Russian Journal of Applied Chemistry, Vol. 77, No. 1, 2004, pp. 92–97. Translated from Zhurnal Prikladnoi Khimii, Vol. 77, No. 1, 2004, pp. 96–101. Original Russian Text Copyright © 2004 by Pashkevich, Mukhortov, Petrov, Alekseev, Asovich, and Barabanov.

> ORGANIC SYNTHESIS AND INDUSTRIAL ORGANIC CHEMISTRY

Synthesis of Tetrafluoromethane by Graphite Fluorination with Elemental Fluorine

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Received November 29, 2002; in final form, May 2003

Abstract—Formation of high-temperature inverse wave of the filtration combustion of graphite fixed bed in fluorine was studied. Scientific principles of the industrial process of the tetrafluoromethane synthesis from graphite and fluorine were developed.

Tetrafluoromethane (TFM), CF_4 , is widely used in the industry for plasma-chemical production of integrated circuits, as refrigerant, flame inhibitor, etc. [1]. The annual world consumption of TFM is about 1000 t today, which determines urgency of the development of its commercial synthesis.

Various methods of TFM preparation are known: fluorination of methane, its chloro and fluoro derivatives, silicon carbide, and polyfluoroethylene with elemental fluorine and fluorination of tetrachloromethane with various inorganic fluorides [1]. However, the synthesis from the elements is the most promising; fluorine is a commercial product, and electrode graphite, which is characterized by high purity and appropriate physicomechanical properties, can be used as a carbon material.

It was found [2–11] that, depending of fluorination conditions and kind of carbon raw material, the products of fluorine reaction with carbon are liquid, solid, and gaseous substances:

$$\mathbf{C}(\mathbf{s}) + \mathbf{F}_2(\mathbf{g}) \rightarrow (\mathbf{CF})_n(\mathbf{s}) + \mathbf{CF}_4(\mathbf{g}) + \mathbf{C}_2\mathbf{F}_6(\mathbf{g}) + \mathbf{C}_3\mathbf{F}_8(\mathbf{g})$$

+
$$C_4F_{10}(g)$$
 + $C_5F_{12}(g)$ + ... (1)

It was shown in [8, 9] that, at $1000-1500^{\circ}$ C, TFM is the single product of the fluorine reaction with graphite. At lower temperatures, hexafluoroethane, octafluoropropane, and higher-molecular-weight per-fluorinated carbons are also formed. At the temperatures lower than 500°C, fluorographite (CF)_n is the main product. At temperatures lower than 100° C, fluorine does not react with graphite, as indicated in numerous papers.

The TFM formation in the fluorine reaction with carbon is accompanied by a heat release $(932 \text{ kJ mol}^{-1})$ sufficient for graphite heating up to the required temperatures. Powdered graphite has effective heat conductivity of about 10^{-2} W m⁻¹ K⁻¹. The filtration combustion mode is realized when fluorine is passed through a heated graphite bed. The combustion wave has inverse structure, since graphite burns out completely, and all the reaction heat is distributed in the graphite bed below the reaction zone along the gas flow direction. In the inverse wave of the filtration combustion, the zone of fluorine uptake is narrower than the zone of highly heated graphite. Therefore, unreacted graphite is subject to prolonged heating before it appears in the reaction zone, and, as a result, volatile impurities (e.g., sulfur) are eliminated. This fact favors preparation of high-purity TFM. It should be noted that, in the inverse wave of the filtration combustion, fluorine breakthrough through the reaction zone is excluded, and thus complete fluorine conversion is provided [12].

As mentioned above, at temperatures lower than 500°C, solid fluorocarbon $(CF)_n$ is the single reaction product [10, 11]. On heating above 500°C, it decomposes to form C_2F_6 , C_3F_8 , C_4F_{10} , etc. [10, 11]. Therefore, to obtain pure TFM, the thermal interaction of the graphite packing in the fluorine-containing area with heat-bearing surfaces should be excluded. This can be realized by feeding fluorine directly into the graphite bed depth.

However, at the reactor startup, fluorine is (in the simplest case) fed into the graphite bed at room temperature, and, in the course of formation of the hightemperature synthesis wave, fluorographite initially accumulates, which then decomposes to form C_2F_6 , C_3F_8 , C_4F_{10} , etc. In addition, since fluorographite is a thermolabile condensed compound, its accumulation is undesirable from the viewpoint of safety of the reactor functioning. Thus, the stage of formation in the graphite packing with the initial temperature of $10-20^{\circ}$ C of a high-temperature wave (1000-1500 K) in which the synthesis proceeds is the most important for production of maximally pure CF₄ in an industrial reactor and the process safety.

We found no studies of carbon ignition in fluorine. Such important characteristics of the industrial process as the time of ignition delay and time of attainment of the reactor operating mode ensuring production of pure TFM (at the content of fluorocarbon impurities no more than 0.1%) are virtually unknown.

In this work, we determined the conditions of formation of a high-temperature wave of filtration combustion of graphite or its mixtures with activated birch charcoal in fluorine and a method for safe and reliable reactor startup.

EXPERIMENTAL

To study the combustion process, we developed a laboratory device (see figure).

A graphite powder was charged into a cylinder (1) with an inner diameter of 68 mm and height of 164 mm. Fluorine was fed into the reactor through a thick-walled copper nozzle (2). In the reactor volume 700 mm in diameter, Chromel–Alumel thermocouples T1–T3 without protective cases were placed. The distance (along the vertical) between the nozzle outlet and thermocouple junction was 14 mm, and the distance between the thermocouple junctions, 30 mm.

In the experiments, the constant fluorine consumption was preset, and samples of the reaction gas for chromatographic analysis on a katharometer were taken from a sampler (3) with a syringe. In addition, the fluorine breakthrough through the sampler (3) was monitored. A KI aqueous solution was used as an indicator.

Formation of the high-temperature zone of the synthesis was judged from the thermograms obtained. The time interval from the beginning of fluorine introduction to attainment of the temperature of 400°C near the junction of thermocouple T1 was considered as the ignition delay time t_{id} .

Fluorine and an F_2 + HF mixture¹ were used as



Scheme of the laboratory device for studying carbon combustion in fluorine.

fluorinating agents, and ground VAZ grade graphite (TU 48-20-54–84) produced by the MEZ (Moscow Electrode Plant) Joint-Stock Company and a mixture of 90% graphite and 10% activated birch charcoal (ABC), as carbon raw materials.

The first series of experiments was performed with VAZ graphite and fluorine. The initial graphite and graphite already used in high-temperature synthesis of CF_4 were used. The results of measurements of the ignition delay time as influenced by fluorine consumption are listed in Table 1. The nozzle outlet diameter *d* and the linear velocity of the fluorine flow at the nozzle outlet also presented. It should be noted that the high-temperature reaction zone could not be formed with spent graphite.

The results of chromatographic analysis of the reaction gas samples, qualitative monitoring of the fluorine breakthrough, and measurement of temperature as a function of time from the beginning of fluorine feeding are given in Table 2.

It follows from Tables 1 and 2 that heat accumulation and ignition proceed in the area between thermo-

Table 1. Time of ignition delay t_{id} at different flow rates W_{F_2} and linear velocities U_{F_2} of fluorine at the nozzle outlet, d = 0.85 mm

Raw material	W_{F_2} , cm ³ s ⁻¹	$U_{\rm F_2}, {\rm m \ s^{-1}}$	t _{id} , s
Graphite	40	71	540
	27	48	No ignition
Graphite*	45 26	79 46	"
Graphite+ ABC	40	71	250
Graphite + ABC*	15	26	No ignition

* After use in high-temperature synthesis of CF₄.

This mixture simulates an anodic gas produced by the Angarsk Electrolysis Chemical Combine.

Raw material	$W_{F_2}, cm^3 s^{-1}$	<i>t</i> _s ,	T, °C			Content, vol %					Breakthrough
		$cm^{3}s^{-1}$	s	T1	T2	Т3	CF ₄	C ₂ F ₆	C ₂ F ₄	CO ₂	C ₃ F ₈
Graphite	40	83	36	42	44	11.5	0.70	_	87.8	_	+
	40	165	36	42	71	80.1	3.12	-	15.5	1.20	+
	40	140	31	45	96	95.6	3.11	_	-	1.27	+
	40	330	29	15	168	98.2	1.22	-	-	0.48	+
	40	435	27	678	281	99.2	0.54	-	_	0.26	+
	40	540	>1100	637	358	96.6	2.68	-	-	0.81	+
	40	623	>1100	627	369	99.3	0.45	-	-	0.14	+
	40	735	>1100	1072	358	99.4	0.41	-	-	0.11	+
	40	825	>1100	>1200	350	99.6	0.25	-	-	0.18	+
	7	68	40	35	37	-	-	-	-	-	+
	7	112	45	35	40	-	23.8	75.7	-	-	+
	7	435	40	26	29	-	-	-	-	-	+
Graphite*	45	53	45	23	25	67.6	_	10.9	19.2	_	+
	45	135	55	25	28	88.1	-	11.9	-	-	+
	45	270	55	25	26	-	-	100	-	-	+
	45	360	55	24	25	-	-	100	-	-	+
	45	570	54	21	23	_	-	100	_	_	+
	26	98	20	25	22	_	-	_	100	_	+
	26	210	22	26	34	_	-	_	100	_	+
	26	298	22	26	34	-	-	-	100	-	+
	26	383	29	25	34	-	-	-	-	-	+
	26	495	29	25	32	-	-	-	-	-	+
	26	600	29	24	24	_	-	-	_	_	+
Graphite +	40	120	57	-	—	100	-	-	_	-	+
ABC	40	278	452	-	_	95.8	3.28	_	_	0.73	+
	40	330	713	-	-	90.5	7.83	-	-	1.65	_
	40	405	748	-	-	91.6	5.69	-	0.5	1.87	_
	40	623	-	-	—	99.2	0.55	-	_	0.22	_
	40	675	-	-	—	99.4	0.58	-	-	-	_
Graphite +	40	180	39	-	_	_		-	100	_	+
ABC*	40	255	35		_	_	-	-	100	_	+
	40	375	35	-	-	49.8	34.9	-	15.3	_	+

Table 2. Composition of the reaction gas and temperatures of thermocouples T1–T3 at various times of the synthesis t_s and fluorine flow rates W_{F_2}

* After the use in high-temperature synthesis of CF₄.

couples T2 and T3, and, as a result, a counterwave of the filtration carbon combustion in fluorine is formed. It propagates upwards the flow, is stabilized in the region of fluorine outlet from the nozzle, and transforms into the inverse wave. The counterwave of carbon combustion in fluorine propagates in the filtration mode; there is no fluorine breakthrough beyond the reaction front. The wave linear velocity between thermocouples T2 and T1 is 900 mm h^{-1} with respect to the level of 600°C.

The time of ignition delay of the initial graphite is several hundreds of seconds. In this time, carbon polyfluoride is accumulated, which then decomposes with formation of gaseous fluoroalkanes containing CF₄. Under the laboratory conditions, after the first 900 s of the synthesis, the product containing 99.5 vol % CF₄ was prepared. The main impurities were C_2F_6 and C_3F_8 .

To control the possibility of shutdown and startup of the industrial reactor of the TFM synthesis after cooling the reaction zone, we made experiments with graphite treated with fluorine in the high-temperature zone and found that, under laboratory conditions at the initial temperature of 15°C, such graphite was not ignited. Hence, to obtain pure TFM and provide stable reactor startup, special measures are required to intensify the ignition.

One of the methods of the ignition intensification is adding certain amount of activated charcoal to the graphite packing. The charcoal has substantially larger specific surface area as compared to graphite and provides higher reaction rate. We performed a series of experiments with graphite + ABC mixture using the above method. The results are given in Tables 1 and 2.

The time of ignition delay for freshly prepared graphite + ABC mixture was 250 s at fluorine flow rate of 40 cm³ s⁻¹; there was fluorine breakthrough through the graphite bed. After 700 s of the synthesis, pure CF₄ was not obtained; the hexafluoroethane impurity was 0.6 vol %. In the case of spent mixture and at fluorine flow rate of 15 cm³ s⁻¹, no ignition was observed.

The above facts show that the time of the ignition delay with ABC as initiator decreases, but the problem of the startup period (accumulation of thermolabile carbon polyfluoride under the synthesis conditions) remains. In addition, the spent graphite + ABC mixture, similarly to pure graphite, has startup characteristics differing from those of the freshly prepared mixture.

Using ABC as initiator in an industrial reactor may have the following substantial disadvantage. In the case of faster ABC burn-out as compared to graphite, the ABC in the region of fluorine feeding into the carbon bed can get exhausted after prolonged reactor functioning, which worsens the reactor startup parameters (time of ignition delay, time of attaining the steady-state mode).

In this work, we suggest the following method of the reactor startup. At startup, a gas forming with fluorine a self-igniting pair is introduced into the graphite bed coaxially to the fluorine flow. After formation of high-temperature (>1000 K) zone, owing to heat liberated in oxidation of this gas with fluorine, feeding of the gas is turned off, and the TFM synthesis is performed.

Taking into account high reactivity of fluorine, readily available methane, propane, ethylene, etc. can be used as a gaseous fuel.

Among the above gases, ethylene is the most reactive with respect to fluorine, since in the fluorine– ethylene system a branched chain reaction mechanism is realized [13]. Therefore, in laboratory trials of this method, we used a mixture consisting of 85 vol % H_2

Tab	le 3. Tin	ie t_{350}	at var	ious	flow	rates	of f	luorine	$W_{\rm F_2}$
and	ethylene	+ hy	drogen	mix	ture	$W_{\rm mix}$,	d	= 0.85	mm

	m s 1	s
26 13 26	46 23 46 25	188 270 128
	26 13 26 14	$ \begin{array}{cccccccccccccccccccccccccccccccccccc$

and 15 vol % ethylene and VAZ graphite (initial and spent). The nozzle for feeding fluorine and gas fuel consists of two coaxial tubes. Fluorine was fed through the axial channel, and a mixture consisting of hydrogen and ethylene, through the ring channel.

The gaseous fuel was fed for 10 s, and then fluorine feeding at a preset flow rate was started. When the temperature near the thermocouple T2 junction reached 350°C, feeding the gaseous fuel was stopped, while feeding fluorine with the preset flow rate was continued.

The time intervals between the beginning of fluorine feeding and attainment of 350°C near the thermocouple T2 junction, t_{350} , for various flow rates of fluorine and gas mixture are listed in Table 3. The compositions of the reaction products after stopping feeding of the ethylene + hydrogen mixture and measurement of the temperature of the graphite bed are listed in Table 4.

At the instant of fluorine feeding into the graphite bed, thermocouple T1 recorded a jump of temperature from the initial value to more than 1300°C, after which it burnt down. Thermocouples T2 and T3 recorded smooth temperature rise, and after approximately 5 min, thermocouple T2 recorded the temperature of 150–300°C.

Table 4 shows that, after stopping the supply of the gaseous fuel, a stable high-temperature inverse wave of the CF_4 synthesis is formed in the graphite bed. The time interval from stopping the gaseous fuel feeding to obtaining pure CF_4 (more than 99.9 vol %) does not exceed 500 s.

No fluorine breakthrough through the graphite bed was observed. All experiments of this series were performed with graphite that worked in the high-temperature zone of the synthesis.

Thus, the use of gaseous fuel allows stable startup of the wave reactor of TFM synthesis without ac-

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4		<i>T</i> , °C		Content, vol %					
t _s , s	T1	T2	Т3	CF ₄	C ₂ F ₆	C ₃ F ₈	CO ₂	HF	
$H_2 + C_2H_4$ mixture									
45	>1300	548	29	97.2	_	2.8	-	_	
90	>1300	644	30	98.8	_	1.2	_	-	
157	>1300	822	39	99.7	_	0.3	_	-	
202	>1300	974	51	99.9	_	0.1	_	-	
270	>1300	>1100	67	99.96	_	0.04	_	-	
300	>1300	>1100	71	99.94	_	0.06	_	-	
15	>1300	207	26	94.48	_	5.52	_	-	
90	>1300	373	26	97.16	_	2.84	_	-	
150	>1300	693	28	99.91	0.06	0.3	_	_	
225	>1300	1189	30	99.96	0.03	0.02	_	_	
315	>1300	>1100	32	99.95	0.03	0.02	_	_	
465	>1300	>1100	48	100.0	_	_	_	_	
600	>1300	>1100	68	99.99	0.01	-	_	_	
743	>1300	>1100	94	99.96	0.03	0.01	_	_	
840	>1300	_	30	99.97	_	0.03	_	_	
150	>1300	_	_	99.50	_	4.50	_	_	
330	>1300	_	_	99.50	_	0.50	_	_	
420	>1300	_	_	100.0	_	_	_	_	
225	>1300	_	_	94.20	_	5.60	_	_	
360	>1300	_	_	99.50	_	0.50	_	_	
472	>1300	_	_	99.90	_	0.10	_	_	
630	>1300	_	_	100.0	_	_	_	_	
105	>1300	_	_	88.50	_	11 50	_	_	
225	>1300	_	_	96 70	_	3 30	_	_	
315	>1300	_	_	99.50	_	0.50	_	_	
405	>1300	_		99.90	_	0.10	_	_	
555	>1300			100.0	_	0.10	_	_	
555	21300							_	
	$C_3H_8 + C_4H_{10}$ mixture								
30	>1300	589	28	-	0.50	_	_	_	
83	>1300	960	29	96.13	0.08	_	0.32	2.75	
150	>1300	>1100	29	99.38	0.03	_	0.04	0.50	
210	>1300	>1100	28	99.75	-	-	-	0.23	
300	>1300	>1100	44	99.92	-	-	-	0.08	
360	>1300	>1100	62	99.95	-	-	-	0.05	
30	>1300	489	30	93.14	0.77	-	0.18	5.42	
105	>1300	>1100	31	87.85	1.31	-	0.24	9.62	
240	>1300	>1100	38	98.78	0.13	-	0.07	0.94	
315	>1300	>1100	52	99.29	0.09	_	0.06	0.56	
480	>1300	>1100	80	99.64	0.03	_	0.03	0.30	
750	>1300	>1100	207	99.91	-	_	0.02	0.07	
855	>1300	>1100	267	99.94	-	_	0.01	0.05	
1065	>1300	>1100	402	99.99		_	–	0.01	

Table 4. Composition of the synthesis products and temperatures of thermocouples T1–T3 at various synthesis times t_s after stopping supply of ethylene + hydrogen or propane–butane mixture*

 \ast No F₂ breakthrough.

cumulation of carbon polyfluoride in the reactor in the starting period.

Fluorine produced at electrolysis plants contains impurities of HF, N₂, and O₂. To reveal the effect of HF on the TFM synthesis, we made experiments with an F₂ + 9 vol % HF mixture simulating electrolysis gas produced by the Angarsk electrolysis chemical combine and found that HF does not affect the starting characteristics and the composition of the synthesis products.

Propane–butane mixture is the most widespread commercial gaseous fuel. Therefore, we performed some experiments on its use to obtain high-temperature zone of TFM synthesis. The scheme of the laboratory device and experimental procedure were the same as above. The results are presented in Tables 3 and 4.

Thermocouple T1 at the instant of fluorine feeding recorded a temperature jump from the initial value to that higher than 1300°C. The pattern of formation of the high-temperature zone was similar to that observed with ethylene–hydrogen mixture.

The above data show that, under the industrial conditions, startup of the reactor of the TFM synthesis from electrode graphite and F_2 in the mode of the inverse wave of the filtration combustion is the most reliable when a gaseous fuel is used. In this case, the process can be organized so as to minimize accumulation of carbon polyfluoride in the reactor volume in the time of formation of the high-temperature zone and ensure the time of attainment of working conditions not exceeding 10 min. The propane–butane mixture can be recommended as the most readily available.

CONCLUSIONS

(1) A laboratory device was developed, and conditions of formation of high-temperature wave of filtration combustion in fluorine of graphite and its mixtures with activated birch charcoal were studied.

(2) At temperatures higher than 1000°C, tetrafluoromethane is the single product of fluorine reaction with graphite.

(3) At the initial temperature of the bed of graphite (or its mixture with activated birch charcoal) of 20°C, the ignition process is instable, and formation of the high-temperature zone of the synthesis depends of the fluorine flow velocity and carbon raw material history.

(4) The method of formation of the high-temperature synthesis zone with a gaseous fuel, which forms with fluorine a self-igniting pair in the graphite bed, was suggested and experimentally examined. This method allows formation of a stable wave of graphite filtration combustion in fluorine. Propane–butane mixture can be recommended for industrial use.

REFERENCES

- 1. Maksimov, B.N., Barabanov, V.G., Serushkin, I.L., et al., Promyshlennye ftororganicheskie produkty: Spravochnik (Industrial Organofluorine Products: Handbook), St. Petersburg: Khimiya, 1996.
- Ruff, O. and Keim, R., Z. Anorg. Chem., 1930, vol. 192, pp. 249–256.
- 3. Ruff, O. and Brettschneider, O., Z. Anorg. Chem., 1934, vol. 717, pp. 1–19.
- Ruff, O., Trans. Farad. Soc., 1930, vol. 34, pp. 1022– 1025.
- 5. Kuriakose, A.K. and Margrave, J.L., J. Phys. Chem., 1965, vol. 69, pp. 2772–2775.
- Ruddorff, O. and Ruddorff, G., Z. Anorg. Allg. Chem., 1947, vol. 253, pp. 281–285.
- Simons, H.J. and Dlock, L.P., J. Am. Chem. Soc., 1939, vol. 61, pp. 2962–2966.
- Timofeev, N.V., Sbornik rabot po sintezy i svoistvam ftoruglerodnykh soedinenii (Coll. of Papers on Synthesis and Properties of Fluorocarbon Compounds), Leningrad: GIPKh, 1967, issue 2, pp. 3–11.
- Timofeev, N.V. and Stepanov, V.P., Materialy 1 Mezhvedomstvennoi konferentsii po khimii i tekhnologii soedinenii ftora (Proc. 1st Interdepartmental Conf. on Chemistry and Technology of Fluorine Compounds), Leningrad: GIPKh, 1973, pp. 23–27.
- 10. Kita, Y. and Watanabe, N., J. Am. Chem. Soc., 1979, vol. 101, no. 14, pp. 3832–3841.
- 11. Watanabe, N., Koyama, S., and Imoto, H., Bull. Chem. Soc. Jpn., 1980, vol. 53, pp. 3093–3099.
- Aldushin, A.P. and Merzhanov, A.G., in *Rasprostranenie teplovykh voln v geterogennykh sredakh* (Propagation of Heat Waves in Heterogeneous Media), Novosibirsk: Nauka, 1988, pp. 8–52.
- 13. Semenov, N.N., *Khimicheskaya fizika (fizicheskie osnovy khimicheskikh prevrashchenii)* (Chemical Physics (Physical Principles of Chemical Transformations)), Moscow: Nauka, 1978.