Journal of Thermal Analysis, Vol. 19 (1980) 449—452

DETECTION OF PRE-IGNITION/POST-EXTINCTION (OSCILLATORY) PHENOMENA IN A CATALYST-AMMONIA-OXYGEN SYSTEM BY A MODIFIED DTA METHOD

A. WOJNOWSKI and J. BARCICKI

Department of Chemical Technology, Institute of Chemistry UMCS, M. Curie — Sklodowska Square 3, 20-031 Lublin, Poland

(Received June 12, 1979)

The paper presents results of examining catalysts by a modified DTA method in a pre-ignition/post-extinction region. The results include a finding of oscillatory and other phenomena in the given temperature range.

Oscillatory phenomena still constitute the subject of many studies [1—4], and the usefulness of thermal methods for the examination of these effects [5] has been emphasized. The present note reports the results of examination of the catalyst ignition/extinction obtained by a modified DTA method. Among others, these results include a discovery of oscillatory phenomena in the presence of catalysts in the given temperature range.

Experimental

The examinations were carried out with an apparatus which made possible direct measurements of the temperature difference between the interior of a catalyst single pellet, i.e. a layer or coil of the catalyst located on the quartz cover of the thermocouple, and a stream of the gas mixture. Measurements were taken with a system of thermocouples and an appropriate recorder. The catalysts employed included commercially available metal oxides and metals in the form of wire [6—9].

Results and discussion

Even during the first experiments it was found that the course of the phenomena in the ignition/extinction region was more complex than could be expected from the literature data [10—12].

The phenomena observed are shown in Fig. 1 A—D. The fact that seems most striking here is the overheating of the catalyst in the region in question, which does not exceed a few degrees and is usually only 1—2°. It seems, therefore, that the observation of these phenomena was possible due to the low activity of the examined samples. Owing to this low activity, a too quick overheating/cooling of the catalyst did not occur and the effects could be observed as if taking place "in slow motion".

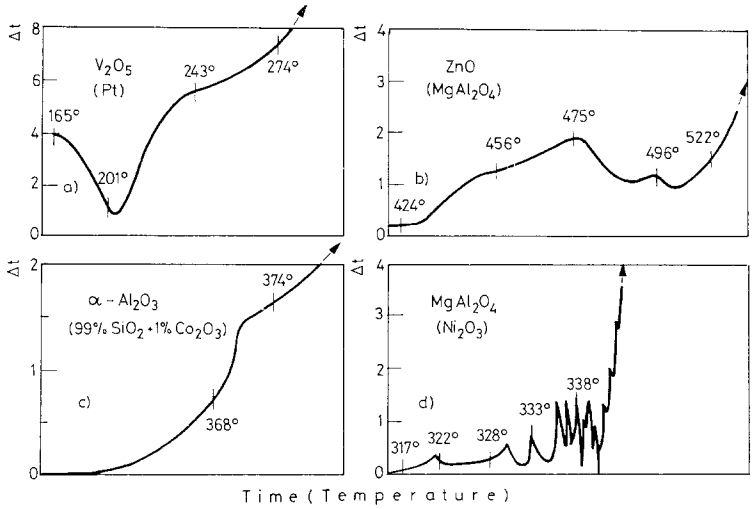

Fig. 1. Pre-ignition phenomena in a catalyst-ammonia-oxygen system: 10vol% NH_3 + 90vol. % air, single pellet of catalyst

Since the reproducibility of the phenomena (temperature range, magnitude of effects) was not high, it is hard to state with any certainty whether or not the effects *B*, *C* and *D* in Fig. 1 are variants of the same kind of phenomenon. However, effects similar to *B* and *C* were observed most often. It is not clear, either, if the phenomena of type *A* observed in the vanadium and platinum catalysts had the same cause, since in the case of platinum they took place in a much smaller temperature range, that is, the effects were much quicker. The question may now be asked is to whether the differences result from the high activity of platinum in the oxidation reactions, or whether they perhaps throw some light on the causes of this activity.

It seems that the main factor determining the reproducibility of the results was the rate of passing through the region of these effects, that is, the rate of temperature changes. The phenomena with a typically oscillatory character were observed most often when the system was cooled at a rate of about 1°/min in the region preceding the extinction (Figs 2 and 3). Heating usually produced merely a single effect of type *B*.

The course of the phenomena is also affected by the sample size or the thickness of the catalyst layer (Figs 2 and 3). The amplitude of the oscillations further depends on the ammonia concentration (with oscillations disappearing at both high and low concentrations) and on the temperature (Figs 2 and 3).

The region of appearance of the phenomena indicates that some thermal effects connected with sorption/desorption may be involved here, although it is difficult to ascertain the usefulness of any of the numerous interpretations suggested in the literature, because the similarity between the phenomena described here and those

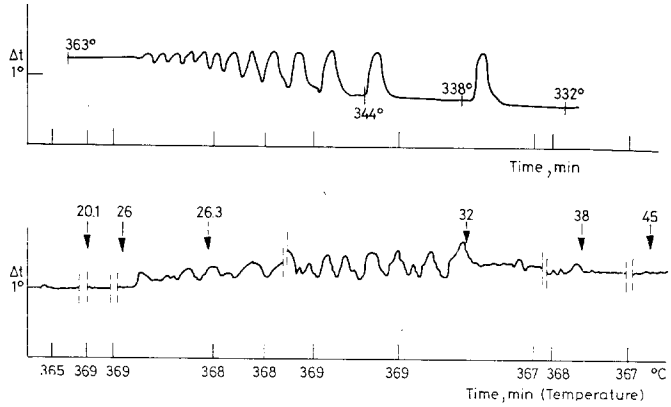

Fig. 2. Oscillatory phenomena in a post-extinction region: 10vol.% NH_3 + 90vol.% air (upper part) and NH_3 concentration (in arbitrary units) indicated with arrows (lower part), $MgAl_2O_4$ catalyst, layer thickness about 0.5 mm

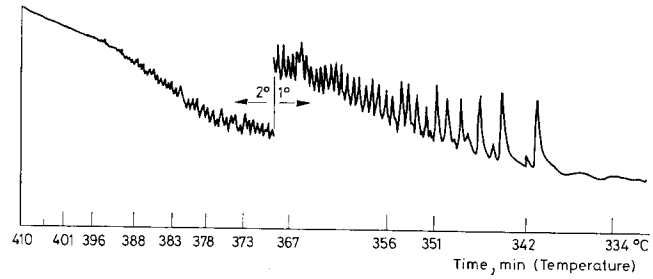

Fig. 3. Oscillatory phenomena in a post-extinction region: 10vol.% NH_3 + 90vol.% air, $MgAl_2O_4$ catalyst, layer thickness about 1.5 mm

known from the literature may be only apparent, while differences in experimental techniques make a comparison of the results difficult.

The effects observed indicate the complexity of the processes taking place at the catalyst ignition/extinction and require further research. The results obtained confirm the usefulness of the presented method for the examination of some aspects of catalysis other than activity.

References

1. U. F. FRANCK, Angew. Chem., 17 (1978) 1.
2. P. VARGHESE, J. J. CARBERRY and E. E. WOLF, J. Catal., 55 (1978) 76.
3. J. E. ZUNIGA and DAN LUSS, J. Catal., 53 (1978) 312.
4. J. BARCICKI and A. WOJNOWSKI, React, Kinet. Catal. Lett., 9 (1978) 59.
5. P. K. GALLAGHER and D. W. JOHNSON, JR., Thermochim. Acta, 15 (1976) 238.

6. J. BARCICKI, W. SWITLUK and A. WOJNOWSKI, Ind. Chim. (Fr.), (1968) 263.
7. J. BARCICKI and A. WOJNOWSKI, Przem. Chem., 47 (1968) 762.
8. J. BARCICKI, A. WOJNOWSKI and J. CHMIEL, Environ. Protect. Eng., 3 (1977) 103.
9. A. WOJNOWSKI and J. CHMIEL, React. Kinet. Catal. Lett., 4 (1976) 443.
10. N. Y. BUBEN, Sbornik rabot po fizicheskoi khimii (dopolnitelnyi tom Zh. Phys. Khim. 1946), Izd. Akad. Nauk SSSR, Moscow 1947, p. 129.
11. V. V. BARELKO, Kinet. katal., 14 (1973) 196.
12. H. BEUSCH, P. FIEGUTH and E. WICKE, Chemie Ing. Tech., 44 (1972) 445.

RÉSUMÉ — L'article présente les résultats de l'examen de catalyseurs, par une méthode d'ATD modifiée, dans la région qui précède l'ignition et suit l'extinction, ainsi que des observations sur l'oscillation et autres phénomènes, dans l'intervalle de températures mentionné.

ZUSAMMENFASSUNG — Es wird über die Ergebnisse der Untersuchung von Katalysatoren durch eine modifizierte DTA-Methode im Bereich vor der Entzündung/nach der Löschung berichtet. Die Ergebnisse enthalten Beobachtungen von Oscillationen und anderen Erscheinungen in dem erwähnten Temperaturbereich.

Резюме — Представлены результаты исследования катализаторов с помощью модифицированного метода ДТА в области предвоспламенения и после тушения. Результаты включают найденные в упомянутой температурной области осцилляционные и другие явления.