A METHOD OF ESTIMATING THE MINIMUM AMOUNT OF MATERIAL REQUIRED TO POISON OR PROMOTE A SUPPORTED METAL CATALYST

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Previous theoretical studies have shown that the range of operation of poisons and promoters on metallic catalysts is short, typically < 5 A. This result is generalised and an estimate is given of the range of operation of a large group of common promoters and poisons. A simple formula is derived which can be used to estimate the minimum weight of poison or promoter which will be effective on a supported metal catalyst.

The phenomena of poisoning and promotion are well known in heterogeneous catalysis, [1]. Catalyst activity is depressed or enhanced by the presence of some entity which is normally more strongly adsorbed at the catalytically active site than the reactants themselves. For supported noble metal catalysts, where the active metal is often present at very low loading, the amount of poison required completely to deactivate the catalyst can be very small, as can the quantity of promoter necessary. It has often therefore been assumed that catalysts can be severely poisoned by undetectable amounts of impurity and that the analysis of poisoning phenomena is thus not worth attempting. The purpose of this note is to show that, at least on metal catalysts, a quantitative discussion of poisoning and promotion is possible and that the levels necessary are often well within the detection capability of modern analytical science.

The present work arises from our theoretical studies which have been reported previously, [2]. As part of a more general theoretical programme to understand the catalytic behaviour of promoted metals, we examined the range of effectiveness of a number of electronegative poisons on a nickel surface. The influence of the poison on the density of electronic states at the metal Fermi level was calculated as a function of distance from the poison. The essential result of the calculations is that poisoning of nickel is a short range phenomenon, even a very

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strong poison such as sulphur being effective over < 5 A. In the present context we assume that the area within range of the poison atom is completely deactivated. The results of the theoretical calculations, although obtained on nickel, are general and can be applied with reasonable confidence to any metal.

Once the poisoning range is known, it becomes easy to estimate the *minimum* amount of poison necessary to deactivate a catalyst to a particular degree. To achieve this, we assume that all of the poison in the catalyst is located at the surface of the active metal and that there will be short range, (< 5 A) repulsive interactions between the poison atoms. If this is not the case, and for example islands of poison or promoter are formed, more material will be required than is indicated in these calculations. Poison atoms located on the catalyst support must also be neglected and this is another factor which will cause the results presented to yield minimum values.

Promoters also act by influencing the density of electronic states available for reaction. Promotion can thus be viewed as the inverse of poisoning, and the arguments developed for one, applied to the other. Our calculations have also indicated that the range of effectiveness of promoters is similar to that noted earlier for poisons, so that the results deduced below are expected to be equally applicable to promotion and poisoning.

We now derive the formula for the calculation of minimum promoter or poison loading and we show that levels of poison should normally be detectable, for example by X-ray fluorescence. The formula offered obviously make no comment on whether an additive will have either poisoning or promotional activity. That will depend on the individual reaction which is being catalysed.

With the assumptions discussed above, two parameters are required to calculate the amount of poison necessary to deactivate a catalyst to a given degree. These are the active metal surface area per unit weight of catalyst and the range of operation of the poison of interest. The available active surface area of the metal catalyst can readily be obtained from a knowledge of the catalyst's loading and its dispersion. If the percentage dispersion is D, then the metal surface area is given by:

$$\mathrm{SA} = L.N.A.D/\left(W_{\mathrm{m}}.1 \times 10^{20}\right)/\mathrm{cm}^{-2}\ \mathrm{g}^{-1} \qquad (1)$$

where L is the metal loading, expressed as % weight, N is the Avogadro number, 6.023×10^{23}, A is the surface area occupied per molecule expressed in A^2 and W_{m} is the atomic weight of the metal.

The only quantity in eq. (1) which is difficult to define with precision is the surface area occupied per metal atom, A. Suggested values for metals of common interest are given in table 1. We have chosen to represent the face centred and body centred cubic metals by their (100) plane and hexagonal close packed metals by their close packed, (001) face, ((0001) in four index notation).

The next stage is to use the theoretical results, referred to earlier, to estimate the poisoning/promotion ranges, R, which are given in table 2. For each element

Table 1
Area occupied by individual surface atoms

Metal	Surface area per atom/A^{-2}
Aluminium	8.16
Chromium	8.28
Cobalt	5.47
Copper	6.51
Gold	8.29
Iron	8.18
Manganese	~ 8.0 *
Molybdenum	9.86
Nickel	6.18
Osmium	7.42
Palladium	7.52
Platinum	7.66
Rhenium	6.62
Rhodium	7.20
Ruthenium	6.29
Silver	8.31
Tantalum	10.76
Titanium	7.54
Tungsten	9.97
Vanadium	9.07
Zinc	6.12

* Because of its complex crystal structure, a precise value for manganese is difficult to define.

we give two values, the most probable range and the maximum range over which it is likely that poisoning/promotion can be effective. The range of poisoning or promotion is determined by a complex balance between electronegativity and atomic size, as has been discussed elsewhere, [3]. The determination of range has been carried out explicitly only for the electronegative elements sulphur, chlorine, phosphorous and carbon, [2a] and for lithium and potassium, [2b]. For other elements we have attempted to consider how these interactions will balance and the range of influence which will result. Where a reducible transition metal acts as to poison another metal, we believe its role will be essentially substitutional. It will replace one active site, but its influence will extend *at most* to its nearest neighbours. Where a non-reducible ion, such as Al^{3+} is the promoter or poison, we suggest that its range will be closer to that of carbon. Although some of the estimates of range are inexact, the error in the quantity of poison or promoter required will very rarely be greater than an order of magnitude if the other assumptions of the method are reliable.

When the range of operation of a poison is known, it becomes trivial to estimate the weight which is required. The total surface area poisoned is given by $N_p.\pi R^2$, where N_p is the number of effective poison atoms per gram of catalyst. If

Table 2
Poisoning and promotion ranges for the elements

Element	Optimum range/A	Maximum range/A	Element	Optimum range/A	Maximum range/A
Aluminium	3.5	5.0	Mercury	1.5	3.0
Antimony	3.5	5.0	Molybdenum	1.5	3.0
Arsenic	3.5	5.0	Nickel	1.5	3.0
Barium	4.0	7.0	Niobium	1.5	3.0
Beryllium	3.5	5.0	Nitrogen	2.0	3.5
Bismuth	3.5	5.0	Osmium	1.5	3.0
Bromine	5.0	7.0	Oxygen	3.5	5.0
Cadmium	3.5	5.0	Palladium	1.5	3.0
Calcium	3.5	5.0	Phosphorous	5.0	7.0
Carbon	1.5	3.0	Platinum	1.5	3.0
Cerium	3.5	5.0	Potassium	3.5	5.0
Cesium	5.0	7.0	Rhenium	3.5	5.0
Chlorine	5.0	7.0	Rhodium	1.5	3.0
Chromium	1.5	3.0	Rubidium	5.0	7.0
Cobalt	1.5	3.0	Ruthenium	1.5	3.0
Copper	1.5	3.0	Scandium	3.5	5.0
Fluorine	5.0	7.0	Selenium	5.0	7.0
Gallium	3.5	5.0	Silicon	3.5	5.0
Germanium	3.5	5.0	Silver	1.5	3.0
Gold	1.5	3.0	Sodium	3.5	5.0
Hafnium	3.5	5.0	Strontium	3.5	5.0
Indium	3.5	5.0	Sulphur	5.0	7.0
Iodine	5.0	7.0	Tantalum	1.5	3.0
Iridium	1.5	3.0	Tellurium	5.0	7.0
Iron	1.5	3.0	Tin	3.5	5.0
Lanthanum	3.5	5.0	Tungsten	1.5	3.0
Lead	3.5	5.0	Vanadium	1.5	3.0
Lithium	3.5	5.0	Yttrium	3.5	5.0
Magnesium	3.5	5.0	Zinc	1.5	3.0
Manganese	1.5	3.0	Zirconium	1.5	3.0

the percentage loss of catalytic activity is P, then the surface area poisoned is given by $\mathrm{SA}.P/100$. Thus N_p can be obtained from:

$$N_p.\pi R^2 = \mathrm{SA}.P/100. \tag{2}$$

If the atomic weight of the poison is W_p, the concentration of poison necessary, expressed in parts per million, (ppm), is simply:

$$\text{Concentration/ppm} = L.A.D.P.W_p/\left(W_m.\pi R^2\right). \tag{3}$$

As an example, let us consider the possible poisoning of a typical platinum catalyst, loading 0.5% by weight and 65% dispersed. Let bromine be the suspected poison and assume that the catalyst has been deactivated by 50%. From eq. (3)

and tables 1 and 2 it can be calculated that at least 65 ppm of bromine are needed to give the required amount of deactivation. The detection limit for bromine which can be achieved by careful X-ray fluorescence analysis is < 20 ppm. It should therefore be possible to establish, by quantitative analysis of the bromine content of the catalyst, whether enough is present to cause the observed extent of deactivation.

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