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CATALYSIS

Effect of Sulfur Compounds and Higher Homologues of Methane on Hydrogen Cyanide Production by the Andrussow Method

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Abstract—The influence of sulfur compounds and higher homologues of methane on the parameters of oxidative ammonolysis of methane was studied.

In [1, 2], the results obtained in technological calculations in terms of the empirical model of HCN production by the Andrussow method (the so-called oxidative ammonolysis of methane, OAM) were considered. The next step in a comprehensive study was to analyze the influence exerted by technological impurities present in natural gas on hydrogen cyanide formation.

The influence of sulfur compounds and higher homologues of methane—unavoidable components of natural gas—on the OAM parameters has been studied in sufficient detail [3–5]. A detailed analysis of patents and other published evidence was made in a monograph [6]. However, quite a number of questions, answers to which are exceedingly important from the standpoint of applications, remain unanswered. In particular, the effect of the time τ of contact with platinoid grids on the loss of catalytic activity upon prolonged action of technological impurities on a catalyst, has not been studied at all. A search of answer to this and other questions was the aim of the present study.

The author has collected during a long time data characterizing the operation of an industrial installation for HCN synthesis. The obtained body of evidence was used to compile a database, part of which is given in Table 1 (total number of measurements 116).

Table 1. Influence exerted by the concentration of sulfur compounds and higher homologues of methane in natural gas on the content of HCN in synthesis gas (selected data)

Starting mixture, vol %			Content in natural gas, mg m^{-3}		Flow rate of mixture, m^3 h^{-1}	T, °C	τ, h	HCN content in synthesis gas, vol %
NH_3	CH_4	O_2	S	C_nH_{2n+2}				
11.00	11.66	15.26	1.06	0.24	7550	930	26	6.16
11.30	12.88	14.86	0.62	1.81	7660	945	94	7.05
10.79	12.55	15.42	0.58	1.54	9380	960	174	7.45
11.00	11.68	15.45	0.17	0.94	7500	930	240	7.31
11.24	12.52	15.71	0.72	0.69	7550	930	378	6.58
11.07	12.28	15.65	0.54	1.69	8700	925	455	7.17
11.39	11.48	15.11	0.61	1.17	7050	930	574	7.01
11.16	12.11	15.28	0.47	0.59	7550	910	656	7.98
10.73	11.29	15.51	0.51	0.02	7630	980	716	7.43
11.70	12.76	15.47	0.17	0.94	8700	945	833	7.57
11.47	12.10	15.74	0.51	0.67	8700	945	908	7.07
11.92	12.13	15.61	0.36	0.60	9640	960	1018	6.61
11.94	12.83	15.52	0.30	0.98	9610	945	1202	6.90
11.24	12.4	16.05	0.30	1.26	9720	970	1250	7.29

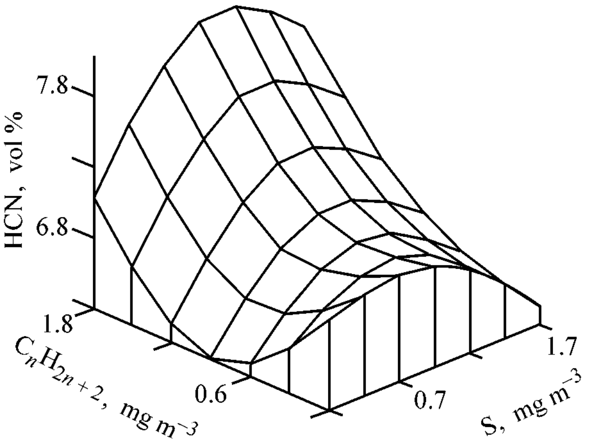

Fig. 1. Hydrogen cyanide concentration in the synthesis gas vs. content of sulfur compounds, S, and higher homologues of methane, C_nH_{n+2}, in natural gas.

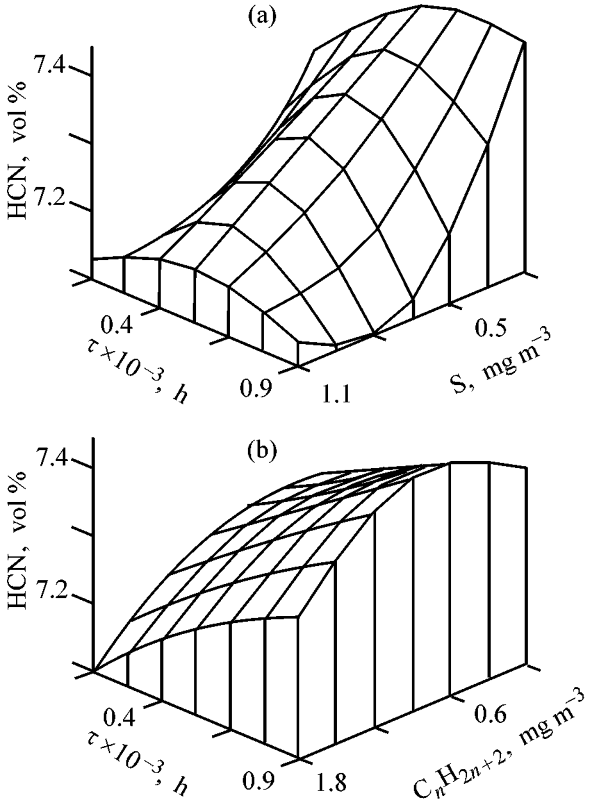

Fig. 2. Hydrogen cyanide concentration in the synthesis gas vs. (a) content of sulfur compounds, S, and (b) higher homologues of methane, C_nH_{n+2}, in natural gas at different times τ of contact with platinoid catalyst.

A preliminary processing of the entire body of information (representation in two-dimensional space) revealed a rather clearly pronounced correlation between the amount of sulfur compounds in natural gas and the volume concentration of hydrogen cyanide in the synthesis gas. There is no relationship between the content of HCN and the amount of C_nH_{n+2}. Therefore, it was suggested that the influence exerted by technological impurities present in natural gas has combined nature. This suggestion was confirmed by plotting the corresponding dependence in three-dimensional space (Fig. 1).

Noteworthy is the fact that the effect of sulfur compounds has extremal nature with a maximum at 1.0 mg m^{-3}: minor amounts block intermetallic compounds inevitably present in the alloy, thereby enhancing its selectivity; further increase in the content of sulfur in the gas leads to poisoning of platinum itself. The obtained results are in full agreement with the data of [7–9]. The influence of higher homologues of methane is on the whole positive in the investigated range of their concentrations, but, with this range expanded further, an abrupt drop in the output of hydrogen cyanide would be expected, as found experimentally by S.S. Bobkov [6]. A virtually similar conclusion is given in a patent [10].

Analysis of the data in Fig. 2 shows that the content of HCN exhibits extremal behavior with the time contact with the platinoid catalyst increasing at fixed content of sulfur compounds; at constant concentration of methane homologues the content of hydrogen cyanide grows with increasing time of passage.

The subsequent processing of the entire body of input data cast some doubts on the existence of a direct dependence of the volume content of HCN in the synthesis gas on the concentration of technological impurities in natural gas. A graphical interpretation of the averaged data of Table 1 (Fig. 3) indicates that this relationship cannot be considered in isolation from the changing flow rate of the starting mixture $Q \times 10^3$ (m^3 h^{-1}) and the spontaneously attained autothermic temperature T (°C) of the process. Anyway, none of the considered parameters (content of sulfur and C_nH_{n+2}, and also Q and T) correlates with the content of hydrogen cyanide in the reaction products.

In this regard, the following assumption seemed to be well justified. The problem in question can only be solved, with an empirical model adequate to the input data constructed, when the concentrations of technological impurities in a mixture supplied to conversion, rather than in natural gas (as it was done before [3–5, 7–10]), are used as control parameters.

A graphical presentation of the results of a representative sampling characterized by constant flow rate of the starting mixture (7550 m^3 h^{-1}) indicates

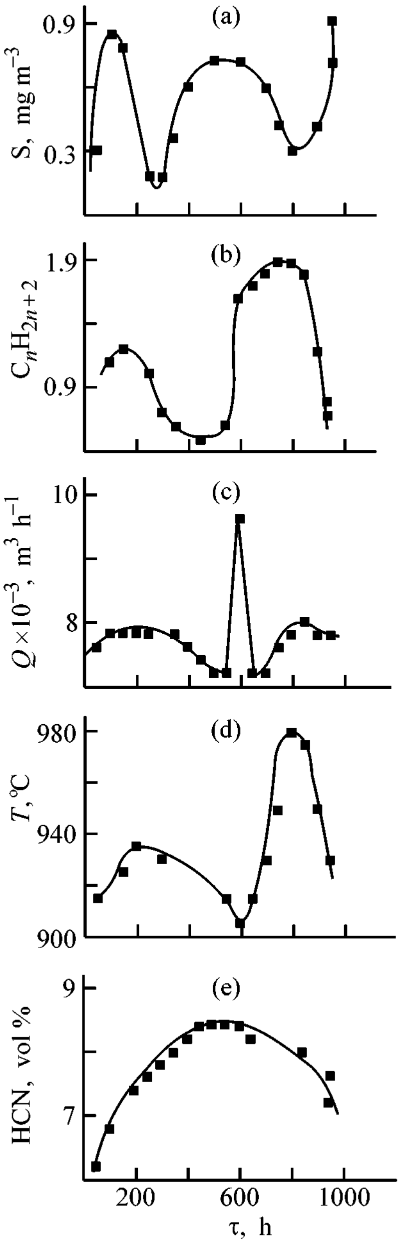

Fig. 3. Selected control parameters and response functions vs. time τ. (Q) Flow rate of the starting mixture and (T) temperature.

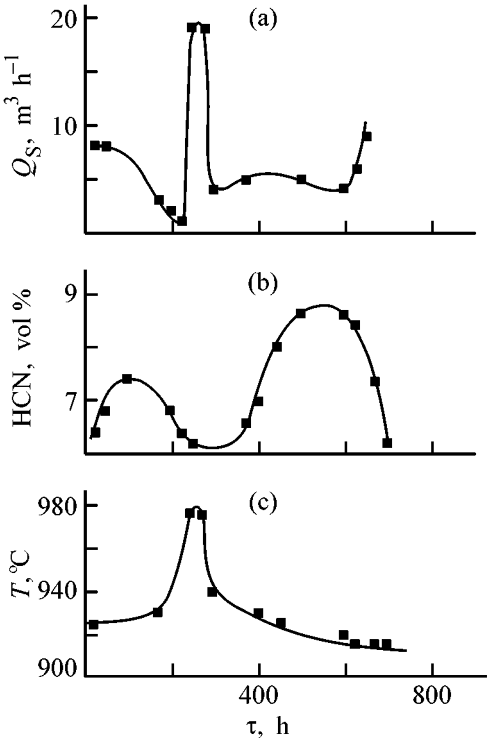

Fig. 4. Selected control parameters and response functions vs. time τ at constant flow rate of the starting mixture (7550 $m^3\ h^{-1}$). (Q_S) Amount of sulfur and (T) temperature.

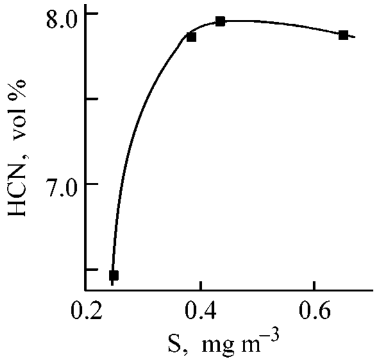

Fig. 5. Effect of the content S of sulfur compounds on the content of hydrogen cyanide in the synthesis gas. Load 7550 $m^3\ h^{-1}$, temperature 915°C.

(Figs. 4a and 4b) that an abrupt increase in the amount of sulfur, Q_S ($m^3\ h^{-1}$), fed into the reactor for HCN synthesis is accompanied by a virtually instantaneous, but not prolonged in any way, decrease in the content of hydrogen cyanide in the synthesis gas.

At the same time, the processing revealed a correlation between the content of sulfur compounds and the autothermic temperature of the process (Figs. 4a and 4c). For example, experiments with approximately constant temperature gave a dependence (Fig. 5) virtually coinciding with Warren's data, with the form of presentation of the content of sulfur compounds—as their concentration in natural gas or in the starting reaction mixture—being of no importance.

The entire body of the obtained data gave new insight into the problem of the influence exerted by technological impurities on the course of the OAM process. The revealed correlation between the content of sulfur compounds and the autothermic temperature suggested a similar relationship for higher homol-

Table 2. Database for determining the nature of the influence exerted by sulfur compounds on parameters of the OAM process.

Starting mixture, vol %			T, °C	τ, h	Natural gas		Amount of sulfur compounds, m^3		Content of HCN in synthesis gas, vol %
NH_3	CH_4	O_2			flow rate, $m^3 h^{-1}$	content of sulfur compounds, vol %	running	integral	
10.93	11.76	15.17	925	73	1080	0.75	8.08	590	7.1
11.30	11.78	15.17	920	141	1100	0.67	7.35	1415	7.4
10.63	12.09	15.50	930	173	1070	0.61	6.52	2505	7.7
11.00	11.68	15.45	930	245	1095	0.17	1.87	3380	7.4
11.12	12.00	15.49	930	265	1100	0.16	1.76	3845	7.0
11.16	11.93	15.41	975	294	1090	1.74	18.98	6745	6.5
11.16	12.11	15.58	930	309	1095	0.36	3.95	10200	6.4
11.06	12.04	15.51	930	333	1115	0.50	5.56	11725	6.8
11.40	12.52	15.24	925	409	1130	0.40	4.53	13595	6.7
11.48	12.16	15.41	920	432	1135	0.51	5.80	15765	7.3
11.12	12.05	15.31	915	577	1105	0.27	2.99	17980	6.3
11.17	12.09	15.65	910	600	1135	0.37	4.20	20095	7.7
11.66	12.27	15.49	915	622	1140	0.72	8.19	23850	8.3
11.05	12.21	15.82	910	653	1120	0.47	5.25	28165	7.9
10.93	12.08	15.55	915	673	1110	0.51	5.65	31780	7.1

ogues of methane, too, the more so as the calorific value of these latter much exceeds the same characteristic for sulfur compounds [11].

Therefore, an assumption was made that the entire body of the previously obtained information reflects the accumulation of sulfur on the surface of a platinoid catalyst, rather than the prolonged nature of the influence of sulfur compounds. To verify (or reject) this hypothesis, a sample was formed (Table 2), characterized by constant flow rate of the starting mixture (7550 $m^3 h^{-1}$). As an additional restrictive condition served the following: all the experiments belonged to the same run. The volume of sulfur compounds in a given period of the run is understood as the current amount of sulfur compounds passed through the reactor, and their progressive total volume, as the integral amount.

The graphical representation of the data of Table 2 indicates that there is no integral effect of sulfur on the course of the OAM process. No prolonged nature of this influence is observed either. Detailed analysis of the obtained data shows that sulfur compounds are to be regarded as catalytic poisons of instantaneous action.

Thus, it became apparent that it is only possible to construct an empirical model of the OAM process that would adequately describe not only the effect of the main technological parameters (as it was done in [6]), but also the influence exerted by sulfur compounds and higher homologues of methane if the following condition is satisfied. Deviations of calculated volume concentrations of methane from experimental values should be regarded as a direct consequence of the unaccounted-for effect of sulfur compounds and higher homologues of methane.

The subsequent statistical processing aimed at developing an empirical model (derived by the Brandon method in the form of a polynomial) took this factor into account and yielded a system of equations, including several submodels. These were the following: (a) calculation of the volume concentration of reagents in the starting mixture (ammonia, methane, oxygen), depending on its preparation conditions; (b) determination of the spontaneously attained process temperature; (c) finding the output parameters of the process (volume content of HCN in the synthesis gas, conversion of reagents into the target product, yield of the target product, etc.).

The results of a technological calculation performed using the derived system of empirical equations indicate (Fig. 6) that, with natural gas containing equal amounts of sulfur compounds and higher homologues of methane, an increase in the amount of impurities leads to a gradual rise in the process temperature, and this dependence passes through a maximum with increasing flow rate of the starting mixture.

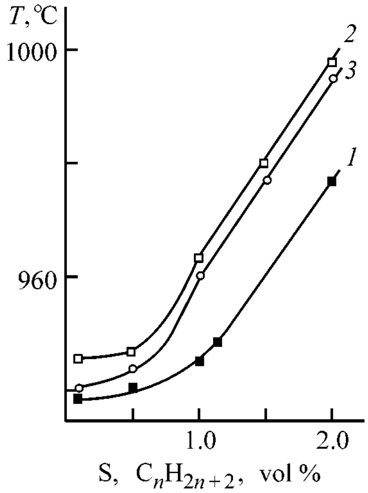

Fig. 6. Process temperature *T* vs. content of sulfur compounds, S, and higher homologues of methane, C_nH_{n+2}, in natural gas at their equal concentrations. Flow rate ($m^3\ h^{-1}$): (*1*) 7000, (*2*) 8000, and (*3*) 9000.

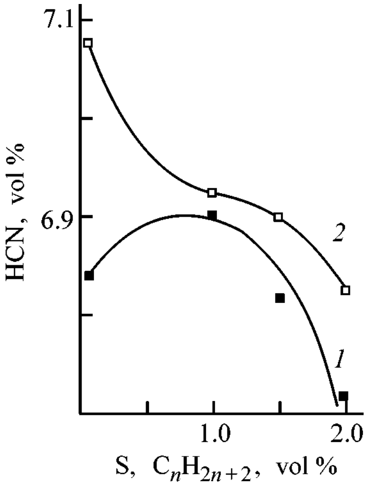

Fig. 7. Effect of the content of (*1*) sulfur compounds, S, and (*2*) higher homologues of methane, C_nH_{n+2}, on the concentration of hydrogen cyanide in the synthesis gas. Content (vol %): (*1*) C_nH_{n+2} 1.03 and (*2*) S 0.56.

An indisputable advantage of the proposed model is that it clearly demonstrates the effect of sulfur compounds and homologues of C_nH_{n+2} in “pure” form. The database in Table 1, characterized by exceedingly wide ranges of variation of all parameters of the OAM process, cannot do this by definition. It can be seen from Fig. 7 that the influence exerted by the content of sulfur compounds has extremal nature; the effect of higher homologues of methane on the content of hydrogen cyanide in the synthesis gas is negative (in calculations, the content of one of the natural gas components under consideration was fixed at the statistical-mean level).

It may be stated that only technological calculations based on the empirical model of the OAM process made it possible to avoid an erroneous conclusion that impurities contained in natural gas affect the HCN formation, drawn in the stage of preliminary processing of the initial database.

CONCLUSIONS

(1) Preliminary processing of experimental data was used to determine the nature of the influence exerted by technological impurities inevitably present in natural gas on parameters of oxidative ammonolysis of methane.

(2) Technological calculations performed using the constructed empirical model of oxidative ammonolysis of methane demonstrated an extremal influence of sulfur compounds and negative effects of higher homologues of methane on the content of hydrogen cyanide in the production gas.

(3) An increase in the time of contact with a platinoid catalyst in the case of presence of sulfur compounds and higher homologues of methane in natural gas exerts negative influence on the volume content of HCN in the synthesis gas.

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