

POSTER

MODIFICATION OF FIBER CARBON MATERIALS FOR IMPROVEMENT OF THEIR CAPACITY TO REMOVE SULFUR COMPOUNDS FROM GAS-AIR MIXTURES

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INTRODUCTION

Evacuation of sulfur compounds (SO_2 , H_2S) from gas-air mixture is particular importance because of their high toxicity as for human beings and catalysts of their high toxicity as for the human beings and catalysts of different industrial processes as well [1,2]. In particular they suppress the work of thermochemical and semiconductor-adsorptive sensors, which register the presence in gaseous mixtures. It is a well-known fact that active carbons (AC) adsorb sulfur compounds, and this property is used in a number of technologies, such as purification of waste gases in atmosphere, for example. In the case of H_2S physical and activated adsorption combined with catalytic oxidation of H_2S with oxygen takes place. It is a well-known fact that the values of adsorption of different substances on carbon materials as well as their catalytic activity depend upon structure of the initial CM and availability of the surface functional groups (SFG). Adsorption and catalytic properties could be also changed by introducing of some active substances, such as some metallic compounds into the SFG or pores. The positive effect of such a modification was found in the case of ammonia adsorption and oxidation of hydrocarbons and some other substances. The change of adsorption capacity and catalytic activity of carbons in these cases is accounted mainly for the different acidity of SFG. In the case of carbons, modified with metallic cations, this change is attributed to the possibility to occur the so-called "chelation" adsorption, when the adsorbed particles occupy vacancies in coordination sphere of the surface complexes producing surface structures as $-\text{C}-\text{O}-\text{Me} \dots \text{Ln}$. On the basis of some data one could expect that modification of CM may enhance the adsorption of sulfur compounds.

EXPERIMENTAL

In our research we studied adsorption of SO_2 and H_2S (0.1-0.3 % mass) from air on different fibrous and granulated CM based on industrial carbons and possibility to improve their adsorption capacity by modification with Fe^{3+} , Co^{2+} , Ni^{2+} and Cu^{2+} cations.

Modification of CM was done by ion-exchange of the given ions from the solutions of their nitrates and by impregnation of CM with nitrates or sulfates. We planned to study the effect of the nature of the modifying agent and its amount as well as the capacity of the above sulfur compounds. All species of active carbons had a well-developed porosity, large value of total pore volume and specific surface area. The oxidized samples contained a lot of SFG capable to bind cation of different metals. The starting carbons had a different ordering in their atomic structure what resulted in different values of their electric conductivity. Adsorption of SO_2 and H_2S was determined in dynamics under the constant flow rate of gaseous mixture. Dynamics activity (DA) in minutes, that is the time of uptake of sulfur compound till their breakthrough, was assumed as the criterion of the adsorbent's efficiency. Sulfur gases were determined by chemical analysis and by special detectors. The "break through" was determined from deviations of ampermeter and voltmeter readings (ΔJ , mA and ΔU , mV). Using J values we evaluated the relative amount of H_2S that was not adsorbed on filter. Although the dependence between J and H_2S concentration was not linear, it enabled us to estimate fairly well the adsorption capacity of different CM.

RESULTS AND DISCUSSION

Table 1 represents data on DA when SO_2 and H_2S are adsorbed from the gas-air mixtures on different CM - starting carbons AC and OCC, carbon cloth (CC) and their modifications, produced by ion-exchange and conventional impregnation with solutions containing 18-20 per cent of impregnator, industrial carbons K-3, K-4, K-6.

Table 1.
SO₂ and H₂S adsorption by the modified carbon materials.

Adsorbent.	DA, min.	
	SO ₂	H ₂ S
OCC-H	13	
OCC-Ni	15	
OCC-Cu	22	
OCC-Co	35	
OCC-Fe	41	
AC		6
AC-Ni		3
AC-Cu		15
AC-Co		24
AC-Fe		25
K-3		21
K-4		44
K-6		55

Experiments proved the modified samples to be much more efficient than initial ones. The amount of the adsorbed gases depended substantially on the nature and quantity of modifier and dropped according to the following sequence Fe > Co > Cu > Ni. It was assumed that adsorption of SO₂ and H₂S in these systems followed the chelation mechanism [3, 4], when the adsorbed molecules occupied vacancies in coordination sphere producing surface complexes --C-O-Me...Ln. We used the thermogravimetric method in order to get some additional data on binding the modifier by carbons. It was found that final properties of the carbon adsorbents were predetermined by properties of the initial carbons -- their composition and electroconductivity. The most efficient ones appeared to have the largest value of electric conductivity and good parameters of their structure. These factors were considered to be of particular importance. As far even trace amount of SO₂ and H₂S can misrepresent the readings of the sensitive elements in detectors for a given admixture and lead to irreversible changes in detectors, we tried to apply AC as filters, protecting the sensors in these detectors from H₂S and SO₂. As it follows from the data presented in Table 2 the efficiency of CM is different. For example, the adsorption capacity of the modified CC, based on activated carbon cloth, is larger than that for the non-activated ones. The most efficient appeared to be Fe- and Co --modifications, average values were found for Cu- modifications, whereas Ni- modifications did not practically adsorb H₂S.

Tests with filters, made from industrial samples K-3, K-4 and K-6 with a large percentage of modifier proved them to be the most efficient. The break through was noted after 10-20 hours. Readings of the thermochemical detector were practically unchanged for about 100 hours in the case of using in it the most efficient carbon sample K-6.

Table 2.
Protection of the adsorption-semiconductor detectors for methane gas using filters made of CM.

Filter material	ΔJ, mkA	Testing time, min
CC-Fe	2000	5
CC-Co	3000	2
CC-Ni	2500	3
CC-Cu	2500	2
CCact-Fe	1000	180
CCact-Co	1050	120
CCact-Ni	2500	1
CCact-Cu	900	60
K-3	12500	1200
K-4	170	2400
K-6	125	6000

CONCLUSIONS

Methods of modification of CM were found. Reasons that determine the adsorption capacity of CM to adsorb SO₂ and H₂S were established. We have shown that filters, which contain the modified carbons, can protect the sensitive elements in hydrocarbon detectors from poisoning with H₂S. Such filters have prospects for their practical application.

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