OXIDATIVE DEHYDROGENATION OF N-BUTANE CATALYZED BY ACTIVATED CARBONS

M. Domingo-García, I. Fernandez-Morales, F.J. López-Garzón, C. Moreno-Castilla

Departamento de Química Inorgánica, F. Ciencias, Universidad de Granada. GRANADA 18071. SPAIN

Introduction

A great interest has been devoted to the study of activated carbons as catalysts supports during the two last decades, due to the versatility of their textural and chemical characteristics as well as to their inertness at moderate temperatures. Having into account these properties and their well known catalytic behaviour in numerous inorganic oxidation reactions [1], more recently, activated carbons are being studied as catalysts itself in some important organic reactions, particularly dehydrogenation and dehydration of hydrocabons and alcohols [2, 3].

On the other hand, since the current chemical industry depends heavily on the use of unsaturated hydrocarbons as starting materials, the dehydrogenation of high alkanes carried out at mild temperatures using catalysts to produce useful olefins, offers a promising alternative.

In this work the dehydrogenation of n-butane in presence and absence of air conditions using an activated carbon obtained from olive stone, H-25, and a demineralised commercial carbon GAe as catalysts is studied

Experimental

Preparation and characterization of the activated carbon H-25 from olive stone as raw material, has been already reported [4].

Demineralization of the commercial activated carbon GAe was carried out by sucesive treatment with HCl and HF solutions. The ash percentage of final product was less than 0.8 %.

The catalytic experiments were performed in a plug-flow microreactor working at atmospheric pressure and temperatures between 623 and 673 K for H-25 and between 483 and 583 K for GAe. The activated carbon, 0.50 g, was heated overnight at 673 K in He flow prior to carry out the dehydrogenation reaction. The feed was a mixture of n-butane and air or helium with a molar ratio of 1:3 giving a total flow of 10 ml/min. Analysis of reactants and products were carried out in a gas chromatograph Perkin Elmer model 3920-B using a 20% BMEA on Chromosorb P-AW, 60/80 column and FID detector.

The conversion values that appear in the Tables refer to the amount of n-butane transformed into alkanes and alkenes.

Results and Discussion

To start with, the anaerobic dehydrogenation of butane in a mixture with helium at 673 K was carried out using sample H-25 as catalyst. The evolution of the conversion and the distribution of the different products with time of reaction are given in Figure 1 and Table 1 respectively. A decrease of conversion with time, which fit quite well to an exponential curve, is observed in the Figure 1. This effect can be atributed to the lost of surface active sites in the catalyst which will be hydrogenated in the course of the reaction. Although the conversión is low it keeps above the 1,2 % in the first hour producing a 96 % of C_4 alkenes, what means a low amount of cracking of butane into smaller molecules; however, 1,3 butadiene is not produced in this reaction Nevertheless, the products distribution remains constant during reaction time.

Quite different results are found for the butane/air reaction with the same catalyst at 623 K, giving a conversion of around 6.5 % and producing also a 96 % of C_4 alkenes but, in this case a significant production of 1,3 butadiene is found. As can be observed in Figure 2, there is no change in conversion with reaction time, and also the production of all products keeps constant. In this reaction the presence of oxygen in the gas flow eliminates the hydrogen fixed on the surface active sites of the catalyst producing water and then avoiding the lost of activity. A mean value of the products distribution under these conditions are given in Table 1.

The influence of temperature on the activity of GAe catalyst for butane/air reaction was also analysed and the results are given in Table 2. An important increase of conversion is found between 523 K and 583 K

following the reactivity the Arrhenius law. As with H-25 catalyst a low proportion of cracking reaction is given but, the most remarkable fact is that with the increase in conversion the production of 1-butene decreases in the same proportion as the production for 1,3 butadiene increases, becaming equivalent at 573 K; however, a very light decrease is observed for the production of cis and trans-butene species, which on the other hand, are almost equal at all temperatures.

Acknowledgment

This work was supported by the DGICYT under contract PB94-0754

References

1. Jüntgen, M. and Kühl, M.; Chemistry and Physics of Carbon (Edited by P.A. Thrower). Marcel Dekker, New York, 1989, Vol, 22, p. 145.
2. Drago, R.S. and Jurczyk, K., Appl. Catal., 1994, A112, 117.
3. Szymanski, G.S., Rychlicki, G. and Terzyk, A.P., Carbon, 1994, **32**, 265.
4. Salas-Peregrín, M.A., Carrasco-Marín, F., López-Garzón, F.J., and Moreno-Castilla, C., Energy & Fuels, 1994, **8**, 239.

Table1.- Products distribution of dehydrogenation of n-Butane in non oxidative and oxidative conditions using H-25 activated carbon as catalyst

Mixture of reactant	T (K)	Time (min)	Products Distribution (%)					
			C_3H_8	C_3H_6	1-C_4H_8	Trans-C_4H_8	Cis-C_4H_8	1,3-BD
Bu/He	673	55	1.7	1.5	32.4	37.4	26.7	0.2
		165	2.0	1.6	32.8	37.2	26.4	0.0
		295	1.8	1.5	33.0	37.4	26.3	0.0
Bu/Air	623	170	1.6	1.7	37.2	23.3	24.1	12.1

Table 2.-Conversion and products distribution of oxidative dehydrogenation of n-Butane using GAe activated commercial carbon

T (K)	Conversion (%)	Products Distribution (%)					
		C_3H_8	C_3H_6	1-C_4H_8	Trans-C_4H_8	Cis-C_4H_8	1,3-BD
483	0.17	0.0	0.0	42.4	26.6	27.7	3.3
513	0.63	0.5	0.3	35.2	27.3	28.7	8.0
533	1.34	0.7	0.4	31.4	25.3	26.7	15.5
573	2.32	1.2	1.2	28.6	21.0	22.2	25.8
583	3.88	1.5	1.5	28.6	19.8	21.2	27.4

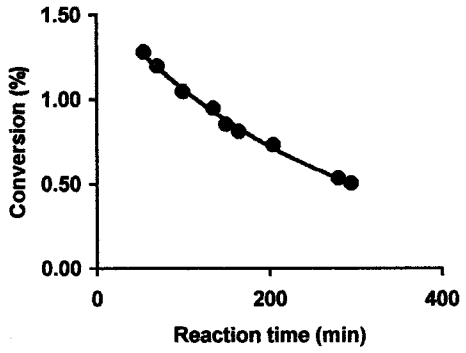

Figure 1.- Evolution of the conversion with reaction time for the non oxidative dehydrogenation of n-Butane at 673 K with activated carbon H-25

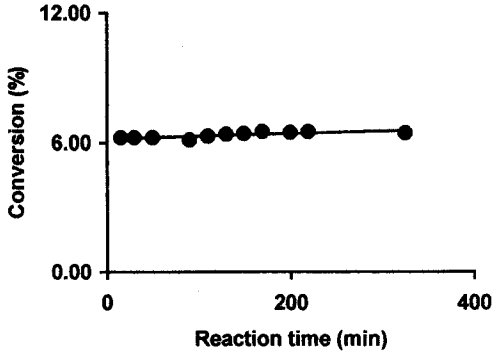

Figure 2.- Evolution of the conversion with reaction time for the oxidative dehydrogenation of n-Butane at 623 K with activated carbon H-25