

Ni-Carbon Mineral Sorbent - Catalyst of Sulfur Dioxide Sorption

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Abstract

The morphology and structure of Ni-carbon mineral sorbent-catalysts on the basis of local mineral raw material were studied by methods of thermoprogrammed desorption and electron microscopy. The specific surface, filamentary carbon diameter sizes and sorption characteristics of sulfur dioxide adsorption were determined.

It was shown that the adsorption capacity of carboncontaining sorbents is influenced by: nature of metals of varying valence, specific surface and density of patterns. Physical and chemical sorption of sulfur dioxide was shown experimentally.

Introduction

At present the environment protection, particularly environmental air pollution prevention, is still one of the most urgent ecological problems. It is well known that the waste gases of many industrial productions and refinery plants contain such sulfur component emissions as H₂S, SO₂, SO₃ etc., affecting not only the animals and plants, but also inducing corrosion of metal constructions and oil pipelines.

In the process of catalytic purification of sulfur oxide-containing waste gases the catalysts are poisoned by sulfur oxides [1], that results in catalyst deactivation [2-3]. The regeneration of poisoned catalysts requires extra power consumption that increases the catalyst costs. Moreover, insufficient availability and expensive costs of catalysts based on noble metals (Pt, Pd), as well as substantial costs of technology for manufacture both of carriers and catalysts prevent their large-scale applications, particularly in processes of exhaust gas purification.

The synthesized carbon-mineral sorbents, i.e., carbonized clays may be used to purify waste gas emissions of sulfur oxides, being the cheapest material that requires no substantial expenses relative to clay mining and catalyst manufacture technology

costs [4-6].

The X-ray phase analysis (RPA) results prove that the natural clays contain oxides of metals showing variable valence, which being activated by carbonization, improve adsorption and catalytic process features.

The data obtained by electron microscopy and other physico-chemical investigation methods [6-7] showed that the tubular-filamentary nanosstructure carbon formed in certain carbonization conditions is promoting extension of specific surfaces and structure porosity.

This paper deals with the results of investigations of SO₂ adsorption on the carbonized clay from Narinkol region of the Republic of Kazakhstan.

Experimental

The chemical analysis of Narinkol clay gave its composition by weight percentage as follows: Na₂ (0.55), MgO (4.61), Al₂O₃ (11.51), SiO₂ (47.28), P₂O₅ (0.11), K₂O (3.16), CaO (15.14), TiO₂ (0.45), MnO (0.11), Fe₂O₃ (4.01) and other substances (13.52).

The catalysts were prepared by clay impregnation with nickel acetate solution. The samples pre-molded in cylinders of d = 1-2 mm and d = 5-6 mm were dried at ambient temperature (12 hours) and then were

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calcinated at 423 K (2 hours) and 623 K (3 hours).

The thermo-catalytic synthesis of carbon-mineral catalysts and sorbent was carried out by propane-butane mixture pyrolysis at 80 cm³/min. flow rate within 673-1073 K temperature range during 10-30 minutes. After the process was completed, the argon is fed into the reactor and cooled down to ambient temperature.

The SO₂ adsorption based on the carbonized sample was studied in the flow reactor by thermo-programmed desorption (TPD) method within 298-773 K temperature range at 17 K/min. rate and further chromatographic analysis of desorption products. The analysis of O₂, CO₂ and SO₂ was proceeded using «Gasochrome-3101» and «LCM-8 MD» gas chromatographs.

The interactions between SO₂ and carbonized samples (0.5 g) pre-treated under vacuum at 3×10⁻⁵ Pa and then exposed at 673 K temperature during 2 hours, were proceeded at 423 K in He (40 cm³/min) flow 0.08-0.1 vol. % SO₂.

The electron microscopy investigations were carried out using the 120000× microscope «EM-125 K».

Results and discussion

The mechanism of catalytic formation of carbon deposits on pure oxides was thoroughly studied by R.Ya.Buyanov et al. [7-9]. The obtained results show that carbon is formed in fine-dispersion graphite structures having morphological patterns differing from each other in their carbide mechanism. Under certain experimental conditions the morphological structure changes and carbon deposits in the form of tubular filaments.

The obtained experimental results are summarized in Table 1. As is seen from the table, the specific surface of the clay increases from 5.21 m²/g to 9.23 m²/g with carbonization temperature (T_{carbon.}, K) rise from 673 K to 823 K. The further T_{carbon.} increase results in specific surface decrease.

The microscopy images (Fig. 1) evidence that the carbonization of clays is followed by the formation of filamentary nanostructure carbon and its diameter depends on the carbonization temperature. The diameters increase with temperature (Table 1).

Moreover, one can see from the images (Fig. 2), that the metal atoms are mainly located on the nanotube ends. This phenomenon is the most evident on the carbonized clay with deposited nickel (Fig. 3, 4),

where quite numerous nanotubes with nickel deposited on their ends are observed. In case of samples with deposited cobalt and copper, the filamentary fibril carbon was not found on the electron microscopy images, evidencing the selectivity of fibril carbon formation on various metals.

Table 1

Effects of carbonization temperature on the specific surface of clays and filamentary carbon

T _{carbon.} , K	D _{carbon.} , nm	S _{specif.} , m ² /g
Clay (non-carbonized)	-	4.60
673	5-7	5.21
723	14	6.35
773	16-25	8.01
873	26-50	9.23
973	60-70	8.38
1073	80-100	4.00

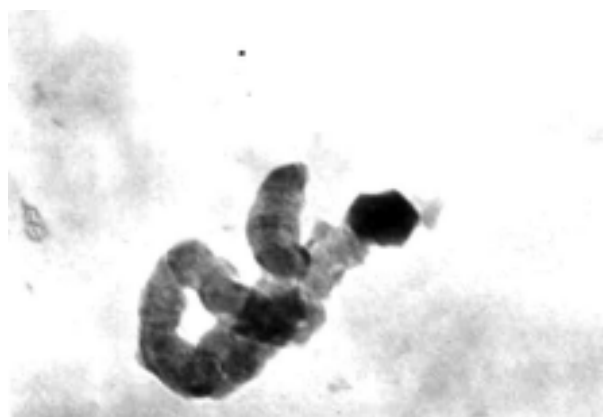


Fig. 1. Clay carbonized at 873 K, d = 700 Å

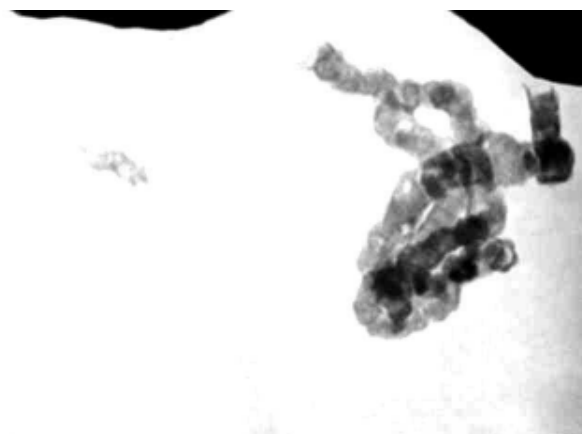


Fig. 2. Clay carbonized at 873 K, d = 400 Å

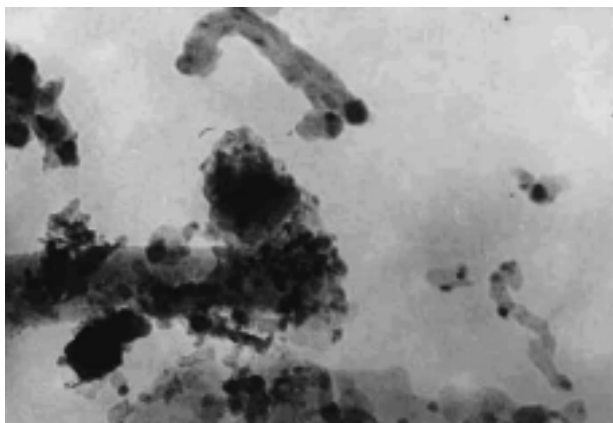


Fig. 3. 1 % Ni/clay catalyst carbonized at 873 K, $d = 140 \text{ \AA}$



Fig. 4. 1% Ni/clay catalyst carbonized at 873 K, $d = 120\text{-}140 \text{ \AA}$

According to the authors [5], the filamentary fibril carbon is a catalytic active center and, moreover, it has a particular property to remove metal from the volume up to the surface.

The electron microscopy images (Fig. 5) were obtained after SO_2 adsorption at 423 K and further SO_2 desorption proceeded at 298-773 K from the carbonized samples having nickel deposits (1 % weight). It is seen from these image that sulfur dioxide (loose form) is adsorbed both on the fibril carbon and on the metals bounded with fibril carbon. After thermo-desorption the surface of sorbent-catalysts samples became uneven with etched sites (Fig. 6).

According to the thermo-desorption data (Fig. 7), after SO_2 adsorption proceeded at 423 K, SO_2 is released in the form of two peaks from the nickel-deposited (1-5 % weight) samples carbonized at different temperatures and from non-modified clay.

The comparative analysis of TPD spectra of SO_2 (Fig. 8, Table 2), after its adsorption at 423 K, from non-carbonized clay and from the clay carbonized at

723 K, showed that SO_2 adsorbs more effectively ($3.73 \text{ cm}^3/\text{g}$) on the carbonized clay than on non-carbonized ($0.35 \text{ cm}^3/\text{g}$) one. In case of nickel-containing catalysts the SO_2 adsorbs still more effec-

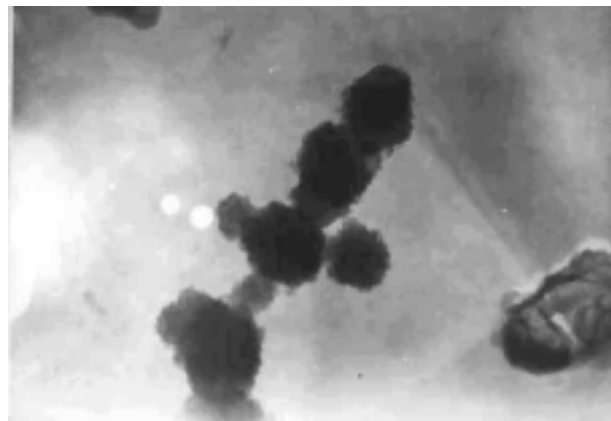


Fig. 5. After SO_2 adsorption at 423 K on 1% Ni/clay catalysts carbonized at 873 K



Fig. 6. After desorption of the SO_2 adsorbed at 423 K from 1% Ni/clay catalyst carbonized at 873 K

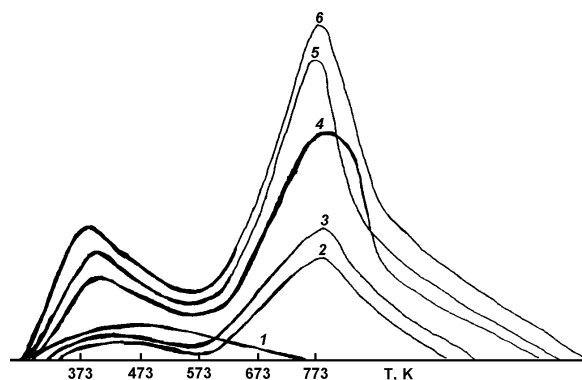


Fig. 7. Thermo-desorption spectra of SO_2 after its adsorption at 423 K from the catalysts carbonized at 723 K: 1 - Clay (non-carbonized); 2 - clay (carbonized); 3 - 0.1% Ni/clay; 4 - 1.0% Ni/clay; 5 - 2.5 % Ni/clay

tively and adsorption depends on nickel content in the clay (% weight). The adsorption of sulfur dioxide increases with the increase of nickel content in the clay. The maximal amount (13.52 cm³/g) of adsorbed SO₂ falls at the clay containing 5 % nickel and minimal amount (5.01 cm³/g) of adsorbed SO₂ falls at the clay containing 0.1 % nickel. The similar dependence of SO₂ adsorption is observed for carbonization temperature and the higher is the carbonization temperature, the more SO₂ is adsorbed. However, at temperatures over 723 K the decreasing in total fraction of adsorbed SO₂ to 6.93 cm³/g ($T_{\text{carbon.}} = 873 \text{ K}$) and 1.0 cm³/g ($T_{\text{carbon.}} = 1073 \text{ K}$) is observed.

The average values of desorption activation energy were calculated and they reached 44.8 kJ/mol, i.e., physically adsorbed (low-temperature, within 298-573 K temperature range of desorption), and 84.8 kJ/mol, i.e., chemo-sorbed (high-temperature, within 573-773 K temperature range of desorption), forms of SO₂.

The filamentary carbon that we have found is a catalytic active center showing selective interactions both with deposited metals and with metals present in

natural sorbents, besides it is the center of SO₂ adsorption. Moreover, the active carbon has a particular property to remove metals from the volume onto the sorbent surface being a main factor to direct involving of metals in adsorption and catalytic processes.

As appears from TPD data the substantial increase of SO₂ adsorption capacity by carbonized sorbing clay

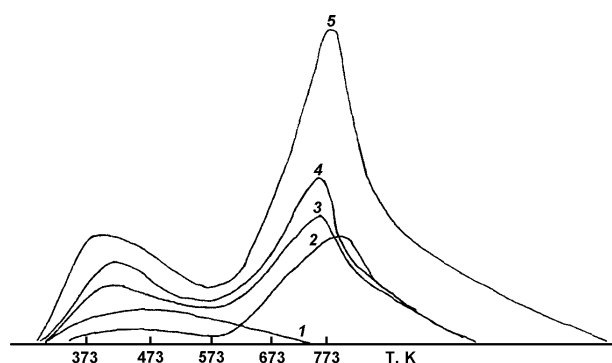


Fig. 8. Thermo-desorption spectra of SO₂ after its adsorption at 423 K from the catalysts carbonized at 723 K: 1 - Clay (non-carbonized); 2 - clay (carbonized); 3 - 2.5 % Co/clay; 4 - 2.5 % Cu/clay; 5 - 2.5 % Ni/clay

Table 2
Thermo-desorption characteristics of sulfur dioxide

Catalysts	$T_{\text{carb.}}, \text{ K}$	Desorption range, K	$T_{\text{max.}}, \text{ K}$	Amounts of desorbed SO ₂		Total amounts of desorbed SO ₂ , (cm ³ /g×cat)	$E_{\text{des.}}, \text{ SO}_2, \text{ kJ/mol}$
				cm ³ /g×cat	%		
Clay (non-carbonized)	-	297~773	423	0,36	100	0,36	54,4
Clay (carbonized)	723	298~503	398	0,60	16,10	3,73	48,43
		503~773	773	3,13	83,90		90,23
0.1% Ni/clay	723	298~593	413	1,01	20,16	5,01	46,32
		593~773	773	4,00	79,84		88,32
1% Ni/clay	723	298~583	373	2,35	17,56	13,38	44,69
		583~773	773	11,03	82,44		88,07
2.5% Ni/clay	723	298~573	393	3,10	25,41	12,20	44,14
		573~773	773	9,10	74,59		89,75
5% Ni/clay	723	298~573	403	3,35	24,78	13,52	44,77
		573~773	773	10,18	75,22		84,81
5% Ni/clay	873	298~5835	393	2,06	29,73	6,93	43,10
		83~773	773	4,87	70,27		86,90
5% Ni/clay	1073	298~573	373	0,34	34,00	1,00	41,30
		573~773	773	0,66	66,00		83,18

and modified catalysts on the clay basis, is related to the formation of active fibril carbon and its interactions with SO₂. The catalysts can be arranged by amounts of adsorbed SO₂ at T_{adsorp.} = 423 K in the following series:

C-Ni/clay > C-Cu/clay > C-Co/clay > carbonized clay > non-carbonized clay

Conclusions

Thus, the clay activation by overcarbonization leads to increase porosity and specific surfaces of sorbents and contribute to the procedure of physical and chemical sorption of sulfur dioxide and that was confirmed by the values of calculated activation energy of sulfur dioxide sorption process.

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