Matching the formal potential of the catalyst with the reversible potential of the reaction. A new way of optimizing Electrocatalysis.

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We offer, for the first time evidence of an "inverted region" for an inner-sphere reaction, the oxidation of hydrazine in alkaline media, catalysed by Fe phthalocyanines confined on graphite surfaces. The classical interpretation of these correlations follows the Sabatier principle that to obtain the highest catalytic activity for a given reaction, the adsorption of the reacting molecule need to be not too weak, not too strong (1) A correlation of this sort is shown in Figure 1 on the left where the "falling region" that is a atributed to a gradually increase in the strength in the adsorption of the reaciong molecules that decreases the fraction of free-active sites is now interpreted as an inveverted region. We have suggested that the Fe(II)(I) formal potential of the catalysts is proportional to the free energy of adorption of the target molecule on the Fe centers as they involve the reduction of Fe(II) to Fe(I) so this served to explain the shape of the asymmetric volcano correlation in Figure 1 on the left.

In this work we use the Savéant (3) formalism that emplys a quadratic correlation between the activation energy and the free energy of the reaction, similar to those used in Marcus model. However, Marcus model applies only to outer-sphere reactions (no bond breaking or bond forming) whereas Savéants model is used for concerted ET reactions that involve bond-breaking at the *rds* . In our case we use the same reasoning but for bond-forming at the *rds*, which is the crucial step in any electrocatalytic reaction. This inverted region appears in unsymmetric parabolic correlations between the reaction rate (log k_o) versus the difference between the $E^{o'}_{Fe(II)/(I),}$ the formal potential of the catalyst and reversible potential of the couple E $_{N2H4/N2}$ in the same media (unaerobic 0.1 M NaOH). The rate-determining step involves the formation of a temporary bond between the Fe center and a nitrogen atom in hydrazine. The potential energy surfaces of the reactant are defined by a Morse type of correlation due to the anharmonicity of the system. The highest catalytic activity is achieved when the formal

potential of the catalyst matches the N_2H_4/N_2 reversible potential. This clearly shows that the formal potential of the catalysts needs to be "tuned" to be exactly the reversible potential of the target molecule to undergo a ET reaction. The later is likely to be valid for many reactions of this sort and might change the way volcano correlations are interpreted.
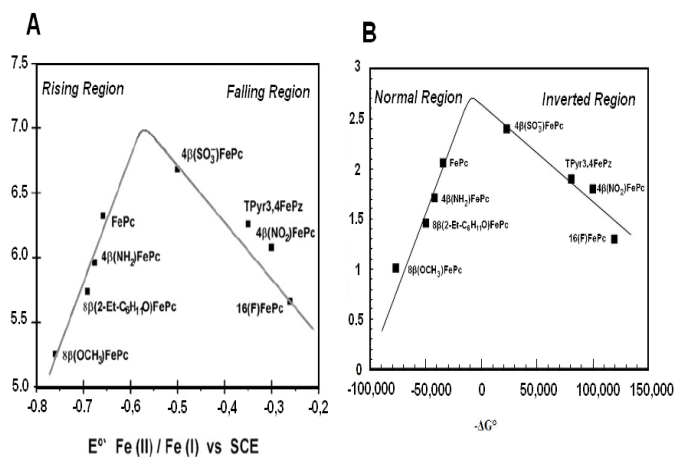

Figure 1. (A) Variation of log(i/Γ complex) (currents normalized for the surface concentration of the catalyst) versus the formal potential of the catalyst for the electrooxidation of hydrazine on FePcs with different substituents. Adapted from ref. [1]
(B) Plot of log k^o versus $-\Delta G^o$ (Jmol^{-1}) constructed with data from Figure 1-A.

References

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