

A new concept for the application of linear free energy relationships in catalysis

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Abstract

Linear free energy relationships (LFERs) have been used in heterogeneous catalysis for a long time. Their application to heterogeneous catalytic systems have been based on the original substituent concept introduced by Hammett [K.J. Laidler, *Chemical Kinetics*, Harper Collins Publishers, New York, 1987, pp. 246–251.]. This work deals with the idea of validating a new concept for the application of LFER in heterogeneous catalysis. Following this idea, the considered reactions center is the active site on the catalyst surface, rather than that of the reacting molecule. The confirmation of a successful application to HDS and hydrogenation reaction will be shown as a preliminary example of the potential of the new approach. The implications for catalyst design will be discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: LFER; Structure–reactivity relationship; Catalyst design

1. Introduction

For more than six decades, empiric correlations between rate (or equilibrium) constants and some structural parameters have been successfully applied to a wide range of chemical reactions. They are currently known as linear free energy relationships (LFERs). One of the most used LFER is based on an equation proposed by Hammett [1], which relates the reaction rate or equilibrium constant to substituent parameters, for the reactions of substituted benzene. According to Hammett, the rate or equilibrium constant (k) in a series of compounds, having a substituent at a given position other than the reaction center, is related to the value

for the unsubstituted compound (k_0) in terms of a two-parameter equation, namely, ρ and σ , such as:

$$\log k = \log k_0 + \rho\sigma \quad (1)$$

where σ depends only on the substituent and ρ is a reaction constant, which varies with the reactions and associated conditions. The σ parameter is related to the polar character of the substituent. In fact, a positive value of σ corresponds to stronger electron attractors than hydrogen. Reactions with positive ρ values are accelerated by an electron withdrawing character of the substituent.

Although LFER are semiempirical correlations, transition state theory provides the bases for their rationalization. The observance of a LFER is equivalent to the existence of a linear

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relationship between the free energy of activation:

$$\log k_i = \log[k_B T/h] - \Delta G^\ddagger/RT \quad (2)$$

where k_B , h and R refer to the Boltzmann, Planck and ideal gas constants, T is the reaction temperature and ΔG^\ddagger is the free energy change of activation. Including the ΔH^\ddagger and ΔS^\ddagger contributions to ΔG^\ddagger , Eq. (2) becomes:

$$\log k_i = \log[k_B T/h] - \Delta H^\ddagger/RT + \Delta S^\ddagger/R. \quad (3)$$

In a reaction family, characterized by a given reaction mechanism, the steric factors of the transition state might be the same for each member of the family. Thus, the difference in the change of entropy between the transition state and the reactants for members of the family, is either negligible or directly correlated with the enthalpy change. So, Eq. (3) can be rewritten as:

$$\log k_i = A + B\Delta H^\ddagger \quad (4)$$

taking the form of a LFER.

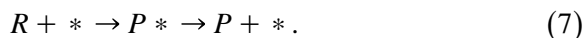
Besides the Hammett equation, some other structure–reactivity relationships have been proposed [2], such as those from Taft [3], Bronsted [4] and the Evans–Polanyi formalism [5]. Their application in heterogeneous catalysis began with the classical work of Mochida and Yoneda [6–8] and followed with a series of promising examples [9–11]. In more recent years, LFERs have been established for complex catalytic systems of significance to the oil refining industry. The new approach involves new set of reactivity parameters evaluated by means of quantum chemistry calculations. Direct correlations between kinetic constants and quantum parameters have been established for a family of chemical reactions when the parameters were evaluated for the associated molecules (reactants) or reaction intermediates [12]. These relationships have also been applied in heterogeneous catalytic systems, although to a lesser extent than in homogeneous reactions [12]. In this regard, a

molecular kinetic model was developed for an acid-catalyzed reaction, such as catalytic cracking [13], which uses the Monte Carlo approach to represent the gas oil as a specific set of molecules. This model predicts a product distribution very close to that obtained experimentally. The LFER approach is used here for the first time, to establish correlations between known kinetic parameters and their calculated quantum parameters. Then, the correlations are used to predict the unknown kinetic parameters for certain molecules from their calculated quantum parameters.

Up to now, the LFER applications in heterogeneous catalysis follows the same principle used in organic reactions, where reactivity parameters of the reactive molecules are correlated to kinetic constants. In this work, the use of catalyst reactivity indices (RIs) instead of reactant parameters in establishing LFERs correlations is proposed and its implications for catalyst design is discussed. The application of this new concept is illustrated for the hydrodesulfurization (HDS) and hydrogenation reactions (HID), currently appeared during the hydrotreatment of petroleum fractions.

2. Concept and methodology

The catalytic conversion of a reactant, R , into a product, P , on an active site, $*$, can be schematized as:



In this reaction, one might consider the active sites as one of the reacting molecules and introduce small differences within a series of active sites, so as to define a family, such as those employed for the construction of LFER. The comparison of the reaction kinetics of molecules that differ slightly in structure has been proven to provide substantial information about a given reaction.

Assuming, that in fact, the LFERs can be considered equivalent to relationships with the

free energy and that the free energy presents an additive characteristic, the introduction of small differences in a molecule (or cluster) might involve only an additive contribution to tag free energy (a summational effect). Providing that the change introduced within the series, in the structure of the cluster forming the active site is small, a LFER might be found.

Additionally, another requirement in order to keep the linearity in the relationship, is that the effect of the structure change on the reaction occurs through an independent interaction. In other words, the interaction causing the effect of the structure change is different than that causing the reaction itself.

Within these constraints, the application of this model (where the active sites are changed within the series) needs, not only that the reactant molecule is kept constant, but also that the change in structure of the active site does not cause new interactions with the reactant molecule. In order to achieve this requirement, the interaction of the reactant molecule with the active site must be a constant factor through the series. The choice of the model reaction must be based on the knowledge of the reaction mechanism.

Dunn [14] proposed to separate the heterogeneous reaction into elementary steps and to model each of them with a simple reaction and then, to apply the additive concept of the free energy. The absence of more than one type of interaction and the possibility of keeping the reaction mechanism through the series are favored by this approach.

In the original concept of the LFER, the substituent influence considers their stabilizing or destabilizing effect on the transition state. The electronic effect of the substituent account for their inductive and resonance influence on the conversion of the reactant molecule into the transition state. The inductive effect reflects a field effect and an electronegativity effect which can hardly be separated and are currently treated together. Highly inductive substituents stabilize electron rich transition states but destabilized

electron deficient species. The ability of the substituent to stabilize or destabilize the transition state through resonance without modifying the charge distribution can be separated into another parameter. The original Hammett parameters contain inductive and resonance components. However, their individual contribution have been separated in order to generate purely inductive parameters [15].

Besides electronic effects, the existence of steric effects might alter the observation of LFER. The incorrect selection of substituents exhibiting steric hindrance might mask the consequences purely due to polar effects. Although Taft has evaluated steric parameters for a liquid phase model reaction, they are usually difficult to quantify. Thus, it is desirable to chose substituents with minimum steric effects. Unfortunately, this is difficult. Most regression trials based on a two-parameter equation fail because other effects have not be taken into account [2]. Therefore, linear correlations are fit using more parameters, but also it is likely that new RIs would be required. In heterogeneous catalysis, the need to applying the regression through four-parameter equations have been demonstrated [16]. It might be obvious to imagine more demanding steric requirements in heterogeneous catalysis, than those present in liquid phase organic reactions. Consequently, most regressions would not work in catalysis, especially, because the reactivity parameters employed for the reactant molecules do not take into account all the effects which are of significant importance in heterogeneous catalysis.

In principle, the actual active site of a catalyst is that which does not hinder sterically the reacting molecule, but instead offers the suitable geometry and the proper electronic structure required for activation of the electron distribution required for breaking and for/or creation of new bonds. Thus, provided that the quantum calculations were performed in a representative cluster of the active site, there should be an electronic parameter associated with a RI suitable for a LFER.

Even for organic molecules and reactions, the reactivity parameters, formerly empirical, have been theoretically evaluated. So far, calculations based on semiempirical methods have proven to be good enough for the evaluation of the quantum parameters used for establishing the LFERs [12]. In an attempt to verify the feasibility of obtaining LFERs using catalyst RIs, we have used different approximation levels of semiempirical calculations, in the present work.

The reactions taken as examples were the HDS reaction of dibenzothiophene and the hydrogenation of biphenyl, evaluated at 530 K and atmospheric pressure. The catalytic activity, from Lacroix et al. [17], for a given sulfide, is taken as the number of converted molecules $\times 10^{-10}/\text{s m}^2$.

The active site was modeled by sulfide clusters of an asymmetric unit cell (Fig. 1). Cluster geometry, responding to the structures identified in Ref. [17], was extracted from crystallographic data [18]. By doing so, we assume to be modeling a cluster representative of the active site.

As a first approach, Restricted Hartree–Fock calculations at the CNDO level [19] were performed employing the MSI's package Zindo [20]. The calculated parameters were: Mulliken Population Distribution (MPD) for the atomic d-orbital, the HOMO and LUMO energy value (E_{HOMO} , E_{LUMO}) and the LUMO–HOMO difference of energies (Δ).

Restricted Open Hartree–Fock (ROHF) cluster calculations were carried out, as a second level of approximation, for the evaluation of the

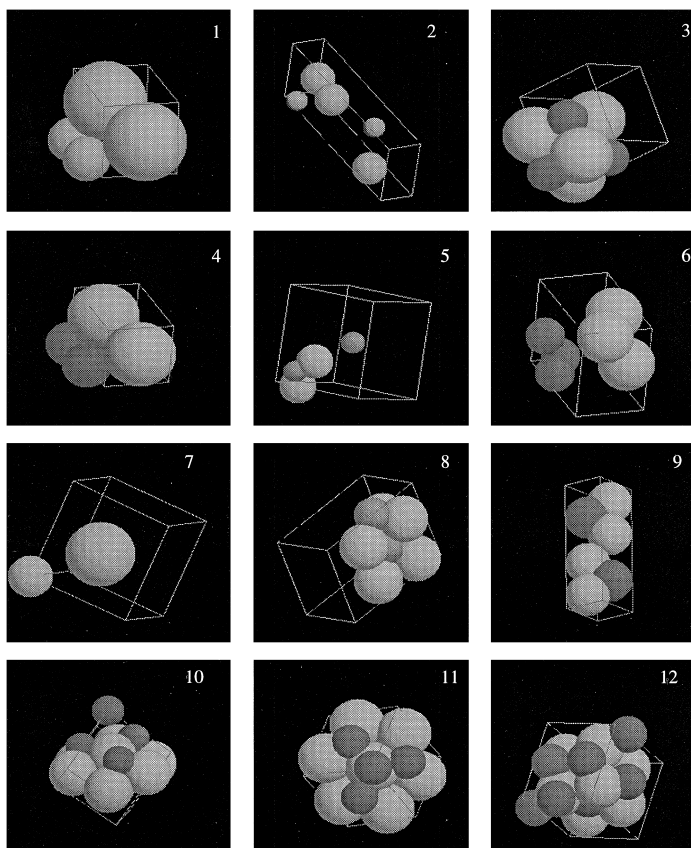


Fig. 1. Evaluated sulfide clusters. (1) VS, (2) Cr_2S_3 , (3) MnS, (4) FeS, (5) Co_9S_8 , (6) NiS, (7) CuS_2 , (8) NbS_3 , (9) MoS_2 , (10) RuS_2 , (11) RhS_2 , (12) PdS.

metal sulfide quantum parameters, within the INDO1 method, also employing the Zindo package from MSI [20]. At this level, the electronic energy partitioning scheme presented by Kollmar [21], for the analysis of ab initio and semi-empirical SCF calculations was used. The resulting value might be associated with the electronic contribution to the bond strength (DBE). Sánchez and Ruette [22] has proposed its use as a tool for bond analysis. Within semi-empirical methods, the following expression is obtained:

$$\text{DBE}(A-B) = \sum_{i,j \in A,B} p_{ij}(h_{ij} + f_{ij}) \quad (8)$$

where h_{ij} , p_{ij} and f_{ij} are the one electron, bond order and Fock matrix elements, as obtained from the INDO1 calculations.

3. Results and discussion

In Figs. 2 and 3, the linear correlations determined for the HDS and for the hydrogenation activity values, at the CNDO level, are shown. The trends in HDS and hydrogenation activities

with the metal sulfide Mulliken d-orbital population and LUMO–HOMO energy separation along the first transition metal series was discussed [16] in terms of the vacancy formation rate (catalyst activation step). The active sites for the HDS reaction have been recently associated [23,24] with anionic vacancy, which might be formed by surface sulfur removal upon reaction with hydrogen. Metals with few valence d-electrons might exhibit the highest electron withdrawing character, and therefore the reduction of the metallic site (anionic vacancy) might occur more readily.

The hydrogenation reactions involve the interaction of the hydrocarbon and hydrogen molecules with the surface. In the frontier orbital picture, the energy changes of a chemical process are governed by the interaction between the frontier orbitals (HOMO and LUMO), interacting with the reactants [25], and so a lower Δ value might imply a higher probability of charge rearrangements in the solid, reducing in this way the energy costs involved in activation of the hydrocarbon double bond. More details are given in Ref. [26].

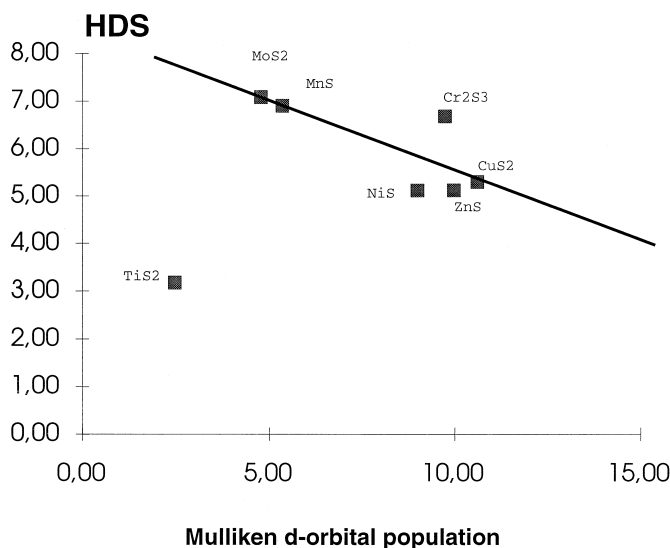


Fig. 2. Linear correlation for the HDS at the CNDO level.

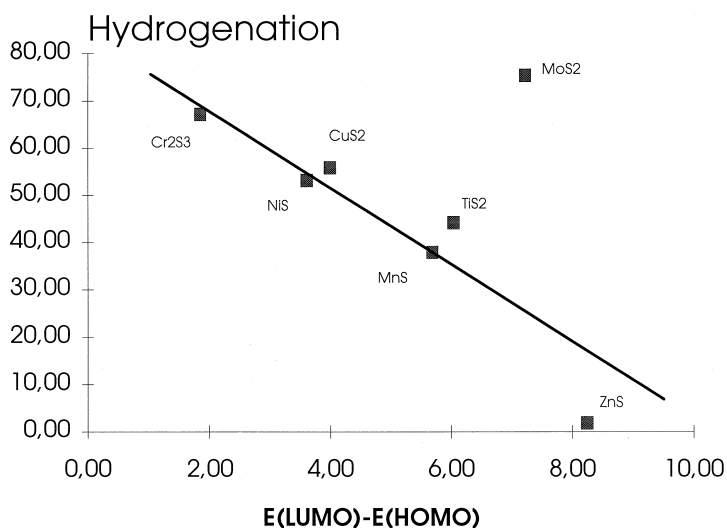


Fig. 3. Linear correlation for the hydrogenation at the CNDO level.

In summary, for HDS, metals with lower valence d-electron density might show a higher vacancy formation rate. Meanwhile, for hydrogenation, a lower HOMO–LUMO energy difference might imply a higher probability of charge rearrangements in the solid, reducing in this way the energy costs involved in the hydrocarbon double bonds activation.

The correlations found between the QM calculated parameters and the experimentally evaluated activity indicates the validity of associating the electronic properties with RIs, as has already been demonstrated in the case of the reacting organic molecules [13]. Besides, the possibilities of explaining the LFERs found with the calculated catalyst RIs, using accepted mechanistic facts of the reference reactions, illustrated the capabilities of this tool for the understanding of the catalytic phenomena. Furthermore, the feasibility of treating the active sites as a reacting compound within a reaction mechanism, for the LFER formalism, has been also confirmed.

CNDO is a rough approximation and it was only a first attempt for confirming the feasibility of using catalyst QM calculated RI for obtaining a LFER. Achieving this step, one might think on taking a further step and using a better level

within the semiempirical methods. Fig. 4 shows the results obtained when fitting the HDS activity data with the DBE values, again a linear relationship has been attained. Such a correlation involving the DBE quantum parameter and the HDS activity, is also in agreement with the role of S vacancies as active site. A detailed explanation of the meaning of this relationship has been given elsewhere [26], but the separation into two distinct lines for each transition metal series within the periodic table need to be clarified. However, it is important to mention the relevance of using normalized activity values in order to find the correlation. The normalization of the experimentally obtained activity values by the S/M ratios accounts for the variations on structures and stoichiometry along the transition series. Regardless of the specific reaction mechanism, the rate of the rate limiting step seems to be determined by the intrinsic reactivity of the unsaturated metal sites.

Improvement in the quality of the calculated RI values leads to a deeper knowledge in the involved catalytic mechanism and the active role of the catalytic site, providing that a LFER holds.

However, for catalyst design purposes, it would be useful to have a single correlation for

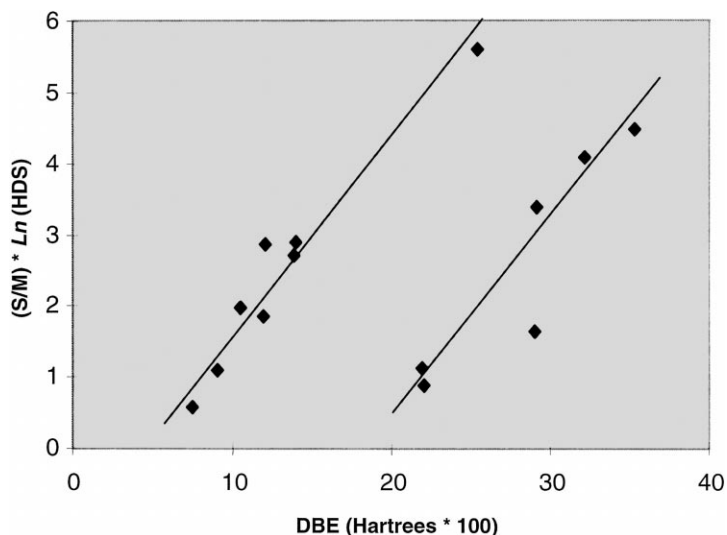


Fig. 4. Linear correlation for the HDS at the INDO1 level.

the whole family of transition metal sulfides, so as to choose the best formulation for achieving a certain activity level. Such a correlation is shown in Fig. 5, for which:

$$(S/M)\ln(\text{HDS}) = A * \text{DBE} + B * \text{VN} + C \quad (9)$$

where $\text{VN} = \text{qt}(\text{M})\text{qt}(\text{S})/\text{RMS}$, $\text{qt}(\text{M})$ = metal (Mulliken) net charge, $\text{qt}(\text{S})$ = sulfur (Mulliken) net charge and RMS = metal–sulfur distance.

VN is regarded as the net charge repulsion potential. The plot shows the quality of the four-parameter linear correlation and corresponds to the observed values vs. the calculated ones. Clearly, this relationship represents a first approximation for a four-parameter LFER. The quality of this LFER is not as good as the others we have shown in this work. In fact, $R^2 = 0.80$ and $s = 0.67$, for a linear regression of Eq. (9).

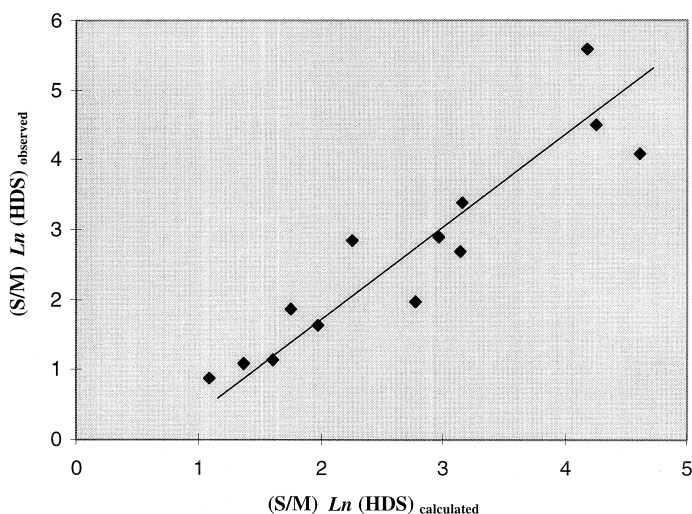


Fig. 5. Quality of the four-parameter linear correlation for HDS activity.

The values found for the fitting parameter were $A = 0.12$, $B = -0.12$ and $C = 2.25$, but their meaning is not well understood. A need for a better four-parameter linear regression remains.

For catalyst design purposes, the use of Eq. (9) is suggested as a first step prior to using the LFERs shown in Fig. 4. So, using Eq. (9) (Fig. 5), the QM parameter of the suitable sulfide could be predicted to achieve a given value of the desired activity. Then, Fig. 4 can be used for a more accurate determination of the selected sulfide and to decide on which line the corresponding data (from Fig. 5) fits.

4. Conclusions

The feasibility of obtaining LFERs when correlating the experimentally evaluated catalytic activity with RIs calculated by quantum mechanics methods on clusters representative of the active sites has been demonstrated. Their implications and uses for catalyst design purposes has been also suggested.

The economic importance of these type of relationships in catalyst development lies in the fact that they could reduce significantly the number of experiments involved. A quantitative correlation between kinetic data and molecular (microscopic) parameters for a given reaction of industrial interest might be of particular value to optimize a catalytic system. Further advantages are encountered on the variety of available molecular modeling software and the accelerated advances in computer hardware, which makes the quantum parameters readily evaluated.

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