JOURNAL OF CATALYSIS 40, 281-285 (1975)

NOTES

The Use of Differential Scanning Calorimetry in Catalyst Studies. The Methanation of Carbon Monoxide over Nickel/Alumina Catalysts

There have been several publications which describe the use of differential thermal analysis (DTA) in catalyst evaluation. For example, Keely (*1*) has described the use of DTA both for studying catalyst calcination and reduction, giving results for dehydration of a mixture of β-$Al_2O_3\cdot 3H_2O$ and α-$Al_2O_3\cdot H_2O$ and the reduction of NiO. Papadatos and Shelstad (*2*) have described the use of a DTA apparatus to screen mixed oxides as catalysts for the oxidation of toluene, while Wedding and Farrauto (*3*) have used the method to compare various catalysts of the copper chromite type for the oxidation of CO and of hexane, and also discuss the use of the method to examine catalyst deactivation. [It is interesting to note that although Wedding and Farrauto (*3*) claim to be using differential scanning calorimetry (DSC), they were in fact using this in the DTA mode; the differences between DTA and DSC are discussed briefly below.] Finally, Landau and Molyneux (*4*) have reviewed the use of DTA in catalyst testing and have described a large amount of otherwise unpublished work from their own laboratories.

This note describes the use of a Perkin-Elmer DSC Ib apparatus in an investigation of the calcination, reduction and catalytic activity for carbon monoxide methanation:

$$CO + 3H_2 \rightarrow CH_4 + H_2O \qquad (1)$$

of coprecipitated Ni/Al_2O_3 catalysts of the type used in hydrocarbon steam-reforming. We attempt to show the versatility of the technique for catalyst testing and the quantitative nature of the results which can be obtained.

The essential difference between DTA and DSC is as follows. In the former technique, equal heat fluxes are supplied to both sample and reference so that the reference temperature increases at a steady rate and any thermal event in the sample is recorded as a temperature difference ΔT between sample and reference. In the latter technique, different heat fluxes are supplied to sample and reference either at constant temperature or when heating or cooling, so that both maintain the same temperature throughout; any difference between sample and reference is recorded as a rate of supply or removal of heat, $d(\Delta H)/dt$. Whereas in DTA the value of ΔT is a qualitative measure of the thermal event which occurs, the value of $d(\Delta H)/dt$ obtained with DSC is completely quantitative, not depending on the heat capacity of the solid involved. This fact, and the fact that small quantities of solid (catalyst) are required, make the technique extremely valuable as a means of determining the kinetics of catalytic reactions in which (a) heat is evolved or taken up and (b) a single product is involved, i.e., the catalyst is selective.

The methanation reaction (1) is particularly suitable, under criterion (a), for examination by DSC as it is exothermic ($\Delta H_{500} = -218$ kJ mol^{-1}), proceeding essentially to completion at atmospheric pressure and at temperatures below about 650 K. Criterion (b) is also fulfilled as nickel is selective for methane formation and carbon deposition will not occur under the conditions used (*5*) (H_2:CO > 2.8), as long as a flow of the reactant gases is maintained (see below). Provided ΔH_T^0 is constant, the rate of the methanation reaction at temperature T will be proportional to $\{d(\Delta H)/dt\}_T$:

$$r_T = -\left\{\frac{dP_{CO}}{dt}\right\}_T = a\left\{\frac{d(\Delta H)}{dt}\right\}_T \qquad (2)$$

where a is a constant. If the rate of reaction is given by a rate expression:

$$\begin{aligned} r &= -\frac{dP_{CO}}{dt} \\ &= k\, P_{CO}{}^{n}\, P_{H_2}{}^{m} \exp(-E/RT), \end{aligned} \qquad (3)$$

then experiments can be carried out with various partial pressures of CO or H_2 or at various temperatures. Further, if differential conditions exist (i.e., rate of flow of reactant over the catalyst $\gg r$), then P_{CO} and P_{H_2} will be determined by the partial pressures of CO and H_2 in the reactant mixture. In the work to be described below, the reaction was studied under differential conditions at atmospheric pressure and using a 3:1 H_2:CO mixture; hence, by measuring $d(\Delta H)/dt$ during a programmed temperature increase, the value of the activation energy for the reaction, as well as a quantity proportional to k, may rapidly be determined and this may be compared with the values for other catalaysts. Some illustrative results are given below which show how the technique may be used to examine the calcination of coprecipitated nickel–alumina samples, the progress of their reduction in hydrogen at 1 atm at 773 K and their optimum catalytic activity; results which show the deactivation of the catalysts will also be presented, and other possible uses of the apparatus will be outlined.

Figure 1 shows typical DSC results for the decomposition (in flowing nitrogen) of samples of $Al(OH)_3$, of basic nickel carbonate, and of a coprecipitate, prepared from solutions of $Al(NO_3)_3$ and/or $Ni(NO_3)_2$ by addition of Na_2CO_3 solution according to the method outlined in Ref. (*6*); the results shown were obtained with a heating rate of 32 K min^{-1}, but similar results were obtained at other heating rates. The reference was in each case a blank aluminum sample holder. Clearly there is considerable interaction between the components in the coprecipitate; X-ray evidence shows that nickel hydroaluminate is present in some such samples before the first endotherm. The position of the endotherms varies considerably with the preparation conditions, and this may be interpreted in terms of different degrees of interaction, crystallite size, etc.

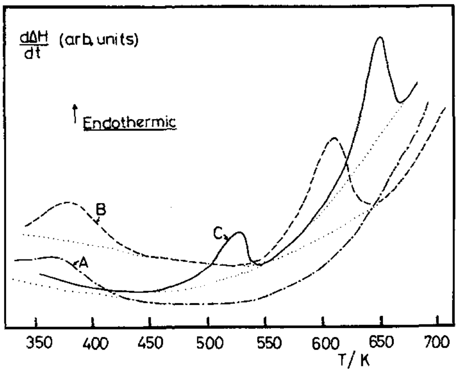

FIG. 1. DSC results for the decomposition in N_2 ($f = 60$ cm^3 min^{-1}) of $Al(OH)_3$ (A), basic nickel carbonate (B) and a coprecipitated sample (C) containing both components (Ni/Al = 5.2). Rate of temperature increase = 32 K min^{-1}.

Figure 2a shows typical recorder traces, superimposed upon one another, of $d(\Delta H)/dt$ versus T (or t) for a catalyst which was pre-reduced in a separate system and then reduced briefly in H_2 at 773 K in the DSC apparatus; the results were obtained with different flow rates (f), ranging from 10 to 120 cm^3 min^{-1}, and as above, the reference was a blank aluminum sample pan. Figure 2b shows plots of $d(\Delta H)/dt$ vs $1/f$ at several temperatures; the value of $d(\Delta H)/dt$ increases as

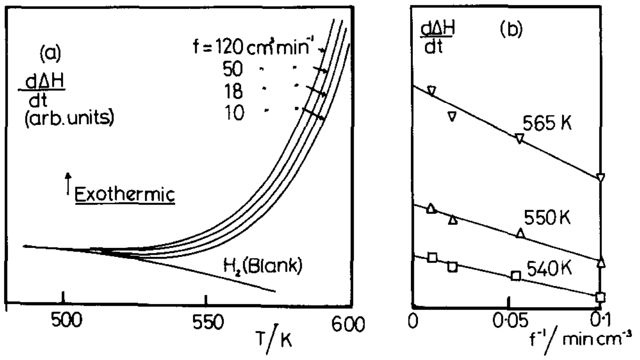

FIG. 2a. Recorder traces of $\{d(\Delta H)/dt\}_T$ vs T for reaction (1), for different flow rates, f. The blank was obtained using hydrogen with a flow rate of 120 cm^3 min^{-1}. Catalyst is a coprecipitated Ni/Al$_2$O$_3$ sample (75% Ni) prereduced in a separate system (see text). (b) Corresponding plots of $\{d(\Delta H)/dt\}_T$ vs $1/f$ at various temperatures.

$1/f \rightarrow 0$, i.e., as the conditions tend to being differential. Strictly speaking, plots of log $\{d(\Delta H)/dt\}_T$ vs $1/T$ (Arrhenius plots) should be constructed using limiting values of $\{d(\Delta H)/dt\}_T$ vs $(1/f \rightarrow 0)$, but we have standardized on the use of a value of f of 120 cm^3 min^{-1}, which enables rapid comparison of various catalysts to be made.

Figure 3a and b show results of experiments carried out using two catalysts prepared under slightly different conditions; catalyst A shown in (a) was calcined at 800 K, compared with catalyst B, shown in (b), which was calcined at 900 K. The calcined samples were reduced in the DSC apparatus at 773 K, using a flow of H_2 at 1 atm ($f = 60$ cm^3 min^{-1}); the reduction process was interrupted at various time intervals, which are shown, when the H_2 flow was replaced by a flow of $CO + 3H_2$ and the kinetics of the reaction were determined. Figure 4a and b show the corresponding Arrhenius plots. Clearly, catalyst A is more active at all stages of reduction; both catalysts are reduced slowly at 773 K, and this contrasts with the reduction of NiO, which can be carried out at the much lower temperature of 600 K [see, for example, Ref. (*7*)]. It should be noted that little useful information regarding the reduction itself can be obtained using DSC, as the reduction of nickel is effectively thermoneutral. Although the work described here is still somewhat qualitative, the relative activities of the samples studied are determined quantitatively, and this is to be contrasted with the DTA method (*3*). If, instead of using a fixed $CO + 3H_2$ feed, variable feed compositions are supplied, it should be possible to determine full kinetic parameters under strictly differential conditions, but this has not yet been carried out.

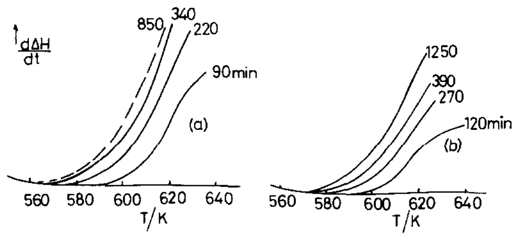

FIG. 3. Recorder traces of $\{d(\Delta H)/dt\}_T$ vs T for reaction (1) with $f = 120$ cm^3 min^{-1} after various periods of reduction in hydrogen; (a) catalyst A, (b) catalyst B (see text).

We have used the technique to look at poisoning of the catalysts and loss of activity due to carbon deposition. For example, we have carried out preliminary experiments on the effect of pulsing H_2S to the sample, when exotherms may be measured for each pulse; if the experiments are carried out under suitable conditions (*8*), the

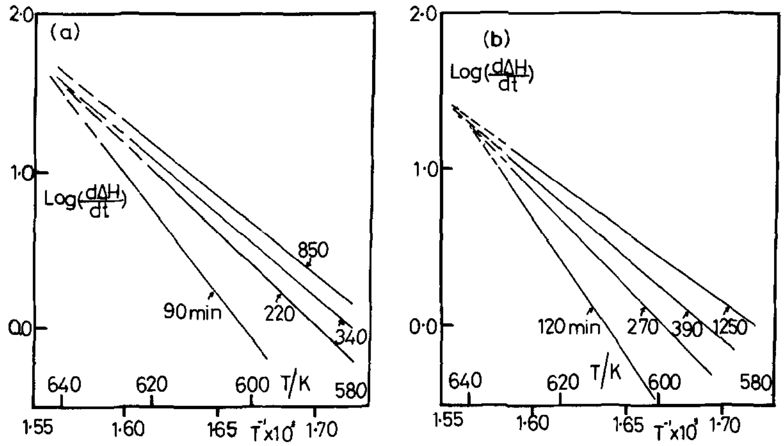

FIG. 4. Arrhenius plots corresponding to the data of Fig. 3; (a) catalyst A, (b) catalyst B.

total area under these exotherms is a measure of the active nickel area of the catalysts. After H_2S adsorption, no activity for the methanation reaction could be observed. By stopping the $CO + 3H_2$ flow over an active catalyst (when the partial pressure of CH_4 builds up), carbon deposition occurs. Subsequently, the methanation activity is considerably decreased, but it is gradually restored, at least partially, by reaction in the $CO + 3H_2$ mixture at higher temperatures, probably by reaction of the carbon with H_2. Figure 5a shows typical results and Fig. 5b shows the corresponding Arrhenius plots.

This note, therefore, shows the versatility of the DSC technique, which may be used either for rapid and reproducible catalyst screening tests or for more rigorous kinetic studies under strictly differential conditions, when it gives an accurate measure of reaction rates. In conjunction with analysis of the effluent gas, it may be used for pulse microcatalytic/calorimetric studies and for temperature programmed desorption or reduction investigations. We are currently examining these various uses, both for methanation and other related reactions over Ni catalysts, and for other catalyst systems.

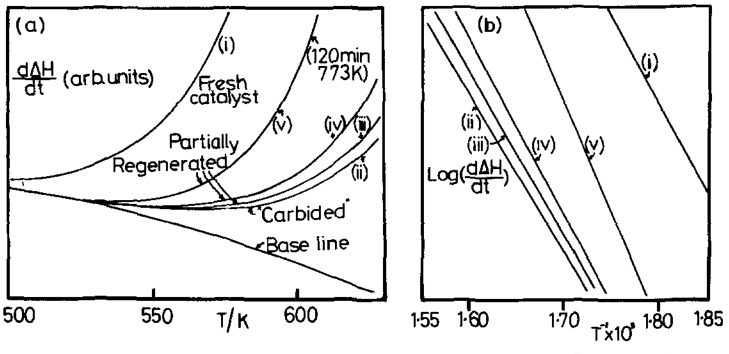

FIG. 5. Effect of the deposition of carbon caused by stopping the $CO + H_2$ flow; (a) plots of $\{d(\Delta H)/dt\}_T$ vs T for the fresh catalyst (i) after carbon deposition (ii) and after partial regeneration in $CO + H_2$ mixtures: (iii) after 10 min at 650 K, (iv) after 30 min at 773 K, (v) after 120 min at 773 K); (b) corresponding Arrhenius plots.

ACKNOWLEDGMENTS

The authors thank P. Hall, R. N. Lewis and D. J. Wright, all undergraduate studies at the University of Bradford, who carried out the majority of the experimental work described herein, Dr. R. Jemison and the late K. Livingston of Laporte Industries Ltd., who contributed to the development of the programme, and Professor M. W. Roberts, who gave us help and encouragement at all stages of the work. We also thank Laporte Industries Ltd. for their financial support and for permission to publish the results.

REFERENCES

1. Keely, W. M., *Proc. Toronto Symp. Thermal Analysis* 131 (1965).
2. Papadatos, K., and Shelstad, K. A., *J. Catal.* **28**, 116 (1973).
3. Wedding, B., and Farrauto, R. J., *Ind. Eng. Chem., Process Des. Develop.* **13**, 45 (1974).
4. Landau, M., and Molyneux, A., *in* "Differential Thermal Analysis" (R. C. McKenzie, Ed.), p. 299. Academic Press, New York, 1972.
5. Mills, G. A., and Steffgen, F. W., *Catal. Rev.* **8**, 159 (1973).
6. Ross, J. R. H., and Steel, M. C. F., *J. Chem. Soc., Faraday Trans. I.* **69**, 10 (1973).
7. Jost, F., Klyachko-Gurvich, A. L., and Rubinshtein, A. M., *Izv. Akad. Nauk SSR, Ser. Khim.* 2105 (1963).
8. Rostrup-Nielsen, J. R., *J. Catal.* **11**, 220 (1968).

TOM BEECROFT
ARTHUR W. MILLER

Laporte Industries Ltd.
Moorfield Road
Widnes WA8 0HE, England

JULIAN R. H. ROSS

School of Chemistry
University of Bradford
Bradford BD7 1DP, England

Received January 16, 1975