

OXIDATIVE DEHYDROGENATION OF *n*-BUTANE OVER A MgO-SUPPORTED MAGNESIUM VANADATE CATALYST

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abstract: The catalytic and non-catalytic oxidative dehydrogenation of *n*-butane were investigated. It was found that in the non-catalyzed reaction the *n*-butane conversion not exceeds 4% at 550°C and the selectivities to butenes are significant only at temperatures below 450°C. Oxidative dehydrogenation was examined in the presence of mixed V-Mg-oxide catalyst comprising 24.5% V₂O₅. It was observed that the catalyst is active and quite selective for butenes and butadiene at reaction temperatures in the range 450 – 550°C. The selectivity to butenes decreased and the selectivity to butadiene increased with increasing conversion at 550°C. The low apparent activation energy observed (7 kcal.mol⁻¹), suggests that the rate-limiting step of the reaction is the reoxidation of the catalytic site by diffusion of the lattice oxygen or directly by gas phase oxygen.

keywords: V-Mg-oxide catalyst, oxidative dehydrogenation, *n*-butane.

Introduction

Vanadium-magnesium-oxides (V-Mg-O) are among the most selective and active catalysts for the oxidative dehydrogenation of *n*-butane to butene and butadiene, the orthovanadate phase being the selective phase [1]. Unfortunately, the selectivity and yield obtained in all literatures are too low to make the process commercially feasible [1-5].

In the present study, the catalytic oxidative dehydrogenation of *n*-butane is investigated over a range of temperatures and contact times for a stoichiometric butane/air ratio. MgO-supported magnesium vanadate is used as catalyst. The non-catalytic oxidative dehydrogenation of *n*-butane is also investigated.

Experimental

Catalyst preparation and characterization

The catalyst was prepared following a method described by Chaar et al. [1]. An appropriate amount of MgO powder was impregnated with a solution containing 1 wt % of ammonium vanadate and 0.5 wt % of ammonium hydroxide at 70°C. The resulting suspension was

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evaporated with stirring until a paste was obtained. The paste was dried for 18 h at 120°C. The resulting solid was calcined at 600°C for 4 h and then pelletized, crushed and sieved to the desired particle size. The catalyst composition used in this work was determined at 24.5 wt % V₂O₅ by means of inductively coupled plasma (SPECTROFLAME-ICP). The surface area of the sample was measured using the BET technique and the crystal phases were identified by X-ray diffraction using a Brüker D5005 diffractometer and Cu K α radiation. Characterization of the catalyst has been performed before and after catalytic test. After catalytic test, the catalyst was recovered by cooling them down in the flow of reactants.

Catalytic test

The oxidative dehydrogenation of *n*-butane was carried out in a fixed bed quartz tube down-flow reactor operated at atmospheric pressure and in the temperature range of 400 – 550°C. The conditions of the catalytic test were described elsewhere [6]. A gas feed with an air to *n*-butane ratio equal to 5 and an hourly space velocity (VVH) of 1000 h⁻¹ with respect to *n*-butane were used. When the effect of the VVH on the catalytic properties of the catalyst was studied, this was varied in the range 500 – 2000 h⁻¹. Quartz chips were used to fill the dead volumes before and after the catalyst bed to minimize potential gas-phase pyrolysis reactions at higher reaction temperatures. In the non-catalytic experiments, the catalyst bed was replaced with quartz chips having the same particle size. The major products formed under these reaction conditions were 1- and 2-butenes, butadiene, CO, CO₂, and cracking products (methane, ethane, ethylene and propylene).

Results and discussion

Catalyst characterization

The specific surface area of the solid as prepared was slightly over 20 m².g⁻¹. In the XRD pattern of this material, presented in figure 1.a, only the peaks indicating the presence of MgO are evidenced. A diffuse band between 20 and 40° is also observed, indicating a much less crystallized or more dispersed form of orthovanadate. Before the catalytic test, this solid was treated in the reactor at 600°C in the flow of reactants for 6 hours. The specific surface area of the resulted catalyst was only 12 m².g⁻¹ and the XRD pattern of this material (fig. 1.b) clearly shown the presence of the crystalline Mg orthovanadate (Mg₃(VO₄)₂). Neither pyro- (Mg₂V₂O₇) nor meta-vanadates (MgV₂O₆) are observed in this pattern. This activated catalyst was tested in the oxidative dehydrogenation reaction.

After catalytic test, the specific surface area remained almost the same and the XRD pattern of the solid was not affected by the test.

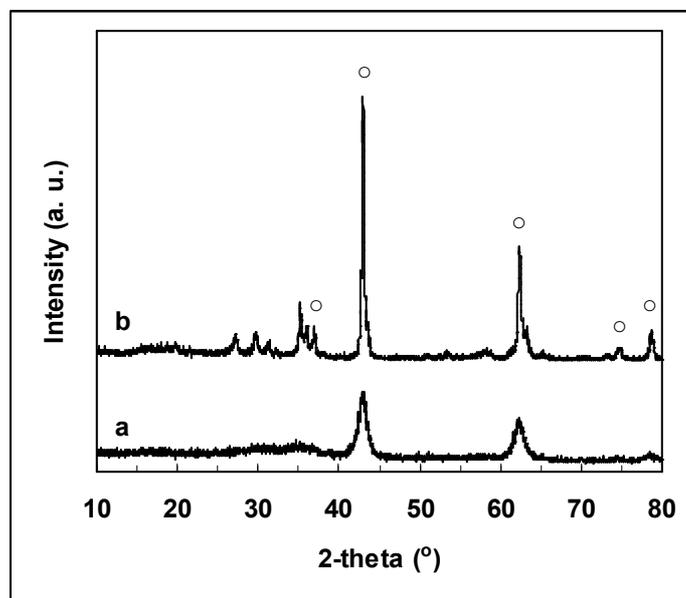


Fig. 1. XRD patterns of the catalyst (a) as prepared and (b) after activation in the flow of reactants (o - peaks corresponding to MgO phase).

Non-catalytic oxidative dehydrogenation

The non-catalytic oxidative dehydrogenation of *n*-butane was investigated using a residence time of 0.6 s. The residence time was calculated by dividing the volume of the quartz chips bed replacing the catalyst (2 cm³) by the volumetric flow rate of the feed

Fig. 2 shows the conversion of *n*-butane and the distribution of products as a function of reaction temperature. The conversion of *n*-butane is very low, at 550°C only 4% of butane being converted. The selectivity to butenes is high (~ 90%) at 410°C, but decreases to 30% as the temperature is increased to 550°C. Butadiene was not detected. The selectivity to cracking products is low at low temperatures and increases up to 54% at 550°C. The selectivity to combustion products (CO_x) is quite low and increases slightly in the range of temperatures used.

Summarizing, the non-catalytic oxidative dehydrogenation reaction of *n*-butane is not important in our conditions and the selectivities to butenes are significant only at temperatures below 450°C. Lemonidou et al. [7] shown that this reaction is very important in the range of temperatures of 530 – 580°C but using an empty reactor. When the reactor was fulfilled with inert quartz particles, only 2.5% of *n*-butane was converted at 580°C.

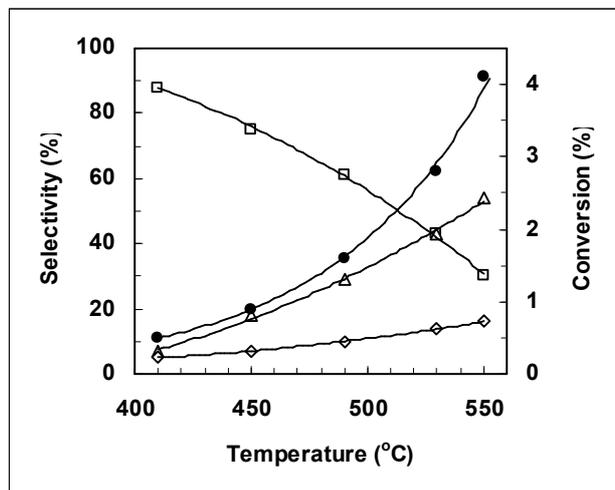


Fig. 2. Effect of reaction temperature on the non-catalytic oxidative dehydrogenation of *n*-butane: *n*-butane conversion (●) and selectivities for butenes (□), CO_x (◇) and cracking products (Δ).

Catalytic oxidative dehydrogenation

The results obtained in the presence of the MgO-supported magnesium vanadate catalyst are shown in figure 3. As expected, an increase in the temperature resulted in an increase in the conversion: from 13% at 450°C to 24% at 550°C. The selectivity for butadiene actually increased (from 17 to 32%), while this of the butenes decreased (from 39 to 31%), but the total dehydrogenation selectivity (TDS) remained almost the same between 490 and 550°C. There was a slight increase in the selectivity for the cracking products and, contrarily to results obtained by Chaar et al. [1], the selectivity for the combustion products decreased with increasing temperature. The same tendency was observed in the tests with a void post-catalytic volume reported by Lemonidou et al. [7].

The effect of the VVH on the conversion and on the total dehydrogenation selectivity at 550°C is shown in figure 4. The conversion decreased linearly when the VVH with respect to *n*-butane was increased from 500 to 2000 h⁻¹ and the total dehydrogenation selectivity increased. These results are in agreement with the fact that the conversion of *n*-butane and the selectivity to butenes and butadiene are inversely related.

The influence of the conversion on the product distribution is depicted in figure 5. While the selectivity to butenes decreases with the conversion from 46 to 28%, the selectivity to butadiene increased from 25 to 33%. The selectivity to butenes decreased due to the formation of butadiene and carbon oxides in a consecutive reaction. The selectivity to cracking products decreases with increasing conversion, probably due to subsequent oxidation to carbon oxides. Finally, Fig. 5 also illustrates the well-known fact that butenes are primary products, with a high selectivity at low conversion (low contact time), while the secondary product butadiene appears at higher contact times.

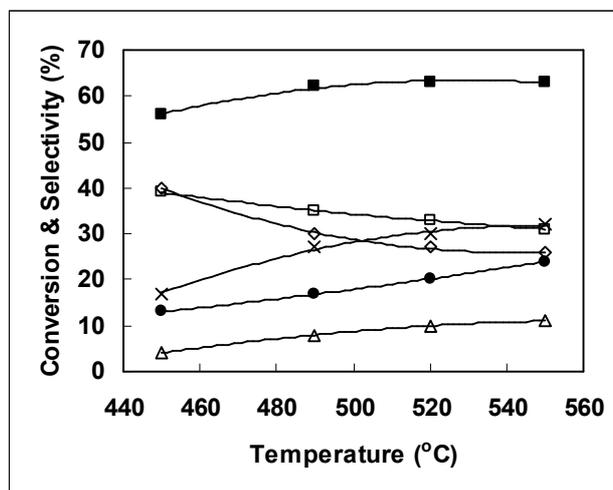


Fig. 3. Effect of reaction temperature on the oxidative dehydrogenation of *n*-butane over $Mg_3(VO_4)_2/MgO$: *n*-butane conversion (●), total selectivity for dehydrogenation products (TDS) (■) and selectivities for butenes (□), butadiene (×), CO_x (◇) and cracking products (Δ).

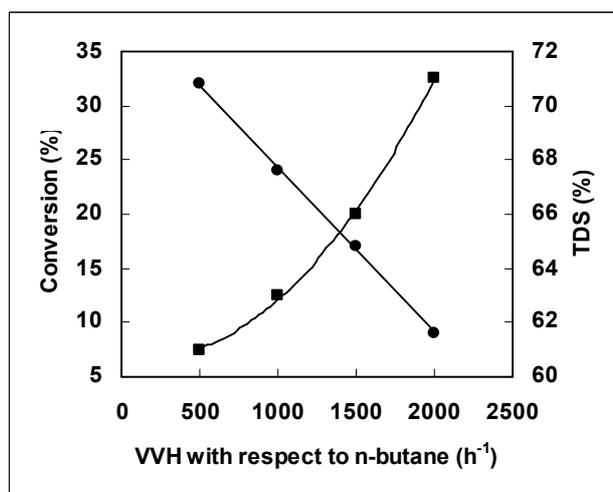


Fig. 4. Effect of VVH on the conversion (●) and on the total selectivity for dehydrogenation products (TDS) (■) in the oxidative dehydrogenation of *n*-butane over $Mg_3(VO_4)_2/MgO$ catalyst at 550°C.

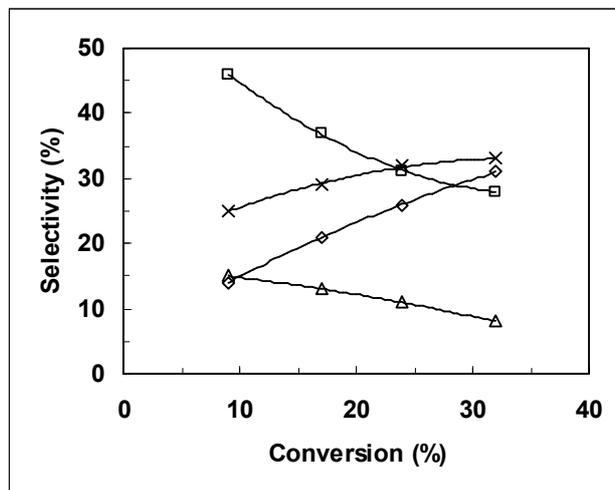


Fig. 5. Effect of conversion on the selectivities in butenes (□), butadiene (x), CO_x (◇) and cracking products (Δ) in the oxidative dehydrogenation of *n*-butane over Mg₃(VO₄)₂/MgO at 550°C.

The apparent activation energy for the reaction of *n*-butane was calculated from the Arrhenius plot over the range from 450 – 550°C (figure 6).

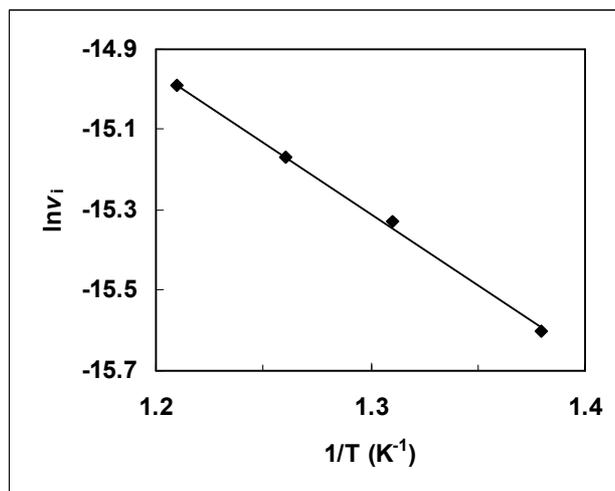


Fig. 6. Arrhenius plot for the *n*-butane conversion on Mg₃(VO₄)₂/MgO catalyst.

The obtained value is low, namely 7 kcal.mol⁻¹. Taking into account that the Mars – van Krevelen mechanism is the reaction mechanism in this case [8, 9], this low value of the apparent activation energy suggests that the rate-limiting step of the reaction is the reoxidation of the catalytic site by diffusion of the lattice oxygen or directly by gas phase oxygen, like in the case of titanium pyrophosphate (TiP₂O₇) catalyst in the same range of

temperatures [10]. Patel et al. [11], reported, for the same reaction in the same range of temperatures, an apparent activation energy equal to 22 kcal.mol⁻¹, but they worked with a rich-oxygen reaction mixture. This means that, when the oxygen content in the feed is not sufficient for the reoxidation of the catalytic site, like in our case, this becomes the rate-limiting step of the reaction.

Conclusion

In the non-catalyzed oxidative dehydrogenation, the *n*-butane conversion not exceeds 4% at 550°C and the selectivities to butenes are significant only at temperatures below 450°C. Butadiene was not detected.

MgO-supported Mg₃(VO₄)₂ catalyst is active and quite selective for butenes and butadiene at reaction temperatures in the range 450 – 550°C. The maximum yield was obtained at 550°C and a VVH of 500 h⁻¹ with respect to *n*-butane, with selectivities in butenes and butadiene of 28% and 33%, respectively, for 32% conversion.

The apparent activation energy for *n*-butane conversion on Mg₃(VO₄)₂/MgO catalyst was 7 kcal.mol⁻¹. This low value suggests that the rate-limiting step of the reaction is the reoxidation of the catalytic site by diffusion of the lattice oxygen or directly by gas phase oxygen.

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