The Oxidative Dehydrogenation of Alkanes C_3—C_4 by Carbon Dioxide

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The oxidative dehydrogenation of propane, butane, isobutane, and their mixtures, by carbon dioxide over manganese-, chromium-, copper-, and silver-based catalysts at temperatures from 700 up to 850 °C at the atmospheric pressure was studied using a continuous reactor. All the tested catalysts have exhibited a low activity for this type of process, which was demonstrated by comparison with the results obtained over the catalyst which did not contain dehydrogenation- and cracking-active sites. The yield of alkenes has been controlled mainly by temperature and the residence time. The highest yield of alkenes was approximately 55 % at the mole ratio of alkanes to CO_2 equal to 1:1.35, the temperature 840 °C, and the space velocity GHSV = 650 $dm^3\ h^{-1}\ dm^{-3}$ (with a gas flow-rate measured at 25 °C). On the basis of a simple equilibrium model, the behaviour of the studied system is discussed. From both the experimental data and theoretical calculations, the potential usefulness of carbon dioxide for improving the yield of alkenes in the dehydrogenation processes and a mild-temperature pyrolysis process is demonstrated. Carbon dioxide seems to be important: as a reactant; to enhance the production of alkenes, especially ethylene; to prevent from coking; as a dilutant of the reaction mixture; and as a heat supporter.

A catalytic conversion of methane by carbon dioxide and by a mixture of carbon dioxide and the water vapour is well known from the production of a technological synthesis gas with various concentrations of carbon monoxide and dihydrogen [1—5]. The activity (α) of individual metals decreases by the following sequence [6]: $\alpha(\mathrm{Ni}) > \alpha(\mathrm{Co}) \gg \alpha(\mathrm{Fe})$. Rhodium supported on aluminium trioxide (0.5—1 mass % of Rh) exhibits even a higher activity than nickel and, moreover, a formation of coke is suppressed significantly. The high activity of rhodium catalysts also results in accelerating other reactions, *e.g.* a formation of benzene from toluene

$$C_6H_5CH_3 + CO_2 \leftrightarrow C_6H_6 + 2CO + H_2 \qquad (A)$$

Other metals from the VIII group are not such efficient as rhodium, their activity can be compared following the sequence [7]: $\alpha(\mathrm{Rh}) > \alpha(\mathrm{Pd}) > \alpha(\mathrm{Pt}) \gg \alpha(\mathrm{Ru})$.

The reaction of carbon dioxide with propane over oxide-based catalysts (Mn/SiO_2, $Cr—Cu/SiO_2$, $K—Cr—Mn/SiO_2$, and Cr/SiO_2) was studied [8, 9]. At approximately 1020 K and a space velocity of 1800 h^{-1}, the selectivity to ethylene and propene was about 60 % at the 80 % conversion of propane and 60 % conversion of carbon dioxide [8]. The reaction mixture contained also methane, carbon monoxide, hydrogen, and water.

The oxidative ability of carbon dioxide is fairly well illustrated by the conversion of methanol to formaldehyde [10, 11] over a $Cr—Mn—Mo/SiO_2$ catalyst, carried out at the temperature of 853—973 K.

$$CH_3OH + CO_2 \leftrightarrow HCHO + CO + H_2O \qquad (B)$$

In the context of the presented chemical processes, applying also another alkanes, the ways of an activation of carbon dioxide, as well as an activation of oxygen generated from carbon dioxide are of interest [12, 13]. Catalysts based on chromium and manganese have shown to be good acceptors of carbon dioxide [13].

In our work, we tested the catalysts based on chromium, manganese, silver, and other metals, *e.g.* calcium and potassium giving a promotion effect. We focused our attention on the oxidative dehydrogenation of propane and butane. A thermodynamic analysis of the investigated system was made, and the results obtained are discussed together with the experimental observations.

EXPERIMENTAL

Chemicals

Carbon dioxide (DUSLO, j.s.c., Šaľa, Slovakia) of the purity 99.7 mass %, containing oxygen and nitrogen as impurities, isobutane (IB) (Fluka), 99.9 mass %, propane (P) (Slovnaft, j.s.c., Bratislava, Slovakia) of the composition w/%: ethane 2.5; propane 96.9; isobutane 0.02; propene 0.2, as well as a mixture of propane and butanes (PB) (Slovnaft, j.s.c., Bratislava, Slovakia) of the composition w/%: ethane 0.05; propane 41.9; propene 0.02; n-butane 29.0; isobutane 28.80; butenes 0.23 were used.

Other chemicals were of anal. grade purity.

Catalysts

The catalysts were either from commercial suppliers or they were prepared by the impregnation of γ-Al_2O_3 used as a support. The composition of the catalysts was estimated by mineralization and atomic absorption measurements.

Catalyst **1** – Mn/γ-Al_2O_3; the surface s_{BET} = 156 m^2 g^{-1} The catalyst was prepared by an impregnation of extruded cylinders (diameter 1 mm, length 2 mm) of γ-Al_2O_3. 21 g of the support were put into a cell and were evacuated for 3 h at 300 °C, 2.67 kPa. Then, the cell was cooled to room temperature and 400 cm^3 of aqueous solution of manganese acetate (1 mass %) was added to the support under vacuum. The impregnation was carried out at a temperature of 100 °C under mild stirring for 4 h. The cell was cooled, the catalyst was decanted and dried. The activation was made by air in a continuous reactor at 800 °C for 1 h. The content of manganese in the activated catalyst was 1.23 mass %.

Catalyst **2** – Mn—Cr—K/γ-Al_2O_3; the surface s_{BET} = 158 m^2 g^{-1} The preparation of this catalyst was similar to the preparation of the catalyst **1;** after impregnation with manganese acetate, the impregnated support was dried and calcinated at 500 °C for 4 h. Then, after cooling to room temperature, 400 cm^3 of $K_2Cr_2O_7$ in water (1 mass %) was added and the impregnation at 100 °C for 4 h was carried out. The decantation, drying, and activation were made under the same conditions as for the catalyst **1**. The content of metals was w_r/%: Mn 0.43; Cr 1.26; K 0.36.

The mixture of oxides (mainly CuO—MnO_2) – the catalyst **3,** in the commercial available form named as Hopkalit; cylinders were crushed and sieved prior to use, particles of about 1—2 mm were applied. The surface s_{BET} = 51 m^2 g^{-1} The content of metals was w_r/%: Cu 27.01; Mn 35.73; Pb 0.58; Mg 0.1; Fe 0.07; Ni 0.006; Si 0.4; Ca 1.9.

The mixed oxide catalyst (**4**) prepared by mechanical mixing from the catalyst **2** (w_r = 1/3) and the catalyst **3** (w_r = 2/3).

The oxidized Mn—Cu—K/γ-Al_2O_3 catalyst (**5**); the surface s_{BET} = 168 m^2 g^{-1} The preparation was similar to that of the catalyst **1.** After impregnation with manganese acetate (400 cm^{3}of 1 mass % aqueous solution to 6.9 g of support), the impregnated support was dried and impregnated by copper nitrate (1 mass % in water), dried and impregnated with potassium carbonate dissolved in water (1 mass %). Each impregnation lasted 4 h. The activation was under the same conditions as for the catalyst **1**. The content of metals was w_r/%: Mn 0.88; Cu 0.28; K 0.36.

The oxidized Mn—K—Ca/γ-Al_2O_3 catalyst (**6**); the surface s_{BET} = 154 m^2 g^{-1} The route of preparation was similar to the preparation of the catalyst **1**. An additional impregnation with calcium nitrate (1 mass % in water) was applied after the impregnation with manganese acetate and the potassium salt. The content of metals in the resulting catalyst was w_r/%: Mn 0.012; K 0.97; Ca 1.11.

A silver catalyst (**7**), 7 mass % of Ag supported on the α-Al_2O_3. This catalyst was from a commercial supply (the catalyst is commonly used for the air oxidation of ethylene to ethylene oxide). The cylinders of the catalyst were crushed and sieved prior to use; particles of 1—2 mm were applied; the surface s_{BET} = 1.1 m^2 g^{-1}

A nonmetal catalyst (**8**). The crushed particles of porcelain (Rashig rings 3 mm) of 1—2 mm; impregnated with sodium hydroxide (5 mass % in water), then dried and calcinated at 800 °C for 3 h. The surface s_{BET} = 5.30 m^2 g^{-1}

Apparatus and Procedure

The experiments were carried out in an apparatus from a temperature-stable stainless steel. A reactor of the inner diameter 8 mm was filled with 5—8 cm^3 of a catalyst, and to the top of the catalyst, the layer of Rashig rings (about 5 cm height) was added to ensure the preheating of the feed. Heating of the reactor was maintained by electricity, the temperature control was within ± 3 °C. The feed was on the top of the reactor. Nitrogen, pressurized air, carbon dioxide, and alkanes were supplied from pressure cylinders, through reduction valves and flow meters; the flow-rate control was ± 5 % relative with respect to the desired value. The reaction mixture from the bottom of the reactor was led, after cooling and splitting of the stream, to a heated sampling valve connected to gas chromatographs. The analysis of all species except dihydrogen, methane, and carbon monoxide, was performed at 0 °C using dihydrogen as a carrying gas with a flow-rate of 30 cm^3 min^{-1} (stainless steel column, 3 mm i.d., 13 m length, 2,4-dimethylsulfolane on the Chromosorb P, TCD). Dihydrogen, methane, and

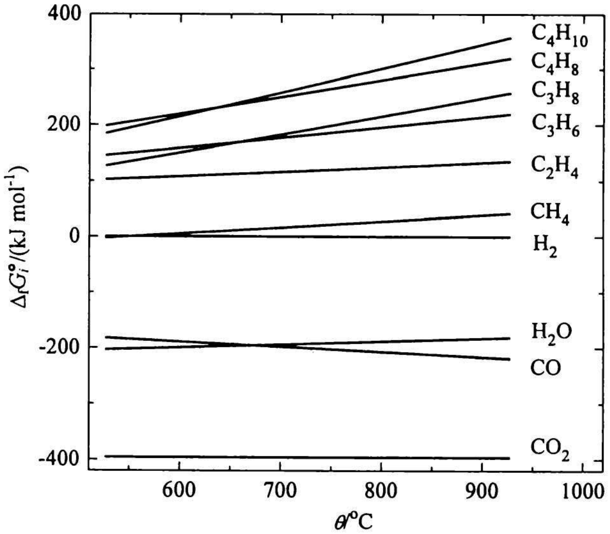

Fig. 1. The Gibbs energy of formation ($\Delta_f G_i^\circ$) *vs.* temperature θ, of compounds considered in the process of oxidative dehydrogenation of alkanes by carbon dioxide. C_4H_{10} – isobutane, C_4H_8 – *trans*-2-methylpropane.

carbon monoxide were analyzed at 75 °C using a glass column (3 mm i.d., 1.2 m length, the molecular sieve 5A activated at 500 °C) and nitrogen as a carrying gas.

Experimental Procedure

Before starting an oxidative dehydrogenation, the reactor with a catalyst was fed by air with a flow-rate of 3 dm^3 h^{-1} at a temperature of 800 °C for 1 h. Then, pure nitrogen (in experiments without carbon dioxide) or pure carbon dioxide (in experiments with carbon dioxide) with a flow-rate desired for the given experiment, was let to flow throughout the reactor, while the temperature in the reactor reached the desired value (about five minutes). The flow of nitrogen was stopped (if it had been on) and the flow of alkanes was switched on to the desired value. The reaction mixture was sampled for the analysis every ten minutes. The constant activity of the catalyst was maintained by a regeneration after every hour of the experiment, using a mixture of nitrogen and air (the flow-rates of nitrogen and air were gradually decreased and increased, respectively) at 800 °C with a total flow-rate of 3 dm^3 h^{-1} During the regeneration, the output stream from the reactor was checked for carbon dioxide; the regeneration was finished when no carbon dioxide was present (usually about 10 min). This procedure of regeneration was sufficient for experiments when the carbon dioxide was utilized. When the feed to the reactor consisted only of alkanes, as the consequence of coking, a very strong deactivation was observed. The regeneration needed to be done every ten minutes.

RESULTS AND DISCUSSION

Thermodynamics

Fig. 1 shows the temperature dependence of the Gibbs energy of formation of the compounds the most frequently occurring in the oxidative dehydrogenation of propane and butane by carbon dioxide, calculated on the basis of the data from [14]. The fact of the low oxidative ability of carbon dioxide is demonstrated perfectly by the lowest Gibbs energy of all the compounds considered. Another important certainty is the lowest Gibbs energy of the methane of all alkanes and alkenes taken into account. This means, that starting from a reaction mixture of C_2 and higher alkanes and carbon dioxide, supposing methane as one of the products in an equilibrium state, a majority of alkanes should be converted to methane and hydrogen.

Table 1*a*. The Oxidative Dehydrogenation of Propane (P), Isobutane (IB), and a Mixture of Propane and Butanes (PB) over the Mn/γ-Al_2O_3 Catalyst (**1**)

Run	a	F(a)	F(CO_2)	θ	GHSV	x(a)	x(CO_2)	s(C_2H_4)	s(C_3H_6)	s(C_4H_8)	Y(C_2—C_4)
		dm^3 h^{-1}	dm^3 h^{-1}	°C	h^{-1}	%	%	%	%	%	%
1	IB	1.5	2	600	540	4.7	7.3	0.9	8.6	81.5	4.2
2	IB	1.5	2	675	540	12.3	32.7	0.6	15.5	61.2	9.6
3	IB	1.5	2	735	540	45.8	40.8	6.5	28.5	44.1	36.3
4	IB	1.5	2	840	540	87.0	64.3	37.6	20.9	8.6	58.4
5	P	1.5	2	730	540	36.0	61.7	19.0	43.6	2.1	23.3
6	P	1.5	2	780	540	62.2	62.7	40.8	28.3	3.1	44.9
7	P	1.5	2	820	540	79.8	81.1	46.2	9.8	5.2	48.8
8	PB	1.5	2	720	540	47.9	43.2	18.9	35.0	14.3	32.7
9	PB	1.5	2	750	540	61.0	54.5	28.9	28.7	11.7	42.3
10	PB	1.5	2	780	540	75.5	53.4	32.3	29.3	7.9	52.4
11	PB	3	4	790	1080	71.2	37.2	32.2	25.4	13.4	50.6
12	PB	3	4	820	1080	84.4	41.8	40.8	21.5	6.8	58.3

Table 1*b*. Analysis of the Reaction Mixtures (Water is not Involved) from Runs in Table 1*a*

Run	w_i/mass %													
	H_2	CO	CH_4	C_2H_6	C_2H_4	C_3H_8	CO_2	C_3H_6	i-C_4H_{10}	n-C_4H_{10}	1-C_4H_8	i-C_4H_8	*t*-2-C_4H_8	*c*-2-C_4H_8
1	0.1	2.3	0.23	0.01	0.02	0.	45.6	0.2	49.2	0.2	0.1	1.6	0.1	0.1
2	0.2	10.7	1.5	0.1	0.1	0.	34.6	1.0	47.7	0.1	0.05	3.7	0.1	0.1
3	0.4	12.3	5.2	0.5	1.7	0.5	28.1	7.5	32.1	0.1	0.3	10.8	0.3	0.2
4	1.7	20.2	8.3	0.	9.2	10.	17.6	10.7	7.	0.9	0.	2.2	1.9	0.3
5	0.3	21.8	4.8	2.8	3.7	36.3	21.3	8.5	0.	0.1	0.1	0.2	0.1	0.
6	0.6	29.1	6.7	1.3	10.5	16.4	27.2	7.3	0.	0.1	0.2	0.5	0.	0.1
7	1.4	40.7	11.4	1.5	15.1	8.7	14.9	3.2	0.	0.4	0.4	1.3	0.	0.
8	0.4	12.2	8.9	1.4	5.4	18.3	25.2	10.0	8.8	5.3	0.6	3.0	0.3	0.2
9	1.2	10.5	12.7	2.5	12.6	21.8	13.8	12.5	4.7	2.6	0.4	4.2	0.3	0.2
10	1.5	14.3	13.9	2.3	15.1	12.2	19.6	13.7	2.0	1.7	0.3	3.3	0.1	0.
11	0.7	11.9	10.5	2.0	12.3	9.1	31.6	9.7	4.2	2.8	0.9	3.2	0.6	0.4
12	1.3	12.7	16.6	0.	19.2	5.8	27.8	10.1	2.7	0.6	1.6	0.6	0.6	0.4

Names of columns represent chemical compounds given by stoichiometric formula: i-C_4H_{10} – isobutane, n-C_4H_{10} – butane, 1-C_4H_8 – but-1-ene, i-C_4H_8 – isobutene, *t*-2-C_4H_8 – *trans*-but-2-ene, *c*-2-C_4H_8 – *cis*-but-2-ene.

Fortunately, the kinetics of a methane formation is not fast, therefore, the formation of methane is usually to a low extent, which is also illustrated by the experiments (Tables 1*a*, 1*b*).

In order to compare experimental results with the situation in theoretical equilibrium, we calculated the equilibrium composition of one reaction mixture which we used in the experiments. The equilibrium composition was calculated by a minimization of the Gibbs energy (G) of the system with respect to the extents of chemical reactions (ξ_j). The initial amounts of substances $n_0(i)$ were taken as values of mole fractions in the starting mixture. A mathematical description of the problem is given by the set of expressions (*1*—*4*). The values of the standard Gibbs energy of formation ($\Delta_f G_i^\circ$) were the same as those given in Fig. 1. The computer program was completed by checking the independence of the chemical reactions [14]. Due to the relatively high temperatures (more than 600 °C) and low pressure (about 0.1 MPa), the ideal behaviour of the gases was supposed in the calculation. In order to find the minimum with a high accuracy and reliability, a combination of random searching and the Nelder—Mead method [15] has been applied. The random search method was important both for ensuring that the global minimum should be found (starting from different initial estimates), and to start the Nelder—Mead method (usually it is not possible to start with the extents of chemical reactions equal to zero). The shape of the minimum was very shallow and the minimization route was strongly curved, therefore, a small simplex was necessary to utilize. Searching was finished when the highest dimension of the simplex was equal to 10^{-18}

$$G = \sum_{i=1}^{N_c} n(i) \left(\Delta_f G_i^\circ + RT \ln \frac{p}{p^\circ} + RT \ln y_i \right) \qquad (1)$$

$$n(i) = n_0(i) + \sum_{j=1}^{N_c} \nu_{j,i} \xi_j \qquad (2)$$

$$y_i = \frac{n(i)}{\sum_{k=1}^{N_c} n(k)} \qquad (3)$$

$$\text{Constraints: } n(i) \geq 0, \quad i = 1, 2, \ldots, N_c \qquad (4)$$

In the equilibrium reaction mixture, 10 compounds at the maximum were considered, numbered: *1* – propane, *2* – carbon dioxide, *3* – propene, *4* – carbon monoxide, *5* – water, *6* – ethylene, *7* – 2-methylpropene, *8* – butane, *9* – dihydrogen, *10* – methane. 2-Methylpropene was chosen as the isomer of butenes, which exhibits the lowest Gibbs energy of formation [14]. The following set of chemical reactions was considered to create the compounds mentioned

$$C_3H_8 + CO_2 \leftrightarrow C_3H_6 + CO + H_2O \qquad (Ca)$$

$$C_4H_{10} + CO_2 \leftrightarrow C_4H_8 + CO + H_2O \qquad (Cb)$$

$$2C_3H_6 \leftrightarrow C_4H_8 + C_2H_4 \qquad (Cc)$$

$$4C_3H_8 + 4CO_2 \leftrightarrow 3C_4H_8 + 4CO + 4H_2O \qquad (Cd)$$

$$C_3H_8 + 3CO_2 \leftrightarrow C_2H_4 + 4CO + 2H_2O \qquad (Ce)$$

$$C_3H_8 \leftrightarrow C_3H_6 + H_2 \qquad (Cf)$$

$$C_2H_4 + CO_2 \leftrightarrow CH_4 + 2CO \qquad (Cg)$$

Of course, the set of the reactions (*Ca*—*Cg*) is not the only one which can be chosen to obtain the compounds desired. The advantage of eqns (*Ca*—*Cg*) is that kinetic preferences usually increase from eqn (*Cg*) up to eqn (*Ca*) going from the starting reaction mixture consisting of propane and carbon dioxide [16], and, in consequence of the kinetics, *e.g.* the dehydrogenation (*Cf*) and the formation of methane (*Cg*) may, or need not be taken into account. In the presented theoretical investigations, the reaction of a coke formation was not supposed, because of the low Gibbs energy of formation of carbon (zero value – the element in the standard state) which should result in the total decomposition of hydrocarbons to carbon and dihydrogen in the total chemical equilibrium state. An exclusion of this reaction is again inferred from the kinetics of the coke formation [16].

From the equilibrium composition, conversions of reactants and selectivities to individual products may be calculated. The conversion of alkanes has been expressed as

$$x_\mathrm{e}(\mathrm{a}) = 100\left(1 - \frac{n_\mathrm{e}(\mathrm{a})}{n_0(\mathrm{a})}\right) \qquad (5)$$

Similarly, the conversion of carbon dioxide

$$x_\mathrm{e}(\mathrm{CO}) = 100\left(1 - \frac{n_\mathrm{e}(\mathrm{CO_2})}{n_0(\mathrm{CO_2})}\right) \qquad (6)$$

Selectivities of the formation of alkanes and alkenes have been calculated with respect to the number of carbon atoms involved in a molecule, *i.e.*

$$s(\mathrm{C_3H_6}) = \frac{3n_\mathrm{e}(\mathrm{C_3H_6})}{D} \qquad (7)$$

$$s(\mathrm{C_2H_4}) = \frac{2n_\mathrm{e}(\mathrm{C_2H_4})}{D} \qquad (8)$$

$$s(\mathrm{C_4H_8}) = \frac{4n_\mathrm{e}(\mathrm{C_4H_8})}{D} \qquad (9)$$

$$s(\mathrm{C_4H_{10}}) = \frac{4n_\mathrm{e}(\mathrm{C_4H_{10}})}{D} \qquad (10)$$

where

$$\begin{aligned} D = {} & 3n_\mathrm{e}(\mathrm{C_3H_6}) + 2n_\mathrm{e}(\mathrm{C_2H_4}) + 4n_\mathrm{e}(\mathrm{C_4H_8}) \\ & + n_\mathrm{e}(\mathrm{CH_4}) + (4n_\mathrm{e}(\mathrm{C_4H_{10}})) \end{aligned} \qquad (11)$$

Eqn (*10*) and the term in brackets in the expression (*11*) is considered only if the starting reaction mixture does not contain butane. The yield of alkenes $Y(\mathrm{C_2}—\mathrm{C_4})$ was also calculated with respect to the number of carbon atoms involved in the compounds in the starting reaction mixture

$$Y(\mathrm{C_2}—\mathrm{C_4}) = \frac{2n_\mathrm{e}(\mathrm{C_2H_4}) + 3n_\mathrm{e}(\mathrm{C_3H_6}) + 4n_\mathrm{e}(\mathrm{C_4H_8})}{3n_0(\mathrm{C_3H_8}) + 4n_0(\mathrm{C_4H_{10}})} \qquad (12)$$

As mentioned in the discussion of Gibbs energy of formation of individual compounds, if the formation of methane is allowed, all components would convert to this product to a maximum extent. This result prompted us to neglect the formation of methane, due to the lower rate of its formation in comparison with rates of the reactions (*Ca*—*Cf*) [16]. Of course, the exclusion of the methane formation is rather drastic. As shown by the experimental data in Tables 1*a*, 1*b*, a discrepancy between the simplified thermodynamic model and a "technological reality" increases with an increasing temperature. The "technological reality" is somewhere between two extreme situations; the first – without the formation of methane, the second – the equilibrium formation of methane. In a real system, the extent of the formation of methane depends on the kinetics, therefore, the catalysis plays a very important role. In spite of the mentioned discrepancy, the simplified thermodynamic model (without the methane and coke formation) can be a tool for the qualitative description of the investigated system.

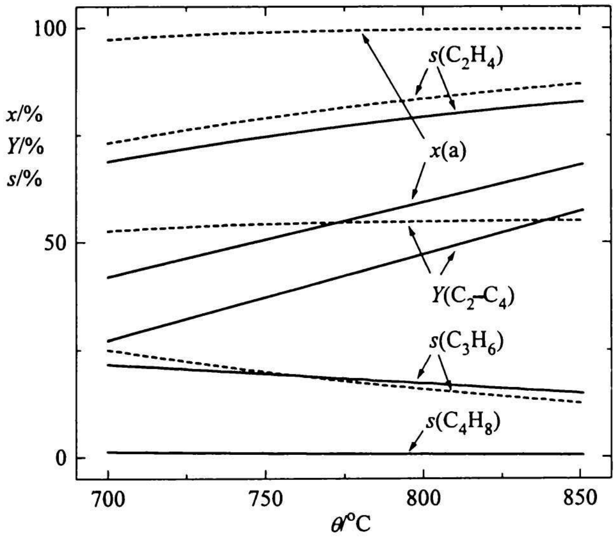

Fig. 2. The chemical equilibrium in the oxidative dehydrogenation of propane by carbon dioxide without the dehydrogenation reaction releasing free dihydrogen (solid lines) and with this dehydrogenation (dotted lines) at various temperatures; 0.425 and 0.575 mole fractions of propane and carbon dioxide at the start.

The importance of the dehydrogenation reaction with the formation of a free dihydrogen (the reaction *Cf*) is fairly well illustrated by the conversion of propane, which without the dehydrogenation reaction (*Cf*) varies from 30 up to 57 %, but, if the dehydrogenation takes place, the conversion close to 100 % can be reached (Fig. 2). The selectivity to the ethylene formation increases with an increasing temperature, on the contrary, the selectivities to a butane and butene formation decrease with increasing the temperature no matter if the dehydrogenation reaction is allowed or not.

Exploratory Experiments

Tables 1*a* and 1*b* contain the results from the oxidative dehydrogenation by carbon dioxide using pure isobutane (I), propane (P), and a mixture of propane and isobutane (PB, the composition is given in Experimental). The catalyst **1** ($\mathrm{Mn}/\gamma\text{-}\mathrm{Al_2O_3}$) was employed in all the experiments involved in Tables 1*a* and 1*b*. The title GHSV denotes the space velocity of

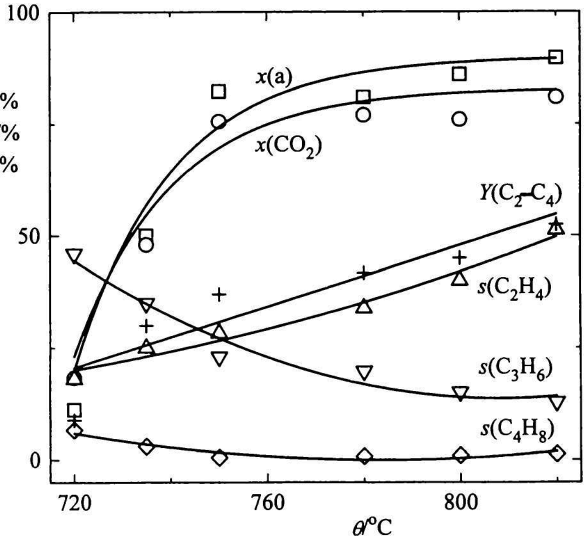

Fig. 3. The temperature dependence of oxidative dehydrogenation of propane by carbon dioxide over Mn—Cr—K/γ-Al_2O_3 (the catalyst **2**), GHSV = 650 h^{-1}, the mole ratio in the feed - CO_2 C_3H_8 = 1.35.

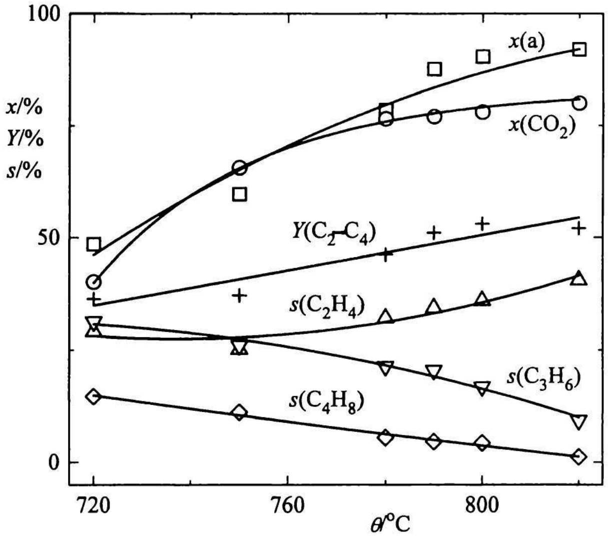

Fig. 4. The temperature dependence of oxidative dehydrogenation of the mixture of propane and butanes (PB, the composition is given in Experimental) by carbon dioxide over Mn—Cr—K/γ-Al_2O_3 (the catalyst **2**), GHSV = 650 h^{-1}, the molar ratio in the feed - CO_2 alkanes = 1.35.

the gaseous phase expressed as a fraction of the volume flow-rate at 25 ℃ and the volume of the bed of a catalyst in the reactor. The content of dihydrogen in the output reaction mixture varied from 0.1 up to 1.8 mass %, which indicates different extents of the dehydrogenation reaction releasing a free dihydrogen and the relatively slow course of the reaction of hydrogen and carbon dioxide. The content of carbon monoxide was within the range from 2.3 up to 50.7 mass %. In accordance with Fig. 2, the yield of alkenes increased with the temperature; the maximum value was more than 50 %. The good yield of alkenes gives an inspiration to utilize isobutane as an intermediate for the production of propene and ethylene employing a manganese catalyst and carbon dioxide as a "consumer" of hydrogen formed during the dehydrogenation. The low content of butenes is in accordance with the thermodynamic calculations, and especially, a very low content of but-2-enes indicates the splittings of alkanes and alkenes C_3—C_4 to be dominant reactions in the investigated system. In experiments with PB, the selectivity to alkenes C_2—C_4 varied from 64 up to 79 %. The content of methane increased with increasing the temperature, which again indicates that the splitting reactions of carbon compounds, accompanied by *in situ* formation of hydrogen, and its subsequent reaction with carbon dioxide, are mostly preferred.

The results obtained on the catalyst **2** (Mn—Cr—K/γ-Al_2O_3), presented in Figs. 3—5, are similar to those obtained over the catalyst **1**, however, the selectivity to C_2—C_4 alkenes was slightly worse. The conversion of carbon dioxide was relatively high in all cases, and the yield of carbon monoxide was high, too. The equilibrium behaviour of the investigated system is illustrated in Fig. 5, which shows the output quantities (x(a), $x(CO_2)$, $s(C_2H_4)$, $s(C_3H_6)$, $s(C_4H_8)$) to be practically independent of the space velocity GHSV.

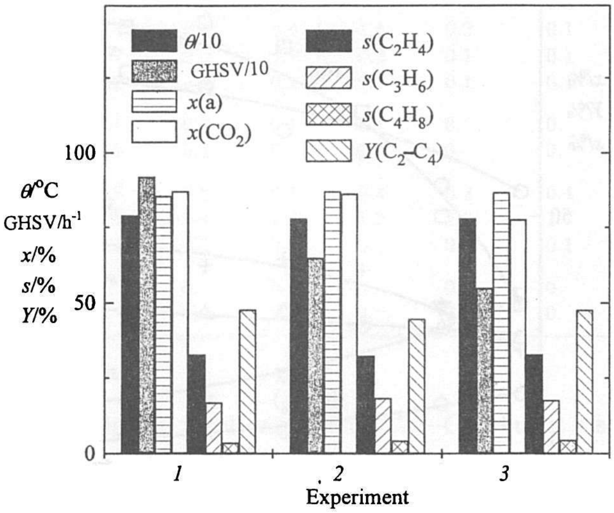

Fig. 5. The oxidative dehydrogenation of the mixture of propane and butanes (PB, the composition is given in Experimental) by carbon dioxide over Mn—Cr—K/γ-Al_2O_3 (the catalyst **2**) under various conditions, the mole ratio in the feed - CO_2 alkanes = 1.35.

The next set of experiments was done using the catalyst **3** (Hopkalit), which is commonly exploited for the removal of oxygen from carbon monoxide (the oxygen is consumed *via* oxidation of carbon monoxide to carbon dioxide). The most important results are in Figs. 6 and 7. The formation of dihydrogen was to a

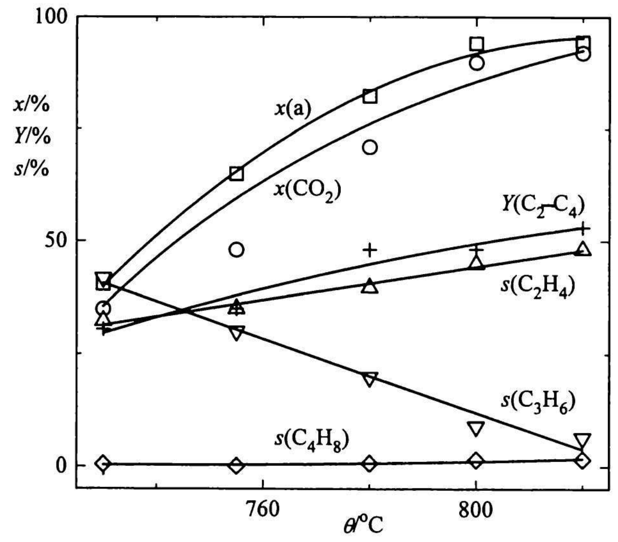

Fig. 6. The temperature dependence of oxidative dehydrogenation of propane by carbon dioxide over Hopkalit (the catalyst **3**), GHSV = 650 h^{-1}, the mole ratio in the feed - CO_2 C_3H_8 = 1.35.

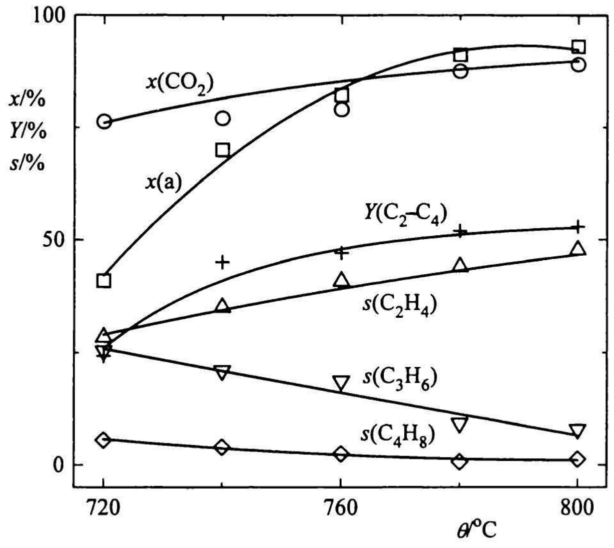

Fig. 8. The temperature dependence of oxidative dehydrogenation of propane by carbon dioxide over Ag/α-Al_2O_3 (the catalyst **7**), GHSV = 650 h^{-1}, the mole ratio in the feed - CO_2 C_3H_8 = 1.35.

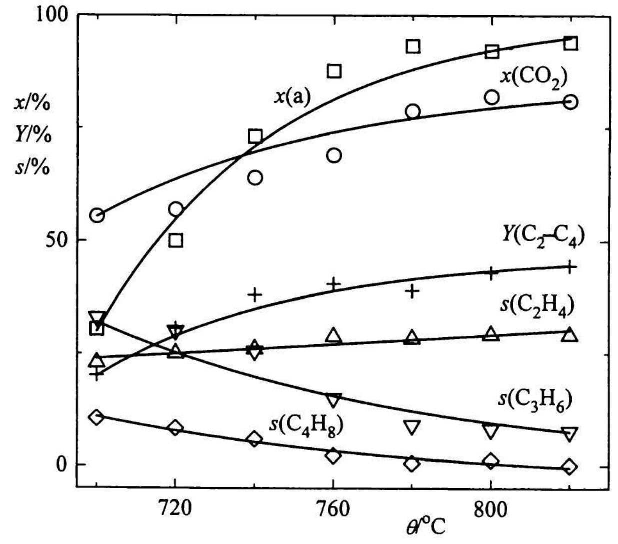

Fig. 7. The temperature dependence of oxidative dehydrogenation of the mixture of propane and butanes (PB, the composition is given in Experimental) by carbon dioxide over Hopkalit (the catalyst **3**), GHSV = 650 h^{-1}, the mole ratio in the feed - CO_2: alkanes = 1.35.

relatively low extent (about 0.5 mass %), the conversion of carbon dioxide was in the range of 25—75 %, which resulted in the content of carbon monoxide from 11 up to 54 mass %. The relatively good conversion of carbon dioxide was not accompanied by the good selectivity to alkenes, which did not exceed 66 %.

The effects of the catalysts **4** (a mechanical mixture of the Mn—Cr—K/γ-Al_2O_3 catalyst and Hopkalit), **5** (Mn—Cu—K/γ-Al_2O_3), and **6** (Mn—K—Ca/γ-Al_2O_3) were similar to the catalyst **2**. However, the catalyst **6** yielded the highest amount of olefines C_2—C_4 under a relatively wide range of operational conditions. For example, using the PB feed, the yield of olefines was 44—62 % per pass at a temperature of 650—740 °C and the atmospheric pressure.

The catalyst **7** (Ag/α-Al_2O_3) behaved similarly to the catalyst **3**. As shown in Fig. 8 the conversions of alkanes and carbon dioxide were relatively high, but the selectivity to alkenes was only in the range of 49—62 %.

In spite of the different kind of the catalysts (catalysts **1**—**7**) tested on the oxidative dehydrogenation of alkanes by carbon dioxide, the behaviour of the reaction system was similar. This observation led us to use the catalyst **8** (crushed porcelain), which did not carry any strong dehydrogenation and oxidative active sites, and the ability of cracking was suppressed by the alkali impregnation. In this case, the bed in the reactor consisted of the catalyst **8**, any other materials were not used for preheating the reactants. The role of a heat conductor was ensured by the catalyst. The data in Tables 2*a* and 2*b* show the similar values of the conversion and selectivities in the oxidative dehydrogenation of propane and the mixture of propane and butane, as it was in the case of the catalysts **1**—**7** The main factor influencing the conversion is the temperature and residence time. The highest conversion of alkanes achieved was 97 %. The reduction of carbon dioxide to carbon monoxide proceeds too, but to the significantly lower extent than it was when using the catalysts **1**—**7** The content of carbon monoxide and dihydrogen varied from 6.7 up to 11.8 mass %, and from 0.6 up to 2.8 mass %, respectively. The selectivity to alkenes

Table 2*a*. The Oxidative Dehydrogenation (Runs 1—4) and Dehydrogenation (Runs 5—11) of Propane (P), and a Mixture of Propane and Butanes (PB) over the Crushed Porcelain Particles (the Catalyst **8**)

Run	a	F(a)	$F(CO_2)$	θ	GHSV	x(a)	$x(CO_2)$	$s(C_2H_4)$	$s(C_3H_6)$	$s(C_4H_8)$	$Y(C_2—C_4)$
		$dm^3\ h^{-1}$	$dm^3\ h^{-1}$	°C	h^{-1}	%	%	%	%	%	%
1	PB	1.5	2	720	650	86.5	22.7	17.7	18.6	5.3	36.0
2	PB	1.5	2	760	650	95.7	23.3	37.2	21.2	4.3	60.0
3	PB	1.5	2	780	650	98.3	33.8	42.8	10.2	1.0	53.0
4	PB	1.5	2	800	650	99.4	35.4	49.5	4.1	0.8	54.2
5*	PB	1.5	0	780	280	82.1		37.7	15.7	0.3	44.1
6*	PB	1.5	0	800	280	86.1		50.0	5.2	0.2	47.6
7*	PB	3	0	760	560	84.8		30.7	13.8	1.8	39.2
8*	PB	3	0	780	560	80.3		36.1	16.8	10.6	51.0
9*	PB	3	0	830	560	90.0		37.8	3.8	0.6	38.0
10*	P	3	0	760	560	57.5		26.8	14.9	0.0	23.9
11*	P	3	0	800	560	77.9	–	7.0	2.8	0.0	7.6

* Very extensive coking was registered, calculated conversions and selectivities are affected by the significant error.

Table 2*b*. Analysis of the Reaction Mixtures (Water is not Involved) from Runs in Table 2*a*

Run	w_i/mass %													
	H_2	CO	CH_4	C_2H_6	C_2H_4	C_3H_8	CO_2	C_3H_6	i-C_4H_{10}	n-C_4H_{10}	1-C_4H_8	i-C_4H_8	t-2-C_4H_8	c-2-C_4H_8
1	0.6	6.8	4.4	2.3	8.3	22.4	36.4	8.7	6.2	1.4	0.4	1.7	0.2	0.2
2	1.0	6.7	10.9	1.9	19.8	9.0	34.6	11.3	2.1	0.4	0.4	1.6	0.2	0.1
3	2.3	11.0	19.8	2.3	21.0	3.3	33.9	5.0	0.7	0.2	0.1	0.2	0.1	0.1
4	2.8	11.8	20.9	2.3	24.0	1.7	33.8	2.0	0.2	0.1	0.1	0.1	0.1	0.1
5*	22.4	0.1	28.9	2.4	22.6	13.7	0.	9.4	0.1	0.2	0.1	0.1	0.	0.
6*	26.3	0.1	29.4	1.0	29.9	10.1	0.	3.1	0.0	0.1	0.	0.1	0.	0.
7*	21.4	0.1	31.6	4.0	19.2	11.7	0.	8.6	1.5	0.8	0.1	0.4	0.2	0.4
8*	17.5	0.1	21.4	4.7	22.8	10.9	0.	10.6	2.5	2.8	1.6	1.2	2.2	1.7
9*	21.8	0.1	39.7	3.2	24.7	7.3	0.	2.5	0.1	0.2	0.1	0.1	0.1	0.1
10*	25.1	0.1	23.1	3.6	10.8	31.3	0.	6.0	0.	0.	0.	0.	0.	0.
11*	43.1	0.1	35.7	5.2	2.8	11.9	0.	11.	0.	0.	0.	0.	0.	0.

* See Table 2*a*.

was also similar, or slightly lower, to those obtained on the catalysts tested before. However, the selectivity to alkenes was lowered by 15—25 % in the case of not using carbon dioxide, while the conversion of alkanes was comparable with the previous runs. Without carbon dioxide the reaction with hydrogen generated by the dehydrogenation of alkanes, as well as formation of carbon monoxide is not possible, therefore, the content of dihydrogen in the output stream is much more higher than in experiments with carbon dioxide; 17—43 mass % in comparison to 0.6—2.8 mass %. The high concentration of dihydrogen illustrates a wider extent of the side and consequent reactions of alkenes, which cause the mentioned lower yield of alkenes, the higher production of hydrogen, ethane and methane and, consequently, the higher production of the coke. These results give a resemblance with splitting of alkanes during the mild-temperature pyrolysis [16, 17]. It may be deduced that carbon dioxide in the oxidative dehydrogenation does not have only the role of the reactant in the reaction system (*Ca*—*Cf*), but it also helps in preventing the coking due to the oxidative-reduction equilibrium with carbon (the reaction: $CO_2 + C \leftrightarrow 2\ CO$) and in lowering the reactivity of the gaseous phase by diluting.

An important feature of the metal-supported catalysts tested in this work is a low activity at temperatures lower than 700 °C which is documented by a high difference between the experimental and the equilibrium conversions of the reactants (Fig. 2 in comparison with Figs. 3—8). The catalysts started to be effective sufficiently at temperatures higher than 700 °C, and from this temperature, if the residence time was long enough, the output composition from the reactor was close to that of the equilibrium. In the context with the catalysts and reaction systems mentioned in the introduction of this work, probably, more active catalysts should be prepared using the rare metals of the group VIII; *e.g.* rhodium which has proven to be very good for the dehydrogenation of toluene [6]. Another

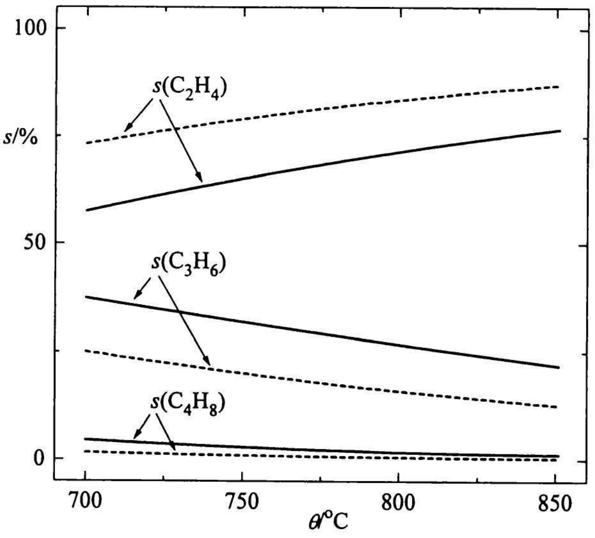

Fig. 9. The comparison of the selectivities (s) in the equilibrium state (eqns (Ca—Cf)) of the oxidative dehydrogenation of propane by CO_2 (dotted lines; n(propane) $n(CO_2) = 1$ 1.35 at the start) and the reactions of propane without CO_2 (solid lines).

perspective class of catalysts should be a combination of lanthanoids with the commonly used dehydrogenation catalysts [18, 19]. For example, such kind of catalyst may be Fe—Gd or Fe—Tb supported on the acid mordenite. The utilization of the latter catalyst has been documented by the oxidative dehydrogenation of methylcyclohexane by carbon dioxide [18], in which the selectivity to methylcyclohexene of 83.5 % at 400—500 °C was exhibited.

Effect of CO_2 in Pyrolysis

A qualitative agreement between the calculated and measured effects of CO_2 on the oxidative dehydrogenation of alkanes prompted us to perform some theoretical investigations in the pyrolysis. The effect of carbon dioxide on the selectivity to the ethylene and propene formation in a state of the theoretical chemical equilibrium (taking into account the reactions (Ca—Cf)) was studied. Fig. 9 shows a higher yield of ethylene in the presence of carbon dioxide, while the yield to propene was decreased. The results obtained allow us to speculate about a potential suitability of carbon dioxide, which can serve not only as the reactant, but also as a heat supporter, and, together with water vapour, as a dilutant of the feed for a mild-temperature pyrolysis.

CONCLUSION

The oxidative dehydrogenation of alkanes by carbon dioxide is represented by a set of reactions similar to reactions in cracking, dehydrogenation, and a mild-temperature pyrolysis. All the mentioned processes are peculiar by the formation of a coke. The carbon dioxide has shown to be very effective in lowering the rate of the coke formation, and the deactivation process, if a catalytic system is utilized, is suppressed, too. The yield of alkenes in the oxidative dehydrogenation strongly depends on the temperature, residence time, and type of the catalyst. The employed manganese-, chromium-, copper-, and silver-based catalysts exhibited relatively low activity, the kinetics of the reactions was controlled by the temperature dominantly. So, these catalysts may be considered as not very suitable for this process. In the future, it would be worthwhile to test the catalysts based on rare metals, or a combination of commonly used dehydrogenation catalysts and lanthanoids. A good catalyst needs to enhance a formation of alkenes, but not to accelerate a methane and coke formation.

A simple model for the calculation of an equilibrium state was developed. The generation of methane under the conditions of carrying out the experiments was slow, and the output stream from the reactor was far from equilibrium, therefore, the formation of methane was excluded from the system of chemical reactions expressing the investigated system. For the same reason as the latter, the reaction giving carbon (a coke formation) was not considered. At temperatures higher than 650 °C, the dehydrogenation possessing a free dihydrogen needs to be taken into account if a realistic picture of the system is desired. In spite of these simplifications applied in the developed thermodynamic model, the results calculated have given some quantitative tendencies of the studied reaction system. The advantage of this model lies in much simpler calculations than they are in the case when a full thermodynamic and kinetic models are applied. The model of the equilibrium state has proven to be a good tool for an investigation of the oxidative dehydrogenation of alkanes, as well as for a pyrolysis of propane and butane.

Some recommendations, concerning a utilization of carbon dioxide in a pyrolysis of hydrocarbons, can be given on the basis of the presented work. Carbon dioxide may be a potential "improver" of the yield of alkenes in a pyrolysis process. Altogether, carbon dioxide seems to be useful: i) as a reactant, ii) to enhance the production of alkenes, especially ethylene, iii) to prevent from coking, iv) as a dilutant, and v) as a heat supporter. The listed potential advantages can serve as the idea how to increase the economy of pyrolysis.

SYMBOLS

a	alkanes
F(k)	flow-rate of the feed k [dm^3 h^{-1}]
G	Gibbs energy of the system [kJ]

GHSV	space velocity; flow-rate of the gas feed at 25 °C per a unit volume of the catalytic bed in reactor [$\mathrm{dm^3\ h^{-1}\ dm^{-3}}$]
$n(\mathrm{i})$	amount of substance of the component i
$n_0(\mathrm{i})$	amount of substance of the component i at the start
$n_\mathrm{e}(\mathrm{i})$	amount of substance of the component i at equilibrium
N_c	number of components
N_r	number of chemical reactions
p	pressure [kPa]
p°	standard pressure [101.325 kPa]
R	gas constant [8.314 $\mathrm{J\ mol^{-1}\ K^{-1}}$]
$s(\mathrm{i})$	selectivity to the component i
T	temperature [K]
w_r	relative mass fraction
$x(\mathrm{i})$	conversion of the component i
$x_\mathrm{e}(\mathrm{i})$	equilibrium conversion of the component i
y_i	mole fraction of the component i in eqn (*3*)
$Y(\mathrm{i})$	yield of the compound i with respect to the number of carbon atoms in the molecule
$\Delta_\mathrm{f}G_i^\circ$	standard Gibbs energy of formation of the component i [$\mathrm{kJ\ mol^{-1}}$]
$\nu_{j,i}$	stoichiometric coefficient, the reaction j, the component i
ξ_j	extent of the reaction j
θ	temperature [°C]

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