Research Perspectives during 40 Years of the *Journal of Catalysis*

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Received 26 July 2002; revised 9 September 2002; accepted 11 September 2002

Abstract

Research developments recorded in the *Journal of Catalysis* over the past 40 years are reviewed. The journal was launched at a propitious time, as is made clear from the accounts presented of various topics newly introduced in the 1960s, which laid the foundation for achievements to come later, notably in catalysis by zeolites but also in reactions catalyzed by metals and transition metal oxides. The early years are shown to have been followed by a period marked by the skilled application of new experimental techniques, especially spectroscopic methods for catalyst characterization and chemisorption. Research in which ideas and methodology were interchanged between homogeneous and heterogeneous catalysis are also indicated. By the middle years perspectives in catalysis were becoming strongly influenced by concerns regarding oil reserves and care of the environment. Examples of fundamental research reflecting this are described. The article briefly digresses to recall the members who have composed the editorial team of the *Journal of Catalysis* over the past 40 years, all of them personally active in basic research and recognizable from their work as sympathetic to the drive for understanding catalysis at the molecular level. In a final section the survey returns to its leitmotiv when some research themes from recent years are collated, among them the continuing progress with zeolite-related catalysis, the search for improved enantioselective catalysts, and the application of techniques in theoretical chemistry to chart catalytic reaction mechanisms.
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1. Introduction

The *Journal of Catalysis* made its appearance in the spring of 1962. It is a tribute to the founding editors, Jan de Boer and Pierce Selwood, and to the members of the original Editorial Board (Fig. 1) that the pattern of subjects chosen for the launch of the new journal proved to be both a welcome and a durable template for recording original research in catalysis. An international authorship was canvassed from the outset and the first volume carried papers from groups working in 15 different countries. It is now common to find that any given volume of the *Journal of Catalysis* has 20–25 countries represented among the indicated locations where the research has been conducted. The international make-up of the authorship has been one of the main factors ensuring that the evolution of ideas and techniques in catalysis worldwide has been rapidly documented and disseminated.

Volume 1 specified that the *Journal of Catalysis* would publish articles dealing with both heterogeneous and homogeneous catalysis and indeed the very first issue carried papers on the NO_x-catalyzed combustion of hydrogen and on enzyme catalysis as well as on heterogeneous catalysis and the surface chemistry of catalysts (Fig. 1). However, the well-known researches of the editors and the members of the Editorial Board gave a tacit signal that the main focus for the new journal would be heterogeneous catalysis and the surface properties of solids. Authors reacted accordingly and during its first 5 years of publication only a small number of papers featured homogeneous catalysis alongside almost 400 articles on heterogeneous catalysis, adsorption, and the characterization of solid catalysts. This has remained the format in spite of an unchanged rubric for soliciting submissions.

2. The early years

It is appropriate to begin by recalling some of the advances in catalysis and the properties of surfaces which were described by authors of the *Journal of Catalysis* articles in the first 5 years after its introduction.

As regards metals and metal-catalyzed reactions, much effort was being directed at unraveling the mechanisms of hydrogenation, isomerization, and hydrogenolysis of hydrocarbons. A novel proposal of the time was that reactive intermediates were π-bonded to the surface [1,2], a view elaborated by Rooney and Webb [3], and by Gault and coworkers [4]. Deuterium exchange, already well established,

JOURNAL OF CATALYSIS

ACADEMIC PRESS
New York and London

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Fig. 1. Cover and contents of the first issue of the *Journal of Catalysis*, in March 1962.

was playing a large part in these mechanistic studies [5]. For the analysis of deuteropropenes Hirota and Hironaka [6] provided additional insight by using microwave spectroscopy and rotation spectra to locate not only the presence but also the position of the D atoms. Considerable progress in measuring metal dispersion by chemisorption, X-ray line broadening, and electron microscopy had already been made by the time the *Journal of Catalysis* appeared, but an advance came in 1965 with the introduction of the "H_2–O_2 titration" method for determining the surface area of supported platinum [7]. This paved the way for the studies which stimulated Boudart et al. [8] to make a distinction between *facile* reactions, which had turnover frequencies (TOFs) which were independent of particle size, and *demanding* reactions, where TOFs were dependent on factors other than the mere number of surface metal atoms, such as particle size distribution, choice of support, and method of preparation. A sideline at the time was the discovery that hydrogen atoms formed by dissociative adsorption of H_2 on supported Pt, or on Pt admixed with oxide, could migrate across the interface with the second phase and diffuse on its surface, or even penetrate its bulk [9]. The term *spillover* was coined and became accepted terminology for what is now regarded as a widely occurring phenomenon with supported transition metals.

The most far-reaching of the advances in catalysis during the first 5 years of the *Journal of Catalysis*, however, was the demonstration of the outstanding potential of zeolites as catalysts. Rabó et al. had reported the work of the Linde Division of Union Carbide on the activity of synthetic faujasite for alkane isomerization at the International Congress on Catalysis in Paris in 1960 [10]. The first publications on the new Linde zeolites in the *Journal of Catalysis*, however, were from Socony-Mobil teams. Shape selectivity [11,12], exceptional activity for catalytic cracking [13], and the catalysis of various organic reactions [14] were all illustrated. The importance of this pioneering work at the Union Carbide and Mobil laboratories is reflected in the enormous extent to which zeolites are used in catalysis today.

The classic solid-acid catalysts such as alumina and silica–alumina were also the subject of many papers in the early volumes of the *Journal of Catalysis.* The generation of carbonium ions and radical ions was much discussed. The nature of the acid sites was a consuming passion, not least in the controversial exchanges between Hirschler [15] and Hall and Porter [16], who were the first to make good use of the Letters section introduced by the editors. A notable contribution was made by Parry [17], who showed that the infrared absorption bands of adsorbed pyridine could be used to discriminate between Lewis and Brønsted acid sites.

Important advances were also made in catalysis by transition metal oxides and halides. In the selective oxidation of C_3 and C_4 alkenes on oxides, Shell groups established the formation of allyl intermediates [18,19], and with bismuth molybdate the first indications of the relevance of the bulk structure were made by Schuit and co-workers [20]. Cimino et al. [21] introduced studies on transition metal

ions as isolated active centers by using dilute oxide solid solutions, e.g., NiO–MgO, as catalysts. However, the role of structure-defined active centers in catalysis was demonstrated most convincingly by Cossee and Arlman [22–25], who proposed a mechanism to explain stereospecificity in the polymerization of propene on the Ziegler–Natta catalyst α-$TiCl_3$/$Al(C_2H_5)_3$.

It will be evident from the above summary that the early 1960s was a period rich in discoveries and innovations. The *Journal of Catalysis* had made an auspicious start in recording so many of these new researches.

The next few years were marked in the *Journal* more by accounts consolidating the ideas and experimental findings of the early 1960s than by advances which were wholly new. Identification of cyclopropane hydrogenation as a structure-insensitive ("facile") reaction [8] was complemented by identifying neopentane isomerization and hydrogenolysis as structure-sensitive ("demanding") reactions [26]. Hydrogenolysis of ethane, another demanding reaction, was shown by Sinfelt and Yates [27,28] to be a case where there were huge differences in activity among transition metals.

Parry's pyridine work [17] was exploited by those investigating acid centers [29,30]. Let us note in passing that numerous researches have subsequently employed his protocol. It is widely applicable, suitable for studies ranging from the weak acidity of alumina, to the strong acidity of decationated zeolites and sulfated zirconia.

Theoretical work included studies on linear free energy relationships (LFER). Established early on by the classic work of Hammett, Taft and others in homogeneous catalysis, Mochida and Yoneda [31] took up the challenge to extend LFER to heterogeneous catalysis. The aim was to predict rates and product distributions by searching for linear relationships between rate data and numerical variables which reflected the reactivity of the reactants and, if possible, the activity of the solid catalysts. The shape of things to come in computing and kinetic analysis was also foreshadowed by Happel and Mezaki [32] in work on reaction-rate modeling.

At the start of the 1970s there was a change of editorship. Jan de Boer retired and the present author took over as the European-based editor. The editorial archive came by ship from Rotterdam to the old port of Bristol and the large wooden crate was opened for inspection in the ancient Custom House more suited to the examination of casks of sherry. The box contained a copy of every *Journal of Catalysis* letter written by Jan de Boer during his editorship of over 500 manuscripts.

New techniques for investigating chemisorption and the properties of solid catalysts were emerging. Ultra-high-vacuum (UHV) equipment had become widely available, so low-energy electron diffraction (LEED) and Auger electron spectroscopy could be used to characterize single crystals of metals and study chemisorbed layers. Photoelectron spectroscopy using both UV and X-ray sources (UPS and XPS) had arrived. Somorjai and co-workers [33,34] pointed the way to transferring results and ideas from UHV-based

techniques to heterogeneous catalysis as normally practised with stimulating work on stepped single crystals of platinum as catalysts for heptane dehydrocyclization and cyclopropane hydrogenolysis, overture to much distinguished single-crystal work on bridging the pressure gap which was to follow in later years.

Research on oxides benefited from studies using electron paramagnetic resonance (EPR) spectroscopy [35–37] and oxygen adsorption as the paramagnetic species O_2^- and O^- was fully authenticated. TiO_2 was shown to be a photocatalyst for oxidation reactions using O_2^-, provided its surface was partially hydroxylated to trap the photogenerated holes [38,39]. In the selective oxidation of alkenes on bismuth molybdate an important advance was the proof using ^{18}O that O^{2-} ions of the catalyst bulk were used [40,41], and specific proposals were made as to the separate functions of bismuth and molybdenum [42]. Also in molybdenum chemistry, there began what was to become a saga in later years, namely the interaction between MoS_2 and cobalt in Co–Mo hydrodesulfurization catalysts and to which reference is made later.

In catalysis by metals the field was still largely dominated by research on the reactions of hydrocarbons. The structure-sensitive character of hydrogenolysis was confirmed by work on alloys. The general consensus was that an ensemble of two or more active metal atoms was needed to bond the hydrocarbon multiply in order to effect hydrogenolysis. Isomerization, too, was confirmed to be a demanding reaction. New terminology was coined for mechanisms, e.g., bond shift, cyclic, and rollover, depending on the bonding and the orientation of the organic intermediate in the chemisorbed state. A novel suggestion here was for *metallo*cyclic intermediates, one member of the ring being a surface metal atom [43].

There were instances at this time of the influence of fundamental work in homogeneous catalysis on mechanisms proposed for heterogeneous catalysis. First, the seminal work of Olah [44] on carbocation formation in superacids was under way and starting to stimulate ideas on catalysis at solid surfaces. A second example was the concept of activity deriving from coordinatively unsaturated (cus) sites. Although inherent in the Cossee–Arlman mechanism for alkene polymerization [22–25], the link to catalysis on transition metal oxides from homogeneous catalysis on complexes was given explicit description by Siegel [45] in a discussion of ethene hydrogenation and H_2–D_2 exchange. A third example is the mechanism of the metathesis of propene to ethene and butene. In 1964 Banks and Bailey [46] presented the important discovery that the reaction could be catalyzed heterogeneously and much discussion followed on the possibility of a cyclobutane intermediate being involved. However, the reaction was already well known in homogeneous catalysis and recent work in that area had led to the view that a chain reaction involving a metal carbene was involved. Rooney and colleagues [47] made the bold step of proposing that a metal carbene $M=CH_2$ was formed in the

heterogeneous reaction and that the catalysis proceeded via a four-membered *metallo*cyclic intermediate. This later became the accepted mechanism.

Homogeneous catalysis itself continued to feature in the *Journal of Catalysis*, both for metathesis [48] and for other reactions [49,50]. In addition, efforts were constantly being made to introduce into catalytically successful metal complex systems in solution the paramount advantage of heterogeneous catalysis in having products separated from the catalyst. It was shown that this could be achieved either by anchoring the complexes on polymers [51] or by supporting the liquid phase and dissolved catalyst as such on a macroporous material [52].

3. The middle years

In 1976 Pierce Selwood retired after 14 years of dedicated service as the American-based editor. He was succeeded by Keith Hall, who brought a wide experience of catalysis by metals, oxides, and zeolites to bear on the editorship. The opportunity was taken at this time to make changes in the Editorial Board, which had remained unaltered since 1962. Twelve new members were appointed, but several of the original Board remained, including Michel Boudart, Charles Kemball, George Schuit, and Paul Weisz, all of whom had contributed greatly as authors and acted as advisers to the editors, and who would continue to do so for many more years. A welcome innovation in the *Journal of Catalysis* in 1973 had been the publication of a Cumulative Subject Index at the end of the year. It is not a trivial matter to do this well and the publishers deserve credit for the detailed cross-referenced entries which have characterized these Indexes ever since. They have many uses and one is to be invoked now, namely to help the present author justify omitting citations of much research that knowledgeable readers might regard as meriting reference in this review. With so much material available, the choice of subjects mentioned has to be selective and to some degree personal. This is a suitable point to apologize to readers conscious of omissions and to ask them to seek solace in finding the work cited in the Indexes. It will be evident also that, with a few exceptions, only research published in the *Journal of Catalysis* is being cited. This also calls for an apology, but in mitigation it can be argued that almost all of the fundamental advances in catalysis that have occurred since the 1960s are cross-referenced somewhere in articles in the *Journal*.

In some cases advances received their first detailed presentation in its pages. One such case is the pair of articles in 1976, by Wentrcek et al. [53] and by Araki and Ponec [54], which established that the nickel-catalyzed reaction of carbon monoxide and hydrogen to methane proceeded via *dissociated* CO (Fig. 2). This work set the scene for others to show that also the Fischer–Tropsch synthesis occurred by this initial step [55,56]. It had been known for years that Fischer–Tropsch catalysts became carbided, but that could
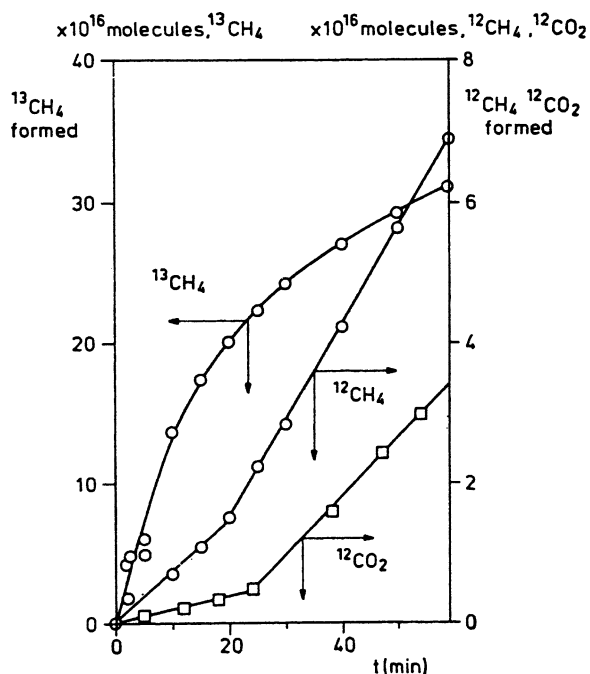
Fig. 2. Initial step in methanation of CO. Reaction of ^{12}CO and H_2 to methane at 250 °C on a nickel surface carrying presorbed ^{13}C. The methane which is rapidly formed is $^{13}CH_4$, showing that the key intermediate is derived from dissociated CO and not from an oxygen-containing species. After Araki and Ponec [54].

be a consequence of side reactions, and hitherto left open was the question of whether the attack of hydrogen on CO *preceded* or *succeeded* the fission of the C–O bond.

It soon became clear that selectivity in CO hydrogenation switched to *methanol* synthesis for metals which chemisorbed CO nondissociatively. Work with noble metals, notably Pd [57], established this criterion. Klier and his group turned attention to the mechanism of methanol synthesis catalyzed by Cu–ZnO/Al$_2$O$_3$ [58–60]. This proved to be a controversial issue, in regard to both the importance of CO$_2$ in the synthesis from CO/CO$_2$/H$_2$ mixtures and the state of copper in the active catalyst. The subject was regularly revisited in the *Journal of Catalysis* [61–64] and elsewhere, including a succession of International Congresses on Catalysis. It was eventually agreed that in line with the recent analysis by to Rozovskii and co-workers [65], and as originally proposed in 1975 [66], the route to methanol is via the hydrogenation of CO$_2$, with CO replenishing CO$_2$ by the water–gas shift reaction. As regards the catalyst, there is no doubt that Cu is the active component, but the nature of the synergy with ZnO is still debated.

Two other stimulating papers at this time concerned the reaction of methanol over the new Mobil shape-selective synthetic zeolite ZSM-5 [67,68]. The catalytic activity of this zeolite for the conversion of methanol to light alkenes and onward to C$_4$–C$_{10}$ hydrocarbons was demonstrated (Fig. 3) and the reaction later became commercialized as the MTG (methanol to gasoline) process. This and related work on ZSM-5 opened the way to many other developments in both fundamental and applied research using this material.

Following events in the Middle East in 1973 it was realized that, while natural gas would remain plentiful, adequate supplies of light crude oil might become less readily available. Since syngas (CO and hydrogen) is readily obtainable from natural gas by steam reforming, the production of hydrocarbons from CO hydrogenation moved higher up the strategic agenda. This was the background to renewal of research on the Fischer–Tropsch route to the higher hydrocarbons and the methanol-synthesis-MTG route to gasoline, examples from which have been mentioned above. At the same time environmental pressure was growing to decrease emis-
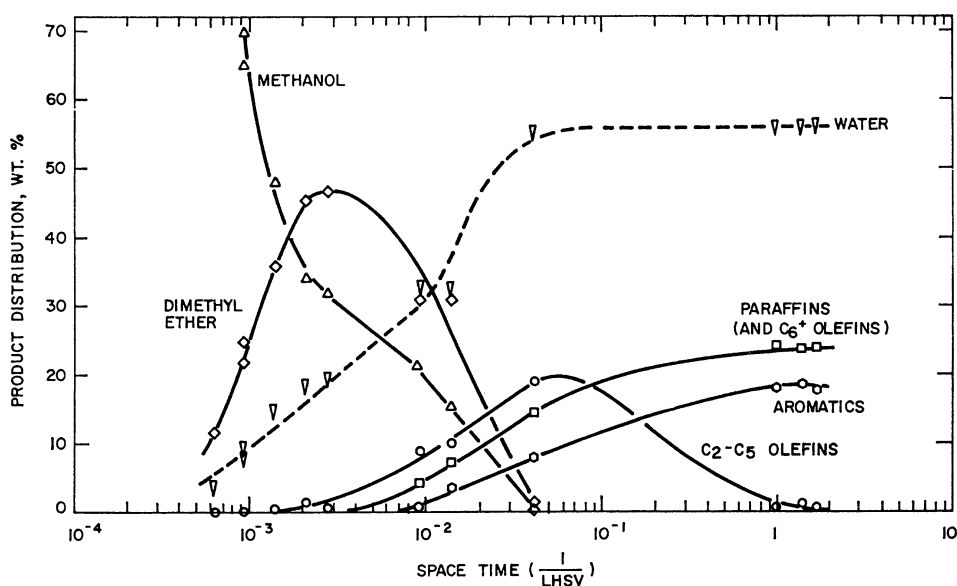

Fig. 3. Conversion of methanol to hydrocarbons on a shape-selective zeolite of ZSM-5 type at 371 °C. The hydrocarbon products are limited to a narrow range of molecular weights terminating abruptly at C$_{10}$. From Chang and Silvestri [67].

sions from air-polluting chemical plants and cars. This last concern was to determine the direction that much agency-funded and industrially sponsored research would take in the following decade.

After catalytic cracking, which by 1980 was being carried out industrially over stabilized zeolites in combination with silica–alumina, the next largest catalytic operation in industry was hydrotreatment, principally hydrodesulfurization (HDS) and hydrodenitrogenation (HDN), but also hydrodemetallation (HDM), partly to reduce unwanted emissions of SO_2 and NO_x and partly to avoid poisoning catalysts used industrially in further chemical processing. The classic hydrotreating catalysts were, indeed are, sulfided Co–Mo/γ-Al_2O_3 and Ni–Mo/γ-Al_2O_3 and their analogues with tungsten instead of molybdenum. A great deal of fundamental work has been directed at sulfided Co–Mo/Al_2O_3, the archetype among HDS catalysts. Three separate proposals were originally made for the structure of this catalyst, all of them in the *Journal of Catalysis* [69–71]. Cobalt was regarded as a promoter, rather than possessing HDS activity per se. Some years later Topsøe et al. [72] added a fourth proposal, one which afforded Co ions a more direct part in HDS catalysis. Their concept of a "Co–Mo–S phase," as it was termed, began to hold sway and various physical techniques (Mössbauer, IR, ^{59}Co NMR, and X-ray absorption spectroscopy) and theoretical treatments were brought to bear on the problem. A consistent view emerged that cobalt was bonded as atoms on the edges of very small crystallites of MoS_2 [73–76]. Cited here are only a few of the dozens of articles published in the *Journal of Catalysis* on this catalyst and its HDS activity in the 1980s and 1990s. For a recent contribution the reader is invited to marvel at the beautiful atomic-scale images of the edge structures obtained by the Danish team using scanning tunnelling microscopy [77].

The other major advances in pollution abatement by catalysis have been the introduction of oxide catalysts for the selective catalytic reduction (SCR) of NO_x emitted by industrial plants and the development of the Pt–Rh/ceria/γ-alumina catalyst wash-coated onto cordierite "monoliths" for the conversion of CO, NO_x, and unburnt hydrocarbons in automobile exhaust gases. Both depended greatly on research into catalyst preparation. V_2O_5 supported on anatase TiO_2 became a front-runner for SCR of NO_x by ammonia during the 1980s and is now used industrially for the removal of NO_x from stack gases. Originally investigated as a selective oxidation catalyst [78], the potential of V_2O_5/TiO_2 as a "monolayer catalyst" was soon recognized and was taken a stage further by Geus and his group [79] and indeed by others [80] who supported the V_2O_5/TiO_2 itself on silica to enhance even more the active area of V_2O_5 in contact with the reactants. Alternatively, the catalyst can be prepared as nanoparticles by spray pyrolysis [81]. As regards the "three-way" automobile exhaust catalyst, given the great effort expended and the achievements made in its development, one might have expected to find more recorded in the
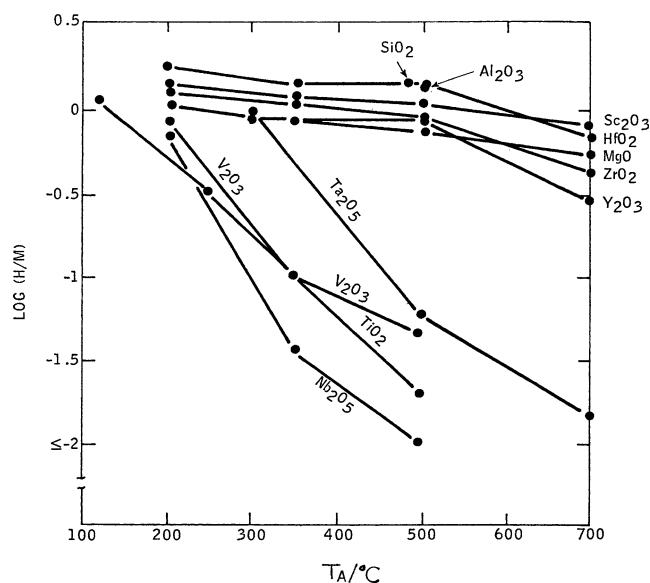

Fig. 4. Strong metal–support interaction. Hydrogen chemisorption at $25\,^{\circ}C$ on supported iridium as a function of the temperature of preactivation in hydrogen. H/M is the atoms of hydrogen adsorbed per atom of iridium. 1 wt% Ir for SiO_2, Al_2O_3, V_2O_3, HfO_2 supports and 2 wt% for others. From Tauster and Fung [91].

Journal of Catalysis than is the case. However, one aspect which is well covered is the role of ceria as a support for the noble metals [82–85], still an important issue with respect to the oxygen storage capacity of the catalyst.

Although a classic catalytic reaction, ammonia synthesis must be briefly mentioned in any survey of fundamental research during this period. The splendid work of Ertl and co-workers on Fe single crystals [86–88] has become a paradigm for showing how UHV-based surface science studies can lead to a detailed enthalpy diagram for a catalytic reaction. The structure-sensitive ammonia synthesis reaction has the dissociative chemisorption of nitrogen as its rate-determining step, activity being exhibited predominantly by the Fe(111) plane [89].

From time to time individual topics excite pulses of activity and result in a plethora of publications. One such event was strong metal–support interaction (SMSI). Initially described by Tauster et al. in a paper in the *Journal of the American Chemical Society* [90], the effect was linked particularly with Pt/TiO_2 and hydrogen chemisorption. This paper is still the one most universally cited, but it deserves recalling that at the same time Tauster and Fung also reported the effect in the *Journal of Catalysis* [91], but in relation to supported iridium, which behaves in the same way as platinum. The effect with iridium is illustrated in Fig. 4. It can be seen that if the noble metal is supported on TiO_2, V_2O_3, Nb_2O_5, or Ta_2O_5, an interaction occurs which degrades activity for hydrogen chemisorption when the supported metal is pretreated in hydrogen at temperatures above

200 °C. The effect is absent when the noble metal is supported on the seven other oxides for which results are cited in Fig. 4. The SMSI phenomenon attracted widespread interest, with most discussion focusing on Pt/TiO_2. It was soon amply confirmed by other workers, as also was the fact that it could be reversed by heating in oxygen. Within the next few years, scores of articles appeared on the subject, including a great number in the *Journal of Catalysis*. Metals other than noble metals were shown to exhibit SMSI and gradually it became recognized that a specific property was needed in the crystal chemistry of the oxide support, namely that the oxide should be capable of reduction by H_2 or CO to a suboxide and become sufficiently mobile to cover and even encapsulate the metal particles [92–97]. It is surprising that this was not appreciated earlier since, except for V_2O_3, the four oxides showing SMSI in Fig. 4 are the very ones able to form suboxides with shear or block structures when heated in hydrogen, and the vanadium oxide sample could be included if some residual V_2O_5 remained from the preparation of V_2O_3 from this oxide.

Another wave which deserves special comment is the flurry of activity in 1985–1995 on the oxidative coupling of methane. The abundant reserves of natural gas, 90% or more of which is methane, and the need of the petrochemicals industry for ethene had made the notion of a high-temperature process involving the coupling of methane to ethane and the oxidative dehydrogenation to ethene all in one operation a very attractive scenario. Basic research interest was initiated by a paper in the *Journal of Catalysis* by Keller and Bhasin [98]. They showed the feasibility of a process and identified suitable active catalysts as those oxides which could release and replenish oxygen from the bulk. For the next 10 years or so, oxidative coupling of methane (OCM) became a hot topic and was often interestingly controversial. A particularly active part was played by Lunsford, who with co-workers published regularly on OCM in the *Journal* and elsewhere [99,100]. Li/MgO, Na/CaO, and lanthanide oxides were among the catalysts found to be most effective. Basic oxides, so often in the background in catalysis compared with oxides exhibiting acidity gained center stage. Virtually every catalyst shown to have OCM activity had strong basic properties [99,101,102]. Methyl radicals formed on the surface and released to the gas phase were shown to be the agents providing the coupling, but the mechanism by which CH_4 was activated to produce them on the basic oxide was much debated [103,104]. Surface science work [105] contributed to the dialogue. However, the early view that high selectivity to C_2 hydrocarbons and suppression of oxidation to CO and CO_2 was due to oxygen ions of the catalyst being directly involved [98] was widely upheld. By the early 1990s industrial interest had faded due to conversions at high selectivity being insufficiently promising for process development. Fundamental research on OCM was regrettably scaled down, but new reactor technology with membranes [106] may yet revive it.

4. The editorial team

A short digression will be made at this point to comment on the editorship during the 40-year history of the *Journal of Catalysis*. The editorial team and its changes are listed in Table 1. The founding editors, Jan de Boer and Pierce Selwood, and their respective replacements, Frank Stone in 1970 and Keith Hall in 1976, have already been mentioned. Next came the hand-over of the American-based editorship to Gary Haller in 1988 and to Nick Delgass in 1994. Both were well known for their contributions to catalytic science before their appointment as editors and they brought enthusiasm as well as experience to the expanding *Journal*. In 1994 the editorial change was accompanied by a new dimension for the *Journal*: there was a 40% increase in page size as well as an increase in content. In 1998, Enrique Iglesia took over from Nick Delgass, strengthening the expertise of the editorial team in the kinetics of catalytic reactions. By contrast, the European-based editorship remained unchanged for over 25 years, with the present author overseeing the passage of several thousand manuscripts and adopting a personal style that many authors and reviewers will recall. When a change came in 1996 a reorganization [107] enabled the new European-based editor, Roel Prins, to have a lighter load. This brought two advantages: the time from submission of articles to publication was shortened and on the personal side Roel Prins was able to sustain his own numerous and diverse contributions to original research concurrently with the editorship. The American-based editors benefited similarly.

This short commentary on the editorships must not conclude without specific reference being made also to the Associate Editors listed in Table 1. Their constant support and individual specializations have been invaluable to the editorial operations and have added greatly to the prestige which the *Journal* has accumulated.

5. The later years

This final section describes some of the research areas which have developed strongly over the past 15 years and which look set to continue to do so. Most of them feature in

Table 1
Editors and Associate Editors during 40 Years of the *Journal of Catalysis* (1962–2002, Vols. 1–212)

Editors
J.H. de Boer (1–15), P.W. Selwood (1–40), F.S. Stone (16–161), W.K. Hall (41–111), G.L. Haller, (112–144), W.N. Delgass (145–173), R. Prins (159–212), E. Iglesia (174–212)

Associate Editors
R.L. Burwell (85–111), R.S. Weber (112–144), M.A. Vannice (145–196), J.W. Niemantsverdriet (165–212), G.J. Hutchings (176–212), D.W. Goodman (176–201), J.A. Dumesic (197–212), D.E. Resasco (204–212)

Numbers indicate the respective volumes for which the Editors and Associate Editors acted.

other articles in this issue, so the accounts here are brief and selective.

The growing interest in fine chemicals has prompted much work on catalysis by supported metals. One manifestation is the challenge to find catalytic systems capable of carrying out reactions enantioselectively and to understand their mode of chiral action. Although this is a field in which homogeneous catalysis is making the running, heterogeneous catalysis has a particular stake as far as the hydrogenation of functionalized C=O bonds is concerned. Nickel modified by pretreatment with chiral acids has long been studied and Hoek and Sachtler gave a first account of tartrate-modified Ni as a catalyst for enantioselective hydrogenation in the *Journal of Catalysis* already in 1979 [108]. However, it is platinum modified with cinchona alkaloids which has been most investigated and particularly for the enantioselective hydrogenation of keto-esters such as methyl pyruvate, which proceeds with high enantioselectivity. This has served as a model reaction for fundamental work and several groups have been active in this research [109–112]. A 1:1 interaction between adsorbed modifier and adsorbed pyruvate is generally regarded as responsible for the enantioselectivity but many points of detail are still debated. New synthetic modifiers described by Baiker and his group are keeping up the excitement in this fascinating subject [113].

A more general contribution to the synthesis of fine chemicals has been coming from catalysis by zeolites. The discovery of shape selectivity has already been cited but what has not been emphasized is the extent to which zeolites have remained with such a high profile in fundamental research in catalysis throughout the past 40 years, both as catalysts per se and as supports for metals or transition metal ions providing bifunctional action. Newly synthesized structures, now familiar from their three-letter acronyms, have abounded. Characterization received a new thrust midterm from magic-angle-spinning nuclear magnetic resonance (MASNMR), X-ray diffraction Rietveld analysis, and high-resolution electron microscopy. The diversity of zeolites for catalysis is illustrated by the scores of papers dealing with them in the *Journal of Catalysis*. A particularly versatile contribution has been made by Corma, who with co-workers has published prolifically during the past 20 years or so, with articles on the catalytic activity of zeolites ranging from the original synthetic small-pore structures to the newest large-pore materials [114,115]. In the late 1980s zeolites were joined by $AlPO_4$ (APO) zeotypes, solids styled as SAPOs or MeAPOs according to the partial replacement of Al or P by silicon or metal atoms, respectively. Like zeolites, these are often markedly acidic, although less so than the aluminosilicates [116,117].

The nanopore dimensions in zeolites and zeotypes such as ZSM-5, Y, and SAPO-11 preclude the entry of bulky organic molecules. However, these species can be reacted on metals or transition metal ions highly dispersed in the new generation of ordered "mesoporous" silicas such as MCM-41. If desired, aluminum can be incorporated during synthesis to generate acidity. Moreover, complexes known for their activity as homogeneous catalysts can be "heterogenized" on these materials [118]. On the petrochemicals front these new supports offer a way for heavy crude oil fractions to be hydrotreated, for example with HDS catalyst mounted on the silica walls [119]. Basic research on these novel mesoporous solids is now well under way.

Another advance in zeolite-related catalysis has been the synthesis at the Enichem laboratories of titanium silicalite TS-1, the titanium analogue of ZSM-5, and the demonstration of its remarkable catalytic properties for the epoxidation of alkenes and the selective oxidation of benzene derivatives using aqueous H_2O_2 as the oxidant [120,121]. In a similar vein, Panov and co-workers [122] have made the novel discovery that iron ions in ZSM-5 constitute a catalyst for selective oxidation using N_2O as oxidant, as in the conversion of benzene to phenol. Painstaking characterization work has shown that whereas the activity of Ti in TS-1 is due to titanium being in solid solution in the MFI framework [123], analogous to the isolated transition metal ions in NiO–MgO solid solutions, the Fe ions in Fe–ZSM-5 active for selective oxidation are in clusters external to the framework [124,125].

Progress in catalysis owes much of its success to the continuing sophistication of physical techniques for characterization, as many of the articles which have been cited illustrate. Techniques for in situ studies are still at a premium. X-ray diffraction, X-ray absorption (EXAFS and XANES), MASNMR, and FTIR spectroscopy probably comprise the most generally applicable physical techniques for characterizing polycrystalline catalysts and the changes occurring in adsorbed species during catalysis. However, the techniques associated with UHV-based surface science are also immensely useful for studying model systems and giving leads to new concepts. Many laboratories are engaged in such studies, and it is to be regretted that studies of chemisorption and catalysis on single crystals using these latter techniques, such as those of Goodman and co-workers with metals [126] and Barteau and co-workers with oxides [127], to mention two examples, are not submitted more often to the *Journal of Catalysis*.

Also underrepresented in recent years in the *Journal* is catalyzed polymerization. Although Ziegler–Natta catalysts and the Cr/silica Phillips catalyst are represented, the brilliant fundamental research in homogeneous catalysis on the polymerization of alkenes by metallocenes (so-called "single-site catalysis") [128] passed by almost unnoticed. There is a hint now that the need to "heterogenize" the catalyst may encourage authors to rectify this omission [129, 130].

Less concern applies to the advances deriving from theoretical work on modeling and simulation. On the whole, these have been well covered in the *Journal of Catalysis*, and deservedly so. They bring the advantage of relating to both catalytic reactions and catalyst structure. On the side of reactions, for example, microkinetic analysis has been skil-

fully applied by Nørskov, Campbell, and others [131–134]. A satisfying aspect is the way in which for a given reaction, such as water–gas shift or methanol synthesis, this work has embraced the full range, from input data obtained on model single crystals, through a set of experimentally justified elementary steps, to final prediction of the rate of reaction on the real catalyst in the working conditions of the industrial process. Also in regard to kinetic analysis, work by Happel et al. [135], Bell and co-workers [136], Hoost and Goodwin [137], and others has been carrying forward the interpretation of transient effects induced by isotopic switching. Turning to catalyst structure and the interaction between surface atoms and reactants, the outstanding development has been the success of applying density functional theory (DFT). Carter and Goddard [138] have followed up previous ab initio work on epoxidation of ethene on silver clusters with DFT studies of methanol oxidation on metals for fuel cells [139]. The work of van Santen and co-workers [140–142] also eminently illustrates the way this exciting new arena for theoretical work is being used and extended. DFT as at present practised can be applied equally to clusters of metal atoms, to small elements of the surfaces of transition metal oxides, and to groups of atoms which comprise the active centers of zeolites, in each case in the presence of adsorbates being activated for reaction. The possible pathways to products can be specified and the respective energies of intermediate states evaluated. This is a fitting high note on which to end this account of advances in catalysis.

6. Conclusion

This survey has attempted to highlight the new discoveries in catalytic science over the past 40 years as reflected in the pages of the *Journal of Catalysis.* Its aim is to have been illustrative rather than comprehensive, while still showing the wealth of knowledge that has been accumulated from fundamental research world-wide. The discoveries comprise theoretical and conceptual advances as well as experimental findings. The understanding of the kinetics and manifold mechanisms of catalysis has undoubtedly progressed. The origins of selectivity are better comprehended. New insight has often been underpinned by work on catalyst structure and surface properties using a host of physical techniques, many of which are themselves highly innovative. However, very significant also are the chemical practices of colloid science, on which novel work in the genesis of catalysts has depended.

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