

## Measurement of the Spatial Distributions of Carbon and Metals within Catalyst Pellets

By CHRISTOPHER J. WRIGHT, JOHN W. McMILLAN, and JOHN A. COOKSON  
(*Harwell Catalyst Unit, Building 521, A.E.R.E. Harwell, Didcot, Oxon.*)

**Summary** A method for determining rapidly and quantitatively the distributions of both carbon and metal atoms within a catalyst pellet using particle beams is described.

THE decomposition profile of carbon or any other poison within a catalyst pellet is a valuable indicator of the mechanism of the laydown reaction, and there are theoretical treatments and experimental observations of the different profiles that occur after both fouling<sup>1</sup> and regeneration processes. Under non-isothermal conditions quite complex patterns have been predicted,<sup>2</sup> and we suggest that in one

of the examples reported here, such patterns can be observed.

Methods described in the literature<sup>3</sup> for quantifying such profiles, *e.g.* quantitative microcombustion in conjunction with visual inspection of the pellet, and sectioning followed by chemical analysis, are all time consuming. Auger spectroscopy is essentially non-quantitative because of surface charging and because the sampling depth may lead to information unrepresentative of the whole pellet.

In contrast the technique used here is relatively rapid. It uses a focussed beam of 1.3 MeV deuterons which react with carbon within the sample (<sup>12</sup>C) to produce <sup>13</sup>C and

emitted protons which can be counted to determine the carbon concentration.<sup>4</sup> Emitted X-rays can also be observed simultaneously although for the results of Figure 3 a separate scan with 3 MeV protons was made to determine the metal concentration. The pellets used were cleaved perpendicular to their long axis, exposed to the deuteron beam on the IBIS accelerator at A.E.R.E. Harwell and examined under vacuum conditions, although similar experiments would be possible in a gas atmosphere. In these results 16,000 proton counts were recorded per point per 1% carbon content, and since no significant loss of information would result from reducing this number by 4 the time taken to scan across a sample could be 3–5 min.

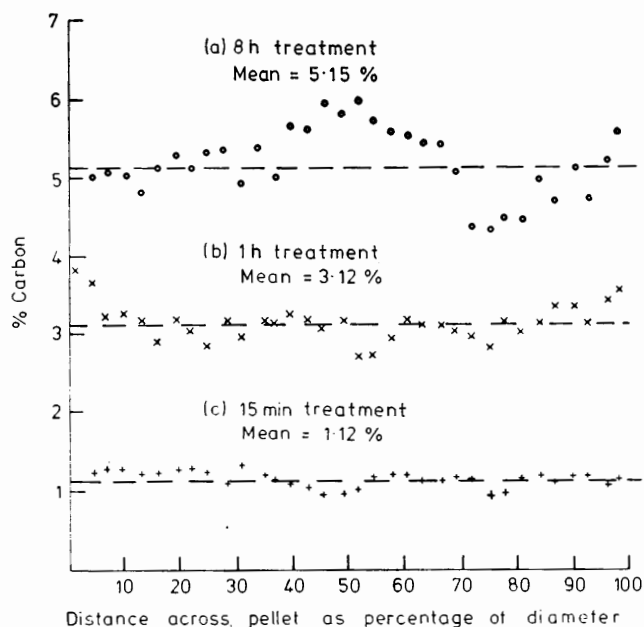


FIGURE 1. A carbon profile determined for a  $\gamma$ -alumina pellet after treatment in a 12:1  $C_2H_2/N_2$  mixture for (a) 8 h, (b) 1 h, and (c) 15 min at 300 °C.

The results in Figure 1 illustrate the type of profile that is found for pellets whose effectiveness factor is 1 for the carbon laydown reaction. The variation from point to point for the carbon concentration determined is due to inhomogeneities within the pellet, and the variation shown here is typical of all the pellets we have examined.

The other two examples in Figures 2 and 3 show, respectively, 'parabolic' laydown and complex laydown where the distribution shows a pair of maxima. The pellets from which the data of Figure 3 were taken had been used for the selective hydrogenation of acetylene in an ethylene stream. So we may speculate that the major source of the carbon was the acetylene and that there was series formation of carbon from the reagent. In this case the analysis of Sagara, Masamune, and Smith<sup>5</sup> shows that for an exothermic reaction we would expect a double humped carbon distribution, of the type found. Although the precise details of the distribution will depend on the sizes of the variable parameters, a curve more or less of the same type will

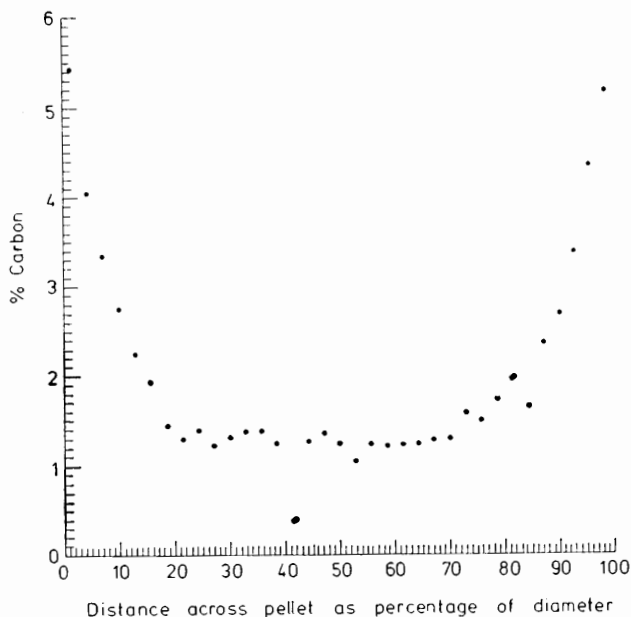


Figure 2. A carbon profile on an industrially used pellet showing 'parabolic' laydown.

always result because of the two opposing forces during the laydown of carbon. The concentration of the reagent is highest at the surface, and the temperature is highest at the centre. Measurement of the X-ray emission from the same samples, Figure 3, showed them to contain palladium in a highly localised band of full width *ca.* 200  $\mu m$  at the edge of the pellet. In this case, although the palladium may have had an influence on the carbon laydown at the edge of the

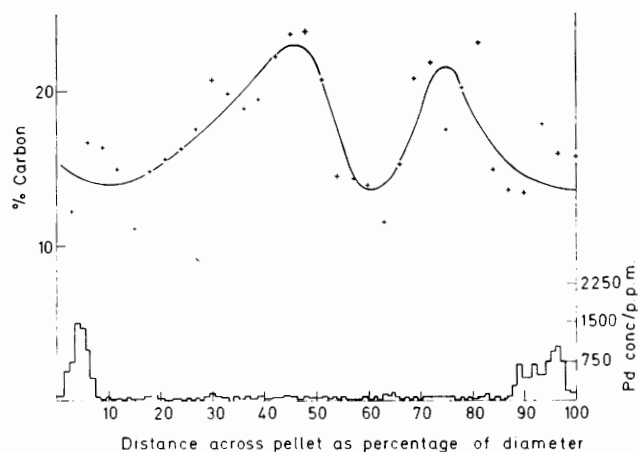


Figure 3. A carbon profile on an industrially used pellet showing a double peaked profile, together with its palladium X-ray profile.

pellet, it is unlikely that its effect could extend into the bulk and so have any influence upon the essential features of the pattern observed. The time taken to determine this concentration of metal with the particle induced X-ray technique is two orders of magnitude shorter than the time

that would have been necessary using an electron microprobe.

In conclusion, the advantages of this technique are (i) its quantitative nature, (ii) its rapidity, (iii) the potential for undertaking measurements in an atmosphere and allowing dynamic observation, (iv) the ability to determine simultaneously the concentrations of heavier elements by observing their X-ray emission, and (v) the ability to

measure in a similar manner the concentrations of other light elements such as B and N.

The Harwell Catalyst Unit is supported by the Chemicals and Minerals Requirements Board of the Department of Industry.

(Received, 29th August 1979; Com. 915.)

<sup>1</sup> For a review see J. Butt, *Catalyst Deactivation in Chemical Reaction Engineering*, Adv. Chem. Series 109, Amer. Chem. Soc., Washington, 1972, and J. T. Richardson, unpublished observations quoted therein; Y. Murakami, T. Kabayshi, T. Hattori, and M. Masuda, *Ind. and Eng. Chem. (Fundamentals)*, 1968, **7**, 599.

<sup>2</sup> M. Sagara, S. Masamune, and J. M. Smith, *Amer. Inst. Chem. Engineers J.*, 1967, **13**, 1226.

<sup>3</sup> P. B. Weisz and R. D. Goodwin, *J. Catalysis*, 1963, **2**, 397; R. J. Rostrop Nielsen, 'Steam Reforming Catalysts,' Teknisk Forlag A/S, Copenhagen, 1975, p. 164.

<sup>4</sup> J. A. Cookson, J. W. McMillan, and T. B. Pierce, *J. Radioanalytical Chem.*, 1979, **48**, 337—357.