

Heterogeneous catalyst structure and function: review and implications for the analysis of dissolved organic carbon and nitrogen in natural waters

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ABSTRACT

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It is the purpose of this paper to provide a brief summary of some of the fundamental concepts of the general chemistry of heterogeneous catalysts, several of which have been recently employed in high-temperature flow-through reactor systems for the analysis of dissolved organic matter in seawater. To avoid the application of these high-temperature catalytic oxidation (HTCO) techniques in an entirely 'black box' manner, it is imperative that the chemical oceanographic community be aware of the structure and function of heterogeneous catalysts, of the advances which have been made in developing such catalysts, and of the inherent limitations to their use as quantitative tools. The information presented herein has been adapted in part from several excellent recent texts and reviews on various aspects of catalyst chemistry, and the interested reader is encouraged to refer to them for greater detail on the subjects touched upon here.

Four general topics will be covered in this review. First, the component parts of heterogeneous catalysts will be defined and the relative advantages and disadvantages of different materials for purposes of organic carbon and nitrogen oxidation will be evaluated. Second, the synthesis and subsequent structure–function relationships of catalysts relative to the reactions carried out will be briefly discussed. Third, those factors known to be responsible for the deterioration of catalytic function and for short- and long-term catalyst deactivation will be assessed. Finally, we will discuss and speculate upon numerous aspects of the application of these catalysts for the specific purpose of accurately quantifying the dissolved organic carbon (DOC) and dissolved organic nitrogen (DON) in seawater. These final two categories will include information obtained from our recent efforts to design and employ different alumina- and aluminosilicate-based catalysts in HTCO systems.

HETEROGENEOUS CATALYSTS — INTRODUCTION AND BACKGROUND

Heterogeneous catalysts are defined as those which occur in a phase which differs from that of the reactants in a given system. Most commonly they are solid-phase materials which mediate reactions between either liquid or gaseous species (Le Page et al., 1987; Richardson, 1989).

Heterogeneous catalysts are differentiated from homogeneous catalysts, which occur in the same phase as that of the reactants and products of a system. Enhancement of the wet chemical oxidation of dissolved organic matter (DOM) by the addition of mercuric or silver nitrates to potassium persulfate or potassium dichromate would be included as reactions which are mediated by homogeneous catalysts (Gupta and Ghosh, 1959; House, 1962; Bauer et al., 1991). The mechanisms involved in homogeneous cat-

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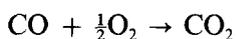
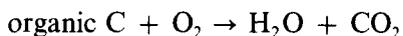
alysis are generally much more amenable to study than those of heterogeneously catalyzed reactions because of the relative ease with which reactants, products and catalysts can be isolated and identified (Orchin, 1984; Richardson, 1989).

In contrast, heterogeneously catalyzed reactions are considerably more complex because of diffusional, adsorptive and absorptive factors which arise as a result of multi-phased systems (Anderson and Pratt, 1985; Richardson, 1989; Spencer, 1989). The rates, kinetics and mechanisms of the reaction are difficult to measure for even simple systems (i.e. those containing two reactants and the catalyst). Therefore, a complete understanding of the full range of interactions and reactions possible for a complex system such as that involving the oxidation of the full complement of naturally occurring organic molecules in natural waters (if, indeed, they are catalytically mediated — see below) is unlikely to be attained. Of more immediate concern is whether quantitative conversion of these compounds actually occurs and, in the absence of understanding the mechanism(s) involved, whether the components of a 'quantitatively successful' system can be identified and assembled to perform in a robust, reproducible manner.

Interest in heterogeneous catalysis has increased dramatically in recent years, largely as a result of the development and use of such catalysts for lowering total hydrocarbon (Σ H_C), carbon monoxide (CO), nitric oxide (NO) and other N-oxide (NO_x) emissions from automobile engines (Blazowski and Walsh, 1975; Kummer, 1980; Taylor, 1984). Catalysts containing the noble metals platinum (Pt) and palladium (Pd) are the most widely used, and they have been shown to be highly efficient (greater than 98%) in converting Σ H_Cs and CO to CO₂ under net oxidizing conditions (Hegedus et al., 1979; Hegedus and Gumbleton, 1980; Summers and Monroe, 1981). No single loading, distribution, or formulation of the noble metal or temperature of operation has been found to be optimal for all applications. In contrast to carbon, organically

bound nitrogen, or 'fuel-N', as well as inorganic N, is largely and readily converted to NO (greater than 95%) under net oxidizing conditions and is apparently insensitive to the initial form of N (Turner et al., 1972; Prasad et al., 1984; Kesselring, 1986). Indeed, one of the major goals of emissions control has been to lower NO and NO_x using secondary catalysts such as Rh under net reducing conditions (see Klimisch and Barnes, 1972; Otto and Yao, 1980). However, reduction of these species by Pt and Pd catalysts is thought to be insignificant under net oxidizing conditions (Taylor, 1984). In comparison with the absence of noble metal catalyst effects, transition metal oxide catalysts can lower significantly the amounts of NO produced (as low as 5–20% of total) from organic N combustion (Prasad et al., 1981).

The equations of interest as they relate to complete organic C, CO and organic N combustion are



In the specific case of nitrogen, organic N appears to oxidize to NO via HCN and NH_x intermediates (Prasad et al., 1984).

The methods employed by the catalyst engineering industry to monitor catalytic performance are the same as those currently in use by the oceanographic community for measuring DOC and DON, namely, nondispersive infra-red (NDIR) spectrometry for CO₂, CO, NO and H₂O vapor, and chemiluminescence detection for NO and NO_x. Thus, noble metal containing heterogeneous catalysts have proven to be excellent for the complete oxidation of gas-phase organic C (derived from incomplete fuel combustion) and CO, and they do not appear to affect significantly the NO produced from organic N combustion. In theory at least they should therefore be useful for quantifying DOC and DON from natural waters. In contrast to their potential for oxidizing organic C and N when

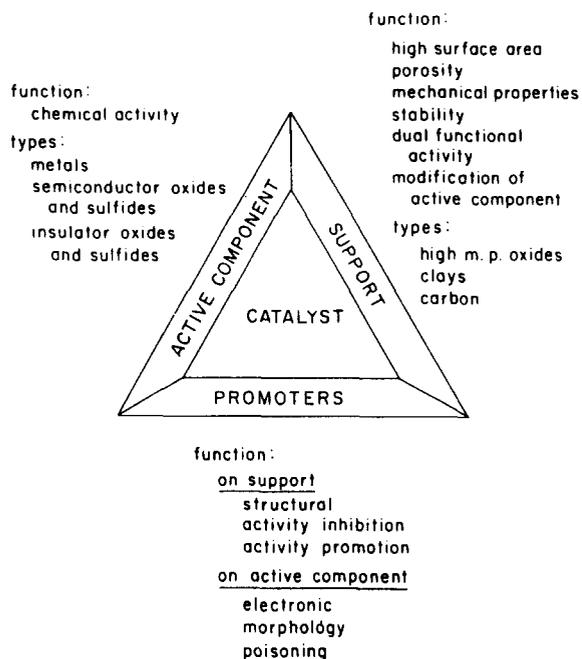


Fig. 1. Schematic illustration of the three major components of a heterogeneous catalyst and their primary functions (from Richardson, 1989).

matrix effects are minimal, however, the severe matrix effects imposed by samples such as seawater may be severely detrimental to heterogeneous catalysts, as will be discussed below. For further information on the mechanisms of, and reactions mediated by, noble metal heterogeneous catalysts, the interested reader should consult the excellent reviews of Taylor (1984) and Prasad et al. (1984) and books by Gates et al. (1979), Pines (1981) and Le Page et al. (1987).

COMPOSITION AND STRUCTURE OF HETEROGENEOUS CATALYSTS

Heterogeneous catalysts are generally considered to be composed of three distinct, yet complementary and necessary, components (Fig. 1). These are: (1) the support; (2) the active component; (3) promoters. The function of each of these components and the better understood functions of some specific component materials will be discussed in turn.

Ideally, the materials which go into the

synthesis of a catalyst should allow it to perform with a high level of activity, little restriction of flow and reasonable stability. Activity is generally achieved by formulating the 'correct' combination of chemicals to be used for each of the three components. In catalyst chemistry much of the knowledge of this aspect is obtained by experience rather than by the ability to predict theoretically and accurately which materials are best suited to a given application. The physical nature of the catalyst particle is also critical in this regard, as the reactants must be able to reach the active sites of the catalyst (Occelli, 1981; Vansant, 1988). This requires a relatively high particle porosity and surface area. The size, shape and mechanical strength of the particle will govern the resistance of the catalyst bed to fluid flow (Richardson, 1989; Spencer, 1989). A wide range of catalyst sizes and shapes is available (see below). The stability of the catalyst particle, that is, its ability to retain its activity under conditions of long-term use, requires that it be resistant to deactivation. The three most important means of catalyst deactivation are fouling, poisoning and sintering, and all catalysts are susceptible to these to a greater or lesser extent. Catalyst optimization thus requires a great deal of attention to the process conditions (including temperature and flow) and how deleterious the conditions (including the fluid, reactants, products and by-products) are to both the short- and long-term stability and activity of the catalyst.

Supports

The main function of the support is to provide the highest possible surface area for dispersion of the active component. It must have a high melting point to minimize the effects of thermal alteration of the support structure. An important additional function of the support is to minimize sintering (migration and coalescence) of the active component. The ability of the support to control sintering is highly dependent upon the degree of loading of the active component onto

TABLE 1

Commonly used support materials (from Richardson, 1989)

Type	Formula	Melting Point (°C)
Basic	MgO	3073
	CaO	2853
	BaO	2196
Amphoteric	ThO ₂	2323
	Cr ₂ O ₃	2708
	La ₂ O ₃	2588
	α -Al ₂ O ₃	2318
Neutral	MgAl ₂ O ₄	2408
	ZnAl ₂ O ₄	2100
Acidic	γ -Al ₂ O ₃	2318
	SiO ₂	1973
	Al ₂ O ₃ -SiO ₂	1818

the support, interaction between the support and the active component, and the operating temperature (Hughes, 1984; Butt and Peterson, 1988). As will be discussed in greater detail, different active components (i.e. metals) behave very differently on supports as a result of the degree of loading, active component mobility and a variety of interactions between the support and active component.

Those materials which best fulfill one or more of the criteria for supports are the high melting point oxides (Table 1). Of these, γ -Al₂O₃, SiO₂ and Al₂O₃-SiO₂ have the highest surface areas and hence are the most commonly used support materials. Activated aluminas are formed by the dehydration of aluminum hydroxides at temperatures of approximately 250–800°C. The transition aluminas include the partially dehydrated γ (Al₂O₃·*n*H₂O, 0 < *n* < 0.6, temperature 600°C or lower) and the nearly anhydrous δ (800°C ≤ temperature ≤ 1000°C) groups (Prasad et al., 1984; Misra, 1986). The aluminosilicates, or zeolites, constitute the other major group of support materials, and their well-defined pore structure (in the range of organic molecular diameters) and ion-exchange capabilities allows for a much greater degree of flexibility and specificity in their application than is possible with the activated aluminas (Breck, 1974; Barrer, 1978; Occelli, 1981).

TABLE 2

Selected active components used in catalysis

Class	Active Components	Reactions
Metals	Fe, Ni, Pt, Pd, Cu, Co, Ag	Redox reactions
		Hydrogenation
		Hydrogenolysis Oxidation
Oxides and sulfides	NiO, ZnO, CoO, CuO	Redox reactions
		Hydrogenation
		Oxidation [Hydrogenolysis]
Oxides	MgO, SiO ₂ , Al ₂ O ₃ , Al ₂ O ₃ -SiO ₂ , zeolites, pillared clays	Carbonium ion reactions Cracking, dehydration, polymerization, isomerization

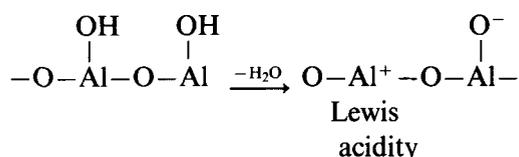
For a given alumina or zeolite, both the pore structure and surface area generally display distinct intermediate temperature optima (Lippens and Steggerada, 1970; Misra, 1986). Although the support should have a porosity sufficient to give the desired surface area, the size and shape of pores is also a consideration when diffusional effects of reactants and products within the catalyst must be considered. As we shall see, activated alumina and zeolitic support materials by themselves can have considerable catalytic activity. Ideally, the support material should not mediate reactions other than those desired for the catalyst as a whole, but this is often not the case.

Active components

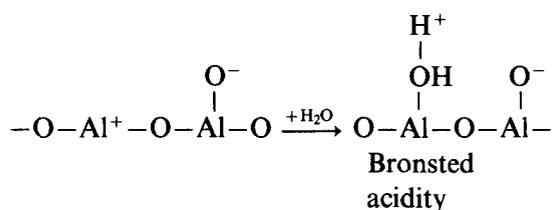
The active component is that portion of the catalyst particle which mediates the primary chemical reaction. The active component may be the support itself, many of which have a variety of catalytic activities, or something which is added to the support at a specific stage of catalyst synthesis. Some active components and the reactions which they mediate are given in Table 2.

Two of the most commonly used supports which also serve as active components are γ -Al₂O₃ and zeolites (alumino-silicates). The

catalytic cracking of C–C bonds has long been known to be accelerated in the presence of alumina and aluminosilicate-based materials over that associated solely with thermal cracking. Whereas thermolytic cleavage of C–C bonds occurs via free-radical splits, catalytic cracking is characterized by ionic rupture of the bond via a carbonium ion mechanism (Tanabe, 1981). Reduction–oxidation reactions are not mediated by these materials because electrons remain localized in valence bonds. However, acid-catalyzed reactions can be mediated by both γ -alumina and zeolites, as a result of their generation of protons in the form of acidic sites (Breck, 1974; Dwyer, 1988; Richardson, 1989). Lewis-type acidity, which promotes ion radical reactions, is generated when alumina is dehydrated:



Lewis acids can serve as electron acceptors from suitable donors such as S- and N-containing organic compounds, which are usually basic in nature. In most applications, however, there is adsorbed water usually present at the surface of the catalyst, thus allowing for the development and predominance of Bronsted acidity:



Carbonium ions (C^+) can arise from proton transfer between a support and various organic molecules, resulting in increased activity and susceptibility of C–C bonds to various rearrangement processes (e.g. cracking) (Ocelli, 1981; Pines, 1981). The promotion of carbonium ion reactions is primarily mediated by Bronsted

acidity and secondarily by Lewis acidity. The hydrogen-bonded proton of Bronsted acidity is available for transfer depending upon localized factors which strengthen or weaken the $\text{H}^+ - \text{OH}$ bond (Richardson, 1989). The crystalline structure of Al_2O_3 (both tetra- and octahedral) allows continua to exist in both the type and strength of acidity existing on different portions of the support.

Zeolites are aluminosilicates which have a highly ordered crystalline structure (Breck, 1974; Barrer, 1978; Rabo, 1981). The basic structure consists of oxygen tetrahedra packed into spherical structures with Al^{3+} and Si^{4+} ions filling the spaces between the oxygen ions. The general formula for zeolites is $\text{Me}_{x/n}^{n+}[(\text{AlO}_2)_x(\text{SiO}_2)_y]w\text{H}_2\text{O}$, where Me is a cationic species and water molecules are removed from the cavities during catalysis (Breck, 1974). Examples of several zeolites are shown in Fig. 2. More than 150 naturally occurring and synthetic zeolites are currently known. The zeolitic structure is defined by cavities that are reached by apertures approximating the effective diameters of organic molecules (Breck, 1974; Imelik et al., 1980; Ocelli, 1981; Vansant, 1988). Ions which are typically part of the zeolite cavity face (e.g. Mg^{2+} , Ca^{2+} , Na^+ or K^+) exert a polarizing influence on molecules trapped in the zeolite cavity, allowing them to be retained. The cation present in a zeolite will have a profound effect on the rates of specific reactions. Sodium is usually the ion present after initial synthesis of a zeolite from sodium silicates and aluminates, but it can thereafter be readily replaced with other desired ions by ion exchange. The acidities of zeolites are many orders of magnitude greater than either alumina (pK_a from approximately +3.3 to –5.6) or $\text{Al}_2\text{O}_3\text{-SiO}_2$ (pK_a approximately less than –8.0) (Rudham and Stockwell, 1977; Dwyer, 1988). Thus, zeolites are sometimes added to alumina and aluminosilicate supports during catalyst preparation to increase the overall acidity of the support. The carbonium-type reactions which may be catalyzed by solid acids (i.e. zeolites, alumina, and $\text{Al}_2\text{O}_3\text{-SiO}_2$)

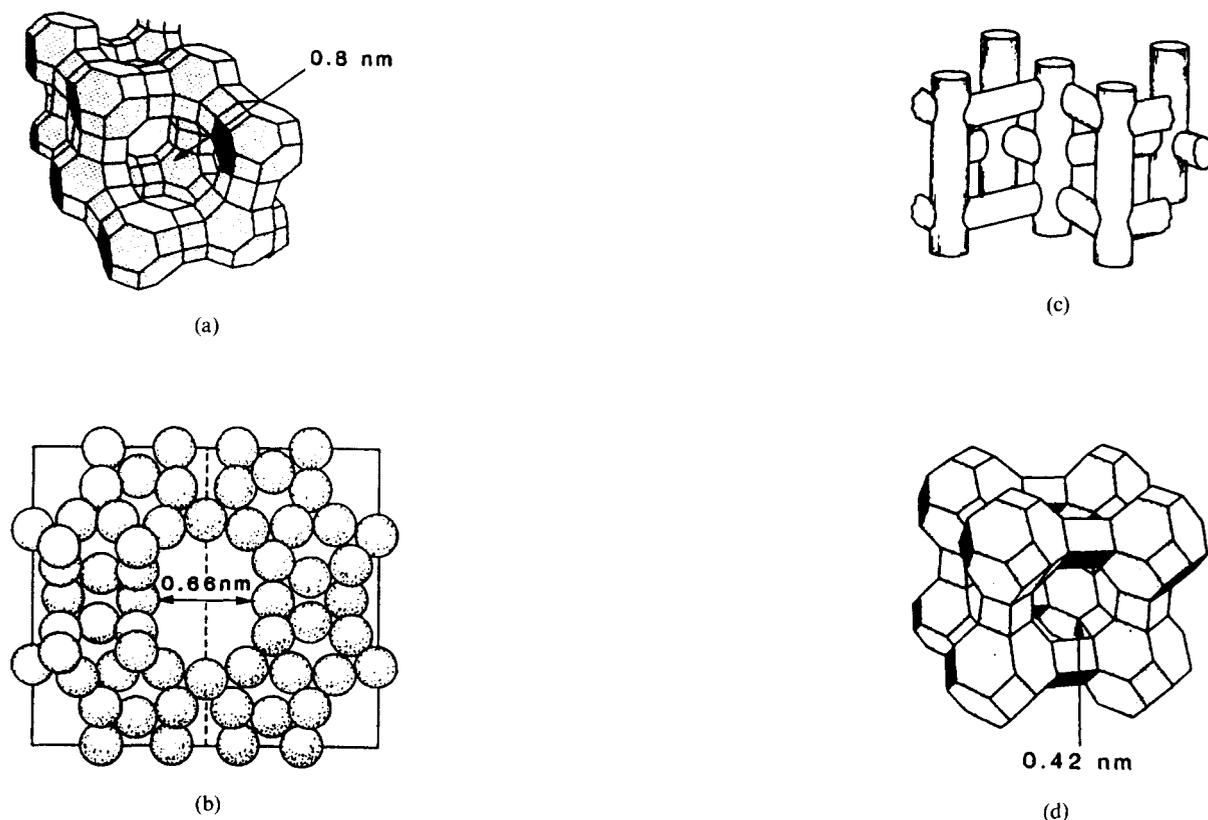


Fig. 2. Some commercially used zeolites and their pore diameters in angstroms.

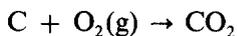
include cracking of C–C bonds, dealkylation, dehydroxylation, dehydrogenation, alkylation, isomerization and graphitic coke formation, the last of which can interfere with catalyst function (see below).

The other major group of active components is metals, which are generally deposited onto a support after its synthesis. Only the *d*-electron transition metals are capable of performing catalytic functions (Bond, 1962; Prasad et al., 1984; Richardson, 1989). These include Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Re, Os, Ir, Pt and Au. The greatest activities are observed for metals with 3, 6 and 8 *d*-electrons; minima are observed for those with 0, 5 and 10 *d*-electrons. The *s*-metals (Groups IA and IIA in the periodic table) are not useful catalysts because of their ready reversion to various ionic states under process conditions. They are, however, commonly used as promoters (see below). The rare earth *f*-metals are also

too reactive to serve as catalysts but also find applications as promoters.

The noble metals Pt and Pd exhibit a high catalytic activity for hydrocarbon oxidation which is attributed to their activation of O–O, C–H and O–H bonds (Bond, 1962; Prasad et al., 1984). For straight-chain hydrocarbons, Pt has been observed to have greater activity than Pd, which has greater activity for aromatic hydrocarbons (Prasad et al., 1984). Their high activities allows both metals to be used at very low loadings (approximately 0.02–0.5 wt.%) in catalytic combustion applications (Summers and Monroe, 1981; Prasad et al., 1984).

The two predominant reactions of carbon (organic or graphitic) with molecular oxygen can be represented as (McKee, 1981)



$$(\text{g}) \Delta G^\circ = -94.628 \text{ kcal mol}^{-1}$$

and



Increasing combustion temperatures favor an increased CO/CO₂ ratio from graphite oxidation, but the presence of many metal-active components (either in pure metallic or oxide forms) results in a corresponding decrease in this ratio (McKee, 1981). The ability of these metals to affect both organic carbon and CO oxidation makes an understanding of their relative role(s) in each process less clear. Moreover, the rate of conversion of CO to CO₂ (independent of their initial formation from organic carbon combustion) is positively correlated with combustion temperature. However, in spite of these complicating factors, it has been well established that numerous metals and their oxides, when used alone, are capable of effectively lowering the combustion temperature of carbon (as powdered graphite) by up to several hundred degrees, the most effective being (in decreasing order) Pb, Co, Cu, Ag, Fe and Pt (McKee, 1981). The Pt-group metals may also enhance C–C bond cleavage via the formation of Pt–C bonds, the ease of cleavage being dependent upon the strength of a particular Pt–C bond. It should be noted that neither Pt nor the other Pt-group metals (Pd, Ru, Rh and Ir) have been found to be the most active catalysts for graphitic carbon oxidation, although they, along with CuO, NiO and Ag metal, are extremely effective in converting CO to CO₂. Indeed, the more common and less costly Cu and Pb oxides have been found to reduce the ignition temperature of graphite by several hundred degrees centigrade and to enhance the rate of oxidation by up to about three orders of magnitude (McKee, 1981). It has also been observed that the presence of water vapor may reduce the rate of oxidation. The effects of these metals on graphite oxidation in oxygen have implications not only for the ability of ‘refractory’ forms of carbon to be oxidized, but also for the ability of a catalyst to perform effectively when graphitic coke is deposited

TABLE 3

Some promoters and their functions (from Richardson, 1989)

Catalyst	Promoter	Function
Al ₂ O ₃	K ₂ O	Reduces coke formation
	HCl	Increases acidity
	MgO	Prevents sintering
Al ₂ O ₃ -SiO ₂	Pt	Increases CO oxidation
Zeolites	Rare earth metals	Increases acidity and thermal stability

during the oxidation of other organic compounds (see below).

Promoters

Promoters are the third component of many catalyst systems, and their addition to the support and active component often results in the enhancement of some aspect of catalyst function (e.g. activity, stability, etc.) (Rosynek, 1977). In general practice, the function of a promoter is determined through trial and error, and the mechanisms behind how promoters work are currently being debated and in many cases are not well understood. A few of the better known functions of some promoters are given in Table 3. Promoters may help maintain the structure and activity of supports. However, one of their most common uses is in the prevention of coke formation on both the catalyst surface and in pores.

Catalyst synthesis

Assembly of the three major components into a functional unit is a lengthy, albeit relatively straightforward, process. The major steps in the process are shown in Fig. 3 and include a series of controlled precipitation and drying phases. For detailed information on catalyst fabrication the reader is referred to Breck (1974), Weiser (1976), Occelli (1981), Oberlander (1984), Misra (1986), Lowe (1988), Occelli et al. (1988) and Richardson (1989).

Briefly, after synthesis of the support, the

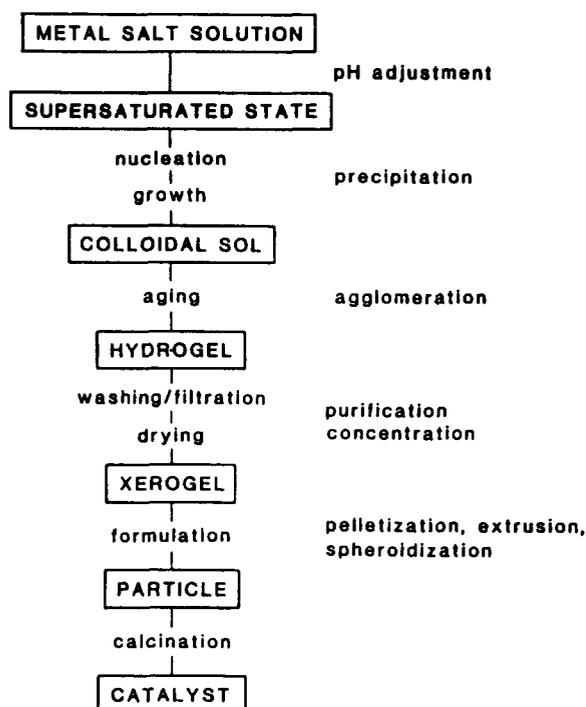


Fig. 3. General steps in the preparation of a heterogeneous catalyst (from Richardson, 1989).

active component is deposited by precipitation, adsorption, ion exchange or impregnation. After deposition of the active component it must then be 'activated', that is, converted to the form in which it is catalytically effective. After deposition, most metals are in an oxidized form. For metal oxides which comprise the active component, no further treatment is necessary. However, for metals which are required to be in the metallic (i.e. zero oxidation state) form a further reduction step is necessary, and this is usually performed in a reducing atmosphere (H_2) at an elevated temperature (approximately 400–500°C). Simultaneous with the reduction, the metal atoms nucleate to form crystallites or agglomerations of metal atoms. Although the reduction and nucleation steps are considered to be critical to both the state and distribution of the active component on the support, both of these steps are highly sensitive to even minor differences in process conditions. It should also be noted that numerous unique problems exist

for the Pt-group metals as active components which may require their re-reduction and redispersion several times throughout the lifetime of the catalyst (see below).

After deposition of the active component the catalyst exists as a powder which may then be formed into any of a variety of shapes depending upon the specific application. The main criteria in selecting an appropriate particle size are that fluid flow through the catalyst bed should be uniform, the pressure drop across the catalyst bed should be minimized, and diffusional effects both within the catalyst bed and at and within the support (i.e. catalyst particle) should also be minimized (Satterfield, 1970; Kesselring, 1986; Richardson, 1989). The most common particle shapes and structures include pellets, extrudates, spherules and granules, all of which have been found to function well in fixed-bed reactors.

CATALYST DEACTIVATION

All heterogeneous catalysts begin to lose their activity from the time they are initially used. Perhaps most disturbing is that initial deactivation often occurs before it can be adequately detected and its effects assessed. If not stored properly (i.e. in inert atmospheres) catalysts may adsorb materials from air which can begin the deactivation process before actual use (see below) (Goodman, 1989). Initial deactivation of a catalyst during use begins immediately as a result of several factors which essentially irreversibly bind active sites on the catalyst (Hughes, 1984; Butt and Peterson, 1988). In fact, initial 'conditioning' of a catalyst, whereby a new steady state is reached during processing of the first several batches of reactants, is really part of the deactivation process resulting in a loss of activity and, hence, efficiency. We have routinely noted when using high-temperature catalytic methods for DOC oxidation that, after a period of non-injection, the first 1–3 injections of seawater, standard compounds or even blank water invariably result in greater NDIR peak areas (see Williams et al., 1993). These then

decrease until an equilibrium is reached with respect to peak areas. This trend may represent a loss in activity of the catalyst, and whether the effect is common to any material (i.e. standards vs. samples) injected is not known. In addition to these rapid losses in activity, long-term (weeks to months) activity losses also occur.

Three major forms of catalyst deactivation have been identified. These are (1) mechanical alterations in the catalyst particle or bed, (2) thermal effects and (3) chemical effects. Any one of the individual processes occurring within each of these categories can result in a loss of catalyst activity and often several act simultaneously.

Mechanical effects

The two main causes of mechanical failure of a catalyst are breakdown of the particle itself and coating of the particle with any of several components of the reaction mixture (Hughes, 1984; Lynwood, 1989). The latter can include the presence of substances occurring concomitantly in the reaction mixture. The mechanical strength of a catalyst can decrease with time because of the effects of high temperatures and chemicals on the support; this results in fissures in the support and a collapse of support pore structures, and thus leads to a loss of surface area. In seawater applications, the presence of sulfate ion may result in the formation under certain conditions of aluminum sulfate, which will weaken alumina-based supports. Of potentially greater concern is the nearly immediate and complete coating which the catalyst at the top of the column experiences as a result of the presence of various salts in seawater. This physical coating essentially removes the catalyst particle, its pores and active sites from contact with the reactants (i.e. DOM molecules) during subsequent applications (injections) of sample. As this portion of the catalytic reactor is that which is first contacted by each sample it must be questioned whether true catalysis occurs or if simple thermal or pyrolytic combustion dominate under these conditions.

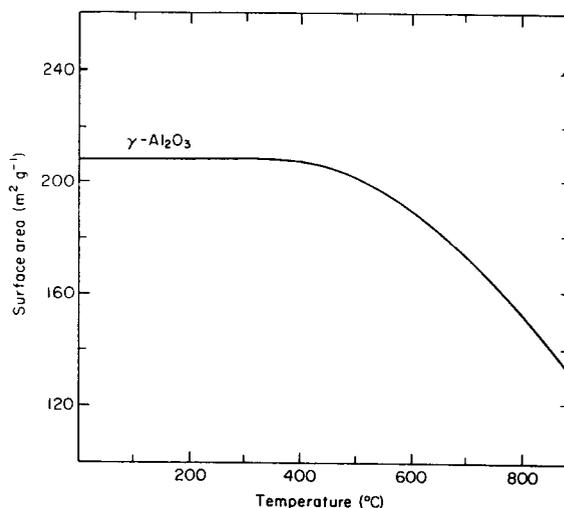


Fig. 4. Loss of surface area from γ -alumina during sintering of the support (from Hughes, 1984).

Thermal effects

The elevated temperatures at which most catalysts are operated may cause volatilization of catalyst components and sintering. Although most active components of catalysts have been evaluated for their volatilization under various processing conditions, the wide variety of rare earth elements used as promoters have received less attention in this respect.

One of the major means of catalyst deactivation is sintering. This is the process whereby either support materials or active component crystallites (usually metals) progressively coalesce to give lower surface-to-volume ratios of the support, the active component or both. In the case of the support, passageways or walls between the pores of the support collapse to form larger pores. The loss of surface area for γ -alumina as a function of temperature is illustrated in Fig. 4. For dispersed metals, the rate of crystallite migration increases dramatically with small increases in reaction temperature (Hermann et al., 1961; Butt and Peterson, 1988). The problem can be exacerbated for several commonly used Pt-group active components when they are used under oxidizing conditions. For example, extensive sintering of Pt

TABLE 4

Effects of process conditions on the extent of dispersion of 2% Pt on γ -alumina (from Butt and Petersen, 1988)

Atmosphere	Temperature (°C)	Time (h)	Dispersion (%)
H ₂	400	12	90
H ₂	700	3	29
O ₂	300	2	69
O ₂	520	2	9
O ₂	800	2	7

and Pd metals (i.e. in the zero oxidation state) can occur rapidly at temperatures above approximately 500°C (Hughes, 1984; Butt and Peterson, 1988). When this is combined with an oxidizing atmosphere, both Pt and Pd may redisperse as the less active forms PtO₂ and PdO on the surface of γ -alumina, resulting in a further decrease in the availability of the metals for catalytic purposes (Lee and Ruckenstein, 1983; Ruckenstein and Dadyburjor, 1983). Furthermore, at temperatures above about 600°C the extent of the interaction between PtO₂ and γ -alumina is weakened even further and larger crystallites form, thus dramatically decreasing the dispersion of Pt on the support as well as the catalyst activity. In addition to a loss of total activity, sintering may also result in qualitative changes in the selectivity of the reactions mediated by the active component (i.e. in products formed). Some examples of the extent of Pt dispersion on γ -alumina under various reaction conditions are given in Table 4. Of further urgency for seawater applications is the observed increase in supported Pt oxidation noted in the presence of chloride ion (Butt and Peterson, 1988).

Chemical effects

The two predominant chemical effects which alter catalyst activity are poisoning and coke formation. Poisoning is generally defined as the chemisorption of a compound to the active component (most commonly metals) and the inactivation of previously active sites. The poison may be present either as an impurity in the process stream or may be formed during

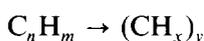
reaction. True poisons need be present only in very small quantities to have a deactivating effect on the catalyst, and poisoning may be reversible or non-reversible. Those metals which are most readily poisoned are the Group VIII and IB elements, i.e. those which exhibit the greatest catalytic activities. The elements which have been found to exert the strongest poisoning effects belong to Groups VB and VIB and include various N-, P- and S-containing compounds (Carnell, 1989). The toxicity of the poison depends upon the availability of empty valence orbitals (usually in the metal) or unshared electron pairs (usually in the poison), with greater availability imparting greater toxicity (Maxted, 1951; Richardson, 1989). Thus, the state in which a given poison exists, which will be at least partially controlled by the processing environment, will determine whether or not it is toxic to a given active component. For example, an oxidized form of S such as sulfate will be much less toxic than a fully reduced form such as hydrogen sulfide, and reduced forms of N such as NH₃ and NH₄⁺ may also be toxic to Pt-containing catalysts (Maxted, 1951). It has been noted that the addition of promoters such as La to the catalyst may help to stabilize Pt against S poisoning.

Various organic molecules, especially unsaturated ones, may also bind strongly with catalytic metals. Other metal ions, especially those with occupied *d*-orbitals, can bond with catalytic metals having empty *d*-orbitals (Richardson, 1989). Thus, Hg²⁺, commonly used as a biological poison and preservative, is toxic to Pt-containing catalysts. As with sintering, the support itself may be subject to poisoning, and alumina and the various zeolites are known to be strongly deactivated by N-containing organic compounds, especially those of a basic nature, which deactivate sites of acidity on the support. Chloride may also have significant effects on the sintering of the support and both the sintering and redispersion of active metal components (Carnell, 1989). In addition, the overall combustion of graphitic carbon has been found to be

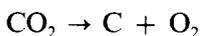
inhibited by the halogens, especially chlorine (McKee, 1981) which is formed in abundance during the high-temperature catalytic oxidation of seawater (J. Bauer, personal observation, 1992). This inhibition may be the result of the formation of stable carbon-halogen complexes.

Coke formation is the deposition on the catalyst of carbonaceous material which is not amenable to significant breakdown under the predominant reaction conditions (Wolf and Alfani, 1982). Coke may arise as a result of direct formation from the reactants in the form of a side reaction or as a by-product of the primary reaction being catalyzed. It is believed, at least in part, to be a direct result of the cracking of hydrocarbon-like structures on Bronsted sites followed by acid-catalyzed polymerization of carbon chains (Naccache, 1985). The structure of coke ranges from aromatic-type structures to highly refractory graphitic material. The amount of coke deposited (as weight per cent) on the catalyst can be significant depending upon the nature of the reactant material and the processing conditions. The major effect of coke is to coat the catalyst particle, thus reducing total surface area and active sites.

Under normal oxidizing conditions, coke (either non-graphitic or graphitic) formation may be represented by two main reactions (Richardson, 1989):



where $(CH_x)_y$ is non-graphitic (i.e. H-containing) carbon deposition, often occurring as polymeric material of an aromatic nature, and



where C represents graphitic (H-deficient) carbon. The former mechanism predominates at the acidic sites of supports and is directly related to the acidity of the support material. The latter mechanism occurs when CO initially dissociates at a catalytic site. Coke is removed from the catalyst ('catalyst regeneration') by burning in oxygen at elevated temperatures, the main

product being CO₂ with smaller amounts of methane and CO. Because of the necessity for higher temperatures in this process, care must be taken to preserve the support structure. In addition, after graphite combustion redispersion of metallic active components may be necessary.

PRELIMINARY CHARACTERIZATION OF CATALYSTS EMPLOYED IN OCEANIC DOM ANALYSES

A variety of techniques is available for the measurement of both bulk (e.g. diffusivity, pore-size distribution, surface area, etc.) and surface (e.g. dispersion, morphology and composition, acidity and activity) properties of catalyst particles (Anderson and Pratt, 1985; Spencer, 1989). We have employed one of these, X-ray photon spectroscopy (XPS), for the analysis of several surface properties (1–3 nm depth) of two of the heterogeneous catalysts which have been employed in our laboratories for DOC and DON analyses. The method essentially involves the ejection of electrons contained in surface materials of the catalyst by low-energy (10^2 – 10^3 eV) X-ray photons. The ejected electrons are collected and counted, giving spectra which are characteristic of the various surface materials.

For each analysis, unground catalyst particles were placed on sample stubs using double-sided tape. Atmospheric exposure of samples was minimized by preparation in an inert atmosphere glove box, and transfers were made using an inert atmosphere device. Analyses were performed with a VG (Stamford, CT) ESCALAB I using Al K α (1486.6 eV) exciting radiation from a dual anode operating at 14 kV and 40 mA. The photoelectrons were collected in a direction normal to the plane of the sample stub. Peak positions were corrected for charging by referencing to the Al 2p peak for alumina at 74.7 eV. The raw peak data were subsequently corrected for instrumental and theoretical variations to give a near-surface compositional analysis on an atomic percentage basis.

The atomic compositions of unused and used 3% Pt-impregnated γ -alumina catalysts

TABLE 5

Near-surface percentage atomic composition of unused and used 3% Pt-impregnated γ -alumina and Co-impregnated F-1-alumina catalysts as determined by XPS analysis

Catalyst	Atomic composition (%)						Carbon speciation (%)		
	C	O	Al	Pt	Na	Σ	GR	HC	CO
Unused 3% Pt	15.0	61.8	22.9	0.01	0.3	100.0	14	80	6
Used 3% Pt	15.5	60.8	22.6	0.00	1.1	100.0	22	75	6
Used Co/CoO	—	—	—	—	10	—	49	51	0

GR — Graphitic; HC — hydrocarbon; CO — carbonyl.

Unused sample of catalyst was analyzed directly from shipping container, used catalysts were analyzed after their use in HTCO unit for the analysis of seawater DOM.

(Sumitomo Chemical, Osaka, Japan) show an absence of measurable amounts of Pt on the surfaces of both catalysts, suggesting that the bulk of the Pt may be fixed within the alumina particles rather than at the immediate surficial region of the particle (Table 5). In addition, the accumulation of sodium may be noted in the used 3% Pt catalyst following light usage (less than 10 ml total), presumably derived from sea salts. This contrasts with the very high loading of sodium (10%) noted for cobaltous oxide on F-1-alumina catalyst (Rosemount Analytical, Santa Clara, CA) after heavy usage (about 100 ml total) (Table 5).

Figure 5(A) shows the C 1s XPS spectra of carbon speciation on samples of the fresh, unused 3% Pt-impregnated alumina catalyst. Although the catalyst was previously unused, and was analyzed immediately after its removal from the manufacturer's storage container, it contained significant carbon in both graphitic (14%) and non-graphitic (80%) forms (Table 5). This strongly implies that adsorption of atmospherically borne forms of organic carbon to the catalyst surface occurs during the various preparation, handling and packaging steps. After light usage of this same catalyst for discrete-injection analyses of seawater DOM, the proportion of graphitic carbon present on the catalyst surface (22%) increased compared with that of the unused sample, whereas the hydrocarbon fraction decreased to 75% (Fig. 5(B); Table 5).

The proportion of carbonyl carbon on both Pt catalyst samples was constant at 6%. In contrast, the cobaltous oxide on F-1-alumina catalyst after heavy usage contained 49% of its surface carbon in graphitic form and 51% in non-graphitic forms (Fig. 5(C); Table 5). Further information on the comparison of DOC and DON measurements conducted using these and several recently synthesized zeolite catalysts is given by Williams et al. (1993).

These preliminary data are intended to illustrate some of the qualitative changes which may occur at the catalyst surface during catalyst use and suggest that some of these changes may be relatively rapid. Whether quantitative evaluation of catalyst deterioration may be accomplished through measurements of this kind is not currently known. However, we feel that further characterizations of catalysts, both before and after usage and under controlled experimental conditions, may help elucidate both the nature and rate at which catalyst deactivation and loss of performance occur during analyses of seawater DOM.

CONCLUSIONS

In summary, it can be stated that a great many factors go into the successful use of heterogeneous catalysts, and numerous precautionary measures must be taken to ensure their proper functioning on anything other than very short

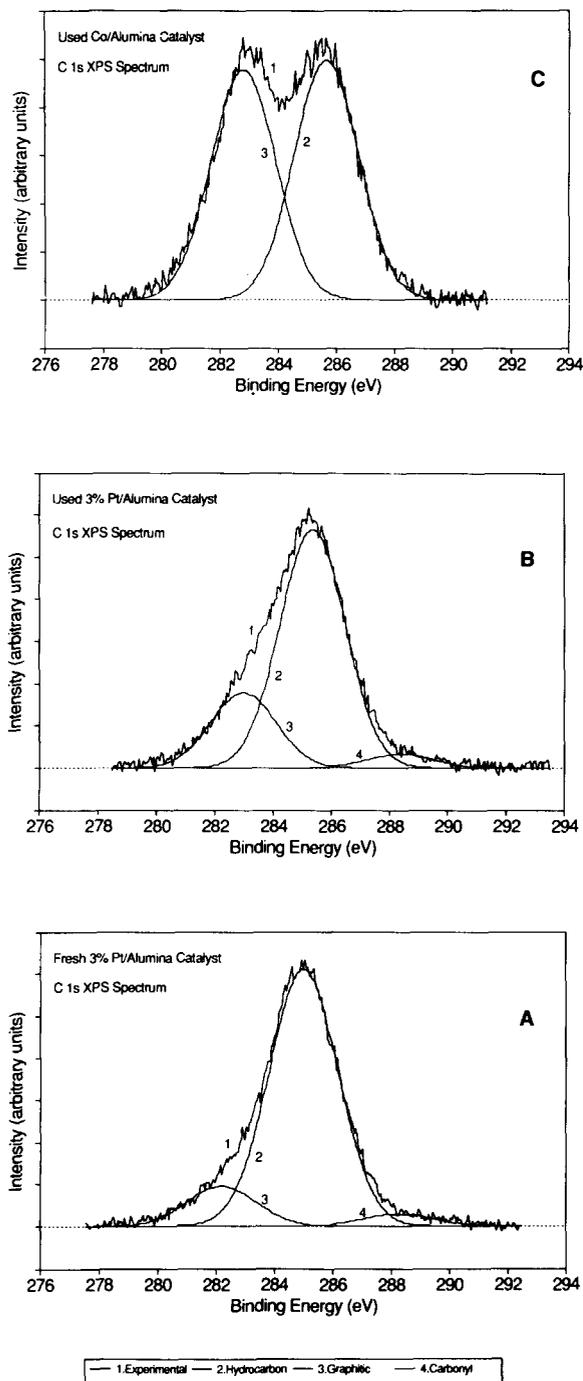


Fig. 5. C 1s XPS spectra of unused (A) and used (B) 3% Pt-impregnated γ -alumina and (C) used Co-impregnated F-1-alumina catalysts showing the speciation of carbon on catalyst surface. Unused sample of catalyst was analyzed directly from shipping container, used catalysts were analyzed after their use in HTCO unit for the analysis of seawater DOM.

time-scales. The available information on heterogeneous catalysts suggests that they may be useful for the routine analysis of DOC and DON in natural waters. An adequate evaluation of heterogeneous catalysis is an exceedingly difficult undertaking under even the simplest processing conditions. Successful application of catalytic systems for the complete oxidation of a variety of complex organic materials in a medium such as seawater therefore presents the chemical oceanographic community with a difficult analytical challenge. Some of the questions that we believe remain to be answered before the definitive use of such catalysts as quantitative analytical tools in the ocean sciences can be assured.

(1) Is a single catalyst capable of quantitatively oxidizing to simple, detectable end-products (i.e. CO_2 and NO) the full complement of DOC and DON molecules in seawater?

(2) What is the effective lifetime of a specific catalyst under conditions of continuous, long-term application of seawater and how can that lifetime be determined?

(3) What are the relative roles of the various components of a high-temperature catalyst system (including the support, active components, promoters and temperature) in the complete oxidation (i.e. combustion) of naturally occurring forms of organic carbon in the environment? Are currently used HTCO systems *catalytically* combusting natural DOC and DON compounds?

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REFERENCES

Anderson, J.R. and Pratt, K.C., 1985. Introduction to

- Characterization and Testing of Catalysts. Academic Press, New York, 457 pp.
- Barrer, R.M., 1978. Zeolites and Clay Minerals as Sorbents and Molecular Sieves. Academic Press, New York, 497 pp.
- Bauer, J.E., Haddad, R.I. and Des Marais, D.J., 1991. Method for the determination of stable carbon isotope ratios in dissolved organic carbon of interstitial and other natural marine waters. *Mar. Chem.*, 3: 335.
- Blazowski, W.S. and Walsh, D.E., 1975. Catalytic combustion: An important consideration for future application. *Combust. Sci. Technol.*, 10: 233.
- Bond, G.C., 1962. Catalysis by Metals. Academic Press, New York, 519 pp.
- Breck, D. W., 1974. Zeolite Molecular Sieves: Structure, Chemistry and Use. John Wiley, New York, 771 pp.
- Butt, J.B. and Petersen, E.E., 1988. Activation, Deactivation and Poisoning of Catalysts. Academic Press, San Diego, CA, 495 pp.
- Carnell, P.J.H., 1989. Feedstock purification. In: M.V. Twigg (Editor), *Catalyst Handbook*, 2nd edn. Wolfe, London, p. 191.
- Dwyer, J., 1988. A critical evaluation of the concepts of Bronsted acidity related to zeolites. In: P.J. Grobet, W.J. Mortier, E.F. Vansant and G. Schulz-Ekloff (Editors), *Innovation in Zeolite Materials Science*. Elsevier, New York, p. 333.
- Gates, B.C. Katzer, J.R. and Schuit, G.C., 1979. Chemistry of Catalytic Processes. McGraw-Hill, New York, 464 pp.
- Goodman, D.R., 1989. Handling and using catalysts in the plant. In: M.V. Twigg (Editor), *Catalyst Handbook*, 2nd edn. Wolfe, London, p. 140.
- Gupta, Y.K. and Ghosh, S., 1959. The silver-catalyzed reduction of persulphate by oxalate in acid solution. *Inorg. Nucl. Chem.*, 11: 320.
- Hegedus, L.L. and Gumbleton, J.J., 1980. Catalysts, computer and cars: a growing symbiosis. *Chemtech*, 10: 630.
- Hegedus, L.L., Summers, J.C., Schlatter, J.C. and Baron, K., 1979. Poison-resistant catalysts for the simultaneous control of hydrocarbons, carbon monoxide and nitrogen oxide emissions. *J. Catal.*, 56: 321.
- Hermann, R.A., Adler, S.F., Goldstein, M.S. and De Baun, R.M., 1961. The kinetics of sintering of platinum supported on alumina. *J. Phys. Chem.*, 65: 2189.
- House, D.A., 1962. Kinetics and mechanism of oxidations by persulfate. *Chem. Rev.*, 62: 185.
- Hughes, R., 1984. Deactivation of Catalysts. Academic Press, London, 265 pp.
- Imelik, B., Naccache, C., Taarit, Y.B., Vedrine, J.C., Coudurier, G. and Praliand, H., 1980. Catalysis by Zeolites. Elsevier, Amsterdam, 351 pp.
- Kesselring, J.P., 1986. Catalytic combustion. In: F.J. Weinberg (Editor), *Advanced Combustion Methods*. Academic Press, New York, p. 237.
- Klimisch, R.L. and Barnes, G.J., 1972. Chemistry of catalytic nitrogen oxide reduction in automotive exhaust gas. *Environ. Sci. Technol.*, 6: 543.
- Kummer, J.T., 1980. Catalysts for automobile emissions control. In: N.A. Chigier (Editor), *Progress in Energy and Combustion Science*, Vol. 6. Pergamon, New York, p. 177.
- Lee, H.H. and Ruckenstein, E., 1983. Catalyst sintering and reactor design. *Catal. Rev.-Sci. Eng.*, 25: 475.
- Le Page, J.-F. et al., 1987. *Applied Heterogeneous Catalysis*. Gulf Publishing, Houston, TX, 516 pp.
- Lippens, B.C. and Steggerada, J.J., 1970. Active alumina. In: B.G. Linsen (Editor), *Physical and Chemical Aspects of Adsorbents and Catalysts*. Academic Press, New York, p. 171.
- Lowe, B.M., 1988. Synthesis mechanisms for zeolites and molecular sieves. In: P.J. Grobet, W.J. Mortier, E.F. Vansant and G. Schulz-Ekloff (Editors), *Innovation in Zeolite Materials Science*. Elsevier, New York, p. 1.
- Lynwood, W.J., 1989. Process design, rating and performance. In: M.V. Twigg (Editor), *Catalyst Handbook*, 2nd edn. Wolfe, London, p. 85.
- Margolis, L.Y., 1963. Catalytic oxidation of hydrocarbons. In: D.D. Eley, H. Pines and P.B. Weisz (Editors), *Advances in Catalysis*, Vol. 14. Academic Press, New York, p. 429.
- Maxted, E.B., 1951. The poisoning of metallic catalysts. In: W.G. Frankenburg, E.K. Rieal and V.I. Komarewsky (Editors), *Advances in Catalysis*, Vol. 3. Academic Press, New York, p. 129.
- McKee, D.W., 1981. The catalyzed gasification reactions of carbon. In: P.L. Walker and P.A. Thrower (Editors), *Chemistry and Physics of Carbon*, Vol. 16. Marcel Dekker, New York, p. 1.
- Misra, C., 1986. *Industrial Alumina Chemicals*. Am. Chem. Soc. Monogr. 184 ACS, Washington, DC, 165 pp.
- Naccache, C., 1985. Deactivation of catalysts. In: J. Oudar and H. Wise (editors), *Deactivation and Poisoning of Catalysts*. Marcel Dekker, New York, p. 185.
- Oberlander, R.K., 1984. Aluminas for catalysis—their preparation and properties. In: B.E. Leach (Editor), *Applied Industrial Catalysis*, Vol. 3. Academic Press, New York.
- Ocelli, M.L., 1981. Zeolites. Union Oil Company of California, Brea, CA (unpublished report), 22 pp.
- Ocelli, M.L., Pollack, S.S. and Sanders, J.V., 1988. Characterization of siliceous zeolites crystallized in the presence of trioctylamine. Part I. Synthesis and crystal properties. In: P.J. Grobet, W.J. Mortier, E.F. Vansant and G. Schulz-Ekloff (Editors), *Innovation in Zeolite Materials Science*. Elsevier, New York, p. 45.
- Orchin, M., 1984. Homogeneous catalysis: a wedding of theory and experiment. *Catal. Rev.*, 26: 59.
- Otto, K. and Yao, H.C., 1980. The reduction of nitric oxide by hydrogen over Pt/g-Al₂O₃ as a function of metal loading. *J. Catal.*, 66: 229.

- Pines, H., 1981. *The Chemistry of Catalytic Hydrocarbon Conversions*. Academic Press, New York, 305 pp.
- Prasad, R., Kennedy, L.A. and Ruckenstein, E., 1981. Oxidation of fuel bound nitrogen in a transition metal oxide catalytic combustor. *Combust. Sci. Technol.*, 27: 45.
- Prasad, R., Kennedy, L.A. and Ruckenstein, E., 1984. Catalytic combustion. *Catal. Rev.—Sci. Eng.*, 26: 1.
- Rabo, J.A., 1981. Unifying principles in zeolite chemistry and catalysis. *Catal. Rev.*, 23: 293.
- Richardson, J.T., 1989. *Principles of Catalyst Development*. Plenum, New York, 288 pp.
- Rosynek, M.P., 1977. Catalytic properties of rare earth oxides. *Catal. Rev.*, 16: 111.
- Ruckenstein, E. and Dadyburjor, D.B., 1983. Sintering and redispersion of supported metal catalysts. *Rev. Chem. Eng.*, 1: 251.
- Rudham, R. and Stockwell, A., 1977. Catalysis on faujasitic zeolites. In: C. Kemball (Editor), *Catalysis*, Vol. 1. Chemical Society, London, p. 87.
- Satterfield, C.N., 1970. *Mass Transfer in Heterogeneous Catalysis*. M.I.T. Press, Boston, MA, 267 pp.
- Spencer, M.S., 1989. Fundamental principles. In: M.V. Twigg (Editor), *Catalyst Handbook*, 2nd edn. Wolfe, London, p. 17.
- Summers, J.C. and Monroe, D.R., 1981. Design factors of dual bed catalysts. *Ind. Eng. Chem. Res. Dev.*, 1981: 23.
- Tanabe, K., 1981. Solid acid and base catalysis. In: J.R. Anderson and M. Boudart (Editors), *Catalysis, Science and Technology*, Vol. 2. Springer-Verlag, New York, p. 231.
- Taylor, K., 1984. Automobile catalytic converters. In: J.R. Anderson and M. Boudart (Editors), *Catalysis, Science and Technology*, Vol. 2. Springer-Verlag, New York, p. 119.
- Turner, D.W., Andrews, R.L. and Siegmund, C.W., 1972. Influences of combustion modification and fuel nitrogen content on nitrogen oxide emissions from fuel oil combustion. *Combustion*, 44: 21.
- Vansant, E.F., 1988. Pore size engineering in zeolites. In: P.J. Grobet, W.J. Mortier, E.F. Vansant and G. Schulz-Ekloff (Editors), *Innovation in Zeolite Materials Science*. Elsevier, New York, p. 143.
- Weiser, H.B., 1976. *The Hydrous Oxides*. McGraw-Hill, New York, 452 pp.
- Williams, P.M., Bauer, J.E., Robertson K.R., Wolgast, D.M. and Occelli, M.L., 1993. Report on DOC and DON measurements made at S.I.O., 1988–1991. *Mar. Chem.*, 41: 271–281.
- Wolf, E.E. and Alfani, F., 1982. Catalyst deactivation by coking. *Catal. Rev.*, 24: 329.