


Editorial

Catalysts for Oxidative Destruction of Volatile Organic Compounds

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On a worldwide scale, concern for our environment has understandably gained high priority in many current political and social agendas. The emission of man-made pollutants to the environment has increased as consumer demand increases, leading to greater industrialization as economies develop. The challenge is to now responsibly control harmful environmental emissions to comply with legislative limits, whilst maintaining living standards and economic growth. Against this background, catalysis is a key enabling technology, and it will play a critical role in solving many of the challenges we face in protecting the environment by controlling emissions, now and in the future.

Volatile organic compounds (VOCs) are a wide-ranging class of species that are common aerial pollutants. Although they share the commonality of being organic species, they are broad in their properties and chemical functionality. They are released into the atmosphere from many sources all around the world, both natural and anthropogenic. The emission of anthropogenic VOCs is of particular concern, as many are intrinsically toxic and can also contribute to deleterious atmospheric chemistry. For example, VOCs react with NO_x to form photochemical smog and ground level ozone, whilst chlorinated VOCs are implicit in the destruction of tropospheric ozone, and many VOCs are potent greenhouse gases with high global warming potentials. It is against this background that we must have technical options to control their emission.

Several different technologies have been developed to control atmospheric VOC emissions including thermal oxidation, adsorption, absorption, and condensation. One of the best options is the process of catalytic oxidation. Compared to thermal oxidation, the incorporation of a catalyst into the oxidation process introduces a number of advantages, such as a decrease in the operating temperature, a reduction of NO_x emissions and harmful partially oxidized by-products, the treatment of very dilute effluent streams, and VOCs can be removed to very low levels. Compared to adsorption and absorption, there is no formation of a solid or liquid secondary waste product from catalytic oxidation.

Many catalysts have been employed for VOC total oxidation, and these can be divided into two groups, those based on supported metals and those based around metal oxides. The former are most commonly focused around platinum and palladium, whilst lately some have used gold-based catalysts. For metal oxides, a wide selection has been investigated, covering single and mixed metal oxides of elements from across the periodic table. The performance of the catalyst is critical in the application, and it is often required to operate under varying conditions of effluent composition and concentration. Despite the variety of catalysts used for VOC oxidation, there is still a need for catalysts with improved performance, and are capable of operating over a suitably wide range of conditions. Furthermore, there is also a need to improve our understanding of how VOC oxidation catalysts operate at a fundamental level, so that improved catalysts can be developed by rational scientific design.

This Special Issue brings together a selection of articles focusing on some of the latest developments around catalysts for the removal of organic pollutants. It includes various aspects of the topic including catalyst synthesis, characterization, improving performance and mechanistic approaches.

Articles have focused on some metal oxide-based catalysts, looking at the catalyst preparation method and how it affects activity. Intiso et al. investigated the influence of preparation of the calcium aluminum oxide catalyst, $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ (mayenite), for the total oxidation of trichloroethylene in the gas phase [1]. The catalyst was prepared using a novel method, employing polymethyl methacrylate (PMMA) as a soft templating agent. The catalyst structure was controlled by the concentration of PMMA in the synthesis, and the most active catalyst was produced with 10% *w/w* PMMA. The advantage of the PMMA templating preparation was demonstrated by benchmarking catalyst activity against a mayenite catalyst prepared by conventional hydrothermal synthesis, and the soft templating catalyst was more active. The increased activity of the soft templated catalyst was related to the increased surface area, and the increased concentration of superoxide (O_2^-) species, which were identified by Raman spectroscopy, and have been shown to be active sites for oxidation on mayenite.

Mixed metal oxide catalysts of ceria and zirconia were prepared by Shah et al. and evaluated for the total oxidation of propane and naphthalene [2]. Catalysts were prepared by mechanical grinding of carbonate precursors followed by calcination, as this is a potentially greener route of preparation compared to alternatives like coprecipitation. The incorporation of zirconia into ceria increased catalytic activity, and the most active catalyst was that with a ceria to zirconia ratio of 95:5. Formation of ceria–zirconia solid solutions were important for high activity, whilst catalysts with higher zirconia content formed segregated phases and were less active. Using surface analysis by x-ray photoelectron spectroscopy, the inclusion of zirconia into the cubic fluorite ceria phase increased the concentration of surface oxygen defects, when compared to pure ceria. The catalytic activity correlated with the concentration of surface oxygen defects, demonstrating that maximizing the nature of the defective surface is a key factor in producing catalysts with enhanced performance.

A silica modified alumina catalyst supported on a structured cordierite monolith was used by El Assal et al. for the total oxidation of dichloromethane [3]. Chlorinated VOCs are some of the most difficult to catalytically oxidize, and they also have significant harmful environmental chemistry. Monoliths with two different channel densities were investigated, and the activity of the catalysts were also determined with and without platinum added by impregnation. High conversion of dichloromethane (>80% at 500 °C) was obtained over the different catalysts on the monolith with 200 channels per square inch, with the most active silica alumina catalyst containing 10 mol% silica. In addition to CO_2 , several by-products such as CO , CH_3Cl , and CH_2O were formed. The amount of by-products were reduced by increasing the silica content, whilst they were significantly reduced when platinum was added. However, platinum addition did not increase conversion, and only increased selectivity to CO_2 . Characterization of the washcoat and comparison with the powdered catalyst showed that the physiochemical properties of the powdered catalyst were retained after the coating process. Key factors of the cordierite monolith affecting performance for dichloromethane oxidation were a low value of the open fraction area, the hydraulic diameter, thermal integrity factor, and the high value of the mechanical integrity factor and geometric surface area.

Zheng et al. studied a range of activated carbon catalysts, modified by various treatments, for the oxidative degradation of ortho-chlorophenol [4]. Ortho-chlorophenol was selected for study as it is an appropriate model for dioxins, which are highly toxic and produced from many incineration and industrial processes. Activated carbon was modified by chemical treatment and by the addition of metal components. For chemical treatments, modification by ammonium hydroxide was the most effective, removing 82% of chlorophenol at 330 °C. Generally, modification by the addition of a metal produced more active catalysts; the best contained cobalt and vanadium, and both removed 93% chlorophenol at 330 °C. Significant differences in product selectivity were observed, ammonium hydroxide treatment produced further dioxin products, whilst vanadium treatment gave complete oxidative conversion. Based on characterization studies and the analysis of the reaction products, different mechanisms were proposed for the vanadium and ammonium hydroxide treated catalysts, providing important understanding in the development of more effective catalysts for the control of dioxin emissions.

As mentioned, many catalysts for VOC oxidation use active precious metal components, but there are relatively few studies that have employed bimetallic catalysts. Using a supported bimetallic palladium-gold catalyst on a hierarchical titania support doped by various elements, Barakat et al. investigated the total oxidation of toluene [5]. The study builds on earlier work that showed there was a catalytic synergy between gold and palladium, and that doping the titania increased activity for VOC oxidation. The study explored the stability of the catalysts over a prolonged time-on-stream. The vanadium containing catalysts demonstrated high stable activity over the 110 h test period. However, whilst doping with niobium also produced a high activity catalyst, it exhibited a surprising cyclic toluene conversion. Diffuse reflectance infrared Fourier transform spectroscopy experiments under operating conditions showed that the presence of varying hydroxyl radicals and carbonaceous species on the catalyst surface were related to the cycling behavior. Further surface analysis revealed that metal-support interactions increased the concentration of mobile oxygen species and enhanced the reducibility of palladium. Accordingly, the cyclic observations of activity were attributed to an enhanced redox scheme.

The adsorbent performance and regeneration process of the sodium form of zeolite Y and silica materials were investigated, with and without platinum, by Yeh et al. for the removal of ethanol [6]. The ethanol adsorption capacity of the material containing platinum was approximately 2.5 times greater than the same material without platinum. After regeneration at high air flow, the platinum containing material demonstrated only a slight decrease in adsorption capacity, whilst without platinum, the adsorption capacity reduced by 8%. Spectroscopic infrared analysis revealed that carbonaceous deposits remained on the surface after regeneration without platinum, but the addition of platinum resulted in the removal of carbonaceous deposits to allow for the restoration of the adsorption capacity. These findings show that the platinum component has a catalytic effect for the oxidation of surface carbon species during regeneration, exerting an important role in the application of the material as an adsorbent. The slight reduction of the adsorption of the Pt-NaY-SiO₂ after regeneration was attributed to a degree of platinum agglomeration from CO at low air flows.

VOCs are primarily aerial pollutants; however, organic species are also common pollutants of water, and catalysis has an important role for water treatment. An article in this Special Issue focuses on this application. Bertram and Nee investigated the fabrication of polydimethylsiloxan beads, which incorporated TiO₂ and was made using a microbubble technique [7]. The approach produced an effective microstructured low-density photocatalyst that was buoyant in water. Synthesizing buoyant photocatalysts with high activity is a key challenge for their deployment in water cleaning processes. The intrinsic photocatalytic activity of TiO₂ was retained on incorporation into the polymer bead surface because synthesis was carried out at low temperature and retained the crystalline TiO₂ structure. Photocatalytic degradation of methylene blue was faster than other buoyant catalysts, and only an order of magnitude slower than a catalyst suspended in solution. This is significant as the buoyant catalyst was only in contact with the water surface; furthermore, no loss of performance was observed on the reuse of the catalyst for five cycles.

In conclusion, this Special Issue brings together a collection of articles concentrating on the removal of a range of organic species using catalytic oxidation. It highlights the broad range of pollutants that have to be dealt with as well as the diversity of approaches and catalysts that can be used. Although we have made progress in developing improved catalysts and understanding how they operate, challenges still remain that need to be overcome, so that we have options to use catalysts to control emissions of all organic pollutants.

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