On the catalytic C-H activation of some silicon dioxide overlayers on thin metal film systems—an observation on the isokinetic effect

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Kinetic data on the exchange reaction betwee hexane and deuterium have recently been reported by Maier and coworkers [1]. The reaction was catalysed by a series of platinum or rhodium systems, some of which had the property that the upper surface was shielded by a silica overlayer. The data are reinterpreted to indicate an isokinetic temperature of 580 K. This observation indicates that all the catalysts behave in a similar manner, which means that the exchange reaction does not require a free metal surface.

Keywords: Isokinetic effect; hexane H/D exchange; selective energy transfer; epitaxially produced catalysts

1. Introduction

In an interesting paper, “Catalytic C-H activation on silicon dioxide overlayer and epitaxial platinum thin film catalysts: a comparison”, Maier et al. [1] study–inter alia–the H-D exchange of hexane over a number of epitaxially produced systems. The composition of the catalyst systems are described very schematically in fig. 1.

The interpretation that the authors present is that hydrogen (D_2) is diffusing through the SiO_2 overlayer, undergoes a dissociative adsorption on the transition metal surface, desorbs as D atoms which rediffuse through the SiO_2 overlayer and react with the hydrocarbon. In short, at steady state conditions, there is a supply of reactive D atoms at the SiO_2 surface.

One of the results that motivates this note is the observation that the exchange rate, expressed in [1] as turnover frequency N_f (reacted molecules cm^{-2} sec^{-1}), is almost as high for systems covered with SiO_2 layers as it is for those systems that expose a bare platinum surface. This is clearly borne out by

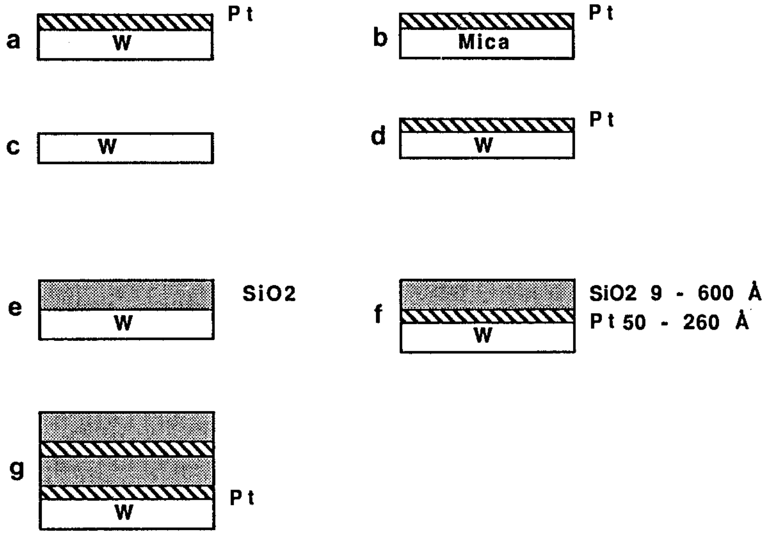

Fig. 1. Different catalysts prepared by Maier et al. [1] in schematic presentation. Items c and e are not catalytically active (as no platinum being present). Item f was also prepared with Rh instead of Pt.

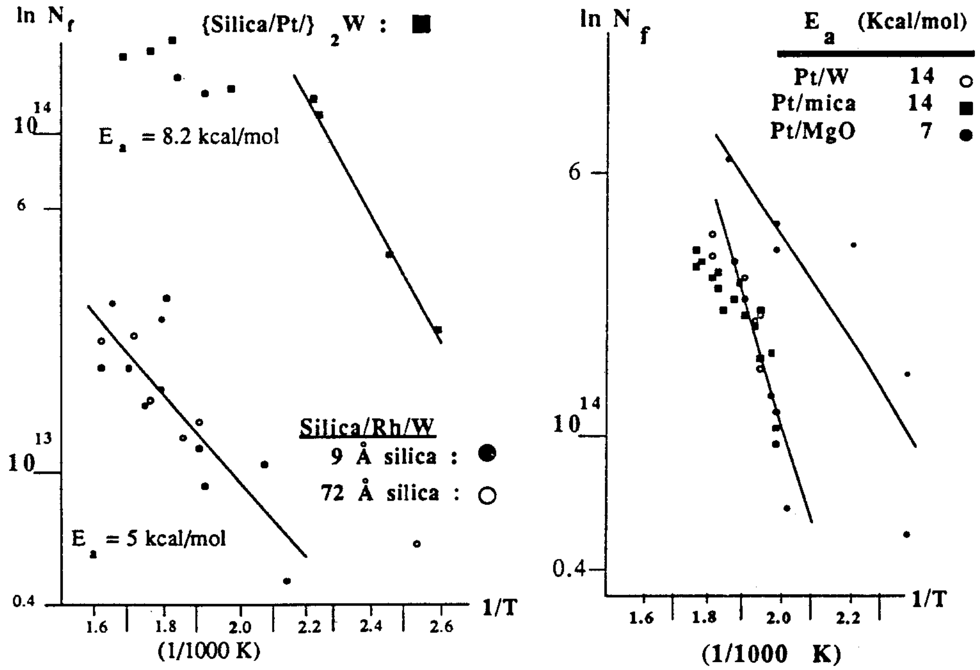

Fig. 2. The data of Maier et al. [1] on the H/D exchange of hexane reproduced from the fig. 10 of their report [1]. The right part represents epitaxial platinum films; the left part represents silica overlayer films.

fig. 2 which is fig. 10 of [1] reproduced here in extenso. This figure presents exchange data for hexane and we will only deal with that part of the paper [1] in this note.

What aroused our interest in the first place is the following circumstance: If the results are not represented as shown, i.e. in two separate graphs, but all data are presented together using one and the same ordinate axis, the lines would appear as in fig. 3. The most striking effect is that the three upper lines intersect in one common point. This is an example of the isokinetic effect (or compensation effect) described, e.g., by Cremer [2]. The coordinate of the point of intersection represents (the inverse of) the isocatalytic temperature that we will denote by Θ in this context.

In the present case one reads from fig. 3:

$$1/\Theta = 1.72 \cdot 10^{-3}\ \mathrm{K}^{-1}$$

i.e., $\Theta = 580$ K.

Before proceeding with any comments on this, it must be noted (fig. 3) that we have taken the liberty to redraw the Arrhenius line(s) for the systems silica/Rh/W. This might be considered a little daring, regarding the high scatter of points in the measurements. This scatter is, however, not worse than that of the points that refer to the uppermost line (Pt/MgO). Of course, one must disregard those points that are found for the high rate, high temperature part of the lines where diffusion control of the rate may occur.

Anyway, the interesting point is that these two new lines intersect at almost the same $1/T$ value as the upper three lines do.

2. The isokinetic or compensation effect

Some words must be said at this stage on the development of theories for the isokinetic effect. This effect was discovered–in the field of catalysis at least–by Constable [3] who found that the two parameters A and E of the Arrhenius equation

$$\ln k = \ln A - E/RT \tag{1}$$

were linearly related to each other:

$$\ln A = \ln Z + bE. \tag{2}$$

This effect has been treated by, among others, Schwab [4], Cremer [2,5], Ruetschi [6], Galwey [7], Conner, Jr. [8] and Kreuzer and March [9]. Interesting observations are made by Bond [10] on the possibility of a set of parallel "compensation lines", by Linert [11] and by Linert and Jameson [12]. Linert [12] stresses for one thing the necessity of applying good statistical criteria since A and E are coupled together in both eqs. (1) and (2). The best criterion of an

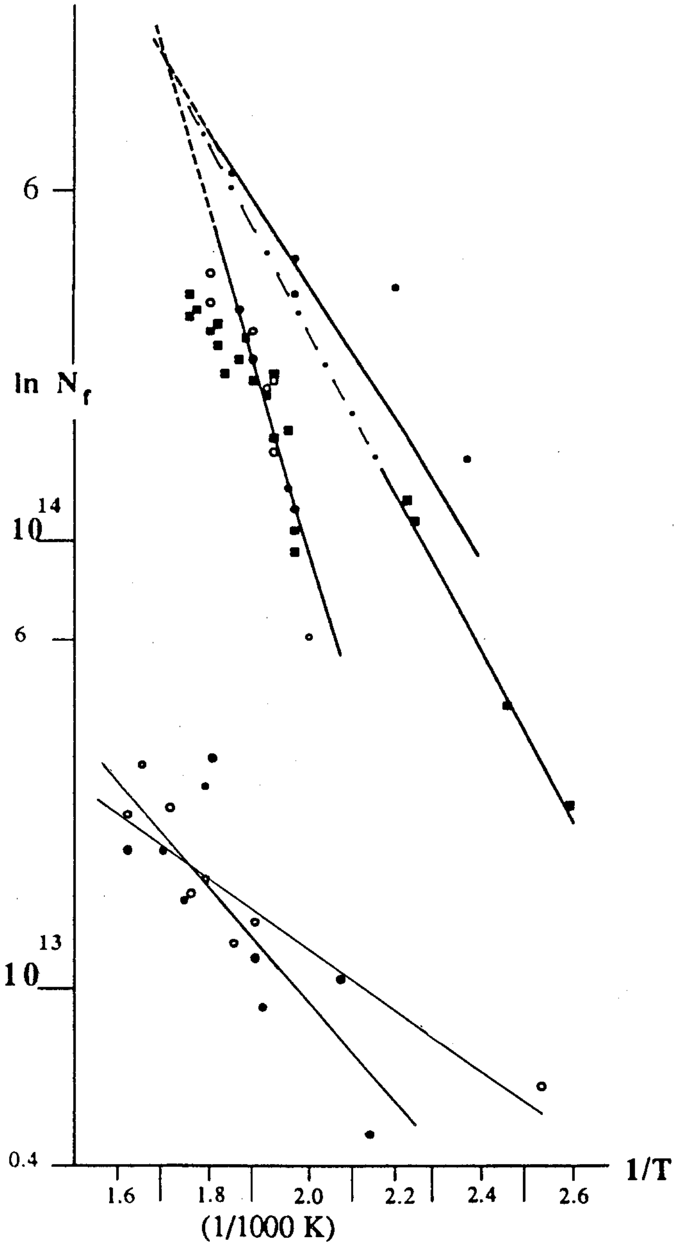

Fig. 3. The data of fig. 2 redrawn to the same ordinate axis. The upper three lines are those drawn by Maier et al. [1]; the lower two have been redrawn by the present author.

isokinetic effect is the intersection of a series of Arrhenius lines in one and the same point (as exemplified here). Furthermore, Linert stresses the fact that isokinetic effects can be observed–with advantage–also for homogeneous systems. This observation immediately reduces the value of those explanations that use concepts from heterogeneous catalysis such as active site distribution [4,5], adsorption energy etc. It seems that the only requirement that must be fulfilled is that of a rate process in a condensed phase. The paper of Kreuzer and March [9] strongly indicates how widely differing bases of explanation have been evoked.

The recent state of knowledge has been summarized by Kral [13].

3. A model for the isokinetic effect

The isokinetic effect has also been treated by the present author [14–16] in terms of a simple but more general model in which the reactant is regarded as a classical, damped oscillator (of the frequency ν) coupled with the surrounding (catalyst, solvent, physisorbed reactants, etc; of a characteristic frequency ω). In the case when $\omega = \nu$ a complete resonance takes place, facilitating the transfer of energy from the surrounding to the reactant. In this way the input of energy more than compensates the loss by various dissipation paths. The dissipation of energy from the excited states corresponds to the damping force in the classical treatment.

The result of this model is a relation between the rate constant, ν and ω, that in its turn gives an expression, eq. (3), for the relation between Θ and ω for every given value of ν.

$$\Theta = \text{Nhc}\ R^{-1}(\nu^2-\omega^2)\omega^{-1}\left\{\pm\pi/2 - \text{arctg}\left(0.5\ \nu\omega\left(\nu^2-\omega^2\right)^{-1}\right)\right\}^{-1}. \quad (3)$$

The details of this model are given in [16]. In fig. 4 we illustrate this relation for a specific value of ν, viz., $\nu = 722\ \text{cm}^{-1}$. The reason for this choice will be obvious from the following discussion. One observes from this figure that the Θ function has a rather flat minimum around $\nu = \omega$; ±10% variation of ω results in only 4% variation of Θ.

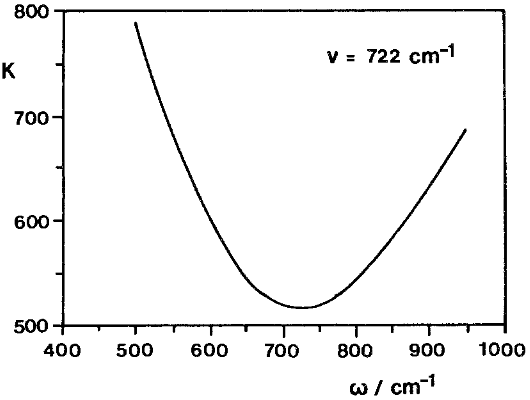

Fig. 4. A graphical representation of eq. (3) for the specific value of $\nu = 722\ \text{cm}^{-1}$.

4. Discussion of the reaction

In order to use the formula presented above one must make some assumption on the values of ν and of ω. It was suggested [14–16] that ν is that frequency that corresponds to that vibrational mode that will distort the reacting molecule towards the structure of the activated state. Hence one must know the reaction mechanism or make some qualified guess about it. To do this in the present case one can recall that it is strongly pointed out by Maier et al. [1] that for the reaction under investigation:

> "H/D exchange is *not* sensitive to the chemical nature of the surface"

and

> "Perhaps a surface may be the only requirement for the observed isotope distributions".

It thus appears that the presence of the Pt (or Rh) surface is not directly important for the reaction mechanism.

This conclusion is of great importance and allows us to depict the probable reaction mechanism as in fig. 5. The hydrocarbon molecule is assumed to be physisorbed on the surface and undergoing a Walden inversion type of reaction with the deuterium atom available at the surface as said above. The activated state must then take the structure of a trigonal bipyramid. The deformation of the reactant that approaches this structure must be the rocking mode of the C–H bonds. By such a rocking there is made available space for attack at the central carbon atom. One can therefore conclude that the CH_2 rocking mode of hexane at 722 cm^{-1} [17] should be used for ν in our equation. This mode is characteristic for n-alkanes in general, the absorption intensity of it building up with the number of CH_2 groups in the alkane [17]. Hence all the four CH_2 groups in hexane have the same rocking frequency and from the point of view presented here one should expect equal probability of attack on any one of the four CH_2 groups. As the corresponding rocking mode of the terminal CH_3 groups also contributes to the vibration absorbing at about 722 cm^{-1} [18], one should expect an almost equal, only slightly lower, probability of reaction of these groups. This is in agreement with the finding of Maier et al. [1] that total deuteriation takes place. Especially noteworthy is the indication that eight H atoms seem to be a little more rapidly exchanged than the six remaining ones

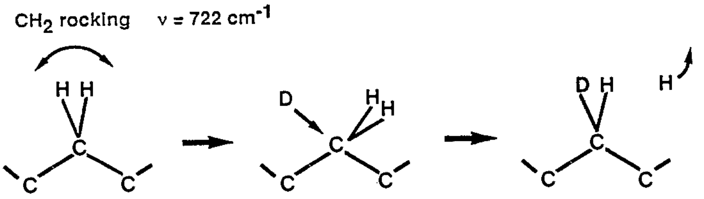

Fig. 5. Schematic model of the substitution reaction.

(fig. 3 a [1]). As the observed Θ (fig. 3 of the present paper) is 580 K one notes from fig. 5 that the input energy must come from a vibration of $\omega = 620$ or 850 cm^{-1}. As it is difficult to find a *common* source corresponding to any of these two frequencies in the varied materials that were studied [1], the following interpretation is proposed:

The energy represented by the ω vibration originates from a vibration mode of physisorbed hexane molecules. The C–C stretching seems a suitable source. There is a rather good agreement between the wave number 850 cm^{-1} needed and the wavenumber of the lowest of the C–C stretching modes of hexane [18]: 826 and 823 cm^{-1} for the TGT conformer, 886 cm^{-1} for the TTT one and 869 cm^{-1} for the GTT conformer (T = trans, G = gauche). Remembering the large uncertainties of the original data and thus of the value of Θ, we conclude that it is this vibration mode that makes possible the appearance of an isokinetic effect in the H/D exchange studied by Maier et al. [1]. One may note that the transfer of energy from the C–C stretching to the CH_2 deformation mode represents *one* of the ways in which energy is dissipated from the first-mentioned, thermally excited, vibration mode in the same way as the dissipation of energy from the latter, reactive, mode is the main cause of the formalism of the model (cf. paragraph 3 and ref. [16]).

The question why the activity of the rhodium based catalysts is lower than that of the platinum based ones is not answered by this analysis. Likewise it does not present any explanation of why the $(SiO_2/Pt)_2W$ system belongs to the same class as the exposed Pt systems, while the $SiO_2/Rh/W$ systems form a separate class of lower activity. Probably there is a subtle balance of geometrical factors that determines the precise outcome of reactivity.

An interesting corollary to our finding appears, however. As all the catalysts, whether they are covered by silica or not, are correlated by having the same isokinetic temperature, we have concluded that the mechanism is the same for all systems. Thus it follows that the H/D exchange reaction (of hexane) on metal surfaces does not require a metal carbon bond to be formed, only the availability of free deuterium atoms that can engage in a nucleophilic attack.

5. On possible ways of experimental verification

Obviously one should like to construct experiments in which one factor could be varied at will and from which variation one could foresee the outcome of the experiment. Such an experiment would be one of crucial importance. Suppose that we performed the experiment with totally deuterated hexane, C_6D_{14}, and normal hydrogen in the gas phase. The wave number of the rocking vibration would be approximately $722/1.41 = 510$ cm^{-1}. As the C–C stretching will not be appreciably changed by the perdeuteration, ν_{C-C} would still be close to 830 cm^{-1}. Hence the possibility of resonance energy transfer would be non existent and the isokinetic temperature very undefined. If, however, some other source of energy common for all the catalyst systems can be traced with vibration frequency close to 510 cm^{-1}, a new isokinetic temperature will be observed, $\Theta = 370$ K. One such possible energy source, analogous to the C–C stretch used above, is the C–C–C bending mode at 533 cm^{-1} [18].

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