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Abstract

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OXIDATIVE CHLORINATION OF METHANE

In the literature of recent years, attention has been directed to the possibility of carrying out, under certain conditions, the reaction of oxidative chlorination of methane ($^{1-2}$). The fundamental essence of such a process consists in combining two reactions: chlorination of the hydrocarbon and oxidation of the hydrogen chloride formed (or taken as the initial chlorinating agent). In general form, the reaction equation may be represented as follows:

$$\mathrm{RH} + \mathrm{HCl} + \tfrac{1}{2}\mathrm{O_2} \rightarrow \mathrm{RCl} + \mathrm{H_2O}$$

or

$$2\mathrm{RH} + \mathrm{Cl_2} + \tfrac{1}{2}\mathrm{O_2} \rightarrow 2\mathrm{RCl} + \mathrm{H_2O}$$

As a catalyst for this reaction, cupric chloride deposited on porous supports was proposed, or else a eutectic melt of cupric chloride and other salts. According to other literature data, chlorination of methane in the presence of molten cupric chloride proceeds in accordance with the following equation:

$$\begin{aligned} \mathrm{CH_4} + 2\mathrm{CuCl_2} &\rightarrow \mathrm{CH_3Cl} + \mathrm{Cu_2Cl_2} + \mathrm{HCl} \\ \mathrm{Cu_2Cl_2} + \mathrm{HCl} + \tfrac{1}{2}\mathrm{O_2} &\rightarrow 2\mathrm{CuCl_2} + \mathrm{H_2O} \end{aligned}$$

When this process is carried out, the thermal effect of the chlorination reaction must partly be compensated by the endothermicity of the cupric chloride regeneration reaction, as a result of which easier and milder regulation of the thermal regime of chlorination is possible. Pure cupric chloride or eutectic salt mixtures, for example $\mathrm{Cu_2Cl_2} + \mathrm{KCl} + \mathrm{CuCl_2}$, are used as chlorine carriers. The use of salt melts, although it simplifies heat removal, creates certain additional difficulties associated, in particular, with the need to circulate the melt in the reaction system at high temperature.

In connection with this, we carried out the principal experiments on the oxidative chlorination of methane on a heterogeneous catalyst, for which cupric chloride deposited on pumice was used.

Schematic of the apparatus

Figure 1: Schematic of the apparatus

Experimental Part

The experiments were carried out in a flow apparatus (Fig. 1). For simplification, the drying devices are omitted from the drawing (a Tishchenko bottle with conc. H_2SO_4 and a U-shaped tube with calcined calcium chloride) on the hydrogen chloride, chlorine, and air lines. The operation of the apparatus is clear from the diagram; we shall indicate only that the reaction tube (*E*), *d*-25 mm, was made of molybdenum glass and held 75 ml of catalyst.

Initially, the catalytic oxidation of hydrogen chloride (in the absence of methane) was studied on this apparatus, as the most important stage of the oxidative chlorination of methane. The catalyst for the experiments on the oxidation of hydrogen chloride, as well as in the subsequent experiments on oxidative chlorination proper, was specially treated pumice impregnated with cupric chloride. The amount of $CuCl_2$ deposited on the pumice was varied in the first experiments from 5 to 20% of the weight of the pumice. However, it turned out that an active catalyst is already formed at a $CuCl_2$ content of 5% in it.

Fig. 1. Schematic of the apparatus: A —chlorine cylinder, —Kipp apparatus (for HCl), —air cylinder, —methane cylinder, —mixer, E —reaction tube, —furnace, —galvanometer, thermocouple, K —reflux condenser with receiver, —Tishchenko bottles with KJ, M_1, M_2, M_3 —traps for chloro derivatives, P_1, P_2, P_3, P_4 —rheometers, respectively for Cl_2, HCl, air, and CH_4

The ratio between the reacting gases was established with the aid of rheometers. The depth of conversion of hydrogen chloride into chlorine (and the degree of chlorination of methane in the oxidative chlorination experiments) was determined by titrating the KJ solution poured into the Tishchenko bottles, as shown in the diagram (see Fig. 1).

Oxidation of hydrogen chloride to chlorine. In studying the oxidation of hydrogen chloride, the influence of temperature and of the duration of operation of the catalyst on the depth of the reaction was determined. The experimental data obtained are presented graphically in Fig. 2. A change in the space velocity from 82 to 215 h^{-1} led to a change in the degree of HCl oxidation from 98 to 86%. With time, the activity of the catalyst decreases somewhat, which is explained by the washing out of cupric chloride by the gas stream from the surface of the support—pumice.

Oxidative chlorination of methane. The process was studied in two variants: 1) chlorination of methane with a mixture of hydrogen chloride and air and 2) chlorination of methane with a mixture of chlorine and air. In these experiments, besides determining the degree of chlorination of methane, the amount of methane burned was also determined, on the basis of the difference in the

Oxidation of hydrogen chloride with air

Figure 2: Oxidation of hydrogen chloride with air

amounts of HCl after the reactor under comparable conditions in the absence and presence of methane. To simplify the calculation, as a first approximation it was assumed that decomposition of the chloro derivatives obtained does not occur, and that combustion of methane proceeds according to the equation:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$

In some experiments, the amount of methane burned as thus determined was checked from the amount of water collected. In doing so it was taken into account that, in the process of oxidation of hydrogen chloride, one mole of water is formed for every two moles of oxidized hydrogen chloride, whereas in the oxidation of methane two moles of water are formed for one mole of methane burned.

Fig. 2. Oxidation of hydrogen chloride with air; a —influence of the experimental temperature, b —change in catalyst activity

Oxidative chlorination of methane with a mixture of hydrogen chloride and air. The results of all three

series of experiments carried out by us on a methane—hydrogen chloride—air mixture are summarized in Table 1.

As follows from the data of Table 1, the chlorination reaction of methane becomes noticeable at a temperature of 350–360°. At these temperatures the oxidation of hydrogen chloride is already taking place and chlorine appears in the reaction mixture. Subsequently the degree of chlorination of methane rapidly increases and at 420–440° passes through a maximum, clearly traceable in all three series of experiments. The presence of this maximum is explained by the fact that, in parallel with the increase in the amount of methane being chlorinated as the temperature rises, the fraction of methane oxidized to CO_2 and H_2O increases and, in addition, apparently, some decomposition of the chlorination products formed takes place.

Combustion of a noticeable fraction of methane is observed at temperatures above 400° and depends to a considerable extent on the ratio hydrocarbon : chlorinating mixture (HCl and air). The maximum amount of combusted methane was observed by us at temperatures of 470–500° in the ratio CH_4 : HCl : air = 1 : 4 : 10.

Decomposition of the chlorination products to carbon was not observed in our experiments, and when the spent catalyst was discharged from the reaction tube there was no coke on the surface of the catalyst.

Table 1

Chlorination of methane with a mixture of HCl + air (in vol. %)

Ratio / initial mixture	Methane	Hydrogen chloride	Air	Temp., °C	Conversion of hydrogen chloride to chlorine	Utilization of chlorine (in % of theory)	Methane chlorinated (in % of initial)	Methane combusted (in % of initial)
Ratio $CH_4 : HCl : air = 1 : 1 : 2.5$	22.2	22.2	55.6	360	30	81	11	5
Ratio $CH_4 : HCl : air = 1 : 1 : 2.5$	22.2	22.2	55.6	400	70	92	42	7
Ratio $CH_4 : HCl : air = 1 : 1 : 2.5$	22.2	22.2	55.6	470	83	95	30	14
Ratio $CH_4 : HCl : air = 1 : 1 : 2.5$	22.2	22.2	55.6	500	87	98	31	16

Ratio / initial mixture	Methane	Hydrogen chloride	Air	Temp., °C	Conversion of hydrogen chloride to chlorine	Utilization of chlorine (in % of theory)	Methane chlorinated (in % of initial)	Methane combusted (in % of initial)
Ratio CH_4 : HCl : air = 1 : 2 : 5	12.5	25.0	62.5	360	30	80	0	7
Ratio CH_4 : HCl : air = 1 : 2 : 5	12.5	25.0	62.5	400	70	85	19	13 (?)
Ratio CH_4 : HCl : air = 1 : 2 : 5	12.5	25.0	62.5	430	78	90	50	7
Ratio CH_4 : HCl : air = 1 : 2 : 5	12.5	25.0	62.5	470	83	92	44	10
Ratio CH_4 : HCl : air = 1 : 2 : 5	12.5	25.0	62.5	500	87	95	43	11

Ratio / initial mixture	Methane	Hydrogen chloride	Air	Temp., °C	Conversion of hydrogen chloride to chlorine	Utilization of chlorine (in % of theory)	Methane chlorinated (in % of initial)	Methane combusted (in % of initial)
Ratio CH_4 : HCl : air = 1 : 4 : 10	6.7	26.7	66.6	360	30	78	10	10
Ratio CH_4 : HCl : air = 1 : 4 : 10	6.7	26.7	66.6	400	70	80	15	13
Ratio CH_4 : HCl : air = 1 : 4 : 10	6.7	26.7	66.6	430	78	90	60	21
Ratio CH_4 : HCl : air = 1 : 4 : 10	6.7	26.7	66.6	470	83	93	55	30

Ratio / initial mixture	Methane	Hydrogen chloride	Air	Temp., °C	Conversion of hydrogen chloride to chlorine	Utilization of chlorine (in % of theory)	Methane chlorinated (in % of initial)	Methane combusted (in % of initial)
Ratio CH_4 : HCl : air = 1 : 4 : 10	6.7	26.7	66.6	500	87	96	50	40

Oxidative chlorination of methane with a mixture of chlorine and air. Under this variant we carried out two series of experiments with different compositions of the reaction mixture. Air was taken in the amount necessary for complete oxidation of the hydrogen chloride formed during chlorination of methane. The results of both series of experiments are presented in Table 2.

As can be seen from the experimental data, chlorination of methane with a mixture of chlorine and air begins at a temperature of 350° and at 420–440° passes through a maximum, as in the case of chlorination of methane with a mixture of hydrogen chloride and air.

Thus, no substantial differences are observed in the course of the reaction of oxidative chlorination of methane when a mixture of chlorine and air is used as the chlorinating agent instead of hydrogen chloride and air. The maximum fraction of chlorinated methane is 50–60%.

Under the optimum temperature conditions of oxidative chlorination of methane with a mixture of chlorine and air ($CH_4 : Cl_2 : \text{air} = 1 : 2 : 5$), a special experiment was carried out to accumulate the chlorination product and investigate it. In the collected product, after its washing, neutralization, and drying, the chlorine content, molecular weight, specific···

weight and refractive index. Table 3 gives the data obtained, which are compared with the corresponding physicochemical characteristics for CCl_4. The average number of chlorine atoms in the reaction product was 3.6. On this basis, using the method described in the literature (^{2}), we calculated the content of CCl_4 in the product, which proved to be equal to ~65%.

Table 2

Chlorination of methane with a mixture of chlorine and air (in vol. %)

Methane	Chlorine	Air	Temp., °C	Conversion of chlorine to hydrogen chloride	Chlorine utilization (in % of theory)	Methane chlorinated (in % of initial)	Methane burned (in % of initial)
Ratio CH_4 : Cl_2 : air = 1 : 1 : 26							
22.2	22.2	55.6	360	30	52.0	13	8
22.2	22.2	55.6	400	70	72.2	18	14
22.2	22.2	55.6	430	78	80.2	48	17
22.2	22.2	55.6	470	83	84.2	42	20
22.2	22.2	55.6	500	87	83.9	50	21
Ratio CH_4 : Cl_2 : air = 1 : 2 : 5							
12.5	25.0	62.5	360	30	50.7	15	12
12.5	25.0	62.5	400	70	68.0	20	15
12.5	25.0	62.5	430	78	80.2	66	22
12.5	25.0	62.5	470	83	85.1	54	28
12.5	25.0	62.5	500	87	90.3	56	41

Table 3

Properties of the chlorination product in comparison with the properties of carbon tetrachloride

Substance	Molecular weight	Chlorine content, %	d_1^{20}	n_D^{20}
Carbon tetrachloride	153.8	92.2	1.5940	1.4602

Substance	Molecular weight	Chlorine content, %	d_1^{20}	n_D^{20}
Chlorination product	140.2	88.5	1.5690	1.4582

Thus, oxidative chlorination of methane makes it possible to obtain substantial yields of carbon tetrachloride.

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Note: Figure translations are in progress. See original paper for figures.