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Fly ash as carrier of catalysts in the Claus process

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ABSTRACT

The study was carried out to obtain catalysts with the use of fly ash as a carrier for removal of H_2S and SO_2 from tail gases of the Claus process.
Fly ashes were from Polish power station. A few type of fly ash was investigated. The structure of fly ash were analyzed by scan microscope with microsonde and XR diffraction. Catalysts were prepared with the use of Ag, Fe(II), Fe(III) compounds. The desulphurization process was carried out in the lab scale at 593 and 453 K.
Introduction of silver in the quantity from 1 to 10 wt. % caused that activity of catalyst increased with the increasing of amount of silver in the catalysts . However introduction of ferric compounds in the quantity from 1 to 10 wt. % on fly ash (carrier) caused that activity of catalysts obtained was different in depending on kind of compounds, kind of anion and amount of iron.
The test was also carried out with the use of French and German industrial catalysts to compare with the catalyst obtained. The catalysts studied were characterized by a similar activity to the industrial catalysts in the conversion of $H_2S + SO_2$ to sulphur.

INTRODUCTION

From the literature dealing with the dry desulphurization process of gases by oxidation of hydrogen sulphide [1, 2] has been resulted that the process takes place on various types of catalysts:

- catalysts based on alumina oxide activated alumina oxide and promoted by various metals
- activated carbon, coke and semicoke activated and promotored by metals
- synthetic and natural zeolites
- titanium and zirconium oxides and others.

The carries of catalysts should have a goold developing surface area because it causes a good dispersion of catalytic substance and formation of more numbers of the active centres. Besides of form of the surface and porosity the second important thing is chemical nature and chemical interaction of its surface [3].
The purpose of this study is to experimentally investigate the fly ashes as carriers of catalyst for the Claus process.

EXPERIMENTAL

The fly ashes from different Polish power station were used as carriers of catalysts. They were determined by K-1, K-2 and W-1 symbols. Their chemical composition is presented in Table 1. Bentonite from Milowice was used as a binder to form the catalysts. The catalysts were prepared by impregnation and pasting methods. The catalysts in the form of pellets were dried at 383K and next calcinated at 633K by 4 hrs (in some cases were calcinated at higher

temperatures). The pellets were pulverized and sieved to obtain a fraction sample of particle sizes between 0,4 and 0,6 mm.
Ferric catalysts were prepared with the following salts:
$FeSO_4 \cdot 7H_2O$, $FeCl_2$, $Fe_2(SO_4)_3 \cdot 9H_2O$ and $FeCl_3$.
Silver catalysts were prepared with the use of $AgNO_3$ solution. Amount of metal added to the mass of catalyst was from 1 to 10 wt. %.
The surface area and pores volumen of carriers and catalyst were studied by adsorption of vapour benzene and BET methods. The results are presented in Table 2. For comparison, the German and French industrial catalysts were studied too.
Testing of the catalysts were carried out in the reactor placed in the electric heater with the use of gas chromatograph, at 473 and 593K and GSVH 600 h^{-1}.
The conversion of H_2S on the carriers and catalysts were investigated according to the reaction: $H_2S + SO_2 \rightarrow 3/2\ S_2 + 2H_2O$

RESULTS
The chemical composition and porosity of fly ashes studied is considerable differ from typical catalysts used in the above mentioned process. (Table 1 i 2). Fly ashes contain oxides and minerals of calcium, silicium, aluminium, potassium, sodium, titanium, and iron. From the scanning microscope with analyzing microsound has been found, that iron in fly ashes is build in the mineral structure. Point analyzing has been showed that iron exists in a small amount near by the such dominated elements as calcium, aluminium and silicium. The study of phase composition of fly ashes by XRD method confirms that iron is build in the minerals as kaolinite, biotite and chlorite.
Fly ashes investigated show a sufficient less porosity from the catalysts used in the Claus process however they prove the activity in this process. May be it is connected with the iron build in the structure of minerals.
Introduction to the fly ash metal phase (silver or iron) has been caused the increase in the activity in the Claus reaction. The activity of silver fly ash catalysts increases with the increase of amount of silver added (1÷10 wt.%).
Iron was introduced, to the fly ash at first, in the sulfate, sulfite, and chloride forms. The catalysts have proved very high activity but they have very low resistant to water. After calcination process, the catalysts had high activity in the Claus process and they were resistant to water.
The amount of iron introduced on fly ash has been effected on the activity of catalyst. It is dependent also on valency of iron and kind of anion in the ferric compounds. Catalysts with the trivalent ferric compounds (calcinated at 633 K) have been proved higher activity in this process than twovalent ferric compounds.
The series of the activity of catalysts with the use of trivalent iron is as follows:
5% Fe^{+3} > 2% Fe^{+3} > 8% Fe^{+3} > 1% Fe^{+3} > 10% Fe^{+3}.
The activity of catalysts with twovalent ferric compounds is dependent on the amount of ferric introduced on fly ash.
The activity of French and German catalysts was similar to those catalysts obtained on the base of fly ashes, but their chemical and physical properties were differ.

CONCLUSION
Fly ashes consisting calcium, silicium, aluminium minerals and other metal compounds may be used as carrier to obtain catalyst for the Claus process.
Introduction of metal phase on fly ash causes in the increase in the activity of the catalysts.
Catalysts obtained in the oxides form proved a high activity and good resistant to water.

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Table 1. Chemical composition of fly ash investigated and Milowice bentonite (binder)

Kind of component	Percentage content of component [wt. %]			
	K-1	K-2	W-1	M – Milowice bentonite (binder)
SiO_2	23,51	41,39	49,15	64,50
Al_2O_3	4,25	12,90	24,53	16,85
Fe_2O_3	3,14	4,61	5,53	2,25
(Fe^{+2}, Fe^{+3})	(0,33; 1,87)	(0,78; 1,91)		
CaO	57,39	22,84	2,70	2,30
MgO	0,87	1,55	2,07	2,80
K_2O	1,00	2,30	2,10	2,05
Na_2O	0,58	1,21	0,29	1,85
TiO_2	0,30	0,78	0,96	0,12
SO_4^{-2}	2,05	0,96	0,70	0,20
Coal	0,20	1,07	7,64	-
Weight-loss on heating	4,09	4,57	9,65	4,20

Table 2. The surface area and volume of pores determined by sorption of benzene vapour.

Sample	Surface area $[m^2/g]$								
	Micropores S_{mic}	Mezopores						$S_{mez}+S_{mic}$	S_{BET}
		$S_{1,5-3}$	S_{3-5}	S_{5-10}	S_{10-30}	S_{30-100}	$S_{mez}=S_{1,5-100}$		
Carrier (fly ash)	16,3	4,2	1,9	1,6	0,9	0,4	9,0	25,3	21
Catalyst on fly ash	20,3	4,4	1,5	1,2	1,0	0,4	8,5	29,3	20
German catalyst	135	130	27,3	4,7	2,2	0,4	164,8	299,8	193
French catalyst	168	125,8	100,6	16,9	3,6	0,6	247,5	415,5	289
	Volume of pores $[m^3/g]$								$\frac{V_{mic}}{V_{mez}}.100$
	Micropores V_{mic}	Mezopores						$\Sigma V_{mic}+V_{mez}$	
		$V_{1,5-3}$	V_{3-5}	V_{5-10}	V_{10-30}	V_{30-100}	$V_{mez}=V_{1,5-100}$		
Carrier (fly ash)	0,00816	0,00483	0,00385	0,00624	0,00572	0,0082	0,02884	0,0370	22,0
Catalyst on fly ash	0,0104	0,00437	0,00310	0,00492	0,00683	0,00893	0,02851	0,03891	26,7
German catalyst	0,0680	0,1505	0,0505	0,0185	0,0136	0,0075	0,2406	0,3086	22,0
French catalyst	0,0840	0,1020	0,1977	0,0588	0,0216	0,0206	0,4007	0,4847	17,3