SELECTION OF AMMONIA OXIDATION CATALYSTS BY A MODIFIED DTA METHOD

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The paper presents a technique of examining catalysts by a modified DTA method in mixtures of reacting gases. The possibilities of using the obtained results for a selection of ammonia oxidation catalysts have been examined. The technique described may also be applied for the selection of catalysts in other reactions.

Thermal methods have been applied for the examination of many aspects of catalytic ammonia oxidation, among others the activities (selectivities) of catalysts of oxidation to NO as the most interesting one [1 — 11]. Since ammonia oxidation comprises three different reactions, each of which has a different exothermicity (producing nitrogen N_2, nitrous oxide N_2O, and nitrogen oxide NO, with exothermicities of 316.7 kJ, 276.1 kJ and 226.4 kJ per mole of NH_3, respectively), a change in the selectivity, produced for instance by a temperature change, will consequently bring about a change in the heat generated on the catalyst. This naturally complicates an unequivocal determination of the activity (selectivity) only on the basis of the heat effects. For this reason, the reports published so far have assumed the occurrence of only one reaction on the catalyst. It seems possible, however, to approach the problem of catalyst selection by the DTA method in a way which will not require such an assumption. This approach is presented below.

Experimental

Experiments were carried out in an apparatus which could operate in a temperature range up to 900° at atmospheric pressure and with a constant flow of gas mixture of any quantitative composition. The apparatus, applied formerly to the examinations of other reactions [12 — 14], consisted of a typical unit for the gas mixture preparation [15], measuring systems with a sample (single pellet) set parallel or perpendicular to the gas flow direction (Figs 1 and 2), and recorders (EZ-10 and Kipp BD-2).

The reactor and the thermocouple (Pt — Pt 10% Rh, 0.2 mm in diameter) covers were made of quartz glass. For this reason the Δt value (catalyst overheating) was measured in relation to the temperature (further denoted as gas temperature, t_g) indicated by the thermocouple placed in the quartz cover, about 2 mm in diameter.
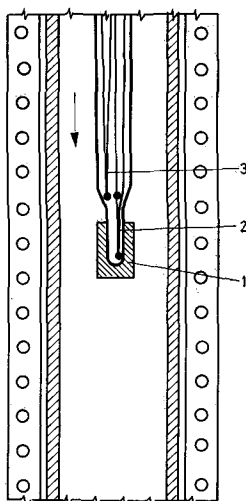
Fig. 1. Measuring system with a parallel setting of the sample; 1 — sample of catalyst, 2 — differential thermocouple; 3 — thermocouple for gas temperature measurement, scale close to 1 : 1
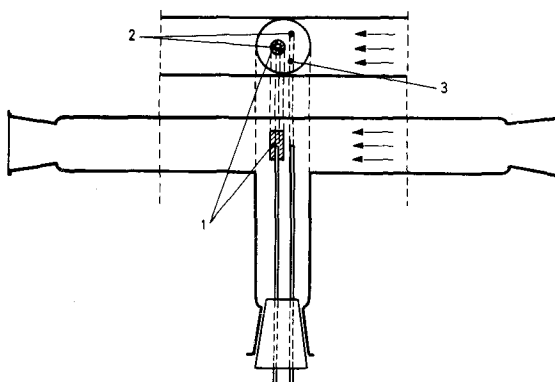

Fig 2. Measuring system with a perpendicular setting of the sample; 1, 2, 3 and scale as in Fig. 1

The measurements were taken at a constant increase and/or decrease in the reactor temperature, at a rate of about 5°/min.

Samples were in the form of single, commercially available metal oxides of various degrees of purity (denoted as "pure" to "p.p.a."); these were placed as water pastes on a thermocouple cover by means of a special device. Metals were applied as wires twined in single coils round a thermocouple cover. The masses of the samples were of the order of several tens of mg.

The gas mixture, composed of 10 vol.% of ammonia and 90 vol.% of air, flowed at a linear rate of 18 cm/sec or 36 cm/sec, depending on the type of the reactor (the reactors had different diameters, and the Reynolds numbers were 145 and 96, respectively).

Results and discussion

Direct results were obtained as values of $t_g = f(\tau)$, where t_g was the gas temperature at a distance of 3 or 5 mm before the catalyst, and τ denoted time, while $\Delta t = f(\tau)$. The results were obtained by recording $t_g = f(\tau)$ and $\Delta t = f(\tau)$ simul-
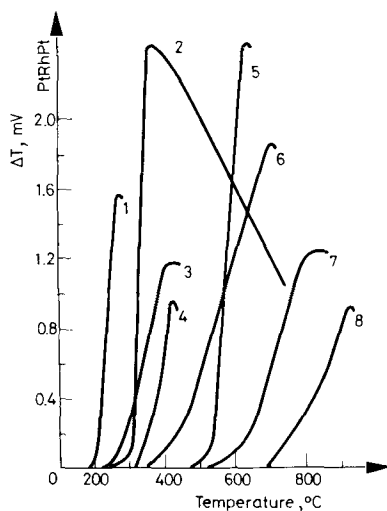

Fig. 3. Catalyst overheating curves; parts before the maxima shown; for catalyst 2 the whole curve is shown. 1-Co_2O_3; 2-Fe_2O_3; 3-CuO; 4-MoO_3; 5-La_2O_3; 6-MgO; 7-Al_2O_3; 8-PbO

taneously but independent by two recorders and after each measurement these results served as the basis for plotting $\Delta t = f(t_g)$ or $\Delta t = f(t_c)$, where t_c (catalyst temperature) is equal to $t_g + \Delta t$. The curves obtained in this way had a characteristic S-shape (Fig. 3, curve 2). In some cases, however, the shape was more complicated, which was connected with phase transformations, oscillatory phenomena [11], etc.

The results obtained may be used for catalyst selection in various ways.

1. The overheating curves characterize the interval of a catalyst's activity, its lower limit in particular (Fig. 3), which thus makes it possible to perform an initial selection of catalysts in cases when the external conditions require an application of catalysts with given operation temperatures. In such cases, the obtained curves make it possible to eliminate from further research the catalysts active at inadequate temperatures [14].

2. The overheating curves may be useful in permitting choice of a temperature interval for detailed studies by more complex methods, since they provide information about characteristic regions, e.g. of phase transformations, etc.

3. If some catalysts are active in the same or similar temperature intervals, then they may be compared directly on the basis of the overheating curves. In view of the identical or similar heat exchange conditions, even on the basis of the Δt values one may state that, for instance, heat is generated more quickly on catalyst 2 in Fig. 3 than on catalysts 3 and 4. It enables one to eliminate from further research catalysts showing the lowest rates of heat generation. A small rate of heat genera-
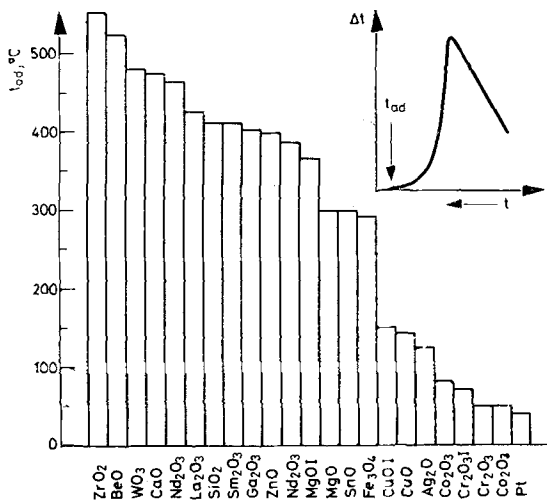

Fig. 4. Catalyst activity sequence measured by the value of the activity disappearance temperature (t_{ad})

tion implies that one cannot expect a high yield of any oxidation product, including NO (differences in the exothermicities of particular reactions are too small — at most about 30% — to account for overheating differences reaching 100% or more).

4. The temperature at which there appears a catalyst overheating of 1 °C (which then continues to rise with the increasing reactor temperature) may be called an activity appearance temperature (t_{aa}), while that at which, during cooling of the reactor, the catalyst overheating is still 1° (and then goes on decreasing) may analogously be called an activity disappearance temperature (t_{ad}). With these definitions, it turns out that sequences of catalysts arranged according to increasing t_{aa} values, and even more so with the t_{ad} values, are very similar (Fig. 4) to the sequences determined by chemical analysis methods [16]. Results obtained in this way may thus constitute a starting point for futher considerations, just like those in papers reported so far. Nevertheless, one should emphasize the simplicity of obtaining results which, in other cases, for instance by gas chromatography, would be

much more time-consuming and would require the application of a complex apparatus [17].

5. Since the initial elimination (cf. item 3 above) is usually insufficient, a comparison of catalysts active in different temperature intervals must take into consideration the influence of heat exchange on the value of overheating. After a calculation of the rates of heat generation [13, 18], one obtains the curves shown in Fig. 5. Their courses will allow an elimination of catalysts in a way analogous to that shown above for the overheating curves. Besides this, they also make possible a choice of curves of fairly slow decreases of rates of heat generation after a maximum, which is advantageous technologically.

6. An analysis of a larger number of heat generation curves [19] reveals that the maxima of catalysts reported in the literature [20] as selective in oxidation to NO lie at much lower temperatures than the maxima of the catalysts regarded as non-selective [21]. Since the literature data [19] report the courses of the most exothermic reactions of oxidation to nitrogen in a temperature interval close to the t_{aa},
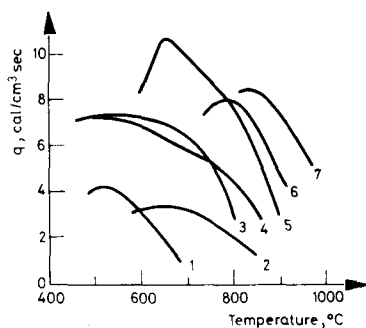

Fig. 5. Heat generation rates for different catalysts; parts of curves after the maxima shown. 1-Pb_3O_4; 2-SnO_2; 3-V_2O_5; 4-Fe_3O_4; 5-La_2O_3; 6-ZrO_2; 7-CaO

and the appearance, followed by the gradual predominance, of other less exothermic oxidation reactions at higher temperatures, the observation presented above may be explained by the scheme offered in Fig. 6. This shows that a high selectivity of oxidation to NO may be expected when the catalyst is active at lower temperatures; otherwise, it would enter the region of homogeneous oxidation (to N_2) before reaching the interval of the oxidation to NO.

7. If we assume that the total heat generated at maximum temperature $t_{q_{max}}$ is derived from the oxidation to nitrogen, then, at the temperature in which $q = 2/3 \, q_{max}$ one may expect the highest rate of oxidation to NO (with the additional assumption that the ammonia consumption remains constant), since the ratio of the exothermicities of oxidations to NO and to N_2 is about 2/3.

8. The assumptions imposed above may now be formulated less rigorously and we may then assume that at the temperature of maximum heat generation there already occur other less exothermic reactions. Thus, the presented technique still

makes an initial catalyst selection possible, for it allows a determination of the limits of the interval of the greatest probability of the occurrence of NO, as equal to $t_{q\max} \leq t \leq t_{2/3\ q\max}$. This will facilitate the choice of a temperature interval for detailed studies by other methods.
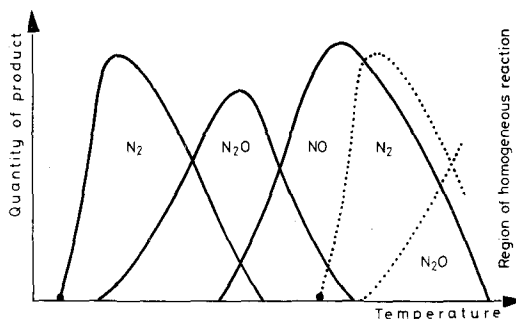

Fig. 6. Scheme of the reaction courses on low- and high-temperature catalysts. — low temperature catalyst; .... high temperature catalyst; ● activity appearance temperature (t_{aa})

Conclusion

It seems that, owing to the simplicity of the apparatus, the short time needed to obtain the results, the easy automation of the measurements, as well as the simple interpretation of the data, the technique described may prove useful for an initial selection of catalysts of ammonia oxidation and of other similar reactions.

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RÉSUMÉ — L'article présente une technique destinée à l'examen des catalyseurs par une méthode d'ATD modifiée, effectuée dans des mélanges de gaz réagissants. In a examiné la possibilité d'utiliser les résultats obtenus pour sélectionner des catalyseurs d'oxydation de l'ammoniaque. La technique décrite peut aussi être appliquée à la sélection de catalyseurs pour d'autres réactions.

ZUSAMMENFASSUNG — Es wird eine Technik zur Untersuchung von Katalysatoren durch eine modifizierte DTA-Methode in einem Gemisch von reagierenden Gasen beschrieben. Die Möglichkeit des Einsatzes der erhaltenen Ergebnisse zur Wahl von Katalysatoren zur Ammoniakoxidation wurde untersucht. Die beschriebene Technik kann auch zur Auswahl von Katalysatoren für andere Reaktionen angewandt werden.

Резюме — Представлен метод исследования катализаторов с помощью видоизмененного метода ДТА в смесях реагирующих газов. Изучена возможность использования полученных результатов для подбора катализаторов окисления аммиака. Описанный метод может быть использован для подбора катализаторов в других реакциях.