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CATALYSTS SUPPORTED ON ALUMINA-SILICA GLASS FIBER FOR NEUTRALIZATION OF WASTE GASES

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Abstract. Technological parameters of catalysts production based on glass fiber have been investigated. Catalysts were made by deposition of different active metal ions on the amorphous glass matrix. The experimental results suggest the modified glass fibers as suitable supports for efficient catalysts for complete oxidation of organic compounds. Complete oxidation of carbon oxide is reached in the temperature range of 220–250 °C (gas hourly space velocity (GHSV) = 882 h^{-1}), and complete oxidation of methane occurs in the temperature range of 400–450 °C (GHSV = 882 h^{-1}). The experimental results made possible to calculate rate constants of oxidation reactions and activation energy.

Keywords: glass fiber, catalytic oxidation, waste gas purification.

1. Introduction

Purification of industrial and exhaust gas emissions is one of the most important environmental problems both in Russia and all over the world, since they contain toxic substances such as carbon monoxide, hydrocarbons, soot particles, and nitrogen oxides. Catalytic combustion, an alternative to conventional flame combustion, has received considerable attention during the last decades. In both processes the organic compounds are completely oxidized by oxygen to carbon dioxide and water. Application of the catalytic combustion in stationary or mobile systems shows significant advantages in controlling pollutant emissions and more efficient use of energy sources. The main advantage of catalytic combustion is the low operating temperatures preventing the formation of toxic compounds.

Nowadays many scientists turn their attention to development of novel efficient supports for catalysts. Generally catalysts must fulfill the following requirements: thermal resistance, large specific surface area, low pressure drop, long operating life, resistance to poisoning, low cost.

The usage of glass fiber materials as a supports for catalytic layers makes possible to develop heat resistant catalysts (up to 1200 °C) with low hydrodynamic resistance. Glass fiber materials in woven form can be designed with a variety of geometric configuration. It offers a large spectrum of options in the reactor design with structured catalytic bed.

The purpose of present study is to develop the preparation technology of glass fiber catalysts containing transition metal oxides for VOCs and CO abatement.

2. Experimental

Commercial alkali free aluminosilicate glass fibers (see Table 1, Fig. 1) in woven form (KT-11) produced by "Polotsk-Steklovolokno" (Polotsk, Belarus) were used as the supports for catalysts.

Table 1. Characteristics of the glass fiber

Max. operating temperature, °C	1200
Content, % Al_2O_3 SiO_2	 4 96
Thickness, h, mm	0.28
Filament diameter, d, mkm	6-9
Sur-face density, g m^{-2}	300
Mesh, mm	1.7×1.7
Weave	Linen

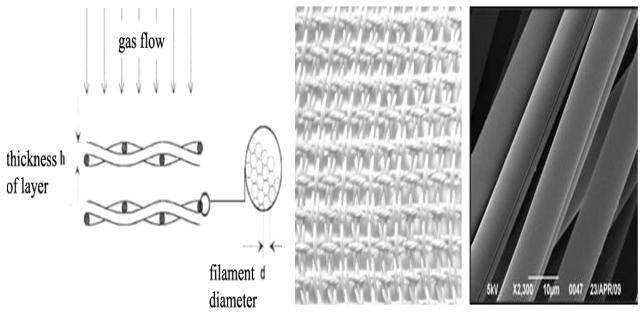

Fig 1. Aluminosilicate glass fiber material

Catalysts were prepared by ion-exchange or impregnation from aqueous solutions of $Co(NO_3)_2$, $Ni(NO_3)_2$, $Cu(NO_3)_2$, $Fe(NO_3)_3$ followed by drying and calcination in the temperature range of 300–550 °C in air for 1 h (Fig. 2) (Витковская *et al.* 2002, Витковская *et al.* 1999).

Atomizer SOLAAR M6 was used in order to determine metal element concentration in samples.

The BET surface area of catalysts was measured using N_2 adsorption-desorption via Sorptomatic 1900 apparatus.

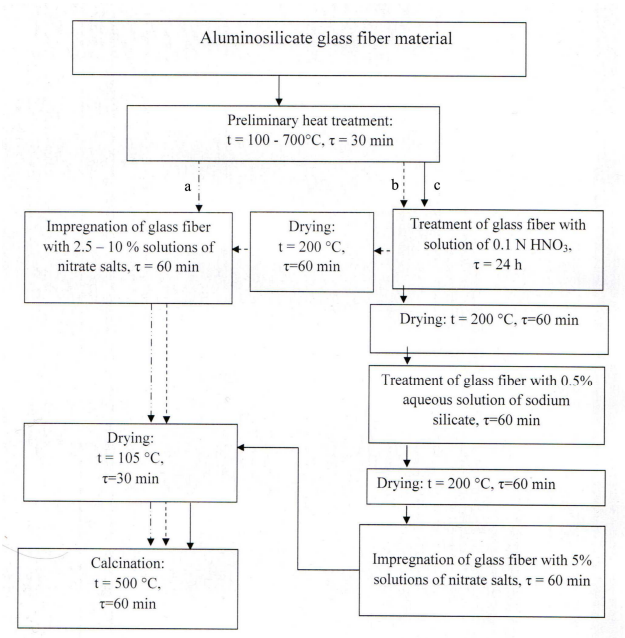

Fig 2. Scheme of catalyst preparation

Complete oxidation of 1 % of methane/carbon oxide in gas-air mixture was chosen as activity test of catalysts. The total gas feed rate was 800–80000 h^{-1}. Load module of catalysts placed into reactor was 73–1093 $kg \cdot m^{-3}$. Measurements carried by the means of Temperature-Programmed Oxidation method.

The investigations of surface morphology were carried out via scanning electron microscopy in a JSM – 6390 electron microscope.

Strength of samples depending on preliminary heat treatment measured using Instron-1122 apparatus.

3. Results and discussions

Lubricant and other impurities on the surface of commercial glass fiber (Дубовый 2003) influence the process of active sites formation. It leads to decrease in specific surface area and metal content of catalysts. These factors influence the catalysts activity and operating life. Therefore, it is necessary to remove lubricant from fiber surface.

To reveal the influence of temperature of preliminary heat treatment on catalyst characteristics we carried out series of experiments composed of preliminary heat treatment of glass fiber in the temperature range of 100–700 °C and further modification by scheme illustrated on Figure 2. The catalytic activity of samples tested at carbon oxide inlet concentration of 1 vol. % in gas-air mixture. From the obtained data (Fig. 3) it is seen that increase in temperature of preliminary heat treatment leads to growth in conversion of carbon oxide. Possibly it is explained by complete removing lubricant from fiber surface and increasing in "active" surface area at 400–700 °C. Further increase in temperature is inexpedient and does not influence the activity of catalysts.

Concentration of impregnating solutions strongly influences the catalytic activity. In order to investigate the influence of concentration of impregnated solutions on conversion of carbon oxide cobalt nitrate was used as precursor of the active components. The most active single metal oxide catalyst for complete oxidation of a variety of organic compounds are found to be oxides of Cr, Mn, Fe, Co, Ni and Cu. These are p-type semiconductor oxides and are able to absorb oxygen by donating an electron from the metal cation. This process leads to a formation of electrophilic oxygen species (O_2^-, O^-) known to be active in deep oxidation (Симонова *et al.* 2001). For this reason cobalt oxide was used as active component deposited on glass fiber supports and tested for the catalytic activity during carbon oxide oxidation.

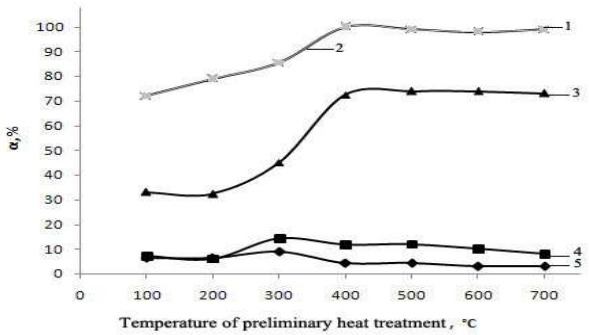

Fig 3. Dependence of CO oxidation on temperature of preliminary heat treatment of support over CoO_x catalysts. Temperature of oxidation process: 1 – 550ºC; 2 – 450 ºC; 3 –350 ºC; 4 – 250 ºC; 5 – 160 ºC; P = 101.701 kPa; C_{CO}= 1 vol. %; load module of catalyst= 1093kg m^{-3}; GHSV 80000 h^{-1}

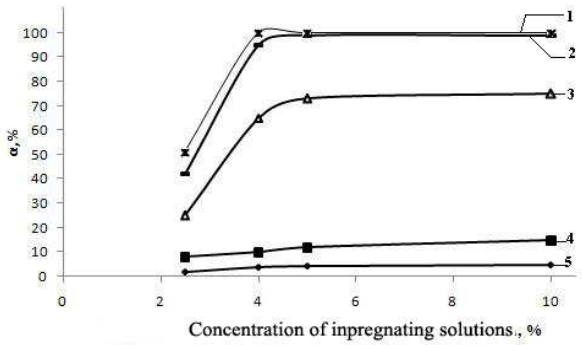

Fig 4. Dependence of CO oxidation on concentration of impregnating solutions over CoO_x catalysts. Temperature of oxidation process:1 – 550°C; 2 – 450°C; 3 – 350°C; 4 – 250°C; 5 - 160°C; P = 101.701 kPa; C_{CO}= 1 vol. %; load module of catalyst= 1093kg m^{-3}; GHSV 80000 h^{-1}

Obtained results showed that increase in concentration of impregnated solutions from 2.5 % to 5 % leads to growth of CO conversion (Fig. 4). Further concentration growth doesn't influence the catalysts activity and results in a change in thickness of metal oxide layer.

The influence of preliminary heat treatment temperature of commercial glass fiber is shown on Figure 5. It is seen that fiber strength decreases with increase in temperature of preliminary treatment.

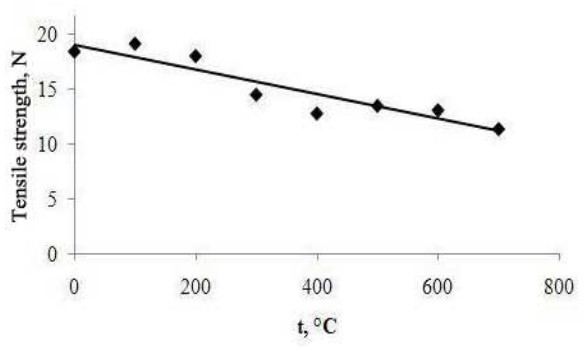

Fig 5. The influence of temperature of preliminary heat treatment on tensile strength of glass fibers

Measurements of specific surface area (Table 2) showed the treatment of commercial glass fiber leads to increase in porosity and specific surface area (SSA). For example, SSA of starting glass fiber is 0.1 m^2g^{-1}, but SSA of Ni-containing catalyst is 1.016 m^2g^{-1}. Mixed oxides containing surface have been reported to have a higher SSA compared to commercial glass fiber material.

Support of the catalyst plays an important role on the process of catalyst preparation affecting the specific surface area, activity, operating life and stability of catalyst.

To increase above mentioned properties we undergone the fiber support to two types of treatment:

1) Impregnation of starting glass fiber with solution of 0.1 N solution of nitric acid during 24 h, and further treatment according to Figure 2, b;
2) Impregnation of starting glass fiber with solution of 0.1 N solution of nitric acid during 24 h, treatment with 0.5 % aqueous solution of sodium silicate and further treatment according to Figure 2,c.

Table 2. Data about metal oxide content on glass fiber surface and specific surface area

N	Catalysts	Metal content of catalysts samples, %				Specific surface area, $m^2\ g^{-1}$
		FeO_x	NiO_x	CoO_x	CuO_x	
1	Glass fiber	-	-	-	-	0.1
2	NiO_x	-	4.13	-	-	1.016
3	CoO_x	-	-	2.57	-	0.5
4	(Fe/Ni/Co/Cu)O_x	0.48	0.58	0.93	0.56	2.35

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The SEM images of the supports after treatment are shown on Fig. 6. The fiber surface presented on Fig. 6, b) is partially covered by the oxide layer. Possibly it influences the catalyst activity and operating life. As it is seen on Fig. 6, c), d) the treatment of support by solution of HNO_3 and aqueous solution of sodium silicate showed the best results. Possibly it is explained by the variation of the ion exchange capacity of the support due to acidic treatment.

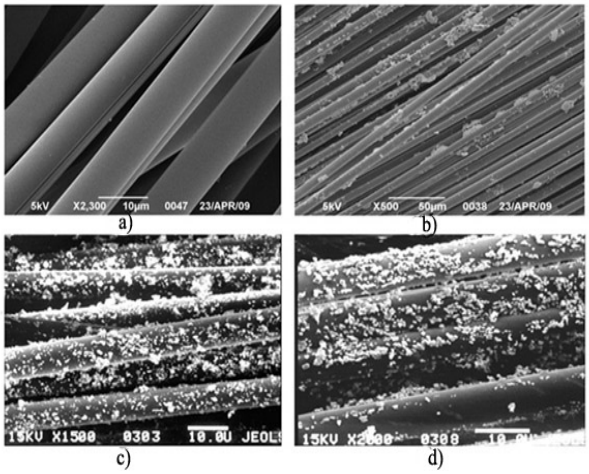

Fig 6. SEM images of the surface of glass fiber catalysts after treatment: a – commercial glass fiber; b – type a of support modification; c – type b of support modification; d – type c of support modification

The strong inorganic acid attacks the siliceous materials surface leaching out non-silicon components (Симонова *et al.* 2001).

The investigations performed showed (Бальжинимаев *et al.* 2002), that composition of glass fiber and leaching conditions influence the morphology of treated material, its absorption properties and strength. Aluminoborosilicate glass fibers were observed to lose tensile strength due to leaching, resulting in increased in SSA and porosity of glass fiber materials.

Since in this investigation non-alkali glass fiber yarns were used we may suppose, that oxygen in crystal lattice bonds hydrogen ions forming silanol groups on glass fiber surface. Then ions from solution replace protons of hydroxyl group, this ion exchange leads to more even distribution of oxides on glass fiber surface (Fig. 6c).

Table 3. Characteristics of the glass fiber supported catalysts for CO and CH_4 oxidation

Cata-lytic layer compo-sition	The ignition temperature, °C		Temperature of 100% conversion		Acti-vation energy, kJ mol^{-1}		Ln(k), min^{-1}		GHSV, h^{-1}
	CO	CH_4	CO	CH_4	CO	CH_4	CO	CH_4	
Glass fiber	-	770	-	900 (α_{max}=38%)	-	211	-	-	882
NiO_x	234	453	340	600	79.35	141.5	18.2	24.5	882
CoO_x	115	457	223	650	74.31	140	21.6	17.5	882
(Co, Ni, Fe, Cu)O_x	143	493	235	604 (α_{max}=25%)	71.79	122.9	20.22	18.68	882
NiO_x	-	540	-	780	-	123.3	-	-	43274
NiO_x	-	545	-	820	-	153.5	-	-	43274

Possibly further impregnation of glass fiber materials with 0.5 % aqueous solution of sodium silicate leads to formation of silica gel on fiber surface. Silanol groups of silicic acid gel then participate in ion exchange with metal ions in solution. Surface of glass fiber treated by this way is shown on Fig. 6d).

The catalytic layer composition strongly influences the catalyst activity (Попова 1991).

The conversion of methane and carbon oxide as function of the temperature is shown on Figs 7, 8. These diagrams show the influence of metal type on conversion of methane and carbon oxide. Obtained results make possible to compose activity row of metal oxides in the oxidation process:

– CO: CoO_x>(Ni/Co/Cu/Fe)O_x>NiO_x;

– CH_4: Ni>Co>(Ni/Co/Cu/Fe).

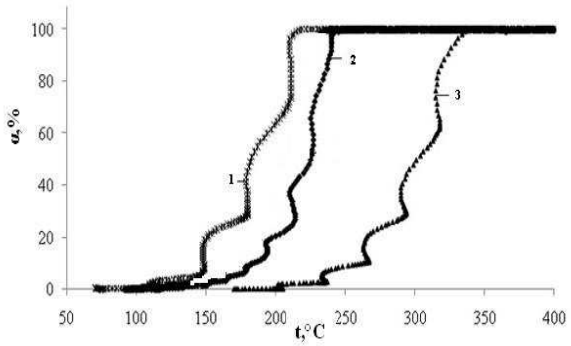

Fig 7. CO conversion as a function of temperature over different catalysts containing: 1 – CoO_x; 2 – (Ni, Co, Cu, Fe)O_x; 3 –NiO_x P = 101.701 kPa; C_{CO}= 1 vol. %; load module of catalyst= 73kg m^{-3}; GHSV 882 h^{-1}

This agrees with data obtained by calculation of rate constants of oxidation reactions and activation energy evaluated from the Arrhenius plots (Table 3). The catalytic activity of CoO_x catalyst during carbon oxide oxidation was seen to be higher than catalytic activity of other catalysts. The activation energy (E_a) of carbon oxide oxidation over CoO_x catalysts is 74.31 kJ mol^{-1}, and the ignition temperature (T_{ig}) over CoO_x catalysts is 115 °C. The catalytic activity NiO_x catalyst during methane oxidation was observed to be higher than catalytic activity of other catalysts (E_a = 141.5 kJ mol^{-1}, T_{ig} = 453 °C).

From the Table 3 it is seen that NiO_x catalysts demonstrate the higher values of activation energy, and therefore these catalysts are exposed to effect of temperature.

All glass fiber catalysts studied in CO oxidation (Fig. 7) demonstrate the sharp increase in CO conversion in the temperature range of 100–220 °C and 100–320 °C over NiO_x catalyst. This behavior shows that the oxidation process occurs in the kinetic area. Above these temperatures the effect of temperature decreases, and the oxidation curve reaches the plateau. This field is characterized by diffusion region, where the oxidation process is limited by the delivery of reagents to active sites.

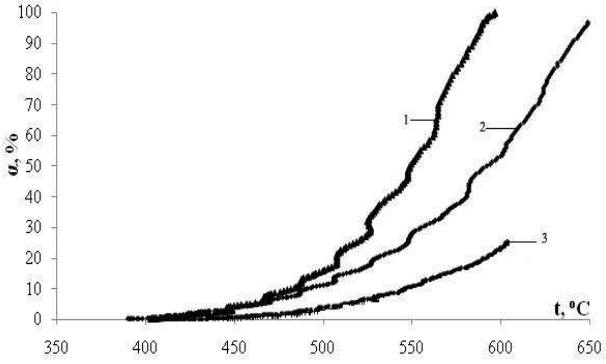

Fig 8. CH_4 conversion as a function of temperature over different catalysts containing: 1 – NiO_x; 2 – CoO_x; 3 – (Ni, Co, Cu, Fe)O_x P = 101.701 kPa; C_{CH_4} = 1 vol. %; load module of catalyst= 73kg m^{-3}; GHSV 882 h^{-1}

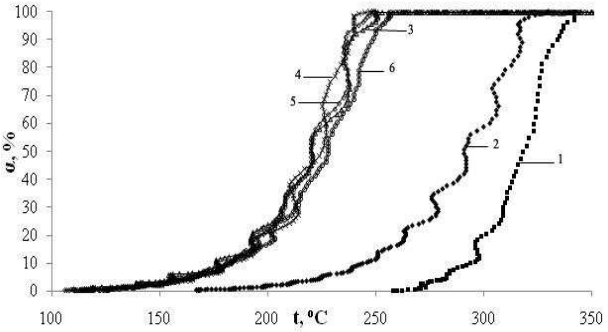

Fig 9. CO conversion as a function of temperature over CoO_x catalyst, oxidation cycles: 1 – first; 2 – second; 3 – third; 4 – fourth; 5 – fifths; 6 – sixth. P = 101.701 kPa; C_{CO}= 1 vol. %; load module of catalyst= 73kg m^{-3}; GHSV 882 h^{-1}

Cycles of CO oxidation over CoO_x catalysts revealed that the reaction rate increases with increasing operating time of the catalysts (Fig. 9), and then reaction rate keeps constant. All catalysts studied demonstrate this behavior during CH_4 oxidation. Therefore catalysts keep constant their catalytic ability.

4. Conclusions

Transition metal oxides such as CoO_x and NiO_x supported on glass fibers are shown to be active catalysts for the oxidation of CO and methane at atmospheric pressure.

Experiments performed made possible to reveal the following conditions of catalyst preparation technology:

1. The temperature of preliminary heat treatment is seen to influence the catalytic activity of catalysts. The optimum heat treatment conditions are reached at temperatures from 400 to 500 °C during 60 min.
2. The concentration of impregnating solutions was found to influence the catalytic activity of catalysts. The optimum concentration of impregnating solution was found in the range of 4–5 wt. % ;
3. The catalytic layer composition strongly influences the rate of CO and CH_4 oxidation.
4. Regions for the CO oxidation over catalysts studied were established. Kinetic region occurs at temperatures below 250 °C, diffusion region observes at temperatures above 350 °C.

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