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Deactivation of $VMgO_x$ Catalysts by Coke in the Process of Isobutane Dehydrogenation with Carbon Dioxide

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Abstract The process of isobutane dehydrogenation in the presence or absence of carbon dioxide was carried out over $VMgO_x$ catalysts with different vanadium loading. The performed tests show that both the reaction atmosphere and physicochemical properties of the catalysts (related to vanadium content) have a great influence on the activity decrease and the carbonaceous deposit formation. Despite small ability of carbon dioxide to remove coke in the Boudouard reaction, the amounts of carbonaceous species deposited on the catalysts after the isobutane dehydrogenation under CO_2 atmosphere were even twice greater in comparison to those deposited in helium stream. Moreover, the rate of coke deposition during the dehydrogenation in the inert gas flow was only slightly dependent on the reaction time, in contrast to the process in carbon dioxide atmosphere. The results show that the coke formation on $VMgO_x$ is enhanced predominantly by surface acidity of the catalysts, which grows with the vanadium content and the presence of CO_2 in the feed.

Keywords Isobutane · Dehydrogenation · Carbon dioxide · $VMgO_x$ catalysts deactivation

1 Introduction

The catalysts deactivation is one of the most serious problems in modern chemical technology. Depending on the process, the catalyst life cycle can vary from a few seconds or minutes, as in the fluid catalytic cracking (FCC) and the dehydrogenation reactions, respectively, to several months or even years, as in the case of ammonia synthesis [1]. The nature of catalyst deactivation is complex, however there are six main causes of the activity loss in the catalytic processes: (a) fouling by coke, (b) poisoning, (c) leaching of the active elements by the reaction mixture, (d) chemical corrosion (vapor–solid and/or solid–solid reactions), (e) thermal degradation (sintering and/or evaporation), and (f) mechanical damage (attrition and/or crushing) [1–3].

The coke deposition on the catalyst surface is one of the main reasons of the activity loss in the case of dehydrogenation reactions. It is well known, that alkenes, aromatics and cyclic compounds are more reactive than saturated hydrocarbons, thus their interaction with acidic centers on the catalyst surface may cause undesirable side reactions, such as oligomerization, aromatization or alkylation to heavier compounds, which are most important coke precursors [3–5].

In most of the papers on the catalytic reactions of hydrocarbons with carbon dioxide an observation prevails, that introduction of CO_2 into the feed can decrease significantly (or even suppress) the coke deposition in comparison with the reaction under an inert gas atmosphere [6–16]. It is unquestionable that carbon dioxide is adsorbed on basic centers and after activation on the catalyst surface it can act as a mild oxidant capable to remove the carbonaceous deposit in the Boudouard reaction [17]. There are only two groups of the scientists working with chromium [18, 19] and vanadium [20] oxides, who found excessive amount of coke formed on the catalyst surface after the dehydrogenation reaction in the presence of carbon dioxide. The proposed explanation of this effect was the enhanced production of unsaturated compounds, which

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exhibit higher capacity to coke formation than the hydrocarbons in feed [18, 19].

The dehydrogenation of C_3–C_4 hydrocarbons under carbon dioxide flow is also investigated in our research group. Especially, the activity of chromium, vanadium and gallium oxide supported catalysts is intensively studied [21–27]. In the previous paper [21] we reported the results of dehydrogenation of isobutane with carbon dioxide over a series of $VMgO_x$ catalysts prepared by citrate method. Further studies showed a lot of differences in the catalysts performance, depending on the vanadium content and the reaction atmosphere, but not correlating in a simple way with the isobutene yield. This paper reports the latter results, proves the possibility of the Boudouard reaction over vanadium–magnesium oxide catalysts and presents our attempt to explain the reasons of faster deactivation of the catalysts under carbon dioxide atmosphere.

2 Experimental

2.1 Catalyst Preparation

The series of $VMgO_x$ catalysts with vanadium pentoxide content from 2.5 to 82 wt% was prepared by citrate method. A transparent aqueous solution of NH_4VO_3, $Mg(NO_3)_2$ and citric acid with a suitable amount of metal cations and COO^- anions (equimolar ratio of Me^{n+}/COO^-), was first evaporated at 353 K while stirring, and then dried at 373 K for next 12 h. The solid precursors were calcined in static air at 923 K for 6 h, pressed to thin discs and crushed to form the final bulk catalyst samples ($d = 0.2$–0.3 mm). All reagents were purchased from POCh in Poland.

2.2 Catalyst Characterization

Specific surface area of the $VMgO_x$ catalysts (BET method) was measured with Quantachrome Autosorb-1 analyzer, using nitrogen at 77 K. The nature of the catalysts surface was tested by temperature-programmed desorption of ammonia and carbon dioxide. Prior the analysis the catalyst samples of 200 mg were outgassed in helium flow for 0.5 h at 900 K. Then the catalysts were cooled down to room temperature and saturated with dry NH_3 or CO_2 for 0.5 h (30 cm^3 min^{-1}). The unadsorbed gases were flushed out by flowing He (60 cm^3 min^{-1}), and finally, the temperature was increased to 900 K at the constant heating rate of 10 deg min^{-1}. Desorbed species were analyzed on-line using gas chromatograph equipped with a thermal conductivity detector. The TCD peak areas were calibrated by injections of dry, gaseous ammonia, and carbon dioxide, respectively.

The decomposition of 2-propanol was used as a test reaction to determine acid–basic properties of the catalyst in the presence and absence of carbon dioxide. $VMgO_x$ catalysts (200 mg) were pretreated at 873 K for 0.5 h in He flow. To carry out the decomposition, 2-propanol vapor was fed into the reactor by passing helium (or pure carbon dioxide) through a 2-propanol bubbler at 288 K at a flow rate of 30 cm^3 min^{-1}. The reaction temperature was 523 K. The products (i.e., propene, acetone, isopropyl ether and unreacted 2-propanol) were analyzed after 15 min time on-stream with an on-line FID chromatograph equipped with 20% FFAP Chromosorb W column.

2.3 Catalytic Activity Tests

The dehydrogenation of isobutane was carried out in a conventional flow type microreactor operated at atmospheric pressure. Prior to the reaction, the catalysts (400 mg) were outgassed at 873 K under He. After 0.5 h the helium stream was changed to the mixture of iC_4H_{10} and CO_2 (or He) with the molar ratio of 1:5 and the total flow rate 36 cm^3 min^{-1}. The reactants and products were analyzed on-line with two gas chromatographs. One of them was equipped with 4 m column (3 mm i.d.) packed with Chromosorb 104 and a flame ionization detector. This chromatograph was used to analyze the hydrocarbons (C_1–C_4). The second chromatograph was equipped with a 3 m column of the same diameter, packed with Carboxen 1000 and a thermal conductivity detector (for CO, H_2 and CO_2 analyses). The isobutane conversion and selectivities toward the products were calculated on the basis of carbon balance, according to Eqs. 1 and 2, where a_i is the number of carbon atoms in the compound i, while n_i and $n_{iC_4H_{10}}$ denotes the molar amount of i hydrocarbon formed and unreacted isobutene, respectively.

$$X_{iC_4H_{10}}(\%) = \frac{(\Sigma a_i \cdot n_i) \cdot 100}{4 \cdot n_{iC_4H_{10}} + \Sigma a_i \cdot n_i} \tag{1}$$

$$S_i\ (\%) = \frac{a_i \cdot n_i \cdot 100}{\Sigma a_i \cdot n_i} \tag{2}$$

Above calculations do not consider the conversion of isobutane to coke, as its formation is time dependent and difficult to estimate directly by simple chromatographic analysis during the continuous flow reaction. Therefore, the calculations are based on the isobutane conversion to gaseous unsaturated and saturated hydrocarbons, i.e., isobutene, n-butenes (n-C_4H_8 and C_4H_6), propene, propane, ethene, ethane, and methane. Coke deposition was estimated separately by the method described below.

The same procedure was used for the 2-propanol decomposition reaction.

2.4 Measurement of Coke Deposition

The catalysts used in the isobutane dehydrogenation experiments were outgassed again and the coke deposit was burned off at 873 K using synthetic air stream (10 min, 30 cm^3 min^{-1}). All the products were collected in a separate bottle and then analyzed chromatographically. The amount of removed carbonaceous deposit corresponded to the molar amount of carbon oxides formed (Eq. 3). Analogically, the Boudouard reaction was carried out in the carbon dioxide stream. The molar amount of gasified coke was calculated according to Eq. 4, where n_{CO} and n_{CO_2} denotes the number of CO and CO_2 moles in the collected gaseous mixture, while $n^{o}_{CO_2}$ is an initial amount of CO_2.

$$n_{C_{coke}}[\text{mol C}] = n_{CO} + n_{CO_2} \quad (3)$$

$$n_{C_{\text{gasified coke}}}\ [\text{mol C}] = \frac{n_{CO}}{n_{CO} + n_{CO_2}} \cdot n^{o}_{CO_2} \quad (4)$$

3 Results and Discussion

3.1 Effects of Vanadium Loading on Dehydrogenation of Isobutane

As shown in Fig. 1, the activity of all tested catalysts in the isobutane dehydrogenation reaction decreased with time, although the rate of deactivation was enhanced by increasing V_2O_5 content and the presence of CO_2 in the feed.

The highest isobutane conversion at the initial stage of the reaction under carbon dioxide atmosphere was observed over $VMgO_x$ catalyst with 20% weight content of vanadium (V_2O_5). The catalysts with lower vanadium loading were less active, although their initial activity was enhanced by the presence of carbon dioxide in the feed. Nevertheless, rapid deactivation of the $VMgO_x$ samples in comparison with the run under helium stream caused considerable decrease of the alkane conversion. Thus, the promoting effect of carbon dioxide disappeared with time on-stream. On the other hand, the activity of vanadium–magnesium oxide catalysts with V_2O_5 content above 20 wt% was much lower under CO_2 atmosphere than that under helium flow.

Looking for the explanation of this phenomenon, we analyzed the degree of coke buildup during the dehydrogenation process in both reaction atmospheres.

3.2 Deactivation of the Catalysts by Deposition of Coke

As we can see from Fig. 2, the rate of coke formation on V_2O_5(20%)MgO surface during the isobutane dehydrogenation with carbon dioxide was strongly dependent on time on-stream. On the other hand, formation of coke under helium atmosphere was less affected by the reaction time, the same decrease of the catalytic activity in the dehydrogenation process. $VMgO_x$ catalysts with higher vanadium loading showed very similar behavior, although considerably larger amount of coke was produced.

Figure 3 shows the amount of carbonaceous deposit formed on $VMgO_x$ catalysts after the isobutane dehydrogenation in the presence and absence of carbon dioxide at 873 K. The data are compared with the results of coke gasification by CO_2. All the analyses were performed for both reaction atmospheres within the first 10 min of the dehydrogenation, where the activity of $VMgO_x$ catalysts was highest. For all tested samples the amount of coke deposited on the catalyst surface during the isobutane dehydrogenation under CO_2 flow was higher than that, in helium atmosphere. Furthermore, the rate of coke deposition was enhanced significantly by vanadium loading. We believe that this was the main reason of faster deactivation of the catalysts with high vanadium content in the dehydrogenation process.

Although the carbon dioxide demonstrated some oxidizing properties, in contrast to diluted oxygen, CO_2 was not able to remove all carbonaceous deposit at the steady-state conditions. Moreover, gasification of coke in the Boudouard reaction was only slightly dependent on $VMgO_x$ composition. Therefore, the rate of coking in the dehydrogenation process had to be considerably faster than the rate of decoking, especially for the catalysts with high vanadium content.

It was reported in the literature that higher coke deposition at processes under CO_2 atmosphere was caused by higher production of olefins [18, 19]. To verify this statement, we calculated the amount of iC_4H_{10} necessary to obtain the required amount of coke and we divided it by the corresponding isobutane conversion to gaseous hydrocarbons, i.e., isobutene, *n*-butenes (*n*-C_4H_8 and C_4H_6), propene, propane, ethene, ethane and methane (Fig. 4).

The results clearly indicate that the above explanation is correct only for $VMgO_x$ catalysts with low vanadium content ($\leq$20 wt%), where the coking to dehydrogenation molar ratio was equal for both reactions (i.e., in the presence and absence of carbon dioxide in the feed). It seems to be very possible that carbonaceous species can be produced by subsequent conversion of olefins produced at the dehydrogenation of isobutane, but also by undesirable disproportionation of carbon oxide, which can be treated as an equilibrium reverse Boudouard reaction (5):

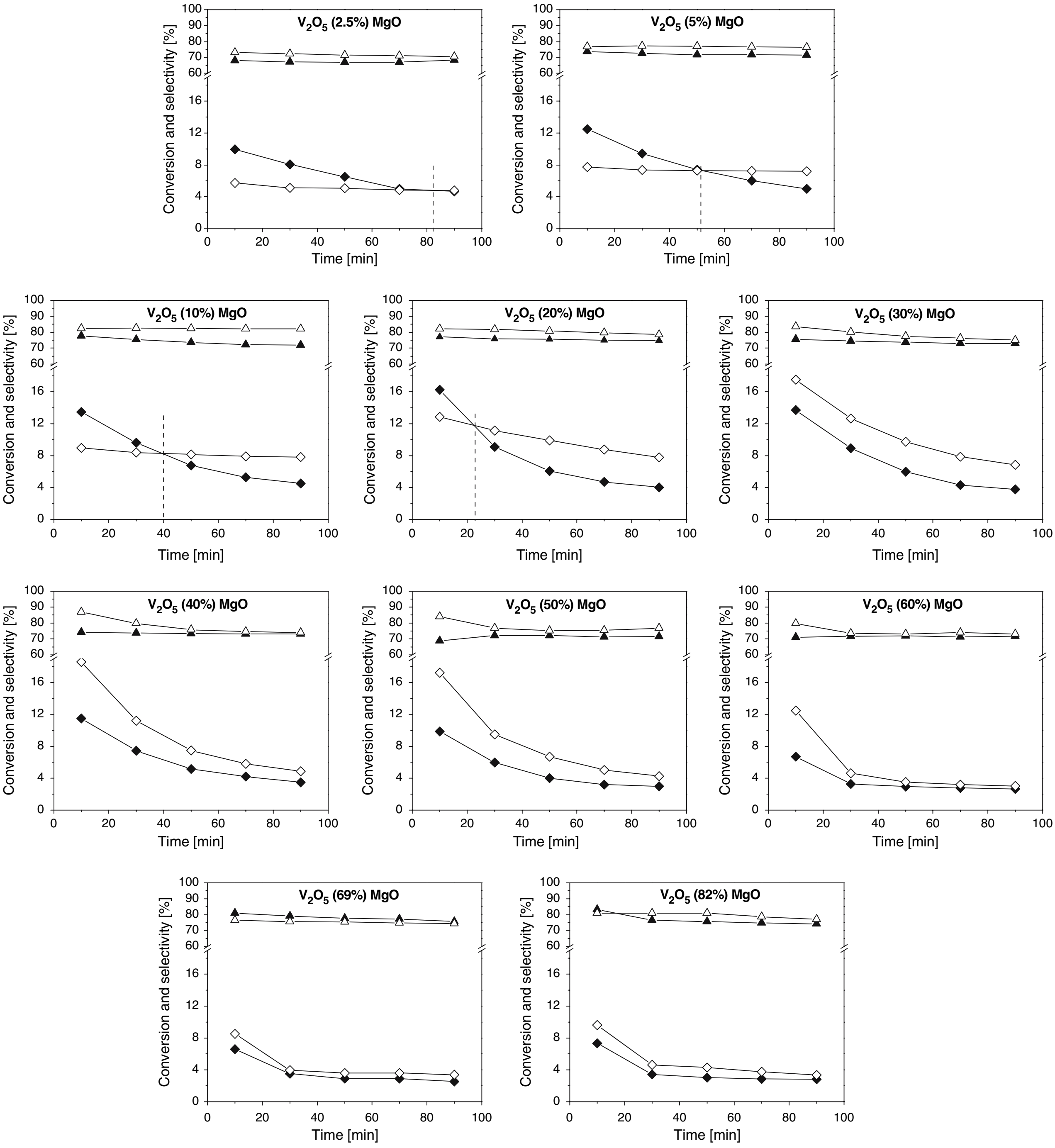

Fig. 1 Effect of time on-stream and vanadium loading on isobutane conversion (diamond markers) and selectivity to isobutene (triangles) in the process at 873 K under CO_2 (solid symbols) or He (open symbols) flow

$$2CO \rightleftharpoons CO_2 + C_{coke} \tag{5}$$

3.3 Effect of the Catalysts Acid–Base Properties on Coke Deposition

It is well-known fact that acidity is favorable for coke formation. Thus, an adequate correlation was found on the basis of the temperature-programmed desorption experiments (the details are given in Table 1).

As shown in Table 1, increase of vanadium loading in $VMgO_x$ can be related to considerable growth in acidity of the catalyst surface. This effect is not surprising, because V_2O_5 is well known for its acidic properties [20]. It should be also underlined that the amount of produced coke has grown in very similar sequence. Thus,

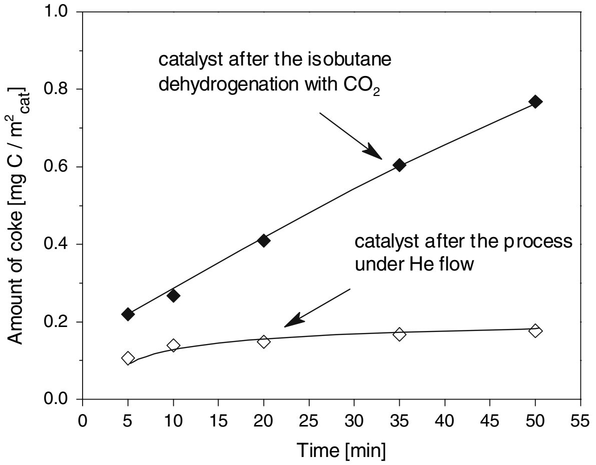

Fig. 2 The effect of time on-stream on the amount of coke formed on V_2O_5(20%)MgO catalyst surface during the isobutane dehydrogenation in the presence and absence of carbon dioxide

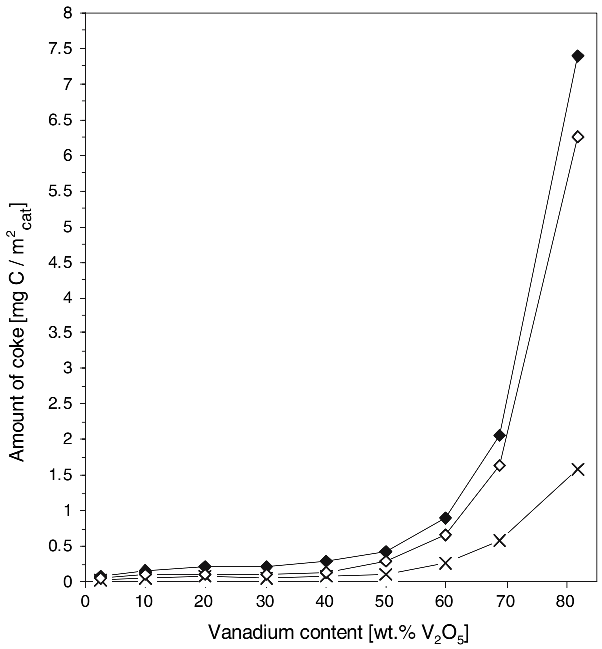

Fig. 3 The effect of vanadium loading on coke deposition in the isobutane dehydrogenation process over $VMgO_x$ catalysts, and the possibility of the Boudouard reaction with CO_2. Diamond markers correspond to coke produced after 10 min of isobutane dehydrogenation in the presence (solid symbols) and absence (open symbols) of carbon dioxide. Crossed symbols represent the coke gasified in the Boudouard reaction after isobutane dehydrogenation under CO_2 atmosphere

it can be concluded that both the increase of vanadium loading and the increase of overall catalysts surface acidity promotes undesirable side reactions, such as production of carbonaceous deposit [3–5]. On the other hand, it is reasonable to assume that the carbon dioxide with its slightly acidic character requires basic sites for

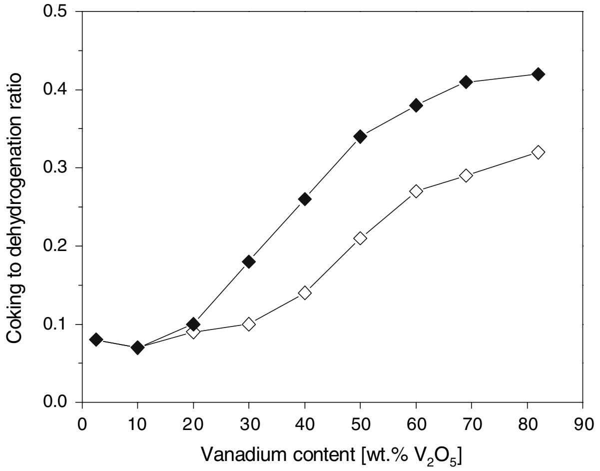

Fig. 4 The effect of vanadium loading on the coking to dehydrogenation molar ratio. Solid symbols—catalysts used in the isobutane dehydrogenation with carbon dioxide, open symbols—process under helium atmosphere

the activation. Thus, adsorption of CO_2 on the catalyst surface should cause an increase of the catalyst acidity. This effect was previously reported for Ga_2O_3 [28] and confirmed for active carbon supported vanadium oxide catalyst by our analysis (i.e., by isopropanol decomposition test reaction in the presence and absence of carbon dioxide) [22]. As shown in Table 2, the same effect was observed over $VMgO_x$ catalysts.

The role of particular centers in 2-propanol decomposition reaction is still under discussion, however it is generally 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. Thus, the overall acidity of $VMgO_x$ catalysts was calculated as a proportion between the selectivities to dehydration and dehydrogenation products. As it is seen from the Table 2, the overall acidity was enhanced by increasing vanadium loading. Moreover, it slightly increased when the carbon dioxide was used as a carrier gas for 2-propanol vapor. We believe that such change of the catalysts surface acid–base properties was the main reason of higher coke deposition during the isobutane dehydrogenation process under carbon dioxide atmosphere in comparison to that under helium flow.

The most possible mechanism by which CO_2 favors the acidity of the catalyst is that carbon dioxide preferentially adsorbs on the basic sites presented on the surface of $VMgO_x$ oxide. Since the acidic and basic sites can be related to vanadium and magnesium oxides, respectively, we may expect that adsorption of CO_2 should result in decrease of concentration of available basic sites. Thus, the largest differences between the coke formation during the process in the presence and absence of carbon dioxide should be seen

Table 1 The results of temperature-programmed desorption analysis

Catalyst	S_{BET} (m^2/g_{cat})	TPD-NH_3 (μmol NH_3/m^2_{cat})	TPD-CO_2 (μmol CO_2/m^2_{cat})	Molar ratio of NH_3/CO_2
V_2O_5(2.5%)MgO	20.83	30.2	23.75	1.27
V_2O_5(5%)MgO	17.53	32.6	17.12	1.91
V_2O_5(10%)MgO	18.02	33.2	16.93	1.96
V_2O_5(20%)MgO	20.86	34.2	13.95	2.45
V_2O_5(30%)MgO	31.91	20.6	8.06	2.56
V_2O_5(40%)MgO	30.28	20.3	7.61	2.66
V_2O_5(50%)MgO	24.94	18.9	5.76	3.28
V_2O_5(60%)MgO	15.32	17.9	3.56	5.03
V_2O_5(69%)MgO	7.74	42.9	4.00	10.75
V_2O_5(82%)MgO	1.08	271.0	19.31	14.03

Table 2 Decomposition of 2-propanol on several VMgO$_x$ catalysts in the presence and absence of carbon dioxide at 523 K

Catalyst	Carrier gas for alcohol vapor	2-Propanol conversion (%)	Selectivity to (%)			Overall acidity $\frac{S_{propene}+S_{DIPE}}{S_{acetone}}$
			Propene	DIPE	Acetone	
V_2O_5(5%)MgO	He	2.59	40.9	–	59.1	0.35
	CO_2	1.51	41.9	–	58.1	0.63
V_2O_5(20%)MgO	He	2.08	35.1	–	64.9	0.54
	CO_2	4.15	38.0	–	62.0	0.61
V_2O_5(40%)MgO	He	3.63	34.6	–	65.4	0.53
	CO_2	4.75	54.1	–	45.9	1.18
V_2O_5(60%)MgO	He	3.18	34.8	7.6	57.5	0.61
	CO_2	4.73	62.4	–	37.6	1.66
V_2O_5(82%)MgO	He	23.16	76.8	1.6	21.7	3.54
	CO_2	28.80	78.9	–	21.1	3.74

for the catalysts with low vanadium content. Nevertheless, the opposite trend was observed experimentally (Fig. 3). This effect can be easily related to gasification ability of carbon dioxide, which decreases with increasing vanadium content in VMgO$_x$ catalysts, as the basic sites are required for CO_2 activation. For example, almost 40% of carbonaceous deposit formed on V_2O_5(20%)MgO catalyst surface during the dehydrogenation process was removed at the subsequent Boudouard reaction (Fig. 3). At the same conditions, the amount of coke gasified by carbon dioxide over V_2O_5(40%)MgO and V_2O_5(82%)MgO samples was only 32% and 22%, respectively.

4 Conclusions

The experimental results show that carbon dioxide stream is able to gasify some part of the carbonaceous species formed on the catalyst surface, although it does not remove all deposit under steady-state conditions. Hence, the rate of coking has to be faster than the rate of decoking. More intensive deactivation of catalysts in the dehydrogenation process under carbon dioxide flow is caused by higher rate of coke formation in comparison to the process in helium atmosphere. Thus, the promoting effect of CO_2 decreases with time on-stream. Analysis of the catalysts physicochemical properties shows that coke formation on VMgO$_x$ is enhanced chiefly by the surface acidity, which grows with both the vanadium loading and the content of carbon dioxide in the feed.

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