Selective catalytic reduction of O_2 with excess H_2 in the presence of C_2H_4 or C_3H_6

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The selective reduction of molecular oxygen with excess H_2 in the presence of alkenes was achieved successfully for the first time: silver supported on alumina catalysts exhibited full conversion of O_2 at temperature as low as 50 °C, while the conversion of ethene or propene remained essentially zero up to 250 °C.

New chemical processes based on the addition of molecular oxygen as an oxidising agent, *e.g.* autothermal reforming (ATR), non-catalytic partial oxidation (POX), catalytic partial oxidation (CPO), are gaining interest for the production of syngas, alkenes and hydrocarbons from various feedstocks, *e.g.*, natural gas, light alkanes, higher hydrocarbons, biofuels and alcohols.[1–6] Using these methods will potentially result in the presence of O_2 impurities in the reactor effluent.[7] Any chemical process involving a hydrocarbon feedstock can potentially be hampered by the presence of molecular oxygen in the reaction feed, as many homogeneous and heterogeneous catalysts are readily poisoned or decomposed by trace levels of O_2. The utilization of selective oxygen traps and distillation techniques are commonly used to decrease the concentration levels of dioxygen. When the residual dioxygen concentration is small and large concentrations of dihydrogen is also present in the feedstock, it may be practical to react these two molecules and form water, which can be easily removed, to further lower the levels of O_2. Obviously, any catalytic material to be used for this matter should not trigger any reaction of the hydrocarbon with either the hydrogen or oxygen in the feed.

Ethene, when used as a monomer for the production of polyethene, must be sufficiently pure to be sent to the polymerization reactor. Trace amounts of dioxygen in part per million quantities can impede polymerization and decrease product yield.[8] The objective of this study was to remove traces of molecular oxygen in an H_2-rich alkene feed (ethene or propene) by reducing the O_2 with the hydrogen present, while preventing the hydrogenation or oxidation of the unsaturated hydrocarbon. Surprisingly, no studies have reported the selective

catalytic reduction of O_2 with excess H_2 in the presence of light alkenes, apart from a patent report in which a Pd-based catalyst was used in combination with sulfur compounds continuously added to the feed.[9] The addition of sulfur compounds to the reaction stream appeared crucial to prevent alkene hydrogenation.[9] Within the present study, a number of catalytic formulations were screened based on Pd, Pt, Cu and Ag with silver supported on alumina or silica showing the most effective activity/selectivity combination which resulted in the removal of the molecular oxygen without leading to removal of ethene or propene. Note that no sulfur compounds were added to our reaction streams.

The catalysts with different metal loadings on the alumina support (Saint-Gobain) were prepared by incipient wetness impregnation at room temperature. The metal precursors used were $AgNO_3$ and $Cu(NO_3)_2$ (Riedel-de-Haën). The appropriate amount of metal precursor was dissolved in distilled deionised 18.2 MΩ water, and then added on the support whilst stirring. The impregnated sample was dried at 80 °C for 12 h and then calcined at 630 °C for 6 h. The metal contents were determined by AAS (atomic absorption spectroscopy) following dissolution of the catalysts in corrosive solutions. The catalytic tests were conducted at ambient pressure using stepwise isotherms between room temperature and 250 °C. The reactor effluents were analysed by on-line gas-chromatography using a gas chromatograph fitted with packed columns (molecular sieve, Chromosorb B and Haysep A, N and T) and TCD and FID detectors. The gases measured included H_2, O_2, CO, CO_2, ethane, ethane, ethyne, propene and propane. The gas hourly space velocity was set at 20 000 h^{-1} with a the total flowrate of 33 cm^3 min^{-1}. The feed composition was 0.2% O_2 + 38.5% H_2 + 18% C_2H_4 or C_3H_6 (balance He).

The alumina support used exhibited a low activity above 100 °C, displaying *ca.* 7% hydrogenation of ethene to ethane and an O_2 conversion of *ca.* 6% at 250 °C (Fig. 1). The fact that alumina can hydrogenate alkenes was already reported and was associated with the presence of Lewis acid and base pairs at the interface between alumina and boehmite domains.[10] Two alumina-supported catalysts based on palladium (0.5 wt%) and platinum (5 wt%) (both samples supplied by Johnson Matthey) were tested; however, although these materials gave complete conversion of O_2 at 60 °C, complete conversion of C_2H_4 to C_2H_6 was also observed (data not shown). In order to reduce the hydrogenation activity, a 1 wt% Cu/Al_2O_3 was also investigated. Some selectivity for O_2 removal over C_2H_4 reaction was observed at 200 °C; however, at higher temperatures significant hydrogenation

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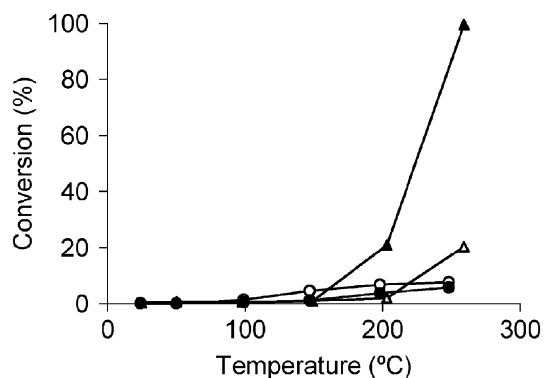[c] Johnson Matthey plc, Orchard Road, Royston, Hertfordshire, UK SG8 5HE

Fig. 1 O_2 (solid symbols) and ethene (open symbols) conversions measured over Al_2O_3 (circles) and 1% Cu/Al_2O_3 (triangles). Feed 0.2% O_2 + 38.5% H_2 + 18% C_2H_4 (balance He).

activity was found with >20% conversion to ethane at 100% conversion of O_2 (Fig. 1).

In contrast, the silver-based catalysts showed excellent O_2 reduction activity, in general, without the concomitant ethene hydrogenation occurring (Fig. 2). Between 0.4 and 7.6 wt% Ag/Al_2O_3 catalysts were compared and showed a decrease in the O_2 reduction light-off temperature with increasing silver loading with 100% O_2 conversion reached at approximately 50, 100 and 150 °C for the 7.6, 1.4 and 0.4% loadings, respectively.† In each case the ethene conversion was negligible (<1%), within the experimental error. Similar results were obtained when supporting the silver on high surface area silica (data not shown).

It is interesting to note that the ethene conversion measured in the case of the bare support was significantly higher than that observed in the case of the sample impregnated with silver. It must be concluded that the presence of silver induced a direct (e.g. via site blocking) or indirect (e.g. via reactant activation) modification of the activity of the support.

The activity of the silver-alumina catalysts was also tested for the O_2 reduction in the presence of propene, to assess whether the outstanding activity pattern was also observed in the case of the presence of an alkene with an allylic hydrogen. The reaction carried out with propene in place led to almost identical results (Fig. 3) as those obtained in the case of ethene
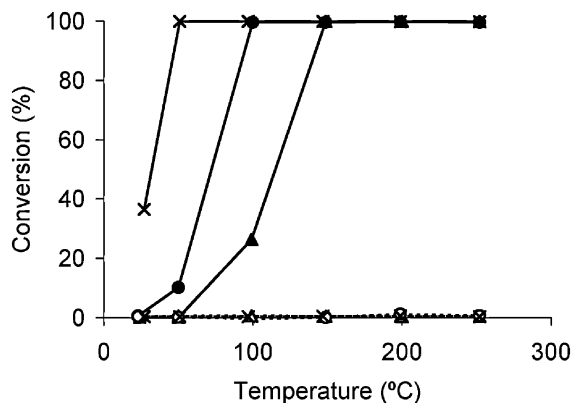

Fig. 2 O_2 (filled symbols) and ethene (open symbols) conversions measured over γ-Al_2O_3–supported catalysts with various silver loadings: 0.4 wt% (triangles), 1.4 wt% (circles) and 7.6 wt% (crosses). Feed 0.2% O_2 + 38.5% H_2 +18% C_2H_4 (balance He).
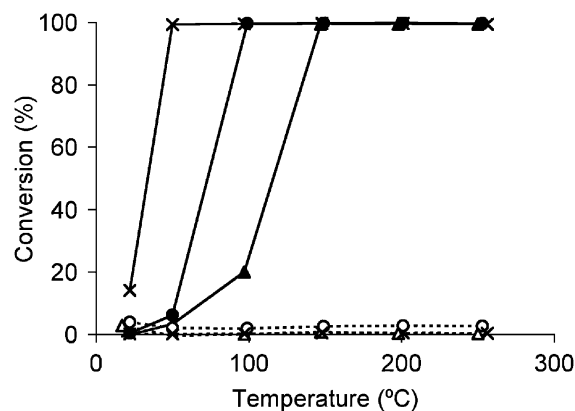

Fig. 3 O_2 (filled symbols) and propene (open symbols) conversions measured over γ-Al_2O_3–supported catalysts with various silver loadings: 0.4 wt% (triangles), 1.4 wt% (circles) and 7.6 wt% (crosses). Feed 0.2% O_2 + 38.5% H_2 + 18% C_3H_6 (balance He).

(Fig. 2). Less than 3% propene conversion was observed, while O_2 reduction was completed at temperatures that were identical to that measured in the ethene case.

The outstanding activity for the selective catalytic reduction of O_2 with excess H_2 in the presence of alkenes observed over the silver-based materials can be rationalized by the fact that (1) silver is known to activate O_2, as in the O_2 + H_2 reaction, ethene epoxidation[11–13] and (2) silver is a poor hydrogenation catalysts, compared with Pt and Pd.[14,15] Moreover, silver is used as a promoter of Pd-based acetylene hydrogenation catalysts used for ethene purification, as the addition of silver strongly inhibits the hydrogenation of ethene to ethane.[16,17]

The combined effect on the 1.4% Ag/Al_2O_3 activity of several gases typically found in hydrocarbon feedstocks was also investigated. 4.8% of carbon monoxide, 2% of carbon dioxide, 0.14% of butadiene and 0.15% of ethyne were added to the ethene-containing feed. Full O_2 conversion was only attained at ca. 200 °C (data not shown), while O_2 removal was already completed at 100 °C in the absence of the additional gases (Fig. 2). Examination of the effect of each individual component indicates that ethyne has the only significant affect and this inhibits the reduction of O_2. Apart from O_2, ethyne was the only molecule that was partly converted, into ethene, leading to a slightly negative ethene conversion value. No ethane was observed. Despite the inhibition observed, it is important to stress that the catalyst remained able to fully reduce O_2 while preventing ethene hydrogenation.

Long term activity tests were performed at 78 °C over 120 h using 1.4 wt% Ag/Al_2O_3 with 0.2% O_2 + 38.5% H_2 + 18% C_2H_4 (balance He) as the feed conditions (data not shown). Although significant deactivation of the catalyst was found with the O_2 conversion dropping rapidly from ∼80 to 50% over the first 10 h, thereafter a much reduced rate of deactivation was observed. Between 10 and 120 h the conversion decreased from 50 to 40%. Following reoxidation of the catalyst at 200 °C, the activity is fully recovered and indicates that this is possibly due to coke formation on the catalyst. Temperature-programmed oxidation of the used catalyst evidenced several CO_2 formation peaks associated with various types of carbonaceous deposits (data not shown). The role of each of those is under investigation. A TEM analysis of the

silver particle size was carried out over the fresh, reduced and used samples (measuring more than 200 particles in each cases). These data show that most of the silver particles have a diameter comprised between 1.5 and 4 nm, but a few very large particles (24 nm) were also observed (data to be reported elsewhere).

To summarise, the selective reduction of molecular oxygen with excess H_2 in the presence of alkenes (ethene and propene) was achieved successfully for the first time. Silver supported on alumina catalysts exhibited full conversion of O_2 at temperature as low as 50 °C, while no significant conversion of the alkene was found up to 250 °C. The combined addition of CO, CO_2, ethyne and butadiene to the feed did not induce any ethene hydrogenation, but resulted in a poisoning that required higher reaction temperatures to maintain full O_2 conversion. The results reported here open the way to new strategies in the way O_2 impurities can be removed from hydrogen-rich alkene-containing feedstocks.

Notes and references

† As an example, the rate of O_2 reduction obtained in the case of the 1.4% Ag/Al_2O_3 at 50 °C was 0.1 µmoles g^{-1} s^{-1}.

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