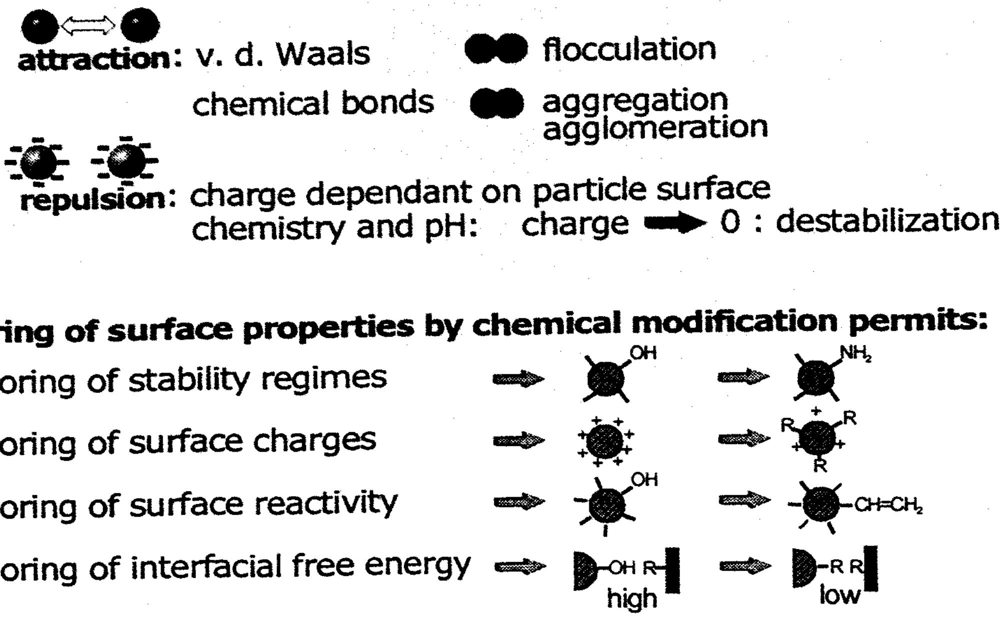
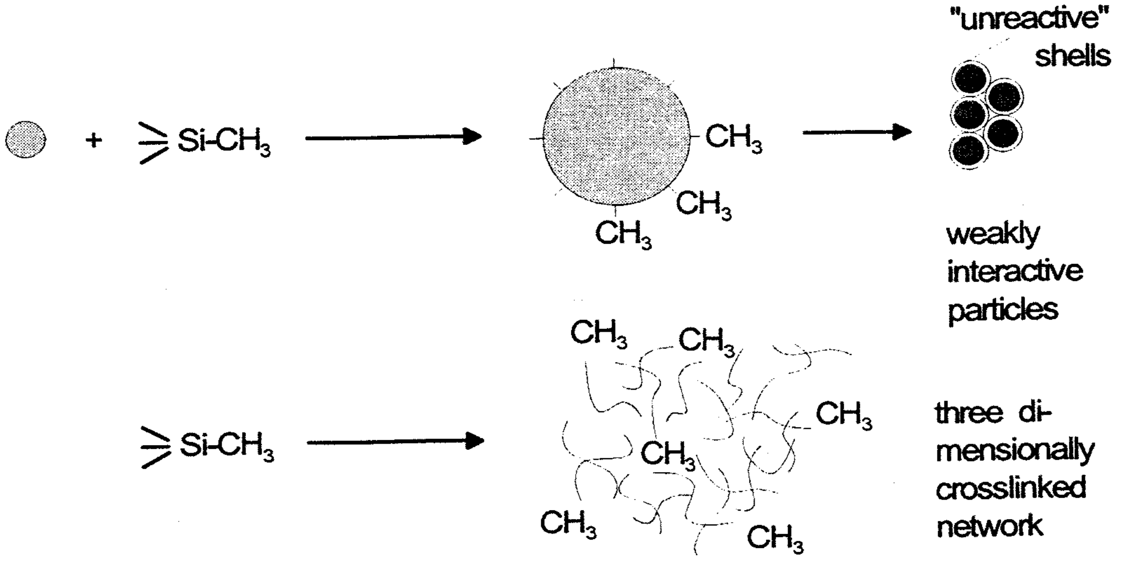


Fig. 2: Colloidal principles and advantages of surface modification of nanoparticulate sols

The surface modification of colloidal particles by „small“ molecules has several advantages. A large variety of surface modifiers can be used, which can be fixed on the surface by several types of chemical bonds, like hydrogen bridges (e.g. in aprotic solvents), complex, covalalent or ionic bonds. If bifunctional molecules are used, the second function also may be of interest, since the surface chemistry of the sol particle can be influenced. Using this approach, the stability regime of the zeta potential curve, the amount of surface charges, the surface reactivity and the interfacial free energy between the particle surface and the matrix (liquids or polymer melts) can be tailored. This approach provides very interesting tools to fabricate „modified“ sols, details of which are described elsewhere [18]. Based on these ideas, a fabrication process for modified sols and redispersible „dry sol-gel powders“ has been established for medium size quantities [19].

3.2. Use of Specific Modification Techniques and Commercialized Products

3.2.1. Production of unreactive surfaces: SiO_2 gels, in general, are brittle due to their three-dimensional crosslinking. In addition to this, they have a poor mechanical strength. To use SiO_2 sols as binders for glass fibers has been tried to be realized in vain for many times; the resulting glass fiber insulation materials are extremely brittle and can be crushed very easily by squeezing. In order to avoid these problems, silica sol has been surface modified by phenyl and methyl silanes in order to avoid particle to particle interaction for these modification techniques, which is described in detail elsewhere [20]. One of the effects of this surface modification is an improved relaxation behaviour of films produced from these modified sols. In a one step coating process films up to 15 µm thickness can be obtained without cracking after 500 ° densification on silica substrates [21]. Based on these results, it was expected that binders fabricated from these materials for glass fibers also show an improved flexibility and glass fiber insulating materials could have been developed based on this technique for industrial use. These glass fibers are flexible like polymer-bonded glass fibers and contain about 5 weight % of the modified binder. In opposition of the simple use of methyl or phenyl silanes, the modified SiO_2 leads to much more flexible systems due to the lower degree of three dimensional crosslinking [22]. The principle is shown in figure 3.



Model for particulate flexible and polymertype unflexible gels

Fig. 3: Principles of the surface modification of silica sols to be used as glass fiber binders (after [21]).

The flexibility of these fiber mats produced in an industrial process is shown in figure 4. The fibers are white, stable up to 500 °C over a long time and easily to be recycled. In case of fire, no toxic components are emitted.

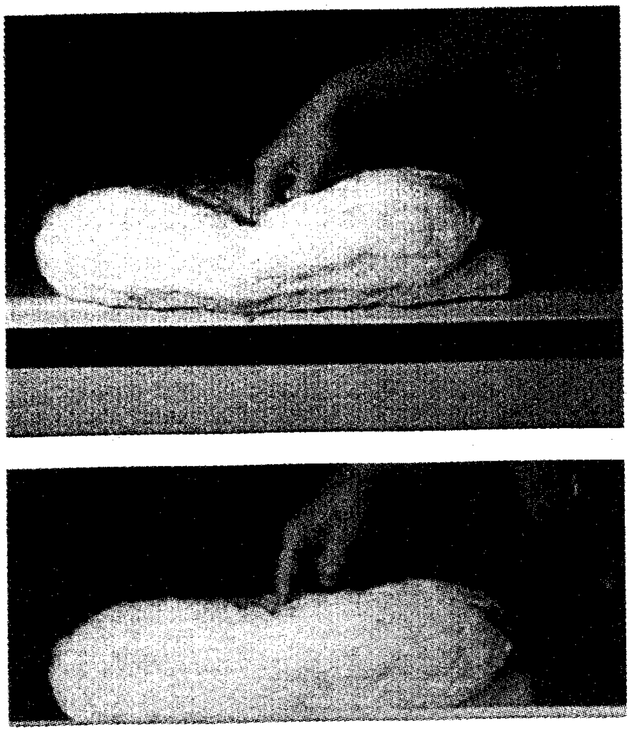


Fig. 4: New glass fiber mats produced by the new binder.

An industrial process has been developed based on this technology [23]. It is planned to produce up to about 70 tons of glass fibers per day at the beginning which requires about 3.5 t of these sol-gel binders per day and about 1000 t per year.

This binder also has shown that it can be used as an adhesive for natural fibers and wood, since it shows an antimicrobial behaviour, and, at the same time self-extinguishing properties in case of fire. The ability of the binding of natural fibers has been used to develop composite materials from hemp, straw and plywood [24].

3.2.2. Polymerizable nanoparticles: As shown elsewhere, the surface modification of many types of nanoparticles like alumina (boehmite, silica or TiO_2) can be carried out by appropriate silanes [25, 26].

In the case of boehmite, a process has been developed for coating the boehmite particles with an epoxy silane and to polymerize the epoxides by use of aluminum alkoxides or the boehmite particles as catalyst by themselves at temperatures of about 130 °C. Using this approach, very hard coatings have been fabricated with abrasion resistance values determined by a taber abrader test and measuring the haze values of about 2 % after 1000 cycles. These systems have been developed for the coating of polycarbonate for automotive glazing. The market expectations of this technology for a fraction of 10 % of the total glazing made from polycarbonate sums up to about 100 t of the sol-gel coating materials per year but the impact on the polycarbonate production is much more important. Further perspective in order to develop new designs for the cars through polycarbonate and to gain a larger market fraction leads to very interesting market volumes of 1000 and more tons per year, but the increased markets for polycarbonate are much more interesting, of course.

Another example for successful commercialization of the polymerizable nanoparticle technology is the fabrication of hard coatings for credit cards, driver's licenses and others. In this case, boehmite particles have been surface modified with methacryloxy silanes and the technology has been built up for off-set printing of these materials on plastic sheets for the fabrication of the described documents. The interesting part of this technology is that the laser damage threshold of these coatings at a thickness of several µm is high enough in order to permit laser writing through the coating into the plastic support. This permits the coating of the plastic sheets before the individual writing of the parts and facilitates the process substantially. About 150 million documents using these techniques are fabricated at present in Germany, but despite the fact that the material's value is rather small (several 100 kg per year), the added value of this technology is high. In figure 5 the principle of the process is shown.

3.3.3. *Easy-to-clean technologies*: The formation of gradient materials by sol-gel techniques has been proved with sol-gel hybrid materials using side chain perfluorinated silanes [27]. Due to thermodynamical effects, the fluorine is upconcentrated on the surface of the coating leading to a low surface free energy with an antiadhesion or, depending on application, with an easy-to-clean effect. The first successful commercialization of this type of coatings has been carried out in a common project together with nanogate, where the largest European group for sanitary ware and the world largest supplier for tile coating materials are involved. Sanitary ware is already very successfully available on the market and tile production is just introduced worldwide. The principles of the process are shown in figure 6. The market volume of this technology is large and is estimated

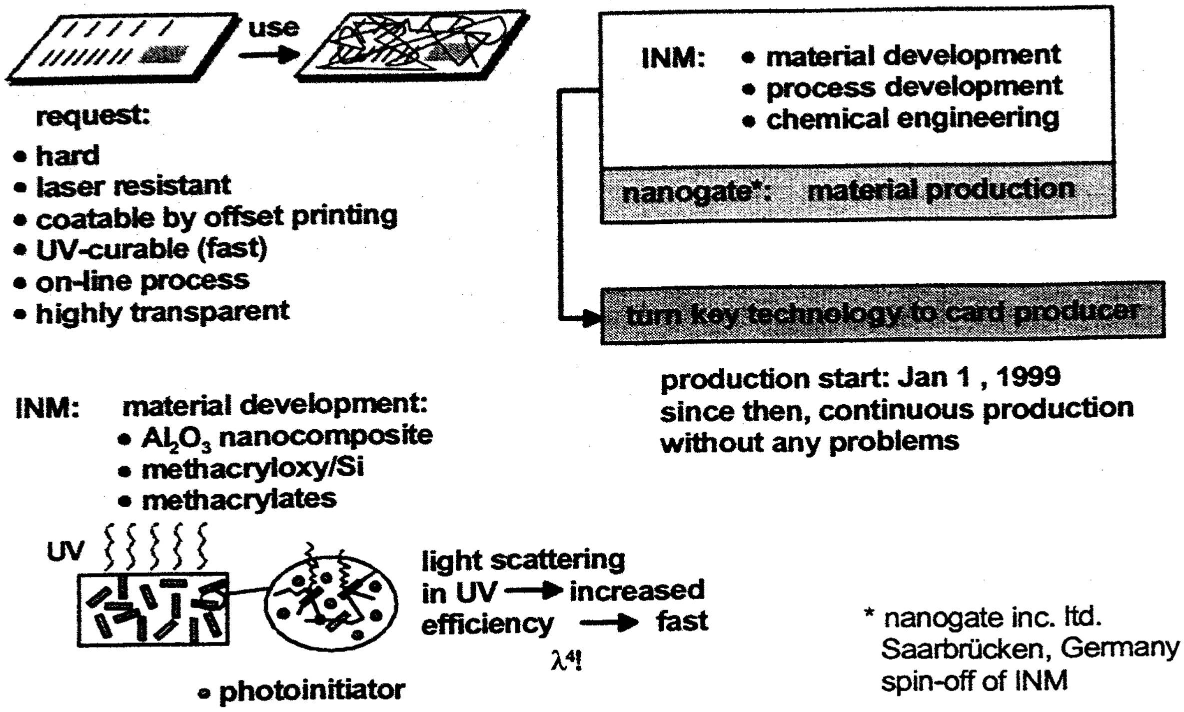


Fig. 5: Scheme of the development of a process for laser writable hard coated systems.

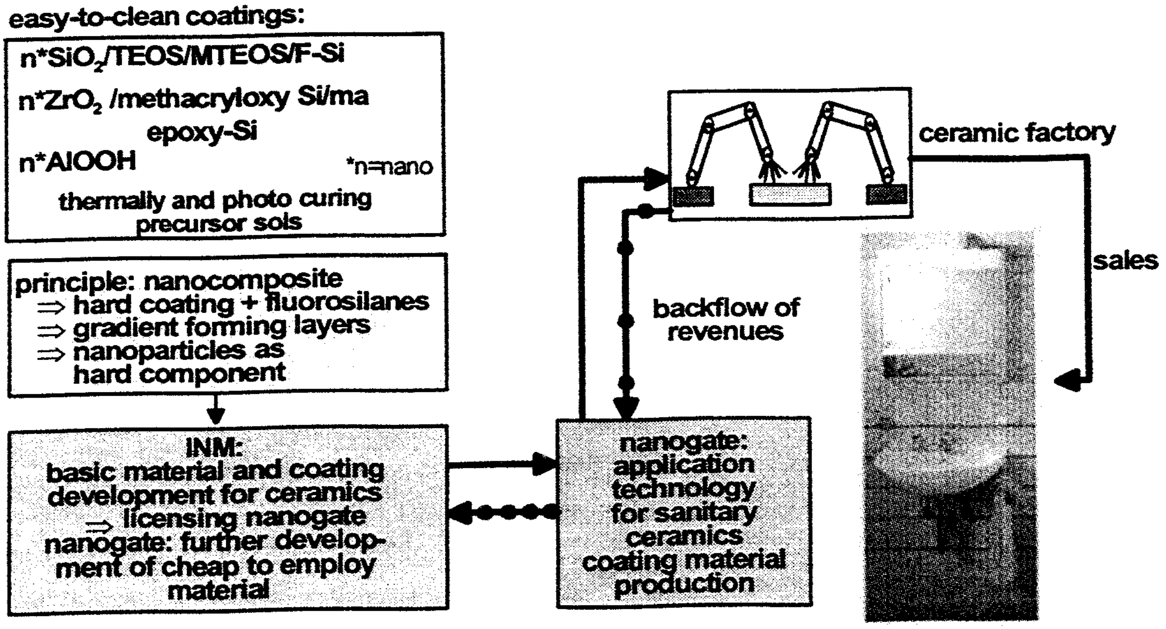


Fig. 6: Principles of the fabrication of easy-to-clean sanitary ware.

to be a couple of billion dollars per year worldwide, but the volume of the coating material again, is expected to be in the range of about 700 t per year.

3.3.4. *Catalytic systems for deodourisation*: The best way for the removal of odours is the decomposition or oxidation into simple components like water, carbon dioxide and nitrogen. The oxidation catalysis can be carried out with finely derived nobel metal on carriers, but also with specific transition metal oxides. However, the activity of transition metals is rather low compared to nobel metals. On the other side, nobel metal catalysts are expensive and in most cases rather difficult to be produced in desired shapes for specific applications. For these reasons, sol-gel binders have been used for binding mixtures of µm-sized powders of cobalt oxides, mangane oxides and cerium oxides. The idea was to produce open structures with large transport channels for a fast gas exchange and to reduce the operating temperatures down to about 300 °C. In figure 7 the microstructure of the catalyst bonded with surface modified sol-gel SiO_2 and sol-gel aluminum oxide as binders is shown. The technique permits to produce layers up to several hundred µm and in thickness on any type of substrates, e. g. ceramic honeycombs or even on stainless steel. The resulting catalyst has an activity of about 10 times of the state of the art and has been commercialized together with one of the world's largest producers of kitchen stoves to remove the smell of cooked and roasted food. This technique provides an improvement of the competitiveness of the company and the catalytic material is produced by nanogate company in the

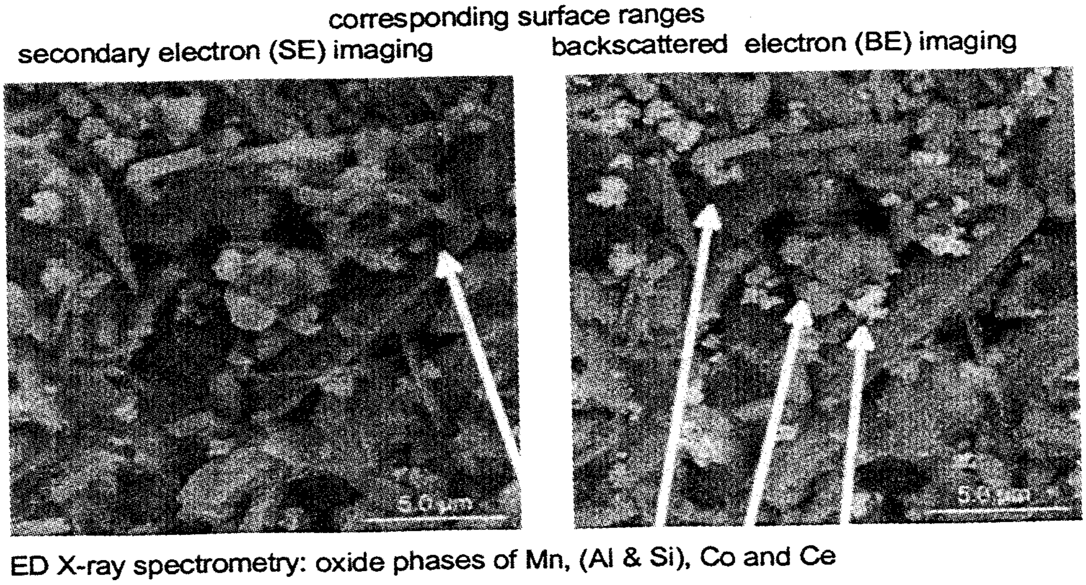


Fig. 7: SEM micrographs of the described oxide catalysts

quantity of several tons per year at present. In figure 8 the whole process is shown schematically. Again, the sol-gel materials produced even in small quantities improve competitiveness substantially.

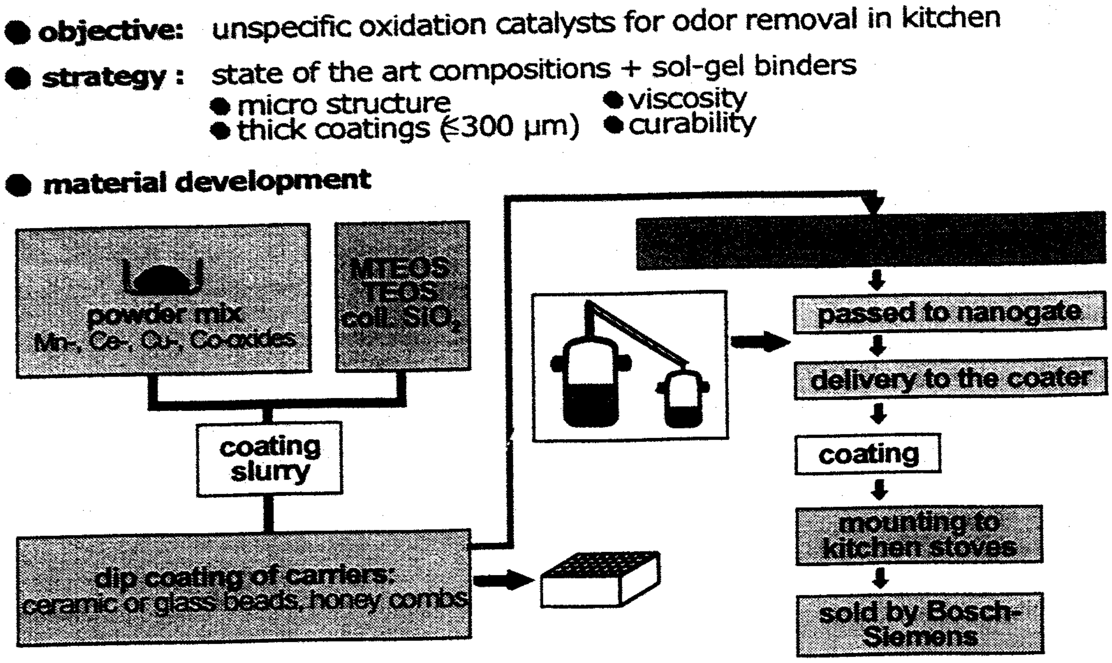


Fig. 8: Scheme of the process of the fabrication and commercialization of deodourisation catalysts.

7. CONCLUSIONS

The few examples show that by using the appropriate approach, sol-gel materials can be produced and successfully commercialized. However, it is necessary to obay certain rules. One of the rules is indicated as the so-called „vertical integration“ which is shown in figure 9. It means that it is not sufficient only to develop materials with excellent properties, but also to provide a technology development on the academia level. This, however, means that the R&D partner has to collaborate in this vertical integration down to a level at which the partner is able to take up the development. This depends strongly on the abilities and the skills of the partners and especially on their size. The requirement for vertical interdisciplinarity is shown schematically in figure 10. As one can conclude from this figure, there are only a few technologies which can be transferred to industry in the basic science state. If one wants to transfer technologies either to smaller companies or to companies not familar with the sol-gel techniques, one has to process the technology down to production, and if production technology also is developed, small and medium sized enterprises become extremely interested in

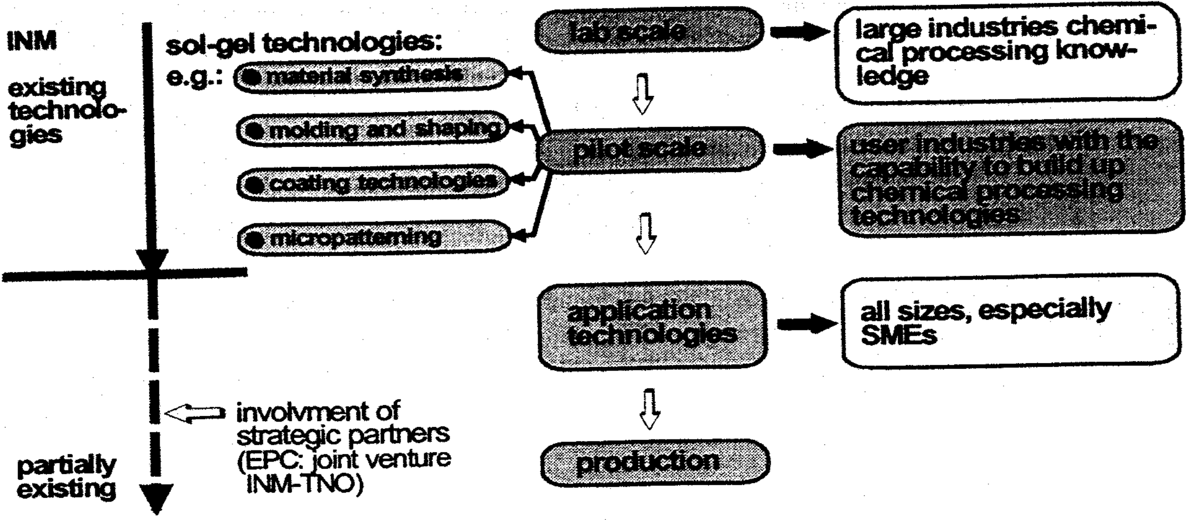
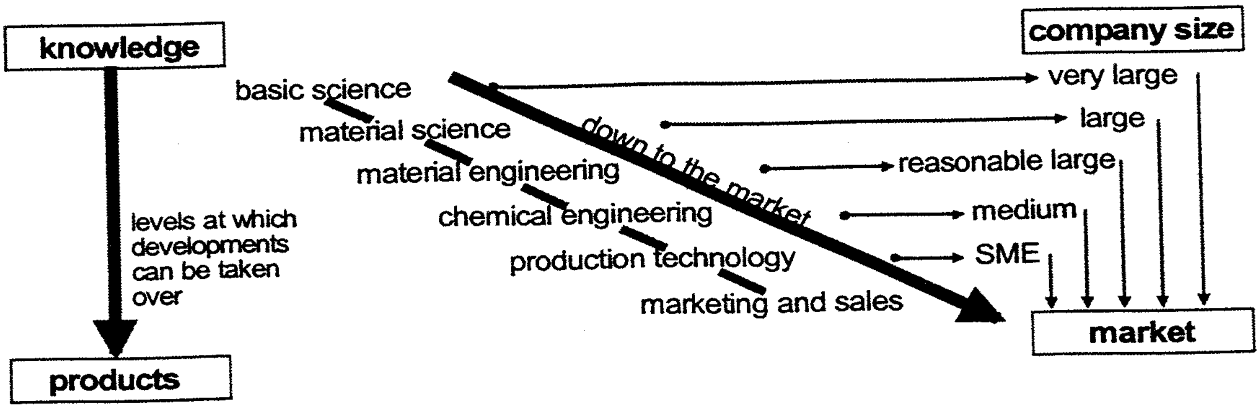


Fig. 9: The vertical route for the successful strategy for the commercialization of sol-gel products.

the new technologies. Summarizing it is to say that sol-gel techniques are a powerful tool for producing and developing new materials but due to the lack of vertical integration in R&D centers, only a small percentage of the developments are transferred into the market.



academica: in most cases only one discipline at the same time

required: interdisciplinary R+D organization with vertical interdiciplinarity

Fig. 10: Strategy and steps „down to the market“

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