

Contents lists available at ScienceDirect

Applied Catalysis A: General



journal homepage: www.elsevier.com/locate/apcata

Pathways of light compounds formation during propane and isobutane dehydrogenation on Al-Cr catalysts

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ARTICLE INFO

Article history: Received 16 February 2010 Received in revised form 7 April 2010 Accepted 13 April 2010 Available online 20 April 2010

Keywords: Light compounds Al-Cr catalyst Dehydrogenation Thermo-cracking Hydrocracking Propane Isobutane

ABSTRACT

Reaction pathways of the light hydrocarbons formation during propane and isobutane dehydrogenation on Al-Cr catalyst have been studied. It was determined that the majority of light compounds are formed not directly from initial paraffin, but from the main product of the paraffin dehydrogenation; olefin. The sequence of the light compounds formation reactions includes: (1) dehydrogenation of the initial paraffin with formation of targeted olefin; (2) consecutive hydrocracking of the newly produced main olefin with formation of the one carbon shorter chain olefin and methane; (3) one carbon shorter chain olefin can be converted by two parallel reactions further. The first reaction is hydrogenation of the one carbon shorter chain olefin to the formation of the one carbon shorter chain paraffin. Another parallel reaction is hydrocracking of the one carbon shorter olefin to the two carbon shorter olefin and methane. If short olefin is ethylene the final product of the hydrocracking reaction is methane. This sequence can be presented by using isobutane dehydrogenation as an example which also includes steps of light compounds formation from C₃ hydrocarbons:

$C_4H_{10} \rightarrow \ C_4H_8 + H_2$	(1)
$C_4H_8+H_2\rightarrow\ C_3H_6+CH_4$	(2)
$C_3H_6+H_2\rightarrow\ C_3H_8$	(3a)
$C_3H_6+H_2\rightarrow\ C_2H_4+CH_4$	(3b)
$C_2H_4+H_2 \rightarrow \ C_2H_6$	(4a)
$C_2H_4 + 2H_2 \rightarrow \ 2CH_4$	(4b)
Obtained reaction pathways of light compounds formation can	be applied to optimize the concept of

Obtained reaction pathways of light compounds formation can be applied to optimize the concept of the dehydrogenation process and explain puzzling phenomena regarding the temperature profile in the fixed bed dehydrogenation process.

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1. Introduction

The paraffin dehydrogenation process on Al-Cr catalyst has been known for about 70 years. There are hundreds of published studies that investigated different aspects of the technology including the catalyst and kinetics of reactions. However, there are still some questions regarding this process that need to be answered. One of these questions is the reaction pathway of the light compounds formation such as methane, ethane, ethylene and others that are

* Tel.: +1 502 634 7423; fax: +1 502 634 7486. *E-mail address:* vladimir.fridman@sud-chemie.com. formed by different cracking reactions during paraffin dehydrogenation.

To the best of our knowledge there are no published experimental studies aimed to determine the reaction pathway of light compounds formation during the dehydrogenation process. Our guess is that this subject has never been considered as an important one. In spite of the absence of the experimental studies regarding the pathway of light compounds formation during dehydrogenation, some authors presented their presumptions based on light compounds composition how these reactions might have happen. For instance, the authors [1] presented schematics of the reaction pathways of all reactions that are observed during isobutane dehydrogenation indicating that light compounds are formed by direct cracking of paraffin. Shmulevich et al. [2] studying kinetics of the

⁰⁹²⁶⁻⁸⁶⁰X/\$ - see front matter © 2010 Elsevier B.V. All rights reserved. doi:10.1016/j.apcata.2010.04.026

isopentane dehydrogenation suggested the model of the light compounds formation that also says that they are formed directly from paraffin:

$$i\text{-}C_5H_{12} \rightarrow \ 0.5CH_4 + 0.5C_2 + 0.5C_3 + 0.5C_4H_8$$

Authors of [3], on the basis of amount of light compounds obtained after thermo-desorption of isobutane and isobutylene, concluded that paraffin is the main producer of light compounds on Al-Cr catalyst. It should be noted that it is pretty common view on this subject.

However, our attempt to explain the main olefin selectivity profile in the Al-Cr catalyst bed using this presumption did not match to the experimental data, thus creating doubts that this assumption is correct. Moreover, the chemistry of the cracking and hydrocracking reactions on the low acidity Al-Cr catalyst also does not support the assumption that initial paraffin is a main source for light compounds formation.

At the same time, we are convinced that understanding the reaction pathway of light compounds formation during the dehydrogenation process is very important for development of a highly selective catalyst. Furthermore, misconception regarding light compounds pathway formation also can be detrimental to quality of the engineering configuration of the dehydrogenation process. In our view there was a necessity in verifying correctness of this presumption. The present study was conducted to give an experimental proof of the reaction pathway of the light compounds formation during propane and isobutane dehydrogenation on Al-Cr catalyst.

2. Experimental

Al-Cr catalyst prepared according to [4] with 20% of Cr_2O_3 has been used for the current study. The kinetic study was conducted in the unit that simulated the cyclic dehydrogenation process. This process operates in the cyclic mode dehydrogenation–regeneration. The following steps were included in one dehydrogenation–regeneration cycle: initial evacuation, the catalyst reduction by H₂, second evacuation, dehydrogenation for 10 min, purge, and regeneration for 15 min. The reaction products were analyzed by a HP 6890 gas chromatograph with special configuration that provides simultaneous analysis of CO, CO_2 and hydrocarbons from methane up to butadiene. The separation of the compounds was conducted with application of the molecular sieve column Supelco 13061U and capillary column J&W Scientific.

The plug reactor with diameter 25.4 mm has been used. The commercial pellets of the catalyst with a diameter of 3 mm were loaded in the reactor. Because the fresh Al-Cr catalyst changes its initial activity during the first few cycles (breaking in period) the catalyst was aged to achieve stable catalyst performance. The aging of the fresh catalyst was conducted at about 600 °C and for 300 cycles after which the catalyst activity achieved the constant value. To verify a stable catalyst performance, in the end of the aging, the catalyst was run for 10 cycles at 567 °C in propane dehydrogenation at LHSV – 1 h⁻¹ at a total dehydrogenation pressure in the reactor of 0.5 atm, or in the case of isobutane dehydrogenation in the end of the aging, the catalyst was run for 10 cycles at 567 °C in isobutane dehydrogenation at LHSV – $2 h^{-1}$ and at a total dehydrogenation pressure in the reactor of 0.5 atm These conditions have been chosen as standard conditions. After completion of the aging test that provided stable catalyst performance the sample was unloaded and used for making the catalyst composite for testing. Before loading, the catalyst was mixed with alpha-alumina chips. Changing of the catalyst loading provided different reaction time from 0.22 up to 1.84s. Experiments were performed in the temperature range between 540 and 630 °C. Each experiment was conducted three times. The average value for yield has been used for calculation.

After the 100 cycles of testing the catalyst was tested again for activity at standard conditions to verify if activity is stable. The results of these tests always indicated that short testing of the catalyst at different conditions did not change its initial performance.

The reaction pathway of the light gas formation during dehydrogenation of paraffins was studied by analyzing the compositions and relative selectivity of the light gas products as a function of the reaction (contact) time. In the case of simple reactions this method can provide preliminary information regarding the reaction pathway. Furthermore the kinetic data were analyzed to obtain dependence between the particular product reaction rates dC_x/dt to dC_y/dt extrapolated to the zero reaction time, which should achieve zero value in the case of consecutive reactions and be different from zero and infinity in the case of parallel reactions [5]. The method of separated reactions [5] also has been applied where conversion of the possible intermediates such as propane, propylene, isobutane, isobutylene, ethane and ethylene in the presence of hydrogen at the reaction conditions was studied.

3. Results and discussion

3.1. Reaction pathways of the light gas formation during propane dehydrogenation on Al-Cr catalyst

During propane dehydrogenation on Al-Cr catalyst the light compounds mixture formed by side reactions consists of methane, ethane and ethylene. The light compounds from propane can be formed by reaction of the thermo-cracking and catalytic cracking.

3.1.1. Reactions of thermo-cracking during propane dehydrogenation

Initially the reaction of propane thermo-cracking was studied where alpha-alumina inert with surface area $0.5 \text{ m}^2/\text{g}$ was loaded in place of the catalyst. This experiment imitated the conversion of the paraffin between catalyst pellets. Propane with purity 99.9% with was passed through the reactor to provide contact time from 0.22 to 1.84 s and at 600 °C. Similar experiments were conducted with a mixture of propane and hydrogen where hydrogen concentration in the feedstock mixture was 30 mol%.

There are only few theoretical possibilities for formation of the light compounds by thermo-cracking from propane and propylene (reactions (1) and (2)).

$$C_3H_8 \rightarrow C_2H_4 + CH_4 \tag{1}$$

$$C_3H_8 \rightarrow C_3H_6 + H_2; C_3H_6 + H_2 \rightarrow C_2H_4 + CH_4$$
 (2)

The outlet gas after propane thermo-conversion contained only two compounds with carbon number less than C_3 such as methane and ethylene. This strongly suggests that propane decomposes only into ethylene and methane by reaction (1). Besides these two compounds a small amount of propylene and coke were formed during propane thermo-decomposition.

It should be pointed out that the rate of propane thermodecomposition was relatively low. For instance, at 600 °C and a reaction time of 1.84 s, the observed propane conversion was only 2.7%, but the maximum yield of all light compounds was lower than 1% (Fig. 1a).

Addition of the hydrogen in propane has a very strong inhibiting effect on the rate of thermo-decomposition of propane (Fig. 1a). The yield of ethylene and methane was down by about four times when compared with conversion of propane without hydrogen (Fig. 1a).

One of the pathways of the thermo-cracking reaction occurs via radical mechanism where the cleavage of the C–C bond under high temperature starts from $CH_3-CH_*-CH_3$ 1- or 2-propyl radical. The assumption is that hydrogen also can generate radical H* that is probably involved in the recombination of new produced



Fig. 1. Yield of the light compounds formed during of propane (a) and isobutane (b) dehydrogenation as a function of reaction time: (1) paraffin without catalyst at 600 °C; (2) paraffin-hydrogen mixture without catalyst at 600 °C; (3) on Al-Cr catalyst at 600 °C.

 $\mathsf{CH}_3\mathsf{-}\mathsf{CH}_*\mathsf{-}\mathsf{CH}_3$ propyl radical and inhibits the thermo-cracking reaction.

3.1.2. Reactions of light compounds formation on the Al-Cr catalyst during propane dehydrogenation

Dehydrogenation of propane was conducted using Al-Cr catalyst with reaction times of 0.22, 0.45, 0.9 and 1.84 s at a dehydrogenation pressure of 0.5 bar and temperatures ranging from 570 to 620 °C. Fig. 2 depicts the dependence between molecular concentration of the light compounds in outlet gas produced at 600 °C during propane dehydrogenation and different reaction time.

Besides propylene, dehydrogenation of propane on Al-Cr catalysts usually leads to formation of the light compounds such as methane, ethane and ethylene (Fig. 2).

Theoretically the light compounds generated during propane dehydrogenation might be formed from propane and propylene by reaction of propane thermo-cracking (reactions (1) and (2)) or by propane and propylene hydrocracking as follows:

$$C_3H_8 + H_2 \rightarrow C_2H_6 + CH_4 \tag{3}$$

$$C_3H_6 + H_2 \rightarrow C_2H_4 + CH_4 \tag{4}$$

Newly produced ethane and ethylene might further be converted by hydrogenation or dehydrogenation reactions into correspondent olefin or paraffin by reactions (5) and (6).

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{5}$$

$$C_2H_4 + H_2 \rightarrow C_2H_6 \tag{6}$$

There is also a possibility for hydrocracking of ethylene and ethane by reaction conversion of ethylene or ethane to methane as drawn below:

$$C_2H_6 + H_2 \rightarrow 2CH_4 \tag{7}$$

$$C_2H_4 + 2H_2 \rightarrow 2CH_4 \tag{8}$$

The character of the curves shown in Fig. 2 is typical for consecutive reactions where methane and ethane are the final products of the initial feedstock transformation and propylene and ethylene are intermediate compounds for formation of ethane and methane.

The first question that needs to be answered is "Is ethane formed from ethylene or is ethylene formed from ethane?". There is no doubt that ethane and ethylene are interconnected. During dehydrogenation of propane they are converted into each other to satisfy the equilibrium. Ethane can be produced by propane hydrocracking by reaction (3)). Newly produced ethane can be dehydrogenated into ethylene (reaction (5)). There is another pathway whereas ethane can be produced differently. The first reaction of this pathway is hydrocracking of propylene to ethylene and methane (reaction (4)) and then ethylene can be hydrogenated to ethane (reaction (6)).

Based on the results of the propane dehydrogenation conducted at different contact time on Al-Cr catalyst the relative selectivity between ethane to ethylene and between ethylene to ethane for product produced during dehydrogenation of propane at 600 °C has been calculated (Fig. 2).

As seen in Fig. 3 the ratio between the rates of ethylene to ethane formation decreases as a function of reaction time and approaches infinity when reaction time is extrapolated to zero, which is an indication that during propane dehydrogenation ethylene is not formed from ethane. The ratio between the rates of ethane to ethylene formation increases as a function of reaction time and approaches zero when reaction time is extrapolated to zero. This dependence is typical for consecutive reactions where ethane is produced from ethylene [5]. Growth of ethane is provided by consumption of ethylene that leads to increasing relative selectivity between ethane and ethylene. Thus, this observation strongly suggests that during propane dehydrogenation ethane is formed from ethylene by consecutive reaction of ethylene hydrogenation.

The hydrogenation reaction of ethylene in the absence of ethane is thermodynamically favorable even at 600 °C where the equilibrium ratio between ethane and ethylene at a total pressure 0.5 bar is about 3–1. Any new molecule of ethylene formed from C_3 compounds in the mixture where there is no ethane breaks the equilibrium of the system and promotes the consecutive hydrogenation.

To verify this presumption, ethylene conversion in hydrogen has been studied on Al-Cr catalyst at 600 °C using different contact times. The initial ethylene concentration was 65 mol%. As seen from Table 1, ethylene can be hydrogenated on Al-Cr catalyst at 600 °C with conversion up to 75%. This supports the assumption about fast hydrogenation of ethylene to ethane at these conditions and confirms the suggested pathway of ethane formation through hydrogenation of ethylene.

The second unknown question was a reaction pathway of methane formation from C_2 compounds. There are two possibilities for production of methane from ethane or ethylene. Methane from C_2 hydrocarbons can be formed by hydrocracking of ethane (reaction (7)), or by hydrocracking of ethylene (reaction (8)). Table 1 presents the product composition of the conversion of ethane and ethylene in the presence of hydrogen. As seen from Table 1 the conversion of ethane in the presence of hydrogen led to very small amount of methane. The amount of methane started to be noticeable when ethylene concentration produced by ethane dehydrogenation was high enough to start forming methane. Unlike



Fig. 2. Propylene and light compounds concentrations in the outlet gas generated during propane dehydrogenation on Al-Cr catalysts at 600°C as a function of the reaction time.



Fig. 3. Relative rates of the ethylene and ethane formation generated during propane dehydrogenation at 600 °C and extrapolated to zero reaction time.

Table 1

Conversion of hydrogen-ethane, hydrogen-ethylene mixtures and concentration of the light compounds in outlet gas produced on Al-Cr catalyst at different reaction time.

Feed composition: hydrogen – 35 mol%, ethylene – 65 mol%						
Temperature (°C)	Contact time (s)	Concentration of products after ethylene hydro-treatment (mol%)			Ethylene conversion (%)	
		CH ₄	C_2H_6	C_2H_4		
600	0.23 0.46 0.92 1.84	0.95 1.54 4.4 7.92	26.9 48.56 50.02 52.4	35.06 22.06 21.46 17.01	27.1 42.7 67.3 75.4	
Feed composition: hydrogen – 35 mol%, ethane 65 mol%						
Temperature (°C)	Contact time (s)	Concentration of products after ethane hydro-treatment (mol%)			Ethane conversion (%)	
		CH ₄	C ₂ H ₆	C ₂ H ₄		
600	0.23 0.46 0.92 1.84	0.06 0.17 0.37 0.75	27.24 26.34 25.96 25.3	2.15 2.73 2.84 3.05	7.3 9.4 11.3 11.5	

ethane, the conversion of ethylene in hydrogen led to about 10 times higher yield of methane than that after conversion of ethane in hydrogen at the same conditions. This strongly suggested that methane is formed from ethylene. It should be noted that a very similar conclusion was reported recently for formation of methane during propane dehydrogenation on Pt-Sn catalyst [6].

The next question was "What is the reaction pathway of ethylene formation?" During propane dehydrogenation ethylene can be formed by hydrocracking of propylene (reaction (4)), or by thermodecomposition of propane (reaction (1)). Comparison of the total amount of light compounds formed during propane dehydrogenation on Al-Cr catalyst with the amount of light compounds formed from propane by thermo-cracking without catalyst (Fig. 1) indicates that thermo-cracking without hydrogen produces about six times lower amount of light compounds than hydrocracking on Al-Cr catalyst. In the presence of catalyst the rate of thermo-cracking of propane to ethylene should be even lower because dehydrogenation of propane leads to generation of hydrogen. As we already mentioned before hydrogen strongly inhibits the propane thermocracking reaction (Fig. 1).

As it was already concluded before ethylene is not formed from ethane, but it can be synthesized from propylene by hydrocracking (reaction (4)). In order to determine the relationship between propylene and ethylene an analysis of relative selectivity was conducted between ethylene and propylene as a function of the reaction time. For ethylene selectivity it was necessary to take into account the fact that a significant part of ethylene produced was converted into ethane by the hydrogenation reaction. Thus, the amount of the ethylene that was formed from the initial compound is equal to the amount of ethylene left in the outlet gas plus the amount of ethane formed from ethylene by hydrogenation to paraffin. Fig. 4 depicts the ratio between rates of C₂ compounds (ethane and ethylene) and propylene formation generated during propane dehydrogenation at 600 °C as a function of the reaction time.

As seen from Fig. 4, the ratio of the rates of ethylene formation to propylene formation increases as a function of contact time and goes to zero when reaction time is extrapolated to zero. This observation is typical for consecutive reactions where propylene is an intermediate compound and source for formation of ethylene and methane by reaction (4). However, this type of dependence can be observed not only for a consecutive reaction, but also in the case where one reaction is thermodynamically limited and another one does not have thermodynamic limitations. This is the case where propane dehydrogenation to propylene is limited by equilibrium, but hydrocracking reaction does not have thermodynamic limitation. Thus, the obtained results presented in Fig. 4 are not enough to prove the presumption that ethylene is formed from propylene.

To confirm the correctness of this assumption, conversions of propylene and hydrogen and propane and hydrogen mixtures have been studied using Al-Cr catalyst at 600 °C with different contact time. The results summarized in Table 2 showed that hydrotreatment of propane do not produce a noticeable amount of light gas. The main reaction during transformation of propane with an excess of hydrogen was still dehydrogenation with production of propylene.

Very little amount of ethane and ethylene (Table 2) was produced during conversion of propane. The discernable amount of light compounds during hydro-treatment of propane was obtained only when propylene concentration was about 10%. In our opinion in this case the newly produced propylene started to produce light compounds.

Unlike the hydro-treatment of propane, hydrocracking of propylene at the same conditions resulted in five times higher yield of methane, ethane, and ethylene (Table 2). Simultaneously with light gas, a significant amount of propane obtained by propylene hydrogenation reaction was seen. This result supported initial assumption that hydrocracking of propylene is the main pathway for ethylene formation not the thermo-cracking of propane.

The obtained data is strong evidence that the majority of the light gas is formed not directly from propane, but from propylene which is intermediate after dehydrogenation of propane by consecutive reaction of hydrocracking.

Below is presented the pathway of the formation of light gases during propane dehydrogenation:

$$C_3H_8 \rightleftharpoons C_3H_6 + H_2 \tag{1}$$

$$C_3H_6 + H_2 \to C_2H_4 + CH_4$$
 (2)

Ethylene by parallel reaction simultaneously with hydroge

3)
$$C_2H_4 \xrightarrow{+H_2} C_2H_6$$

+ 2H₂ 2CH₄ (3)

Ethylene by parallel reaction simultaneously with hydrogenation to ethane is converted by the hydrocracking reaction to methane.

3.2. Reaction pathways of the light gas formation during isobutane dehydrogenation on Al-Cr catalyst

Isobutane dehydrogenation is accompanied by formation of five compounds with hydrocarbon number less than C_4 : methane, ethane, ethylene, propylene and propane. There are much more theoretical possibilities for formations of these compounds from isobutane than from propane.

3.2.1. Reactions of thermo-cracking during isobutane dehydrogenation

Thermo-cracking of isobutane also have more options than thermo-cracking of propane, which can happen by following reactions presented below:

$$i-C_4H_{10} \to C_3H_6 + CH_4$$
 (9)

$$i-C_4H_{10} \rightarrow C_2H_4 + C_2H_6$$
 (10)

$$i-C_4H_8 \to C_3H_4 + CH_4 \tag{11}$$

$$i-C_4H_8 \to 2C_2H_4 \tag{12}$$

 $CH_3 - CH - CH_3 \rightarrow CH_3 - C = CH_2 + H_2$

Unlike n-butane, the structures of isobutane and isobutylene prohibit cracking of these compounds to two C_2 molecules such as ethane and ethylene that eliminates the possibility of reaction (10), (12), and (17) but there is still possibility to produce C_2 molecules by reactions (14) and (15).

$$i-C_4H_{10} + H_2 \rightarrow C_3H_8 + CH_4$$
 (13)

 $i-C_4H_{10} + 2H_2 \rightarrow C_2H_6 + 2CH_4$ (14)

$$i-C_4H_{10}+H_2 \rightarrow C_2H_4 + 2CH_4$$
 (15)

$$i-C_4H_8 + H_2 \rightarrow C_3H_6 + CH_4 \tag{16}$$

$$i-C_4H_8 + H_2 \rightarrow C_2H_6 + C_2H_4$$
 (17)

Similar to propane, isobutane thermo-cracking has been studied in the quartz plug type reactor which was loaded with α -Al₂O₃ inert



Fig. 4. Relative rates of the ethylene and ethane formation to propylene generated during propane dehydrogenation at 600 °C and extrapolated to zero reaction time.

only, having a surface area of 0.5 m^2/g . Isobutane having a purity of 99.7% was passed through the reactor at different reaction times and at 600 $^\circ\text{C}.$

The results of these experiments are summarized in Fig. 1b. As a result of the isobutane thermo-decomposition only two products with an amount of carbon less than C_4 were observed in the outlet gas: methane and propylene. No C_2 compounds were seen in the products. Besides methane and propylene only isobutylene and coke were formed during thermo-decomposition of isobutane.

Similar to propane thermo-cracking, isobutane thermoconversion was inhibited by hydrogen significantly (Fig. 1b).

3.2.2. Reactions of light compounds formation on the Al-Cr catalyst during propane dehydrogenation

Reaction pathway of light compounds formation during isobutane dehydrogenation was studied by testing Al-Cr catalyst at different temperatures in the range 540–620 °C and different reaction times at dehydrogenation pressure 0.5 atm using the same approach that was applied for propane dehydrogenation.

The results of dehydrogenation of isobutane on Al-Cr catalyst at 600 °C presented in Fig. 5 demonstrated that the outlet gas contained the products of the side reactions and included methane, ethane, ethylene, propane and propylene. The character of the curves presenting molecular concentration of light gas compounds in the outlet gas as a function of the reaction time provides the first clue regarding the pathway of their formation. The curves of the propylene and propane concentrations as a function of the reaction time are typical for that obtained for consecutive reactions where propylene is the intermediate compound and propane is the final compound.

There are no doubts that propylene and propane are interconnected and can be converted into each other depending on equilibrium. The question was "What compound is formed first during isobutane dehydrogenation?" Propane theoretically can be formed from isobutane by reaction (13) following dehydrogenation to propylene. Propylene theoretically can be formed from isobutane by thermo-cracking reaction (10) and from isobutylene by hydrocracking reaction (16). If propylene is formed first, because the shift in equilibrium when propylene appears in gas phase without propane the hydrogenation reaction to propane should follow.

Fig. 6 presents the ratio between the rates of propane to propylene and propylene to propane as a function of the reaction time. As seen in Fig. 6, the relative amount of propylene to propane decreases with increasing of the reaction time and approaches infinity when reaction time is extrapolated to zero. This is an indication that propylene is not produced from propane. Contrary to that the ratio between the rates of the propane and propylene formation grows as function of reaction time and approach zero when

Table 2

Conversion of hydrogen-propane and hydrogen-propylene mixtures and concentration of the light compounds on Al-Cr catalyst at different reaction time.

Feed composition: hydrogen – 60 mol%, propane – 40 mol%					
Temperature (°C)	Contact time (s)	Concentration of products after propane hydro-treatment (mol%)			
		CH ₄	C_2H_6	C_2H_4	C_3H_6
580	0.23	0.02	0.01	0.02	3.76
	0.46	0.08	0.04	0.03	6.41
	0.92	0.22	0.11	0.06	9.99
	1.84	0.51	0.26	0.07	10.92
Feed composition: hydrogen	– 60 mol%, propylene – 40 mol%				
Temperature (°C)	Contact time (s)	Concentration of products after propylene hydro-treatment (mol%)			
		CH ₄	C ₂ H ₆	C_2H_4	C ₃ H ₈
	0.23	0.2	0.07	0.09	7.3
580	0.46	0.55	0.24	0.18	9.4
	0.92	0.11	0.54	0.45	11.3
	1.84	2.47	1.43	0.76	11.5



Fig. 5. Isobutylene and light compounds concentrations in the outlet gas generated during propane dehydrogenation on Al-Cr catalysts at 600 °C as a function of the reaction time.

reaction time is extrapolated to zero. This is a clear indication that propane formation is the consecutive reaction to the propylene formation [5] and that propane is formed by consuming propylene by reaction hydrogenation.

The next question was "What compound propylene is formed from?" It can be formed from isobutane by reaction (10) or from isobutylene from reaction (16) where isobutylene is an intermediate compound formed by dehydrogenation of isobutane. To answer this question relative selectivity of formation of propylene to isobutylene was studied. The rate of propylene production was calculated taking into account that propane produced was produced from propylene.

Fig. 7 depicts the ratio between of the rates of propylene and isobutylene formation at 570 °C at different reaction times extrapolated to a zero. This temperature is chosen because at this condition the contribution of the reaction of conversion of propylene to C_2 compounds is still very little, which makes it easier to interpret the results.

The character of the curves presented in Fig. 7 indicates that there is a high probability that propylene is produced by consecu-

tive reactions of isobutylene hydrocracking. However, this data is not enough to prove this point. This type of dependence between relative selectivity of propylene to isobutylene can be observed in the case whereas propylene is formed from isobutane by thermocracking (reaction (10)) and hydrocracking (reaction (13)), which can grow without thermodynamic restrictions as a function of reaction time and where isobutane dehydrogenation to isobutylene is restricted by equilibrium.

To have an additional argument to determine whether propylene is formed from isobutylene or isobutane hydrocracking of isobutane with 40 mol% of hydrogen and isobutylene with 40 mol% of hydrogen was studied at similar conditions and the results were compared to each other. The results of this study presented in Fig. 8 show that the yield of C_3 compounds is about 2.5 times higher when using isobutylene feedstock instead of isobutane feedstock.

The observation that isobutane conversion in the presence of hydrogen still leads to the production of C_3 products can be explained by the high rate of reaction of isobutane dehydrogenation to isobutylene even at a high partial pressure of hydrogen. Because this reaction is still very fast, following hydrocracking of



Fig. 6. Relative rates of the propylene and propane formation generated during isobutane dehydrogenation at 600 °C and extrapolated to zero reaction time.

+ U



Fig. 7. Relative rates of the propane and propylene formation to isobutylene generated during isobutane dehydrogenation at 570 °C and extrapolated to zero reaction time.

isobutylene leads to propylene production. The rate of the hydrocracking reaction with formation of methane and propylene is a function of partial pressure of isobutylene. During dehydrogenation of isobutane on Al-Cr catalyst the partial pressure of newly formed isobutylene in these experiments increased from 0 to 25 mol%, which further is converted to propylene. However, during isobutylene hydrocracking the isobutylene partial pressure was significantly higher, and that provided the higher yield of C₃ products.

Thus, the observation that isobutylene feedstock produces much more propylene and propane on Al-Cr catalyst can be an argument that isobutylene is a main source of these compounds formation. The further transformation of propane and propylene on Al-Cr catalyst was already discussed and determined before.

Below is presented the pathway of the formation of light gases during isobutane dehydrogenation:

$$C_4 H_{10} \rightleftharpoons C_4 H_8 + H_2 \tag{1}$$

$$C_4H_8 + H_2 \rightarrow C_3H_6 + CH_4$$
 (2)

$$C_{3}H_{6} \xrightarrow{+H_{2}} C_{3}H_{8}$$

$$C_{3}H_{6} \xrightarrow{+H_{2}} C_{2}H_{4} + CH_{4}$$

$$C_{2}H_{4} \xrightarrow{+H_{2}} C_{2}H_{6}$$

$$C_{2}H_{4} \xrightarrow{+2H_{2}} 2CH_{4}$$

$$(3)$$

Thus, unlike previously expressed common view on the light compounds formation pathway [1–3,7] stating that the main source of the light compounds formation during paraffin dehydrogenation is initial paraffin, the current study showed that light gas is mostly formed from targeted olefin such as propylene or isobutylene by consecutive reaction of hydrocracking and hydrogenation.

The suggested reaction pathway of the light gas formation on Al-Cr catalyst is in a very good agreement with the carbonium ionic theory of the reaction cracking and hydrocracking, which postulates that the first step of the reaction is a formation of a carbonium cation. As follows from review of Pines [8], weak acids can catalyze the conversion of olefins in which the double bond is attacked resulting in formation of a carbonium cation. The strong super acid besides double bond can attack stable alkanes [8]. However, these types of acid sites do not exist on the surface of Al-Cr dehydrogenation catalyst that is designed to suppress strong acid sites by alkali metal.

The information regarding light compounds formation pathways is extremely useful for understanding of the existing paraffin dehydrogenation technology and optimization of the process. For instance, the fixed bed dehydrogenation process on Al-Cr catalyst has a puzzling phenomenon that did not have clear explanation before such as hot spot formation on the bottom of the catalyst bed. Knowing correct reaction pathway of light gas formation helps to understand it much better. An analysis of the thermo-chemistry of the light compounds formation reactions presented in this article indicated that the majority of them are exothermal (Table 3). The reaction of ethylene hydrocracking to methane is very exothermic (Table 3). No doubts



Fig. 8. Concentration of the C₃ products (propylene and propane) generated during conversion of the isobutylene-hydrogen and isobutane-hydrogen mixtures on Al-Cr catalysts at 600 °C at different reaction time.

Table 3

Heat of the reactions dehydrogenation and cracking occur during isobutane and propane dehydrogenation.

Reaction	Name and type of reaction	Heat of reaction at 600 $^\circ\text{C}\left(J/mol\right)$
Main reaction		
$i\text{-}C_4H_{10}\rightarrow i\text{-}C_4H_8\text{+}H_2$	Dehydrogenation-endothermic	121,800
$C_3H_8 \rightarrow C_3H_6 + H_2$	Dehydrogenation-endothermic	128,290
Reaction of the light gas formation		
$i-C_4H_{10} \rightarrow C_3H_6$ + CH_4	Thermo-cracking-endothermic	78,470
$i\text{-}C_4H_8 + H_2 \rightarrow C_3H_6 + CH_4$	Hydrocracking-exothermic	-43,330
$C_3H_6 + H_2 \rightarrow C_3H_8$	Hydrogenation-exothermic	-128,290
$C_3H_6 + H_2 \rightarrow C_2H_4 + CH_4$	Hydrocracking-exothermic	-47,200
$C_2H_4 + H_2 \rightarrow C_2H_6$	Hydrogenation-exothermic	-141,900
$C_2H_4 + 2H_2 \rightarrow 2CH_4$	Hydrocracking-exothermic	-211,000

that these reactions contribute to the above described phenomenon.

and methane. The last reaction is hydrocracking of ethylene to methane.

4. Conclusions

From above presented results the following conclusions have been made:

- The main sources for production of light compounds during dehydrogenation of propane and isobutane are propylene and isobutylene. The contribution of the direct conversion of paraffin to light compounds is much smaller.
- The main pathway of the light compounds formation during propane and isobutane dehydrogenation includes hydrocracking of propylene and isobutylene to the one carbon shorter chain olefin and methane. The newly formed one carbon atom shorter olefin further by parallel reactions is hydrogenated to paraffin, or by hydrocracking is converted to two carbon shorter olefin

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