JOURNAL OF CATALYSIS **168,** 532–537 (1997)
ARTICLE NO. CA971657

NOTE

On the Isokinetic Effect of Neopentane Hydrogenolysis over Metal Catalysts

The hydrogenolysis of neopentane is a classics in catalysis; e.g., a recent compilation by Somorjai (1) of kinetic results of this reaction contains a long list of metals as catalysts and a variety of supports for the metal particles used as catalysts. During later years the detailed kinetics of this reaction has been followed, inter alia, over Pd catalysts, notably supported on zeolites and on silica gel (2–7). It was recently found (4) that the parameters of the Arrhenius treatment of the results indicated a compensation effect.

It is commonly agreed that the phenomenon of "compensation effect" is poorly understood. So much more important it is to investigate simple reactions in order to try to discover the essential features of this phenomenon. Simple reactions are chosen as the many steps of more complicated ones might obscure the simple pattern and the simple rules sought for.

The aim of the present paper is to apply a model of selective energy transfer (8) that has been shown to work well for small molecules and that has a certain generality. This model is based on the assumption that the activation of the molecule up to the activated state is described by the excitation of that vibrational mode of the molecule that perturbs the structure of the molecule towards that of the activated state.

The data were presented (2–7) as turnover numbers, N (molecules of reacted neopentane per surface Pd atom per second). As the pressure of the reactants were kept constant in all the experiments (2–7), i.e., $p_{\mathrm{NP}} = 6$ Torr and $p_{\mathrm{H}_2} = 60$ Torr, and the temperature range was rather limited (ΔT was typically 40 K) it is possible to use the experimental turnover frequencies as a measure of the true rate constant. Inherent in this approach is the assumption that the reacting neopentane is weakly adsorbed.

$$d \ln N/d(1/T) = d \ln k/d(1/T), \qquad [1]$$

where the rate constant is denoted k. Any isokinetic effect that relates to N also relates to k.

If an isokinetic effect is observed it holds that

$$\ln A = bE_a + c, \qquad [2]$$

where A and E_a are the conventional Arrhenius parameters. It is well known (9–10) that this equation can define an isokinetic temperature, T_{iso}, as it can be shown that

$$T_{\mathrm{iso}} = 1/bR, \qquad [3]$$

where R is 1.987 cal/mol $K = 8.31$ kJ/mol.

It is also well known that Eqs. [2] and [3] transform into

$$\ln k = \ln Z + E_a/\, R(1/T_{\mathrm{iso}} - 1/T). \qquad [4]$$

This means that at $T = T_{\mathrm{iso}}$, $\ln k$ is constant and equal to $\ln Z$ for any of the (very similar) systems concerned. It has been strongly pointed out by Exner (11) that the best criterion for the isokinetic effect is that, for a series of similar and related catalysts (systems), the Arrhenius lines intersect in one and the same point, T_{iso}. The relation between the two criteria for the compensation effect and the isokinetic effect is still a matter of debate; e.g., very recently Corma *et al.* (12–13) have pointed out that, for the sake of clarity, it would be wise to strictly separate between the two concepts. The present authors fully agree with this:

(a) The compensation effect thus defined means "only" that there is a linear relation between $\ln A$ and E_a, implying that the increase of the preexponential factor is compensated by a similar increase of the activation energy.

(b) The isokinetic effect is defined by the existence of a common intersection point of Arrhenius lines describing the kinetics of a series of similar reacting systems.

Thus the major argument for an isokinetic effect is criterion (b). Only if this is found to hold, the corresponding compensation line—Eq. [2], criterion (a)—can be used to support the interpretation. In the present paper we will use this approach. If the value of T_{iso} derived from the two criteria are the same it must be accepted—and explained.

One should be aware that situations can appear—and are rather frequently found (14)—where two groups of experiments can result in two different values of $\ln Z$ (Eq. [4]) but the same T_{iso}. If all the experimental points were unsuspectedly used for an analysis according to Eq. [2] an erroneous value of T_{iso} would be obtained.

Indeed, the curious and astonishing matter concerning the isokinetic effect is really that one can find so many systems for which $\ln Z$ is constant even if the activation energy differs. Trivially, such a situation must imply a very good

0021-9517/97 $25.00

calibration of specific surface, number of available sites, number of metal atoms per gram of catalyst or whatever entity is used to define the specific rate (turnover frequency) of the reaction. But there must be also some more basic reason for the constancy of ln Z and it seems to us that this problem has not been fully solved. Some small variations of Z can, however, often occur. It has been been pointed out by Bond (14) that one can often find a set of parallel lines, the slope of which give T_{iso} and the interlinear distances of which are attributed to different values of ln Z in Eq. [4]. This might indicate that ln Z can take on only some few preferred values. The reason for the disrepute of the application of Eq. [2] might to some extent be that one has tried to join together with one line points that should really be related to two or several parallel lines.

Against this background, it was of a tremendous interest when we found a linear relation between ln A and E_a from the data reported in (1). The slope of the line was found to be $b = 1.06$ mol/kcal, giving a value of $T_{\text{iso}} = 475$ K. Our interest arouse because a similar line of a similar slope was reported in (4), giving the isokinetic temperature of about 520 K, i.e., close to that of the Somorjai collation.

This finding was also of great interest in view of a model of selective energy transfer from catalyst to reactant, proposed as an explanation of the isokinetic effect (8, 15). It turns out (8, 15), that if there is a complete resonance between the molecular vibrations of the reactant (accepting energy) and of the catalyst system (releasing energy) it holds that

$$T_{\text{iso}} = Nhc/2R \cdot \nu \approx 0.715\nu. \qquad [5]$$

Here ν is the vibration frequency of that vibration mode of the reacting molecule (expressed as cm^{-1}) that most strongly distorts the structure of the molecule towards the structure at the activated state. The excitation of this vibration mode will thus lead into reaction. If the conditions of relation [5] are valid, the necessary value of ν describing the neopentane hydrogenolysis can be calculated as $520/0.715 = 727$ cm^{-1}. This is very near the calculated frequency characterizing the symmetric carbon–carbon stretching vibration of neopentane, viz. 724 cm^{-1} (16) and near the experimental value, 733 cm^{-1} (17). Hence one might infer, not surprisingly perhaps, that the stretching of the C–C bonds is the vibration that must be activated for the hydrogenolysis reaction.

Because of this result we decided to look closer into the information embedded in the experimental results (2–7). Before going into the details of this, it is of importance to stress the similarity of T_{iso} for the data collected for different metals (1) and of those for one and the same metal (4). This similarity indicates, in its turn, that the same mechanism is operating, the same frequency of vibration is activated, independently of the nature of the metal used as catalyst. We conclude—and this will be the basis of the present work—that such a condition would be upheld only if the reacting molecule is very weakly adsorbed, i.e., the difference between heat of adsorption for the various metals of (1) is very small because the heats of adsorption as such are low.

We will now treat the kinetic data from the reports (2–7). The brutto turnover frequencies reported (N) are corrected to represent only that part of the observed reagent disappearance that is caused by hydrogenolysis reactions. Thus $N_{\text{corr}} = N(1 - S_i)$, where S_i is the selectivity for isomerization.

From the data in Refs. (2–7) we can now match the possible intersection point of Arrhenius lines against the slope of the corresponding ln A versus E_a lines as discussed above. Turning first to the data of zeolite L supports (4) we find a good agreement between the temperature at which the Arrhenius lines intersect (Fig. 1a; $1000/T_{\text{iso}} = 2.06$ K^{-1};

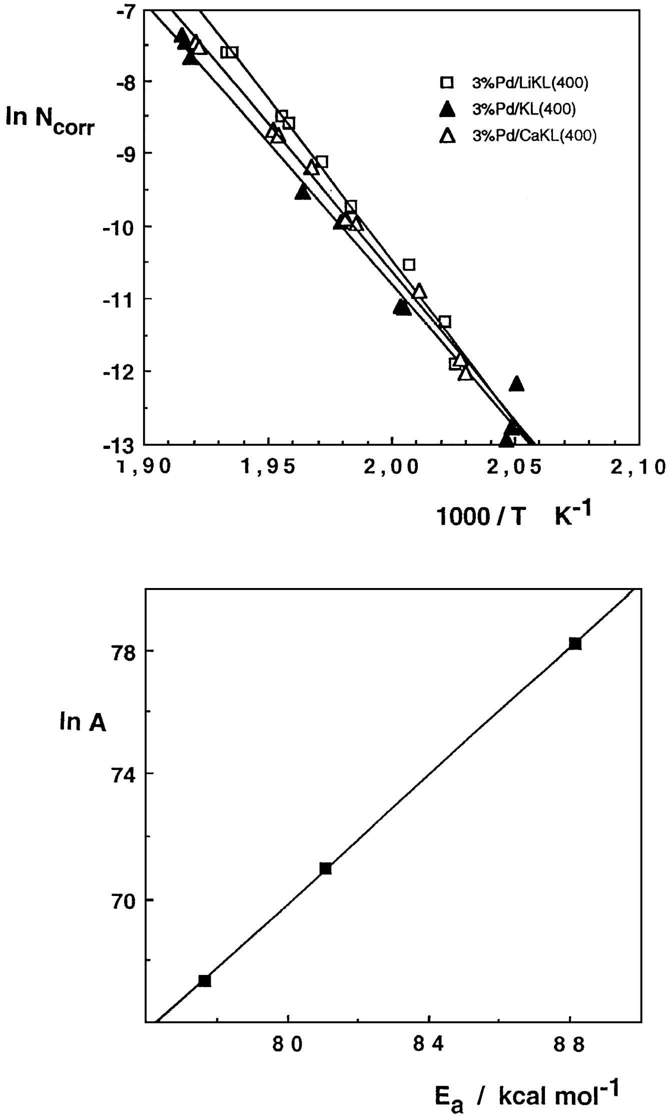

FIG. 1. (a) The Arrhenius graphs for the data of Pd on Zeolite L supports (4). (b) The compensation line (Eq. [2]) from the data of (4).

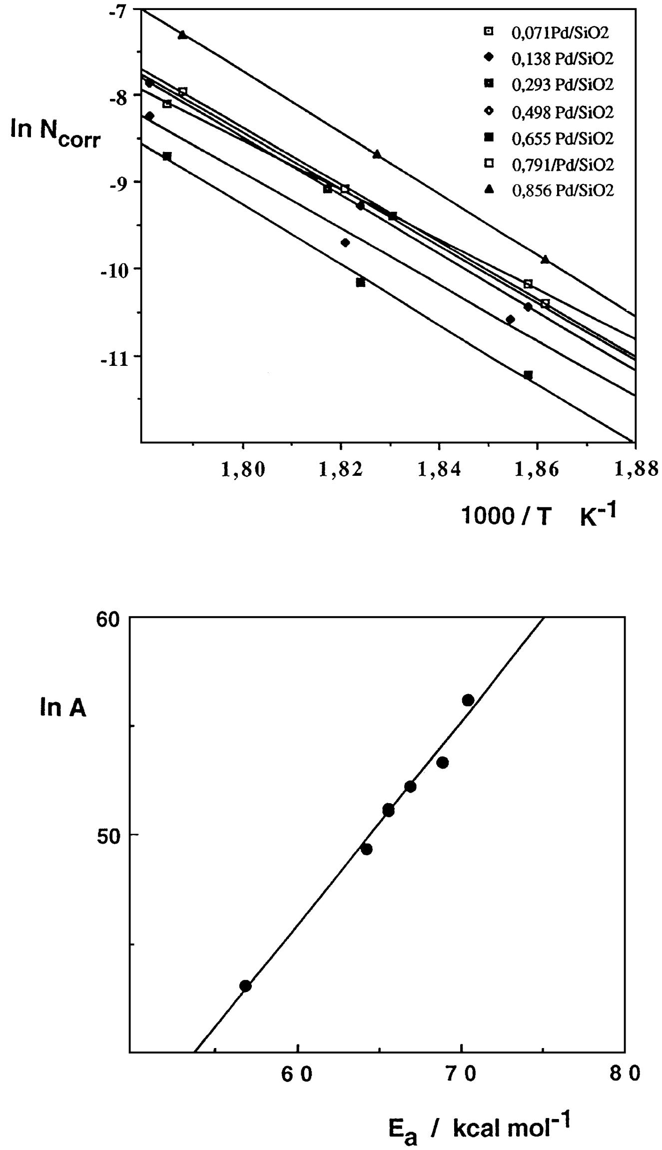

FIG. 2. (a) The Arrhenius graphs for the data of Pd on silica supports (2). (b) The compensation line (Eq. [2]) from the data of (2).

$T_{iso} = 485$ K) and the T_{iso} calculated from the slope of ln A versus E_a (Fig. 1b; $b = 1.038$; $T_{iso} = 485$ K). This almost ideal set of data indicates that the quality of measurement is such (so high) that it is possible to use Eq. [1] without the need of fearing any stochastic errors influencing the result.

Next we examine a series of differently dispersed palladium particles, all on silica support (2). Figure 2a indicates that there is a series of lines with almost the same slope. For those that do intersect there is a range of intersection (dependent on the choice of almost parallel lines to intersect) at $1000/T \approx 1.81$–1.85 K^{-1}. This yields $T_{iso} = 546$ K. The result in Fig. 2b supports this interpretation; $b = 0.925$ or $T_{iso} = 544$ K.

From this not so ideal set of data one learns that points in a ln A versus E_a diagram may give rise to a compensation line, the slope of which indicates a value of the isokinetic temperature close to that found by the Exner/Linert method even if some points do not correspond to lines intersecting at the isokinetic point. The requirement for this is that the extra points happen to be spread out rather evenly on both sides of the line (i.e., that the extra Arrhenius lines are found at both sides of the intersection point).

Next one can consider the data for Y zeolites as support with differing palladium loading (NaY (3) and in one case HY (7)). Applying the same technique we found a point of intersection at $1000/T = 1.87$ K^{-1} or $T_{iso} = 534$ K. This intersection was defined only by the lines for 4% Pd/NaY and 7% Pd/NaY, whereas the (coinciding) lines for 2% Pd NaY and 5.2% Pd/HY clearly has another ln Z value.

Figure 3a gives the Arrhenius lines from a recent investigation (5, 6) on Pd/Au supported on silica with a total metal

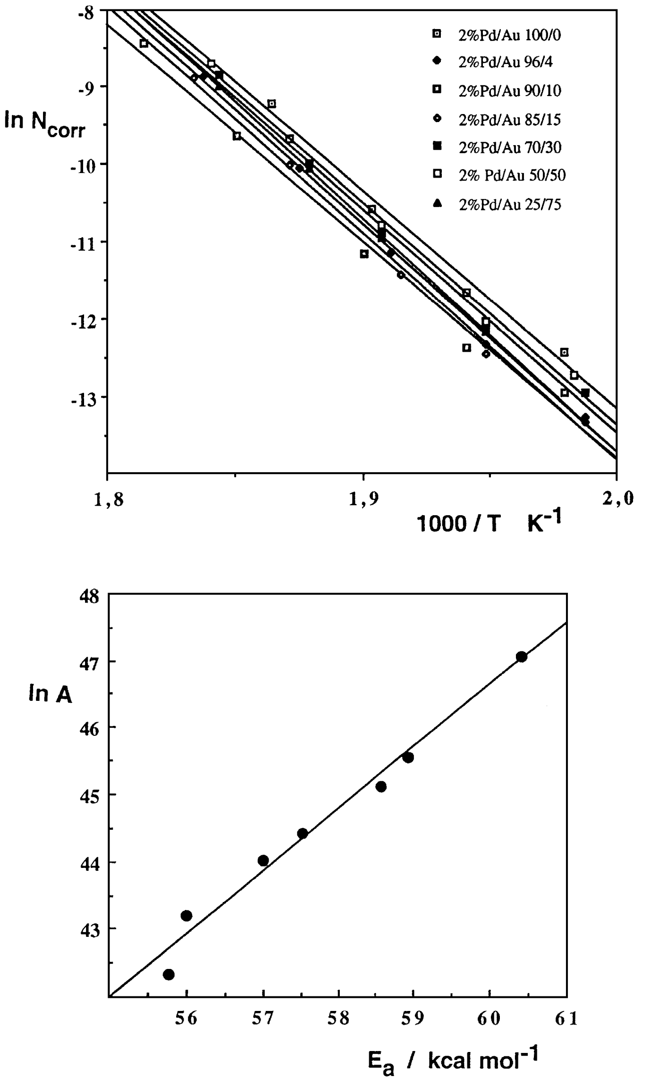

FIG. 3. (a) The Arrhenius graphs for the data of 2% Pd/Au on silica supports (5, 6). (b) The compensation line (Eq. [2]) from the data of (5, 6).

TABLE 1

Isokinetic Temperatures for the Different Catalyst Systems and the Assignment of Vibrations of the Support

Support	T_{iso}/K	Reference T_{iso}	$\omega_{\mathrm{support}}$/cm^{-1}	Reference ω
Zeolite Y	534	Refs. (3) and (7)	760–789	(18)
Zeolite L	485	Fig. 1	767	(18)
SiO_2	543–546	Fig. 2, Fig. 3	794–797	(19)
SiO_2	547	Fig. 4	794–797	(19)
Al_2O_3	555	Ref. (20)	845	(21)

Note. The support vibration wave numbers are taken from experimental infrared spectra.

loading of 2% (5, 6). The same pattern appears as we found in Fig. 2a: A series of almost parallel lines and some lines intersecting one another. The point of intersection gives $1000/T = 1.83$ K^{-1}, i.e., $T_{\mathrm{iso}} = 546$ K. When all the data are collected in a ln A versus E_a diagram one finds a rather good correlation line with slope $b = 0.927$ or $T_{\mathrm{iso}} = 543$ K. Thus also in this case the two criteria for the isokinetic effect can be used to strengthen each other. (It should be noted that in Fig. 3a one could almost equally well chose another range of intersection, viz. $1000/T = 1.95$–2.0 K^{-1}. This range has not been used, however, as it is broader and not agreeing with the slope observed in Fig. 3b as the first one is.)

For the sake of easy reference, the data obtained are recollected in Table 1. One notes that those systems that has silica as support show quite similar T_{iso}. This is so much more obvious if one selects from the collation of Somorjai (1) those systems that have silica support. The result of this selection is given in Fig. 4 and indicates a series of three parallell lines with slope $b = 0.92$, corresponding to $T_{\mathrm{iso}} = 547$ K. The systems with zeolite support show somewhat lower values of T_{iso}.

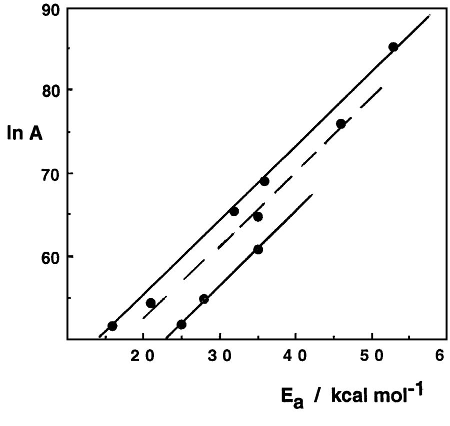

FIG. 4. The compensation effect for those systems quoted by Somorjai (1) that use silica supports. The three lines are drawn by hand with a common slope to illustrate the possibility of parallel lines in a set of scattered points.

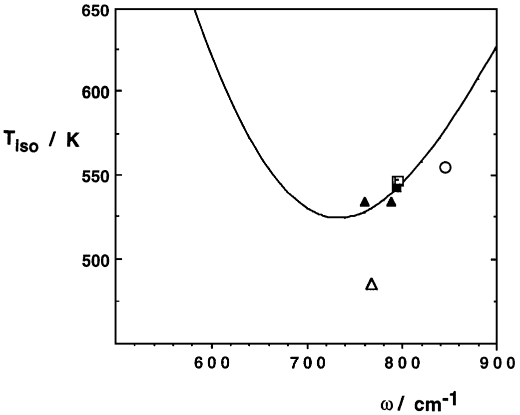

FIG. 5. T_{iso} as a function of ω, Eq. [6], for the fixed value of $\nu = 733$ cm^{-1} (full-drawn curve). The points are originating from the T_{iso} values (deduced as described in the text) as the ordinate values and with the wave numbers of the infrared absorption for the respective carriers as the abscissa values, respectively. These experimentally found wave numbers (selected as near to 733 cm^{-1} as possible) are chosen from literature as indicated in Table 1. Zeolite Y (▲), Zeolite L (△), SiO_2 (■), SiO_2 (Fig. 4) (□), Al_2O_3 (○).

In order to more completely describe our analysis, let us introduce the full formula for T_{iso} as it appears from the model of selective energy transfer (8). In this model the isokinetic temperature is derived by considering the selective excitation of the bond breaking vibrational mode (frequency ν). It is assumed that the energy necessary for exciting this vibration is obtained from vibrators of the catalyst system, the frequency of these vibrators being denoted ω.

$$\begin{aligned} T_{\mathrm{iso}} &= Nhc\,R^{-1}(\nu^2 - \omega^2)\omega^{-1} \\ &\quad \times \{\pm\pi/2 - \mathrm{arctg}(0.5\nu\omega(\nu^2 - \omega^2)^{-1})\}^{-1}. \end{aligned} \quad [6]$$

Especially if $\omega = \nu$, in which case one gets maximum efficiency of resonance energy transfer, Eq. [6] transforms to the previously given Eq. [5]. The form of this function is depicted in Fig. 5 where the curve is calculated for the specific value of $\nu = 733$ cm^{-1}. This value is chosen because it is the experimental value (17) of the symmetric C–C stretch of neopentane. The identification is corroborated by theory (16) giving 724 cm^{-1} as indicated above. In Fig. 5 we have also introduced the results of the above calculations of T_{iso} (Table 1) using as abscissa values the wave numbers experimentally found in the infrared spectra of the support materials. Those wave numbers have been chosen that are close to the wave number of the sym C–C stretch of neopentane and they are also collected in Table 1.

One notes that the points (T_{iso}; ω) thus defined adhere quite closely to the calculated curve. This means according to our model (8)—quite unexpectedly—that the vibrational energy that is activating the reacting molecule comes from the support. To illustrate the implications of this discovery, one might envisage the reacting molecule to be situated in a radiative field, represented by the emission infrared spectrum of the supporting systems. This field might interact with the C–C vibrations and thus activate the molecule. (The palladium particles are of course the origin of the active hydrogen atoms needed for the hydrogenolysis reaction.) This interpretation lifts away the problem that the metal phonons, that should otherwise be the foremost candidates as an energy source, have much too low frequencies.

The only exception from the above-mentioned close adherence of the isokinetic points to the calculated curve is the point representing the zeolite L systems. The differing position of the point of the L zeolites can possibly be explained by assuming that the unidimensional character of the L-zeolite channels affects the neopentane molecule so that the T_d symmetry is resolved into two C_{2v} systems, perpendicular to each other. That one directed along the flow might have the lowest symmetric C–C stretching frequency. If this vibration corresponds to the reactive mode, a low value of ν in Eq. [6] and consequently of T_{iso} might be understood.

Recently, another investigation has been published (20), in which Pd/Al_2O_3 was used as catalysts for the neopentane hydrogenolysis. Although the material is somewhat limited, one can observe an isokinetic effect with $T_{iso} = 555$ K. It might be of interest, however, that the infrared spectrum of Al_2O_3 presents a band at 845 cm^{-1} (21). This gives a point (555 K; 845 cm^{-1}), quite close to the curve of Fig. 5.

The major result of the present investigation is the confirmation of an isokinetic effect for the reaction concerned. It has been demonstrated that both the criteria for such an effect (the criterion of Exner (11) and Eq. [2]) must be used in symbiosis with each other. Of major importance in this work is that the model of selective energy transfer explains not only the magnitude of the isokinetic temperature but that it also can describe fairly well the variation of T_{iso} with the driving frequency ω.

On the mechanistic level, the conclusion of the presented analysis is, that the neopentane molecule is activated on the surface without being strongly adsorbed. In agreement with this, the frequency ν that is found from Eqs. [5] and [6] is the one for the free molecule. Even if molecular vibrations do not change the frequency very much on coordination (adsorption) this similarity to the free molecule data corroborates our assumption that the neopentane molecule is just weakly adsorbed. Hence it is also allowed, as we have done, to compare data from a variety of metals, recorded in the compilation of Somorjai (1). It must be strongly stressed that such a nonadsorptive process was suggested by Maier and co-workers (22) for a D/H exchange reaction, a result supported by considerations, similar to the present one (23).

As the final conclusion stands our interpretation that the symmetric C–C stretch is the vibration mode that must be activated in order for the molecule to react. Judging from the values of the activation energy, the symmetric stretching vibration is populated up to vibration levels of about 20–30, reaching 40 in some cases. When a suitable prolongation of the carbon–carbon bonds has been achieved, there is space enough for a hydrogen atom, already adsorbed on the surface, to attack one of the carbons. It is somewhat strange that it is the symmetric, not the asymmetric, stretching of the tetrahedral unit that is activated. The reason for this may be that the anharmonicity is stronger for the asymmetric vibration, thus hindering an easy resonance transfer of energy up to high vibration levels.

For these high levels of excitation, one might also expect a complete breakdown of the normal mode approximation in describing the intramolecular motions (24). This effect is well identified for the case of benzene C–H stretching (24). Instead of a molecular mode the vibration tends to correspond to a local stretching of a single bond: a C–H in the case of benzene and a C–C bond in the present case.

ACKNOWLEDGMENT

We express our gratitude to the Royal Swedish Academy of Sciences (KVA) and the Polish Academy of Sciences (PAN) for their support and assistance in making this cooperation possible.

REFERENCES

1. Somorjai, G. A., "Introduction to Surface Chemistry and Catalysis." Wiley, New York/Chichester/Brisbane/Toronto/Singapore, 1994.
2. Karpinski, Z., Butt, J. B., and Sachtler, W. M. H., *J. Catal.* **119**, 521 (1989).
3. Homeyer, S. T., Karpinski, Z., and Sachtler, W. M. H., *Rec. Trav. Chim. Pays-Bas* **109**, 81 (1990).
4. Karpinski, Z., Gandhi, S. N., and Sachtler, W. M. H., *J. Catal.* **141**, 337 (1993).
5. Juszczyk, W., Karpinski, Z., Lomot, D., Pielaszek, J., and Sobczak, J. W., *J. Catal.* **151**, 67 (1995).
6. Juszczyk, W., Ph.D. dissertation, Institute of Physical Chemistry of Polish Acad. Sci., Warsaw, 1994.
7. Karpinski, Z., unpublished results.
8. Larsson, R., *J. Mol. Catal.* **55**, 70 (1989).
9. Cremer, E., *Adv. Catal.* **7**, 75 (1955).
10. Galwey, A. K., *Adv. Catal.* **26**, 247 (1977).
11. Exner, O., *Collect. Czech. Chem. Commun.* **37**, 1425 (1973).
12. Corma, A., Llopis, F., Monton, J. B., and Weller, S., *J. Catal.* **142**, 97 (1993).
13. Corma, A., Llopis, F., Monton, J. B., and Weller, S., *J. Catal.* **148**, 415 (1994).
14. Bond, G. C., *Z. Phys. Chem. (N.F.)* **144**, 21 (1985).
15. Larsson, R., *Catal. Today* **1**, 93 (1987).
16. Schnyder, R. G., and Schachtschneider, J. H., *Spectrochim. Acta* **21**, 169 (1965).
17. Rank, D. H., Saksena, B. D., and Shull, E. R., *Discuss. Faraday Soc.* **9**, 187 (1950).
18. Breck, D. W., "Zeolite Molecular Sieves." Wiley, New York/London/Sidney/Toronto, 1974.
19. Haccuria, M., *Bull. Soc. Chim. Belges* **62**, 428 (1953).
20. Juszczyk, W., Lomot, D., Karpinski, Z., and Pielaszek, J., *Catal. Lett.* **31**, 37 (1995).
21. Crowell, J. G., Chen, J. G., and Yates, J. T., Jr., *Surf. Sci.* **165**, 37 (1986).

22. McEwen, A. B., Maier, W. F., and Smith, D. A., *in* “Catalysis 1987” (J. W. Ward, Ed.), p. 823. Elsevier, Amsterdam, 1988.
23. Larsson, R., *Catal. Lett.* **10**, 317 (1991).
24. Swofford, R. L., Long, M. E., and Albrecht, A. C., *J. Chem. Phys.* **65**, 179 (1976).

Z. Karpinski
R. Larsson*

Institute of Physical Chemistry
Polish Academy of Sciences
ul. Kasprzaka 44/52, 01-224 Warsaw, Poland
**Group of Catalysis Research, Chemical Center*
University of Lund, 221 00 Lund, Sweden

Received November 6, 1995; revised February 10, 1997; accepted February 18, 1997