ELSEVIER

Catalysis Today 53 (1999) 647–659

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Thermal stability of metal-supported catalysts for reduction of cold-start emissions in a wood-fired domestic boiler

Magali Ferrandon [a,*], Magnus Berg [b,1], Emilia Björnbom [a]

[a] *Royal Institute of Technology, Department of Chemical Engineering and Technology, Chemical Reaction Engineering, SE-100 44 Stockholm, Sweden*

[b] *TPS Termiska Processer AB, Studsvik, 611 82 Nyköping, Sweden*

Abstract

The aim of the present work is to develop a catalyst based on a mixture of manganese oxides and platinum supported on a metallic monolith for abatement of emissions from wood combustion, particularly during the cold-start phase. The activity and the thermal stability of the catalysts have been studied in the laboratory, before performing tests in a wood-stove. The effect of the hydrothermal treatment at 900°C on the adherence of the washcoat onto a metallic substrate was studied using scanning electronic microscope. It revealed well-adhering washcoat onto the metallic support due to the growth of the alumina whiskers during the treatment. The influence of the amount of washcoat, as well as the influence of the concentration of manganese oxides in it (Mn: 5 to 20 mol%/Al_2O_3) on the activity of fresh and hydrothermally-treated catalysts were studied. The activity tests were carried out using a mixture of carbon monoxide, naphthalene and methane in the presence of air, steam and carbon dioxide to resemble the flue gases from wood combustion. On the fresh catalysts, containing the same total amount of manganese, a high concentration of manganese oxides in the washcoat favoured the oxidation of carbon monoxide and naphthalene, whereas a lower concentration of manganese oxides in the washcoat gave higher activity for the oxidation of methane. An increased total amount of manganese oxides in the catalysts, which had the same amount of washcoat, resulted in an increase in activity for the oxidation of the three combustibles. After thermal treatment at 900°C for 270 h in steam, most of the manganese oxide catalysts were activated for the oxidation of carbon monoxide and naphthalene while only being slightly deactivated for the oxidation of methane. The addition of manganese oxides in the washcoat, however, lowers the temperature of the γ- to α-alumina phase transformation. Platinum (0.5 mol%) was added to the manganese oxide (10 mol%) catalyst to improve its activity. A platinum catalyst was also tested for comparison. The platinum and the mixed catalysts showed similar activity for the oxidation of carbon monoxide and naphthalene, while the mixed catalysts were more active for the oxidation of methane. A similarly mixed MnO_x–Pt (10–0.5 mol%) catalyst supported on Al_2O_3 stabilised with 3% lanthanum, but at larger scale, was tested in a wood-stove. The possibility of pre-heating the catalyst during the start-up phase was studied. The tests revealed a strong decrease of the carbon monoxide and unburned hydrocarbons emissions during the start-up phase when the catalyst was pre-heated with hot air compared with no pre-heating or no catalyst. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Manganese oxides; Platinum; Metallic monolith; Naphthalene; Carbon monoxide; Methane; Oxidation; Deactivation; Thermal ageing; Cold-start; Wood combustion

1. Introduction

Combustion of wood or wastes from the forestry industry is an attractive alternative to the utilisation of fossil fuels for energy supply since they have the

---

[*] Corresponding author. Tel.: +46-0-8-790-82-81; fax: +46-0-8-10-85-79

E-mail addresses: mafe@ket.kth.se (M. Ferrandon), magnus.berg@tps.se (M. Berg)

[1] Tel.: +46-(0)-155-22-13-78; fax:+46-(0)-155-22-13-98

0920-5861/99/$ – see front matter ©1999 Elsevier Science B.V. All rights reserved.

PII: S0920-5861(99)00152-2

advantage of being renewable and do not contribute to the increase of CO_2 in the atmosphere. The wide spread use of small-scale combustion of wood in traditional stoves causes, however, environmental and health problems. In Sweden, several hundred cases of cancer are believed to be caused every year by the emissions from small-scale combustion of wood. The emissions contain carbon monoxide, volatile organic compounds (VOC), polynuclear aromatic hydrocarbons (PAH) and particulates. Small-scale wood stoves contribute to more than 25% of the VOC and 50% of the PAH emissions although wood consumption represents only 5% of the total fuel consumption in Sweden [1].

In the initial stage, during reloading and in the final stage of a wood burning cycle, as much as 90% of the total emissions can be released. During the start-up phase when the combustion temperature is low the excess air ratio is also low due to vaporisation of volatiles. This leads to high emission levels of carbon monoxide and organic compounds, especially heavy compounds. When combustion stabilises, the combustion temperature increases and the level of unburned compounds decreases rapidly. During reloading, high emission levels occur as a result of rapid volatilisation leading to low excess air levels. In the final stage of the combustion cycle, when only a small amount of fuel remains, the excess air ratio increases and the combustion temperature decreases, this leads to a higher emission of carbon monoxide, however, the level of unburned hydrocarbons is relatively low as at this stage the fuel is almost fully devolatilised.

It is possible to lower the emissions of unburned compounds by complete catalytic oxidation to carbon dioxide and water at moderate temperatures. High conversion of unburned compounds over the catalyst and thus very low emissions for wood-fired boilers equipped with such catalysts have previously been demonstrated during work in which the design and the optimal integration of the catalyst was investigated [2]. With different catalysts, conversions over 80% were achieved and mean carbon monoxide emissions well below 300 ppm (measured according to the Standard Swedish Testing Procedure) were obtained. However, this Standard Procedure does not include the start-up phase. In the start-up and final stage of a wood burning cycle, it is difficult to achieve complete combustion, even with the presence of a catalyst. Also, the catalyst may be covered with tar and soot and therefore it may not work effectively during these periods and the catalyst may suffer from the condensation of tar which can lead to its deactivation. Furthermore, some of the inorganic compounds, such as sulphur compounds, may poison the active phase at low temperatures [3]. In stoves equipped with catalyst, the flue gas is usually led through a by-pass during the start-up period and hence the catalyst is not used when it is needed the most. It is important to find a method to minimise the length of time for the temperature to reach the light-off of the catalyst. Pre-heating of the catalyst has the potential to control emissions during a cold-start. This could be possible either by using an electrical heated catalyst (EHC) or by injecting hot air through the catalyst. EHC systems are however too expensive and complicated. The second alternative seems to be more economically attractive since a fan is already available in today’s stoves and only a coil upstream of the catalyst needs to be added. Thus, high emissions during the start-up phase may be controlled and at the same time the catalyst could be placed in a position where maximum peak temperatures are avoided.

The efficiency of the pre-heating may be influenced by the catalyst support. Metallic monoliths present some advantages over ceramic monoliths such as higher thermal conductivity, lower heat capacities and greater thermal and mechanical shock resistance. Moreover, they can be made with thinner walls than their ceramic counterparts, which results in lower pressure drop for the same cell density and higher contact surface area per unit of volume which provides more effective conversion. Any flow maldistribution concentrates the ageing (both thermal and poisoning) to certain areas of the monolith. Compared to the ceramic monolith, the metallic monolith, with its higher thermal conductivity, suffers less from thermal ageing due to maldistribution, thus delaying catalytic and structural thermal damage [4]. The lower heat resistance of metallic supports compared to that of ceramic supports does not have to be a limitation in wood boiler applications since the maximum temperatures in the flue gas duct can be kept below 900°C. Some disadvantages may however be attributed to the metallic monolith. For example, the deposition of washcoats on metallic monoliths is not as well developed yet as on ceramic monoliths. The non-porous nature of the metal foil, coupled with the mismatch in the thermal expansion between the foil and the ceramic washcoat, contributes to a washcoat adhesion problem during thermal cycling. The cost of metallic monoliths is higher than that of ceramic monoliths [4].

This paper reports the results of a study on metal-supported catalysts for the minimisation of the emissions during the cold-start stage. The active phases chosen were manganese oxides and platinum since their combination is active for the total oxidation of carbon monoxide and hydrocarbons and at the same time stable under the prevailing conditions [5]. In the first part of the study, the adherence of the alumina layer onto the metallic substrate before and after hydrothermal treatment at 900°C for 270 h was studied using scanning electronic microscope. In the second part, the effect of the number of washcoat dips (1–4) and also the effect of the concentration of manganese oxides in it (Mn: 5, 6.67, 10 and 20 mol%/Al_2O_3) on the activity of fresh and hydrothermally-treated catalysts were studied. The activity tests were carried out using a mixture of carbon monoxide, naphthalene and methane in the presence of air, steam and carbon dioxide to resemble the flue gases from wood combustion. In the third part of the study, platinum (0.5 mol%) was added to the manganese oxides to improve the activity. For comparison, a platinum catalyst was also prepared. Finally, a full-scale metal-supported catalyst containing a mixture of manganese oxides and platinum on alumina stabilised with 3% lanthanum was prepared and tested in a wood-stove. The beneficial combination of catalytic components and the high thermal conductivity of the substrate were used to speed up the ignition and to minimise the cold-start emissions.

2. Experimental part

2.1. Catalyst preparation

2.1.1. Pre-treatment of the substrate

Metallic monoliths were obtained from Emitec (Germany). The substrates consist of an alloy of iron, chrome and aluminium. To obtain a better adherence of the washcoat onto the substrate, the later was subjected to treatment in our laboratory, the details of which are proprietary information. Alumina, formed by the oxidation of bulk aluminium, migrates to the surface providing a textured whisker structure, as seen in Figs. 1 and 2. The mean size of the whiskers varies between 1 and 2 μm. The alumina whiskers completely cover the metal surface. The advantage associated with the alumina film is its compatibility with alumina-containing washcoat, which substantially eases application and ensures its adhesion to the

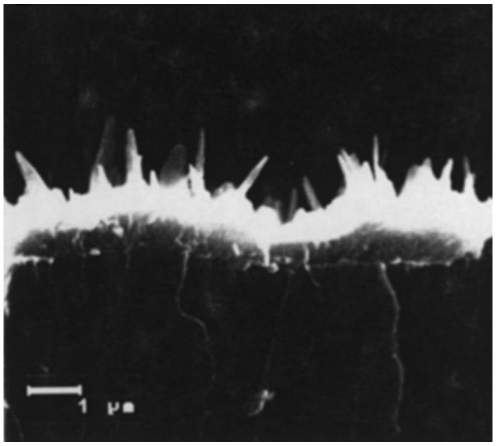

Fig. 1. SEM picture of the whiskers. Sideview.

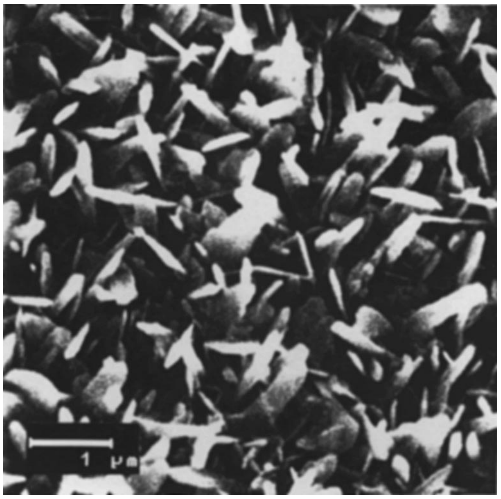

Fig. 2. SEM picture of the whiskers. View from above.

substrate. Also, the alumina layer completely covers the metal surface, thus rendering the alloy highly oxidation-resistant.

2.1.2. Preparation of the washcoat

γ-Alumina (Puralox SBA-170, Condea Chemie, Germany) was used as a support for the preparation of lab-scale catalysts. Condea Chemie supplied alumina doped with 3% lanthanum (Puralox SBA-130/L3) for the manufacturing of the full-scale catalyst. The active components consisted of manganese oxides and platinum. In a slurry containing either γ-alumina alone or γ-alumina stabilised with lanthanum, manganese nitrate, $Mn(NO_3)_2 \cdot 4\ H_2O$ (Merck, Germany, 98.5 %) and urea (Merck, Germany, pro analysi) were added with a molar ratio Mn : urea of 1 : 9 [6]. Platinum nitrate (Chempur, Germany, 54.44%) was also used for the preparation of the mixed MnO_x–Pt catalyst. The slurries were ball-milled overnight in order to bring down the alumina mean particle size and to obtain homogeneous suspensions. Thereafter, the suspensions were stirred for 5 h at 90°C under inert atmosphere. At this temperature, the decomposition of urea causes the precipitation of manganese hydroxide ions which anchor to the alumina surface via reaction with its OH groups [7]. The gels obtained were dried overnight at 200°C. The loadings for manganese were: 5, 6.67, 10 or 20 mol% and for platinum: 0.5 mol% of the washcoat counted as Al_2O_3.

2.1.3. Deposition of the washcoat onto the substrate

The washcoat impregnated with the active phases was mixed with an organic binder. This organic binder was prepared according to the procedure described by Pettersson et al. [8]. The addition of an organic binder reduces stress caused by surface tension during evaporation of the solvent. In order to get suitable slurries for dip coating, the slurries were ball-milled for 24 h. The particle size distribution of the powder in the slurries showed over 90% of the alumina particles to be $<3\ \mu m$, when using a Brookhaven X-ray disc centrifuge (BI-XDC) particle sizer. The metallic monoliths were immersed in the slurries for around 5 min. After withdrawal of the monolithic samples from the slurries, the excess slurries were removed by blowing air through the channels. The number of dips varied from 1 to 4. Between the dips, the catalysts were dried at 200°C for a few hours. Finally, all the samples were calcined at 800°C for 4 h in air. The choice of the calcination temperature is based on the values of the temperatures obtained in a flue duct of a wood-stove. In order to be used for deactivation treatments and characterisation, a part of the impregnated washcoat was treated separately in the same way as the monolithic catalysts.

2.2. Hydrothermal treatment

Deactivation treatments were applied both to the lab-scale monolithic catalysts and to the impregnated washcoat powders. The hydrothermal treatment was performed with an air flow of 1 l/min with ≈10% steam, at 900°C for 270 h.

2.3. Characterisation

The surface area was determined by nitrogen adsorption using a Micromeritics ASAP 2000, after outgassing the samples in a vacuum at 250°C.

The microstructure of monolithic catalysts was investigated by scanning electron microscopy (SEM) using a Zeiss DSM 940 with a resolution of 20–50 Å.

The phase compositions of the samples before and after hydrothermal treatment were investigated by powder X-Ray diffraction using a Siemens Diffraktometer 5000 operating with the following parameters: Cu K_α radiation, 30 mA, 40 kV, Ni filter, 2θ scanning range 20–80°, and scan step size 0.02.

2.4. Activity measurements in laboratory

The activity of the fresh and hydrothermally-treated catalysts for the oxidation of carbon monoxide, methane and naphthalene in a gas mixture (Table 1) was tested. The catalysts tested were based on 400 cpsi metallic monolithic substrate (Section 2.1.1) with a cylindrical shape (diameter: 20 mm, height: 25 mm). Manganese oxides and platinum were the active phases tested alone or mixed, deposited on γ-Al_2O_3 (Section 2.1.2). The reactor used was a

Table 1
Composition of the gas mixture used for the activity measurements

Component	Concentration
Naphthalene	50 ppm
Methane	200 ppm
Carbon monoxide	2550 ppm
Water	12 vol%
Carbon dioxide	12 vol%
Oxygen	10 vol%
Nitrogen	balance

vertical Inconel tube placed in a tubular furnace. During the activity tests, the temperature of the furnace was increased from 100° to 800°C with a heating rate of 3°C/min. The total flow of the gas mixture was 2.5 l/min, corresponding to a space velocity of 19 100 h^{-1}. The contents of methane and naphthalene in the exit gases were determined every 24 s using a gas chromatograph, HP5890 equipped with a flame ionisation detector. Carbon monoxide was analysed by a non-dispersive infrared spectrophotometer (NDIR, Rosemount, BINOS 100). The conversion of carbon monoxide, methane and naphthalene was presented as a function of the temperature of the gas upstream of the catalyst, assumed to be close to the temperature at the catalyst inlet.

2.5. Demonstration of the potential of catalyst pre-heating in a wood fired boiler

To verify the expected advantages of pre-heating a metallic monolith, a full-scale catalyst was integrated in a commercial 30 kW wood-fired boiler (model CTC V30, CTC Parca AB, Sweden). The catalyst prepared was based on an 100 cpsi metallic monolithic substrate of the same kind as described in Section 2.1.1 and it contained a mixture of manganese oxides (10 mol%) and platinum (0.5 mol%) deposited on alumina stabilised with 3% lanthanum (Section 2.1.2). The shape of the catalyst was half a cylinder (diameter: 200 mm) divided into four segments, each with a length of 50.8 mm, separated by ≈10 mm. The aim of the segmentation was to increase the mass transfer within the catalyst section as a result of the mixing of the gases between the segments and the increased turbulence in the channels due to an increased number of inlet sections [9]. This catalyst could be fitted in a section underneath the grate before the convection section in the downdraft boiler where the maximum temperature could be kept around 800°C.

The boiler was equipped with a flue gas fan. The damper was automatically closed when the fuel feeding door was closed, thereby switching directly from over-firing to down-draft. This procedure did not allow any by-pass of the catalyst during the cold-start phase and thus this boiler was especially suitable for a pre-heated catalyst.

The wood used was well-seasoned birch wood with a moisture content of ≈12%, cut into 47 cm long pieces. The boiler is normally lit by 4 kg of finely-chopped wood that is allowed to burn for 15 min, after which a bed of glowing char remains. On top of this, a full batch of wood, 20–25 kg, was added which was then lit by the glowing char. Since this investigation focused on the start-up phase, which extends over a period of 10 min, only the first small batch was used.

An electric hot air heater introduced through the ash pit door pre-heated the catalyst. The heater had to be switched off and the ash pit door closed before the ignition of the fuel, at which point the catalyst started to cool down. Other solutions could of course be chosen if the catalyst was installed in a commercial unit but this study is a first attempt to demonstrate the potential of this method. For experiments with and without preheating, the temperature and the emissions of carbon monoxide and total hydrocarbons (THC) during the first 10 min after ignition of the first small batch of wood were measured. Also, for comparison, experiments without any catalyst in the boiler were included. The temperature of the catalyst was measured in the last catalyst segment or, in the case of experiments without any catalyst, in the position where the last segment would normally be placed. In all experiments in the wood fired boiler the concentration of carbon monoxide and THC was measured in the same position downstream of the catalyst. Carbon monoxide was analysed by a non-dispersive infrared spectrophotometer, (NDIR, Rosemount, NGA 2000), and THC by using a flame ionisation detector (FID, Mess Analystechnik, Thermo-FID). The THC was quantified as methane equivalents. The flue gas flow was ≈100 Nm^3/h, corresponding to a space velocity of 32 000 h^{-1}.

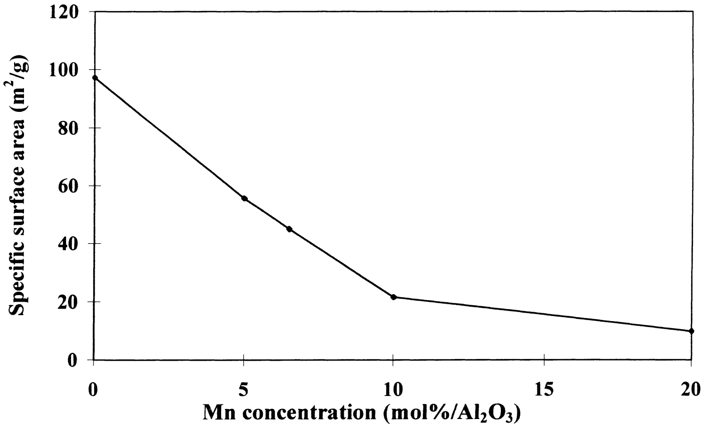

Fig. 3. Specific surface area of MnO_x/γ-Al_2O_3 catalysts with different concentrations of manganese, after hydrothermal treatment at 900°C, for 270 h in presence of 10% steam.

3. Results and discussion

3.1. Characterisation

3.1.1. BET-surface area measurement

The BET surface area of all the fresh catalysts, calcined at 800°C, was around 155 m^2/g. After hydrothermal treatment the surface area decreased for all the samples. This decrease was larger at higher concentrations of manganese in the washcoat, as can be seen in Fig. 3. For a concentration of manganese higher than 10 mol%/Al_2O_3, the further decrease in surface area was small.

3.1.2. Scanning electronic microscope

Prior to the analysis by the SEM, the samples were sputtered with gold and platinum to give a better contrast. SEM pictures revealed that the presence of cracks in the washcoat was already observed after calcination at 800°C for 4 h, this is due to the mismatch in the thermal expansion between the metal foil and the washcoat. Fig. 4 shows a enlargement of a part of the washcoat deposited on the alumina whiskers growing on the metallic surface. The whiskers act as anchors for the washcoat when deposited onto the substrate. Fig. 5 shows the layer of washcoat deposited on the metallic substrate after the hydrothermal treatment. It can be seen that the whiskers become bigger when exposed to higher temperature. The small spots on the picture are agglomerates of sputtered gold and platinum, which had been formed during the hydrothermal treatment.

Fig. 4. SEM picture. Enlargement of a section of layer of washcoat onto the metallic substrate after calcination at 800°C for 4 h.

3.1.3. X-ray diffraction

Mostly γ-alumina and little δ-alumina phases were detected on the sample containing only alumina calcined at 800°C for 4 h. After hydrothermal treatment, the δ-alumina phase has increased and θ-alumina phase has appeared on the sample containing only alumina. XRD analyses carried out on all the fresh samples (calcined at 800°C) containing manganese oxides

Table 2
characteristics of the MnO_x/γ-Al_2O_3 catalysts

Catalyst labels	Washcoat (g)	Number of dips	Mn (mol%/Al_2O_3)	Total Mn (10^{-4} mol)
M1(20)3.4	0.17	1	20	3.4
M2(10)3.4	0.34	2	10	3.4
M3(6.67)3.9	0.59	3	6.67	3.9
M4(5)3.9	0.80	4	5	3.9
M4(6.67)5.3	0.80	4	6.67	5.3
M4(10)9.0	0.85	4	10	9.0
M4(20)16.3	0.83	4	20	16.3

Fig. 5. SEM picture of the layer of washcoat onto the metallic substrate (Fig. 4) after hydrothermal treatment at 900°C for 270 h in steam.

revealed the presence of MnO_2 and Mn_2O_3phases. No α-Al_2O_3 phase was detected on fresh samples containing manganese oxides deposited on Al_2O_3. After thermal treatment at 900°C for 270 h in steam, XRD analyses of the different manganese oxide catalysts with the various amount of manganese (5, 10 and 20 mol%/Al_2O_3) showed the presence of corundum (α-Al_2O_3) whose intensity was stronger for the samples containing an amount of manganese of 10 and 20 mol%/Al_2O_3. On all the hydrothermally-treated samples containing manganese oxides, both Mn_2O_3 (Bixbyite-C) and Mn_3O_4 (Hausmannite) phases were detected. Probably, there are also other manganese oxides phases which cannot be detected due to their low amount or because of their amorphous structure. According to literature, γ-Al_2O_3 phase is converted into the stable α-Al_2O_3 phase between 1000° and 1100°C, this phase has a low surface area [10]. The presence of manganese oxides lowered the temperature of the γ- to α-phase transition by around 200°C, which has also been observed by Tsyrul'nikov et al. [11].

3.2. Activity tests on the manganese oxide catalysts

The influence of (i) the number of the dips for a given total amount of active phases in the catalysts and (ii) the amount of manganese oxides in the catalysts for a given total amount of washcoat were studied through the activity testing of some catalysts. Catalyst samples M1(20)3.4, M2(10)3.4, M3(6.67)3.9 and M4(5)3.9 were prepared with varying numbers of γ-Al_2O_3 washcoat dips and varying concentrations of manganese in the washcoat, but maintaining a similar amount of manganese in the samples (Table 2). The first figure in the denotation of the catalyst stands for the number of dips; the figure in parentheses gives the concentration of manganese oxides in the washcoat (mol%) and the third figure reflects the total amount of manganese in the catalysts (10^{-4} mol). The total amount of manganese in the catalysts M4(5)3.9, M4(6.67)5.3, M4(10)9.0 and M4(20)16.3 was varied, using the same washcoat loading (Table 2). The catalysts were tested before and after the hydrothermal treatment at 900°C for 270 h in steam. The temperatures required for 50% conversion of carbon monoxide, naphthalene and methane for the catalysts before and after hydrothermal treatment are given in Table 3.

Naphthalene is oxidised at lower temperatures than carbon monoxide and methane is oxidised at higher temperatures than naphthalene, for all the MnO_x catalysts.

Table 3
Temperatures for 50% conversion of carbon monoxide, naphthalene and methane for the fresh (F) and hydrothermally treated (HT) $MnO_x/\gamma\text{-}Al_2O_3$ catalysts

Catalyst Labels	T_{50} (°C)								
	CO			$C_{10}H_8$			CH_4		
	F	HT	ΔT^a	F	HT	ΔT^a	F	HT	ΔT^a
M1(20)3.4	420	514	94	365	342	**−23**	720	748	28
M2(10)3.4	472	480	8	375	330	**−45**	702	722	20
M3(6.67)3.9	522	430	**−92**	385	320	**−65**	678	714	36
M4(5)3.9	554	408	**−146**	395	317	**−78**	678	712	34
M4(6.67)5.3	487	456	**−31**	364	317	**−47**	669	682	13
M4(10)9.0	456	331	**−125**	336	272	**−64**	650	676	26
M4(20)16.3	378	344	**−34**	288	313	25	626	716	90

[a] $\Delta T = T_{50}$ (HT) − T_{50} (F).

3.2.1. Effect of the washcoat thickness

3.2.1.1. Fresh catalysts. The activities of the catalysts M1(20)3.4, M2(10)3.4, M3(6.67)3.9 and M4(5)3.9 are compared to see the effect of the number of washcoat dips and the concentration of manganese in it when the total amount of manganese in the four catalysts is approximately the same (Table 3).

The light-off temperature for the oxidation of carbon monoxide increases with increasing number of dips and decreasing concentration of manganese in the catalysts (Table 3). Already at low temperatures, there is some difference between the conversion of carbon monoxide for the various catalysts. The same trend is observed in oxidation of naphthalene, i.e. the oxidation is larger on a lower number of washcoat dips (higher concentration of manganese in the washcoat). However, there is less difference between the light-off temperatures of the catalysts for the oxidation of naphthalene than for carbon monoxide. Indeed, the difference in temperature for 50% conversion between catalyst M1(20)3.4 and catalyst M4(5)3.9 is 30°C for naphthalene while it is 134°C for carbon monoxide.

The oxidation of methane is favoured on catalysts prepared with several washcoat dips (lower concentration of manganese oxides). The activity of the catalysts containing three and four washcoat dips is similar. The oxidation of methane is a slow reaction, therefore the dispersion of the active phases becomes a more important factor for the reaction.

3.2.1.2. Hydrothermally-treated catalysts. The activity of the catalysts for the oxidation of carbon monoxide is inverted after hydrothermal treatment. Whereas catalyst M1(20)3.4 has the best activity among the fresh catalysts M1(20)3.4, M2(10)3.4, M3(6.67)3.9 and M4(5)3.9 catalysts, it has the lowest activity after treatment. For the oxidation of carbon monoxide catalyst M1(20)3.4 shows a considerable decrease in activity, catalyst M2(10)3.4 shows almost no change and catalysts M3(6.67)3.9 and M4(5)3.9 show significant enhancement after hydrothermal treatment, as seen in Table 3. Indeed, the light-off temperature is decreased by around 150°C for catalyst M4(5)3.9.

Just as for carbon monoxide, the order of activity for the oxidation of naphthalene of the treated catalysts is inverted compared to one of the fresh catalysts. After hydrothermal treatment, the activity is enhanced for all the catalysts, especially with an increasing number of dips of washcoat.

After hydrothermal treatment, the light-off temperature of all the catalysts for the oxidation of methane is increased by around 20–35°C.

The results from the activity of the hydrothermally-treated catalysts for the oxidation of all the combustibles show the highest activity for M4(5)3.9, followed by M3(6.67)3.9, M2(10)3.4 and M1(20)3.4. One major reason for this observation is the difference in surface area, which is lower for the washcoats with higher manganese contents, since the sintering of the washcoat is increased with an increased manganese concentration, as noted in Section 3.1.1. The high sintering of the M1(20)3.4 and M2(10)3.4 catalysts also leads to greater encapsulation of a part of the manganese oxides than it does for the M3(6.67)3.9 and M4(5)3.9 catalysts. The enhancement of the activity of MnO_x catalysts after hydrothermal treatment at 900°C, as observed for the oxidation of carbon monoxide and naphthalene in most of the cases, has been discussed by several authors [5,11,12]. Tsyrul'nikov et al. [11] observed an increase in catalytic activity of manganese oxides catalysts deposited on γ- and α-Al_2O_3 for the oxidation of butane, benzene, and particularly, carbon monoxide. They attributed the increase of activity to the formation of $Mn_3O_{4.2}$ which has a defective structure that is close to the structure of Mn_3O_4 spinel. Probably, naphthalene oxidation is more affected than that of carbon monoxide by the presence of the new active phase since the enhancement effect is already seen for catalyst M1(20)3.4 which suffered from the largest loss of surface area. The beneficial effect of the presence of the new phase and the decrease in surface area affect the oxidation in opposite directions. Depending on the extent of the loss of surface area, the effect of the new phase is more or less visible, which could lead to either a positive or negative effect or no effect at all.

Compared to the other treated catalysts and the fresh M1(20)3.4, M2(10)3.4, M3(6.67)3.9 and M4(5)3.9 catalysts, the hydrothermally-treated M4(5)3.9 catalyst is more active for the oxidation of carbon monoxide and naphthalene. A catalyst with a low concentration of manganese oxides seems to be a good choice for this application. However, it could be of interest to study how much the amount of manganese can be increased without risk of washcoat sintering.

3.2.2. *Effect of the amount of manganese oxides*

3.2.2.1. Fresh catalysts. Catalysts M4(5)3.9, M4(6.67)5.3, M4(10)9.0, and M4(20)16.3 are compared to see the effect of the amount of manganese on the activity of carbon monoxide, naphthalene and methane oxidation. All catalyst samples contain approximately the same amount of washcoat (4 dips, 0.8 g).

The increasing amount and concentration of manganese oxides appears to improve the oxidation of carbon monoxide to a larger extent than it does the oxidation of naphthalene and methane, shown in Table 3. Indeed, the difference between the light-off temperature of catalyst M4(5)3.9 and catalyst M4(20)16.3 is around 175°C for carbon monoxide whereas it is 100°C for naphthalene and 50°C for methane. As expected, the catalyst with the highest amount of manganese in the washcoat, M4(20)16.3, gives the highest activity for the oxidation of the three components.

3.2.2.2. Hydrothermally-treated catalysts. After hydrothermal treatment, the oxidation of carbon monoxide is improved for the M4(5)3.9, M4(6.67)5.3, M4(10)9.0 and M4(20)16.3 catalysts. The strongest enhancement is observed for the M4(5)3.9 catalyst. However, M4(10)9.0 catalyst has the best activity amongst the treated catalysts for the oxidation of carbon monoxide.

The enhancement of the activity for oxidation of naphthalene after hydrothermal treatment was observed for the three catalysts, M4(5)3.9, M4(6.67)5.3 and M4(10)9.0, with the strongest decrease in light-off temperature for the M4(5)3.9 catalyst, as was also the case for carbon monoxide. Amongst the catalysts, M4(10)9.0 catalyst shows the largest activity.

Some deactivation was observed for the oxidation of methane for all the catalysts. The M4(10)9.0 catalyst has the best activity amongst the hydrothermally-treated catalysts, M4(5)3.9, M4(6.67)5.3, M4(10)9.0 and M4(20)16.3, for the oxidation of methane.

The M4(10)9.0 catalyst with a concentration of manganese oxides of 10 mol%/Al_2O_3 (with a total amount of manganese of 9.0×10^{-4} mol) seems to be the optimum between a high activity due to the presence of the new manganese oxide phase and stability due to its relatively high surface area after thermal treatment.

3.3. *Activity tests on the platinum and mixed manganese oxide–platinum catalysts*

Following the tests described in Section 3.3, 10 mol% manganese was used to prepare a catalyst

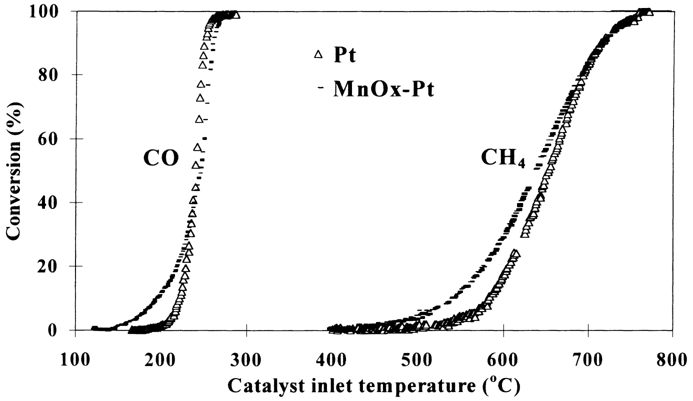

Fig. 6. Conversion of carbon monoxide and methane for the Pt (0.5 mol%/γ-Al_2O_3) and mixed MnO_x–Pt (10–0.5 mol%/γ-Al_2O_3) catalysts.

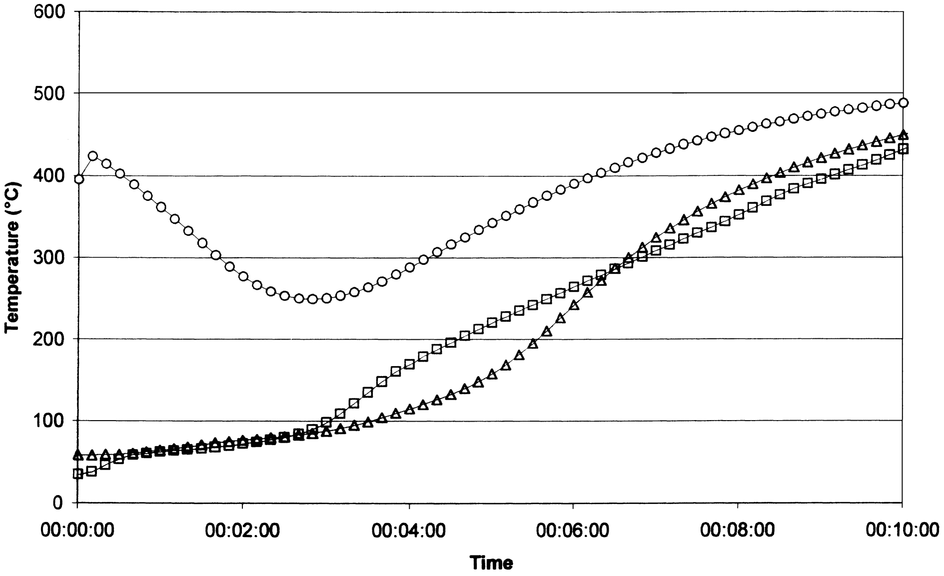

Fig. 7. Temperature measured in the last catalyst segment. With pre-heating (○), without pre-heating (△) of the MnO_x–Pt (10–0.5 mol%/La–Al_2O_3) catalyst and without catalyst (☐).

containing a mixture of manganese oxides and platinum (0.5 mol%). A platinum catalyst was also chosen for comparison. The catalysts were studied for the oxidation of carbon monoxide, naphthalene and methane. The results of the activity tests are shown in Fig. 6.

At 50% conversion, both the platinum and the mixed catalysts showed similar activity for the oxidation of carbon monoxide and naphthalene, while the mixed catalyst had somewhat higher activity for methane. Also, at low conversions, the mixed catalyst showed larger conversion than the platinum catalyst for the oxidation of all the combustibles, as was the case for carbon monoxide and methane, as shown in Fig. 6.

3.4. Full-scale tests

The full-scale tests were performed according to the description in Section 2.5. Fig. 7 shows the

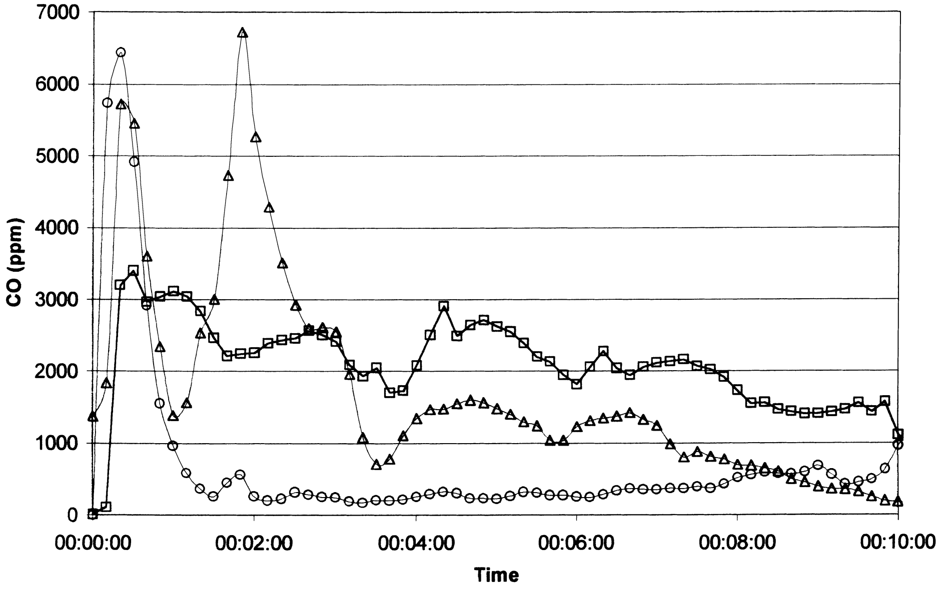

Fig. 8. Carbon monoxide concentration measured downstream of the MnO_x–Pt (10–0.5 mol%/La–Al_2O_3) catalyst. With pre-heating (○), without pre-heating (△) and without catalyst (□).

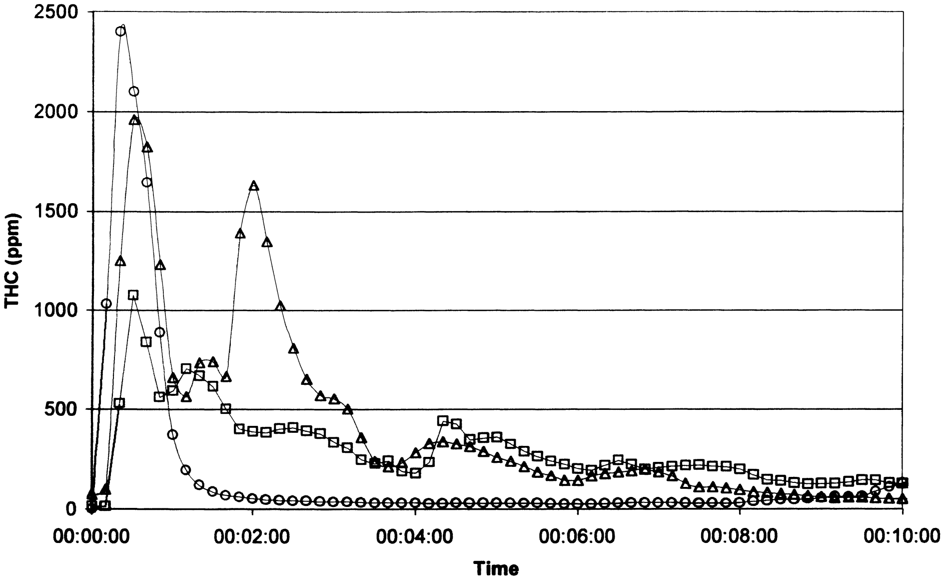

Fig. 9. Total hydrocarbon (THC) concentration measured downstream of the MnO_x–Pt (10–0.5 mol%/La–Al_2O_3) catalyst. With pre-heating (○), without pre-heating (△) and without catalyst (□).

temperature profile during the first 10 min of tests performed with and without pre-heating of the catalyst, as well as one experiment without any catalyst. Since the pre-heating of the catalyst is interrupted just before the fuel is ignited, the temperature of the pre-heated catalyst decreases during the first 3 min. After this period, the hot flue gases increase the temperature of the pre-heated catalyst and after 8–10 min

Table 4
Average carbon monoxide and total hydrocarbon concentrations during the start-up phase for the three different conditions studied

	No catalyst	MnO_x–Pt (10–0.5 mol%/La–Al_2O_3) catalyst	
		Without pre-heating	With pre-heating
CO-concentration (ppm)	2010	1980	690
THC-concentration (ppm)	350	330	180

no significant difference in temperature between the different experiments remains. For this type of catalyst, the ignition temperature of carbon monoxide in the laboratory tests was around 240°C (Fig. 6) and since the minimum measured temperature of the catalyst is 250°C a good effect on the conversion of carbon monoxide over the pre-heated catalysts could be expected. All the THC, except methane, are also expected to be oxidised in the same range of temperature. This is also shown in Figs. 8 and 9 where the carbon monoxide and THC concentrations, respectively, for the same three experiments as shown in Fig. 7, are measured downstream of the catalyst. Combustion of batches of wood logs in small-scale boilers and stoves is known to be very unstable and dependent, for example, on how the logs are arranged and the homogeneity of the fuel. Due to this, the experiments will never be totally reproducible which, especially in combination with the transient conditions during start-up, complicates the evaluation of the experimental results. It is however clear that the pre-heated catalyst results in lower emissions during the period from 1 up to 8 or 9 min, the latter part of the period being the time when the effect of pre-heating can no longer be seen on the temperature measurements. When the ignition temperature of the catalyst is reached, the carbon monoxide emissions from the experiments without any pre-heating are lower than the emissions when operating without any catalyst, which could be expected. In Table 4, the concentrations of carbon monoxide and THC are shown for the three types of experiments performed. Each value is the average of the concentrations measured every 10 s during the first 10 min, based on at least two different experiments. The reduction of carbon monoxide during these 10 min with the pre-heated catalyst compared with the boiler operating without any catalyst is 67%. Further conversion could be expected if the space–velocity is lowered or the pre-heating temperature of the catalyst is further increased. Another advantage with pre-heating the catalyst is that the deactivation may be reduced, especially for a boiler designed without any possibility to by-pass the catalyst during start-up, since the condensation of tars on the cold catalyst surface contributes significantly to the deactivation.

4. Conclusions

The emissions during the start-up phase can be reduced by using a catalyst which has a low ignition temperature, combined with pre-heating of the catalyst during the start-up phase.

On the fresh catalysts containing the same total amount of manganese, a high concentration of manganese oxides in the washcoat favoured the oxidation of carbon monoxide and naphthalene, whereas a lower concentration of manganese oxides in the washcoat gave higher activity for the oxidation of methane. Increasing the amount of manganese oxides in the catalysts with the same amount of washcoat resulted in an increase in activity for the oxidation of carbon monoxide, naphthalene and methane.

After hydrothermal treatment at 900°C for 270 h in steam, most of the manganese oxide catalysts were activated for the oxidation of carbon monoxide and naphthalene and slightly deactivated for the oxidation of methane. The addition of manganese in the washcoat, however, increases the sintering of the washcoat due to an increased formation of α-alumina phase. The catalyst with a concentration of manganese oxides of 10 mol%/Al_2O_3 and four washcoat dips was the most resistant towards hydrothermal treatment.

The platinum (0.5 mol%) and the mixed (10–0.5 mol%) catalysts showed similar activity for the oxidation of carbon monoxide and naphthalene, while the mixed catalyst was more active for the oxidation of methane.

The experiments in the boiler using the full-scale catalyst have shown that pre-heating of the catalyst significantly reduces the emissions of carbon monoxide and unburned hydrocarbons during the start-up phase. During the first 10 min of the burning cycle a 67% reduction of carbon monoxide as well as a significant reduction of THC were achieved with the pre-heated catalyst compared with no catalyst.

Acknowledgements

The financial support for this work, given by the European Commission, the FAIR-programme, CT95-0682 and the Swedish National Board for Industrial and Technical Development (NUTEK) are gratefully acknowledged. Thanks are given to Inga Groth for help with the SEM, to Lars Pettersson for help with the preparation of the organic binder, to Massoud Pirjamali for the GC maintenance at the Division of Chemical Technology, the Royal Institute of Technology (KTH) and to Emitec for supplying the metallic monoliths. Thanks are also given to Christina Hörnell (KTH) and Michael Morris (TPS) for help with the English.

References

[1] J. Carnö, M. Berg, S. Järås, E. Björnbom, Kemisk Tidskrift 8 (1995) 56 (in Swedish).

[2] M. Berg, N. Berge, Proceedings of the 2nd Olle Lindstöm symposium on renewable energy, bioenergy, submitted for publication.

[3] J.T. Kummer, Prog. Energy Combust. Sci. 6 (1979) 177.

[4] M.V. Twigg, D.E. Webster, Metal and coated-metal catalysts, in: A. Cybulski, J.A. Moulijn (Eds.), Structured Catalysts and Reactors, New York, 1998.

[5] M. Ferrandon, J. Carnö, S. Järås, E. Björnbom, Part I and Part II., Appl. Catal. A 180(1/2) (1999) 153.

[6] M.F.M. Zwinkels, O. Haussner, P.G. Menon, S.G. Järås, Catalysis Today, in press.

[7] X. Xiaoding, H. Vonk, A. Cybulski, J.A. Moulijn, in: G. Poncelet, P. Grange, P.A. Jacobs, B. Delmon (Eds.), Preparation of Catalysts VI, Elsevier, Amsterdam, 1995, p. 1069.

[8] L.J. Pettersson, M.F.M. Zwinkels, Method for coating of metallic surfaces with oxidic layers, in preparation.

[9] M. Berg, N. Berge, Abatement of emissions from small-scale combustion of biofuels, Final report of FAIR-project No 95-0682, 1998.

[10] D.J. Young, P. Udaja, D.L. Trimm, in: B. Delmon, G.F. Froment (Eds.), Catalyst Deactivation, Elsevier, Amsterdam, 1980, p. 331.

[11] P.G. Tsyrul'nikov, V.S. Sal'nikov, V.A. Drozdov, S.A. Stuken, A.V. Bubnov, E.I. Grigorov, A.V. Kalinkin, V.I. Zaikovskii, Kinetika i Kataliz 32(2) (1991) 439–446 (in Russian).

[12] P.G. Tsyrul'nikov, O.N. Kovalenko, L.L. Gogin, T.G. Starostina, A.S. Noskov, A.V. Kalinkin, G.N. Krukova, S.V. Tsybulya, E.N. Kudrya, A.V. Bubnov, Appl. Catal. A 167 (1998) 31–37.