

Selective Oxidative Dehydrogenation of Isobutane over a $Y_2O_3-CeF_3$ Catalyst

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The multi-valence anion modified complex catalyst $Y_2O_3-CeF_3$ was found to be selective for the oxidative dehydrogenation of isobutane to isobutene at a relatively high conversion.

The production of gasoline octane enhancers (*i.e.* methylene *tert*-butyl ether, or MTBE) has led to new commercial developments in isobutene production. The relatively abundant liquefied petroleum gas (LPG) contains mainly propane and butane. Catalytic oxidative dehydrogenation of isobutane is a promising route to isobutene¹⁻⁴. In this process, catalytic selectivity is the most important factor since with an alkane and oxygen mixture, the thermodynamically favoured products are CO_2 and H_2O . Thus for this process catalysts must be designed which inhibit the oxidation effectively.⁵ We designed the CeF_3 promoted yttrium oxide catalyst which is active in isobutane oxidative dehydrogenation. It has a relatively high selectivity at high isobutane conversion.

The catalyst was prepared from CeF_3 and Y_2O_3 which were mixed in equal mole ratios, crushed to a powder and then stirred with deionized water to form a paste. The paste was dried at $100^\circ C$ for 2 h and calcined at $850^\circ C$ for 4 h. The catalytic activity and selectivity for the oxidative dehydrogenation were determined using a conventional flow system (fixed bed microreactor, 6 mm internal diameter) with a reaction temperature of $460-540^\circ C$; pressure of 1 atm; space velocity of $6000\ h^{-1}$; the feed was isobutane: $O_2 = 1:1$ or isobutane: $O_2:N_2 = 2:3:5$. The products were analysed by on-line gas chromatography.

The catalyst was particularly active for the selective production of isobutene from the oxidation of isobutane with molecular oxygen. Isobutene selectivity was much higher than with pure or complex oxides (over a Y_2O_3 catalyst, the isobutene selectivity was only 37.1% at 34.5% isobutane conversion at $500^\circ C$ and space velocity of $6000\ h^{-1}$ without N_2

feed). Fig. 1 shows the results of catalytic oxidative dehydrogenation of isobutane over the prepared catalyst. The conversion increased steadily with increasing temperature at above $460^\circ C$ while the selectivity dropped. The byproduct was predominantly propene, but CO and CO_2 were also formed, especially when the partial pressure of oxygen was increased. The isobutane conversion increased markedly with a slight decrease in isobutene selectivity when the oxygen partial pressure increased. This reaction can be run with pure (undiluted) gases. At $500^\circ C$ without N_2 , the isobutane conversion reached 15.4%, the selectivity 71.3% and the isobutene obtained 10.9%.

These catalysts were stable under the reaction conditions and under an 84 h test the activity and selectivity remained almost constant. This implied that the composition of the catalyst did not change and F^- was not lost.

XRD results indicated that the catalyst was composed of orthorhombic YF_3 , hexagonal YOF , cubic CeO_2 and (or) cubic $CeOF$. The XRD lines of CeO_2 and $CeOF$ are almost the same, so it is difficult to separate them. This result clearly showed that in the preparation of the catalyst, O^{2-} and F^- exchanged places in the solid lattices. This would cause anion defects, similar to complex oxides with different valence cations.^{6,7} The formation of the anion defects favours the activation and transfer of O_2 to active oxygen species, thus favouring the oxidative dehydrogenation of isobutane to isobutene.

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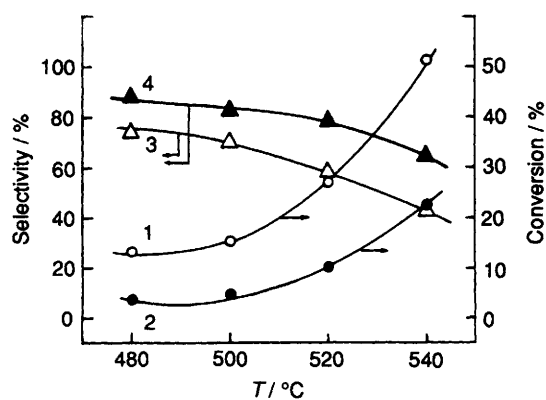


Fig. 1 Isobutane conversion and isobutene selectivity on $Y_2O_3-CeF_3$ catalyst. Lines 1 and 3 represent no N_2 feed, lines 2 and 4 with a N_2 feed.

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