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A Discussion on Kinetic Compensation Effect and Anisotropy

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A discussion on the so-called kinetic compensation effect, which has been observed in several heterogeneous catalytic processes and in particular in the direct synthesis of dimethyldichlorosilane, is presented. A possible explanation about the origin of the phenomena in relation to the anisotropic character of the reaction is proposed. A complementary explanation about the mechanism of promoters' action on the direct synthesis reaction is also proposed. These findings were obtained by comparison with analogous characteristics of another silicon reaction, namely, the silicon etching by alkaline solutions, for which similar phenomena are observed.

Introduction

The temperature dependence of the kinetics of heterogeneous reactions is usually represented by the classical Arrhenius law,

$$k = k_0 \exp(-E/(RT)) \tag{1}$$

where the preexponential term k_0 is often referred to as the frequency factor and E is the activation energy. For a group of similar or comparable rate processes, for example, for systematic series of similar reactants, catalysts, or solvents, several researchers have reported a correlation between the observed values of the frequency factor and the activation energy. Thus, a change in one Arrhenius parameter is compensated for by a correspondent change in the other. This behavior is more commonly referred to as the "kinetic compensation effect" (KCE) or "isokinetic effect", but different fields of chemistry often refer to it by different names, such as "the θ-rule" in heterogeneous catalysis. This compensation is usually expressed by

$$\ln k_0 = aE + b \tag{2}$$

where a and b are constants characteristic of the particular group of reactions to which the relationship applies. Equation 2 can also be expressed by the so-called Cremer−Constable relation:

$$\ln k_0 = \ln k_i + \frac{E}{R}\frac{1}{T_i} \tag{3}$$

where k_i is called the isokinetic constant ($b = \ln k_i$), and T_i is called the isokinetic temperature or compensation temperature ($a = 1/(RT_i)$). Similar compensation behavior can also be noticed in adsorption equilibrium parameters (Van't Hoff equation) and in other physical−chemical processes, such as those cited by Conner and Schwartz.[4]

Several possible explanations, some of more fundamental character than others, have been proposed in the literature to elucidate this behavior. In a review article on the compensation effect in heterogeneous catalysis, Galwey[9] summarized the following explanations for the KCE: (a) existence of a threshold temperature of onset of reaction; (b) energetically heterogeneous catalyst surface; (c) more than one active surface; (d) variation of the availability of surface reactant; (e) relationship between entropy and enthalpy;[3] (f) use of power law to represent the rate for surface reactions.

Galwey[9] mentioned, however, that there is no hypothesis of general acceptance. Another important aspect is the quantitative criterion for the detection of the compensation effect, because certain simple statistical procedures usually employed to estimate k_0 and E can generate cross-correlated estimates of these parameters. The false detection of the compensation effect due to spurious correlation among the Arrhenius parameters should be avoided using more appropriate statistical procedures, as proposed by Krug.[11]

The behavior described by eqs 2 or 3 has been observed for several groups of heterogeneous reactions in the literature.[9] This effect was also observed for the direct synthesis of dimethyl-dichlorosilane (DMDCS) by the reaction between methyl chloride (MeCl) and silicon, also called the Rochow reaction.[14] This reaction occurs at temperatures ranging from 280 to 360 °C, at which MeCl and DMDCS are both in the vapor phase.

The main objective of the present paper is to discuss the compensation effect observed in the direct synthesis reaction. For this purpose, we gathered information on the compensation effect observed in the direct synthesis process as well as in another similar reaction involving silicon, namely, the alkaline etching of silicon. The discussion on the analogy of the phenomena in the two reactions suggests a more fundamental explanation for the compensation effect observed in these processes.

Compensation Effect in the Direct Synthesis

Lieske et al.[14] studied the action of promoters on the direct reaction (reactions between silicon and methyl chloride, catalyzed by copper) and found a mutual dependency between the Arrhenius parameters k_0 and E_a obtained for different promoters (Zn, Sb, Sn, Zn + Sn, Zn + Sb, and without promoters). The parameters exhibit a genuine (i.e., free of statistical errors) and

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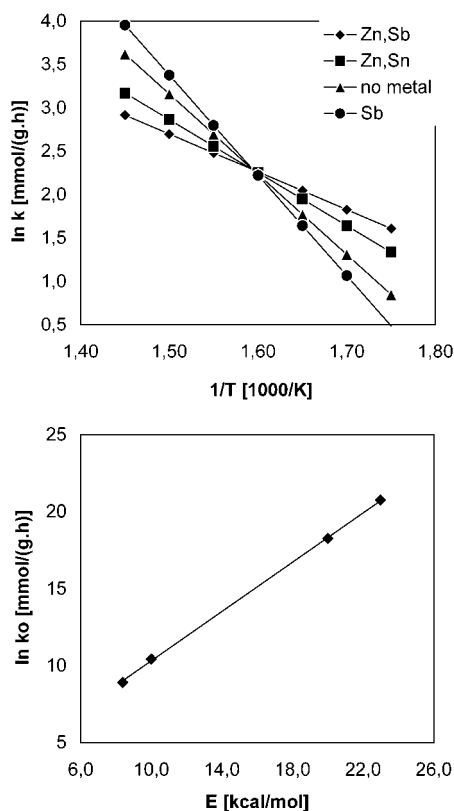
Figure 1. Arrhenius plot (a) and Cremer−Constable Diagram (b), showing the compensation effect for different promoters on the reaction between methyl chloride and silicon (extracted from ref 15 used with permission from editors).

Figure 2. Electronic microscopy picture showing erosion figures in (111) and (100) planes of silicon (extracted from ref 2 with permission of Academic Press, Inc).

precise compensation effect, closely following the Cremer−Constable relationship. Figure 1 illustrates a sample of their results, and each straight line in the Arrhenius diagram (Figure 1a) represents a different promoter. The isokinetic temperature was found to be about 330 °C. They concluded that the isokinetic effect is a characteristic of this reaction and occurs if the mass contact composition (the type and amount of the promoters, of the copper component, and of the silicon quality) is changed. According to Lieske et al.,[14] the causes for the isokinetic effect remained ignored and no justified mechanistic explanation of the isokinetic effect could be pointed out at that time.

As mentioned by Lieske et al.,[14,15] the most serious implication arises from the value of the isokinetic temperature (T_i), which amounts to about 330 °C, that is, this value is positioned just within the range of usual reaction temperature. As consequence, the order of the rate constants for different promoters will be reversed by a mere variation of the reaction temperature, if the isokinetic temperature is passed. If a promoter A is more efficient than a promoter B at a temperature $T < T_i$, then the opposite will happen for a temperature $T > T_i$. This can be seen in Figure 1a. According to Lieske et al.,[14,15] this is probably one of the reasons for the contradictions in the literature on the effect of promoters on the direct synthesis. Although compensation temperature is within the range of experimental measurements, Lieske et al.[15] showed that the consistency and the genuineness of the compensation effect on the direct synthesis were detected and demonstrated by their data, following the criteria proposed by Krug.[11]

For the mass contact (mixture of silicon, catalyst, and promoter) to be considered as promising, they should exhibit significant deviations of catalytic activity at temperatures close
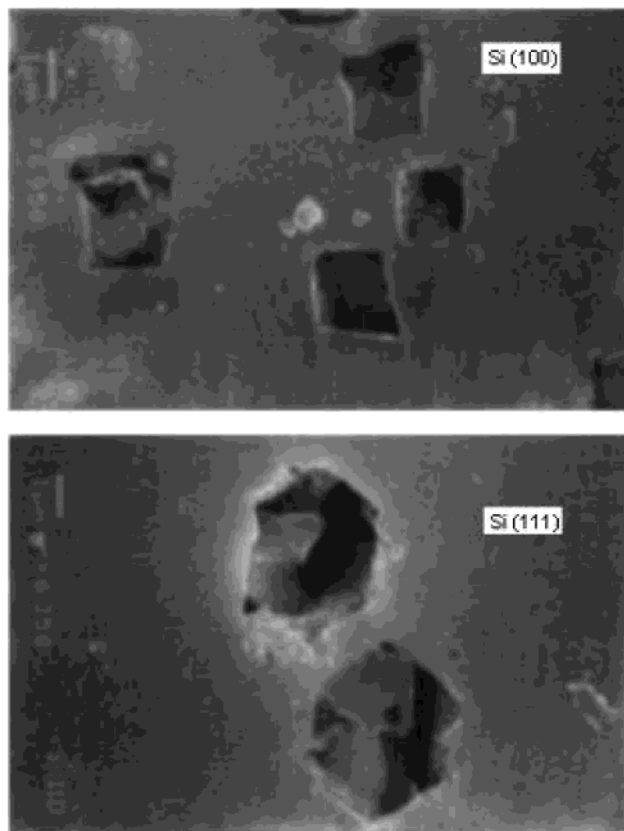
to the isokinetic temperature (T_i), at which all of the rate constants should be the same by definition. Taking into account the effect of the compensation, Lieske et al.[14] without success tried to correlate the promoters' effect with characteristics of the deposits of the alloy Cu_3Si. Their data showed no correlation between the promoters' presence and the content or average size of the catalyst particles (alloy Cu_xSi_y) nor between those and the catalytic activity. Although Lieske et al.[14] have found that it is possible to have some control on the temperature dependence of the reaction by changing the catalyst composition, the causes of the isokinetic compensation effect for the direct synthesis in terms of the nature and number of active sites still remained obscure.

The research about the mode of action of the promoters cannot be based on the activation parameters. In other words, it is not possible to discuss the changes in activation energy in terms of changes of the reaction mechanism or to interpret differences in frequency factors as differences in the number of active sites.

Anisotropy

Banholzer et al.[1,2] studied the reactivity of the (100) and (111) faces of silicon in the reaction with methyl chloride. Examining those faces after the reaction, using scanning electronic microscopy, they observed erosion figures ("pits") that are characteristic of each studied face, as shown in Figure 2. The development of those pits indicates that one or more stages of the reaction are anisotropic. Those pits remain up to silicon conversions of about 60%.

The anisotropic reaction exhibited by the direct synthesis has some similarities to the etching of silicon made in the electronic industry.[2] Several organic and inorganic alkaline aqueous

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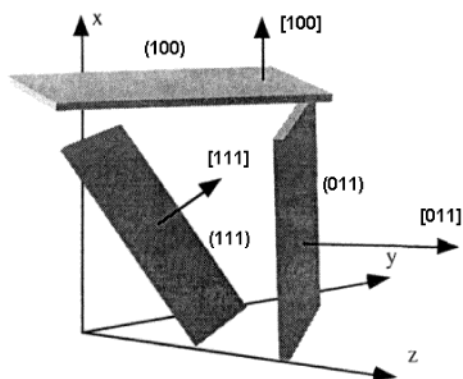
Figure 3. Draw of the locations of the planes with smaller Miller indexes.[8]

solutions have been developed that dissolve Si preferably in one or two crystallographic directions. This erosion usually has its smallest speed in the ⟨111⟩ direction resulting in the exhibition of the {111} planes. Figure 3 shows the position of the planes with the smallest Miller indexes in relationship to the space axes.

The smaller erosion speed experienced by the plans in the ⟨111⟩ direction has been associated with the number of available free connections on the silicon surface ("dangling bonds"). Furlan[8] questions that statement because there is usually a 100-fold ratio between the reaction rates observed along the ⟨100⟩ and ⟨111⟩ directions or ⟨110⟩ and ⟨111⟩ directions, while the difference of the connection densities for the same pair of planes is only about 2-fold.

Seidel et al.[16] claim that the anisotropic effect is attributed to the differences between activation energies of the several bond geometries on each surface. Figure 4 shows the atomic distributions for different crystallographic plans of a silicon crystal.

The etching of crystalline silicon occurs in two stages. The first one is the oxidation of the silicon, and the second is the dissolution of the formed oxide. The direct synthesis proceeds in a similar way; the silicon reacts with MeCl catalyzed by the Cu_xSi_y alloy, forming a volatile product, the DMDCS. However, no generally accepted mechanism of the direct synthesis reaction has emerged so far.[12]

According to Furlan,[8] the parameters that affect the speed and the quality of the anisotropic erosion of silicon are the concentration of the solution, the temperature, the concentration of doping agents in the substrate, the mass transport, and the protection against broad erosion. In the case of the direct synthesis, this last factor would correspond to the thickness of the native oxide layer. Thus, in the silicon erosion by KOH as well as in the direct synthesis of DMDCS, the emergence of well-defined erosion figures is guided by the layer of silicon oxide. According to Yilmaz et al.,[21] the thickness of the silicon oxide layer influences both the activity and the selectivity. Banholzer et al.[2] presented a pictorial diagram showing the formation of the active phase and the anisotropic reaction of the silicon with MeCl. The oxide mask disciplines the erosion, making it visibly anisotropic and containing the front of erosion progress, as shown in Figure 5. If the oxide layer is removed, the spatially organized erosion of the silicon is replaced by a widespread attack on the whole silicon surface.

The rate of silicon etching by alkaline solutions, such as KOH, depends on the crystallographic direction of the silicon. The etch rate distribution for different planes has been measured by several authors (e.g., Yang et al.[20]) as a function of the temperature and of the face of the silicon monocrystal, as shown in Figure 6.
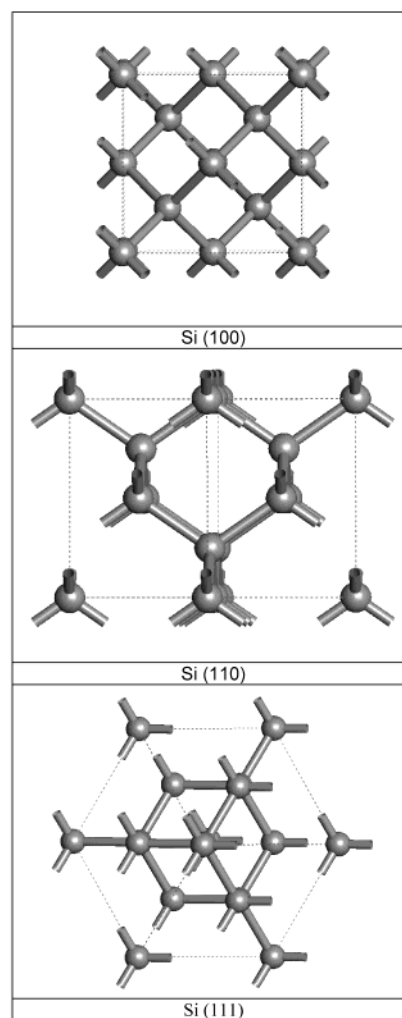

**Figure 4.** Atomic structures of the crystallographic planes of the silicon crystal.

Seidel et al.[16] measured etching rates of silicon by ethanolamine solution at different silicon plans under a temperature range between 20 and 115 °C. They presented an Arrhenius diagram, indicated in Figure 7, showing the curves extrapolated for infinite temperature at which, according to those authors, differences of energy among the important superficial states responsible for the anisotropy would not exist. The extrapolated curves for different plans intercepted each other at a point located about 300−400 °C rather than infinite.

However, those authors did not mention the fact that the behavior shown in Figure 7 is exactly a characteristic diagram of the existence of the compensation effect. Moreover, the crossing point corresponds to the isokinetic temperature for the etching process. This means that all of the silicon plans would be eroded at the same rate if the etch process could be carried out at this isokinetic temperature. The data on anisotropic etching of silicon in alkaline solutions, presented by Seidel et al.,[16] were obtained at the range 20−115 °C, which is quite far from the calculated compensation temperature (~355 °C). The extrapolated lines in the Arrhenius diagram presented in Figure 7 show a very defined concurrence, which, as pointed out by Krug,[11] is an indication that the linear compensation is due to chemical factors rather than due to spurious propagation of measurement errors.

These evidences suggest a strong relationship between the anisotropy and the compensation effect for these reactions involving silicon. The isokinetic temperature in the direct
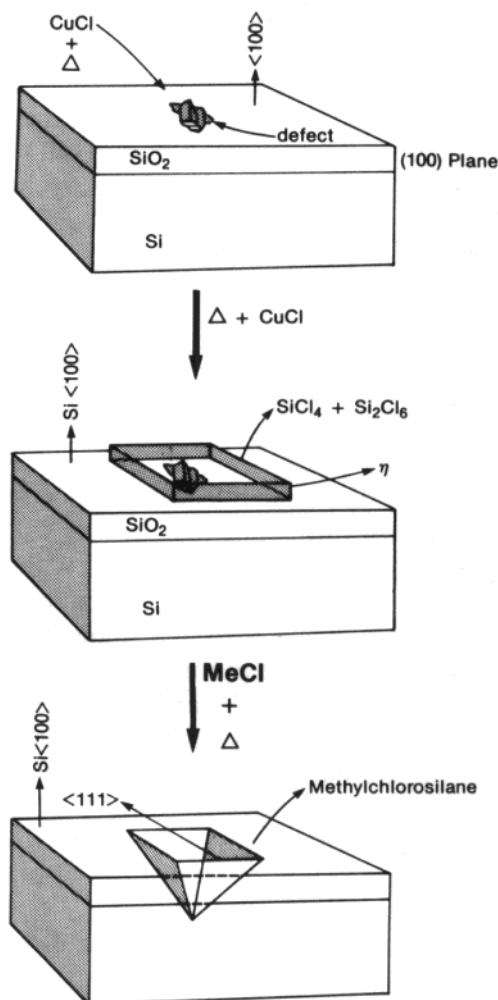
Figure 5. Anisotropic active phase formation (extracted from ref 2 with permission of Academic Press, Inc).
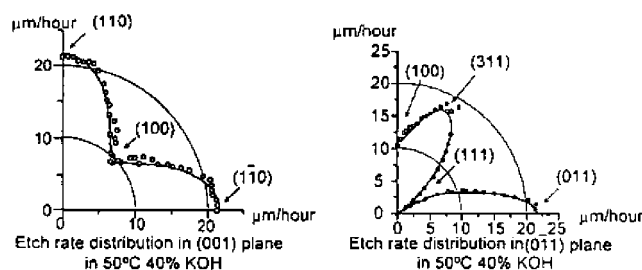

Figure 6. Polar graph of silicon etching by KOH (reprinted from ref 20 with permission from Elsevier Science).

synthesis and that calculated for anisotropic etching are essentially the same, which could indicate that some similar elementary steps would be involved in one and the other reaction and possibly the isokinetic temperature would be related to some property of the silicon crystal. More recently, Larsson and Lieske[12] have applied the "selective energy transfer model" to the direct synthesis of DMDCS. This model had been proposed earlier for heterogeneous reactions,[5,13] wherein the isokinetic temperature was shown to have a direct correspondence with surface vibrational energy modes. According to this model, at the isokinetic temperature the efficiency of ressonance energy transfer for the reacting species is maximized, and the dynamics of the energy transfer to and from molecular vibrations would be the underlying reason for the isokinetic effect. The frequencies of the rocking vibration of the Si−CH$_3$ and Si−OH bonds
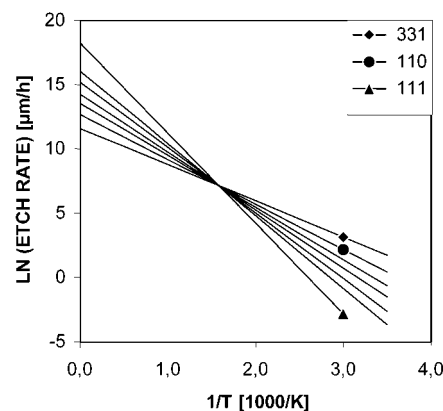
Figure 7. Arrhenius diagram for lateral etching rates in ⟨100⟩ directions of the silicon crystal from the data taken from ref 16.
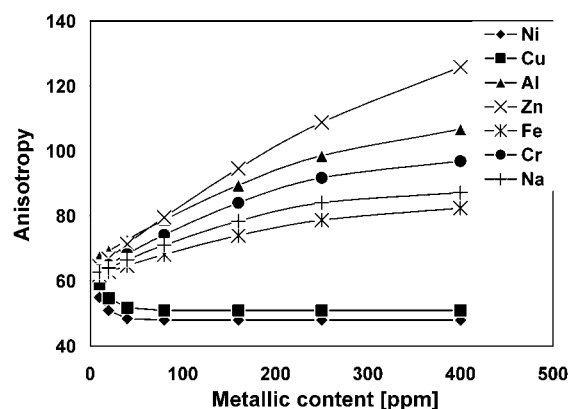
Figure 8. Effect of metallic impurities on the anisotropy of the etching of crystalline silicon by KOH solution from the data presented by Hein et al.[10]

are rather similar, and so are the isokinetic temperatures of direct synthesis and alkaline etching.

From the analogy of the phenomena in the two reactions, a more fundamental explanation for the compensation effect observed in these processes may be suggested. As pointed out earlier, among the possible explanations given by Galwey,[9] the kinetic compensation effect in these silicon reactions seems to be due to the existence of more than one active surface and, more specifically, due to the existence of more than one active crystallographic solid surface, possibly with different energy levels and availabilities. This is fairly consistent with the theoretical framework presented by Conner and Schwartz[4] based on the existence of multiple reaction paths and the interdependence of the energetic and probabilistic factors of the reactive states of the system.

The Promoters Role and Compensation Effect

In another work in the microelectronics area, Hein et al.[10] showed that besides the impurities normally present in the silicon, called dopants,[17] impurities present in the etching alkaline solutions may affect the anisotropic erosion of silicon. Figure 8 shows the effect of different metallic impurities in the aqueous KOH solution on the anisotropy, which was defined by those authors as the relationship between the erosion rates of the {100} and {111} planes. It is interesting to compare the performance of some elements in both the etching and the direct synthesis processes. For instance, Cu and Ni, recognized as the best catalysts for the direct synthesis of DMDCS, reduce the anisotropy, while Zn and Al, recognized among the best promoters or cocatalysts of the direct synthesis of DMDCS,

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increase the anisotropic character of the etching process. The addition of metallic impurities affects both the speeds and the angle of erosion of the planes during silicon etching.

From the comparison between these results and the known effects of these elements on the direct reaction with MeCl catalyzed by Cu_3Si, we can suggest that these impurities would act as promoters on the silicon etching by KOH in the analogous way that they act in the direct synthesis. Following that parallel, we can also suppose that the promoters act in similar way in the anisotropic character both in the alkaline etching and in the direct synthesis of DMDCS. For the direct synthesis process, this anisotropic behavior depends on the nature of the promoter as well as on the way the copper was added, influencing also the habit of the Cu_3Si phase.[7] The contact angle between the crystals of Cu_3Si and the silicon surface can be made different depending on the promoter type and content, resulting in different reactivities and selectivities.

Besides the reaction rate, the selectivity also seems to be correlated with the anisotropy of the reaction. Falconer and Yilmaz[6] verified that the selectivity on the (100) and (111) planes are different at different reaction times, and the reaction in the [111] direction was more selective for the formation of DMDCS than in the [100] direction. Then, if Zn accelerates the reaction and increases the selectivity to DMDCS, it is possible to infer that the effect of Zn is to accelerate the erosion of some specific (100), (110), and (331) planes, which have different selectivities and activities. However, to know which plan would be involved, more specific experiments would be necessary.

Concluding Remarks

The available information in the literature on the occurrence of the compensation effect, anisotropy, and promoters' influence on the process of direct synthesis of DMDCS and on the processes of etching of silicon by alkaline solutions was discussed and compared. These comparisons show that the compensation effect and the anisotropy occurrence are related in some way in these processes, strongly suggesting that the fundamental or mechanistic aspects capable of explaining these effects in one reaction can be used similarly to explain the occurrences in the other reaction. Additional evidences for this analogy are the observations regarding the effect of metallic impurities.

Among the possible explanations put forwarded by Galwey,[9] the presented discussions indicated that the anisotropic character of these reactions seems to be responsible for the existence of compensation effect, which means that more than one active surface are present, each one related to a crystallographic plan.

Although no specific set of experiments to prove such ideas has been made by now, it is believed that the compensation effect in the direct synthesis is caused by the change in the ratio between the rates of the different planes being eroded. Therefore, the KCE would be strongly linked to the anisotropic character of the reaction. It is possible that two or more types of active sites exist, with different energies associated with different angles of erosion, which depend on the charge density of the silicon surface, which can be altered by the presence of metallic promoters or impurities.

Even though these claims have arisen from a discussion on two specific silicon reactions, they would infer interesting extensions, because these ideas can be investigated to extend this analogy to other similar reactions in which isokinetic effect, anisotropy or both are observed.

Important and sound speculative consequences for other areas of chemistry and physics may arise from the concepts here discussed, such as the following:

(a) Experimental observation of the compensation effect in thermal decompositions of solids, with or without melting, could be explained by differences in preparation of the samples submitted to thermal analysis, which would cause exposition of a different amount of crystalline faces with distinct anisotropic behavior.

(b) During crystallization, different faces of the crystal may grow with different rates, resulting in an anisotropic growth. The possibility of the presence of compensation effect in crystal growth should be investigated, as long as the change in crystallization temperature leads to changes in crystalline habits.

(c) Several structure-sensitive catalytic reactions, such as the oxidation of alcohols on MoO_3 catalysts,[18,19] may exhibit compensation effect for catalysts with different fractions of exposed crystalline faces. Presumably, the reported compensation effect of many catalytic reactions can be ascribed to the anisotropy of the different faces of the existing crystals in the catalyst (different activity, availability or both of each crystalline face).

(d) Following these ideas, it can be also expected that a homogeneous catalyst that was supported on a crystalline material may exhibit compensation effect, because the electronic interaction between the catalyst and the different exposed faces of the support can be distinct. Future investigations on the site differentiation after supporting, for example, in metallocene catalysis for olefin polymerization, should consider such issues.

Finally, the proposed ideas on the existence of a correlation between compensation effect and anisotropy may motivate some revision of the published literature along with a proposition of new specific experiments to get further insight on these interesting phenomena.

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