The Compensation Effect for Some Hydrodesulfurization Catalysts and a Simple Model for Catalysis

In a recent paper (*1*) a model for catalysis has been applied to calculate the isocatalytic temperature (θ) of catalytic reactions. θ relates to the slope of the linear relation between $\ln A$ and E_{exp}. It is this latter relation [1] that describes the "compensation effect" for a family of similar catalysts (*2*):

$$\ln A = bE_{exp} + c \qquad [1]$$

$$\theta = (bR)^{-1}. \qquad [2]$$

In these relations A is the preexponential factor and E_{exp} is the experimental (apparent) energy of activation in the Arrhenius formula:

$$\ln k = \ln A - E_{exp}/RT. \qquad [3]$$

c of Eq. [1] is a constant. If Eq. [1] holds exactly it also holds that [3] transforms to

$$\ln k = \ln Z + E/R \, (1/\theta - 1/T). \qquad [4]$$

Hence, if $T = \theta$, $\ln k = \ln Z$ (= constant) for all the catalysts in the family of interest. Therefore θ is named the isocatalytic temperature. Incidentally, it follows that c of Eq. [1] is equal to $\ln Z$ of Eq. [4].

The present note is intended to exemplify the possible applicability of the model to a catalytic reaction other than that used in the first paper (*1*), viz., to hydrodesulfurization (HDS).

For some HDS catalysts it has been shown by Mitchell and co-workers (*3*) that Eq. [1] holds quite well. The specific reaction studied was the hydrogenation of thiophene. This observation has recently been discussed by Bond (*4*). The model of catalysis alluded to above treats the catalytic effect in terms of a selective transfer of

energy from the catalyst into that very vibrational mode of the reacting molecule which will cause the molecule to react (*5*). Suppose the energy is taken from a set of vibrators, belonging to the catalyst and having the frequency ω, and suppose that the frequency of the critical vibration mode of the molecule is ν. The point of the argument is that when ω is close to ν, a state of resonance will exist, causing an effective energy transfer. The consequence of this model has been treated in some detail in Ref. (*1*). By applying the classical mechanics of a forced, damped (harmonic) oscillator it was shown (with ν and ω expressed as wavenumbers/cm^{-1}) that

$$\theta = \frac{Nhc}{R} \frac{\nu^2 - \omega^2}{\omega} \cdot \frac{1}{\pm\pi/2 - \text{arc tg} \dfrac{\nu\omega}{2(\nu^2 - \omega^2)}} \qquad [5]$$

or

$$\theta = \frac{Nhc}{R} \frac{\nu}{2} \qquad [6]$$

if $\nu = \omega$.

The damping of the classical oscillator is considered to correspond to the dissipation of energy from the partially activated molecule to the solid phase on which it is adsorbed. In order to apply Eqs. [5] and [6] to the material presented by Mitchell and Scott (*3*) (and represented in Fig. 1) one must try to deduce what molecular vibration of the thiophene molecule is of critical importance in bringing the molecule to such an activated state that it reacts. As the main *initial* reaction products seem to be H_2S
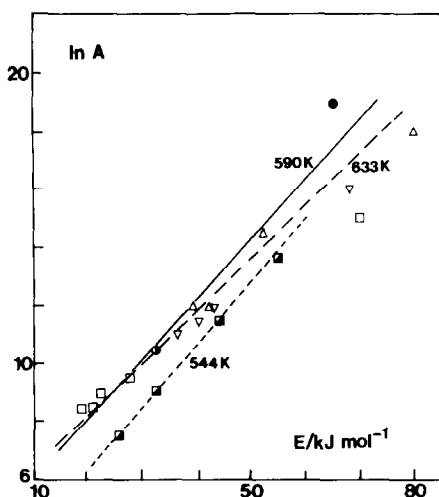
568

FIG. 1. The logarithm of the preexponential factor versus the experimental energy of activation for a series of HDS catalysts. Data and notation from Mitchell and Scott (3). The full line is the one proposed by Mitchell and Scott. The dashed lines are those given by Bond (4) from somewhat more selected material.

and 1,3-butadiene, 1-butene, and cis-2-butene (6–9), the stretching mode of the aromatic ring that most strongly affects the C–S bonds seems to be the most reasonable choice. According to Loisel and Lorenzelli (10) this vibration for the free molecule, ν_3, is found at 834 cm^{-1} (solid as well as liquid state).

In want of good information on the shift of this frequency upon coordination (adsorption) of thiophene to a metal atom we have chosen to use the value 834 cm^{-1} for ν to construct the function $\theta = \theta(\omega)$ from Eq. [5]. The graph is given in Fig. 2.

One might compare the result with the data given by Mitchell and Bond, respectively ($\theta = 590$ K (3) and $\theta = 633$ and 544 K (4)). The mean value of these numbers is $\theta = 590 \pm 35$ K. The minimum of the graph of Fig. 2, calculated from Eq. [6], is 596 K. The agreement is as good as can be expected for a simple theory like the present one. There are, indeed, only a few other quantitative treatments of the compensation effect (11, 12), although there is a

plethora of qualitative discussions. The minimum of the curve of Fig. 2 is actually the most relevant datum of comparison. It is obvious that any improvement in a catalyst system, whether it is made by trial and error or systematically by adding certain active ingredients as promoters, should aim at achieving as large a slope for Eq. [1] as possible. This means as small a θ as possible. Lacking detailed information on the infrared spectra of the catalyst systems used in the original investigations (3), we must approach the question of the nature of the vibrator ω in a rather general way.

Three subquestions can be formulated:

Is the ω-vibrator only delivering energy?

Is the ω-vibrator delivering energy as well as taking part in the atom transfer of the chemical reaction?

Is the range of interaction so large that the support can also supply energy ("strong support interaction")?

Let us now consider a conventional HDS system of sulfided (Co)-Mo/Al$_2$O$_3$ + H$_2$. In such a system one can identify some candidates for the role of the vibrator ω.

(1) The Mo–O stretching vibrations of MoO$_3$ remaining after the sulfidation might be a "long-range" source. They are given, e.g., at 995, 880, and 820 cm^{-1} (13), 994,
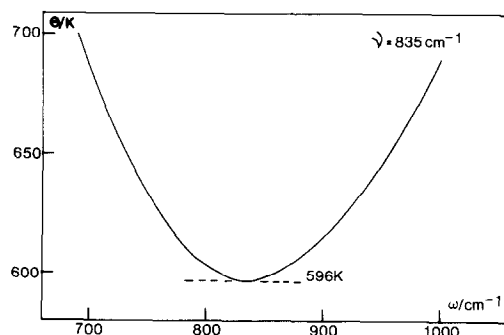

FIG. 2. The isocatalytic temperature calculated from Eq. [5] as a function of the catalyst frequency ω. The value for ν has been chosen as 834 cm^{-1}, corresponding to the free, solid thiophene C–S stretching vibration.

864, and 819 cm^{-1} (14), or 992, 868, and 822 cm^{-1} (15).

(2) The support Al_2O_3 might also be a "long-range" supply of energy. It will show vibrations at many different frequencies depending on the physical state of the oxide. For example, a layer of aluminium oxide freshly formed on aluminium has been shown recently to have EELS peaks at 845 and 880 cm^{-1} (16).

(3) The hydrogen of the system is probably present in the form of S–H groups. There are recent indications (17) that the MoS_xH_y system thus formed vibrates at 662 cm^{-1} with a combination mode at 847 cm^{-1}. The intensity of the latter vibration is increasing rapidly with hydrogen sorption (17) and might be dominating at the pressure used in the HDS treatment.

Any one of these types of vibrator might be appropriate as far as the application of Eq. [5] is concerned. Obviously the catalytic efficiency is critically dependent on the precise correspondence between the vibrators ν and ω (within the model discussed). Indeed, the much-discussed influence of Co on MoS_2/Al_2O_3 systems for HDS catalysis *might* be due to the fine-tuning of the C–S vibration of thiophene so that it will better coincide with the vibrations of the catalyst system. Conversely, one can envisage the role of Co to be one affecting the frequencies of the catalyst system so that they will better coincide with that of the thiophene vibration. In order to avoid misunderstandings, it must be firmly assured that the present model is not in conflict with the concept that the transition metal atoms of, e.g., $Mo(Co)S_2$ should be the active sites of coordination of thiophene. Conversely, the process of coordination must affect the C–S bond strength (and thus ν_{CS}).

The present treatment is beset by the following difficulty, namely the use of the experimental energy of activation to express the law of compensation. This E_{exp} is often called the apparent energy of activa-

tion. It is not expected to be directly related to the dynamics of the process. Instead the true energy of activation, E, is the proper choice. This is too complicated a problem to be treated in a short note, but it will be further discussed in a future paper (18). It will be shown that under first-order conditions $E_{exp} \approx E$. The application of Eq. [5] should not be attempted for systems where the relation $E \approx E_{exp}$ is not fulfilled.

REFERENCES

1. Larsson, R., *Chem. Scr.*, in press.
2. Schwab, G. M., *Z. Phys. Chem. B* **5**, 405 (1929).
3. Mitchell, P. C. H., and Scott, C. E., *Bull. Soc. Chim. Belg.* **93**, 619 (1984).
4. Bond, C. G., *Z. Phys. Chem. N.F.* **144**, 21 (1985).
5. Larsson, R., *Chem. Scr.* **12**, 78 (1977).
6. Owens, P. J., and Amberg, C. H., *Adv. Chem. Ser.* **33**, 182 (1961).
7. Desikan, P., and Amberg, C. H., *Canad. J. Chem.* **42**, 843 (1964).
8. Kolboe, S., and Amberg, C. H., *Canad. J. Chem.* **44**, 2623 (1966).
9. Gates, B. C., Katzer, J. R., and Schuit, G. C. A., "Chemistry of Catalytic Processes." McGraw-Hill, New York, 1979.
10. Loisel, J., and Lorenzelli, V., *Spectrochim. Acta A* **23**, 2903 (1967).
11. Conner, W. C., *J. Catal.* **78**, 238 (1982).
12. McCoy, B. J., *J. Chem. Phys.* **80**, 3629 (1984).
13. Bielanski, A., Dyrek, K., and Kozłowska-Rog, A., *Bull. Acad. Pol. Sci. Chim.* **20**, 1055 (1972).
14. Jonson, B., Larsson, R., and Rebenstorf, B., *J. Catal.* **102**, 29 (1986).
15. Barraclaugh, C. G., and Stals, J., *Aust. J. Chem.* **19**, 741 (1966).
16. Crowell, J. G., Chen, J. G., and Yates, J. T., Jr., *Surf. Sci.* **165**, 37 (1986).
17. Wright, C. J., Sampson, C., Fraser, D., Moyes, R. B., Wells, P. B., and Riekel, C., *J. Chem. Soc. Faraday Trans. 1* **76**, 1585 (1980).
18. Larsson, R., *Chem. Scr.*, in press.

RAGNAR LARSSON

Inorganic Chemistry 1, Chemical Center
University of Lund
Box 124, S-221 00 Lund, Sweden