

OXIDATIVE DEHYDROGENATION OF n-BUTANE, III.
KINETIC AND CATALYTIC ACTIVITY OF FERRIC OXIDE

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Catalytic activity of ferric oxide was evaluated in the oxidative dehydrogenation of n-butane. The apparent activation energy determined in the kinetic region was 37.7 kcal/mol. The activity of this oxide was undetectable up to 430°C. Reaction product distributions are shown as functions of temperature in the range of 430-650°C.

Каталитическую активность окиси железа (III) измеряли в окислительном дегидрировании n-бутана. Кажущаяся энергия активации равна 37,7 ккал/моль. Активность окисла не удалось обнаружить вплоть до 430°C. Распределение продуктов реакции представлено в зависимости от температуры в интервале 430-650°C.

INTRODUCTION

As part of a continuing study on n-butane oxidative dehydrogenation (OXD) reaction over different oxides, the activity and kinetics on ferric oxide have been investigated.

RESULTS AND DISCUSSION

The apparatus, operation conditions and detailed procedures have been described earlier [1,2].

The reactor was packed with ferric oxide diluted with quartz. The total BET surface area of this oxide was determined to be $10.08 \text{ m}^2/\text{g}$.

The reaction over ferric oxide can only be detected above 430°C , where the total n-butane conversion is 0.2%. This temperature is significantly greater than that obtained with nickel oxides ($200\text{--}300^\circ\text{C}$) [2] but little lower than that with quartz (500°C) [1].

Since in this study it was necessary to use high temperatures due to the low activity of the oxide, the product composition is the result of three kinds of reactions that can be present under these severe conditions, namely: dehydrogenation (butenes and butadiene), combustion (carbon dioxide and small quantities of CO) and cracking (ethylene and propylene). Data of total butane conversions and yields in dehydrogenation, cracking and combustion products, as functions of temperature are shown in Fig. 1b.

The reaction is more selective to C_4 olefins at low conversion (low temperatures) while the selectivity to combustion products passes through a maximum at approximately 580°C . Cracking reaction becomes significant at 530°C and increases rapidly with temperature. The yields of C_4 olefins and CO_2 tend to reach a maximum at temperatures around 650°C . Cracking becomes the main reaction at temperatures above 600°C .

The temperature dependence of the specific rate is given, in Arrhenius coordinates, in Fig. 1a. As can be seen, the line shows a breaking point in the region of $550\text{--}560^\circ\text{C}$. It must be stressed that the cracking reaction is already significant at these temperature conditions (Fig. 1b). The Arrhenius parameters in each of the regions (low and high temperature) are:

$$\begin{array}{l} 430\text{--}550^\circ\text{C} \quad E_a=37.7 \text{ kcal/mol}; \quad \log A = 3.29 \\ 560\text{--}640^\circ\text{C} \quad E_a=19.7 \text{ kcal/mol}; \quad \log A = -1.47 \end{array}$$

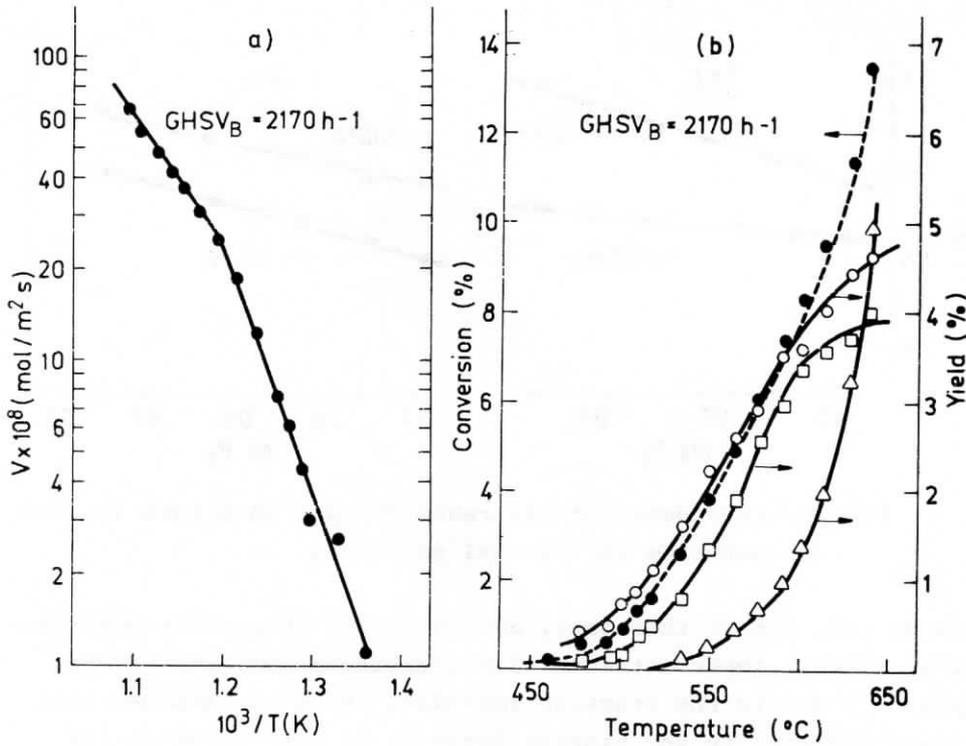


Fig. 1. (a) Arrhenius plot. (b) Conversion of n-butane (----) and yields (—) in total C_4 olefins (o), combustion (\square) and cracked products (Δ)

The orders of the reaction with respect to oxygen (m) and butane (n) partial pressure were determined at 510°C and 570°C (Fig. 2), with the aim to compare reaction order results in the absence (510°C) and presence (570°C) of the cracking reaction. The reaction orders are :

$T = 510^\circ\text{C}$	$m = 1.05$	$n = 1.11$
$T = 570^\circ\text{C}$	$m = 0.33$	$n = 1.28$

The apparent activation energy reduces to one half of the value at low temperature, which we could therefore, ascribe to intraparticle diffusion limitation, as was postulated on nickel

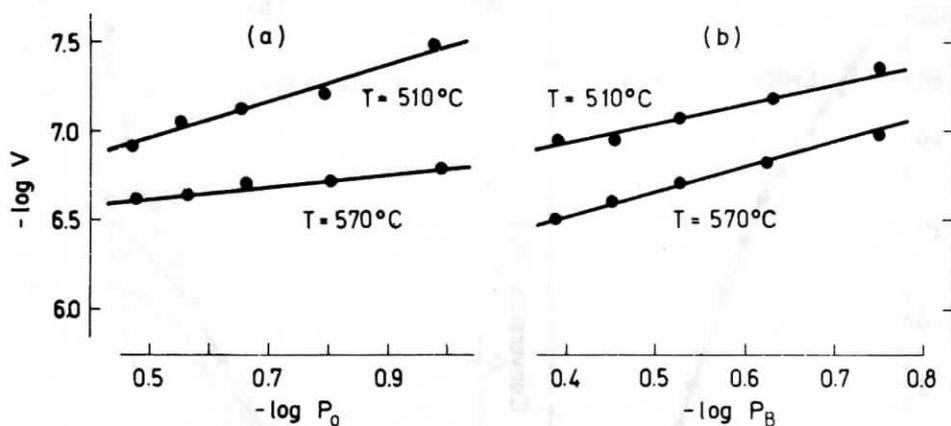


Fig. 2. Dependence of the reaction rate on oxygen (a) and n-butane (b) partial pressures

oxide [2]. But in this case, as the change in product distribution is very important after the breaking point temperature, possibly due to the cracking reaction, it can be assumed that the difference in the kinetic behavior of the system is the result of the interaction of two phenomena: an intraparticle transport limitation and a change from the low to the high temperature reaction mechanism, as was found for the oxidation of hydrocarbons [1]. This is also confirmed by taking into account the reaction orders and the pre-exponential factors in the two regions.

CONCLUSION

Ferric oxide is a very stable catalyst under the conditions used here. Its activity remains almost uniform for long times even under severe conditions. Selectivity in C_4 olefins is low due to the cracking reaction, which is significant at the high temperature conditions where the catalyst was active.

In the region of $550\text{--}560^\circ\text{C}$ a sudden change is observed in the activation energy which can be explained by the combined effect of a change in the reaction mechanism and intraparticle

transport limitations. A correlative change in the product distribution on the effluent reactor stream was also noticed.

It can be concluded that the activity of ferric oxide is significantly lower than that of nickel oxide but a little higher than that of quartz. This is in agreement with the apparent activation energy values over these oxides [1,2].

REFERENCES

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2. E.E. Gonzo, L.C. Romero, J.C. Gottifredi: *React. Kinet. Catal. Lett.*, in press.