

Activation of alkanes by gold modified lanthanum oxide

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Introduction

Direct activation of alkanes and their conversion to light alkenes, preferably to ethene and propene, is a topic of significant interest to both industry and academia. Currently, many catalysts are based on the use of platinum group metals or first row transition metals, due to the availability of empty d-orbitals, which are needed to activate the C-H bond, which is normally the rate determining step [1, 2]. In these cases, selectivity is often an issue as the products, are more reactive than the starting material and the temperatures needed to activate the reactants lead to over oxidation to CO_x.

Reported here is the first highly active, selective and, notably, stable supported gold based catalyst for the partial oxidation of C₂₊ aliphatic alkanes to alkenes, namely *n*-butane into light alkenes, using molecular oxygen. This reaction is of particular industrial importance due to the fact that *n*-butane is an abundant undesirable side product of steam cracking of naphtha [3].

Experimental

Gold catalysts were prepared by deposition-precipitation with a number of supports (La₂O₃, CeZrO₄, ZrO₂, TiO₂ and Nb₂O₅). Differential reaction conditions were used for comparison of the catalysts performances wherein 20 mg of catalyst and 40 mg SiC were used in a flow containing 0.57% O₂, 1.14% *n*-butane and balance He with a total flow rate of 220 cm³ min⁻¹. The long term stability of 0.2% Au/La₂O₃ was evaluated using 50 mg of catalyst with a feed of 5% O₂, 10% *n*-butane, 10% N₂ (internal standard) and balance He with a total flow rate of 80 cm³ min⁻¹ and 48 h time on stream. Tests were performed between 500 and 650 °C.

Results and Discussion

From the tests of the fresh supports the highest reaction rate and selectivity to alkenes was found for La₂O₃. The remainder of the supports explored demonstrated low selectivity, in agreement with previous findings [5]. With the exception of the gold doped La₂O₃, gold modification decreased both conversion and selectivity for the tested supports. In the case of the La₂O₃ sample, addition of gold did not significantly affect the rate of reaction but increased the selectivity to alkenes by a factor of 1.7. These results also showed that the 0.2% Au/La₂O₃ is nearly four times more active and over twice as selective compared with BiOCl, which has previously been reported as one of the best catalysts for this process [5].

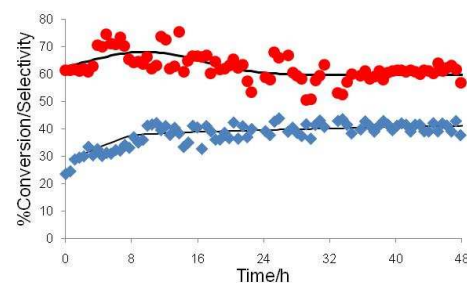


Figure 1: Conversion (♦) and selectivity to alkenes (●) for 0.2% Au/La₂O₃ at 650 °C

Figure 1 reports the conversion and alkene selectivity of 0.2% Au/La₂O₃, as a function of time on stream under the high conversion conditions. The catalyst had an average conversion of 38.1% with a selectivity of 62.5% after 48 h on stream. This equates to an average alkene production yield of 22.9%. Importantly, little deactivation was observed over 48 h with the mass balance maintained through this time period indicating that carbon laydown and/or modification of the surface sites is not a major problem.

The origin of the increase in the catalyst performance on addition of gold to lanthanum oxide may be due to the ability of La₂O₃ to stabilize cationic Au. Recently, we reported that, even at high temperatures, Au/La₂O₃ retained much of the cationic gold character of the initially prepared catalyst when compared with many other supports [6]. On supports other than La₂O₃ gold is easily reduced to the zero valent oxidation state thermally, even under oxidising conditions.

The 0.2% Au/La₂O₃ catalyst is particularly notable as it is highly active, selective to propene and ethene and stable on stream over a 48 h period. Maintaining cationic gold is thought to be critical for the stability and this catalyst design provides the possibility of applying gold based catalysts over a much wider temperature range than has been previously reported.

References

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