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Glass-fiber catalysts: Novel oxidation catalysts, catalytic technologies for environmental protection

B.S. Balzhinimaev [1], E.A. Paukshtis [1], S.V. Vanag [1], A.P. Suknev [1], A.N. Zagoruiko *

Boreskov Institute of Catalysis, Pr. Lavrentieva, 5, Novosibirsk 630090, Russia

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ABSTRACT

Novel glass-fiber based catalysts containing extra-low amounts of noble metals (0.01–0.02 mass% of Pt or Pd) demonstrate unique performance in many catalytic reactions, resulted from the ability of the glass fibers to stabilize the transient metals in the glass bulk in a highly dispersed form. Moreover, specific heat/mass transfer properties, original geometry, high flexibility and high mechanical strength of such catalysts give the way to develop really new catalytic processes and novel reactor designs. The paper is dedicated to the successful research and development (from fundamental research issues to pilot and semi-industrial tests) of different catalytic oxidation processes based on application of fiber-glass catalysts for solution of various environmental problems, namely: purification of automotive exhausts, incineration of VOCs (volatile organic compounds) in waste/vent gases, utilization of chlorinated VOCs and dioxins abatement in waste gases, sulphur dioxide oxidation for purification of waste gases and for conditioning of flue gases of coal-fired powerplants.

1. Introduction

The glass-fiber materials of silicate origin are for a long time produced in industry and are widely used as perfect heat and electric insulators. At the same time these materials are much less known as catalyst supports despite their obvious advantages such as high thermal stability (up to 1200 °C), high mechanical strength, improved hydrodynamic properties as well as the possibility to create the new types of structured catalytic beds and the catalytic reactors with new flexible designs.

The glass-fiber catalysts (GFCs) reveal unique catalytic performance in many oxidation reactions due to the ability of the glass fibers to stabilize the highly dispersed nanoclusters of transient metals in the glass bulk [1–6]. This results in high catalytic activity and high catalyst resistance to poisoning and deactivation in aggressive reaction media. Notably, excellent catalyst performance is achieved at very low noble metal content (0.01–0.02 wt.%) thus providing quite reasonable pricing for the catalyst.

The unique catalytic properties of GFCs in many oxidation reactions provide their high attractiveness for application in various environmental processes, mostly connected with abatement of toxic and harmful compounds in industrial waste gases and automotive exhausts. The present paper shortly considers the features of GFC preparation and their application in various areas of environmental catalysis.

2. Catalyst preparation and characterization

The industrial production of glass materials includes making of glass melt, manufacturing of separate fibers with typical size of 5–10 μm, twisting of these fibers into threads (0.3–1.0 mm in diameter) with final manufacturing of glass-fiber fabric (Fig. 1). In average the leached silicate glass material used for production of GFCs contains 97–99.5 wt.% SiO_2 and 0.5–3 wt.% Al_2O_3. The glasses modified by zirconia may additionally contain up to 10% ZrO_2.

The literature data on molecular structure of silicate glasses, especially of those modified with zirconia, are still rather controversial and disputable. Nevertheless, among the numerous known models of glass structure the most adequate are those proposed earlier by Greaves et al. [7] and by us [2] on the base of IR and NMR studies data. In particular, it was established that the network of SiO_4 tetrahedra are interconnected randomly with each other via bridging oxygen atoms. But this network is not continuous and is interrupted by protons bounded with non-bridging oxygen. In other words, more dense silicate layers are alternated with less dense interspaces containing H-bonded hydroxyl groups. The presence of protons is very important because the introduction of different cations into the bulk of glass matrix occurs namely via ion exchange with these protons.

Platinum introduction into the bulk of the glass fibers and its stabilization in the highly dispersed state was performed in two

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* Corresponding author. Tel.: +7 383 3309770.
E-mail addresses: balzh@catalysis.ru (B.S. Balzhinimaev), zagor@catalysis.ru (A.N. Zagoruiko).
[1] Tel.: +7 383 3309770.

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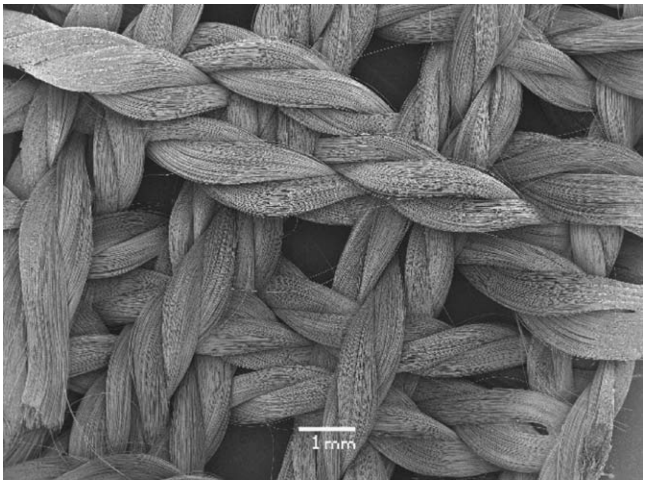

Fig. 1. Typical view of the glass-fiber catalyst.

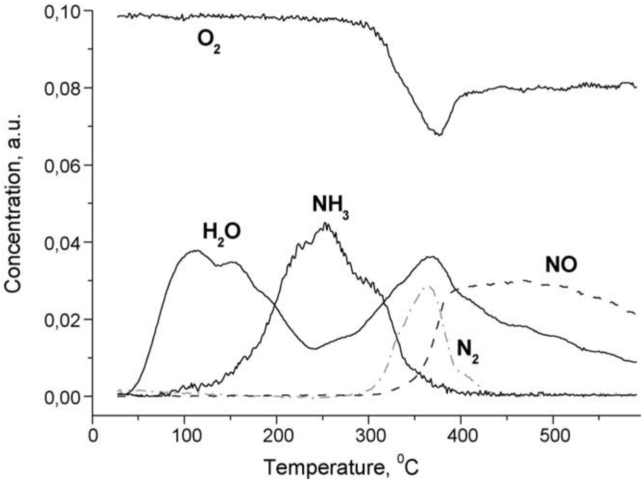

Fig. 3. PO profile of the washed out and dried sample (see curve 1 in Fig. 2).

stages. First stage included ion exchange of Pt amine complexes with protons of glass matrix:

$$[\mathrm{Pt(NH_3)_4}]^{2+}_{\mathrm{solution}} \underset{-2\mathrm{H}^{+}_{\mathrm{solution}}}{\overset{2\mathrm{OH}^{-}_{\mathrm{glass}}}{\rightleftarrows}} [\mathrm{Pt(NH_3)_4}]^{2+}_{\mathrm{glass}}$$

The second stage is sample calcination at elevated temperatures targeted to reduction of Pt(II) cations into Pt clusters within the bulk of glass fibers:

$$[\mathrm{Pt(NH_3)_4}]^{2+} \xrightarrow{\mathrm{T,O_2}} \mathrm{Pt} + 2\mathrm{N_2} + 5\mathrm{H_2O} + 2\mathrm{H^+}$$

The catalyst samples were investigated by UV–vis diffusion reflectance spectroscopy (UV–vis DRS) and temperature-programmed oxidation (TPO) technique. UV–vis spectra were recorded without any GFC sample pretreatment using Shimadzu 2501 spectrometer, equipped with the diffusion reflection accessory ISF-240 for the range of 11,000–52,000 cm^{-1}. TPO experiments with ion-exchanged and dried sample included its linear heating in 1%O$_2$ + He flow up to ~600 °C (temperature ramp rate—10 K/min, GHSV = 11,000 h^{-1}) with continuous gas phase analysis using the quadrupole mass-spectrometer VG Sensorlab-200D.

As seen in Fig. 2 the spectrum of dried and washed sample (curve 1) practically coincides with that of [Pt(NH$_3$)$_4$]Cl$_2$ (curve 2) in the impregnating solution (see the typical bands at 44,600, 42,000 and 35,000 cm^{-1}), meaning that platinum species, incorporated into the glass bulk, are similar to those in the initial tetraammonia complex. After sample calcination at 300 °C the intensity of the 44,600 cm^{-1} band in the spectra sharply decreases and the appearance of the band of 38,900 cm^{-1} is simultaneously observed, being an evidence of Pt(II) reduction to small charged Pt clusters. These results are in good agreement with TPO data (Fig. 3) demonstrating that water and ammonia desorb at low temperatures (the ability of glass fibers to absorb polar and easily polarizable molecules was shown earlier in [3]), then N$_2$ formation due to Pt reduction occurs starting from ~300 °C followed by ammonia oxidation to NO at higher temperatures. The final Pt content in Pt/GFC measured with Inductively Coupled Plasma (ICP) technique (using Optical Emission Spectrometer Optima 4300 DV) was equal to 0.02 wt.%.

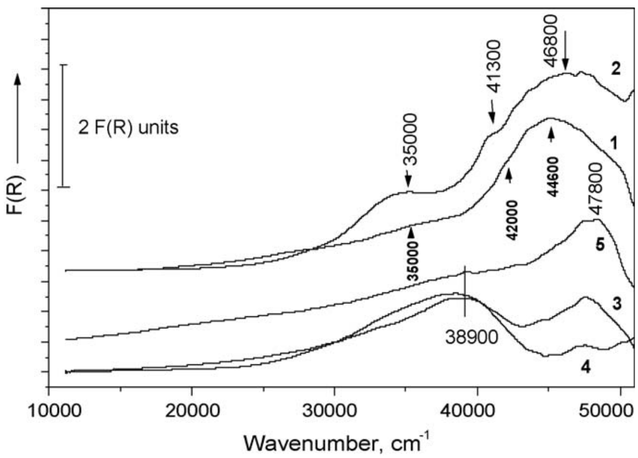

Fig. 2. UV–vis spectra for Pt/GFC samples: (1) ion-exchanged with solution of [Pt(NH3)$_4$]Cl$_2$, washed out with water and dried at 110 °C; (2) spectrum of impregnating solution; (3) calcined in air at 300 °C; (4) calcined in air at 500 °C; (5) calcined at 350 °C without preliminary washing out and drying.

The band of 38,900 cm^{-1} may be attributed to d–d transitions in small charged platinum clusters due to the following reasons: (a) electron microscopy data of GFC samples [3] shows the presence of Pt species with a size not exceeding ~1 nm and the absence of metal particles at the outer fiber surface. Fig. 2 shows the comparative data for the sample prepared without washing and drying procedures (curve 5). In this case the appearance of intensive band 47,800 cm^{-1}, corresponding (according to electron microscopy data [3]) to metal particles of 5–8 nm in size located at the fiber surface, is observed; (b) position of absorbance bands, corresponding to d–d transitions of transient metals ions, is sensible to electro-donor ability of ligands. For example, for platinum (II) the replacement of oxygen ligands for ammonia results in band shift from 20,000–25,000 to 32,000–36,000 cm^{-1}. Platinum atoms have higher electron density than ammonia, therefore, the bands of these transitions must have the higher frequency and bands of 38,000–40,000 cm^{-1} quite probably belong to ions of two-valent platinum surrounded by metal atoms, e.g. $(\mathrm{Pt}_n)^{\delta+}$ clusters.

As it was shown earlier by combination of XPS and ion etching methods [3] the Pt clusters are localized in the upper layers of glass fibers at the depth up to 10 nm.

3. Environmental applications of GFCs

3.1. Incineration of volatile organic compounds

Incineration of volatile organic compounds (VOCs) is a very important and very common environmental protection problem which may be met in almost all branches of modern industry–chemistry, petrochemistry and refinery, machinery, wood

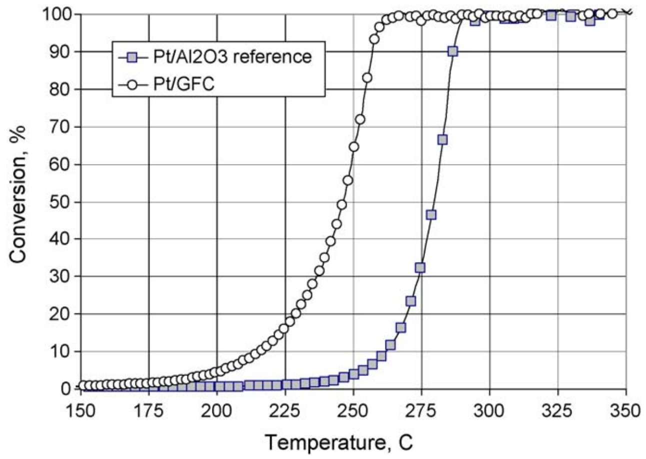

Fig. 4. Conversion of ethylbenzene into CO_2 *vs* temperature under programmed temperature rise of Pt/GFC and reference catalyst. Feed gas composition: ethylbenzene—1.2 vol.%, oxygen—16 vol.%, balance—helium. Gas flow rate—2.2 l/h, catalyst loading—0.22 g.

processing and paper production, agriculture and many others. Such VOCs may be represented by different hydrocarbons, organic acids, spirits, ethers etc.

The most efficient way for abatement of VOCs is their deep catalytic oxidation to harmless products:

$$C_xH_yO_z + O_2 \Rightarrow CO_2 + H_2O$$

Pt-based GFCs have demonstrated extremely high oxidation efficiency in such reactions. Fig. 4 shows lab data on comparative performance of Pt-based GFC with the commercial alumina-supported Pt catalyst in the reaction of deep oxidation of ethylbenzene. It is seen, that GFC provides much higher activity than conventional Pt/Al_2O_3 catalyst, despite the fact that GFC contains ~30 times less platinum than the commercial catalyst (0.02 wt.% of Pt in GFC *vs* 0.56% Pt in reference catalyst).

The GFC-based process of catalytic incineration of VOCs (mostly isoprene, isobutylene and CO) in the waste gases of synthetic rubber production facilities was successfully commercialized at Nizhnekamskneftekhim Company site (Nizhnekamsk, Russia) in 2008. The industrial reactor with waste gas loading up to 15,000 st. m^3/h was charged with 1 tonne of GFC, structured in a form of vertical spiral cartridges [8] (see Fig. 5).

Though the operation conditions were quite complicated (the waste gases have decreased oxygen content as low as 2–3 vol.%, the water vapor content was reaching 80 vol.% and the gas flow was contaminated with dust particles) the application of GFC leads to increase of abatement efficiency from maximum 70–80% observed earlier for conventional catalyst up to 99.5–99.9%. Catalyst continuous operation for more than 16 months has revealed no any decrease of catalyst activity, thus giving the ground for quite optimistic estimation of possible GFC lifetime.

3.2. Incineration of chlorinated VOCs and dioxins

The special problem within the VOC incineration is abatement of chlorine-containing hydrocarbons. The first problem here is complicated by possible formation of extremely toxic product of incomplete oxidation (phosgene, dioxins, etc.) which may be even more hazardous than the initial wastes. The second problem is low stability and fast degradation of practically all known conventional oxidation catalysts in presence of Cl-containing compounds.

The special family of advanced GFC was synthesized for destruction of chlorinated VOCs. The laboratory tests have demonstrated high efficiency of modified Pt/GFC in respect to deep oxidation of chlorinated hydrocarbons (chlorobenzene, dichloroethane, polyvinylchloride production wastes etc.): practically complete conversion of initial Cl-VOCs with their residual content in oxidation products below 1 vppm; 100% selectivity of oxidation into CO_2, water and HCl (no CO and Cl_2 formation); no formation of harmful oxidation by-products (phosgene, dioxins) [9]. GFCs have also demonstrated extremely high resistance to deactivation in the Cl-containing reaction media (no decline of catalytic activity was observed during more than 100 h of resource tests).

These catalysts were tested in a pilot reactor at the Volograd Department of Boreskov Institute of Catalysis (Volgograd, Russia) for oxidative destruction of Cl-containing wastes from real PVC production plant where the GFC was structured in a form of vertical radial bed [10] (see Fig. 6). The reactor loaded with 10 kg of GFC has provided the incineration capacity of 5–8 kg of liquid Cl-containing wastes per hour with conversion of Cl-VOCs at the level of ~99.9% without formation of any hazardous oxidation by-products.

The recent data obtained in collaboration with US Environmental Protection Agency have also demonstrated very high efficiency of modified GFCs in respect to oxidative destruction of dioxins. The residual content of dioxins after such oxidation was

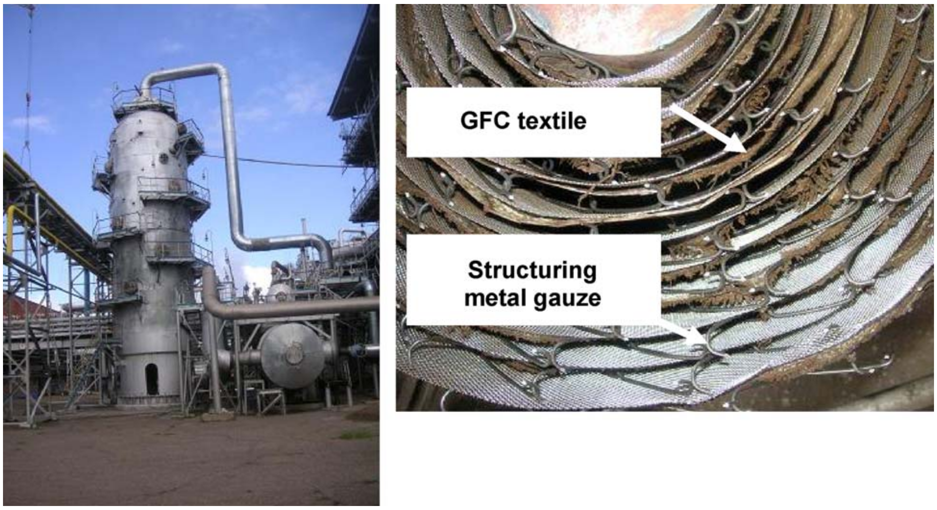

Fig. 5. Commercial VOC incineration reactor at Nizhnekamskneftekhim Company (left) and internal structure of the GFC spiral cartridge (right).

Fig. 6. External view of the GFC radial bed for incineration of chlorinated hydrocarbons.

provided at the level below 0.1 ng/l without formation of secondary dioxins and other toxic by-products. It opens the way to application of GFC for solution of the very important environmental problem—abatement of dioxins in waste gases of municipal waste incinerators.

3.3. Catalytic purification of automotive exhausts

The purification of exhaust gases from vehicle and stationary engines also deals with catalytic incineration of CO and hydrocarbons but it is complicated (especially in case of diesel engines exhausts) by necessity to provide abatement of nitrogen oxides and particulate matters (PM) as well.

Earlier pilot studies performed at certified diesel testing stands have confirmed the advanced catalytic properties of GFCs in respect to this application [11]. In particular, it was shown the purity of exhausts of the typical Russian tractors and trucks diesel engines may be improved up to the modern requirements of Russian national standards or European standards (not less than Euro-4) by application of Pt/GFC-based catalytic neutralizer, which is much more simple and cheap, than conventional ones with much higher content of noble metals.

Pilot tests of GFC-based catalytic filter were also performed at the stationary diesel 4 MW electricity generator, which was characterized with high NOx (up to 2000 vppm) and PM content. The filter was made of two spiral catalytic cartridges with external diameter of 0.8 m (see Fig. 7) situated directly in the exhaust gas duct, so no separate reactor body was needed. This filter has provided fulfillment of all environmental requirements. Notably, the maximum pressure drop at the filter in the tests was observed at the appropriate level (below 10 kPa) despite the extremely high gas velocities in the gas duct (up to 40 m/s). No rise of the pressure drop was seen during the tests due to high catalyst mechanical stability and efficient oxidation of soot particles by GFC preventing the accumulation of particulates in the filter.

3.4. Sulfur dioxide oxidation

Oxidation of SO_2 to SO_3 is widely used for solution of environmental problems connected with abatement of sulfur dioxide in non-ferrous metallurgy, chemical industry, energy production etc. Earlier performed studies [5] have demonstrated the high potential of GFC application for such purposes. Pt-based GFC in this reaction demonstrate high activity, good thermal stability, low “ignition” temperature and high resistance to deactivation.

GFC-based process of SO_2 oxidation may be also used for conditioning of flue gases from coal-fired powerplants. The ash particulates in the flue gases of such powerplants are often characterized with high electric resistance, limiting the efficiency of particulate removal in electrostatic precipitators (ESP). The injection of small quantities of SO_3 (as low as 2–10 vppm) into the flue gas stream may decrease the ash resistance and significantly improve the ESPs dust removal performance.

The special study [12] has demonstrated that GFC create a good basis for construction of compact catalytic reactors for controlled SO_3 production for described purposes. Investigation of various fiber-glass based and conventional catalyst samples have shown that the best SO_2 oxidation performance is observed for the Pt/GFC using the silica-zirconia fiber-glass support with Pt content of $\sim$0.01 wt.%. This catalyst was tested in the pilot reactor at Byisk Oleum plant (Byisk, Russia) in the media of real industrial gases produced by combustion of elemental sulfur, containing 7–9% SO_2. These tests have shown the low value of ignition temperature for this GFC (as low as 360–370 °C) and complete absence of its deactivation after more than 1000 h of continuous operation.

Fig. 7. Structure of the GFC cartridge with structuring corrugated stainless gauze (left) and catalytic filter for abatement of diesel exhausts (right).

4. Conclusion

It may be concluded that the noble metal catalysts on the base of glass-fiber material represent itself the new generation of highly efficient oxidation catalysts which may be successfully applied for solution of numerous environmental protection problems, such as purification of automotive exhausts, incineration of VOCs (volatile organic compounds) in waste/vent gases, abatement of chlorinated VOCs and dioxins, sulphur dioxide oxidation for purification of waste gases and for conditioning of flue gases of coal-fired powerplants.

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