

Indications for a Surface Temperature Excess in Heterogeneous Catalysis

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We explored the surface temperature excess $\Delta T = T^r - T^m$ (real reaction temperature T^r , measured catalyst temperature T^m) on the basis of experimental data, a gradually curved Arrhenius plot for CO oxidation reactions over Pd/ γ -Al₂O₃ catalysts. Such a plot could be an indication of the surface temperature excess in the 2-dimensional reaction surfaces of catalysts. The positive or negative surface temperature excess could be developed to be a general explanation for a gradually curved Arrhenius plot of a gas–solid catalytic system. This is a new insight into solving the puzzle on such common phenomena in heterogeneous catalysis. By using the reciprocal of the real reaction temperature T^r in the hypothetical 2-D reaction surface, instead of the experimentally determined catalyst temperature T^m or the gas temperature T^g , the gradually curved Arrhenius plot becomes linear. We investigated the implications of such a difference among T^r , T^m , and T^g . The surface temperature excess could be the effect of coupling between the fluxes of a chemical reaction and heat transport in the 2-D reaction surface. Its order of magnitude is 10 K for the present model system.¹ The surface temperature excess increases exponentially with the reaction temperature.

Introduction

The discriminating aspect of heterogeneous catalysis is that a chemical reaction takes place in the interface between the catalyst and the medium. Chemisorption of the reactant molecules and the conversion reaction itself are limited to the adsorbed monolayer in the interface. That the reaction can only take place in the interface itself has special thermodynamic consequences for the conversion rates and their relation to the dissipation of the reaction heat. In this paper the notion of a “Gibbs dividing surface”,² which characterizes a heterogeneous thermodynamic system in equilibrium, is extended to nonequilibrium systems. The “2-D reaction surface” where catalytic reactions really take place is defined to distinguish from the inactive catalyst surface. The surface temperature excess does not exist in the large percentage of inactive catalyst surfaces. Like the Gibbs dividing surface, this two-dimensional reaction surface is a separate thermodynamic system. It has all the excess thermodynamic parameters assigned to it, by which the complete heterogeneous system differs from the two adjacent three-dimensional homogeneous “bulk” phases put together. In addition to excess values for enthalpy, entropy, and excess amounts of adsorbed molecules, the reaction surface has also heat fluxes and reaction rates involving adsorbed reactant species assigned to it as surface excesses. Thermodynamic relations are valid for the local excess properties. But the fluxes and forces for the irreversible surface processes follow the rules for the thermodynamics of irreversible processes.^{3,4} The reaction surface is a convenient 2-D representation of heat fluxes and conversion rates in an active heterogeneous catalyst.⁵ In such a catalyst the temperature T^r in the reaction surface differs from the temperature T^m of the catalyst particles or the gas temperature T^g . This is because of the heat which is generated by the processes in the reaction surface. This heat must be transported

away, transferred to the bulk phases, and dissipated in the volume of the reactor. There could be steady-state temperature gradients in the boundary layer of a catalyst surface and heat transport limitations causing a temperature difference between the catalyst particles T^m and the ambient medium T^g . Coupled fluxes of heat and mass do exist in the boundary layers. And, indeed, as an additional transport property, thermal diffusion in the boundary layer can be important to a catalyst surface temperature in heterogeneous catalysis.⁴

But technologically important, and certainly more interesting from a theoretical viewpoint, seems the possibility of a surface temperature excess, $\Delta T = T^r - T^m$, in the 2-dimensional reaction surface of an active heterogeneous catalyst. The anisotropic interface may have been reduced to a 2-D thermodynamic system by definition, but this reaction surface still contains the adsorbed molecules which participate in the catalytic reaction. Therefore, the reaction surface must also have its own heat capacity and it can store amount of excess enthalpy as latent heat. This implies that an active catalyst surface can have a surface temperature excess $\Delta T (=T^r - T^m)$. The heat which is generated at the temperature T^r of the reaction surface must flow into the bulk catalyst particles at the temperature T^m . It is, however, T^r rather than T^m that controls the reaction rate \mathcal{R} and also the selectivity of a heterogeneous catalytic process through the Arrhenius equation (eq 1),

$$k = A \exp(-E_a/RT^r) \quad (1)$$

in which k is the reaction rate constant for the conversion process in the interface.

T^m values can be measured in combination with the corresponding reaction rates, and these thermokinetic data can be used to construct “Arrhenius plots” and obtain the activation energy E_a of the catalytic reaction. But, quite often, these experimental plots are gradually curved^{6–10} rather than straight. A linear relation between the logarithm of the reaction rate

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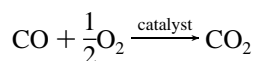
constant k and the inverse of the reaction temperature ($1/T^m$) is predicted by the Eyring theory for activated chemical rate processes.^{11,12} This kinetic theory for activated rate processes connects the constants k and E_a from Arrhenius' law (eq 1) with the quantum-mechanical potential energy diagram for the interaction of the atomic species, which are involved in the conversion. Experimental curves bending upward or downward would indicate that the activation energy E_a of the catalytic process is, somehow, a function of the reactor temperature. But most authors hold the belief that the activation energy E_a of a reaction should not, and certainly not strongly, depend on the temperature. Therefore, they have come up with ad hoc explanations for every single system with such a curved Arrhenius plot. A characteristic example is the study by Liu et al.,⁶ involving a microporous one-dimensional zeolite catalyst. To explain the observed kinetics they had to assume a transition between rate-limiting mechanisms: from single file diffusion to reaction controlled kinetics with increasing temperature. The apparent activation energy of the overall process would then gradually decrease because of this transition.^{6,7} Others have suggested the transition from a reaction controlled regime at low temperatures to mass transfer limited conversion rates at high temperature^{13,14} or that the rate-determining step in the catalytic process changes from a desorption limitation at a low temperature to adsorption of reactant molecules as the limiting step at high temperatures.¹⁵ Again, the effective E_a in the process would then vary in the experimental range of temperatures. For a kinetically controlled chemical reaction E_a is typically of the order of 100 kJ/mol, whereas diffusion-limited reactions have characteristic activation energies of the order $E_a = 10$ kJ/mol.

A most interesting observation was, however, made by van de Runstraat et al.¹⁶ They simulated a reaction with a curved Arrhenius plot and discovered that the activation energy E_a will, actually, remain constant, whereas the surface coverage of the reaction intermediate and the order of the reaction change with increasing temperature. This is one example that the Arrhenius hypothesis of a nearly constant activation energy remains valid in the end, even though the Arrhenius plot is gradually curved.

Of course, we shall not deny that there may sometimes be unexpected anomalies in a heterogeneous reaction system. Apparently nonlinear Arrhenius plots for specific cases can indeed be the result of complications in the chain of elementary reaction steps. We also do accept the existence of gradual transitions to other types of rate limitations when the reaction temperature is altered. But, in general, a chemical reaction constitutes a chain of elementary transformations. The rate of a kinetically limited conversion is then determined by one elementary step. Such a step should have its own, specific, temperature-independent activation energy. In many cases one and the same elementary step will remain rate determining over a considerable temperature range. In all those many cases the activation energy E_a of the catalytic reaction should not change with temperature and the real Arrhenius plots are linear or straight.

Catalytic CO Oxidation, Experimental Case

We shall explore the consequences of the proposed surface temperature excess in one active heterogeneous catalyst. The CO oxidation



is a very well documented reaction. This simple reaction is catalyzed by Pt, Pd, and V catalysts and shows a distinct, well-

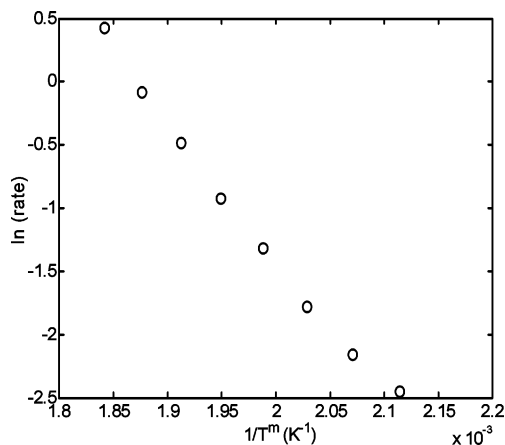


Figure 1. Gradually curved Arrhenius plot (reproduced using data in Figure 7 in the paper by Perry et al.¹).

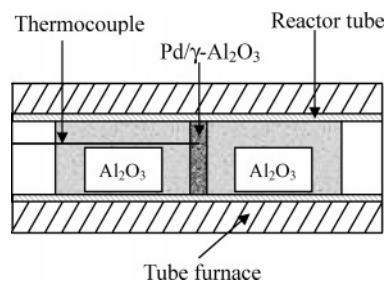


Figure 2. Schematic of the differential packed bed reactor using a conventional heating system (replotted on the basis of the paper by Perry et al.¹).

measured, and gradually curved Arrhenius plot with each of these catalysts. This has been observed in the experiments with Pd/Al₂O₃ catalysts,^{1,8} a single crystalline Pt(100) surface,⁹ and a Pd/SiO₂ catalyst.¹⁰ Wei, from our own department, obtained the curved Arrhenius plot for CO oxidation with a vanadium catalyst.¹⁷ In all these experiments a plot of the logarithm of the reaction rates as a function of the inverse catalyst temperatures ($1/T^m$) had upward curvatures, as in Figure 1. The slope of the plots is steeper at the high-temperature end. Apparently, E_a increases with the temperature T^m . In our analysis we shall use the experimental results by Perry et al.¹

Perry studied the CO oxidation over a 5 wt % Pd catalyst on a porous γ -Al₂O₃ support using both conventional and microwave heating systems. The rapid heating via microwave and its large-scale nonisothermality make it an interesting subject.^{18,19} However, because of the hot spots in the catalysts it is very difficult to measure the temperature accurately to be used in kinetics study, which does not fit our requirement here. Therefore, here, the set of experimental data from Perry et al. using conventional heating and a differential reactor was chosen, where the catalyst bed has almost uniform temperature.

The schematic of the reactor is shown in Figure 2. Thin layer catalyst particles, 5 wt % Pd/ γ -Al₂O₃ Escat 14 (Engelhard), were sandwiched between two inactive support materials in a tube reactor. This thin layer catalyst included 3 mg of active catalyst diluted in about 50 mg of inactive support γ -Al₂O₃ to achieve radial uniformity of catalyst distribution across the packed bed. A tube furnace was used to heat up the reactor tube inside. The catalyst temperature T^m was measured in a steady state (the catalyst bed reached an equilibrium temperature) using a fixed digital controller thermocouple, embedded in the small catalyst particles, which can measure the temperature within the error of 0.1 °C. This fits our requirement on small errors in temperature measurements for this study. Reaction rates \mathcal{R}

were measured for the different catalyst temperatures and plotted as a function of $1/T^m$ in their Figure 7,¹ which is the same as our Figure 1.

A differential reactor enables direct measurement of reaction rates. Normally, the conversion in a differential reactor is only a small percentage, below 5% or 10%. In such a low conversion system, temperature and concentration gradients along the reactor tube are negligible and the reaction rate in the catalyst thin layer is assumed to be uniform. This simplifies the interpretation of the experimental data considerably.

In Perry's publication,¹ there is no suggestion of a model to explain the curvature in this Arrhenius plot. The data were reported as such, and the theoretical implications were not discussed. But we shall try to interpret the thermochemical kinetics behind these purely experimental data, with our idea of a distinct surface reaction temperature T^r in mind.

The exponential in Arrhenius' expression for a rate constant has, in fact, not one but two variables, E_a and T^r , which could vary with the imposed experimental conditions and the resulting reaction rates. The traditional interpretation is that the activation energy E_a can be calculated from measured temperatures T^m at the catalyst surface and the corresponding reaction rates or rate constants. But, inversely, if we had obtained a value of E_a from some theory, experiment, or assumption, then we might just as well calculate the real temperatures in the reaction surface as process variables. The measured reaction rates are now a sensor, which is indicative of the temperature T^r in the thermodynamically defined reaction system. Since a constant E_a is predicted by the Eyring theory for a chemical reaction,^{11,12} this is a straightforward method to access the temperature T^r which is the alternative variable of the Arrhenius equation. This reaction temperature T^r in the 2-D reaction surface is not measurable in a direct way with a thermocouple or IR camera. These methods determine the temperatures in the adjacent, three-dimensional bulk phases, of the medium (T^g) and of the catalyst particles (T^m). But in heterogeneous catalysis the measured reaction rates indicate the real temperature T^r in our hypothetical 2-D reaction surface.

A curved Arrhenius plot like Figure 1 can be used to obtain the temperature T^r . Such a plot ought to be a straight line if E_a is the same in all experimental points. The reason that the plot appears to be curved could, of course, be that E_a varies with T , which is the general assumption in such cases. But the alternative explanation is that erroneous values of the reaction temperature have, somehow, been used to construct the abscissa ($1/T$) for the plot. In our chosen experiments¹ these were the T^m values which had been measured with a thermocouple in the bulk of the catalyst. But these temperatures T^m of the catalyst particle are not necessarily equal to the reaction temperatures T^r which is defined inside the separate two-dimensional thermodynamic system in which the catalytic processes take place.

Interpretations of Curved Arrhenius plots

Perry ignored the curvature of the Arrhenius plot for good reasons. Indeed it is difficult to think of a fitting ad hoc kinetic model which explains why E_a in this particular catalytic reaction should *increase* with the measured temperature of the catalyst particles. But as it is, the calculation of activation energies from the slopes at different measured temperatures in Figure 1 leads to a temperature-dependent activation energy E_a . This classical result is shown in Table 1.

The magnitudes of these calculated activation energies indicate that reaction rates were controlled by the kinetics of the catalytic reaction over the whole temperature range of the

TABLE 1: Activation Energies for CO Oxidation Catalyzed by Pd/ γ -Al₂O₃¹

T^m (K)	473	483	493	503	513	523	533	543
E_a (kJ/mol)	54	65	76	86	94	102	110	121

experiment. The values are too high for a diffusion rate-limiting reaction (with $E_a = 10$ kJ/mol at most). And we see no signs of a gradual change in the rate-limiting mechanism either. Normally, the apparent activation energies would then tend to decrease with increasing reaction temperatures. But here E_a increases, rather drastically, at the higher catalyst temperatures.

Following our proposition, this calculated increase could be an artefact, caused by using erroneous temperature values in constructing the Arrhenius plot. Therefore, the problem is to find the real reaction temperature and to extract ΔT values for the individually measured data points from the experiment in Figure 1.

The procedure is started by calculating one experimentally plausible and constant reference value E_a° for the activation energy E_a at a chosen reference temperature $T^\circ = T^{m^\circ}$, which belongs to the original Arrhenius plot. The activation energy $E_a = E_a^\circ$ simply determines the constant slope of the real Arrhenius plot. This plot becomes a straight line when the abscissa is $1/T^r$ instead of $1/T^m$. The assumed E_a° , because of the linearity of the Arrhenius plot, fixes the real temperatures T^r in the reaction surface for all the measured reaction rates \mathcal{R} in the corresponding catalytic systems.

This procedure of "straightening the Arrhenius plot" is illustrated in Figure 3. For a start, we have chosen the activation energy for the lowest temperature of an experimental point in Figure 1 as a plausible reference value E_a° . This is because reaction rates diminish, and eventually vanish, toward the low temperature end of the Arrhenius plot. At low rates the heat generation in the reaction surface is relatively small. This heat is transferred from the reaction surface to the catalyst particle and will then flow out of the catalyst surface at $T = T^m$ into the ambient gas (at $T = T^g$) by heat transfer. According to irreversible thermodynamics,^{3,5} the heat flow from the reaction surface to the catalyst will be proportional with the surface temperature excess $\Delta T = T^r - T^m$, whereas the heat transfer from the catalyst into the medium is driven by the temperature difference $T^m - T^g$.

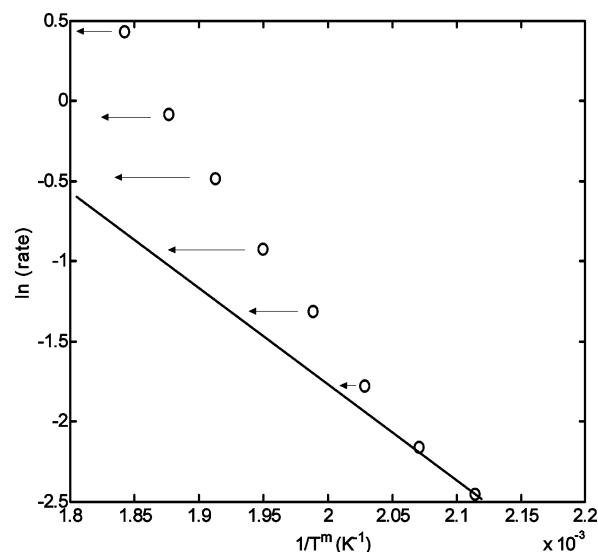


Figure 3. Temperature shift from the measured catalyst T^m to the real reaction T^r by assuming constant activation energy of the surface reaction. (Circles correspond to T^m and the line represents T^r .)

At very small reaction rates the reaction temperature T^r will not differ too much from the measured catalyst temperature T^m , and neither will T^m be much different from the gas temperature T^g . Ideally, there must be some reference point T^0 , with a negligibly small reaction rate, where all these temperatures are approximately equal ($T^g = T^m = T^r = T^0$). Therefore, a direct method to obtain the real reaction temperature T^r from experimental data is through Arrhenius' equation and using the reference temperature T^0 where the reaction rate extremely small:

$$\ln \frac{\mathcal{R}(T)}{\mathcal{R}(T^0)} = -\frac{E_a}{R} \left(\frac{1}{T} - \frac{1}{T^0} \right) \quad (2)$$

This T^0 would be close to the experimental value for T^m at the lowest reaction rate in an experimental set of data. In CO oxidation (Table 1) the activation energy was $E_a = 54$ kJ/mol at the lowest temperature ($T^m = 473$ K). Even though there was still a measurable reaction rate at this temperature, this $E_a = 54$ kJ/mol might be a reasonable approximation for $E_a = E_a^0$. All the corresponding data from this particular experimental setting could then be introduced into eq 2 as the reference values T^0 , $\mathcal{R}(T^0)$, and E_a^0 , respectively. At this reference point the surface temperature excess $\Delta T = 0$, by definition. The values for ΔT in all the other experiments were calculated by $\Delta T = T^r - T^m$, where T^r was calculated using eq 2.

Perry's experimental reaction rates, as indicated in Figure 3, are now obtained at a lower $1/T$ than in the original Figure 1. The higher temperatures T^r ($> T^m$) on the straightened Arrhenius plot also indicate that the temperature in the reaction surface is decisive for the rate of an activated catalytic process.

The temperature excess $\Delta T = T^r - T^m$ is a real temperature difference. It can cause a flux of the reaction heat in the two-dimensional reaction surface, from the domain with the high-temperature T^r to the transfer point with the catalyst which is at T^m . In the steady state the generated reaction heat (or heat flux) is proportional with the reaction rate \mathcal{R} , which, itself, increases exponentially with the temperature T^r . The heat flux is also proportional with its driving force, the surface temperature excess ΔT , as in Fourier's law. Consequently, the reaction rate and the surface temperature excess ΔT have a linear relation. The surface temperature excess ΔT should then, in a consistent model, increase exponentially with the reaction temperature T^r .

This proposition is explored in Figure 4. We have plotted logarithm of ΔT as a function of T^r . The relation seems not to be linear at all although we should have anticipated this result. The deviation from a linear relation is due to an inherent systematic error in our approach. Selecting E_a for the lowest T^m as a reference point ($T^m = T^r = T^0$), we have overlooked that there must already have been a measurable rate \mathcal{R} and, therefore, a measurable heat production and heat flux within the nonisothermal reaction surface at the pertinent reaction temperature T^r . This oversight is felt most intensely at the low end of the temperature scale because we have forced ΔT to become zero in the chosen reference point.

Since the present model system is in a kinetically controlled regime, heat and mass transfer is not a limiting step anymore. The generated heats from surface reactions were transported away to the catalyst particle and to the gas phase before the reaction surface and the catalyst particle can reach the same temperature in steady state. Because of the higher thermal conductivity of the solid catalyst particle than the gas mixture, it received heat easier and faster from the reaction surface than

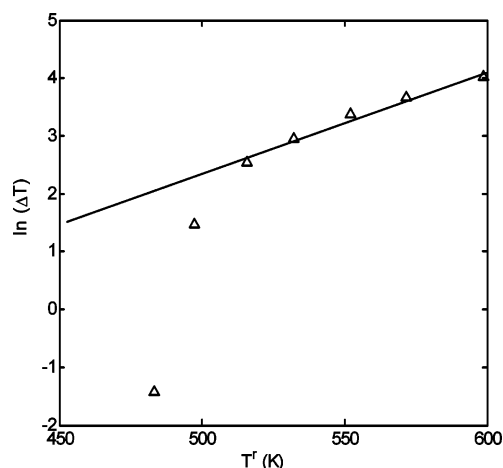


Figure 4. Relation between the reaction temperature T^r and the logarithm of the surface temperature excess ΔT before the correction by using a linear relation between T^r and logarithm of ΔT .

TABLE 2: Reaction Temperatures T^r and Temperature Excesses ΔT after the Correction by Using a Linear Relation between T^r and Logarithm of ΔT

T^m (K)	483	493	503	513	523	533	543
T^r (K)	498	510.9	525.1	539.4	556.1	574.5	598.6
ΔT (K)	15	17.9	22.1	26.4	33.1	41.5	55.6

the gases. Consequently, in the steady state, the temperature of the catalyst particle is slightly higher than the gas mixture.⁵ This means that there are heat fluxes from the 2-D reaction surface to the catalyst particle and from the catalyst particle to the gas phase in a steady state as long as there is a reaction going on the active catalyst surface. There are surface temperature excesses in all experiments of our model system, larger or smaller, depending on the reaction rate. Therefore, the value of the ΔT at the lowest temperature is, in fact, not zero and hence must be corrected. The correction procedure has been started with Figure 4.

The predicted linear relation of $\ln(\Delta T)$ with T^r is indeed observed in Figure 4 at the higher reaction temperatures, with larger reaction rates. To correct the methodical error on ΔT the linear relation at the high temperatures must be extrapolated downward. A tangent line is made through the highest temperature point in Figure 4 downward, which gives a new set of temperature excesses ΔT and the reaction temperatures T^r (Table 2). Using this new set of reaction temperatures T^r and measured reaction rates, we replot the Arrhenius plot. From this new Arrhenius plot, the actual activation energy for our model reaction is obtained; that is, $E_a = 63.8$ kJ/mol. The real activation energy of the catalytic reaction is lowered less by the interaction with the catalyst than would be assumed in the original (classical) estimates of Table 1.

Since we assumed that the reaction temperature T^r is equal to T^m at the lowest catalyst temperature $T^m = 473$ K to obtain Figure 4, the lowest temperature point was missing in Figure 4. Therefore we cannot obtain the reaction temperature at $T^m = 473$ K by extrapolation method in Figure 4. But we can use the Arrhenius equation to obtain it. We introduced the measured data, Perry's experimental reaction rate at $T^m = 533$ K and the corresponding $T^r = 574.5$ K as reference, and the newly obtained activation energy $E_a = 63.8$ kJ/mol into eq 2. For the catalyst temperature $T^m = 473$ K this gave $T^r = 487.9$ K and the corresponding temperature excess $\Delta T = 14.9$ K. These values are well within the range of expectation for this low temperature of heterogeneous catalytic reactions. This illustrates the internal consistency of our mathematical corrections.

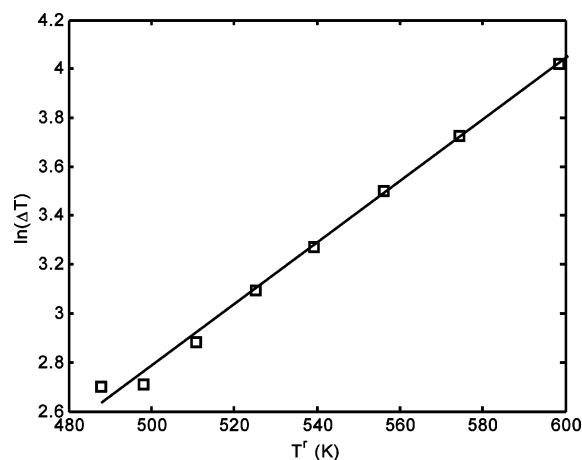


Figure 5. Relation between the reaction temperature T^r and the logarithm of the surface temperature excess ΔT after the correction by using a linear relation between T^r and logarithm of ΔT .

The new set of T^r and $\ln(\Delta T)$ is replotted in Figure 5. However, it does not show an expected perfect linear relation. The reason is when we correct ΔT by making a tangent line in Figure 4, T^r is also changed together with ΔT . But now the deviation from linear relation is rather small.

The temperature excess is important in the thermokinetic modeling of the reaction for catalyst development. A catalyst like Perry's shows relatively high-temperature excesses ΔT . The reaction temperatures T^r exceed the catalyst temperatures T^m by tens of degrees, which accelerates the catalytic process.

Catalytic Reaction Surface

The discussion which is illustrated by Figure 1 and Figures 3–5 demonstrates that expanding the notion of a “Gibbs dividing surface” to a “2-D reaction surface” by including irreversible processes in the assigned excess parameters can, at least, result in a consistent, alternative model for an active catalyst. In this thermodynamic model the temperature T^r of the reaction surface is an important property. It differs from the temperature T^m of the catalyst particles by the surface temperature excess ΔT . The upward or downward curvatures of Arrhenius plots for individual catalytic processes indicate that this temperature difference can be positive or negative, depending on the chosen catalyst and reaction, etc. The effect of ΔT can, therefore, accelerate or reduce the rate of a catalytic reaction.

In a heterogeneous catalytic system the chemisorption of the reactant molecules and the conversion reaction itself are characteristically limited to a monolayer of molecules at the catalyst surface. In our model we have assigned the special properties of the molecular species in this monolayer in terms of the thermodynamic excess quantities of the reaction surface. The conversion rate itself is an excess rate: it is very large in the reaction surface and negligible in the two adjacent bulk phases. There is also an excess energy or enthalpy, which is assigned to—i.e. stored in—the reaction surface. This energy or enthalpy is contained in bonds and vibrations of chemisorbed species which participate in the reaction as reactants, products, or the more complex activated state which determines the reaction rate \mathcal{R} . The amount of energy which is released during the conversion of reactants into product molecules is proportional with the conversion rate \mathcal{R} . The production rate of reaction enthalpy increases, therefore, exponentially with the reaction temperature T^r .

In a steady state, the released enthalpy surplus must be first temporarily physically stored in the separate thermodynamic system of the reaction surface. At the molecular level this system will only contain chemisorbed reactants and products. The products of the conversion are, therefore, molecular species in an excited state.

The relaxation of these molecules, slowly or fast, to a ground-state energy constitutes the microscopic equivalent of a heat flow in the two-dimensional reaction surface. This heat flow will be proportional with $(T^r - T^m) = \Delta T$, as in Fourier's law. The heat surplus that is generated by the conversion should eventually flow out of the reaction surface and be transferred to the catalyst at the surface temperature T^m because there should be no energy accumulation in the 2-D reaction surface in a steady state.

But within the 2-D reaction surface there is also a possible exchange of energy between excited states of the adsorbed reactant and product molecules. A fraction of the initially temporarily stored excess enthalpy in the reaction surface is not transferred “up the reaction path” to reactant molecules, and by creating excited reactant species, it contributes to the rate of the conversion reaction. In the language of the thermodynamics of irreversible processes: it could create a “cross effect”, an extra, thermally driven contribution to the activated conversion rate.

This issue would be intensively investigated and discussed in the following paper, in which irreversible thermodynamics is applied to the 2-D reaction surface. The coupling between heat flux in the 2-D reaction surface and the reaction rate may cause a deviation from a linear relation between the driving forces ΔT and the fluxes of reaction rates.

Such a coupling between a thermal flux and a chemical conversion is forbidden in homogeneous bulk systems by the Curie–Prigogine principle but not in an anisotropic or two-dimensional reaction surface, which thermodynamically represents the active heterogeneous catalyst surface. This coupling would discriminate between thermodynamic properties of homogeneous and heterogeneous catalysis in a hitherto unexplored fashion. Such a study of coupling could give new insights about thermal properties affecting rate enhancement and selectivity in active heterogeneous catalysts.

There exist several experimental observations on excess thermal energies of chemisorbed species which participate in the catalytic oxidation of CO on Pt catalysts. One is the observation by Watanabe et al.²⁰ and Mullins et al.,²¹ who investigated the energy excesses in product molecules after CO oxidation reactions. They report that CO₂ molecules are ejected from the Pt surfaces where they were produced with a translational, vibrational, and rotational energies in excess of what would be expected from a thermal equilibrium at the catalyst surface temperature T^m . These results are also discussed in the review paper by Nieuwenhuys.²²

King et al.²³ investigated CO oxidation on a Pt(110) catalyst. Using the technique of single-crystal adsorption microcalorimetry, they found that, with CO dosed onto an oxygen-saturated overlayer, the CO₂ (product) molecules carried little (9 ± 17 kJ/mol) internal energy in excess of thermal equilibrium at T^m . But, with oxygen gas attacking an adsorbed CO overlayer, the product CO₂ molecules had a definitely positive excess energy of 52 ± 21 kJ/mol.

The essential aspect of all these results is that, even after desorption, the CO₂ molecules were at higher energy levels than would correspond to the thermal equilibrium at T^m . Along a

different line of reasoning it is found, again, that the actual temperature T^* , which controls the rate of the catalytic reaction, was different and higher than the measured temperature in the catalyst. The real reaction temperature T^* indicates how much extra bond energy is stored, temporarily, in the heat capacity of the CO₂ product molecules. The heat capacity of the reactant and product molecules and the temporary storage of a part of reaction enthalpy in the reaction surface, which is used later by next surface reactions, create the effective temperature T^* of the reaction surface. The temperature T^* , in turn, determines the reaction rate, via Arrhenius' equation. The heterogeneous catalytic system comes into a steady state, both chemically and thermally. In the thermally equilibrated reaction surface T^* represents a steady percentage of the chemisorbed molecules populating excited states.

Conclusion

The real reaction temperature T^* in the 2-D reaction surface of an active heterogeneous catalyst is different from the measured temperature T^m in the catalyst surface or the temperature T^s of the medium. In the exothermic CO oxidation reaction over a supported Pd catalyst, the assumption of a surface temperature excess $\Delta T = T^* - T^m$ leads to a consistent kinetic model for the reaction. In this model the corrected Arrhenius plot for catalytic CO oxidation on a Pd/ γ -Al₂O₃ catalyst is linear, with a constant activation energy $E_a = 63.8$ kJ/mol.

In this catalytic system the surface temperature excess ΔT is positive, between 10 and 60 K depending on the reaction rate. This temperature excess in the reaction surface accelerates the reaction rate at the catalyst surface, whereas the activation energy of the catalytic reaction is higher than anticipated. This results in new predictions for the activity and the selectivity of the chosen catalyst under process conditions. The reaction surface, which is considered as a separate thermodynamic system in the modeling of heterogeneous catalysts, opens an

alternative line in the investigations on better and more selective catalyst materials.

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