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KINETICS ASSISTED DESIGN OF CATALYSTS

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Whether thermokinetic data obtained on model large single crystals at low surface coverage can be used successfully to calculate yields on real catalysts at high surface coverage is a question that is considered in the conjecture presented in this note.

1. The problem of non-ideal surface kinetics

If rate constants of elementary steps entering in a catalytic cycle are known, it is now possible to calculate on a personal computer the yields obtained in a catalytic reactor operating with a conceptual catalyst under specified process conditions [1]. This possibility provides the researcher with another powerful tool to design new catalytic cycles and materials by systematic trial and error called molecular engineering. Kinetics as well as other means of assistance in the feedback loop of molecular engineering or design of catalysts have been discussed in a recent book [2].

In the case of kinetics on heterogeneous catalysts, the difficulty is not only to come up with reasonable elementary steps of the cycle and with their experimental, calculated, or estimated rate constants, but with the dependence of these rate constants on surface coverage. This dependence has been established by generations of chemists dealing with solid surfaces. The reason for this dependence is twofold.

First, at sufficiently low surface coverage, adsorptive molecules probe the details of surface structures, including defects, with atoms of varying surface coordination numbers and sites with diverse multiplicity and symmetry. The result is a spectrum of binding modes, adsorption entropy and enthalpy values, and kinetic parameters. As surface coverage increases, lateral attractive or repulsive interactions become more important with the similar consequence of thermodynamic and kinetic parameters in the adsorbed layer varying with surface coverage. To account for the effect of surface coverage on kinetic parameters appears to be such a formidable problem that the almost universal reaction of surface kineticists is to ignore it altogether. The result is the traditional treatment of heterogeneous catalytic kinetics associated with the names of Langmuir and Hinshelwood [3].

The validity of this kind of "ideal" kinetics has been questioned justifiably and repeatedly [4]. Its validity has been argued to be an excellent approximation in the case of reactions that require only a single atom or a simple site in the rate determining step of the catalytic cycle and in addition are run under conditions of sufficiently high surface coverage [5]. Then, the remaining empty sites are sufficiently dilute to behave ideally in the surface solvent of an almost complete monolayer that effectively erases the intrinsic structural differences of the underlying surface. In any event, there exist now many examples of such reactions run on metals under the above conditions for which turnover rates determined on different crystallographic planes of large single crystals are very similar, and also very similar to turnover rates measured on supported clusters of the same metal with size between 1 and 10 nm [3].

This remarkable agreement between rate data obtained on large single crystals and on supported metal catalysts suggests that the former provide the standards by which work on the latter can be assessed [6], provided that the rates are measured in both cases under comparable conditions of sufficiently high surface coverage.

2. Is it possible to calculate catalytic rates from data at low surface coverage?

The question addressed in this Letter is a new one. Is it possible to calculate the rate of a catalytic reaction at normal or high pressures on an industrial type of catalyst, from kinetic parameters measured on large single crystals at very low pressures, *i.e.*, under conditions of low surface coverage? Recently this question has been answered positively by Oh et al. at General Motors in the case of the oxidation of carbon monoxide on Rh(111) and on Rh supported on alumina [7]. The question was answered negatively by Bowker et al. [8] at Imperial Chemical Industries in the case of ammonia synthesis when data obtained by Ertl's group on single crystals of iron [9] were extrapolated to industrially relevant pressures and temperatures. In the work of Bowker et al., the disagreement between extrapolated values of conversion and representative values reported on an industrial catalyst was enormous (4 to 5 orders of magnitude). By contrast, Stoltze and Nørskov at Haldor Topsøe report excellent agreement [10–12] between conversion data also calculated from the iron single crystal data of the Ertl group [9] and observed data at high pressures and temperatures on a commercial KM1 Topsøe iron catalyst.

It is hard to delve into the possible reasons behind the positive and negative answers to the same question obtained by Bowker et al. on the one hand and Stoltze and Nørskov on the other hand. Until the discrepancy is explained, it will be assumed that the latter authors are correct.

3. A conjecture

Indeed, a conjecture can be presented that suggests in general the possibility of a positive answer to the question posed in this Letter. The conjecture is based on the formalism developed over the years by M.I. Temkin as discussed in detail elsewhere [3]. Temkin's formalism originated in his treatment of the kinetics of ammonia synthesis on iron catalysts [13] that was later expanded and generalized by himself and his school. The formalism acknowledges the non-ideality of the catalytic surface by postulating a distribution function of the standard free energy of adsorption of a chosen reactant, ΔG°. The value of $(\Delta G^\circ/\mathrm{RT}) = t$ is assumed to vary between $t = t_0$ on a bare surface to $t = t_1$, on a filled surface. The shape of the distribution function is described by a parameter γ. The relation between the thermodynamic quantity ΔG° and the corresponding rate constant k is of the Brønsted type: $k = \mathrm{const}[\exp(-\Delta G^\circ/\mathrm{RT})]^\alpha$ with a Brønsted parameter α. The following results are perfectly general [13]. But for clarity and because of the papers discussed above, they will be presented for the case of ammonia synthesis. For the turnover rate v of that reaction in the forward direction, it is assumed that chemisorption of dinitrogen is the rate determining step and adsorbed nitrogen is the most abundant reactive intermediate. With these assumptions, when rates are integrated over the distribution between $t = t_0$ and $t = t_1$, a simple result obtains for the forward turnover rate v averaged over the entire surface:

$$v = \left\{ k[\mathrm{N_2}] \frac{[\mathrm{H_2}]^3}{[\mathrm{NH_3}]^2} \right\}^m \tag{1}$$

with $k = \tau k^0\ (K^0)^{-m}$; $m = \alpha - \gamma$, and τ a numerical quantity. The constant k^0 is the rate constant for adsorption of dinitrogen *at the value* t_0 *corresponding to zero surface coverage*. The constant K^0 is the equilibrium constant for

$\mathrm{NH_3} + {*} \mathrel{⊜} \mathrm{N}{*} + \frac{3}{2}\mathrm{H_2}$

also corresponding to *the value* t_0 *corresponding to zero surface coverage*. It follows that the rate can be calculated if the kinetic and thermodynamic parameters at zero surface coverage are known and if the parameter m is known. Now, if the surface had been an ideal surface characterized by a single value of both k and K, the forward rate for ammonia synthesis would have been for the same mechanism:

$$v = \frac{k[\mathrm{N_2}]}{\left\{1 + K[\mathrm{NH_3}]^2/[\mathrm{H_2}]^3\right\}^{1/2}}. \tag{2}$$

The close similarity between eqs. (1) and (2) was first pointed out [14] by noting that, in a certain range of concentrations:

$$\frac{1}{\left\{1 + K[\mathrm{NH_3}]^2/[\mathrm{H_2}]^3\right\}^{1/2}} = \left\{K[\mathrm{NH_3}]^2/[\mathrm{H_2}]^3\right\}^{-m}$$

if as is usually the case, $0 < m < 1$ as for example for ammonia synthesis on iron.

Thus, if the needed kinetic and thermodynamic parameters are known at low surface coverage, and if the rate is calculated on the basis of an *ideal* surface, it is *possible* that an approximately correct result will be obtained. That the approximation can be an excellent one follows from the work of Stoltze and Nørskov who followed the above prescription, ignoring completely the non-ideality of the surface on which the formalism of Temkin is based, a formalism that for ammonia synthesis is supported by many thermodynamic (adsorption isotherms) and kinetic (rates of adsorption, kinetic isotope effect) data.

It is clear that a truly zero coverage, structural effects would show up so that a single value of kinetic parameters at zero coverage is not expected. But in the formalism of Temkin, it is shown that the contribution to the average rate due to sites at very low or very high values of surface coverage is relatively quite small. For details, the reader is referred to ref. [3]. It is not claimed here that the approximation made in calculating a surface catalytic rate from low coverage data by ignoring completely the non-ideality of the adsorbed layer is necessarily going to be good or even excellent.

The message of this letter is that the successful examples of Oh et al. [7] and of Stoltze and Nørskov [10–12] may not be accidental but find some justification in the Temkin formulation of non-ideal surfaces. This observation should encourage others to try for other surfaces and reactions what has been successfully attempted in these two cases.

Let us note that Oh et al. have made in their analysis a small concession to surface non-ideality by assuming a modest linear decrease of the heat of adsorption of carbon monoxide with surface coverage by the latter. But as discussed elsewhere [15], this decrease was probably compensated by a corresponding increase with coverage of the activation energy of chemisorption by dioxygen, as prescribed by Temkin's formalism. Clearly much remains to be done to handle consciously and properly the reality of non-ideal surface behavior. The conjecture sketched in this letter is designed to encourage others to handle this problem instead of ignoring it. A clear understanding of the problem will determine the future of kinetics assisted design of catalytic cycles and materials [1].

4. Conclusion

In summary, it is conjectured that the rate of a catalytic reaction on a non-ideal surface may be calculated approximately from kinetic parameters obtained on a sparsely covered surface with the assumption that the rate can be described as if the surface were ideal. This conjecture follows from the Temkin formalism that expresses rates on a non-ideal surface by means of a rate expression that resembles closely that prevailing for an ideal surface and contains only kinetic parameters pertaining to low surface coverage.

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