

ADVANCES IN CATALYSIS

VOLUME 34

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ADVANCES IN CATALYSIS

VOLUME 34

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Preface

There is something notable about this volume. In four chapters, it demonstrates the diversity of science that constitutes the field of catalysis as well as the cohesiveness of its parts. It covers *technique* of materials analysis, quantum chemical *theory*, a branch of catalytic *practice*, and the discussion of a major *phenomenon* of solids.

Each chapter is a comprehensive overview, but the emphasis is on the current horizon of knowledge. Each should serve not only the researcher, teacher, or practitioner of catalytic science alone, but those in chemistry and materials science with spillovers to solid-state physics and other “disciplinary” practices that deal with the transformation of solids or the fate of molecules that contact solids.

The state and capabilities of quantum chemical modeling of silicon dioxide framework structures (silica, aluminosilicates, zeolites) are discussed by Zhidomirov and Kazansky. Here are basic theoretical approaches to a class of catalytic compositions which contribute the probably most massive quantities of catalysts used by man’s (petroleum and chemical) industries.

The action of transition metals in the carbonylations of alcohols is treated by Dekleva and Forster. This is a field of important chemistry, from the point of view of coordination chemistry as well as catalysis. It is also another example of cross-stimulation between basic science and technological utility.

Conner, Pajonk, and Teichner discuss the once mysterious phenomenon of molecular “spillover,” or migration of hydrogen and other molecular species across boundaries of heterogeneous compositional regions of solids. Its implications extend to many aspects of solid-state science and practices.

The pursuit of catalytic science has itself helped to catalyze something, namely the development of sophisticated physical tools for probing the physical-chemical state of solid constituents at the molecular and atomic scale. Bart discusses near-edge X-ray absorption spectroscopy, still a rapidly moving activity. It also is an interesting example of an important symbiosis between seemingly remote scientific endeavors: between “big machine” and high-energy particle physics and the science of chemical catalysis and solid-state structures.

PAUL B. WEISZ

Georg-Maria Schwab, 1899–1984

Georg-Maria Schwab died on 23 December 1984, just 5 months after he had presided so successfully over the 8th International Congress on Catalysis in Berlin. Schwab had originally studied chemistry in that city, graduating Ph.D. in 1923 with a thesis directed by E. H. Riesenfeld on the Thermodynamic Properties of Ozone. As part of that work Schwab dissolved ozone in liquid hydrogen, isolating a blue-black complex, which must say something about the imperturbable nature of his character. His first catalyst work, with E. Pietsch on the decomposition of methane, led to his Habilitation thesis, taken at Würzburg on the catalytic decomposition of ammonia. In 1928/9, now in Munich, he collaborated again with Pietsch in working out the kinetic consequences of reaction along the line between two adjacent surface phases, the "Adlineation" theory. In 1929 he published with E. Cremer on the Compensation Effect, which he called the theta rule, theta referring to the catalyst preparation temperature assumed to fix the thermodynamic distribution of active centers. In 1931 appeared his comprehensive textbook, "Katalyse vom Standpunkt der Chemischen Kinetik," which appeared in English translation in 1937. In 1938 he published, with Elly Agallidis (Mrs. Schwab), his first paper on the parahydrogen conversion by organic radicals, which he continued on migrating to Greece in 1939. Here he was Head of the Inorganic, Physical and Catalytic Chemistry Department at the Nikolaos Kanellopoulos Institute in the Piraeus, at which he carried out his important studies of the formic acid dehydrogenation on a series of metal alloys. This he reported to the Faraday Society Discussion at Liverpool in 1950, a pioneer effort in which he successfully correlated activation energy changes on alloying with the Hume-Rothery electron concentration parameter. In 1950 he became Director of the Institute of Physical Chemistry at Munich University, and there followed a long series of investigations inspired by the ideas of electron transfer at catalyst surfaces, first on semiconducting oxides, and later on supported catalysts, both metals on oxides, and oxides on metals. In his very latest papers (1983/84) Schwab returned to the Compensation Effect, seeking an explanation in terms of an activation energy distributed among a number of square terms. Although catalysis was his main theme, Schwab also contributed to solid-state reactions, chromatography, infrared and Raman spectroscopy, and was much interested in the history of chemistry. Schwab was active on a number of committees and served as President of the Research Council of the Fraunhofer Foundation for Applied Science.

Among the honors received by Schwab were membership of the Bavarian, "Leopoldina," Heidelberg, and Vienna Academies, and an Honorary Pro-

fessorship of the University of Caracas. He received Honorary Doctorates from the Universities of Berlin, Paris, Liège, and Hamburg, and the Liebig Medal of the German Chemical Society. He was an Honorary Member of the German Bunsen Society for Physical Chemistry. He received the St. George's Order of Greece, and was an officer of the Order of the Belgian Crown.

Schwab was a man of equable and humorous temperament, a rock-climber in earlier days and latter a skier, with a mountaineer's preference for deep snow over the piste. Professor and Mrs. Schwab had a party with old students each semester in the convivial surroundings of a famous Munich beer-cellar and the laboratory staff and students made an annual expedition to the mountains for skiing. During the time my wife and I were in Munich in 1963, Professor and Mrs. Schwab went to great lengths to make our stay there as enjoyable as possible, and I have no doubt other visiting Professors found the same hospitable reception. Professor Schwab is survived by his wife and by a son and two daughters who are married with families.

DANIEL D. ELEY

Georgii Konstantinovich Boreskov, 1907–1984

Catalysis science has suffered a severe bereavement—on August 12, 1984, a leading scientist in the field of catalysis, an eminent chemical engineer, an outstanding organizer of science and industry, the Director of the Institute of Catalysis of the Siberian Branch of the USSR Academy of Sciences, a great teacher, and a remarkable man, academician Georgii Konstantinovich Boreskov passed away.

G. K. Boreskov was born in Omsk on April 20, 1907. On graduating from the Odessa Chemical Institute in 1929 he became head of an industrial laboratory of catalysis. It was under his leadership that the first home catalysts for SO_2 oxidation and methods of calculating commercial reactors were developed. Later he summarized his experience in the book "Catalysis for Sulfuric Acid Production," which was published in 1954 and retains its value to the present day.

Boreskov emphasized the necessity of taking into account the effect of the reaction medium on the catalyst, particularly when describing kinetics of heterogeneous catalytic reactions. This problem was also the subject of his last report at the 8th International Congress on Catalysis in West Berlin shortly before his death.

People who knew Professor Boreskov at the beginning of his scientific career recall him as a man with an inquisitive mind, encyclopedic knowledge, diligence, and energy. He was also a gifted engineer and organizer. Georgii Konstantinovich took an active part in all steps of research from laboratory experiments and catalyst investigations to projection of large-scale reactors and optimization of processes.

Boreskov supported the idea of a chemical approach to catalysis, according to which the mechanism of catalytic action consists of an intermediate chemical interaction of the catalyst with a reactant.

The theoretical activity of Boreskov is intimately associated with all states in the formation and development of the modern science of catalysis. He treated the catalytic process by considering all related phenomena. It is from just such a concept that a new trend, mathematical modeling of catalytic (and chemical, in general) processes, arose. Now, with mathematical modeling of chemical reactions as the basis, a special branch of science, concerned with the theoretical basis of chemical technology, has been formed.

As a technologist, Boreskov showed a keen interest in new possibilities of catalysis, i.e., the expansion of the application of catalytic methods both in technology and energetics, as well as for new nontrivial solutions of chemical engineering problems.

Boreskov had a sharp sense of the new and always supported the appearance of novel trends in catalysis. He directed experiments on the application of catalysis for fuel combustion and participated in the development of new methods to carry out catalytic processes—performance of reactions in unsteady state conditions (a promising way of performing exothermal reactions with low adiabatic heat).

The creation of the Institute of Catalysis was Boreskov's life work. He was the director of the Institute from the time of its foundation in 1958. He formulated the main research problems of the Institute: the development of scientific bases for foreseeing catalytic action and scientific bases of catalyst preparation and mathematical modeling, combined with solutions of applied problems essential for modern industry. In a fairly short period of time the Institute has gained world-wide recognition. In 1980 it received an International "Gold Mercury" prize.

Boreskov was a tireless supporter of international cooperation in catalysis. He contributed to the Organization of International Congress on Catalysis by serving as president from 1972 to 1976 and on his initiative, regular bilateral seminars on catalysis—Soviet–Japanese (1971) and Soviet–French (1972)—were organized. Boreskov was the chief coordinator in the USSR in the Soviet–American Scientific cooperation on the problem of "Chemical Catalysis" in 1973–1980. He was a member of the editorial board of a number of authoritative journals, both foreign and Soviet.

The scientific activity of Boreskov has been highly valued by the Soviet and foreign scientific communities. He was a full member of the USSR Academy of Sciences and was elected an Honored Member of the New York Academy of Sciences, Foreign Member of the Academy of Sciences of the German Democratic Republic, and Honored Doctor of Poitiers University (France) and of Wrocław Polytechnical Institute (Poland). The Government of Bulgaria decorated Boreskov with a first degree Kirill and Mefodii Order. The Soviet Government gave him the highest award of the USSR—the Hero of Socialist Labor.

Fond memories of Professor G. K. Boreskov will always remain in the hearts of those who knew this great scientist and this great man.

K. I. ZAMARAEV
YU. I. YERMAKOV

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Spillover of Sorbed Species

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I. Introduction

Solid catalyst surfaces are by their very nature heterogeneous. Steps, kinks, edges, and vacancies on supported metals, mixed oxides, and sulfides give rise to catalytically "active sites." This concept of active sites was used by Langmuir and Hinshelwood to express the kinetics of heterogeneous reactions. For supported metals in particular, the support was initially perceived only to disperse the active metal, increasing and preserving its effective surface area. More recently, it has been accepted that the support can influence the activity of the metal [e.g., strong metal-support interaction (SMSI)].

Langmuir-Hinshelwood kinetics assumes that the number of active sites initially present or induced by the reactants is fixed and that the reacting species adsorb and interact at the isolated sites. No mobility from a site across the surface is taken into account.

Limited mobility of sorbed species has long been understood. The exchange of species from one position to another, either on the surface or through the bulk, has been well established (1). More unique is the mobilization of a sorbed species from one phase onto another phase where it does not directly adsorb. This has been defined as "spillover."

The phenomenon of spillover was first noticed in the 1950s (2) when it was observed by Kuriacose that the decomposition of GeH_4 on a Ge film was

increased by contact with a Pt wire used to measure the conductivity. Taylor proposed that the wire provided a "porthole" for the recombination of H to H₂ (3) ("reverse spillover"). The first direct experimental evidence for spillover was presented by Khoobiar in 1964, who documented that the formation of tungsten bronzes (H_xWO₃) was possible at room temperature for a mechanical mixture of WO₃ with Pt/Al₂O₃ (4). Sinfelt and Lucchesi postulated that reaction intermediates (presumably H) had migrated from Pt/SiO₂ onto Al₂O₃ during ethylene hydrogenation (5). During the ensuing score of years over 400 papers involving spillover have been published. The First International Symposium on the Spillover of Adsorbed Species (FISSAS) was held in 1983 in Lyons (6).

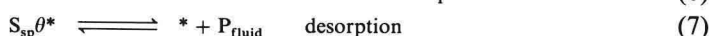
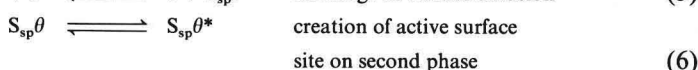
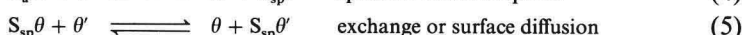
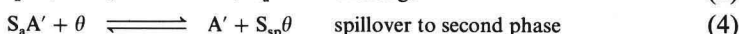
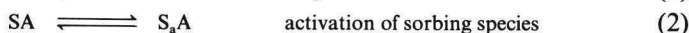
Reviews of the publications have appeared in 1973 (7), 1980 (8), and recently from a historical perspective in 1983 (9). The focus of this article is to present our current understanding of the phenomenon and articulate the unknown aspects of spillover.

First, it is necessary to define spillover. During the recent international symposium a definition was proposed and affirmed by the congress (10).

Spillover involves the transport of an active species sorbed or formed on a first phase onto another phase that does not under the same condition sorb or form the species.

And offered as a comment: The result may be the reaction of this species on the second phase with other sorbing gases and/or reaction with, and/or activation of the second phase.

Mechanistically this can be generally visualized as a sequence of steps, viz:



where S_{fluid} is the species sorbing from fluid (gas or liquid), A, A' are the sites able to adsorb S, S_a is the activated sorbed species, S_{sp} is the spiltover species (usually equivalent to S_a), θ , θ' are the phases unable to sorb S directly, $S_{\text{sp}}\theta^*$, * are the possible active sites or new phases resulting from θ , and P_{fluid} is the possible product of the creation of the new active site or phase.

These seven steps initially simplify the discussion of the phenomena related to spillover. As the most common example, hydrogen is adsorbed from the gas phase onto a metal (Pt, Pd, Ni, etc.), where it dissociates to atomic hydrogen ($S_aA = \text{HPt}$, etc). Spillover occurs if the atomic hydrogen is then

able to be transported onto the support ($\text{PtH} + \theta \rightarrow \text{Pt} + \text{H}_{\text{sp}}\theta$, equivalent to Step 4).

We hope objectively to access what is known and what is not known about spillover. Our specific focus is on the phenomena and the catalytic consequences.

Spillover may result in a spectrum of changes in the nonmetallic phase onto which it occurs. In the weakest sense, the spiltover species (e.g., H_{sp} , for spiltover hydrogen) is transported across the surface of this phase as a two-dimensional gas. It may exchange with similar surface species (e.g., $\text{OH} + \text{D}_{\text{sp}} \leftrightarrow \text{OD} + \text{H}_{\text{sp}}$). The spiltover species may react with the surface (e.g., $\text{H}_{\text{sp}} + \text{M}-\text{O}-\text{M}' \rightarrow \text{M}-\text{O}-\text{H} + \text{M}'$), which can result in the creation of surface defects and/or active sites. Further, the bulk of the solid may be transformed into a different structure (as in the transformation of oxides to hydrogen-bronzes). In each of these cases, the second phase is no longer an inert. It is not serving to promote the inherent activity on the first phase. The second phase is participating directly in the transport, exchange, and reaction with the spiltover species. In some cases it is able to become catalytically active on its own and thereby to participate directly in subsequent catalysis.

The remainder of this article will be divided into five sections. First, we will discuss the types of phenomena associated with spillover. This will include enhanced adsorption, exchange with the surface, and the bulk transformation of the second phase. In the second section we will discuss the mechanism of spillover, the nature of the surface and spiltover species, and the kinetic and mechanistic implications. In the third section we will consider the spillover of species other than hydrogen. In the fourth section we will discuss the aspect of spillover with the most significant catalytic implications: surface activation of the second phase (e.g., the support of the metal) and the resulting catalysis. In the final section we will bring together the general conclusions of the earlier sections and discuss the implication of spillover to catalysis and other heterogeneous processes.

We recognize that the phenomenon of spillover is still controversial, and yet the potential implications are far reaching. Therefore, we will take this opportunity to advance some hypotheses concerning the phenomena associated with spillover and their consequences.

II. Phenomena Associated with Spillover

For the sake of clarity the most important consequences of spillover are summarized and discussed in the following four subsections. First, the enhanced adsorption by mono- and bimetallic supported catalysts is described. This deals mainly with abnormal hydrogen adsorption quantities

and rates. The second subsection describes isotopic exchange with the surface. The third subsection relates bulk changes in materials exposed to spillover, and the last subsection reports on strong metal-support interaction (SMSI) and its relation to spillover. These last two phenomena occur with less refractory and more easily reducible inorganic oxides.

The very important problems of catalytic activity and reaction mechanism involving spillover will be discussed in Sections III and V.

A. ENHANCED ADSORPTION

Literature data are mainly centered around hydrogen adsorption on group VIII, VI, and I metals (mono- or bimetallic systems) supported on refractory inorganic oxides such as Al_2O_3 , SiO_2 , zeolites, or carbons. The studies involving SMSI have focused on TiO_2 as a support.

Enhanced adsorption of H_2 is generally reported to occur at atmospheric pressure (or lower pressures of H_2) at temperatures about 200°C . However, many cases are described for adsorption at ambient temperatures (and below).

Although this article is devoted to recent experimental and theoretical developments in the ever-growing field of research on spillover, it is of interest to recall here, very briefly, some important results published earlier in the literature (7, 8). These results are expressed as ratios H/M_t , where H stands for the number of H atomic species adsorbed per total number of metallic atoms, M_t , in supported catalysts, and are shown in Table I according to the review published by Sermon and Bond in 1973 (7). Figure 1 represents the three combination cases where spillover may occur; it distinguishes the primary spillover effect (case A) from the secondary spillover effects (cases B and C) (7, 11). In general, the ratio H/M_s , where M_s is the total number of surface metal atoms of the catalyst, rarely exceeds 2 (12) for the most commonly encountered metals. Large values of H/M_t indicated enhanced adsorption attributed to a spillover of adsorbed hydrogen according to one (or more than one) of the schemes depicted in Fig. 1. Values of H/Pt_t as high as 64 and 6.8 for $\text{Pt}/\text{Al}_2\text{O}_3$ and Pt/SiO_2 catalysts, respectively, have been quoted by Altham and Webb (13), while H/Pt_t ratios between 3 and 277 have recently been calculated by Sermon and Bond (11) for reverse spillover involving the two platinized bronzes H_xWO_3 and H_xMoO_3 .

Now, turning to the kinetics of spillover-enhanced adsorption, it may be induced that if spillover occurs, the rate of adsorption increases. For instance, Fujimoto and Toyoshi (14) found increased rates of H_2 adsorption with active carbon as a support for cobalt (case A spillover) or added as a diluent to this metal (cases B and C). The extent of the increases depended on the

TABLE I
Maximum Values of n_H/n_M Measured for Some Supported Metals by
Hydrogen Adsorption^a

Metal	Support	Maximum ^b n_H/n_M	Temperature of adsorption (°C)	Hydrogen pressure (cm Hg)	Ref. ^c
Pd	SiO ₂	(4.0) ^d	−196	40	47
	Al ₂ O ₃	5.0			49 ^e
	Al ₂ O ₃	3.2	25		50
Pt	SiO ₂	1.35	20	0.1	5
	SiO ₂	(1.5) ^d	−196		33
	SiO ₂	(1.6) ^d	−196	10 ^{−3} –10 ^{−6}	18
	Al ₂ O ₃	2.44	250	12	34
	Al ₂ O ₃	2.19	250	12	24
	Al ₂ O ₃	2	300		31
	Al ₂ O ₃	1.5	200	0.9	37
	Al ₂ O ₃	> 1	200	0.9	39
	Al ₂ O ₃	10.0			49 ^e
	C	75	250	60	23
	Zeolite	1.4	21		10
	Zeolite	2	100		25
	Zeolite	2	200	5–20	42
		1.92	250	< 25	14
Rh	Al ₂ O ₃	1.39	25	0 ^f	54

^a After Sermon and Bond (7).

^b n_M is the total number of metal atoms; n_H is the number of chemisorbed H atoms.

^c These references belong to the original paper (see Ref. 7 of the present chapter).

^d The validity of characterization of supported metals by hydrogen adsorption at −196°C is questionable.

^e Values obtained by D. V. Sokolskii and E. I. Gil'debrand, reviewed by Popova (49).

^f Extrapolated to zero pressure.

contact between the metallic component and active carbon, in this case Co/C (noted CC). This is shown in Fig. 2, where TM stands for “treated mixture” [active carbon (AC) mixed with CC and bound with polyvinyl alcohol]. SM is the simple physical mixture of AC with CC. Moreover, Fujimoto and Toyoshi found that the amount of adsorption does not vary with the source of spillover hydrogen (Ni, Cu, Fe), with the metal loading, or with use of pure or sulfided metals. The amount of hydrogen uptake at 400°C at equilibrium is the same. Similar H₂ adsorption is measured on pure AC. Thus, its extent