

Carbon Containing Compositions

R.M. Mansurova*, Z.A. Mansurov*, Soh Deawha**

Abstract

With the use of the electron microscopy and X-ray phase analysis the regularities of carbon deposit formation in process of methane and propane pyrolysis on the zeolites, Kazakhstan natural clays, chrome and bauxite sludge containing metal oxides of iron subgroup, have been studied. In process of over-carbonization the trivalent iron was reduced to metal form. In addition, the carbon tubes of divers morphology had been impregnated with ultra-dispersed metal particles. The kinetic parameters of carbon formation in process of methane decomposition on the zeolite CoO mixture surface were investigated by method of thermo-gravimetric analysis. The morphology and structure of formed carbon fibrils, with the metal particles fixed at their ends, have been investigated, the formation of branched carbon fibrils pattern, so called octopus, being found.

Key Words : Carbon materials, coal, tube formation

1. Introduction

Carbon containing materials are considered to be promising for solving the problems of environment protection from pollution, purification of sewage disposal, separating valuable components from them. The high thermal, chemical and radiation resistance of fibrous coals makes possible to use them in more severe regimes of exploitation compared to polymer sorbents. Contrary to grain absorbents the fibrous coals are characterized by their greater rate and complete sorption-desorption processes [1,2].

Carbon monoxide, hydrocarbon gases and liquids are the raw materials for catalytic carbon obtaining, while metal oxides, sludge and clays are used as catalysts-carries. Over-carbonization was achieved through the use of flow reactor in carbon pyrolysis process on the surface of salts or metal oxides of transition elements (pyrolysis is carried out at temperature range from 350 to 1,025 °C). As a result of the pyrolysis the catalytic

carbon with up-rated specific surface exceeding ordinary sizes by five or ten times, is formed on the catalyst surface. It is due to the morphology of carbon deposits, being fibril, tube formation and clusters of 1,500, 3,000 Å diameters. Besides, there is occurred dissemination of metal particles of 200-800 Å diameter. It is necessary to underline that the carbon fibril formation has sophisticate character and sometimes gives rise to branched structures evidenced by the fact that one metal particle initiates formation of several carbon fibrils in different directions, so-called 'octopus' effect [3-5].

2. Experiment

a) Substances and over-carbonized samples preparation

Over-carbonization of chrome sludge was carried out in flow running conditions in the quartz reactor (d=30mm) with propane-butane mixture (60%+40%). A pounded fraction (a=0.25-0.5mm) fed by (30g) charges into the reactor was used in this experiment. The process was carried out at temperatures $T = 500-800$ °C, time of contact being $t = 20-80$ min, gas flow rates up to 3-7 l/hour. Carbon content of over-carbonized

* Combustion Problems Institute, Kazakstan

E-mail : mansurov@lorton.com

** Myongji University, Korea,

E-mail : dwshoh@wh.mju.ac.kr

samples was estimated by combustion of the sample of 1-2 g mass placed in ceramic boat in the horizontal tube furnace at the temperature $T = 800\text{ }^{\circ}\text{C}$ for 40 minutes. Carbon concentrations were determined as sample mass differences before and after combustion.

Natural zeolite of Altyn-Amel deposit in Kazakhstan has an averaged composition (%): SiO_2 47.9; TiO_2 0.84; Al_2O_3 17.6; Fe_2O_3 0.6; FeO 0.6; MnO 0.12; CaO 7.3; MgO 4.7; Na_2O 2.6; K_2O 0.5; P_2O_5 0.1; SO_3 0.1. Zeolite was granulated in laboratory conditions China clay being added as binder. Cobalt oxide (11) was added by mechanical mixing with beforehand ground zeolite (0.5 mm). Concentrations of added CoO were 2; 4; 10; 15 mass %. The specific surface measured by volumetric method was about $4.6\text{ m}^2/\text{g}$. Walnut shells (WS) and grape kernels (GP) carbonization was proceeded in argon flow in quartz reactor, the 0.5-0.8 mm fraction being used in this experiment. The process temperature $T = 25, 900\text{ }^{\circ}\text{C}$, carbonization time 1 hour.

b) Physicochemical investigation method

The experiment aimed at investigation of kinetic parameters of carbon deposit formation process was carried out by thermo-gravimetric analysis in the «Dyupon-591» unit. The morphology and carbon microstructure formations were determined by electron-microscopic analysis using the IBM-LC 100 unit. X-ray phase analysis of source and over-carbonized samples was carried in the 'DRON-05' diffractometer at accelerating voltage 35kV and with using of tubes with cupric cathode (nickel shield). The filming was proceeded at 2 g/min rate within 600mm/h diagram band, the angle interval being from 2 to 500 degree.

Mossbauer spectra were obtained by ESR spectrometry method at room temperature using the ESR spectrometer of homodine type, working in 3-cm range.

3. Results and Discussion

a) Kinetics of carbon deposits process

In this work the rate, activation energy and temperature of carbon formation occurred in process of methane decomposition on the surface of zeolite- CoO mixture have been investigated by

thermogravimetric analysis method (TGA). In the Fig.1 the TGA curves obtained in process of initial zeolite over-carbonization without metal oxide addition are presented. At higher temperatures the process of carbonaceous deposits formation occurs less intensively, than for the samples with metal addition, and it is due to the simple thermal non-catalytic decomposition of metal on the surface of zeolite.

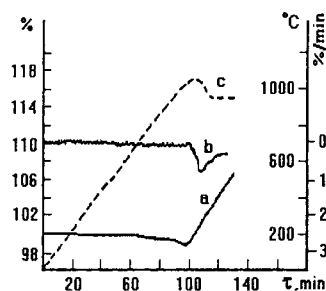


Fig.1. TGA curves of over-carbonization process of pure zeolite: a - change in sample mass (%), b - rate of change in sample mass (%/min), c - curve of temperature increase.

For the samples with cobalt oxide addition the process of over-carbonization occurs in a wide temperature range (Fig.2.). All TG curves, obtained for mechanical zeolite- CoO mixtures, have identical form at different initial temperatures of over-carbonization. The low temperature process of carbon deposits formation is running through intermediate compounds resulted of propane adsorption on the acid centers created at certain temperatures on the catalyst.

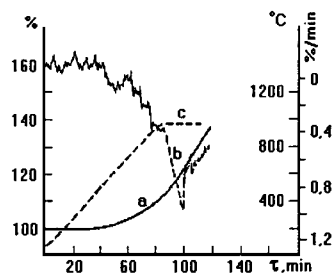


Fig.2. TGA curves of over-carbonization process of zeolite with CoO addition : a - change in sample mass, b - rate of change in sample mass, c - curve of temperature increase.

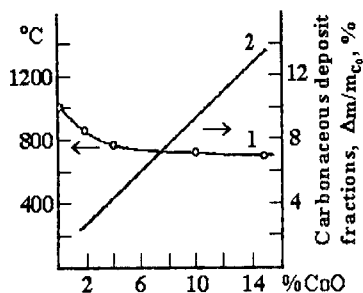


Fig.3. Over-carbonization starting temperature (1) and cobalt yield on carbon dependence upon heterogeneous zeolite - CoO, (2) mixture decomposition

Basing on the investigation results there were obtained dependencies of the temperature of over-carbonization starting and carbon yield on the heterogeneous hydrocarbons mixture compositions. The value of change in over-carbonization starting temperature (curve 1) decreases with an increase of CoO content, and the value of gain in carbonaceous deposits mass (curve 2) increases with an increase of metal concentration in mixture. As is evident from these data, the mechanical adding of CoO practically effects no the coke formation in the low-temperature region while its significant effects being noted for high-temperature region of this process. The major quantitative characteristics of over-carbonization process of zeolite containing samples are shown in the table 1.

The kinetic parameters, i.e., activation energy pre-exponential factor (Fig.4), were calculated. The equation $dm/dt = K_0 e^{E_0/RT}$ was used for quantitative processing of TGA data.

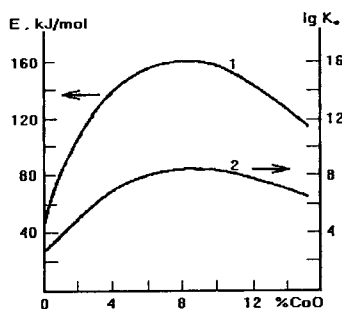


Fig.4. Activation energy E_0 (1) and pre-exponential K_0 (2) dependence on the composition of mechanical zeolite - CoO mixture.

Table 1. Major experiment results of over-carbonization of heterogeneous zeolite - CoO mixture with methane.

CoO mas. %	mass, mg	starting temperature, °C	Mass of carbonaceous deposits for 120 min, mg	Gain in sample mass resulting, %	E_0 , kJ/mol	LgK_0
0	27.70	910	2.44	8.8	42.1	3.44
2	29.34	580	10.16	34.6	104	4.74
4	31.81	500	14.31	44.9	136	7.12
10	26.54	480	15.23	57.4	148	8.21
15	27.43	400	17.12	62.4	117	6.83

When the CoO is added in amounts from 2 to 10%, the increase of E_0 and K_0 values is observed. Thus, the dependencies of carbonaceous deposits formation on the natural zeolite mixed with cobalt oxide (II) on the reaction temperature and zeolite-CoO ratio are obvious. The CoO content of the sample being increased the mass of carbonaceous deposit gains linearly to it.

b) Structure and physicochemical characteristics

The over-carbonization enables to obtain larger surfaces with a number of active centers exceeding that of source sample. The electron-microscopic photograph of over-carbonized chrome sludge (Fig.5) shows that the formation of carbonaceous deposits leads not only to chemical processes (formation of metal carbide and carbide transfer to the carbon fibril) but also to physical processes (carrying of the particles to the carbon mass).

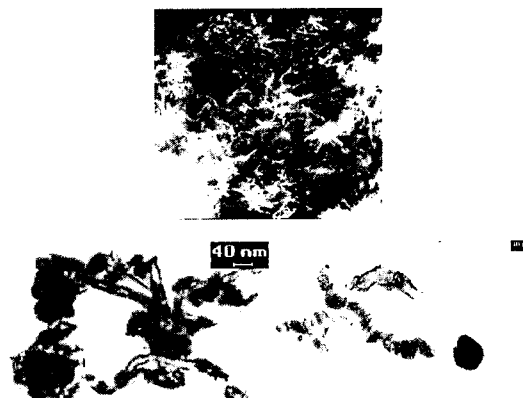


Fig.5. Electron-microscopic photograph of over-carbonized chrome sludge at $T = 800$ °C.

The formation of branched carbon fiber starting from one center, the occurrence of so-called octopus phenomenon are noted here [4,5]. The results obtained by electron microscopy method applied in the RAS Sibir Division's Institute of Catalysis proved that the threadlike carbon formed in process of chromite sludge over-carbonization is hollow nano-tubes with metal particle on their ends.

c) Moessbauer spectra for over-carbonized samples.

Table 2. Mossbauer spectra characteristics for chrome sludge samples

Sample	E_s , mms-1	E_Q , mms-1	H, kOe	S, %
1	0,17	1,46	-	40
	0,36	1,52	-	60
2	0,16	1,51	-	46
	0,34	1,60	-	54
3	0,0	-	335	9
	0,16	1,53	-	46
	0,36	1,62	-	45
4	0,02	-	336	17
	0,20	1,51	-	48
	0,37	1,61	-	35
5	0,04	-	337	24
	0,20	1,45	-	41
	0,30	1,66	-	35

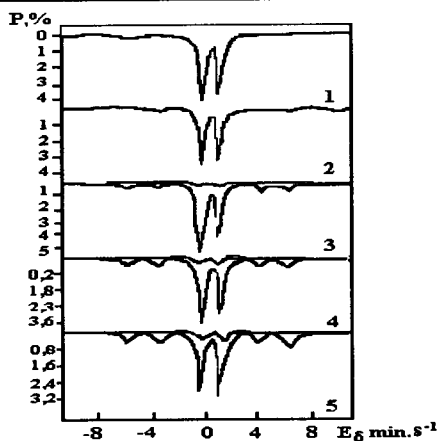


Fig. 7. NGR-spectra of chrome sludge + CaO(4%) system, over-carbonized at $T = 800 \text{ }^\circ\text{C}$: 1 source sample; 2 $t = 20$; 3 $t = 40$; 4 $t = 60$; 5 $t = 80$ min.

The Mossbauer spectra for the samples of CoO containing chrome sludge over-carbonized at $T=750 \text{ }^\circ\text{C}$ during exposure time 20, 40, 60, 80 min,

are presented in the Table 2, Fig.6. They can be classified into two groups, one of which containing source sample and first sample over-carbonized during $t=20$ min that are an asymmetrical doublet. The second one contains the second, the third and the fourth samples (40, 60, 80 min respectively), where the six lines spectrum is added to the same doublet.

The asymmetrical spectrum doublet is the super-position of two doublets available in all spectra and showing almost equal parameters. The doublet with lesser isomeric shift corresponds to trivalent iron ions in a tetrahedral medium and with greater one - to trivalent iron ions in an octahedral medium. The area of spectrum components, as a first approximation, corresponds to relative iron content of each component.

The parameters obtained by computer processing of these spectra are given in the table 2. There: E is an isomeric shift relatively to the metal iron, E_Q , mm/s, is a quadrupolar splitting, H is a field at iron nuclei, kilooersted, S is a relative component content in terms of percentage.

4. Conclusion

From the given results it can be concluded that the adsorptive-catalytic systems on chrome and bauxite sludge and clay base are used successfully as sorbents for wastewater purification.

References

- [1] R. A. Buyanov. Catalyst coking. Novosibirsk; Nauka, 1983.-207p.
- [2] R. A. Buyanov, V. V. Chesnokov. Carbon fibrils formation regularities in the process new composite materials synthesis. Chemistry in the interests of stable development. 1995.'3. p.177-186.
- [3] Z. A. Mansurov. Overcarbonized adsorptive catalytic systems. KazSU Bulletin. 1998.'3. p. 98-104.
- [4] Z.A. Mansurov. Overcarbonised Adsorptive Catalytic Systems. Eurasian ChemTech Journal 2 (2000) 59-68
- [5] R.T.K. Baker, P.S. Harris. Chemistry and Physics of Carbon, Marsel Dekker Inc., New-Youk-Basel. 1978, Vol.14, p.83-105.