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Study of the Reaction of Ozonolysis of Coal-Tar Crude Benzene

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Abstract

The effect of ozonation on the change of the componental composition of coal-tar crude benzene was studied. It was established that ozonation facilitated the decrease of the amount of unsaturated sulphur compounds and a relative increase in the share of benzene.

Key words: coal-tar benzene, ozonation

INTRODUCTION

At the present time, the production capacity of benzene in the world exceeds 50 million tons. The largest producers of benzene are countries of North America, Western Europe, and Northeast Asia. Together, their share is three-quarters of the world capacities [1]. According to the prognosis, up to 2020, the demand for benzene will grow on average by 2.8 % a year and in the end, will amount to 57 million tons [2, 3].

In this regard, alternative sources of the preparation of aromatic hydrocarbons, which in particular, include the products of coalcoking, are of great interest.

Unsaturated and sulphur compounds are contained in raw benzene. It is known that even minor impurities of sulphur in benzene and toluene used in organic synthesis processes cause a fast catalyst poisoning, and resinous substances formed as a result of polymerisation of un-

saturated compounds cover the surface of the catalyst and deactivate it. Thus, in order to prepare pure products from raw benzene, it should preliminary be purified.

Almost all the productions of coal-tar benzene are based on the sulphuric-acid method of the purification of the benzene-toluene-xylene fraction (BTX) that allows obtaining benzene of the brand “for nitration”. However, this process is accompanied by the accumulation of a sour pitch, the utilization of which is associated with certain problems [4, 5]. At the present time, the catalytic hydrotreatment method that combines in one technological process hydrogenolysis of sulphur compounds and hydrogenation of unsaturated hydrocarbons is spread. This provides the preparation of a pure product that is a valuable raw material for the chemical synthesis of organic compounds, however, the method itself is rather expensive [6, 7].

One of the possible methods of the purification of coal-tar crude benzene is its ozonation. The method has long established itself when purifying waste water from phenols; it is used in the oxidative purification of oil diesel fractions [8, 9]. Ozone is characterized by a selective electrophilic addition to unsaturated compounds, polycyclic arenes and heteroatomic compounds [10]. In addition to the unique chemical activity of ozone, advantages of the method include soft conditions of the process providing intensive proceeding of reactions at moderate temperatures, even when catalysts are absent [11–13]. With respect to crude benzene that is a mixture of three major products, *viz*, benzene, toluene and xylene, the ozonation method may contribute the preparation the fraction BTX and subsequent isolation of pure benzene. Moreover, in comparison with traditional methods when using ozone, mineral wastes, the separation of which from products of the reaction and utilization require large additional expenses, are not formed [14–17].

The goal of the present work is the study of the effect of ozonolysis on the component structure of coal-tar crude benzene in the presence of a catalyst.

EXPERIMENTAL

Crude benzene (CB) of the production of the Coke JSC (Kemerovo) corresponding to the requirements TU 1104-241419-395-167-2001 was used as the study object. Five major individual compounds that are benzene (62.89 %), toluene (32.28 %), xylenes (1.38 %), cyclopentadiene (1.14 %), octadiene (1.91 %) (Table 1) have been identified in the original sample of CB.

We have earlier shown [18] that ozonation of crude benzene even in the absence of catalysts allows decreasing the amount of unsaturated and sulphur compounds. In the work [18], initial crude benzene was ozonated; the resulting ozonated mixture was passed through an adsorption column filled with silica gel ASCG to remove resinous oxygen-containing compounds. The mixture of hydrocarbons obtained on the outlet of the column was separated by distillation using the dephlegmator with the height of 40 cm up to the temperature of 80.1 °C in order to isolate the benzene fraction. The characteristic of this fraction is given in Tables 1, 2.

In this work, the reaction of ozonation of crude benzene was carried out following the same methodic, at the atmospheric pressure in the thermostated reactor of the bubbler type with a continuous supply of the ozone oxygen mixture. However, unlike [18], tests were carried out in the presence of metals oxides (CuO, NiO) with a sample weight of 0.1 g. The characteristics of the initial metal oxides are represented in Table 3. The volume of the treated sample of CB is equal to 50 mL. Ozone was obtained in a generator OGBK-02K (MELP Co., St. Petersburg) using a barrier discharge. Process conditions: the concentration of ozone in the ozone-oxygen mixture is 30 mg/L, temperature is 25 °C, and duration is 1 h. The treatment of the ozonated product, removal of resinous oxygen-containing compounds and isolation of the benzene fraction were carried out according to the above method. Major properties of this benzene fraction of the ozonated CB in the presence of CuO and NiO are given in Table 1.

For a comparative analysis of results of the impact of the ozonolytic treatment on the com-

TABLE 1

Componential composition of the initial crude benzene (CB) and benzene fractions, mass %

Substances	Samples				
	Initial CB	Benzene fraction without ozonation	Ozonated CB		
			without catalyst	in presence of CuO	in presence of NiO
1,3-Cyclopentadiene	1.14	1.51	1.10	0.86	0.31
Benzene	62.89	77.15	79.8	82.18	88.50
Toluene	32.28	18.48	16.30	13.55	9.00
Xylenes	1.38	2.20	2.10	2.10	1.50
3,5-Octadiene	1.91	0.66	0.70	1.31	0.69

TABLE 2

Properties of crude benzene and benzene fractions

Samples	Acidic number, mg/100 g	Bromine number, g/100 mL	Content of CS ₂ , %
Initial CB	1.100	3.400	0.480
Ozonated CB without catalysts	3.600	2.678	0.301
Same in the presence of CuO	4.889	2.144	0.150
Same in the presence of NiO	5.213	0.968	0.140

position of the benzene fraction, separate tests on its isolation from the initial CB without ozonation were carried out. The initial CB was passed through an adsorption column and the resulting mixture of hydrocarbons at the outlet of the column was separated according to the above method for the isolation of the benzene fraction (see Table 1).

The acidic number of initial crude benzene and benzene fractions obtained was determined according to the reaction of these mixtures with KOH, the bromine number was obtained with bromide-bromate mixture, and the content of carbon disulphide was defined by the iodometric titration.

The chromatographic-mass spectrometric analysis was conducted using the instrument Hewlett Packard that includes the gas chromatograph HP-5890 of the series II and mass selective detector HP-5971. The capillary column is HP-5MS (5 % diphenyl, 95 % dimethylsiloxane) with the size 30 m × 0.25 mm × 0.25 μm. The gas-carrier is helium; the flow rate is 1 mL/min. The temperature heating mode of the column: 2 min at 50 °C, the increase of the temperature up to 300 °C with the rate of 10 °C/min, 30 min at 300 °C. The temperature of the evaporator is 280 °C; of the ion source is 175 °C. The scanning rate is 1.2 scan/s in the area of 30–650 amu. Oxygen-containing products before chromatography were previously etherified by a methanolic solution of HCl. The identification of components by mass spectra was conducted using information search system AMDIS and Agilent ChemStation. IR absorption spectra were registered on a spectrometer Tensor-27 of the Bruker Company in the area of wave numbers of 400–4000 cm⁻¹ (the resolution is 2 cm⁻¹, number of scans of the sample is 64) using a liquid cuvette with windows from KBr.

RESULTS AND DISCUSSION

Absorption bands of the following structural fragments (ν , cm⁻¹) were discovered when studying the sample of CB by the IR spectroscopy method (Fig. 1): of bonds C–H of aromatic rings (3040, 1610, 1500) with a high degree of mono- and bisubstitution of the aromatic hydrogen (690, 740, 780); weakly intense adsorption in the area of the stretching (2940, 2850) and bending vibrations (1460, 1380) indicate the low total content in products of com-

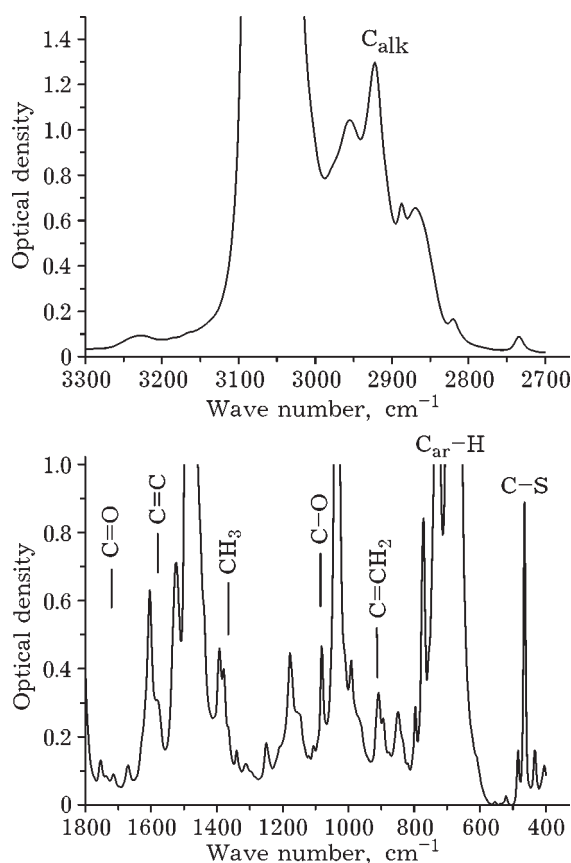


Fig. 1. IR spectra of initial crude coal-tar benzene.

pounds of the aliphatic type at increased intensities of adsorption bands of methyl groups (1380) and cycloalca(e)nes (1005, 975, 910); oxygen-containing structures are presented with mono- and dicarbonic aromatic (3400, 2720, 1690, 1270) and aliphatic (1710) acids (1715, 1210), ketoesters and lactones (1770, 1840); minor amounts of heteroatomic compounds (2750, 1060–1100, 480–500) are also identified in the composition of CB.

The process of ozonation of CB in the presence of metals oxides is accompanied by the intense formation of oxygen-containing products, as a result of which the acidic number is increased (see Table 2). At that, the prod-

uct colour changes from initial bright yellow to bright orange. Resinous products become poorly soluble in benzene and condensed on the reactor walls.

As a result of ozonation, the content of unsaturated and sulphur compounds in the product decreases. For example, the bromine number value that characterizes the presence in the products of compounds with unsaturated bonds C=C decreased by 37 % in the sample of the initial SB and up to 78 % in the sample of the ozonated CB without catalysts.

The content of carbon sulphur constituting the major proportion of sulphur-containing components decreases in the presence of copper oxide by 68.8 %, of nickel oxide by 71 %.

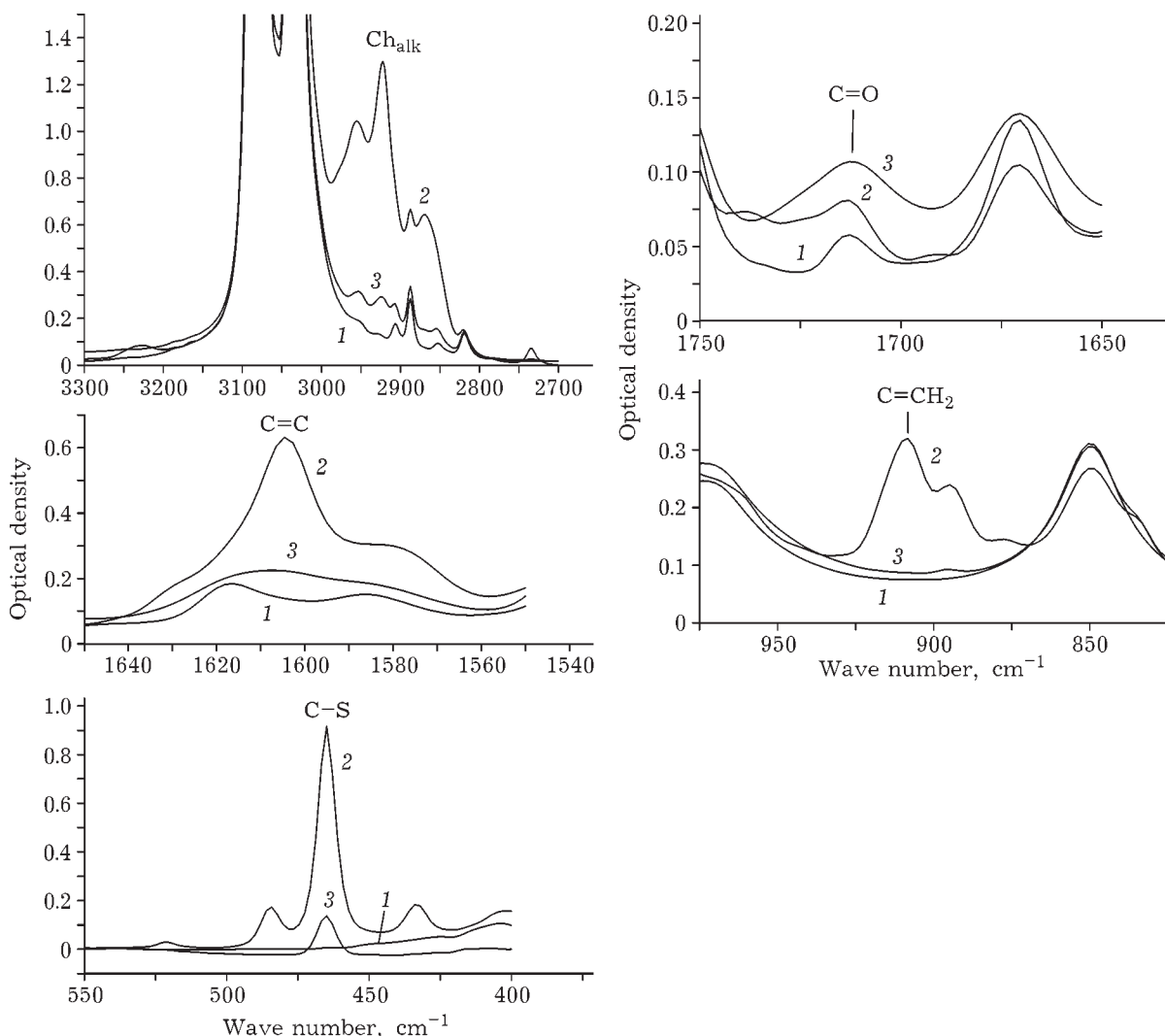


Fig. 2. IR spectra of benzene of ch. d. a. grade (pure for analysis) (1), initial (2) and ozonated crude benzene in the presence of NiO (3).

TABLE 3

Characteristics of metal oxides of os. ch. grade (especially pure)

Samples	S_{sp} , m ² /g (total, BET)	V_{pores} , cm ³ /g (BET)	Density, g/cm ³
CuO	4.98	0.02	6.31
NiO	0.11	0.07	6.67

Five major individual compounds, *viz.*, benzene, toluene, *o*-, *p*- and *m*-xylynes that are almost 92 % from the sum of all compounds identified chromatographic (see Table 1) were identified in the initial sample by the chromatography-mass spectrometry method. Other compounds are represented by cyclodienes. Thiophenes and nitrogen-containing compounds are not identified chromatographically, probably, due to their low content in the product. CB treated under these conditions was undergone to the adsorption purification from resinous products on a column with silica gel. The hydrocarbon fraction of the ozonated CB, according to data of mass spectrometry, is mainly represented by benzene (~82 %) and toluene (~13 %); the remaining part (~2 %) falls on conjugated dienes.

The treatment by ozone had the most noticeable impact on the content of unsaturated compounds of the cyclic character (cyclodienes), which agrees with the results of the identification of the bromine number. The content of methylbenzene (toluene), *viz.*, by 57 % in the sample of the initial CB and by 72 % in the sample of the ozonated CB without catalysts is significantly reduced (see Table 1, Fig. 2). The content of the target component (benzene) increases.

The data obtained by chemical methods are confirmed by the results of IR spectroscopy (see Fig. 2). The proportion of the unsaturated bonds C=C (880–900 cm⁻¹) is reduced, which agrees with the data of the chemical analysis of crude benzene. The adsorption bands of alkenes (1630, 900 cm⁻¹), cycloalkenes (880 cm⁻¹) are reduced. A weak adsorption at 480 cm⁻¹ may indicate the presence of sulphur compounds. A weak-intensive adsorption in the area of the stretching (2940, 2850 cm⁻¹) and bending vibrations (1460, 1380 cm⁻¹) indicate a low total content in products of compounds of the aliphatic type. Reducing the intensity of the bands, in com-

parison with initial crude benzene, is apparently associated with entering into the reaction with ozone alkyl substituents of benzene rings.

The process of ozonation of crude benzene in the presence of a copper oxide is also characterized by the reduction of the band of the adsorption of aliphatic groups C-H in the area of the stretching (2940, 2850 cm⁻¹) and bending (1460, 1380 cm⁻¹) vibrations, adsorption bands of unsaturated bands CH=CH (1610, 880–900 cm⁻¹) are indistinguishable. A low intensity of adsorption at 2920 cm⁻¹ indicates a small presence of monoalkyl substituted benzenes (toluene), and in the interval of 450–500 cm⁻¹, on the presence of sulphur compounds (C-S). The content of CS₂ in the presence of a copper oxide is reduced in a less extent than in case of nickel oxide.

The prevailing type of reactions with benzene hydrocarbons is radical. They proceed on the C-H bond at carbon atoms in the α -position to the aromatic ring not affecting the cycle, moreover, their probability increases with the increase of the number of substituents [10]. Unsaturated hydrocarbons interact with ozone according the mechanism of the electrophilic addition to the bond C=C with the formation of mono dicarboxylic aliphatic acids and aldehydes or are converted into polymer-like cross-linked structures. Sulphur compounds react with ozone forming SO₂ and sulphoxides.

According to the data of IR spectroscopy, the product obtained by ozonolysis in the presence of catalysts is close to benzene of ch. d. a. grade (pure for analysis). Results of the IR spectroscopic study and chromatographic-mass spectrometric analysis show that these oxides have a similar catalytic effect on the ozonolytic treatment process. Further works will be devoted to the research on the kinetics of ozonolysis on specially prepared oxide and platinum catalysts.

CONCLUSION

Thus, the use of the ozonolytic treatment in the presence of metal oxides followed by the adsorption purification allow increasing the content of the most target valuable component that is benzene. The ozonation process of initial crude benzene in the presence of a catalyst promotes

the decrease of the content of unsaturated compounds of the cyclic nature, as well as the removal of sulphur-containing components.

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