

Editorial

Reflections on Catalytic Selective Oxidation: Opportunities and Challenges

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Currently, and looking forward, there is an ever increasing demand to perform chemical transformations with optimized atom and energy efficiency. In parallel, there is also growing interest in diversification of chemical feedstocks from more traditional ones. For example, effective and economic transformation of biorenewable chemical feedstocks and shale-gas, are just two that can be highlighted. These targets are demanding and challenging, and the required shift in industrial production of energy and chemicals will not be possible without advances in catalysis.

This Special Issue focuses on selective catalytic oxidation, as it offers significant potential as an approach to achieving green and efficient chemical transformations of a broad range of substrates. Selective oxidation offers many challenges, not least of which is the control of product selectivity to the required products. Control of selectivity can be particularly challenging, as the desired products are less thermodynamically favoured compared to carbon oxides. This can be a particular problem if high temperatures are required to activate stable molecules, as these conditions can result in significant sequential over-oxidation of the desired products. A number of strategies have been developed to minimise such affects, and perhaps one of the most common is to utilise oxidants which are more active than molecular oxygen. A number of oxidants can be employed for selective catalytic oxidation, and depending on scale, reaction efficiency and relative cost of the oxidant and product, specific oxidants can be economic to use (e.g., hydrogen peroxide). However, the use of molecular oxygen, preferably directly from air, to achieve high yields of target products selectively must be the ultimate aim.

There are some large scale selective catalytic oxidation processes that operate commercially. Formaldehyde is a bulk commodity chemical with a large worldwide market, it has many important uses, with major applications for thermosetting resins, manufacture of polyurethane foam, thermoplastics and adhesives. The two major industrial processes for production of formaldehyde are from the catalytic oxidation of methanol. One method is via an oxidation-dehydrogenation reaction using a silver-based catalyst. The alternative is direct oxidation of methanol to formaldehyde by oxygen using a mixed metal oxide iron molybdate catalyst [1]. The iron molybdate catalysed process is becoming increasingly prevalent, since it operates at a lower temperature than the silver catalysed process, and the catalyst is more robust. These advantages mean that the cost per tonne of formaldehyde production using iron molybdate catalysts is lower and yields a higher return on capital investment [2]. The industrial iron molybdate catalyst consists of a mixed metal oxide phase, $\text{Fe}_2(\text{MoO}_4)_3$, together with excess MoO_3 . $\text{Fe}_2(\text{MoO}_4)_3$ is considered to be the active/selective phase, with MoO_3 being selective but with low activity, and Fe_2O_3 unselective forming CO_2 . It has been reported that the catalyst must contain both $\text{Fe}_2(\text{MoO}_4)_3$ and excess MoO_3 in order to achieve high activity, selectivity and life-time. Catalyst deactivation is due to loss of molybdenum, and it is proposed that the excess MoO_3 ensures that no iron rich phase is formed during the catalyst lifetime. Hence, although the iron molybdate catalyst is used industrially, and has been for many years, scope still exists to develop improved catalysts and improve our understanding of the process.

One area in which selective catalytic oxidation has huge potential to contribute is for the direct conversion of alkanes. One current process that stands out in this field is vanadium phosphate catalysts, which are important industrial catalysts employed for the selective oxidation of *n*-butane to maleic anhydride by molecular oxygen [3]. $(VO)_2P_2O_7$ is the acknowledged active phase of Vanadium Phosphate catalysts for *n*-butane selective oxidation charged into the reactor. It is usually prepared through calcination of $VOHPO_4 \cdot 0.5H_2O$, which undergoes a topotactic transformation to retain the precursor morphology in the final catalyst.

The introduction of oxygen into an alkane through selective oxidation is conceptually very simple. However, practically it is difficult to achieve at levels of activity and selectivity that would currently be required for processes that are efficient enough to be economically viable. Nevertheless the selective catalytic oxidation of *n*-butane to maleic anhydride is a tangible indicator that it is achievable. One of the greatest and longstanding challenges in selective catalytic oxidation is the direct conversion of methane to methanol. The strong C–H bond in methane has meant that many approaches trying to use oxygen have employed high temperatures to activate the molecule. Consequently, over many decades the literature contains examples of numerous different catalysts used for gas phase methane selective oxidation, but none of these demonstrate outstanding performance [4].

Some of the most successful catalysts systems for methane partial oxidation have adopted approaches like using strong acids to activate the C–H bond, and some of these approaches are promising, but could be difficult to put into application. It is possible to draw inspiration from nature, as there are enzymes that can oxidise methane, and other alkanes, selectively to oxygenates under mild conditions, demonstrating fundamental feasibility. Against this background there are examples of heterogeneous catalysts that can oxidise methane and ethane selectively to oxygenated compounds, but generally these utilise hydrogen peroxide as the oxidant, examples of recent work in this area for ethane selective oxidation are included in this Special Issue [5].

An interesting area of research for selective oxidation has seen a focus on lower temperature approaches in the liquid phase, as opposed to gas phase approaches at higher temperature [6]. In particular, the use of supported metal nanoparticles demonstrates great promise. As mentioned above, some of these approaches use hydrogen peroxide, but there is also a considerable number that use molecular oxygen. For example, gold-palladium nanoparticles supported on titania are able to selectively oxidise toluene to benzyl benzoate with an exceptionally high yield under relatively mild conditions [7]. There are other examples of selective toluene oxidation that use metal oxide-based catalysts [8]. Metal nanoparticle catalysts have been very successful for the selective oxidation of a wide range of substrates for many less demanding reactions, like the selective oxidation of alcohols [9]. The Special Issue contains examples of selective oxidation driven by light using gold-based catalysts [10], and selective oxidation of ethers [11]. Lower temperature oxidation opens up possibilities of transforming low value biorenewable feedstocks, such as glycerol into more valuable chemical products [12]. These areas have now become major topics of research for selective oxidation using supported nanoparticulate catalysts.

Catalytic selective oxidation also opens other potential routes for chemical transformations, which can show advantages over other chemical pathways. A good example of this is the partial oxidation of short chain alkanes to alkenes by oxidative dehydrogenation (ODH). Dehydrogenation of alkanes to the corresponding alkenes is thermodynamically limited and high temperatures are required to achieve acceptable equilibrium yields. The switch to an oxidative route removes such limitations, but control over selectivity to the desired alkenes at acceptable levels of conversion is key to success [13]. For short chain alkanes the relatively high temperatures required using metal oxide and phosphate catalysts result in over oxidation of the alkene products with the formation of carbon oxides. The key features of the catalyst are discussed in the Special Issue, and it is clear that progress in catalyst development is being made, but further improvements are necessary [14]. It may be that totally new approaches are required to achieve commercial targets.

The range of possible applications for selective catalytic oxidation is vast; and so far its potential has not been fully realised. For example, it can be employed for efficient transformation of existing petrochemical feedstocks, or, equally, to provide new routes for the production of useful chemicals from bio-derived sustainable feedstocks. There is also the possibility to carry out ammoxidation reactions, and this is an area that is being actively studied [14,15]. Furthermore, selective oxidation can have an important role in preferentially oxidising one component over another in a mixture of the components, such as oxidising carbon monoxide selectively in hydrogen, for applications such as fuel cells. Although advances are continually being made in catalyst discovery and development, there is still a requirement to produce high yields of desired products for many reactions employing selective catalytic oxidation. Hence, there are still many challenges to be met in this field of catalysis research and plenty of opportunities to make a real impact for chemical manufacture and upgrading.

Conflicts of Interest: The author declares no conflict of interest.

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