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

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Abstract

The "warm walls" (WW) plasma-chemical reactors (PCR) synthesized catalyst samples (types LTC-1–3) give up by activity compared to their industrial analogues; and these synthesized in PCR with "cold walls" (CW) (types LTC-7–9) have a commensurable activity compared to those of the industrial catalysts used by the Bulgarian company CHIMCO-Vratza. Their activities were 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.

The enhanced catalytic activity of the plasma-chemically synthesized samples is owing to: the faulty crystal lattice structure of the catalytically active phases; the nanodispersed sample composition (the crystal sizes of the catalytically active phases ranges from 10 to 40 nm); the presence of Cu_2O in the fresh samples, apart form the presence of CuO; the content of cuprous oxides—30–38 mass%; the even distribution of the ultradispersed components, the high porosity, specific surface and dispersity of the phases.

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

The high specific surface of the plasma-chemically synthesized samples for low-temperature steam conversion of CO, their homogenous chemical composition, high formation rate of their active surface by reduction, high activity and thermal resistance, represent a precondition to extend the investigation on developing a plasma-chemical technology for their industrial synthesis in the catalyst workshops.

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

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].

A portion of the test results is shown in Table 1.

Catalyst activity, depending on the mass ratio of solid and gas phase in the reaction zone, goes through a maximum. Their porosity reaches 70–80%. The increased activity of the catalysts obtained by plasma-chemical method (PCM) could be explained by the more even distribution and high porosity of the components [1].

Continuos tests (20 days periods) with catalysts LTC-4P and LTC-8P have been carried out with industrial gas with a volume of 800 cm^3. High indices with respect to the catalyst stability and activity were found under the conditions of stage-increasing volume rate, pressure, temperature and steam/gas ratio. The average residual content of CO output of the reactor was by 10% lower than at use of standard catalysts.

Some properties of catalysts for LTSCCO, obtained by PCM [2] with different compositions are shown in Table 2. Sample No. 5 has the highest activity (493 K, 0.15 vol.%; 473 K, 0.20 vol.%; 453 K, 0.40 vol.% CO). The sample obtained by co-precipitaion and than overheated at the same temperature is inactive. LTC-8 industrial samples, as well as the catalyst obtained under the conditions of LTP with the same chemical composition, are three-phase catalysts (Cu_2O, complex spinel, Al_2O_3).

A catalyst for methanol synthesis with an optimal composition of $2CuO{\cdot}ZnO{\cdot}0.16Al_2O_3$ [4] was synthesised by the PCM. Crystal size of Cu is 30–40 nm, of ZnO is 40–70 nm,

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Table 1
Some properties of carbon oxide conversion catalysts

Sample[a]	Crystal size (nm)	Activity (residual content of CO (vol.%)/rate constant)			Specific surface area (m^2/g)	
		473	493	453	Reduced catalyst	Cu
LTC-8P	31	0.3/15.4	0.2/17.6	0.8/11.1	127.0	2.1
LTC-4P	19	0.2/17.8	0.1/19.8	0.4/14.9	87.0	2.0
LTC-8	23	0.5/13.0	0.35/14.8	1.5/8.8	80.0	12.0
LTC-4	21.2	0.3/15.3	0.5/14.6	1.5/9.0	65.0	12.5

[a] LTC: low-temperature catalyst.

Table 2
Composition and properties of catalysts for LTSCCO obtained by PCM

Number	Composition (mass%)		Activity			Specific surface area (m^2/cm^3)	Particles diameter (nm)
	CuO	Complex spinel	Al_2O_3	Rate constant (s^{-1})	Residual content of CO (%) at 493 K		
1	37.0	32.5	30.5	17.5	0.2	137	29.8
2	43.3	13.8	38.8	–	–	148	26.3
3	27.7	18.9	53.4	–	–	116	38.4
4	43.0	29.4	27.6	17.5	0.2	145	26.2
5	46.5	40.8	12.7	17.5	0.2	124	35.0
6	63.8	18.7	17.5	–	–	148	27.1
7	27.1	55.5	17.4	17.5	0.2	138	28.5
8	20.1	41.2	38.7	13.1	0.6	142	29.4
9	17.1	42.7	40.2	–	–	140	30.0
10	51.3	25.1	23.6	16.0	0.3	116	39.0
11	52.7	6.8	40.5	17.5	0.2	123	31.6
12	30.5	46.0	23.5	18.8	0.15	133	31.6
13	51.5	42.2	6.3	–	–	121	36.6
14	30.9	25.3	43.8	17.5	0.2	133	31.2
15	48.6	31.6	29.8	17.5	0.2	118	38.7

Table 3
Activity and copper crystal sizes of plasma-chemically synthesised catalyst before and after overheating [4]

Number	Overheating temperature (K)	Temperature (K), residual concentration of CO (vol.%)			Copper crystal sizes (nm)
		453	473	493	
1	Without overheating	1.0	0.3	0.2	31.0
2	723	1.0	0.3	0.2	61.0
3	873	1.5	0.4	0.2	96.0
4	1023	8.9	4.4	2.8	110.0

for example a little bit larger than those of the standard catalyst. It was establish that after reduction, the copper crystal sizes of the standard and the plasma-chemically synthesised (PCS) catalysts are practically identical. For measuring the influence of the temperature on the activity in the process of LTSCCO, copper–zinc–aluminium catalysts were tabletted and overheated at 723, 873 and 1023 K for 3 h. The activity measurement results are given in Table 3.

As shown in Table 3, the overheating temperature, unlike the precipitated catalysts, has a significantly lower influence on the "plasma" catalyst activity. When raising the overheating temperature of the "plasma" catalyst to 873 K, its phase composition and activity do not change, while the mixed catalyst practically completely loses its activity at 673–773 K [6]. At 1023 K, cuprous oxide recrystallization in the catalyst comes on, and its conversion into a hardly reducible modification that leads to a significant activity reduction and to an increase of the cuprous oxide crystals; and at the same time, a caking process run.

Catalyst samples obtained by the PCM have an increased thermal resistance compared to the samples obtained by

Table 4
"Plasma" and standard catalysts' activity in the process of LTSCCO at a pressure of 2.8 MPa [4]

Number	Sample	Activity, residual content of CO (vol.%)				
		A 24 h period	Two 24 h period	Three 24 h period	Four 24 h period	Five 24 h period
1	LTC-4	0.21–0.26	0.25–0.37	0.37–0.47	0.47–0.78	0.78
2	LTC-4P	0.19–0.24	0.24–0.32	0.32–0.42	0.42–0.65	0.65–0.69
3	LTC-8	0.18–0.23	0.23–0.31	0.31.0.36	0.36–0.60	0.60–0.81
4	LTC-8P	0.16–0.22	0.22–0.28	0.28–0.34	0.34–0.51	0.50–0.72

mixing and precipitation. The result of investigating LTC-8P and LTC-4P catalysts' activity is shown in Table 4, compared to those of the standard ones. Experiments were carried out with a model plant at a pressure of 2.8 MPa.

The aim of this paper is to present our investigations tests about catalytic activity of the PCS and/or regenerated catalysts for low-temperature steam conversion of CO (LTSCCO) under the conditions of electric-arc low-temperature plasma in plasma-chemical reactors (PCR) type (with "cold walls" (CW) or "warm walls" (WW)).

2. Results and discussion

As it was already mentioned here before, one of the most important criteria for the catalysts efficiency is their activity. The investigation test concerning the PCS samples activity were carried out on a line plant submitted to us for use in the laboratory of Professor D. Shishckov (Department of Technology of Inorganic Substances, University of Chemical Technology and Metallurgy, Sofia) (Fig. 1), at a pressure of 2 MPa, within the temperature range 473–573 K, volume rate of the steam–gas mixture of 1500, 3000, 6000 and 10,000 h^{-1}. A model gas with the following composition (vol.%) was used: CO, 3.5; CO_2, 15.7 and H_2:N_2 = 3:1 up to 100 vol.%; the steam–gas ratio ranges from 0.7 to 1.3.

The test results of the LTC-1–3 samples' activity is represented in Tables 5 and 6. These results are not satisfactory, because a relatively high conversion degree is reported to be within the range 523–573 K, where the equilibrium rate of conversion is lower. It could be expected that the use of an effective PCP products quenching would lead to getting a more active catalyst composition.

The sample has not completely lost its activity at 523 K after 2 h overheating at 773 K as it is seen in Table 6. The samples are tested for activity, as the results are represented in Tables 7–9.

All three samples have comparable activities, as the highest activity has sample LTC-4 at which steam/gas ration (0.7–1.0) was varied. Catalyst activities tend to equalise at volume rates up to 30,000 h^{-1}.

Bearing in mind measured the catalytic activity of samples LTC-4–6 and the correlation between the activity and the total specific surface, Al_2O_3 content is increased in that test

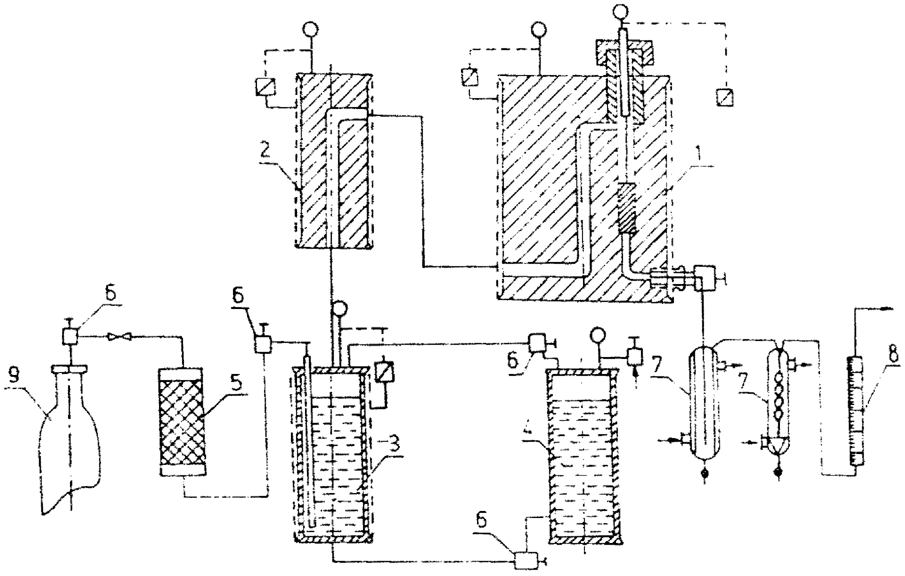

Fig. 1. Scheme of a plant for testing the activity of catalyst samples for steam LTC of CO: 1, catalytic reactor; 2, condenser; 3, steam-saturator; 4, water vessel; 5, reactor of ZnO; 6, valves; 7, cooler; 8, flowmeter; 9, model gas cylinder.

Table 5
Activity of PCS samples of type LTC-1 and LTC-2 for LTSCCO, with the following composition of the model gas (vol.%): CO, 3.3; CO_2, 13 and H_2:N_2 = 3:1 up to 100 vol.%

Number	T_r (K)	V ($\times 10^3$ h^{-1})	Steam:gas ratio	Residual content of CO (vol.%)		Conversion degree, α (%)	
				LTC-1	LTC-2	LTC-1	LTC-2
1	473	3	0.82	1	1	–	–
2	493	3	1.0	0.84	0.75	73.92	76.70
3	523	3	0.7	0.62	0.82	80.71	74.54
4	573	3	0.7	–	0.18	–	94.68
5	573	6	0.7	–	0.5	–	84.42
6	573	10	0.7	–	0.76	–	76.39

Table 6
Activity of PCS samples of type LTC-3 for LTSCCO, with the following composition of the model gas (vol.%): CO, 4.2; CO_2, 19.8 and $H_2:N_2 = 3:1$ up to 100 vol.%, at a steam:gas ratio = 0.68

Number	T_r (K)	V ($\times 10^3$ h^{-1})	Steam:gas ratio	Residual content of CO (vol.%)		Conversion degree, α (%)	
				Fresh sample	After overheating[a]	Fresh sample	After overheating[a]
1	473	1.5	0.68	0.83	–	79.58	–
2	473	3	0.68	1.0	1.98		51.83
3	483	3	0.68	0.51	–	80.71	–
4	528	3	0.68	0.27	0.37	93.32	90.85
5	528	6	0.68	0.37	0.65	90.85	83.98
6	528	10	0.68	0.46	0.84	88.64	79.33
7	548	3	0.68	0.30	–	92.58	–
8	548	6	0.68	0.34	–	91.58	–
9	548	10	0.68	0.42	–	89.62	–
10	568	10	0.68	0.33	–	91.84	–

[a] The sample is overheated for 2 h at $T_p = 773$ K.

series, with the purpose to increase the specific surface, on the one hand, and the thermal resistance and activity, on the other hand.

Catalytic activity of samples LTC-7–9 was tested for activity (see Tables 10–12).

Due to the fact that all three samples demonstrate a satisfactory catalytic activity, the investigation tests were hold only for catalytic reactor temperatures of 473 and 493 K. After 3 h heating at a temperature of 773 K, the samples are tested for activity within the temperature range 473–523 K. The sample LTC-7, that was obtained at the lowest temperature, showed the lowest thermal resistance. The other two samples (LTC-8 and LTC-9) demonstrated good activity at temperatures of 493 and 523 K. Probably, the enhanced thermal resistance of samples LTC-8 and LTC-9 is owing to the increased content of Al_2O_3 (25 mass%) compared to the samples with a low content of Al_2O_3 (14 and 20 mass%). The enhanced thermal resistance of samples LTC-8 and LTC-9 is seen in Figs. 2 and 3. Overheating the conventional catalysts up to 773 K, leads to their complete deactivation due

Table 7
Activity of PCS samples of type LTC-4 for LTSCCO, with the following composition of the model gas (vol.%): CO, 3.3; CO_2, 13.0 and $H_2:N_2 = 3:1$ up to 100 vol.%

Number	T_r (K)	V ($\times 10^3$ h^{-1})	Steam:gas ratio	Residual content of CO (vol.%)		Conversion degree, α (%)	
				Fresh sample	After overheating[a]	Fresh sample	After overheating[a]
1	473	3	0.82	0.10	0.74[b]	96.87	77.00[b]
2	473	6	0.82	0.66	–	79.47	–
3	473	3	1.0	0.22	–	93.13	–
4	473	6	1.0	0.72	–	77.62	–
5	473	10	1.0	0.99	–	69.31	–
6	493	3	0.7	0.28	0.22	91.26	93.13
7	493	6	0.7	0.47	0.67	85.36	79.16
8	493	10	0.7	0.79	–	75.46	–
9	493	3	1.0	0.12	–	96.24	–
10	493	6	1.0	0.14	–	95.62	–
11	493	10	1.0	0.24	–	92.50	–
12	493	20	1.0	0.90	–	72.08	–
13	523	3	0.7	0.07	–	97.81	–
14	533	6	0.7	0.06	–	98.12	–
15	533	10	0.7	0.10	–	96.87	–
16	533	20	0.7	0.37	–	88.46	–
17	533	40	0.7	0.92	–	71.46	–
18	563	3	0.7	0.06	–	98.12	–
19	563	6	0.7	0.07	–	97.81	–
20	563	10	0.7	0.12	–	96.24	–
21	573	20	0.7	0.30	–	90.64	–
22	573	40	0.7	0.65	–	79.78	–

[a] The sample is overheated for 3 h at $T_p = 773$ K.

[b] The steam:gas ratio = 0.7.

Table 8
Activity of PCS samples of type LTC-5 for LTSCCO, with the following composition of the model gas (vol.%): CO, 4.2; CO_2, 19.8 and H_2:N_2 = 3:1 up to 100 vol.% and a steam:gas ratio = 0.68

Number	T (K)	V ($\times 10^3\,h^{-1}$)	Residual content of CO (vol.%)		Conversion degree, α (%)	
			Fresh sample	After overheating[a]	Fresh sample	After overheating[a]
1	473	3	0.57	1.23	85.94	69.85
2	483	6	0.39	0.72	90.36	82.26
3	483	6	0.91	–	77.62	–
4	498	3	0.41	0.43	89.87	89.38
5	523	3	0.23	–	94.30	–
6	523	6	0.29	–	92.82	–
7	523	10	0.33	–	91.84	–
8	528	3	–	0.28	–	93.07
9	528	6	–	0.53	–	86.92
10	528	10	0.31	0.86	92.33	78.84
11	548	6	0.26	–	93.56	–
12	568	10	0.34	–	91.59	–
13	568	3	0.31	–	92.33	–
14	568	6	0.36	–	91.10	–
15	568	10	0.37	–	90.85	–
16	568	20	0.44	–	89.13	–
17	568	40	0.48	–	88.14	–
18	568	60	0.63	–	84.47	–

[a] The sample is overheated for 3 h at $T_p = 773$ K.

to the transformations occurring in the crystal structure of the catalytically active phases.

Some of the test results on the regenerated samples' activity are represented in Table 13. A conclusion could be drawn that Loyna-1961 catalyst was not regenerated.

The nanodispersed particles (NDP) size for the most dispersed samples ranges from 10 to 40 nm depending on the preparation conditions, as it is proved by means of the electron-microscope analysis. According to the X-ray diffraction pattern analysis, CuO, Cu_2O, ZnO, $CuAl_2O_4$ and elemental Cu are basic components of the samples. The specific surface of the samples decreases after reduction and passivation. The catalyst synthesised in a CW reactor displays a higher activity (see Table 14). Within the

Table 9
Activity of PCS samples of type LTC-6 for LTSCCO, with the following composition of the model gas (vol.%): CO, 4.2; CO_2, 19.8 and H_2:N_2 = 3:1 up to 100 vol.% and a steam:gas ratio = 0.68

Number	T_r (K)	V ($\times 10^3\,h^{-1}$)	Residual content of CO (vol.%)		Conversion degree, α (%)	
			Fresh sample	After overheating[a]	Fresh sample	After overheating[a]
1	473	3	0.40	0.98	90.11	75.92
2	483	3	0.31	0.80	92.30	80.31
3	483	6	0.71	–	82.51	–
4	498	6	0.67	–	83.51	–
5	523	3	0.17	0.17	95.79	95.79
6	523	6	0.21	–	94.80	–
7	523	10	0.33	–	91.84	–
8	528	6	–	0.37	–	90.85
9	528	10	0.31	0.58	92.80	85.69
10	528	20	0.63	–	84.84	–
11	548	6	0.28	–	93.07	–
12	548	10	0.33	–	91.84	–
13	548	20	0.38	–	90.61	–
14	548	40	0.64	–	84.22	–
15	563	6	0.30	–	92.58	–
16	563	10	0.34	–	91.59	–
17	563	20	0.46	–	88.64	–
18	563	40	0.54		86.60	–
19	563	60	0.75	–	81.53	–

[a] The sample is overheated for 3 h at $T_p = 773$ K.

Table 10
Activity of PCS samples of type LTC-7 for LTSCCO, with the following composition of the model gas (vol.%): CO, 4.15; CO_2, 20.4 and H_2:N_2 = 3:1 up to 100 vol.% and a steam:gas ratio = 0.7

Number	T_r (K)	V ($\times 10^3$ h^{-1})	Residual content of CO (vol.%)		Conversion degree, α (%)	
			Fresh sample	After overheating[a]	Fresh sample	After overheating[a]
1	473	3	0.11	1.71	97.24	57.81
2	473	6	0.20	–	94.99	–
3	473	10	0.33	–	91.74	–
4	473	20	0.62	–	84.53	–
5	493	3	0.08	0.51	97.99	87.26
6	493	6	0.14	–	96.49	–
7	493	10	0.30	–	92.49	–
8	498	20	0.60	–	85.03	–
9	523	40	0.90	–	77.61	–
10	523	3	–	0.23	–	94.25
11	523	6	–	0.30	–	92.49
12	523	10	–	0.56	–	86.02

[a] The sample is overheated for 3 h at $T_p = 773$ K.

Table 11
Activity of PCS samples of type LTC-8 for LTSCCO, with the following composition of the model gas (vol.%): CO, 4.15; CO_2, 20.4 and H_2:N_2 = 3:1 up to 100 vol.% and a steam:gas ratio = 0.7

Number	T_r (K)	V ($\times 10^3$ h^{-1})	Residual content of CO (vol.%)		Conversion degree, α (%)	
			Fresh sample	After overheating[a]	Fresh sample	After overheating[a]
1	473	3	0.09	0.82	97.94	79.59
2	473	6	0.12	1.33	96.99	67.06
3	473	10	0.21	–	94.74	–
4	473	20	0.62	–	84.53	–
5	493	3	0.09	0.18	97.74	95.49
6	493	6	0.09	0.36	97.74	90.99
7	493	10	0.14	0.60	96.49	85.03
8	493	20	0.38	–	90.50	–
9	493	40	0.58	–	85.53	–
10	493	60	0.64	–	84.04	–
11	523	6	–	0.15	–	96.24
12	523	10	0.17	0.17	–	95.74
13	523	20	–	0.15	–	96.24
14	523	40	–	0.27	–	93.24
15	523	60	–	0.40	–	90.00

[a] The sample is overheated for 3 h at $T_p = 773$ K.

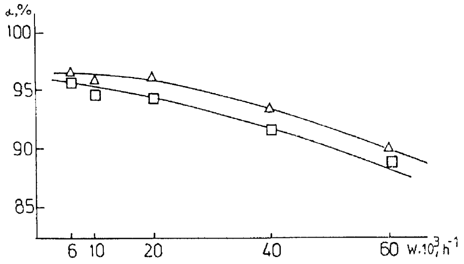

Fig. 2. Conversion degree, α (%) upon the process of LTSCCO on PCS catalysts of type LTC-8 and LTC-9 at 493 K (the samples are heated for 3 h at 773 K) depending on the volume rate of the steam–gas mixture: (▽) LTC-8; (☐) LTC-9.

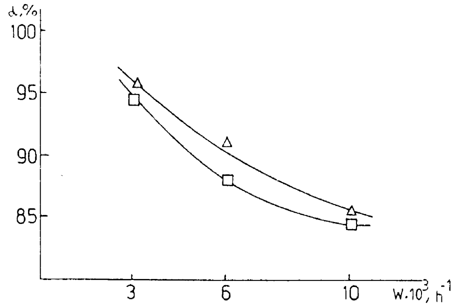

Fig. 3. Conversion degree, α (%) upon the process of LTSCCO on PCS catalysts of type LTC-8 and LTC-9 at 523 K (the samples are heated for 3 h at 773 K) depending on the volume rate of the steam–gas mixture: (▽) LTC-8; (☐) LTC-9.

Table 12
Activity of PCS samples of type LTC-9 for LTSCCO, with the following composition of the model gas (vol.%): CO, 4.15; CO_2, 20.4 and H_2:N_2 = 3:1 up to 100 vol.% and a steam:gas ratio = 0.7

Number	T_r (K)	V ($\times 10^3\ h^{-1}$)	Residual content of CO (vol.%)		Conversion degree, α (%)	
			Fresh sample	After overheating[a]	Fresh sample	After overheating[a]
1	473	3	0.13	0.52	96.74	87.01
2	473	6	0.16	–	95.99	–
3	473	10	0.28	–	92.99	–
4	473	20	0.49	–	87.76	–
5	493	3	0.14	0.22	96.49	94.49
6	493	6	0.16	0.49	95.99	87.76
7	493	10	0.20	0.62	94.99	84.53
8	493	20	0.32	–	91.99	–
9	493	40	0.45	–	88.76	–
10	493	60	0.66	–	83.54	–
11	523	6	–	0.17	–	95.74
12	523	10	–	0.21	–	94.74
13	523	20	–	0.23	–	94.24
14	523	40	–	0.34	–	91.49
15	523	60	–	0.45	–	88.76

[a] The sample is overheated for 3 h at $T_p = 773$ K.

Table 13
Activity of PCS samples of type LTC-OMR and LTC-NMR, and a deactivated catalyst LTPC for LTSCCO, with the following composition of the model gas (vol.%): CO, 3.5; CO_2, 15.7 and H_2:N_2 = 3:1 up to 100 vol.%

Number	T_r (K)	V ($\times 10^3\ h^{-1}$)	Steam:gas ratio	Residual content of CO (vol.%)			Conversion degree, α (%)		
				LTC-OMR	LTPC[a]	LTC-NMR	LTC-OMR	LTPC[a]	LTC-NMR
1	473	3	0.7	1.00	1.00	1.00	–	–	–
2	513	3	0.7	1.84	1.00	1.00	46.57	–	–
3	523	3	0.7	1.00	0.80	1.00	–	76.53	–
4	548	3	0.7	1.14	0.27	0.74	66.66	92.04	78.28
5	548	6	0.7	–	0.77	–	–	77.40	–
6	573	3	0.7	0.86	0.26	0.66	74.93	92.33	80.61
7	573	6	0.7	–	0.50	–	–	85.29	–
8	573	10	0.7	–	0.69	–	–	79.73	–
9	573	3	1.3	0.95	–	0.84	72.17	–	75.36
10	573	10	1.3	–	1.00	–	–	70.72	–

[a] Already processed catalyst of type Loyna-1961 for LTSCCO, with a specific surface area of 27 m^2/g before and 17 m^2/g after activity testing.

temperature range 473–523 K, the residual content of CO is 0.06–0.2 vol.% at a volume rate of 3000 h^{-1} and it increases at raising the volume rate. The conversion degree (α, %) decreases, respectively.

The overheating temperature, impacts significantly less the activity of PCS samples compared to precipitated catalysts. The residual content of CO was 0.18%, in 3 h, at a volume rate of 3000 h^{-1}, temperature of the catalytic reactor of 493 K, and at raising the overheating temperature of the PCSC type LTC up to 773 K, while the mixed catalyst was practically completely deactivated at 673–773 K. A recrystalization of CuO within the catalyst composition runs at 923 K. As a result of that, the activity is significantly decreased and the CuO crystals grow.

In our opinion, the increased catalytic activity of the PCS catalyst for LTSCCO, is owing to: the faulty crystal lattice of the catalytically active phases; the ultradispersed composition of the samples; the presence of Cu_2O in the fresh samples; the content of Cu oxides within the range 30–38 mass%. Most probably, the enhanced thermal resistance of the “plasma” samples is due to the high content of Al_2O_3 (25 mass%). The synthesised by PCM under the conditions of quasi-equilibrium electric-arc LTP catalysts for LTSCCO have an even distribution of the finely dispersed components, high porosity, high specific surface and dispersity, enhanced activity and thermal resistance.

The very low catalytic activity of the regenerated catalysts, could be due to: the caking and the agglomeration of NDP; the presence of inoxidated coarse-dispersed Cu; the presence of hardly reducible spinel. For instance the residual content of CO was 0.66 vol.% at a temperature in the catalytic reactor of 573 K at a volume rate of 3000 h^{-1}. The cuprous oxide is reduced in the course of formatting the active surface to a coarse-crystal Cu that in the course of conversion is easily caked. That explains the lowered catalytic activity after reduction.

Table 14
Activity of PCS samples[a] (LTC-7, LTC-8 and LTC-9) for LTSCCO, with the following composition of the model gas (vol.%): CO, 4.15; CO_2, 20.4 and the remainder H_2:N_2 = 3:1 up to 100 vol.% at a steam:gas ratio = 0.7

Number	T (K)	V ($\times 10^3\ h^{-1}$)	Conversion degree (α%)					
			LTC-7 (T_r = 1000 K)		LTC-8 (T_r = 1800 K)		LTC-9 (T_r = 2700 K)	
			Fresh sample	After overheating[b]	Fresh sample	After overheating[b]	Fresh sample	After overheating[b]
1	473	3	97.2	57.8	97.7	79.6	96.7	87.0
2	473	6	95.8	–	97.0	67.1	96.0	–
3	473	10	91.7	–	94.7	–	93.0	–
4	473	20	84.6	–	84.6	–	87.8	–
5	493	3	98.0	87.3	97.7	95.5	96.5	94.5
6	493	6	96.5	–	97.7	90.1	96.0	87.8
7	493	10	92.5	–	96.5	85.0	95.0	84.5
8	493	20	85.0	–	90.5	–	92.0	–
9	493	30	77.6	–	85.5	–	88.8	–
10	493	60	–	–	84.0	–	83.4	–
11	523	3	–	94.2	–	–	–	–
12	523	6	–	92.5	–	96.2	–	95.7
13	523	10	–	86.0	–	95.7	–	94.7
14	523	20	–	–	–	96.2	–	94.2
15	523	40	–	–	–	93.2	–	91.5
16	523	60	–	–	–	90.0	–	88.8

[a] Plasma-chemically synthesise samples with the following composition (mass%): CuO, 30; ZnO, 45; Al_2O_3, 25.
[b] The sample was overheated for 3 h at a temperature of 773 K.

3. Conclusions

The experimental investigation tests on the PCS and/or regeneration of catalysts for LTSCCO 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. It is experimentally proved that the optimal temperature range in the PCR for synthesis of samples with maximum dispersity and catalytic activity is from 2000 to 3800 K.

   The WW PCR synthesised catalyst samples (LTC-1–3) give up by activity compared to their industrial analogues; and these synthesised in PCR with CW (LTC-7–9) have a commensurable activity compared to those of the industrial catalysts used by the Bulgarian company CHIMCO-Vratza. The catalysts synthesised by us are more active than their analogues synthesised by some Russian scientists [1–4]; and there is no other literature data on that problem in the reference licensed and periodical literature at this stage.
2. The enhanced catalytic activity of the PCS samples is owing to:
   - the faulty crystal lattice structure of the catalytically active phases;
   - the nanodispersed sample composition (the crystal sizes of the catalytically active phases range from 10 to 40 nm);
   - the presence of Cu_2O in the fresh samples, apart from the presence of CuO;
   - the content of cuprous oxides, 30–38 mass%;
   - the even distribution of the ultradispersed components, the high porosity, specific surface and dispersity of the phases.

   Most probably, the enhanced thermal stability of the “plasma” samples is due to the high content of Al_2O_3 (25 mass%).
3. The regenerated samples display a low specific surface (10–12 m^2/g) and low catalytic activity that is owing to the caking and the agglomeration of the ultradispersed particles; the presence of an unreacted coarse-dispersed elemental Cu; the content of a hardly reactable spinel ($CuAl_2O_4$); the unstable, in some cases, operating conditions of the electric-arc plasmatron;
4. The high specific surface and dispersity of the PCS samples for LTSCCO, their homogenous chemical composition, high formation rate of their active surface by reduction, high activity and thermal stability, all that represent a precondition to extend the investigation on developing a plasma-chemical technology for their industrial synthesis in the catalyst workshops.

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