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OXIDATIVE DEHYDROGENATION (OXD) OF n-BUTANE I. ACTIVITY OF NATURAL QUARTZ II. KINETIC AND CATALYTIC ACTIVITY OF NICKEL OXIDES

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The oxidative dehydrogenation of n-butane on nickel oxide catalysts and on natural quartz, used as catalysts diluent, were studied. It is assumed that oxygen ions from the oxide lattice participate in the initial step of the reaction.

Исследовали окислительное дегидрирование н-бутана на катализаторе окиси никеля и на природном кварце, используемом в качестве разбавителя катализатора. Полагают, что ион кислорода из матрицы окисла принимает участие в инициирующей ступени реакции.

INTRODUCTION

Oxidative dehydrogenation (OXD) has significant thermodynamic and process condition advantages as compared with the conventional dehydrogenation process in producing olefins and diolefins. For this reason, increasing attention has been directed to it recently [1-3].

A redox mechanism, initially proposed by Mars-van Krevelen, was postulated to explain experimental results obtained for

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the catalytic OXD of propylene [4] and butene [5,6].

The production of diolefins by the OXD of alkanes is not generally successful, due to the low reactivity of these compounds [7-11]. The yield of butene and butadiene was always very low, independently of the catalyst used [12-14].

The study of n-butane OXD on different first period transition metals oxides was carried out, with the aim to correlate reaction parameters with the thermodynamic properties of the oxides. In this paper, a study of the OXD of n-butane on nickel oxides is presented. Since the oxides used as catalysts have to be diluted in natural quartz, kinetic results in the absence of metal oxide are also presented.

EXPERIMENTAL

The reaction was studied in a tubular reactor of 9 mm diameter mounted vertically inside a controlled electrical heater. In the absence of metal oxide compound, quartz particles 60/80 mesh were used. In the experimental runs with the metal oxides, a bed of "black" nickel oxide (Merck) diluted with quartz in a ratio 1.2:1, was used. The BET surface area of the oxide was 3.75 m^2/g [15]. The reactant gas mixture, high purity oxygen and nitrogen, and 94% volume n-butane, was passed downward through the reactor at a fixed total flow rate of 215 NTP ml/min.

The reactor was operated under differential conditions. Thus, the reaction rate V was directly obtained from the n-butane conversion (x) as: $V=F_B \cdot x/S$, where F_B is the n-butane flow rate and S, the mass or the catalyst surface area charged in the reactor. The reaction rate V may be expressed as:

$$V = k\, p_O^m\, p_B^n$$

where k is the rate constant, m and n the order of reaction and p_O and p_B the partial pressure of oxygen and n-butane respectively.

RESULTS AND DISCUSSION

(a) Natural Quartz. The reaction rate is detectable starting from 400°C and the butane conversion overcomes 0.1% only after the temperature exceeds 500°C (Fig. 1b). A linear regression analysis of experimental data (Fig. 1a) leads to the values of the Arrhenius parameters shown in Table 1.

Carbon dioxide, C_4 olefins and unreacted butane were the main products present in the effluent gas up to 55°C, while cracking products (ethylene and propylene) were formed, besides carbon dioxide and C_4 olefins, at temperatures above 600°C. Thus, the reaction orders determined at 550°C and 614°C are shown in Table 1.

There can be seen an important change in the reaction orders obtained at low and high temperature. This effect may be due to a change in the mechanism of the reaction at different temperatures, which leads to the different product distribution observed. Nevertheless, the reaction order in n-butane (n), at low as well as at high temperature is always larger than unity, suggesting a poor or no surface coverage by the hydrocarbon.

Table 1

Arrhenius parameters (space velocity of n-butane 2170 h^{-1}, $C_4H_{10}:O_2:N_2$=20:15:65 mol %) and reaction orders

	Arrhenius parameters			reaction orders	
	E_a (kcal/mol)	log A	T (°C)	in oxygen (m)	in butane (n)
Quartz	43.6	4.60	550	1.30	3.40
			614	0.50	2.64
Nickel Oxides					
Series A	14.7	-1.29	-	-	-
Series B(LT)	19.4	-0.03	360	0.29	0.53
Series B(HT)	10.3	-3.02	420	0.41	0.28

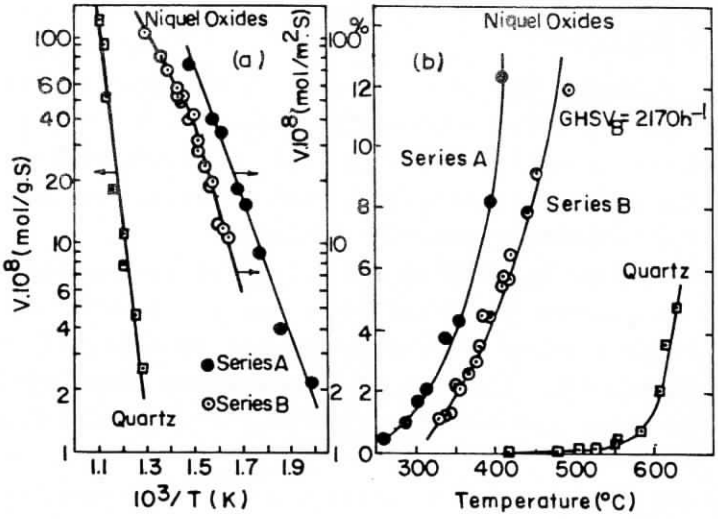

Fig. 1. (a) Arrhenius plot; (b) Conversion of n-butane

(b) Nickel Oxides. The "black" hydrous nickel oxide loses water producing $Ni_2O_3 \cdot 2H_2O$ and $Ni_2O_3 \cdot H_2O$, as it is heated [16,17]. It starts to decompose at temperatures of 340°C, but it is stable up to 410-430°C in the presence of oxygen [18].

With the purpose of studying this oxide in its initial state, a series of runs have been carried out at temperatures between 200°C and 500°C (Fig. 1, Series A). The reaction exothermicity is very high and the pressure drop through the bed increases rapidly as the reactor temperature reaches 413°C. After this series of experiments the catalyst was "regenerated" by circulating an oxygen-nitrogen mixture at 450°C. This treatment produces an important bed temperature increment, whose magnitude cannot be attributed to coke combustion, but rather to a reoxidation process; suggesting that during the Series A runs, the catalyst was reduced to a lower oxide (NiO) and eventually to metal as was found by Pilipenko et al. [11]. During this treatment, the pressure drop diminished until it reached values near the initial ones.

With the reoxidized catalyst, a second series of runs was

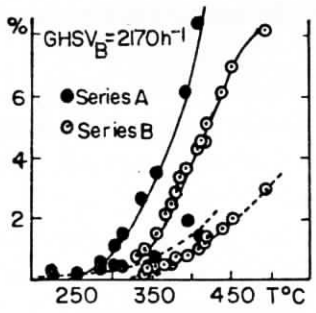

Fig. 2. Yields of combustion products (——) and total C_4 olefins (----) as a function of temperature. $C_4H_{10}:O_2:N_2$=20:15:65 mol %

carried out between 340-500°C (Fig. 1, Series B). After this series, the oxygen-nitrogen mixture at 450°C and also at 540°C was circulated. No heating effects were observed, indicating that, in this case, the catalyst has not been reduced. At this point, X-ray diffraction data confirm that the nickel was present as NiO, by repeating all the experimental runs with this catalyst, between 320-450°C, results in complete agreement with that of Series B were obtained (see Fig. 1).

In the Arrhenius plots for Series B, a sharp change in the slope of the line is observed for temperatures greater than 400°C, suggesting a severe internal diffusion limitation effect on the reaction rate or a change on the reaction mechanism. Arrhenius parameters as well as reaction orders for Series A and Series B, at low (LT) and high temperature (HT), are summarized in Table 1. When the internal diffusion transport affects the chemical kinetic process, the activation energy can be reduced to half the true value and the order of reaction can be (m+1)/2 for the limiting reactant and n/2 for the other [19,20]. Surprisingly, in this case, these figures are met.

The reaction poducts detected over both nickel oxides, were CO_2 and C_4 olefins (butenes, butadiene); cracking as well as other oxygen-containing compounds were absent (see Fig. 2).

Small amount of CO was observed at temperatures greater than 400°C.

The black nickel oxide is more active than NiO (Fig. 1b). Nevertheless, in both cases, a similar product distribution was obtained, which changes only slightly with temperature (Fig. 2).

CONCLUSION. Due to the low butane conversion on natural quartz, even at high temperature, it can be regarded as a good diluting agent for the catalysts.

The black hydrous oxide and NiO accelerate the butane OXD (Fig. 1b). On NiO there is an important transport limitation effect when temperature is greater than 400°C. The changes observed in the reaction rate for temperatures lower and higher than 400°C cannot be attributed to a modification in the mechanism of reaction, as in the case of oxidation reaction, due to the fact that the product distribution remains almost the same in the long temperature range investigated (Fig. 2).

It can also be argued that the oxygen responsible for initial hydrogen atom abstraction from n-butane is an oxygen ion from the oxide lattice [21]. The higher activity of "black" nickel oxide, compared with NiO, is possibly due to the greater instability and lability of the lattice oxygen responsible for the reaction.

REFERENCES

1. C.N. Wolf, R.I. Bergman, M. Sittig: Chem.Week, 113 (1966).
2. F.C. Newman: Ind.Eng.Chem., 62, 42 (1970).
3. L.M. Welch, L.J. Croce, H.F. Christmann: Hydrocarbon Process., 57, 131 (1978).
4. J.M. Peacock, A.J. Parker, P.G. Ashmore, J.A. Hockey: J. Catal., 15, (I) 373, (II) 379, (III) 387, (IV) 398 (1969).
5. PH.A. Batist, C.J. Kapteijns, B.C. Lippens, G.C.A. Schuit: J. Catal., 7, 33 (1967).
6. K. Keizer, PH.A. Batist, G.C.A. Schuit: J. Catal., 15, 256 (1969).

7. P. Boutry, J.C. Daumas, R. Montarnal: C.R. Acad, Sci. Paris, Serie C, 264, 81 (1967).
8. P. Boutry, P. Courty, J.C. Daumas, R. Montarnal: Bull. Soc. Chim. France, 4050 (1968).
9. V.G. Sitnikov, M.M. Andrushkevich, R.A. Buyanov, L.M. Plyasova, V.S. Babenko, G.N. Kustova, I.N. Klimik: Kinet. Katal., 15, 841 (1974).
10. I.Sh. Itenberg, M.M. Andrushkevich, R.A. Buyanov, G.A. Khramova, V.G. Sitnikov: Kinet. Katal., 17, 867 (1976).
11. F.S. Pilipenko, A.L. Tsailingol'd, G.A. Stepanov: Kinet. Katal., 17, 842 (1976).
12. V.K. Skarchenko: Int.Chem.Eng., 9,1(1969).
13. D.J. Hucknall: Selective Oxidation of Hydrocarbons, Academic Press, London 1974.
14. L.C. Romero, J.F. Rödl, S.R. Mohedas, L. Mercado: Lat. Am. J. Chem. Eng. Appl. Chem., 14, 193 (1984).
15. E.E. Gonzo: Appl. Catal., 2, 359 (1982).
16. C.F. Bell, K.A.K. Lott: Modern Approach to Inorganic Chemistry, Sec. Ed. Butterworth & Co. Ltd., London 1966.
17. K.M. Mackay, R.A. Mackay: Introduction to Modern Inorganic Chemistry. International Textbook Co. Ltd., London 1974.
18. E. Foote, B.C. Smith: J. Am. Chem. Soc., 20, 1344 (1908).
19. M. Boudart, G. Djega-Mariadasson: Kinetics of Heterogeneous Catalytic Reactions, Princeton University Press 1984.
20. E.E. Gonzo, J.C. Gottifredi: J. Catal., 83, 25 (1983).
21. J.H. Lunsford, M.B. Ward, T. Yang: in Proc. Climax Third International Conference on the Chemistry and Uses of Molybdenum, H.F. Barry and P.C.H. Mitchell - eds., Michigan 1979.