

Note

Detection of catalytic oscillations by differential thermal analysis

P. K. GALLAGHER AND D. W. JOHNSON, JR.

Bell Laboratories, Murray Hill, N. J. 07974 (U. S. A.)

(Received 5 September 1975)

We have discussed the applicability of DTA to studies of catalysis in earlier work^{1–3}. The technique is conceptually simple, is quick and sensitive, and commercial equipment is readily available. In this brief note we wish to report that we have observed by DTA certain oscillatory or instability phenomena^{4,5} which involve rapid changes in the catalytic activity. We also illustrate how its rapid response and high sensitivity make it suitable for the study of these oscillations which may be more difficult to detect by other techniques⁴.

EXPERIMENTAL PROCEDURES AND RESULTS

Nominally 15 mg samples were placed in the sample pan of the DSC cell of a DuPont Model 900 DTA apparatus. An atmosphere of 2% CO, 2% O₂, 96% N₂, and with or without 150 ppm of SO₂ was flowed through the cell at a rate of 0.5 l min⁻¹. The heating rate was 10°C min⁻¹. Some typical examples of DTA curves exhibiting oscillations are shown in Fig. 1. In order to be sure the effect was not instrumental, we also performed an experiment using the Mettler 200 DTA system which confirmed our observations.

DISCUSSION

Danchot and Cakenberghe⁴ observed oscillations for the oxidation of CO on Pt wires and thin films by following electrical resistance or photo-voltaic effects. The samples in which we observe oscillations in the DTA pattern all contain Pt in significant amounts. Those illustrated in Fig. 1 have Pt contents ≥ 2400 ppm so that a significant amount of the observed activity, particularly in the presence of SO₂, is due to Pt^{6,7}. Danchot and Cakenberghe⁴ attribute these oscillations to the applicability of the Langmuir–Hinshelwood mechanism in which the reaction takes place between CO and O₂ molecules adsorbed upon the surface of the Pt. The exothermicity of the reaction markedly raises the temperature of the catalyst desorbing the product CO₂. However, at higher temperatures O₂ is preferentially adsorbed and the sample must cool in order to adsorb enough CO before reacting again. This gives rise to cycles whose period and amplitude depend upon many things, e.g., thermal transport, concentrations in the gas phase, etc.

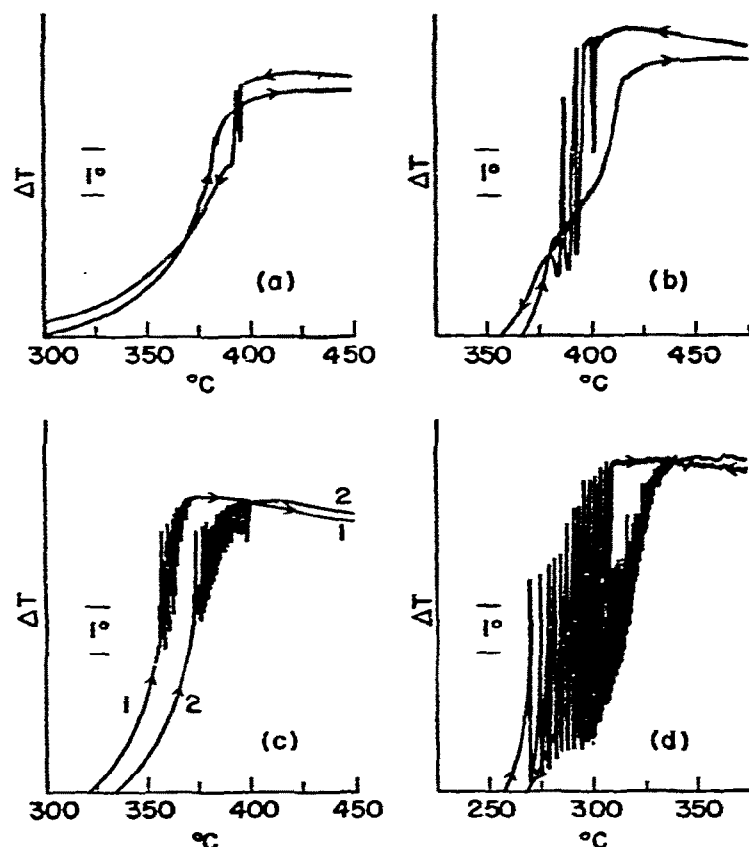


Fig. 1. DTA Curves for 15 mg of the indicated catalysts and atmospheres. Heating rate, $10^{\circ}\text{C min}^{-1}$ and flow-rate, 0.51 min^{-1} . (a) $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3 + 2400 \text{ ppm Pt}$, ground single crystals, 2% CO , 2% O_2 , 96% N_2 . (b) $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3 + 2500 \text{ ppm Pt}$, freeze dried, 2% CO , 2% O_2 , 96% $\text{N}_2 + 300 \text{ ppm SO}_2$. (c) $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3 + 5500 \text{ ppm Pt}$, ground single crystals, 2% CO , 2% O_2 , 96% N_2 . (d) $\text{La}_{0.7}\text{Pb}_{0.3}\text{MnO}_3 + 5500 \text{ ppm Pt}$, ceramic preparation, 2% CO , 2% O_2 , 96% $\text{N}_2 + 300 \text{ ppm SO}_2$.

The examples in Fig. 1 were selected in order to illustrate a wide range in the observation of this effect. Figure 1a shows essentially the threshold of the observable effect. It is characteristically more obvious on the cooling curve as can also be seen in Fig. 1b where the effect has become greater. The exact nature of the oscillations is not precisely reproducible under our experimental conditions as illustrated by successive heating curves shown in Fig. 1c. Figure 1d is our most pronounced example of this effect. The oscillations are as large as 4°C in amplitude with a varying period of 2–30 sec. They, of course, represent a combination of the actual catalytic effect and the experimental and instrumental response characteristics. Obviously further work would be necessary to establish the actual catalytic response curves.

ACKNOWLEDGEMENTS

The authors are grateful to Mrs. E. M. Vogel for some experimental assistance and to Mr. R. J. H. Voorhoeve for helpful discussions.

REFERENCES

- 1 D. W. Johnson, Jr. and P. K. Gallagher, *Thermochim. Acta*, 7 (1973) 303.
- 2 D. W. Johnson, Jr., P. K. Gallagher, E. M. Vogel and F. Schrey, *4th International Conference on Thermal Analysis, Budapest, Hungary, July 1974, Therm. Anal.*, 3 (1975) 181.
- 3 P. K. Gallagher, D. W. Johnson, Jr. and E. M. Vogel, *5th Conference on Catalysis in Organic Synthesis, Boston, April 1975*, to be published in the proceedings thereof.
- 4 J. P. Danchot and J. Van Cakenberghe, *Nature Phys. Sci.*, 246 (1973) 61.
- 5 K. M. Yu and J. M. Douglas, *Chem. Eng. Sci.*, 29 (1974) 163.
- 6 P. K. Gallagher, D. W. Johnson, Jr., J. P. Remeike, F. Schrey, L. E. Trimble, E. M. Vogel and R. J. H. Voorhoeve, *Mater. Res. Bull.*, 10 (1975) 529.
- 7 P. K. Gallagher, D. W. Johnson, Jr., E. M. Vogel and F. Schrey, *Mater. Res. Bull.*, 10 (1975) 623.