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THE STRUCTURE SENSITIVITY AND INSENSITIVITY OF CATALYTIC REACTIONS IN LIGHT OF THE ADSORBATE INDUCED DYNAMIC RESTRUCTURING OF SURFACES

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Catalytic reaction structure sensitivity, catalytic reaction structure insensitivity, adsorbate induced surface restructuring, restructuring of surfaces

The classification of catalytic reactions to structure sensitive and structure insensitive types has stood up well to the tests of experiments over the past two decades. Model studies using metal single crystal surfaces explored the relationship between the reaction kinetics and the atomic surface structure. These investigations uncovered the adsorbate induced dynamic restructuring of metal surfaces on the timescales of chemisorption, catalytic reactions and on longer times controlled by mass transport. The causes of reaction structure sensitivity and insensitivity are reinterpreted in view of the dynamic restructuring of the metal catalysts.

1. Introduction

One of the most successful classifications of catalytic reactions is the one that divides them into two groups: those that exhibit variations of turnover rates with particle size changes of dispersed catalyst particles are called structure sensitive while those with unchanging rates are called structure insensitive [1,2]. This division based on experiments stood up to the tests of time. Single crystal studies confirmed the structure sensitivity of ammonia synthesis over iron [3] and rhenium [4] surfaces and of ethane hydrogenolysis over nickel and platinum [5]. It also confirmed the structure insensitivity of ethylene hydrogenation [6] over Pt and Rh and CO hydrogenation over nickel and rhodium [7]. An interesting correlation has been found between homogeneous and heterogeneous catalysis that places all of the reactions that can be carried out by both homogeneous and heterogeneous catalysts (hydrogenation, carbonylation, hydroformylation) in the structure insensitive class [8].

In recent years strong experimental evidence has been accumulating indicating that the structure of metal catalyst surfaces is not rigid but changes in response to its changing chemical environment [9]. This restructuring occurs on the time scale of adsorption (10^{-3} sec), of turnover times of catalytic reactions (seconds) or on longer time scales leading to deactivation or regeneration of catalytic processes. Thus, the surface is dynamic, its structure changes as the nature of the local surface chemical bonds are altered [10].

The question arises how structure sensitivity and insensitivity of catalytic reactions can be interpreted in light of surface restructuring and the new dynamic model of surface structure that advocates continually changing topology instead of a rigid surface atomic environment. In this paper we aim to address this question. First we review the experimental evidence for surface restructuring, then we shall suggest reasons for structure sensitive and insensitive catalytic reactions by presenting three examples: ammonia synthesis over iron, the hydrodesulfurization of thiophene and ethylene hydrogenation.

2. The restructured surface; when clean and when adsorbate covered

a) *Clean surface relaxation and reconstruction.* Low energy electron diffraction-surface crystallography studies show that the interlayer distance is shorter between the first layer of atoms at the clean surface and the second layer than interlayer distances in the bulk [11]. This is schematically shown in fig. 1. Atoms in the first layer always contract toward the bulk, the magnitude of contractions (often called relaxation) increases with atomic roughness (defined as the reciprocal of the packing density). This is shown in fig. 2. Thus, the more open is the surface (less nearest neighbors), the more marked is the relaxation, the movement of surface atoms from their bulk-like equilibrium positions. Drastic restructuring occurs at the lower coordination step site on the surface as shown in fig. 3 as a consequence. The large relaxations strongly influence the bonding among atoms near the surface especially for those solids with highly directional bonding (metals and covalent insulators for example). As a result, reconstruction occurs [12]. The surface atoms move into new structural arrangements that maximize their bonding in their new equilibrium positions; surface reconstruction takes place. One example is shown in fig. 4. The clean Ir(110) surface reconstructs into the "missing row" (1 × 2) surface structure, with large troughs between rows

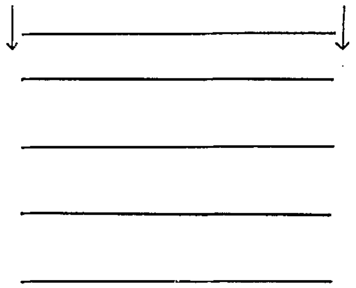


Fig. 1. Clean metal surface relaxation.

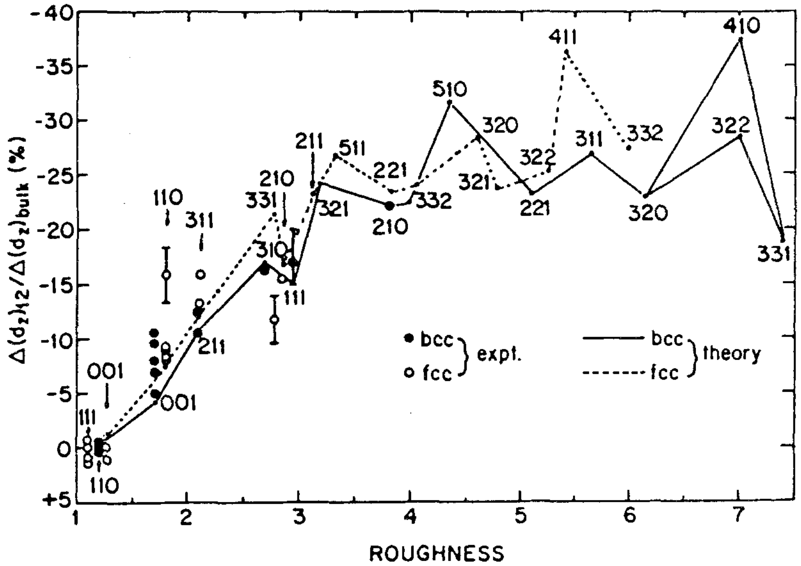


Fig. 2. Variation in the magnitude of relaxation at clean metal surfaces as a function of surface roughness (defined as 1/packing density).

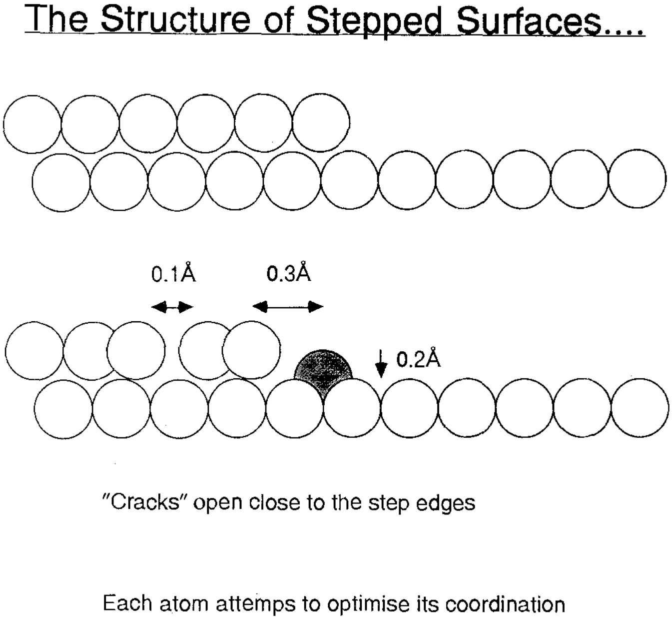


Fig. 3. Restructuring at a step site on a clean metal surface.

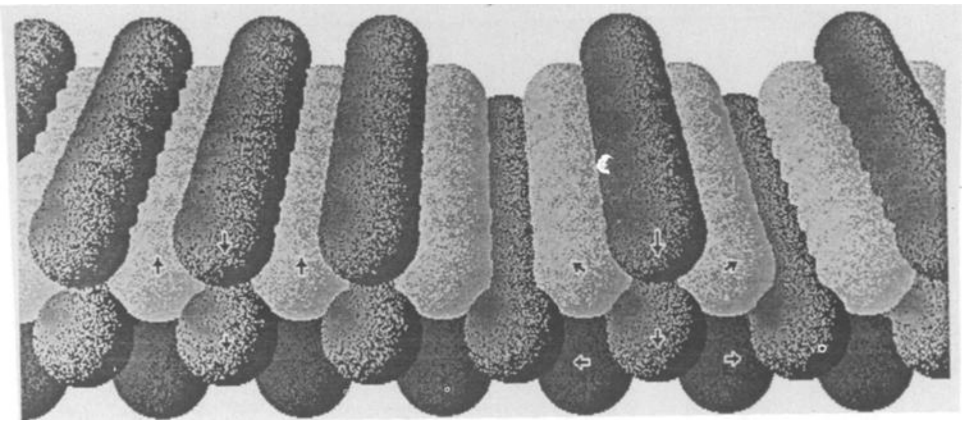


Fig. 4. Reconstruction of the iridium (110) surface to a "missing row" structure. Relaxation of atoms in the top three atomic layers at the surface occur.

of atoms and relaxation of atoms in the new structure can be detected down to the third atomic layer [13].

b) *Adsorbate induced restructuring of surfaces.* When an atom or a molecule chemisorbs, it usually forms chemical bonds with its nearest neighbor substrate atoms that are just as strong as the bonds between substrate atoms [10]. Thus, there is a thermodynamic driving force for restructuring upon adsorption. This is shown in fig. 5 for the chemisorption of one-half monolayer of carbon on the Ni(100) surface. The four-fold unit cell of the clean surface expands and rotates by a small angle to maximize Ni–C bonding [14]. The enlarged Ni–Ni distance near the carbon provides a bigger space for the carbon atom to occupy a site that is closer to Ni atoms in the second layer to be able to better bond to them. The surface stress induced by this lattice expansion is relieved by the small periodic rotation of the nickel surface atoms around the carbon bonding site. Upon reaction with hydrogen, the carbon atoms react to produce methane, CH_4, which desorbs. The surface then restructures again so that nickel atoms move into the positions they occupied before the carbon chemisorption occurred. The nickel surface is now ready for the next carbon readsorption event.

Another example of adsorption induced restructuring is the chemisorption of sulfur on Fe(110) [15]. The surface structure that forms is shown in fig. 6. The sulfur atoms form four equal strength bonds with their nearest neighbor iron atoms that rearrange to produce a four-fold site. The restructuring of the iron surface into these Fe_4S-like clusters that form a periodic array increases the metal-metal distances between the different clusters leading to a weakening of some of the iron-iron bonds. The energy needed for this process is compensated by the formation of the newly produced four Fe–S substrate-adsorbate chemical bonds which are quite strong. Reactive desorption of sulfur leads to reestablish-

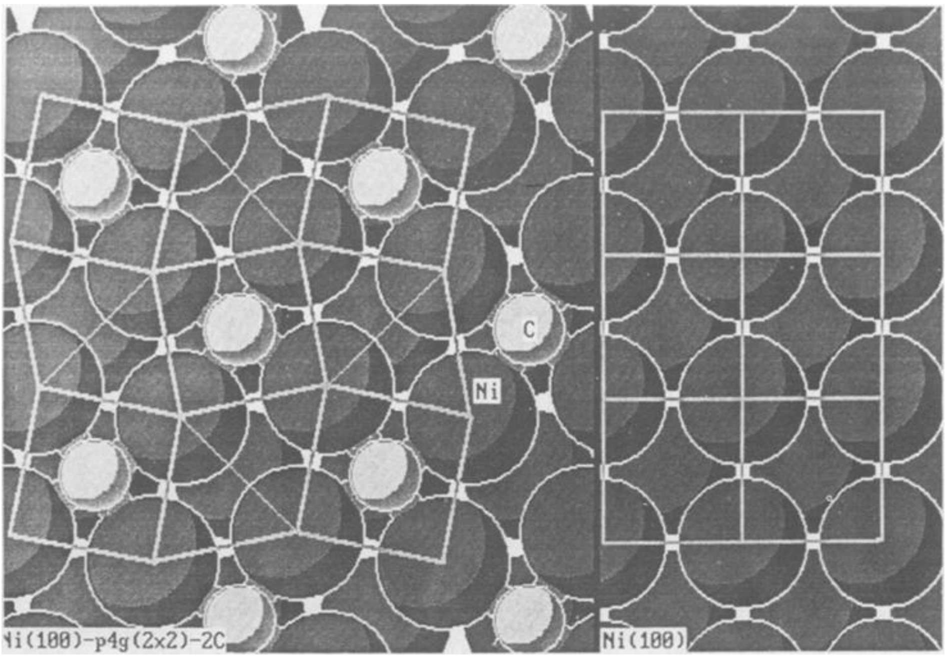


Fig. 5. Carbon chemisorption induced restructuring of the nickel (100) crystal face.

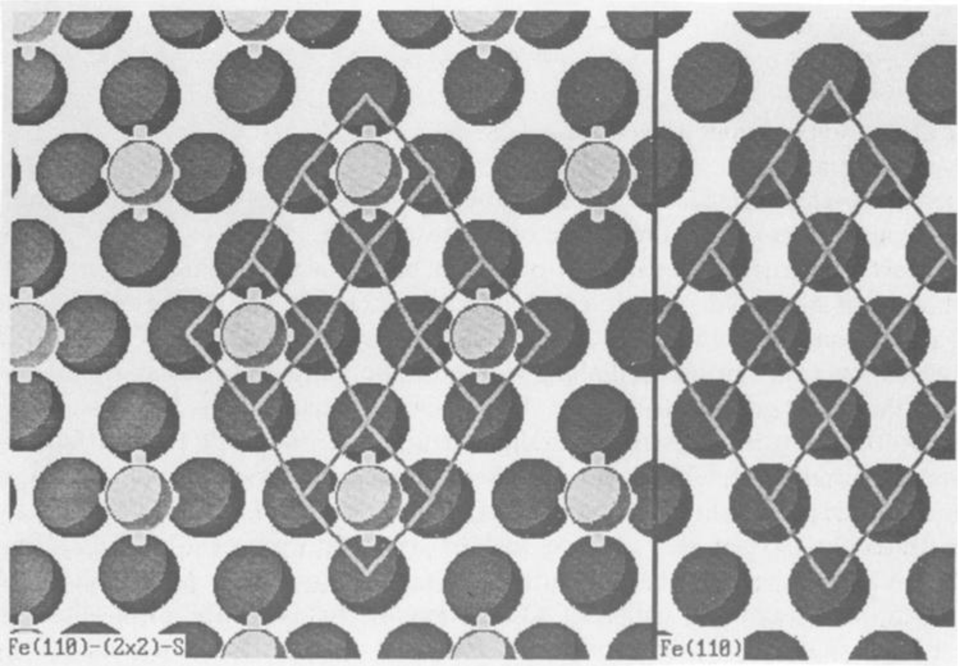


Fig. 6. Sulfur chemisorption induced restructuring of the iron (110) crystal face.

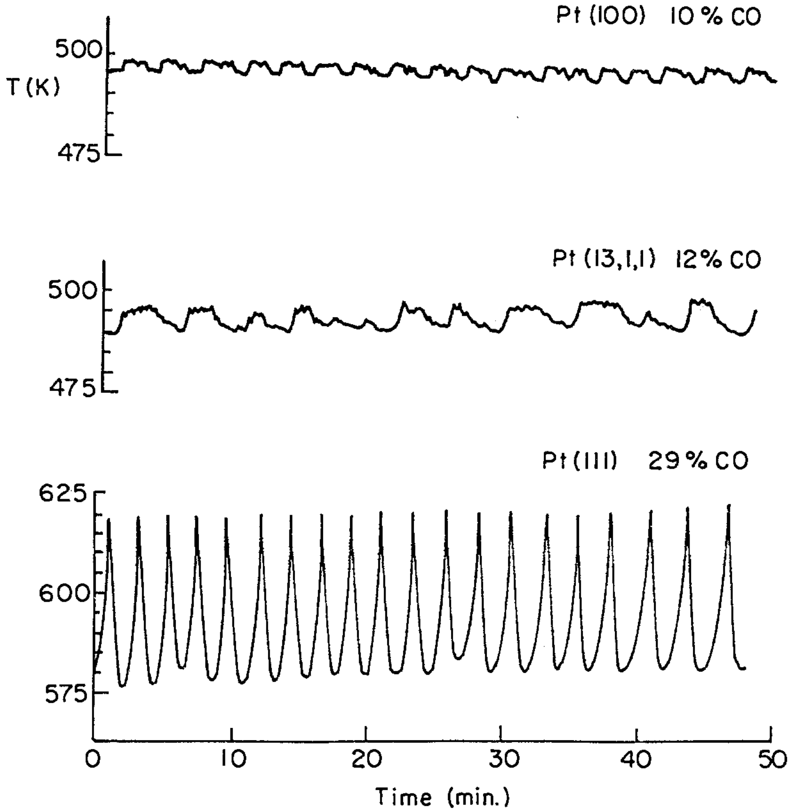


Fig. 7. Periodic temperature changes observed during CO oxidation over different platinum crystal faces.

ment of the clean metal surface structure. Adsorption induced restructuring of these types occurs on the time scale of chemisorption.

However, restructuring can also occur on time scales that are longer, on the time scale of a catalytic reaction or longer. An example of surface restructuring that occurs on the time period of a catalytic reaction turnover is CO oxidation [16]. This reaction can be oscillatory with periodic temperature changes as much as 50° that can readily be observed (fig. 7). One mechanism has been established by Ertl et al. that involves the periodic restructuring of the Pt(100) surface that drives the oscillation of the reaction. Since dioxygen dissociatively chemisorbs with a higher probability on one type of surface structure, one surface reaction path is on an oxygen rich surface that exists in the presence of this surface structure. The other surface structure that has a much lower probability of O_2 chemisorption is covered with CO. Oscillations occur as restructuring alternates the two branches of this exothermic reaction. Another mechanism for this reaction that leads to oscillations of the reaction rate is the periodic oxidation of

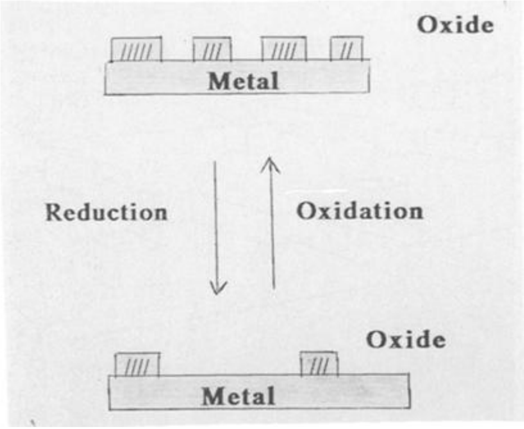


Fig. 8. Scheme of the oxidation and reduction of platinum that can occur during CO oxidation.

the metal and the reduction of the oxide [17] (fig. 8). Oxidation and reduction also lead to periodic restructuring of the surface.

There are many adsorption induced surface restructuring processes that are slow compared to chemisorption and catalytic reaction turnover times because they depend on mass transport [10]. Chemisorption is often the first step to initiate the formation of a bulk compound, sulfur chemisorption to produce sulfides or oxygen chemisorption to form oxides. In these circumstances restructuring may take hours and is reversible only on a similar time scale if at all. Thus, adsorbate induced restructuring can be of many classes that occur on different time scales. It is an all pervasive phenomenon that occurs at surfaces and interfaces that participate in chemical change.

3. The dynamic restructuring model of surfaces

Our physical model of surfaces that we use to explain known phenomena has undergone major changes that are perhaps useful to review. In the 1930s the *homogeneous surface model* was developed as shown in fig. 9 that viewed the surface as a smooth discontinuity [12]. Electrons may spill out of the surface by

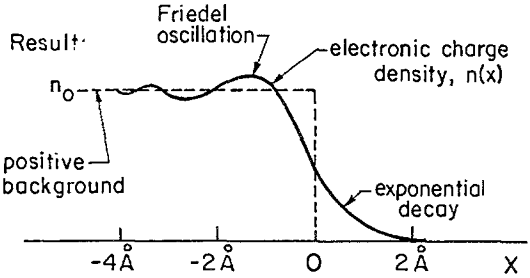


Fig. 9. The homogeneous surface model.

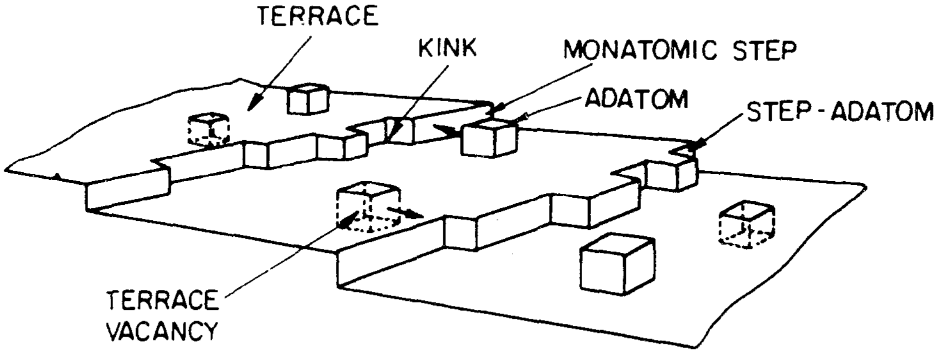


Fig. 10. The heterogeneous rigid surface model.

tunneling to give rise to the surface space charge and their periodic motion to the Friedel oscillations. This picture explained changes of work function from crystal face to crystal face and the formation of a space charge at insulator and solid-liquid interfaces. In the 1950s the *heterogeneous rigid surface model* was proposed as shown in fig. 10. Various surface sites, atoms at steps, kinks, ad-atoms and vacancies could be identified by experiments and successful theories of crystal growth and evaporation could be developed by invoking the important roles of these different surface sites and atom transport from one site to another [12]. The surface was assumed to be rigid, the surface atoms all occupying their bulk-like equilibrium positions. It was assumed that from knowledge of the bulk structure, the surface structure could be deduced. This model was successful in explaining the chemical importance of steps and kinks and of vacancies in compound (oxides, sulfides, arsenides) surfaces.

The new *dynamical restructuring model* views the surface atoms as flexible, constantly changing their equilibrium positions in response to the changing chemical bonding environment imposed by the dynamics of chemisorption and chemical reactions. They exhibit relaxation and reconstruction when clean then shift into new surface structures when chemisorption occurs which are altered again as the surface chemical bond is changed by desorption.

Below we shall attempt to explain structure sensitivity and insensitivity of catalytic reactions in light of the dynamical restructuring surface model.

4. Structure sensitive and insensitive reactions as a consequence of dynamically restructuring metal surfaces

a) *Ammonia synthesis on iron*. The formation of ammonia is one of the most surface structure sensitive reactions known [18]. When carried out on single crystal surfaces at high pressures (20 atm, 400°C 3 : 1 $H_2 : N_2$ ratio) the (111) and (211) crystal faces are orders of magnitude more active (over a factor of 300) than the (110) close packed surface of this bcc metal. The activity of the (100) surface is quite low as well. The presence of 7-coordinated atomic sites that are present in the second layer in large concentrations only in the (111) and (211) surfaces is suggested to be responsible for their high catalytic activity. These sites, that were identified using a rigid lattice model, dissociate dinitrogen with near zero activation energy.

The iron (111) and (211) surfaces exhibit relaxation when clean and will certainly restructure in the presence of chemisorbed nitrogen atoms. Nevertheless the structure sensitivity of this reaction points to a correlation between the surface structure of a clean iron crystal face and its surface structure in the presence of chemisorbed nitrogen that is active for the ammonia synthesis. Although the two structures are different, there must be a structural relationship to explain the structure sensitivity of ammonia synthesis. This correlation will be explored by modern surface science techniques that include diffuse low energy electron diffraction (LEED) to determine the structure of disordered surfaces and the scanning tunneling microscope (STM).

b) *Hydrodesulfurization (HDS) of tiophene over Mo and Re surfaces [19]*. This reaction removes sulfur from the five member heterocyclic C_4H_4S molecule and produces H_2S and butenes without breaking any C–C bonds. Single crystal studies found it structure insensitive on Mo and structure sensitive over Re under identical reaction conditions (270°C, 1 atm, 10-fold excess H_2). This is shown in fig. 11.

LEED surface crystallography studies revealed that clean Mo single crystal surfaces are disordered at 300 K and above. The surface atoms appear to be displaced randomly from their bulk-like equilibrium positions (they order at lower temperatures). When sulfur chemisorbs, the surface remains disordered. This then could be the reason for structure insensitivity of the HDS reaction since neither the clean nor the catalytically active sulfur covered surface exhibits long range order. However, the rhenium crystal surfaces remain ordered during the reaction and also in the presence of chemisorbed sulfur that is detectable by STM and, therefore, the reaction remains structure sensitive over this metal.

c) *Ethylene hydrogenation over Pt and Rh.* At 300 K this reaction occurs at high rates (10^2 ethylene molecules produced per second per surface atom) at atmospheric pressures in excess of H_2 [6]. The reaction is structure insensitive; its kinetics (rate, activation energies) are the same on crystal surfaces, dispersed particles, films and metal foils. Surface science studies revealed that the active surface is covered by a monolayer of ethylidyne whose structure is shown in fig. 12.

This layer of chemisorbed molecules does not hydrogenate rapidly during the catalytic reaction but remains on the surface for over a million turnovers as indicated by ^{14}C labelling studies [20]. While H_2 dissociation is not inhibited by the presence of this strongly bound molecular hydrocarbon overlayer as shown by facile H_2/D_2 exchange in its presence, the adsorption of ethylene on the metal

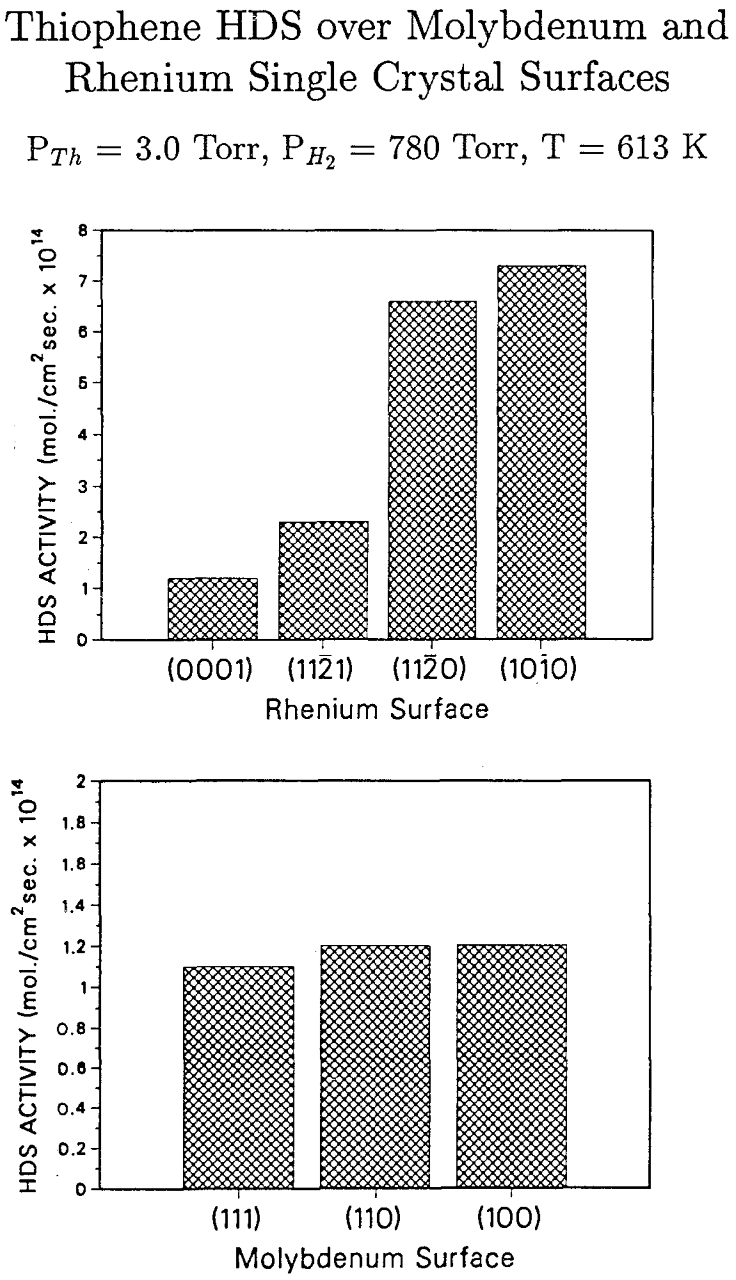
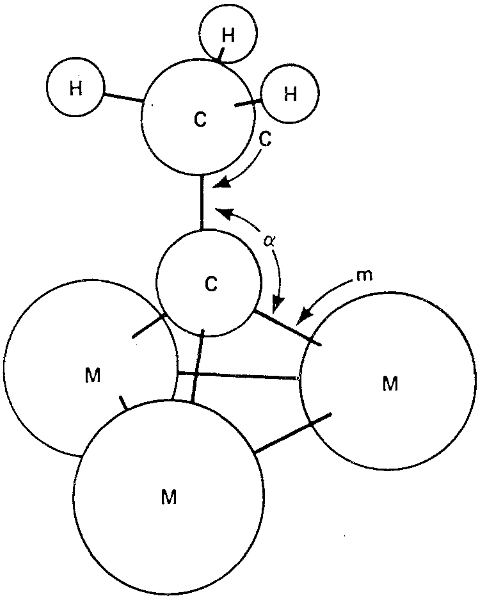


Fig. 11. The structure insensitivity and sensitivity of tiophene hydrosdesulfurization over molybdenum and rhenium crystal surfaces, respectively.

surface is not possible as there is not enough space in between the ethylidyne surface species where ethylene could fit in and react. A likely possibility is ethylidyne induced surface restructuring of Pt and Rh that creates large enough

Different ethylidyne species: bond distances and angles
(r_C = carbon covalent radius; r_M = bulk metal atomic radius)



	C [Å]	m	r_M	r_C	α [°]
$Co_3(CO)_9CCH_3$	1.53 (3)	1.90 (2)	1.25	0.65	131.3
$H_3Ru_3(CO)_9CCH_3$	1.51 (2)	2.08 (1)	1.34	0.74	128.1
$H_3Os_3(CO)_9CCH_3$	1.51 (2)	2.08 (1)	1.35	0.73	128.1
Pt (111) + (2 X 2) CCH_3	1.50	2.00	1.39	0.61	127.0
Rh (111) + (2 X 2) CCH_3	1.45 (10)	2.03 (7)	1.34	0.69	130.2
H_3C-CH_3	1.54			0.77	109.5
$H_2C=CH_2$	1.33			0.68	122.3
$HC\equiv CH$	1.20			0.60	180.0

Fig. 12. The ethylidyne structure on the Pt(111) crystal face.

sites in between the chemisorbed stagnant C_2H_3 species for gas phase C_2H_4 adsorption, reaction with H atoms and desorption as C_2H_6. If this model is correct, it would explain the structure insensitivity of this reaction as the active sites are created only during the reaction, by the first monolayer of chemisorbed C_2H_4 that induces the surface restructuring.

The concept that the active sites do not exist on the clean catalyst surface but are created during the reaction is powerful enough to explain why any surface reaction may be structure insensitive. It lacks experimental proof however. STM studies are in progress that attempt to monitor the state of atomic surface structure during the reaction to verify the possibility of surface restructuring.

5. Promotion of the rates of C–O bond hydrogenation by the oxide-metal interface

CO hydrogenation catalysis has benefited greatly from the rediscovery of the unique catalytic behavior of oxide-metal interfaces first observed by Schwab and his co-workers [21]. The effect is commonly referred to as strong metal-support

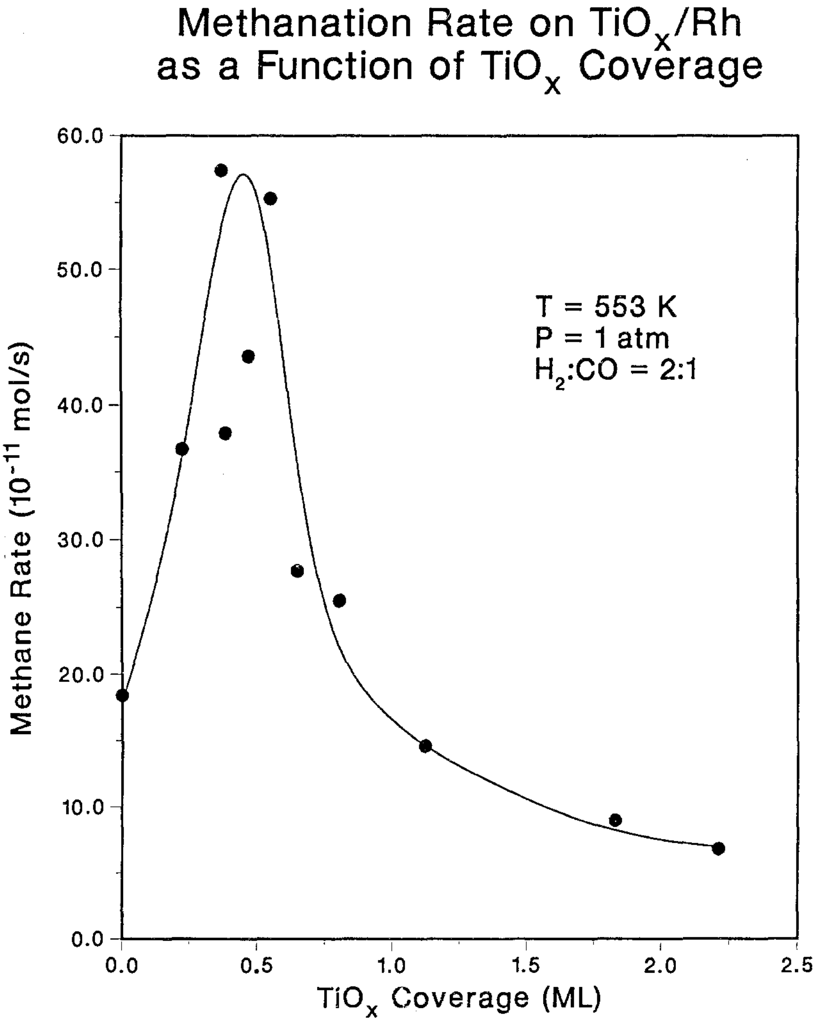


Fig. 13. CO hydrogenation rate over the rhodium-titanium oxide catalyst as a function of oxide coverage of the metal.

interaction or SMSI. Touster [22] reported large enhancement in the CO hydrogenation rates for transition metal catalysts when supported on high surface area titanium oxide. Subsequent studies of catalyst activation involving reduction and reoxidation using H_2 and O_2 respectively indicated that the catalyst is activated by optimizing the oxide-metal interface area. Since the same catalytic behavior can be obtained by depositing the metal on the oxide support or by deposition of oxide islands on the transition metal, the oxide-metal periphery area is implicated as the active site responsible for the increased reaction rates. A typical reaction rate behavior exhibits a maximum with increasing oxide coverage over a transition metal catalyst as shown in fig. 13 for CO hydrogenation [23] over TiO_2 on Rh. The oxide alone is inactive while the metal is active for methane formation. At about 50% of a monolayer of oxide coverage, which corresponds to the optimum oxide-metal interface area, the reaction rate exhibits a maximum.

This large oxide-metal interface catalysis effect is observed for several transition metals including Ni, Rh, Co and Fe and for several oxides including TiO_2, La_2O_3, MgO and ZrO_2. In addition to CO activation, other molecules that have CO bonds (CO_2, acetone, alcohols) are also activated for hydrogenation [24].

This oxide-metal interface activation phenomenon is under intense investigation in many laboratories as several new catalyst systems have been reported and patented based on SMSI. The scanning tunneling microscope (STM) has been able to image the oxide-metal interface on the atomic scale. It is suggested that the periodic restructuring of metal atoms that drives the catalytic reaction can occur at faster rates at the oxide-metal interface leading to enhanced catalytic activity. It is hoped that STM experiments that are performed while the reaction is occurring can investigate the dynamic changes of surface structure at the oxide-metal interface and elsewhere on the surface of the active catalyst.

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