

Deactivation and Regeneration of Chromia and Vanadia Catalysts in Alkane Dehydrogenation.

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Introduction

In a previous study we examined the deactivation and regeneration of vanadia catalysts after use in butane dehydrogenation [1]. In that study we showed that vanadia catalysts could be regenerated by a treatment in an oxygen containing gas at room temperature. In this paper we have extended the study to include chromia catalysts and will compare the deactivation and regeneration processes of the two oxides.

Materials and Methods

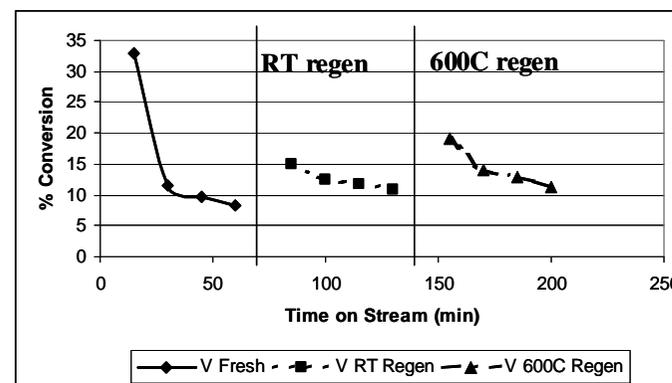
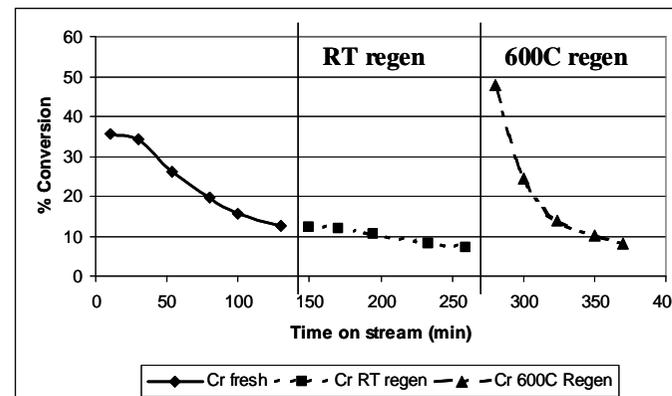
The catalysts were prepared by impregnation. Oxalic acid was added into aqueous NH_4VO_3 ($\text{NH}_4\text{VO}_3/\text{oxalic acid} = 0.5$ molar) for 3.5 % VO_x loading to ensure dissolution of NH_4VO_3 . 6 % loading chromia was achieved using ammonium dichromate solution. The θ -alumina support ($S_A > 101 \text{ m}^2 \cdot \text{g}^{-1}$) was supplied by Johnson Matthey, UK. The samples were dried at 393 K overnight and calcined at 823 K for 6 h. Activity and selectivity was determined using a fixed-bed, continuous-flow, reactor. The catalysts were reduced in situ at 873 K. The system was purged then n-butane introduced (GHSV = 14,400) at atmospheric pressure. Reaction products were analysed at regular intervals using an online GC. Regeneration of the catalysts was carried out using 2 % O_2/Ar . The catalyst was purged with argon at 873 K for 0.5 h to remove adsorbed reactant/products from the catalyst surface. Then, the catalyst was cooled to room temperature in a flow of argon. Once at room temperature the gas flow was switched to 2 % O_2/Ar and the catalysts heated to 873 K with a programmed heating rate of $10 \text{ deg} \cdot \text{min}^{-1}$. The temperature was maintained at 873 K until regeneration was complete. The total process was monitored by online MS.

Results and Discussion

Both catalysts were tested for n-butane dehydrogenation at 873 K. The catalysts deactivated as shown in the figures. They were then regenerated by cooling the catalysts to 293 K and subjecting them to 2% O_2/Ar . The vanadia catalyst regenerated achieving ~70% of the activity observed after regeneration at 873 K.

In contrast, the chromia catalyst did not regenerate after 293 K oxygen treatment, only after regeneration at 873 K did the catalyst regain its activity.

The reasons behind the difference relate to the stability of alkyl fragments on the surface of chromia and vanadia. The nature of the carbon deposited on both catalysts in relation to the species desorbed during room temperature oxygen treatment will be discussed in detail. The extent of the carbon laydown will also be discussed from temperature programmed oxidation studies.



Significance

Understanding the type and reactivity of surface carbonaceous species and the variation in behaviour with oxide catalyst is of importance in terms of designing new processes and consideration of retro-fits.

Reference:

1. Jackson, S.D. and Rugmini, S., *J. Catal.*, 251, 59, (2007)