Catalysts, commercial or laboratory made, show a decline in activity when they are used in reactions. This behaviour, detrimental to the industrial efficiency and often not well understood by the laboratory chemist, may result, in principle, from many reasons. One of the most suspected is the presence in the reactants of poisons which cover permanently the catalyst and compete therefore for the chemisorption of reagents. But also, the reaction products undergo a further evolution, like polymerization or cracking, and their deposit on the surface of the catalyst is comparable to poisoning. These phenomena, however, are to be distinguished from the sintering which is an additional, if not the main, cause of the loss in activity. The sintering may result in the decrease of the active area and in the change of the structure of the surface. For instance, the porous oxide catalyst or the porous support of the active metal may exhibit a narrowing or closing of its pores. The permeability of the catalytic bed decreases together with the loss of accessible area. The porous, high surface area oxide catalyst may also change its surface structure by surface recrystallization, and by formation or vanishing of surface defects, whose role may be important in catalysis.

In the case of an active metal like platinum deposited on a high surface area carrier, if the carrier itself is preserved from any modification, the metal which initially is in a highly dispersed state, may sinter and this results in the growth of its crystallites and in the change of its surface structure.

These phenomena, which are here reunited in a general term of sintering are responsible for the decrease of the catalytic activi-
ty and also, very often, for a change in the reaction selectivity. Moreover, in the case of poisoning of a catalyst a reactivation process is required in order to remove the materials (poisons, coke, tar) covering the active surface. This reactivation may result in a sintering of porous catalysts or carriers or in a grow of metal particles.

The understanding of the influence of these various factors on the catalytic activity and selectivity is still very poor. Besides, a clear definition of the catalytic activity is still lacking. Generally based on kinetic results (e.g. number of moles of the reactant transformed per unit time, per unit mass of the catalyst or of the active metal in the catalyst or per unit area of the catalyst or active metal in the catalyst) the activity may also imply the activation energy and the preexponential factor, because its change with the temperature may not be simple.

On the other side the catalysts are active through their surface properties (particular crystal surface planes, or surface defects or surface coordination of active atoms or ions). These surface properties impose a particular catalytic activity and selectivity which may undergo a change if these properties are modified, for instance through the recrystallization process.

In the search for correlations between the catalytic activity and the sintering, considered in the most general sense, it is necessary to determine if a reaction under study is a structure sensitive reaction (or demanding reaction) or a structure insensitive reaction (or facile reaction). This very interesting concept, suggested by BOUDART (1) for reactions catalyzed by supported metals (mainly platinum), was recently applied also to oxide catalysts (2). The determination of this characteristic of the reaction (demanding or facile) requires a series of catalysts of the same type, differing only by the size of particles of the active component, like platinum crystallites. The increase of their size may be achieved by a progressive heating of a given platinum catalyst or by a progressive increase of the platinum content in a series of catalysts.

In this way, BOUDART showed that for platinum on alumina catalysts the catalytic activity, expressed as the number of molecules of the reagent, converted per unit time per surface platinum atom (turnover number) at a given temperature, decreases for certain reactions (like hydrogenolysis of neopentane) when the size of platinum crystallites increases. On the other hand for facile reactions like hydrogenation of benzene, the turnover number remains constant when the particle diameter increases.

The number of surface defects or coordinatively unsaturated sites increases when the particles diameter decreases (3). Certain reactions therefore require these defects, whereas other are produced on any type of active surface.