



## Dehydrogenation of C<sub>3</sub>–C<sub>4</sub> paraffins on Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts in fluidized and fixed bed reactors

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### ABSTRACT

Thermodynamic calculations for dehydrogenation of a model C<sub>3</sub>–C<sub>4</sub> paraffin mixture indicate that there is a complex mutual effect of the components on the equilibrium yield of olefins. Each component can act simultaneously: (i) as a diluent shifting the dehydrogenation equilibrium of the mixture components to the desired olefin and (ii) as an additional source of hydrogen to the reaction zone, which shifts the dehydrogenation equilibrium to the left. Experiments on dehydrogenation of model C<sub>1</sub>–C<sub>4</sub> paraffin mixtures on Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalysts in fluidized and fixed beds show an increase of the total conversion of C<sub>3</sub>–C<sub>4</sub> paraffins to olefins and an increase of the total process selectivity to olefins.

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### 1. Introduction

Processing of C<sub>3</sub>–C<sub>5</sub> paraffins from gas condensate, associated petroleum gas (APG) and natural gas liquids (NGL) is a key problem of the Russian Federation oil-and-gas industry. Catalytic dehydrogenation yielding olefin and diolefin hydrocarbons is one of the methods used for processing these substances. These hydrocarbons (propylene, *n*-butenes, isobutylene, butadiene, isoprene) are precursors for producing synthetic rubbers, plastics, motor fuel constituents (MTBE, alkylates) and other important chemicals. The annual bulk volume of olefins, without propylene, produced by dehydrogenation in Russia is 600,000–700,000 tons. The world industry utilizes several processes for dehydrogenation of C<sub>3</sub>–C<sub>5</sub> paraffins using different production engineering and catalysts [1–5]. Thus, about one half of the known processes use Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> (Cr<sub>2</sub>O<sub>3</sub> is the active component) as a catalyst. In our country, two plants use vacuum dehydrogenation of *n*-butane to butadiene (Catadien Process) in a fixed bed with Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst supplied by Süd Chemie/Houdry Division for 30 years. In other countries, this catalyst is used for dehydrogenation of propane and isobutene (Catofin Process). In Russia about 10 plants perform dehydrogenation of isobutane, *n*-butane and isopentane in a fluidized bed with Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. There are no processes and catalysts for dehydrogenation of propane to propylene in our country.

Updating the existing dehydrogenation methods aimed at increasing the yield of olefin hydrocarbons and process selectivity is a very important problem today. Dehydrogenation of hydrocarbon mixtures (APG or NGL) without preliminary separation of the components is an interesting to intensify the olefin production. In the present report we consider the theoretical and experimental feasibility of the C<sub>1</sub>–C<sub>4</sub> paraffin mixture dehydrogenation without preliminary separation of the individual components.

### 2. Experimental

Supported chromium oxide catalysts were prepared by incipient wetness impregnation with an aqueous solution of CrO<sub>3</sub> with KOH or NaOH additive according to the earlier reported procedure [6]. Two types of supports were used in the present study: (i) microspherical (70–150 μm) amorphous product of gibbsite thermal activation in a centrifugal flash reactor (CEFLAR<sup>TM</sup>) [7] and (ii) macrospherical (2–3 mm) γ-Al<sub>2</sub>O<sub>3</sub> [8]. After the impregnation with chromium oxide, the catalysts were dried at 110 °C for 12 h and calcined in air at 700 °C for 2 h.

The catalytic characteristics were measured in a continuous flow reaction system consisting of fluidized bed or fixed-bed quartz-glass reactors with a gas chromatograph for on-line product analysis. The catalyst weight was 5 g. The catalysts were reduced in hydrogen flow before the each test at the reaction temperature. The activity measurements were carried out at 560–600 °C under atmospheric pressure. Dehydrogenation was carried out for 10 min. After the dehydrogenation, the catalyst was flushed with nitrogen

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**Table 1**  
Dependence of the equilibrium degree of isobutane conversion to isobutylene on temperature and composition of the initial mixtures.

No	Initial mixture composition (vol.%)				Temperature (°C)/equilibrium degree of isobutene conversion to isobutylene (%)				
	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	C <sub>3</sub> H <sub>8</sub>	H <sub>2</sub>	CH <sub>4</sub>	540	560	570	580	590
1	100	–	–	–	43.9	55.5	60.3	64.5	68.1
2	50	–	50	–	34.3	44.2	49.0	54.0	58.4
3	50	50	–	–	52.2	60.1	63.6	67.1	70.5
3	50	–	–	50	57.5	65.5	69.1	72.5	75.8
4	5	–	–	95	87.7	–	92.9	–	95.0

**Table 2**  
Dependence of the equilibrium degree of propane conversion to propylene on temperature and composition of the initial mixtures.

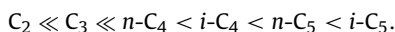
No	Initial mixture composition (vol.%)				Temperature (°C)/equilibrium degree of propane conversion to propylene (%)				
	C <sub>3</sub> H <sub>8</sub>	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	H <sub>2</sub>	CH <sub>4</sub>	540	560	570	580	590
1	100	–	–	–	28.4	34.9	38.5	42.0	45.8
2	50	–	50	–	14.4	21.2	23.9	28.2	31.9
3	50	50	–	–	24.2	31.3	34.6	38.5	42.5
4	50	–	–	50	36.4	43.8	47.5	51.1	55.24
5	5	–	–	95	71.8	–	81.6	–	86.5

and regenerated for 30 min with diluted air. The regeneration temperature was 650 °C.

### 3. Results and discussion

#### 3.1. Thermodynamic aspects

It is well known that the dehydrogenation degree is limited by a thermodynamic equilibrium. At similar temperature and pressure values, the dehydrogenation equilibrium degree (reactivity) rises in the paraffin series with an increase in the number of carbon atoms and the degree of the paraffin branching [1]:



Thermodynamic calculations of model hydrocarbon mixture dehydrogenation performed using “HYSYS” software package indicate a complex mutual effect of the components on the equilibrium yield of olefins. Each component can act simultaneously as a diluent shifting the dehydrogenation equilibrium of the mixture components to the desired olefin, and as an additional source of hydrogen to the reaction zone, which shifts the dehydrogenation equilibrium to the left. The overall effect depends on the position of the component in the reactivity series relative to the other component.

Table 1 suggests that in the model mixture of C<sub>3</sub>–C<sub>4</sub> hydrocarbons (the ratio of gases is similar to that in NGL) propane acts as a diluent of isobutene and increases the equilibrium conversion of isobutene to isobutylene. In this case, the effect of propane on the isobutene dehydrogenation is similar to that of an inert diluent such as methane, but is less evident due to the hydrogen generation during its dehydrogenation.

**Table 3**  
Catalytic characteristics of propane, isobutane and model propane–butane mixture dehydrogenation in a fluidized bed of (16 wt.% Cr<sub>2</sub>O<sub>3</sub>–1.5 wt.% K<sub>2</sub>O)/Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at constant feed space velocity of inlet gases and mixtures.

Catalytic properties <sup>a</sup>	Composition of initial feedstock (wt.%)		
	Propane = 99.9	Isobutane = 99.8	Propane = 42.2 isobutane = 57.8
Propane conversion (%)	34.8	–	34.4
Propylene yield (wt.%)	31.0	–	31.0
Selectivity to propylene (wt.%)	89.0	–	90.0
Isobutane conversion (%)	–	55.0	57.3
Isobutylene yield (wt.%)	–	51.5	53.6
Selectivity to isobutylene (wt.%)	–	93.4	93.5

<sup>a</sup> Process conditions: temperature 560 °C, reaction time 10 min, feed space velocity of individual gases and gas mixtures 400 h<sup>-1</sup>.

Since isobutane is dehydrogenated easier than propane, the equilibrium degree of propane conversion to propylene decreases in the presence of isobutane (see Table 2). In this case, isobutane affects the propane dehydrogenation in the same way as hydrogen dilution. Therefore, a detrimental effect of isobutane on the propane dehydrogenation is caused by hydrogen. The concentration of the latter in the reaction medium increases due to the isobutene dehydrogenation.

#### 3.2. Catalytic tests

The thermodynamic calculations were experimentally tested during dehydrogenation of a number of model paraffin mixtures using both fixed and fluidized beds with Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst developed at the Boreskov Institute of Catalysis [6,9]. The catalytic experiments performed on the dehydrogenation of a propane–butane mixture fully confirmed the conclusions of the thermodynamic calculations for the isobutane dehydrogenation and partially confirmed those for the propane dehydrogenation.

For example, Tables 3 and 4 present the obtained data on the dehydrogenation of isobutane and propane as well as their mixtures (the volume ratio close to 1:1) in a fluidized bed filled with fresh Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. The experiments were carried out in two reaction modes: (a) at constant feed space velocity of both individual paraffins and mixtures (Table 3) and (b) at constant feed space velocity of individual paraffins in the mixture (Table 4). Concerning possible benefits of the industrial application of propane–isobutane mixture dehydrogenation, mode (a) corresponds to the situation when the isobutene production has to be decreased by some reasons. In such a case, propane could be added to the isobutane feed to keep the olefins productivity constant. Mode (b) can be used to increase the reactor productivity by doubling the overall paraffin

**Table 4**

Catalytic characteristics of propane, isobutane and model propane–butane mixture dehydrogenation in a fluidized bed with (16 wt.% Cr<sub>2</sub>O<sub>3</sub>–1.5 wt.% K<sub>2</sub>O)/Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst at constant feed space velocities of isobutane and propane.

Composition of initial feedstock (wt.%)		Feed space velocity $V$ (h <sup>-1</sup> )	$T$ (°C)	Catalytic properties			
<i>i</i> -C <sub>4</sub> H <sub>10</sub>	C <sub>3</sub> H <sub>8</sub>			Olefin Yield (wt.%)		Olefin Selectivity (wt.%)	
				<i>i</i> -C <sub>4</sub> H <sub>10</sub>	C <sub>3</sub> H <sub>8</sub>	<i>i</i> -C <sub>4</sub> H <sub>10</sub>	C <sub>3</sub> H <sub>8</sub>
99.8	0.2	400	560	49.4	0.6	92.2	–
			580	56.7	1.5	90.4	–
			590	56.6	2.1	85.9	–
			600	58.8	2.6	85.3	–
0	99.9	400	580	–	33.0	–	80.0
			590	–	34.7	–	75.9
			600	–	33.7	–	62.7
56.9	43.1	800 (400+400)	560	49.3	25.8	96.0	95.4
			580	57.3	32.9	92.5	96.5
			590	58.2	36.3	90.7	99.5
			600	58.3	40.7	81.6	100.9

**Table 5**

Effect of dilution with methane on the catalytic characteristics of propane and isobutane dehydrogenation in a fluidized bed with (16 wt.% Cr<sub>2</sub>O<sub>3</sub>–1.5 wt.% K<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub> catalyst.

Paraffin	Mixture composition		Feed space velocity (h <sup>-1</sup> )	$T$ (°C)	Olefin Yield (wt.%)	Olefin Selectivity (wt.%)	Paraffin conversion (%)
	Paraffin (wt.%)	Methane (wt.%)					
Propane	99.9	0	400	580	33.0	80.0	39.1
				560	31.0	89.0	34.8
	73.3	26.7	800	580	41.8	88.5	47.2
				560	34.0	88.5	38.4
Isobutane	99.8	0	400	580	57.0	90.5	63.0
				560	51.0	92.1	
	78.3	21.6	800	580	64.1	91.0	70.4
				560	55.0	90.8	60.5

**Table 6**

Effect of dilution with methane on the catalytic characteristics of propane dehydrogenation in a fixed bed with spherical (18 wt.% Cr<sub>2</sub>O<sub>3</sub>–0.4 wt.% Na<sub>2</sub>O)/Al<sub>2</sub>O<sub>3</sub> catalyst at 590 °C.

Reaction mixture composition (wt.%)		Catalytic characteristics		
C <sub>3</sub> H <sub>8</sub>	CH <sub>4</sub>	Propylene Yield (wt.%)	Selectivity towards propylene (wt.%)	Propane conversion (%)
99.9	–	42.9	90.8	47.3
71.7	28.36	48.9	91.2	53.6

feed rate. It should be noted that industrial fluidized bed reactors for dehydrogenation of light paraffins are typically operated at much lower space velocity (up to 200 h<sup>-1</sup>) than our laboratory reactor. So, the results obtained at the laboratory reactor demonstrate general trends for the olefin mixture dehydrogenation and cannot be used for direct prediction of the industrial reactor performance.

Table 4 suggests that when isobutane is mixed with propane (first version), the yield of isobutylene increases by 2 wt.% at the reaction temperature 560 °C. However, no significant reduction of the propylene output predicted by the thermodynamic calculations is observed. It is likely that the additional amount of propylene resulting from the side reaction of isobutane cracking partially compensates the above reduction. As a result, the calculated total selectivity towards propylene increases and exceeds 100% in some cases. Using the second version when the isobutylene yield remains constant and the dehydrogenation selectivity increases at temperatures up to 590 °C one can achieve efficient propane dehydrogenation to propylene.

Similar results were obtained for the reaction performed in a fixed bed with granular Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> catalyst. When the feed space velocity is constant and the feedstock is diluted with propane, the yield of isobutylene can rise by 3–5 wt.% depending on the process temperature.

As it follows from the thermodynamic calculations, both ethane and methane, which are inert in this process, are efficient diluents

of propane. Tables 5 and 6 suggest that the dehydrogenation of the model methane–propane mixture (component concentrations are similar to those in APG) results in a significant increase in the propylene yield (by 3–8 wt.%), which is accompanied by an increase in the selectivity towards propylene. A similar beneficial effect of dilution with methane (or ethane) was observed for the dehydrogenation of paraffin C<sub>4</sub>.

#### 4. Conclusions

The experiments on dehydrogenation of the model C<sub>1</sub>–C<sub>4</sub> paraffin mixtures showed that in order to produce more butene, it is advantageous to dehydrogenate either C<sub>3</sub>–C<sub>4</sub> paraffin mixtures or NGL, which will also provide additional propylene. To direct the process towards higher propylene output, one should dehydrogenate a methane–propane mixture, APG or a NGL–APG mixture prepared in definite proportions.

Both versions allow one to:

- increase the total conversion of C<sub>3</sub>–C<sub>4</sub> paraffins to olefins;
- increase the total process selectivity to olefins;
- avoid double separation of hydrocarbons (before and after dehydrogenation);
- increase the total concentration of propylene in the final product, which is a by-product of cracking during dehydrogenation of the

individual C<sub>4</sub>–C<sub>5</sub> paraffins. The present industrial dehydrogenation plants process propylene together with C<sub>1</sub>–C<sub>2</sub> hydrocarbons as a flue gas due to its low concentration in the mixture making isolation unprofitable.

## References

- [1] B.M. Weckhuysen, R.A. Schoonheydt, *Catalysis Today* 51 (1999) 223.
- [2] D. Sanfilippo, I. Miracca, *Catalysis Today* 111 (2006) 133.
- [3] M.M. Bhasin, J.H. McCaina, B.V. Vora, T. Imai, P.R. Pujadó, *Applied Catalysis A: General* 221 (2001) 397.
- [4] R.A. Buyanov, N.A. Pakhomov, *Kinetika i Kataliz* 42 (2001) 72.
- [5] N.A. Pakhomov, *Industrial Catalysis in Lectures*, vol. 6, Calvis, Moscow, 2006, p. 53 (in Russian).
- [6] RF Patent No 2322290/V.V. Molchanov, N.A. Pakhomov, L.A. Isupova, V.A. Balashov et al. (2008). Priority of 18.12.2006.
- [7] L.A. Isupova, Yu.Yu. Tanashev, I.V. Kharina, E.M. Moroz, et al., *Chemical Engineering Journal* 107 (2005) 163–169.
- [8] B.P. Zolotivskii, R.A. Buyanov, G.A. Bukhtiyarova, et al., *Russian Journal Applied Chemistry* 70 (1997) 299.
- [9] N.A. Pakhomov, V.V. Molchanov, B.P. Zolotovskii, V.I. Nadtochiy et al., *Catalysis in Industry, Special issue* (2008) 13 (in Russian).