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Butane dehydrogenation over Pt/alumina: activation, deactivation and the generation of selectivity

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Abstract

The dehydrogenation of butane over a Pt/alumina catalyst has been studied using pulse-flow techniques. The selectivity to butenes is generated as carbonaceous material is deposited. The final catalyst is sensitive to whether reduction has taken place in hydrogen or butane, with the more effective dehydrogenation catalyst being generated from a hydrogen reduction.

Keywords: Platinum; Dehydrogenation; Butane; Deactivation; Activation

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1. Introduction

The relative demand of propene, butene and isobutene present a need and an 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 most feasible 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 [1,2]. The industrial catalytic processes fall into two categories, those based on platinum as the active phase [3,4] and those based on chromia as the active phase [5]. However, in both cases the catalytic process is complex with a series of competing reactions occurring simultaneously including significant carbon laydown resulting in catalyst deactivation. None of the current industrial processes are ideal and ways of improving the process, including the use of oxidative dehydrogenation, are always being sought [2,6–9]. In this paper, we have studied the processes occurring when butane is pulsed over a Pt/alumina catalyst under dehydrogenation conditions. Using this methodology, we can see that the catalyst without any carbon deposit is highly active but with poor selectivity. The role of pre-reducing the catalyst has also been examined and it is clear that the activation and the deactivation processes occurring in the first few seconds on-line during butane dehydrogenation reaction are fundamental in obtaining the desired selectivity.

2. Experimental

The catalyst used throughout this study was Pt/alumina and was prepared by impregnation. H_2PtCl_6 (Johnson-Matthey) was dissolved in de-ionised water and the solution added to γ-alumina (Engelhard Al-3992E, S.A. 180 $m^2\ g^{-1}$). The resulting suspension was dried and heated to 313 K for 16 h and calcined at 823 K for 3 h. The Pt loading of the sample was 0.66% w/w. The dispersion of the catalyst, measured

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by CO chemisorption, was 78% and the particle size from TEM was measured at <2 nm [10].

Pulsed reaction studies were performed in a dynamic mode using a pulse-flow microreactor system with on-line GC. Using this system the catalyst (typically 0.25 g) could be reduced in situ in flowing 5% H_2/N_2 (30 $cm^3\,min^{-1}$) by heating to 573 K and holding at this temperature for 3 h. After 3 h, the gas flow was switched to helium (50 $cm^3\,min^{-1}$) and the temperature adjusted to the desired reaction temperature. In pulse mode reaction gases were admitted by injecting pulses of known size (typically 5 cm^3, 13.3 kPa) into the helium carrier-gas stream and hence to the catalyst. After passage through the catalyst bed the total contents of the pulse were analysed by GC. Carbon deposition was measured in the pulse mode by difference for each pulse. In all tests, the amount of butane in the pulses was kept constant.

3. Results

No dehydrogenation or isomerisation activity was observed when butane was passed over the support material in the absence of platinum. When aliquots of butane are passed over an unreduced catalyst carbon dioxide and carbon monoxide are produced as well as lower hydrocarbons such that by the fourth pulse of butane all the oxygen associated with the platinum has been removed. The yield of C-4 products is shown in Table 1.

Although carbon oxides are produced in the first pulse as the butane reduces the platinum oxide, the highest yield product is methane at 52.4%, however this rapidly drops to 4.4% by pulse no. 6. Over the first six pulses, the conversion also drops as the yield of dehydrogenated products increases, however, the carbon deposition consistently increases over the same period (Table 2).

Over a reduced catalyst, a small amount of carbon monoxide is detected in the exit of the first pulse. The amount of oxygen removed would approximate to 1% of the oxygen that is associated with the platinum, however, it is more likely that this small carbon monoxide evolution results from a reaction with the support. Once again, methane has the largest yield in the first pulse at 40.3%. The conversion and yield of the C-4 products is shown in Table 3.

Table 1
Conversion and C-4 yields at 673 K over unreduced Pt/alumina

Pulse no.	Conversion (%)	Isobutane (%)	1-Butene (%)	*Trans*-2-butene (%)	*Cis*-2-butene (%)
1	100	0	0	0	0
2	94.5	0	0.7	0.5	0.5
3	72.5	4.1	3.3	2.2	1.7
4	53.2	4.2	5.3	3.8	3.2
5	42.9	3.8	6.3	4.4	3.8
6	36.8	3.3	6.7	4.5	3.8

Table 2
Dehydrogenation yield and cumulative carbon deposition at 673 K over unreduced and reduced Pt/alumina with a butane feed, and dehydrogenation yield and cumulative carbon deposition at 673 K over a reduced Pt/alumina with a 2:1 co-feed of butane/oxygen

Pulse no.	Unreduced catalyst		Reduced catalyst		Butane/oxygen	
	Yield butenes (%)	$\sum$ Carbon ($\times 10^{19}\,g^{-1}$)	Yield butenes (%)	$\sum$ Carbon ($\times 10^{19}\,g^{-1}$)	Yield butenes (%)	$\sum$ Carbon ($\times 10^{19}\,g^{-1}$)
1	0	1.89	0	3.52	0	2.69
2	1.6	4.72	3.3	6.82	2.6	5.51
3	7.2	6.97	13	8.75	10.3	6.80
4	12.4	8.57	17.3	10.06	12.7	7.37
5	14.4	9.88	18.5	11.30	13.2	7.59
6	14.9	10.94	19.1	12.50	13.3	7.68

Table 3
Conversion and C-4 yields at 673 K over reduced Pt/alumina

Pulse no.	Conversion (%)	Isobutane (%)	1-Butene (%)	*Trans*-2-butene (%)	*Cis*-2-butene (%)
1	100	0	0	0	0
2	88.9	3.7	1.4	1.1	0.8
3	62.9	4.8	4.8	4.6	3.5
4	53.6	4.3	6.4	6.2	4.7
5	47.8	3.9	6.9	6.6	5
6	45.1	3.6	7.1	6.7	5.3
7	41.5	3.5	7.4	6.9	5.6

Table 4
Conversion and C-4 yields for co-fed butane/oxygen 2:1 at 673 K over reduced Pt/alumina

Pulse no.	Conversion (%)	Isobutane (%)	1-Butene (%)	*Trans*-2-butene (%)	*Cis*-2-butene (%)
1	100	0	0	0	0
2	91.5	0.4	1.1	0.8	0.6
3	68.5	5.3	3.8	3.6	2.9
4	55.0	5.1	4.7	4.4	3.6
5	48.6	4.7	4.9	4.6	3.7
6	42.4	4.7	4.8	4.6	3.8

As with the unreduced catalyst, the conversion over the reduced catalyst decreases over the seven pulses. The amount of carbon deposited increases however, as does the yield of dehydrogenated products (Table 2).

The link between conversion/yield and carbon deposition was further investigated by oxidative dehydrogenation. A reduced catalyst was subjected to mixed pulses of butane and oxygen (C_4H_8:O_2, 2:1 molar). The variation of conversion and C-4 product yield is shown in Table 4 and the carbon deposition and overall dehydrogenation yield in Table 2. The amount of carbon oxides produced in each pulse was relatively constant at ∼18% (measured as $\sum CO_x/\text{butane} \times 4$).

In a separate experiment, butane and oxygen were sequentially pulsed over a reduced catalyst with the amounts of butane and oxygen the same as in the co-feed experiment. Butane was pulsed first followed by oxygen then butane then oxygen, this sequence was repeated three times. As expected the oxygen pulse removed some of the deposited carbon as carbon dioxide. The amount of carbon removed was approximately 7% of the previous butane pulse. The effect of this was to keep the butane conversion high and limit the dehydrogenation yield (Table 5).

Table 5
Conversion and C-4 yields for sequential pulses of butane followed by oxygen (2:1 molar ratio) at 673 K over reduced Pt/alumina

	Pulse no.					
	1	2	3	4	5	6
Conversion (%)	100	95.3	74.6	75.0	68.7	49.5
Butene yields (%)	0	1.4	2.5	7.8	9.3	14.4

4. Discussion

All the results show quite clearly that the Pt/alumina system is highly active, however not for the desired reaction. No butenes are observed from the initial pulse over the catalyst; methane and carbon are the main products. Of course this does not mean that the catalyst is not producing butenes in situ, only that they are not exiting the catalyst bed. Comparable experiments using propane as the feed gave similar results [11]. From Table 2, it is clear that as carbonaceous material is deposited on the catalyst surface the yield of dehydrogenated products increases. This can be interpreted as the carbonaceous residue blocking high activity sites that catalyse C–C bond fracture and decomposition of butane and butene. Once the residue poisons these sites, the remaining sites can catalyse the dehydrogenation reaction. Indeed, the selectivity of the catalyst to dehydrogenation rests upon the deposition of carbon to eliminate unselective sites. In Table 5 where, in-between butane pulses, an oxygen pulse is used to remove around 52% of the deposited carbon from the previous butane pulse, the conversion remains high but the selectivity to dehydrogenation is low. This positive effect of the residue is maintained but eventually, over a longer time frame, the carbon deposit also acts to reduce the efficacy of the dehydrogenation sites [2,4,11,12]. At a carbon deposition level of $\sim 6.85 \times 10^{19}$ carbon atoms g^{-1}, dehydrogenation yields of 3, 7, and 10% are all recorded (Table 2), therefore the extent of carbon deposition does not define dehydrogenation yield. These results suggest that the presence of oxygen, as well as carbon deposition, influences the dehydrogenation yield. The presence of oxygen on the catalyst allows a higher yield of alkenes than the extent of carbon deposition would indicate, however, the final yield achieved is lower than that attained with no oxygen present. Therefore, we can view the oxygen as having two roles, at low carbon coverages the oxygen aids dehydrogenation by occupying high energy sites thereby allowing more dehydrogenated products to exit the reactor. At high carbon coverages, addition of oxygen rather than aiding the production of dehydrogenated product acts to clean the catalyst of carbonaceous residue hence lowering the yield.

In the case of propane dehydrogenation, no difference was found between catalysts that had been reduced by hydrogen or were reduced in situ by propane [13]. However, with butane the position is more complex. When we compare the C-4 product yields in Tables 1 and 3 for an equivalent conversion (Table 1, pulse no. 5, 43% and Table 3, pulse no. 7, 42%), we find the catalyst that has been reduced in hydrogen has a higher yield of dehydrogenated products and a different butene profile. For both the unreduced and reduced catalysts, the principal C-4 product is 1-butene, the thermodynamically least favoured butene. If we examine the butene profile for the unreduced catalyst, we find that after the third pulse the 2-butenes are in their equilibrium ratio (1.16:1), however, the 1-butene to 2-butene ratio is constant and well removed from equilibrium. With the reduced catalyst the 2-butene ratio is constantly moving towards equilibrium, but the ratio with 1-butene remains constant throughout. Therefore, for both catalysts we can postulate that the primary product is 1-butene, which isomerises at a constant rate into *trans*-2-butene. Hence for the unreduced catalyst there is rapid equilibration between the *cis*- and *trans*-2-butenes, whereas the attainment of equilibrium between the 2-butenes is slower over a reduced catalyst. Therefore, with the reduced catalyst the laydown of carbon is generating a surface where the activity for isomerisation increases, whereas no such process is occurring on the unreduced catalyst. This bias towards the 1-butene is also found in the industrial processes [12].

All of the systems produce isobutane in approximately equal yield that is independent of the butane conversion but is slowly decaying (isobutene was not observed). It is probable that most of the isobutane is formed not on the platinum but on the alumina support via an acid catalysed reaction [2]. This reaction will be insensitive to the reduction process and the zero yield on pulse no. 1 is likely to be due to secondary reaction of the isobutane on the platinum once formed, rather than lack of formation. In these systems, a significant portion of the carbon deposited is associated with the support [2,7,11], and much of the chemistry that the deposit undertakes on the surface is acid catalysed. Hence the isobutane formation is likely to be more sensitive to carbon deposition as a deactivation medium. The slightly higher yield found when oxygen is co-fed may be due to a slight cleaning effect of the oxygen on the acid sites of the support and hence maintaining a lower deactivation of these sites.

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