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Kinetics under dynamic conditions of the oxidative dehydrogenation of butane with doped V/MgO

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Abstract

The oxidative dehydrogenation of butane on a V/MgO doped catalyst has been studied under anaerobic conditions. Fe, Co and Mo were used as dopants with atomic ratios to V of 1:20 and 1:100. Under these conditions, the oxygen from the catalyst lattice is consumed by the reaction and the degree of solid oxidation changes during the process.

A kinetic model is applied in which the relation between the reaction rates and the degree of catalyst oxidation is taken into account.

The V/MgO-Fe (1%) is the most promising doped catalyst for increasing the yield to butenes + butadiene. The effect of the doping in the kinetic scheme supposes an increase in the butane oxidation constant to CO_x, and a decrease in the formation of butadiene from butane and in the deep oxidation of butadiene. The final effect is an improvement in the selectivity to butenes + butadiene.

Keywords: Oxidative dehydrogenation; Butene; Butadiene; Transient kinetics

1. Introduction

The use of a two-zone fluidized bed reactor has been shown as a suitable method for increasing the yield to butadiene in the oxidative dehydrogenation of butane [1]. In this reactor, two zones are created by feeding the oxygen-containing stream and the hydrocarbon at different points. The catalyst circulates between an oxidizing and a reducing zone, and thus operates under dynamic conditions. This operation system constitutes an alternative to the circulating bed reactor as employed, for example, by DuPont [2] for the production of maleic anhydride. The oxidation state of each particle of the catalyst varies over the time, in the same way that the degree of oxidation of the catalyst changes along the bed, despite the fact that the full reactor is operating under steady state conditions. In order to predict the performance of this reactor, the conventional kinetic models obtained under steady state conditions are no longer useful, and any kinetic equations must be obtained under dynamic conditions, varying the degree of oxidation with time.

A V/MgO catalyst, widely studied in the literature, was employed in previous works. The kinetic of this catalyst under dynamic conditions (varying the oxidation degree over the time) had previously been studied [3], and the kinetic constant for each reaction was related with the degree of oxidation of the catalyst. The resulting model allowed us to take into account the changes in selectivity with the degree of oxidation. The aim of this work is to determine the effect of some dopants (Fe, Co and Mo) on the performance of the catalyst under dynamic conditions and to develop a kinetic model for the most promising of these modified V/MgO catalysts.

2. Experimental

The reaction experiments were performed under anaerobic conditions in a fluidized bed reactor, thus ensuring the isothermicity of the bed, feeding a $110\,\mathrm{N\,cm^3\,min^{-1}}$ butane/helium mixture (4% C_4H_{10}) at the reaction temperature ($T = 525$–$575\,^\circ\mathrm{C}$). The superficial gas velocity used in the bed was 1.5 times the minimum fluidization velocity of the solid. The catalyst load ($W_o = 5$–$30\,\mathrm{g}$) was initially fully oxidized, and is reduced by the introduction of the reacting feed, since the only oxygen available for reaction comes

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from the catalyst lattice. The changes in the product composition over time were followed by gas chromatography (C.E. Instruments GC-8000top with a Molecular sieve 10 A 80/100 and a Chromosorb P AW 80/100 columns). In order to obtain enough experimental data along the time on stream, each experiment was repeated twice, taking samples at different times.

The original V/MgO catalyst, with a vanadium content of 24 wt.% as (V_2O_5), was prepared by impregnation of commercial MgO powder with an aqueous ammonium metavanadate and ammonium hydroxide solution in accordance with a previously reported procedure [4]. The solid was dried at 100 °C overnight and calcined in air at 550 °C for 6 h. The initial fine powder was pressed into pellets, then crushed and sieved to a 100–320 μm size.

The resulting catalyst was doped with Fe, Co and Mo, by the method of incipient wetness: a 50 g sample was impregnated with 60 ml of an aqueous solution of the corresponding salt, $Fe(NO_3)_3 \cdot 5H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ or $MoCl_5$. Two atomic ratios of dopant to V were used for each: 1 and 5%. The solid obtained was calcined at 600 °C for 12 h. The final catalyst was termed Fe-1, Fe-5, Co-1, Co-5, Mo-1 or Mo-5 according to the dopant used and the atomic ratio (checked by ICP analysis). An average BET surface area of $29\,m^2\,g^{-1}$ was obtained in the calcined samples. The minimum fluidization velocity was about $1.2\,cm\,s^{-1}$.

3. Results

3.1. Catalyst efficiency

Several anaerobic reaction tests were carried out with the V/MgO reference catalyst and with the doped samples, under the experimental conditions described in the above section, in order to compare their activity and selectivity in the oxidative dehydrogenation of butane. The temperature T and catalyst load W_o were fixed at 550 °C and 15 g, respectively.

No improvement was observed with the Co doped catalysts. Improvements in selectivity or activity were found only with Mo-5 and with Fe (both 1 and 5% atomic ratio) catalysts.

The beneficial effect of Mo was only observed in the selectivity to butadiene at low butane conversion, but the selectivity to valuable dehydrogenation products (butanes and butadiene) is clearly lower than that obtained with the undoped catalyst, as can be observed in Fig. 1. The presence of Fe resulted in an improvement in the total selectivity to butenes + butadiene measured at isoconversion. The Fe-5 catalyst improved this selectivity, but only at butane conversions below approximately 60% (Fig. 1). However, the Fe-1 catalyst showed a different behavior, the improvement in selectivity to butenes + butadiene being reached at butane conversions higher than approximately a 40% value, allowing higher yields to the desired products. Therefore the catalysts with Fe, mainly Fe-1, were selected for a detailed kinetic study.

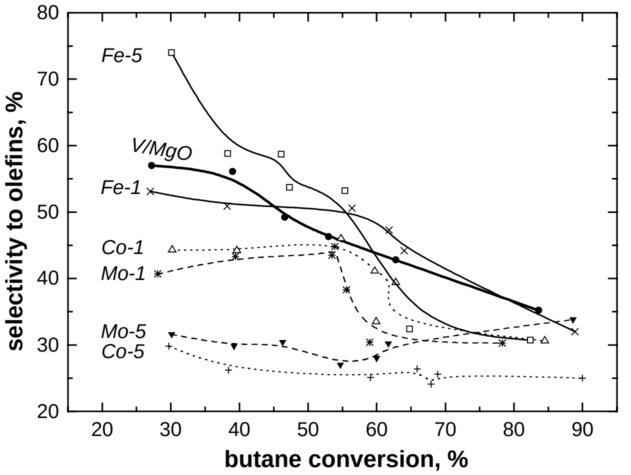

Fig. 1. Selectivity to olefins (butenes+butadiene) for the different prepared catalysts as a function of butane conversion, under anaerobic conditions. $W_o = 15$ g, $T = 550\,°C$.

3.2. Kinetic model

The reaction scheme employed (see Fig. 2) considers every step in the transformation of butane to butene, butadiene and carbon oxides. The cracking of butane yielding light C_2^+ hydrocarbons (mainly methane, ethylene and propylene) has also been included in the model. The reaction of coke formation has not been considered in the model given the small amount measured by means of further combustion experiments carried out with the catalyst used in the oxidative dehydrogenation experiments. The mass balance for each gaseous compound leads to Eqs. (1)–(5), in which the n_i parameters gives the dependency of each reaction on the degree of oxidation of the catalyst, θ_o:

$$\frac{dx_b}{d\tau} = (k_1\theta_o^{n_1} + k_2\theta_o^{n_2} + k_4\theta_o^{n_4} + k_7\theta_o^{n_7})(1 - x_b) \tag{1}$$

$$\frac{dY_{bte}}{d\tau} = k_1\theta_o^{n_1}(1 - x_b) - (k_3\theta_o^{n_3} + k_5\theta_o^{n_5} + k_7\theta_o^{n_7})Y_{bte} \tag{2}$$

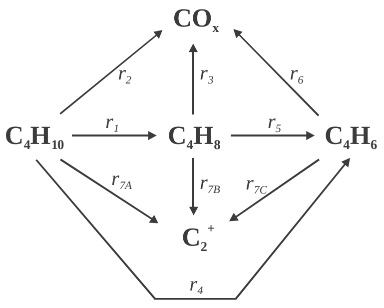

Fig. 2. Proposed reaction scheme.

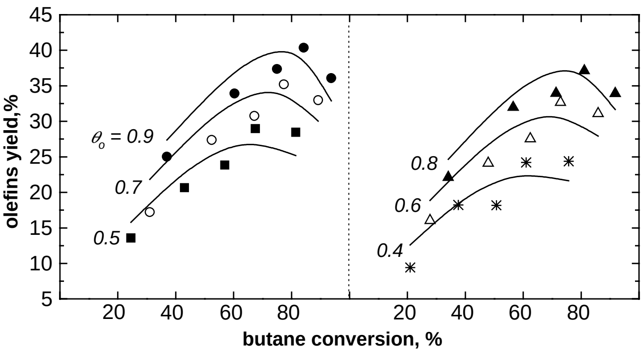

Fig. 3. Comparison between the experimental yield to olefins (butenes + butadiene) and the predictions of the selected model (lines) for the Fe-1 catalyst at $T = 550\,^{\circ}\mathrm{C}$.

$$\frac{\mathrm{d}Y_{\mathrm{btd}}}{\mathrm{d}\tau} = k_4\theta_{\mathrm{o}}^{n_4}(1 - x_{\mathrm{b}}) + k_5\theta_{\mathrm{o}}^{n_5}Y_{\mathrm{bte}} - (k_6\theta_{\mathrm{o}}^{n_6} + k_7\theta_{\mathrm{o}}^{n_7})Y_{\mathrm{btd}} \tag{3}$$

$$\frac{\mathrm{d}Y_{\mathrm{c}}}{\mathrm{d}\tau} = k_7\theta_{\mathrm{o}}^{n_7}[(1 - x_{\mathrm{b}}) + Y_{\mathrm{bte}} + Y_{\mathrm{btd}}] \tag{4}$$

$$\frac{\mathrm{d}Y_{\mathrm{cox}}}{\mathrm{d}\tau} = k_2\theta_{\mathrm{o}}^{n_2}(1 - x_{\mathrm{b}}) + k_3\theta_{\mathrm{o}}^{n_3}Y_{\mathrm{bte}} + k_6\theta_{\mathrm{o}}^{n_6}Y_{\mathrm{btd}} \tag{5}$$

x_b being the butane conversion, τ the spatial time referred to the catalyst weight ($W_{\mathrm{o}}F^{-1}$, $\mathrm{g\,s\,mol^{-1}}$) and Y_i the yield to the i compound. The i compounds are btd (butadiene), bte (butanes), c (cracking products), co$_x$ (carbon oxides).

Several dynamic experiments were carried out under anaerobic conditions at different T and W_{o} values in order to obtain the parameters of the proposed kinetic model. By combining those performed at the same temperature but with different spatial times, graphs of the yield to each product versus butane conversion may be obtained for each value of θ_{o}. As an example, Fig. 3 shows the experimentally obtained (data points) olefin yields versus butane conversion for several θ_{o} values at $T = 550\,^{\circ}\mathrm{C}$ with the Fe-1 doped catalyst.

The shape of the experimentally obtained Y_i versus x_{b} plots for each i compound and different θ_{o} values (such as those shown in Fig. 3) gives some insight into the dependency of each reaction on the degree of oxidation of the catalyst. In this context, several submodels were tested, each with a different supposed dependence of each reaction (n_i) on the degree of oxidation of the catalyst (θ_{o}). The model selection was made by comparing the experimentally observed curves with those predicted by the model, and also by the statistical parameters obtained in the multivariable fitting. This was done using *Scientist*® software. The statistical criteria considered are the *Model Selection* criteria (MSC), the correlation coefficient (CC) and the correlation coefficient for the fitting of butadiene (CCB).

The best fit was obtained with a model in which the deep oxidation of hydrocarbons (reactions 2, 3, and 6 in the reaction scheme of Fig. 2) was independent of θ_{o} The hydrocarbon cracking (7A, B, and C) was also independent of θ_{o}, and all the other reactions were first order dependent with θ_{o}. Thus the selected kinetic model has the following n_i values: $n_1 = 1$, $n_2 = 0$, $n_3 = 0$, $n_4 = 1$, $n_5 = 1$, $n_6 = 0$, $n_7 = 0$.

This implies that the best selectivity was obtained with a fully oxidized catalyst. At first sight this seems to contradict the results of other authors, e.g., [5], who found higher selectivity with low oxygen partial pressure. The apparent contradiction can be explained by taking into account that these other authors were working in aerobic conditions. There is consequently a fast reaction between weakly adsorbed oxygen coming from the gas phase (in the usual experimental system) that is not produced in our reaction system (where all the oxygen for the reaction is obtained by reducing the catalyst). These results are in good agreement with other previous works [6,7].

In the selected submodel, reaction (4) was removed from the reaction scheme because the constant k_4 was clearly smaller than any other constant k_i and its standard deviation larger than its value. The values of the kinetic constants at $T = 550\,^{\circ}\mathrm{C}$ and the statistical parameters of the final simplified submodel are given in Table 1, for the catalyst

Table 1

Values of the kinetic constants for the proposed kinetic model ($n_1 = 1$, $n_2 = 0$, $n_3 = 0$, $n_4 = 1$, $n_5 = 1$, $n_6 = 0$, $n_7 = 0$, $k_4 = 0$), Fe-1 catalyst

	k_i at 550 °C ($\mathrm{mol\,kg^{-1}\,s^{-1}}$)	Arrhenius dependence			k_i at 550 °C (V/MgO) ($\mathrm{mol\,kg^{-1}\,s^{-1}}$)
		$\ln k_{\mathrm{o}\,i}$	E_{a}/R (K)	r	
k_1	$2.74\mathrm{E}^{-4} \pm 5.24\mathrm{E}^{-5}$	22.25	25304	0.977	$3.39\mathrm{E}^{-4}$
k_2	$2.29\mathrm{E}^{-5} \pm 8.24\mathrm{E}^{-6}$	23.84	22105	0.973	0
k_3	$4.09\mathrm{E}^{-4} \pm 1.20\mathrm{E}^{-4}$	18.33	12931	0.969	$5.35\mathrm{E}^{-4}$
k_5	$9.38\mathrm{E}^{-4} \pm 9.75\mathrm{E}^{-5}$	8.48	8431	0.953	$2.21\mathrm{E}^{-3}$
k_6	$1.04\mathrm{E}^{-4} \pm 3.28\mathrm{E}^{-5}$	0.86	50603	0.926	$2.01\mathrm{E}^{-4}$
k_7	$8.75\mathrm{E}^{-6} \pm 1.61\mathrm{E}^{-6}$	49.49	28730	0.985	$6.83\mathrm{E}^{-6}$
MSC[a]	2.97				2.66
CC[b]	0.98				0.96
CCB[c]	0.96				0.95

[a] Model selection criterion.

[b] Fitting correlation coefficient.

[c] Fitting correlation coefficient for the butadiene yield.

Fe-1. The Arrhenius dependence of these kinetic constants and the correlation coefficient are also shown in Table 1.

Finally, the simulated results are plotted in Fig. 3 (in lines). As may be seen, the experimental trends agree with those predicted by the model.

3.3. *Kinetic effect of the doping*

The last column in Table 1 shows the kinetic constants obtained for the undoped V/MgO catalyst [3]. A comparison of the kinetic constants of the doped (1% Fe) and the original catalyst shows the effect of the doping: an increase in the butane oxidation constant to CO_x, and a clear decrease in the formation of butadiene from butane and in the deep oxidation of butadiene. The final effect is a decrease in butadiene yield and larger butene production, which jointly result in an improvement in the selectivity to butenes + butadiene.

4. Conclusions

The doping of a V/MgO catalyst with Fe, Co or Mo, with atomic ratios of dopant to V of 1:20 and 1:100, produces a broad effect on activity and product selectivity for the oxidative dehydrogenation of butane. Doping with Fe increases the selectivity under anaerobic conditions.

The kinetic model used previously for undoped catalysts is perfectly adaptable for doped ones. A comparison of the new kinetic constants with those of the reference catalysts allows a diagnosis of this effect. The kinetics obtained is also well suited for the simulation of a reactor in which the catalyst operates under dynamic conditions.

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