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OXIDATIVE DEHYDROGENATION OF n-BUTANE
IV. KINETIC AND CATALYTIC ACTIVITY OF COPPER OXIDE

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Copper oxide is moderately active and selective in the oxidative dehydrogenation of n-butane. Selectivity to C_4 olefin is almost constant in the range of 200-520°C. The apparent activation energy determined between 200 and 360°C was 18.8 kcal/mol, and 9.2 kcal/mol at higher temperatures.

Окись меди умеренно активна и селективна в окислительном дегидрировании н-бутана. Селективность к олефину C_4 почти постоянна в интервале температур 200-520°C. Кажущаяся энергия активации в интервале температур 200-360°C равна 18,8 ккал/моль, а при более высоких температурах она равна 9,2 ккал/моль.

INTRODUCTION

In preceding reports by the authors dealing with n-butane oxidative dehydrogenation (OXD) reaction over natural quartz, nickel oxides [1] and ferric oxide [2], both activity and kinetic parameters were examined. In the following section, a study of the OXD of n-butane on copper oxide will be presented, based on results obtained in our laboratory.

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RESULTS AND DISCUSSION

All of the experimental data were obtained using the system reported in the previous paper [1] under the same experimental conditions.

A 20 mm bed height of copper oxide diluted with natural quartz in a ratio of 1.2:1 was packed in the reactor. The BET surface area of the oxide, measured by a gravimetric technique based on n-hexane adsorption [3] was 29.2 m^2/g.

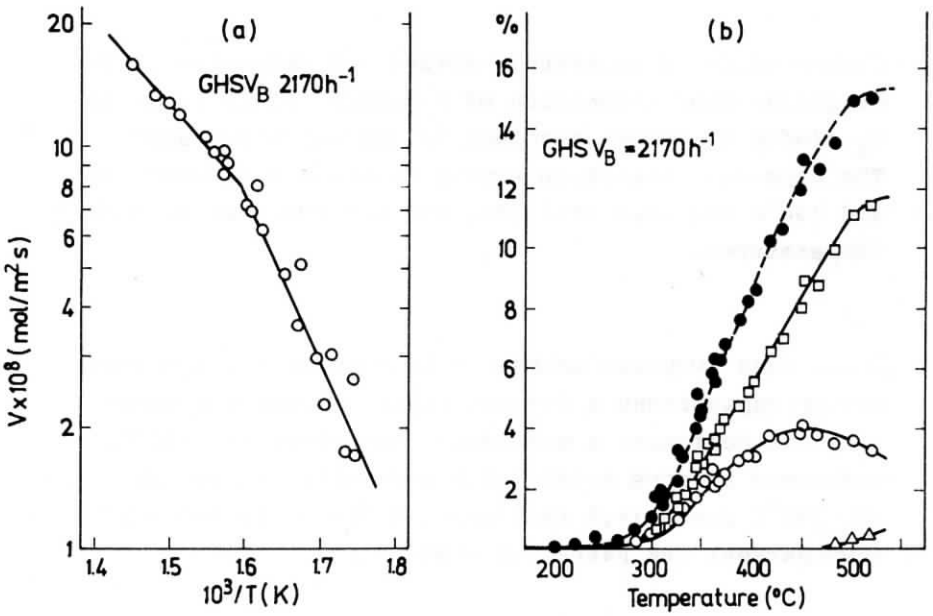

Fig. 1. (a) Arrhenius plot. (b) Conversion of n-butane(---) and yields (——) in total C_4 olefins (●), combustion (□) and cracked products (△)

Figure 1b shows the influence of the reaction temperature on the catalytic activity of pure copper oxide at an oxygen to butane molar ratio of 0.75. The total butane

conversion begins to be detected at temperatures around 200°C, reaching 1% conversion at 300°C. Between 300°C and 500°C, a sharp increase in butane conversion is observed up to 15%. The reaction rate at 352°C, evaluated with respect to the overall butane conversion, is 7.4×10^{-8} mol/m^2s, which agrees with the value reported by Levin et al. [4] for this reaction using copper oxide supported on α-Al_2O_3.

The catalytic activity of copper oxide is comparable to that of nickel oxide [1] and is higher than that observed with ferric oxide [2]. Nevertheless, the specific catalytic activity of copper oxide per unit surface area is three times lower than on nickel oxide.

As can be seen in Fig. 1b, the reaction products detected up to 450°C are carbon dioxide and C_4 olefins (butenes and butadiene), while cracking products (ethylene and propylene) are detected at temperatures higher than 450°C. Figure 1b also shows that the selectivity in dehydrogenation products is always greater than that found with nickel or ferric oxides [1,2] and remains almost constant and independent of reaction temperature.

The reaction rate dependence on the temperature is shown in an Arrhenius plot in Fig. 1a. A breaking point is observed between 350-360°C. A linear regression analysis of experimental data leads to the following values of Arrhenius parameters in each region:

LT: 204 - 360°C E_a=18.8 kcal/mol; log A=-0.55
HT: 364 - 418°C E_a= 9.2 kcal/mol; log A=-3.87

The orders of the reaction with respect to oxygen (m) and n-butane (n) partial pressure for a power law kinetic expression are (Fig. 2):

Low temperature range (LT): m=0.18, n=0.51
High temperature range (HT): m=0.09; n=0.42

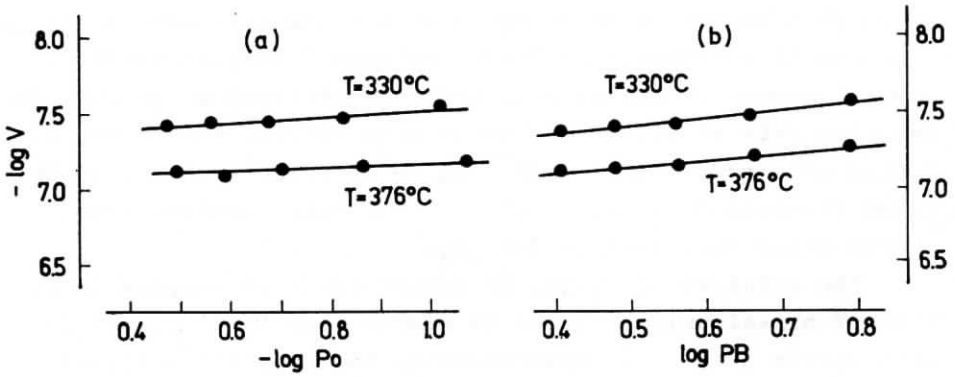

Fig. 2. Dependence of the reaction rate on oxygen (a) and n-butane (b) partial pressure

No change either in the specific surface area or in the XRD spectra of the oxide were observed after a catalyst test, in agreement with the results reported by Levin et al. [4].

The change in the kinetic behavior of the system when the temperature rises above 360°C may be explained taking into account the redox mechanism proposed for the OXD reaction [1]. An increase in reaction temperature will favor the activity of lattice oxygen which could explain the increase of CuO activity with temperature (Fig. 1b). After a certain temperature has been reached, however, the lattice oxygen is so active that the rate of disappearance is more rapid than the rate of catalyst reoxidation due to the oxygen in gaseous phase. This could lead to a net oxide reduction (even if no Cu_2O can be detected after performing a given reaction test) [5]. This phenomenon could also be the reason for slight selectivity changes, both in dehydrogenation and combustion products, observed in the whole range of temperature investigated. Nevertheless, under more severe experimental conditions, the partial pressure of oxygen in the gases leaving the reactor can be estimated as 0.06 atm at 450°C. This value is several orders of magnitude greater than the equilibrium oxygen pressure for

the system CuO (s) $\rightleftharpoons$ Cu_2O (s) + 1/2 O_2 (g) [6].

Although the approximate apparent activation energy reduction to one half could be explained by pore diffusion limitation effects, this cannot be demonstrated by observing the simultaneous reaction order changes [7].

CONCLUSIONS

Copper oxide (CuO) is a moderately active and selective catalyst for n-butane oxidative dehydrogenation. Its activity is comparable with that observed for nickel oxides but is greater than that observed for ferric oxide. The selectivity to dehydrogenation products (butenes and butadiene) is greater than previous findings with other oxides and is almost independent of reaction temperature. The changes observed in activation energy and reaction orders, in the region of 350-360°C, might be explained by assuming a competitive reaction mechanism in which temperature effects on the rate of disappearance of lattice oxygen and the rate of catalyst reoxidation are involved.

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