Determination of Crystallographic Planes on the Surface of Supported Metallic Crystallites

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The percentage of metal surface atoms with different co-ordination numbers is calculated for $Pd/\gamma\text{-}Al_2O_3$ catalysts from gas chemisorption measurements.

The activity and selectivity of metal-supported catalysts are frequently related to metal dispersion. This, however, is only a rough approximation, since even 'structure insensitive' reactions can take place at different rates on points of the metal crystal with different co-ordination numbers.[1] Thus, a more realistic relation has to take into consideration not only the dispersion or crystallite size of the metal but also the proportion of metal surface atoms with different co-ordination numbers. If we could develop a simple method for finding this proportion it should then be possible to find how the differences in metal co-ordination on supported metal catalysts affect the catalytic activity, and hence enable catalysts with the maximum number of metal atoms in the desired co-ordination to be prepared. We report a method for calculating this proportion from gas chemisorption studies on metal-supported catalysts, in this case $Pd/\gamma\text{-}Al_2O_3$ catalysts. Details of the experimental procedure and catalyst preparation can be found elsewhere.[2]

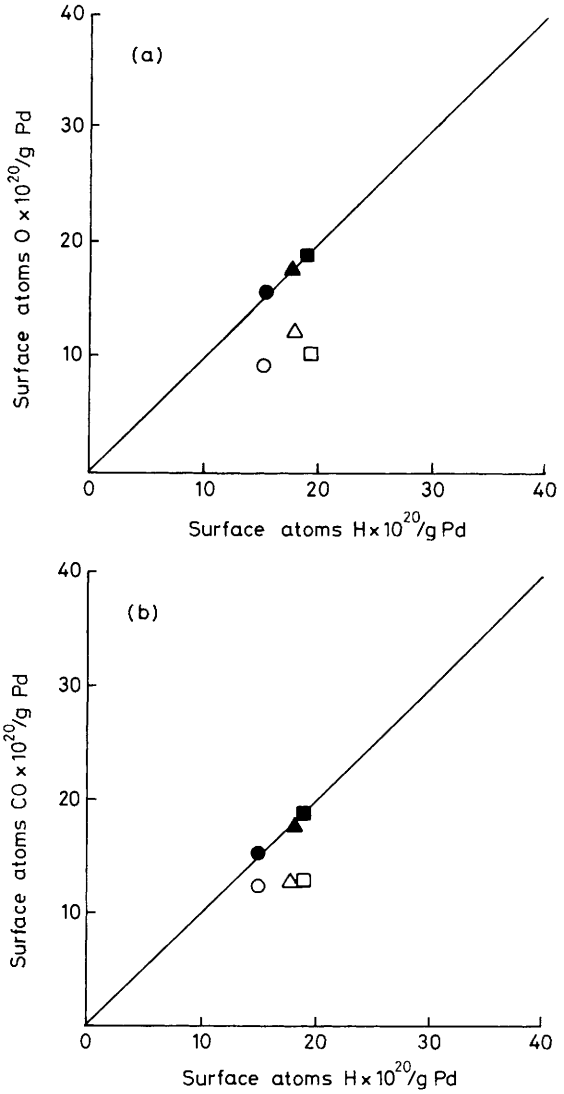

Figure 1. Comparison of number of surface atoms measured by (a) O_2 and H_2 and (b) CO and H_2 chemisorption considering a statistical distribution of planes (○ = Pd/Al_2O_3 0.47%; □ = Pd/Al_2O_3 0.9%; △ = Pd/Al_2O_3 4.75%) from ref. 2 and considering the percentage of crystallographic planes shown in Table 1 (solid symbols).

The experimental results in Figure 1, (a) and (b), open points, show that for $Pd/\gamma\text{-}Al_2O_3$ the number of metal surface atoms, calculated from H_2, O_2, and CO chemisorption data [assuming, as is usual, that there is a fixed distribution of metal atoms in different co-ordinations: 33% each in (111), (110), and (100)], depends on the type of gas chemisorbed. These results indicate that the assumption made is not correct and that in this metal-supported catalyst there are preferential orientations of crystal growth as has been established by high resolution electron microscopy for some systems.[3]

The preferential growth will depend on factors including the method of metal deposition, reduction and/or activation procedure, nature of the support, *etc.*

In the case of metals with face centred cubic structure the most probable surface plane orientations of low Miller index (high co-ordination number) are (111), (100), and (110),[4] and if one takes their partial contribution to the total metal surface of the supported metal as x, y, and z respectively, it is possible to write equations (1)—(3), where O_S, H_S, and

$$O_S/H_S = Ax + By + Cz \quad (1)$$

$$CO_S/H_S = A'x + B'y + C'z \quad (2)$$

$$1 = x + y + z \quad (3)$$

CO_S are the number of atoms of O and H, and molecules of CO adsorbed per gram of metal. A, B, C and A', B', C' are the stoicheiometries for O and CO chemisorption on planes (111), (100), and (110) of Pd monocrystals reported in the literature:[5] 0.25, 0.5, 1; 0.5, 0.7, 1, respectively. Now by carrying out appropriate adsorption experiments with H_2, O_2, and CO and solving the system of equations it should be possible to calculate not only the total number of surface atoms but also the fraction of them lying in each of the three most probable crystallographic planes mentioned before. The system of equations can be solved by finding the x, y, and z values which minimize the function given in equation (4).

Table 1. Percentages of crystallographic planes from three-planes fitting.

Catalyst[a]	% (111)	% (100)	% (110)
0.47	2	71	27
0.90	52	10	38
4.75	32	0	68

[a] Percentage of Pd (wt%) on Al_2O_3.

$$\psi = |O_S/H_S - Ax - By - Cz| + |CO_S/H_S - A'x - B'y - C'z| \quad (4)$$

Calculations were done for three $Pd/\gamma\text{-}Al_2O_3$ catalysts in which chemisorption measurements with three gases (H_2, O_2, and CO) had been carried out (unfortunately, most chemisorption studies have only dealt with two gases), and the results are given in Table 1. It can be seen that two crystal surface orientations are in clear majority on these catalysts, and that by considering the three planes in the percentage given in Table 1, the number of surface atoms measured is now independent of the nature of the gas used for the measurements [Figure 1(a) and 1(b), solid points].

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References

1 A. Benedetti, G. Cocco, S. Enzo, and E. Pina, *React. Kinet. Catal. Lett.*, 1980, **13**, 291.

2 M. A. Martin, Ph.D. Thesis, Universidad Complutense, Madrid, 1983.

3 M. J. Yacamán and J. M. Domínguez E., *J. Catal.*, 1980, **64**, 213; M. J. Yacamán, A. Gómez, and D. Romeu, *Kinam*, 1980, **2**, 303.

4 S. Ino, *J. Phys. Soc. Jpn.*, 1969, **27**, 941; M. C. Dejonquères and F. Cyrot-Lackman, *Surf. Sci.*, 1975, **50**, 257; W. Romanowski, *ibid.*, 1969, **18**, 373; S. N. Khana, J. P. Bucher, J. Buttet, and F. Cyrot-Lackman, *ibid.*, 1983, **127**, 165.

5 H. Conrad, G. Ertl, J. Koch, and E. E. Latta, *Surf. Sci.*, 1974, **43**, 462; W. Erley and H. Wagner, *J. Chem. Phys.*, 1980, **72**, 2207; J. P. Biberian and M. A. Van Hove, *Surf. Sci.*, 1982, **118**, 443; J. C. Tracy and P. W. Palmberg, *J. Chem. Phys.*, 1969, **51**, 4852; R. M. Lambert, *Surf. Sci.*, 1975, **49**, 325; H. Conrad, G. Ertl, J. Küppers, and E. E. Latta, *ibid.*, 1977, **65**, 235; T. W. Orent and S. D. Bader, *ibid.*, 1982, **115**, 323; G. Ertl and P. Prau, *ibid.*, 1969, **15**, 443; H. Conrad, E. Ertl, and E. E. Latta, *ibid.*, 1974, **41**, 435; J. P. Muscat, *ibid.*, 1981, **110**, 85; R. J. Behm, K. Christmann, and G. Ertl, *ibid.*, 1980, **99**, 320; M. G. Cattania, V. Penka, R. J. Behm, K. Christmann, and G. Ertl, *ibid.*, 1983, **126**, 382.