CENTENARY LECTURE *

Molecular Ingredients of Heterogeneous Catalysis

By Gabor A. Somorjai
MATERIALS AND MOLECULAR RESEARCH DIVISION,
LAWRENCE BERKELEY LABORATORY AND
DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF CALIFORNIA, BERKELEY, CALIFORNIA 94720, USA

1 Introduction

When Professor Thomas asked me to join up with him for a symposium on catalysis, I was happy to oblige. Catalysis science stands on two legs, surface science and the solid state chemistry of metastable materials (Figure 1). In the last ten years a scientific revolution has occurred that has converted catalysis from art to science. From the surface science side, this has been due to atomic level characterization of model, low surface area and real, high-surface area catalysts. As a result, the preparation of catalysts and their application in the chemical and petrochemical technologies have become science driven. That is, the molecular level under-standing that is obtained by research in the laboratory controls the development of chemical or petrochemical catalysis-based technology. Two examples of recently developed high technology catalysts are the catalytic converter and the new generation of zeolites (Figures 2 and 3). These could not have been developed
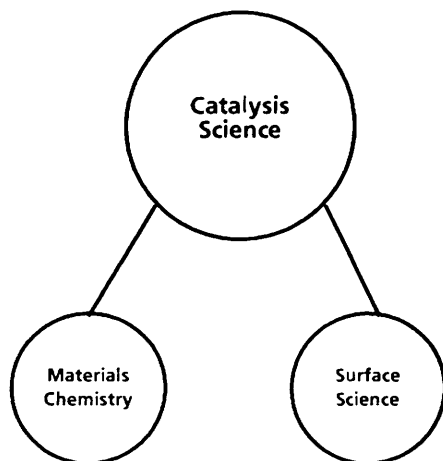

Figure 1 *Schematic representation of the close relationship between the materials chemistry of metastable high surface area materials, surface science, and catalysis science*

* Delivered at the Scientific Societies' Lecture Theatre, London, November 7th 1983.

Figure 2 *The catalytic converter for the complete combustion of automobile exhaust. It oxidizes unburned hydrocarbons, and carbon monoxide to carbon dioxide and water, and reduces nitrogen oxides to dinitrogen simultaneously*

without the molecular level characterization of their structure and composition by electron spectroscopies and solid-state n.m.r. that lead to the establishment of the all important correlation between their atomic structure and composition and performance.

Let me review this recent development of the molecular science of heterogeneous catalysis from the surface science side, where much of my research is concentrated, and perhaps also show the direction the field might take in the near future. My investigations utilize mostly small area single crystal catalysts and use the full repertoire of surface science techniques for their characterization. The most
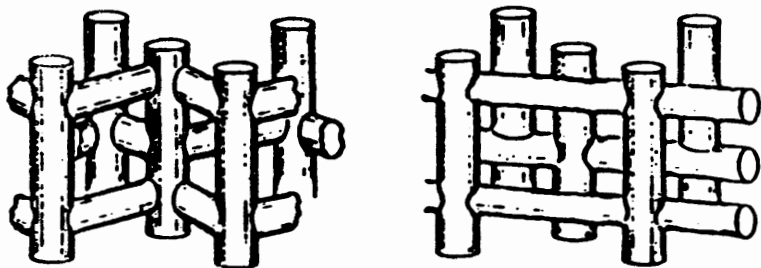
ZSM-5 Channel Structure   ZSM-11 Channel Structure

Figure 3 *Two recently synthesized zeolites with large silicon to aluminium ratios*

frequently used tools for surface characterization include low energy electron diffraction (LEED), Auger electron spectroscopy (AES), and high resolution electron energy loss spectroscopy (HREELS).[1] The work horse for the catalytic studies was the low-pressure, high-pressure apparatus,[2] shown in Figure 4. After appropriate characterization the sample is enclosed in an isolation chamber that can be pressurized to atmospheric pressures (up to 100 atm) with the reactant gases. These can be circulated by a pump and when the sample is heated to the reaction temperatures, the rate and the product distribution can be monitored with a gas chromatograph. The high pressure loop acts as a microreactor that can be operated in the flow or in the batch modes. When the reaction is complete, the isolation cell is opened and the sample is now in an ultra-high vacuum environment again. After performing surface analysis to identify the surface composition and structure that was present under the reaction conditions, the surface may be modified and the high pressure reaction study can be continued.
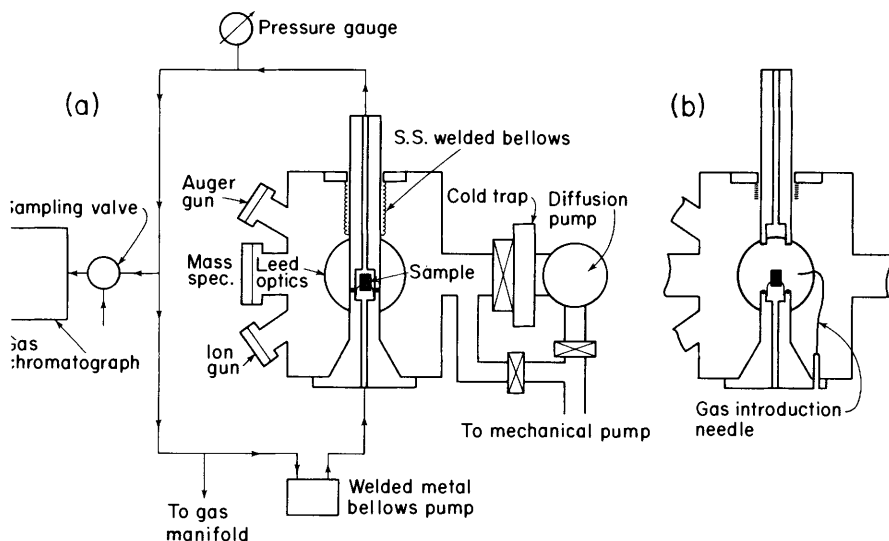

Figure 4 *Schematic representation of the experimental apparatus utilized to carry out the catalytic reaction rate studies on single crystal or polycrystalline surfaces of low surface area at low and high pressures in the 10^{-7} to 10^{+4} torr range*

When using model catalysts it is essential to establish if close similarity exists between the behavior of the model and the real catalyst systems. This was found to be the case for several reactions that include the hydrogenation of carbon

[1] G. A. Somorjai, 'Chemistry in Two Dimensions: Surfaces', Cornell University Press, 1981, Library of Congress Catalog Card No. 80-21443.

[2] A. L. Cabrera, N. D. Spencer, E. Kozak, P. W. Davies, and G. A. Somorjai, *Rev. Sci. Instrum.*, 1982, **53**, 1888.

monoxide over rhodium,[3] the hydrogenation of cyclohexene,[4] and the ring opening of cyclopropane.[5]

We investigated in some detail several important catalytic reactions, including the conversion of hydrocarbons over Pt crystal surfaces,[6-8] the synthesis of ammonia over iron[9] and rhenium[10] crystals, the hydrogenation of carbon monoxide over iron[11] and rhodium,[12] and the photodissociation of water over TiO_2, $SrTiO_3$,[13] and iron oxides.[14] From these studies three molecular ingredients of heterogeneous catalysis were identified. These are:

> The Atomic Structure of the Surface
> The Carbonaceous Deposit
> The Oxidation State of Surface Atoms

We shall discuss each one of these ingredients and give examples of their roles in catalytic surface reactions.

2 Atomic Surface Structure

Figure 5 compares the rates of ammonia production on three single crystal surfaces of body centered cubic iron[9] at high pressures. The (111) face is about 430-times more active than the closest packed (110) crystal face while the (100) face is 32-times as active as the (110) face. The rate limiting step in this reaction is the dissociation of N_2 and it appears that this process occurs with a near zero activation energy on the (111) iron surface while there is a larger activation energy on the other iron crystal surfaces. It has been proposed that the active site for breaking the very strong N_2 bond is a seven co-ordinated iron atom that is present in the second layer under the surface. There is a theory being developed[15] that relates the concentration of nearly degenerate electron vacancy states, the density of hole states near the Fermi level, to the ability of a given site to break and make chemical bonds in a transient manner by charge fluctuations. The sites with the largest number of nearest neighbours (highest co-ordination) have the highest density of electron-hole states and thus, they should be the most active during catalytic reactions. Unfortunately they are located in the bulk and are not accessible to the incoming reactants. However, atoms in the second layer of an open surface structure are accessible but are still surrounded by a large number of neighbours. These are then the most active sites in many catalytic reactions.

[3] B. A. Sexton and G. A. Somorjai, *J. Catal.*, 1977, **46**, 167.
[4] S. M. Davis and G. A. Somorjai, *J. Catal.*, 1980, **65**, 78.
[5] D. R. Kahn, E. E. Petersen, and G. A. Somorjai, *J. Catal.*, 1974, **34**, 294.
[6] W. D. Gillespie, R. K. Herz, E. E. Petersen, and G. A. Somorjai, *J. Catal.*, 1981, **70**, 147.
[7] S. M. Davis, F. Zaera, and G. A. Somorjai, *J. Am. Chem. Soc.*, 1982, **104**, 7453.
[8] S. M. Davis, F. Zaera, and G. A. Somorjai, *J. Catal.*, 1984, **85**, 206.
[9] N. D. Spencer, R. C. Schoonmaker, and G. A. Somorjai, *J. Catal.*, 1982, **74**, 129.
[10] N. D. Spencer and G. A. Somorjai, *J. Catal.*, 1982, **78**, 142.
[11] D. Dwyer and G. A. Somorjai, *J. Catal.*, 1979, **56**, 249.
[12] D. G. Castner, R. L. Blackadar, and G. A. Somorjai, *J. Catal.*, 1980, **66**, 257.
[13] F. T. Wagner and G. A. Somorjai, *J. Am. Chem. Soc.*, 1980, **102**, 5494.
[14] C. Leygraf, M. Hendewerk, and G. A. Somorjai, *J. Catal.*, 1982, **78**, 341.
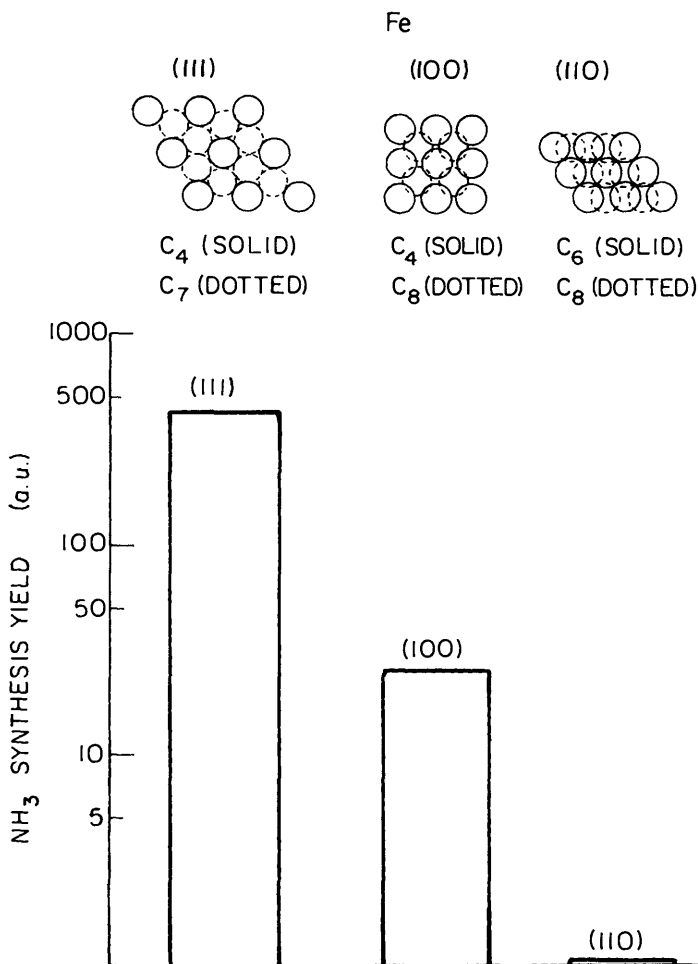[15] L. Falicov and G. A. Somorjai, *Proc. Natl. Acad. Sci.*, 1984, to be published.

Figure 5 *The remarkable surface structure sensitivity of the iron catalysed ammonia synthesis*

Although this theory will have to be tested further and proven by careful experiments, the available experimental data on the structure sensitivity of catalytic reactions can be explained by it. Figure 6 shows the rate of ammonia formation from N_2 and H_2 over hexagonal close-packed rhenium crystal surfaces.[16] Again the open (11$\bar{2}$0) crystal face is about 10^3-times more active than the closest packed (0001) hexagonal surface, thus exhibiting a profound structure sensitivity that is even more pronounced than that on iron.

For catalysed hydrocarbon reactions on platinum, which is an excellent catalyst,

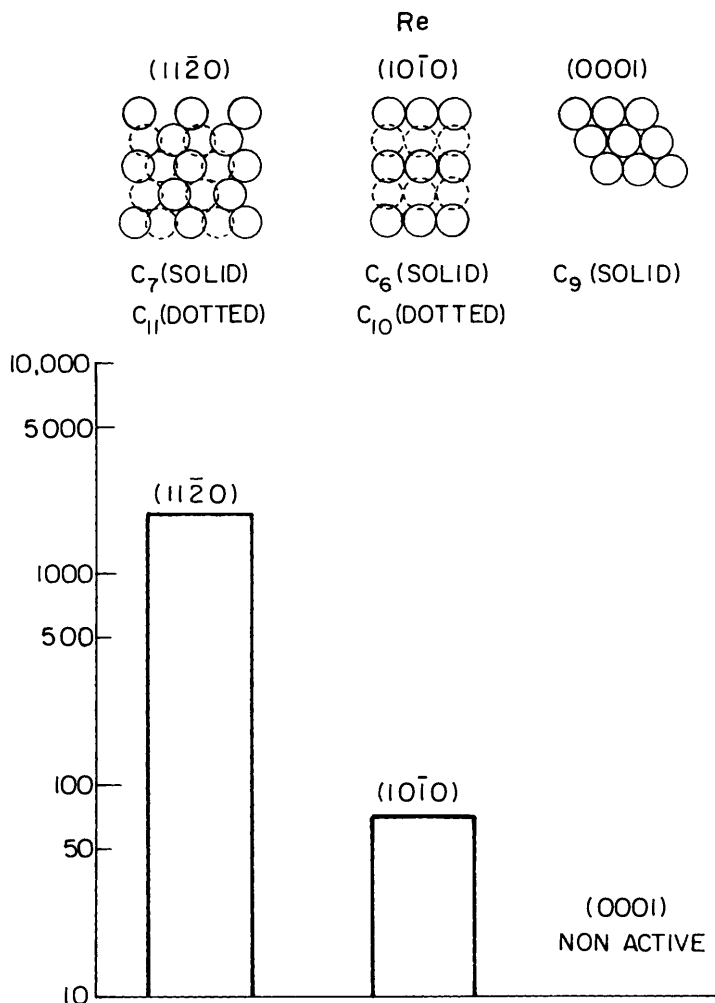[16] M. Asscher and G. A. Somorjai, *Surf. Sci.*, 1984, in press.

Re

(11$\bar{2}$0)   (10$\bar{1}$0)   (0001)

C_7(SOLID) C_6(SOLID) C_9 (SOLID)
C_{11}(DOTTED) C_{10}(DOTTED)

Figure 6   *The structure sensitivity of ammonia synthesis on rhenium single crystal surfaces*

there are four crystal surfaces with very different atomic surface structures that exhibit very different reaction selectivities. These are the flat (111) and (100) surfaces that have hexagonal and square unit cells, respectively. The other two surfaces have ordered steps of atomic heights and one has ledges (or kinks) in the steps as well. These are shown in Figure 7. The test reactions that best demonstrate the structure sensitivity over Pt are the conversions of n-hexane and n-heptane into other organic molecules.[6] n-Hexane may be converted into benzene upon dehydrocyclization or into methycyclopentane by a cyclization reaction. These are shown in Figure 8. It may isomerize to branched butanes or undergo C–C bond
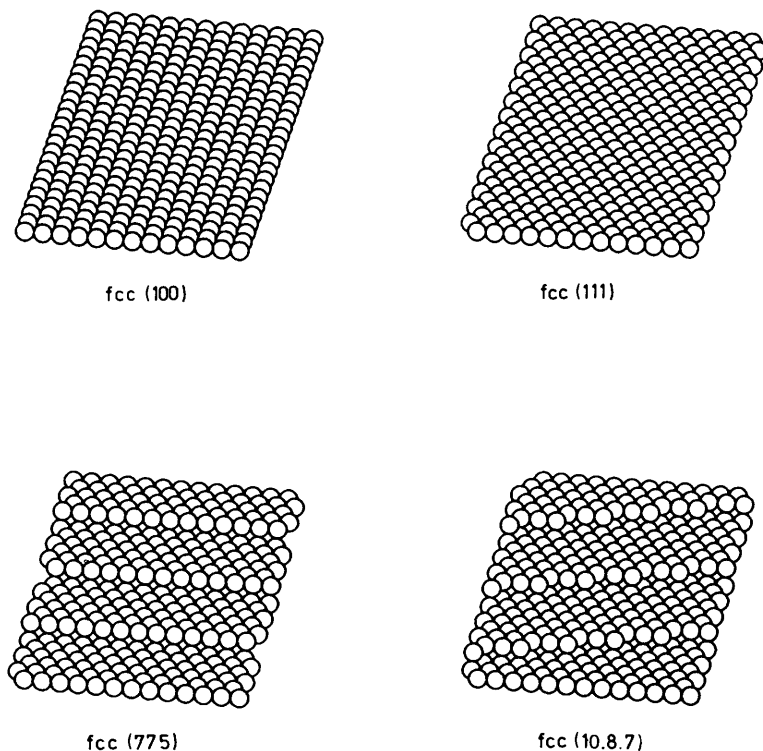
326

fcc (100)   fcc (111)

fcc (775)   fcc (10.8.7)

Figure 7 *Idealized atomic surface structures for the flat platinum (111) and platinum (100), the stepped platinum (775) and kinked platinum (10,8,7) surfaces*

breaking (hydrogenolysis) to produce C_1—C_3 fragments (methane to propane). The first three of these reactions are desirable when the aim is to produce high octane gasoline while the fourth reaction is undesirable as it leads to the production of gases of much less value as fuels. Figure 9 shows that the hexagonal surface produces much more aromatic product than the square (100) crystal face. In fact, a stepped surface with (111) orientation terraces that are five atoms wide is perhaps the best catalyst we have found so far to carry out the dehydrocyclization reaction. Conversely, the (100) flat surfaces with the square unit cells are much better isomerization catalysts, as shown in Figure 10, than the hexagonal crystal surface of Pt.[7] Thus, depending on the catalyst preparation, one may obtain superior dehydrocyclization or isomerization activity that is certainly well documented in the patent literature. The hydrogenolysis reaction that is also shown in Figure 10 is most active on surfaces that contain a large concentration of ledge or kink sites.[8] It is often necessary to 'poison' these sites by the adsorption of sulphur or other strongly bound additives that bind more strongly to the ledge sites than to the other surface sites (step or terrace sites). This way, the ledges cannot participate in
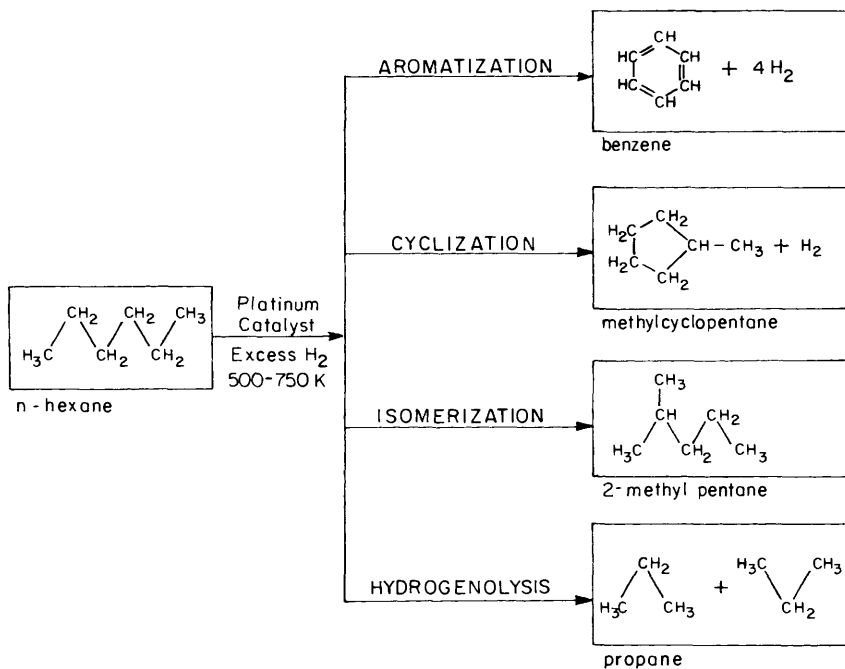
Figure 8 *Skeletal rearrangement reactions of hydrocarbons catalysed by platinum with high activity and unique selectivity. Depicted here are the several reaction pathways which occur simultaneously during the catalysed conversion of n-hexane, C_6H_{14}. The isomerization, cyclization, and aromatization reactions that produce branched or cyclic products are important in the production of high octane gasoline from petroleum naphtha. The hydrogenolysis reaction that involves breaking of C–C bonds yields undesirable gaseous products*

hydrocarbon reactions because they are masked by the selective adsorption of additives while the rest of the higher co-ordination surface sites remain clean and thereby active and selective.

3 The Carbonaceous Deposit

A catalytically active metal surface is always covered with a carbonaceous deposit. By labelling the reactant organic molecules with ^{14}C isotope, the residence time of this carbonaceous layer can be monitored.[17] It is found that it is usually ten- to fifty-times larger than the turnover time for the catalytic hydrocarbon conversion reactions. This is shown in Figure 11 under the label of the irreversible adsorption along with the hydrogen to carbon ratio of this deposit. As the reaction temperature is increased, the deposit becomes successively dehydrogenated as its stoicheiometry varies from C_2H_3 to C_2H and finely it looses all its hydrogen, and becomes graphitic. The metal surface retains its catalytic activity as long as the

---

[17] S. M. Davis, F. Zaera, and G. A. Somorjai, *J. Catal.*, 1982, **77**, 439.

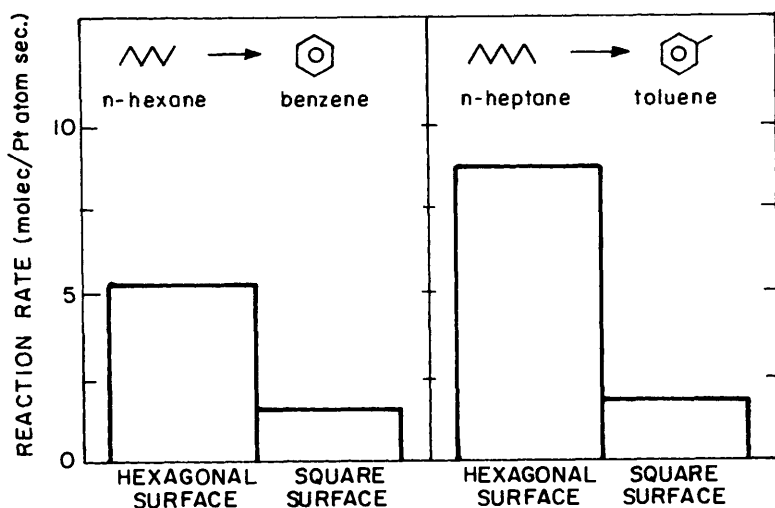## STRUCTURE SENSITIVITY OF ALKANE AROMATIZATION

Figure 9 *Dehydrocyclization of alkanes to aromatic hydrocarbons is one of the most important petroleum reforming reactions. The bar graphs shown here compare reaction rates for n-hexane and n-heptane aromatization catalysed at 573 K and atmospheric pressure over the two flat platinum single crystal faces with different atomic structure. The platinum surface with the hexagonal atomic arrangement is several times more active than the surface with a square unit cell over a wide range of reaction conditions*

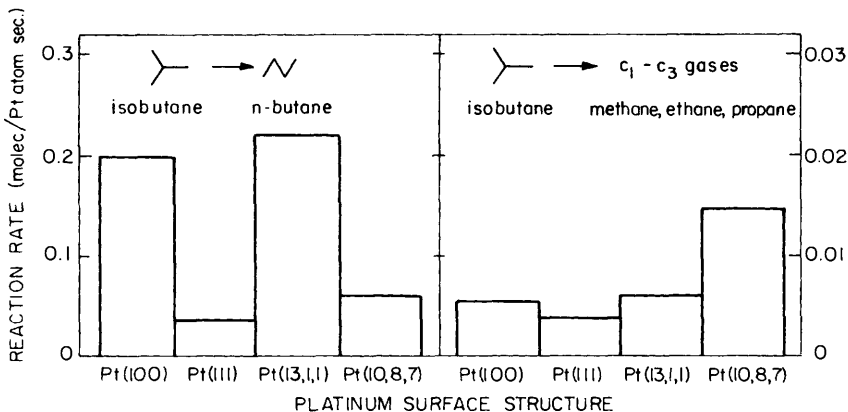## STRUCTURE SENSITIVITY OF LIGHT ALKANE SKELETAL REARRANGEMENT

Figure 10 *Reaction rates are shown as a function of surface structure for isobutane isomerization and hydrogenolysis catalysed at 570 K at atmospheric pressure over four platinum surfaces. The rates for both reaction pathways are very sensitive to structural features of the model single crystal catalytic surfaces. Isomerization of these light alkanes favoured on the platinum surfaces that have a square (100) atomic arrangement. Hydrogenolysis rates are maximized when kinked sites are present at high concentrations, as in the platinum (10,8,7) crystal surface*

carbonaceous deposit contains hydrogen, but becomes completely inactive (poisoned) in the presence of the graphitic overlayer.
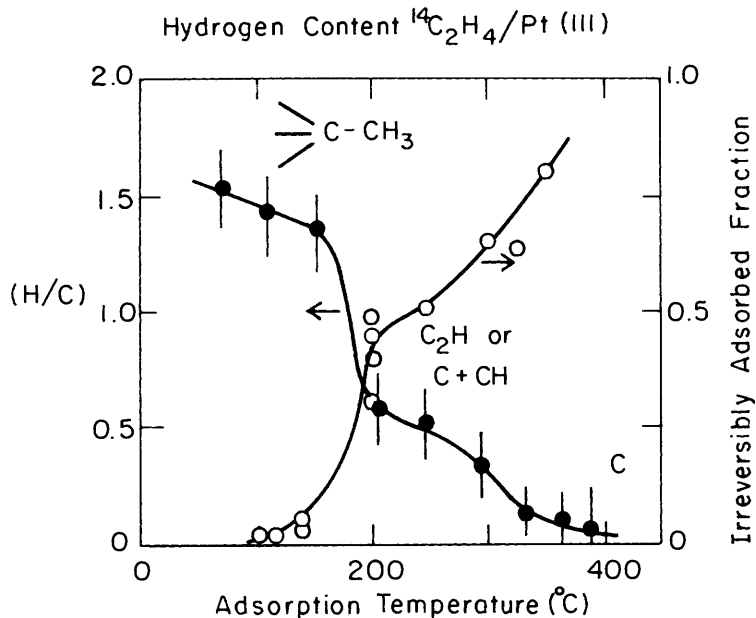

Hydrogen Content $^{14}C_2H_4$/Pt (III)

Figure 11 *Carbon-14 labelled ethylene C_2H_4 was chemisorbed as a function of temperature on a flat platinum surface with hexagonal orientation, Pt(111). H/C composition of the adsorbed species was determined from hydrogen thermal desorption studies. The amount of pre-adsorbed ethylene, which could not be removed by subsequent treatment in hydrogen at atmospheric pressure represents the irreversibly adsorbed fraction. The adsorption reversibility decreases markedly with increasing adsorption temperature as the surface species becomes more hydrogen deficient. The irreversibly adsorbed species have very long surface residence times of the order of days*

The sequential dehydrogenation of adsorbed organic monolayers with increasing temperature can be readily demonstrated by temperature programmed thermal desorption studies. Figure 12 shows the evolution of hydrogen from adsorbed layers of C_2H_4, C_3H_6, and C_4H_8.[18] At well-defined temperatures, hydrogen evolves at a maximum rate until complete dehydrogenation and graphitization of the remaining carbon occurs at the highest temperatures.

LEED and HREELS studies reveal the structure of organic monolayers at each stage of chemisorption. At lower temperature ($< \sim 300K$) the organic molecules exhibit ordered molecular structures. Figure 13 shows one of the ordered surface structures of benzene[19] on the Rh(111) crystal face that was determined by LEED and Figure 14 shows the HREELS spectra of benzene and its deuterated form.[20]

[18] M. Salmeron and G. A. Somorjai, *J. Phys. Chem.*, 1982, **86**, 341.
[19] M. A. Van Hove, R. Lin, and G. A. Somorjai, *Phys. Rev. Lett.*, 1983, **51**, 778.
[20] B. E. Koel, J. E. Crowell, C. M. Mate, and G. A. Somorjai, *J. Phys. Chem.*, 1984, in press.
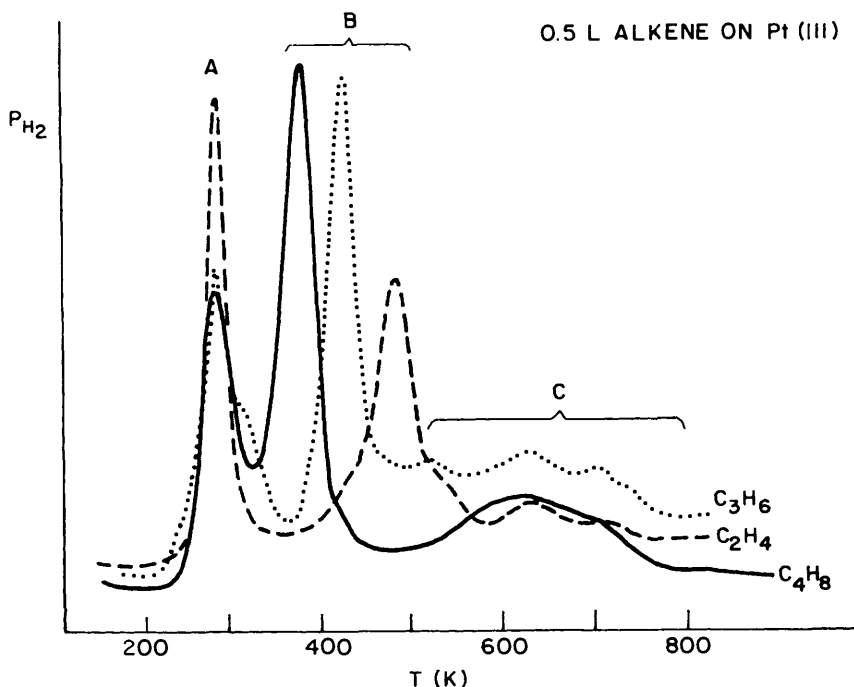
0.5 L ALKENE ON Pt (III)

Figure 12 *Hydrogen thermal desorption spectra illustrating the sequential dehydrogenation of ethylene, propylene, and cis-2-butene chemisorbed on* Pt(111) *at about* 120 K *(the heating rate is 12 K per second)*

The C_{3v} symmetry is clearly compatible with the molecular structure shown in Figure 13 with the molecule lying with its π ring parallel to the surface and the centre of the ring above a three-fold hollow. Figure 15 shows the surface structures of chemisorbed ethylene, propylene, and butene on the Pt(111) crystal face.[21] These molecules form alkylidyne species upon adsorption near 300 K with the C–C bond that is closest to the metal surface, perpendicular and elongated to a single C–C bond length. Similar alkylidyne structures have been found on other transition-metal surfaces, including Pd, Rh, and Ni.[22] The carbon atom that binds the molecule to the metal prefers the three-fold hollow site. Figure 16 compares the molecular structure of the ethylidyne molecule on the Pt(111) surface with a structure of ethylidyne containing trinuclear metal cluster compounds. The symmetry, the bond distances, and the bond angles in these clusters are very similar to the molecular structure of chemisorbed ethylene on the transition-metal surface. This similarity indicates the predominance of localized bonding of adsorbed sur-

[21] R. J. Koestner, J. C. Frost, P. C. Stair, M. A. Van Hove, and G. A. Somorjai, *Surf. Sci.*, 1982, **116**, 85.
[22] R. J. Koestner, M. A. Van Hove, and G. A. Somorjai, *Surf. Sci.*, 1982, **121**, 321.

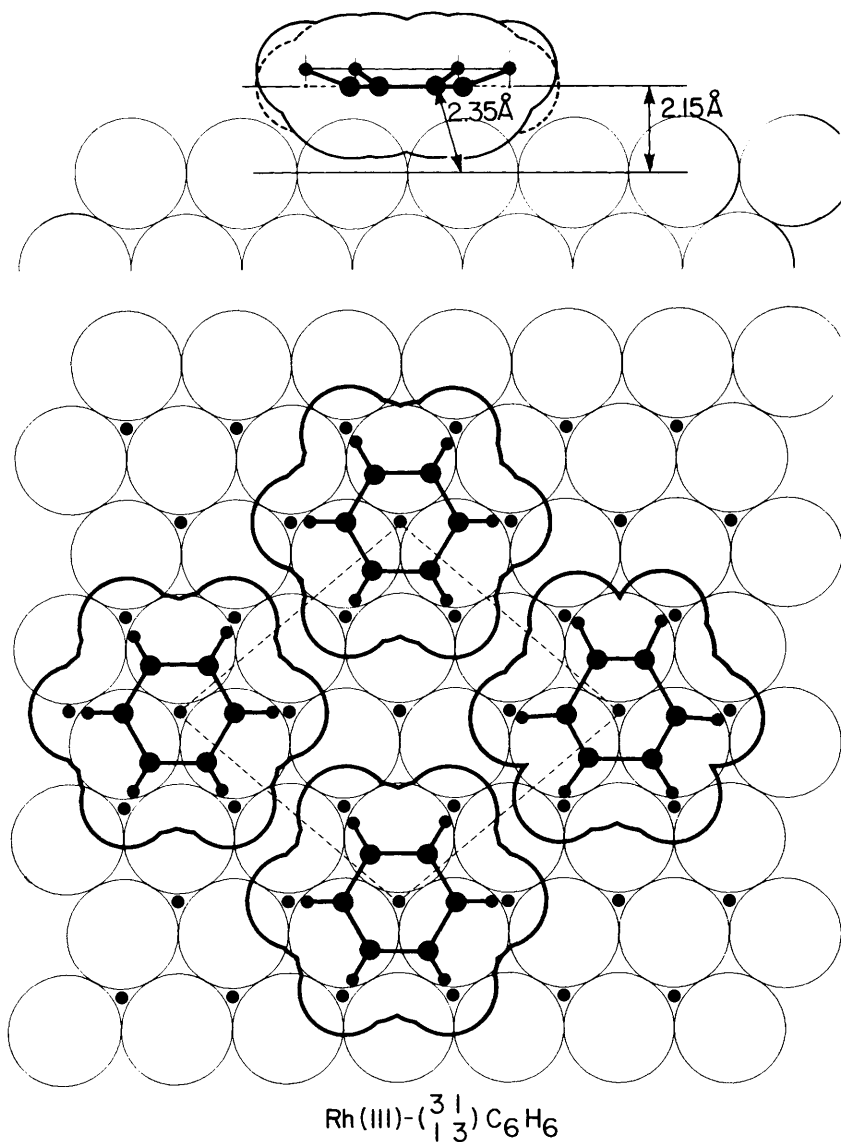$$Rh(III)-\begin{pmatrix}3 & 1\\ 1 & 3\end{pmatrix} C_6 H_6$$

Figure 13 *The surface structure of benzene as determined from low energy diffraction studies and surface crystallography*

face species, an important conclusion in our scrutiny of the surface chemical bond.[23]

[23] G. A. Somorjai, 'Proc. 9th Intl. Conf. on Atomic Spectroscopy', XXII CSI, Tokyo, June 1982, 'Recent Advances in Analytical Spectroscopy,' ed. K. Fuwa, Pergamon Press, 1982, p. 211.
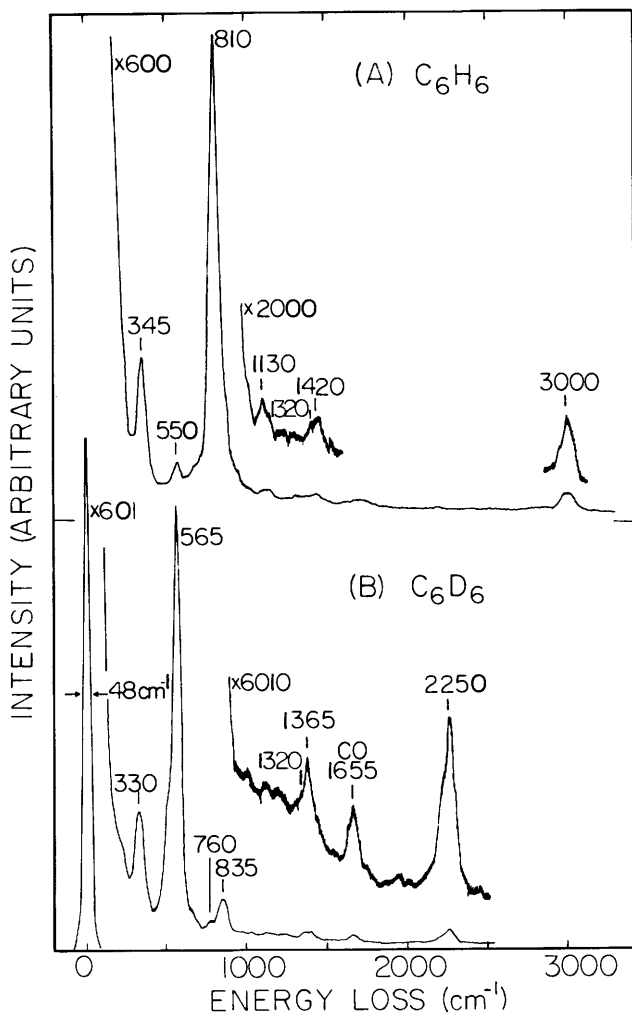
Figure 14 *The vibrational spectra of benzene and deuterated benzene as determined by high resolution electron energy loss spectroscopy*

Figure 17 shows the sequential change of the vibrational spectrum of chemisorbed C_2H_4 on the Rh(111) crystal face as the temperature is increased.[24] The molecule decomposes and there is evidence for the presence of CH, C_2, and C_2H species on the surface in the spectra. Figure 18 shows schematically many of these species that were detectable by HREELS (not by LEED because these

---

[24] B. E. Koel, J. E. Crowell, C. M. Mate, and G. A. Somorjai, *J. Phys. Chem.*, submitted for publication (1984).

333
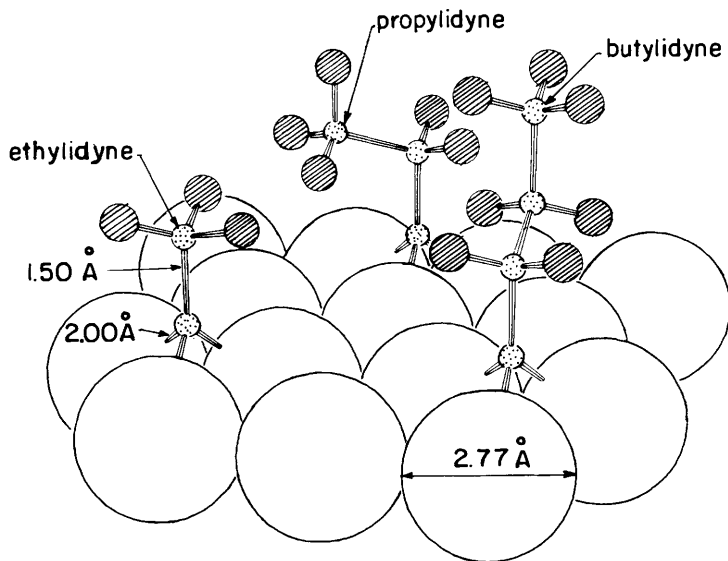
Pt (III) + ethylidyne , propylidyne and butylidyne

Figure 15 *Surface structures for alkylidyne species formed on platinum (111) after the adsorption and rearrangement of ethylene, propylene, and butenes. These structures were determined by LEED surface crystallography*

fragments are disordered) and also $-CH_3$ that has not been observed as yet.[25] It is believed that the location of these organic fragments is governed by the necessity of tetrahedral symmetry for the bonding carbon atoms. That is, a $\equiv CH$ fragment occupies a three-fold site with bonding to three metal atoms; a CH_2 fragment has two metal bonds at a bridge site, and by analogy a $-CH_3$ fragment should have one metal bond and be localized at a top site. If this is the desired bonding configuration of the various fragments, it explains the mechanism by which a three-fold strongly-binding sites is freed by successive hydrogenation of the fragments and becomes available to the next incident molecule.

The alkylidyne molecules are present only under conditions of catalysed reactions at low temperatures, as they decompose above 400 K on most transition-metal surfaces. This restricts their importance by and large to hydrogenation reactions, which having low activation energies may proceed well below 400 K. Recent studies of C_2H_4 hydrogenation over Pt and Rh(111) crystal faces indicate that it occurs on top of the ethylidyne layer that remains ordered and its residence time is much longer than the turnover time of C_2H_4 hydrogenation.[26]

[25] C. Minot, M. A. Van Hove, and G. A. Somorjai, *Surf. Sci.*, 1982, **127**, 441.
[26] F. Zaera and G. A. Somorjai, *J. Am. Chem. Soc.*, 1983, in press.

Different ethylidyne species: bond distances and angles
(r_C = carbon covalent radius; r_M = bulk metal atomic radius)
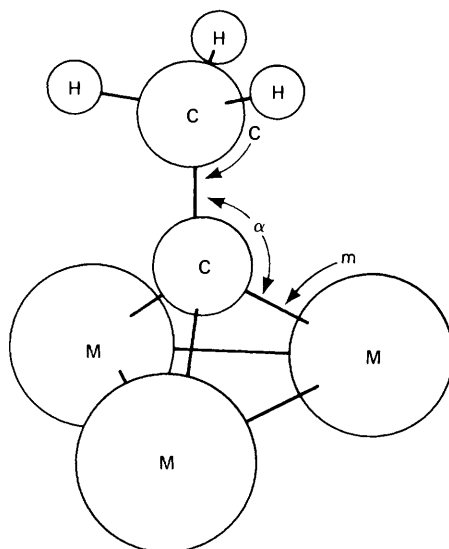
	C [Å]	m	r_M	r_C	α [°]
Co_3 $(CO)_9$ CCH_3	1.53 (3)	1.90 (2)	1.25	0.65	131.3
H_3 Ru_3 $(CO)_9$ CCH_3	1.51 (2)	2.08 (1)	1.34	0.74	128.1
H_3 Os_3 $(CO)_9$ CCH_3	1.51 (2)	2.08 (1)	1.35	0.73	128.1
Pt (111) + (2 × 2) CCH_3	1.50	2.00	1.39	0.61	127.0
Rh (111) + (2 × 2) CCH_3	1.45 (10)	2.03 (7)	1.34	0.69	130.2
$H_3C - CH_3$	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

Figure 16 *The surface structure of ethylidyne, the bond distances and angles, are compared with several tri-nuclear metal cluster compounds of similar structure*

For other catalysed hydrocarbon reactions that occur at an appreciable rate only at higher temperatures the organic fragments are the permanent fixture on the surface during the reaction. Their main role appears to be H-transfer to the adsorbed reaction-intermediates as the C–H bonds retain the hydrogen more easily than the bare transition-metal surface. H–D exchange studies using pre-deuterated
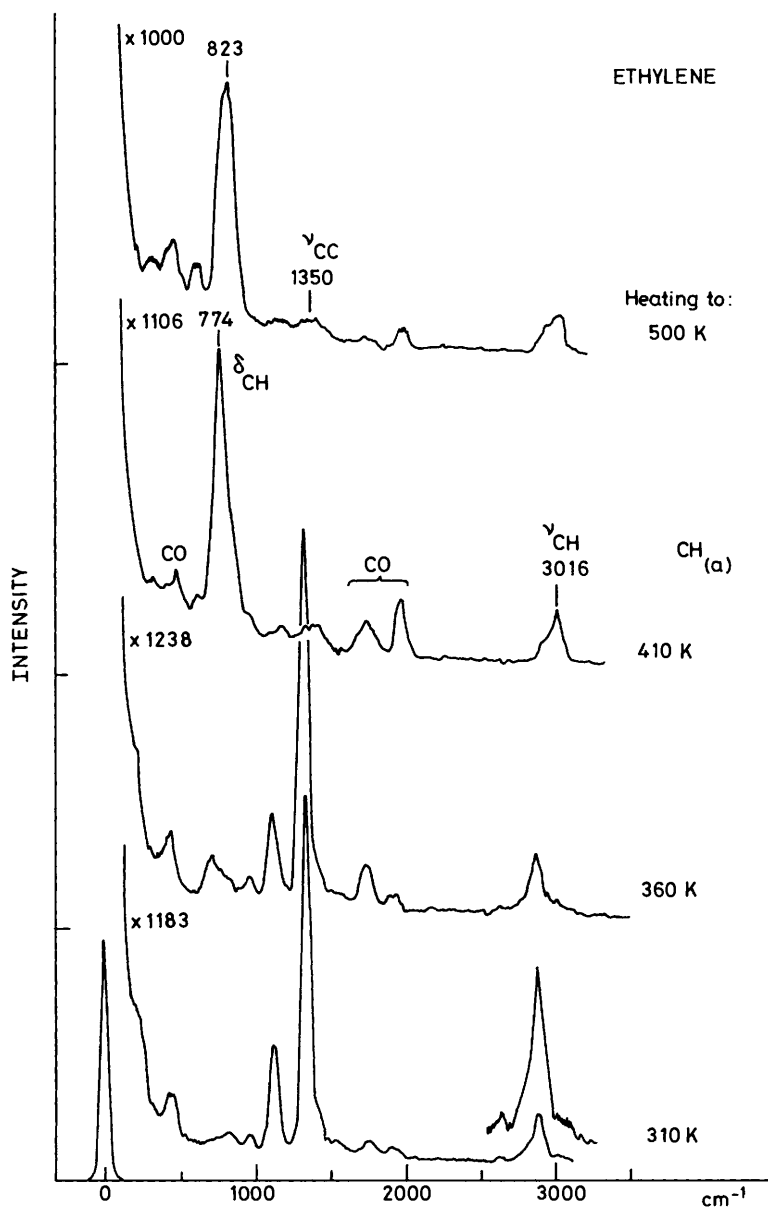
335

Figure 17 *Changes of the vibrational spectrum of chemisorbed ethylene as a function of increasing temperature. Sequential decomposition is clearly visible from the vibrational spectrum obtained by high resolution electron energy loss spectroscopy*
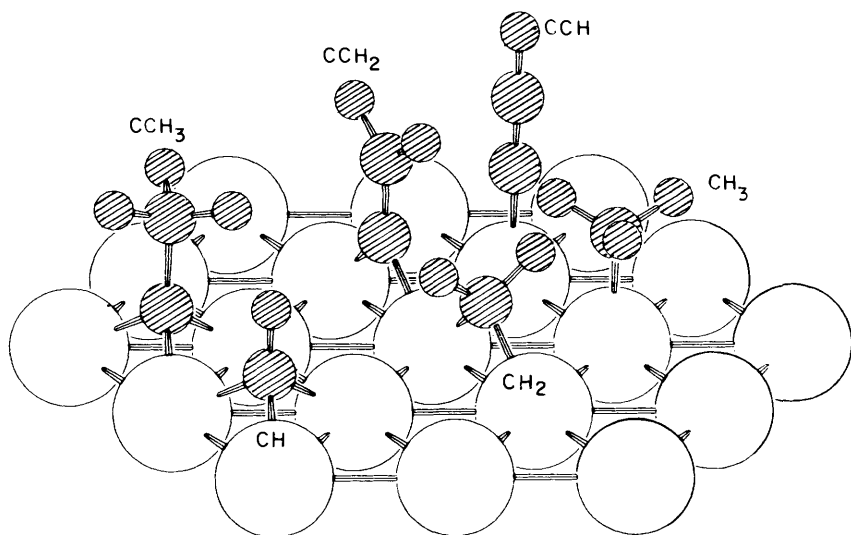
Figure 18 *Schematic representation of the various organic fragments that are present on metal surfaces at high temperature. The presence of CH, C_2, C_2H, CH_2, and C–CH$_3$ species have been detected*

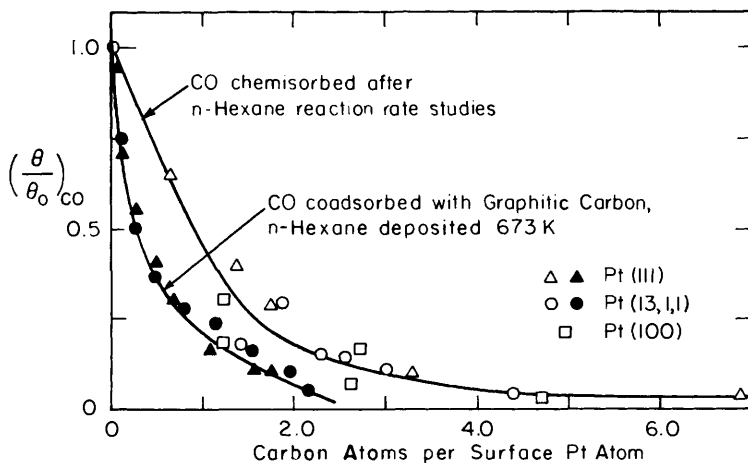CO Chemisorption on Carbon Covered Pt(III), Pt(IOO) and Pt(I3,I,I)

Figure 19 *Fractional concentrations of uncovered platinum surface sites determined by* CO *adsorption–desorption as a function of surface carbon coverage on the* (100), (111), *and* (13,1,1) *platinum crystal surfaces. A comparison is made between the* CO *uptake determined following n-hexane reaction studies and* CO *uptake determined when* CO *was co-adsorbed with graphitic surface carbon*

fragments or reactants indicate that the rate of H–D exchange is at least an order of magnitude faster than the turnover rate of most hydrocarbon conversion reactions. Thus, the hydrogen atoms in the C–H bonds of the strongly held organic fragments are readily transferred to the adsorbed intermediates whereas the carbon atom does not exchange easily.

Fortunately not all of the metal sites are covered with the organic fragments, although AES studies indicate that more than a monolayer of carbon is present on the surface under catalytic reaction conditions. We can titrate the remaining bare metal-sites by the chemisorption of CO at low pressures which, under the same conditions, does not absorb on the carbonaceous deposit.[6] Figure 19 shows the fraction of the bare metal surface $(\theta/\theta_0)_{CO}$ that is present after the reaction where θ_0 is the concentration of chemisorbed CO on the initially clean metal-surface before the reaction. About 5—20% of the Pt is uncovered, the bare-metal area decreasing with increasing reaction temperatures. Of course at higher hydrogen pressures (all hydrocarbon conversion reactions are carried out in the presence of excess hydrogen) the fraction of uncovered metal increases.

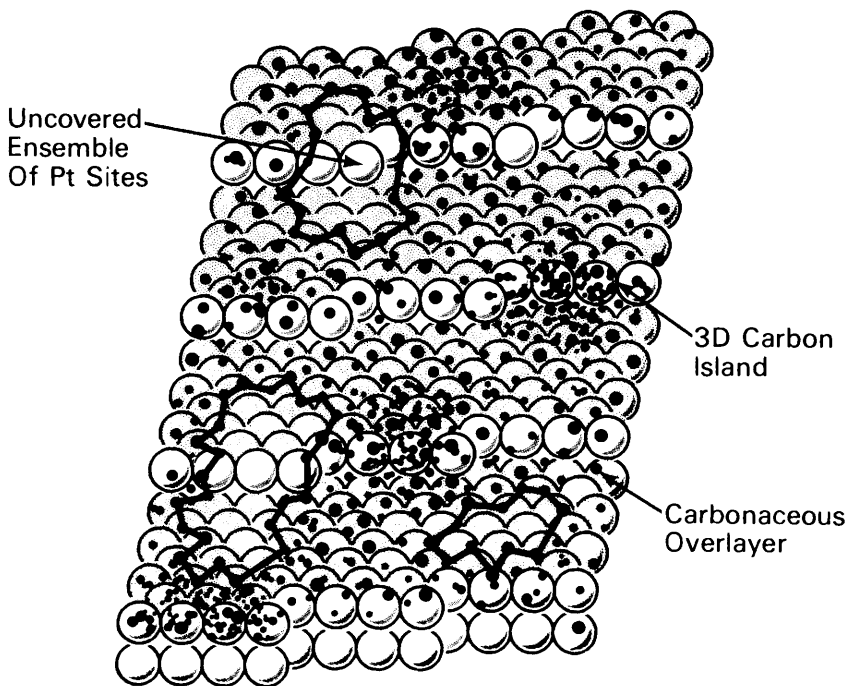## MODEL FOR THE WORKING PLATINUM CATALYST

Figure 20 *Model for the working platinum catalyst that was developed from our combination of surface studies using single crystal surfaces and hydrocarbon reaction rate studies on these same surfaces*

From these studies a molecular model of the working Pt catalyst can be constructed and is shown in Figure 20. There are bare-metal islands whose structure is determined mostly by the catalyst fabrication.[6] The incident reactant molecules adsorb and undergo chemical rearrangements on these metal islands. Then the adsorbed intermediates diffuse onto the carbonaceous deposit, pick up one or more hydrogen atoms, and desorb as the products. Once the carbon deposit loses all its hydrogen and becomes graphitic, hydrogen transfer, which is an important part of the catalytic reactions, can no longer occur and the catalyst surface becomes inactive.

4 Oxidation State of Surface Atoms

The importance of different oxidation states of transition-metal ions can well be demonstrated through the studies of the CO/H_2 reaction over rhodium.[12] The metal produces mostly methane, as shown in Figure 21, because it dissociates CO
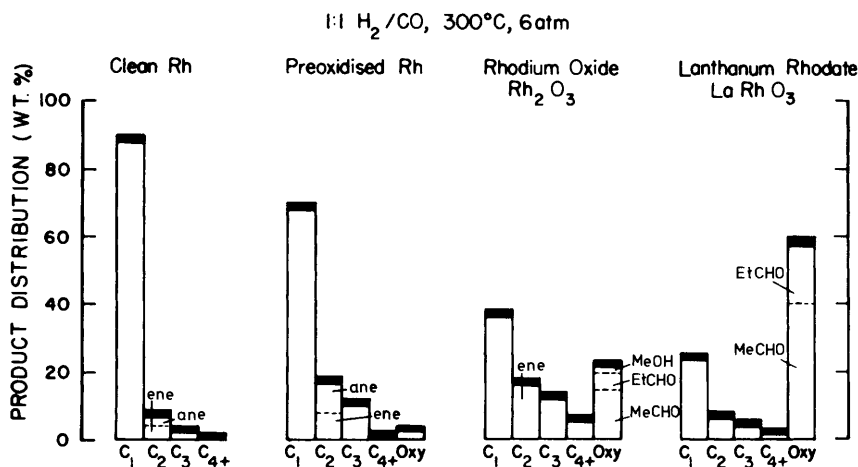

Figure 21 *Product distribution in the carbon monoxide hydrogenation reaction on various rhodium compound surfaces*

and has superior hydrogenating ability. However, over Rh_2O_3 surfaces a large fraction of oxygenated molecules CH_3CHO, CH_3OH, and C_2H_5OH form. When the rhodium ion is incorporated into the crystal lattice of a refractory oxide such as La_2O_3 in the form of $LaRh_2O_3$ the products of the CO/H_2 reaction are exclusively oxygenated hydrocarbons.[27] This drastic change in reaction selectivity has several causes. Figure 22 shows the heats of adsorption of CO and D_2 on the rhodium metal, Rh_2O_3, and $LaRhO_3$ surfaces. Rh_2O_3 binds CO more weakly and D_2 more strongly than the rhodium metal. However, the active $LaRhO_3$ appears to have at least two binding states, indicating that the transition metal is present on the active surface in at least two different oxidation states.

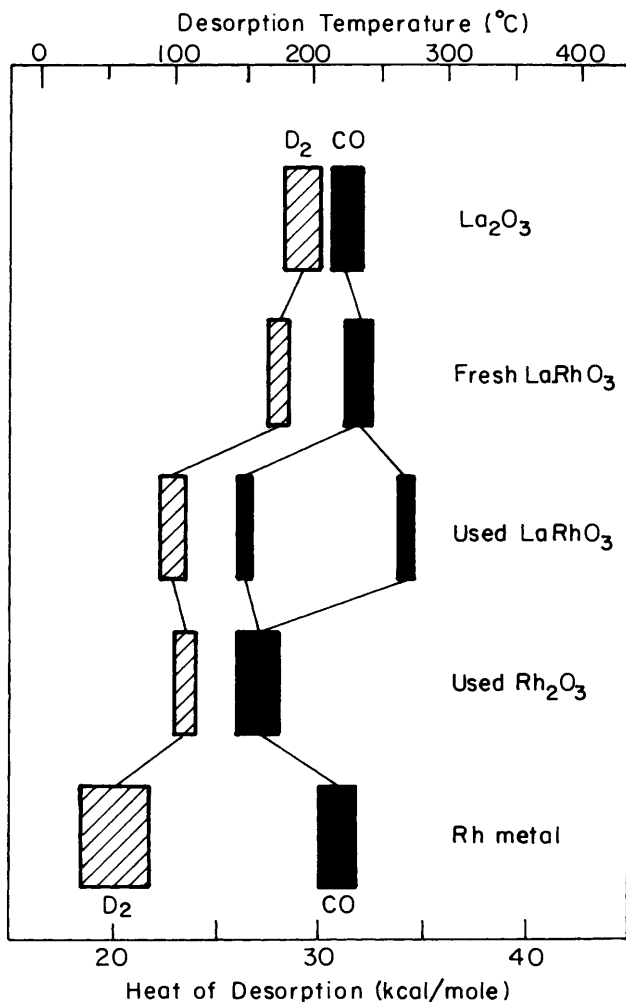[27] P. R. Watson and G. A. Somorjai, *J. Catal.*, 1982, **74**, 282.

Figure 22 *Heat of desorption* (kcal mole^{-1}) *of* CO *and* D$_2$ *from lanthanum oxide, fresh and used lanthanum rhodate, fresh and used rhodium oxide and rhodium metal. The spread of each value represents the variation with surface coverage rather than experimental uncertainty*

Rhodium oxide has a unique ability to carbonylate olefins, an important step toward the formation of oxygenated species. When C$_2$H$_4$ is added to the CO/H$_2$ reactant mixture it is carbonylated quantitatively to propionaldehyde. On rhodium metal, ethylene was hydrogenated fully to ethane. Thus, oxidation of the metal reduces its hydrogenation ability and makes it active for carbonylation.

The difficulty is to maintain the higher metal oxidation states that produce desireable products under conditions of the catalytic reactions that occur in a

highly reducing atmosphere. The refractory oxide support plays a key role in this circumstance. The Auger spectra of Rh_2O_3 before and after the CO/H_2 reaction indicates that the oxide is reduced to the metal within an hour with the corresponding change of the product distribution from the oxygenated species to methane. However, $LaRhO_3$ does not loose its lattice oxygen and the Rh^{3+} ion is fixed in the crystal lattice by the large lattice energy. Thus, the higher oxidation state transition-metal ion is kinetically stabilized in the reducing reaction mixture and remains stable indefinitely as long as the temperature is not increased too high. The so-called strong metal support-interaction is often used to stabilize one or more different oxidation states of transition-metal ions. Thus, the catalyst support plays an important chemical role in most catalyst systems in addition to providing high surface areas on which the metal component may be finely dispersed.

Another example of the importance of the changing oxidation state of transition-metal ions at the surface is shown by the catalytic cycle leading to the photocatalysed dissociation of H_2O or $SrTiO_3$ surfaces.[28] This is shown in Figure 23. The oxide surface is completely hydroxylated in the presence of water and the Ti ions are in the 4 + formal oxidation state. When the surface region is irradiated with light of energy 3.1 eV or larger, electron-hole pairs are generated. The electron is utilized to reduce the Ti^{4+} to the Ti^{3+} formal oxidation state. The electron vacancy induces charge-transfer from the hydroxy-group, producing OH radicals that dimerize to H_2O_2 and split off oxygen that evolves.[29] The reduced Ti^{3+}-containing surface can now adsorb another water molecule that acts as an oxidizing agent to produce Ti^{4+} again and a hydroxylated surface, evolving hydrogen in the process. Clearly changes of oxidation states of transition metal ions are frequently indispensable reaction steps in catalytic processes.
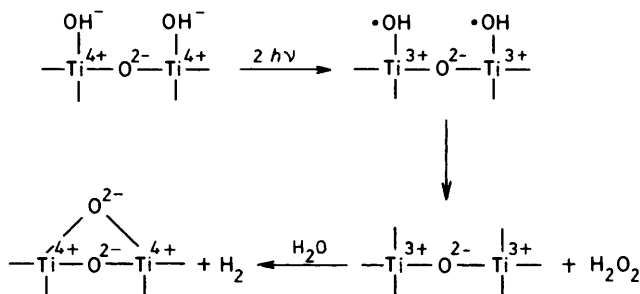

Figure 23 *A proposed mechanism for the photodissociation of water over* TiO_2 *and* $SrTiO_3$ *surfaces*
(Van Damme and Hall, *J. Am. Chem. Soc.*, 1980, **101**, 4373)

5 The Building of Catalysts

By giving the examples of surface and catalytic studies on well characterized systems I hoped to demonstrate the understanding that could be achieved of the

[28] F. T. Wagner, S. Ferrer, and G. A. Somorjai, in 'Photoeffects at Semiconductor-Electrolyte Interfaces', ed. A. J. Nozik, ACS Symposium Series No. 146, 1981, p. 159.
[29] H. Van Damme and W. K. Hall, *J. Am. Chem. Soc.*, 1979, **101**, 4373.

molecular ingredients of important catalytic systems. We can now utilize this understanding to build better systems by alteration of their structure or their state of surface charge. Below we discuss two examples of deliberate catalyst modifications: the effects of gold and potassium on transition-metal catalysis.

A. The Effect of Gold on the Selectivity and Activity of Pt Catalysts.—The influence of gold on Pt hydrocarbon conversion catalysis has been studied by condensing Au on Pt crystal surfaces. Gold forms epitaxial layers on Pt and upon heating it forms an alloy in the near surface region.[30] This Au–Pt alloy has a markedly different selectivity and activity for the conversion of n-hexane into other hydrocarbons as shown in Figure 24. The isomerization rate goes up as compared to that on clean Pt
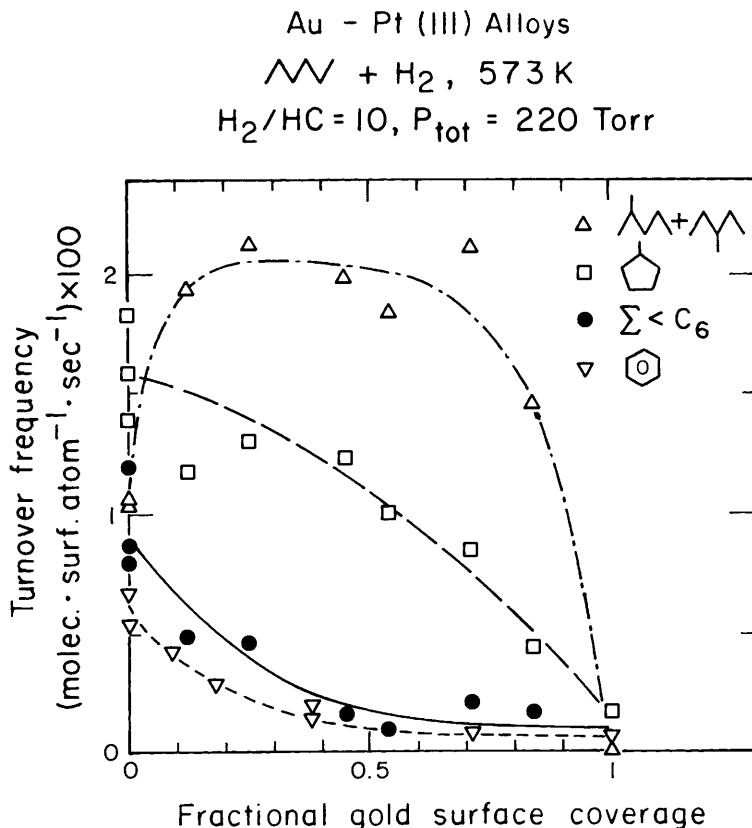

Figure 24 *The rate of formation of various products from n-hexane as a function of fractional gold surface coverage for gold–platinum alloys that were prepared by vapourizing and diffusing gold into Pt(111) crystal surfaces*

[30] J. W. A. Sachtler, M. A. Van Hove, J. P. Biberian, and G. A. Somorjai, *Surf. Sci.*, 1981, **110**, 19.

while the hydrogenolysis and dehydrocyclization rates are reduced exponentially with increasing gold concentration.[31] This remarkable selectivity and activity alteration can be explained by a change of structure of the Pt(111) surface induced by gold alloying. By substitution of a gold atom, the high co-ordination three-fold Pt sites are eliminated much faster than the two-fold and one-fold bridge and top sites. This is commonly called the ensemble effect. As a result, the chemistry that requires the adsorption of molecules and surface intermediates at the three-fold sites is eliminated while the chemical reactions that require adsorption at bridge or top sites are not attenuated. Although subtle electronic changes may also occur at the alloy surface sites, most of the results can be rationalized by this selective high co-ordination site elimination model.

Similar observations were reported by Boudart *et al.* for the production of water from H_2 and O_2 over Pd–Au alloy surfaces. Small amounts of gold increased the rate of this reaction by fifty-fold.

It should be noted that gold is a very poor catalyst for both of these reactions. Nevertheless, its presence as an alloying constituent can beneficially influence the selectivity and the reactivity of transition metal catalysts.

B. The Effect of Potassium on the Bonding and Reactivity of Carbon Monoxide and Hydrocarbons.—Potassium has a high heat of adsorption when present in low coverages on transition-metal surfaces (Figure 25). Simultaneously it also reduces the work function of the transition metals, indicating large charge-transfer between the metals.[32] A model that assumes that potassium is ionized when adsorbed on the transition-metal surface explains these results. As the potassium concentration
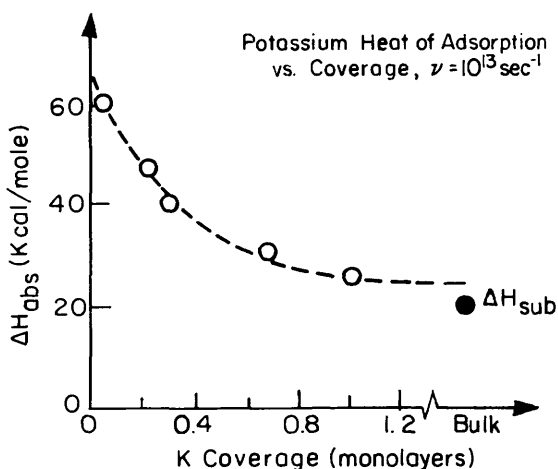

Figure 25 *The heat of adsorption of potassium on platinum single crystal surfaces as a function of potassium coverage*

[31] J. W. A. Sachtler and G. A. Somorjai, *J. Catal.*, 1983, **81**, 77.
[32] E. L. Garfunkel and G. A. Somorjai, *Surf. Sci.*, 1982, **115**, 441.

increases the charged species repel each other and depolarization occurs; the potassium layer becomes metallic and its heat of adsorption approaches rapidly the heat of sublimation of potassium metal.

Potassium has a strong influence on the heat of adsorption of CO on transition-metal surfaces. This is shown in Figure 26. In the absence of potassium, CO desorbs at a maximum rate from the Rh(111) surface at 400 K. However, when co-adsorbed with 50% of a monolayer of potassium, it desorbs at 600 K indicating a 12 kcal
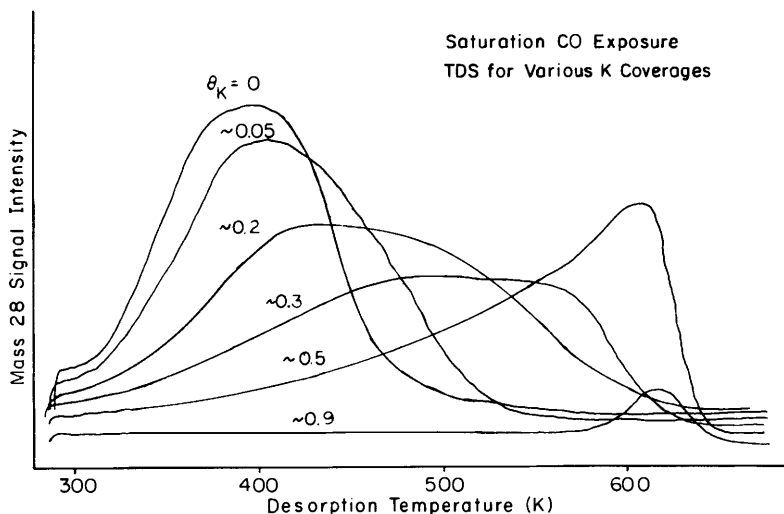

Figure 26 CO *thermal desorption spectrum from clean platinum and when co-adsorbed with potassium on platinum crystal surfaces*

increase of its binding energy.[33] The HREELS spectra of CO on Pt(111) also exhibits major changes that are shown in Figure 27. In the absence of CO, two well-defined CO stretching frequencies are detectable that are associated with CO at a top and at a bridge site adsorbed with its CO bond perpendicular to the surface.[33] As the potassium is added to the Rh surface, CO shifts to the bridge site and its stretching frequency decreases by more than 300 cm^{-1}.[34] This corresponds to a gradual change of bond order with increasing potassium coverage from 2 to 1.5. This indicates that the electron transferred from the potassium to the transition metal density of states can populate the antibonding molecular orbitals of CO, thereby weakening the C–O bond. Simultaneously the metal–carbon bond is strengthened as charge density in this bonding orbital must increase.

Potassium is often used as a beneficial additive to transition-metal catalysts utilized for the hydrogenation of carbon monoxide. Its presence increases the

[33] E. L. Garfunkel, J. E. Crowell, and G. A. Somorjai, *J. Phys. Chem.* 1982, **86**, 310.
[34] J. E. Crowell and G. A. Somorjai, 'Summary Abstract for the American Vacuum Society 30th National Vacuum Symposium', Nov. 1—4, 1983, Boston, Massachusetts, *J. Vac. Sci. Tech.*, submitted for publication (1983).
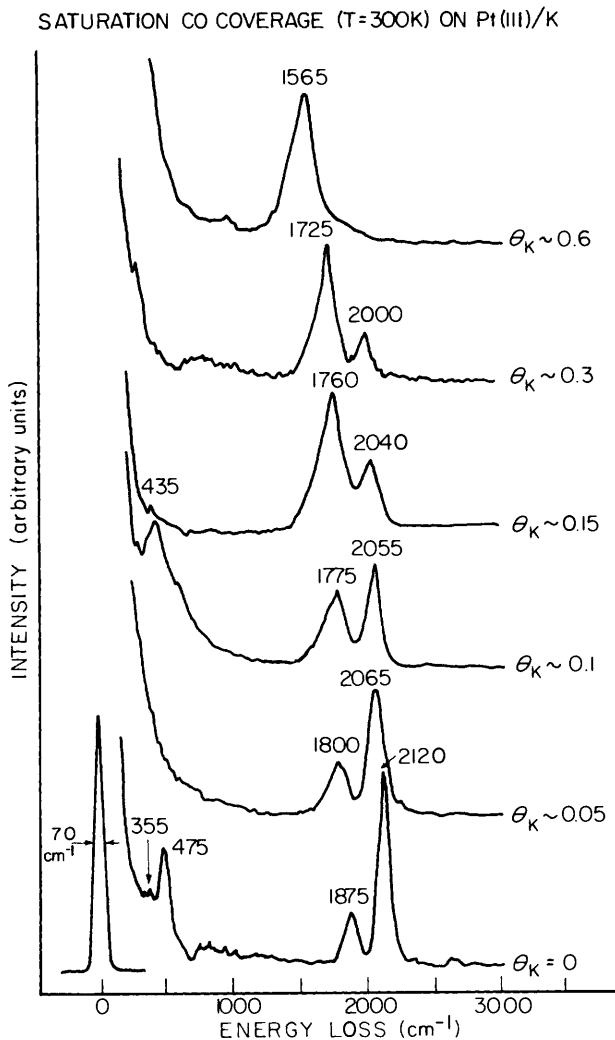
SATURATION CO COVERAGE (T=300K) ON Pt(III)/K

Figure 27 *Vibrational spectra of CO at the saturation coverage when chemisorbed on* Pt(111) *at* 300 K *as a function of a pre-adsorbed potassium coverage*

molecular weight of hydrocarbon products, as would be expected if the dissociation rate of carbon monoxide is enhanced.

Potassium, however, is a non-selective poison for hydrocarbon reactions on platinum surfaces.[35] The reason for this is revealed in recent surface studies. The presence of potassium increases the activation energy for the breaking of C–H

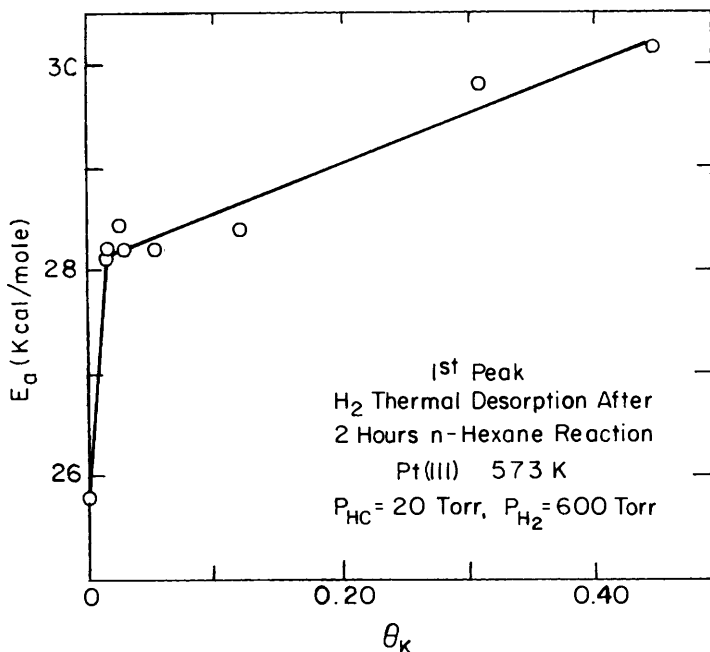[35] F. Zaera and G. A. Somorjai, *J. Catal.*, 1983, **84**, 375.

Figure 28   *Activation energy of the hydrogen β-elimination from carbonaceous deposits after n-hexane reactions over platinum (111) surfaces as a function of potassium coverage*

bonds, which is an important step in most hydrocarbon conversion reactions. This is shown in Figure 28. Thus, the surface residence time of the molecules increase and this reduces the catalytic turnover rates.

There is little doubt that potassium influences the catalytic reaction by charge transfer, that is, by electronic changes. It has large effects on some molecules when co-adsorbed with them (CO, N_2) and virtually no effects on others (NO, PF_3).[36] It would be of value if we could predict by the use of theoretical techniques whether charge transfer between the molecular orbitals of adsorbates and the charge density that is altered by the adsorption of potassium on the transition-metal surface could or could not take place.

6 New Reactions, New Processes
As our understanding of how catalysts work increases through the application of molecular surface science, it will be increasingly possible to find catalysts for reactions for which good catalysts do not seem to exist. There are many important reactions of small molecules such as CO_2, CH_4, H_2O, and N_2 that may be investigated. CO_2 could be well utilized as a source of carbon-containing chemicals if it could be hydrogenated to $HCOOH$ or dissociated to CO. Figures 29—31

[36] E. L. Garfunkel. J. J. Maj, J. C. Frost, M. H. Farias, and G. A. Somorjai, *J. Phys. Chem.*, 1983, **87**, 3629.
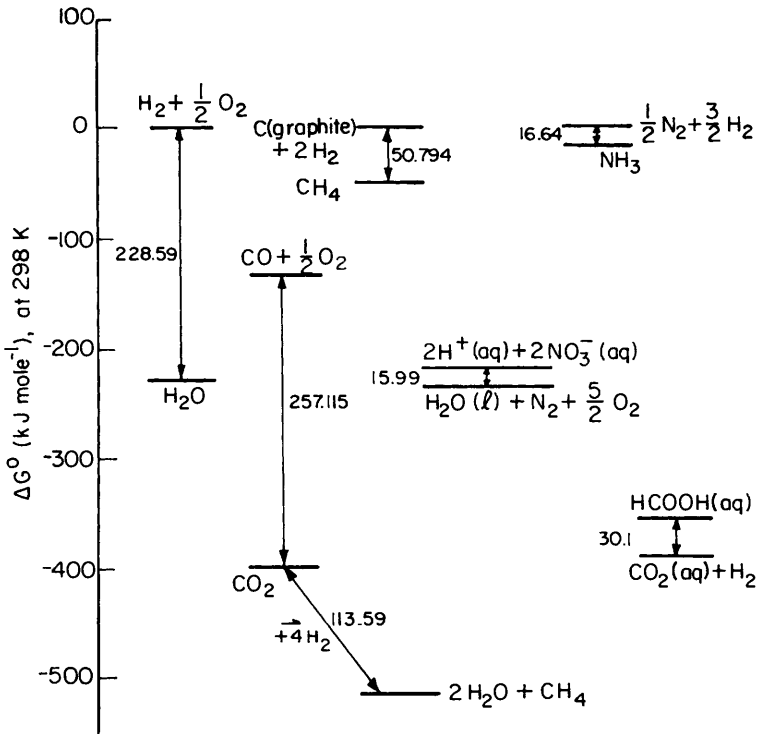
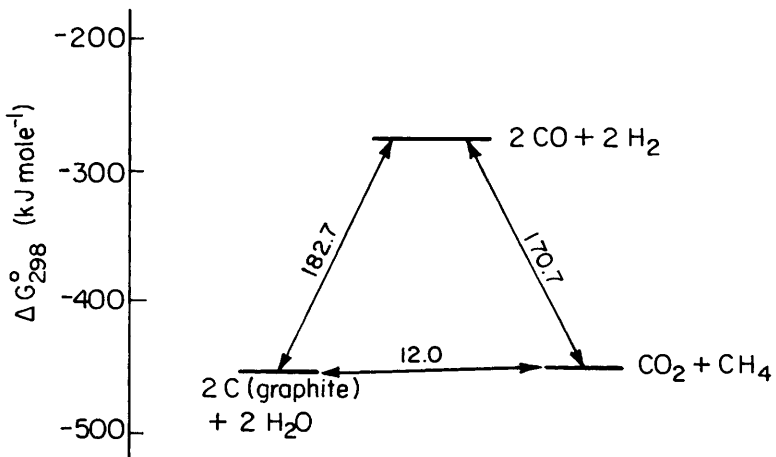**Figure 29** *Standard free energies for several chemical reactions*

Figure 30 *Standard free energies for several chemical reactions*

show the free energy changes associated with several reactions. While CO_2 hydrogenation is thermodynamically feasible, its dissociation to CO and O_2 requires the input of excess energy in the form of light or heat. The reaction of carbon with water to produce CH_4 and CO_2 is thermoneutral, as shown in Figures 29—31. This reaction may represent a desirable alternative for carbon gasification with water to CO and H_2, a very endothermic reaction indeed.

The partial oxidation of methane to CH_2O and CH_3OH should be feasible by suitable catalyst surfaces.[37] These reactions are shown in Figure 31. Finally, the oxidation of nitrogen to nitric acid ($N_2O + 5/2\ O_2 + H_2O \rightarrow 2H^+ + 2NO_3^-$) is thermodynamically feasible, as pointed out by G. N. Lewis in 1923.[38]

'Even when starting with water and air, we see by our equations that nitric acid should form until it reaches a concentration of about 0.1M where the calculated
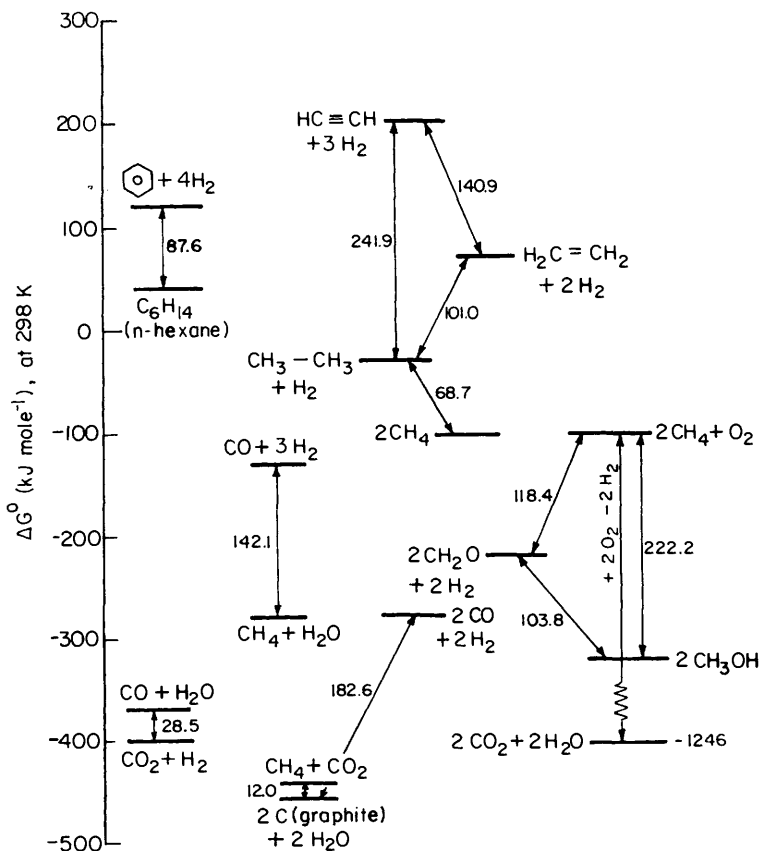

Figure 31 *Standard free energies for several chemical reactions*

[37] M. M. Khan and G. A. Somorjai, *J. Catal.*, to be published (1984).
[38] G. N. Lewis and N. Randall, 'Thermodynamics', McGraw Hill, 1923.

equilibrium exists. It is to be hoped that nature will not discover a catalyst for this reaction, which would permit all of the oxygen and part of the nitrogen of the air to turn the oceans into dilute nitric acid.'[38]