Commentary on industrial processes

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A brief commentary on the three papers presented in the session on ‘industrial processes’ is presented. In particular, emphasis is placed on the factors considered to be crucial for an industrial process, namely: catalyst activity, the selectivity of the overall catalysed reaction and the lifetime over which the performance is observed. Control of selectivity is viewed as being most important, and examples of how this is achieved through the use of membrane reactors and catalyst design are described.

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The three preceding papers (McLeary et al. 2005; Ratnasamy et al. 2005; Twigg 2005) highlight a number of factors that are of crucial importance in the application of catalysis to industrial processes. The papers, however, do not represent a step change from those preceding them, rather there is a continuous flow of catalysis as pure science into applied catalysis, and these papers ably demonstrate the continuous thread of the subject. Professor Catlow, in opening his lecture in an earlier session, stated that the purpose of the discussion meeting was the ‘development of an understanding of catalysis at a molecular level’. It is this understanding that aids the application of catalysis to industrial practice, and the three papers on this topic emphasize the statement made by Catlow.

Although fundamental understanding lies at the heart of successful commercialization of catalytic science and technology, there are three factors that have to be addressed in any industrial process, namely:

(i) **activity**—the amount of product made per unit mass of catalyst per unit time (mol product kg\(^{-1}\) catalyst h\(^{-1}\));
(ii) **selectivity**—the catalyst needs to make sufficient product and minimize by-product formation; and
(iii) **lifetime**—the catalyst has to be durable.

Of these, it can be argued that selectivity is now considered to be the most important. Catalyst activity at the industrial scale can be regulated by the amount of catalyst used in the application, whereas reactor design currently permits the use of catalysts with lifetimes ranging from a few seconds to decades. The current emphasis on green chemistry, however, has strengthened the need for catalysts that give only the desired products, since the disposal of unwanted products is problematic.

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by-products is rapidly making many processes non-competitive. It is in this area that catalysis has made dramatic innovations in recent years, and the three papers on industrial processes highlight all these points.

Professor Maschmeyer selected membrane catalytic reactors in view of the important advances being made in this field (McLeary et al. 2005). However, given the importance of membranes in biological systems for the control of the supply or removal of key reagents, this topic is ideal for highlighting some of the potential similarities in biological and chemical catalysis. Maschmeyer has highlighted four applications that exemplify the main ways in which inorganic membranes can be used in industrial processes; for example the removal of H$_2$ from dehydrogenation reactions to drive the thermodynamically limited reactions, or the control of oxidant delivery in selective oxidation to limit over-oxidation. In the past 10 years, significant advances have been made in the reproducibility and durability of inorganic membranes, in particular the fabrication of microporous zeolites on oxide or metal substrates, as described by Professor Thomas in his introductory lecture. In this respect, Maschmeyer is correct in highlighting their use, since now is the time for the catalysis community to embrace a more widespread investigation of these materials. Maschmeyer highlighted the potential for the use of membranes in the production of fuels since they permit simultaneous conversion and separation, thereby driving operation beyond equilibrium limits. While we can anticipate that the initial commercial application will be in the production of improved fuels, Maschmeyer highlighted the need to improve oxidation processes, and it is here that membranes offer immense scope, particularly for the direct oxidation of benzene to phenol. Phenol is a commodity chemical that is produced in high tonnages but the current process requires the co-production of acetone. Membranes will offer the scope to decouple phenol synthesis from acetone manufacture since the membrane permits effective control of the oxidant delivery for the difficult chiral oxidant of benzene.

In the second presentation, Dr Ratnasamy (Ratnasamy et al. 2005) emphasized the progress that has been achieved in the design of oxidation catalysts on the basis of clean technology. In this respect, emphasis was placed on improved atom efficiency with the use of oxygen and hydrogen peroxide as oxidants in place of stoichiometric oxygen donors. At present, many oxidation reactions carried out in the fine chemicals industry use non-green technology that has been operating for decades. It is in this arena that catalysis can play a major role. Ratnasamy highlighted a number of valuable new catalysts which are effective for the oxidation and hydroxylation of hydrocarbons crucial for the manufacture of chemical intermediates in the production of polyester fibres, polycarbonates, etc. The availability of new metallosilicates in recent years has also been advantageous. In this respect, the development of the well-documented titanosilicalite molecule sieve TS-1 has been most significant, as it effectively catalyses the oxidation of benzene to phenol, toluene to cresols, and phenols to catechol and anthraquinone. Ratnasamy also exemplified a further approach in the design of benign oxidation catalysis, namely the encapsulation of metal complexes within microporous and mesoporous frameworks. In this respect, the use of copper acetate dimers within zeolites as a catalyst for the regioselectivity oxidation, with O$_2$, of L-tyrosine to L-dopa, represents a clear example of

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the progress achieved in this field. Similarly, the encapsulation of copper phthalocyanine complexes with zeolite Y using a ‘ship-in-a-bottle’ synthesis provides an elegant example of how encapsulation can manipulate the stereochemistry of metal complexes to produce highly strained structures with enhanced reactivity.

The emphasis in the final presentation by Dr Twigg (Twigg et al. 2005) concerned small molecule reactions and the removal of pollutants in car exhausts. The introduction of this catalytic technology has made major contributions to air quality around the world and represents one of the most significant recent examples of the success of the application of catalytic technology to solve a long-standing problem. Twigg emphasized how a detailed understanding of metal and metal oxide stability and volatility plays a major part in the design of effective catalysts. In effect, only two metals, Pt and Pd, meet the stringent requirements on these two operating parameters. Twigg also emphasized that these catalysts have to operate under non-steady state conditions to achieve the reduction of both NO\textsubscript{x} compounds, as well as hydrocarbon and carbon monoxide, since these two classes of pollutants require different oxygen concentrations together with the catalyst to ensure near complete conversion. This transient operation of a catalyst is something that can and should be applied in other processes, and we can expect major advances in this in the future. Many of the points made by Twigg were applicable to both petrol and diesel emissions but, in the latter part, he addressed the pressing need to control the emission of carbon particulates from diesel engines. The key here appears to be a recognition that, although carbon is not readily oxidised by oxygen at temperatures lower than 500 °C, a temperature inaccessible for the catalytic converter downstream of a diesel engine, if NO\textsubscript{2} is used this reaction proceeds rapidly at 250 °C. Hence, the carbon particulates are trapped on a porous filter and oxidized by NO\textsubscript{2} that is generated from the oxidation of NO that is continuously recycled. This example shows great ingenuity in solving a difficult problem and, I am confident, is just a harbinger of major future applications of catalytic science in industrial processes.

References

