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Ageing of palladium, platinum and manganese-based combustion catalysts for biogas applications

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Abstract

During recent years, catalytic combustion of low heating value gases has received increased attention. The purpose of the present work was to study the effect of ageing for 30 days at 1000°C in air saturated with 12% steam on Pd- and Pt-impregnated as well as Mn-substituted lanthanum hexaaluminate materials. Both hexaaluminate powders and 400 cpsi cordierite monoliths, washcoated with hexaaluminate powder, were aged. Powders were characterised by BET and XRD, whereas the catalytic activity of the washcoated monoliths was evaluated in a bench-scale rig for conversion of synthetic gasified biomass. The surface areas decreased significantly during the first day of ageing, whereas further ageing had only a minor influence. The pure lanthanum–alumina sample was a mixture of the hexaaluminate $LaAl_{11}O_{18}$ phase and the less preferable perovskite $LaAlO_3$ phase, which increased after ageing. The Mn-substituted lanthanum–alumina mainly showed pure hexaaluminate phase both before and after ageing. The catalytic activity tests showed that Pd-impregnated lanthanum hexaaluminate was the most active catalyst for combustion of carbon monoxide and hydrogen, retaining low light-off temperatures also after 30 days of ageing. However, the ignition temperature for 50% conversion (T_{50}) of methane was approximately 300°C higher than for the fresh sample. Pt-impregnated samples were less active than the Pd ones. The Pt-loading decreased after ageing, whereas the Pd-loading remained fairly constant. However, the amount of Pd oxide decreased after ageing. Further, the Mn-substituted samples were less active than the precious metal ones. Here, the activity for the combustion of carbon monoxide was substantially affected by ageing. The formation of nitrogen oxides from ammonia was lower over the aged samples than over fresh ones; the Mn-substituted sample aged 30 days showed the lowest yield, only 30% of ammonia was converted to nitrogen oxides. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Catalytic combustion; Gasified biomass; Ageing; Hexaaluminate; Palladium; Platinum; Manganese

1. Introduction

Today, catalytic combustion is an ultra-low emission technology for gas turbines, verified by several pilot-scale tests [1,2]. Development and commercialisation are directed towards the use of natural gas. However, the use of catalytic combustion for non-fossil fuels, such as gasified biomass, can also be advantageous with respect to stable combustion of the low-heating value (LHV) fuel and potential low emissions of fuel-NO_x [3]. Further, this fuel is rich in hydrogen and carbon monoxide. Therefore, it can be catalytically ignited at substantially lower temperatures than methane fuels. Nevertheless, it is of principal interest to have a high selectivity of the catalysts to molecular nitrogen (N_2) formation since the biogas

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contains high levels of ammonia. However, both with gasified biomass and natural gas, catalytic combustion is limited by the fact that the catalytic materials must withstand very high temperatures, e.g. 900–1000°C for hybrid applications, during prolonged operation [4].

At the required operating temperature most catalysts undergo deactivation [5]. Poisoning [6] as well as sintering, encapsulation and evaporation of the active sites and washcoat can severely reduce the activity of the catalysts. The thermal stability of the catalysts is strongly dependent on the support. Phase transformation, due to the high temperature, significantly reduces the surface area of the most common supports, resulting in pore closure and encapsulation of the active catalytic sites. The gas atmosphere, especially with steam present, can affect sintering too [7]. One promising sintering-resistant support is modified alumina, especially the thermally stable hexaaluminate composition [8]. Further, evaporation of the active phase also has to be considered as an important factor. Most of the active components have significant vapour pressure at a temperature of 1000°C and above. Recent work indicates that the loss of noble metal could be so rapid that 70% of the metal would be lost after 15 h of operation [9].

The objective of the present work is to study the effect of ageing on catalytic combustion of gasified biomass. A selection of promising catalyst compositions, such as lanthanum hexaaluminate-supported palladium and platinum, and manganese-substituted lanthanum hexaaluminate, has been studied before and after ageing in humid air at 1000°C for 30 days. Powder materials have been characterised by AAS, BET, XRD and SEM and the activity of catalytic combustion of a synthetic fuel resembling gasified biomass has been studied over washcoated cordierite monoliths.

2. Experimental

2.1. Preparation of the catalysts

To begin with, two hexaaluminate materials were prepared namely lanthanum hexaaluminate, $LaA1_{11}O_{18}$ (LHA), and lanthanum–manganese hexaaluminate, $LaMnAl_{11}O_{19}$ (LMHA). Palladium and platinum samples were prepared by impregnation of LHA, with an approximate loading of 0.8 (PdLHA) and 1.5 wt.% (PtLHA), respectively. Furthermore, two other compositions of LHA were synthesised, in which the ratio between La and Al was varied. The amount of aluminium was increased by 15 (15LHA) and 30 mol% (30LHA) compared to the stoichiometric amount.

The catalysts were prepared by carbonate precipitation [10,11]. Nitrates of lanthanum, aluminium and manganese, dissolved in excess of water, were added dropwise (100 ml/min) to a stirred water solution of ammonium carbonate, the pH of which was adjusted by adding dropwise an aqueous solution of 9 vol.% ammonia. The system was stirred vigorously, the pH was kept around 9 and the temperature slightly above room temperature (25°C). The precipitate was then allowed to settle for 1 h. The precipitate was centrifuged, washed with isopropanol and centrifuged again. The powder was dried at 200°C for 24 h and calcined step-wise to 1000 and 1200°C. Samples were collected after each step for further characterisation. The powders calcined at 1200°C were mixed with water to obtain a slurry with a dry content of 20 wt.% and then ball-milled for 24 h. Palladium and platinum nitrate solutions were added to two samples of the LHA slurry in an amount to give the right weight percentage of the element in the slurry, 0.8 wt.% Pd and 1.47 wt.% Pt, respectively. Cordierite monoliths (400 cpsi cylinder 16 mm diameter, 14 mm length) were dipped into the washcoat slurry and held there for about 30 s. The excess slurry was carefully blown off with pressurised air. The monoliths were dried in a microwave oven for 15 min at 500 W. This procedure was repeated until a layer of about 16–20 wt.% had been applied onto the monoliths. Finally, the monoliths were calcined at 1000°C for 4 h and the remaining slurries were first dried at 200°C for 24 h and then calcined at 1000°C for 4 h.

2.2. Ageing

Both hexaaluminate powder samples and monoliths were aged in a tubular furnace at 1000°C with a flow of air saturated with 12% steam. Powder samples were collected after 1, 5 and 15 days, whereas monoliths were taken out after 15 days. Moreover, the monoliths and the powder of LHA and LMHA were aged up to 30 days with the same procedure.

2.3. Characterisation of the catalysts

The X-ray diffraction patterns (XRD) were recorded with a Siemens Diffractometer 5000 scanning 2θ from 10° to 80° using monochromatic Cu Kα radiation. Specific surface area was measured according to the Brunauer–Emmet–Teller (BET) method with nitrogen adsorption at liquid nitrogen temperature on a Micrometrics ASAP 2000/2010. Bulk analysis for the detection of the amount of metal (La, Al, and Mn) was performed by plasma-emission spectrometry, ICP-AES, on the samples, melted with $LiBO_2$ and dissolved in HNO_3. For the analysis of Pt and Pd the samples were dissolved in aqua regia and then analysed by plasma-mass spectrometer, ICP-QMS. Pd samples were also analysed by SEM-Edax, electron microscopy with energy dispersive X-ray spectrometry.

2.4. Activity tests

The catalytic activity of the washcoated monoliths was evaluated for conversion of LHV fuel. The gases simulated the composition of a fuel from gasification of biomass, i.e., the main components were carbon monoxide, hydrogen, methane, nitrogen, carbon dioxide, water and ammonia. The fuel mixture was combusted catalytically over the monolith in excess of air (300%), at atmospheric pressure in a tubular quartz reactor [3] and an hourly gas space velocity of 50 000 h^{-1}. All the catalysts were tested after they had undergone a temperature ramp in a stream of air. The composition of the inlet gas is shown in Table 1. The temperature ramps were different depending on the catalyst, e.g. from 140 to 800°C for both PdLHA and PtLHA and from 200 to 850°C for LMHA.

Table 1
Composition of the inlet gas for the activity tests (space velocity=50 000 h^{-1} and λ=4.0)

Gas	N_2	O_2	H_2	CO	CO_2	CH_4	NH_3	H_2O
Volume concentration (%)	84.0	9.6	1.2	1.6	1.4	0.5	0.02	1.6

3. Results and discussion

3.1. Visual analysis

A change in colour was observed between fresh samples and aged samples of PtLHA and PdLHA. The Pt sample changed from a dark grey to a light grey. The lighter colour of the aged sample is in line with the bulk analysis, which showed a loss of platinum. This is in line with evaporation of the active phase in noble metal impregnated catalysts at high temperature shown by Dalla Betta [9]. The fresh powder of PdLHA had salmon colour while the 15th day sample showed a grey colour. The same tendency was observed for the monolith washcoated with palladium: while the fresh monolith appeared salmon, both the 15 and the 30 days sample were grey. The salmon colour of the fresh PdLHA sample indicates the Pd–La oxide structure, whose colour is between brown and orange. The grey colour of the 15th day sample indicates the presence of PdO_x or Pd metal, which appears black. The LHA and LMHA powders did not undergo any change in colour, maintaining white and grey colour, respectively.

3.2. BET analysis

A sharp and approximately exponential decrease in the surface area during the first day of ageing was observed for all the samples, cf. Table 2. The percentage of lost surface area after 1 day was about 25–46%. The areas of LHA and LMHA increased after the ball-milling procedure (30 m^2/g after calcination at 1200°C in dry air and 41 m^2/g after the ball-milling of the powders calcined at 1200°C). The increases in surface area due to the ball-milling were completely lost after the first day of ageing. The effects of the ageing in humid air at 1000°C became smoother as the time increased. After 15 days of ageing, only 7% of the surface area that the LHA sample had at the end of the first day was lost. Ageing for 30 days of LHA resulted in a decrease of surface area, i.e., 29 to 27 to 25 m^2/g after 1, 15 and 30 days, respectively. The surface area of LMHA was more strongly influenced by the first day ageing, showing a decrease of about 46% compared to the fresh one. Nevertheless, LMHA retained a surface area of 19 m^2/g after 15 days of ageing. The catalysts prepared with excess of aluminium, i.e., 15LHA and 30LHA, were more stable.

Table 2
BET analysis results[a]

Samples	Surface area				Surface area decrease (%)		
	Fresh	1 day	15 days	30 days	0–1 day	1–15 days	15–30 days
LMHA	41	22	19		46.3	13.6	
LHA	41	29	27	25	29.3	6.9	7.4
PdLHA	41	31	27		24.4	12.9	
PtLHA	41	31	27		24.4	12.9	
15LHA	{22}	22	21		0	4.5	
30LHA	{26}	26	25		0	3.8	

[a] Surface areas are expressed in m^2/g. The number between parentheses indicates the surface areas of non ball-milled samples. % (0–1) indicates the lost surface area from 0 to 1 day of ageing.

After 15 days of ageing they showed a decrease of only 4% compared to the initial surface areas. On the other hand their surface areas were lower compared to the stoichiometrically prepared sample, LHA.

3.3. XRD analysis

The LHA sample was a mixture of the hexaaluminate, $LaAl_{11}O_{19}$, and the less preferable perovskite, $LaAlO_3$, phases. On ageing of LHA as well as of PdLHA and PtLHA, perovskite peak heights increased and hexaaluminate peak heights decreased. The 30 day samples showed only minor differences compared to the 15 day samples. The loadings of the noble metals on the samples were too low to allow XRD analysis of the species Pt and Pd metal as well as Pd oxide and Pd–La oxide.

The LMHA sample was mainly composed of pure hexaaluminate phase. The hexaaluminate peak heights increased during the ageing. The perovskite phase peak heights decreased on ageing for the LMHA sample as well as for 15LHA and 30LHA. A comparison of the different structures of the LHA and LMHA samples is reported in Fig. 1. For LHA and LMHA sharper peaks were observed after ageing. This suggests the formation of larger crystallites, a decrease of the amorphous character or even a combination of both.

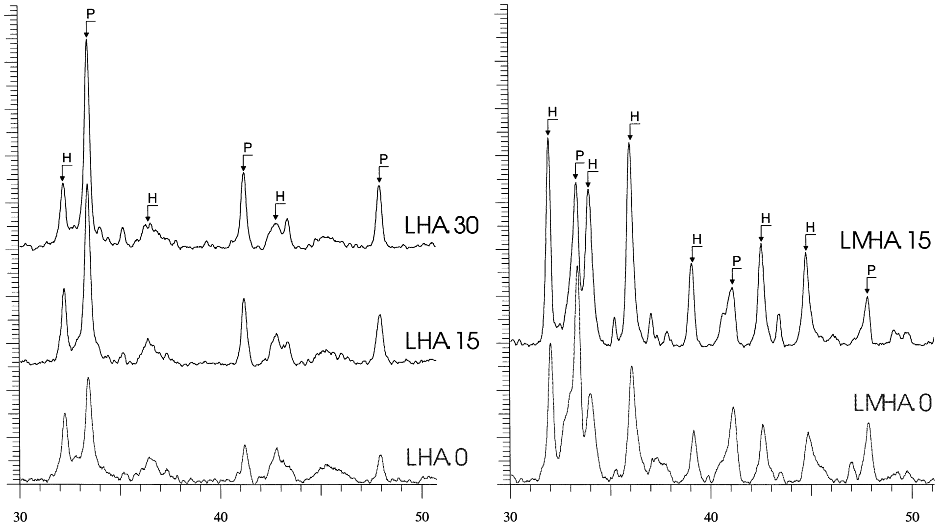

Fig. 1. XRD plots for LHA and LMHA, respectively.

Table 3
Results of the bulk analysis, ICP-QMS and SEM-Edax, on PdLHA and PtLHA both before and after ageing

Samples	Metal (wt.%) [ICP-QMS]	Total (wt.%) [SEM-Edax]	Theoretical (wt.%) [SEM-Edax]
PtLHA.0	1.32		1.47
PtLHA.15	1.28		
PdLHA.0	0.12	0.5 (±0.1)	0.80
PdLHA.15	0.23	0.5 (±0.1)	

3.4. Bulk analysis

The chemical analysis of the bulk of the catalysts showed that the preparation method gave rise to a higher ratio between Al and La than the calculated one (Al/La=14 instead of 11 for LHA). The composition with respect to the main elements Al, La and Mn did not change after ageing of LHA. After ageing a decrease in the noble metal content was observed for the samples impregnated with platinum (13 200 ppm fresh compared to 12 800 ppm after 15 days of ageing). This confirms the hypothesis of evaporation of the active phase due to the high temperature in presence of steam [9]. Unfortunately, the same analysis cannot be used for the palladium samples, since palladium metal and palladium–lanthanum oxide are soluble whereas palladium oxide is insoluble in aqua regia. Surprisingly, by analysis after dissolution in aqua regia, a higher palladium loading was detected in the aged sample compared to the fresh one, cf. Table 3. The higher palladium loading could be explained by the fact that the fresh sample contained more PdO than the aged sample. The larger amount of Pd in the aged sample indicates a higher loading of Pd in the form of Pd metal. Further semi-quantitative analysis by SEM-Edax indicated that the global loading of palladium did not change during the ageing, i.e., about 0.5 wt.% compared to the theoretically loading of 0.8 wt.%.

Based on the results from bulk and visual analysis, the following points were concluded:

1. Palladium–lanthanum oxide is present in the fresh sample.
2. The amount of PdO in the fresh sample is higher than in the aged ones.
3. The amount of palladium metal is higher in the aged samples than in the fresh one.

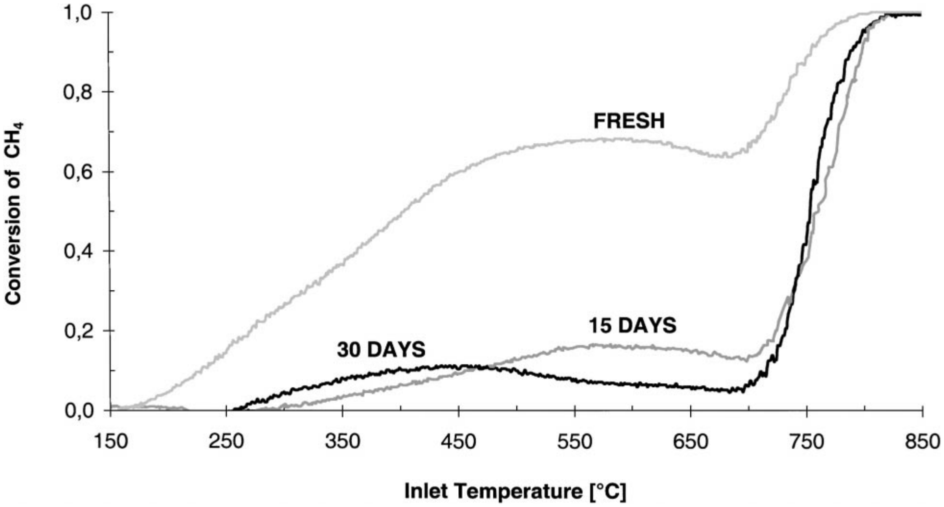

Fig. 2. Conversion of methane for Pd catalysts, fresh and aged 15 and 30 days, respectively.

Table 4
Increased T_{50} for aged samples[a]

Samples	$T_{50}^{(CO)}$	$T_{50}^{(CH_4)}$	$T_{50}^{(H_2)}$	$\tau_{50}^{(CO)}$	$\tau_{50}^{(CH_4)}$	$\tau_{50}^{(H_2)}$
15 days ageing						
PdLHA	219	747	219	4.5	39.2	6.5
PtLHA	316	704	316	14.8	11.9	14.8
LMHA	741	693	651	40.6	3.8	28.2
30 days ageing						
PdLHA	212	753	208	3.0	40	4.1
LMHA	761	705	679	43.4	5.0	32

[a] Temperatures are expressed in °C. τ_{50} (%)=$100[(T_{50}^{\text{aged}}-T_{50}^{\text{fresh}})/T_{50}^{\text{fresh}}]$, calculated by using the absolute scale, K, is a measure of the decrease in activity of the catalysts.

4. The total amount of palladium is approximately constant during the ageing.

3.5. Activity tests

3.5.1. Conversion of CO, H_2 and CH_4

The fresh samples of all the catalysts were tested and compared with the samples aged 15 days and, for PdLHA and LMHA, 30 days as described above. As expected, the precious metal-impregnated catalysts, PdLHA and PtLHA, showed higher activity compared to the Mn-substituted catalysts. On the other hand, manganese samples showed the lowest yield of nitrogen oxides.

The well-known but not fully understood behaviour of methane conversion over the palladium catalyst (PdLHA) that results in a plateau in conversion when palladium oxide is transformed to palladium metal, was observed [12]. This peculiar shape became smoother with ageing, as the conversion of methane decreased, see Fig. 2. The effects of long-time ageing on PdLHA catalysts resulted in a sharply decreased activity for the conversion of methane, whereas the performance for the conversion of both carbon monoxide and hydrogen was maintained. The temperature corresponding to 50% conversion (T_{50}) of carbon monoxide in the sample aged 15 days increased only by 4.5% compared to the fresh sample, which gave $T_{50}^{(CO)}=198$°C, cf. Table 4 concerning the T_{50} val-

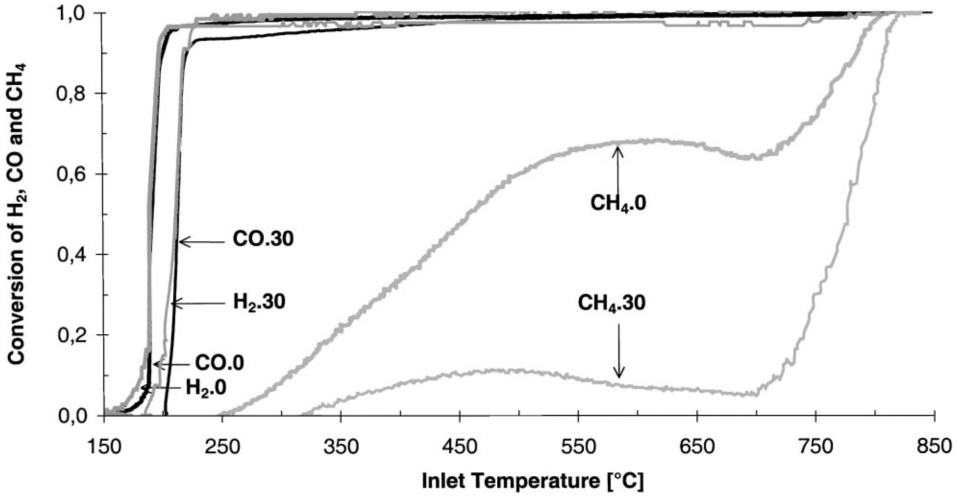

Fig. 3. Conversion plots for PdLHA. Comparison between fresh sample (fuel.0) and aged for 30 days (fuel.30).

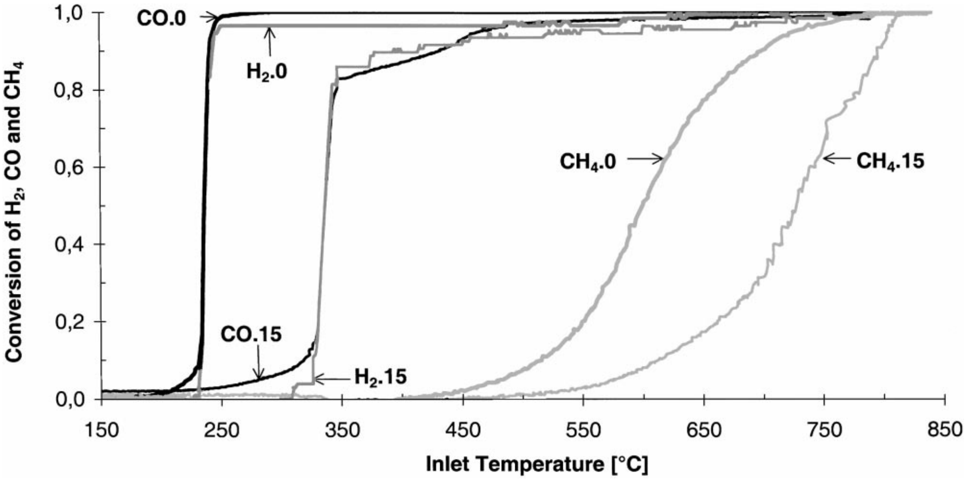

Fig. 4. Conversion plots for PtLHA. Comparison between fresh sample (fuel.0) and aged for 15 days (fuel.15).

ues. The conversion of methane was instead strongly affected by the ageing. The T_{50} for methane increased from 460°C for the fresh sample to 747°C for the sample aged for 15 days, i.e., an increment of about 40%. Further ageing up to 30 days under the same conditions did not affect the conversion of carbon monoxide and hydrogen; the light-off temperatures (T_{10}) for the conversion of carbon monoxide and hydrogen only rose 3% for carbon monoxide and 8% for hydrogen compared to the fresh sample, see Fig. 3. The conversion of methane only changed slightly, i.e., T_{50} increased only 6°C compared to the 15 days sample.

The fresh platinum sample (PtLHA) was less active than the palladium one (PdLHA.0). Ageing up to 15 days influenced the activity of the catalyst with respect to the conversion of all the components of the fuel. The behaviour of the aged sample shifted to about 100°C higher temperatures compared to the fresh one. The decrease in activity was almost the same for the three components, i.e., T_{50} increased by 12–15% for

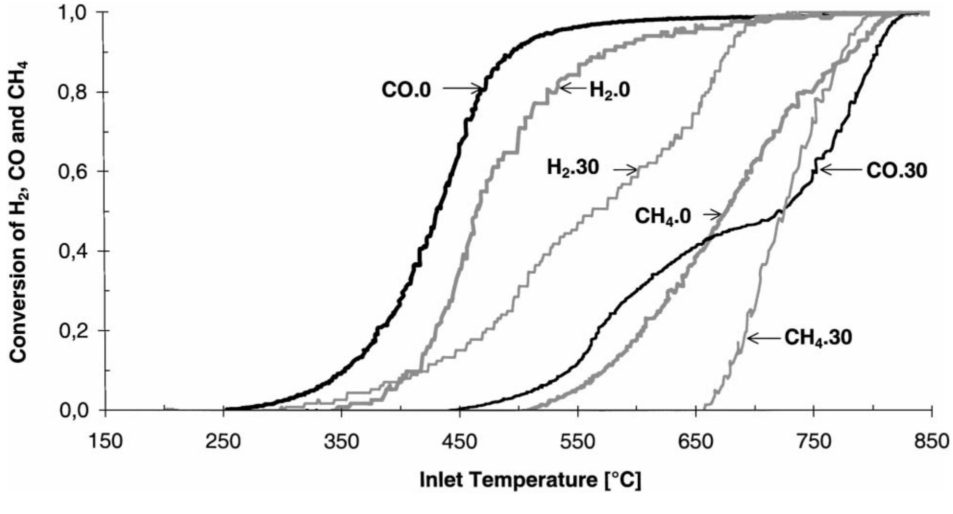

Fig. 5. Conversion plots for LMHA. Comparison between fresh sample (fuel.0) and aged for 30 days (fuel.30).

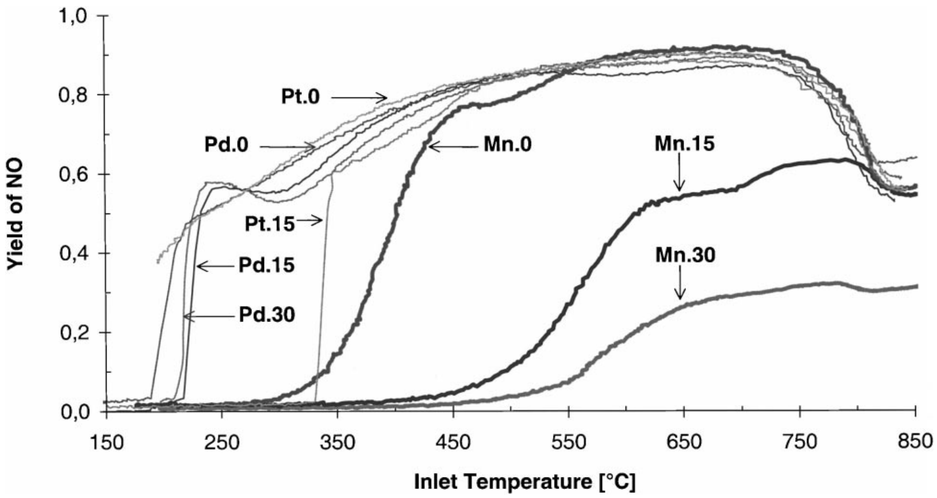

Fig. 6. Production of NO on combustion. Comparison between aged and fresh samples of PdLHA catalysts (Pd, day of ageing), PtLHA catalysts (Pt, day of ageing) and LMHA catalysts (Mn, day of ageing). The other N-compounds formed from NH_3 are not shown here (NO_2+N_2).

carbon monoxide, methane and hydrogen, see Table 4 concerning the T_{50} values and Fig. 4. Still, aged Pt catalyst showed higher activity for methane combustion than aged Pd.

The manganese-substituted sample (LMHA) was less active than the precious metal samples. Over precious metal samples the light-off temperature for carbon monoxide and hydrogen increased only a few degrees on ageing for 15 and 30 days, although the light-off temperature for methane became significantly higher. The behaviour of LMHA after the ageing was different from that of the Pd- and Pt-impregnated samples. The manganese-substituted catalyst activity was strongly affected with respect to the combustion of carbon monoxide and hydrogen, whereas the activity for the conversion of methane was not so strongly influenced (Fig. 5). The activity for carbon monoxide combustion was seriously lowered over the aged samples. That is, the $T_{50}{}^{(CO)}$ increased from 448°C for the fresh, to 741°C after 15 days of ageing to 761°C for the 30 days aged catalyst, respectively (Table 4 concerning the T_{50} values). The behaviour of the LMHA sample, both after 15 and 30 days of ageing, turned out to resemble that of the LHA monolith in carbon monoxide conversion. The activity for the combustion of methane was not strongly affected. The ignition temperature in the aged samples was shifted by 80°C, although the temperature for 50 and 95% conversion increased only 30°C. Characteristic for LMHA is that the shape of the conversion curves changed considerably between the fresh and the aged samples, especially for carbon monoxide.

3.5.2. Conversion of fuel-N

The effects of ageing on the formation of molecular nitrogen and fuel-NO_x have been studied. Over the noble metal catalysts examined, the effects of ageing turned out to be negligible, whereas positive effects were observed for the lanthanum–manganese sample, cf. Fig. 6. The calculated yield for both nitrogen oxide and nitrogen dioxide is based on the inlet concentration of ammonia in the corresponding test over fresh LHA. The results showed that ammonia is converted at temperatures resembling those for carbon monoxide, to mainly molecular nitrogen and NO_x, see Table 4. The amount of nitrous oxide is expected to be very low, based on earlier studies [13]. In all the performed tests, nitrogen dioxide was lower than 5–10%.

Over noble metal-impregnated monoliths, i.e., both PdLHA and PtLHA, ammonia was ignited instantaneously together with carbon monoxide and hydrogen. Temperatures corresponding to 50% conversion of ammonia are reported in Table 5 in the T_{50} columns. The

Table 5
T_{50} with respect to the conversion of ammonia[a]

Samples	$T_{50}{}^{(\mathrm{NH_3})}$	$\tau_{50}{}^{(\mathrm{NH_3})}$
PdLHA.0	198	
PdLHA.15	217	6.1
PdLHA.30	216	5.8
LMHA.0	384	
LMHA.15	581	30
LMHA.30	551	25.4
PtLHA.0	220	
PtLHA.15	343	25

[a] Temperatures are expressed in °C. τ_{50} (%)=100[($T_{50}{}^{\mathrm{aged}} - T_{50}{}^{\mathrm{fresh}})/T_{50}{}^{\mathrm{fresh}}$], calculated by using the absolute scale, K.

formation of nitrogen was low and reached less than 10% yield, but increased appreciably above 700°C up to a maximum of 50% yield. For PdLHA the strong increase in the selectivity for molecular nitrogen occurred at the same temperature at which PdO is reduced.

Over LMHA, NO_x is produced in the temperature range of 500–700°C. The activity for the conversion of ammonia to nitrogen was higher in the aged samples than in the fresh one. A minimum yield of NO_x, i.e., about 30%, was reached over LMHA aged for 30 days at 800°C. This correlates to that LMHA also is the least active sample for conversion of ammonia.

4. Conclusions

Ageing studies at high temperature in presence of steam have demonstrated that palladium-impregnated lanthanum hexaaluminate maintains the activity for the ignition of carbon monoxide and hydrogen and that manganese-substituted lanthanum hexaaluminate increases the selectivity against NO_x formation.

Analysis performed on the catalyst powders showed that the surface area dropped significantly after 1 day ageing in steam, from approximately 41 to 22–31 m^2/g. However, the surface area dropped only a few percent on further ageing, suggesting that heat treatment in steam only gave a sharp initial decrease for the samples pre-calcined in dry air. The inverse behaviour was observed for changes in the crystal phase. XRD analysis of the lanthanum hexaaluminate samples showed that the less wanted perovskite phase, $LaAlO_3$, was formed in parallel to the formation of the hexaaluminate phase. On further ageing perovskite peak heights increased and hexaaluminate peak heights decreased. Although the perovskite

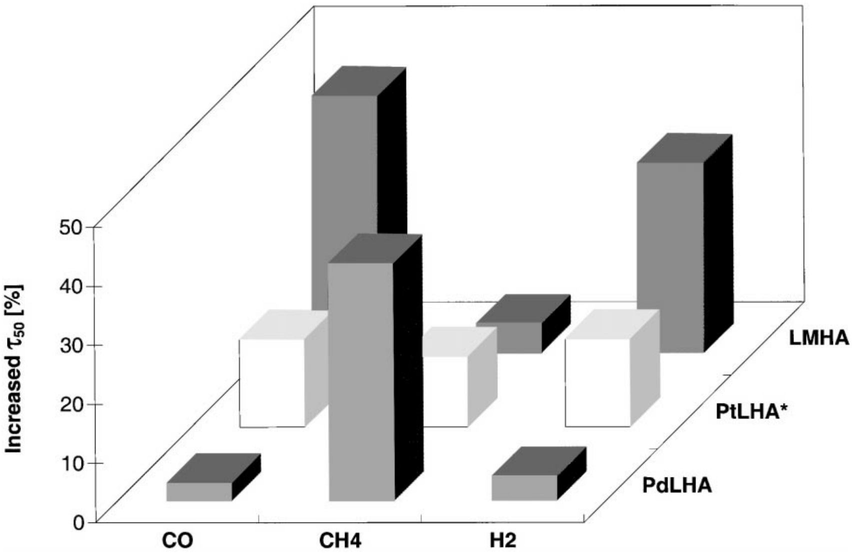

Fig. 7. Comparison between PdLHA, PtLHA and LMHA. PtLHA* indicates that the sample was aged for 15 days, whereas the other two were aged for 30 days. τ_{50} (%)=100[($T_{50}{}^{\mathrm{aged}} - T_{50}{}^{\mathrm{fresh}})/T_{50}{}^{\mathrm{fresh}}$], where all the temperatures are expressed in K.

phase seemed to grow, only a small decrease of the surface area was observed. Only after long time exposure does the initial relation between hexaaluminate and perovskite phases change, indicating that this is a slow process. Addition of 15 and 30 mol% aluminium during the synthesis increased the amount of hexaaluminate phase formed upon ageing, although the surface area did not improve. The manganese-substituted lanthanum hexaaluminate samples showed stronger peaks from the hexaaluminate-phase than from the perovskite, which decreased upon further ageing.

Analysis of the bulk of the noble metal-impregnated catalysts showed that platinum evaporates during the ageing, also shown by Dalla Betta [9]. Palladium is less volatile than platinum [5], nevertheless sintering is believed to occur on palladium particles, which leads to less active catalysts. Thus, neither platinum nor palladium can be considered suitable for catalysts, which have to maintain activity at a temperature above 1000°C.

Conversion of synthetic gasified biomass over fresh and aged samples was evaluated in a bench-scale rig operating at atmospheric pressure and with a hourly gas space velocity of 50 000 h^{-1}. Fresh precious metal samples showed low light-off temperature for carbon monoxide and hydrogen. Palladium catalysts were more active than platinum ones up to the temperature where, upon combustion of methane, palladium oxide is reduced (500–800°C) and a plateau or decrease of the reaction rate was observed. At these temperatures the platinum catalysts turned out to be more active. Lanthanum–manganese samples did not show the same activity for the light-off of the fuel, although the activity above 700°C was equal to that of the precious metal. At these temperatures, the onset of homogeneous reactions and mass transfer limitations are likely to level out the differences between the catalysts under the experimental conditions used.

After ageing up to 30 days, the light-off temperature for carbon monoxide and hydrogen was only increased a few degrees over the palladium sample, although the light-off temperature for methane was significantly increased. This behaviour of the palladium catalyst is suggested to be caused by sintering and/or evaporation of the active phase, which has been proved to occur at the ageing temperature [9]. Further, a colour change in the palladium samples suggested that mixed lanthanum palladium oxide was present in the fresh sample, but that the aged samples were mainly composed of palladium oxide and larger clusters of palladium metal. The fact that the catalyst maintained its activity at low temperature for the ignition of carbon monoxide and hydrogen suggests that only a small amount of active phase is responsible for this reaction. As shown in a previous study [14], this amount can be fixed at 0.2 wt.% or even lower. The activity for carbon monoxide was seriously lowered over the aged manganese sample, although the light-off temperature for methane only increased by 35°C. The selectivity for the conversion of ammonia into molecular nitrogen increased on ageing. An increased selectivity from 40 to 70% was observed in the 30 days aged sample, although the 15 days aged sample showed only a minor improvement compared to the fresh one. The lowest yield of nitrogen oxide was 30%.

The results in this study point out that ageing decrease the catalytic activity of Pd-, Pt-, and Mn-combustion catalysts in three different ways. The decrease in activity of the catalyst is reported as the value τ_{50} (%)$=100[(T_{50}{}^{\mathrm{aged}} - T_{50}{}^{\mathrm{fresh}})/T_{50}{}^{\mathrm{fresh}}]$ in Tables 4 and 5 and is also depicted in Fig. 7. First, ageing of the Pd-impregnated catalysts significantly increased the ignition temperature of methane though hydrogen and carbon monoxide showed similar activity compared to a fresh sample. Secondly, the effects of ageing on the Pt-impregnated samples turn out to be that the ignition temperatures of all components are increased uniformly. Finally, the influence of ageing on LMHA is that only the ignition temperatures of carbon monoxide and hydrogen are significantly increased. The fact that the catalysts show special properties might be useful to control the temperature profiles in the combustor.

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