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Plasma-chemical preparation of nanostructured catalysts for low-temperature steam conversion of carbon monoxide: properties of catalysts

Gheorghy P. Vissokov*

Institute of Electronics, Bulgarian Academy of Sciences, 72, Tsarigradsko Chaussee Bulvd., 1784 Sofia, Bulgaria

Abstract

The conditions and the process parameters of the plasma-chemical synthesis and/or regeneration of catalysts for low-temperature steam conversion of CO under the conditions of electric-arc low-temperature plasma have been investigated, as depending on the plasma-chemical process parameters and the plasma-chemical reactors (PCR) type (with "cold walls" (CW) or "warm walls" (WW)), samples that have the following properties were obtained: specific surface, up to 56 m^2/g; particle sizes, 10–60 nm, in some cases, up to 200 nm; faulty crystal lattice structure; phases of ZnO, CuO, Cu_2O and $CuAl_2O_4$.

The temperature from 2000 to 3800 K was experimentally provided as the optimal temperature range in the PCR for synthesis of samples with maximum dispersity and catalytic activity.

A complex physicochemical analysis of the plasma-chemically synthesised and/or regenerated sample by the following methods was performed: X-ray diffraction patterns, electron-microscope, chemical and other analyses.

Keywords: Plasma-chemical preparation; Nanostructured catalysts; Low-temperature steam conversion of carbon monoxide; Properties

1. Introduction

The first investigations on plasma-chemical preparation of nanostructured catalysts (NC) for low-temperature steam conversion of carbon monoxide (LTSCCO) were found in the periodical and licensed literature [1–8].

The catalyst synthesis was perform in multi-jet plasma-chemical reactor (PCR) [1]. The row-material (a mixture of powdered metals) was subject to a chemical processing. After that it was directly fed to the PCR mixer. The obtained catalyst sample composition is as follows (mass%) (Table 1).

The good contact between the initial phases under the conditions of low-temperature plasma (LTP) and the short time period (up to 10^{-3} s) of temperature treatment lead to a formation of spinel structured aluminates and Cu_2O in the synthesised products that normally miss in the precipitated and mixed catalysts. The unreduced catalyst LTC-8P comprises nanodispersed particles (NDP) with a specific shape and a diameter of 10–50 nm.

Tests were carried out on pressing the catalyst that is an analogue of LTC-8 synthesised under plasma conditions. When the pressure raises, tablet strength increases and achieves a maximum of 380 kg/cm^2 at a moulding pressure of 3500 kg/cm^2, and after that decreases. By addition of graphite, polyvinyl alcohol and carboxymethyl cellulose to the catalyst powder tablet strength achieves 700 kg/cm^2 at the same moulding pressure. Increasing the average diameter of the particles from 25 to 65 nm, the table strength falls from 610 to 280 kg/cm^2. The aim of this paper is to present our investigations tests about conditions and the process parameters of the plasma-chemical synthesis and/or regeneration of catalysts for low-temperature steam conversion of CO (LTSCCO) under the conditions of electric-arc low-temperature plasma, their physicochemical properties, as depending on the plasma-chemical process parameters and the plasma-chemical reactors (PCR) type (with "cold walls" (CW) or "warm walls" (WW)).

2. Results and discussion

Our experimental tests were performed on a plasma-chemical plant whose general scheme is given in Fig. 1.

* Fax: +359-2-9753-201.
E-mail address: marinela_panayotova@hotmail.com (G.P. Vissokov).

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Table 1
Composition of the catalyst samples

	CuO	Al_2O_3	ZnO	Cr_2O_3
Low-temperature catalyst-8P	37.3	24.5	28.2	–
Low-temperature catalyst-4P	54.0	21.0	11.0	14.0

The following main cycles of experimental tests were carried out:

(1) Plasma-chemical synthesis (PCS) of a catalyst type LTC-1, -2 and -3 in a reactor with "warm walls" (WW) at an average mass temperature in the plasma-chemical reactor (PCR) of 1000–3800 K, at a flow-rate of plasma-forming gas (Ar) of 0.87 g/s and an oxidant (O_2) flow-rate of 0.25 g/s. A mixture/charge of the following ingredients was used: elemental Cu, Zn, Al and $Al(OH)_3$ in such a mass ratio that after their oxidation, a catalyst with the following composition would be obtained: CuO 38 mass%, ZnO 48 mass% and Al_2O_3 14 mass% for LTC-1 and -2; and CuO 35.7 mass%, ZnO 44.1 mass% and Al_2O_3 20.2 mass% for LTC-3.
(2) PCS of a catalyst type LTC in a reactor with "cold walls" (CW) for an average mass temperature in PCR within the temperature range of 1000–3700 K, at a flow-rate of plasma-forming gas (Ar) of 0.89 g/s and an oxidant (O_2) flow-rate of 0.25 g/s. A mixture/charge of the following ingredients was used: elemental Cu, Zn, Al and $Al(OH)_3$ in such as a mass ratio that after the oxidation under the conditions of electric-arc LTP catalyst samples with the following composition (mass%) would be obtained: for LTC-4 (T_{rmta}, reactor mass temperature average is 1500 K)—CuO 38, ZnO 48 and Al_2O_3 14; and LTC-5 ($T_{rta} = 3700$ K)—with the same mass composition; LTC-6 ($T_{rta} = 1400$ K)—CuO 35.7, ZnO 44.1 and Al_2O_3 20.2; LTC-7 ($T_{rta} = 1000$ K), LTC-8 ($T_{rta} = 1800$ K) and LTC-9 ($T_{rta} = 2700$ K) with the following composition (mass%): CuO 30; ZnO 45 and Al_2O_3 25.
(3) Plasma-chemical regeneration of already processed catalyst samples for LTSCCO produced by CHIMCO-Vratza, Bulgaria, type "Loyna-1961", in an reactor with CW within the temperature range of 1000–2400 K, at a plasma-forming gas (Ar) flow-rate of 0.79 and 1.12 g/s and an oxidant (O_2) flow-rate of 0.25 g/s.

Some of the conditions for PCS of samples type LTC and their compositions are given in Table 2. The process parameters of the PCP on synthesising the samples type LTC-1, LTC-2 and LTC-3 in a reactor with WW are represented in Tables 3–5.

The PCS of NP, particularly when their obtaining is related to the chemical reaction running and an effective quenching

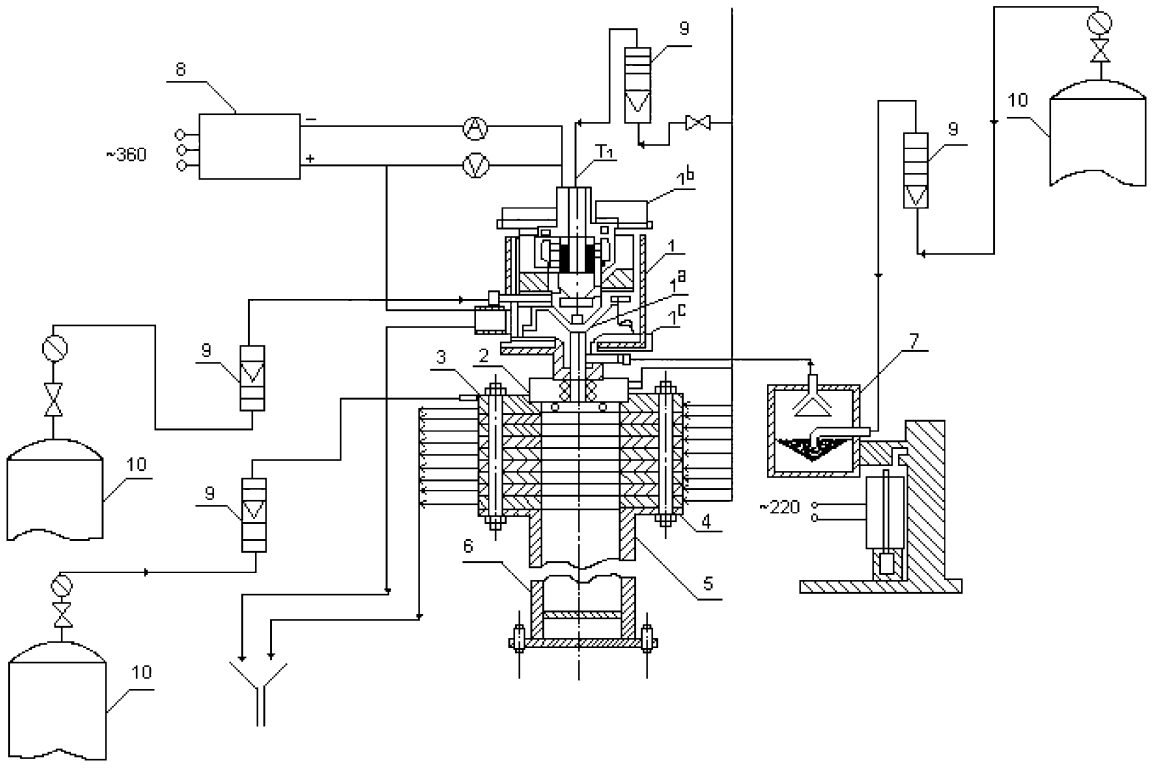

Fig. 1. Scheme diagram of plasma-chemical installation for synthesis and/or regeneration of nanodispersed catalysts NDC for ammonia production: 1, electric-arc DC plasmatron; 1^a, thoriated tungsten cathode; 1^b, copper water-cooled anode; 1^c, plastic adjusting ring; 2, CW PCR; 3, quenching device; 4, copper water-cooled sections of the quenching device; 5, powder-trapping chamber; 6, filter; 7, vibration powder-feeding device (if necessary, a piston type vibration powder-feeding device can also be used); 8, current rectifier; 9, flow-rate meters; 10, bottles with plasma-forming, powder-carrying and quenching gases; T_1, temperature of inlet water; T_2, temperature of outlet water.

Table 2
Conditions for PCS of samples type LTC and chemical composition

No.	Catalyst sample	Experimental conditions			Catalyst composition		
		Type[a] (PCR)	T_{rmta} (K)	I (A)	CuO (mass%)	ZnO (mass%)	Al_2O_3 (mass%)
1	LTC-1	WW	1600	200	38	48	14[b]
2	LTC-2	WW	3800	300	38	48	14
3	LTC-3	WW	2300	200	35.7	44.1	20.2
4	LTC-4	CW	1500	200	38	48	14
5	LTC-5	CW	3700	300	38	48	14
6	LTC-6	CW	1400	200	37.5	44.1	18.2
7	LTC-7	CW	Up to 1000	100	30	45	25
8	LTC-8	CW	1800	200	30	45	25
9	LTC-9	CW	2700	300	30	45	25

[a] PCR WW, plasma-chemical reactor with "warm" walls; PCR CW, plasma-chemical reactor with "cold" walls.
[b] Concerning the samples with 14 mass% content of Al_2O_3, 7% of the last one are obtained by thermal decomposition of $Al(OH)_3$.

is performed, have a high dispersity, high specific surface and a lot of defects in the crystal lattice. Due to that, synthesising the catalyst samples is based on the metal powders of the corresponding ingredients, with the purpose to run an oxidation chemical reaction and getting a high effective catalyst with a degenerated crystal structure. Considering the contemporary state of the problem [1–4] and the potential of the process equipment in our laboratory, plasma-chemical tests for synthesising a low-temperature catalyst type LTC have been performed, whose main parameters are represented in Tables 3–5.

As it is seen from Tables 3–5, the samples specific surface is within the range 35–50 m^2/g, the highest specific surface has the sample obtained at $T_{rmta} = 3800$ K (LTC-2). We could judge by the X-ray diffraction patterns (Fig. 2(1)) for the phases present in the sample, that is for the completeness of the separate ingredients' oxidation. Peaks of ZnO, CuO, Cu_2O and elemental Cu are observed. That proves the fact that a portion of Cu has not reacted, and the remainder quantity has been oxidised to CuO and Cu_2O. From the X-ray diffraction patterns appearance could be concluded that Al and Zn are completely oxidised, as a por-

Table 3
Process parameters of PCP for synthesising catalyst type LTC-1 in PCR with WW ($I = 200$ A)

No.	U (V)	W (kW)	H_{ape} (J/kg)[a]	T_{apt}[b] (K)	T_{art}[c] (K)	Specific surface (m^2/g)
1	28	5.6	2050	4000	1800	45[d]
2	28	5.6	2530	4900	2600	45
3	25	5.0	1680	3300	1700	45
4	28	5.6	1640	3200	1400	45
5	30	6.0	2460	4700	2200	45
6	27	5.4	1300	2500	1000	45
7	25	5.0	1330	2600	1000	28[e]
8	27	5.4	1340	2600	1000	28
9	27	5.4	1700	3300	1500	28
10	30	6.0	2510	4800	2100	28

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh, unreduced sample right after getting it.
[e] For a sample, tested for activity and passivated.

Table 4
Process parameters of PCP for synthesising catalyst type LTC-2 in PCR with WW ($I = 300$ A)

No.	U (V)	W (kW)	H_{ape}[a] (J/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	Specific surface (m^2/g)
1	28	8.4	3900	7500	3800	51[d]
2	28.5	8.55	–	–	–	51
3	29	8.70	3790	7300	3800	21[e]
4	28	8.40	–	–	–	21

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh unreduced, sample after getting.
[e] For a sample, tested for activity and passivated.

Table 5
Process parameters of PCP for synthesising catalyst type LTC-3 in PCR with WW ($I = 200$ A)

No.	U (V)	W (kW)	H_{ape}[a] (J/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	Specific surface (m^2/g)
1	29.0	5.8	2220	4300	2200	49[d]
2	29.0	5.8	1940	3800	2000	49
3	30.0	6.0	2390	4600	2300	49
4	31.0	6.2	2800	5400	2800	49
5	28.0	5.6	2540	4900	2500	49
6	26.0	5.2	2030	3900	1900	35[e]
7	26.0	5.2	2150	4100	2000	35
8	27.0	5.4	2480	4800	2600	35
9	27.5	5.5	2630	5100	2800	35
10	27.0	5.4	2330	4500	–	35
11	26.5	5.3	2260	4400	2300	30[f]
12	26.5	5.3	2260	4400	2300	30
13	26.5	5.3	2310	4500	2400	30
14	26.0	5.2	1990	3800	2800	30
15	26.0	5.2	2040	3900	2100	30

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh, unreduced sample right after getting it.
[e] For a fresh, unreduced sample right after tabletting.
[f] For a sample, tested for activity and passivated.

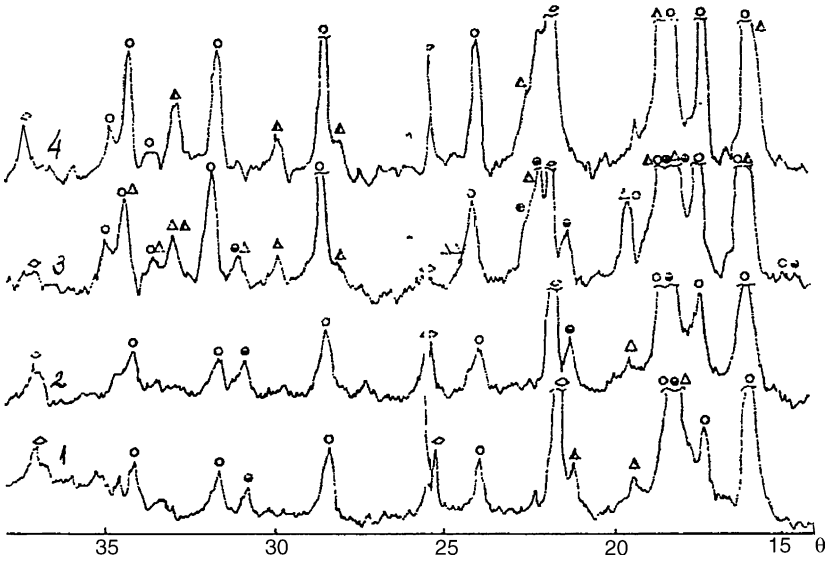

Fig. 2. X-ray diffraction patterns of plasma-chemically synthesised sample catalysts type LTC for low-temperature steam conversion of CO: 1, sample LTC-2 (PCR-WW); 2, sample LTC-7 (PCR-WW); 3, sample LTC-8 (PCR-CW); 4, sample LTC-8 tested for activity; (△) CuO; (○) ZnO; (●) Cu_2O; (◆) Cu; (◓) $CuAl_2O_4$.

tion of Cu is bonded to Al_2O_3 in the form of $CuAl_2O_4$ spinel.

The electron-microscope photograph of sample LTC-2 (Fig. 3) shows that the crystal sizes are about 20–40 nm and that the particles are mono-disperse. ND powder is compounded by particles with almost spherical shape, but there are particles reported to be with a well-shaped crystal structure are also observed.

The absence of an effective quenching of the PCS products gives us a base for testing the possibility to synthesise samples in a reactor with CW (II cycle of investigation). The preliminary investigation tests (Table 6) showed that the specific surface of the samples ranges from 30 to 40 m^2/g.

Regardless of the high radial and axial temperature gradients of the reactor with CW, it allows fixing non-equilibrium structures and defects in the crystal lattice of the phases,

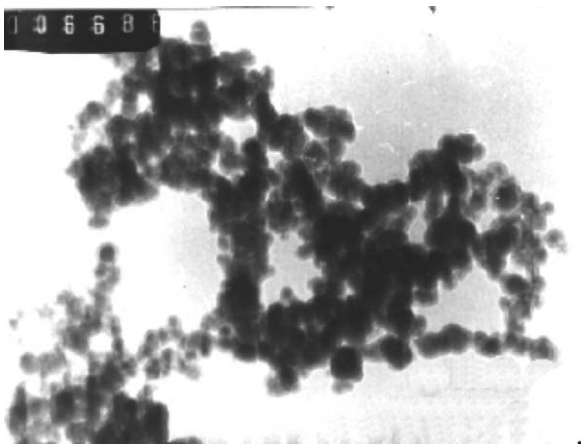

Fig. 3. Electron-microscope photograph of LTC-2 sample, magnification 98 000×, 1 mm = 10.2 nm.

Table 6
Process parameters of PCP on the preliminary investigation test for synthesising catalyst of type LTC-5 in PCR with CW

No.	I (A)	U (V)	W (kW)	H_{ape}[a] (MJ/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	S (m^2/g)
1	100	27.0	2.7	0.8	1600	Up to 1000	34
	100	26.0	2.6	0.8	1600	Up to 1000	34
	200	26.0	5.2				
2	200	28.0	5.6	2.1	4100	1800	31
	200	27.0	5.4				
	200	26.0	5.2				
3	350	26.0	9.1	3.6	6900	3000	36
	350	25.5	8.9				

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.

Table 7
Process parameters of PCP for synthesising catalyst of type LTC-4 in PCR with CW (I = 200 A)

No.	U (V)	W (kW)	H_{ape}[a] (MJ/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	Specific surface (m^2/g)
1	32.0	6.4	2.78	5400	2300	32[d]
2	33.0	6.6	2.57	5000	2000	32
3	25.0	5.0	1.64	3200	1100	32
4	25.0	5.0	–	–	–	20[e]
5	28.0	5.6	1.93	3700	1300	20

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh, unreduced sample right after getting it.
[e] For a sample, tested for activity and passivated.

Table 8
Process parameters of PCP for synthesising catalyst of type LTC-5 in PCR with CW ($I = 300$ A)

No.	U (V)	W (kV)	H_{ape}[a] (MJ/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	Specific surface (m^2/g)
1	30.0	9.0	3.7	7,100	2900	37[d]
2	37.0	11.0	15.04	10,300	4600	37
3	36.0	10.8	4.92	9,500	4400	37
4	31.0	9.3	3.62	7,000	3100	29[e]
5	33.0	9.9	3.90	7,500	3400	29
6	31.0	9.3	4.2	8,000	4000	27[f]

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh, unreduced sample right after getting it.
[e] For an unreduced sample after tabletting.
[f] For a sample, tested for activity and passivated.

Table 9
Process parameters of PCP for synthesising catalyst of type LTC-6 in PCR with CW ($I = 200$ A)

No.	U (V)	W (kV)	H_{ape}[a] (MJ/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	Specific surface (m^2/g)
1	25.0	5.0	1.80	3500	1500	34[d]
2	27.0	5.4	2.02	3900	1700	34
3	27.0	5.4	1.80	3500	1300	34
4	26.0	5.2	1.85	3600	1500	34[e]
5	24.0	4.8	1.48	2900	1200	34
6	44.0	4.8	1.78	3400	1600	34
7	26.0	5.2	1.64	3200	1300	30[f]
8	24.0	4.8	1.65	3200	1400	30
9	25.0	5.0	1.74	3400	1600	30
10	23.0	4.6	1.47	2800	1200	30

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh, unreduced sample right after getting it.
[e] For an unreduced sample after tabletting.
[f] For a sample, tested for activity and passivated.

which from their side are precondition for fixing an increased catalytic activity. The PCS process parameters of LTC-4, -5 and -6 samples are represented in Tables 7–9.

The sample LTC-5 has the highest specific surface, as it is seen in Table 8.

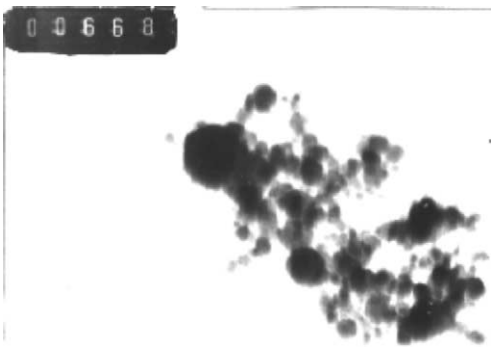

Fig. 4. Electron-microscope photograph of sample LTC-4, magnification 98 000×, 1 mm = 10.2 nm.

Table 10
Process parameters of PCP for synthesising catalyst of type LTC-9 in PCR with CW ($I = 300$ A)

No.	U (V)	W (kV)	H_{ape}[a] (MJ/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	S (m^2/g)
1	23.5	7.05	3.04	5900	2500	49[d]
2	23.0	6.90	2.76	5300	2300	49
3	23.5	7.05	2.81	5400	2100	49
4	25.0	7.50	3.34	6500	3000	35[e]
5	25.0	7.50	3.19	6200	2800	26[f]
6	25.0	7.50	3.67	7100	3200	26
7	25.5	7.65	3.57	6900	3100	26

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh, unreduced sample right after getting it.
[e] For a sample after tabletting.
[f] For a sample, tested for activity and passivated.

The electron-microscope analysis (Fig. 4) shows that the particles have an oval, almost spherical shape, with a little bit larger size (20–60 nm) compared to those synthesised in PCR with WW.

It is obvious that there are phases of ZnO, Cu_2O, CuO and elemental Cu (and probably phases of $CuAl_2O_4$) available in the samples obtained in a reactor with WW, as proved by the X-ray diffraction patterns analysis performed (see Fig. 2(2)).

The plasma-chemical synthesis process parameters of the samples LTC-7, -8 and -9 are represented in Tables 10–12, respectively. It is seen that the specific surface is raising from 40 to 56 m^2/g.

Peaks of the $CuAl_2O_4$ spinel are found aside from the abovementioned phases of ZnO, Cu_2O, CuO, as it is seen from the X-ray diffraction pattern of sample LTC-8 (Fig. 2(3)). Besides, the elemental Cu has a much finer

Table 11
Process parameters of PCP for synthesising catalyst of type LTC-7 in PCR with CW ($I = 200$ A)

No.	U (V)	W (kW)	H_{ape}[a] (MJ/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	S (m^2/g)
1	28.5	2.85	0.93	1800	–	56[d]
2	30.0	3.00	1.12	2200	1000	56
3	28.5	2.85	1.04	2000	–	56
4	27.5	2.75	–	–	–	34[e]
5	30.0	3.00	–	–	–	34
6	29.0	2.90	–	–	–	34
7	28.0	2.80	0.80	1600	1000	24[f]
8	27.5	2.75	–	–	–	24
9	27.5	2.75	–	–	–	24
10	28.0	2.80	1.03	2000	1100	24
11	28.0	2.80	1.00	1900	1000	24

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh, unreduced sample right after getting it.
[e] For a sample after tabletting.
[f] For a sample, tested for activity and passivated.

Table 12
Process parameters of PCP for synthesising catalyst of type LTC-8 in PCR with CW ($I = 200$ A)

No.	U (V)	W (kW)	H_{ape}[a] (MJ/kg)	T_{apt}[b] (K)	T_{art}[c] (K)	S (m^2/g)
1	25.0	5.0	2.13	4100	1600	40[d]
2	27.0	5.4	3.18	6100	2800	40
3	27.0	5.4	2.42	4700	1900	40
4	26.5	5.3	2.18	4200	1700	29[e]
5	26.0	5.2	2.15	4100	1700	29
6	27.0	5.4	2.13	4100	1600	29
7	26.5	5.3	2.18	4200	1600	24[f]
8	26.5	5.3	2.10	4100	1500	24
9	26.5	5.2	1.95	3800	1400	24
10	26.5	5.3	2.35	4500	2000	24
11	26.5	5.3	2.42	2400	2000	24

[a] H_{ape}, average plasma enthalpy.
[b] T_{apt}, average plasma temperature.
[c] T_{art}, average reactor temperature.
[d] For a fresh, unreduced sample right after getting it.
[e] For a sample after tabletting.
[f] For a sample, tested for activity and passivated.

structure. It could be almost certainly claimed that also a phase of the intermetal compound Cu_9Al_4 exists within the catalytic composition.

Comparing the X-ray diffraction pattern of the reduced and quenched sample LTC-8 (Fig. 2(4)) to that of the fresh one (Fig. 2(3)), the following conclusion could be made: one portion of CuO and Cu_2O is caked and is partially transformed into a coarse-dispersed elemental Cu as a result of the increased temperature, and the remainder forms $CuAl_2O_4$ spinel with Al_2O_3.

Our literature studies have shown that there are no reports on the regeneration of already processed deactivated catalysts for low-temperature steam conversion of CO (LTSCCO) under the conditions of LTP. Nevertheless, we have performed a series of experimental tests on activating an already processed low-temperature catalyst (LTC) type Loyna-1961 that had been stayed for a long time (2–3 years) in the open air. To provide an even supply to the PCR, the processed catalyst sample has been ground in a ball mill achieving particle sizes of up to 200 μm and less. The powder has been fed to the PCR by means of a vibration powder-feeding device. The process parameters of the plasma-chemical process are represented in Table 13.

The specific surface of samples processed under the conditions of electric-arc LTP is 11–22 m^2/g. In our opinion, the low specific surface values of the PCS samples are due to the ineffective reaction products quenching.

We have produced about 250–300 cm^3 from each sample, sample LTC-OMR (low-temperature catalyst, regenerated in an oxidative medium) and LTC-NMR (low-temperature catalyst, regenerated in a neutral medium), under the following process parameters: (1) For sample LTC-OMR: current, consumed by the plasmatron, of 200 A; voltage of 22–25 V; power, respectively, of 4.4–5.0 kW; average mass temperature in PCR of 1000–1200 K (plasma average mass temperature of 1900–2600 K); specific surface after plasma-chemical treatment of 17 m^2/g, and after testing the activity 12 m^2/g. (2) For sample LTC-NMR: current consumed by the plasmatron of 200 A; discharge voltage of 22–23.5 V; power, respectively, of 4.4–4.7 kW; mass temperature average in PCR of 1100–1500 K (plasma mass temperature average of 2100–2600 K); specific surface after plasma-chemical treatment of 18 m^2/g, and after testing the activity 11 m^2/g;

The obtained powdered material was pressed at a pressure of 4000 kg/cm^2, and after that fractions of 0.40–0.80 mm were prepared. These fractions were tested for activity.

To characterise the sample phase compositions, an X-ray diffraction pattern analysis of the following samples was made: fresh catalyst type Loyna-1961, processed and regenerated samples LTC-OMR and LTC-NMR (see Fig. 5).

Table 13
PCP process parameters of the performed investigation tests for regenerating an already processed deactivated catalysts type Loyna-1961 for LTSCCO (at average temperature)

No.	I (A)	U (V)	W (kW)	D_{ar} (g/s)	D_{pcg}[a] (g/s)		H_{ape} (kJ/kg)	T_{apt} (K)[b]	T_{art} (K)[c]	S (m^2/g)
					O_2	Ar				
1	100	25.5	2.55	0.79		0.28	1.27	2500	1300	12
2	200	23.0	5.60	0.79		0.28	1.55	3000	1500	12
3	300	20.0	6.00	0.79		0.28	1.46	2800	1400	11
4	100	25.5	2.55	1.19		0.28	0.84	1400	800	12
5	200	23.5	4.70	1.19		0.28	1.20	2300	1000	18
6	300	23.5	7.05	1.19		0.28	2.00	3900	2000	17
7	100	27.0	2.70	0.79	0.25		1.00	1900	800	17
8	200	25.5	5.10	0.79	0.25		2.20	4200	1800	20
9	300	22.0	6.60	0.79	0.25		2.06	4000	1400	22
10	100	26.5	2.65	1.19	0.25		0.78	1400	800	14
11	200	25.5	5.10	1.19	0.25		1.30	2500	1200	16
12	300	25.0	7.50	1.19	0.25		2.45	4700	2400	15

[a] Powder caring gas.
[b] Average plasma temperature.
[c] Average reactor temperature.

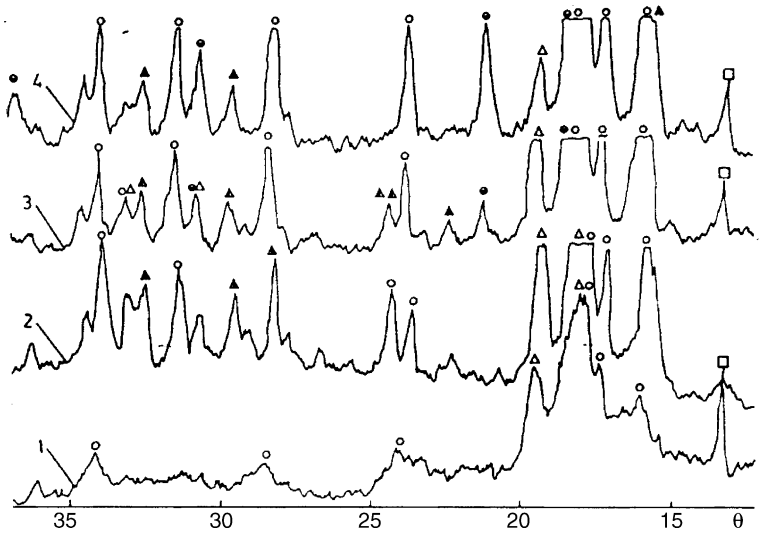

Fig. 5. X-ray diffraction patterns of plasma-chemically regenerated samples of catalysts for low-temperature steam conversion of CO: 1, fresh catalyst of type Loyna-1961; 2, an already processed catalyst of type Loyna-1961; 3, catalyst of type LTC-OMR; 4, LTC-NMR.

X-ray diffraction patterns of samples tested for activity are represented in Fig. 6. As it can be seen, a phase of ZnO is observed in all samples. Phases of Cu_2O and $CuAl_2O_4$ spinel were also observed in the plasma-chemically regenerated samples. Normally, they are not observed in the industrial catalyst. From the generalised view of the X-ray diffraction pattern, it could be concluded that the fresh catalyst has a finely dispersed structure compared to the already processed and the plasma-chemically regenerated ones. That is an a priori information that allows to be claimed that the regenerated under the conditions of LTP catalysts must have lower activity compared to that of the fresh catalyst. The fact that in the already processed samples, a substantial portion of the Cu is as spinel is impressing.

Peaks of elemental Cu were observed in X-ray diffraction pattern of plasma-chemically regenerated samples after testing their activity. Obviously, in the course of reduction, Cu_2O is reduced to a coarse-crystal Cu that is subsequently caked. That could explain the low specific surface and the lack of catalytic activity. A comparison to the X-ray diffraction pattern of a plasma-chemically synthesised under the conditions of LTP sample of type LTC-7 ($S = 56\,m^2/g$) shows the finely dispersed structure of the latter sample compared to that of the regenerated samples (see Fig. 7).

Electron-microscope photographs of the following samples are represented in Fig. 8: catalysts regenerated under the conditions of LTP in a neutral medium (LTC-NMR); in

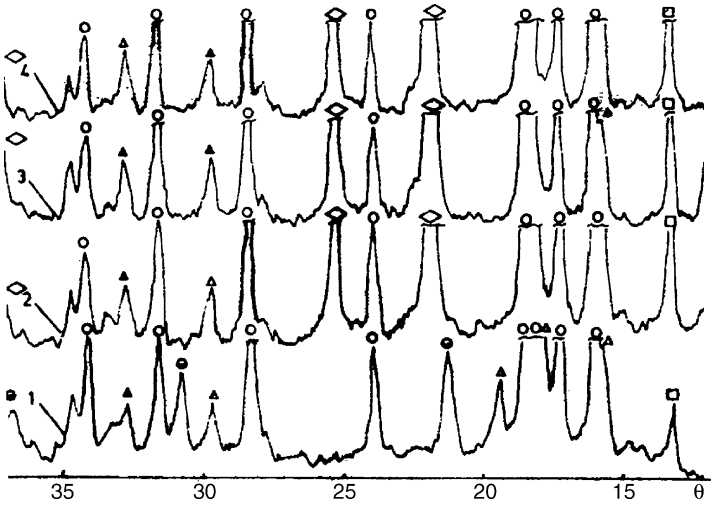

Fig. 6. X-ray diffraction patterns of plasma-chemically regenerated catalysts samples and tested for activity of the LSCCO process: 1, catalyst of type LTC-NMR; 2, catalyst of type LTC-NMR and tested for activity; 3, catalyst of type LTC-OMR and tested for activity; 4, an already processed catalyst and tested for activity; (△) CuO; (○) ZnO; (●) Cu_2O; (◇) C; (⊜) $CuAl_2O_4$.

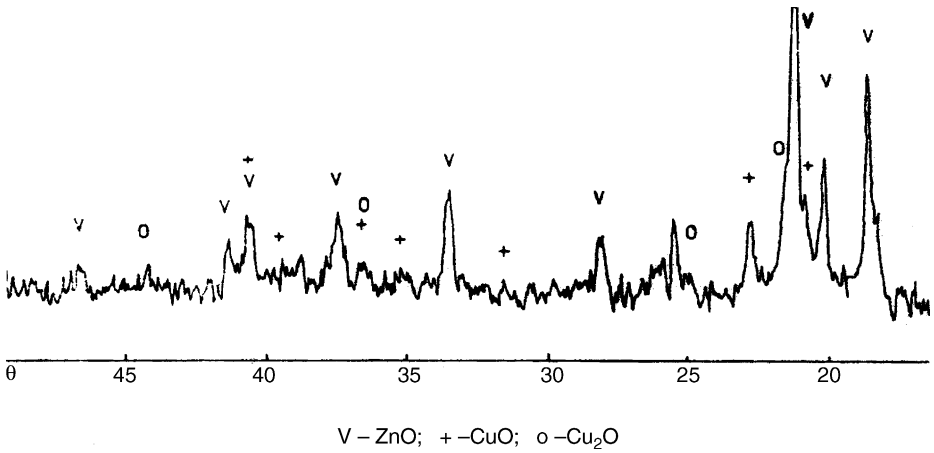

Fig. 7. X-ray diffraction pattern of a plasma-chemically synthesised sample of type LTC-7, $S = 56\,m^2/g$.

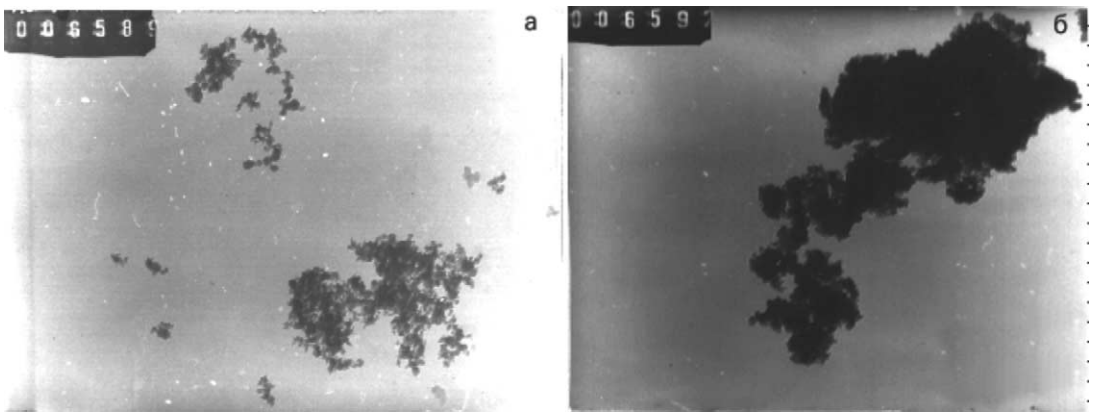

Fig. 8. Electron-microscope photographs of a regenerated catalyst of type LTC-OMR (a) and LTC (b), magnification 36 000×, 1 mm = 28 nm.

an oxidative medium (LTC-OMR); and an already processed catalyst (LTPC, i.e. low-temperature processed catalyst).

The particles already subjected to plasma influence have an oval shape, but not completely spherical. That proves the fact that particles are not completely evaporated in the PCR. The particle sizes are as follows: for sample LTC-NMR, 30–60 nm; for sample LTC-OMR, 100–200 nm; and for sample LTPC, about 1–2 μm.

Results obtained in all three cycles of investigation are generalised in Table 14. The conditions for preparation and some physicochemical properties of the catalyst samples synthesised under the conditions of electric-arc LTP are also

Table 14
Preparation conditions and physicochemical properties of some plasma-chemically synthesised or regenerated catalysts for low-temperature steam conversion of CO

Catalyst preparation, conditions (regeneration)	Synthesis, medium (regeneration)	Specific surface of the, S (m^2/g)		Crystal sizes (nm)	Phases registered by the X-ray (diffraction analysis)
		Fresh catalyst	Reduced catalyst		
Synthesis in a CW reactor, $T_r = 1000\,K$	Oxygen	32	–	15–60	CuO, Cu_2O, Cu, $CuAl_2O_4$, ZnO, Cu_9Al_4, $ZnAl_2O_4$
Synthesis in a WW reactor					
$T_r = 1300\,K$	Oxygen	45	–	10–40	CuO, ZnO, Cu
$T_r = 5100\,K$	Oxygen	51	–	10–40	
Regeneration in a CW reactor					
$T_r = 1000\,K$	Oxygen	17	12	60–200	CuO, Cu_2O, ZnO, $CuAl_2O_4$
$T_r = 1300\,K$	Argon	18	11	20–60	
Deactivated catalyst of type Loyna-1961	–	27	17	150–600	CuO, ZnO, C, $CuAl_2O_4$, $ZnAl_2O_4$

represented. It is obvious that the samples specific surface, depending on the type of PCR and the preparation conditions, is widely ranged from 17 to 51 m^2/g.

3. Conclusions

The experimental investigation tests on the plasma-chemical synthesis and/or regeneration of catalysts for low-temperature steam conversion of CO under the conditions of direct-current, quasi-equilibrium, electric-arc LTP; the complex physicochemical characterisation of the samples; and the interpretation of the test results, allow formulation of the following contributions and conclusions:

1. The conditions and the process parameters of the plasma-chemical synthesis and/or regeneration of catalysts for low-temperature steam conversion of CO under the conditions of electric-arc LTP have been investigated, as depending on the PCP parameters and the PCR type (with CW or WW), samples that have the following properties were obtained: specific surface, up to 56 m^2/g; particle sizes, 10–60 nm, in some cases up to 200 nm; faulty crystal lattice structure; phases of ZnO, CuO, Cu_2O and $CuAl_2O_4$.
2. This is the first time world-wide, when an attempt is made to regenerate already processed, deactivated catalysts for low-temperature steam conversion of CO. The conditions for plasma-chemical regeneration of an already processed catalyst of type Loyna-1961 stayed for 2–3 years in the open air have been investigated.
3. A complex physicochemical analysis of the plasma-chemically synthesised and/or regenerated samples has been performed by the following methods: X-ray diffraction patterns, electron-microscope, chemical and other analyses; as their activities are defined by using a model gas simulating the industrial one for temperatures and a volume rate of the steam–gas mixture similar to those used in the industrial process of low-temperature steam conversion of CO.

Due to the bonding of a portion of the elemental Cu in the $CuAl_2O_4$ spinel crystal lattice, the plasma-chemically synthesised samples of type LTC have a high thermal resistance which exceeds that of their conventional industrial analogues.

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