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Sticking probability determinations on supported catalysts

Mike Bowker and Glyn Roberts
Leverhulme Centre for Innovative Catalysis and Surface Science Research Centre,
Department of Chemistry, University of Liverpool, PO Box 147, Liverpool L69 3BX, UK

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Abstract. This paper deals with measurements that go a little way towards overcoming the knowledge gap that exists between the adsorption on well defined single-crystal surfaces and that on real catalysts and reports data on the sticking of oxygen on the surfaces of real supported catalysts, measured in a vacuum system.

We first consider whether measurements of the sticking of oxygen on real surfaces are possible. In particular, the following equation, which was reported in an earlier paper [1], describes the approximate relationship between pressure inside the pore (P) and outside the catalyst (P_0):

$$P_0/P = 1 + 2gSl/r. \tag{1}$$

Here S is the probability of sticking on the active component of the catalyst, g is the fraction of the pore area that is active and l and r represent the length and radius of the pore. Equation (1) is derived from simple mass-balance considerations for a pore treated as a box. Nevertheless, it gives an idea of the conditions under which S can be determined. For making such a measurement in an accurate way it is essential that the ratio P_0/P is close to unity. In general for a catalyst the ratio l/r is large (and may be very large depending on the configuration of the catalyst mounted in a UHV system), while g usually represents a few per cent of the total area. As a result S usually needs to be low to be accurately measured.

Adsorption measurements have been carried out on two catalysts that represent opposite extremes in terms of equation (1)—that is, one catalyst that is expected to have a very low value for S and one that has a relatively high value. The former is a catalyst of silver supported on an alumina of the type used in the industrial epoxidation of ethylene and the latter is Europlatinum 1. The value for S at 300 K on Ag is $\simeq 5 \times 10^{-4}$ for the fastest adsorbing plane whereas on Pt it is $\simeq 0.1$ [2]; both metals show strong structural anisotropy for oxygen adsorption. Also, the total surface area of the former is $\simeq 1\ \mathrm{m}^2 g^{-1}$, whereas that of the latter is $185\ \mathrm{m}^2 g^{-1}$, and the pore radii are, on average, a factor of 300 different. Under these conditions P_0/P for the Ag catalyst is at most 1.01 and so we can be confident of accurately measuring S. On the other hand P_0/P for the Pt catalyst is of the order of $\simeq 10^3$ and we would therefore expect a large pressure drop

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down the pore and a much lower uptake than would be anticipated for the P_0 value; as a result a very low value for S would be found.

These features have been borne out by uptake measurements on the two types of catalyst determined in a UHV system using thermal desorption to measure the amount of oxygen adsorbed. For the Ag catalysts S was determined to be 10^{-6} at 300 K at zero coverage, and it increased ten fold at 480 K indicating an activation barrier of 16 kJ mol^{-1}. These parameters agree with those determined by Campbell for an Ag(111) surface [3] and show that the catalyst almost exclusively consists of the close-packed planes. In contrast, the Pt/SiO_2 catalysts gave an anomalously low apparent sticking probability, of the order of $\sim 10^{-5}$, which is consistent with the large pressure drop down the pores anticipated from the arguments given above.

References

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