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Environmental catalysis into the 21st century

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Abstract

This paper describes existing catalyst technologies and trends in research as we enter the 21st century. Catalytic technologies developed during the 20th century for end-of-pipe clean up of pollutant emissions will continue for mobile and stationary sources. The catalytic problems associated with the fuel-efficient lean-burn engine, with lower emissions of greenhouse gases, offers significant challenges, especially for lean NO_x reduction with on-board fuels. Monitoring pollutants using catalytic sensors will play a key role in controlling emissions from mobile and stationary sources. Decomposing ambient ozone using 'passive' catalytic technologies will find increasing application by the year 2000. Photocatalysis will continue to be the subject of research, but applied only in 'niche' markets. The proton exchange membrane fuel cell will be a major focus for research in electrocatalysis and catalytic fuel processing to make hydrogen from hydrocarbons. This technology holds great promise for stationary and vehicular power generation. The manufacture ('Green Chemistry') of chemicals with decreased waste and pollutants will continue to be actively pursued by many chemical manufacturers with increasing successes. The feasibility of catalytic combustion for stationary power generation with ultra-low emissions will be decided early in the 21st century.

Predictions for the possibility of commercial successes will be made. ©2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Environmental catalysis research is undergoing a transition from pollution abatement to pollution prevention. Research for advanced fuel cells and catalytic combustion, both promise power generation with ultra-low emissions, are under intensive investigation worldwide. New and cleaner catalytic routes are changing the way in which bulk and fine chemicals are made.

During this transitional phase, catalytic pollution abatement technology will continue to be used commercially with further improvements in effectiveness required. Emissions from the internal combustion engine will remain a focal point for new technologies, which improve fuel economy and decrease emissions of greenhouse gases (i.e. CO_2). Lean-burn internal combustion engines promise significant improvements in fuel economy, but the problem of NO_x abatement remains to be solved.

Monitoring pollutants to extremely low concentrations in automobile exhausts, chemical processes, commercial and residential buildings is also under intense investigation using sensors which could contain catalysts.

The abatement of traces of pollutants from the air using 'passive catalysis' is a new and exciting way to improve the quality of the air we breathe. Catalysts deposited on heat-exchanger surfaces can be utilized to

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decompose ambient ozone and hydrocarbons. Photocatalysis continues to show effectiveness, but for special applications only.

The objective of the current survey is to present the catalytic technologies that will be the focus of research as we enter the 21st century.

2. Catalysts for the 21st century automobile

The demands of a catalyst to function in the hostile environment of the automobile exhaust has resulted in the development of materials never before needed in catalysis [1]. During the latter part of the 20th century, we have seen the widespread use of an entirely new structure; the ceramic and metallic monolithic substrate as a support for the catalytic washcoat. It allows high conversion efficiencies at high gaseous throughput, provides a high geometric surface area with lower pressure drop, excellent high-temperature and thermal-shock resistance and can be conveniently oriented in the exhaust train in any number of directions. The carrier material, most notably activated high surface area Al_2O_3, has been modified by the use of oxide stabilizers, i.e. La, Si, Ba, etc. to maintain high surface areas after experiencing temperatures up to 1100°C in the high H_2O content of the automobile exhaust. The dispersion of the catalytically active precious metal components has been stabilized against sintering by using rare-earth metal oxides in the catalyst formulation.

The zirconia-based electrochemical O_2 sensor provides computer controlled feedback for the combustion process to maintain the engine air-to-fuel ratio within a narrow range for efficient three-way catalysis. Combinations of CeO_2 and ZrO_2 play an integral role in providing oxygen storage capacity (OSC), which broadens the conversion efficiency for NO_x, CO and HC, during the rich/lean perturbations, associated with the feedback control system. Truly, the automobile catalyst has resulted in the development of materials durable under extreme environments previously thought impossible in conventional catalytic processes. Further improvements, however, are still required to meet evermore stringent emission standards worldwide.

The precious metals used in modern three way catalysts (TWC) are primarily Pt and Rh combinations or only Pd deposited on high surface area alumina. In each case, proprietary base-metal oxides are used to promote the activity and stability of the catalyst. The composite washcoat is deposited on a ceramic honeycomb with 400–600 cells per square inch with wall thickness of 0.004–0.006 in. From the fundamental understanding of the positive and negative interactions that occur in multi-component catalysts, some manufacturers have developed segregated or layered washcoat structures adding great flexibility in optimizing the chemistry of the finished catalyst. A high Pd loaded catalyst with small amounts of Pt and Rh is prepared in two washcoat layers. Deactivation by compound formation between active species is virtually eliminated by locating the Pd and Rh in separate layers. Furthermore, the NO_x reduction activity of the Rh function is maintained by segregating it from the CeO_2. Some of the Pd is deposited on the OSC to enhance oxygen storage and the kinetics of CO oxidation and water gas shift reactions. The remainder of the Pd is deposited on the alumina, which provides better NO_x and HC performance [2]. Thus the washcoat is formulated in two distinct layers permitting the positive aspects of each function to be preserved [3].

The close-coupled catalyst has been a very significant technological advancement in meeting the cold-start hydrocarbon emission problem associated with the ultra-low emission vehicle (ULEV). Catalysts mounted close to the exhaust ports of the engine will benefit from the hot exhaust and, thus, will reach hydrocarbon light-off temperatures within 10 s [4]. A larger TWC catalyst is located downstream in an underfloor position to function during other driving modes. The close-coupled design, however, exposes the catalyst to hotter overall temperatures increasing the likelihood of carrier and/or metal sintering. One preparation selectively oxidizes the HC with minimal CO oxidation to avoid high temperatures during rich engine excursions and high CO concentrations. This novel Pd containing catalyst has temperature stability to 1050°C. Proprietary metal oxides are added to stabilize the Al_2O_3 and Pd against excessive sintering. The more stringent test cycle (US 06 modification to the US FTP to include aggressive driving modes of high speed and load) will add additional high-temperature stress to close-coupled catalysts. This technology is expected to be incorporated into model year 2000 vehicles.

A major challenge for the next generation of fuel-efficient engines is to develop a catalyst capable of NO_x reduction with on-board fuel in the presence of large excesses of O_2 [1]. If, and when, available, lean-burn gasoline engines with fuel efficiencies approaching 25% greater than the stoichiometric engine could be commercialized. Accompanying the fuel economy benefits will be a proportionate decrease in CO_2 emissions. Catalytic lean-NO_x reduction is available for stationary engines with NH_3 as the reductant; however, for automotive applications it is more practical to use on-board derived fuel. Research for active, selective and stable catalysts, which will utilize on-board derived hydrocarbons as reductants, has not been successful [5], and although research will continue into the next century the likelihood of success is low.

In the absence of a lean NO_x catalyst, the automobile manufacturers have developed a hybrid partial lean-burn engine which operates lean during cruise conditions, resulting in 5–10% fuel economy savings. The NO_x generated during lean modes is stored in an alkali-earth metal oxide, i.e. BaO, which is incorporated into a TWC. Periodically, the air-to-fuel ratio is forced rich for a short time in which the stored NO_x is reduced on the TWC [6]. This system is commercially available in Japan, where low sulfur-containing fuels are used. In locations where the gasoline sulfur content is higher, i.e. US and Europe, the large concentration of acidic sulfur oxides present in the exhaust adsorb more strongly than the NO_x, poisoning the alkaline sites. If the short rich pulse is conducted at temperatures in excess of 650°C, almost complete regeneration is feasible. This engine management strategy, coupled with new materials research, will continue into the 21st century. In parallel, the petroleum companies are expected to decrease sulfur levels in the gasoline to <50 ppm.

3. Passive catalytic technologies

When a catalytic system does not require any instrumental control, such as controlled heating, adjustments in gaseous composition, etc. it operates in a ‘passive’ as opposed to an ‘active’ mode. Classical approaches to pollution control have been to passively abate emissions at the tailpipe or stack by placing the catalyst in series with the exhaust to be treated. No adjustments in the gas composition are required for the catalyst to function. In contrast, the automobile TWC functions with feedback control of the air-to-fuel ratio in order to maximize simultaneous conversion of all three pollutants and, therefore, is an active system.

3.1. Radiator catalysts for destruction of ambient ozone

In a new technology, called the PremAir® catalyst systems [7], a catalytic coating is applied to a radiator which converts ambient ground-level ozone passively. This technology can be applied to both mobile and stationary applications. As ozone-containing air passes over the coated radiator or condenser, the catalyst converts the ozone into oxygen as shown in Fig. 1. Studies have also shown this configuration is effective for other pollutants in addition to ozone [8].

Demonstrations of this technology have occurred for on-the-road vehicle tests [9] and stationary heat exchange surfaces. Test vehicles included Ford Contours and Taurus’ as well as Volvo’s S70 and S90. Typical results on the Volvo vehicles are shown in Fig. 2. Here, ozone conversion is plotted vs. the space velocity through the radiator. Since the catalyzed radiator is a typical reactor, all the classical reaction-engineering approaches apply.

Depending on the space velocity, ozone destruction varies from 95% to ∼80% for a high surface-area radiator to 80% to ∼50% for a low surface-area radiator. Also shown in this figure are laboratory results on the same radiators to show that the lab test rig agrees with the on-the-road tests.

Stationary applications involve the coating of air-conditioner condensers and other stationary

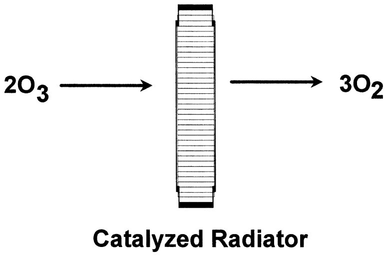

Fig. 1. Catalyst on a catalyzed radiator destroys ozone.

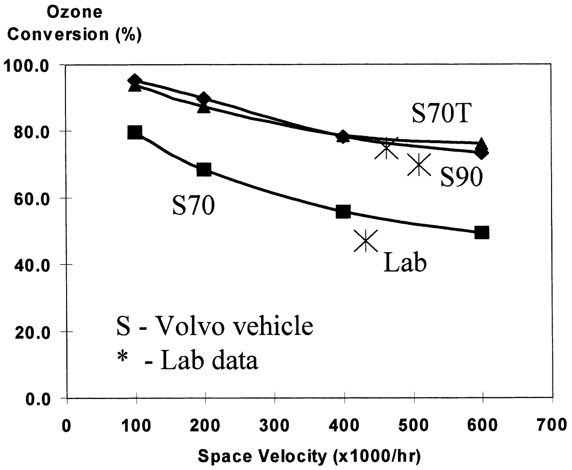

Fig. 2. Ozone conversion is a function of space velocity through the radiator.

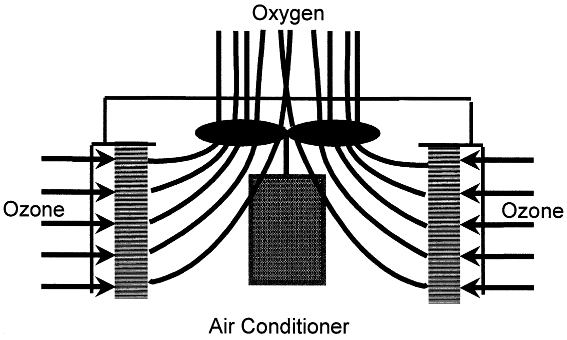

Fig. 3. Catalyzed coating can be applied to air conditioner condensers.

heat-exchange surfaces. Field tests have also been conducted on catalyzed air-conditioner condensers. This concept is depicted in Figs. 3 and 4. Ozone-containing air passes through the catalyzed heat exchanger of an air condenser. The ozone conversion maintained a steady rate over the summer test period at ca. 90% ozone destruction.

The regulatory and analytical framework for addressing urban ozone has been historically based on reducing the emissions of ozone precursors (i.e. VOC and NO_x). Additionally, regulatory programs and control systems have generally focused on the ozone levels at a downwind site, where the peak ozone level often occurs after a series of complex photochemical reactions, atmospheric mixing, and transport of ozone and

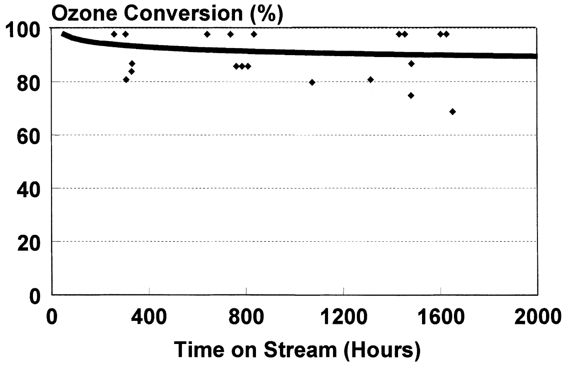

Fig. 4. Summer long test on commercial air conditioner.

its precursors. The PremAir® catalyst, on the other hand, directly reduces ozone pollution and produces its most significant effects in the vicinities where motor vehicle and population activity are most intense. An assessment of the PremAir® catalyst should recognize this difference when comparing its air quality benefits with those of other ozone control strategies. This technology is presently being considered for implementation on the ultra-low emission vehicles to offset tailpipe emissions.

3.2. Photocatalytic destruction of hydrocarbons in air and waste waters

Photocatalytic destruction of hydrocarbons is an excellent example of a practical passive application. Surfaces, such as windows, mirrors, indoor wall tiles, etc. are coated with a thin transparent film of photocatalytic TiO_2. Indoor hydrocarbons, originating from equipment, cooking or smoking odors, adsorb on the photocatalyst where sunlight assists in decomposition to carbon dioxide and water passively. Other candidates for this technology are sky scraper windows, traffic lights, road sign reflectors, computer and TV screens, etc. [10].

Destruction of hydrocarbons in waste waters can be accomplished by a combination of photocatalytic and activated carbon. Furthermore, heavy metal ions such as Cr^{+6} can be reduced to less environmentally harmful Cr^{+3} using Fe-modified TiO_2 in the presence of sunlight [11]. Studies showing the reduction of Cu ions have been investigated using nanosized TiO_2 photocatalysts [12].

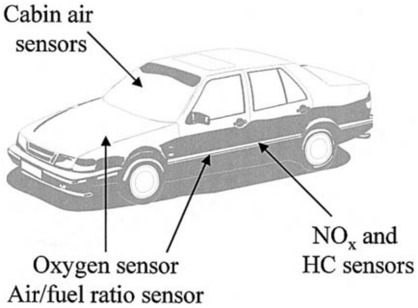

Fig. 5. Applications of catalytic sensors.

4. Catalytic sensors

Sensor technology for mobile applications has become a market opportunity since the operation of the motor vehicles is closely monitored using on-board diagnostics (referred to as OBD). There are a number of possible applications for catalytic automotive sensors as shown in Fig. 5.

The first true catalytic sensor for the automobile revolutionized the approach to engine control and emissions reduction. The oxygen sensor [1], introduced in the 1970s, consists of a yttrium-doped ZrO_2 dense ceramic (which has oxygen ion conductivity) formed in the shape of a thimble and mounted on a spark plug assembly. The ceramic is coated on both sides with porous platinum electrodes forming an electrochemical cell. The outer side is in the exhaust gas while the inner has reference air. A porous oxide layer is deposited on the exhaust electrode as protection against erosion and deposits. This electrochemical cell develops a potential (E) as given by the Nernst equation (Eq. (1)), where E_0 is the standard state voltage and R, T, n and F the universal gas constant, the absolute temperature, the number of electrons transferred and the Faraday constant, respectively. The voltage varies as the ratio of the partial pressure of O_2 [PP O_2] in air and exhaust.

$$E = E_0 + \left(\frac{RT}{nF}\right) \ln \frac{[\mathrm{PP\ O}_{2(\mathrm{air})}]}{[\mathrm{PP\ O}_{2(\mathrm{exhaust})}]} \qquad (1)$$

The Pt catalyzes the conversion of the O_2 by the CO or HC and the voltage generated reflects the amount of O_2 remaining at the surface of the electrode. A change from an O_2 deficiency to an excess results in a step change in EMF response of the electrochemical cell as shown in Fig. 6. This signal is fed back to the engine control system which adjusts the air-to-fuel ratio towards a stoichiometric mixture.

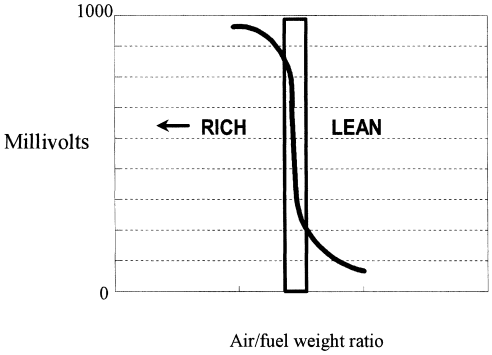

Fig. 6. Voltage response for varying air-to-fuel ratios in the automotive oxygen sensor.

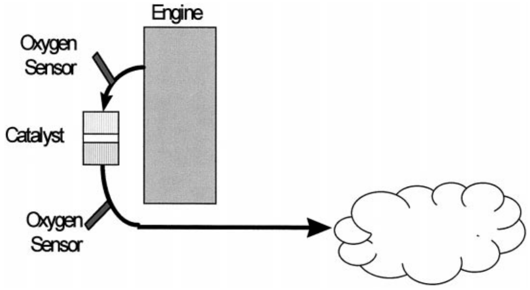

Fig. 7. Arrangement of dual oxygen sensor for on-board diagnostic monitoring.

Currently, dual oxygen sensors, positioned before, and after, the catalyst, are used to ‘sense’ or monitor the hydrocarbon content of the exhaust via a correlation with the oxygen storage capacity of the TWC. The difference in voltage between the inlet and outlet oxygen sensors is transmitted to the dashboard, alerting the driver of a malfunction of the catalyst. Such a system is called on-board diagnostics (OBD) [13] as shown in Fig. 7.

The key to using the dual oxygen sensor for OBD is to find a suitable relationship between the change in oxygen storage of the TWC and hydrocarbon activity or conversion. Such a relationship has been developed and is as shown in Fig. 8, which depicts a region of sensitivity where the dual oxygen sensor methodology can be used to monitor hydrocarbon efficiency. Note that there is substantial variability in this measurement

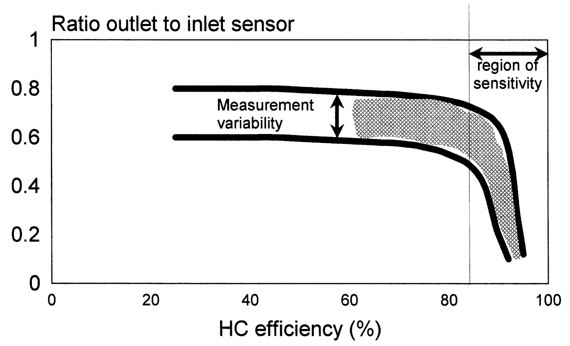

Fig. 8. Correlation of hydrocarbon efficiency and ratio of signals from the dual oxygen sensor.

and the technique has not been proven for ultra-low emission vehicles.

A sensor is under development for detecting NO_x in automobile exhaust utilizing a combination of electrochemistry and catalysis. The O_2 present in a small sample of exhaust gas is electrolytically reduced at the Pt/ZrO_2 cathode. CO or HC then reduce the residual NO_x over Rh. A signal correlating the amount of NO_x reduced is measured [14].

With the increased use of sensors in many industrial applications, there will certainly be many future markets for catalysts.

5. Benign manufacturing

Chemical companies are improving their processes by generating more desirable products with less by-product waste. By eliminating pollution control equipment and waste disposal, economic benefits are clearly derived. ‘Green manufacturing’ will continue to be a high priority for chemical production well into the 21st century. The field is extremely broad and many details are confidential to specific manufacturers, but Anastas and Warner [15] describe the overall goals in a new monograph.

There are many examples in the literature, but most noteworthy is the desire to replace mineral and Lewis acid catalysts with solid acid catalysts, especially for alkylation reactions. Extensive research has been conducted; however, little success has been achieved mainly due to coke formation and subsequent catalyst deactivation. Nevertheless, research will continue but with little chance of commercial success.

There has been considerable commercial success in other areas of benign manufacturing. For example, phenylethanol was traditionally produced by the reaction of benzene with ethylene oxide over $AlCl_3$. Product purification, disposal of the Lewis acid and the special equipment needed to carry out the reactions adds considerable expense to production. Hoelderich [16] has circumvented these disadvantages while producing the same product by hydrogenating phenylethylene oxide using Cu and B promoted ZSM-5 as the solid acid catalyst. Thus, the entire manufacturing route has been improved by using the appropriate catalyst. Hoelderich [17] has recently provided other examples.

Panov et al. [18] has reported that phenol can be produced by reaction of benzene with nitrous oxide (produced during the production of adiponitrile for nylon) over Fe promoted ZSM-5. The uniqueness is that N_2O usually must be decomposed before discharge into the atmosphere, because it is a strong greenhouse gas. Therefore, a by-product pollutant is now used as a reactant. This process will be commercialized by Monsanto [19].

Homogeneous catalysts perform special reactions, i.e. hydroformulation, chiral synthesis, etc. for which heterogeneous catalysts are not as active or selective. The process difficulty is separation of the expensive catalyst and ligands from the final reaction product, which often involves energy-consuming distillations. It, therefore, can be characterized as an environmental issue. Attempts to bond homogenous catalysts to supports in order to permit easy, low energy-consuming separations while retaining activity, selectivity and resistance to leaching has been a goal for many years. Patent applications are now being filed [20] in which claims are made that heteropolyacids can be used as effective binding agents for some homogeneous catalysts. This could have a major impact on the chemical and pharmaceutical industries if indeed the claims can be translated to real processes.

6. Catalysts for energy and power generation

6.1. The proton exchange membrane fuel cells

Considerable progress in fuel-cell systems has been made over the last ten years, thus opening

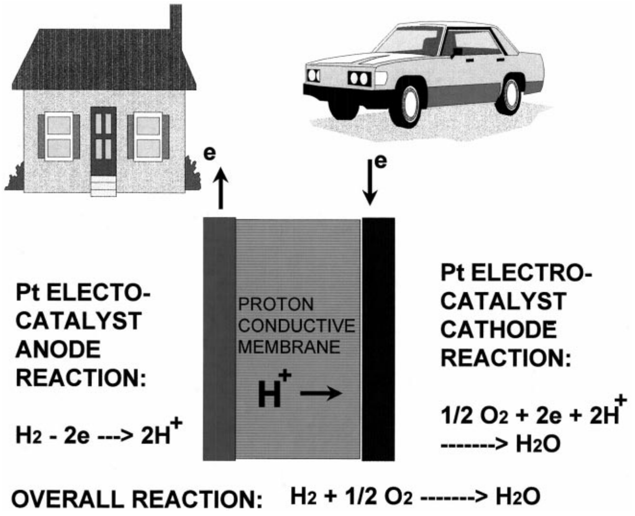

Fig. 9. Proton exchange membrane fuel cell using H_2 and O_2 as fuels.

the commercial door for possible use in stationary and mobile source applications [21]. The fuel cell directly converts chemical energy into electricity, thereby eliminating the mechanical process steps that limit thermodynamic efficiency. The fuel cell can be two-to-three times as efficient as the internal combustion engine with little, if any, emission of primary pollutants; carbon monoxide, hydrocarbons and nitric oxides.

The key development has been the improved performance of the proton exchange membrane (PEM) fuel-cell electrochemical system [22]. This includes decreased Pt use in the anode and cathode as well as improvements in CO tolerance of the anode. Hydrocarbons cannot be directly converted electrochemically at the anode but hydrogen, with a Pt electrocatalyst, is sufficiently active. Therefore, it is necessary to convert readily available fuels, such as natural gas (stationary applications) and gasoline (mobile applications) to H_2. With the improved efficiency of the fuel cell, the amount of CO_2 generated during H_2 production from hydrocarbon processing is significantly decreased relative to the internal combustion engine. The production of synthesis gas from hydrocarbons for ammonia and methanol is widely practiced and, therefore, catalysts and process conditions are very well known [23]. Desulfurization of the hydrocarbon fuel, steam reforming, water gas shift and purification of small amounts of CO present in the exit gas from low-temperature shift are routinely addressed in large-scale manufacture of H_2. These processes must now be modified and miniaturized for integration into the fuel cell [24]. Reduction in size, weight and cost are key factors that must be addressed to develop a cost-effective system. This challenge will require modified and/or improved catalysts and the reactor design.

The unit operations for a sulfur-containing hydrocarbon fuel are;

$$\begin{aligned}&\text{desulfurization} \rightarrow \text{steam reforming} \rightarrow \text{water gas shift}\\&\rightarrow \text{CO removal from } H_2 \rightarrow H_2\\&\rightarrow \text{ anode compartment} \rightarrow \text{excess } H_2 \text{ combustion}\end{aligned}$$

A cartoon of the electrochemical system is shown in Fig. 9. Purified H_2 (<5 ppm CO) is delivered to the Pt-containing anode, where it is electrocatalytically oxidized to H^+. The protons migrate through the Nafion (fluoropolymer of sulfonic acid) and combine with the reduced O_2 at the Pt cathode forming water.

Since each cell generates <1 V, it is necessary to stack them in series to meet the desired voltage and power requirements for the target application.

The steam-reforming and water–gas shift reactions are well known, although catalytic engineering will be required to reduce their size, weight and cost for the fuel-cell application. The anode electrokinetics are greatly hindered by traces of CO present from the hydrocarbon steam reforming and water–gas shift processes. For this reason, a more CO tolerant Pt/Ru anode was developed, but still the CO must be decreased to <5 ppm. For large-scale production of H_2 for the ammonia industry, pressure swing adsorption is used to reduce the CO content of the H_2. This technology is not practical for fuel-cell applications, because of excessive size and cost related to compressors. An alternative method is to oxidize the CO to CO_2. Ideally, the catalyst must selectively oxidize about 1% (10 000 ppm) CO to <5 ppm without oxidizing any of the 40–70% H_2 present. Large amounts of water and carbon dioxide from the upstream hydrocarbon reforming reactions are also present and can inhibit the catalyst performance.

Dailmer–Benz Ballard is aggressively developing technology for automotive applications (model year 2004) using methanol as the source of H_2 [25]. Plug Power [26] is forecasting production of residential fuel cells powered by natural gas by the year 2001.

The most highly desired technology is the direct electrochemical oxidation of hydrocarbon fuels, thereby eliminating the necessity to reform the hydrocarbon. Research will continue in this area, but breakthroughs in electrocatalysts and membranes are necessary.

6.2. Catalytic combustion for ultra-pure emissions

An ideal combustion process is one that delivers high energy with zero emissions. The implementation of catalytic combustion has been a dream for three decades since its discovery in the early 1970s [27], but material limitations has hindered commercialization. A lean-fuel air mixture, with a composition giving an adiabatic temperature rise of about 900 to 1000°C, is presented to a monolith catalyst [1]. Oxidation is initiated and conversion proceeds down the channel of the catalyzed monolith. When the residual fuel/air mixture and temperature reach flammability, homogeneous or thermal reaction occurs completing the combustion process to a high level of efficiency. The combustion products have <2 ppm each of HC, CO and NO_x. The latter does not form substantially, because the maximum temperature of 1300°C is below that required for the $N_2 + O_2$ reaction.

During the past decade, new catalysts, substrate materials and engineering concepts have brought this technology closer to commercialization. A family of high-temperature Pd-containing catalysts [28] and thermally stable monoliths has been developed [29] which hold promise for eventual commercialization. The most popular process concept [30] is one in which alternate channels of a metallic monolith are coated with catalyst. The fuel air mixture in the uncatalyzed channels cools the catalyzed channel protecting the substrate and catalyst against excessively high temperatures. The gas-exit temperature is sufficiently high to initiate thermal combustion.

Field demonstrations are now in progress and positive results will predict whether wide-scale commercialization is likely [31].

7. Conclusions

Catalysis will continue to play a major role in both, pollution abatement and prevention as we move forward to the next century. The exciting applications of pollution sensing, benign manufacturing, fuel cells, NO_x decomposition or reduction with hydrocarbons in lean environments, passive catalysis and catalytic combustion will represent new challenges for catalytic R&D. The need for product improvement for pollution abatement technologies will continue. We can expect greater fuel efficiency, cleaner manufacturing and less waste production to dominate catalytic research well into the 21st century.

Environmental catalytic technologies that will likely be commercially successful within the next five years are:

1. NO_x reduction in partial lean-burn gasoline engines.
2. Ambient decomposition of ozone by catalyzed radiator surfaces.
3. Catalytic sensors for on-board diagnostics.
4. PEM fuel cells with hydrocarbon fuel processors for stationary applications.
5. Benign manufacturing for selective processes.

The following will represent even greater catalyst challenges for commercial success:

1. NO_x decomposition or reduction with hydrocarbons in full lean environments.
2. Replacing mineral acids with solid acids for alkylation.
3. Bonding homogeneous catalysts to supports.

4. Fuel cells which directly convert hydrocarbons electrochemically.
5. The application of PEM fuel cells for mobile sources.
6. Extensive use of photocatalysis.
7. Catalytic combustion for ultra-low emissions.
8. Catalytic zero emission vehicle

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