Lowering the operating temperature of selective oxidation catalysts

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By incorporating palladium into oxidative dehydrogenation catalysts, a key step in the usual Mars–van Krevelen redox cycle has been by-passed, resulting in a decrease in operating temperature of around 200 °C.

In the partial oxidation of hydrocarbons by gas-phase oxygen, the desired reaction (*i.e.* oxidative dehydrogenation, oxygen insertion, or ammoxidation) has to compete with total combustion. In general, chemisorbed oxygen will react with adsorbed hydrocarbons to generate waste products, unless it can first form lattice oxide ions—the species implicated in selective partial oxidation.[1] By definition, therefore, metals usually catalyse total combustion, while metal oxides have the potential to generate added-value products. This potential is realised when hydrocarbon molecules are adsorbed near available oxide ions, which in turn can be replenished as soon as they are consumed in the selective reaction.

The parent materials used in this study, iron(III) oxide and bismuth molybdate, both belong to a category of catalysts that function by a cyclic redox mechanism, first described by Mars and van Krevelen.[2] In this cycle, the mobility of oxygen through the lattice is crucial to the overall process of replenishing oxide ions close to the hydrocarbon adsorption sites. Since the mobility of lattice oxygen is strongly dependent on temperature, it can become rate limiting when the operating temperature is lowered.[3] Eventually, a threshold is reached (usually at about 300 °C), below which the mobility is so low that the oxide has negligible catalytic activity. However, we have been able to induce partial oxidation activity at operating temperatures within the range 100–200 °C and even lower, by incorporating palladium into Fe_2O_3 and Bi_2MoO_6. This dramatic reduction in temperature is brought about by a change in the prevailing reaction mechanism.

The method by which Pd is introduced into the metal oxide is critical to inducing low temperature activity. We have found that controlled precipitation is the optimum route, resulting in reproducible catalysts that do not require any special activation procedures. The incorporation of Pd into iron(III) oxide (Pd–Fe–O) and bismuth molybdate (Pd–Bi–Mo–O) is described in detail in a family of patent filings.[4]

XPS of freshly dried precipitate of Pd–Fe–O (as used in activity tests) showed Pd in the +2 state (Pd $3d_{5/2}$ E_b = 337.3 eV) and Fe in the +3 state (Fe $2p_{3/2}$, E_b = 710.6 eV). XRD revealed the material to be amorphous, which was also the case when the precipitation was carried out in the absence of Pd.

As bismuth molybdate catalysts require calcination in order to form the active binary phases,[5] our precipitate of Pd–Bi–Mo–O was also subjected to the same thermal treatment, before characterisation and testing. XRD of the calcined Pd–Bi–Mo–O showed it to be a mixture of α-bismuth molybdate (monoclinic $Bi_2Mo_3O_{12}$) and β-bismuth molybdate (monoclinic $Bi_2Mo_2O_9$), with no evidence of a crystalline Pd-phase. Without Pd, the bismuth molybdate catalyst was also a mixture of two allotropes, but these were the β- and γ-(orthorhombic Bi_2MoO_6) forms.

In common with other metal oxides, conventional catalysts derived from iron oxide are not active for butene oxidation below 300 °C.[6] However, when fresh samples of Pd–Fe–O made by coprecipitation were exposed to a feed of 14% but-1-ene in air at 100 °C, there was a delay (2–10 min, depending on Pd content) and then reaction began. Starting temperatures as low as 80 °C (for a catalyst containing 4% Pd by mass) and 60 °C (10% Pd) were recorded. In order to assess whether this low temperature activity was due to a synergy between the palladium and iron oxide phases or was primarily a result of the preparative method, we also tested palladium oxide and iron oxide prepared by essentially the same precipitation method. Neither showed any activity at such low temperatures. However, some reduction in operating temperature could be induced by impregnating Fe_2O_3 with Pd (4% by mass). This material was capable of achieving 50% butene conversion with 35% selectivity to butadiene at a feed temperature of 200 °C, but showed no activity below 150 °C.

Initial butadiene yield of the coprecipitated Pd–Fe–O catalysts was poor (*ca.* 10%), and their sensitivity to the butene/air feed ratio was high. During the first few hours on line, the yield improved and the sensitivity declined, before stabilising. For example, after 5 h on line, 4%Pd–Fe–O converted 50% of the hydrocarbon in a 20% butene/air feed with 70% butadiene selectivity; after the same time in a 14% butene/air feed, it converted 55% with 60% selectivity. The on-line improvement in yield appeared to be closely related to the blocking of non-selective (combustion and isomerisation) sites by carbon. As shown in Table 1, the catalysts could be 'regenerated' by heat treatment in flowing air (550 °C), during which the retained carbon was displaced as CO_2.

Pd–Bi–Mo–O required a higher operating temperature and a leaner hydrocarbon feed (12.5% butene/air) than Pd–Fe–O. After no activity was observed at 150 °C, the bed temperature was raised to 200 °C, whereupon reaction began as soon as the gas feed was introduced. The initial conversion of butene was 55%, with 45% selectivity to butadiene. Again, the performance improved with time, before stabilising after 30 min at 60% conversion and 60% butadiene selectivity. By contrast, unmodified bismuth molybdate showed only short-term activity under the same conditions (Fig. 1). Its temperature had to be raised to 350 °C before activity could be sustained (80% conversion; 70% selectivity). The fact that the selectivity of Pd–Bi–Mo–O (at 200 °C) was not as high as that of the unmodified bismuth molybdate (at 350 °C) may reflect the change in phase composition caused by the presence of Pd.

Both Pd–Fe–O and Pd–Bi–Mo–O are derived from catalysts that conform to a redox mechanism, in which the movement of

Table 1 Oxidation of butene over 4%Pd–Fe–O as function of catalyst condition[a]

Catalyst condition	Conversion/ (%)	Selectivity (%)			
		CO_2	*trans*-But-2-ene	*cis*-But-2-ene	Butadiene
Fresh	65	45	14	12	15
Aged on line	54	36	3	2	59
Regenerated	70	42	13	11	21

[a] Feed: 14% butene/air; contact time: 0.6 s; feed temperature: 100 °C.

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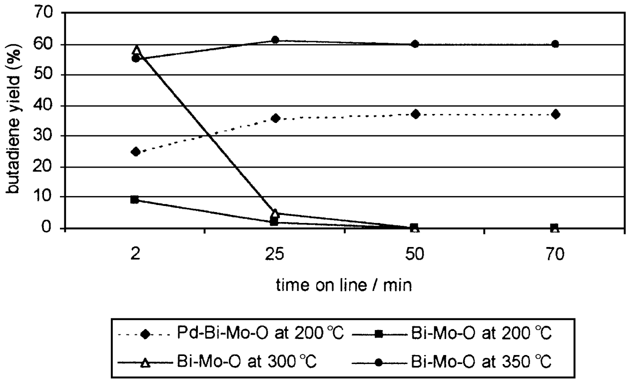

Fig. 1 Yield of butadiene as a function of time, over unmodified and Pd-modified bismuth molybdate, at operating temperatures of between 200 and 350 °C (feed: 12.5% butene/air; contact time: 0.6 s).

lattice oxygen is a key step in the selective partial oxidation of hydrocarbons.[7] The performance (preferred feed-composition; product distribution; activity/selectivity correlation) of the Pd-containing materials is similar to that of the unmodified catalysts, except in terms of operating temperature. Our working model, therefore, is one in which the same alkene adsorption sites are present in both forms, but the role of Pd is to supply selective oxygen at lower temperatures, by-passing the need for transport through the lattice.

A TAP study of the initial steps in the butene to butadiene reaction over 4%Pd–Fe–O, compared to a conventional α-Fe_2O_3 catalyst, provides support for this model.[8] Even at 150 °C, unmodified Fe_2O_3 is capable of converting butene/O_2 to butadiene, but only for a short time. At this temperature, it only forms butadiene, while it is consuming O_2. Although the same applies to Pd–Fe–O, it continues to consume O_2 indefinitely. The presence of the Pd enables the catalyst to activate gas-phase oxygen into selective species at low temperatures, leading to sustainable oxidative dehydrogenation under conditions where Fe_2O_3 does not usually function.[6] This mechanistic short cut enables low-temperature activity to be achieved by redox catalysts in which oxygen mobility would normally be the limiting factor. It cannot, however, overcome some of the other factors (such as product desorption) that can prevent low-temperature activity—as we have found to be the case for the conversion of propene to acrolein over Pd–Fe–O and Pd–Bi–Mo–O.

During the past thirty years, there have been a number of reported examples of heterogeneously catalysed oxidation reactions at unexpectedly low temperatures. In most cases, the reaction has been the total oxidation of a simple molecule.[9–13] Furthermore, these instances of low-temperature activity have appeared to be isolated and exceptional effects, associated with very specific compositions, preparations or interactions. We believe that our studies of Pd-incorporation into metal oxides illustrate a more general phenomenon that can allow the normal activity of a redox catalyst to be achieved at temperatures much lower than previously expected. Indeed, the Pd–Fe–O family of catalysts is particularly versatile, exhibiting catalytic activity at exceptionally low temperatures for CO oxidation[14] and the water–gas shift reaction,[4] as well as for the partial oxidation of hydrocarbons described here. For each reaction, the minimum operating temperature is about 250 °C below that observed for unmodified iron(III) oxide.

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