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Published in: Chemical Engineering Journal

DOI: 10.1016/j.cej.2019.122741

Published: 01/02/2020

Document Version Accepted author manuscript

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Link to publication

Please cite the original version: Matveyeva, A. N., Wärnå, J., Pakhomov, N. A., & Murzin, D. (2020). Kinetic modeling of isobutane dehydrogenation over Ga2O3/Al2O3 catalyst. *Chemical Engineering Journal*, *381*, –. Article 122741. https://doi.org/10.1016/j.cej.2019.122741

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Kinetic modeling of isobutane dehydrogenation over Ga_2O_3/Al_2O_3 catalyst

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Abstract: Kinetic modeling was done for isobutane dehydrogenation using an alumina supported gallia catalyst in a fixed bed reactor at atmosphere pressure, 520–580 °C and a short residence time (ca. 0.03–0.3 s). A complex reaction network was taken into account considering formation of not only isobutane, but also a range of other hydrocarbons in various side reactions. Parameter investigation revealed an adequate description of the experimental data. The apparent activation energy of isobutane dehydrogenation was estimated to be 195 kJ/mol.

Keywords: kinetic modeling, dehydrogenation, isobutane, Ga₂O₃.

Notation	
A_0	pre-exponential factor
\overline{A}_{ι}	mean pre-exponential factor
C _{est}	component concentration estimated by the model (mol. %)
\bar{c}_{est}	mean value of all the data points (mol. %)
c _{exp}	component concentration obtained from experiment (mol. %)
D	denominator
$E_{A,i}$	activation energy (kJ/mol)
$E^{est}_{A,app}$	estimated apparent activation energy (kJ/mol)
$E^{obs}_{A,app}$	observed apparent activation energy (kJ/mol)
$k_{iC_4H_{10}}$	isobutane transformation rate constant (mol/(min \cdot g \cdot atm ⁿ))
k_{2}^{+}	forward reaction rate constant (mol·(mol. %)/(min·g)
K_i	adsorption constant of respective step ((mol. %) ^{-1})
k_i	rate constant multiplied by the adsorption constant (mol/(min $\cdotg)$
n	reaction order
P_i	component partial pressure (atm)
Q	sum of squared residuals ((mol. %) ²)
$r_{iC_4H_{10}}$	isobutane transformation rate $(mol/(min \cdot g))$
r_2	reaction rate of respective step $(mol/(min \cdot g))$
R^2	degree of explanation (%)
\overline{T}	mean temperature of the experimental data sets (K)
Wf	weight factor
Z	active surface site (metal)
ZO	vacant site (metal with oxygen)
Greek letters	
τ	residence time under work conditions (s)
θ_{ZO}	proportion of vacant sites
θ_{ZO_i}	surface coverage

1. Introduction

Processing of C_3 – C_5 alkanes, which are a part of the natural gas liquids (NGL), is one of the main directions in the petrochemical industry. Among other processing methods, catalytic dehydrogenation has a special role being able to generate corresponding olefins and dienes, which, in turn, are valuable intermediates in production of a range of valuable chemicals. Current industrial dehydrogenation processes are optimized to produce olefins with the purity suitable for synthesis of polymers.

Industrial dehydrogenation processes use chromia- or platinum-based catalysts generally supported on alumina and promoted with alkali metals [1]. Although substantial improvements have been made for both type of catalytic materials, several economic, environmental, and technological challenges have still to be solved.

In the recent years, an increased attention has been given to the gallium oxide-based catalysts, both supported [2]–[8] or not supported ones [9]–[15], as potential candidates for dehydrogenation of lower alkanes.

Of great interest is the use of Ga_2O_3 -based catalysts for oxidative dehydrogenation of alkanes C_2-C_3 [16], which inspired by the work of Nakagawa et al. reporting exceptionally high activity of bulk Ga_2O_3 in dehydrogenation of ethane in the presence of CO_2 [17],[18]. Moreover, gallium oxide exhibits a much higher activity than Cr_2O_3 and Fe_2O_3 , while Al_2O_3 and SiO_2 are almost inactive for these reactions [19]. This order of reactivity is consistent with the H/D exchange reactions [20], for which Ga_2O_3 , together with chromium and zinc oxides, are considered the most active.

Even though dehydrogenation reactions have been studied for almost a century, there is still an interest in elucidation of the reaction mechanism, particular because this reaction is catalyzed by a vast array of materials [21]. A detailed investigation of the dehydrogenation reaction mechanism and the nature of intermediates was performed on Pt and Pt–Sn catalysts using isotopic labeling experiments [22], infrared spectroscopy [23]–[27], DFT calculations [28]–[30] and microcalorimetry [31],[32] along with other methods.

Most experimental results suggest that dehydrogenation of light alkanes proceeds via the reverse Horiuti-Polanyi mechanism first proposed for hydrogenation reactions [33], which consists of four main steps: dissociative adsorption of an alkane (step 1.1), C–H bond cleavage of a second hydrogen atom (step 1.2), subsequent desorption of both hydrogen and olefin (step 1.3), and formation of a hydrogen molecule (step 1.4). It that can be presented as (where Z is the active surface site, for example, Pt):

 $C_nH_{2n+2}(g) + 2Z \rightleftharpoons C_nH_{2n+1}Z + HZ \text{ (step 1.1)},$

 $C_nH_{2n+1}Z + Z \rightleftharpoons C_nH_{2n}Z + HZ \text{ (step 1.2)},$

 $C_nH_{2n}Z \rightleftharpoons C_nH_{2n}(g) + Z \text{ (step 1.3),}$

 $2HZ \rightleftharpoons H_2(g) + 2Z$ (step 1.4),

This mechanism follows the so-called Langmuir-Hinshelwood kinetics, where all the surface sites of the catalyst are considered identical. Notably, that either the dissociative adsorption of an alkane (step 1.1) [34]–[36] or the second C–H bond cleavage (step 1.2) [37]–[41] have been suggested as the rate-determining (limiting) step of the dehydrogenation reaction.

There are no evidences of major fundamental differences in the reaction mechanism on metal oxide and noble metal catalysts, although mechanistic studies involving metal oxide catalysts are more rare.

It is believed that the dehydrogenation mechanism on chromia-based catalysts is somewhat different, as both the chromium and the oxygen atoms are believed to participate in the reaction [42],[43]. Alkane adsorption was proposed [44],[45] as the rate-determining step on the

chromia/alumina catalyst for isobutane dehydrogenation, whereas the surface reaction of the adsorbed alkyl group was suggested [42],[46],[47] for dehydrogenation of propane and n-butane.

For gallia-based catalysts, calculations using DFT method on Ga_2O_3 (100) surface [48] showed that the propane dehydrogenation mechanism is similar to the one proposed for ethane dehydrogenation over CrO_x catalysts [36],[49],[50]. The initial C–H activation takes place involving a radical, which can adsorb on the Ga site as an alkyl species, or can directly undergo the second C–H cleavage step. Moreover, desorption of both hydrogen and alkene was found to be energetically unfavorable, which was used to explain the rapid coking and a relative low activity of bulk GaO_x -based dehydrogenation catalysts.

It can be thus concluded, that no systematic research on the mechanism of isobutane dehydrogenation reactions on Ga₂O₃ catalysts is available.

In this work, based on our previous study reporting the kinetic regularities [51], a kinetic model has been proposed for the first time, including the main (dehydrogenation) and side (cracking and isomerization) reactions, and the subsequent kinetic modelling was performed for isobutane dehydrogenation over alumina supported gallia catalyst.

2. Experimental part

2.1. Reactants

Isobutane was acquired from KINEF refinery (Russia). Its purity, tested by gas chromatography, was 99.5 mol.%, the remaining part being 0.3% isobutene and 0.2% n-butane. Ethane, propane, butenes, as well as larger hydrocarbons were present in trace amounts.

2.2. Catalyst preparation

Catalyst employed in this work was Ga_2O_3 supported on alumina with the loading of 6 wt. % based on the metal, hereafter referred to as $6Ga/Al_2O_3$. Preparation of the catalyst was done using capillary impregnation of calcined alumina (700°C), which was obtained from thermal activated gibbsite [52] by a slow dropwise addition of aqueous solution of $Ga(NO_3)_3 \cdot 8H_2O$ under vigorous stirring in a flask, drying the impregnated solid at 90–110°C for 2 h and then calcining at 700 °C for 4 h in static air.

Information on activity measurements, as well as details on analysis of products and calculations of activity and selectivity can be found in [51]. Reactions conditions are shown in Table 1.

	<u> </u>	D 11 1 1	-			
Series	Catalyst	Residence time in	Temperature	Volume fraction of		
	volume (cm^3)	the reactor $l(s)$	(°C)	i - C_4H_{10} in helium		
1	0.41	0.058-0.062	520-580	1		
2	0.88	0.123-0.131	520-580	1		
3	1.41	0.197-0.212	520-580	1		
4	2.20	0.280-0.300	520-580	1		
5	0.90	0.125, 0.130, 0.135	520, 550, 580	0.1–1		
6	0.43	0.060	580	0.1–1		
Note: The first value is at 520 °C, the last value is at 580 °C.						

Table 1. Reaction conditions applied in kinetic tests utilized for modelling.

2.3. Parameter estimation

The kinetic parameters were estimated from the laboratory experiments by nonlinear regression with the Simplex and Levenberg–Marquardt methods [53] using the ModEst (Model Estimation) software [54]. For parameter estimation the plug flow reactor model was used.

The parameter estimation routine minimizes the objective function, the sum of squared residuals (Q),

which is defined as:

$$Q = \sum (c_{exp} - c_{est})^2 \cdot w_f, \qquad (1)$$

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where c_{exp} is the component concentration obtained from experiments and c_{est} is the component concentration estimated by the model, w_f is the weight factor for the experimental point. The weight factor was set to unity for all experimental points. Statistical analysis was performed by the Monte Carlo Markov Chain (MCMC) method, which is based on the Bayesian approach [55].

3. Result and Discussion

3.1. Power law kinetics

Catalyst deactivation was not observed for at least 60 consecutive cycles thus allowing to measure activity in the current work from the first cycle [56].

Small particle sizes of the used catalyst (below 150 μ m) and low isobutane conversion levels (0.4–17.5 mol. %) as a result of short residence times have allowed to eliminate the effect of mass transfer on the reaction kinetics.

Based on the Arrhenius expression, the kinetic parameters were determined, which are described in details in [51]. The observed apparent activation energy ($E_{A,app}^{obs}$) was equal to 191 kJ/mol. The observed isobutane transformation rates as well the reaction orders (*n*) with respect to isobutane were dependent on temperature and residence time, as shown in Fig. 1. Large deviations observed at a residence time of ca. 0.03 s indicate a larger contribution of thermal reactions to the observed parameters (*r*, *k*, *n*) discussed in detail in the previous communication [51]. Thus, excluding the experimental data related to 0.031–0.033 s from calculations of these parameters, the equation for isobutane transformation rate (mol/(min·g)) in the range of 520–565 °C and residence time of 0.058–0.300 s can be expressed as:

$$-r_{iC_4H_{10}} = k_{iC_4H_{10}} \cdot P_{iC_4H_{10}}^{n}, \qquad (2)$$

where the isobutane transformation rate constant $k_{iC_4H_{10}}$, (mol/(min·g·atmⁿ)) is:

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$$k_{iC_4H_{10}} = 6.9706 \cdot 10^8 \cdot e^{\frac{-E_{A,ap}^{obs}}{R \cdot (T+273.15)}},$$
(3)

A phenomenological expression for temperature dependence of the reaction order is:

$$n = 1799.2847 \cdot e^{-7327.8912/(T+273.15)} + 0.5252, \tag{4}$$

Given equations are also valid for temperatures above 565 °C, but for a residence time larger than 0.123 s.



Fig. 1. The dependence of the observed reaction order with respect to isobutane (b) on temperature and the residence time for the supported 6 wt. % gallia catalyst.

3.2. Reaction network

The network of chemical reactions involves a wide range of light and heavy by-products. Besides the main reactions of dehydrogenation and thermal cracking, other processes can occur, such as consecutive dimerization, polymerization and aromatization, which ultimately lead to the coke deposition. The main objective of this work was to develop a model with a low number of reaction steps and kinetic parameters that could adequately describe the essential features of the reaction kinetics and low isobutane conversion being far from equilibrium.

Based on the experimental data for isobutane dehydrogenation over gallia/alumina catalyst given in [51], a set of reactions was selected (I–IV), excluding the backward reactions (Fig. 2).



Fig. 2. Products distribution in isobutane dehydrogenation for the supported gallia at 520 °C and residence time ~0.062 s.

Isobutane dehydrogenation (I) and demethylation (II) reactions were clearly dominating. Further secondary reactions of propene, resulting in a slight excess of methane, were neglected.

$$iC_4H_{10} \rightarrow iC_4H_8 + H_2, \tag{I}$$
$$iC_4H_{10} \rightarrow C_3H_6 + CH_4, \tag{II}$$

The amount of coke deposited on the catalyst during dehydrogenation was not taken into account, since the effect of coke on the total mass balance was less than 1%.

The feedstock used in experiments contained n-butane, which can lead to formation of ethane and ethene, and thus was also included in kinetic analysis. The total content of 1-butene, cis- and trans-2-butenes was denoted as C_4H_8 in reaction III.

$$nC_4H_{10} \rightarrow C_4H_8 + H_2, \tag{III}$$

Since the amounts of formed 1-butene and 2-butenes were larger than converted n-butane, an additional route for these products generation should be considered. According to [51] high temperatures, beneficial for dehydrogenation (800–900 K), also favor isomerization of isobutane to n-butane (IV).

$$iC_4H_{10} \rightarrow nC_4H_{10},$$
 (IV)

The reaction steps leading to the formation of propane and C_5 were not considered since there were no significant contributions of them to the overall isobutane conversion (less than 1%).

Finally, considering all the above-mentioned features of reaction kinetics, the following major components were included in kinetic modeling: *1*) i-C₄H₁₀; *2*) n-C₄H₁₀; *3*) i-C₄H₈; *4*) C₄H₈; *5*) C₃H₆; *6*) CH₄.

3.3. Mechanism

As noted above, the Horiuti–Polanyi mechanism is the most often utilized mechanism for explaining dehydrogenation of alkanes. The detailed mechanism for isobutane dehydrogenation and the corresponding reaction routes shown in Table 2 are based on the mechanism proposed by Carra et al. for n-butane dehydrogenation on a supported chromia catalyst [42]. The main difference is that the dissociative adsorption of the alkane (step 1.1) is considered in the current work through the following two steps (where ZO is the vacant site in which Z=metal, O=oxygen):

 $C_4H_{10}(g) + ZO \rightleftharpoons C_4H_9ZOH \text{ (step 2.1) adsorption}$

 $C_4H_9ZOH + ZO \rightleftharpoons C_4H_8ZOH + ZOH$ (step 2.2) C-H cleavage

Kinetic modeling of isobutane dehydrogenation over Cr₂O₃/Al₂O₃ supported this mechanism of surface reactions on dual sites, even if a direct dissociative adsorption of alkane was also considered [43]. Other desorption models were, therefore, not considered in this work.

It should be noted that hydrogen does not affect the state of the active ZO sites, since no reduction peaks were observed for Ga_2O_3/Al_2O_3 .

The bimolecular reaction path way cannot be ruled out due to formation of C_5 hydrocarbons in isobutane isomerization [57],[58]. Nevertheless, in modeling performed in the current work, a monomolecular mechanism was considered (Table 2, steps 1, 9, 12), since isomerization was not major reaction pathway.

3.4. Rate equations

In order to properly analyze the complex reaction system a set of elementary reactions was proposed. Linear combinations of elementary steps, multiplied by the corresponding stoichiometric numbers given in Table 2 were grouped into reaction routes. Thus, stoichiometric numbers were chosen in a way that no intermediates would appear in the overall equations for each route. Routes are essentially different, and it is impossible to obtain one route through multiplication of another route by a number. The total number of independent routes P was determined by the expression proposed by Horiuti and further developed by Temkin [59]: the sum of elementary steps (12) with balance (link) equations minus the number of independent intermediates including the vacant sites (9). The balance equation in the current case corresponds to the total coverage of sites equal to unity.

Steps		Routes			
		N ⁽²⁾	N ⁽³⁾	N ⁽⁴⁾	
1) $iC_4H_{10}(g) + ZO \equiv iC_4H_9ZOH$	1	0	0	1	
2) $iC_4H_9ZOH + ZO \rightarrow iC_4H_8ZOH + ZOH$		0	0	0	
3) $iC_4H_8ZOH \equiv iC_4H_8(g) + ZOH$		0	0	0	
4) $2ZOH \equiv H_2(g) + 2ZO$		0	1	0	
5) $iC_4H_{10}(g) + ZO \equiv C_3H_7ZOCH_3$		1	0	0	
6) $C_3H_7ZOCH_3 + ZO \rightarrow C_3H_6ZOCH_3 + ZOH$		1	0	0	
7) $C_3H_6ZOCH_3 \equiv C_3H_6(g) + ZOCH_3$		1	0	0	
8) $ZOCH_3 + ZOH \equiv CH_4(g) + 2ZO$		1	0	0	
9) $nC_4H_{10}(g) + ZO \equiv C_4H_9ZOH$		0	1	-1	
10) $nC_4H_9ZOH + ZO \rightarrow C_4H_8ZOH + ZOH$		0	1	0	
11) $C_4H_8ZOH \equiv C_4H_8(g) + ZOH$		0	1	0	
12) $iC_4H_9ZOH \rightarrow C_4H_9ZOH$		0	0	1	
$N^{(1)}: iC_4H_{10} \rightarrow iC_4H_8 + H_2; N^{(2)}: iC_4H_{10} \rightarrow C_3H_6 + CH_4;$					

Table 2. The detailed mechanism and routes $(N^{(n)})$ of the isobutane dehydrogenation over aluminasupported Ga₂O₃. Blue color = independent intermediates and the vacant site.

 $N^{(3)}$: $\mathbf{nC}_4\mathbf{H}_{10} \rightarrow \mathbf{C}_4\mathbf{H}_8 + \mathbf{H}_2$; $N^{(4)}$: $\mathbf{iC}_4\mathbf{H}_{10} \rightarrow \mathbf{nC}_4\mathbf{H}_{10}$.

The concentrations of the adsorbed intermediates were expressed as surface coverages (θ_{ZO_i}) according to the ideal case of chemisorption on surface reactions sites developed by Langmuir [60] assumes that all the surface sites are identical, binding energies of the reactants are the same independent of the surface coverage, and interactions between adsorbed species may be neglected [61]. The quasi-equilibrium approximation was assumed for the adsorption and desorption of the reactants, Eqs. 5–12:

$$\theta_{iC_4H_9ZOH} = K_1 P_{iC_4H_{10}} \theta_{ZO}, \tag{5}$$

$$\theta_{iC_4H_8ZOH} = P_{iC_4H_8}\theta_{ZOH}/K_3, \tag{6}$$

$$\theta_{ZOH} = \theta_{ZO} \sqrt{P_{H_2}/K_4},\tag{7}$$

$$\theta_{C_3H_7ZOCH_3} = K_5 P_{iC_4H_{10}} \theta_{ZO},$$
(8)

$$\theta_{C_3H_6ZOCH_3} = P_{C_3H_6}\theta_{ZOCH_3}/K_7, \qquad (9)$$

$$\theta_{ZOCH_3} = \theta_{ZO}^2 P_{CH_4} / \theta_{ZOH} K_8, \tag{10}$$

$$\theta_{nC_4H_9ZOH} = K_9 P_{nC_4H_{10}} \theta_{ZO}, \tag{11}$$

$$\theta_{C_4H_8ZOH} = P_{C_4H_8}\theta_{ZOH}/K_{11}, \qquad (12)$$

where K_I etc. represent the adsorption constant of respective steps; $P_{iC_4H_{10}}$ is the partial pressure of isobutane etc.

The value of θ_{ZO} can be determined from the site balance:

$$\theta_{ZO} + \theta_{iC_4H_9ZOH} + \theta_{iC_4H_8ZOH} + \theta_{ZOH} + \theta_{C_3H_7ZOCH_3} + \theta_{C_3H_6ZOCH_3} + \theta_{ZOCH_3} + \theta_{nC_4H_9ZOH} + \theta_{C_4H_8ZOH} = 1,$$
(13)

giving thus

$$\theta_{ZO} = \frac{1}{D},\tag{14},$$

where

$$D = 1 + P_{iC_4H_{10}}(K_1 + K_5) + \sqrt{\frac{P_{H_2}}{K_4}} \left(\frac{P_{iC_4H_8}}{K_3} + \frac{P_{C_3H_6}P_{CH_4}K_4K_7}{P_{H_2}K_8} + \frac{P_{C_4H_8}}{K_{11}} \right) + K_9P_{nC_4H_{10}},$$
(15)

Assuming that C-H cleavage steps in each route are the slow steps while other steps are in quasi-equilibria, the following rate equations for the rates along different routes were obtained:

$$r_2 = k_2^+ \theta_{iC_4 H_9 Z O H} \theta_{Z O} = k_2^+ K_1 P_{iC_4 H_{10}} / D^2, \tag{16}$$

$$r_6 = k_6^+ \theta_{C_3 H_7 Z O C H_3} \theta_{Z O} = k_6^+ K_5 P_{i C_4 H_{10}} / D^2, \tag{17}$$

$$r_{10} = k_{10}^+ \theta_{nC_4 H_9 Z 0 H} \theta_{Z 0} = k_{10}^+ K_9 P_{nC_4 H_{10}} / D^2,$$
(18)

$$r_{12} = k_{12}^+ \theta_{iC_4 H_9 Z O H} = k_{12}^+ K_1 P_{iC_4 H_{10}} / D, \tag{19}$$

where k_2^+ etc. are the rate constants of respective steps.

3.5. Parameter estimation

The initial parameter estimation demonstrated that several terms in the denominator can be neglected resulting in the following expression

$$D = 1 + K_1 P_{iC_4 H_{10}} + K_9 P_{nC_4 H_{10}},$$
(20)

Non-linear regression using a plug flow reactor model was performed to compare the kinetic model with experimental data. The independent variables were concentrations of $i-C_4H_{10}$, $n-C_4H_{10}$, $i-C_4H_8$, C_4H_8 , C_3H_6 , CH_4 measured at the inlet and outlet of the reactor. Consequently, for the matter of convenience, in the calculations instead of partial pressures of components their concentrations in mol. % were used with a following set of equations instead of eq. (16–19):

$$r_{2} = k_{2}^{+} K_{1} c_{iC_{4}H_{10}} / D^{2}, r_{6} = k_{6}^{+} K_{5} c_{iC_{4}H_{10}} / D^{2}, r_{10} = k_{10}^{+} K_{9} c_{nC_{4}H_{10}} / D^{2}, r_{12} = k_{12}^{+} K_{1} c_{iC_{4}H_{10}} / D, (21)$$

where c_i etc. is the respective concentration of compound *i* and

$$D = 1 + K_1 c_{iC_4 H_{10}} + K_9 c_{nC_4 H_{10}},$$
(22)

In the final model, the temperature dependences of the rate constants were expressed as:

$$k_i^+ K_j = \overline{A}_i \cdot e^{\left(\frac{-E_{A,i}}{R}\left(\frac{1}{T} - \frac{1}{\overline{T}}\right)\right)},\tag{23}$$

$$\overline{A}_{i} = A_{0} \cdot e^{\frac{-E_{A,i}}{R \cdot \overline{T}}},$$
(24)

where \overline{T} is the mean temperature of the experimental data sets equal to 550 °C.

The degree of explanation defined as:

$$R^{2} = \left(1 - \frac{\left(|c_{exp} - c_{est}|\right)^{2}}{\left(|c_{exp} - \bar{c}_{est}|\right)^{2}}\right) \cdot 100\%,$$
(25)

Where \bar{c}_{est} represents the mean value of all the data points, had a very high accuracy of 99.95%.

The values of parameters and their standard errors are presented in Table 3.

Estimated parameters	Value ± standard error	Relative standard error (%)	
$k_2^+K_1$, mol/(min·g)	$0.251 \cdot 10^{-6} \pm 0.661 \cdot 10^{-8}$	2.6	
$k_6^+K_5$, mol/(min·g)	$0.172 \cdot 10^{-7} \pm 0.180 \cdot 10^{-8}$	10.4	
$k_{10}^+ K_9$, mol/(min·g)	$0.672 \cdot 10^{-5} \pm 0.175 \cdot 10^{-6}$	2.6	
$k_{12}^+K_1$, mol/(min·g)	$0.827 \cdot 10^{-8} \pm 0.177 \cdot 10^{-9}$	2.1	
E_2 , kJ/mol	195 ±23	1.2	
E_6 , kJ/mol	300 ± 27	7.2	
E_{10} , kJ/mol	131 ± 2.8	2.1	
E_{12} , kJ/mol	157 ± 3.2	2.1	
K_{l} , (mol. %) ⁻¹	$0.597 \cdot 10^{-6} \pm 0.224 \cdot 10^{-6}$	37.6	
K9, (mol. %) ⁻¹	$0.237{\cdot}10^1\pm0.577{\cdot}10^0$	24.3	

Table 3. The estimated parameters and their relative standard errors.

In the proposed kinetic model, the concentrations of the reactant and the main products in good agreement with the experimental data (Fig. 3) with low values of parameter errors.



Fig. 3. Comparison between experimental and calculated data points for all compounds (in mol. %), where A=iC₄H₁₀; B=iC₄H₈; C=C₃H₆; D=CH₄; E= nC₄H₁₀; F=C₄H₈.

Results from MCMC analysis presented in Fig. 4 point out on the presence of potential numerical correlations between parameters. MCMC method provides a tool for the evaluation of the reliability of the model parameters by treating all the uncertainties in the data and the modelling as statistical distribution. Parameter estimation results described by the contour plots relate parameters, which could in general compensate each other. In particular, elongated contour plots indicate some correlation between parameters, especially for k_{12} and the corresponding activation energy (Fig. 5).

Other parameters were, however, well identified, which is visible from the cycle-like shape of contour plots.



Fig. 4. The correlation matrix of the parameters using MCMC method.





Fig. 5. Correlation between k_i (rate constant multiplied by the adsorption constant) and the corresponding activation energies.

3.6. Validation of activation energy

The general expression for the activation energy it is very well known [62,63]:

$$E_{A,app}^{est} = -R \frac{\partial \ln r}{\partial \frac{1}{T}}, \qquad (26)$$

From Table 2 it is clear that isobutane is consumed along routes $N^{(1)}$: $iC_4H_{10} \rightarrow iC_4H_8 + H_2$; $N^{(2)}$: $iC_4H_{10} \rightarrow C_3H_6 + CH_4$; and $N^{(4)}$: $iC_4H_{10} \rightarrow nC_4H_{10}$. The overall rate of isobutane consumption is thus the sum of the rates along these routes:

$$r = r^{(I)} + r^{(II)} + r^{(IV)}, \qquad (27)$$

And subsequently can be expressed through the respective reaction steps:

$$r = r_2 + r_6 + r_{12}, \tag{28}$$

Resulting in

$$E_{A,app}^{est} = -R \cdot \frac{\partial ln(r_2 + r_6 + r_{12})}{\partial \frac{1}{T}},\tag{29}$$

The estimated apparent activation energy was equal to 200 kJ/mol, which is close to the value obtained graphically ($E_{A,ap}^{obs} = 191$ kJ/mol).

The estimated apparent activation energies for isobutane and n-butane dehydrogenation (I and III) as well as for isobutane isomerization (IV) are much smaller (195, 131 and 157 kJ/mol, respectively) than for the cracking reaction (II) producing methane and propene (300 kJ/mol), indicating an efficient use of the supported gallia catalyst to produce C_4 olefins.

The values of the apparent activation energy for isobutane thermal cracking obtained in the absence of any catalyst at 575–580 °C were ranging from 226 to 193 kJ/mol [64], while isobutane cracking to propene with methane formation in the presence of Ga₂O₃/Al₂O₃ catalyst gives values of the apparent activation energy between 226 to 292 kJ/mol. This apparent contradiction can be explained by effective recombination of the radicals generated in thermal cracking on the surface of a heterogeneous catalyst, as reported in [51], thus substantially hindering the thermal contribution to cracking.

Thus, an excellent correspondence of the estimated values to the experimental data presented in Fig. 6 for the main components and for conversion confirms that the reaction network can adequately describe the experiments not requiring inclusion of any additional parameters.



Fig. 6. Fit of the model to the experimental data for compounds in mol. % $(A - iC_4H_{10}, B - iC_4H_8, C - C_3H_6)$ and conversion as a function of temperature (°C) and residence time (τ , s).

4. Conclusions

Kinetics of isobutane dehydrogenation and the accompanying reactions over supported gallia catalyst was elaborated by applying non-linear data fitting. The model was based on the surface reactions using the theory of stationary complex reactions considering several reaction routes occurring on ideal surfaces, i.e. assuming that the sites are identical and that lateral interactions between adsorbed species can be neglected. The value of the degree explanation ($R^2 = 99.95\%$) confirms capability of the model to describe the kinetic data giving also statistically reliable values of parameters. Ga₂O₃/Al₂O₃ catalyst was observed to be more selective towards dehydrogenation than to cracking exhibiting a lower apparent activation energy towards dehydrogenation compared to cracking.

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