JOURNAL OF CATALYSIS 48, 445–446 (1977)

Chemisorption and Magnetization Measurements

Van Meerten *et al.* (*1*) have recently given magnetization results for hydrogen and for several hydrocarbons adsorbed on nickel–silica. The method was the double-primary low field permeameter. In their second paragraph it is implied that there is some disagreement between the results of Martin *et al.* (*2*) and our own. The purpose of this letter is to show that Van Meerten *et al.* have confused the symbols α and ϵ used by Martin and by ourselves, respectively, and that they have misquoted Martin's equation.

Our definition (*3*) of ϵ, the change in magnetic moment of the adsorbent caused by the chemisorption of hydrogen, is as follows:

$$\epsilon(\mathrm{H}) = (\Delta M_0/M_0)\cdot\beta(\mathrm{Ni})\cdot n(\mathrm{Ni})/n(\mathrm{H}),$$

where M_0 is the saturation magnetization extrapolated to absolute zero, $\beta(\mathrm{Ni})$ the Bohr magneton number of nickel, $n(\mathrm{Ni})$ the moles of nickel metal in the sample, and $n(\mathrm{H})$ the moles of hydrogen *atoms* chemisorbed. The definition of α used by Martin *et al.* (*2*) is the same except for the last term. They use $n(\mathrm{H_2})$, the moles of hydrogen molecules. Consequently $\alpha = 2\epsilon$. Reported values for $\epsilon = \alpha/2$ are -0.71 (*3*), -0.72 (*4*), and -0.73 (*5*). It is true that saturation magnetizations change with temperature. Martin *et al.* (*2*) refer to this in their relation $\alpha = \alpha_{\mathrm{mes}} M_0/M_s$ where M_s is the saturation magnetization at any temperature. This is the relation misquoted by Van Meerten *et al.* It is meaningless to say that ϵ varies with the temperature at which the magnetization is measured.

The matter referred to above does not invalidate all of the conclusions reached by Van Meerten *et al.* (*1*) concerning the bonding and surface reactions of hydrogen, benzene, cyclohexene and cyclohexane. The chief conclusions given in their abstract are, with minor exceptions, the same as those previously reached for the same systems by essentially the same experimental method. One conclusion is that chemisorption of the hydrocarbons stops at partial coverage. It was previously shown (*6*) that a nickel surface with chemisorbed cyclohexene to maximum capacity is still capable of chemisorbing a substantial quantity of hydrogen under conditions precluding hydrogenation. This could not have occurred if the cyclohexene had completely covered the nickel. Similar results have been obtained for benzene (*7*). Another conclusion (*1*) is that the approximate number of bonds between hydrocarbon and nickel can be found by the method described. This is indeed true and it has been applied to many adsorbates. Martin and his associates (*2*, *5*) have extended the scope and reliability of such measurements by using saturation magnetizations. The results are all in reasonably satisfactory agreement with those reported earlier provided that attention is paid to the possibility of preferential adsorption on certain metal particle sizes (*2*) and to the maximum temperature reached by the adsorbed molecule. Martin and Imelik (*8*) have shown that the bond number of chemisorbed benzene on nickel rises almost vertically with maximum holding temperature in the room temperature region. This means that a change of a degree or two can

ISSN 0021-9517

alter the bond number by increasing dissociation of the molecule. The heat of adsorption is itself sufficient to raise the temperature of the nickel particles by several degrees (*9*) and thus, in this case, to increase the bond number. A final point in this connection is that the bond number ζ as used by the writer for any molecule X on nickel is $\zeta = \epsilon(\mathrm{X})/\epsilon(\mathrm{H}) = \epsilon(\mathrm{X})/0.72$. Martin (*8*) defines the bond number as $\alpha(\mathrm{X})/\beta(\mathrm{Ni}) = \alpha(\mathrm{X})/0.606$. Martin's bond numbers are, therefore, about 16% larger which is measurable but not too significant. It is also concluded by Van Meerten *et al.* (*1*) that a weakly bound form of dissociatively adsorbed hydrogen is active in hydrogenation. This is identical with an earlier conclusion reached by a similar method to the effect that for hydrogenation to take place it is necessary for the nickel–hydrogen bond to be sufficiently attenuated by ample chemisorbed hydrogen (*10*).

This letter will be concluded with a brief comment on the usefulness of the low field magnetization method. There is no question that this method can yield much information. It is simple and inexpensive. It may be used at temperatures and pressures at which many catalytic reactions take place. It is, however, essential that the adsorbent be superparamagnetic at the temperature and frequency of measurement. There is also the problem, referred to above, that the results may be affected by preferential adsorption on certain particle sizes. The field gradient coil magnetometer described by Lewis (*11*) and the superconductive magnets used by Martin (*12*) and by Richardson and Desai (*13*) permit determination of saturation magnetizations with more convenience than was formerly possible.

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Received January 21, 1977