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Adsorption-catalytic process for carbon disulfide removal from air

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Abstract

Adsorption-catalytic process for carbon disulfide removal by means of the use of adsorbent and catalysts on the basis of carbon materials is developed. The process consists of adsorption of carbon disulfide from purified air, its steady desorption in inert gas flow, hydrolysis of carbon disulfide with hydrogen sulfide yielding, and oxidation of generated hydrogen sulfide to elemental sulfur. Efficient catalysts for carbon disulfide hydrolysis (5% TiO_2, 1% CaO/KAU) and hydrogen sulfide oxidation (Fe-EDTA/carbopon) are developed. The most favorable parameters, which provide a complete carbon disulfide removal from air, are determined for all steps of the purification process.

Keywords: Adsorption-catalytic process; Carbon disulfide; Hydrolysis

1. Introduction

The use of carbon disulfide as a fumigant commonly causes public health problems and accordingly, necessitates intermittent rendering harmless the air in storages. Carbon disulfide removal is also a problem of current interest for viscose-manufacturing plants where carbon disulfide is used in large quantities for cellulose xanthate production.

Since CS_2 possesses high toxicity with a maximum permissible concentration in air of 0.005 g/m^3, its emission into atmosphere even in small amounts is inadmissible.

Air purification from CS_2 is a sufficiently complicated task, which is solved in different ways. Thus, the authors [1] recommend the use of NaOH aqueous solution as an absorbent for purification of waste gases of viscose fibre production from sulfur compounds (H_2S, CS_2). It is suggested to desorb absorbed carbon disulfide from the absorbent by heating, condense it and return to the production cycle, while air outlet the absorber is directed to a column with activated carbon for adsorption recovery of residual CS_2.

In our opinion, CS_2 recycle can be expedient only at relatively high concentrations otherwise the process will be very power consuming. Moreover, it is not clear what to do with the spent activated carbon that contaminates adsorbed CS_2.

To remove CS_2 from gases, liquid organic absorbents are proposed: a mixture of heterocyclic nitrogen-containing compounds and aliphatic amine alcohols [2], on one hand, and aliphatic polyamines [3] on the other. Neither the opportunity of regeneration of these compounds, nor utilization of the formed products – dithiocarbamate salts – is reported in the patents.

According to the process disclosed in [4], CS_2-containing air undergoes hydrolysis with water vapour over the catalyst (Pd/C, Pd/SiO_2 or H_3PO_4/Al_2O_3) at elevated temperatures. Gas flow outlet catalytic reactor, which contains the products of oxidizing hydrolysis of carbon disulfide (SO_2, H_2S and CO_2), is treated with aqueous alkaline solution. The latter generates wastewaters, which, in turn, contain alkaline metal sulfites, sulfides and carbonates. There is no information in the patent regarding technology for the wastewaters neutralization.

According to the process [5], sulfur compounds, which are produced in cellulose processing, are burnt in air excess

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at 800 °C. It is suggested that sulfur-containing compounds including CS_2 undergo catalytic oxidation at 300–500 °C [6,7].

It is necessary to note that thermal and thermocatalytic processes for CS_2 and other sulfur compounds oxidation demand significant power consumption due to an unavoidable need to heat the whole volume of the purifying air for high temperatures. In doing so, sulfur dioxide is one of the main products of sulfur compounds oxidation. Sulfur dioxide neutralization requires a large volume of alkali consumption and is connected with the wastewaters generation that contain alkaline metal sulfites, which are also necessary to remove.

In our opinion, it is more reasonable to use adsorption-catalytic approach developed by the present authors. The suggested approach consists of CS_2 adsorption from air, the following desorption in an inert gas flow, CS_2 hydrolysis with hydrogen sulfide yield and oxidation of the latter to elemental sulfur.

2. Experimental

Various carbon materials (CM) were tested as catalyst supports (Table 1). The catalysts for CS_2 hydrolysis were made by varying both active component composition (TiO_2 and CaO content) and preparation conditions. CM were impregnated with a solution of titanium and calcium chlorides. A number of consequent reactions proceed in the case of $TiCl_4$ interaction with water. Titanium hydroxychlorides of variable composition and HCl are formed as the products. The samples were treated by ammonia and water vapour to neutralize HCl and to convert titanium hydroxychlorides and calcium chloride into corresponding hydroxides. Then, the samples were calcined in a nitrogen flow at 450 °C to convert titanium and calcium hydroxides into corresponding oxides and also to remove NH_4Cl being formed. Different conditions of the catalysts preparation are given in Table 2.

The interaction of calcium chloride, HCl and titanium hydroxychlorides with ammonia can proceed with different level of conversion degree depending on preparation conditions. Unreacted chlorides can block active sites of the catalyst; thus, the samples were washed off after calcination until Cl^- ions were absent in rinsing water.

In order to choose the most efficient catalyst from a large number of synthesized samples (Table 3) and provide an immediate, sufficiently correct information for the catalyst's activity, the experiments were carried our employing a pulse-type microcatalytic gas chromatography reactor. The catalyst sample of 0.02 g was loaded into the reactor of 3 mm diameter and held in He flow (60 ml/min) at 300 °C over 1 h. Then, 0.4 μl of carbon disulfide and 0.24 μl of water (CS_2:H_2O molar ratio is 1:2) were injected into the reactor by means of a syringe.

The chromatographic column of 3 m length and 3 mm diameter with polysorb-1 as a stationary phase was used to separate initial reactants from the hydrolysis products.

The catalysts of H_2S oxidation were prepared by impregnation of the CM samples with complexonate Na_2[Fe-EDTA(OH)] solution (concentration 0.26 mol/l, pH 8.2). The impregnated sample was taken from the solution and demoisturized a little by means of a filter paper. A part of the damp sample was used to measure its activity. Another one was used to determine the active component content in the catalyst. The active complex was washed away from the sample and iron content in the obtained solution was determined using atomic-absorptive spectroscopy.

Table 1
Nature and physical–chemical characteristics of carbon materials

Number	Carbon material	Origination	Surface area (by nitrogen adsorption) (m^2/g)	Average pore diameter (Å)	Thermostability limit (°C)
1	KAU granulated activated coal	Fruit seeds	950	28	400
2	SAU granulated activated coal	Synthetic polymer	830	4	180
3	Carbon linen "carbopon"	Viscose fibre	780	23	150

Table 2
Variants of preparation of the catalysts

Number	Steps of the samples treatment after impregnation						
	Drying up to air-dry state	Treatment in N_2 flow saturated by NH_3 at 25 °C over 1 h Temperature of NH_4OH solution 25 °C	Treatment in N_2 flow saturated with NH_3 at 350 °C over 2 h Temperature of NH_4OH solution (°C)				Calcination of N_2 flow at 450 °C over 2 h
			25	50	70	90	
1	–	$+^{(1)}$	–	–	–	–	$+^{(2)}$
2	–	$+^{(1)}$	$+^{(2)}$	–	–	–	$+^{(3)}$
3	–	$+^{(1)}$	–	$+^{(2)}$	–	–	$+^{(3)}$
4	–	$+^{(1)}$	–	–	$+^{(2)}$	–	$+^{(3)}$
5	–	$+^{(1)}$	–	–	–	$+^{(2)}$	$+^{(3)}$
6	$+^{(1)}$	$+^{(2)}$	$+^{(3)}$	–	–	–	$+^{(4)}$

Comment: $+^{(n)}$, sequence of stages.

Table 3
Effect of composition and conditions of the catalysts preparation on their activity in CS_2 hydrolysis (catalyst portion, 0.02 g; He flow rate, 60 ml/min)

Catalyst support	Active components (%, w)	Variant of preparation (from Table 2)	Degree of chlorides hydrolysis (%)	Washing of Cl^--ions	CS_2 conversion degrees (%)
KAU	0.5 CaO, 5.0 TiO_2	1	44	–	33.8
				+	36.9
SAU			40	–	20.5
				+	21.6
Carbopon			4	–	5.9
				+	5.9
KAU	1.0 CaO, 5.0 TiO_2	1	50	–	26.3
				+	34.9
		2	74	–	30.8
				+	45.9
		3	65	–	31.8
				+	38.8
		4	70	–	28.6
				+	38.9
		5	71	–	27.4
				+	39.7
		6	84	–	26.3
				+	56.0
	1.0 CaO	3	61	–	21.6
				+	25.1
	5.0 TiO_2	3	65	–	34.9
				+	26.3
	1.0 CaO, 10.0 TiO_2	3	69	–	29.6
				+	28.6

The measurements of activity of the CM and the catalysts on their basis were carried out in a flow reactor (d_{int} = 0.75 mm, fixed bed) at room temperature. The gas mixture (0.03 vol.% H_2S in air) was directed into the reactor with a damp sample. Space velocity of the gas mixture comprised 850 h^{-1} (0.07 mg H_2S/g_{CM} min). To characterize the efficiency of the research samples, H_2S breakthrough time was measured.

Experiments for adsorption-catalytic air purification (CS_2 hydrolysis + H_2S oxidation) were carried out in a laboratory unit having two flow reactors with a fixed catalyst bed (Fig. 1).

Air flow from the cylinder 1 was directed through the rheometer 7 into the saturator 9 with carbon disulfide. To decrease carbon disulfide evaporating rate, it was covered with a water layer. CS_2 concentration in air outlet the saturator was adjusted by a plunge depth of an inlet tube into CS_2 layer and by rate of air. The air flow with given CS_2 concentration went to the adsorber 11. Granular activated carbon AG-3, which is manufactured by wood carbonization was used as an efficient CS_2 adsorbent. To reduce the adsorbent breakthrough time, applied CS_2 concentration in air was kept at relatively high level (15–20 vol.%). Completeness of adsorption was determined by the time when CS_2 appears in air flow outlet the adsorber. Adsorption capacity until CS_2 breakthrough comprised 1.1 g CS_2/g of carbon.

It is necessary to note that in the conditions described above, complete absorption of CS_2 is reached in a wide range of its concentrations in air – from 0.05 up to 25 vol.%. Carbon disulfide is not hydrolyzed over titanium–calcium catalysts in the presence of oxygen but is oxidized to sulfur dioxide. Therefore, CS_2 desorption from the adsorbent surface was carried out by nitrogen. Nitrogen from the cylinder 2 through the rheometer 7 and system of three-way valves came to the adsorber 11. A steady CS_2 desorption was achieved by a programmed elevation of temperature in the adsorbent bed (0.10–0.15 °C/min).

Nitrogen with desorbed CS_2 was directed to a water saturator 10 that had electrical heating. Gas flow from the saturator containing vapour of CS_2 and water went into hydrolysis reactor 12 with the catalyst 5% TiO_2, 1% CaO/KAU. The catalyst volume was 3.4 cm^3, the grain size, 1–2 mm. The reactor was preliminarily heated up to given temperature in a nitrogen flow that came from the cylinder 2 through the three-way valves 17 and 18.

The gas mixture outlet of the hydrolysis reactor was cooled in the condenser 13; unreacted water was separated in a collector 14. Gas flow, which contains hydrolysis products (H_2S and CO_2), was mixed with air at ratio of 1:1.3–1.4 and directed to the reactor 15 for H_2S oxidation. The air volume, which is required for oxidation, is let into the system through a nozzle connected to the atmosphere and located between the collector 14 and the oxidation reactor 15 due to some pressure discharge in the system (about 700 mm of Hg), which was created by means of a water-jet pump 16.

1.7 g of damp (0.7 g of air-dry sample) Fe-EDTA/carbopon catalyst (0.34 mmol of complex/g of catalyst) was

preliminarily loaded into the oxidation reactor. Hydrogen sulfide content in initial gas mixture was 1.5–2.6 vol.%, molar ratio H_2S: O_2 = 1:5–8. Hydrogen sulfide oxidation was carried out at room temperature and gas mixture space velocity equal to 200 h^{-1}.

The following parameters were varied in the experiments for adsorption-catalytic air purification in a laboratory unit with flow reactors:

- temperature of hydrolysis (from 230 up to 310 °C),
- nitrogen velocity (4.0 and 5.5 ml/min),
- water temperature in the saturator 10 (from 80 up to 85 °C).

3. Results and discussion

At the first stage of our study, the experiments were targeted to find the optimal compositions of catalysts for carbon disulfide hydrolysis and hydrogen sulfide oxidation.

Since titanium–calcium catalysts show a high activity in carbon disulfide hydrolysis [8], it was interesting to obtain and test in CS_2-hydrolysis the catalytic systems on the basis of porous catalyst supports modified by relatively small amounts of titanium dioxide and calcium oxide.

The data for the effect of the catalyst composition and conditions of the samples preparation on their activity in CS_2 hydrolysis are presented in Table 3. As it can be seen, the sample made on the basis of KAU activated carbon by version 6 with the following washing off of Cl^--ions possesses the highest catalytic activity with CS_2 conversion degree of 56%. The composition of this catalyst is: CaO, 1.0%; TiO_2, 5.0%; KAU, the rest. It is interesting to point out that the highest degree of chlorides hydrolysis (84%) is observed in this sample preparation.

Accordingly, this catalyst was selected for the following tests in flow conditions.

It is known that hydrogen sulfide is readily oxidized to elemental sulfur while it contacts with Fe-EDTA aqueous

Table 4
Operating time of CM and the catalysts on their basis at air purification from hydrogen sulfide

CM	CM operating time until H_2S breakthrough	Fe-EDTA content in catalyst sample, (mmol/g_{cat})	Catalyst operating time until H_2S breakthrough (min)
KAU	12	0.40	235
SAU	28	0.45	15
Carbopon	11	0.29	1270

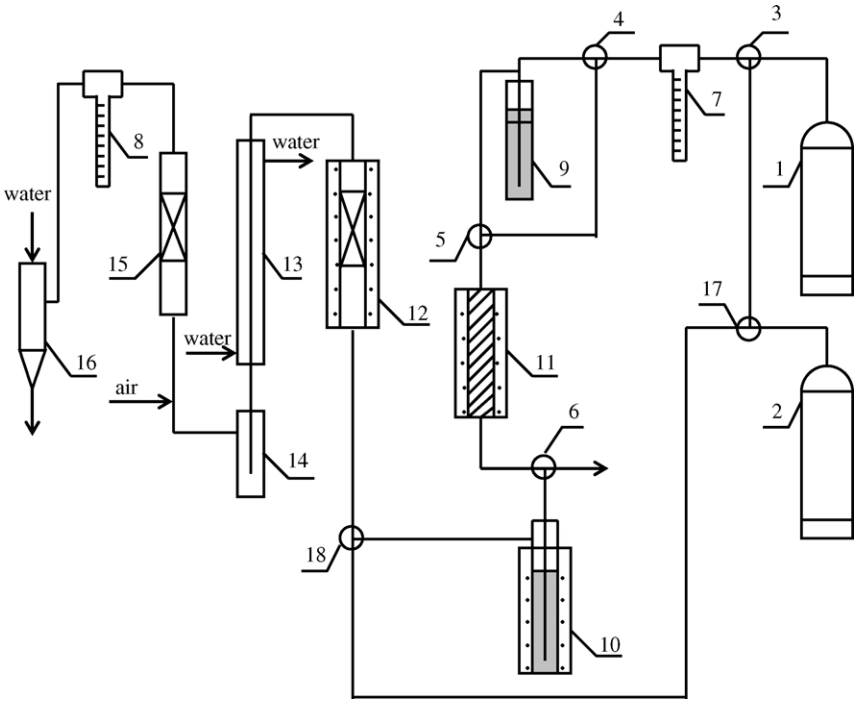

Fig. 1. Flow sheet of the experimental unit for adsorption-catalytic purification of air from carbon disulfide: (1) cylinder with air, (2) cylinder with nitrogen, (3–6, 17, and 18) three-way valves, (7 and 8) rheometers, (9 and 10) saturators with CS_2 and water, (11) adsorber, (12) reactor for CS_2 hydrolysis, (13) condenser, (14) collector, (15) reactor for H_2S oxidation, and (16) water-jet pump.

Table 5
Conditions and experimental results for hydrogen sulfide oxidation over the catalyst Fe-EDTA/carbopon (the catalyst volume, 3 cm^3; gas mixture space velocity, 200 h^{-1})

Number	H_2S content in gas mixture before mixing with air (vol.%)	H_2S content in gas mixture after mixing with air (vol.%)	O_2 content in gas mixture after mixing with air (vol.%)	Hydrogen sulfide specific load (mg H_2S/g_{cat} min)	Operating time of the catalyst until H_2S breakthrough (min)
1	4.0 ± 0.4	1.7 ± 0.2	12.0	0.35 ± 0.04	180
2	4.6 ± 0.4	2.0 ± 0.2	12.0	0.40 ± 0.04	156
3	5.4 ± 0.4	2.4 ± 0.2	11.9	0.48 ± 0.04	125

solution (EDTA-ethylenediaminetetraacetate) [9,10]. The catalytic process can be described by the following reactions:

$$H_2S + 2\text{Fe-EDTA}^- \rightarrow \tfrac{1}{8}S_8 + 2\text{Fe-EDTA}^{2-} + 2H^+$$

$$2\text{Fe-EDTA}^{2-} + \tfrac{1}{2}O_2 + H_2O \rightarrow 2\text{Fe-EDTA}^- + 2OH^-$$

Our earlier studies demonstrated that heterogenized catalytic systems Fe-EDTA/anionite also possess high activity in this process [11–14].

As follows from Table 4 data, the catalyst on the basis of the carbon fibre (carbopon) reveals the greatest efficiency. The catalysts on the basis of granular CM are less efficient despite the greater active complex content in them. It seems to be caused by diffusive limitations. Small diameter of carbopon fibre (5–10 μm) provides a higher mass transfer rate versus the catalysts on the basis of KAU and SAU, the grain diameter of which is 1–2 mm, i.e., 100 times larger. Hence, it is expedient to use the catalyst Fe-EDTA/carbopon for hydrogen sulfide oxidation.

The results for CS_2 hydrolysis in a flow system (reactor 12, Fig. 1) are presented in Fig. 2. As it can be seen from the obtained data, CS_2 conversion degree rises with the temperature increase up to 280–300 °C and with the decrease of feed flow rate and water vapour content. It is possible to assume that activity of the catalyst is low due to strong competitive water adsorption on its surface at high water vapour content in the mixture (curve 3). The most favorable conditions for 100% CS_2 conversion are demonstrated by curve 1 in Fig. 2. They are: temperature, 280–290 °C; CS_2:H_2O molar ratio, 1:3–4; and gas mixture space velocity, 75–80 h^{-1}.

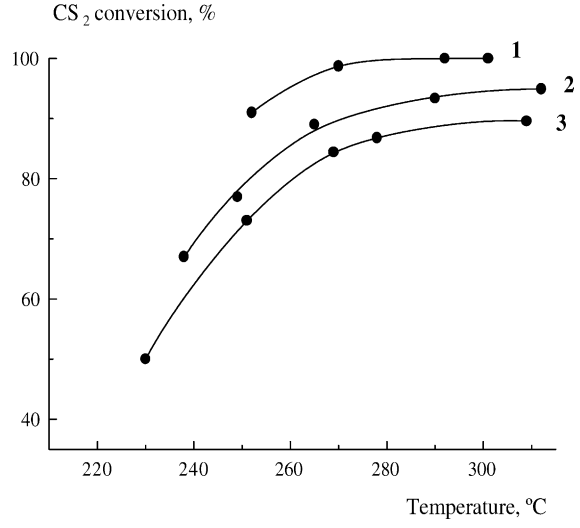

Fig. 2. CS_2 conversion degree vs. temperature at various experimental conditions: (1) flow rate of nitrogen, 4 ml/min; CS_2 and water vapour content in gas mixture, 2.3 and 8.6 vol.% (feed flow rate, 4.5 ml/min). (2) Flow rate of nitrogen, 5.5 ml/min; CS_2 and water vapour content in gas mixture, 2.2 and 9.0 vol.% (feed flow rate, 6.2 ml/min). (3) Flow rate of nitrogen, 5.5 ml/min; CS_2 and water vapour content in gas mixture, 2.0 and 18 vol.% (feed flow rate 6.9 ml/min).

The results of the experiments for catalytic oxidation of hydrogen sulfide obtained at CS_2 hydrolysis are shown in Table 5. As it can be seen in the table, the operating time of the catalyst Fe-EDTA/carbopon with 100% conversion degree comprises 2–3 h for the catalyst sample weight of 0.7 g (in air-dry state) and H_2S flow rate of 0.35–0.48 mg/g_{cat} min.

The operating time of the reaction system until the hydrogen sulfide breakthrough can be varied depending on the amount of the catalyst and H_2S concentration in a purifying gas mixture.

4. Conclusions

Adsorption-catalytic method for carbon disulfide removal from air with the use of the adsorbent and the catalysts on the basis of carbon materials is suggested and experimentally tested.

Highly efficient catalytic systems for CS_2 hydrolysis (5% TiO_2, 1% CaO/KAU) and H_2S oxidation to elemental sulfur (Fe-EDTA/carbopon) are developed.

The most favourable parameters of the purification process, which provide complete recovery of carbon disulfide, are determined for all steps of the process including: CS_2 adsorption by activated carbon, its desorption in an inert gas flow, carbon disulfide hydrolysis and hydrogen sulfide oxidation over the synthesized catalysts.

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