Catalyst Temperature Profiles under Poisoned Conditions

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The poisoning of catalyst pellets and the effect on mass transport has been considered in detail by Wheeler (1955) and by others. Two extreme cases were identified, namely, homogeneous poisoning in which the poison was uniformly distributed throughout the pellet, and pore mouth poisoning where the poison affected the outer layers first. There have been a number of detailed studies of poisoning utilizing these concepts, notably the study of time-dependent poisoning processes by Masamune and Smith (1966) and of Gorring and Carberry (1966). Almost all of this work has considered isothermal conditions only. The one exception is the work of Sagara et al. (1967) where a detailed analysis was presented of the effects of temperature on parallel and series fouling of catalyst pellets.

In this communication we report some measurements of temperature profiles in a single catalyst pellet under conditions where poisoning occurred. Unlike the work of Sagara (1967), poisoning in the present work was caused by impurities in the feed stream and was therefore of the kind designated as Type I poisoning in the excellent and comprehensive review of Butt (1970).

The experimental measurements were made using the same type of system as described previously (Hughes, 1970). Basically, a single spherical catalyst pellet containing embedded thermocouples of 0.0025-cm platinum/platinum-rhodium wire and a separate surface junction was supported in an axial flow vertical reactor. Temperature rises were recorded during the exothermic catalyzed reaction between hydrogen and ethylene. The pellet (radius 0.63 cm) was made from a powder containing 5% nickel supported on silica alumina, the nickel being deposited by impregnation. The results described below refer to a single catalyst pellet which was first operated in the active condition and was subsequently deliberately poisoned. Poisoning of the catalyst pellet was achieved if the ethylene stream was not purified from traces of oxygen. Normally, purification was achieved using a reduced manganese dioxide bed; if this were bypassed a poisoned pellet resulted. A similar poisoning effect has been observed by others (Boudart, 1966; Hahn, 1970) for the hydrogenolysis of cyclopropane over a platinum catalyst.

A comparison of the intraparticle temperature profiles obtained with the active pellet (upper curve) and when the pellet was deliberately poisoned (lower curve) are shown in Figure 1. Since the same pellet was used in both sets of experiments the physical properties were identical. Similar flow rates and ethylene concentrations were used so that the results are directly comparable. The appreciable difference in the overall temperature level between the active and poisoned pellet is evident. Although a different initial temperature was employed for the active case, this is not important since it had previously been established that for an active pellet the ultimate temperature level was virtually independent of the starting temperature. Another point of difference is the shape of the intraparticle temperature profiles. For an active condition of the pellet a very steep temperature gradient was obtained just inside the pellet surface. All the temperature rise was located within this narrow zone and the remainder of the pellet was at a uniform temperature (the drop of temperature of 1 to 2°C at the pellet center is caused by slight asymmetry of the temperature field surrounding the pellet). Conversely, the poisoned pellet shows a much more gradual temperature gradient which is almost linear up to the point where the flat central profile is found. The intraparticle temperature rise was observed to be not very different for both active and deactivated conditions of the pellet.

The effect of variations in the concentration of ethylene on the intraparticle temperature profiles in the poisoned pellet is illustrated in Figure 2. Both the surface temperature and the maximum intraparticle temperature rise increase with increase in the concentration of ethylene. An interesting feature of these curves is that the point inside the pellet at which the profiles become flat appears to occur at the same radius for all concentrations of ethylene used. It should be pointed out that no time de-

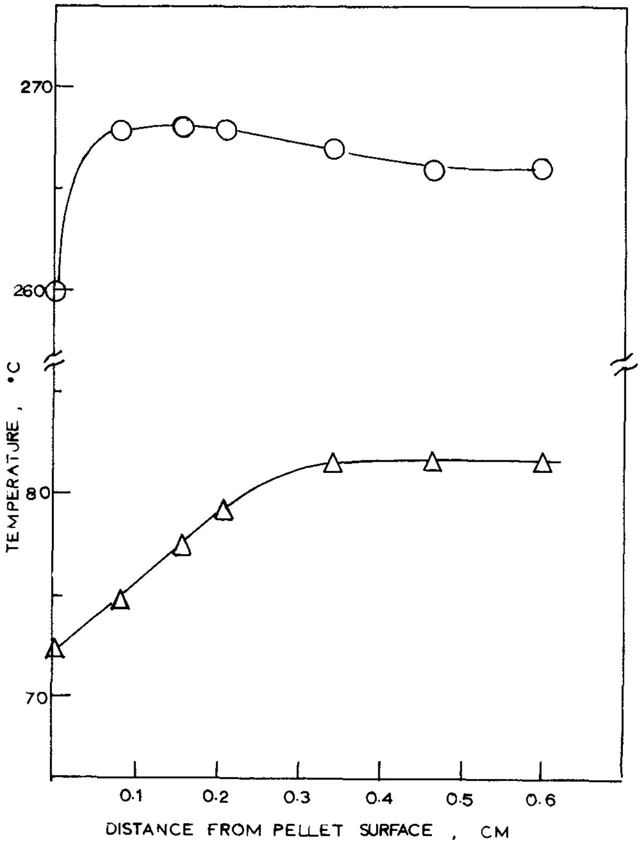

Fig. 1. Comparison of intraparticle temperature profiles for active and poisoned pellet: ○ = active pellet, 24% C_2H_4, flow = 21 cm^3 s^{-1}, T_{initial} = 20°C; △ = poisoned pellet, 20.7% C_2H_4, flow = 20 cm^3 s^{-1}, T_{initial} = 54°C.

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pendence of poisoning was observed throughout the few hours duration of these experiments.

Previous work by the authors had suggested that measurements of the gas phase temperature adjacent to the pellet were not reliable because of the severe temperature gradients in this region. An estimate of the relative magnitude of the interphase temperature rise may be obtained, however, by comparing the surface temperatures for the active and poisoned pellet. This comparison is given in the upper part of Figure 3, where surface temperatures are plotted against the concentration of ethylene in the gas phase. Also shown in the lower part of the figure is the intraparticle temperature rise plotted on the same basis. It is apparent that not only is the surface temperature of the active pellet much higher than the poisoned pellet but that the surface temperature of the active pellet is much more sensitive to concentration changes. The maximum intraparticle temperature rises lie on the same straight line for both the active and the poisoned pellet.

Of primary interest from a design point of view is the relative magnitude of the interphase and intraparticle temperature rises. From the results reported here, it is clear that while a lumped parameter assumption that the intraparticle temperature rise may be neglected in comparison with the interphase temperature rise is justified for the active pellet, this is not necessarily so when the pellet is poisoned. In the latter case the intraparticle temperature rise may reach a value of 50% or more of the interphase temperature rise and therefore should be considered in any precise analysis when poisoning is present.

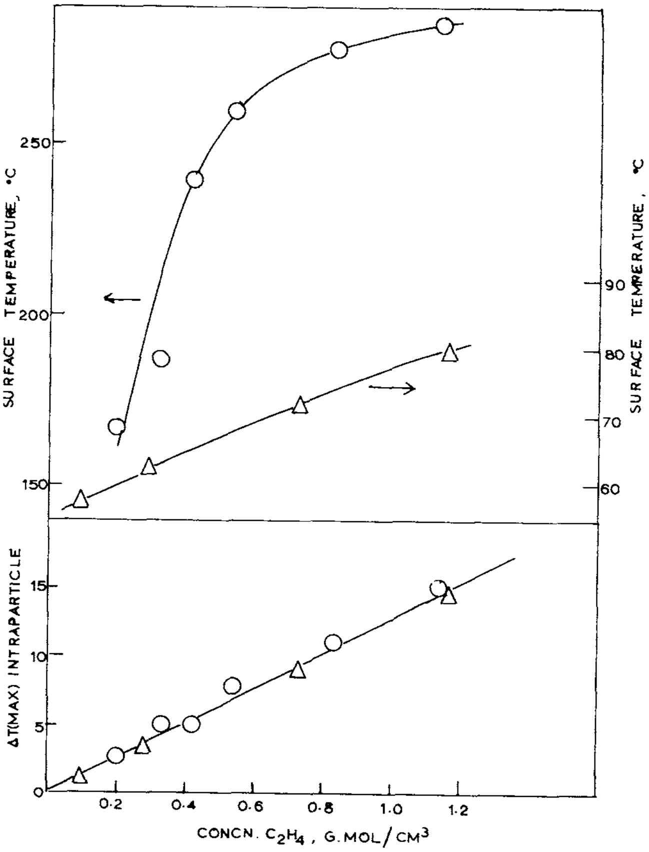

Fig. 3. Comparison of surface temperature and maximum intraparticle temperature rise for active (○) and poisoned (△) pellet.

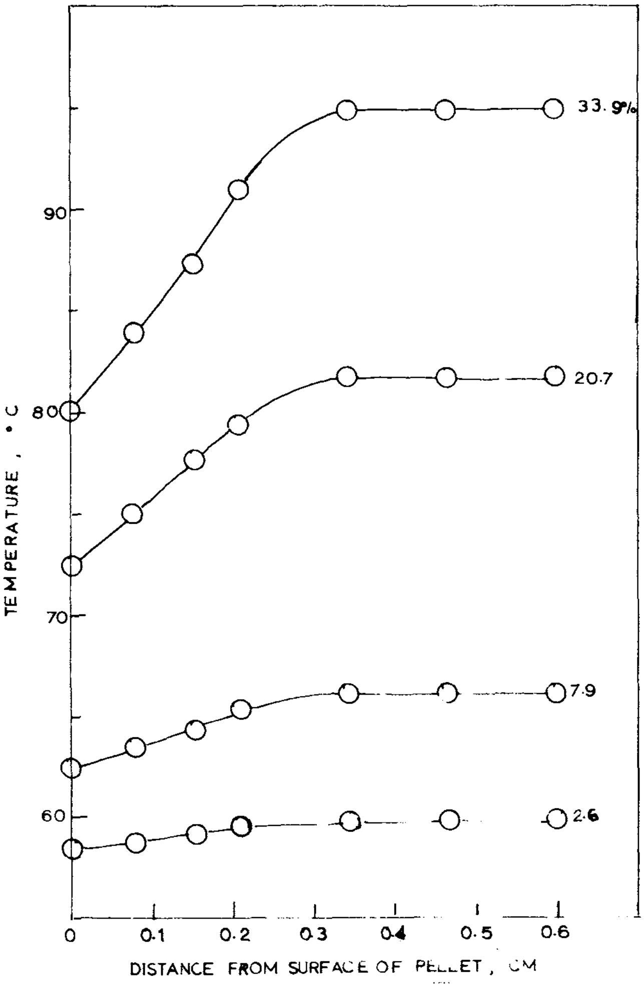

Fig. 2. Variation of intraparticle temperature profiles with ethylene concentration, poisoned pellet. Initial temperature 54°C. Flow rate 20 cm^3 s^{-1}. C_2H_4 % on curves.

Furthermore, although an unequivocal decision on the type of deactivation is not possible from temperature profile data alone, the results obtained do suggest that pore mouth poisoning is predominant. If homogeneous poisoning were present, it would not be expected that the maximum temperature rise in the active and poisoned pellet would be almost equivalent. The linearity of the ascending temperature portion of the poisoned pellet also suggests that poisoning is not homogeneous.

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