

Catalyst deactivation and regeneration in alkane dehydrogenation: “can’t see the wood for the trees”?.

S. David Jackson* and Sreekala Rugmini.

WestCHEM, Department of Chemistry, The University, Glasgow G12 8QQ, Scotland.
sdj@chem.gla.ac.uk

Introduction

A series of vanadia catalysts have been prepared and characterised using UV-Visible excited Raman spectroscopy [1] and earlier studies on 1%V and 3.5%V on alumina showed that isolated VO_x species are much more effective at catalysing carbon deposition during butane dehydrogenation than the polyvanadate species. Equally it was observed that polyvanadate species are more effective at dehydrogenation compared to the isolated vanadia species [2]. In this paper, we report the results of our investigation on θ -alumina supported vanadia catalysts for the direct dehydrogenation of n-butane to butenes and butadiene. Three different vanadia loadings (1, 3.5 and 8%V) on θ -alumina have been prepared. All the catalysts were evaluated and temperature programmed oxidations were carried out on the coked catalysts to study the nature of the carbon deposit.

Materials and Methods

The catalysts were prepared by impregnation. Aqueous NH₄VO₃ (99+%, Aldrich) solution was used to prepare the catalyst with a 1 % w/w V loading. Oxalic acid (99%, Aldrich) was added into the solutions (NH₄VO₃/oxalic acid = 0.5 molar) for high VO_x loadings (3.5 and 8 % V). The θ -alumina support (101 m².g⁻¹, S.A.) was supplied by Johnson Matthey. The samples were dried at 393 K overnight and calcined at 823 K for 6 h. The catalysts were tested using a fixed-bed, continuous-flow, reactor. The catalyst was reduced in hydrogen for 1 hour at 873 K. Subsequently, n-butane was introduced at 873 K (GHSV = 14,400) and atmospheric pressure. Reaction products were analysed at regular intervals using an online GC. Regeneration of the catalysts was carried out using 2 % O₂/Ar. The catalyst was purged with argon at 873 K then catalyst was cooled to room temperature in a flow of argon. Once at room temperature the flow was switched to 2% O₂/Ar and the catalysts heated to 873 K at 10 deg.min⁻¹. The temperature was maintained at 873 K until regeneration was complete. The process was monitored by online mass spectrometry (MS).

Results and Discussion

As expected online MS indicated that all hydrocarbon components were rapidly swept out of the reactor at 873 K when the gas stream was switched from butane to argon and no other gases apart from argon were detected during the cool-down period. However when 2 % O₂/Ar was passed over the sample at room temperature C-4 species were evolved. Figure 1 shows the evolution of butane, (butenes and butadiene were also desorbed) from the three catalysts and the alumina support. From the desorption profiles it can be seen that the amount of retained C-4 is proportional to the amount of VO_x on the surface. These species were desorbed from the catalyst on contact with oxygen at room temperature. Desorption of C-4 gases that are strongly adsorbed and stable at 873 K in an inert atmosphere, but are easily displaced by an oxidising gas at room temperature is surprising. This desorption process can

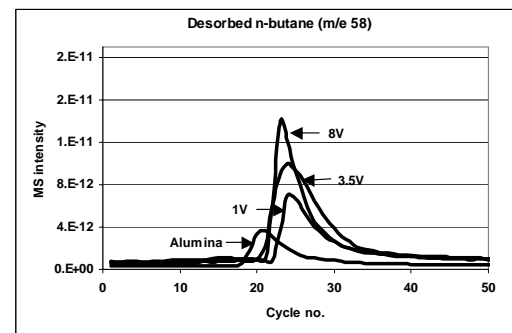
be viewed as an oxidative displacement, resulting in recombination of reaction intermediates (hydrogen and alkyl, alkenyl, and alkadienyl) from the surface of reduced VO_x species and acid sites on the alumina. To understand the effect of these species on deactivation, the gas flow was switched back to argon and the catalyst reheated to 873 K. Once at 873 K the flow was switched to butane and the activity measured. The activity recorded was > 75% of that regained after a full regeneration involving heating in O₂/Ar at 873 K. Indeed after an hour on

stream there was no difference detectable between a room temperature regeneration and regeneration at 873 K. When a TPO was run following this desorption, combustion of carbon was observed.

This reaction/regeneration cycle can be repeated and

Figure 1.

Desorption of butane at room temperature a similar evolution of C-4



gases at room temperature observed (not shown). The TPO patterns of first use and regenerated catalysts show the presence of different types of coke species on the catalysts' surface over and above the C-4 gases that are desorbed at room temperature. Note that the removal of this coke has little effect on the regeneration of activity. This suggests that much of the polyaromatic/polyolefinic/graphitic coke identified by spectroscopy, is not associated with the VO_x species but with the support. The TPO of the 3.5V fresh catalyst after reaction showed two different types of coke species, whereas regenerated catalyst showed only one peak in its TPO. These results are in agreement with the reactivity profiles and the UV-Visible DRS in recording a change between the fresh catalyst and a regenerated one.

Significance

The discovery of strongly bound reaction intermediates as the main cause of deactivation rather than the widely viewed polyaromatics is a considerable step forward in our understanding and our ability to develop new systems that do not deactivate.

References.

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2. Jackson, S. D., Rugmini, S., Stair, P.C. and Wu, Z., *Chem. Eng. J.*, 120, 127 (2006).