

DEACTIVATION AND POISONING OF CATALYSTS

Edited by

Jacques Oudar

Henry Wise



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*ECOLE NATIONALE SUPERIEURE
DE CHIMIE DE PARIS
PARIS, FRANCE*

Henry Wise

*SRI INTERNATIONAL
MENLO PARK, CALIFORNIA*

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Preface

In recent years the research effort in heterogeneous catalysis has shifted from studies of chemical reaction kinetics and mechanisms to investigations of specific surface reactions, identification of surface intermediates, and interpretations of catalytic processes in terms of crystal structure, imperfections, surface coordination, and electronic interactions between substrate and overlayer. Therefore, it is timely to examine the problem of catalyst deactivation and poisoning on the atomic level in an attempt to relate fundamental observations in surface science to industrial experiences. Transition metal catalysts, which are in widespread use by the petroleum and petrochemical industries, are particularly prone to catalyst deterioration during prolonged operation. The main causes for deactivation can be identified as physical, such as crystallite sintering, and chemical, such as deposition of feed stream impurities or formation of surface residues by side reactions. However, the physical or chemical steps involved in these processes have not been elucidated in sufficient detail to understand the various processes causing such debilitating effects.

During the last decade the availability of advanced surface-sensitive analytical tools and the use of well-defined metal surfaces have given considerable impetus to the study of surface phenomena. In this book we focus primarily on chemically induced effects associated with bonded surface species that cause catalyst activity decline and in some cases a change in catalyst specificity. The offending surface species may be in the form of feed impurities, as in metal poisoning, or reaction intermediates, as in the case of coking.

In Chapter 1 the thermodynamic aspects of sulfur-metal and carbon-metal interactions are presented. The results obtained in experimental studies with well-defined surfaces under well-controlled conditions are analyzed in Chapter 2. The third chapter is devoted to the general features of poisoning of dispersed metal catalysts. Chapter 4 treats the important subject of coking of metal catalysts. The remaining chapters address the problems of deactivation encountered with catalysts used in petroleum refining and petrochemical processing.

Throughout the book the authors attempt to relate the observations made in catalytic processing to concepts derived from surface studies. The information presented reflects the state of the art in this important area of heterogeneous catalysis. As a result, the book will be invaluable to research scientists engaged in basic or applied research and, hopefully, will provide new approaches to the solution of the problem of catalyst deactivation and poisoning.

Jacques Oudar
Henry Wise

Contributors

Jacques Barbier Professeur, Laboratoire de Catalyse Organique,
Université de Poitiers, Poitiers, France

Jean-Pierre Franck R & D Project Manager for Catalytic Reforming,
Kinetics and Catalysis, Institut Français du Pétrole, Rueil-Malmaison,
France

Germain P. Martino Adjoint au Directeur de Recherches, Direction de
Recherche "Cinétique et Catalyse," Institut Français du Pétrole, Rueil-
Malmaison, France

Jon McCarty Program Manager, Catalysis Group, Materials Research
Laboratory, SRI International, Menlo Park, California, U.S.A.

Claude Naccache Directeur de Recherche, Institut de Recherches sur
la Catalyse, Centre National de la Recherche Scientifique (CNRS),
Villeurbanne, France

P. E. Højlund Nielsen Senior Scientist, Haldor Topsøe A/S, Lyngby,
Denmark

Jacques Oudar Professeur, Laboratoire de Physico Chimie des Surfaces,
Ecole Nationale Supérieure de Chimie de Paris—E.N.S.C.P., Paris
France

vi / Contributors

J. R. Rostrup-Nielsen Deputy Director, R & D Division, Haldor
Topsøe A/S, Lyngby, Denmark

David L. Trimm Professor, School of Chemical Engineering &
Industrial Chemistry, University of New South Wales, Kensington,
New South Wales

Henry Wise Scientific Fellow, Materials Research Laboratory, SRI
International, Menlo Park, California, U.S.A.

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1

Sulfur and Carbon Interactions with Metal Surfaces

HENRY WISE and JON McCARTY SRI International, Menlo Park,
California

JACQUES OUDAR Ecole Nationale Supérieure de Chimie de Paris,
Paris, France

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I. INTRODUCTION

On metal surfaces the presence of adsorbed species containing sulfur, carbon, and halogens is the most serious cause of catalyst poisoning. The presence of such foreign species on the catalyst surface not only can block reactions sites, but can induce changes in surface morphology due to faceting, result in preferential segregation of one component in a multicomponent metal catalyst particle, enhance sintering as a result of adsorbate-induced diffusional transport of metal surface components, and modify metal-support interactions.

In the following sections, the various phenomena associated with catalyst deactivation by adspecies are examined in terms of structural phenomena and adsorption energetics. These studies carried out during the last two decades with modern surface-sensitive techniques, such as Auger electron spectroscopy (AES), low-energy electron diffraction (LEED), and x-ray photoelectron spectroscopy (XPS), have provided some insight into the causes of and cures for surface poisoning of metal catalysts.

II. THERMODYNAMICS OF ADSORPTION AND SEGREGATION

The thermodynamic properties of the surface-adlayer interface play an important part in controlling the compositional and structural heterogeneities caused by catalyst poisoning. Of primary interest to our subject is the adsorption equilibrium which is established between the gas phase in contact with the solid surface. Closely related to it is the segregation and dissolution equilibrium, which deals with the interface between the bulk solid and the surface region.

Equilibrium adsorption (or segregation) is accompanied by a decrease in the total energy of the system. Because of differences in local environment, the bonding of adspecies at the surface can exhibit configurations different from those encountered in the bulk phase.

To obtain a relationship between the equilibrium surface density of adspecies and their concentration in the gas phase it is most useful to employ the Gibbs "dividing surface" [1,2]. It states that the total value of any extensive property Y for the entire system, with reference to a dividing plane parallel to the surface, is the sum of that property in the bulk phase Y^b , that in the gas phase Y^g , and that of the surface Y^s (generally called the surface excess).^{*} For a system with an interface, the surface excess internal energy E^s is

$$E^s = TS^s + \sum \mu_i N_i^s + \gamma A \quad (1)$$

^{*}The assumption is made that the value of Y^b and Y^g extend to the dividing surface.

where γ is the surface tension of the surface, N_i^S the surface excess of component i , S^S the surface excess entropy, and μ_i the chemical potential of component i .

A small change in the surface properties yields for the surface excess internal energy

$$dE^S = T dS^S + \sum \mu_i dN_i^S + \gamma dA \quad (2)$$

which on subtraction from the differential form of Eq. (1) results in the Gibbs adsorption equation

$$d\gamma = -\frac{1}{A}(S^S dT + \sum N_i^S d\mu_i) \quad (3)$$

At constant temperature one obtains the Gibbs adsorption isotherm

$$d\gamma = -\sum \Gamma_i d\mu_i \quad (4)$$

where $\Gamma_i = N_i^S/A$ is the specific surface excess. In the case of an adsorbate it represents the surface coverage. For an ideal gas

$$\mu_i = \mu_i^\circ + RT \ln p_i \quad (5)$$

where μ_i is the chemical potential of the gas and p_i the partial pressure of component i . Therefore, for a single gas-phase component the adsorption isotherm [Eq. (4)] reads

$$d\gamma = -RT \Gamma_i d \ln p_i \quad (6)$$

or

$$\Gamma_i = -\frac{1}{RT} \left(\frac{d\gamma}{d \ln p_i} \right)_T \quad (7)$$

The isothermal change in surface tension in the presence of an adsorbate is obtained by integration of Eq. (6):

$$\gamma = \gamma_0 - RT \int \Gamma_i d \ln p_i \quad (8)$$

* The surface tension is defined as the work (dW) required for the reversible formation of an interface area increment dA [i.e., $\gamma = \lim_{dA \rightarrow 0} (dW/dA)$].

For the case of Langmuir-type nondissociative adsorption the analytical expression between Γ_1 and p_1 reads

$$\Gamma_1 = \frac{b_1 P_1}{1 + b_1 P_1} \quad (9)$$

where b_1 is a constant of the order of the adsorption site density, and $P_1 = p_1/p_1^*$, with p_1 the partial pressure of the gas-phase component in equilibrium with the solid surface, and p_1^* the partial pressure of the gas-phase component at which saturation coverage of the surface is attained. On integration of Eq. (8) one finds

$$\gamma = \gamma_0 - b_1 RT \ln(1 + P_1) \quad (10)$$

where γ_0 is the surface tension of the clean surface. It is quite apparent that the adsorbed species cause a significant lowering in surface tension with progressive adlayer coverage.

For dissociative adsorption, for which the Langmuir isotherm reads

$$\Gamma_2 = \frac{b_2 P_2^{1/2}}{1 + b_2 P_2^{1/2}} \quad (11)$$

the integrated form of the Gibbs adsorption isotherm reads

$$\gamma = \gamma_0 - 2b_2 RT \ln(1 + P_2^{1/2}) \quad (12)$$

For evaluation of the heat of adsorption we consider the change in chemical potential of the system $d\mu_j$ associated with the transfer of a small mass of component j from the gas phase to the solid surface. The term $d\mu_j$ is the sum of two terms, the partial molar entropy and the partial molar volume*:

$$d\mu_j = \frac{\partial \mu_j}{\partial T} dT + \frac{\partial \mu_j}{\partial p} dp = -\bar{S}_j dT + RT d \ln p_j \quad (13)$$

For the surface at constant coverage Γ_j the change in chemical potential is†.

*For an ideal gas the partial molar volume is $\bar{V} = RT/p$

†The quantities with primes (superscript) refer to the surface.

$$d\mu_j' = \frac{d\mu_j'}{dT} dT = -\bar{S}_j' dT \quad (14)$$

At equilibrium $d\mu_j = d\mu_j'$, so that

$$d \ln p_j = -\frac{1}{RT} (\bar{S}_j' - \bar{S}_j) dT \quad (15)$$

By defining the isosteric heat of adsorption as $\Delta H_a = T(\bar{S}_j' - \bar{S}_j)$ one obtains

$$\left(\frac{d \ln p_j}{dT} \right)_{\Gamma_j} = \frac{\Delta H_a}{RT^2} \quad (16)$$

An analogous expression may be derived for the isosteric heat of segregation from the bulk phase to the surface

$$\left(\frac{d \ln X_j}{dT} \right)_{\Gamma_j} = -\frac{\bar{S}_j' - \bar{S}_j^b}{RT} = \frac{\Delta H_{\text{seg}}}{RT^2} \quad (17)$$

where the superscript b refers to the bulk phase, and X_j to the mole fraction of component j in the bulk phase.

Based on the Gibbs adsorption isotherm [Eq. (8)] a surface adsorbate causes a decrease in the surface tension of a solid. The magnitude of the adsorbate effect on the surface tension of a metal has been evaluated from the adsorption isotherms of sulfur on the low index planes of silver [3]. For Ag(110) at 873 K the results indicate significant changes in surface tension as the adlayer density exceeds one-half saturation coverage (Table 1). Similar considerations apply to the other low-index crystal planes of silver. Thus surface reconstruction and surface transport would be favored with progressive surface coverage.

Similarly, for a multicomponent solid solution, such as a metal alloy surface, enrichment is to be expected with the component of lowest surface free energy. For a completely miscible binary alloy, whose components (subscripts 1 and 2) have similar atomic radii (perfect solution), the Gibbs adsorption isotherm reads

$$\frac{\bar{X}_1^s \bar{X}_2^s}{\bar{X}_1^b \bar{X}_2^b} = \exp \left[\frac{(\gamma_2 - \gamma_1) a_1}{RT} \right]$$

TABLE 1 Change in Surface Tension of Ag(110) at 873 K with Sulfur Coverage

Gas-phase composition $\text{PH}_2\text{S}/\text{PH}_2$	Equilibrium adsorbate density [(S atom/cm ²) $\times 10^{-14}$]	Surface tension difference $\gamma_0 - \gamma$ (erg/cm ²)
0	0	0
5.6×10^{-3}	0.75	0
7.4×10^{-3}	2.07	0
1.0×10^{-2}	4.90	0
1.3×10^{-2}	6.41	31
1.8×10^{-2}	6.78	52
3.2×10^{-2}	6.97	95
5.6×10^{-2}	7.00	152

Source: Calculations based on data from Ref. 125.

where X represents the mole fraction of the two components on the surface (s) and in the bulk (b), and a_i the average molar surface area of the two components. For alloys with components of different atomic radii, the elastic strain theory needs to be applied, as discussed in a recent review [4].

In addition, the surface composition will be affected by adspecies which preferentially form bonds with individual components of an alloy. Such adsorbate-induced effects have been examined for the Pt/Sn alloy system [5] in the presence of oxygen and hydrogen. The components of this system have considerably different surface free energies, as evidenced by their heats of sublimation* (300 kJ/mol for Sn and 510 kJ/mol for Pt). Also, they exhibit different affinities for H_2 and O_2 . As could be expected, the surfaces of PtSn and Pt_3Sn become enriched with tin on annealing in vacuum. The adsorption of oxygen causes a further enrichment with tin to which oxygen is more strongly bonded. Reduction of the alloys in hydrogen carries the excess of tin back into the bulk and causes an enrichment of the surface with Pt relative to the annealed state.

Also, changes of substrate surface composition induced by sulfur adatoms have been observed, with surface segregation of copper in

*The heat of sublimation is related as a first approximation to the surface free energy of a metal.

Cu₃Au and Cu₈Au₃ alloys [6], nickel in Cu-Ni alloys [7], and palladium in Pd-Ag alloys [8]. For the latter system a thermodynamic model has been proposed [9,10] based on the approximations of a binary regular solution with solute-solute and solute-solvent interactions.

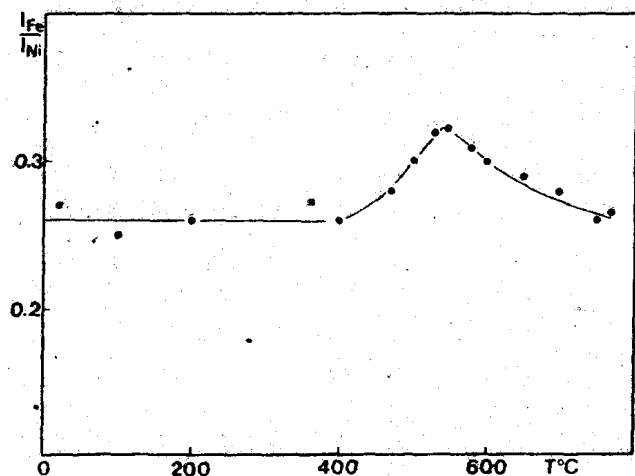
In addition, the surface composition changes may depend on the surface orientation, as has been shown by scanning Auger electron spectroscopy in the case of Cu-Ni alloys [7]. Single-crystal studies with Ni₃Fe have shown no changes in the surface composition compared to the bulk for the clean (111), (100), and (110) planes, as well as for the (100) and (110) planes covered with sulfur [11]. However, reversible changes in the surface composition occur between 673 and 1023 K with sulfur adsorbed on the (111) plane. They may be related to order-disorder transitions [11] (Fig. 1a and 1b).

III. ADSORBATE-INDUCED SURFACE MODIFICATION

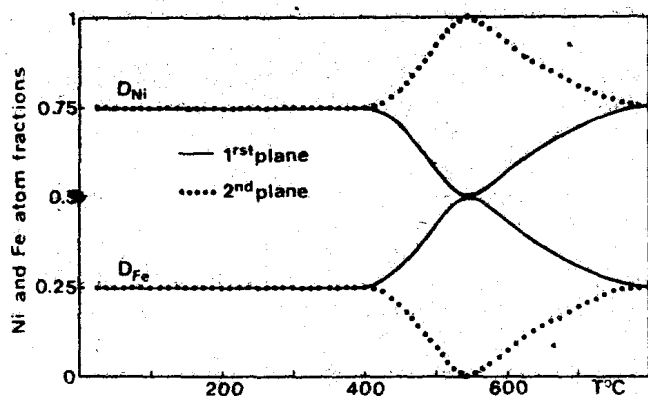
The adsorption of a strongly bonded species may induce complex changes in the structure of a metallic substrate. Thus the interplanar spacing normal to the surface may be altered (surface relaxation). Also, rearrangement of the atoms in the topmost plane of the crystal may occur (surface reconstruction). Finally, the adsorbate can cause drastic changes in the equilibrium shape of the crystal, which can induce instability of certain monatomic steps (two-dimensional faceting) or planes (three-dimensional faceting). The unstable steps or planes break up into segments or planes of new orientations. In general, these phenomena are reversible and on removal of the surface impurity the surface recovers to its original structure.

A. Surface Relaxation

Because surface atoms are in an asymmetrical environment compared to the bulk atoms, the first interplanar spacing normal to the surface is different from the bulk spacing. In most cases a contraction has been observed by electron diffraction or ion scattering. It appears that adsorption restores the first interlayer spacing to a value nearly identical to that of the bulk crystal. In some cases an expansion of the lattice has been observed. Thus, for the Ni(110) surface an inward relaxation of $4 \pm 1\%$ for the clean surface and an outward relaxation of $6 \pm 3\%$ for a surface covered with 0.5 monolayer of sulfur have been measured by low-energy ion scattering [12]. Similar effects have been observed [13] in LEED analysis of C/Ni(100) and O/Fe(100) [13,14].



(a)



(b)

FIGURE 1 (a) Thermal effect on the surface composition of the sulfur-covered (111) face of Ni_3Fe as determined by Auger electron spectroscopy. I_{Fe} and I_{Ni} are the heights of the Auger peaks of Fe and Ni in the derivative mode. (From Ref. 11.) (b) Calculated nickel and iron atom fractions in the first and second planes versus temperature for S-(111) Ni_3Fe as determined from the curve in Fig. 1a. (From Ref. 11.)