Correlations between substituent effects for surface reactions and catalytic reactions

Mark T. Buelow, Andrew J. Gellman [*]

Department of Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, USA

Abstract

Minor changes or substitutions in the structure or composition of reactants can have profound effects on reaction kinetics. The effects of substituents on surface and catalytic reaction kinetics can be understood through the use of semi-quantitative empirical correlations such as the Hammett relation. These correlations provide a basis for comparison of reaction kinetics in varying environments. For example, comparisons can be made between reaction kinetics measured on single crystals under ultra-high vacuum (UHV) conditions and reaction kinetics measured on catalysts at high pressures. Doing so offers a means of translating insights obtained from studies of surface chemistry into the field of catalysis. One such insight is into the nature of the transition states for heterogeneously catalyzed reactions. An example discussed in this article compares β-hydride elimination of alkoxides on Cu(111) with alcohol dehydrogenation over ZnO–Cr$_2$O$_3$. In both systems inductive substituents (R) decrease the reaction rate suggesting that the transition state for the rate limiting step in both reactions has an electron deficient carbon atom (RC$^{\delta+}$ $\cdots$ H). A second example, phenyl coupling on the Ag(111) surface exhibits an increase in rate due to inductive substituents. This observation is consistent with observations of homogeneously catalyzed phenyl coupling described in the literature. These comparisons demonstrate the potential for using Hammett correlations measured in surface science studies to understand important issues in catalysis. © 1998 Elsevier Science B.V.

Keywords: Surface reactions; Catalysis; Hammett correlations

1. Introduction

Given that catalysis is fundamentally a problem in controlling reaction kinetics, it follows that our understanding of surface catalyzed reactions would benefit greatly from a deeper understanding of the nature of transition states and the activation barriers to surface reactions. Complex catalytic reactions are usually described as single or branching sequences of elementary steps leading from reactants through reaction intermediates to one or more products.

$$R \xrightarrow{k_a} I_1 \xrightarrow{k_r} I_2 \xrightarrow{k_d} P$$
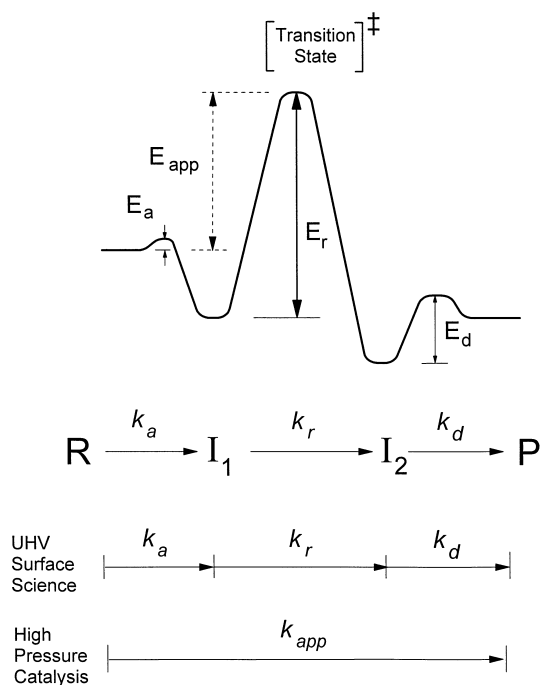
---
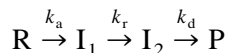
[*] Corresponding author.

Fig. 1. One dimensional potential energy surface of a hypothetical catalytic reaction. In each elementary step an intermediate proceeds from an initial state to the next intermediate by passing over an activation barrier. A transition state exists at the top of each barrier. The kinetics of each elementary step can be selectively studied with surface science techniques. High pressure catalysis studies typically measure reaction rates for the entire sequence of steps, the overall rate of which is determined by the slowest step with the largest activation barrier. The activation energies are E_a (adsorption), E_r (surface reaction), E_d (desorption) and E_{app} (apparent activation energy). The rate constants are k_a (adsorption), k_r (surface reaction), k_d (desorption) and k_{app} (apparent rate constant for the overall reaction.

Each elementary step converts one species into the next by passing over an energy barrier (Fig. 1). This activation barrier (E_a) is the dominant term in the rate constant (k) and controls the kinetics of each step [1]. The magnitude of the activation barrier is determined by the energy difference between the intermediate and the activated complex or transition state. While our understanding of the nature of many reaction intermediates is quite detailed, our understanding of the nature of the transition states for surface reactions is comparatively sparse. Some characteristics of the transition states for several important surface reactions have been obtained through the use of substituent effects. The reactions studied include β-hydride elimination of alkoxides [2,3], coupling of alkyl groups [4], and symmetric coupling of phenyl groups [5]. This paper summarizes the insights into these reactions that have been obtained from surface science experiments in ultra-high vacuum (UHV) and establishes the initial connections to observations made of the same reactions under high pressure catalytic conditions.

While studies of catalytic reactions must by their nature measure the kinetics of complex reaction pathways which convolute the kinetics of multiple steps, surface science approaches are better able to isolate individual elementary steps. It is crucial, however, to determine the relevance of surface science results by making comparisons to the catalytic systems that are so often cited as the motivation for surface science research. In some instances it is possible to make direct comparison between rate constants, activation energies, or product distributions measured for reactions on single crystal surfaces and on high surface area catalysts [6,7]. Another approach which is suggested in this paper is the comparison of substituent effects on reactions performed on single crystal surfaces and on

catalysts. Such an approach requires measurement and comparison of reaction kinetics using sets of substituted reactants (i.e., RCH_2OH, R = H, CH_3, CF_3, C_2H_5, etc.). The effects of the substituents on the reaction kinetics can be used to establish linear free energy relationships (LFERs) such as the Hammett relation,

$$\log\left(\frac{k_R}{k_H}\right) = \rho\sigma_R,$$

where σ_R is the Hammett parameter for any given substituent. The rate constants for the substituted and unsubstituted reactants are k_R and k_H, respectively while ρ is characteristic of the reaction. Linear free energy relationships have been used to characterize a number of heterogeneously catalyzed reactions [8]. Surface science results can be compared to these catalytic results by comparison of the linear free energy relationships determined for a reaction studied on both a single crystal surface in UHV and over a catalyst at high pressure.

In order to make a meaningful comparison between reaction kinetics on single crystal surfaces and on catalysts, several conditions must be satisfied. The reaction rates on both must be limited by the same elementary step. Generally, there are more steps involved in catalytic processes than in reactions studied on single crystal surfaces. Thus, in real catalytic systems more steps have the potential to be rate determining. As illustrated in Fig. 1, the rate constant for the catalytic process is a convolution of several elementary rate constants while in the idealized surface science experiment one can isolate a given elementary step. Nonetheless, if the rate of the catalytic reaction is dominated by the barrier to one elementary step and this is the same step that is isolated in the surface science experiment, substituent effects measured in both systems should be comparable.

1.1. Substituent effects

Comparison of the reaction kinetics of molecules that differ slightly in structure provides substantial information about a reaction [8,9]. For a given reaction, such as deprotonation or dehydration,

$$RCO_2H \rightarrow RCO_2^- + H^+$$

$$RCH_2CH_2OH \rightarrow RCH=CH_2 + H_2O$$
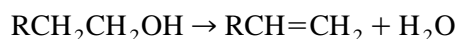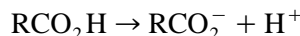
differences in kinetics among the substituted reactants can be correlated to properties of the substituents (R), provided that the rate limiting step is the same for all reactants and does not change as a result of substitution. The most common form of substitution is isotopic substitution which can be used to probe reaction mechanisms. For example, the kinetics of breaking a C–H or C–D bond differ substantially. Although the potential energy surfaces for the two processes are identical, the kinetics differ because of differences in zero point energy. Non-isotopic substitutions are more complex in nature in the sense that they influence the potential energy surface of the reaction under observation. The use of electronegative substituents will influence reaction kinetics by altering the activation barriers for polar transition states such as the one expected for a reaction such as deprotonation.

$$RCO_2H \rightarrow \left[RCO_2^{\delta-} \cdots H^{\delta+}\right]^{\ddagger} \rightarrow RCO_2^- + H^+$$
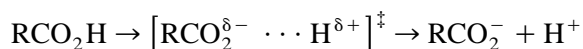
In a complex chemical reaction involving a number of elementary steps, the comparison of rates within a set of substituted reactants can be meaningful provided that the mechanism remains the same for all substituted reactants and, consequentially, that the rate limiting step is the same in each case.

An appreciation of the manner in which substituents alter reaction kinetics can be obtained from transition state theory. Within the framework of transition state theory, intermediates pass from one intermediate to the next through a transition state [1]. The rate constant for each such step is expressed as: $k = \nu \exp(-E_a/RT)$. The values of the pre-exponent, ν, and activation energy, E_a, depend only on the relative properties of the initial state and the transition state. For a set of substituted molecules whose structures are sufficiently similar, the variation in ν is minor compared to the effect of E_a. The magnitude of the activation energy is relative and the effect of the substituent is on the energies of both the initial state and the transition state.

Substituents can stabilize or destabilize reaction intermediates and transition states in a variety of ways. Substituents with different inductive abilities probe changes in the electronic structure or electron distribution on going from reactant to transitions state [9,10]. The inductive effect can be divided into a through space field effect or a through-the-bond electronegativity effect. Since it is quantitatively difficult to separate these effects, they are typically treated together and simply called the inductive effect [11]. The current understanding is that field effects dominate under most circumstances [10,11]. Electronegativity effects are generally negligible if the highly electronegative atom of the substituent is separated from the reaction center by more than one atom [10]. That is the case for all substituents discussed in this paper and thus all inductive effects described in this work can be attributed to field effects. Field effects are due to the interaction of polar substituents with the charge distribution of the reactant or the transition state. They are not the result of changes in the charge distribution induced by the presence of the substituent. Field effects can stabilize or destabilize a given charge distribution, but they will not alter the charge distribution. Highly inductive substituents stabilize electron-rich species and destabilize electron-deficient species, thus, measurements of activation barriers provide information about changes in the nature of charge separation in the transition state relative to the initial state. An illustration of this effect for the β-hydride elimination reaction in adsorbed ethoxides is given in Fig. 2. In that case the substituted ethanols in the gas phase serve as the reference energy level and there is very little effect of fluorination on the heat of formation of the substituted ethoxides. Using this reference scale one can ascribe the effects of fluorine substitution to its influence on the energy of the transition state which in this case has a carbon atom which is cationic or electron deficient with respect to the initial state ethoxide (or ethanol).

Inductive effects which can be used to probe the electronic structure of transition states can be masked by steric effects that result from changes in the size or shape of the reactant species. Steric hindrance is generally an unwanted substituent effect from the point of view of analysis because it is difficult to quantify. Therefore, it is desirable to utilize substituents that will minimize steric effects. Steric considerations are especially important for surface reactions since the reacting species are in such close proximity to a relatively large rigid structure. In the work described in this paper most of the substitutions have replaced hydrogen with fluorine. This substitution is probably so effective because the relatively small difference in size between groups such as $-CH_3$ and $-CF_3$ minimizes steric effects [12].

Fluorine is an ideal substituent for determining electronic properties of reactants and transitions states on surfaces. The high electronegativity of fluorine can have dramatic stabilizing or destabilizing effects on polar species. The inductive ability of fluorine will energetically destabilize a cationic or electron deficient species and will stabilize an electron rich or anionic species. Furthermore, as mentioned, the small size of fluorine also minimizes the concern of steric hindrance with the surface. The C–F bond is also extremely strong which renders the substituent stable on several metal surfaces. Since fluorine substitution is not done at the reaction center for any the reactions studied in this work,
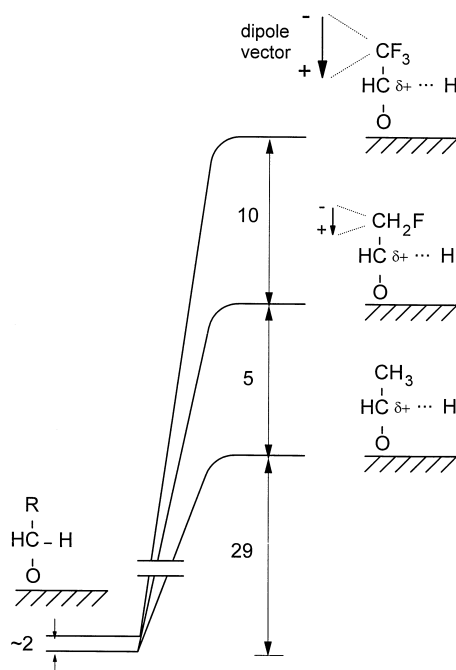
Fig. 2. Schematic illustration of substituent effects on β-hydride elimination in ethoxides. The activation barrier increases with increasing inductive character of the substituent. The manner in which a highly inductive substituent can destabilize a transition state is illustrated. For this example, a positive charge at the α-carbon is destabilized by the dipole of the fluorinated methyl group. The units of the activation energies are kcal/mol.

the fluorine only influences energetics through field effects and does not induce changes in charge distribution at the reaction center.

1.2. Linear free energy relationships

Substituent effects can be quantified empirically through the establishment of linear free energy relationships (LFERs) which correlate reaction rate constants (k) with empirically defined substituent constants (σ) [9]. Linear free energy relationships have been used extensively in physical organic chemistry, but have only received minor attention in the field of heterogeneous catalysis [8,9]. One type of LFER for a given reaction is based upon the Hammett equation whose general form is,

$$-\left(\Delta G_R^\ddagger - \Delta G_0^\ddagger\right)/RT \propto \log k_R/k_0 = \rho\sigma_R.$$

The values $\Delta G_R^\ddagger$ and $\Delta G_0^\ddagger$ are the free energies of activation for the reaction using substituted and unsubstituted reactants. The rate constant for the substituted reactant k_R is normalized by reference to the rate constant for the unsubstituted reactant, k_0. The reference substituent is hydrogen for the Hammett relationship and the reaction used for the empirical determination of the substituent constant is the equilibrium dissociation of substituted benzoic acids ($\sigma_R = K_R/K_H$). The effects of a substituent on the rate of a reaction or on an equilibrium constant can arise from a number of different physical mechanisms, as mentioned above. The inductive effect can be quantified for a given substituent using the inductive substituent parameter, σ_I. A highly inductive substituent will have a large positive value of σ_I. The reaction constant (ρ), the slope of the LFER, is unique to the reaction

under study and provides valuable insight into the electronic structure of the transition state for the reaction. Roughly speaking, if $\rho < 0$, then the transition state for the reaction must have an electron deficient center adjacent to the substituent ($R-C \rightarrow [R-C^{\delta+}]^{\ddagger}$). In this case, this atom must be electron deficient with respect to the initial state and the substituent is energetically destabilizing the transition state with respect to the initial state. If $\rho > 0$, the opposite is the case and the transition state must have a reaction center which is electron rich with respect to the initial state ($R-C \rightarrow [R-C^{\delta-}]^{\ddagger}$). If $\rho = 0$, the initial state and transition state have the same charge separation, if any.

An extensive set of substituent constants has been compiled for over 500 different substituents [11]. These constants have been defined in a number of ways and have been evaluated using many different reactions. Care must be taken in choosing among the different definitions of the substituent constants since not all are based upon the same property. The original Hammett constants, σ_p and σ_m [9], were based upon the acid dissociation constants of various benzoic acids in aqueous solution. These constants contain inductive and resonance components. The inductive and resonance contributions have been factored out based upon correlations using substituents expected to have no resonance effect to generate purely inductive, σ_I, constants [11]. Since their original conception, these constants have been used to establish LFERs for many different reactions. A testament to the utility of this method is that the constants of a given type obtained from many different laboratories, under many different reaction conditions all agree rather well [11]. As the substituent constants are experimentally derived their values contain a certain degree of error and not all values have been determined with equal accuracy. Most researchers have placed their substituent constants on the same scale as the original Hammett constants so that any choice of substituent constants of a given type is valid within the accuracy of the constants. As an example of an alternative set of substituent parameters, the Taft parameters (σ^*), are based upon the hydrolysis of esters in both an acidic and a basic solution. The σ^* values are important since they represent the first definition of a substituent parameter that contains only an inductive contribution. However, the validity of values determined in this way has been disputed. Arguments against σ^* are that the transition state for ester hydrolysis is different in acid and basic solution and is likely to be solvated differently and that the constants for alkyl groups contain a steric component [13]. In spite of this the σ^* constants seem to be useful for the correlation of rate constants of reactions in aliphatic systems. Unfortunately, the original Taft parameters (σ^*) are not on the same scale as the Hammett parameters ($\sigma^*_{CH_3} = 0.0$ and $\sigma^*_{CF_3} = 2.0$ while $\sigma_{I,CH_3} = 0.01$ and $\sigma_{I,CF_3} = 0.38$) [13]. These substituents (CH_3 and CF_3) represent the extremes of the substituent parameters used for the data presented in this paper. This suggests that an appropriate scaling factor for the work reported here would be ~ 5. In this paper we have chosen to use inductive substituent constants (F or σ_I from Table 1 in Ref. [11]) which are based on correlations using the Hammett parameters rather than the Taft parameters.

2. Experimental

The measurements of surface reaction kinetics made in our laboratory have been accomplished using several ultra-high vacuum (UHV) chambers with base pressures $\sim 10^{-10}$ Torr all of which have been described in detail elsewhere [2–5]. The chambers are equipped with instrumentation for Temperature Programmed Desorption/Reaction Spectroscopy (TPD, TPRS), Fourier Transform-Infrared Reflection Absorption Spectroscopy (FT-IRAS), High Resolution Electron Energy Loss Spectroscopy (HREELS), Auger Electron Spectroscopy (AES), and Low Energy Electron Diffraction (LEED). The single crystal metal surfaces are mounted on a liquid nitrogen cooled manipulator that

can be resistively heated to provide temperature control from $T < 100$ K to $T > 1000$ K. The surfaces can be exposed to adsorbates to create intermediates that mimic those proposed to exist on catalyst surfaces [14]. These intermediates can be characterized by the various spectroscopic techniques.

TPR and TPD spectroscopy are the methods used to obtain all the rate constants presented in this article. The initial intermediates for the surface reaction of interest are generated on the surface in a variety of ways, but all at temperatures low enough that the intermediates are stable. The surface is then heated in front of a mass spectrometer and the desorption of product gases is monitored. The mass spectrometer signal can be analyzed using various techniques to provide values of the rate constant. If desorption is the rate limiting step, the result is a measure of the kinetics of desorption (TPD), however, if the desorption is fast compared to the reaction step, then the reaction is rate limiting and the desorption of the product is a measure of the reaction rate (TPRS). The details for the acquisition of the rate constants for β-hydride elimination [2,3], alkyl coupling [4], and phenyl coupling [5] can be found in the literature.
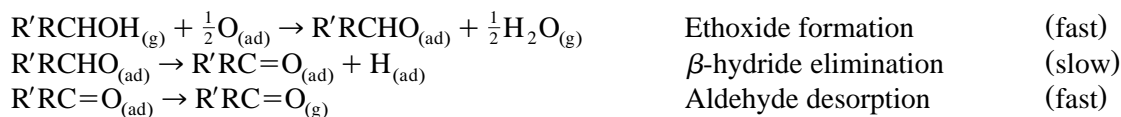
3. Results

This article describes substituent effects for several different reactions on metal surfaces and then draws comparisons with results obtained on supported catalysts in several different laboratories around the world. The first reaction is the β-hydride elimination of alkoxides on Cu(111) [2,3]. The results of the study of this reaction will be compared to observations of ambient pressure dehydrogenation of alcohols on a ZnO–Cr_2O_3 catalyst as published by Gulková and Kraus [15,16]. The second reaction, alkyl coupling, also provides an example of the use of substituent effects in a surface reaction although, thus far, we have found no high pressure analog to this process [4,17–19]. Finally, the coupling of phenyl groups to form biphenyl will be discussed [5,20–27]. Comparison will be made to an important solution phase reaction known as the Ullmann biaryl coupling reaction. The effect of substituents on the phenyl coupling reaction will be compared with substituent effects on the alkyl coupling reaction.

3.1. β-hydride elimination

Dehydrogenation occurs in many technologically important processes including the production of aldehydes and ketones from alcohols and the production of olefins from alkanes [28–32]. The most commonly proposed mechanism for the dehydrogenation of alkyl groups on surfaces is β-hydride elimination. This process has been observed in UHV surface science studies [2,3,14,31–35] and in real catalytic processes [28–30]. Although the mechanistic details are well documented, information about the nature of the transition state for β-hydride elimination is lacking [31,32]. With the use of substituent effect probes, the electronic characteristics of the transition state for β-hydride elimination in alkyl and in alkoxides have been determined on the Cu(111) surface. The conclusion of these investigations is that during β-hydride elimination the carbon atom at which the C–H bond is being broken is electron deficient in the transition state with respect to the initial state (R–CH $\rightarrow$ [R–C$^{\delta+}$ $\cdots$ H]‡) [2,3,35].

A fairly detailed understanding exists of the mechanism of primary and secondary alcohol dehydrogenation on metal surfaces [31]. The first step in the reaction of an alcohol with many metal surfaces is deprotonation of the hydroxyl to yield an adsorbed alkoxide. Alkoxides have been identified on many surfaces using a variety of spectroscopic techniques. With the use of FT-IRAS the

orientation of several ethoxides has been determined [36]. It has been determined that the alkoxides are bound to the surface through the oxygen atom. On some surfaces deprotonation occurs when the surface is clean, but for other surfaces such as those of copper or silver, the surface must first be oxidized [31,32]. On these pre-oxidized surfaces, the adsorbed alcohol deprotonates to form the alkoxide and water. Under appropriate conditions all of the pre-adsorbed oxygen will leave the surface as water. The alkoxides are stable species at low temperatures but ultimately decompose during heating by the β-hydride elimination reaction in which the C–H bond adjacent to the oxygen atom is cleaved to deposit hydrogen on the metal surface. The remaining product is an aldehyde or ketone which then desorbs from the surface. The mechanism of this process can be expressed as:

$$R'RCHOH_{(g)} + \tfrac{1}{2}O_{(ad)} \rightarrow R'RCHO_{(ad)} + \tfrac{1}{2}H_2O_{(g)} \qquad \text{Ethoxide formation} \qquad \text{(fast)}$$
$$R'RCHO_{(ad)} \rightarrow R'RC=O_{(ad)} + H_{(ad)} \qquad \text{β-hydride elimination} \qquad \text{(slow)}$$
$$R'RC=O_{(ad)} \rightarrow R'RC=O_{(g)} \qquad \text{Aldehyde desorption} \qquad \text{(fast)}$$

Substituted ethanols react on the surface to form ethoxides and then deprotonate to form acetaldehydes. On the Cu(111) surface fluorination of the methyl group in ethoxide to give $CF_3CH_2O_{(ad)}$ results in an increase in the overall reaction barrier of ~ 15 kcal/mol [2].

In order to be absolutely certain that the rate determining step is in fact the β-hydride elimination reaction for both ethoxide and trifluoroethoxide, the dehydrogenation of selectively deuterated ethoxides were studied. Deuterium substitution at the β-position decreased the rate for both ethoxide and trifluoroethoxide. Thus, β-CH dissociation is rate determining for both intermediates and fluorination does not change this fact. The amount by which isotopic substitution decreased the rate was also the same for both, indicating that the mechanism of the bond breaking process is not significantly altered by fluorination.

In trying to understand the effects of substituents on the overall kinetics of this process it is important to know whether the effect of fluorination is on the energetics of the initial state alkoxide or the transition state. To test the effect of fluorination (R', R = CH_3, CFH_2, CF_2H, CF_3) on the heats of adsorption of alkoxides on Cu(111) the equilibrium reaction,

$$CF_3CH_2OH_{(g)} + CH_3CH_2O_{(ad)} \Leftrightarrow CF_3CH_2O_{(ad)} + CH_3CH_2OH_{(g)}$$
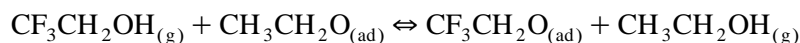
was studied [2]. This was accomplished by exposing the surface to a mixture of ethanol and trifluoroethanol concurrently until equilibrium coverages of each ethoxide were formed. The relative coverage of ethoxide vs. trifluoroethoxide was determined by monitoring the desorption of the corresponding acetaldehyde of each with a mass spectrometer. The heats of dissociative adsorption were found to differ by ~ 2 kcal/mol. The minimal effect of fluorination on the heat of adsorption is a general conclusion carried to our analysis of other reactions involving the use of fluorine substituent effects. Based on this, it has been concluded that the major contribution to the increase in activation energy that results from fluorination of the methyl groups is a transition state effect.

β-hydride elimination has been studied in an extensive set of alkoxides on the Cu(111) surface (primary: $CF_nH_{3-n}CH_2O_{(ad)}$, $n = 0–3$ and secondary: $RR'CHO_{(ad)}$, R, R' = CH_3 or CF_3) [2,3]. The Cu(111) surface was chosen due to its success as a catalytic dehydrogenation catalyst and thus much of the early work which served as the basis for this investigation was performed with this material [30–32]. Increasing the inductive character of the substituent by adding fluorine increased the activation energy for β-hydride elimination (Fig. 2). For the ethoxides full fluorination of the methyl group resulted in an increase of 15 kcal/mol in the activation energy. Since it has been demonstrated that fluorination does not significantly affect the ethoxide formation energetics, the effect of fluorination is to destabilize the transition state. On this energy scale, using the gas phase ethanols as
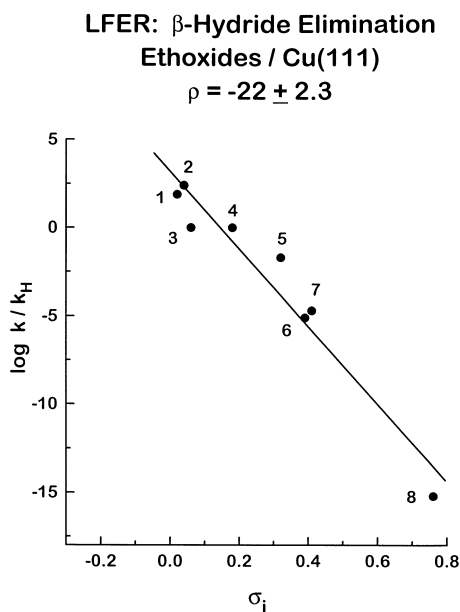
LFER: β-Hydride Elimination
Ethoxides / Cu(111)
ρ = -22 ± 2.3

Fig. 3. Linear free energy relationship (LFER) for β-hydride elimination of primary and secondary alkoxides on Cu(111). The rate constants, k/k_H, are evaluated at 300 K and referenced to the rate constant for methoxide. The substituent constants, σ_I, are the inductive parameters, F, obtained from Table 1 of Ref. [11]. The slope of the plot is the reaction constant, $\rho = -22 \pm 2.3$. The rate constant for β-hydride elimination is lowered by inductive substituents as indicated by the negative slope of ρ. $1 = (CH_3)_2CHO_{(ad)}$, $2 = CH_3CH_2O_{(ad)}$, $3 = CH_3O_{(ad)}$, $4 = CH_2FCH_2O_{(ad)}$, $5 = CHF_2CH_2O_{(ad)}$, $6 = CF_3CH_3CHO_{(ad)}$, $7 = CF_3CH_2O_{(ad)}$, $8 = (CF_3)_2CHO_{(ad)}$.

the reference state, the transition state for the β-hydride elimination reaction must be electron deficient with respect to the initial ethoxide (or ethanol).

The primary goal of this article is to illustrate the correlation that can be made between substituent effects that we observe on single crystal metal surfaces and observations made using supported catalysts for similar reactions. The results of our observations on surfaces have been quantified in the form of a LFER plotted in Fig. 3. The rate constants for β-hydride elimination in several alkoxides are given relative to that for methoxide. The quantity $\log k/k_H$ is plotted against the inductive substituent constants, σ_I, for the β-hydride elimination of primary and secondary alkoxides on Cu(111). The resulting linear correlation has a reaction constant (slope), with a value of $\rho = -22 \pm 2.3$. It is interesting to note that this value is larger than those typically found in solution phase where $|\rho| < 7$ and is closer in magnitude to those typically found for gas phase reactions [9,10].
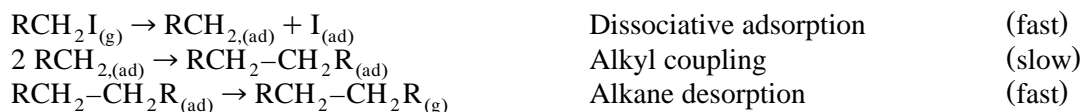
The results of our study of β-hydride elimination in alkoxides on surfaces can be compared to the results of studies of the dehydrogenation of alcohols on supported catalysts. The two reactions are very similar although the alcohol dehydrogenation process involves several steps, one of which is thought to be β-hydride elimination. Gulková and Kraus [15,16] studied the dehydrogenation of many primary and secondary alcohols on a Na modified ZnO–Cr$_2$O$_3$ catalyst. This work was done at atmospheric pressure and 360°C in a model flow reactor. With the use of deuterium labeling, they determined that the α-CH bond dissociation was rate determining in their system. (Note: We refer to dissociation of the α-CH bond in alkoxides of the form RCH$_2$O$_{(ad)}$ as β-hydride elimination in order to retain consistency with discussions of the same reaction in adsorbed alkyls of the form RCH$_2$CH$_{2,(ad)}$). Since this is the same rate determining step as in our UHV study on Cu(111), the results are expected to be comparable. They plotted their results in a LFER using Taft substituent

constants, σ^*, and found a strong correlation with a reaction constant of $\rho^* = -1.43$. The negative slope of the LFER led them to conclude that the transition state was electron deficient which is entirely consistent with our description of charge separation in the transition state for β-hydride elimination on the Cu(111) surface. As mentioned in Section 1.2, the scale of the substituent constants (σ^* vs. σ_I) used in this comparison differ by a factor of ~ 5. This alone does not account for the difference in magnitude between the results on Cu(111) and the ZnO–Cr$_2$O$_3$ catalyst. However, since entirely different surfaces are involved and the reactions are carried out under different conditions, it is not expected that the magnitudes should be the same. It is possible that the ZnO metal-oxide surface may stabilize the charge build-up of the transition state to a greater extent than the copper metal surface. For the purposes of this article, it is sufficient to point out that the basic trend in rate constants for the alcohols on the two materials is the same.

3.2. Alkyl coupling

Carbon–carbon bond formation is important for many heterogeneously catalyzed processes including the Fischer–Tropsch (FT) process [28]. Alkyl coupling is important in that it is a termination step in the FT process. Alkyl coupling is also important because it is the reverse of hydrocarbon cracking [28,29]. In a hydrocarbon cracking process, alkyl coupling is an undesired side reaction since it increases the length of the carbon chain. Therefore, an understanding of the factors which influence alkyl coupling kinetics is important for its suppression. In spite of its widespread occurrence, the nature of C–C bond formation is not well understood. Alkyl coupling has been identified in several surface science studies [4,17–19], but kinetic information for this process is lacking in the catalytic literature.

The effects of fluorinated substituents on the alkyl coupling reaction have been measured on the Ag(111) surface using several alkyl groups (RCH$_{2,(ad)}$: R = H, CH$_3$, CH$_2$CH$_3$, CH$_2$CF$_3$) [4]. The results of these measurements can be combined with the results of Zhou et al. [18,19] to make an extensive LFER. The Ag(111) surface was chosen because alkyl groups on its surface selectively couple to form long alkanes rather than undergoing β-hydride elimination [4,17–19]. The adsorbed alkyl groups are formed by the dissociative adsorption of the appropriate alkyliodide. Upon heating, the alkyl groups dimerize to form an alkane which desorbs rapidly from this surface. The reaction mechanism can be expressed as:

$$\text{RCH}_2\text{I}_{(g)} \rightarrow \text{RCH}_{2,(ad)} + \text{I}_{(ad)} \qquad \text{Dissociative adsorption} \qquad \text{(fast)}$$
$$2\,\text{RCH}_{2,(ad)} \rightarrow \text{RCH}_2\text{–CH}_2\text{R}_{(ad)} \qquad \text{Alkyl coupling} \qquad \text{(slow)}$$
$$\text{RCH}_2\text{–CH}_2\text{R}_{(ad)} \rightarrow \text{RCH}_2\text{–CH}_2\text{R}_{(g)} \qquad \text{Alkane desorption} \qquad \text{(fast)}$$

The substituent effect is illustrated in Fig. 4. The effect of fluorination is clearly to decrease the rate of coupling as the inductive character of the substituent is increased. The reaction constant is $\rho = -15 \pm 2.7$. This is consistent with a transition state which is electron deficient with respect to the initial state of alkyl species on Ag(111). With the observation of ν_{CH} mode softening in IR spectra [37] and theoretical calculations by Zheng et al. [38], it has been concluded that alkyl species have a partial negative charge on the surface as a result of back-bonding from the filled d-band of the metal to the σ_{CH}^* anti-bonding orbital of the alkyl species. Such an electron rich species (RCH$_{2(ad)}^{\delta-}$) would be stabilized by an adjacent inductive group like trifluoromethyl. If the transition state lacked this negative charge, stabilization of this initial state would result in an increase in the barrier to coupling. It is important to emphasize that the potential energies are only meaningful with respect to a reference
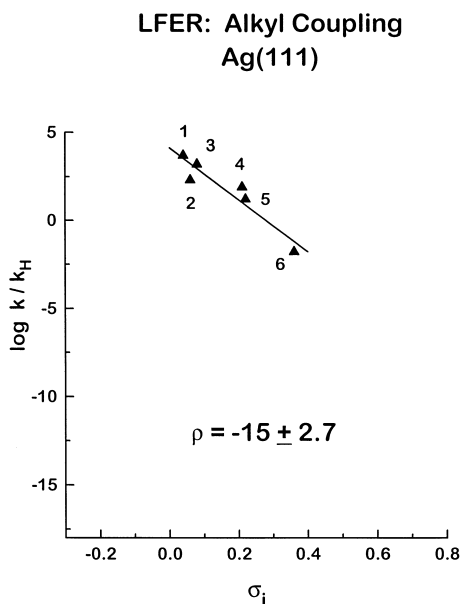
LFER: Alkyl Coupling
Ag(111)

Fig. 4. Linear free energy relationship (LFER) for alkyl coupling reaction on Ag(111). The constants, k/k_H, are evaluated at 300 K and referenced to the rate constant for methyl–methyl coupling. The substituent constants, σ_I, are based upon the inductive parameters, F, obtained from Table 1 of Ref. [11]. The slope of the plot is the reaction constant, $\rho = -15 \pm 2.7$. The rate constant for alkyl coupling is lowered by inductive substituents as indicated by the negative slope of ρ. $1 = (CH_3)_2CH-CH(CH_3)_2$, $2 = CH_3CH_2CH_2-CH_2CH_2CH_3$, $3 = CH_3CH_2-CH_2CH_3$, $4 = CH_3CH_2CH_2-CH_2CH_2CF_3$, $5 = CH_3CH_2-CH_2CH_2CF_3$, $6 = CF_3CH_2CH_2-CH_2CH_2CF_3$.

state, thus all we can claim is that the transition state is electron deficient with respect to the initial state.

3.3. Phenyl coupling

The formation of symmetric and asymmetric biaryls is an important reaction in organometallic synthesis. The Ullmann reaction, which can be described as copper catalyzed nucleophilic aromatic substitution on an aryl halide, has proven to be successful at formation of biaryls and several reviews of this process in solution phase can be found in the literature [20–23]. The mechanism of the Ullmann reaction is still the subject of debate [20–27]. It is generally accepted that an aryl-copper species reacts with an aryl halide. One issue is whether the coupling occurs on the Cu surface or in solution phase. Experiments in UHV environments have demonstrated that the Ullmann reaction can be carried out entirely on a copper surface [5,24,25], but in solution phase a homogeneous reaction cannot be ruled out. For coupling on the Cu surface, two possibilities exist, both of which are initiated by the formation of a surface bound aryl species by dissociation of the aryl-halogen bond. The copper-aryl species may then react with other surface aryl groups formed in similar fashion or directly with adsorbed aryl-halide to produce biaryl. Both reactions have been witnessed, however, the phenyl–phenyl coupling reaction dominates at low coverages and occurs at high temperatures [24,25].

One interesting feature of the phenyl coupling reaction is that it is an analog of the alkyl coupling reaction, but uses reactants with no C–H bond adjacent to the metal surface. Thus, there is no opportunity for the back-donation of electrons from the metal that renders the alkyl groups electron-rich. To probe the effects of this difference, substituent effects have been measured for the coupling of phenyl groups on the Cu(111) surface. A set of substituted iodobenzenes were used to

determine the electronic nature of the transition state for phenyl coupling [5] ($I–C_6H_4–R$, $R = H$, m-CH_3, p-F, m-F, and o-F). Only the symmetric coupling reactions were studied and the coverage of phenyl groups was kept low so only the coupling of adsorbed phenyl groups was observed. At approximately 175 K the C–I bond dissociates to form phenyl groups and iodine on the surface, reaction (1). At approximately 380 K, phenyl groups couple to form biphenyl, reaction (2) which rapidly desorbs, reaction (3).
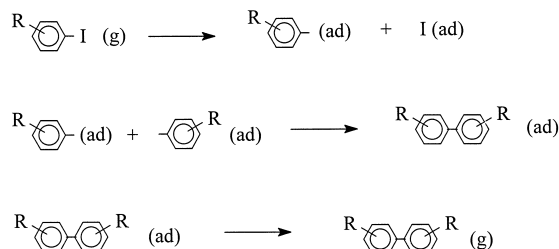
Xi and Bent [24,25] demonstrated that the coupling reaction is the rate determining step.

Increasing the inductive character of the substituent increases the phenyl coupling rate. This is opposite to the effect on the alkyl coupling reaction. A LFER correlating reaction rate constants with substituent constants yields a slope of $\rho = 2.9 \pm 1.5$ (Fig. 5). In this LFER the rate constants are plotted vs. the $\sigma°$ substituent constants so that there is no resonance contribution [9]. Using the $\sigma°$ parameters allows comparison to the other reactions presented in this paper that also use inductive

LFER: Phenyl Coupling
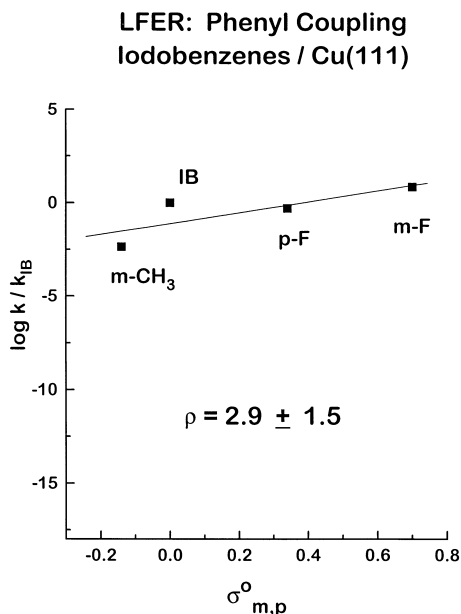**Iodobenzenes / Cu(111)**

Fig. 5. Linear free energy relationship (LFER) for the symmetric phenyl coupling reaction on Cu(111). The rate constants, k / k_{IB}, are evaluated at 300 K and referenced to the rate constant for iodobenzene. The substituent constants, $\sigma_m°$ or $\sigma_p°$, are the normalized Hammett parameters with no resonance component obtained from Ref. [9]. The slope of the plot is the reaction constant, $\rho = 2.9 \pm 1.5$. The rate constant for phenyl coupling is increased slightly by inductive substituents as indicated by the positive value of ρ. Note: IB = iodobenzene, the substituents of the other phenyl groups are given on the figure.

parameters with no resonance component. The rate constants increase due to a lower activation barrier resulting from a transition state that is electron-rich with respect to the surface phenyl species. This result can be directly contrasted to alkyl coupling on the Ag(111) surface, where $\rho = -15$ [4]. The correlation is not as good for the phenyl coupling reaction, but the LFER is clearly different from alkyl coupling, both in magnitude and in sign. This is partly the result of the bonding of the initial intermediates with the surface. As mentioned above adsorbed phenyl groups lack the $\sigma_{C-H}*$ anti-bonding orbitals that are responsible for back-bonding in alkyl groups. Thus, the initial states will be affected differently by inductive substituents.

Comparison can be made between the phenyl coupling reaction on the Cu(111) surface and the homogeneously or heterogeneously catalyzed Ullmann biaryl synthesis carried out in solution. It has been found that the reaction constant for copper assisted nucleophilic substitution is positive and small in magnitude, $\rho = 0.0$ to 1.1, indicative of a nucleophilic process [21]. In general it is observed that inductive substituents increase the rate of the Ullmann reaction in solution, as they do on the Cu(111) surface. For CuBr catalyzed condensation of $C_6H_5O^-K^+$ with bromobenzenes at 170°C, the reaction constant is 0.61 [26]. This result also seems to be true for nickel complexes where $\rho \sim 1$ for the reaction of *o*-anisylnickel(II)bromide with *para* substituted bromobenzenes in benzene solution and 80°C [27]. This result is comparable to the result obtained on the Cu(111) surface of a small positive value for ρ and an electron rich or nucleophilic transition state. One striking contrast is the coupling of *o*-F substituted phenyl groups on the Cu(111) surface which occurred at a much lower rate than other phenyl groups. By comparison *ortho* substitution of electron withdrawing groups is observed to cause a remarkable increasing in the rate of coupling in solution phase reactions [21]. On the surface it may be that steric effects are much more pronounced than in solution and inhibit the reaction for the *ortho* substituted reactants.

4. Discussion

One of the primary goals of the work described in this paper has been to correlate systematic trends observed in surface reactions with trends observed in catalytic systems. In order for meaningful comparison to be made between surface science and high pressure catalytic studies, a few conditions must be satisfied. First, it is crucial that the kinetics of the same step are being compared. In the catalytic process where many steps are involved, the overall rate is controlled by the rate determining or the slowest step. The rate law for a sequential mechanism includes rate constants and equilibrium constants for steps up to and including the rate determining step. The rate determining step of the catalytic study must be clearly identified so that the rate constant for the same step may be measured in the surface science study. Identification of the rate determining step in catalytic work is often difficult. The ability of the surface scientist to control surface intermediates by controlling surface exposure and temperature make isolation of one reaction step easier. It must also be clearly established that mass transfer to and from the catalyst surface is not rate limiting in the high pressure studies. Second, since substituted and unsubstituted species may react with different mechanisms, it must be established that all species used in the LFER react via the same mechanism with the same rate determining step. A substituent may inhibit the reaction to such an extent that an alternative reaction pathway may become preferred. Third, in order to obtain a meaningful LFER, a wide range of substituents with a wide range of σ values must be used. Unfortunately, this point is often missed in the literature. Alkyl substituents alone cannot provide a wide enough range of inductive character to adequately correlate electronic properties since alkyl groups all have nearly the same inductive

ability and very similar substituent constants ranging in value from $\sigma = -0.02$ to 0.03 [10,11]. Studies of alkyl substituted compounds are common in the literature [14,29,30,34], but data using species with substituents having a significant range of inductive abilities is very limited. Another limitation is the need to compare the reaction on the same surfaces in both studies. Different surfaces may stabilize charge at the reaction center to a different extent. Reactions taking place on different surfaces may exhibit differing magnitudes of the reaction constant, but the sign should remain the same provided the surface does not cause a change in the reaction mechanism. Thus, a reversal in sign of the reaction constant for a reaction on two different surfaces would indicate a change in mechanism or rate determining step.

Substituent effects have been used to determine the effect of molecular structure on the dehydrogenation of alcohols on supported catalysts [8,15,16,39–41]. The work performed by Gulková and Kraus [15,16] on ZnO–Cr_2O_3 correlated best with our study. As mentioned earlier, the conclusion that the transition state is electron deficient for α-CH bond breaking during alcohol dehydrogenation is the same as our conclusion on $Cu(111)$ surfaces, the difference being that the magnitude of the effect is different. The LFER for both sets of data resulted in a negative reaction constant, ρ. The work by Gulková et al. utilized the most extensive range of inductive substituents of any we found in the catalytic literature. It also satisfied the criterion of identifying the same rate determining step as our study, breaking of the α-CH bond. The weakness of the comparison is that the surfaces used are different. Differences in the magnitude of the reaction constant may perhaps be accounted for by this one discrepancy. Similar studies of alcohol dehydrogenation on hydroxyapatite [39], supported Cu [40], Pt, Pd and Rh [41], resulted in a positive reaction constant ρ. However, these studies utilized a very limited range of substituents consisting only of alkyl substituted secondary alcohols. Our work and that of Gulková et al. are rooted on a much firmer basis of inductive substituents. Even if the positive reaction constants are accepted, it is not clear that the rate determining step is the same as that of our study. For example, if deprotonation of the hydroxyl group is rate determining, a positive reaction constant would be expected since inductive substituents would destabilize a transition state of the form, $RCH_2O^{\delta-} \ldots H^{\delta+}$. As further demonstration of the weakness of using alkyl groups to determine electronic properties, the dehydrogenation of alcohols on Pt, Pd, and Rh are better fit by steric substituent constants, E_s, than by inductive constants, σ^* [41].

In order for correlations of the type presented in this paper to have value, we offer a few suggestions. First, the need to identify the rate determining step in high pressure catalytic processes is affirmed, yet again. Direct correlations can only be made if it is known that the same reactions are being compared. Linear free energy relationships used to determine electronic properties must be based upon a wide range of inductive substituents. We suggest fluorinated alkyl groups as an excellent choice of inductive substituents. Rate constants must be evaluated for molecules with more structural variation than different alkyl chain length. These points are also important to the surface scientist. A further responsibility of the surface scientist is to study the kinetics of catalytically relevant reactions on surfaces reasonably approximating the real catalyst.

5. Conclusions

Substituent effects can be a valuable tool for probing the electronic properties of transition states for reactions occurring on metal surfaces. Knowledge of the transition state can greatly aid in prediction of reaction kinetics through LFERs which provide a means of quantifying the effect of substituents. Most importantly it has been shown that these LFERs offer a means to compare surface

reactions occurring in the pristine environment of the surface science laboratory with those of the catalysis laboratory. The general conclusions of our studies correlate well with the conclusions drawn from high pressure catalytic reaction studies.

Substituent effects indicate that the transition state for β-hydride elimination is electron deficient with respect to the initial state. This seems to be a typical result of elimination reactions even in heterogeneous catalysis. Measurements of alcohol dehydrogenation at atmospheric pressure on $ZnO–Cr_2O_3$ also pointed to the same conclusion that the transition state is electron deficient [15,16]. The transition state for the coupling of alkyl groups on Ag(111) is also electron deficient with respect to the initial state. In contrast, the coupling of phenyl groups involves a transition state that is electron rich. This is entirely consistent with a nucleophilic aromatic substitution process such as the Ullmann biaryl synthesis reaction.

Acknowledgements

References

[1] K.J. Laidler, Chemical Kinetics, Harper Collins Publishers, New York, 1987.
[2] A.J. Gellman, Q. Dai, J. Am. Chem. Soc. 115 (1993) 714.
[3] Q. Dai, A.J. Gellman, J. Phys. Chem. 97 (1993) 10783.
[4] A. Paul, A.J. Gellman, J. Am. Chem. Soc. 117 (1995) 9056.
[5] J.M. Meyers, A.J. Gellman, Surf. Sci. 337 (1995) 40.
[6] F. Zaera, A.J. Gellman, G.A. Somorjai, Acc. Chem. Res. 19 (1986) 24.
[7] J.A. Rodriguez, D.W. Goodman, Surf. Sci. Rep. 14 (1/2) (1991) 1.
[8] M. Kraus, Adv. Catal. 29 (1980) 151.
[9] P.R. Wells, Linear Free Energy Relationships, Academic Press, New York, 1968.
[10] R.W. Taft, R.D. Topsom, Prog. Phys. Org. Chem. (1987) 1.
[11] C. Hansch, A. Leo, R.W. Taft, Chem. Rev. 91 (1991) 165.
[12] D.R. Lide, Handbook of Chemistry and Physics, CRC Press, Boston, 1991.
[13] C. Hansch, A. Leo, Substituent Constants for Correlation Analysis in Chemistry and Biochemistry, Wiley, New York, 1979.
[14] B.E. Bent, Chem. Rev. 96 (1996) 1361.
[15] D. Gulková, M. Kraus, Collect. Czech. Chem. Commun. 57 (1992) 2215.
[16] D. Gulková, M. Kraus, J. Mol. Catal. 87 (1994) 47.
[17] A. Paul, B.E. Bent, J. Catal. 147 (1994) 264.
[18] X.-L. Zhou, F. Solymosi, P.M. Blass, K.C. Cannon, J.M. White, Surf. Sci. 219 (1989) 294.
[19] X.-L. Zhou, J.M. White, J. Phys. Chem. 95 (14) (1991) 5575.
[20] P.E. Fanta, Synthesis 1 (1974) 9.
[21] J. Lindley, Tetrahedron 40 (9) (1984) 1433.
[22] R.G.R. Bacon, H.A.O. Hill, Q. Rev. 19 (1972) 95.
[23] M. Goshaev, O.S. Otroshchenko, A.S. Sadykov, Russ. Chem. Rev. 41 (12) (1972) 1046.
[24] M. Xi, B.E. Bent, Surf. Sci. 278 (1992) 19.
[25] M. Xi, B.E. Bent, J. Am. Chem. Soc. 115 (1993) 7426.
[26] A.J. Paine, J. Am. Chem. Soc. 109 (1987) 1496, and references therein.
[27] T.T. Tsou, J.K. Kochi, J. Am. Chem. Soc. 101 (1979) 7547.
[28] C.N. Satterfield, Catalysis in Industrial Practice, McGraw-Hill, New York, 1991.
[29] H. Noller, W. Kladnig, Catal. Rev. -Sci. Eng. 13 (2) (1976) 149.
[30] A.A. Balandin, Adv. Catal. 10 (1958) 96.
[31] R.J. Madix, Adv. Catal. 29 (1980) 1.
[32] I.E. Wachs, R.J. Madix, Appl. Surf. Sci. 1 (1978) 303.

[33] F. Zaera, J. Am. Chem. Soc. 111 (1989) 8744.
[34] F. Zaera, Chem. Rev. 95 (1995) 2651.
[35] J.G. Forbes, A.J. Gellman, J. Am. Chem. Soc. 115 (1993) 6277.
[36] S.C. Street, A.J. Gellman, J. Phys. Chem. 100 (20) (1996) 8338.
[37] J.-L. Lin, B.E. Bent, Chem. Phys. Lett. 194 (1992) 208.
[38] C. Zheng, Y. Apeloig, R. Hoffmann, J. Am. Chem. Soc. 110 (1988) 749.
[39] C.L. Kibby, W.K. Hall, J. Catal. 29 (1973) 144.
[40] M. Hájek, K. Kochloefl, Collect. Czech. Chem. Commun. 34 (1969) 2739.
[41] M. Hájek, J.C. Duchet, K. Kochloefl, Collect. Czech. Chem. Commun. 35 (1970) 2258.