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# APPLICATION OF THERMAL ANALYSIS TO THE INVESTIGATION OF CATALYSTS

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A short review of the possibilities of application of thermal analysis to the investigation of catalysts is given: analysis of catalysts, investigation of the processes during the preparation of catalysts, desactivation of catalysts, and interaction of reactants or catalytic poisons with the catalysts. Several examples are mentioned.

The oldest field of application of the methods of thermal analysis is the investigation of the composition of minerals and rocks. As some minerals (e.g. silicates) are used as catalysts and as processes of a similar kind – which may be observed by thermoanalytical methods – take place in a number of other catalysts during their heating or cooling, the analysis (phase analysis) of catalysts represents the oldest application of thermal analysis for the investigation of catalysts. This application is a very important one, because the catalysts used in practice are often rather complex systems, in many cases obtained by empirical procedures, so that it is necessary to identify the individual components or to determine their relative proportions in the catalysts. The data obtained about the composition of the catalyst are then correlated with its catalytic activity, selectivity, or resistance against desactivation. Differential thermal analysis was used, for example, for the determination of the phase composition of the catalysts of the type Bi–Mo–O, and of the influence of this composition on their activity in the oxidation of butene [1–3].

In our laboratory thermoanalytical methods were also used for the determination of the phase composition of a catalyst, of the type Fe–Mo–O, applied to the oxidation of methanol to formaldehyde. This catalyst was prepared on the basis of results obtained by a statistical optimalization experiment. The analysis of the process of preparation and of the X-ray diffraction data led to the assumption that the catalyst represents a system consisting of iron(III) molybdate and molybdenum trioxide.

For qualitative analysis DTA was used: in the heating curves (20°/min up to 1150° in air) endothermic peaks were observed in the temperature range 800–850°, corresponding to the melting and sublimation of the free $MoO_3$ present, as well as other endothermic peaks around 1000°, corresponding to the melting and subsequent decomposition of $Fe_2(MoO_4)_3$. The quantitative determination of both these components was performed by thermogravimetry: the loss in mass at 850° corresponded to the sublimation of the free $MoO_3$ present, whereas the loss in mass at 1050° corresponded to the sublimation of $MoO_3$ formed by the decomposition of the $Fe_2(MoO_4)_3$ present.

Both DTA and TG were used in the same manner for the analysis of a series of catalysts prepared by a solid-state reaction between $Fe_2O_3$ and $MoO_3$. For this series of catalysts, ranging from pure $Fe_2O_3$ to mixtures of $Fe_2O_3$ and $Fe_2(MoO_4)_3$, pure $Fe_2(MoO_4)_3$, mixtures of $Fe_2(MoO_4)_3$ and $MoO_3$, and finally to pure $MoO_3$, an unambiguous dependence of the activity and selectivity of these catalysts on their composition was established in the oxidation of methanol [4].

All cases of the analysis of already-prepared catalysts in fact represent the investigation of processes which take place during the thermal decomposition of catalysts at temperatures above the temperature of their preparation or of their use in the catalytic reactor.

The methods of thermal analysis, however, give us the further possibility to follow at least some of the processes occurring during the preparation of catalysts. This is due to the fact that in many cases first a precursor is prepared, usually a precipitate of hydroxides or thermally unstable salts of the elements in question, alone or on a suitable support. This catalyst precursor is further heated to a gradually increased temperature in a defined or even variable atmosphere. During this procedure a number of processes take place: e.g. dehydration, decomposition of carbonates, nitrates, etc. and finally the formation of oxides (in some cases mixed ones) of the elements in question. Sometimes this step is further followed by a reduction of the oxides formed to the corresponding metals by the action of a suitable reducing atmosphere.

With regard to the fact that the final properties of a catalyst are influenced to a significant extent by the manner of its preparation, it is useful to use this possibility of studying the process of the formation of catalysts, at least from their precursors in the course of the thermal activation, in such a way that this process is simulated directly in a suitable apparatus for thermal analysis.

As an example of this procedure may be mentioned the DTA of a precursor, represented by a mixed precipitate of nickel hydroxide and hydrogel of alumina. In those catalysts where the formation of aluminate was observed, after the reduction a higher degree of dispersion of nickel in the surface and therefore a higher activity was achieved [5].

In a number of catalysts it is necessary to choose conditions of preparation ensuring that the temperature and the duration of the thermal activation of the precursor will be sufficient for the formation of a desired catalyst, but that exceeding of the necessary values will not cause the sintering of the catalyst, the decrease of its surface, and thereby also the decrease of its catalytic activity.

From this point of view we have recently investigated some catalysts of the type Ni – Mo – O. For example, the decomposition of an initial precipitate, representing a defined compound of Ni and Mo, was studied by means of simultaneous DTA, TG, DTG and EGD [6].

From the results of thermal analysis, practical conclusions concerning the procedure for the preparation of catalysts were deduced: e.g. determination of the temperatures to which the precursor is gradually heated, of the temperature region in which it is necessary to supply a stream of air (which prevents the reduction of molybdenum by the released ammonia), as well as of the temperature and time after the reaching of which it is necessary to terminate the activation.

Another point which is very interesting for those working in catalysis is the question of catalyst desactivation, resulting either from structural changes in the catalyst (here a comparison of the thermal analysis of the desactivated catalyst with that of the fresh active one might be very useful), or from the formation on the surface of a catalyst of a deposit (mostly of carbon) which occupies its active centres. Such a deposit can be very well studied by thermal analysis [7]. Thermal analysis may also be applied to the investigation of the interaction with the catalyst of various adsorbed substances, either reactants (original substances, intermediates or products of the catalytic reaction for which the catalyst in question is used) or catalytic poisons. In this application the initial system at the beginning of the thermal analysis is formed by the catalyst onto which the appropriate substances were adsorbed beforehand (usually in vacuo). In the course of the heating of a sample prepared in this way a gradual desorption of the adsorbate (or of the products of its interaction with the catalyst) takes place, the rate of this depending on the temperature of the sample. This technique is usually called programmed thermal desorption [8].

The common feature of the above-mentioned applications is the fact that they may be performed by means of usual types of apparatus for thermal analysis, usually by DTA, TG and/or EGA. However, it is necessary to work in a defined atmosphere, in some cases with passage of a stream of a gas above the sample. If the possibility to pass the gas directly through a layer of the sample is given, the temperature-dependence of the reactivity of the catalyst may be directly simulated [9]. Beyond the scope of thermal analysis in the proper sense of the word lie techniques which on the one hand use the equipment usual in thermal analysis, e.g a differential thermocouple or a thermobalance, but on the other hand work at constant temperature with a variable composition of the atmosphere around the sample. The optimum application of these techniques (as well as of methods of genuine, i.e. thermally programmed thermal analysis) with a controlled atmosphere needs a special modification of the apparatus: the flow of gas through the sample in a conveniently adapted sample holder, in TG at least especially flat crucibles making possible the fast exchange of gases with the sample. These techniques with a controlled atmosphere also give rise to further problems in the interpretation of results, due to the appearance of chromatographic effects [10]. In spite of the problems involved, all methods of thermal analysis in the investigation of catalysts may be considered very prospective ones.

## References

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Résumé — On présente une rapide vue d'ensemble sur les possibilités d'application de l'analyse thermique à l'étude des catalyseurs: l'analyse des catalyseurs, l'étude des processus ayant lieu lors de la préparation des catalyseurs, la désactivation des catalyseurs, l'interaction de réactifs ou de poisons sur les catalyseurs. Plusieurs exemples sont mentionnés.

Zusammenfassung — Eine kurze Übersicht über die Möglichkeiten des Einsatzes der Thermoanalyse zur Prüfung von Katalysatoren wird gegeben: Analyse der Katalysatoren, Prüfung der Vorgänge während der Herstellung von Katalysatoren, Inaktivierung von Katalysatoren, Wechselwirkungen zwischen Reagenzien oder Katalysatorengiften und den Katalysatoren. Eine Anzahl von Beispielen wird erwähnt.

Резюме — Приведено короткое обозрение о возможности применения термического анализа к исследованию катализаторов: анализ катализаторов, исследование процессов во время получения катализаторов, дезактивация катализаторов, взаимодействие реагентов и каталитических ядов с катализаторами. Упомянуты некоторые примеры.