

Deactivation and regeneration of chromia and vanadia catalysts in alkane dehydrogenation

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ABSTRACT

The deactivation and regeneration of a 6 % CrO_x/alumina catalyst and a 3.5 % VO_x/alumina catalyst has been studied after use in butane dehydrogenation at 873 K. Both catalysts deactivate due to carbonaceous deposits and with both catalysts the isomerisation reaction from 1-butene to cis and trans-2-butene is poisoned more effectively than the dehydrogenation reaction. The chromia catalyst deactivates three times faster than the vanadia system but the total amount of carbon deposited is similar indicating that the nature of the deposit on the chromia system is much more deleterious. The vanadia catalyst can be regenerated at room temperature in a flow of oxygen by removal of reaction intermediates, which desorb as butane, butene and butadiene. Over 75 % of the activity can be retrieved and by 1 hour on stream no difference can be discerned, whereas no significant desorption is detected from the chromia catalyst at room temperature and no regeneration is observed. TPO of both systems show different profiles with the deposit on the chromia catalyst more resistant to oxidation, which suggests a more dehydrogenated or more graphitic type material, which would be in keeping with the faster deactivation. After regeneration at 873 K the chromia catalyst recovers all its activity, whereas even after 873 K regeneration the vanadia catalyst does not recover all its activity.

This is likely due to a change in structure and electronic properties of the polyvanadate species.

KEYWORDS: butane dehydrogenation, chromia, vanadia, deactivation, regeneration

INTRODUCTION

Changes in the relative demand of propene and isobutene are presenting a need and opportunity for on purpose manufacture of these chemicals, as opposed to their traditional sourcing as by-products from steam cracking and catalytic cracking. While various schemes have been proposed for the on-purpose production, the only one active on a commercial scale at present is catalytic dehydrogenation of the relevant alkane.

The dehydrogenation of light alkanes has been known as a catalytic process for a significant number of years [1]. Industrial chemical processes use chromia or platinum based catalysts generally supported on alumina and promoted with alkali metals [1-3]. These processes operate at the high temperatures and low pressure needed to achieve reasonable equilibrium yields (~50 % conversion at 873 K and 1 bar for propane and butane). The high temperatures required to achieve sensible yields for the dehydrogenation reaction leads to catalyst deactivation by coke deposition [4, 5]. All operate in a cyclical fashion to mitigate against the severe catalyst deactivation that is observed and in some cases to offset the large heat fluxes.

In this paper we continue our study of vanadia and chromia catalysts, using butane as the probe

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alkane and concentrating on the deactivation and regeneration of the catalysts.

EXPERIMENTAL

Preparation of catalysts

The catalysts were prepared by incipient wetness impregnation with θ -alumina as the support. The θ -alumina support (1/20" trilobes, Surface area = $101 \text{ m}^2 \cdot \text{g}^{-1}$, Pore volume = $0.60 \text{ ml} \cdot \text{g}^{-1}$) was supplied by Johnson Matthey, UK. Before impregnation, the alumina was pre-dried at 353 K overnight. Aqueous NH_4VO_3 (99+ %, Aldrich) solution was used to prepare a catalyst with a 3.5 % w/w V loading: oxalic acid (99 %, Aldrich) was added ($\text{NH}_4\text{VO}_3/\text{oxalic acid} = 0.5$ molar) to ensure dissolution of NH_4VO_3 . Aqueous ammonium dichromate (99+ %, Aldrich) was used to prepare a catalyst with a 6 % w/w Cr loading. After impregnation, the samples were mixed thoroughly using a rotavap for 2 h at 350 K and dried by purging with air at 393 K overnight. Finally the samples were calcined at 823 K for 6 h. A catalyst nomenclature of 3.5V and 6Cr will be used to designate the 3.5 % $\text{VO}_x/\text{alumina}$ and the 6 % $\text{CrO}_x/\text{alumina}$ respectively.

XRD analysis

The crystalline structure of the support and catalysts was studied by X-Ray Diffraction analysis with a Siemens D 5000 instrument using $\text{CuK}\alpha$ radiation and operated at 40 kV and 30 mA.

UV-visible diffuse reflectance spectroscopy

UV-visible spectra were obtained using a Varian Cary 5000 Win UV-Vis.-NIR spectrophotometer equipped with a Diffuse Reflectance Attachment (Harrick) with full environmental control. Catalyst reduction was carried *in situ* using H_2 at a flow rate of $10 \text{ cm}^3 \text{ min}^{-1}$.

Nitrogen adsorption

The surface area of the support and the catalysts were determined from the nitrogen adsorption curve using Micromeritics Gemini III 2375 Surface Area Analyzer after degassing the samples at 393 K overnight.

Dehydrogenation activity evaluation

The activity and selectivity of each catalyst was determined using a fixed-bed, continuous-flow,

reactor. The catalyst (0.25 cm^3) was reduced in pure hydrogen ($40 \text{ cm}^3 \cdot \text{min}^{-1}$) for 1 hour at 873 K. The flow was switched to argon and the system purged for 30 minutes. Subsequently, n-butane was introduced at a flow rate of $60 \text{ cm}^3 \cdot \text{min}^{-1}$ at 873 K (GHSV = 14,400) and atmospheric pressure. Reaction products were analysed at regular intervals using an online GC (Agilent 6890 Series -FID, Varian Chrompack Capillary Column CP7568). Regeneration of the catalysts was carried out using 2 % O_2/Ar . After a dehydrogenation reaction, 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.

The conversion and selectivity were calculated (on a carbon basis) from the reaction products (P), the total amount of n-butane fed to the reactor (X) and amount of butane out (Y) along with reaction products.

$$\% \text{Conversion} = [(X-Y)/X] * 100$$

$$\% \text{Selectivity} = [P/(X-Y)] * 100$$

The yield of a specific product was obtained by multiplying the n-butane conversion by the corresponding selectivity.

RESULTS/DISCUSSION

The surface area of the alumina used as the common support was $105 \text{ m}^2 \cdot \text{g}^{-1}$; the chromia and vanadia catalysts had surface areas of $101 \text{ m}^2 \cdot \text{g}^{-1}$ and $94 \text{ m}^2 \cdot \text{g}^{-1}$ respectively. As expected there is a loss in surface area upon impregnation. XRD analysis of both catalysts revealed only the diffraction pattern for θ -alumina; no evidence was observed for crystalline phases of vanadium or chromium oxides. At these loadings this is to be expected. Previous studies [6, 7] indicate that higher Cr and V surface densities are required before crystalline phases are detected. Temperature programmed reduction revealed reduction peaks at $\sim 643 \text{ K}$ for 6Cr and $\sim 823 \text{ K}$ for 3.5 V, which is in keeping with literature results [7, 8].

The reduction was also followed by UV-visible Diffuse Reflectance Spectroscopy (UV-vis DRS). The behaviour of the 3.5V has been reported previously [7]. Briefly before reduction the catalyst is in a V(V) oxidation state with a charge transfer band at 290 nm (34480 cm^{-1}). Over the course of the reduction the spectrum changes to give a spectra typical for a V(III) state with d-d transitions around 575 nm and 625 nm. Once reduced the 3.5V sample does not regain its original state even after high temperature oxidation. With the as-prepared 6Cr catalyst there are bands at 280 and 370 nm typical of LMCT bands for Cr(VI) species as well as bands that are typical of Cr(III). As reduction progresses the Cr(VI) bands disappear and bands typical of Cr(III) in Oh symmetry are observed at 380 nm, 460 nm and 620 nm. This final spectrum is stable under reduction, reaction and regeneration conditions. Analysis of the Cr(VI) content by wet chemical analysis gave a value of 0.27 % in the as-prepared material, indicating that approximately 5 % of the chromium present in the 6Cr catalyst is Cr(VI). This is very much in keeping with the literature [9] where it was found that at calcination temperatures above 823 K caused reduction of the Cr(VI) present to Cr(III).

The catalysts were tested under identical conditions. The conversion selectivities and yields are reported in Table 1. After 15 min on stream both catalysts give similar product yields. Both catalysts deactivated and the deactivation could be described by a simple first order deactivation relationship, $\ln(C_t/C_0) - 1 = -k_d t + \ln(kt_0)$. The

deactivation constant for 6Cr was 0.016 min^{-1} and 0.0053 min^{-1} for 3.5V. When deactivation is compared on a product basis the rate of deactivation is not identical for the butane isomers. 1-Butene rate of decay is systematically less over each catalyst such that even though 1-butene is the least thermodynamically favoured isomer yet it is always present above the equilibrium value and as the catalysts deactivate it becomes more dominant (Figure 1). As 1-butene is the primary product this indicates that for both chromia and vanadia catalysts the isomerisation reaction is poisoned more effectively than the dehydrogenation reaction suggesting that each reaction has a unique site.

Carbon deposition is the main cause of deactivation in alkane dehydrogenation catalysts. Deposition of carbon occurs through progressive dehydrogenation, condensation, polymerisation and cyclisation of hydrocarbon species on the catalyst surface. To remove this carbonaceous deposit and restore activity the catalysts were treated with low concentration oxygen in argon. Two regeneration processes were investigated; the first involved switching the flow from butane to argon to purge the system then to 2 % O_2/Ar at 873 K and holding until carbon dioxide evolution ceased. Once carbon dioxide evolution ceased the gas flow was switched back to argon then butane. The second methodology involved switching the flow from butane to argon at 873 K and maintaining this for 0.5 h to purge the catalyst. Then, the catalyst was cooled to room temperature in flowing argon. Once at room temperature the

Table 1. Conversion, selectivity and yield after 15 min on stream at 873 K and 1 barg.

Sample	Conv. (%)	% Selectivity (Yield)				
		1-butene	Trans-2-butene	Cis-2-butene	1,3-butadiene	C1-C3s
θ -Alumina	5.8	0.73 (0.04)	0.60 (0.03)	--	--	21.2 (1.2)
6Cr	40.5	19.2 (7.8)	15.7 (6.3)	12.1 (4.9)	4.2 (1.7)	2.0 (0.8)
3.5V	32.9	20.4 (6.7)	16.9 (5.6)	13.1 (4.3)	5.7 (1.9)	3.4 (1.1)

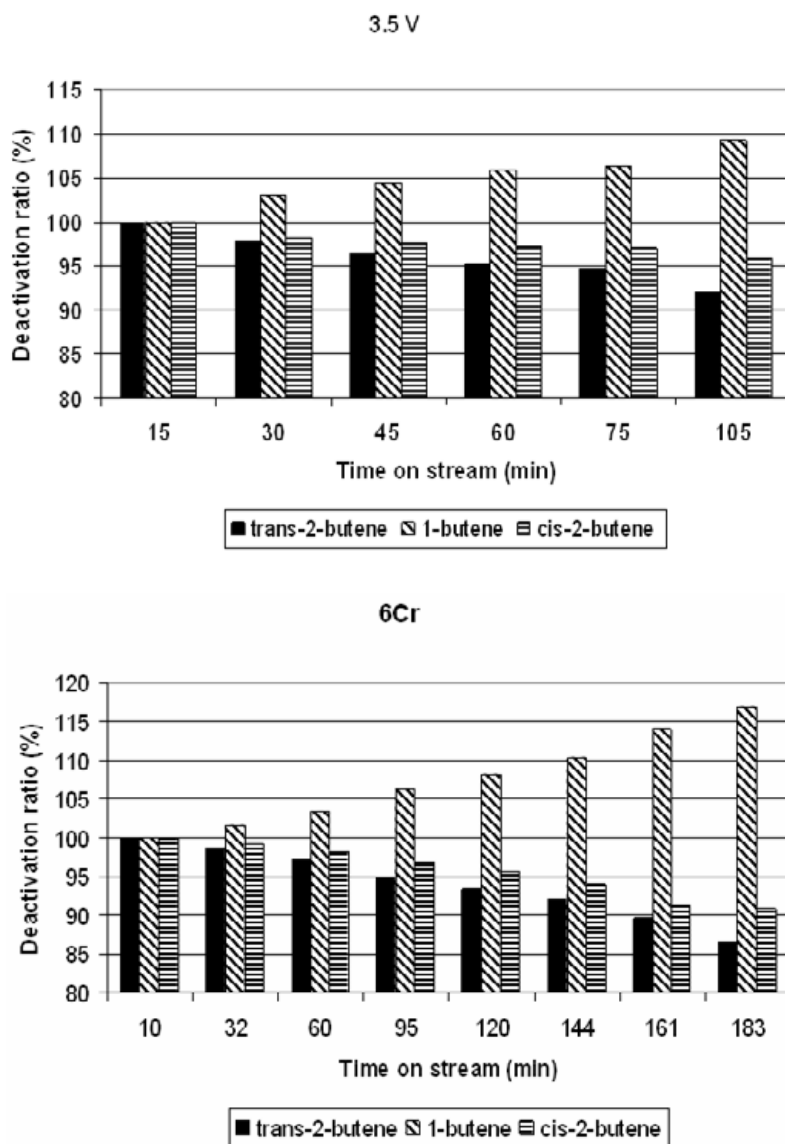


Figure 1. Comparison of butene isomer deactivation.

gas flow was switched to 2 % O₂/Ar and after a period the catalyst heated to 873 K. After all carbon dioxide evolution had ceased the flow was switched back to butane.

Using the first methodology there was an immediate evolution of carbon monoxide followed by carbon dioxide when the flow was switched from butane to 2 % O₂/Ar for both 3.5V and 6Cr. Once the evolution has ceased the butane flow was restored and the activity measured. The results are shown in Figure 2. Initially carbon monoxide is produced as the oxygen is limited.

Once the amount of carbon on the surface reduces the main product is carbon dioxide. From the evolution an amount of carbon deposited on the catalysts could be calculated. The amount of carbon deposited on the 6Cr catalyst was calculated at 14 mmole.g⁻¹, while the amount deposited on the 3.5V catalyst was 13 mmole.g⁻¹. These values are considerably higher than the amounts of chromium and vanadium on the catalysts which were 1.1 mmole.g⁻¹ and 0.7 mmole.g⁻¹ respectively. The 3.5V value is higher than that found by Krause *et al.* [10] but their data was

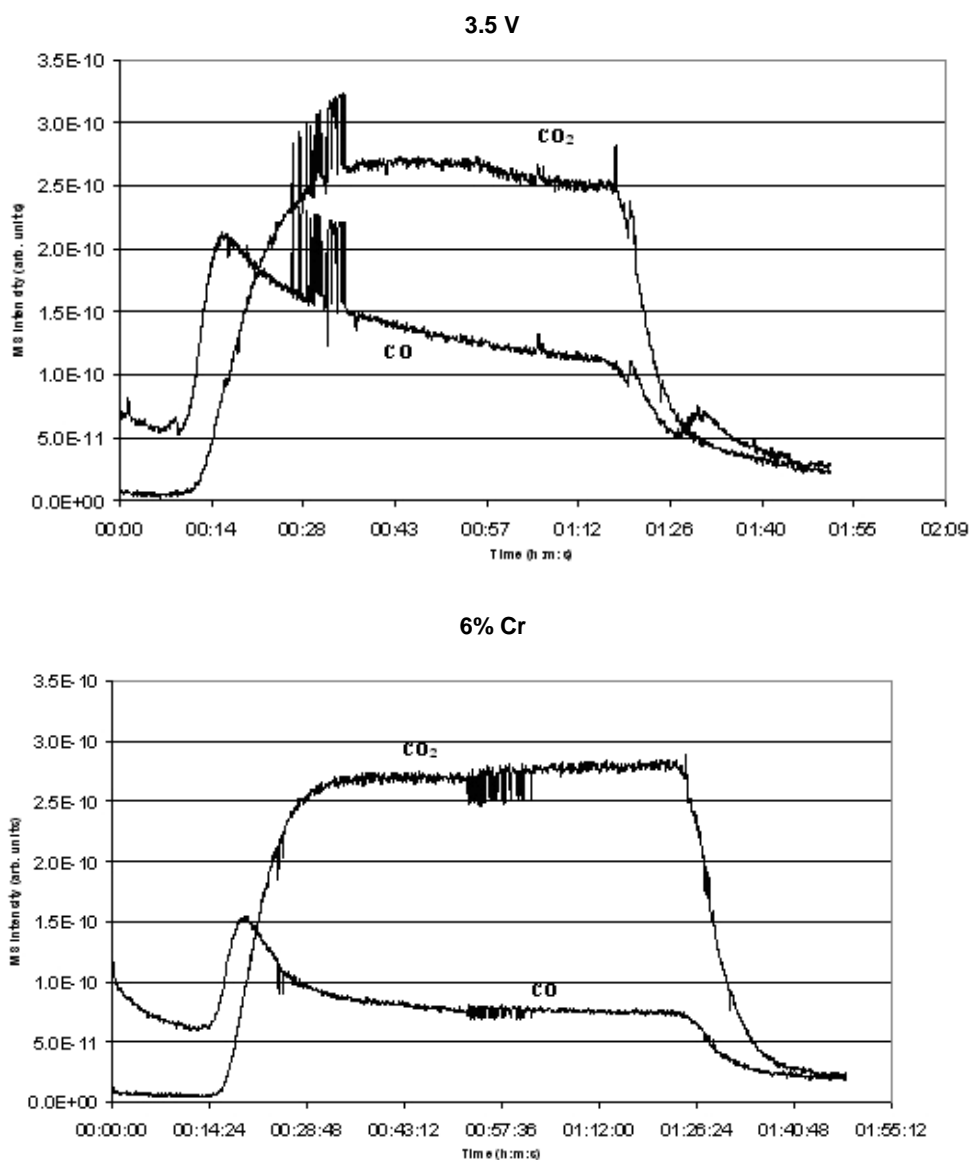


Figure 2. CO and CO₂ evolution after flow switched to 2 % O₂/Ar at 873 K.

taken at 15 min on stream whereas our data is taken after 2 h on stream. Previous studies [8, 11] have also shown that much of the carbon deposited is not associated with the chromia or vanadia but with the alumina support and indeed although the catalysts have deactivated they were not totally inactive. After this treatment the flow was switched back to n-butane and the activity and selectivity measured. From Figure 3 it is clear that the 6Cr regains all activity and has similar selectivity to the fresh catalyst; with the 3.5V catalyst not all the activity is regained but the

selectivity does not change. As noted above in the UV-visible spectroscopic study, the chromia system is stable through reduction/reaction/regeneration whereas the vanadia system is not. An *in-situ* XPS study also confirmed the instability of the vanadia system [12]. Therefore the inability of the vanadia to regain full activity may not be due to retention of carbon but to a change in the structural and/or electronic properties of the catalyst [13].

Using the second method, as expected online MS indicated that all hydrocarbon components were

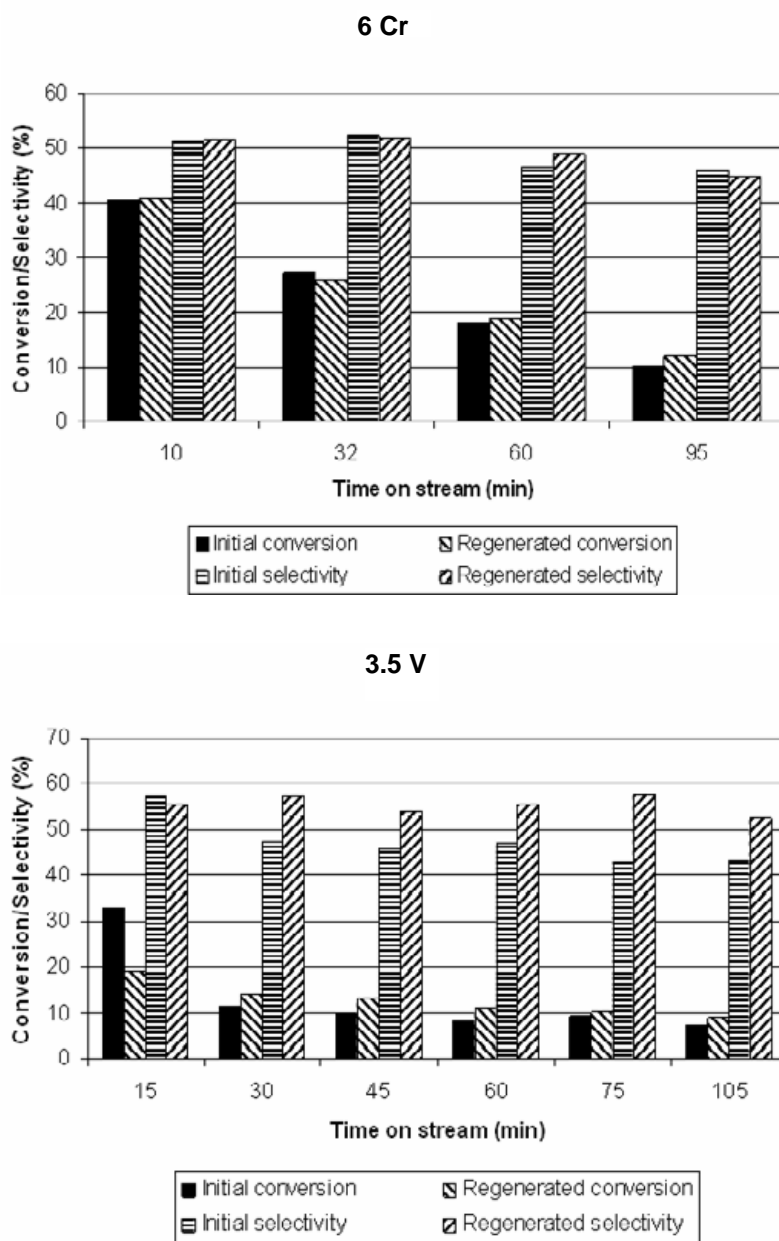


Figure 3. Conversion and selectivity of fresh and regenerated catalysts at 873 K.

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 the argon carrier were detected during the cool-down period for both catalysts. When 2 % O₂/Ar was passed over the 3.5V sample at room temperature CO₂ and C-4 species were evolved (Figure 4). 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

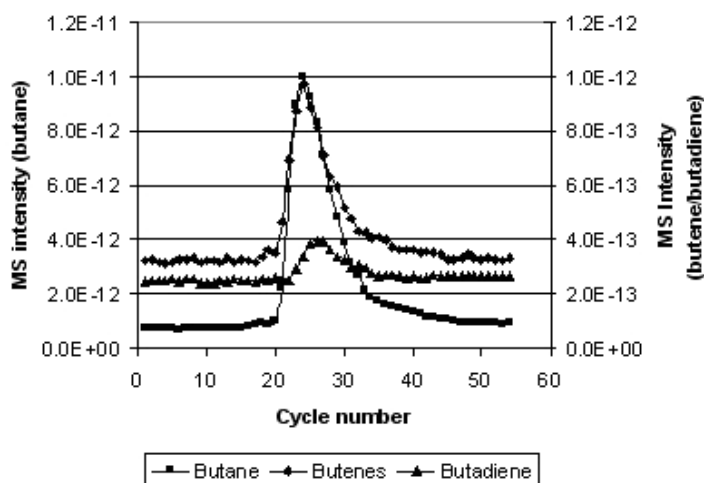


Figure 4. Room temperature desorption of butane, butenes and butadiene from a 3.5V catalyst after use at 873 K.

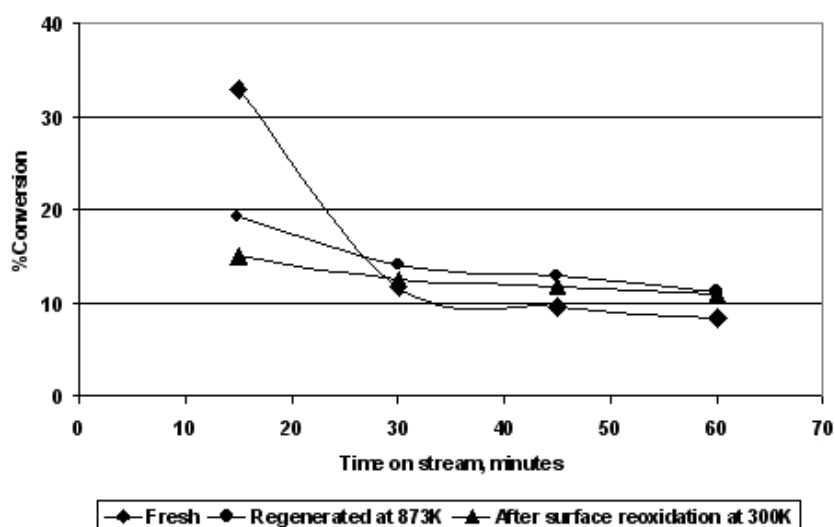


Figure 5. Regained dehydrogenation activity after surface and bulk reoxidation for 3.5V.

heating in O_2/Ar at 873 K (Figure 5). Indeed after an hour on stream there was little difference detectable between a room temperature regeneration and regeneration at 873 K. When a TPO was run following a room temperature desorption, combustion of carbon was observed giving two well resolved evolutions of carbon dioxide at 723 and 843 K (Figure 6) confirming that a significant amount of carbon was still retained by the catalyst. This recovery of activity after room temperature regeneration indicates that most of

the deposit associated with the vanadia is in the form of reactive intermediates rather than significantly dehydrogenated or polymerized material. As well as removing the deposit and freeing potential reaction sites the oxygen can also increase the oxidation state of the vanadium [12] and change the structural properties [13].

These results are in marked contrast to the 6Cr sample where only a small evolution of gases took place at room temperature, which was very

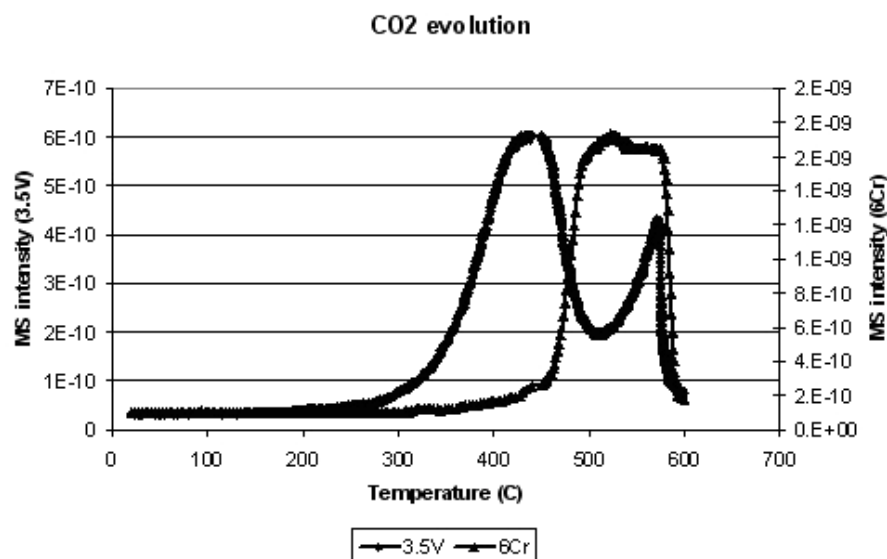


Figure 6. TPO of 3.5V and 6Cr catalysts.

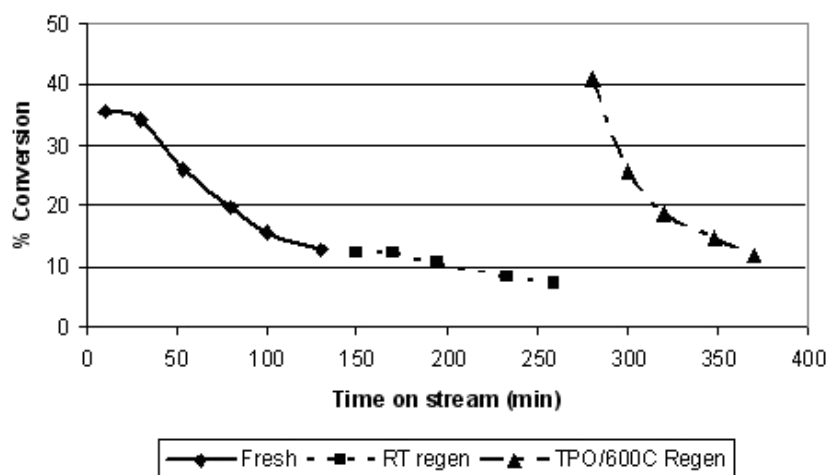


Figure 7. Conversion over fresh 6Cr, after a RT regeneration and after a TPO or 873 K regeneration.

similar to that from the alumina support [7]. To determine whether this small evolution had any effect on activity, 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 identical to that observed before the treatment at room temperature, i.e. no regeneration had occurred (Figure 7). After a period the flow was again switched to argon and the catalyst cooled. Once at room temperature a TPO was performed

(Figure 6) revealing two poorly resolved evolutions of carbon monoxide at 803 and 848 K with a leading edge shoulder at 773 K. After the TPO the temperature was held at 873 K and the flow switched to butane. The activity recorded was equivalent to that of a fresh catalyst (Figure 7).

When we compare the TPO profiles in Figure 6 it is clear that the deposit on the chromia catalyst requires much higher temperatures to combust than the deposit on the vanadia catalyst suggesting

a much more dehydrogenated species on the surface. Our results are in agreement with Krause and co-workers [14] who found, when studying isobutene dehydrogenation over a chromia catalyst that heating the catalyst to 853 K in an oxygen containing gas was required for full regeneration. Typical species detected over chromia catalysts from propane dehydrogenation at 873 K were pyrene ($C_{16}H_{10}$) and benzo-fluoranthenes ($C_{18}H_{10}$ and $C_{20}H_{12}$) [8]. Nevertheless the material found on the 3.5V catalyst is also aromatic in nature. Wu and Stair [15] studied this system using *in situ* Raman spectroscopy and concluded that 2D, sheet-like coke species were formed, while Vass *et al.* [12] using NEXAFS also confirmed the presence of disordered carbon. Therefore both catalysts produce polynuclear aromatics and given the coincidence of carbon dioxide evolution we propose that the second evolution in both TPOs is due to combustion of the aromatic species. The lower temperature peak in the 3.5V TPO may be related to combustion of the intermediates detected at low level in the gas phase during the study by Vass *et al.* [12].

CONCLUSIONS

In conclusion, we have examined the deactivation and regeneration of chromia and vanadia catalysts after use in butane dehydrogenation at 873 K. Both catalysts deactivate due to carbonaceous deposition and with both catalysts the isomerisation reaction between 1-butene and cis and trans-2-butene is poisoned more effectively than the dehydrogenation reaction. Both systems form polynuclear aromatics, although some of these are formed on the support [8]. However there are also significant differences. The chromia catalyst deactivates three times faster than the vanadia system but the total amount of carbon deposited after equal times on stream is similar. This indicates that the nature of the deposit on the chromia system is much more deleterious. The vanadia catalyst can be regenerated at room temperature in a flow of oxygen containing gas by removal of reaction intermediates, which desorb as butane, butene and butadiene. Over 75 % of the

activity can be retrieved and by 1 hour-on-stream no difference can be discerned. Whereas no significant desorption is detected from the chromia catalyst at room temperature and no regeneration is observed. TPO of both systems show different profiles with the deposit on the chromia catalyst more resistant to oxidation, which would suggest a more dehydrogenated or more graphitic type material and this would be in keeping with the faster deactivation. After regeneration at 873 K the chromia catalyst recovers all its activity and *in situ* UV-visible spectroscopy indicates that the system cycles through the same species, whereas even after 873 K regeneration the vanadia catalyst does not recover all its activity. This is likely due to a change in structure and electronic properties of the polyvanadate species [12, 13].

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