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LETTER TO THE EDITOR

Comments on A. Corma *et al.*, "On the Compensation Effect in Acid–Base Catalyzed Reactions on Zeolites"

In many reports of kinetic studies it is stated that a group of rate processes exhibits a compensation effect. It is generally accepted that a compensation effect arises when a linear relation between ln A and E (the logarithm of the preexponential factor and the activation energy) is detected for a single reaction taking place over different catalysts or different reactions over one catalyst. For a perfect linear relation between ln A and E, the representation of the reaction rate constant in an Arrhenius plot determines a series of straight lines which intersect in a single point. However, it is not clear what we should understand when we talk about the occurrence of a compensation effect, because an apparent linear relation between ln A and E does not guarantee the existence of isokinetic parameters. Indeed, small deviations from a straight line in a ln A vs E plot are usually reflected as isokinetic parameters with considerable dispersion.

If all of the experiment points lie on a straight line in a ln A vs E plot, then there will be a single intersection in an Arrhenius plot. For this case only, we can calculate the isokinetic parameters with no error. It can be shown that an indetermination $\Delta \ln A$ in the preexponential factors of two related reactions reflects in the intersection of their Arrhenius plots as (1)

$$\Delta \ln k = 2\,\Delta \ln A\,(E_1 + E_2)/|E_1 - E_2|, \qquad [1]$$

$$\Delta(1/T) = 4R\,\Delta \ln A/|E_1 - E_2|. \qquad [2]$$

The error in the determination of isokinetic parameters depends on the scatter in ln A and the difference between activation energies. We will see a very small error in the ln A vs E plot might originate a large uncertainty in the isokinetic parameters. For example, for $\Delta \ln A = 1$ and $E_1 - E_2 = 10$ kJ/mol, the indetermination in the isokinetic temperature is about 300 K.

Great caution must be exercised before establishing the existence of isokinetic parameters, as we will see by examining some of the data presented by Corma *et al.* (2). For example, in the transalkylation reaction of *meta*-xylene over different Y zeolites, the linear regression coefficient is about 0.925. Figure 1, however, shows that isokinetic parameters are not determined; i.e., a single point of concurrence cannot be found.

The compensation effect would appear, at first sight, to be unchallenged when analyzing the reactions on a given catalyst presented by Corma *et al.* For the sample HYD-1, the linear regression coefficient is 0.9989, and then one would expect that the isokinetic parameters should be undoubtedly determined. Figure 2, however, shows three points of concurrence spread over 500 K. This case is particularly interesting, since this large dispersion is a direct consequence of the small difference in activation energy between two of the reactions (see Eq. [2]). From all the studied zeolite-catalyzed reactions, the isokinetic parameters are clearly determined only for reactions on sample HYD-4. In this case, the three points of concurrence are in a range of only 3 K. This is due to the extremely high linear regression coefficient in the ln A vs E plot (0.9999) and the absence of reactions with similar activation energies. These considerations do not invalidate the conclusions in the paper published by Corma *et al.*, but it must be pointed out that their parameter d does not represent the isokinetic temperature.

The criterion used by Corma *et al.* to establish the existence of a compensation effect, that is, the linear relation between ln A and the activation energy, has been

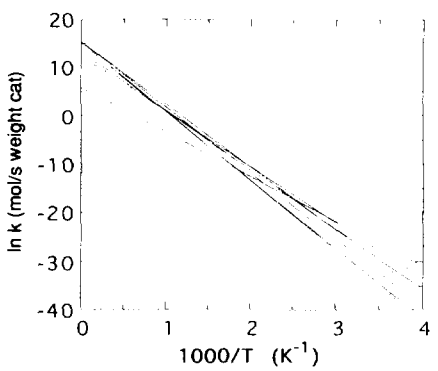

FIG. 1. Arrhenius plot for the transalkylation of *meta*-xylene over Y zeolites showing the nonexistence of an isokinetic temperature (from the data in Ref. (2)).

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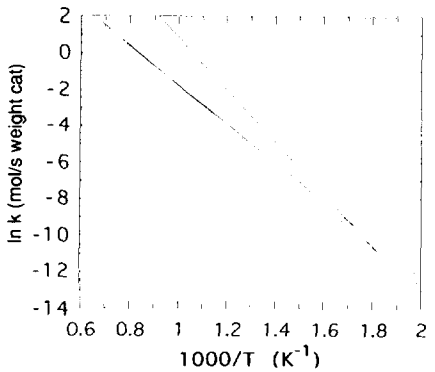

FIG. 2. Arrhenius plot for the three reactions over HYD-1 studied by Corma *et al.* in Ref. (2).

considered by Agrawal to lead to a false compensation effect (3, 4). According to Agrawal, a true compensation effect can only be established when a single point of concurrence appears in a ln k vs $1/T$ plot. Although we think that it is a matter of what we understand by a compensation effect, we want to stress that isokinetic parameters cannot be directly inferred from a ln A vs E plot.

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