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Pt-containing catalysts on a base of woven glass fiber support: a new alternative for traditional vanadium catalysts in SO_2 oxidation process

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Abstract

Pt-containing catalysts (0.01–0.12% Pt), supported on leached sodiumsilicate glass fiber were tested in sulfur dioxide oxidation (10–20% SO_2) at 420–700 °C. Catalysts showed high activity and good thermal resistance.

1. Introduction

Platinum is well known as the most active catalyst for sulfur dioxide oxidation. Before 1940s, industrial sulfuric acid production was done using metal platinum gauzes, which were later replaced with less expensive and more resistant to poisons vanadium catalysts. Since then, the catalyst improvement was directed towards higher activity at low temperatures <400 °C. At present, one of industrial challenges is the processing of highly concentrated sulfuric gases up to 20–30% SO_2. It requires catalysts that should be thermally stable at 700–750 °C.

Recently, the interest in the practical use of platinum catalysts was renewed. Major efforts were aimed at improving the durability of expensive platinum by depositing it on appropriated supports that provide high dispersion of active metal, thermal stability, resistance against sulfating, and have optimal geometry with good aerodynamic parameters. For this purpose, multi-channeled ceramic monoliths coated with highly dispersing materials resistant to sulfuric acid such as silica [1] were suggested. Catalysts on a base fiber glass woven support also seem to be rather promising [2–4].

Commonly applied industrial technology for production of woven fiber glass material consists of several stages:

1. Melting of initial Na–Si glass beads. Chemical composition of the average material is 65–80% SiO_2, 16–18% Na_2O, 1.5–5% Al_2O_3.
2. Passing the melted mass through spinneret and producing the elemental fibers of 7–10 μm in diameter.
3. Twisting the elemental fibers into threads of 0.1–1 mm in diameter.
4. Weaving from threads the textiles of different shapes and density.
5. Leaching of the woven fiber glass textiles by inorganic acids, that results in Na^+ cations replacement by H^+.
6. Calcination at 900 °C to produce textile as a good electric insulator.

After leaching, but without calcination this material can be regarded as a support for catalyst preparation. Its impregnating by the water solutions of Pt, Pd, Ag, Cr, Ni, etc. compounds followed by appropriate thermal treatment can lead to a formation of active catalytic material.

Catalysts on the fiber glass woven supports ensure low pressure drop and uniform gas flow distribution along the bed cross-section excluding the occurrence of hot spots, rather typical in the highly exothermal reactions. The small size of the elemental glass fiber (∼10 μm) guarantees low internal diffusion limitations, and hence, the efficient use of the active component and high performance.

The goal of this work was to study the possibility of using Pt on fiber glass supports for oxidation of SO_2 at various reaction conditions.

2. Preparation and characterization of woven fiber glass catalysts

As a starting material for catalyst preparation we used commercial sodiumsilicate glass fiber (Na–SiGF) textile (80% SiO_2, 18.5% Na_2O, 1.5% Al_2O_3) available from

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Belarus plant "Steklovolokno". Its specific surface area, corresponding to the geometrical surface of a elemental fiber ranged within 1–1.5 m^2/g. Textile was spun from threads of 1 mm in size with density of 16 square holes per square centimeter. Leached glass fiber material contained practically pure SiO_2 (98–99%) without loss in fibers' flexibility and mechanical strength. In this case, BET-measured specific surface did not change, but the obtained silica material exhibited specific structure and properties essentially different from those of the conventional silica materials. According to IRS, TEM and NMR ^{29}Si, ^{23}Na studies [5], this material can be most adequately represented as a pseudo layered intercalation structure (Fig. 1). Here, layers of three tetrahedrons (for simplicity Si atoms are presented without oxygen) are separated by interlayer spaces where the hydroxyl groups are located. The different cations (Pt, Pd, etc.) via ion exchange, even large Cs^+, may be incorporated into interlayers space providing the pillaring effect, as in clays. Of course, the presented model is rather rough approximation to real structure of leached silicate glass.

Pt-containing catalysts were synthesized using two methods. Samples 1–3 (see Table 1) are prepared by impregnation of leached sodium woven fiber glass with $Pt(NH_3)_4Cl_2$ solution at room temperature. Then it is separated from solution, dried at 110 °C, calcined at 300 °C for 2 h followed by reduction in hydrogen flow at 300 °C for 2 h. Samples 4–6 (second method) are prepared by impregnation of the same silica material with the same solution but at elevated temperatures. Then the samples are washed out by double deionized water to remove Pt compounds weakly bounded with support. The drying and calcination procedures were the same as for previous method. Depending on Pt concentration in impregnating solution the synthesized samples contained 0.01–0.12 wt.% of platinum.

Our previous TEM and XPS studies [6] show that two types (M1 and M2) of particles might form depending on preparation procedure. First type are the metal particles sized from tens to hundreds angstroms are located on the outer surface of the fibers (Fig. 2a). The metallic state of particles is confirmed by microdiffraction pattern (Fig. 2b) with characteristic interplanar distances: 2.25, 1.95, 1.4, 1.2 Å, etc. Depending on Pt loading the average size of metal particles changed from 20 Å (sample 1) to 50 Å (sample 3).

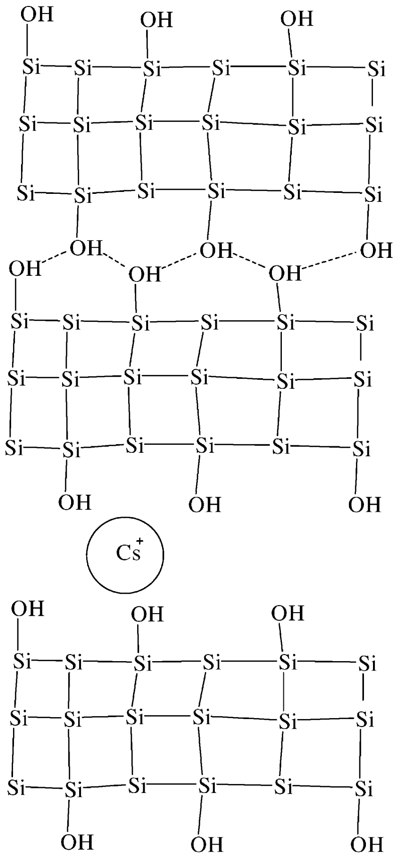

Fig. 1. Possible structure of leached silica glass fibers.

The second type of Pt species are so dispersive that they are not observed by high resolution electron microscopy. The small clusters (up to 10 Å in size) appear under heating by electron beam only (Fig. 2c) due to partial sintering of Pt particles with atomic size. These clusters or ions are located in the bulk of glass fiber up to hundred angstroms of depth which is confirmed by XPS data combining with ion etching [6]. In XP spectra of Pt 4f we observed two components appearing due to spin-orbital splitting with binding energy of 72.4 and 76.7 eV which correspond to Pt^{2+} in $Pt(OH)_2$ [7]. This evidenced that Pt is chemically bonded with the glass matrix. The intensity of Pt 4f spectra was decreasing

Table 1
SO_2 conversion at 420 and 485 °C on Pt/SiGF samples and commercial vanadium sulfuric acid catalysts

Catalyst	Pt (%)	Type of Pt particles	X^{420} (%)	X^{485} (%)
1	0.01	M1	25	47
2	0.05	M1	38	88
3	0.12	M1	55	93
4	0.01	M2	–	–
5	0.03	M2	52	90
6	0.07	M1 + M2	58	92
SVD (Russia) (6.5% V_2O_5, K/V = 2.5)	–	–	29	85
IC-1-6 (Russia) (7.5% V_2O_5, Na/K/V = 1.3/2.9/1)	–	–	59	88

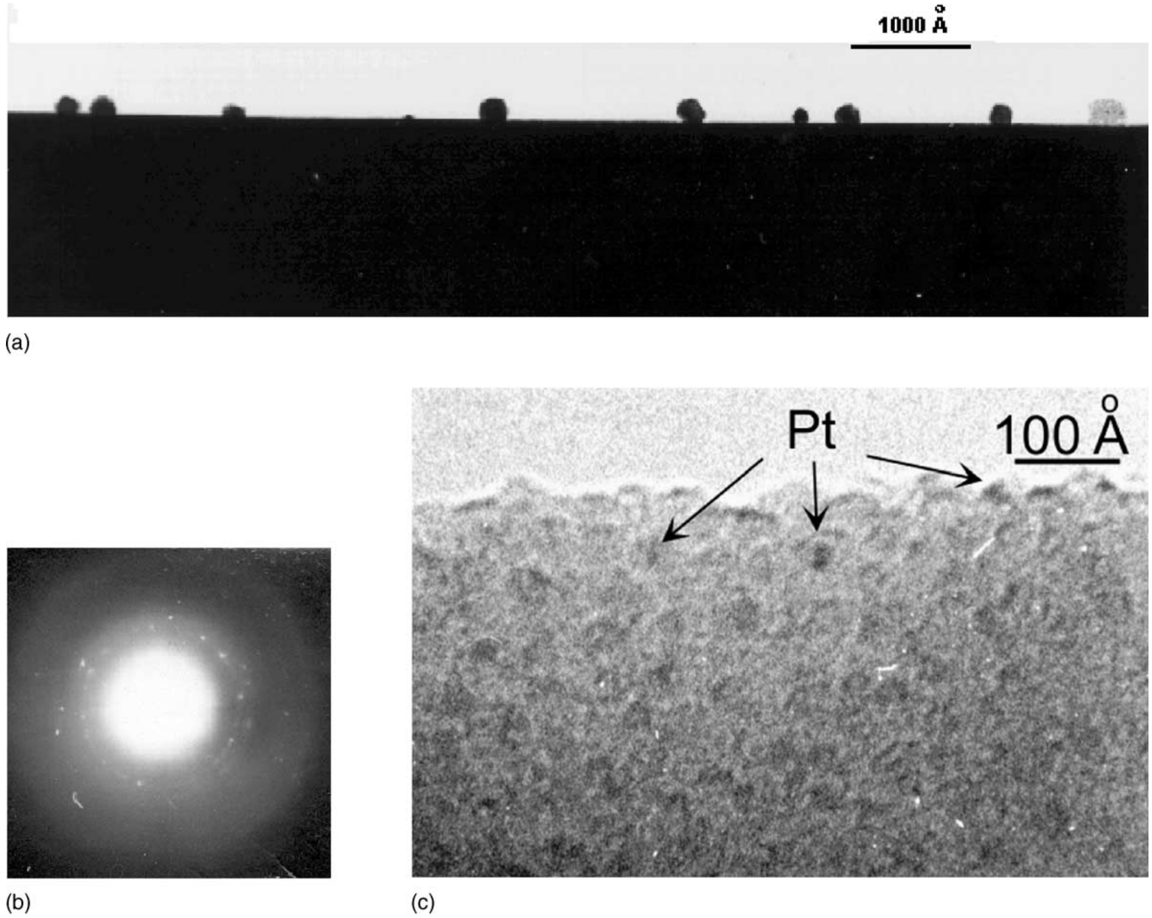

Fig. 2. TEM image of sample 3 (a); its microdiffraction pattern (b); HREM image of sample 4 (c).

with etching time, and after 4 min corresponding approximately to 100 Å of XPS depth analysis, it has disappeared. It means, that charged Pt species are actually located in the bulk of glass fiber.

3. Testing of Pt/SiGF catalysts in SO_2 oxidation

The activity of Pt catalyst in SO_2 oxidation was measured in a flow reactor (quartz tube of 27 mm in diameter) at 420 and 485 °C. The 100 cm^2 of textile (5 g) was cut on 3 mm × 3 mm pieces and loaded into reactor. To avoid the possible overheating the textile pieces were diluted by 20 cm^3 of 2 mm × 2 mm quartz pieces. Feed gas was 10 vol.% SO_2 + 18.9 vol.% O_2 + 71.1 vol.% N_2 and gas space velocity provided the contact time $\tau = 0.9$ s. The catalyst activity was characterized by the conversion of SO_2 at both temperatures X^{420} and X^{485} (see Table 1). Concentration of SO_2 was determined using a chromatographic analysis. For comparison we have also measured the activity of several commercial vanadium sulfuric acid catalysts. SVD is an oldest Russian sulfuric acid catalyst supported on diatomic earth. It has low relatively V_2O_5 content and low potassium/vanadium atomic ratio. IC-1-6 is developed by Boreskov Institute of Catalysis in early 1980s and is characterized by high sodium + potassium/vanadium ratio, as well as high V_2O_5 content. The artificial silica with optimized pore structure serves as a support. Both of these factors provided the best IC-1-6 performance in sulfuric acid production especially at low temperatures. The 5 g of catalyst powder (0.5–1 mm in size) diluted with 20 cm^3 of quartz powder was loaded into the same reactor. As seen from Table 1 data, Pt/SiGF catalysts reveal high SO_2 conversion at 420 and 485 °C comparable to those exhibited by the best commercial catalysts. For the samples containing Pt on the outer surface only (samples 1–3) SO_2 conversion is increasing with the Pt content, achieving the highest value at Pt loading 0.12%.

Based on electron microscopy data, the specific surface area of Pt particles increases from 0.015 m^2/g_{cat} for 0.01% Pt/SiGF sample to 0.07 m^2/g_{cat} for 0.12% Pt/SiGF. This means the increase of SO_2 conversion can be explained by the rise of active surface of Pt metal particles. Unfortunately, we did not measure the reaction rate because we persued just testing-comparison aim. Nevertheless, we did it in our previous paper [8] devoted to deep oxidation of *n*-butane over the same Pt/SiGF catalysts. It was shown clearly that turnover frequency in this reaction was constant TOF $\approx$ 2 s^{-1} in wide Pt loading range (up to 0.4 wt.%). The closely spaced TOF values were observed for Pt catalysts supported on traditional silica or alumina. This evidenced that the state and performance of Pt particles deposited on glass fibers are close to those supported on conventional carriers. As to samples with highly dispersed Pt species (clusters or ions) located inside fibers, it is more reasonable to compare the catalyst activity in terms of reaction rate referred to platinum atom. In this case atomic catalytic activity of these samples in *n*-butane oxidation was on one to two orders higher than for Pt metal particles. Based on data presented in Table 1, we believe that similar regularities take place in SO_2 oxidation also. Indeed, when Pt is located in the fiber bulk the same SO_2 conversion is obtained at much lower Pt loading (compare samples 5 and 3).

It was important to check the capabilities of Pt/SiGF catalysts in SO_2 oxidation at elevated temperatures (>650 °C), which are typical for processing of highly concentrated sulfuric gases. In such severe conditions, conventional vanadium catalysts tend to be thermally unstable. We believed that localization of Pt species in the fibers bulk can provide not only the high dispersion of Pt, but also it can essentially prevent sintering compared to the Pt deposited on outer surface of fibers. To verify this, we experimentally tested catalysts containing 0.01 and 0.03% Pt localized in the fibers bulk only (samples 4 and 5).

The tests were performed in a flow reactor on a highly concentrated feed gas (20 vol.% SO_2, 20 vol.% O_2, 60 vol.% N_2) at temperature 700 °C. The contact time varied from 0.36 to 1.5 s by changing of catalyst loading (0.4–1.6 g). Under such severe conditions, the experimental conversion values have reached the equilibrium conversion (X_{eq}) equal to ∼52%.

According to Fig. 3, both samples exhibit similar performance. Conversion of SO_2 attains the equilibrium 1 at the contact time of approximately 1 s. Samples' activity is also similar at smaller contact times ($X = 35$ and 37% at $\tau = 0.36$ s). The conversion remained unchanged at 700 °C for 48 h of running. The studied catalysts thus showed remarkable thermal stability. To confirm this result, we exposed the sample containing 0.03% Pt to accelerated aging. The sample was additionally calcined in muffle at 800 °C for 10 h, and then tested again at 700 °C at the same conditions. No activity loss was detected (Fig. 3). According to the XRD and XPS analysis high-temperature tests caused no crystallization of the silica fiber glass, as well as decrease in Pt loading.

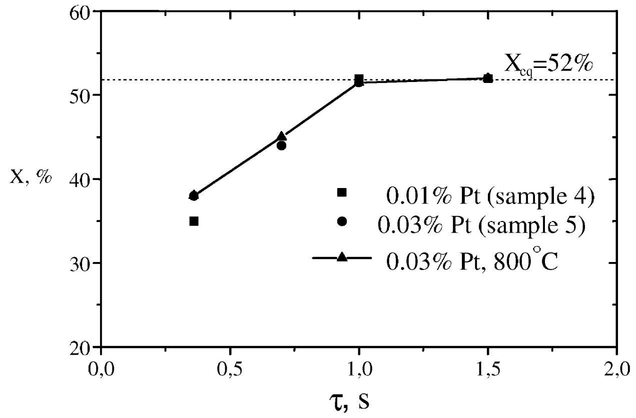

Fig. 3. Influence of contact time on SO_2 conversion over 0.01% Pt/SiGF (sample 4), 0.03% Pt/SiGF (sample 5) and sample 5 calcined at 800 °C.

Hence, the presence of highly dispersed Pt species located in the bulk of glass fibers was found to be responsible for the enhanced activity in SO_2 oxidation. It is believed that Pt species (clusters or ions) are in non-equilibrium (metastable) state that is main reason, likely, of high catalyst performance.

The stabilization of Pt species in glass matrix is possible due to the following reasons. First, they are chemically bonded with matrix because Pt^{n+} ions were introduced into glass via ion exchange with nH^+ of hydroxyl groups of leached glass fibers. Second, it is difficult to imagine that positively charged Pt species located in very narrow interlayered space are capable of coalescencing and sintering. Most probably the sintering process will take place when the woven support loses the glass property due to its phase transition to amorphous or crystal states. Anyway, we never observed the formation of crystal silica and metallic platinum.

The localization of active Pt species inside of glass fibers brings the problem of their accessibility for reacting molecules from gas phase. At present it is difficult to reveal the internal diffusion limitation contribution to measured activity in SO_2 oxidation. Moreover, the diffusion mechanism is not clear because at elevated temperatures the glass matrix structure becomes rather labile. Recently, we have showed that diffusion rate depends on mostly the reaction temperature and electrophysical properties of reacting molecules (dipole moment, polarizability, etc.) [9]. At low temperatures (up to 100–150 °C) the latter plays the crucial role, so the reaction between non-polar molecules does not proceed at all. Therefore, we are inclined to believe that reaction of SO_2 oxidation proceeds without diffusion limitation at studied range of temperature.

Thus, along with appropriate hydrodynamic properties (low pressure drop, additional feed gas mixing, etc.), as well flexibility in the construction of wide variety shape and geometry, the Pt-based woven glass fiber catalyst showed high activity in SO_2 oxidation and high thermal stability. Therefore, these new catalysts can be considered as a promising alternative for vanadium conventional sulfuric acid catalysts, especially for processing of highly concentrated SO_2 feed gases.

Acknowledgements

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