REVIEWS

Catalytic Abatement of Water Pollutants

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The paper reviews solid-catalyzed oxidation and reduction processes for the treatment of wastewater that contains small concentrations of toxic compounds and for which separation is not economical while biological treatment is not feasible. Specifically, the objectives are (1) to understand the interactions between catalytic materials and various pollutants, (2) to provide a database for catalyst selection, and (3) to assess the potential of these processes for commercialization. The review suggests the following well-investigated solutions: (1) Supported metal (Ru/CeO_2, Pt/CeO_2, and Ru/C) and metal oxides (CuO−ZnO−CoO, MnO_2/CeO_2, CoO/Bi_2O_3, and V_2O_5/Al_2O_3) are the most promising catalysts for the destruction of refractory organic compounds with nearly 100% selectivity to CO_2; (2) CoO/CeO_2 and MnO_2/CeO_2 are the most active catalysts for ammonia oxidation at temperatures of 263−400 °C; (3) activated carbon, preferably in the presence of copper ions, is an active catalyst for the oxidation of cyanides and sulfur-containing compounds; (4) catalytic hydrodechlorination (HDC) of chloroorganics and hydrodenitrification (HDN) of nitrates emerge as promising processes for wastewater treatment. To overcome mass-transfer resistance, catalysts should be constructed as fibers, cloth, or powder. Novel processes that incorporate separation at room temperature (e.g., by adsorption) and reaction at elevated temperatures are described. Suggestions for new directions of research are made.

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1. Introduction

Wastewater treatment has become a major social, technological, economical, and political problem. Modern legislation in every country imposes environmental regulations and health quality standards that steadily become more restrictive. Three general strategies can be adopted by the industry to comply with these limitations: (*i*) to minimize waste production by developing new “clean” technologies that will replace existing technologies; (*ii*) to improve the performance of the existing technologies and units by the implementation of new advanced methods for environmental protection, and (*iii*) to build closed industrial water-recycling systems without any wastewater discharge.

The nature of pollutants and their concentrations in industrial wastewater depend on their source. Industrial wastewater typically leaves the units at higher temperatures than communal and agricultural wastewater. Because of the high concentrations of toxic materials in industrial wastewater, it is necessary to apply specific processes for their separation, transformation, and further decomposition. A variety of biological, physical, and chemical processes and their combinations are available for these purposes, but each technique has its inherent limitations in applicability, effectiveness, and cost.

Biological treatment is highly effective for the removal of most contaminants. Despite their success and cost effectiveness, biodegradation processes are inherently slow, do not allow for high degrees of removal, and are not suitable for compounds that are toxic for the microorganisms. The sludge formed during biological treatment has to be disposed of either by landfilling or by burning, and the cost of these disposal methods should be accounted for. Sludge disposal may pose additional environmental problems. Evidently, the biological treatment of industrial wastewater is of

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limited use only, and additional treatment by other methods is frequently required.

The chemical industry generates wastewater that contains toxic compounds in small concentrations so that their economic recovery is not feasible and, in many cases, their biological treatment is not feasible since they are poorly biodegradable or toxic. For example, aromatic compounds such as phenols are considered to be toxic to the microbial population at concentrations above 70−200 mg/L (Katzer et al., 1976; Metcalf & Eddy, 1991). The halogenated compounds are not removed efficiently by existing biological treatment techniques, either because they are metabolized very slowly or because they are resistant to microbial attack under prevailing treatment conditions (Adrieaens and Vogel, 1995). Ammonia inhibition makes the biological process extremely slow at an ammonia concentration above 300 mg/L (Wiesman, 1994). Cyanides and cyanide-producing substances can have harmful effects on biological treatment processes (Fewson, 1988).

It is necessary to develop effective treatment options using less conventional techniques, such as chemical and catalytic processes for aqueous streams. Chemical oxidation is a popular method since the reactants are inexpensive, but oxidative techniques may be prohibitively expensive when used to achieve complete oxidation of all contaminants present in the wastewater. The partial oxidation of organic pollutants to intermediate compounds which are amenable to biological treatment is possible and less expensive to complete oxidation. Reductive processes are typically more expensive and less popular, but in special cases they are indispensable (Kalnes and James, 1988).

Catalysis plays a major role in pollutants abatement from gas streams and in atmospheric protection and remediation (Armor, 1992). Its leading role in this field is expected to be preserved in the future. Catalytic processes for wastewater treatment offer several advantages. They can be performed under milder conditions (temperatures and pressures). Another great advantage of catalytic methods is the possibility to treat only a single pollutant, or a group of similar pollutants, out of a complex mixtures of pollutants (as in selective catalytic reduction). This opportunity is of special interest when a mixture of pollutants and useful compounds should be processed. By proper choice of the catalyst, it is possible not only to control the degree of conversion of pollutants but also to select different reaction routes, in order to select the optimal reaction intermediates and products and avoid the formation of secondary pollutants.

Katzer and co-workers (1976) were the first to evaluate the catalytic liquid-phase oxidation as a potential wastewater treatment technology. They demonstrated that catalytic oxidation may not be economically attractive for low concentrations of pollutants because of the energy requirement to heat up a wastewater stream. These methods become economically feasible only with high organic concentrations which provide sufficient heat for a self-sufficient process.

Catalytic methods, however, are not widely used for wastewater treatment in the industry for several reasons: Reaction rates are slow at room temperature, and even at higher temperatures they are significantly limited by mass-transfer resistance. Also, catalytic processes require major engineering efforts in modeling and optimal designing of complicated three-phase industrial reactors. The development of new catalysts and catalytic processes requires an extensive and expensive basic and applied research activity. Properties of the catalyst like lifetime, susceptibility to poisoning, and mechanical stability may be improved successfully only by running pilot plant experiments which are rather expensive. The high investment cost in the development of a suitable catalyst and a catalytic process is usually compensated by the high economic efficiency of such units. We expect that in the nearest future catalytic methods will find an extensive application for abating reactants that are not biodegradable or that are toxic to the biological treatment and for complementing existing, typically biochemical, technologies. We expect that stricter environmental regulations and the expensive land requirement for the slow biological processes will make chemical and especially catalytic wastewater treatment methods more attractive.

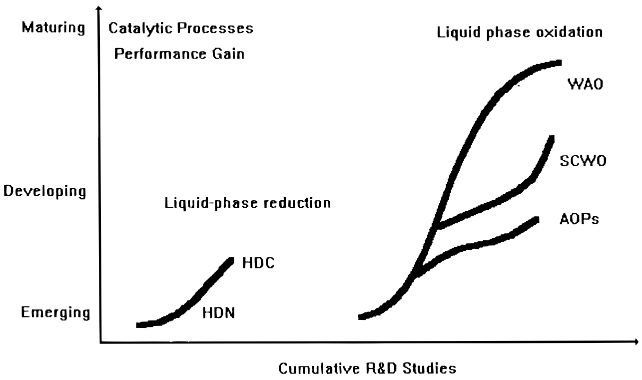

Figure 1. Maturity of the available catalytic abatement techniques in water treatment.

The goal of this work is to review the recent published literature (1976−1997) dealing with solid-catalyzed oxidation and reduction abatement of refractory water pollutants. Specifically, the objectives are (1) to understand the interactions between catalytic materials and various pollutants, (2) to provide the database for catalyst selection, and (3) to assess the potential of these processes for commercialization.

A computer search in the Chemical Abstracts files, using the key words *wastewater/pollution/catalytic*, indicates that about 200 papers appeared in this field in the past two decades, with most in the last decade. Figure 1 quantitatively portrays the state of various technological approaches capable of reducing hazardous pollutants using catalytic performance. It shows that the majority of catalytic abatement research was devoted to oxidation processes, which are currently used for wastewater treatment in more than 200 plants worldwide.

We describe below several catalytic oxidation methods for pollutant abatement along with their advantages and shortcomings: Wet air oxidation (WAO) is an established technology that involves the liquid-phase oxidation of dissolved organics or oxidizable inorganic compounds using a gaseous source of oxygen (usually air) at high temperatures (200−350 °C) and pressures (70−230 atm) which severely affects the economy of this technology (Mishra et al., 1995). Under these conditions, the solubility of oxygen in wastewater is substantially enhanced, the diffusion of oxygen and organics are also enhanced, and most of the pollutants are oxidized. The WAO process becomes self-sustained thermally when the chemical oxygen demand (COD) of the feed exceeds 20 g/L and at sufficiently higher feed CODs it can be a net energy producer. This method is rather expensive because of the required large investments in high-pressure equipment and the high cost of running the reaction at high pressures and temperatures.

The efficiency of supercritical water oxidation (SCWO) for contaminant destruction at temperatures and pressures above its critical point, typically around 500 °C and pressure of 276 atm, may be even higher than that of WAO; this high efficiency should be weighed against the high cost of the supercritical unit (Gloyna and Li, 1995).

The reviewed use of solid catalysts in oxidative destruction methods for pure compound solutions reveals that the incorporation of solid catalysts to the WAO and SCWO reaction environments may enhance reaction rates and enable one to carry out these processes at lower temperatures and reactor residence times. It may also cause optimized reaction pathways that are otherwise difficult to achieve through noncatalytic processes. Various combinations of photocatalysts and UV light were developed to achieve higher reaction rates in aqueous streams. These advanced oxidation processes (AOPs) have been reviewed elsewhere (Matthews, 1992) and are not within the scope of this work.

The use of solid catalysts in the oxidative destruction of a pure compound solution is reviewed in the next chapter. One important consideration in any catalytic process is the possible formation of partial oxidation products, which in turn may be toxic, and this information is reviewed. Engineering issues of reactor and catalyst design and those associated with the catalytic oxidation process optimization are also discussed here. In chapter 2 we also describe a novel and efficient method for the catalytic regeneration of adsorbents (particularly for activated carbons (AC)).

Although conventional and advanced oxidative degradation processes have been suggested for the disposal of many pollutants, they were found to be of limited effectiveness for certain groups of pollutants like halogenated organics (Surprenant et al., 1985). The reductive abatement of these pollutants currently receives considerable attention. Emerging reductive catalytic technologies, such as hydrodechlorination (HDC) and hydrodenitrification (HDN), are analyzed in chapter 3.

2. Oxidation Processes

Noncatalytic aqueous-phase oxidation requires long residence times (1 h) and relatively severe temperatures (200−450 °C) and pressures (70−250 atm). Catalytic oxidation processes have currently industrially applied for wastewater treatment, but the process is limited by relatively slow rates because of the absence of suitable active solid catalysts capable of stable operation in the liquid-phase oxidation of refractory compounds. These processes may be prohibitively expensive when used to achieve the complete oxidation of all organics present, to CO_2 and H_2O. As an alternative, the partial oxidation of the organics may be used to render the wastewater more amenable to other methods of treatment (typically biological).

The sources of oxidants may be either air and dioxygen (in most of investigations), dissolved hydrogen peroxide (Al Hyek and Dore, 1990; Borup and Ashcroft, 1992), or ozone (Luo, 1989). The rate of oxidation by air is limited by the low solubility of oxygen in water and the slow rate of air-to-liquid mass transfer. The enhanced solubility of oxygen at elevated pressures provides a strong driving force for catalytic reactions. The elevated pressures are also required to keep water in the liquid state at high temperatures.

The following subsections describe the catalysts employed, their stability and durability, and the reported results of the catalytic abatement of aromatic compounds such as phenols and of aliphatic compounds such as carboxylic acids, as well as of inorganic compounds like cyanides, ammonium, and sulfur-containing ions. These subsections describe the key operational parameters required for fast catalytic oxidation; these are the pollutant concentration, temperature of the reaction media, pressure, and the degree of contact between pollutants, catalysts, and oxidants under consideration. The destruction efficiencies and reaction rates at the investigated parameters are tabulated in the corresponding tables.

2.1. Catalysts: Activity and Longevity. 2.1.1. Catalytic Agent. A catalyst for water-phase oxidation should possess the following properties: (i) Exhibit high oxidation rates; in many cases, the reaction is diffusion-limited and under such conditions the rate should be enhanced by better contact between the phases. (*ii*) Be nonselective and exhibit complete oxidation. (*iii*) Be physically and chemically stable in hot acidic solution. *(iv)* Maintain a high activity for a prolonged use at elevated temperatures and be insensitive to poisons in the stream. (*v*) Be mechanically strong and resistant to attrition.

Conventional catalytic agents used for oxidation reactions can be divided into three classes: metals, metal oxides, and metal salts and their complexes. A variety of solid catalysts, including metal oxides of Cu, Mn, Co, Cr, V, Ti, Bi, and Zn, as well as noble metals (Ru, Pt, and Pd), have been tested as active components of catalysts in the oxidation of water pollutants (Table 1). Homogeneous catalytic systems, such as the soluble transition-metal salts, are generally more effective than solid catalysts (Imamura et al., 1988), but the dissolved catalysts are, in many cases, toxic and steps should be taken to separate them from the solution.

The correlation of catalytic activity with physicochemical properties provides preliminary information for the selection of catalysts and suggests a possible catalytic performance for each reaction. Metal oxides as oxidation catalysts are characterized by high electron mobility and positive oxidation states, as determined Cby the d-shell electron configuration of the metals (Krylow, 1970). They may be classified according to the stability of the oxide (Golodets, 1983). The most stable oxides in the high oxidation state ($\Delta H°_{298} > 15.5$ kJ/mol of O) are of metals such as Ti, V, Cr, Mn, Zn, and Al. Oxides with intermediate stability ($\Delta H°_{298} = 9.6-15.5$ kJ/mol of O) include those of Fe, Co, Ni, and Pb. High oxidation state oxides that are unstable ($\Delta H°_{298} < 9.5$ kJ/mol of O) and include noble metals like Pt, Pd, Ru, and Au, as well as Ag. The usefulness of this criterion for the metal oxide catalyst classification is that presumably the metals that do not form the stable bulk oxides (i.e., noble metals) remain in their reduced metal form during oxidation reactions at moderate temperatures.

Another consequence of this classification is that there exists some optimal strength of metal−oxygen interaction in an oxide catalyst. The activity of an oxide catalyst is inversely related to the strength of chemi-

Table 1. Summary of Catalysts Used in Oxidative Abatement of Water Pollutants

compd type	metals	refs	catalytic agent/ support oxides of	refs
aromatic compds	Ru, Rh, Pt, Ir; Rh/TiO_2, Pt/TiO_2, Ir/TiO_2, Ru/TiO_2, Ni/TiO_2, Ag/TiO_2; Pt/Al_2O_3, Pd/Al_2O_3, Ru/Al_2O_3, Ni/Al_2O_3, Ag/Al_2O_3; Rh/CeO_2; Ru/CeO_2	Frish et al., 1994; Oguchi and Nitta, 1992; Higashi et al., 1991; 1992; 1994	V, Mn(II), Cr, Co, Cu(II); Al; Zr; Ni; V/Al, Mn/Al, Cr/Al, Co/Al, Cu/Al; Cu/Si; Cu−Zn; Cu−Zn−Co/Al; Cu−Co−Ti/Al; Mn/Ce, Co/Bi, Cu/Si−Mg−Ca	Aki et al., 1996; Ding et al., 1995; Elliot et al., 1993; Imamura et al., 1986; Frish et al., 1994; Krajnc and Levec, 1994; Katzer et al., 1976; Pintar and Levec, 1992a,b; 1994; Kochetkova et al., 1992a,b; Ito et al., 1989; Jiang et al., 1990; Jie et al., 1991; Jin et al., 1992; Tukac and Hanika, 1994; Njiribeako et al., 1978; Farha et al., 1978; Seiyama, 1982
		Imamura et al., 1982a,b; 1988; Okitsu et al., 1995	Cu−Zn/Al−cement; Cu/Zn/aluminate cement	
	phosphmolybdovanadium heteropolyacids			Kholdeeva et al., 1992
aliphatic compds	Pt, Pd/Al_2O_3; Ir/CeO_2, Pt/CeO_2, Ru/CeO_2, Rh/CeO_2, Pt/TiO_2; Pt/ZrO_2 Pt, Pd/honeycomb Au/, Au-Pd/oxides; Ru/C	Frish et al., 1994	Co(II), Co(III), Ti, Mn(II), Fe, Zr, Cu/Al; Co/Al; Zn/Al; Cu−Zn, Cu−Ni, Ni−Bi, Cu−Mn, Zn/Bi, Sn−Bi, Mn/Ce, Co/Bi; Cu−Mn−La/Zn−Al	Baldi et al., 1974; Dooley and Knopf, 1987; Frish et al., 1994; Levec et al., 1976; Levec and Smith, 1976; Krajnc and Levec, 1994; Haseba and Inoue, 1988; Jahan and Kung, 1994; Ito et al., 1989; Imamura et al., 1982a,b; Mitsui et al., 1989; Imamura and Ando, 1989
		Takahashi et al., 1987; Yamaguchi et al., 1992; Duprez et al., 1995; Gallezot et al., 1997		
inorganic compds				
ammonia	Pt, Pd, Ru, Rh; Pt/TiO2 Co/, Fe/, Cu/, Ni/; Pt/TiO2	Oba et al., 1985; Higashi et al., 1991;	Mn(II), Cr, Co, Ce(II); Fe Co/Ce; Mn/Ce, Ni/Ce; Co/Bi, Co/Ti	Imamura et al., 1985; Ding et al., 1995
		Birbara and Genovese, 1991		
cyanides, sulfides	AC, AC fiber, Cu-exchanged zeolites, Cu, Cr(III)-exchanged resins			Ummarino, 1988; Wei and Cao, 1993; Yan, 1991; Matatov and Grigor'ev, 1987

sorption of reactants (volatile organics and oxygen), provided that their adsorption is sufficiently strong to achieve a high surface coverage. This consideration leads to the well-known qualitative behavior known as “volcano” plot (Bond, 1974).

The classification of oxides according to their electrical conductivity also reflects their catalytic properties (Bielanski and Haber, 1991): *n*-type metal oxides are generally not active as oxidation catalysts, although V_2O_5 (Golodets, 1983) is a notable exception, but *p*-type metal oxides are generally active catalysts, because they are electron-deficient in the lattice and conduct by means of positive “holes”. Insulators have very low electron (or “positive hole”) mobility and are generally not active as catalysts but are often used as catalyst supports (Satterfield, 1991).

Several studies have ranked catalysts according to their reactivity. While this order depends on the reactant (pollutant) and operating conditions, we do not expect it to vary significantly and list below several examples. Imamura et al. (1988) ranked noble metal and metal oxide catalysts according to the total organic carbon (TOC) conversion achieved in 1 h, during the oxidation of PEG-200 (polyethylene glycol with an average molecular weight of 200) at 200 °C and pH 5.4. They found the following order:

$$\mathrm{Ru} = \mathrm{Rh} = \mathrm{Pt} > \mathrm{Ir} > \mathrm{Pd} > \mathrm{MnO}$$

where all catalysts include 5 wt % metal or metal oxide supported on CeO_2 (Ru, Rh, and Pt exhibited 100% conversion). Recall that metal oxide catalysts are generally less active than supported noble metals, but they are somewhat more resistant to poisoning. Oxidation of *p*-chlorophenol catalyzed by noble metals supported on alumina (Al_2O_3) or titania (TiO_2) at 150 °C and under 3 atm of oxygen pressure showed the following order of activity (Okitsu et al., 1995):

$$\mathrm{Pt} \gg \mathrm{Pd} > \mathrm{Ru} > \mathrm{Rd} > \mathrm{Ag}$$

The catalytic activity of metal oxides during phenol oxidation showed the following typical order (Kochetkova et al., 1992a):

$$\mathrm{CuO} > \mathrm{CoO} > \mathrm{Cr_2O_3} > \mathrm{NiO} > \mathrm{MnO_2} > \mathrm{Fe_2O_3} > \mathrm{YO_2} > \mathrm{Cd_2O_3} > \mathrm{ZnO} > \mathrm{TiO_2} > \mathrm{Bi_2O_3}$$

Mixtures of metal oxides frequently exhibit greater activity than the single oxide. Cobalt, copper, or nickel oxide in combination with the following oxides of iron(III), platinum, palladium, or ruthenium are reported as effective oxidation catalysts above 100 °C (Levec and Pintar, 1995 and references within). Pintar and Levec (1994) reported that a CuO/ZnO/γ-Al_2O_3 catalyst (42/47/10 wt %) and CuO−ZnO−CoO catalyst (9.3/6.9/1.4 wt %) supported on steam-treated porous cement are more effective for phenol oxidation and more stable in a hot oxidizing phenolic aqueous solution than a catalyst containing 10% CuO on γ-Al_2O_3 used in earlier works (Sadana and Katzer, 1974). Kochetkova et al. (1992b) also observed that a mixture of CuO−CoO−TiO_2/Al_2O_3 oxides on a cement carrier provided more activity and stability, in the oxidation of phenol in aqueous solutions below 200 °C, than supported CuO/γ-Al_2O_3.

Heteropolyacids and metallocomplexes were also tested as catalysts: These include complexes of transition metals with polyethyleneimine (Butina et al., 1984), hematin (Sublette, 1990), phtalocyanines and metallophtalocyanines (Akhmadulina et al., 1988; Andreev et al., 1993; Ledon et al., 1990), and other ligands (Signalova and Galutkina, 1990). Activated carbon (AC) was found to be an active catalyst for the oxidation of cyanides and sulfur-containing compounds (see section 2.2.2).

2.1.2. Catalyst Support. The support serves three important functions in the catalytic system: (*i*) It increases the surface area of the metal or metal oxide by providing a matrix that enables their dispersion as very small particles. (*ii*) It inhibits the sintering of the active catalyst material and improves its hydrophobity and its thermal, hydrolytic, and chemical stability. (*iii*) The support stability is critical as it will govern the useful lifetime of a catalyst. Typical supports for metal and metal oxide catalysts are presented in Table 1.

Oxide supports could enhance the activity of the metal catalyst (Frish et al., 1994). For instance, the TOC conversion after 1 h at 200 °C and pH 5.4, during the catalytic oxidation of PEG-200 in the presence of a 5 wt % Ru catalyst over various supports, showed the following order of catalyst activity (Imamura et al., 1988):

$$CeO_2 > \gamma\text{-alumina} > \text{NaY zeolite} > ZrO_2 > TiO_2$$

The corresponding BET surface areas (m^2/g) were

$$135.7 \qquad 138.5 \qquad 509.8 \qquad 15.2 \qquad 3.8$$

Okitsu et al. (1995) studied the effect of the platinum supported on various titania (TiO_2) on the oxidative decomposition of *p*-chlorophenol and found the rate of the reduction on TOC to be higher on the catalyst with anatase-type titania than that with a rutile-type. The catalytic activity was increased with decreasing sizes of titania.

2.1.3. Catalyst Deactivation. Catalyst deactivation occurs due to the poisoning of the catalytic agents, due to the reduction of the catalyst surface (sintering), or due to the elution of the catalyst.

Catalyst deactivation commonly occurs due to surface-deposition of contaminants in the feedstock or in the process equipment. The use of noble metals for water-phase oxidation applications appears to be limited by their high sensitivity to poisoning. Trace contaminants formed during the oxidation of halogen-, phosphorus-, and sulfur-containing compounds, such as chlorine, chloride (Baker et al., 1989; Frish et al., 1994), or sulfur (Simonov, 1990), are generally poisonous for oxidation catalysts. There have been efforts to develop efficient catalysts that are resistant to poisoning: for example, alkali- and alkaline-earth-supported catalysts are used for the destruction of halogenated organic chemicals (Berty, 1991).

One of the important sources of solid catalyst deactivation in liquid-phase oxidation processes is connected with the exposure to hot acidic water, which promotes the solubility of some metal oxides. The dissolution of the metal in the hot acidic reaction medium prevents the use of catalysts which themselves are soluble in hot acidic water or can be transformed to a soluble state during reaction in the presence of oxygen. For example, copper ions were shown to be leached out from a CuO/Al_2O_3 commercial catalyst during phenol oxidation (Sadana and Katzer, 1974). The activity of the same type of catalyst after five to seven runs decreased by 40% and the copper ions concentration in the solution increased to 150 mg/L (Pintar and Levec, 1994).

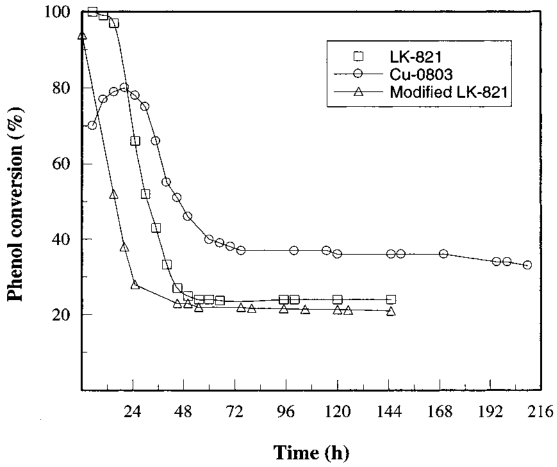

Figure 2. Changes in activity of several commercial copper-containing catalysts expressed as phenol conversion in a continuous trickle-bed reactor (Fortuny et al., 1995).

The level of active component elution from a metal oxide catalyst depends also on reactor configuration. Metal ions concentrations, due to leaching from a CuO–ZnO–CoO catalyst during phenol oxidation in a trickle-flow reactor (with a low ratio of the liquid-to-solid), were found to be lower than those for runs performed in a slurry reactor (with a high ratio of liquid-to-solid) (Levec and Pintar, 1995). At elevated temperatures increased levels of dissolved metal ions from V_2O_5/Al_2O_3 and Cr_2O_3 catalysts have been found in effluents following hydrolysis reactions involving inorganic compounds (Ding et al., 1996). Catalyst elution may become a major consideration in catalyst use for water pollution control not only because of loss of catalyst but also due to the toxicity of metal ions (such as Cr) to aquatic organisms.

Most ceramic preparation methods, such as sol-gel, coprecipitation, and high-temperature aerosol decomposition methods, have been adapted for preparing metal oxide catalysts. Ceramic and cement carriers are used to improve longevity (mechanical strength, chemical and hydrolytic stability, and hydrophobicity) of oxidation catalysts. Numerous studies have shown that the properties of a catalytic agent or support largely depend on the manufacturing process and pretreatment process. As an example, Figure 2 presents the decline in phenol conversion during its oxidation in a continuous trickle-bed reactor using the commercial catalysts: The catalyst that is most active initially (TopsØe LK-821) declined to a residual activity of only 25% (Fortuny et al., 1995). Harshaw Cu-0803 catalyst reached 80% conversion but showed approximately 40% residual activity after 72–144 h. Figure 3 presents batch phenol concentrations using a CuO–ZnO/Al_2O_3 catalyst supported on cement and pretreated at different temperatures in an oxygen stream (Levec, 1990), showing again the sensitivity to the manufacturing process.

2.2. Pollutants Abatement. Catalytic liquid-phase oxidation has been tested for the treatment of waste streams generated by various industries and processes; these include wastewater from the petrochemical industries, from hydrodesulfurization of flue gas, from catalytic hydrogenation and coal gasification, from

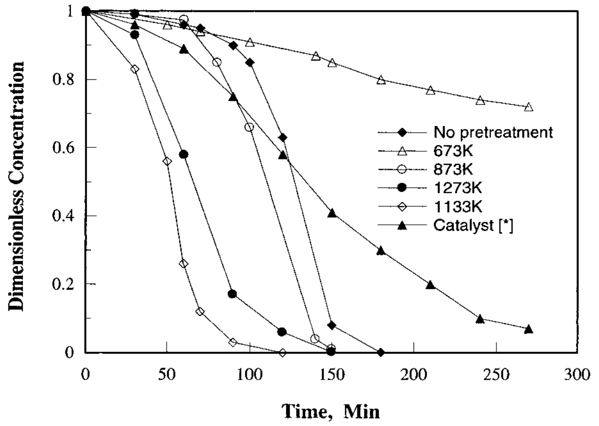

Figure 3. Relative activities in oxidation of phenol of supported CuO–ZnO/Al_2O_3 catalysts pretreated at different temperatures (Levec, 1990) ([*] data for catalyst prepared by Farha et al., 1978).

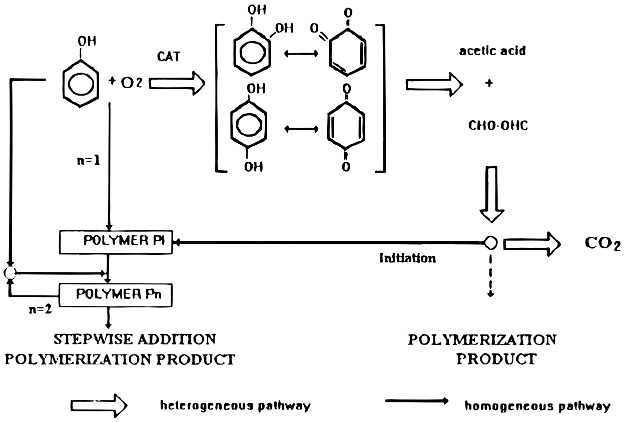

Figure 4. Simplified reaction pathway of phenol oxidation over supported copper oxide catalysts in a slurry reactor (Levec and Pintar, 1995).

pesticide and detergent production, from pulp and paper manufacturing units, and from electroplating and metallurgical operations. The following subsections describe the results of catalytic abatement studies classified by the nature of the pollutant.

2.2.1. Organic Compounds. Phenol and Aromatic Compounds. Catalytic studies for the oxidation of phenol, which has been frequently used as a model substance, were performed with many industrial and specially designed catalytic systems (Tables 2 and 4). Most studies prior to 1976 have focused on demonstrating the feasibility of catalysts and evaluating their activity (Katzer et al., 1976 and references herein) and are not reviewed here.

Catalyst Selection. Copper oxide is the most active catalyst for phenol oxidation in the temperature range of 160–250 °C. Several studies were performed with copper oxide or its mixture with other oxides in the last years (Table 2).

Mixtures of copper oxide with oxides of Co, Zn, and Ti exhibit greater activity than that of the single copper oxide. Pintar and Levec (1992a) reported that a CuO/ZnO/γ-Al_2O_3 catalyst (42/47/10 wt %) was more effective for phenol conversion than a catalyst containing 10% CuO on γ-Al_2O_3 (Katzer et al., 1976) and that the CuO/ZnO/CoO (9.3/6.9/1.4 wt %) catalyst supported on steam-treated porous cement showed even a higher activity (Pintar and Levec, 1992b). Also, a mixed CuO/CoO/TiO_2/γ-Al_2O_3 catalyst supported on cement was found to be effective and stable (Kochetkova et al., 1992b). The catalytic activity of various mixtures of copper oxide with other metal oxides in phenol oxidation showed the following order:

CuO > CuO/MnO > CuO/ZnO > CuO/ZnO/CoO

Imamura et al. (1982a,b, 1986, 1987) developed several catalytic systems (oxides of Mn/Ce and Co/Bi) to improve the liquid-phase oxidation and found that the MnO_2/CeO_2 composite catalyst exhibits much higher activity than even a homogeneous copper catalyst.

In contrast with metal oxide catalysts, very little research has been reported on phenol oxidation over metal catalysts. Imamura et al. (1988) reported that the activities of Ru, Pt, and Rh were higher than those with a homogeneous copper catalyst. Ruthenium showed the highest activity among the three catalysts and indicated a high possibility for it to be used as a promoter for the MnO_2/CeO_2 catalyst. Higashi et al. (1991) reported that phenol completely decomposed within 80 min in the presence of 5% Pt/Al_2O_3 catalyst in an autoclave at 150 °C.

These catalysts show similar trends in destruction efficiency and reaction rates for other aromatic compounds including benzene, benzoic acid, chlorobenzene, chlorophenols, nitrophenol, and pyridine (Table 3). Experiments of catalytic oxidation of the substituted phenols on the supported CuO/ZnO/CoO catalyst showed the following order of activity:

p-nitrophenol > *p*-chlorophenol > phenol

The corresponding values of the activation energy (kJ/mol) were

89 90 137

in a flow differential liquid-full fixed-bed reactor (Pintar and Levec, 1994), and

p-chlorophenol > phenol > *p*-nitrophenol

in a slurry batch reactor (Pintar and Levec, 1992b).

Mechanism. Metal oxide catalysts are capable of initiating free radicals, and two methods of radical generation have been suggested: (1) the catalyst activates reactant molecules directly and facilitates their decomposition into radicals, or (2) the catalyst accelerates the decomposition into radicals, with the hydroperoxides either being present in the system or forming slowly by the first mechanism. Haber (1991) reports that the oxidation reaction of aromatic compounds may start by the activation of either the dioxygen (electrophilic oxidation) or the hydrocarbon molecule (nucleophilic oxidation).

Oxygen may participate in a reaction either as an adsorbed species on the catalyst surface or as a part of the lattice oxygen presented in the metal oxides. Adsorbed oxygen may come from oxides of Cu, Cr, Co, Fe, Mn, and Ni, and lattice oxygen may come from vanadium oxide (Novakova, 1971). Thus, the presence of catalysts creates an ionic environment that enhances heterolytic reactions. Both free radical (homolytic) and ionic (heterolytic) oxidation reaction mechanisms have been proposed for the oxidation of aromatic compounds, resulting in a ring-opening reaction.

The reaction is believed to occur by free-radical initiation on the catalyst surface, homogeneous propagation, and either a homogeneous or a heterogeneous termination process. Radical initiation could occur by

Table 2. Listing of Studies into Catalytic Oxidation of Phenol

		operating conditions						
catalyst	reactor type[a]	temp. (°C)	press. (atm)	C_0 (g/L)	conv. (%)	reaction time (min)	reaction rate[b] r_0	refs
Ru/CeO_2	S	200	10	2.0	94.8	60		Imamura et al., 1985
Pt/γ-Al_2O_3	S	200	10	1.0	58	175		Higashi et al., 1991
Cr_2O_3	F	390	241	0.5			8.4	Ding et al., 1995
V_2O_5	F	390	241	0.5			7.8	Ding et al., 1995
MnO_2 (TGS-3)	S	50−60	1	0.5−2.0	90[c]	30		Jie et al., 1991
CuO/γ-Al_2O_3	S	114−200	3.4−17	3.6−5.1	99[c]	9		Katzer et al., 1976
CuO/γ-Al_2O_3	TB	120−160	6−12	5	80[c]	30		Fortuny et al., 1995
V_2O_5/Al_2O_3	F	390−410	241	0.23−8.4			22.5[c]	Ding et al., 1995
MnO_2/CeO_2	F	390	241	2.0			2.6[c]	Ding et al., 1995
MnO_2/CeO_2	F	220	10	2.0	92.7	20		Imamura et al., 1988
CuO−ZnO/cement	FB	380−390	230	5.0		0.25	1.1	Krajnc and Levec, 1994
CuO−ZnO−CoO	TB	50−210	3−8.0	0.1−0.5	100	1		Pintar and Levec, 1994
CuO−CoO−TiO_2	S	14−200	0.8−1.8	4−5.5	85	30		Kochetkova et al., 1992b

[a] Reactor type: B, batch; S, slurry; TB, trickle bed; FB, fixed bed; F, flow. [b] $r_0 = (C_0 - C_f)/t$, where C_0 is the initial concentration in mg/kg, C_f is the final concentration in mg/kg, and t is the residence time in min. [c] CO_2 formation.

Table 3. Listing of Studies into Catalytic Oxidation of Aromatic Compounds

			operating conditions						
catalyst	compd[a]	reactor type[b]	temp. (°C)	press. (atm)	C_0 (g/L)	conv. (%)	reaction time (min)	initial rate[c] (mg/min)	refs
Cr_2O_3	1,3-dbc	F	390	241	1			7.9	Ding et al., 1995
V_2O_5/Al_2O_3	1,3-dcb	S	390	241	2			5.3[d]	
V_2O_5/Al_2O_3	1,4-dcb	S	343−412	67	1.4−2.0			5.3[d]	Jin et al., 1992
Pt/Al_2O_3	1,4-dcb	F	418	276	1			7.5	Ding et al., 1995
CuO−ZnO−CoO	1,4-nph	FB	150−190	30	0.1−2.0	90	60		Pintar and Levec, 1994
Pt/TiO_2	1,4-nph	S	150	10	2	70[d]	30		Higashi et al., 1992
Pt/TiO_2	ntb	S	250	10	2	93[d]	30		Higashi et al., 1994
Pt/Al_2O_3	py	F	418	276	1			7.5	Ding et al., 1995
CoO/Bi_2O_3	py	S	270	10	1	17.1	60	1.0	Imamura et al., 1986
V_2O_5	py	F	412	671	1			0.5	Jin et al., 1992
MnO_2/CeO_2	py	S	270	10	2	22.1[d]	60	2.0	Imamura et al., 1986
MnO_2/CeO_2	py	F	418	263	2			9.8	Ding et al., 1995
Al_2O_3	py	S	418	276	5			0.07	Frish et al., 1994
CuO−ZnO−CoO	1,4-chp	FB	150−190	30	0.1-0.5	>90	30−200		Pintar and Levec, 1994
CuO−ZnO/$Al_2O_3^-$	1,4-nph	S	105−130	1.5−10	2.0	90	60		Pintar and Levec, 1992a

[a] Abbreviations: py, pyridine; dcb, dichlorobenzene; nph, nitrophenol; chp, chlorophenol. [b] Reactor type: B, batch; S, slurry; FB, fixed bed; F, flow. [c] Destruction. [d] CO_2 formation.

dissociative adsorption of phenol or by hydroperoxide decomposition on the catalyst. One of the characteristics of branched chain reactions is an exhibition of the critical catalyst concentration phenomenon: a slight increase in catalyst concentration induces a dramatic change in the rate of the process. This has been observed only during phenol oxidation performed in a slurry reactor (Sadana, 1979). The oxidation involves an induction period, in which the generation of radicals is poor, and a higher steady-state activity period with a fast free-radical reaction regime, as was observed during phenol oxidation (Sadana and Katzer, 1974). The conversion of phenols was markedly affected by pH, having a maximum of activity at a pH of about 11 (Pintar and Levec, 1995). This pH value is higher than the pK_a values of substituted phenols, and consequently the phenolate anion (PhO^-), yielding phenoxy radicals (PhO), was considerably more reactive than the protonated form (PhOH). A comparison of the results obtained in slurry and fixed-bed reactors supports the conclusion that the distribution of intermediate products, and consequently the oxidation rate depends on the reactor system utilized.

Phenol oxidation results in the formation of a variety of partial oxidation and polymerization products (Table 4). The reaction mechanisms were derived through the identification of reaction intermediates and products. The catalytic oxidation of phenol progressed mainly through 1,4-benzenediole formation; it seems that a substituent bond in the para position of the benzene ring breaks during the formation of benzenedioles (i.e., electrophilic oxygen attack). The benzene ring opening is not the rate-limiting step in the catalytic phenol oxidation, unlike the mechanism suggested for the noncatalyzed reaction (Delvin and Harris, 1984). The observation of intermediates, such as 1,4- and 1,2-benzenediole, 2,5-cyclohexadiene-1,4-dione, and 3,5-cyclohexadiene-1,2-dione (quinones), which once formed are easily transformed further to low molecular products (mostly acids) and carbon dioxide, is evidence to that effect.

The formation of polymeric products markedly reduced the extent of total oxidation, with only 50−60% of the initial carbon content being converted via a propagation route to carbon dioxide. In reactors with the high solid-to-liquid ratio, like a trickle-bed reactor, the polymerization reactions are suppressed (Pintar et al., 1992).

Kinetics. The kinetic data for phenol catalytic oxidation are summarized in Table 8. Significant disagreement is reported on the apparent activation energy values: for phenol oxidation catalyzed over supported copper oxide these values vary from 84 to 176 kJ/mol (Pintar and Levec, 1994). The lower apparent activation energy may be due to the polymerization reaction involved.

The rate of phenol disappearance (r_P, mol/(g_{cat} h)) during oxidation in a slurry reactor has been expressed

Table 4. Product Distribution in Catalytic Oxidation of Phenol

reactor type[a] →	S	S	S	S	TB	FB
catalyst →	noncatalyzed	CuO/alumina	CuO/alumina	CuO−ZnO−Al_2O_3	CuO−ZnO−CoO	CuO−ZnO−CoO
(refs) →	(Devlin and Harris, 1984; Thornton and Savage, 1992)	(Sadana and Katzer, 1974)	(Otha et al., 1980)	(Pintar and Levec, 1992b)	(Pintar et al., 1992)	(Pintar and Levec, 1994)
phenol conversion (%)	100	95	90	20	95	95
1,2-benzenediole	+		+	+	+	+
1,4-benzenediole	+		+	+	+	+
2,5-cyclohexadiene-1,4-dione	+	+	−	+	+	+
3,5-cyclohexadiene-1,2-dione	+	+	−	−	−	−
1,4-dioxo-2-butene	+	−	−	+	−	+
acids[b]	A, M, F, S, P, Ma, Ac, Ox, Gly	−	Ma	A	A	Ma
carbon dioxide	+	+	+	+	+	+
polymeric products:	+	−	+	−	−	−
4-phenoxylphenol	+	−	+	−	−	−
2,2′-biphenol	+	−	+	−	−	−
dibenzofuran	+					

[a] Reactor type as in Table 2. [b] Acids: B, benzoic; P, propionic, A, acetic; Ad, adipinic; By, bytiric; Fo, formic; Fu, fumaric; Ac, acrylic; Gly, glyyoxalic; Hex, hexalyc; O, oxalic; Mu, muconic; Ma, maleic; Mal, malonic; S, succinic.

Table 5. Listing of Studies into Catalytic Oxidation of Aliphatic Compounds

			operating conditions						
catalyst	compds	reactor type[a]	temp. (°C)	press. (atm)	C_0 (g/L)	conv. (%)	reaction time (min)	initial rate (mg/min)	refs
Rh/CeO_2	PEG-200	S	200	10	2.0	100	60		Imamura et al., 1988
Pd/CeO_2	PEG-200	S	200	10	2.0	49.7	60		
Ir/CeO_2	PEG-200	S	200	10	2.0	74.8	60		
Ru/CeO_2	PEG-200	S	200	10	2.0	100	60		
	formaldehyde	S	200	10	2.0	96−98	60		
	acetamide	S	200	10	2.0	51.6	60		
	PPG-1000	S	200	10	2.0	54.3	60		
	propanol	S	200	10	2.0	47.2	60		
	butanol	S	200	10	2.0	9.8	60		
MnO_2/CeO_2	tristearin	S	220	10	2.0	33.4	50		Imamura and Ando, 1989
	PEG-200	S	220	10	2.0	55.4	60	20.3	Imamura et al., 1986
	n-butylamine	S	220	10	2.0	5.4	60	0.9	
CuO−ZnO	2-propanol	S	380	230	0.5	98	30	26.6	Krajnc and Levec, 1994
Co_2O_3	aminaacids	S	200	10	2.0	99	30		Ito et al., 1989
	amines		200	10	2.0	>99	60		
	aminoalhogols		200	10	2.0	>99	60		
CoO/Bi_2O_3	*n*-butylamine	S	220	10	1	5.4	60	0.8	Imamura et al., 1986
CoO/Bi_2O_3	PEG-200	S	220	10	1	62.2	60	20.3	

[a] Reactor type as in Table 2.

as a sum of heterogeneous conversion to carbon dioxide and homogeneous polymerization contribution:

$$r_P = k_{het} C_P C_{O_2}^{1/4} + k_{hom} C_P \Sigma C(P_n) \qquad (1)$$

where k_{het} is the apparent rate constant for the heterogeneous oxidation steps, k_{hom} is the lumped homogeneous polymerization rate constant that accounts for initiation (phenol plus glyoxale) and propagation steps, C_P and C_{O_2} are the phenol and oxygen liquid-phase concentrations, and $\Sigma C(P_n)$ is the total concentration of all polymers of all possible chain lengths (Pintar and Levec, 1994).

On the other hand, the measured rate of liquid-phase phenol disappearance per unit weight of catalyst (supported mixture of copper, zinc, and cobalt oxides) in a differential liquid-full operated fixed-bed reactor (Pintar and Levec, 1994) was found to be independent of space time and well-described by a rate equation of the Langmuir−Hinshelwood type:

$$r_P = \frac{k_{sr} K_P K_{O_2}^{1/2} C_P C_{O_2}^{1/2}}{1 + K_P C_P} \qquad (2)$$

where k_{sr} is the apparent surface reaction constant, K_i are the adsorption constants, and C_i are the reactant concentrations.

Summary. Dissolved phenol can be oxidized in the presence of a CuO catalyst, or its mixture with CoO or ZnO, at temperatures of 150−200 °C and oxygen pressures of 1−235 atm. The reaction proceeds via a free-radical mechanism and the solid−liquid volume ratio affects the rate and product distribution. Reaction times imply the existence of diffusion limitations. Detailed investigations are needed to get kinetic data for the reliable design of oxidation reactors and for cost reduction by the optimization of the operating conditions (see section 2.3).

Aliphatic Compounds and Acetic Acid. The aliphatic compounds that have been studied for oxidative catalytic abatement include alcohols, amines, carboxylic and amino acids, and polymers like PEG-200 and PPG-1000. The most effective catalysts that were selected for the oxidation of aromatic compounds show similar trends in destruction efficiency or reaction rates during abatement of aliphatic compounds (Tables 5−7).

The catalytic oxidation of acetic acid has been studied more extensively (see Tables 6 and 8). Many research

Table 6. Listing of Studies into Catalytic Oxidation of Acetic Acid

catalyst	reactor type[a]	operating conditions temp. (°C)	press. (atm)	C_0 (g/L)	conv.[b] (%)	reaction time (min)	reaction rate (mg/min)	refs
Pt		395		1.0	97	5		Frish et al., 1994
Fe_2O_3	TB	250−280	67−73	0.06−0.7	10−20[c]	60		Levec and Smith, 1976
TiO_2	F	394−466	280	0.7			3.7	Frish et al., 1994
Ru/CeO_2	S	200	10	2.0	44.5	60		Imamura et al., 1988
Pt/Al_2O_3	S	418	276	0.7			5.44	Frish et al., 1994
Pt/TiO_2	S	418	276	1.0			5.43	Frish et al., 1994
Cu:Mn:La oxides/$ZnO-Al_2O_3$	TB	250−280	67−73	0.06	3−15			Levec et al., 1976
CoO/Bi_2O_2 (5:1)	S	248	10	2.0	100	60		Imamura et al., 1982a,b
		225		5.0	87.1	60		
		180		5.0	25.9	60		
MnO_2/CeO_2	S	247	10	2.0	99.5	60	50	Imamura et al., 1986
MnO_2/CeO_2	S	300−440	276	2.0			0.4	Frish et al., 1994
Co_2O_3	S	200	4	0.6	43	180		Ito et al., 1989

[a] Reactor type as in Table 2. [b] Destruction. [c] CO_2 formation.

Table 7. Listing of Studies into Catalytic Oxidation of Carboxylic Acids[a]

catalyst	reactor type[a]	acid[b]	operating conditions temp (°C)	press. (atm)	C_0 (g/L)	conv.[c] (%)	reaction time (min)	refs
Co_2O_3	S	F	200	4	1.0	100[d]	60	Ito et al., 1989
		P	200	4	1.0	55[d]	180	
		B	200	4	1.0	51[d]	255	
Ru/CeO_2	S	F	200	2.0	2.0	100 (pH 2.9)	60	Imamura et al., 1988
	S	F	200	2.0	2.0	63.7 (pH 1.9)	60	
MnO_2/CeO_2	S	F	200	1.0	2.5	100	60	Imamura et al., 1988
CoO/Bi_2O_3	S	F	200	1.0	2.5	25.9	20	Imamura et al., 1988
		P	200	1.0	2.5	79.0	20	
		By	200	1.0	2.5	83.4	20	
		V	200	1.0	2.5	50.9	20	
		Hex	200	1.0	2.5	81.6	20	
		O	200	1.0	2.5	0	20	
		Ad	200	1.0	2.5	97.4	20	
		S	200	1.0	2.5	100	20	
		Gly	200	1.0	2.5	82.5	20	
CuO−ZnO	F	B	380	230			0.5	Krajnc and Levec, 1994

[a] Reactor type as in Table 2. [b] Acids as in Table 4. [c] Destruction. [d] CO_2 formation.

Table 8. Kinetic Data for Aqueous Phase Catalytic Oxidation[a]

catalyst	compds	reactor type[b]	operating conditions temp. (°C)	press. (atm)	C_0 (g/L)	E^c	A	m	n	refs
MnO_2/CeO_2	am	F	410−470	276	0.05−0.1	105.7	4.9×10^6	0.5	0.8	Ding et al., 1996
TiO_2	ac	F	394−466	280	0.7	237	7.94×10^{16}	1	0	Frish et al., 1994
MnO_2/CeO_2	ac	S	394−466	240−390	0.2−0.8	44.1	4.22×10^1	1	0	Frish, 1992
Ru/C	ac	B	175−200	100	5−20	100.5[d]	1.8×10^{10}	0	0.65	Gallezot et al., 1997
CoO−BiO	ac	S	248	10	5.0	105.9				Imamura et al., 1982a,b
CuO/Al_2O_3	ph	S	114−200	3−17	3−5	57.4 (127)		1	1.5	Katzer et al., 1976 (Sadana and Katzer, 1974)
CuO/Al_2O_3	ph	S	121−288	5−30	0.2−0.5	85.7		0.44	0.55	Otha et al., 1980
CuO/Al_2O_3	ph	TB	120−160	3−17	5	76−85		1	0.5	Fortuny et al., 1995
V_2O_5/Al_2O_3	ph	F	390−410	240	0.3−1.0	38.1[d]	1.35×10^3	1	1	Ding et al., 1995
MnO_2/CeO_2	ph	F	390−410	240	0.3−1.0	48.3	9.28×10^3	1	1	
MnO_2/CeO_2	be	F	390−430	240	0.5−1	112.9	9.36×10^7	1	1	
V_2O_5/Al_2O_3	be	F	390−430	240	0.5−1	67.1	2.99×10^6	2	2.2	
V_2O_5/Al_2O_3	1,4-dcb	S	343−412	100−670	1−1.5	55.1	316.2	1	0	Jin et al., 1992
MnO_2/CeO_2	1,3-dcb	F	390−450	240	0.3−1.0	150.5[d]	8.47×10^9	1	0	Ding et al., 1996

[a] Global rate equation: $-\mathrm{d}[C]/\mathrm{d}t = A \exp\{E/RT\}[C_0]m[O_2]n$, where E is in kJ/mol, T is in K, $R = 8.314$ J mol^{-1} K^{-1}, and $k_0 = [1/\mathrm{s}]$ for first-order models and [L mol^{-1} s^{-1}] for second-order models. $[C_0]$ is the initial pollutant concentration at the ambient conditions. Abbreviations: be, benzene; ph, phenol; ac, acetic acid; dcb, dichlorobenzene; am, ammonium. [b] Reactor type as in Table 2. [c] Destruction. [d] CO_2 formation.

studies of aromatic and aliphatic organic oxidation during noncatalytic and catalytic oxidation report the formation of refractory acetic acid.

Some of the earlier studies had shown that noble metals (0.1 wt % Pd) or the CuO/ZnO catalyst are inactive for the oxidation of an acetic acid solution. Recently, Imamura et al. (1982a,b; 1988) investigated catalytic composite metal oxide catalysts and found that composites of cobalt and bismuth oxides (with a Co/Bi molar ratio of 5:1) and manganese oxide on cerium oxide (Mn/Ce ratio of 7:3) exhibit activity for the oxidation of refractory lower carboxylic acids at 180−400 °C. Although the Mn/Ce oxide catalyst has been effective in destroying acetic acid, as well as most of the other refractory organics, more information on its effectiveness in the destruction of real waste streams and

Table 9. Listing of Studies into Catalytic Oxidation of Inorganic Compounds

		operating conditions					
catalyst	reactor type[a]	temp. (°C)	press. (atm)	C_0 (g/L)	conv. (%)	reaction time (min)	refs
					Ammonium		
CoO/CeO_2	S	263	10	1.0	50.2	60	Imamura et al., 1985
CoO/Bi_2O_3	S	263	10	1.0	46.0	60	
Co/TiO_2	F	263	70	1.0	50.0	60	
Ni/CeO_2	F	263	100	1.0	19.6	60	
MnO_2/CeO_2	F	410−470	276	1.0	20−50	0.1−2	Ding et al., 1995
MnO_2/CeO_2	S	263	10	1.0	50.0	60	Imamura et al., 1985
Pt, Pd, Ru−Rh (W1-501)	S	250	70	2−4	93.0	60	Oba et al., 1985
					Cyanide		
activated carbon (AC)	F	30		10	100	6	Weber and Corapcioglu, 1981; Chen et al., 1991; Lin et al., 1990, 1991; Wei and Cao, 1993
impregnated AC	F	30−50		0.03	93	45	Tian et al., 1988; Zhang et al., 1989
MoS_2	F	30		5	>95	60	Lin et al., 1990
					Sulfide		
AC, AC fiber		30−40		9−10	100	30	Sekaran et al., 1993; Vil'danov et al., 1991
Ptz, M-Ptz/polyethylene[b]		30		5.58	90	60	Akhmadullina et al., 1988; Zhang, 1990, 1991
MoS_2		30		5.8	60	30	Andreev et al., 1993
Cu, Cr ion exchangers	S	30−50		6	90	30	Matatov and Grigor'ev, 1987; Matatov, 1989

[a] Reactor type as in Table 2. [b] Abbreviations: Ptz, phtalocynine. M-Ptz, metalphtalocyanine.

reusability is required for its commercialization. As has been noted above, the Mn/Ce oxide catalyst and Ru/CeO_2 catalyst have also been found to be very effective for the destruction of phenolic compounds. Recently, Duprez et al. (1995) and Gallezot et al. (1997) demonstrated that the Ru/C catalyst exhibits higher activities for acetic acid oxidation than those of Ru/TiO_2 or Mn/Ce oxide catalysts.

From Tables 6 and 7 one can see that multicomponent oxide catalysts like MnO_2/CeO_2, CuO/Co_3O_4, and $Co_3O_4/BiO(OH)$ are considerably more active than monocomponent catalysts. The catalytic oxidation destruction efficiencies intensify with increasing molecular weight of the carboxylic acids.

To explain the mechanism of acetic acid oxidation, Levec and Smith (1976) assumed the formation of intermediates or free radicals and proposed the following elementary steps:

$$CH_3\,COOH + \oplus \rightarrow CH_3COOH{-}\oplus \tag{2a}$$

$${}^{1}\!/_{2}O_2 + \oplus \rightarrow O{-}\oplus \tag{2b}$$

$$CH_3COOH{-}\oplus + O{-}\oplus \rightarrow HCHO + CO + H_2O + \oplus \tag{2c}$$

$$HCHO + O{-}\oplus \rightarrow HCOOH + \oplus \tag{2d}$$

$$HCOOH + O{-}\oplus \rightarrow CO_2 + H_2O + \oplus \tag{2e}$$

$$CO + O{-}\oplus \rightarrow CO_2 + \oplus \tag{2f}$$

where $\oplus$ denotes a vacant adsorption site, which may be different for the two adsorbates and $O{-}\oplus$ denotes an oxidized site capable of acting as a catalyst for the reaction 2e. Acetic acid initially adsorbs onto an active site, reacts with adsorbed oxygen, and goes through several intermediate steps, and the latter involves the formation of formaldehyde, carbon monooxide, formic acid, and eventually carbon dioxide plus water.

Baldi and co-workers (1974) studied the conversion of formic acid to carbon dioxide catalyzed by a commercial CuO−ZnO catalyst at 200−240 °C. Formic acid oxidation was found to be first-order with respect to both oxygen partial pressure and formic acid concentration. The formic acid may undergo the thermal gas-phase decomposition to CO_2 and H_2 (decarboxylation) or CO and H_2O (dehydration). Water molecules act as a catalyst in the decarboxylation reaction 3a.

$$HCOOH \rightarrow CO_2 + H_2 \tag{3a}$$

$$HCOOH \rightarrow CO + H_2O \tag{3b}$$

The oxidation of the formate ion is slower than that of formic acid.

Available kinetic parameters for catalytic oxidation of acetic acid are given in Table 8. The observed activation energy for pseudo-first-order appears to be within 38−237 kJ/mol in various conditions. The order with respect to substrate concentration was in the range of 1−1.5 and the order with the respect to oxygen for the oxidation of formic acid (Baldi et al., 1974) and acetic acid (Levec and Smith, 1976) was found to be 1 and 1.5, respectively.

One generalized kinetic model is based on simplified reaction pathways involving the formation and destruction of rate-controlling intermediates in the aqueous-phase oxidation of aromatic and aliphatic organics such as acetic acid (Li et al., 1991).

2.2.2. Inorganic Compounds. Ammonia. Nitrogen appears in water and wastewater streams in organic molecules as well as in nitrate, nitrite, and ammonia. During biological degradation the organic nitrogen is transformed into ammonia. In industrial effluents the ammonia concentration reaches 0.5 g/L (as N) and nitrate concentrations may be in the range of 2.7−12.5 g/L (Wiesmam, 1994). Ammonia formation as an intermediate in catalytic oxidation of nitrogen-containing organics was proved to be fast at 200 °C, but further oxidation of ammonia was quite difficult.

Applications of catalysts for the destruction of NH_4^+ and NH_3 in waste streams are listed in Table 9. Imamura and co-workers (1982a,b; 1985) found that MnO_2/CeO_2 (80:20) and CoO/Bi_2O_3 (5:1) composite oxides were remarkably active as catalysts for ammonia oxidation. Ammonia conversion reached 46% with a cobalt−bismuth composite catalyst, compared with 20.5% in the absence of a catalyst. The reaction proceeded rapidly in the high pH region, indicating that ammonia was more reactive that the ammonium ion. Ammonia conversion with the participation of the MnO_2/CeO_2 catalyst was found to increase to 20−50% at a temperature of 263 °C and 60 min reaction time (Imamura et al., 1985). Ammonia conversion over the same catalyst occurred with 1 s of residence time at the temperature of 450 °C and pressure of 276 atm (Ding et al., 1995). The major products of these oxidation processes are N_2 and N_2O, while the formation of NO_x is thermodynamically unfavorable (Golodets, 1983).

Cyanides. The chemical methods that have been proposed for the destruction of cyanides, like oxidation by ozone or hydrogen peroxide or oxidative chlorination by chlorine dioxide, are too expensive or too slow and in most cases produce undesirable toxic compounds and are not employed in commercial application. Additional difficulties arise from the fact that many metal complexes of cyanides have a low degree of dissociation and can precipitate under alkaline conditions to form a sludge.

Several studies (Table 9) describe the AC-catalyzed oxidation of cyanide to cyanate by molecular oxygen:

$$2CN^- + O_2 \rightarrow 2CNO^- \quad (4)$$

This reaction is promoted in the presence of dissolved Cu^{2+}, Cd^{2+}, Ni^{2+}, Ag^+, and SO_2^{2-} and Cl^- ions (Tian et al., 1988; Zhang et al., 1989; Bursova and Moiseeva, 1989; Lin et al., 1990; Tarkovskaya et al., 1993). Cu^{2+} ions in the form of $CuCl_2$, $CuSO_3$, or $CuSO_4$ are the most active promoters. This process was shown to reduce CN^- concentration from 40 to 0.1 mg/L within 3−10 min. The most effective conditions were reported to be at temperatures of 50−100 °C and a solution with molar ratios of CN^-/Cu^{2+} of about 4.00 (Chen et al., 1991) and SO_4^{2-}/CN^- ratio of about 2; pH should be maintained between 6.5 and 9.0, preferably at 8.0. This reaction is limited by film mass-transfer resistance, and the overall reaction rate of cyanide removal depends on mixing conditions (Weber and Corapcioglu, 1981).

A mechanism for AC-catalyzed CN^- oxidation (Chen et al., 1991) is based on the following experimental observations: (*i*) Cyanides are oxidized in the adsorbed state by dissolved oxygen. (*ii*) The presence of cupric ions enhances the rates of adsorption and of cyanide decomposition. (*iii*) Sulfite addition to the wastewater enhances the rate. The suggested mechanism incorporates the following steps:

$$CN^- + AC \rightarrow AC{-}CN^- \quad (5a)$$

$$4CN^- + Cu^{2+} \rightarrow Cu(CN)_4^{2-} \quad (5b)$$

$$Cu(CN)_4^{2-} + AC \rightarrow AC{-}Cu(CN)_4^{2-} \quad (5c)$$

$$AC{-}CN^- + SO_3^{2-} + O_2 \rightarrow CNO^- + SO_4^{2-} + AC \quad (5d)$$

$$AC{-}Cu(CN)_4^{2-} + SO_3^{2-} + O_2 \rightarrow CNO^- + SO_4^{2-} + AC{-}(CN)_3^- \quad (5e)$$

$$2CNO^- + 1.5O_2 + H_2O \rightarrow N_2 + 2CO_2 + 2OH^- \quad (5f)$$

$$2AC{-}Cu^{+2} + HCO_3^- + OH^- \rightarrow CuCO_3 + Cu(OH)_2 + H_2O + 2AC \quad (5g)$$

$$CNO^- + 2H_2O \rightarrow CO_3^- + NH_4^+ + H_2O \quad (5h)$$

Another proposed mechanism takes into account the role of oxygen and also incorporates several suggestions about the structure of intermediate cyano complexes (Wei and Cao, 1993).

Adsorption of cyanides on AC is enhanced by the presence of Cu^+, Cd^{2+}, Ni^{2+}, and Ag^+ ions in the wastewater, while the adsorption capacity increases with an increasing metal/CN ratio only in the case of Cu^{2+} (She et al., 1988, Wei and Cao, 1993). The adsorption of cyanide on AC was best-described by a Freundlich isotherm (Weber and Corapcioglu, 1981) of the form $Q_{CN} = 17.4C_{CN}^{0.9}$, while data in Chen et al. (1991) were described by $Q_{CN} = 1.141C_{CN}^{0.422}$ (for NaCN solution) and $Q_{CN} = 3.655C_{CN}^{0.523}$ (for $CuCN_4^{2-}$) (Q_{CN}, mg/mg of carbon, is the amount of cyanide adsorbed, and C_{CN}, mg/L, is the cyanide concentration remaining in solution).

Sulfur-Containing Ions. Typical contaminants in this group are sulfide S^{2-}, thiosulfate $S_2O_3^{2-}$, tetrathionate $S_4O_6^{2-}$, trithionate $S_3O_6^{2-}$, and sulfite SO_3^{2-}. All of these ions are converted to the sulfate ion SO_4^{2-} via various chemical and biochemical reactions at natural conditions. To avoid this, all sulfur-containing ions should be removed before the wastewaters are discharged by converting them into elemental sulfur.

Several catalytic systems are studied or are in various stages of development to achieve oxidative desulfurization of wastewaters (Table 9). AC was found to be an active catalyst for sulfide oxidation, and various additivities change dramatically the activity and selectivity of sulfide oxidation on AC. As an example, catalytic cracking of wastewater heavily polluted with Na_2S (up to 9 g/L) achieved 100% efficiency in the presence of a carbon fiber catalyst at room temperature (Vil'danov et al., 1991). Tannery wastewaters, containing 0.7−1.6 g of S^{2-}/L, were also reported to be completely converted with rice bran-based AC as a catalyst. A packed-bed flow reactor was found to be more efficient for this process than a batch reactor (Sekaran et al., 1993).

The possible reactions taking place in an AC-catalyzed system are (Andreev et al., 1995) the following:

$$2HS^- + O_2 \rightarrow 2S^\circ + 2OH^- \quad (6a)$$

$$2HS^- + 3O_2 \rightarrow 2SO_3^{2-} + 4H^+ \quad (6b)$$

$$2SO_3^{2-} + O_2 \rightarrow 2SO_4^{2-} \quad (6c)$$

$$2SO_3^{2-} + O_2 + 2HS^- \rightarrow 2S_2O_3^{2-} + 2OH^- \quad (6d)$$

Thiosulfate and tetrathionate can be oxidized to sulfate by air in the presence of copper and iron sulfides under mild temperatures. In the presence of CuS or Cu_2S catalysts $S_2O_3^{2-}$ is oxidized to sulfate by a series-parallel reaction path involving $S_4O_6^{2-}$ as an intermediate product. However, in the presence of $CuFeS_2$ or chalcopyrite (which contains Fe^{3+}) thiosulfate is rapidly and quantitatively oxidized to tetrathionate which then undergoes slow oxidation to sulfate. The reported oxidation reaction data exhibit a pseudohomogeneous first-order kinetics (Chanda and Rempel, 1985).

2.3. Engineering Considerations Associated with Catalytic Oxidation. Several engineering aspects have to be optimized in order to make the catalytic processes economical. These are mainly reactor design and mass-transfer limitations, process energetic, and flow.

The contacting of three phases in a continuous process is a well-investigated area of the reactor engineering which is covered well in many review articles (Goto et al., 1977; Sarona and Nigam, 1996). The description below highlights the main solutions and the specific characteristics of oxidation in aqueous solution. Enhanced solubility of oxygen in aqueous solution at elevated pressures provides a strong driving force for catalytic reactions. Oxygen flux can be improved by using soluble and active oxidants like hydrogen peroxide or ozone. Oxygen flux can also be increased by reducing the mass-transfer resistance. The film mass transfers between the air bubble and the liquid bulk and between the fluid and the catalyst can be reduced by improving agitation and by inducing smaller air (or oxygen) bubbles. The main resistance is often due to the slow diffusion through the catalyst. Dissolved oxygen diffusity (D) is about 10^{-5} cm^2/s. The penetration depth of oxygen $(D/k)^{1/2}$ is about 0.1 cm (100 μm) for slow reactions (reaction time of 1000 s = 1/k) and about 0.01 cm (1000 μm) for fast reactions (10 s). These values suggest that most of the data concerning oxidations of phenol and other aromatic (Tables 2 and 3) and aliphatic compounds (Tables 5−7), which typically require 10−60 min for significant conversion typically using catalysts that are a few millimeters in diameter, are limited by pore diffusion. Indeed, limitations due to intraparticle diffusion have been found to be significant in catalytic systems with particle diameters as low as 20 μm (Baldi et al., 1974; Otha et al., 1980; Pintar and Levec, 1994; Fortuny et al., 1995). For particles larger than 40 μm, it has been proposed that the oxidation of phenol occurs predominantly on the outer surface (Kochetkova et al., 1992a,b; Levec and Pintar, 1995).

Pore diffusion can be eliminated, of course, by using homogeneous catalysts, which, however, are difficult to separate and to recycle. Heterogeneous catalysts should be organized, therefore, as small grains (powder) or as fibers. Powdered catalysts may be too difficult to separate by sedimentation, and catalytic fibers may be too expensive for most applications. AC fibers have been used in several applications (Heilshorn, 1991). Recently Barelko and co-workers (1996) patented a cloth catalyst made of woven silica fibers and impregnated with various active metals (Pd and Pt). We are currently testing this catalyst, and initial results with it show rates that are significantly faster than those in pellet catalysts.

Most aqueous-phase catalytic oxidation studies were carried out in either slurry reactors or fixed-bed reactors in which the two fluid phases flow through a stationary bed of a catalyst either concurrently upward (bubble column fixed bed) or downward (trickle bed) (Goto et al., 1977). Trickle-bed reactors avoid the disadvantage of separating small catalyst particles from fluid product streams associated with slurry reactors, and they also avoid the limitation of flow rates encountered with upflow through a fixed bed.

As discussed above, reactions undergoing a free-radical mechanism are affected by the catalyst weight as well as by the volume of liquid phase present in a reactor. The kinetic model for catalytic phenol oxidation in a liquid-full fixed-bed reactor (eq 2) was found to be quite different from that developed from the data of a slurry reactor (eq 1) (Levec and Pintar, 1995). The rate of such reactions are affected by the ratio of liquid-to-solid volumes. In reactors with a high ratio of liquid-to-solid (which is typical for a slurry reactor), homogeneous reactions (like polymerization) are enhanced, while these reactions are suppressed in a trickle-bed reactor, or liquid-full fixed-bed reactor, in which the liquid-to-solid ratio is low. Figure 5 presents the comparison of these reactors during phenol oxidation on a copper oxide containing a composite catalyst: In a trickle-bed reactor the phenol is oxidized to CO_2 and H_2O and the conversion in TOC is proportional to that of phenol; in a slurry reactor, part of the phenol converts to polymeric products which contribute to TOC and there is a difference between TOC and phenol conversion.

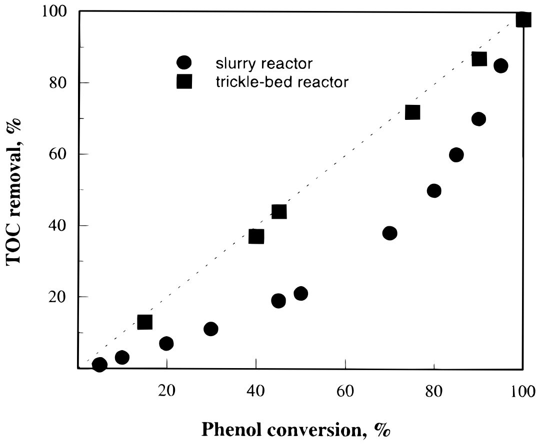

Figure 5. Comparison of total organic carbon (TOC) removal versus phenol conversion in slurry and trickle-bed reactors (Pintar et al., 1992).

Oxidation of phenol and other organic compounds can be conducted only at elevated temperatures. The need to heat up the stream and to recover the heat adds, of course, to the process cost. One way to overcome this problem is to separate the pollutant at low temperatures and decompose them in a concentrated solution. Such an application, using adsorption and catalytic oxidative regeneration, is described in the next section. This technological approach is especially adapt to highly dilute solutions.

Wastewater typically includes a significant fraction of solid particles that may clog catalyst beds and filters. The feed stream should be screened and filtered, if necessary, and the catalytic beds should be subject to backwash and other methods for unclogging the bed.

2.4. Decontamination of Water Using Adsorption and Catalytic Oxidation.

While adsorption and catalysis are well-established technologies, their combination for pollutant abatement purposes has been employed in only a few cases. Adsorption of organic pollutants by AC is a well-established technology, but its cost is still a prohibitive factor. For economic and environmental reasons, spent AC is not disposed but undergoes several cycles of regeneration. Thermal regeneration of AC is the most common process, but it requires high temperatures (800−850 °C) and consequently is usually not conducted in situ, requiring shipment of the spent AC to special regeneration units and thus contributing significantly to its cost. These conditions typically result in adsorption capacity loss up to 15% and weakening of the carbon structure. Moreover, high-temperature regeneration is economically feasible only for large systems that use more than 200 000 t granular AC per year (Sonyheimer et al., 1988).

Table 10. Listing of Studies into Catalytic Regeneration of AC

catalyst impregnated	compd adsorbed	regeneration temp. (°C)	refs
Pt, Pd; CuO, Cr_2O_3, Co_3O_4, V_2O_5	toluene, benzene, styrene	200−350	Nwankwo and Turk, 1975
MnO	dyes, surface active agents	280−350	Koganovskii and Kaninskaya, 1981
Fe_2O_3	phenol	350	Prodan et al., 1988
FeO_3, CuO	dyeing wastewater	280−350	Koganovskii et al., 1981
Fe_2O_3, CuO, Cr_2O_3	phenol, halogenated phenols	250−280	Matatov-Meytal and Sheintuch, 1997

Table 11. Listing of Studies into Catalytic Decontamination of Water Using Reductive Processes

			operating conditions						
catalyst	compd^a	reactor type^b	temp. (°C)	press. (atm)	C_0 (g/L)	conv. (%)	reaction time (min)	initial rate (mg/min)	refs
					HDC				
Pd/carbon	2-chp	S	35	2.3	10	99	60	490	Hoke et al., 1992
	2,3-dcp		35	2.3	10	99	120	560	
	2,3,5-tcp		35	2.3	10	87	180	177	
	pcp		50	2.3	10	98	4980	76	
Pd/carbon	2-chp	S	35	1	10	99	30−60	480	Hoke et al., 1992
Pd/carbon	tce	S	55	2.3		84	10	3.7	Kovenklioglu et al., 1992
	tcb		55	2.3		93	10		
					HDN				
Pd/SiO_2	nitrite	S	10	2.5	0.1	99	40	65^c	Horold et al., 1993a
$Pd-Cu/Al_2O_3$	nitrate	S	10	2.5	0.1	82	50	3.13^d	Horold et al., 1993b

[a] Abbreviations: tcb, trichlorobenzene; dcb, dichlorobenzene; nph, nitrophenol; chp, chlorophenol; tce, trichloroethylene. [b] Reactor type: S, slurry. [c] (mg/min·g of metal). [d] (mg/min·g of cat).

Thus, catalytic regeneration of spent adsorbents, especially, of granular AC was considered by several authors as an alternative to thermal regeneration (Table 10 and references herein). Catalytic regeneration for ACs impregnated with a catalyst has first been applied by Nwankwo and Turk (1975). Metal oxides like Cr_2O_3, CuO, Co_3O_4, V_2O_5, MoO_3, and WO_3 and metals like Pt and Pd are used as catalysts. Impregnation of the adsorbent with a catalyst provides intimate contact in a single unit, reduces diffusion paths, and accelerates the desorption rate, but it may diminish the adsorption capacity and may lead to metal elution. The degree of recovery of adsorption capacities was found to vary with the nature of the adsorbate and catalyst. Koganovskii and co-workers have studied the availability of AC impregnated with oxides of manganese, iron, and a mixture of Fe_2O_3, CuO, and Al_2O_3 for catalytic oxidative regeneration of spent AC after the adsorption of organics from liquid solutions (dyes and surface active agents) in the same adsorption column at 280−350 °C. Despite the fact that due to impregnation of ACs with a catalyst the adsorption capacity declined by about 20% (Koganovskii and Prodan, 1988), catalytic regeneration in situ in the adsorption column at 280−350 °C as opposed to high-temperature thermal regeneration was claimed to be an efficient technology for wastewater treatment. In a recent investigation into low-temperature catalytic regeneration of AC loaded with phenol (Matatov-Meytal and Sheintuch, 1997) we found that the adsorption capacity of impregnated with metal oxide catalyst Filtrasorb-400 granular AC was completely restored even after 10 cycles (Figure 6). Under similar conditions only partial recovering of the adsorption capacity was obtained for spent carbons loaded with *p*-chlorophenol and *p*-bromophenol.

Another regeneration technique which uses desorption of the toxic compounds from AC by hot water at temperatures up to 180 °C and elevated pressure has been suggested by Levec and Pintar (1994); the desorbed organics can be subsequently abated either by catalytic liquid-phase oxidation in a trickle-bed or wet air oxidation reactor.

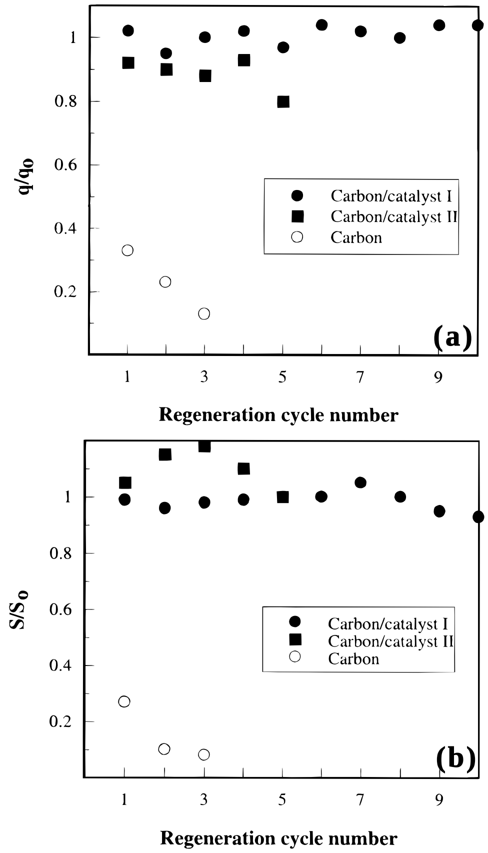

Figure 6. Degrees of recovered adsorption capacity (q/q_0) and of recovered surface area (S/S_0) vs regeneration cycle number during a periodic adsorption−regeneration process. The AC adsorbent was impregnated with a mixture of $Fe_2O_3-CuO-Cr_2O_3$ of 5.1 wt % (catalyst I) or 10.1 wt % (catalyst II). Regeneration was applied at 250 °C with 5% oxygen in nitrogen (Matatov-Meytal and Sheintuch, 1997).

3. Reduction Processes

General recognition of the role of reductive processes in wastewater treatment began with the report of Kalnes and James (1988), who demonstrated that for

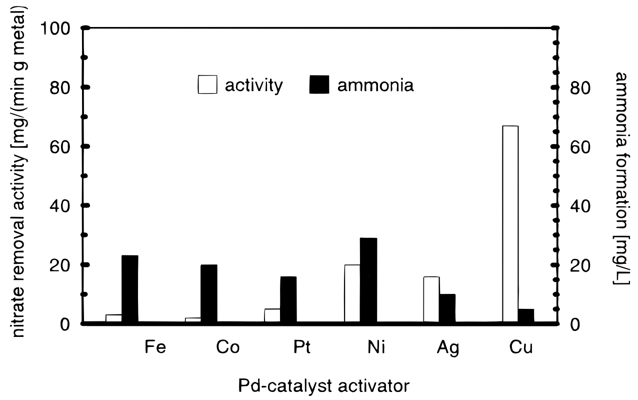

Figure 7. Nitrate removal activity of a palladium catalyst after activation by a second metal (Horold et al., 1993a).

halogenated organic wastes, such as polychlorinated benzenes, reductive treatment, especially hydrodechlorination (HDC), is economically more attractive than direct incineration. Reductive processes can replace or complement the oxidative technologies described earlier. Below, we review catalytic reduction processes for the abatement of two groups of pollutants: chlorinated organics and nitrates.

3.1. Hydrodechlorination. A typical HDC reaction may be expressed as

$$C_lH_mCl_n + nH_2 \rightarrow C_lH_{n+m} + nHCl \tag{7}$$

This process converts the chlorinated organic pollutant into the corresponding organic compound and chlorine is removed as hydrochloric acid. Recently, a number of investigators have examined the use of hydroprocessing for treating or recycling chlorinated organic wastes (Hagh and Allen, 1990a,b; Chen and Allen, 1991; Gioia et al., 1993; Kim and Allen, 1994). The catalysts employed in these HDC reactions have included noble and transition metals on silica or alumina supports, or on carbonaceous supports (Balko et al., 1993). Despite the attention HDC has received for treating liquid organic wastes, there are few reports of direct aqueous-phase catalytic HDC demonstrated as a viable remediation technique (Table 10). Kovenklioglu and coworkers (1992) studied the direct HDC of a variety of chlorinated hydrocarbons (carbon tetrachloride, chloroform, trichloroethylene, trichlorobenzene etc.) at the concentration range of 10−150 mg/L, on commercial noble-metal catalysts (Pd, Pt, and Rh) supported on carbons, at temperatures of 25−55 °C and near atmospheric pressure. Catalyst screening studies with a shaker and autoclave hydrogenation reactors have shown that a commercial Pd catalyst is the most effective catalyst (46−89% conversion). The initial rates of HDC on Pd/C exhibit the first-order dependence of the hydrocarbon concentration and are independent of hydrogen pressure. Activation energies at different catalyst loadings in the temperature range of 16−30 °C were found to vary, without trend, from 29−38 kJ/mol.

The HDC rate on Pd/C was found to be much higher than on Pd/alumina, because the hydrocarbon does not adsorb on alumina. When the carbon support does not readily adsorb the reactant hydrocarbon, the HDC rates drop significantly. These results confirm the role of the carbon support in providing an efficient path for reaction, yielding significantly faster reaction rates in comparison with direct adsorption rates from solution onto the palladium catalyst.

Hoke et al. (1992) investigated direct HDC of chlorophenols dissolved in water by hydrogen (at 2.3 atm) and hydrazine over a Pd/carbon catalyst. Complete conversion of various monochlorophenols (MCP), dichlorophenols (DCP), trichlorophenols (TCP), and pentachlorophenols (PCP) to phenol (with yield 91−99%) was achieved at 35−50 °C when hydrogen was used as the reducing agent. The reaction time for complete conversion to phenol increased with the degree of chlorine substitution and varied from 30 min for MCP to 83 h for PCP. This process is still in the developing stage and the long-term performance of the catalyst is yet to be studied.

3.2. Hydrodenitrification. The abatement of nitrate from drinking water becomes necessary for several communities, particularly in intensively cultivated regions, since water quality standards are violated. Nitrates are stable and highly soluble ions with a low potential for adsorption or coprecipitation. A number of processes are currently available for the removal of nitrate from water, like biological denitrification, ion exchange, reverse osmosis, and electrodialysis (Kapooz and Viraraghavan, 1997 and references herein).

Nitrate removal can also be achieved using chemical reduction by $Fe(OH)_2$, which generates large quantities of iron sludge (Sova, 1986) and by powdered aluminum (Murphy, 1991).

Catalytic processes for nitrate/nitrite removal have recently attracted significant attention. The application of catalytic liquid-phase hydrogenation for nitrate and nitrite abatement mainly to nitrogen from drinking water was recently examined (Horold et al., 1993a,b). Nitrate is reduced to intermediate nitrite, which itself is reduced to nitrogen or ammonia, depending on the active metal catalyst.

$$NO_3^- + H_2 \rightarrow NO_2^- \tag{8}$$

$$NO_2^- + H_2 \rightarrow N_2 + OH^- \tag{9}$$

$$NO_2^- + H_2 \rightarrow NH_4^+ + 2OH^- \tag{10}$$

Most of the catalysts investigated (noble and transition metals Pd, Pt, Ru, Ir, Rh, Cu, and Ni, supported on alumina and silica) reduce nitrite mainly to ammonia. Complete reduction of nitrite to ammonia was achieved on Ru, Ir, Rh, and Cu, Ni catalysts, while both products (gaseous nitrogen and dissolved NH_4 which is undesirable in drinking water) were observed with Pd and Pt catalysts. Only the palladium catalyst was found to be suitable for a selective nitrite reduction to nitrogen. Activity and selectivity to nitrogen depend on the preparation mode of the catalyst and the support.

Different metals of groups VIII and Ib of the periodic table were examined for the activation of the palladium catalyst in the reduction of nitrate. The activity and selectivity of the catalysts depend on the nature of the second metal and on the two-metal ratio. A Pd−Cu catalyst (3.75:1.25 wt %) shows nitrate removal activity but also exhibits a higher ammonia formation rate (Figure 7). The activity of this catalyst, supported on alumina at room temperature, was 3.13 mg of NO_3^-/(min · g of catalyst) that is about 30 times higher than that of the corresponding denitrification bioprocess with microorganisms *Paracoccus denitrificant* DSM 1403.

The process is still in the development stage and kinetic parameters are yet to be studied (see Table 11).

Summary

Decontaminantion of water using solid-catalyzed oxidation and reduction processes has been analyzed. It is apparent that most of the toxic compounds for which biological treatment is not feasible, and that appears in concentrations for which separation is not economical, are amenable to abatement using catalytic oxidation processes. The review of catalytic abatement of dissolved pollutants suggests the following well-investigated solutions: (*i*) Dissolved phenol may be oxidized in the presence of a CuO catalyst or its mixture with ZnO or CoO at temperatures of 150−200 °C and oxygen pressure of 1−235 atm. The reaction proceeds via a free-radical mechanism and the solid/liquid volume ratio affects the rate and product distribution. (*ii*) Supported metal (Ru/CeO_2 and Pt/CeO_2 as well as Ru/C) and metal oxides (CuO−ZnO−CoO, MnO_2/CeO_2, CoO/Bi_2O_3, and V_2O_5/Al_2O_3) are the most-promising catalytic systems for the destruction of aromatic as well as aliphatic organic compounds showing high activity and nearly 100% selectivity to CO_2. (*iii*) Low-molecular-weight organic acids, particularly acetic acid, which are formed as oxidation byproducts, may be oxidized on Ru/Al_2O_3 or MnO_2/CeO_2 and CoO/BiO(OH) complex oxide catalysts at temperatures of 180−250 °C; Ru/Al_2O_3 and MnO_2/CeO_2 catalysts are also highly active catalysts for phenol oxidation at temperatures of 200 °C. (*iv*) CoO/CeO_2 and MnO_2/CeO_2 composite oxides are the most active catalysts also for ammonia oxidation at temperatures of 240 °C. Thus, the combination of these catalysts provides a good system for the abatement of phenol, organic acid, and ammonia. (*v*) Activated carbon, preferably in the presence of dissolved copper ions, is the most promising catalyst for the oxidation of cyanide and sulfur-containing compounds. (*vi*) Aqueous-phase catalytic reduction emerges as a potential process for cleaning water from chlorinated compounds and nitrates over supported metal catalysts. (*vii*) The decontamination of wastewater using adsorption of dilute pollutants from water, on well-established adsorbents like AC impregnated with a catalyst, followed by catalytic regeneration in situ, may emerge as an efficient technology for wastewater treatment.

Applications of catalytic abatement to real wastewater require highly active, nonselective catalysts, capable of long-life operation in hot water, without structural and/or performance degradation, are required. The reviewed studies show that it may be possible to develop a broad-based catalytic abatement process for a range of pollutants that appear in real wastewater, with high activity and a long-life of operation in hot water. There are several technological problems that need to be addressed: (*i*) The catalytic oxidation of most pollutants like phenol, carboxylic acids, and halogen- and nitrogen-containing compounds requires relatively high temperatures, resulting in increased energy costs and the need for efficient energy utilization. The adsorption−catalytic regeneration process seems to be very attractive because its energy investment is relatively minor. (*ii*) Most of the reported works deal with pure components while data reported on pollutant mixtures and on real wastewater are lacking. (*iii*) New approaches for overcoming the slow diffusion in water, involving fiber supports and powder adsorbents, should be tested. (*iv*) Reductive catalytic processes like hydrodechlorination (HDC) of chloroorganics and hydrodenitrification (HDN) of nitrates/nitrites emerge as promising processes for wastewater treatment.

In selecting a wastewater treatment process among biological, chemical, (WAO and SCWO) and catalytic methods one should consider the toxicity and concentrations of the pollutants and the nature of the waste stream. Bioprocesses are suitable for nontoxic pollutants at low concentrations in streams that may include a large fraction of solids. For chemical destruction methods to be thermally self-sufficient, the pollutants concentration should be high. Catalytic methods are suitable for a large group of compounds (see above), in streams with low or high concentrations which are typically free of solids; high solid concentrations can be treated in a slurry reactor, which makes catalyst separation and recycle a difficult problem. Current data suggest that catalytic processes are slower than bioprocesses at room or low temperatures; better catalysts should be developed for such applications.

Acknowledgment

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Nomenclature

d = diameter
E = energy of activation
n, m = reaction order
t = reaction time
k = apparent rate constant
C = liquid phase concentration
K = adsorption constant
Q = adsorption capacity
D = diffusion coefficient

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