Fiber glass supported catalysts and pure platinum: laser ignition of catalytic combustion of propane

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A pure platinum (Pt) catalyst and a new industrial catalyst, the silica fiber glass catalyst (SFGC) doped with only 0.2% Pt, were studied and compared. For propane–air catalytic combustion, the ignition of the reaction and its stability were investigated. The reaction, ignited by a laser beam, propagated as a wave front with constant amplitude and velocity along both catalysts, $\sim$10 mm/s for Pt, and 1–2 mm/s for SFGC. Laser ignition thresholds and the parameter space for front propagation were determined for both catalysts. Spatial instability (resulting in the destruction of the homogeneous regime of combustion and in the formation of hot spots) was found for Pt, but not for SFGC. The new catalyst (SFGC) containing only 10^{-3} of Pt has the same catalytic activity as pure Pt and better spatial stability.

KEY WORDS: Pt catalyst; fiberglass support; propane combustion; stability; laser ignition

1. Introduction

The new catalyst, the silica fiber glass catalyst (SFGC) obtained by doping of Pt into a fiber glass woven matrix [1], has demonstrated important advantages compared to the standard catalysts [2]: less platinum is required, Pt losses are diminished by up to two–three orders of magnitude, catalytic activity is increased, more effective (cassette type) design of industrial reactors becomes possible, exploitation of the reactor is simplified, and production price is lowered. SFG catalysts are starting to be used in wide scale industrial production of fertilisers, sulphuric and nitric acids, for industrial exhausts purification and for water denitrification.

The instabilities of this new catalyst were not investigated previously. They are important both for the theoretical understanding of catalysis, and for the theory of industrial reactors. Temporal instabilities (usually resulting in temporal oscillations), and spatio-temporal instabilities (resulting in the destruction of homogeneous regime of reaction, in hot spots formation and in complex spatio-temporal behavior) are well known in chemistry (see, e.g. [3,4]).

Wave phenomena in heterogeneous catalysis were predicted in 1975 [5] and discovered experimentally by Barelko et al. in 1978 [6]: domain structures, waves, and autowaves (in ammonia oxidation with a platinum wire catalyst). The term autowaves means highly nonlinear waves in active media with specific properties, for example, autowaves annihilate each other under collisions, contrary to classical waves [7]. Nonstationary waves (pulsating domains, and propagating waves that change the direction of propagation) were observed in the ethylene oxidation reaction as early as in 1976 [8]. Later, numerous wave phenomena were found, with different catalysts (Ni, Pt ribbon, Pd/Al_2O_3) [9–12]. Two-dimensional waves were discovered and investigated [13–17] by Ertl et al. in ultrahigh vacuum conditions (isothermal waves). Now, new experimental facilities are developing to overcome this limitation (see, for example [18]). For approaches used for theoretical analysis of patterns see, e.g. [19,20].

In this paper, we investigate ignition of the reaction, propagating waves, and spatial instabilities observed just after ignition. We compare catalytic thermal waves and patterns in SFGC, and in the traditional catalyst, pure Pt. The catalytic combustion of propane is studied. Propane and methane are among the main hydrocarbon fuels in use in industry and households. To our knowledge, there are still no investigations of wave dynamics in propane catalytic combustion even with the traditional Pt catalyst. Investigations of wave processes on SFG catalysts have been started in this work. Another aspect of the present work is the ignition of wave transitions in catalytic reactions by a laser beam [21].

2. Methods

2.1. Catalysts

The silica fiber glass catalyst (SFGC) (supplier: Chemphyst, glass@aha.ru) was in the form of woven tissue (figure 1). We worked with a single thread, consisting of 300 fibers of 7 μm diameter. They contained 0.2 wt% of Pt. The glass matrix contained 96–97 wt% SiO_2, 3% Al_2O_3 and 0.5% Na_2O, with a specific surface area 1–2 m^2/g. The Pt-wire (supplier: Goodfellow, info@goodfellow.com, diameter 0.125 mm) was of 99.95% purity. Before measurement, the wires were heated by electric current (1.5 A) for 45 min in flowing air.

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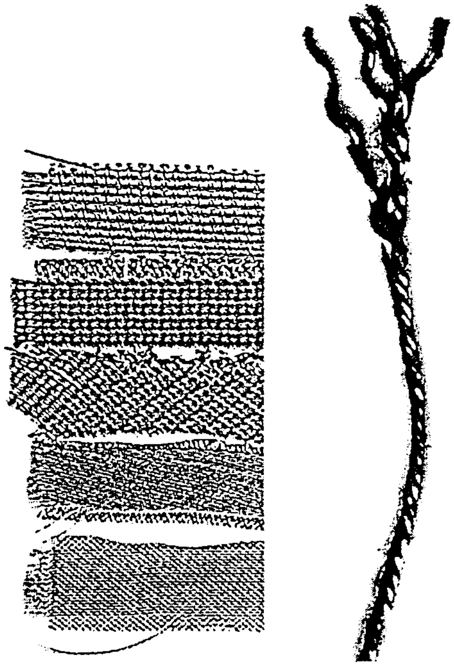


Figure 1. Silica fiber glass (SFG) catalysts doped with 0.2% Pt. (Left) woven catalytic tissues and (right) a thread (0.5 mm in diameter) consisting of elementary glass filaments 7 μm in diameter.

2.2. Reactor

The catalysts were installed in a quartz cell (supplier: Hellma, 131-QS, inner dimensions 10 mm ×10 mm × 30 mm. The catalysts were fixed by copper nodes along the axis of the cell and orientated along the direction of the gas flow. If not noted otherwise, the air flow rate was fixed at 24 l/h, corresponding to a gas flow velocity of 67 mm/s in the reaction chamber. The flow rate of propane was varied between 0.5 and 5 l/h (corresponding to additional ∼1.4–14 mm/s) for changing the propane concentration. In the reaction chamber, the gas flowed parallel to the catalytic filament, allowing the study of the propagation of the ignition wave, parallel and antiparallel to the flow.

We used a Nd-YAG laser (YAG 904, ALY 120 micro control wavelength: 1.06 μm, maximal power 12 W, pulse energy 10*-3 J). The laser power was controlled by the repetition rate and checked by calibrations. Light emission due to the reaction and the subsequent heating of the catalyst was recorded by a video camera (Sony, DC-77RR-CE) on a video cassette recorder (Sony, EVO -9650P, Hi8), with subsequent computer analysis of the images.

3. Results

3.1. Wave front propagation

Both on Pt and on SFGC, the reaction front induced by the laser beam propagated stably with a constant amplitude and velocity, until the reaction zone covered the whole catalyst (figure 2). On the Pt catalyst, the front velocities were five to ten times faster than those on the SFG catalyst (cf. time labels in figure 2 (a) and (b)). Wave front propagation was observed only in a narrow region of propane concentration. They were different for the two catalysts: 2.1–4.8% for the Pt, 2.6–5.1% for the SFGC (figure 2) (the stoichiometric concentration of propane in air is 4 vol%).

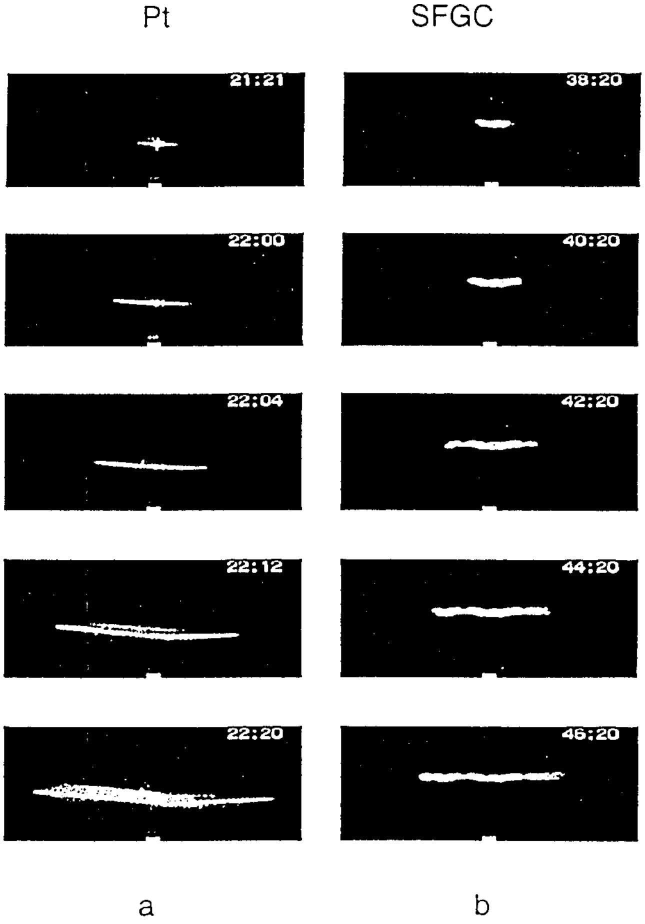


Figure 2. Propagation of the ignition wave front. (a) Pt wire catalyst, propane concentration is 3.5 vol% and (b) SFG catalyst, propane 3.4 vol%. The catalyst length is 30 mm. The laser spot igniting the reaction front is seen on the upper record of (a). The rectangle below labels the former position of the laser spot. Gas flow velocity is 7 cm/s, from left to right. Video records, 25 frames/s. Time label shows (seconds: frame number).

3.2. No propagation

For propane concentration outside of this narrow region, the reaction proceeded under the laser beam only, and did not propagate along the catalysts (figure 3, no-propagation region). The reaction looked like the upper record of figure 2(a), but did not change with time. It is quite natural that the velocities diminished to zero when approaching the no-propagation region (figure 3 (a) and (b)).

3.3. Domain instability

For Pt, a spatial instability (domain instability, DI) was found. It resulted in the decay of homogeneous combustion to several hot spots. We observed one stable hot spot, or two hot spots, as a transient regime in the 3 cm reactor.

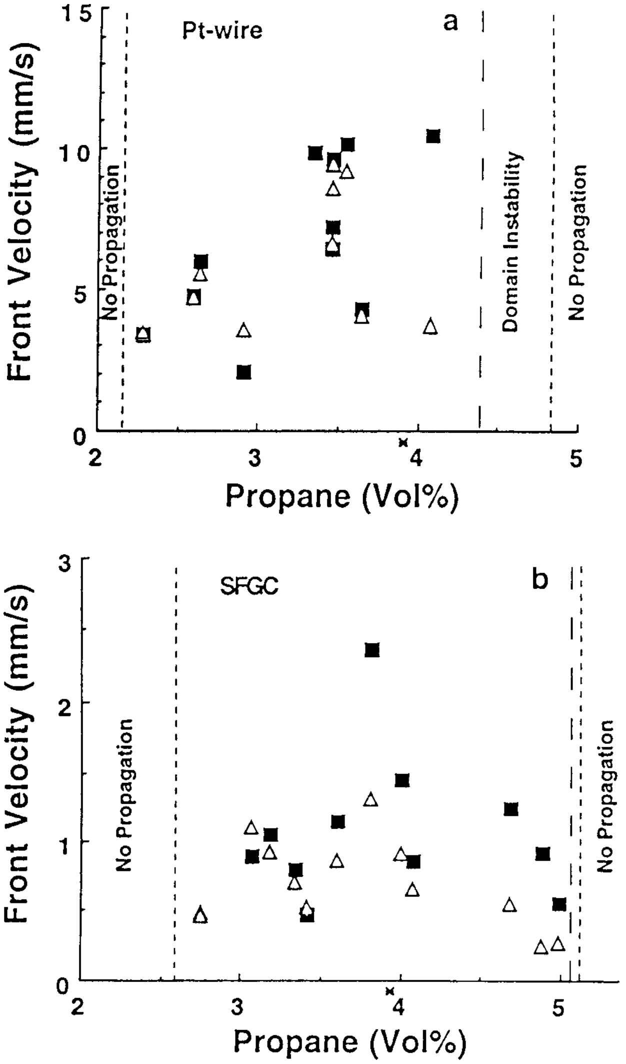
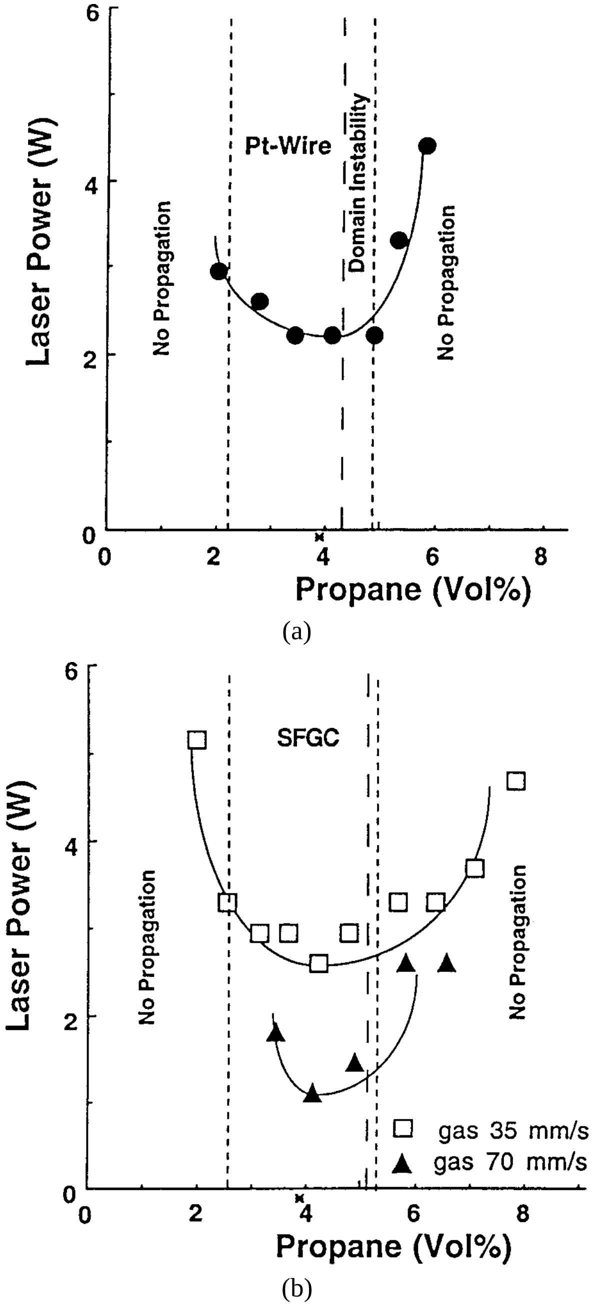


Figure 3. Front propagation velocities. The asterisk on the abscissa labels the stoichiometric composition. It is seen that for the SFG catalyst as compared to Pt: wave propagation is observed at higher propane concentrations (both boundaries, left and right, are shifted to the right); the propagation of the ignition wave is an order of magnitude slower; the domain instability region was not found. (■) Antiparallel and (△) parallel.



(a)

(b)

Figure 4. Minimal laser power required for ignition of the reaction. The lines are drawn as a guide to the eye. The reaction can be ignited also in the domain instability region, and even in the no-propagation region (compare with figure 3).

The boundaries of the DI region were 4.4–4.8%, figure 3(a). Inside the DI region, the steady front propagation lost stability, and the reaction front stopped before reaching the ends of the catalyst. The laser induced reaction did not cover the full length of the catalyst, and a localized reaction zone was formed.

3.4. No domain instability was found in the SFG catalyst

It may mean either that it did not exist for the SFGC, or that it existed, but that the DI region was narrower than the concentration range that we could stably maintain (~0.1%).

3.5. Laser ignition threshold

The different values of the laser ignition thresholds for Pt and SFGC seen in figure 4 do not reflect their distinct catalytic properties. The difference is due to unequal laser light reflection coefficients. The important information on these graphs is how the ignition threshold depends on the parameters. The thresholds for Pt and SFGC depended similarly on the propane concentration.

Minimal ignition energy was observed inside the wave front propagation region. Outside of this region, the reaction could be ignited also (but required a higher laser energy), but did not propagate along the catalyst and was not sustained after switching off the laser. Interestingly, increasing the gas flow rate significantly reduced the ignition threshold (figure 4(b), compare gas flows 35 and 70 mm/s). These results can be explained by the *hypothesis* of homogeneous–heterogeneous mechanisms in catalytic combustion, i.e., inhibitory metastable products are generated in the boundary layer near the catalytic surface [22].

3.6. Paradoxical front velocities

Approaching the domain instability region, an unexpected velocity behavior was found. Near the right boundary of the wave front propagation (figure 3(a)), the velocity measurements gave strange results. They became poorly reproducible, dependent on the location along the catalyst and on the direction of propagation. What could be expected here, is that the reaction front was advected by the gas flow: $C_+ = C_0 + C_{\text{gas}}$, $C_- = C_0 - C_{\text{gas}}$, where C_+ is the velocity of front propagation in the direction of the gas flow (parallel to the gas flow), C_- is the velocity of propagation in the opposite direction (antiparallel to the gas flow), C_0 is the front velocity in the motionless gas, and C_{gas} is the gas flow velocity. This mechanism should result in $C_+ > C_-$. However, the opposite was observed in the experiment (figure 3): $C_+ < C_-$. In the last snapshot in figure 2(a), a non-symmetric propagation is seen: the propagation to the left is faster than the progagation to the right. This symmetry-breaking becomes much more pronounced when approaching the right (high concentration) boundary of the front propagation region (figure 3(a)).

This means that another mechanism is involved. When propane concentration was increased, we observed the formation of hot domains (see domain instability region in figure 3(a)). Inside the DI region, the steady front propagation lost stability, and the reaction front stopped before reaching the end of the catalyst. Abnormal dependence of velocity on direction may mean that the mechanism leading the formation of the hot domains affected the front velocity even before the hot domains were actually formed.

For SFGC, where domain instability (DI) was not found, the front velocity anomaly $C_+ > C_-$ was nevertheless observed near the same boundary where the Pt catalyst displayed DI (figure 3(b)). It would be interesting to check in mathematical models if velocities C_+ and C_- really reflect the approach to the instability region. Maybe they can be used to detect the pattern-forming instability even before the hot domains are created.

3.7. Comparing Pt and SFG catalysts

Pure Pt and SFGC exhibited similar catalytic properties for the reaction, although SFGC contained only 0.2 wt% Pt. For the SFG catalyst as compared to Pt:

- Wave propagation was observed at higher propane concentrations at both boundaries.
- The propagation of the ignition front was an order of magnitude slower.
- Domain instability was not found.

4. Discussion

The well known classical silica gel catalyst at first glance seems similar to the new proposed silica fiber glass catalysts (SFGC). But there are fundamental differences that arise from the amorphous state of the matrix in the fiber glass catalyst [23], while in the classical silica gel it is in a mixed, or polycrystalline state. This results in drastic changes of mechanical and catalytic properties.

Let us compare ignition of SFGC and Pt catalyst. The velocity of the front propagation on the SFGC is an order of magnitude slower than on the Pt wire (figure 3). This can be explained by the significantly higher thermal conductivity of Pt, and the smaller diameter of the Pt wire compared to the SFGC thread. The front propagation velocity is [5]

$$v \approx (l/d)^{1/2} g, \tag{1}$$

where l is the thermal conductivity, d is the diameter, and

$$g = \int [Q_+(T) - Q_-(T)]\,\mathrm{d}t \tag{2}$$

is the integral over the front, where Q_- is the heat loss, and Q_+ is the heat production of the reaction, dependent on the activity of the catalyst. Substitution of the respective values for thermal conductivity $l = 71.7$ W/(m K) for Pt and $l = 1.38$ W/(m K) for SFGC, diameters d (0.125 mm for Pt and 0.5 mm for SFGC) and keeping multiplier g the same, gives a velocity an order of magnitude higher for Pt, in agreement with our measurements.

Since $Q_+(T)$ in equation (2) reflects the catalytic activity, and no variations in $Q_+(T)$ were required to explain the difference, the front velocity measurement is in agreement with the conclusion about the same catalytic activity of both catalysts obtained in [22] by direct rate measurements.

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