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BOND LENGTH–BOND ENERGY CONCEPT AND ITS IMPACT ON THE SURFACE CHEMISTRY OF OXIDES

JACEK ZIÓŁKOWSKI

Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek, 30-239 Kraków (Poland)

ABSTRACT

In addition to experimental evidence, theoretically argued models of elementary molecular steps of chemical reactions are useful for better identification.

INTRODUCTION

Various methods of thermal analysis are frequently used to follow phase transformations or chemical reactions involving solid crystalline materials and developing or beginning on their surfaces. Important progress has been made in understanding the macro-mechanisms of such processes; less is known, however, about their elementary molecular steps. In addition to experimental evidence, theoretically argued models are useful in identifying these steps.

The aim of this paper is to draw attention to the bond length–bond strength–bond energy concepts which have already found application in catalysis on oxide catalysts, but could also be useful in other fields of surface chemistry.

The formation of a crystal surface may be considered to be a result of cutting the crystal along a given crystallographic plane in such a way as to break the weakest (i.e., the longest) bonds. In this way we obtain a nearly flat, periodic mosaic of atoms that is non-uniform both geometrically and energetically. The geometrical map of such a mosaic may be easily constructed on the basis of crystallographic data. In constructing an energy map the concept of bond strength is useful.

The electrostatic bond strength, s (known to be applicable also to highly covalent bonds) was originally defined by Pauling [1] as the valence of a cation, z, divided by its coordination number, k:

$$s = \frac{z}{k} \tag{1}$$

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so that the sum of the strengths of all bonds around an ion is equal to its valence:

$$\sum_{1}^{k} s_i = z \tag{2}$$

As reported by Brown [2], it was later pointed out that the bond strength must depend on the cation–anion distance, R. Various empirical methods for calculating cation–oxygen bond strengths as a function of bond length have been proposed, two of which have become widely applicable and accepted; the inverse power function:

$$s = \left(\frac{R}{R_1}\right)^{-N} \tag{3}$$

and the exponential function:

$$s = \exp\left(\frac{R - R_1}{B}\right) \tag{4}$$

where s is the bond strength expressed in valence units (vu), R is the bond length in Å and R_1, N and B are empirical parameters given in the literature [2].

Recently [3,4] we have proposed for the same purpose a coulombic-type equation:

$$s = \frac{dz}{R - R_0} \tag{5}$$

and we have demonstrated that the bond strength defined in such a way is directly proportional to the bond energy, E (which may be expressed, e.g., in kcal mol^{-1}):

$$E = Js \tag{6}$$

The empirical parameters d and R_0 (related to the ionic radii) have been given [3] for over 200 cations; J is simply the standard atomization energy of a simple oxide of the considered cation per valence unit of cation [4].

Equations (5) and (6) can be applied in constructing the energy map of the surface of oxide crystals. In particular, it is possible to indicate the undersaturated (and thus active) surface atoms. Undersaturation is quantitatively defined as the sum of the strengths or energies of the missing bonds that were cut out in the process of surface formation. The undersaturated surface atoms are bound to the lattice with the strength (energy) of the residual, existing bonds. The increased activity of the undersaturated atoms means that on the one hand they can be more easily extracted from the surface, and on the other they are endowed with some unexploited binding ability and are ready to react with species approaching the surface from the surrounding gaseous or liquid phase.

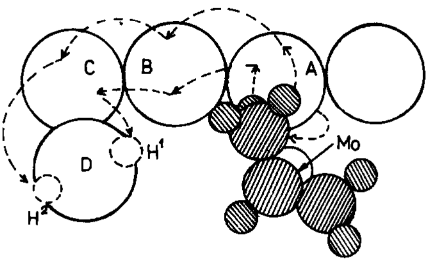

Fig. 1. Structure of active site on the (101) face of MoO_3, on which propylene is selectively transformed into acrolein.

The ideas outlined above have recently been applied to construct the bond strength model of active sites, BSMAS [5], and the crystallochemical model of active sites, CMAS [6], on oxide catalysts. Details are given in the papers cited. In this paper we wish to illustrate the possibilities of these models by considering briefly the mechanism of the oxidation of propylene to acrolein on the (101) face of MoO_3, which is highly selective in this reaction. Figure 1 shows the structure of an active site; only active Mo and O atoms are indicated. The reaction is considered to be composed of five stages (some of them comprising several elementary steps):

(I) Adsorption of propylene over undersaturated Mo.

(II) Abstraction of the first α-hydrogen and its transfer to O_D along the row of the undersaturated oxygens, $O_AO_BO_C$.

(III) Formation of the CH_2CHCHO_AH intermediate and its decomposition with desorption of acrolein.

(IV) Transfer of the second hydrogen (liberated in the latter stage) to O_D and desorption of water (H_2O_D).

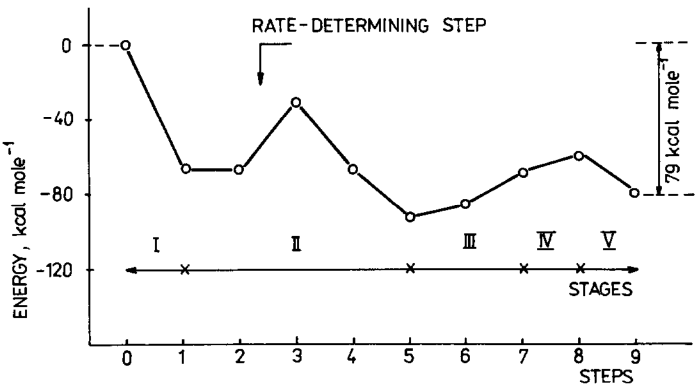

Fig. 2. Energetic pathway of the oxidation of propylene to acrolein on the (101) face of MoO_3.

(V) Reoxidation of the catalyst with O_2 molecules, during which the anion vacancies at O_A and O'_D positions are filled and the catalyst reaches its initial state (O'_D denotes the vacancy on which propylene was originally adsorbed).

Knowing the local undersaturations resulting from eqns. (5) and (6) and from the MoO_3 structure (bond lengths) and taking into account the energies of bonds in molecules, one can easily calculate the energetic reaction pathway, which is shown in Fig. 2. Assuming that the step with the highest enthalpy constitutes the rate-determining step, one can conclude that in the case under consideration this step consists in abstraction of the first α-hydrogen from the molecule of propylene. This remains in agreement with the literature data. On the other hand, the agreement of the calculated heat of reaction (79 kcal mol^{-1}) with that taken from thermochemical tables (81 kcal mol^{-1}) is a good internal check of the model.

It is interesting to note that quite recently the bond length–bond energy concept has been used in calculating the surface energy of solids [7].

The author's belief is that the concepts outlined above could find applications in many other problems with the surface chemistry of solids.

REFERENCES

1 L. Pauling, J. Am. Chem. Soc., 51 (1929) 1010.
2 I.D. Brown, in M. O'Keeffe and A. Navrotsky (Eds.), Structure and Bonding in Crystals, Vol. 2, Academic Press, New York, 1981.
3 J. Ziółkowski, J. Solid State Chem., 57 (1985) 269.
4 J. Ziółkowski and L. Dziembaj, J. Solid State Chem., 57 (1985) 291.
5 J. Ziółkowski, J. Catal., 84 (1983) 317.
6 J. Ziółkowski, J. Catal., 100 (1986) 45.
7 J. Ziółkowski, Proc. IXth Eur. Chemistry of Interfaces Conf., Zakopane, Poland, May 1986, Mater. Sci. Forum, in press.