MgO/CaO-loaded porous carbons for carbon dioxide capture

Effects accompanying regeneration process

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Abstract Nanoporous carbons loaded with both MgO and CaO were prepared by a simple heating of mixtures consisting of poly(ethylene terephthalate) and natural dolomite. Preparations were carried out at temperatures ranging from 850 to 1,000 °C that ensured complete thermal decomposition of the dolomite contained in the mixtures to the oxides. An influence of the PET/dolomite weight ratio and temperature of the preparation process on the porosity of the obtained composite products and on CaO and MgO crystallite sizes are discussed using the results of nitrogen adsorption/desorption at 77 K and X-ray diffraction analyses, respectively. Performances of the hybrid materials as sorbents for carbon dioxide were examined using thermogravimetric analyses. Finally, possibility of regeneration of the spent sorbent materials together with a side—effect accompanying this process are discussed on the basis of thermogravimetric measurements. As found, a part of CO_2 captured by the hybrid sorbents gets adsorbed weakly and another portion is fixed strongly. During thermal regeneration, the strongly fixed CO_2 reacts with carbon material. In this way small fraction of a sorbent is lost.

Keywords Porous carbon · MgO · CaO · CO_2 · Sorption · Regeneration

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Introduction

Porous carbon materials are widely used as adsorbents for purification of gases and liquids. Because of a wide spectrum of applications, various sorts of these specific materials are offered on the market [1]. Depending on the preparation route, raw materials, and eventually on the additional treatments, properties of activated carbons may be very different. Activated carbons may reveal differences in pore structure and specific surface area, which are one of key factors influencing adsorption. For example, microporous carbons usually effectively adsorb contaminants of a small molecular size and mesoporous ones are efficient for adsorption of large molecules [2, 3]. Besides porosity, presence of different oxygen-containing surface functional groups gives to the activated carbons specific features, like enhanced selectivity toward certain adsorbates. For instance, high content of the oxygen functionalities on the surface of activated carbons is beneficial for adsorption of SO_2, CO_2, or phenols [4–6].

Both efficiency and selectivity of carbon adsorbents can be modified by loading to their structure suitable additives, intentionally chosen for a specific application [7]. Therefore, porous carbon materials supporting certain chemicals are used as highly effective adsorbents for special applications, including respiratory protection or purification of air for clean rooms [8, 9]. The additive-loaded activated carbons are also used as catalysts support [10] or as materials being highly efficient during removal of contaminants from air in closed ventilation systems. The high parameters of such composite sorbents are a consequence of a synergic effect, resulting from both physical adsorption and chemical interaction between the additive present in the material and the target adsorbate. Loading of additives into porous carbons is typically realized through impregnation of commercially available carbon adsorbents with suitable organic or

inorganic agents [11]. However, heating of some carbon precursors mixed with certain chemicals can be also used as an appropriate method to prepare porous carbon materials carrying additives [12, 13].

In this work, we present our results on the preparation and properties of carbon adsorbents loaded with two basic oxides, CaO and MgO. These hybrid sorbents were obtained through pyrolysis of natural dolomite contained in mixtures with poly(ethylene terephthalate) (PET). The natural dolomite was a source of the oxides and the latter served as a synthetic carbon precursor. Till now such a one-step route was not reported. Selection of the precursors for preparations was not unintended. We believed that because of MgO and CaO content, obtained porous products would be active in removal of gaseous contaminants of acidic character from air. Porous carbon materials alone [14, 15] as well as MgO and CaO [16, 17], are known as revealing a potential in fixation of such gases. For that reason, these find an application for removal of acidic gases, principally SO_2, from gaseous streams generated by industry. Porous carbons supporting CaO were also reported [18] to be effective for this purpose. However, these composite sorbents were prepared by means of the conventional impregnation of commercial activated carbons with suitable calcium compounds.

MgO itself and some other magnesium compounds are known to be agents capable to create pores in carbon materials [19]. Therefore, pyrolysis of various carbon precursors with numerous magnesium compounds is considered as a suitable method for preparation of porous carbon materials. Depending on magnesium compound used, obtained nanocarbons can be rich in mesopores or/and in micropores. As reported in our previous work [20], gases being freed from some MgO precursors may react with a char formed from carbon precursor and thus play a role as pore creating agents. Recently we reported on the preparation and properties of porous carbons supporting MgO [13]. These sorbents could be successfully prepared by the heating of a synthetic carbon material mixed with natural magnesite. According to our preliminary results, these hybrid materials reveal a potential to capture SO_2 traces from air at room temperature.

Dolomite is a natural carbonate material undergoing thermal decomposition with evolution of CO_2. The gas can react with carbon materials like char at ca. 800–850 °C and thus microporosity can be created [21]. Hence, heating of both the dolomite and suitable carbon precursor was thought to be a suitable route to prepare porous carbon material supporting both MgO and CaO. Obtained composite materials were examined as regenerable sorbents for CO_2. As we noticed, regeneration of the CO_2-saturated sorbent materials was accompanied by certain changes in a mass of samples, even the process was carried out in an inert medium. For that reason, despite reporting

preparation procedure and properties of obtained hybrid materials, in this work we try to explain mechanism of the CO_2 capture and reasons of the mass loss, accompanying the regeneration process.

Experimental

Materials

The raw dolomite used in this research was mined from deposits located near Ząbkowice (Poland), and its basic chemical composition is given in Table 1. This material served as a source of MgO and CaO. Before use, the raw dolomite was pulverized and dried for 24 h in air atmosphere at 140 °C. The commercial grade PET purchased from Boryszew Ltd., (Poland) was chosen to be a carbon precursor. Before use, the material was ground to a form of a fine powder.

Preparations

At first, the powdered PET was mechanically mixed with the dolomite powder (DOL) in three weight proportions (83:17, 50:50, and 30:70). In order to obtain a homogeneous mixes of these raw materials, each PET/DOL mixture was heated (10 °C min^{-1}) to 265 °C under argon gas flow (100 cm^3 min^{-1}) and kept at the final temperature for 1 h. The temperature was high enough to melt PET contained in the mixtures. After cooling down, the obtained solid products were ground and once more subjected to the described fusing/grinding procedure. Subsequently, ca. 15 g of the pulverized PET/DOL mixtures were placed in a tubular furnace and pyrolysed in an argon atmosphere (100 cm^3 min^{-1}) at temperatures up to either 850, or 900, or 1000 °C. In each case, the temperature ramp rate was 10 °C min^{-1} and the final temperature was maintained for 1 h. After the thermal treatment, whole system was allowed to cool down to room temperature, and obtained hybrid products were finally ground to a form of a fine powder.

Methods

The X-ray diffraction (XRD) patterns for the prepared materials were recorded using a Philips X'Pert PRO diffractometer operating with the Cu K$_\alpha$ radiation ($\lambda =$ 1.54056 Å). The mean sizes of MgO and CaO crystallites were calculated according to Scherrer's formula:

$$D = \frac{\lambda}{\beta \cos \theta}$$

where D is the mean crystallite size (nm), λ is the wavelength of Cu–K$_\alpha$ radiation (nm), θ is the Bragg's angle (°),

Table 1 Basic chemical composition of the raw dolomite, with reference to oxides (according to manufacturer's data)

Compound	Content/wt%
CaO	29.44
MgO	19.75
SiO_2	1.43
Fe_2O_3	0.14
Al_2O_3	0.11

and β is the calibrated width of a diffraction peak at half-maximum intensity (rad).

All thermogravimetric (TG) analyses were carried out using Netzsch STA 449 C precise thermobalance. In order to examine mass changes accompanying the preparation process, measurements were carried out in argon flow (30 cm^3 min^{-1}). For the evaluation of CO_2 uptake by the prepared sorbent materials, 10 mg samples were first pre-heated under nitrogen flow (99.999%, 30 cm^3 min^{-1}) to 110 °C. The temperature was maintained until mass indication became stable. After cooling to 30 °C, the inert gas was replaced with CO_2 (99.995%, 30 cm^3 min^{-1}). Exposing to this gas at the temperature was continued until constant weight was achieved. Subsequently, the regeneration step was carried out in situ according to two different temperature regimes. For that purpose, CO_2 flow was stopped and nitrogen gas was introduced to the system (30 cm^3 min^{-1}). Simultaneously, the temperature was raised (10 °C min^{-1}) either to 200 °C or to 850 °C. The final temperature was maintained until mass indication became stable. After that, the measurements were stopped.

The nitrogen adsorption/desorption isotherms at 77 K were measured with use of Quadrasorb SI (Quantachrome Instruments, USA) analyzer. Prior to the measurements, samples were degassed by the means of heating at 290 °C under a high vacuum for 12 h. The specific surface areas (S_{BET}) were determined on the basis of N_2 adsorption data by Brunauer–Emmett–Teller (BET) model. In addition, micropore surface areas (S_{micro}), external surface areas (S_{ext}), and total surface areas (S_{total}) were calculated by the α_s method.

Results and discussion

Thermogravimetric (TG) studies

In order to examine mass changes resulting from heating of used materials, appropriate TG measurements were carried out in argon atmosphere. Changes in mass of the PET, the dolomite, as well as of equivalent mixture of them, are illustrated by TG curves drawn in Fig. 1.
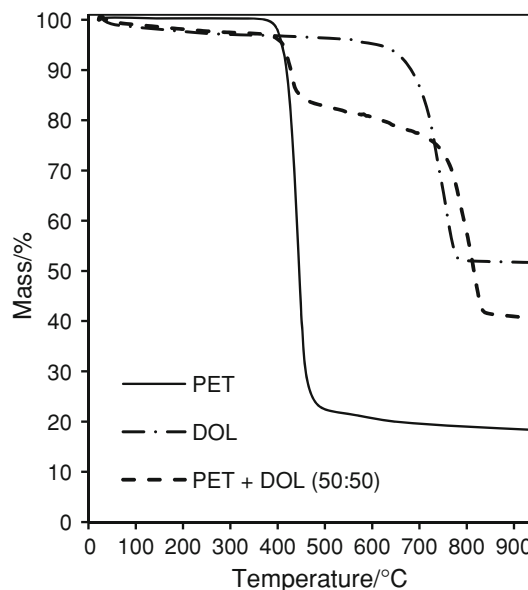
Fig. 1 TG curves for raw PET, raw dolomite (DOL), and raw PET/DOL (50:50) mixture

The raw PET material reveals a rapid one-step decomposition that could be observed in a temperature range from ca. 380 °C to ca. 470 °C, with the maximum rate at ca. 420 °C. Similar to PET, the natural dolomite also undergoes one-step decomposition, however, at higher temperatures, i.e., from ca. 610 °C to ca. 780 °C. The thermogram measured for the PET/DOL mixture confirms two distinct mass drops accompanying the heating. The first decrease in the mass, observed at temperature ca. 420 °C must be resulting from the thermal decomposition of PET contained in the mixture. The other distinct drop in the mass occurs at temperatures 740–830 °C. Compared to TG results collected for the pure dolomite, this range is slightly shifted to higher temperatures region. Moreover, the residual mass registered after this measurement (41%) is by 6% higher than calculated, taking into account residual masses found after heating of PET and DOL alone. Both, the higher than expected residual mass and the shift in temperature of the second drop in the mass, seem to be effects analogous to those observed for systems consisting of PET and thermally decomposable magnesium compounds, described in detail elsewhere [22]. For that reason we did not perform additional research aiming at explanation of these results.

X-ray diffraction (XRD) results

Representative XRD pattern measured for the material obtained through heating of the raw PET/DOL mixture, is shown in Fig. 2. As expected, presence of both CaO and MgO as dominating inorganic phases in the sorbent, could be certainly confirmed. Taking into account XRD patterns
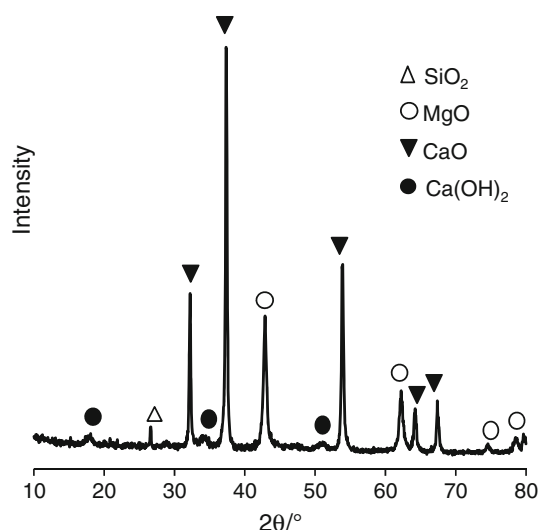
Fig. 2 XRD pattern of the hybrid material obtained through heating of raw PET/DOL (50:50) mixture at 850 °C

Table 2 CaO and MgO mean crystallite sizes in sorbents prepared from PET/DOL 50:50 at different temperatures and from dolomite heated at 850 °C

Preparation temperature/°C	Mean crystallite size/nm	
	CaO	MgO
PET/DOL 50:50 850	71.3	23.1
PET/DOL 50:50 900	56.5	22.1
PET/DOL 50:50 1000	64.3	29.8
DOL 850	195.8	49.8

measured for the raw dolomite (not shown) and for PET/DOL mixture subjected to heating (Fig. 2), liberation of CO_2 during the preparation process could be easily deduced. Such behavior is a known general feature of many carbonates including dolomite. Hence, CaO and MgO are obvious products of the thermal decomposition of the dolomite. Despite the oxides, the XRD pattern measured reveals peaks approving certain content of SiO_2 and $Ca(OH)_2$ in the material. The silica is an impurity naturally present in the mineral (Table 1) and certain amounts of calcium hydroxide must be formed through hydration of the hygroscopic CaO by humidity included in the atmosphere. This apparently takes place during handling of a sample as well as during measurements. All the mentioned phases could be detected also in samples prepared from the other PET/DOL mixtures.

For comparison, sorbent materials were also prepared from the PET/DOL (50:50) mixture at 900 and 1,000 °C. Application of the higher temperatures for preparations did not affect the phase composition of the products. Despite that, the increase in preparation temperature did not cause a significant alteration in the mean size of CaO and MgO crystallites (Table 2).

In contrast, mean crystallite sizes determined for these phases, but formed from the sole dolomite, are considerably larger. Formation of the large agglomerates in the solid remained after heating of the dolomite, must be due to easy sintering of neighboring smaller CaO and MgO species, remaining in a direct contact during thermal treatment. Analogous observations were reported by others [23] studying reaction of CO_2 with lime. On the other hand, the relatively small crystallites found in the hybrid materials must be resulting from an effective separation of fine

dolomite particles by PET material. This reduces possibility of the sintering effect. Thus, formation of the larger species must be diminished. Comparable effects were also observed for other systems, for example composed of carbon and titania [24].

Specific surface areas of the composite materials: an influence of PET/DOL weight ratio and temperature of the preparation process

As displayed on Fig. 3a, relative amounts of PET and dolomite taken for preparations are crucial for nitrogen adsorption at 77 K on obtained products. Nitrogen uptake at relative pressures below 0.5, increases markedly along with PET loading in a raw mixture. The shapes of the presented isotherms at the low relative pressure region, like in type I according to IUPAC recommendation [25], indicate the presence of micropores. Despite that, all the isotherms reveal hysteresis loop between adsorption and desorption branches, like in type IV isotherms. This must be due to a capillary condensation characteristic for mesoporous materials. Hence, the shapes of the measured isotherms can be considered as resultant from overlapping of type I and IV isotherms. In contrast, thermal treatment of the raw PET and dolomite at the same temperature, 850 °C, results in obtaining materials revealing very low N_2 uptake, Fig. 3b. The char obtained from PET shows negligible N_2 adsorption in micropores and adsorption of nitrogen on the solid produced from the sole dolomite proceeds in both micropores and mesopores. For comparison, PET/DOL (50:50)-based sorbent materials were also prepared at higher temperatures, i.e., at 900 and 1,000 °C. Relative position of the measured isotherms (not shown) indicated noticeable decrease in N_2 adsorption along with temperature applied for the preparation process. The observations regarding porous structure of all the materials are well reflected by the calculated BET, total, external, and micropore surface areas (Table 3).

Both BET and total specific surface areas determined for all the hybrid materials range from over 100 m^2 g^{-1} to ca. 350 m^2 g^{-1}, and tend to decrease along with dolomite

Fig. 3 Nitrogen adsorption/desorption isotherms (measured at 77 K) for **a** the composite materials prepared at 850 °C and **b** PET and dolomite, both heated at 850 °C
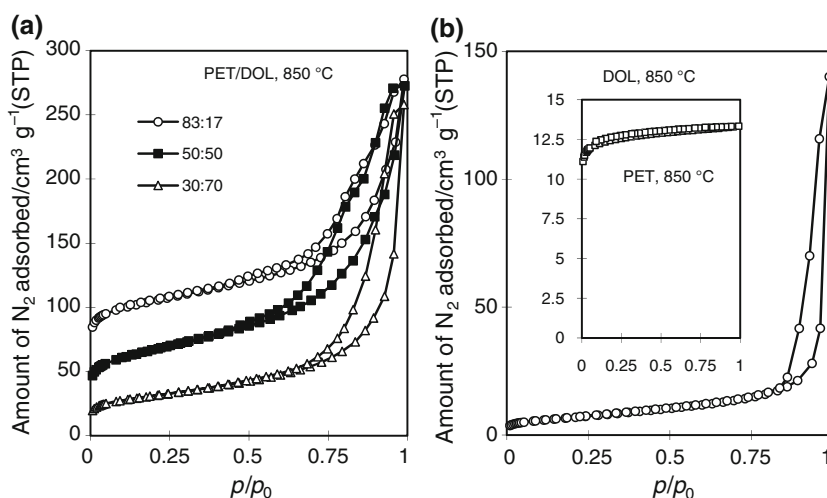
Table 3 Textural parameters calculated from N_2 adsorption data, for PET, dolomite, and PET/MAG materials, all heated at 850 °C

Material/°C	S_{BET}/m^2 g^{-1}	α_s		
		S_{total}/m^2 g^{-1}	S_{ext}/m^2 g^{-1}	S_{micro}/m^2 g^{-1}
PET/DOL 83:17 850	331	347	111	236
PET/DOL 50:50 850	221	256	134	123
PET/DOL 30:70 850	106	114	90	24
DOL 850	25	27	26	1
PET 850	34	37	3	34
PET/DOL 50:50 900	184	203	112	91
PET/DOL 50:50 1000	171	188	110	78

loading in the raw mixtures. Such a trend is known to be resultant from a pore-blocking effect, frequently observed in chemically modified activated carbons or impregnated ones [26]. In the case of PET/DOL-based samples, the regular lowering in pore structure parameters must be caused by increasing contents of CaO and MgO crystallites incorporated into the carbon matrix. Considering the values of the external surface areas and micropore areas presented in Table 3, it may be stated that lowering of micropore area is a key reason why the total area decreases along with loadings of the oxides. The mesopore areas of the resultant materials are not much affected by the PET/DOL ratios. An impact of the preparation temperature on the porosity of the sorbent materials is comparable, however, less obvious. Hence, the decrease in micropore area escalating along with preparation temperature is a cause of specific surface area decrease. This is a known trend reported by others [27]. In contrast to the carbon materials loaded with MgO and CaO, heating of dolomite and PET alone, produces materials revealing very low adsorption of nitrogen and consequently low pore parameters. In view of above observations, an essential role of the dolomite in creation of porosity in the char formed from PET can be evidently

concluded. Taking into account the fact that PET/DOL mixtures consist of decomposable carbonate material and both MgO and CO_2 are generated in the mixture during heating, porosity may be developed in processes analogous to those reported in details in our previous work [20]. Hence, mesopores may be due to MgO and/or CaO presence while CO_2 released from the dolomite may react with the char produced from PET and thus create micropores.

Performance of the composite materials during carbon dioxide capturing and effects accompanying regeneration process

In order to examine capability of the sorbent materials to capture CO_2 gas, appropriate tests were carried out using suitable for this purpose [28, 29] precise thermobalance. Results attained for the sorbents prepared from PET/DOL mixtures are presented in Fig. 4. For reference, results of analogous tests carried out for the pyrolysed PET and dolomite are also shown. Materials prepared at 850 °C were chosen for testing because higher preparation temperatures adversely influenced pore structure parameters of the products.

Two series of measurements were conducted, both beginning with CO_2 adsorption step carried out at 30 °C. However, while desorption of CO_2 in nitrogen atmosphere for the first series was conducted at temperatures up to 200 °C (Fig. 4a), samples subjected to the second series were heated to 850 °C (Fig. 4b).

In both series of measurements, comparable increases in a mass of the tested samples can be observed during their exposition to CO_2. Uptake of the gas markedly increases along with the PET/DOL ratio used for preparations, to achieve ca. 9 wt% for material holding the lowest amounts of MgO and CaO and, at the same time being the richest in carbon material. It should be noticed that at the beginning of CO_2 sorption branches, TG curves registered for materials poorer in the oxides are steeper compared to those holding more oxides. This directly confirms an increase in the rate of CO_2 sorption by the hybrid sorbents along with the PET/DOL ratio. Taking into account textural parameters (Table 3) of the studied composite materials, one may notice a known tendency [30], i.e., an increase in amount and rate of CO_2 adsorbed along with micropore area.

In each run, exchanging CO_2 with N_2 results in a rapid mass drop observable already at the beginning of heating to either 200 or 850 °C. This immediate loss confirms that at least some quantities of total CO_2 captured were weakly adsorbed on the sorbent materials. Residual masses of the samples registered after heating to 200 and 850 °C are very different. As a rule, mass drops determined for the materials exposed to N_2 at the lower temperature are lesser compared to those measured for samples heated to 850 °C. Moreover, while CO_2-saturated PET/DOL 83:17 sample loses upon heating to 200 °C ca. 5% of its mass related changes registered for two other hybrid materials are only ca. 3 wt% and ca. 0.5 wt% for PET/DOL 50:50 and PET/DOL 30:70, respectively. So, the residual mass determined after heating to 200 °C increases along with MgO and CaO loading in the tested material. A noteworthy fact is that the residual masses were always above 100%. This confirms that heating to 200 °C is not enough for complete regeneration of the CO_2-saturated PET/DOL-based materials. In view of above discussion, it may be stated that some part of CO_2 captured by the sorbents is fixed weakly due to physical adsorption or weakly chemisorbed, and another portion is bound strongly, presumably due to some chemical interaction between CO_2 and the oxides included in the sorbent materials.

Confirmation of this statement comes from results gained for DOL and PET-based samples. CO_2 uptakes revealed by the materials are quite low, and reach only ca. 2 wt%. However, both of them behave very different during next steps of the TG measurements. Heating of the first material (originally mixture of mainly MgO and CaO) in nitrogen atmosphere to 200 °C causes almost no change
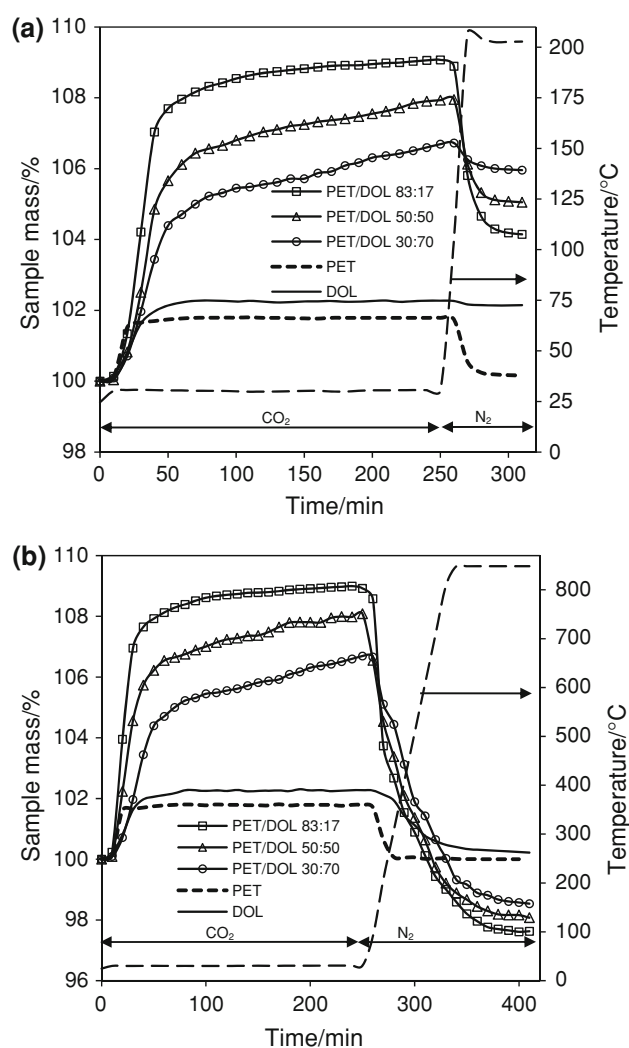

Fig. 4 Results of CO_2 sorption (at 30 °C) and desorption at **a** up to 200 °C and **b** up to 850 °C

in the mass. On the other hand, exposing to analogous conditions of the sole char formed from PET results in a complete desorption of the CO_2 previously adsorbed. These facts evidently point the oxides as accountable for the strong fixing of the CO_2. That is why the hybrid materials richer in CaO and MgO fix more CO_2 bound strongly. On the other hand, significant amounts of CO_2 adsorbed weakly by samples poor in the inorganic additives, must be related to adsorption in micropores. As a consequence, performances of more microporous sorbents, i.e., those containing less MgO and CaO, are superior in this case.

Following considerations given above, the low CO_2 uptake by the mixture of MgO and CaO formed from the dolomite seems to be divergent from the trends observed for strong binding of CO_2. Because reaction between the solid and the gas is predominantly a surface process, the low performance of the mixture must be resulting from

comparatively large CaO and MgO crystallites, Table 2, [23]. The large species reveal low specific surface area and thus low contact area with an adsorbate. For that reason, amounts of CO_2 captured by the sole dolomite-based sorbent is so low. Lack of microporosity in the material must be another reason of the poor performance.

Very interesting and unexpected results were collected for the second series of measurements, Fig. 4b. Heating of the CO_2-saturated hybrid materials to 850 °C is accompanied by an unpredicted reduction of sample mass, to 2–3% below an original level. On the contrary, heating of the materials obtained from sole PET or sole dolomite, results in expected return of the mass to the initial level, without any additional loss. Hence, desorption of CO_2 from the MgO/CaO-loaded nanoporous carbons must be accompanied by some processes resulting in the noticeable loss. Considering results of our related studies, the mass decrease observed during heating of the hybrid materials to 850 °C, appears to be due to the gasification of the carbon by the strongly fixed CO_2, being freed from the exhausted hybrid materials during regeneration. Proceeding of such reaction was confirmed by temperature programmed desorption studies reported by us in our earlier work [22].

In view of above statements, the hybrid materials supporting more oxides are capable to fix strongly more CO_2. As a natural consequence, larger amounts of the gas are released at high temperatures from the sorbents richer in MgO and CaO. Thus, more CO_2 is available for the reaction with the carbonaceous component of the hybrid sorbents while regenerated. In effect, determined mass losses tend to be more apparent for sorbent materials containing more MgO and CaO. As confirmed by TG curves in Fig. 4b, the gasification process considered here can take place only in hybrid sorbents and does not occur when non-hybrid samples, i.e., the char or MgO/CaO alone, are examined according to the same manner. Weak adsorption of CO_2 and easy desorption of the gas at relatively low temperature must be a reason of why such a loss is not observed for the char alone. On the other hand, the dolomite-based sample consists only of thermally stable oxides and do not contain any carbon material. For that reason, no additional loss due to carbon gasification by the CO_2 can take place even the gas is strongly fixed and released at high temperature.

Conclusions

Results described in this work led us to several important findings and conclusions. The preparation method proposed is simple and readily available raw materials can be used. We confirmed that employing natural dolomite for preparations may result in twofold benefit. During preparations, the mineral undergoes thermal decomposition to MgO and CaO and to CO_2 gas. These products are capable to create either mesopores or micropores in suitable carbon materials, like the char formed from PET. Hence, dolomite may act as a specific activating agent to produce porous carbons from the synthetic precursor. The second advantage is that the oxides remain in the structure of the product and play a role of a specific agents enhancing sorption of acidic adsorbates like CO_2.

Because resultant sorbent materials reveal significant microporosity, a part of the total amount of CO_2 captured is weakly fixed. On the other hand, presence of the metal oxides results in proceeding of a chemical interactions resulting in a strong binding of the gas. In both cases, heating of the CO_2-saturated hybrid sorbents in an inert atmosphere results in desorption of the gas. However, while physisorbed CO_2 can be released easily at relatively low temperature, portions of the gas fixed strongly require much more drastic conditions to be desorbed. Thus, CO_2 captured by the sorbents can be released in a controlled way: a part of CO_2 can be desorbed at low temperatures, and the other parts, strongly bound, require more rigorous temperature conditions to be desorbed.

The sorbents studied can be regenerated and therefore be used more than one time. However, because a part of carbon material is lost during regeneration process, the contents of MgO and CaO contained the in regenerated material must gradually increase. This may entail changes in parameters and in performance of the sorbent.

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