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Properties and efficiency of a Pt/Al_2O_3 catalyst applied in a solid fuel thermo-accumulating furnace

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Abstract: A prototype of a solid fuel thermo-accumulating furnace has been developed. In order to achieve a higher combustion efficiency, a Pt/Al_2O_3 catalyst in the form of 3 ± 0.3 mm spheres was applied, which enabled further combustion of flue gases within the furnace. Experimental investigation of the influence of the catalyst on the conversion of CO has been done for different operation regimes and positions of the catalyst. Paper presents selected results regarding CO emission during wood and coal combustion. Investigations suggest a considerable effect of the catalyst and a strong influence of the catalyst position to CO emission reduction. The microstructure of the catalyst beads, characterized by selective chemisorption of CO, has shown the decrease of the number of Pt sites as a consequence of blockage by coke deposits formed during the combustion of solid fuel.

Keywords: Pt/Al_2O_3 catalyst, emission reduction, solid fuel, thermo-accumulating furnace.

INTRODUCTION

The usual problems found in solid fuel household heating systems are low combustion efficiency, small heat transfer intensity and high emission. The problems in residential heating are treated nowadays from various aspects,[1–4] with emission of pollutants being one of the most important.[2–4]

A prototype of an innovative thermo-accumulating solid fuel furnace, aimed for residential heating purposes, has been developed and tested. The furnace provides efficiency over 75 %, considerable energy savings, emission of pollution that meets European standards and possibility of firing both low- and high-rank solid fuels. The basis for the development of the furnace was a registered patent.[5] The furnace is presented and described in details in Ref. 6.

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In order to achieve higher combustion efficiency, a Pt/Al_2O_3 catalyst, in the form of 3 ± 0.3 mm spheres, was applied in the furnace prototype, providing further combustion of flue gases within the furnace. An experimental investigation of the influence of the catalyst on the conversion of CO into CO_2 was performed for different operation regimes and positions of the catalyst. All furnace tests were performed in accordance with the European Standard for solid fuel-fired furnaces (EN 12815). The microstructure of the catalyst beads, characterized by selective chemisorption of CO, was studied and compared to the structure of the beads after use in the furnace.

EXPERIMENTAL

Catalyst preparation

The employed support was commercial $(\gamma+\theta)$–Al_2O_3 in the form of spheres with a diameter of 3 ± 0.3 mm, from Rhone Poulenc. The platinum catalyst was prepared by impregnation of a dry support with an aqueous solution of chloroplatinic acid. Before the Pt deposition, the support was dried for 4 h at 120 °C. An adequate amount of an aqueous solution of hexachloroplatinic acid was added to the support (about 5 $cm^3\ g^{-1}$ support) by the incipient wetness method. The concentration of chloroplatinic acid in the impregnating solution was 1×10^{-2} mol l^{-1}. After the adsorption of chloroplatinic acid during 3 min, the catalyst was filtered, rinsed with distilled water, air-dried at 110 °C for 2 h and finally reduced in a flow of H_2/N_2 mixture. The reduction was performed under a stepwise increase of temperature up to 500 °C. At this temperature the catalyst was reduced during 5 h. A catalyst with the following characteristics was synthesized: Pt amount 0.12 wt. %; specific area – S_{BET} – 110 $m^2\ g^{-1}$; pore volume – 0.68 $cm^3\ g^{-1}$ and supported Pt layer thickness – 100 μm.[7]

Catalytic activity test

The Pt/Al_2O_3 catalyst was tested for combustion of a gas mixture designed to simulate the approximate concentrations of pollutants in the furnace. The activity tests were performed in the apparatus presented earlier.[8] The activity of the catalyst was investigated in the temperature range 100–400 °C, with a space velocity of 17 500 h^{-1}, defined as the ratio between the gas flow rate and the volume of catalyst. The synthetic gas mixture composition was: CO, 1.17 vol. %; C_3H_6, 800 ppm; H_2, 1.36 vol. %; NO_x, 1120 ppm.; CO_2, 6 vol. %; H_2O, 5 vol. %; O_2, 4.6 vol. % and N_2, the rest. The composition of feed stream corresponds to a redox potential of 0.4 V, which was calculated according to the equation presented in Ref. 8.

Catalytic activity in the furnace

The furnace operating at different regimes, firing wood and coal, with and without catalyst, was experimentally tested. The furnace and the experimental set-up are shown in Fig. 1.

The flue gases flow through the three drafts (1a–1c), while combustion of solid fuel (wood biomass, coal) occurs on a horizontal grate (2). The air enters the furnace through the opening under the grate. In order to examine the influence of the position of the catalyst on its ability to reduce CO emission, the catalyst (3) was placed in two vertical positions (denoted as upper and lower), within the central draft (1b), with flue gases flowing downward and around the catalyst. The flue gases leave the furnace through the stack (4), used for flue gas sampling and temperature and flow rate measurements. The airflow rate is controlled by changing the flue gas fan speed. This fan is connected to a variable (0 – 220 V) ac supply (5). During the experiments, when the furnace had attained a steady state (after the initial firing), the ac voltage was kept constant at 110 V. This enabled the whole amount of fuel (about 1.5 kg) in the combustion chamber (1a) to burn out before the next fuel feeding an hour later. The furnace as a whole was placed on a high-precision balance (±10 g), in order to monitor the weight loss between consecutive fuel feedings, *i.e.*, the combustion dynamics.

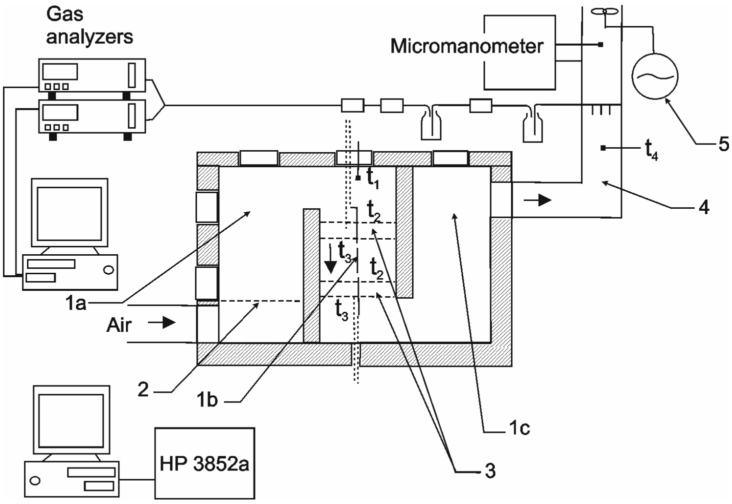

Fig. 1. The solid fuel furnace with the experimental set-up; 1a – combustion chamber; 1b – central draft; 1c – third draft; 2 – grate; 3 – catalyst; 4 – stack; 5 – variable (0 – 220 V) ac power supply.

Gas samples were taken from the stack and continuously analyzed. The gas sampling probe, made according to EN 12815 Standard, was water-cooled on the outside of the stack, in order to dry the flue gas samples. The gas analyzers were controlled by a PC, memorizing the measured concentrations data every three seconds. The flue gas temperatures were measured with type K, class I thermocouples at a number of points, such as at the top of the middle draft (t_1), at the catalyst entrance and exit sections (t_2 and t_3) and at the furnace exit (t_4). The thermocouple signals were measured with a digital voltmeter on an HP3852a data acquisition system, and memorized every 5 seconds.

CO uptake measurements

The CO uptake of the catalysts before and after the catalytic activity tests in the furnace was obtained at a temperature of 24 ± 0.2 °C. The measurements were performed on a pulse gas chromatographic apparatus. Before the chemisorption measurements, the catalyst samples (about 0.5 g) were treated at 500 °C in a helium flow for 1 h. After cooling in a helium flow to room temperature, the CO was pulsed (pulse volume 0.1 cm^3) into the helium stream (30 cm^3 min^{-1}) through the adsorption cell. The catalyst adsorbed the CO pulses until saturation and the fraction of CO not adsorbed was detected by a thermal conductivity detector (TCD).

RESULTS AND DISCUSSION

In order to compare different operation regimes of the furnace, with different air excess, the measured values of the CO concentration in the dry flue gases CO_{meas} were converted to concentration values at referent oxygen content in the flue gases CO_{ref}, all given in vol. %, according to Eq. (1):

$$CO_{ref} = \frac{20.9 - O_{2ref}}{20.9 - O_{2meas}} CO_{meas} \tag{1}$$

The referent oxygen content in the flue gases, according to the EN 12815 Standard, is $O_{2\mathrm{ref}} = 13$ vol. %. The measured oxygen content in the flue gases is $O_{2\mathrm{meas}}$. The flow rate of CO (released carbon-monoxide in time, given in mg s^{-1}) is calculated as:

$$\dot{m}_{\mathrm{CO}} = \dot{V}_{\mathrm{fg}}\mathrm{CO}_{\mathrm{ref}} \tag{2}$$

where $\dot{V}_{\mathrm{fg}}$, m^3 s^{-1}, is the volume flow rate of the flue gases and CO$_{\mathrm{ref}}$, mg m^3, is the referent CO concentration, previously converted from vol. % to mg/m^3. Since the flue gas sampling was performed (with the results memorized) every three seconds, the mass of CO released in 3 s is:

$$m_{\mathrm{CO}}(3\mathrm{s}) = 3\dot{m}_{\mathrm{CO}} \tag{3}$$

and the cumulative CO emission (given in g) from the beginning of the test until the moment of observation τ, $E_{\mathrm{CO}}(\tau)$ is calculated by the expression in Eq. (4):

$$E_{\mathrm{CO}}(\tau) = \frac{1}{1000}\sum_{0}^{\tau} m_{\mathrm{CO}}(3\mathrm{s}) \tag{4}$$

Experiments with synthetic gas mixture

From Fig. 2, it is evident that the Pt/Al$_2$O$_3$ catalyst showed satisfactory performances for the removal CO and propylene.

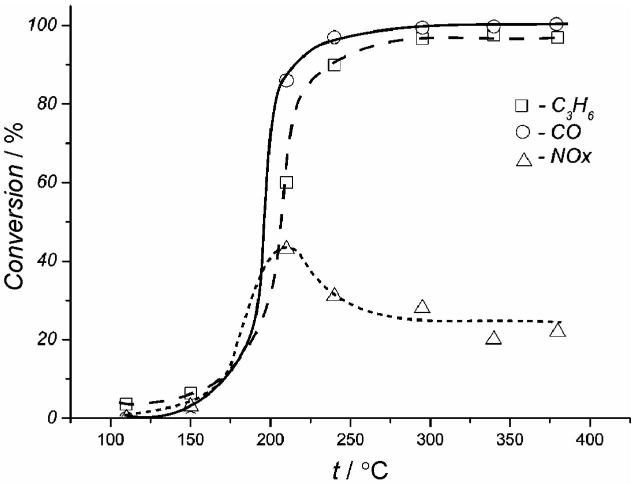

Fig. 2. The performance characteristics of the Pt/Al$_2$O$_3$.

Their conversions exceeded 90 % at temperatures above 225 °C. Although oxidizing conditions were applied (with a redox potential $R = 0.4$ V), a conversion of NO$_x$ was registered. The NO$_x$ conversion curve passed through a maximum at 210 °C and then decreased to a value of 20 %. This is the result of competitive reactions of CO and propylene with NO$_x$ and oxygen. Probably, above 210 °C oxidation reactions of CO and propylene prevailed and NO$_x$ removal was hindered due to a shortage of the reducing agents.

Experiments with wood

The furnace was examined in three operation regimes, with fuel consumption of about 1.5 kg h^{-1} in each. For the basic one (without the catalyst), wood was supplied to the furnace every 30 minutes (0.750 kg) in the beginning, but it was found that this amount of fuel was optimal for 40 minutes of operation and fuel feeding was adjusted accordingly. In the other two regimes, the catalyst was mounted in the upper and the lower position, respectively. The changes of temperature of the flue gases at the catalyst entrance section and CO concentration in the outlet flue gases at 13 vol. % O$_2$ with time are shown in Figs. 3 and 4, for both operation regimes with the catalyst.

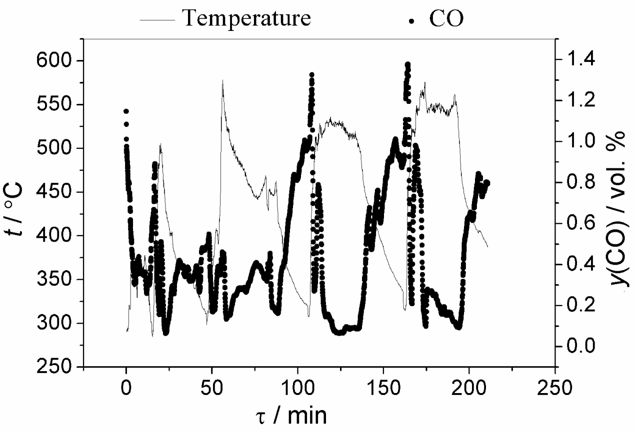

Fig. 3. Time dependence of the flue gases temperature at the entrance section of the catalyst in the upper position and the CO concentration in the outlet flue gases, for wood combustion.

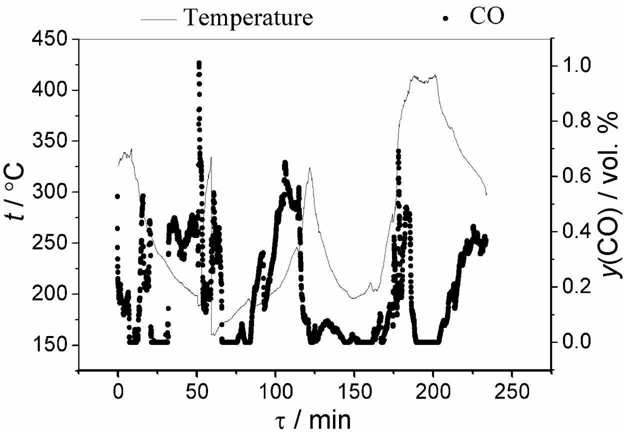

Fig. 4. Time dependence of the flue gases temperature at the entrance section of the catalyst in the lower position and the CO concentration in the outlet flue gases, for wood combustion.

The experimental results for the effect of the catalyst on the CO concentration in the flue gases at 13 vol. % O$_2$ (averaged over the fuel feeding intervals) and on the cumulative CO emission are given in Figs. 5 and 6.

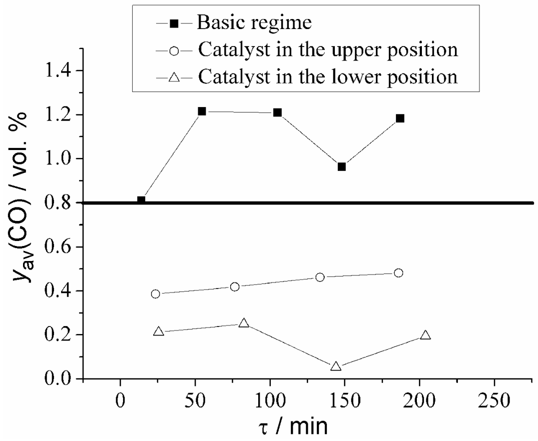

Fig. 5. Effect of the catalyst on the CO concentration in the flue gas, averaged over fuel feeding intervals, for wood combustion.

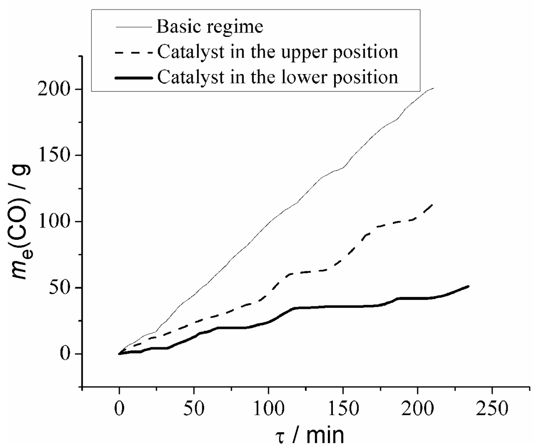

Fig. 6. Effect of the catalyst on the cumulative CO emission, m_e(CO), for wood combustion.

Compared to the basic regime, both those with the catalyst were obviously advantageous. After a quick and very intense increase immediately after fuel feeding, the CO concentration decreased very soon to a value of 0.8 vol. % (Figs. 3 and 4), permitted by the EN 12815 Standard. The average CO concentration (Fig. 5) in the case of the catalyst in the upper position was around 0.4 vol. %, *i.e.*, much lower than the permitted value. Further enhancement was obtained by mounting the catalyst in the lower position, when the presence of the catalyst completely removed CO for a significant period of time between two fuel feedings (Fig. 4) and the average CO concentration was about or lower than 0.2 vol. % (Fig. 5). The positive effects of the catalyst on the reduction of CO emission were even more obvious when the cumulative CO emission during the experiments were considered (Fig. 6). The cumulative emission after 200 minutes of operation for the catalyst in the lower position was 5 times lower compared to the basic regime and for the catalyst in the upper position it was reduced to one half.

The catalyst proved to be more efficient when placed in the lower position than in the upper one (in the zone with higher temperatures). The performance characteristics of the catalyst (Fig. 2) showed that the temperature interval of maximum catalyst efficiency for CO conversion was at temperatures above 200–225 °C, while Figs. 3 and 4 show that for both regimes with the catalyst, the temperatures at the catalyst entrance section was, most of the time, also higher than these. Thus, the better efficiency of the catalyst in the lower position can not be assigned to temperature but most probably to the flow conditions. In this regime, the flue gases enter the catalyst zone and flow over catalyst beads uniformly, so the catalyst is utilized more efficiently. The catalyst in the upper position disturbs the flow and the temperature field in the central draft considerably and it is likely that an intense recirculation zone exists above the catalyst zone (Fig. 1).

Experiments with coal

The experiments were carried out for two operation regimes, the basic one (without the catalyst) and the regime with the catalyst in the upper position. The amount of air supplied in both regimes was sufficient for the combustion of 1.5 kg h^{-1} of coal. In the basic regime, 1.5 kg of coal was supplied once an hour. It was noted during the experiment that with time the grate became covered with a huge amount of unburnt fuel and ash. In order to avoid this in the regime with catalyst, the furnace was supplied with 0.750 kg of coal every 30 minutes.

The CO concentration was low, almost zero, for most of the time between fuel feedings (Fig. 7). The flue gas temperature at the catalyst entrance section did not change considerably, in the range of 320 – 365 °C, and probably did not affect the catalytic conversion of CO much. The results for cumulative CO emission (Fig. 8) showed that the presence of the catalyst, even in the upper position (less suitable for reducing CO), significantly contributed to a lowering of the CO concentration levels in the flue gases. After 120 minutes of operation, the CO emission was 20 % lower with the catalyst than without.

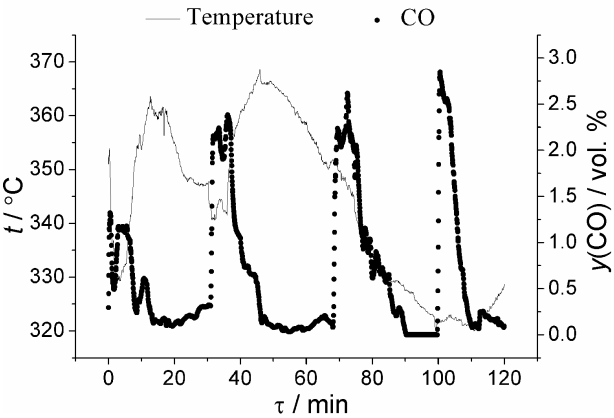

Fig. 7. Time dependence of the flue gases temperature at the entrance section of the catalyst in the upper position and the CO concentration in the outlet flue gases, for coal combustion.

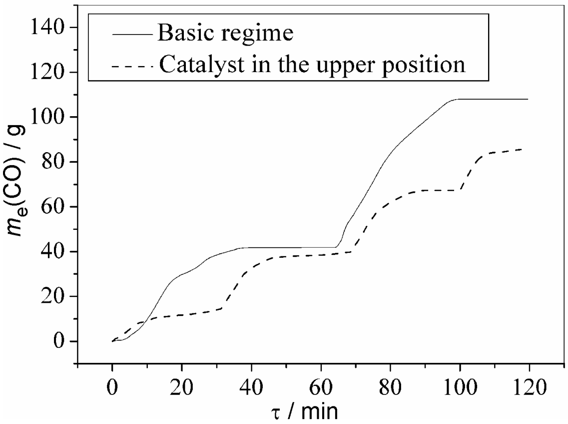

Fig. 8. Effect of the catalyst on the cumulative CO emission, for coal combustion.

Microstructure of the Catalyst Beads

CO uptake measurements (Table I) clearly show that the number of exposed Pt sites which can participate in the surface reactions significantly decreased, by about 50 %, regardless of the type of employed solid fuel.

TABLE I. CO uptake for the Pt/Al_2O_3 catalyst samples

Pt/Al_2O_3 catalyst samples	Fresh	After wood combustion	After coal combustion
CO uptake μmol g^{-1}	1.51	0.84	0.80

There are several possible mechanisms for the reduction of the exposed Pt sites, such as sintering of the Pt due to the high temperature treatment, physical blockage of the Pt sites by deposits formed during the combustion of the solid fuels or catalyst coking caused by surface reactions. Bearing in mind the applied temperature range (150–500 °C), it is unlikely that sintering of the Pt occurred. Previous investigations showed that sintering of Pt commences above 600 °C.[9] Therefore, the drop of CO uptake is ascribed to the blockage of the Pt sites. Furthermore, a visual survey of the discharged catalyst showed black deposits only on the half of the sphere facing the flue gases stream. The other half of the sphere retained the appearance of the fresh catalyst. These facts could lead to the conclusion that the deposits originated from the flue gases stream. The deposits were not formed during reaction on the catalyst surface; otherwise the whole sphere would be covered with the black deposits. Also, it should be noted that the black-colored deposits were more pronounced when coal combustion was applied. Although a decrease in the available Pt sites was registered, there is no evidence of a decrease of the catalyst performances in the furnace. However, for long-term application of the catalyst, removal of the deposits by a suitable method (washing, controlled incineration) should be considered.

CONCLUSION

A series of experiments were performed on a prototype of a thermo-accumulating solid fuel furnace, to investigate the possibility of increasing the combustion efficiency (with respect to the transformation of CO) by means of a Pt/Al_2O_3 catalyst, employed in the form of 3 ± 0.3 mm spheres. Tests were performed in accordance with the corresponding European Standard for solid fuel-fired furnaces. Selected results regarding the activity of the catalyst during wood and coal combustion in the furnace, as well as of a catalytic activity test with a synthetic gas mixture are presented. The measured and average values of the concentration of CO, as well as the cumulative emission of CO, showed that the presence of the catalyst considerably reduces CO emission, for both employed fuels – wood and coal. Investigations also suggest a strong influence of catalyst position to reducetion of CO emission, as well as the importance of the flow conditions within the furnace. The microstructure of the catalyst beads, characterized by selective chemisorption of CO, evidenced a decrease in the number of Pt sites as a consequence of blockage by coke deposits formed during the combustion of the solid fuels.

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ИЗВОД

ОСОБИНЕ И ЕФИКАСНОСТ Pt/Al_2O_3 КАТАЛИЗАТОРА У ТЕРМО-АКОМУЛАЦИОНОЈ ПЕЋИ НА ЧВРСТО ГОРИВО

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У прототипу термо-акумулационе пећи на чврсто гориво, примењен је Pt/Al_2O_3 катализатор, у облику сфера величине 3 ± 0.3 mm, са циљем да повећа ефикасност сагоревања и накнадно сагори гасове унутар пећи. Утицај катализатора на конверзију CO је експериментално испитан при различитим операционим режимима пећи и позицијама катализатора. Приказани су резултати промене емисије CO у току сагоревања дрвета и угља. Истраживања су показала значајан ефекат катализатора на смањење емисије CO, као и значај положаја катализатора. Микроструктура катализатора, испитана селективном хемисорпцијом CO, је показала да у току сагоревања чврстих горива у пећи долази до депоновања угљеника на катализатору што доводи до блокирања и смањења броја Pt активних центара.

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