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VOLUME 40

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Preface

With Volume 39, Paul Weisz retired as our co-editor of *Advances in Catalysis*, a sad break for us, his colleagues for 37 years. His achievements in catalysis were recently honored by his receipt of the U.S. National Medal for Technology. We would like to give him thanks for all his editorial work, and it is good to know that we may still rely on his advice as he joins the Advisory Board. At the same time, we give a hearty welcome to Dr. W. O. Haag who joins us as a co-editor. We wish him well in his work for *Advances in Catalysis*, beginning with the following introductory remarks for Volume 40.

D. D. ELEY
H. PINES

As Drs. Eley and Pines have pointed out, readers of this 40th volume of *Advances in Catalysis* will notice a change in the list of editors. I would like to add my appreciation to Paul Weisz for helping to guide this publication through an astonishing growth period in the science of catalysis, driven by new techniques, methods, and catalytic materials, and by an enormous growth in industrial applications. In a very commendable article, John Meurig Thomas [*Angew. Chem.* **106**, 963 (1994)], takes the reader on an enjoyable journey through this and earlier periods in the development of our catalytic science. Paul Weisz's long-standing contribution to the catalytic community as a dedicated and wise editor deserves our thanks. I have reason to believe that Dr. Weisz, who has always been concerned with the relevance of science, would approve of the selections; all the articles deal with fundamental aspects of heterogeneous catalysis and their relationship to potential or currently practiced industrial applications.

Two chapters deal with oxidation of aliphatic hydrocarbons. In the first article, Harold Kung summarizes the data and current understanding of the oxidative dehydrogenation of paraffins. He shows that high selectivity to the desired olefins is associated with oxide catalysts with a high heat of removal of lattice oxygen. The fifth article deals with the oxidation and ammonoxidation of propylene to acrolein and acrylonitrile, respectively. Moro-oka and Ueda show that the high activity and selectivity of new multicomponent bismuth molybdates can be understood in terms of the resulting lattice vacancies. New design principles for highly selective olefin oxidation catalysis based on modified bismuth molybdate have resulted from this study.

The difficult task of examining the role of catalysis in coal liquefaction has been taken on by Mochida and Sakanishi. They show the catalytic requirements in various stages of coal conversion and the many complex interactions of the catalyst with coal constituents. They also point out directions for future catalysis research needed for more economical coal liquefaction, a commendable feature for processes requiring a long lead time.

The chapter "Fundamental Studies of Transition-Metal Sulfide Catalytic Materials" by Chianelli, Daage, and Ledoux reviews current understanding of the relationship between structural and other properties of these catalysts and their catalytic activity and selectivity in hydrodesulfurization. In view of increasing environmental demands, this field has been heavily researched. The authors show how systematic studies and applications of novel methods can provide considerable understanding of these important catalysts.

Two years ago, *Advances in Catalysis* featured a chapter on chemisorbed intermediates in electrocatalysis. In this issue we follow up with a chapter by Wendt, Rausch, and Borucinski, "Advances in Applied Electrocatalysis." The successful commercial application of electrocatalysis requires a detailed, fundamental knowledge of the many catalytic phenomena such as adsorption, diffusion, and superimposition of catalyst micro- and nano-structure on the special requirements of electrode behavior. Considerable understanding of the status and limitations of electrolysis, fuel cells, and electro-organic syntheses has been obtained and provides a sound basis for future developments.

WERNER O. HAAG

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Oxidative Dehydrogenation of Light (C₂ to C₄) Alkanes

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I. Introduction

The low cost of light alkanes and the fact that they are generally environmentally acceptable because of their low chemical reactivity have provided incentives to use them as feedstock for chemical production. A notable example of the successful use of alkane is the production of maleic anhydride by the selective oxidation of butane instead of benzene (1). However, except for this example, no other successful processes have been reported in recent years. A potential area for alkane utilization is the conversion to unsaturated hydrocarbons. Since the current chemical industry depends heavily on the use of unsaturated hydrocarbons as starting material, if alkanes can be dehydrogenated with high yields, they could become alternate feedstock.

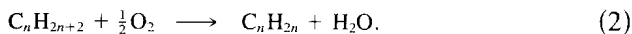
Dehydrogenation of alkanes can be carried out thermally to produce molecular hydrogen as a by-product:



The thermodynamics of this reaction for light alkanes (C₂ to C₄), however, is such that the equilibrium greatly favors the alkane at low temperatures at atmospheric pressure. The equilibrium shifts to the side of the products as the temperature increases. The temperature for 50% conversion of alkane to the corresponding alkene ranges from about 720°C for ethane to about 600°C for propane and butane (2). In addition, the number of molecules in the product is larger than that in the reactant. Thus, operation at elevated pressures preferred in practice would shift the equilibrium conversion in the unfavorable direction. Catalytic dehydrogenation at such high temperatures has a number of disadvantages. At these temperatures, undesirable side reactions are difficult to control. The most significant side reaction is cracking of the alkane into smaller molecules. One effect of this is rapid coking of

the catalyst (3). Finally, the dehydrogenation reaction is highly endothermic, and heat must be added to sustain the reaction. In practice, the heat released by burning off the coke on the catalyst in the regeneration process is used to supply part of the heat required for reaction.

An alternate method of dehydrogenation is by reaction of alkane with oxygen:



The formation of the very stable product, water, makes this reaction very thermodynamically favorable. Thus, in principle, practically complete conversion can be obtained even at low temperatures and high pressures. This provides great advantages over the nonoxidative process based on engineering and economic considerations. The many other possible reactions between oxygen and alkenes, other desired unsaturated hydrocarbon products, as well as alkanes, place a high demand for selective catalysts. For example, reactions with oxygen could result in oxygen-containing organic products such as alcohols, ketones, aldehydes, acids, and combustion product carbon oxides. In most cases, these other reactions are much more thermodynamically favorable than the desired oxidative dehydrogenation reaction. Thus, to be able to carry out the oxidative dehydrogenation reaction with high yield is a very challenging catalytic problem.

Other oxidants could be used instead of oxygen. In the 1960s, many patents and reports have appeared using bromine, sulfur, and, especially, iodine and their compounds as the oxidant. Some of these have been summarized in the treatise by Hucknall (4). The advantages of using these oxidants is that high selectivity for dehydrogenation could be obtained. For example, 86% yield of ethene was reported in the oxidative dehydrogenation of ethane using a mixture of HCl, H₂O and O₂ over a Fe–Al oxide catalyst (5). However, small amounts of chlorohydrocarbons were also formed. The corrosive nature of the halogen and sulfur gases and the potential environmental concern over their use have deterred commercialization of these processes. This paper covers only oxidation using oxygen, although a few examples using nitrous oxide are also mentioned.

II. Gas-Phase Reaction of Alkanes with Oxygen

Thermal reactions of light alkanes with oxygen in the combustion process have been studied extensively (6, 7). These studies were typically conducted at high temperatures—flame temperatures. The elementary reactions of the hydrocarbon species often involve reactions with atomic (H, O) or free radical species (OH, alkyl, etc.). The initiation step is the homolytic cleavage of C—C single bonds to form alkyl radicals. The C—C bonds are the weakest bonds in an alkane molecule (Table I). The chain-propagation step

TABLE I
Typical Bond Energies^a

Bond type	Energy (kJ mole ⁻¹)
C–C	376
Primary C–H	420
Secondary C–H	401
Tertiary C–H	390
Allylic C–H	361
Vinylic C–H	445

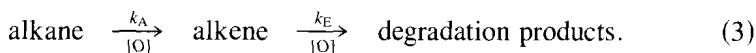
^a"CRC Handbook of Chemistry and Physics,"
71st ed., pp. 9–95, 1990.

involves reactions of alkane with the atomic or radical species, which abstracts a hydrogen atom from the alkane molecule to produce another alkyl radical. The activation energy and the preexponential factor of the rate constants for reactions important in the combustion of light alkanes have been reported (7). Table II shows the activation energy for reactions of ethane and propane that are relevant to the discussion of the catalytic oxidation reactions.

TABLE II
Activation Energies and Rate Constants of Some Gas-Phase Reactions of Ethane, Ethene, Propane, and Propene (Derived from Ref. 7)

Reaction	E_a (Kcal Mole ⁻¹)	k (sec ⁻¹ or cm ³ mol ⁻¹ sec ⁻¹) at 873 K
$C_2H_6 \longrightarrow CH_3 + CH_3$	88.31	2.4×10^{-3}
$C_2H_6 + O \longrightarrow C_2H_5 + OH$	6.36	6.6×10^{11}
$C_2H_6 + OH \longrightarrow C_2H_5 + H_2O$	1.81	3.1×10^9
$C_2H_4 + O \longrightarrow CH_3 + HCO$	1.13	1×10^{12}
$C_2H_4 + O \longrightarrow CH_2O + CH_3$	5.00	2.5×10^{13}
$C_2H_4 + OH \longrightarrow C_2H_3 + H_2O$	1.23	2.4×10^{12}
$C_2H_4 + OH \longrightarrow CH_3 + CH_2O$	0.96	1.2×10^{12}
$C_3H_8 \longrightarrow CH_3 + C_2H_5$	84.84	1.3×10^{-5}
$C_3H_8 + O \longrightarrow i \text{ or } n\text{-}C_3H_7 + OH$	3.00	9×10^5
$C_3H_8 + OH \longrightarrow i \text{ or } n\text{-}C_3H_7 + H_2O$	0.85	3.5×10^8
$C_3H_8 + H_2O \longrightarrow i \text{ or } n\text{-}C_3H_7 + H_2O_2$	18.00	1.6×10^8
$C_3H_8 + O_2 \longrightarrow i \text{ or } n\text{-}C_3H_7 + HO_2$	47.50	6×10^1
$C_3H_6 \longrightarrow C_3H_5 + H$	78.00	10^{-5}
$C_3H_6 \longrightarrow C_2H_3 + CH_3$	85.80	10^{-5}
$C_3H_6 + O \longrightarrow C_2H_5 + HCO$	0.00	3.5×10^{12}
$C_3H_6 + O \longrightarrow C_2H_4 + CH_2O$	0.00	4×10^{13}
$C_3H_6 + O \longrightarrow CH_3 + CH_3CO$	0.60	8×10^{12}
$C_3H_6 + OH \longrightarrow CH_3 + CH_3CHO$	0.00	3.5×10^{11}
$C_3H_6 + OH \longrightarrow C_3H_5 + H_2O$	0.00	3.5×10^{12}
$C_3H_6 + OH \longrightarrow C_2H_5 + CH_2O$	0.00	8×10^{11}

From the activation energies and the preexponential factors, the rate constants at 873 K can be calculated. They are listed in Table II. They show that for the gas-phase homogeneous reactions, the reactions of O atoms and OH radicals with ethene are very rapid and somewhat faster than their reactions with ethane. This fact would limit the maximum yield of ethene. It is well known that if the reactions of an alkane and an alkene are both first order in the hydrocarbon, then the maximum yield for the alkene of about 35% would be obtained when the rate constants, k_A and k_E , for the two reactions have equal values:



If the rate constant k_E is larger than k_A , that is, the alkene reacts more rapidly than the alkane, the maximum yield would be lower.

The same consideration applies to the reaction of propane. The reactions of O atoms and OH radicals are more rapid with propene than with propane. In fact, the differences in the rate constants are larger for the reactions of C_3 's than C_2 's. This would result in a lower maximum yield for propene from propane than for ethene from ethane.

Another aspect of the gas-phase homogeneous oxidation reaction at high temperatures is that the major reaction of the alkyl radicals (ethyl and propyl) is their reaction with molecular oxygen to form alkene and O_2H radical:



Thus dehydrogenation is the primary reaction in the oxidation of alkane, and most of the degradation products are formed from secondary reactions. This has been demonstrated experimentally (8). For example, butenes and butadiene are formed with high selectivities at low conversions in the oxidation of butane.

III. Studies of Catalytic Oxidative Dehydrogenation in the 1960s

Prior to the 1960s, studies on the catalytic oxidation of alkanes emphasized their combustion. Significant activities on oxidative dehydrogenation of alkane began in the 1960s. One of the earlier reports that appeared in 1961 on oxidative dehydrogenation of pentane and 2-methylbutane (isopentane) mentioned the importance of the nature of surfaces on the conversion and selectivity (9). However, the authors did not conduct their studies with specific catalysts. An attempt to use Group VIII metal oxides for oxidative dehydrogenation of butane at 340–440°C did not succeed. Apparently, the reactor was not designed to minimize gas-phase homogeneous reactions,

such that the conversion of butane was about the same with and without the catalyst (10). On the other hand, cobalt molybdate was reported to greatly enhance the formation of butadiene from a mixture of butane and oxygen than from simple dehydrogenation (11). Interestingly, an Sb-Mo oxide catalyst was reported to oxidize 2-methylpropane to methacrolein with 49% selectivity at 22% conversion, and propane to acrolein with 29% selectivity at 15% conversion using a mixture of alkane, air, ammonia, and water at 508°C (12). Thus there was evidence early on that the oxidation of alkane could result in various type of product, depending on the catalyst and the hydrocarbon. The relationship among the selectivity for different products, the nature of the catalyst, and the alkane are discussed further later.

Other catalysts for alkane oxidative dehydrogenation have also been reported in the patent literature. For example, it was claimed that a Na and Li phosphomolybdate produced 17% butadiene and 5% butenes at 600°C with a 1:1 mixture of butane and oxygen (13).

IV. Oxidative Dehydrogenation of Ethane

Unlike higher alkanes, ethane contains only primary C—H bonds, and the dehydrogenation product ethene contains only vinylic C—H bonds. As shown in Table I, these are strong bonds. Thus one would expect that, compared to other alkanes, the activation of ethane would require the highest temperature, but the reaction might be the most selective in terms of the formation of alkene. Indeed, this appears to be the case.

There have been many reports on this reaction and a large number of catalysts have been studied. Figure 1 shows a summary of the performance of the better catalysts. The data points are divided into two groups according to whether the reaction temperature was below or above 600°C. In general, the selectivity for dehydrogenation was higher for data collected at the higher temperatures. These higher temperature data cluster about the line corresponding to the case of $k_A = k_E$ of Eq. (3). This suggests that for these catalysts at the conditions tested, the rate constant of oxidation of ethane is comparable to the rate constant of oxidation of ethene, and a maximum yield of ethene of about 35% could be achieved. The data points of lower temperatures fall below this line. Thus their rate constants of oxidation of ethene are larger than those of ethane. The data in the figure indicate that none of the oxide catalysts known is more active for ethane activation than for ethene activation.

It has been demonstrated, however, that the activity of an oxide catalyst for ethane oxidation can be preferentially increased by treating it with chloride or sulfide (14). If a Co-Zr-P-Na-K oxide catalyst was treated with CH_3Cl , an ethene selectivity of 85% at 55% ethane conversion was obtained at 675°C, compared with 74% selectivity at 32% conversion on the

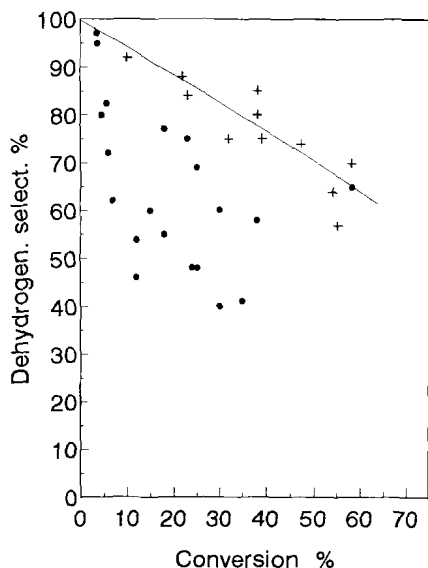


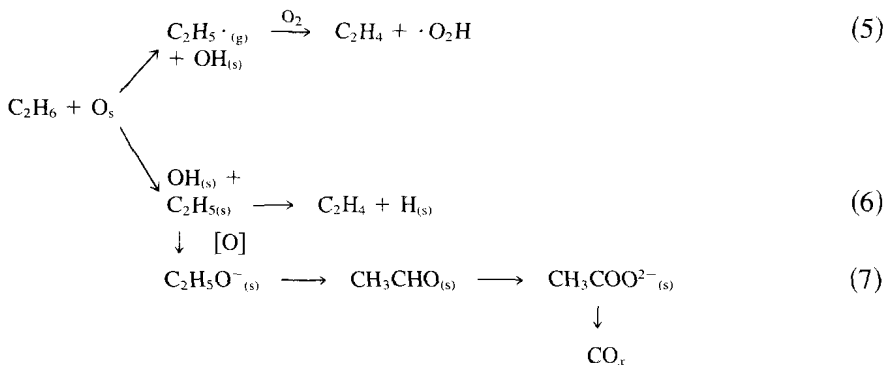
FIG. 1. Selectivity for oxidative dehydrogenation of ethane to ethene. Data taken from Table 3. (●) Reaction under or (+) above 600°C. Solid line denotes selectivity-conversion relationship for $k_A = k_E$.

same catalyst but without the chloride treatment. Likewise, the catalyst showed 85% selectivity at 68% conversion after being treated with sulfate. At such a high reaction temperature, it is possible that chlorine or sulfur desorbed into the gas phase and promoted homogeneous dehydrogenation reaction. The use of N_2O instead of O_2 as the oxidant has also been studied. High selectivities for ethene were obtained at low conversions (15, 16), but the reported data were not superior in terms of the dehydrogenation yield to those shown in Fig. 1.

It is interesting to note that the catalysts that show good selectivities at the higher temperatures generally do not contain easily reducible metal ions, such as V, Mo, or Sb. Many of the catalysts for the lower-temperatures operation, on the other hand, contain these reducible cations. In a study using a Li-Mg oxide, it was established that gas-phase ethyl radicals could be generated by reaction of ethane with the surface at about 600°C (17). These radicals could be trapped by matrix isolation and identified by electron spin resonance spectroscopy.

The dependence of ethene selectivity on the conversion of ethane for the better catalysts shown in Fig. 1 shows that the selectivity is high at low conversions and decreases as the conversion increases. This trend is consistent with a reaction pathway that consists of mostly sequential reactions [Eq. (3)]. Depending on the reaction temperature, the reaction network may involve two parallel reaction pathways shown below, which is modified from

that presented in Ref. 17. The first step in both pathways is the breaking of a C—H bond of ethane to form an ethyl species. The ethyl species could react further on the surface [Eqs. (6) and (7)] or, at sufficiently high temperatures, desorb into the gas phase to react with an oxygen molecule to form ethene [Eq. (5)]. The contribution of the heterogeneous–homogeneous pathway increases with increasing temperature.



The surface reaction consists of two competitive pathways. Their relative rates determine selectivity. The ethyl species may undergo further dehydrogenation to form ethene [Eq. (6)] or be oxidized to ethoxide and then to acetaldehyde or acetate [Eq. (7)], and possibly to carbon oxides. The formation of ethoxide is favored at lower temperatures and in the presence of water vapor (18, 19). Other surface reactions are also possible. They are discussed later.

An alternate view regarding selectivity has been proposed for SiO₂-supported V₂O₅ (20). In this proposal, ethane could be activated in two ways. One was by dissociative adsorption across a V=O bond to form H—V—OC₂H₅. α - or β -elimination of the ethoxide would result in acetaldehyde or ethene, respectively. The other way was by dissociative adsorption across a V—O—* bond to form *—OH and V—C₂H₅. The latter species would lead to combustion products.

The nature of the O_(s) species for ethane activation probably varies depending on the catalyst. On reduced Mo/SiO₂, the surface O[−] species generated by the decomposition of N₂O has been shown to react readily with ethane (15), and O[−] has also been suggested as the active species for the Li–Mg oxide catalyst (17). Oxygen vacancies or surface vanadyl groups may also be active sites.

It is worth noting that catalysts containing metal cations that form stable carbonates may do so under reaction conditions. La₂O₃ and Pr₂O₃ have been found to convert to La₂O₂CO₃ and Pr₂O₂CO₃, respectively, under reaction conditions (21, 22). It is probable that the alkali and alkali earth cations in

TABLE III
Summary Data of Oxidative Dehydrogenation of Ethane

Oxide catalyst	Temp. (°C)	Ethane conv. (%)	Ethene select. (%)	Ref.
Co—Zr—P—Na—K	675	32	74	14
Li—Na—Mg	600–650	38	85	66
Li—Mg	600–650	38	80	66
Li—Ti—Mn	650	23	84	67
		47	74	
Li—Ti	650	10	92	67
		21	88	
Li—Mg	600	39	74	17
		55	57	
	625	54	64	
Sr—Ce—Yb	700	58	70	68
B ₂ O ₃	550	4	97	69
B—Si		4	95	69
—Zn		35	41	
—La		6	82	
—Al		38	58	
—Mg		4	80	
Mo—V—Sb	400	23	75	70
Mo—V—Ta	400	18	77	70
		25	69	
Mo—V—Nb	400	58	65	70
CrPO ₄	550	30	60	71
Cr—ZrP ₂ O ₇	550	24	48	71
V—P	325–360	6	72	56
		15	60	
		18	55	
		25	48	
		30	40	
Sm ₂ O ₃	500	12	54	21
Gd ₂ O ₃	500	12	46	21
Mo—V—Nb	390	7	62	72

many of the catalysts in Table III form carbonates if the reaction temperature is below their decomposition temperatures.

Very high selectivities for ethene at high conversions could be achieved in the absence of gaseous oxygen. As mentioned before, under such conditions, the catalysts would be deactivated by coking. If the catalyst is an oxide, deactivation by reduction also occurs. The catalysts must be regenerated by treatment with oxygen in a cyclic operation (23).

V. Oxidative Dehydrogenation of Propane

Propane contains one secondary carbon, and the secondary C—H bonds are weaker than the primary C—H bonds (Table I). Therefore, propane is