

Catalytic properties of activated carbon surface in the process of adsorption/oxidation of methyl mercaptan

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Abstract

Activated carbons of different origins were used as adsorbents of methyl mercaptan (MM). Before the MM breakthrough capacity tests were carried out, the surface of carbons was characterized from the point of view of its chemistry (Boehm titration) and porosity (adsorption of nitrogen at its boiling point). The results showed that the ability of carbon to adsorb methyl mercaptan depends strongly on its surface chemistry, particularly on the presence of basic oxygen-containing groups and ash content. Catalytic effect of one metal, iron, was studied in more details. It was found that introduction of iron enhances the removal capacity significantly as a result of electron transfer reaction in which thiolate ion is oxidized to dimethyl disulfide (DMDS). This reaction likely involves the reduction of iron sites, which are regenerated after further re-exposure to oxygen. DMDS as a main reaction product is strongly adsorbed in small pores. Water is required for the formation of DMDS since it facilitates the dissociation of MM. That dissociation occurs in water film when the pH of the local system is greater than the apparent pK_a of MM in the confined pore space.

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1. Introduction

Natural gas is a vital component of the world's supply of energy. It is one of the cleanest, safest, and most useful of all energy sources. Because natural gas generated energy provides means for day-to-day needs and activities and energy production from fossil fuel has detrimental effects on the environment, the US Department of Energy is developing improved natural gas power systems that are cleaner and more fuel efficient-fuel cells. Fuel cells are expected to play a major role in the nation's energy future. They are pollution-free power sources capable for on-site power generation. Since there is no combustion, there is no emission of the pollutants commonly produced by boilers and furnaces. For fuel cell application, natural gas is converted to H_2 and CO in a steam-reforming reactor, which yields the highest percentage of hydrogen [1–3].

Natural gas fuel contains naturally occurring reduced sulfur compounds such as hydrogen sulfide, mercaptans and tetrahydrothiophene. These compounds, due to their ability to poison the catalyst, are detrimental to subsystems within the fuel processor and to the fuel cell stacks and must be completely removed from the fuel prior to the fuel reforming operation.

In this paper, activated carbons are used as adsorbents for the removal of methyl mercaptan, an odoriferous sulfur-containing compound, from air. It is commonly added to natural gas for leak detection purposes. Activated carbons are well known for their exceptional ability to adsorb some acidic gases [4–9]. The application of activated carbons to remove hydrogen sulfide (one of the natural gas contaminants) is widely described in literature.

The main objective of this research is to study the efficiency of activated carbons for methyl mercaptan (MM) removal and to link their performance as MM adsorbents to their surface and structural characteristics. It was described previously, that among the features of carbon, which are responsible for MM immobilization at ambient conditions,

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are the pore size and pore volume [10–13], surface oxygen groups [11], surface pH [12], and the affinity of carbon to adsorb water [10,12]. Results described in this paper address subtle but important effects of surface basicity and the inorganic matter content and one of its main constituents, iron, on the performance of carbons as methyl mercaptan adsorbents. Chemical and physical features of the methyl mercaptan molecule [14] show that it can be adsorbed at room temperature on the activated carbon surface in small pores via dispersive interactions. On the surface of the carbons, MM is converted to dimethyl disulphide (DMS) whose adsorption at room temperature is much stronger than that of MM [14]. It has been pointed out in the literature that different functional groups on the surface and/or metal ions such as iron can catalyze the oxidation of mercaptans to disulfides [14–18,20]. Moreover, the impregnation of activated carbons with various chemicals such as potassium iodide, potassium iodate, potassium carbonate and ammonia enhances their sorption capacity several times [18].

2. Experimental

2.1. Materials

Adsorption of MM was performed on several samples of activated carbons of various origins. Among the carbons studied were BAX-1500 (wood based carbons-Westvaco), S208 (coconut shell based carbon-Waterlink Barnabey and Sutcliffe), Centaur[®] (bituminous coal based catalytic carbon-Calgon), BPL (bituminous coal-Calgon), and PCB (coconut shell-Calgon). The initial samples were washed in a Soxhlet apparatus to a constant pH of a leachate. To account for the effect of ash and its iron constituents, the PCB sample (25 mL) was impregnated with 0.05 M solution of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (100 mL), stirred for 20 h, then heated at 200 °C for 3 h and washed with water in a Soxhlet apparatus to remove excess of iron and chloride. Since introduction of iron caused a decrease in the pH, the obtained sample was stirred in a small volume of 0.01 M NaOH for 5 h to increase the pH to the level where dissociation of CH_3SH is enhanced [10]. The final sample is designated as PCB/Fe.

2.2. Methods

2.2.1. CH_3SH breakthrough capacity

Dynamic tests were carried out at room temperature to evaluate the capacity of the sorbents for CH_3SH removal under wet conditions. Adsorbent samples were ground (1–2 mm particle size) and packed into a glass column (length: 370 mm; internal diameter: 9 mm; bed volume: 6 cm³) and prehumidified with moist air (relative humidity 80% at 25 °C) for 1 h. The amount of water adsorbed was estimated from the increase in the sample weight. Moist air (relative humidity 80% at 25 °C) containing 0.3% (3000 ppm) CH_3SH was then passed through the column of adsorbent

at 0.5 L/min. The breakthrough of CH_3SH was monitored using a Micromax monitoring system (Lumidor) with an electrochemical sensor calibrated with MM. The test was stopped at the breakthrough concentration of 50 ppm. The adsorption capacities of each sorbent in terms of mg of CH_3SH per gram of carbon were calculated by integration of the area above the breakthrough curves, and from the CH_3SH concentration in the inlet gas, flow rate, breakthrough time, and mass of sorbent. For each sample the CH_3SH test was repeated at least twice. The determined capacities agreed to within 4%.

2.2.2. pH of carbon surface

Carbon powder (0.4 g) was placed in 20 mL of water and equilibrated during the night. Then the pH of the suspension was measured. For exhausted samples, an additional letter 'E' is added (pHE).

2.2.3. Sorption of nitrogen

Nitrogen isotherms were measured using a ASAP 2010 (Micromeritics) at –196 °C. Before the experiment, the samples were heated at 120 °C and then outgassed overnight at this temperature under a vacuum of 10^{-5} Torr to a constant pressure. The isotherms were used to calculate the specific surface areas (S), micropore volumes (V_{mic}), total pore volumes (V_{t}), average micropore sizes (L_{mic}), and pore size distributions (DFT) [21–23].

2.2.4. Thermal analysis

Thermal analysis was carried out using TA Instruments Thermal Analyzer. The instrument settings were: heating rate of 10 °C/min in nitrogen atmosphere with 100 mL/min flow rate.

2.2.5. Ash content

Total ash content was evaluated as residue after heating in air to 1000 °C.

2.2.6. Boehm titration

Surface chemistry was evaluated using the Boehm titration method [24]. For the purpose of this research, a simplified approach was used for determination of total number acidic or basic groups. One gram of carbon sample was placed in 50 mL of 0.05 N sodium hydroxide or hydrochloric acid. The vials are sealed and shaken for 24 h and then 10 mL of each filtrate was pipetted and the excess of base or acid was titrated with HCl or NaOH. The numbers of acidic sites were calculated under the assumption that NaOH neutralizes acidic groups and HCl neutralizes basic groups.

2.2.7. XRF

X-ray fluorescence analysis was applied to study the elements present in the carbon. For this purpose, SPECTRO Model 300T Benchtop Multi-Channel Analyzer from ASOMA Instruments Inc. was used. It contains a titanium

(Ti) target X-ray tube with Mo-2mil filter and high-resolution detector without a filter. A home-developed method was selected to identify the metals. Acquisition conditions were the following: voltage, 24 kV; current, 80 μ A; count time, 40 s and warm-up, 4 min. Instrument reference temperature: 20 °C and background conditions: lower ROI, 12.000 and upper ROI, 17.000. The amount of iron in carbon was determined based on the calibration curve.

3. Results and discussion

To investigate the ability of activated carbons to adsorb methyl mercaptan, breakthrough tests were carried out at room temperature. Methyl mercaptan breakthrough curves obtained for the samples studied are collected in Fig. 1. Based on the breakthrough times, the performances of the carbons differ significantly. Methyl mercaptan adsorption capacities for the carbons along with the amount of water pre-adsorbed are presented in Table 1. The highest amount adsorbed was found for the Centaur[®] carbon even though the breakthrough test had to be stopped at 26 ppm due to the fact that strongly catalytic nature of this carbon facilitates fast oxidation of MM to dimethyl disulfide (DMDS), which is not detected by the sensor used in our experiments. The capacities of BPL and S208 carbons are also high compared to those for BAX and PCB. To understand what governs the process of MM adsorption on different carbon samples, a deeper insight on the nature of carbons under investigation and the surface features that lead to the differences in their capacities is needed.

A chemical analysis of the carbon surface was done using Boehm titration [24]. The amounts of basic and acidic groups present on the surface of the carbons studied are summarized in Table 2. As expected, the larger the amount of basic groups the higher the pH of the carbon surface. The basicity of the carbon surface is the result of the presence of

Table 1

MM breakthrough capacities and the amount of water pre-adsorbed for the carbons studied

Sample	Amount of water adsorbed (mg/g)	Amount of MM adsorbed (mg/g)
BAX	163.4	28.2
PCB	78.2	85.5
PCB/Fe	89.7	284.0
S208	92.6	162.2
BPL	98.3	172.6
Centaur [®]	98.3	400.0

oxygen-containing surface groups of pyrone-type and/or oxygen-free Lewis basic sites [25–29]. Moreover, ash and its chemical composition can also affect the overall basicity of activated carbons. Pyrone-like structures are combinations of carbonyl and etheric non-neighboring oxygen atoms at the edges of the basal plane and are formed by air re-exposure of heat-treated carbons [27–29]. Such basic oxygen containing groups on the carbon surface could affect the dissociation of MM and oxidation of CH_3S^- ions to disulfides [4,14,16–18]. They may also attract MM via weak acid–base interactions. To see this effect, the density of surface groups was calculated taking into account the numbers of groups and the specific surface areas collected in Table 3. Fig. 2 shows the dependence of MM adsorption capacity on the density of basic groups. It is interesting that a good correlation is found for all the samples except PCB. Both BPL and S208 samples are very active towards the adsorption of MM even though they are less basic than PCB. This suggests a contribution of other factors, such as catalytically active ash, to the adsorption/oxidation process.

Since the inorganic phase present in a certain amount in all the carbon samples can affect their respective MM adsorption/oxidation process, its quantity for each sample was evaluated using thermal gravimetry [10,11,13]. The amounts of ash are collected in Table 2. The results indicate

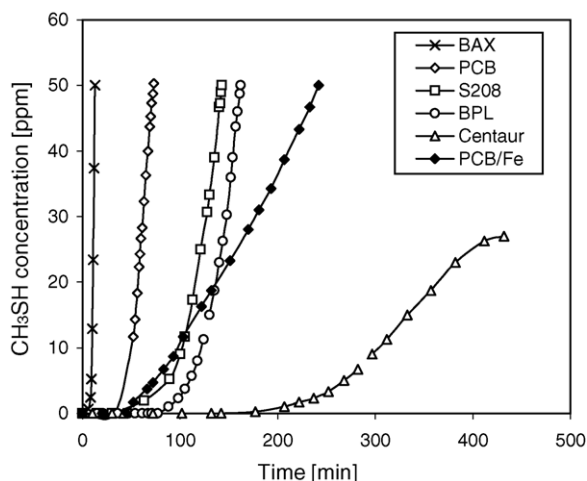


Fig. 1. MM breakthrough curves for the carbons studied.

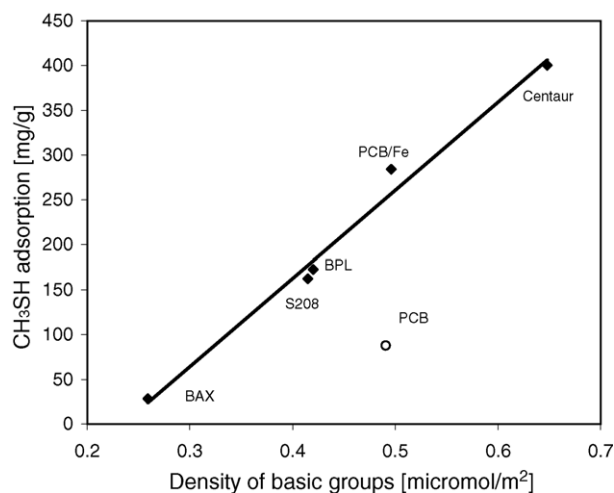


Fig. 2. Dependence of MM adsorption capacity on the density of basic groups.

Table 2
pH of the carbon samples, ash content, and results of the Boehm titration (numbers of surface groups)

Sample	pH	Ash content (%)	Basic (mmol/g)	Acidic (mmol/g)	All (mmol/g)
BAX	6.00	2.11	0.35	0.9	1.25
PCB	7.74	2.76	0.50	0.20	0.70
PCB/Fe	7.80	0.84	0.45	–	–
S208	6.98	1.22	0.45	0.30	0.75
BPL	6.97	8.96	0.40	0.45	0.85
Centaur®	6.66	2.90	0.40	0.25	0.65

that BPL has the highest ash content, which could contribute to its good performance in MM adsorption/oxidation. On the other hand, the amount of ash in PCB is similar to that found in the other carbons studied.

Since for the PCB sample, the ‘crude’ ash content analysis failed to explain the deviation from the general trend of MM capacity dependence on surface basicity, the evaluation of quality and relative quantities of metals, which may affect the capacity, mainly potassium and iron, [18,19] was carried out using the XRF method. The results are shown in Fig. 3. BPL carbon is obviously rich in iron and its amount is much higher ($\approx 0.45\%$) than that for the other samples studied. As shown above, its MM removal capacity for this carbon is the highest. On the other hand, a good performance of S208 can be linked to the presence of potassium, which is a natural component of a coconut-shell precursor. The poor performance of BAX can be related not only to its relatively low ash content but also to its highest surface acidity.

To check the hypothesis about the crucial role of iron in the MM oxidation process, the PCB sample was impregnated with iron chloride which was mainly converted to oxides as described in the materials’ preparation procedure. The impregnation process was designed not to significantly affect the pore sizes of the material. In fact, the pore size distribution presented in Fig. 4 shows only slight changes in the volume of pores, mainly in large micropores after the modification process. Although all carbons but BAX and BPL can be considered as microporous, the latter one has the most open porous structure. The iron content in PCB/Fe was evaluated using XRF and the results are included in Fig. 3. It is clearly seen that after introduction of iron, its content for PCB carbon is comparable to that for BPL coal based carbon (0.4%), but the total ash content becomes even lower than

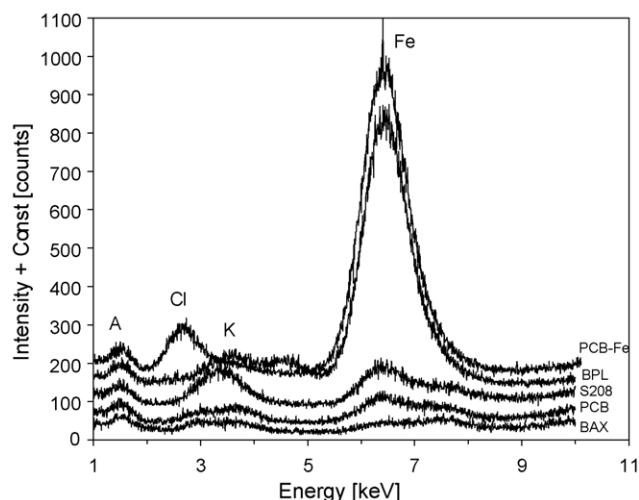


Fig. 3. XRF analysis for the carbons studied.

that in the initial PCB sample (Table 2). This apparent inconsistency may be the result of dissolution of some silica or alumina components in NaOH during the surface neutralization process. Moreover, after modification, a chloride peak appears which most likely is the result of incomplete washing. That increase in iron content affects the performance of PCB carbon in the process of MM adsorption oxidation. After iron modification, the change in the MM capacity of PCB/Fe sample versus surface basicity follows the trend generally observed for the other carbons. It is interesting to note that the breakthrough curve for PCB/Fe (Fig. 1) differs from that one obtained for its unmodified counterpart. Its shape suggests two different slopes, which may represent different kinetics of the adsorption process, related to the carbon phase and the catalytic participation of iron.

Since the presence of iron and potassium has the obvious effect on the behavior of carbons, the mechanisms of oxidation on those catalytic centers should be established. This should be done without neglecting the main, pH dependent, mechanism of CH_3SH oxidation on the activated carbon surface described elsewhere [10–13]. Briefly, in both ‘island’ and ‘dry’ mechanism, it is assumed that that adsorbed MM reacts with oxygen.

In the ‘dry’ mechanism, MM and oxygen are adsorbed from a gas phase on the dry carbon surface, where reaction takes place [12]. Water and DMDS are the reaction products.

Table 3
Structural parameters of carbons calculated from nitrogen adsorption at -196°C

Sample	S_{DFT} (m^2/g)	V_{mic} (cm^3/g)	V_t (cm^3/g)	$V_{<10 \text{ \AA}}$ (cm^3/g)	$V_{<50 \text{ \AA}}$ (cm^3/g)	$V_{\text{mic}}/V_{\text{tot}}$	L_{mic} (\AA)
BAX	1351	0.505	1.290	0.101	1.086	0.392	13.2
BPL	953	0.373	0.688	0.163	0.587	0.542	11.7
PCB	1018	0.431	0.546	0.247	0.478	0.789	10.6
PCB/Fe	907	0.351	0.447	0.243	0.377	0.785	9.4
S208	1084	0.439	0.465	0.299	0.454	0.944	9.7
Centaur®	617	0.243	0.293	0.161	0.257	0.829	9.5

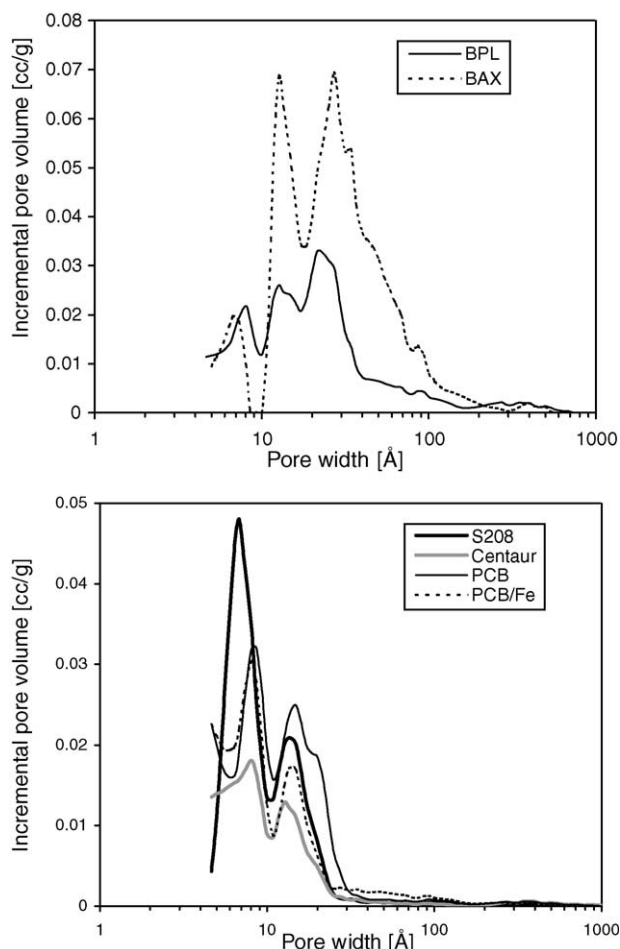


Fig. 4. Pore size distributions (DFT) for the carbons studied.

The latter species is adsorbed on the carbon surface while the former one is desorbed.

The 'island' mechanism assumes that adsorption takes place in wet conditions. Water adsorbed on the carbon surface is able to form clusters or small islands, where MM and oxygen first are dissolved in molecular form and later, depending on the pH, MM can dissociate to thiolate ions [12]. Oxidation occurs due to the surface reaction between adsorbed thiolate ions and dissociatively adsorbed oxygen in water 'islands' and/or between adsorbed MM and oxygen on a dry part of the carbon surface. The product of reaction, DMDS, is adsorbed in a molecular form on the carbon surface.

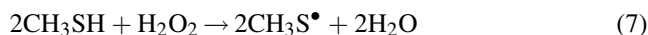
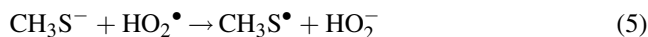
For the dry mechanism, one cannot expect any pH dependence for the adsorption capacity due to the lack of water on the surface. The 'island' mechanism proposes two scenarios, which can coexist. While the first one, on the dry part of the surface, is similar to the 'dry' mechanism, the second scenario is definitely pH dependent due to the presence of a dissociation step. It follows that in the case of MM adsorption on activated carbons, the pH dependence, however expected due to the chemistry of adsorbate, cannot be so clearly seen as in the case of hydrogen sulfide removal described elsewhere [5,30,31]. It was found that to improve

the feasibility of MM removal the pH of the carbon surface, which is a crucial parameter, should be greater than 7.6 to enable the dissociation of MM and formation of thiolate ions. That value was found taking into account the equilibrium constants for the reactions and processes taking place on the surface [12].

Although the pH of most of our carbons is less than 7.6, it should be taken into consideration that we measure the pH of the suspension, which can be different from the pH inside the carbon pores. Nevertheless, the lowest pH of the BAX carbon could be a good reason to explain its poor MM adsorption capacity.

The effect of potassium on the local pH can also explain the enhanced adsorption of MM on S208 carbon. Water-soluble potassium species increase the pH and thus, promotes the dissociation of MM resulting in more thiolate ions, which are further oxidized to DMDS.

To explain the influence of iron, its catalytic redox abilities have to be explored. It is possible that besides the mechanism described above, the following reactions promoted by Fe^{3+} occur in the presence of moisture and oxygen from air:



As seen from the above listed reactions, the role of iron is to promote formation of thiolate radicals and reduction of oxygen resulting in the presence of very active superoxide species, which form radicals, either in wet or dry conditions of the MM removal process.

Although it is understandable that the surface chemistry has complex and significant effects on the performance of activated carbons as MM adsorbents, the process of adsorption/oxidation cannot be effective without a developed pore structure where the products of surface reactions have to be stored. Analyzing the structural parameters of carbons collected in Table 3, differences in porosity can be seen. Based on those results, BAX is the most porous sample and Centaur® the least porous sample of all carbons studied. This is supported by the results of pore size distributions (PSDs) presented in Fig. 4. While all of the structural parameters indicate that BAX carbon has the superior porous structure, its MM removal capacity is very small. Besides the acidic nature of the carbon mentioned above, another reason for its poor performance lies in its small volume of pores less than 10 Å and its large average micropore size. Small sizes of MM (4.2 Å) and DMDS (5.3 Å) molecules [32] suggest that very small pores should be the most active for MM

adsorption/oxidation. In such pores, the adsorption forces are stronger and adsorption energy is high due to the overlapping of the adsorption potentials. On the other hand, in the case of BPL whose volume of small pores is not exceptional as well, a plausible explanation for its high MM adsorption capacity is in surface chemistry and the presence of iron, which acts as a catalyst of the oxidation process. As indicated above, a lack of chemically active centers on the PCB carbon surface is an important factor suppressing the oxidation process. High microporosity is not able to compensate that. However, after introduction of iron, a decrease in surface area, total pore volume and volume of micropores was observed; the volume of pores smaller than 10 Å remained the same and average micropore size was significantly reduced (Table 3). Smaller micropore size increases the energy of adsorption, which could have also led to an increase in adsorption capacity. Centaur[®] carbon is the only carbon with all the characteristics needed for efficient MM removal. Its catalytic nature is supported by a large relative volume of micropores and very small size of micropores [33].

4. Conclusions

This work demonstrated the efficient application of activated carbons for removal of methyl mercaptan from air. The results suggest that desulfurization of gaseous fuels, such as digester gas or natural gas, would also be efficient providing that a small amount of oxygen needed for oxidation is present. The research reveals the complexity of the process of MM adsorption/oxidation on different carbon samples. The nature of each individual sample is unique and affects the adsorption process. Chemistry of the carbon surface is very important for the efficient MM removal. The adsorption capacity of carbons depends on the density of basic oxygen-containing groups on the surface as well as the presence of catalytically active metals in an inorganic matter. Although the results showed that the differences in structural characteristics are not crucial for the removal process, adsorption/oxidation cannot be effective without a developed pore structure and presence of small pores, where the product of methyl mercaptan adsorption/oxidation—dimethyl disulfide is stored.

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