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Conversion of Lower Hydrocarbons in the Presence of Carbon Dioxide: The Theoretic Analysis and Catalytic Tests over Active Carbon Supported Vanadium Oxide

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Abstract The results of thermodynamic analysis of methane oxidative coupling and dehydrogenation of C_2–C_4 hydrocarbons in the presence of carbon dioxide were compared to the corresponding results in an inert gas atmosphere. Moreover, conversion of alkanes in some undesirable side reactions, such as decomposition of alkanes to the synthesis gas or to carbon oxide and water, as well as the gasification of coke by carbon dioxide in the Boudouard reaction, were investigated. Finally, the results of the theoretical calculations were compared with the experimental data obtained over VO_x/C_{act} catalyst. The results are discussed in relation to the acid–base properties of the catalyst surface and the atomic charge on the hydrogen most susceptible to abstraction (i.e., the weakest C–H bond in hydrocarbons). Thus, the changes of the catalytic performance in the presence and absence of carbon dioxide are explained.

Keywords Dehydrogenation of C_2–C_4 · Methane coupling · VO_x/C_{act} catalyst · Carbon dioxide

1 Introduction

It is well known that lower unsaturated hydrocarbons are valuable sources for modern chemical industry. At present, they are mainly produced as a by-product of steam cracking or fluidized catalytic cracking of naphtha, but this source is not sufficient for growing demand. High availability and relatively low price of alkanes make them suitable source for production of olefins by selective dehydrogenation processes. Also, the possibility of methane coupling to higher hydrocarbons (especially C_2), takes a lot of interest [1–3]. As the processes in an inert gas atmosphere bring a lot of disadvantages (i.e. thermodynamic limitations, operation at high temperatures and fast deactivation of catalysts), an attractive alternative is introduction of oxidizing agent into the reaction zone. Oxidative dehydrogenation and coupling give several benefits: the reactions are exothermic, what allows working at lower temperatures, the presence of oxygen prevents the catalyst reduction and deactivation by coke, and mainly, the reactions become practically irreversible. Unfortunately, there are also a lot of difficulties, such as low selectivity to olefins caused by hard to control deep oxidation reactions, the necessity of the heat removal, and finally, the flammability of the reaction mixture [2, 3]. For these reasons, the processes where the molecular oxygen is replaced by a less reactive oxidizing agent, such as CO_2 or N_2O, seem to be very promising and attract a lot of interest [3–6].

Generalized reactions of methane coupling to higher hydrocarbons in the presence of carbon dioxide can be expressed by Eqs. 1 and 2, while the dehydrogenation of alkanes to olefins proceeds in accordance with Eq. 3

$$nCH_4 + (n-1)CO_2 = C_nH_{2n+2} + (n-1)CO + (n-1)H_2O \tag{1}$$

$$nCH_4 + nCO_2 = C_nH_{2n} + nCO + nH_2O \tag{2}$$

$$C_nH_{2n+2} + CO_2 = C_nH_{2n} + CO + H_2O \tag{3}$$

Beside the main reactions, the side-reactions of the hydrocarbons decomposition to the synthesis gas (Eq. 4) and carbon dioxide and water (Eq. 5) cannot be excluded. Moreover, carbon dioxide can react with hydrogen and with carbon deposit at the subsequent reactions (6) and (7).

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$$C_nH_{2n+2} + nCO_2 = 2nCO + (n+1)H_2 \tag{4}$$

$$C_nH_{2n+2} + (2n+1)CO_2 = (3n+1)CO + (n+1)H_2O \tag{5}$$

$$H_2 + CO_2 = CO + H_2O \tag{6}$$

$$C_s + CO_2 \rightarrow 2CO \tag{7}$$

It is also believed, that carbon dioxide can reoxidize the reduced catalyst surface in agreement with Mars and van Krevelen mechanism [7].

Beside the presence of carbon dioxide, both length of the carbon chain and its branching are important factors deciding about the hydrocarbon conversion. This effect can be explained on the basis of dissociation energy of the weakest C–H bond and stability of the carbocations or radicals formed. It is well known, that high stability of light alkanes is the reason why their activation is more difficult in comparison with other hydrocarbons. The tetrahedral arrangement of C–H bonds protects the carbon atoms, what makes the hydrogens more exposed and susceptible to abstraction. The stronger C–H bond is the stronger must be the activation (Table 1). Consequently, the reactivity of lower straight-chained hydrocarbons increases with the number of carbon atoms [8, 9]. Additionally, order of the carbon atom considered and its nearest surroundings have great effect on the stability of carbocations and radicals. Hence, the activity trend of hydrogens in the abstraction process decreases in the following sequence: benzyl ≈ allyl > *t*-butyl > isopropyl > ethyl > methyl [10]. Carbocations can be formed by a heterolytic dissociation of C–H bonds at the transition metal centers on the catalyst surface, while the radicals are primarily formed by homolytic reaction at high-temperatures over poorly reducible catalysts [8–10].

2 Experimental

VO_x/C_{act} catalyst was prepared by impregnation of active carbon (Merck) particles with 0.2–0.3 mm diameter in 0.1 M citric acid solution of NH_4VO_3. The amount of ammonium metavanadate was adjusted to yield 20 wt% of V_2O_5 content in the final bulk catalyst. Prior to the reaction, fresh samples of the catalyst were first activated at 923 K in carbon dioxide flow (30 $cm^3\ min^{-1}$), and then the catalyst bed was cooled down to the reaction temperature under helium atmosphere.

The catalytic dehydrogenation of C_2–C_4 hydrocarbons and coupling of methane in the presence and absence of carbon dioxide were carried out under atmospheric pressure in a flow-type quartz micro-reactor packed with 400 mg of the catalyst. The reaction temperature was 873 K, and the reactant was introduced as 1:5 alkane/CO_2 (or He) mixture at the total flow rate of 35 $cm^3\ min^{-1}$. The products were analyzed on-line using two gas chromatographs. One of them, used for the hydrocarbons analysis, was equipped with Chromosorb 104 and Porapak Q columns and a flame ionization detector (FID). The other gaseous products (i.e. carbon oxides, hydrogen) were analyzed by a chromatograph equipped with a thermal conductivity detector (TCD) and Carboxan 1000 column.

The specific surface area of the catalyst (BET method) was obtained from nitrogen adsorption isotherm measured with Quantachrome Autosorb-1 analyzer. The total numbers of acidic and basic sites of the catalyst were measured by temperature-programmed desorption of gaseous ammonia (TPD-NH_3) and carbon dioxide (TPD-CO_2) respectively. The sample of 200 mg was activated with CO_2, outgassed in helium stream and cooled to the room temperature. After saturation with ammonia or carbon dioxide for 0.5 h (30 $cm^3\ min^{-1}$), the unadsorbed gases were flushed out of the reactor by flowing helium (60 $cm^3\ min^{-1}$) until the TCD signal returned to the initial value. Finally, the temperature was increased to 873 K at the heating rate of 10 K min^{-1}. Desorbed species were analyzed on-line. Independently, the decomposition of 2-propanol was used as a test reaction to determine and verify acid-basic properties of the catalyst in the presence and absence of carbon dioxide. To carry out the decomposition, 2-propanol vapor was introduced into the reactor by bubbling helium (or pure carbon dioxide) gas through the alcohol container at 288 K. The reaction temperature

Table 1 The weakest C–H bond dissociation energy of some light hydrocarbons [8, 10]

Hydrocarbon	The weakest C–H bond (the carbon order)	C–H bond dissociation energy (kJ/mol)
Methane	CH_3–**H** (1°)	438.4
Ethane	CH_3CH_2–**H** (1°)	419.5
Propane	CH_3HC–**H**CH_3 (2°)	401.3
n-Butane	CH_3CH_2HC–**H**CH_3 (2°)	390.8
Isobutane	$(CH_3)_3C$–**H** (3°)	388.2
Ethylene	$CH_2 = CH$–**H**	444.0
Propene	$CH_2 = CH\text{-}CH_2$–**H**	360.7

was 523 K. The products were analyzed after 15 min with an on-line FID chromatograph with 20% FFAP Chromosorb W column. Except for the propene, acetone, isopropyl ether and unreacted isopropanol, small amount of some undefined compound was detected, but in the calculation of selectivity it did not give a considerable effect.

Theoretical analysis included the thermodynamic calculations of dehydrogenation and coupling reactions of lower hydrocarbons (C_1–C_4) in the presence and absence of carbon dioxide. The possibility of some side reactions with CO_2 (Eqs. 4–7) was also considered. Equilibrium conversions of hydrocarbons were investigated under atmospheric pressure at the temperatures from 373 to 1273 K. The molar ratio of C_nH_{2n+2}:CO_2 (or He) was predetermined as 1:5. The thermodynamic data of reagents (i.e. $H°_{298}$, $S°_{298}$ and C_p) were taken from the academic handbook [11].

More detailed description of the catalyst preparation and the theoretical calculation procedure is reported elsewhere [12, 13].

3 Results and Discussion

3.1 Thermodynamic analysis

Table 2 shows the main reactions of methane coupling (A1, B2) and dehydrogenation of light hydrocarbons (C1–I1) in the presence of carbon dioxide. Calculated for them standard enthalpies are compiled with the values obtained for the reactions in the inert gas atmosphere (A2–I2).

On the basis of thermodynamic analysis of one-step dehydrogenation of C_2–C_4 hydrocarbons and methane coupling in the presence of carbon dioxide, equilibrium conversions of hydrocarbons were estimated at the temperatures from 373 to 1,273 K. The same calculation was done for the processes in the inert gas atmosphere. The results are compiled in Fig. 1.

All the reactions considered are allowed thermodynamically. Nevertheless, the equilibrium conversions calculated for the processes in the inert gas atmosphere (A2–I2) are much lower than data obtained in the presence of carbon dioxide (A1–I1). From the literature [3, 4, 14] it is known, that the oxidative dehydrogenation of hydrocarbons can also proceed via a two-step pathway, where the dehydrogenation (C2–I2) is accompanied by subsequent reverse water gas shift reaction (6). In such case, carbon dioxide reacts with hydrogen to form water and carbon monoxide, which shifts the equilibrium to produce olefins. The thermodynamic calculation of the two-step reaction model shows that the equilibrium conversion of hydrocarbon (for example: propane [14], isobutane [12] or ethylbenzene [3]) can be even several percent higher than that for the one-step dehydrogenation process.

The other advantage of the processes carried out in the presence of carbon dioxide is the possibility of prolonging the duration of catalyst active work, as the carbonaceous deposit on the catalyst surface can be partially removed by the Boudouard reaction (7). The equilibrium conversion of coke (C_s) depends strongly on both the temperature and the

Table 2 Standard enthalpies calculated for the reactions of C_1–C_4 hydrocarbons conversions in the presence and absence of CO_2

Lp.	Reactions in the presence of CO_2	$\Delta H°_{298}$ (kJ/mol)
A1	$2CH_4 + CO_2 = C_2H_6 + CO + H_2O$	106.4
B1	$2CH_4 + 2CO_2 = C_4H_4 + 2CO + 2H_2O$	284.8
C1	$C_2H_6 + CO_2 = C_2H_4 + CO + H_2O$	178.4
D1	$C_3H_8 + CO_2 = C_3H_6 + CO + H_2O$	165.7
E1	$nC_4H_{10} + CO_2 = CH_3CH_2CHCH_2 + CO + H_2O$	167.3
F1	$nC_4H_{10} + CO_2 =$ *cis* $CH_3CHCHCH_3 + CO + H_2O$	160.4
G1	$nC_4H_{10} + CO_2 =$ *trans* $CH_3CHCHCH_3 + CO + H_2O$	156.1
H1	$nC_4H_{10} + 2CO_2 = CH_2CHCHCH_2 + 2CO + 2H_2O$	319.5
I1	$iC_4H_{10} + CO_2 = iC_4H_8 + CO + H_2O$	159.0
Lp.	Reactions in the inert gas atmosphere	$\Delta H°_{298}$ (kJ/mol)
A2	$2CH_4 = C_2H_6 + H_2$	65.1
B2	$2CH_4 = C_4H_4 + 2H_2$	202.1
C2	$C_2H_6 = C_2H_4 + H_2$	137.0
D2	$C_3H_8 = C_3H_6 + H_2$	124.3
E2	$nC_4H_{10} = CH_3CH_2CHCH_2 + H_2$	126.0
F2	$nC_4H_{10} =$ *cis* $CH_3CHCHCH_3 + H_2$	119.1
G2	$nC_4H_{10} =$ *trans* $CH_3CHCHCH_3 + H_2$	114.7
H2	$nC_4H_{10} = CH_2CHCHCH_2 + 2H_2$	236.8
I2	$iC_4H_{10} = iC_4H_8 + H_2$	117.7

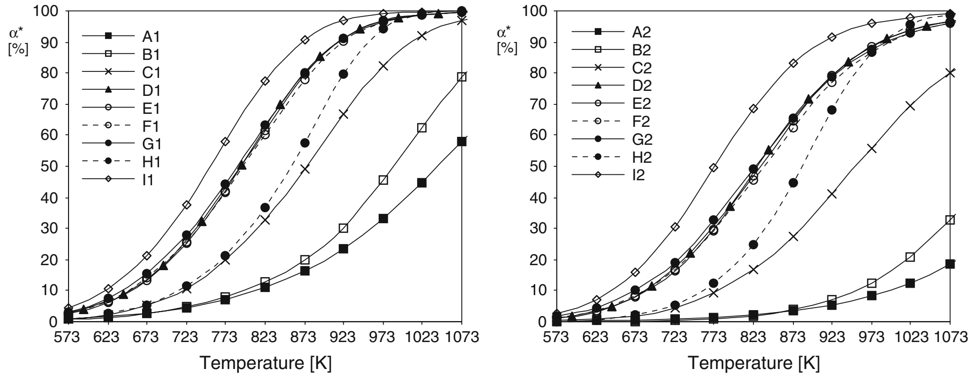

Fig. 1 The equilibrium hydrocarbon conversions of C_1–C_4 hydrocarbons in the presence (A1–I1) and absence (A2–I2) of carbon dioxide as a function of the reaction temperature. Molar ratio $C_nH_{2n+2}/CO_2(He) = 1/5$

molar ratio of C_s/CO_2 (Fig. 2). Nevertheless, the conversion reaches more the 50% at moderately high temperatures (873 K) and high partial pressures of carbon dioxide. Comparison of these data with the results calculated for the C_1–C_4 hydrocarbons suggests that carbonaceous deposit can be efficiently removed from the catalyst surface during the methane coupling and ethane dehydrogenation processes. This assumption is based on the fact that the equilibrium conversions of the both hydrocarbons are relatively low, thus the degree of coking also cannot be too high.

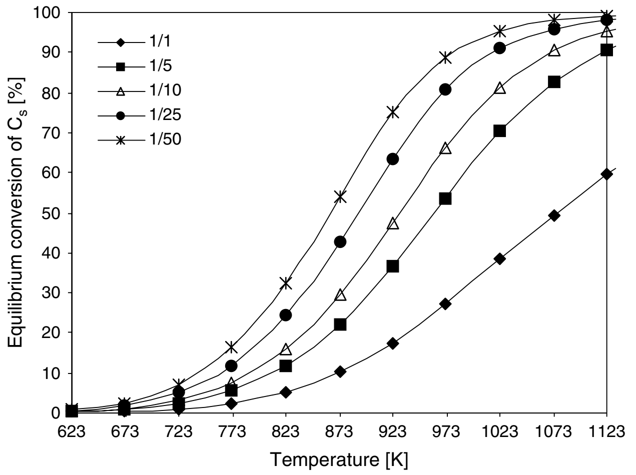

Fig. 2 The equilibrium conversion of coke in the Boudouard reaction as function of the temperature. The molar ratio of C_s/CO_2 varies from 1/1 to 1/50

When the processes in the carbon dioxide atmosphere are considered, the reactions of the hydrocarbons decomposition to synthesis gas (4) or oxidation to carbon oxide and water (5) cannot be omitted. The thermodynamic analysis shows that the equilibrium conversions of hydrocarbons in these exothermic reactions (Table 3) are much higher than those in the corresponding coupling and dehydrogenation reactions (Fig. 1). However, the catalytic experiments show that under the process conditions (i.e. short contact time of reagents with the catalyst bed) these decomposition reactions have greater weight only in the case of C_1–C_2 hydrocarbons [3, 4].

3.2 Catalytic Experiments

The catalytic tests performed over active carbon supported vanadium oxide showed that the experimental results correspond to the theoretical calculations. Conversion of particular hydrocarbons clearly increases with the carbon chain length and the degree of branching (Fig. 3). However,

Table 3 The standard enthalpies calculated for the decomposition reactions of C_1–C_4 hydrocarbons and their equilibrium conversions at 723 and 775 K

Reactions of decomposition C_nH_{2n+2} in the presence of CO_2	ΔH^o_{298} (kJ/mol)	α^*_{723} (%)	α^*_{773} (%)
$CH_4 + CO_2 = 2CO + 2H_2$	247.6	15.9	30.2
$CH_4 + 3CO_2 = 4CO + 2H_2O$	330.4	12.6	21.9
$C_2H_6 + 2CO_2 = 4CO + 3H_2$	430.4	43.7	77.5
$C_2H_6 + 5CO_2 = 7CO + 3H_2O$	554.4	20.4	34.1
$C_3H_8 + 3CO_2 = 6CO + 4H_2$	603.1	99.5	100
$C_3H_8 + 7CO_2 = 10CO + 4H_2O$	768.5	32.2	47.1
$nC_4H_{10} + 4CO_2 = 8CO + 5H_2$	816.0	75.5	100
$nC_4H_{10} + 9CO_2 = 13CO + 5H_2O$	1023.0	18.5	29.7
$iC_4H_{10} + 4CO_2 = 8CO + 5H_2$	822.9	91.9	100
$iC_4H_{10} + 9CO_2 = 13CO + 5H_2O$	1030.0	19.1	30.5

The molar ratio of $C_nH_{2n+2}:CO_2 = 1:5$

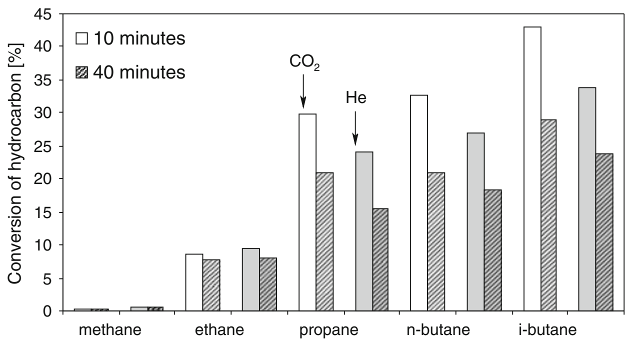

Fig. 3 The percentage conversion of light hydrocarbons over VO_x/C_{act} in the presence (white bars) and absence (grey bars) of carbon dioxide. The data were taken after 10 and 40 min of the reaction

the catalyst and its physicochemical properties have also the grate influence on the reaction course.

In the catalytic processes the initial activation of the C–H bond requires the existence of chemical affinity between the hydrocarbon and the catalyst surface. As the majority of alkanes ($C_n \geq 3$) have a negative charge on the most reactive hydrogen [8, 10], their activation is favored on the electrophilic surfaces like acidic oxides. Nevertheless, too strong interaction with the catalyst surface may cause further degradation (coking or isomerization) of the dehydrogenation products. Thus, higher hydrocarbons require basic sites to promote the selectivity to olefins [8, 9, 15]. This effect can be explained on the basis of electron-donating nature of olefins, which have more basic character than the corresponding paraffins. For this reason, the olefins interact stronger with acidic catalysts than with basic ones. On the other hand, methane and ethane have a positive charge on their hydrogens. Consequently, both these molecules will be more effectively activated on the basic catalysts, while the selectivity will be improved by the acidic surfaces [8, 10, 15].

All the considered reactions were performed over vanadium oxide (20 wt% of V_2O_5) supported on active carbon. High specific surface area of catalyst (705.3 m^2/g_{cat}) contributed to high dispersion of the active element and favored its high catalytic activity. Nevertheless, much more important for further discussion are the acid–base properties of the catalyst surface. The graphical illustration of the TPD-NH_3 and TPD-CO_2 experiments can be found elsewhere [13]. The total desorption of ammonia (the acidity measurement) was 1.39 mmol NH_3/g_{cat} while the amount of carbon dioxide, which desorbed from the basic sites, was four time smaller (0.31 mmol CO_2/g_{cat}). The results of 2-propanol decomposition reaction confirmed the dominating acidic character of VO_x/C_{act} surface, as the selectivity to propene was above 87% in the both reaction atmospheres (Table 4).

The overall acidity was calculated as a proportion between the selectivities to dehydration and dehydrogenation products. The role of particular centers in 2-propanol decomposition reaction is still under discussion, however it is conventionally accepted that acidic sites are responsible for the dehydration activity giving propene and isopropyl ether, while the basic sites promote dehydrogenation of isopropanol to acetone [16–19]. It is also established that formation of propene requires strong Brønsted acid sites or the co-existence of Brønsted and Lewis sites of medium strength, such as those in amphoteric oxides [16, 17]. Moreover, isopropyl ether formation is favored on the Lewis acid sites [16], while the dehydrogenation to acetone, which mainly occurs on basic centers, can also be enhanced by available surface acid/base redox sites [18, 19].

When the carbon dioxide was used as a carrier gas for 2-propanol vapor, both the alcohol conversion and the overall acidity slightly increased (Table 4). This effect can be related to the nature of the catalyst support. From the literature [20, 21] it is known that the majority of oxygen-functional groups are formed on carbon surface during the temperature treatment of the material in oxidizing atmosphere, here in the carbon dioxide flow. Carbons with high oxygen content show acidic surface properties and cation exchange behavior. On the other hand, when the carbon is heated under an inert gas, the existing surface oxygen-groups decompose and the overall basicity increases [20, 21].

Considering above statements, the active carbon supported vanadium oxide catalysts should improve the activation of larger hydrocarbons, which have a negative charge on the weakest bonded hydrogen (butanes). Nevertheless, as the presence of carbon dioxide in the reaction atmosphere increases the overall acidity of the catalyst surface, the selectivity to butenes should decrease. On the other hand, activation of C_1–C_2 hydrocarbons requires basic sites, thus the presence of carbon dioxide is supposed to both decrease the alkane conversion and improve the selectivity to olefins. The experimental results presented in the Table 5 confirm this hypothesis.

Table 4 Decomposition of 2-propanol on VO_x/C_{act} catalyst in the presence and absence of carbon dioxide at 523 K

Carrier gas for alcohol vapor	2-Propanol conversion (%)	Selectivity to (%)			Overall acidity $\frac{S_{C_3^=}+S_{DIPE}}{S_{C_{3}one}}$
		$C_3^=$	DIPE	C_3one	
He	31.5	87.41	0	12.59	6.9
CO_2	35.6	87.94	0.02	12.04	7.3

Table 5 The results of methane coupling and C_2–C_4 hydrocarbons dehydrogenation in the presence and absence of carbon dioxide over VO_x/C_{act} catalyst

C_nH_{2n+2}	Reaction in CO_2	(%)	Reaction in He	(%)
Methane	Conversion of CH_4	0.4	Conversion of CH_4	0.6
	Yield of CO_2	1.2		
	Selectivity of		Selectivity of	
	Ethane	91.6	Ethane	91.7
	Ethylene	8.4	Ethylene	8.3
	$C_{n > 2}$	<0.1	$C_{n > 2}$	<0.1
Ethane	Conversion of C_2H_6	8.7	Conversion of C_2H_6	9.4
	Yield of CO_2	8.2		
	Selectivity of		Selectivity of	
	Methane	17.0	Methane	19.0
	Ethylene	82.4	Ethylene	80.0
	$C_{n > 2}$	0.7	$C_{n > 2}$	1.0
Propane	Conversion of C_3H_8	29.7	Conversion of C_3H_8	24.1
	Yield of CO_2	13.2		
	Selectivity of		Selectivity of	
	Methane	5.0	Methane	5.8
	Ethane	2.0	Ethane	2.8
	Ethylene	4.4	Ethylene	4.5
	Propene	88.7	Propene	87.0
n-Butane	Conversion of n-C_4H_{10}	32.8	Conversion of n-C_4H_{10}	26.8
	Yield of CO_2	15.6		
	Selectivity of		Selectivity of	
	Methane	4.1	Methane	4.8
	C_2	7.3	C_2	8.0
	Propane	1.4	Propane	1.3
	Propene	8.4	Propene	8.2
	n-Butene-1	20.0	n-Butene-1	22.5
	n-Butenes-2	35.0	n-Butenes-2	38.9
	Butadiene	23.8	Butadiene	16.2
Isobutane	Conversion of i-C_4H_{10}	43.0	Conversion of i-C_4H_{10}	33.7
	Yield of CO_2	14.8		
	Selectivity of		Selectivity of	
	Methane	4.9	Methane	4.7
	C_2	1.1	C_2	0.7
	Propane	0.9	Propane	1.2
	Propene	7.4	Propene	5.8
	Isobutene	85.2	Isobutene	87.3
	n-Butenes	0.5	n-Butenes	0.4

Analysis of products after 10 minutes of the process at 873 K

The highest conversion over active carbon supported catalysts was noted for isobutane, whose dissociation energy of the weakest C–H bond was the lowest (Table 1). Moreover, the negative charge (−0.088 [10]) on the most reactive hydrogen caused stronger interaction of the molecule with the acidic catalyst surface (especially in the presence of carbon dioxide) and improved the selectivity of isomerization and degradation reactions.

During the dehydrogenation of n-butane and propane the total selectivity to butenes and propene respectively was almost equal in the both reaction atmospheres. This effect can be related to a slightly higher charge on the reactive hydrogens, equal to −0.051 for both molecules [10]. Additionally, the difficulties in desorption of n-butenes from the acidic surface caused their further dehydrogenation. Consequently, the selectivity to butadiene in the presence of carbon dioxide was higher than in the inert gas atmosphere.

Finally, the positive charge on the hydrogens in the methane and ethane (+0.087 and +0.002 respectively [10]) was the reason why the conversion of both hydrocarbons was higher under helium flow, as the overall basicity of the catalyst surface was a little higher in comparison to the reaction in carbon dioxide. Moreover, high carbon oxide yields in the methane coupling and ethane dehydrogenation proves considerable contribution of the reactions (4) and (5) to the total conversion of both hydrocarbons.

4 Conclusions

The presented results of thermodynamic calculations for methane coupling and dehydrogenation of C_2–C_4 hydrocarbons show that the equilibrium conversion of hydrocarbon can be related both to the dissociation energy of the weakest C–H bond, and to the stability of formed particles (carbocations and/or radicals). The activity trend of light hydrocarbons conversion clearly increases with the carbon chain length and the degree of branching. Although, the thermodynamic analysis show that the presence of carbon dioxide enhances the equilibrium conversion of all considered hydrocarbons, the experimental results over active carbon supported vanadium oxide indicate that physicochemical properties of the catalyst surface have a great influence on its specific activity. The knowledge of acid–base character of both the reactants (especially the properties of hydrocarbon) and the catalyst is crucial for precise description of the reaction course. Therefore, increasing VO_x/C_{act} surface acidity in the presence of carbon dioxide contributes to decrease of both methane and ethane conversion, as these hydrocarbons requires basic sites for activation. On the other hand, higher hydrocarbons (i.e. propane, n-butane and isobutane) are activated on the acid sites, but too strong interaction with the catalyst surface can promote some undesirable reactions, such as formation of coke and isomerization.

As the processes under the carbon dioxide flow are carried out at high temperatures, the non-oxidative mechanism of coupling and dehydrogenation can not be definitely excluded. Similarly, the other reactions of carbon dioxide (i.e. the reverse water gas shift reaction, gasification of coke, decomposition of hydrocarbons to synthesis gas and oxidation to carbon monoxide and water) can also proceed, but their contribution to the overall process is limited.

References

1. General aspects. http://media.walley.com/product.data/excerpt/23/04714178/0471417823.pdf
2. Bhasin MM, McCain JH, Vora BV, Imai T, Pujadó PR (2001) Appl Catal A Gen 221:397
3. Wang S, Zhu ZH (2004) Energy Fuels 18:1126
4. Krylov OV, Mamedov AX, Mirzabekova SR (1995) Catal Today 24:371
5. Wang Y, Otsuka K (1997) J Catal 171:106
6. Michorczyk P, Ogonowski J (2002) Nafta-Gaz 6–7:347
7. Mars P, van Krevelen DW (1954) Chem Eng Sci Spec Suppl 3:41
8. Banares MA (1999) Catal Today 51:319
9. Mamedov EA, Cortes Corberan V (1995) Appl Catal A Gen 127:1
10. Busca G, Finocchio E, Ramis G, Ricchiardi G (1996) Catal Today 32:133
11. Handzlik J, Ogonowski J (1995) Ćwiczenia tablicowe z technologii organicznej. skrypt PK, Kraków
12. Ogonowski J, Sikora E, Skrzyńska E (2004) Czasopismo Techniczne 1-Ch:121
13. Ogonowski J, Skrzyńska E (2005) React Kinet Catal Lett 86:195
14. Michorczyk P, Ogonowski J (2003) React Kinet Catal Lett 78:41
15. Blasco T, Lopez Nieto JM (1997) Appl Catal A Gen 157:117
16. Ortiz-Islas E, López T, Navarre J, Bokhimi X, Gómez R (2005) J Mol Catal A Gen 228:345
17. Diez VK, Apesteguia CR, Cosimo JI (2000) Catal Today 63:53
18. Chen X, Shen Y-F, Suib SL, O'Young CL (2001) J Catal 197:292
19. Hasan MA, Zaki MI, Pasupulety L (2002) J Mol Catal A Gen 178:125
20. Fanning PE, Vannice MA (1993) Carbon 31:721
21. Boehm HP (1994) Carbon 32:759