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TG study on real role of active carbon support in propane dehydrogenation with CO_2

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ABSTRACT

Active carbon was used as a support for chromium(III) oxide phase. The synthesized materials appeared to be very active catalysts of the propane dehydrogenation in the presence of CO_2. An influence of the Cr content on the catalytic activity and selectivity was observed. The best results were achieved over the sample containing about 5 wt.% of Cr. A negative effect of activity decay with time-on-stream was found. The reasons of the observed deactivation were explained using the thermal analysis method. A behavior of the fresh and used samples was tested in a temperature range of 25–1000 °C in different atmospheres (inert gas, air or CO_2). It was found that the catalytic runs resulted in a partial decomposition of surface O-containing groups, which together with CrO_x species play a role of active centers. Moreover, a formation of inactive carbonaceous deposit on the catalyst surface was observed.

1. Introduction

Active carbons are relatively cheap materials, which can be synthesized by chemical or physical activation starting from, e.g. wood, coal, lignite, coconut shell, peat, fruit pits, polymers or petroleum processing residues. An extremely expanded surface area, a unique surface composition as well as stability both in acidic and basic media are features of active carbons finding interest in the catalysis field. It is not therefore surprising that these materials are widely studied as supports of catalytically active phase. Many active carbon supported catalysts have been already commercialized (e.g. active carbon supported noble metals for hydrogenation processes) [1]. Active carbon appeared to be a very promising candidate for a support of alkane dehydrogenation catalysts as well. Their catalytic performance was tested in the dehydrogenation of ethylbenzene and isobutane in the presence of carbon dioxide [2–5]. However, conversion of propane to propene via the direct dehydrogenation route is even more important research subject.

Propene is a very important raw material used as a feedstock for variety of chemical intermediates and polymers. Nowadays, it is obtained predominantly as a primary ethene co-product from steam cracking of natural gas or naphtha and from fluid catalytic cracking of liquid petroleum products. Additionally, small propene sources are “on-purpose” technologies, such as: dehydrogenation of propane, olefin metathesis and natural gas base process—methanol to olefins (MTO).

Growing demand on propene, driven mainly by increasing demand on polypropylene, acrylonitrile, propylene oxide and cumene, stimulates studies aimed at finding new methods of propene production from alternative sources and an improvement of propene yield from conventional sources. Recently, the dehydrogenation of propane with CO_2 has been studied [6–8] as an alternative technology for non-oxidative dehydrogenation of propane. In the new process, propene is obtained with higher yield than in the traditional one. This promoting effect of CO_2 is explained by its participation in:

(1) direct oxidation of propane to propene ($C_3H_8 + CO_2 = C_3H_6 + CO + H_2O$) [9,10];
(2) hydrogen consumption by reverse water–gas shift reaction ($CO_2 + H_2 = CO + H_2O$), which shifts propane dehydrogenation equilibrium [11–14];
(3) coke gasification ($CO_2 + C_{coke} = 2CO$), which slows down the deactivation rate of catalyst [11,13].

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A great variety of catalysts have been tested in the dehydrogenation of propane in the presence of CO_2 [9–24]. Different oxides (Ga, Cr, V, Fe, Zr and Zn) were used as the active components, while potassium oxide was used as a promoter. Inorganic oxides (SiO_2, Al_2O_3, TiO_2, ZrO_2, MgO), mesoporous sieves (MCM-41, SBA-15, MSU-*x*) and carbonaceous materials (diamond, active carbon) were tested as the supports. Some of these studies have demonstrated that promoting effect of CO_2 on the dehydrogenation of propane strongly depends on properties of support [9,10,13,15,21].

In the presented work, we have shown the promoting effect of active carbon support in the catalytic process of propane dehydrogenation in the presence of carbon dioxide. The real role of this support in the studied reaction has been discussed basing on the results of TG analysis of fresh and used chromium oxide supported on active carbon in inert and oxidizing (the presence of air or CO_2) atmospheres.

2. Experimental

2.1. Materials

Carbon (Cheviron-Carbon GmbH) with a low ash content of 0.31 wt.% was initially activated with 90% HNO_3 at 90 °C for 1 h. After washing and drying (180 °C, 2 h), the resulting active carbon (AC) was impregnated by the incipient wetness technique with an aqueous solution of chromium(III) nitrate. An amount of $Cr(NO_3)_3{\cdot}9H_2O$ used was calculated to obtain the supported catalysts containing 2.5, 5.0, 7.5 and 10.0 wt.% Cr, respectively. The impregnated samples were dried at 180 °C for 3 h in air, and subsequently calcined at 650 °C for 3 h in argon atmosphere.

2.2. Characterization methods

The calcined materials were characterized with respect to structure by powder X-ray diffraction (XRD). XRD patterns were recorded in 2θ range of 10–75° using a Siemens D5005 instrument operated at 40 kV and 60 mA with a Cu Kα X-ray source at room temperature. Moreover, texture of the obtained samples was determined using adsorption of nitrogen at −196 °C. The adsorption–desorption isotherms were collected in an ASAP 2010 instrument (Micromeritics). Prior to the analysis, the active carbons were outgassed at 350 °C for 12 h. The collected data were analyzed by the BET, *t*-plot and Horwath-Kawazoe models.

TG analysis was performed on a Mettler Toledo TGA/SDTA 851 instrument equipped with a mass spectrometer Thermo Star (Balzers) in a constant flow of argon, air or CO_2 (80 ml/min). Approximately, 25 mg of each sample was heated in a platinum pan from 30 to 1000 °C with a heating rate of 10 °C/min.

2.3. Catalytic study

The dehydrogenation of propane in the presence or absence of CO_2 was carried out in a flow-type reactor packed with 200 mg of catalyst (grain size 0.2–0.3). The feed was a mixture of C_3H_8:CO_2 or C_3H_8:He (16.7 vol.% of C_3H_8 and 83.3 vol.% of CO_2 or He) at the molar ratio of 1:5. The total flow rate of the feed was 30 ml/min. Prior to the catalytic runs, the catalysts were preheated in dry He stream at 600 °C for 1 h and then the reaction was carried out at a required temperature in the range between 500 and 650 °C. The reaction products and unreacted substrates were analyzed using two gas chromatographs. One of them, equipped with a glass column (3 m × 3 mm) packed with Porapak Q and a flame ionization detector, was used for the analysis of hydrocarbons. The second chromatograph was equipped with a stainless steel column (3 m × 3mm) packed with Carboxen 1000 and a thermal conductivity detector (for H_2, CO and CO_2 analyses). Propane conversion (C_p), products yield (Y_i) and selectivity (S_i) were calculated according to the following equations:

$$Y_i(\%) = \frac{(a_i/3)n_i}{n_{C_3H_8} + n_{C_3H_6} + 2/3n_{C_2H_6} + 2/3n_{C_2H_4} + 1/3n_{CH_4}} \times 100$$

$$S_i(\%) = \frac{(a_i/3)n_i}{n_{C_3H_6} + 2/3n_{C_2H_6} + 2/3n_{C_2H_4} + 1/3n_{CH_4}} \times 100$$

$$C_p(\%) = \frac{Y_p}{S_p} \times 100$$

where a_i is a number of carbon atoms in a compound *i*, n_i the number of moles of compound *i*, Y_p the yield of propene and S_p is the selectivity to propene.

3. Results and discussion

3.1. Catalyst characterization

The calcined AC based samples modified with chromium were studied by XRD. The recorded patterns are shown in Fig. 1. It should be noticed that the catalysts containing a relatively small amount of Cr exhibit rather amorphous nature. An increase in the Cr loading results in an appearance of crystalline phase of chromium oxide.

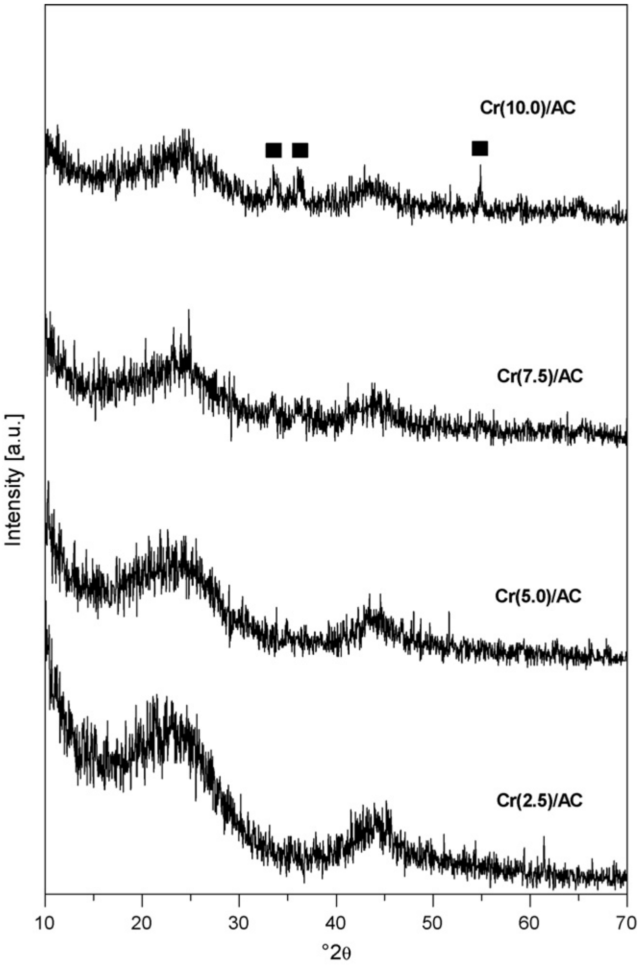

Fig. 1. X-ray diffraction patterns of the chromium-modified active carbon samples (■, α-Cr_2O_3).

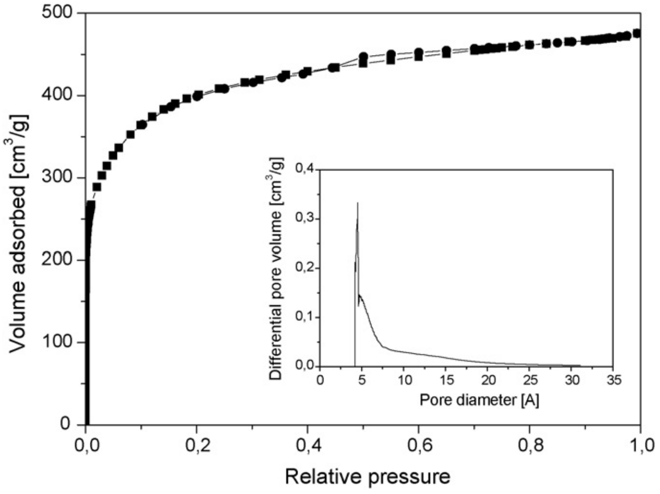

Fig. 2. Isotherm adsorption–desorption of N_2 at −196 °C and pore size distribution determined by the Horwath-Kawazoe model for the AC sample.

The presence of this phase, which is manifested by three diffraction lines at about 33.5°, 36.1° and 54.8° 2θ, is most distinct for the Cr(10.0)/AC sample. The observed diffraction peaks can be indexed as (1 0 4), (1 1 0) and (1 1 6), respectively, and are characteristic for rhombohedral α-Cr_2O_3 with space group $R\bar{3}c$.

The textural properties of the calcined materials were determined by the adsorption of N_2 at −196 °C. An example of adsorption–desorption isotherm recorded for the non-modified active carbon is presented in Fig. 2. The shape of the collected isotherms, which can be determined as type I according to the IUPAC classification, demonstrates that the studied samples are typical microporous solids. The calculation of pore size distribution based on the Horwath-Kawazoe model confirms this conclusion. The pore size distribution curves (Fig. 2, inset) indicate that a majority of pores existing in the AC-based samples possesses an extremely small size <7 Å.

The nature and size of pores were not essentially changed after the modification with chromium oxide. For the samples containing Cr (not shown), submicropores still play a dominant role. On the other hand, the specific surface area determined formally using the BET or Langmuir equation decreases with raising the Cr loading (Table 1). A similar effect was found for the micropore volume calculated according to the *t*-plot method. It should therefore be assumed that chromium oxide species are deposited mainly on an external surface of the active carbon support. The formed clusters and crystallites of Cr_2O_3 partially block an access to the micropores. However, even for the sample with the highest chromium content (Cr(10.0)/AC), the BET surface area is as high as 875 m^2/g and micropore volume exceeds 0.250 cm^3/g.

3.2. Catalytic activity

The obtained samples were tested as catalysts of the dehydrogenation of propane to propene in the presence of carbon dioxide. The optimal catalyst composition was determined for the reaction performed at a thermodynamically reasonable temperature of 600 °C. An influence of the Cr loading on the initial propane conversion and the products selectivity is demonstrated in Fig. 3A and B, respectively. The non-modified active carbon support exhibits a quite reasonable activity in the process, which can be carried out with propane conversion of 16.5% in this case. Active carbons are typical acid-type solids with acidity attributed to the surface oxygen-containing species like carbonyl and carboxyl groups. It is most likely that the process of propane dehydrogenation is catalyzed by such active sites present on the AC surface.

Table 1
Textural parameters of the studied active carbon-based catalysts

Sample	BET surface area (m^2/g)	Langmuir surface area (m^2/g)	*t*-Plot micropore volume (cm^3/g)
AC	1414	1890	0.379
Cr(2.5)/AC	1337	1789	0.383
Cr(5.0)/AC	1156	1544	0.314
Cr(7.5)/AC	1004	1346	0.290
Cr(10.0)/AC	875	1161	0.258

The propane conversion increases with the Cr content and reaches maximum of 51.3% for the Cr(5.0)/AC catalyst. Further enrichment of a sample in chromium results in a slight decay of its catalytic activity. This effect should be attributed to the formation of α-Cr_2O_3 phase (detected by XRD), which has been found to be poorly active in the alkane dehydrogenation [25]. Therefore, it could be concluded that a high dispersion of chromium is a key parameter influencing the catalytic activity of the active carbon-based samples. The propane conversion achieved over the studied catalysts is correlated with selectivity towards propene, which is the main reaction product. It is found that when the propane conversion increases, a decrease in the propene selectivity is observed. Nevertheless, a high selectivity towards propene (>80.0%) was obtained for all the studied catalysts. Three side products (methane, ethane and ethylene) of C_3 hydrocarbons cracking were formed with selectivity below 10%.

It should be stressed that the activity observed for the Cr(5.0)/AC catalyst is indeed very high compared to other catalysts previously studied in the propane dehydrogenation with CO_2 [10,14]. An effect of temperature on the rate of homogeneous phase reaction (empty reactor) and the catalytic performance of the Cr(5.0)/AC sample is comparatively presented in Fig. 4A and B, respectively. The propane conversion and selectivity towards propene were measured for the reactions performed in the absence and presence of CO_2. It is found that the conversion of propane in the gas phase begins at temperature about 550 °C. This process is so slow that even at 650 °C only 8.5% (in inert atmosphere) or 9.0% (in CO_2-containing atmosphere) of propane is converted. The homogeneous phase reaction results in a formation of mainly cracking products. An introduction of solid catalyst leads to a significant increase in both activity and selectivity of the process. It is observed that regardless to the feed composition, an increase in the reaction temperature causes an increase in the propane conversion and a drop in selectivity towards propene over the Cr(5.0)/AC catalyst. This effect is the most distinct when the maximal reaction temperature of 650 °C is reached. Nevertheless, the promoting effect of carbon dioxide on the catalytic performance is clearly observed. CO_2 can be involved in the propane transformation via two independent reaction paths. Carbon dioxide can play a role of an oxidizing agent:

$$C_3H_8 + CO_2 = C_3H_6 + H_2O + CO.$$

It is also possible that a two-steps reaction occurs. First step is propane dehydrogenation to propene:

$$C_3H_8 = C_3H_6 + H_2.$$

The formed hydrogen is subsequently converted by CO_2 to water and carbon monoxide according to the reverse water–gas shift reaction (RWGS):

$$H_2 + CO_2 = H_2O + CO.$$

The molar fractions of the products formed during the reaction over the Cr(5.0)/AC catalyst in the presence and absence of CO_2 are presented in Fig. 5, respectively. It can be found that in both cases

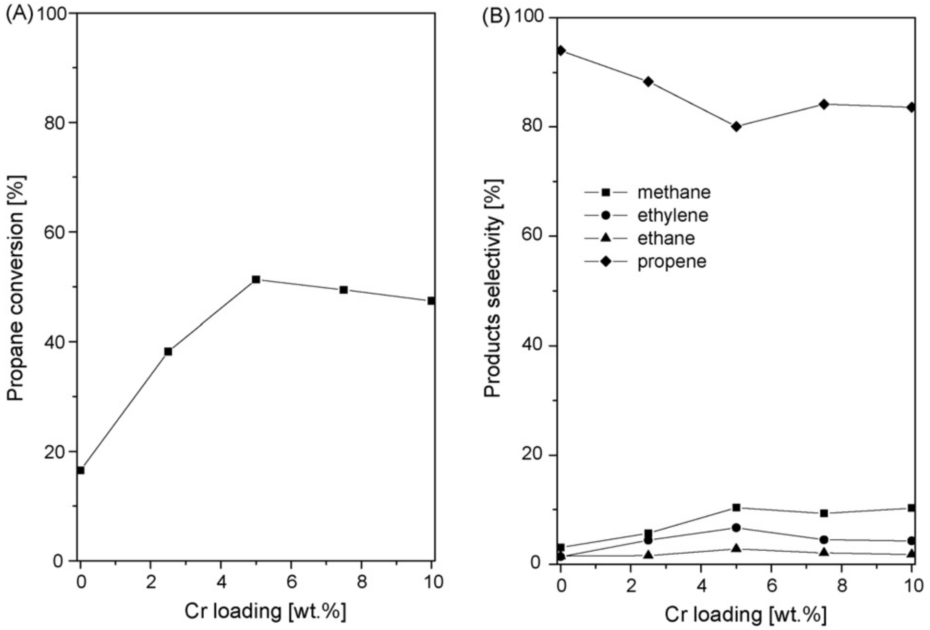

Fig. 3. Propane conversion (A) and products selectivity (B) achieved in the initial period of the reaction over catalysts with different Cr contents (reaction conditions: temperature = 600 °C; catalyst = 0.2 g; propane:CO_2 = 1:5; feed flow rate = 30 ml/min).

hydrogen appears among the reaction products. Therefore, it can be concluded that the studied catalyst is active in the direct dehydrogenation of propane to propene. It should be assumed that in the presence of CO_2 a part of H_2 is eliminated by the RWGS reaction, what is manifested by an increase in the amount of CO produced. However, a participation of the oxidative propane dehydrogenation as a competitive reaction in the propene formation cannot be excluded as well.

Unfortunately, the studied active carbon-based catalysts undergo a fast deactivation with time-on-stream. The rate of activity loss expressed in term of relative yield of cracking (methane, ethylene and ethane) or dehydrogenation (propene) products for the Cr(5.0)/AC sample is presented in Fig. 6. It is observed that the deactivation is faster in the CO_2-rich atmosphere compared to inert one. This effect could be attributed to the higher yield of propene formed in the reaction performed in the presence of carbon dioxide. The produced propene can be a precursor of inactive coke deposited on the catalyst surface. On the other hand, CO_2 is too mild oxidizing agent to remove effectively the carbonaceous deposit. It should, moreover, be noticed that both in the presence and absence of CO_2, the yield of the reaction products decreases with time-on-stream. However, the catalysts lose their activity in the formation of cracking products faster than in the dehydrogenation of propane to propene. The cracking process is commonly catalyzed by acidic surface sites. Therefore, it could be suspected that during the reaction acid sites are preferentially poisoned or decomposed.

3.3. Thermal analysis

A first attempt of explanation of deactivation mechanism led us to the application of the thermogravimetric method. We have tested a behavior of four samples (AC, fresh Cr(5.0)/AC and used

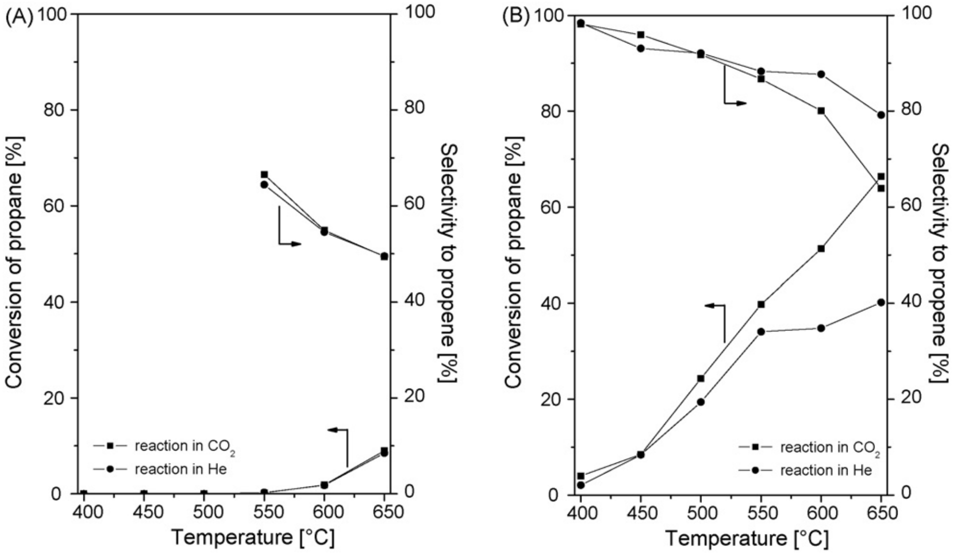

Fig. 4. Influence of reaction temperature on the initial propane conversion and propene selectivity for the process performed in the homogeneous phase (A) or in the presence of the Cr(5.0)/AC catalyst (B) in CO_2 and He atmosphere (reaction conditions: catalyst = 0 or 0.2 g; propane:CO_2 or propane:He = 1:5; feed flow rate = 30 ml/min).

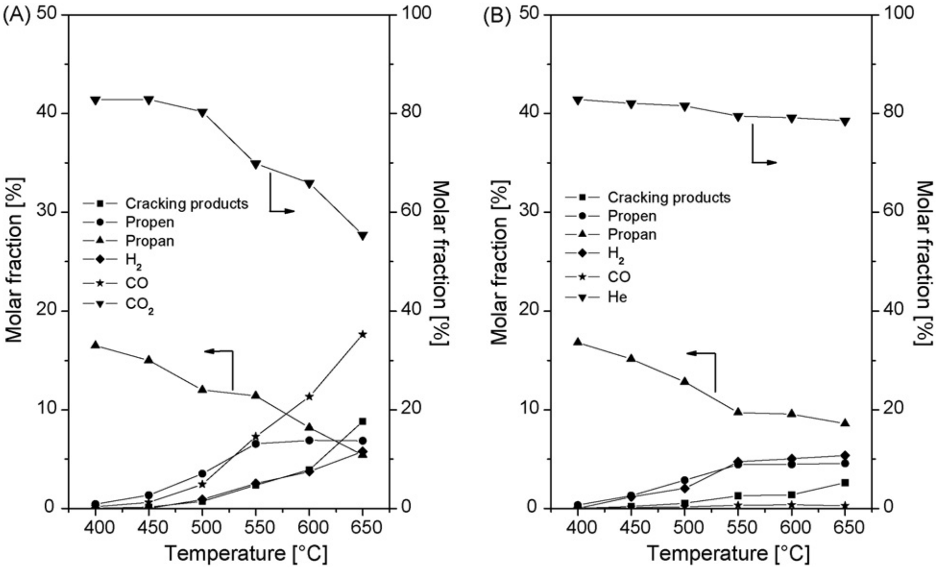

Fig. 5. Influence of reaction temperature on the molar fractions of the products for the process performed in CO_2-containing (A) and inert (B) atmosphere over the Cr(5.0)/AC catalyst (reaction conditions: catalyst = 0.2 g; propane:CO_2 or propane:He = 1:5; feed flow rate = 30 ml/min).

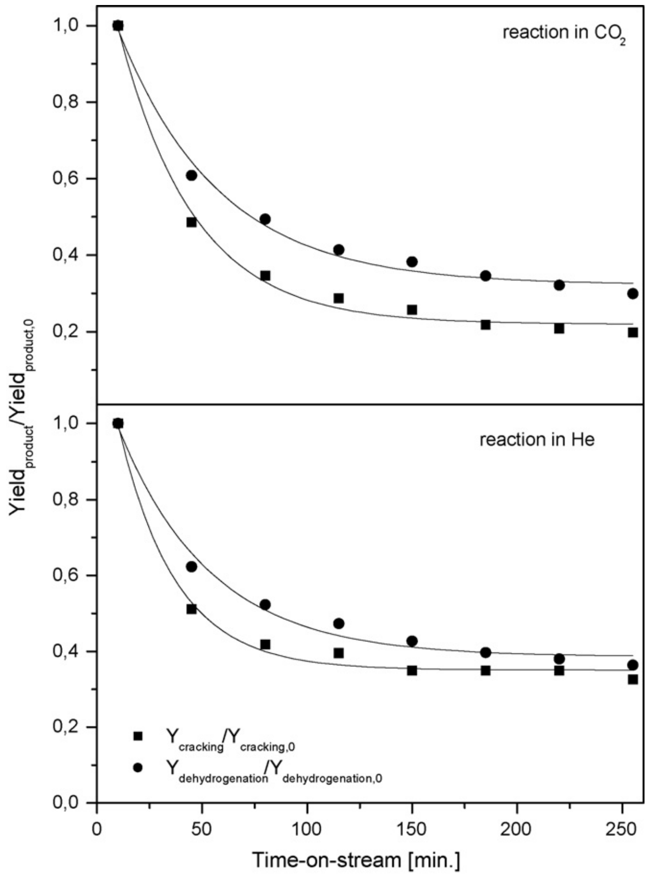

Fig. 6. Rate of deactivation of the Cr(5.0)/AC catalyst measured as a ratio between the actual yield of cracking (or dehydrogenation) products and the initial yield of cracking (or dehydrogenation) products (reaction conditions: temperature = 600 °C; catalyst = 0.2 g; propane:CO_2 or propane:He = 1:5; feed flow rate = 30 ml/min).

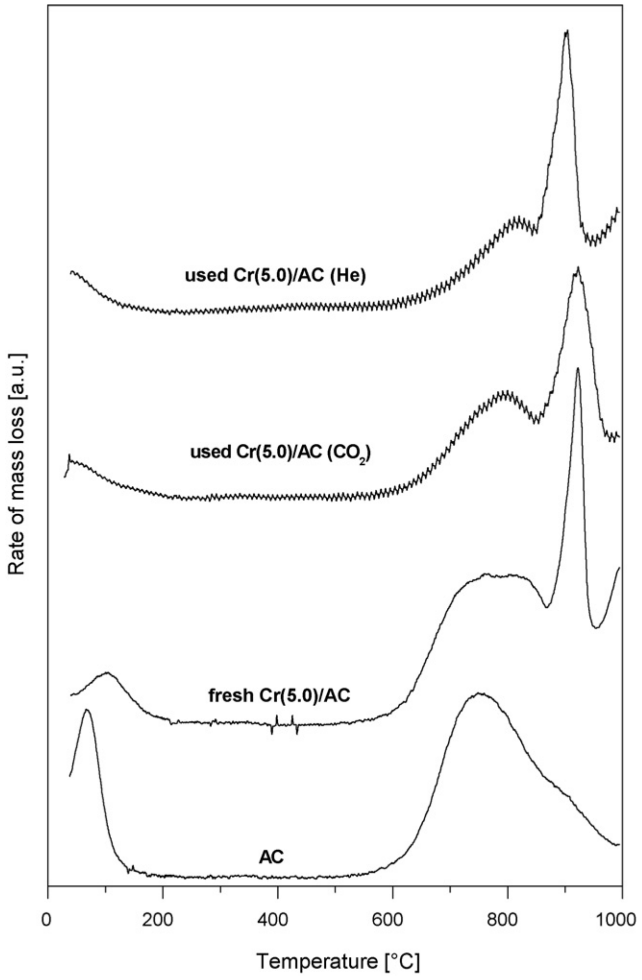

Fig. 7. DTG curves recorded for the active carbon-based catalysts in the argon atmosphere (measurement conditions: sample ~0.025 g; Ar flow rate = 80 ml/min; temperature range = 30–1000 °C, heating rate = 10 °C/min).

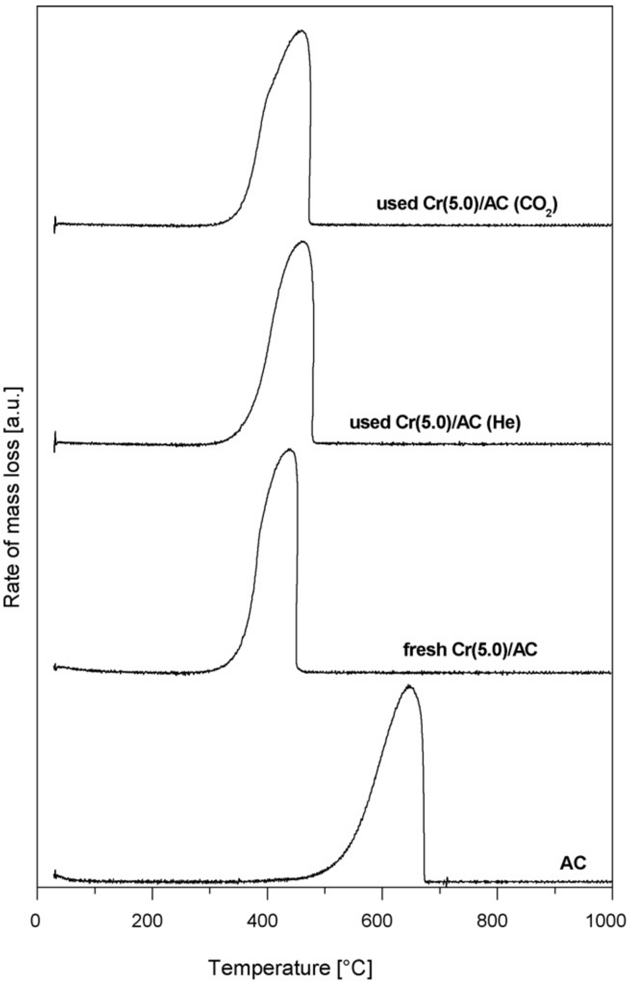

Fig. 8. DTG curves recorded for the active carbon-based catalysts in the air atmosphere (measurement conditions: sample ~0.025 g; air flow rate = 80 ml/min; temperature range = 30–1000 °C, heating rate = 10 °C/min).

Cr(5.0)/AC after the reaction performed in He or CO_2) at elevated temperatures in inert atmosphere. The obtained results are shown in Fig. 7. The decomposition of the AC sample undergoes in two stages. At lower temperatures (<150 °C), the removal of chemisorbed water from the surface is observed. An increase of temperature to about 550 °C results in the decomposition of surface groups, which are partially stable up to 1000 °C. The DTG curve recorded for the Cr(5.0)/AC is similar to that measured for AC. It should, however, be noted that an additional mass loss at about 920 °C is observed for Cr(5.0)/AC. This effect can be assigned to reduction of Cr(III) to metallic chromium by carbonaceous support. The thermal analysis performed for the Cr(5.0)/AC sample used in the catalytic runs in the CO_2 and He atmosphere shows a significant decrease in the detected total mass loss. It is clear that an amount of oxygen-containing surface species was drastically reduced during the catalytic reaction. The decrease in a number of surface sites is more pronounced after the catalytic run in inert atmosphere. Taking into account the catalytic role of carbonyl/carboxyl groups in the conversion of propane it should therefore be concluded that the presence of carbon dioxide in the feed partially protects the active carbon-based catalysts against deactivation.

Apart from the decomposition of active centers, a formation of carbonaceous deposit encapsulating the active phase of chromium oxide can be a reason of the catalyst deactivation. The samples presented above (AC, fresh Cr(5.0)/AC and used Cr(5.0)/AC after the reaction performed in He or CO_2) were tested by the thermal analysis in the air atmosphere as well. The DTG curves collected in the presence of oxygen (Fig. 8) exhibit a significantly higher total mass loss compared to that observed in the inert atmosphere. Oxidation of the non-modified active carbon begins at temperature of about 460 °C and reaches a maximum of rate at 650 °C. The sample lost 99.68% of its initial mass up to 680 °C, when oxidation was completed. An introduction of chromium on the active carbon surface caused a clear shift of oxidation process towards lower temperatures. Evidently, CrO_x present in the samples is a catalytically active phase in carbon gasification. The fresh Cr(5.0)/AC catalyst starts to be burned at temperature as low as 300 °C. There is not further mass loss above 460 °C in the case of this sample. It should be stressed that the presence of the introduced chromium oxide results in lower total mass loss (86.89%) than for the AC material. Similar DTG profiles were recorded for the Cr(5.0)/AC sample used in the catalytic runs. It should, however, be noticed that the decomposition of carbonyl/carboxyl groups in the course of the propane dehydrogenation stabilized slightly the carbonaceous support. The Cr(5.0)/AC catalyst used in the reaction is gasified starting from 310 °C. Moreover, a difference in stability between the samples used in the inert and CO_2 atmosphere can be distinguished. The gasification of the catalyst used in the process performed in the presence of CO_2 is more intensive compared to the same sample exposed to the mixture of helium and propane. The Cr(5.0)/AC catalyst used

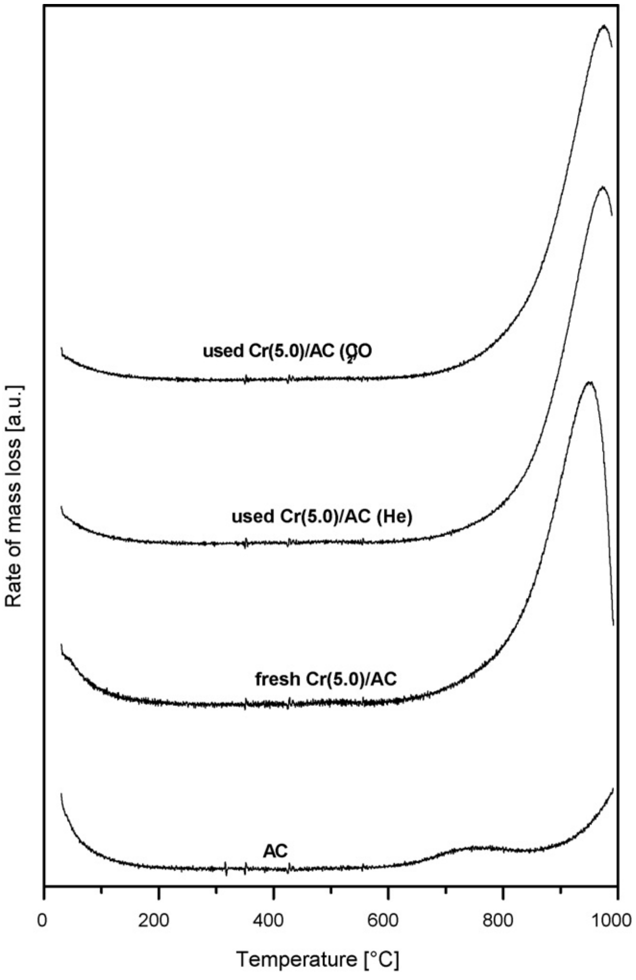

Fig. 9. DTG curves recorded for the active carbon-based catalysts in the CO_2 atmosphere (measurement conditions: sample ~0.025 g; CO_2 flow rate = 80 ml/min; temperature range = 30–1000 °C, heating rate = 10 °C/min).

in the reaction with He lost 88.14% of its initial mass, whereas this catalyst used in the CO_2-containing feed—88.51%. An increase in the total mass loss observed for the used catalysts in comparison to the fresh sample suggests that the carbonaceous deposit was formed during the dehydrogenation process. Therefore, it should be concluded that the drop in the catalytic activity observed with time-on-stream can be attributed to both removal of carbonyl/carboxylic groups and the formation of inactive coke on the catalyst surface.

Finally, the interaction between CO_2 and the active carbon-based samples was studied by TG. The resulting DTG profiles are shown in Fig. 9. It should be noticed that CO_2 is much less effective oxidizing agent compared to air. The non-modified active carbon reacts with carbon dioxide above 850 °C. The maximum observed between 640 and 830 °C in the DTG curve recorded for this sample should be attributed to the decomposition of surface groups, which was also detected for the measurement performed in the inert atmosphere. The catalytic effect of CrO_x phase on gasification of the AC support with CO_2 was found. It begins at about 650 °C for the fresh Cr(5.0)/AC sample. The used catalysts are more resistant for gasification by CO_2. Depending on the reaction conditions, the Cr(5.0)/AC sample begins to be oxidized at 670 (CO_2 atmosphere) or 690 °C (He atmosphere). The TG measurements performed in the CO_2 atmosphere evidence that temperature used in the catalytic experiments was too low for the reaction between carbon dioxide present in the reactant feed and the active carbon support.

4. Conclusions

The CrO_x-containing active carbons appeared to be extremely active catalysts for the propane dehydrogenation in the presence of carbon dioxide. It was found that the catalytic activity and selectivity strongly depended on the Cr loading. The highest propane conversions were achieved for the sample with the Cr content closed to 5 wt.%. An increase in the Cr loading resulted in the formation of crystalline α-Cr_2O_3 phase, a partial blocking of micropores and a decrease in the catalytic activity. Unfortunately, the active carbon-based catalyst underwent a fast deactivation.

The thermal analysis method was applied to study the reasons of the activity loss. TG experiments performed in the flow of inert gas showed that the active carbon support exhibited the presence of carbonyl- and carboxyl-like surface species which played a role in the catalytic process. A gradual decrease in the surface concentration of these groups was observed after the catalytic run. On the other hand, inactive coke was formed in the course of the propane dehydrogenation on the catalyst surface. This effect was confirmed by TG measurements in the O_2-rich atmosphere. Additionally, it was proved that CO_2 was practically inert in a relation to the carbonaceous support in the conditions used during the catalytic process.

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