Probing the Catalyst Structure by Electroconductivity using Computer Simulation Analysis

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If combined with proper Monte-Carlo analysis, electric conductivity of disperse solids may be used as a tool for probing their physical and geometrical structure.

Nowadays, it is generally accepted that the activity and efficiency of a catalyst system is not only determined by its chemical and electronic properties – the geometrical and topological structure is also of tremendous importance. The formation of a catalyst structure depends on numerous factors and includes a large number of topochemical and physical processes. In a detailed paper by de Bruijn and Kuipers it is pointed out that catalyst simulation would be a promising tool for catalyst investigation.[1]

The goal of the present report is to demonstrate the capability of computer simulation as a method of analysing the catalyst structure and its evolution and revealing and identifying the characteristic features of a solid catalyst on various stages of its biography. Electroconductivity was used as a probe for the phase-structure state of a catalyst because this transport property depends critically on the geometrical structure and intergranular contacts. To gain a theoretically understandable correspondence between the geometrical and the electrical characteristics we have developed a versatile program package based on the Monte-Carlo (MC) approach.[2]

The analysing power of electroconductivity has been tested for several model and real objects, each with some notable peculiarities in conductivity behaviour. We have considered both monodisperse and polydisperse multicomponent solid systems.

The conductivity of dispersed solids belongs to percolation phenomena. It is essentially governed by the spatial distribution of the conducting phase and by the intergranular contact barriers. The experimentally observable parameters of the concentration dependence of conductivity are the position of the percolation threshold (where conductivity grows sharply from the badly-conducting phase level) and the slopes of the graph below and above this threshold. On the theoretical side, for monodispersed systems, we have developed several MC models. In these models the real physical space is represented by a three-dimensional discrete lattice, whose sites are to be occupied by either of the species considered. The bonds connecting neighbouring sites represent electrical contacts with conductivities defined according to the model assumptions. The input model parameters are the position and the width of contact barrier distribution (the limiting values of conductivity of intergranular barriers), the degree of friability (measured by the average number of contacts per grain) and the degree of inhomogeneity (either introduced by a conventional parameter or simulated by means of a special MC procedure).

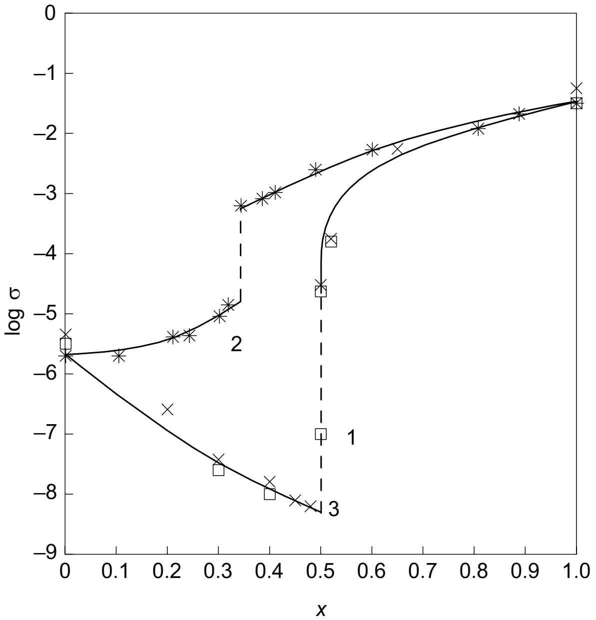

Fig. 1 Electroconductivity of $Fe_3O_4 + NiO$ *versus* the volume fraction x of Fe_3O_4: 1 (□) experimental data, 2 (∗) simulation of homogeneous mixture, 3 (×) simulation with extra disaggregation.

Having considered a series of oxide mixtures ($Fe_3O_4 + MgO$, $Fe_3O_4 + NiO$, $Ni + ZrO_2$) we succeeded in finding an interpretation of the experimental data in terms of the above model parameters.[3] An example of such an analysis is given below, based on the concentration dependence of conductivity σ of a $Fe_3O_4 + NiO$ system (see Fig. 1, curve 1). In homogeneous mixtures the percolation transition would occur at conducting phase fraction $x_c \simeq 0.3$ (curve 2). The relatively high percolation threshold in the considered sample ($x_c \simeq 0.5$) may be explained by the inhomogeneity of phase distribution. A simulation with the use of a “disaggregating” procedure (curve 3) leads to a perfect agreement with the experimental results. The same is also observed for $Ni + ZrO_2$ mixture.

Another feature of the measured conductivity graph is its negative slope in the below-threshold region. This means that heterophase contacts are even worse conductors than homophase badly-conducting phase barriers. This also gives evidence for the absence of chemical interaction between the components, since the possible product, nickel ferrite, would manifest in an enhanced conductivity. The same conclusions may be drawn for a $Fe_3O_4 + MgO$ mixture, which is characterized by a zero slope of the graph.

A detailed discussion of some other interesting properties of monodisperse mixtures may be found in ref. 3. We emphasize that the models considered not only give a qualitative theoretical picture, but provide a quantitative description of real physical systems as well.

Having tested the theoretical approach for monodisperse mixtures we then considered several cases of polydisperse systems dealing mainly with the class of supported catalysts (with low dispersed and high dispersed phases called as supporting and supported phases, respectively). Since the geometrical scales of the supported phase, the supporting phase and the whole sample differ by many orders of magnitude, the simulations were performed in two stages. The properties of individual grains were simulated in the first stage, then the obtained results were used as input to simulate the whole sample (composed of many grains) at the second stage. We analysed the cases of small, moderate and large intrinsic surface area of the support. We studied the

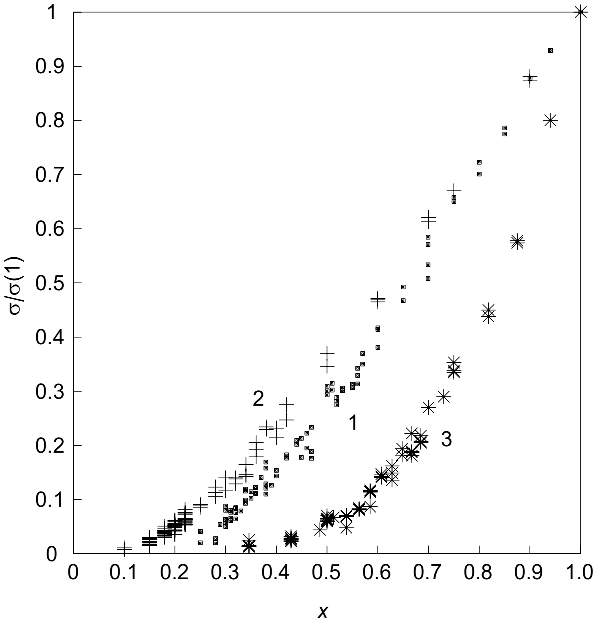

Fig. 2 Theoretical predictions for electroconductivity of three polydisperse systems *versus* surface coverage fraction *x* (continuous support): 1 (·) smooth support surface, 2 (+) support with open pores, 3 (∗) support with blind pores.

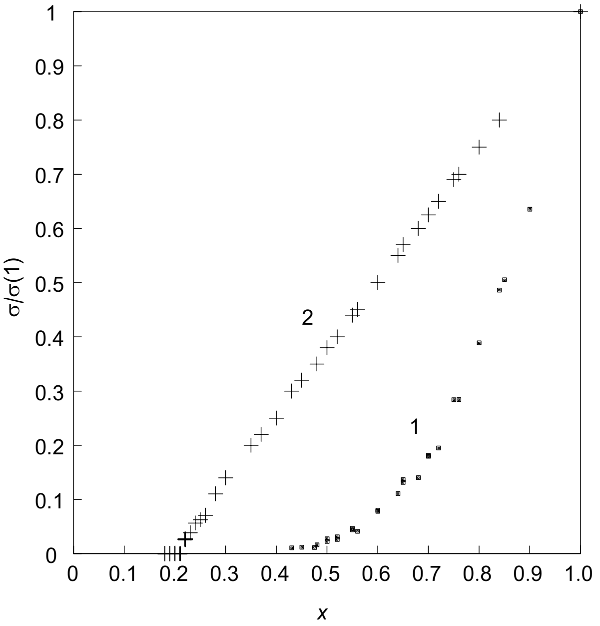

Fig. 3 Theoretical predictions for electroconductivity of polydisperse systems *versus* surface coverage fraction *x* (granulated support): 1 (·) random uniform distribution of supported phase, 2 (+) distribution correlated with intergranular contacts.

dependence of the net conductivity of a system on the degree of the conducting coverage of a surface, x. For completeness, we assumed the supported phase to be the conducting one ($\sigma = 1$) and the support to be isolating ($\sigma = 0$). When x achieves some critical value x_c, this is manifested in the appearance of the overall conductivity which then grows monotonically with growing x. The conductivity behaviour depends both on the structure of the supporting phase and the distribution of the supported phase.

If the supporting phase has a continuous structure (a single grain, a sintered film, a sponge, *etc.*) then the role of the surface area is manifested in the position of the percolation threshold and in the behaviour of the conductivity in the nearby threshold region (see Fig. 2). A large intrinsic support surface may lead to opposite consequences, depending on the structure of the pores. As compared with a smooth surface (curve 1, $x_c \simeq 0.27$), the open pores provide extra paths for current, thus enhancing the conductivity and lowering the percolation threshold (curve 2, $x_c \simeq 0.15$). The blind pores accumulate the conducting material in dead-ends, thus suppressing the conductivity and raising the percolation threshold (curve 3, $x_c \simeq 0.42$).

If the supporting phase has a granulated structure, the intergranular contacts play the dominant role. Then, only the location of the supported phase is important, while the surface area has only a small influence (see Fig. 3). When comparing the random uniform distribution (curve 1) and the distribution correlated with contact points (*i.e.* every intergranular contact is obliged to belong to supported phase, curve 2), we observe that not only does the percolation threshold shift but in addition, the shape of the curve changes generally. These distributions may thus be discriminated experimentally. Hence, even a small amount of supported phase may lead to visible effects in conductivity character, if located in contact regions. Since a chemical interaction or a phase transformation usually starts with intergranular contacts, many important processes of a catalyst's biography (such as oxide reduction, formation of chemical compounds in the course of its preparation or exploitation, *etc.*) may be detected in their very early stages.

Thus, electroconductivity measurements have been shown to be a sensitive tool for probing the geometrical and physical structure of a catalyst. A comparison of experimental results with theoretical predictions would enable one to draw some conclusions about the structure of the pores of the supporting material and on the character of the supported phase distribution. Such information is important for the development of principles of synthesis of catalysts with predicted properties.

Financial support of this work by the International Science Foundation (grant no. M63000) is gratefully acknowledged.

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Received: Moscow, 5th December 1994
Cambridge, 28th February 1995; Com. 4/07649D