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Catalytic behaviour and characterisation of $CuO_{1-z}(La_2O_3)_{z/2}$ based catalysts deposited on γ-Al_2O_3 and prepared in situ with $0.0 \leqslant z \leqslant 1.00$, without and with addition of Pd

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$(CuO)_{1-z}(La_2O_3)_{z/2}$ based catalysts with $0.0 \leqslant z \leqslant 1.0$ supported on γ-Al_2O_3 have been prepared in situ and the phases formed have been identified by XRD, SEM and TEM/EDS studies. The catalyst with $z = 0.5$ exhibited the best catalytic activity for oxidation of CO ($T_{50} = 295$ and 390°C with degrees of conversions of 93 and 92% at 450°C under rich and lean conditions, respectively) and C_3H_6 (291 and 414°C; 93 and 83%) and reduction of NO (405°C; 60 and 0%). This catalyst contained appreciable amounts of the perovskite phase $LaAl_{1-x}Cu_xO_3$ and the enhanced catalytic properties are ascribed to the presence of this phase. Addition of Pd to this catalyst implied that the degree of conversion of NO increased and that the light-off temperatures for all involved gas species decreased. Ageing experiments revealed that $LaAl_{1-x}Cu_xO_3$ decomposed and that Cu containing Pd particles were formed during this procedure which in turn deteriorated the catalytic properties of the catalyst.

Keywords: oxide based catalysts; CuO–La_2O_3–Al_2O_3; Pd; XRD; SEM-TEM/EDS

1. Introduction

With increasingly stringent air quality requirements, it is of major importance to develop new and more efficient systems for removing undesirable pollutants emitted from combustion sources. The three-way catalyst (TWC), used for many years to abate pollutants emitted from internal combustion engines and which simultaneously oxidises hydrocarbons (HC) and carbon monoxide and reduces nitrogen oxides (NO_x) to carbon dioxide, nitrogen and water, consists typically of a ceramic or metallic substrate coated with a support and a noble metal based catalyst. γ-alumina is usually chosen as supporting material because it adheres well to the catalytically active material, i.e. noble metals such as platinum, palladium and rhodium, and because it can be produced with high specific surface area.

However, since precious metals are rare and expensive, great interest has been focused on preparation of new oxide-based catalysts having e.g. perovskite or zeolite structures. The catalytic properties of copper oxides deposited on α- or γ-Al_2O_3 have been extensively studied with respect to the ability to oxidise CO and HC in automobile exhausts [1] and to reduce NO_x in flue gases in the presence of ammonia and oxygen [2,3]. Friedman et al. [4] and Strohmeier et al. [5] have investigated surface and bulk properties of copper oxide supported on α- and γ-alumina. They concluded that these properties of the catalysts were affected by both the metal loading and the calcination temperature. Thus high loading of copper yielded large agglomerates of copper oxide, and high calcination temperatures (above 900°C) resulted in formation of $CuAl_2O_4$.

In a recent investigation we have impregnated the alumina support with La_2O_3 in order to minimise undesirable reactions between deposited metal oxides and γ-alumina [6]. This procedure is known to stabilise γ-Al_2O_3 up to temperatures above 800°C, i.e. to prevent its transformation to corundum [7,8]. Matsuda et al. [9] have thus reported that addition of small amounts of La_2O_3 to γ-alumina gives rise to the formation of La–β-Al_2O_3 at 1000°C, resulting in an improvement of the thermal stability combined with a preservation of a high specific surface area. However, larger La_2O_3 additions caused $LaAlO_3$ to form which in turn decreased the specific surface area.

It is well-known that many perovskites of the general composition ABO_3 exhibit good catalytic properties. Chan et al. [10] have thus recently shown that a partial replacement of the A and B element in $LaCoO_3$ and $LaMnO_3$ by Sr and Cu, respectively, yielded an increased activity for CO oxidation. The authors attrib-

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uted this effect to an increased mobility of oxygen within the perovskite structure. In a previous investigation we have shown that a perovskite phase of the composition $LaAl_{1-x}Cu_xO_3$ was formed when a γ-Al_2O_3 washcoat was impregnated several times with a water solution containing La^{3+} and Cu^{2+} ions, with subsequent calcinations in between [11]. Furthermore we found that the formed material exhibited catalytic activity for oxidation of CO and HC, but not for reduction of NO. In the first part of this article we will describe how we have optimised the catalytic properties of $(CuO)_{1-z}(La_2O_3)_{z/2}$ supported on γ-Al_2O_3 by varying the composition, z, of the catalyst and the amount of oxide material applied.

It is well known that well dispersed Pd supported on γ-Al_2O_3 catalyses the oxidation of CO and HC and reduction of NO_x in gas compositions close to the stoichiometric point [6]. The second part of this article will deal with the catalytic properties of the optimised $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalyst promoted with Pd. The conditions used to deposit Pd onto the optimised oxide material will be discussed in some detail. The activity of these catalysts will be related to the observed phases, the morphology of the catalysts, the oxidation state of Cu and the interaction between Cu and Pd.

2. Experimental

2.1. Preparation of catalysts

The following starting materials, all of pro analysi quality, have been used; Disperal Alumina powder from Condea Chemie, $La(NO_3)_3{\cdot}6H_2O$ (Kebo AB), $Cu(NO_3)_2{\cdot}3H_2O$ (Merck), $Al(NO_3)_3{\cdot}9H_2O$ (Merck), $Pd(NH_3)_4(NO_3)_2$ (Johnson Matthey), $Pd(O_2C_2H_3)_2$ (Merck) and monolith cordierite structure containing 64 square channels per square centimetre (Corning Glass). The gases NO, CO, He, C_3H_6 and O_2 were supplied by AGA Gas AB.

A boehmite sol was prepared by slurrying 15 g Disperal in 100 ml of a 0.12 M HCl solution. Monolith samples with a length of 15 mm and a cross section containing 69 channels were dipped into the boehmite sol and then dried in air at 100°C. The channels were blown free before drying in order to maintain them open. This procedure was repeated until the desired amount (wt% WC) of washcoat was obtained. The alumina was stabilised by calcination at 550°C for 2 h in air, whereby the boehmite modification transformed to γ-Al_2O_3.

The salts of copper and lanthanum of different proportions were dissolved in 0.1 M HNO_3. The total metal content of the solutions was always 0.08 g/ml and the copper–lanthanum content was varied according to the formula $(CuO)_{1-z}(La_2O_3)_{z/2}$ with $z = 0.00$, 0.25, 0.50, 0.75 and 1.00. The in situ preparation of the catalysts was then performed in the following way: (i) the monolith furnished with the washcoat was dipped in the Cu–La solution; (ii) after drying the formed metal salts were decomposed by slow heating to 500°C; (iii) this procedure was repeated until the desired amount of the catalyst material on washcoat was achieved (CW (in wt%) = weight oxide/(weight oxide + weight γ-Al_2O_3) × 100); (iv) finally the catalysts were calcined at 900°C for 24 h in air.

Pd was applied onto γ-Al_2O_3 and the optimised Cu–La catalyst using two different routes. In the first route, a 15 mM water solution of $Pd(NH_3)_4(NO_3)_2$ with pH = 10–10.5 was used for impregnation. Excess liquid was evaporated off by heating the assembly at 95°C for 1.5 h. The assembly was then kept at 120°C for 30 min, followed by oxidation in air at 550°C for 30 min. The final catalyst contained 14 μmol Pd/g catalyst. In the second route, a $Pd(O_2C_2H_3)_2$-saturated acetone solution was used for the impregnation, but otherwise the procedure was as described above. In this case the final catalyst contained 10 μmol Pd/g catalyst.

2.2. Characterisation of prepared catalysts

The prepared catalysts were characterised by measurements of specific surface area and catalytic activity, by morphology studies, and by phase and element analysis.

2.2.1. Specific surface area

The specific surface areas were determined by the BET method, using nitrogen adsorption. The determinations were based on five experiments performed at relative pressures of nitrogen in the range 0.05–0.21. The cross section area per absorbed nitrogen molecule was assumed to be 0.162 nm^2. The nitrogen measurements were performed with a Digisorb 2600 instrument (Micromeritics). To correlate the specific surface area with the amount of applied oxides, the data are presented as m^2 per gram washcoat.

2.2.2. Measurements of catalytic activity

The light-off performance (defined as below) of the prepared catalysts was screened using a gas flow reactor set-up. Synthetic car exhaust was prepared by mixing NO, CO, C_3H_6, O_2 and He. Mass-flow controllers (Bronkhost, El-Flow, HI TEC.), were used to regulate the amount of each gas. Two gas mixtures were used. The first one had the composition 0.98 vol% O_2, 0.10 vol% NO, 1.60 vol% CO and 0.03 vol% C_3H_6 balanced with He and the second one 0.79 vol% O_2, 0.10 vol% NO, 1.60 vol% CO and 0.03 vol% C_3H_6 also balanced with He, yielding S-values of 0.9 and 1.1, respectively. The S-values are defined as in ref. [12] by the expression:

$$S = (2[O_2] + [NO])/([CO] + 9[C_3H_6]) .$$

These mixtures will be referred to as rich ($S = 0.9$) or lean ($S = 1.1$) below. The gas flow was kept constant in all experiments at a space velocity of 68000 h^{-1}.

The gas mixtures were fed into a quartz tube reactor, heated in a tube furnace. The temperature of the inlet gas was measured by an encapsulated Pt/Rh thermocouple in front of the catalyst. The samples were heated from 100 to 600°C at a rate of 3°C/min. The variation in gas composition with temperature was measured with a quadrupole mass spectrometer (Balzers QMG 420). The gas fed into the mass spectrometer was collected via a quartz capillary placed 1 mm after the catalyst. The capillary inlet hole was about 10 μm yielding a pressure of 2×10^{-6} Pa in the mass spectrometer. During the measurements the following mass numbers and corresponding ions were registered, 4 – He^+; 12 – C^+; 14 – N^+; 18 – H_2O^+; 28 – CO^+ and N_2^+; 30 – NO^+; 32 – O_2^+; 40 – $C_3H_4^+$; and 44 – CO_2^+ and N_2O^+. No catalytic activity was observed from the reactor set-up within the temperature range 100 to 600°C, using the gas-mixtures given above.

Before each measurement the catalyst was equilibrated in the appropriate gas mixture by heat treatment at 600°C for about 30 min. After the equilibration the furnace set-up was allowed to cool to a temperature slightly below 100°C, and the light-off curves given below were then recorded.

To compare the recorded mass spectra with each other they were normalised by recording the mass spectrum for a commercial TWC, containing 2.1 mg Pt–Rh per g catalyst (with a Pt : Rh weight ratio of 5 : 1). From these recordings it was found that the conversion degree of CO, C_3H_6 and NO became constant in the temperature range 400 to 600°C. Accordingly it was assumed that the signals recorded at 600°C corresponded to 100% conversion of respective gas. This assumption was also confirmed by recording spectra obtained when the space velocity was varied from 50000 to 120000 h^{-1}. It was also assumed that no conversion occurs at 100°C, implying that the signal levels in all recorded spectra could be directly related to each other at that temperature. The light-off temperature, T_{50}, is defined as the temperature of the inlet gas temperature where 50% of the observed maximum conversion degree of each gas species occurs.

2.2.3. *Phase and element analysis and morphology studies*

Samples for morphology studies were prepared by cutting the monoliths parallel with the channels. A thin layer of carbon was evaporated onto the samples in order to avoid electric charge effects. The morphology and element distribution of the samples were studied in a scanning electron microscope (SEM, JEOL 880) equipped with a windowless energy-dispersive spectroscopy (EDS) detector system (Link AN 10000). Magnifications ranging from 50 to 100000 were used with the SEM working both in secondary (SE) and back scattered electron (BSE) mode, and the element distributions were recorded by having the EDS system working in mapping mode. Surface areas of about 600 μm^2 were used for determining the overall composition of the samples. The data given below, are mean values from more than ten measurements.

Samples obtained by gently scratching off material from the surface and interior of the monolithic structure were used for phase analysis. The crystalline phases were identified by means of their X-ray diffraction patterns, obtained in a Guinier-Hägg camera using Cu $K_{\alpha 1}$ radiation and Si as internal standard. The obtained photographs were evaluated with a computerised scanner system [13] and the obtained spectra were matched to tabulated JCPDS data. Lattice parameters of the crystalline phases were determined using the program package PIRUM [14].

Some samples were also characterised by transmission electron microscopy studies. A part of each sample was gently crushed and then transferred onto a holey carbon film, supported by a Ni-grid, and investigated in a TEM unit (JEOL 2000FX) equipped with an energy dispersive spectrometer (LINK 10000). The La, Cu and Al content of individual fragments was determined by spot analysis. The electron beam was focused to a size of 20– 30 nm, and in all cases phase identifications and crystallinity were verified by their electron diffraction patterns.

3. Results and discussion

The preparation conditions used, together with results from the measurements of specific surface areas and catalytic properties are summarised in table 1.

3.1. *Catalytic activity*

3.1.1. *In situ prepared* $(CuO)_{1-z}(La_2O_3)_{z/2}$

Typical light-off curves for CO, C_3H_6 and NO, recorded under rich conditions ($S = 0.9$) for the catalysts impregnated with solutions with $z = 0.00$, 0.25, 0.50, 0.75 and 1.00 are given in figs. 1a–1c. The catalysts prepared with $z = 0.00$, 0.25 and 0.50 exhibited light-off curves for oxidation of CO which were composed of two S-shaped steps (see curves A, B and C in fig. 1a). The first step appeared in the temperature range 190 to 250°C and only under rich conditions. Catalysts with $z = 0.75$ yielded normal S-shaped light-off curves for oxidation of CO but the sample with $z = 1.00$ did not show any activity. The highest degree of conversion of CO at 450°C (93%) and the lowest light-off temperature (295°C) was found for catalyst C with $z = 0.5$. Oxidation of C_3H_6 yielded normal S-shaped light-off curves and catalyst C exhibited the highest degree of conversion (93%) and lowest light-off temperature (291°C). Reduction of NO was only observed for samples that exhibited a two-step behaviour in their light-off curves for conversion of CO. The lowest light-off temperature for conversion of NO was found for the catalyst C with $z = 0.5$ (405°C) and this catalyst also exhibited the highest degree of conversion (60%) at 450°C.

Table 1
Preparation conditions and catalytic activities of the $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalysts with $z = 0.00, 0.25, 0.50, 0.75$ and 1.00 and of Pd-containing catalysts

Sample z-value	WC (%)	CW (%)	Spec. area (m^2/g Al_2O_3)	Degree of conversion in % at 450°C for						Light-off temperatures, T_{50}, for					
				CO		C_3H_6		NO		CO		C_3H_6		NO	
				$S = 0.9$	$S = 1.1$	$S = 0.9$	$S = 1.1$	$S = 0.9$	$S = 1.1$	$S = 0.9$	$S = 1.1$	$S = 0.9$	$S = 1.1$	$S = 0.9$	$S = 1.1$
A; 0.00	16	30	[a]	70	64	78	60	0	0	347	385	323	407	522	> 600
B; 0.25	13	20	98	76	65	73	69	10	0	308	385	303	390	457	> 600
C; 0.50	15	41	43	93	89	87	80	60	0	295	388	299	382	405	> 600
D; 0.75	13	32	68	63	33	65	50	0	0	380	445	390	428	540	> 600
E; 1.00	15	36	[a]	0	3	7	0	0	0	600	550	543	539	> 600	> 600
F; γ-Al_2O_3 washcoat			128	0	0	10	10	0	0	> 600	> 600	550	540	> 600	> 600
G; 10 μmol Pd dep. on γ-Al_2O_3, AR [b]				100	100	100	100	100	25	320	326	320	315	331	326
H; 10 μmol Pd dep. on sample C, AR [b]				100	100	100	100	100	27	218	252	240	252	260	253
I; 14 μmol Pd dep. on sample C, TR [b]				98	100	100	100	65	0	270	275	279	298	347	> 600

[a] Not determined. [b] AR = deposit via the "acetate" route; TR = deposit via the "tetra-amine" route.

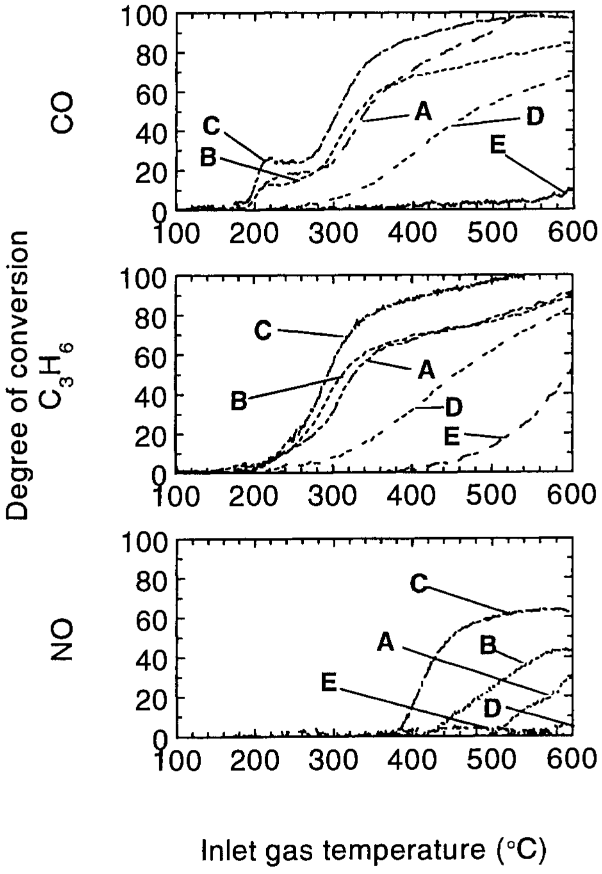

Fig. 1. Light-off performance of CO, C_3H_6 and NO, recorded under rich conditions for the $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalysts with $z = 0.0$ (A), 0.25 (B), 0.50 (C), 0.75 (D) and 1.00 (E).

The two-step behaviour can be understood as follows:

(i) during the first step the following reaction occurs:

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$

(ii) at the end of the first step in addition the additional reaction starts:

$$C_3H_6 + 3O_2 \rightarrow 3CO + 3H_2O$$

implying that more CO is generated and the increase in degree of conversion is hampered;

(iii) at higher temperatures C_3H_6 is completely oxidised according to the following reaction:

$$C_3H_6 + \frac{9}{2}O_2 \rightarrow 3CO_2 + 3H_2O$$

Under lean conditions ($S = 1.1$), all catalysts exhibited activity for oxidation of CO and C_3H_6, and normal S-shaped light-off curves were obtained. Catalyst C with $z = 0.5$ showed the lowest light-off temperatures (390 and 414°C) and the highest degree of conversion at 450°C (92 and 83%) for oxidation of CO and C_3H_6, respectively. Under lean conditions, this catalyst did not exhibit any activity for reduction of NO.

The degree of conversion varied with the amount of material deposited, and an optimum in the catalytic properties was found for the catalysts with $z = 0.5$ and with CW-values (see above) in the range 40 to 50 wt%.

In conclusion, under rich conditions a maximum degree of conversion at 450°C and minimum light-off temperatures for CO, C_3H_6 and NO were found for the $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalyst with $z = 0.50$ having a CW-value in the range 40 to 50 wt%. Under lean conditions no catalyst exhibited activity for reduction of NO while the one with $z = 0.5$ exhibited the best catalytic behaviour in the oxidation of CO and C_3H_6.

3.1.2. Pd deposited onto γ-Al_2O_3 and optimised $(CuO)_{1-z}(La_2O_3)_{z/2}$ material

The light-off curves recorded for sample G (10 μmol Pd deposited onto γ-Al_2O_3 using the "acetate" route) are shown in fig. 2. Under rich conditions this palladium catalyst exhibits simultaneous conversion of CO, C_3H_6 and NO. At 450°C the degree of conversion was 100% for all components. Under lean conditions we also observed simultaneous conversion of these gases. However, a maximum degree of conversion of NO was found at 350°C, where about 40% of the NO was converted compared with 25% at 450°C.

Addition of 14 μmol Pd to the $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalyst with $z = 0.50$ via the "tetra-amine" route (sample I) yielded a catalyst which exhibited T_{50}-values of 270 and 279°C under rich conditions for oxidation of CO and C_3H_6, respectively, while the corresponding value for reduction of NO was 347°C. Under lean conditions the T_{50}-values for the conversion of CO and C_3H_6 were 275 and 298°C, respectively, and no conversion of NO was recorded. The SEM and TEM studies can be interpreted in terms of that Cu is dissolved in the "tetra-amine" solution during the impregnation procedure and the subsequent heat treatment yields particles of a Pd–Cu alloy rather than Pd particles (see below), implying that the expected promotion behaviour is partly lost. In this connection it can be noted that using $PdCl_2$ as precursor for Pd also causes formation of a Pd–Cu alloy.

Addition of 10 μmol Pd to the $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalyst with $z = 0.50$ (sample H) via the "acetate" route yielded a catalyst which exhibited normal S-shaped light-off curves. Substantially lower T_{50}-values for all gas species were recorded both under rich and lean conditions, compared to those recorded for Pd deposited onto γ-Al_2O_3. Thus the difference in the light-off temperatures between samples G and H recorded under rich conditions is considerable, 102, 80 and 71°C for CO, C_3H_6 and NO, respectively, which in turn implies that simultaneous conversion was not observed in this case.

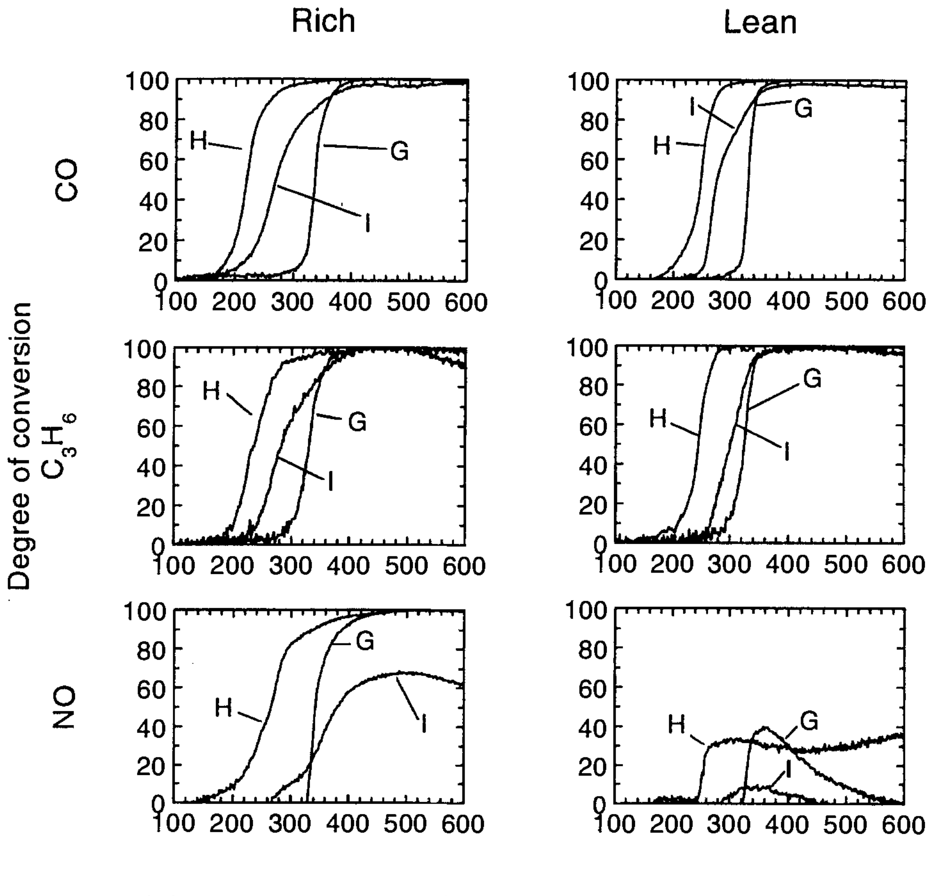

Fig. 2. Light-off performance of CO, C_3H_6 and NO, recorded under rich and lean conditions for the catalysts G, H and I.

At 450°C 100% conversion was found for all species. Under lean conditions the corresponding difference was of the order of 70°C for CO, C_3H_6 and NO. Simultaneous conversion was thus seen in this case but the degree of conversion for NO was only 27% at 450°C while 100% conversion was observed for the other gas species.

In conclusion, when Pd is deposited onto the $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalyst with $z = 0.5$ via the "acetate" route (sample H) one obtained a catalyst which exhibits better catalytic properties than the catalyst $(CuO)_{1-z}(La_2O_3)_{z/2}$ with $z = 0.5$ (sample C) and the catalyst G (Pd supported on γ-Al_2O_3).

3.1.3. *Ageing of the* $(CuO)_{1-z}(La_2O_3)_{z/2}$ *catalyst without and with Pd addition*

In order to investigate the stability of the $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalyst with $z = 0.5$ (sample C), the following experiment was performed. As described above the catalyst was equilibrated under rich conditions (30 min at 600°C) and then cooled to 100°C in the same atmosphere. The light-off curves for CO, C_3H_6 and NO were then recorded. When the temperature reached 600°C the atmosphere was changed from rich to lean and the catalyst was equilibrated in the lean atmosphere for 30 min. The catalyst was then cooled to 100°C, and then a new set of data was recorded. This procedure was repeated four times. Besides the catalyst C the catalysts I and H were exposed to the same procedure.

For the catalyst C, the light-off curves recorded under rich condition showed an increase in T_{50} with 15°C for the oxidation of CO (this difference is named ΔT_{50} below and in table 2). This increase is mainly due to an increase in the onset temperature, defined as the temperature where significant conversion of the reactant could be recorded, accompanied with a decrease in size (degree of conversion) of the first step in the light-off curve (see fig. 1). The second step in the recorded curves does not seem to be affected by the repeated heating/cooling procedure under rich and lean conditions. The T_{50} value for oxidation of C_3H_6 did not change during this procedure, while that for reduction of NO increased with 50°C. The degree of conversion at 450°C for CO and C_3H_6 was not affected by this procedure while that of NO was reduced from 60 to 0%.

Under lean conditions a ΔT_{50}-value of -110°C was recorded for CO. This remarkable decrease was found to be due mainly to the fact that the temperature of maximum conversion decreased substantially, while the onset temperature remained almost constant. Furthermore the degree of conversion of CO decreased during this ageing procedure from 87% to 59%. In the case C_3H_6 we observed a ΔT_{50}-value of -42°C but no change in the degree of conversion. As shown above, the freshly prepared catalyst C did not exhibit any activity for reduction of NO under lean conditions, and accordingly no ageing effect could be observed.

Corresponding measurements for the catalyst I yielded light-off curves with similar shapes as the ones given in fig. 2. Almost the same T_{50}-values were obtained during the ageing procedure, and the degree of conversion at 450°C was also found to be the same. For sample H we observed an increase of the T_{50}-values for oxidation of CO and C_3H_6 of 10 and 25°C under rich and lean conditions, respectively. For NO T_{50} increased by 45°C under rich conditions and by 25°C under lean conditions. The degree of conversion was not affected by the ageing procedure. The observed ΔT_{50}-values are summarised in table 2 and will be discussed in more detail below.

3.2. *SEM, TEM and EDS studies*

SEM studies of monoliths supplied with different amounts of γ-Al_2O_3 revealed that the surface of the monolith was not completely covered with γ-Al_2O_3 for loading less than 10 wt%. From these studies it was concluded that a loading level of 13–16 wt% of γ-Al_2O_3 yielded a satisfactory coverage of γ-Al_2O_3 over the entire monolith.

A SEM micrograph, obtained in BSE mode, of the impregnated γ-Al_2O_3 surface of sample C is shown in fig. 3. The bright spots in the micrograph were found to contain Cu and La, and their sizes were less than 100 nm. The number of particles increased with increasing amount of catalyst addition. TEM-EDS studies revealed that these particles had a metal composition of $LaAl_{1-x}Cu_x$ with $0 \leqslant x \leqslant 0.3$ but grains having La or Cu as the main constituent could every now and then be found. The X-ray analysis (see below) suggested that the chemical compositions of these particles is $LaAl_{1-x}Cu_xO_3$, La_2O_3 and Cu_2O, respectively. Particles of this type were also found in the interior of the washcoat. The TEM-EDS studies furthermore revealed that Cu and La are well distributed, as all γ-Al_2O_3 grains contained Cu and La in almost the same ratio as in the pre-

Table 2
Observed ΔT_{50}-values in connection with the ageing procedure (see text). The samples are labelled as in table 1

Sample	CO		C_3H_6		NO	
	$S = 0.9$	$S = 1.1$	$S = 0.9$	$S = 1.1$	$S = 0.9$	$S = 1.1$
C	+15	−110	0	−47	+50	–
H	+10	+25	+10	+25	+45	+25
I	+5	+5	+5	+5	+5	+5

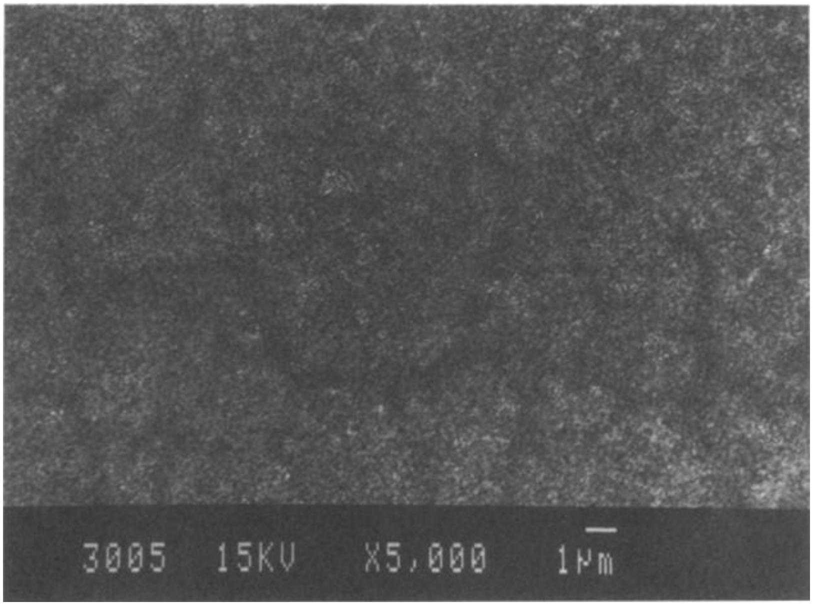

Fig. 3. SEM micrograph recorded in BSE mode showing the morphology of the catalyst C.

cursor solution. Corresponding studies of the aged material yielded the same results.

Samples containing small amounts of catalytic material (CW = 14 wt%) exhibited a morphology very similar to that of the washcoat both in SE and BSE mode. As above, the TEM-EDS studies revealed that both Cu and La were well distributed on the surface as well as in the interior of the washcoat. In this case we could not detect any particles. SEM studies of samples containing larger amounts of the catalytic material (CW = 62 wt%) showed that small particles were present within the washcoat but larger particles, 0.5–1 μm in size, were also found, preferentially at the surface of the washcoat. The composition of these particles and of those occurring in the agglomerates formed at the surface of the washcoat (see fig. 3) was the same as for the catalyst C (see above), but a few grains of the composition La_2CuO_4 were also found.

Recalling that the best catalytic properties were found for catalysts having a loading level of 40–50%, these studies indicate that in order to obtain the optimum catalytic properties the washcoat must be slightly supersaturated with respect to Cu and La, implying that small Cu–La-containing particles are formed. Addition of too large amounts of Cu and La tends to promote the formation of larger and less catalytically active particles.

SEM and TEM studies combined with EDS measurements of sample I showed that no Pd was present in the interior of the washcoat (the detection limit for Pd is ~ 0.5 at%). At the surface of the washcoat, however, 30–100 nm large particles could be found. Besides Pd, these particles also contained Cu and the composition varied from particle to particle according to the formula $Pd_{1-y}Cu_y$ with $0 < y \leqslant 0.5$. The washcoat contained substantially less Cu in the vicinity of these particles and in some case we could not detect any Cu at all (the detection limit for Cu is ~ 0.5 at%). Fig. 4 is a schematic drawing illustrating these observations.

TEM-EDS studies of Pd-impregnated materials according to the "acetate" route revealed Pd contents in the range 0.5–1.0 at% at the surface as well as in the interior of the washcoat. No Pd particles could be found.

3.3. X-ray and electron diffraction studies

The X-ray and electron diffraction studies were performed on samples which had been exposed to reducing atmosphere ($S = 0.9$). The X-ray pattern of sample A could be ascribed to Al_2O_3, $CuAl_2O_4$, Cu and Cu_2O. Both the X-ray and electron diffraction patterns recorded for samples containing La revealed the presence of a cubic perovskite phase, which according to the SEM and TEM studies most probably have the composition $LaAl_{1-x}Cu_xO_3$ and samples with $z = 0.25$ and 0.50 also contained Cu and Cu_2O. Finally, the X-ray pattern of samples with $z = 0.75$ contained reflections which

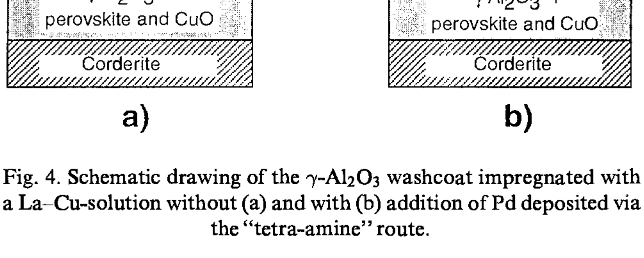

Fig. 4. Schematic drawing of the γ-Al_2O_3 washcoat impregnated with a La–Cu-solution without (a) and with (b) addition of Pd deposited via the "tetra-amine" route.

Table 3
Phase content of the catalysts $(CuO)_{1-z}(La_2O_3)_{z/2}$ with $0 \leqslant z \leqslant 1$ exposed to reducing conditions ($S = 0.9$). All samples contained Al_2O_3 as main constituent

z-value [a]	CW (wt%)	Phase content as determined by XRD [b]	Phase content as determined by SEM/TEM-EDS studies
0.00 [A]	30	$CuAl_2O_4$, Cu/Cu_2O	$CuAl_2O_4$, Cu/Cu_2O
0.25 [B]	44	$LaAl_{1-x}Cu_xO_3{}^{vw}$, Cu/Cu_2O	Cu/Cu_2O
0.50 [C]	41	$LaAl_{1-x}Cu_xO_3$, Cu/Cu_2O	$LaAl_{1-x}Cu_xO_3$, Cu/Cu_2O
0.50	62	$LaAl_{1-x}Cu_xO_3$, Cu/Cu_2O	$LaAl_{1-x}Cu_xO_3$, Cu/Cu_2O
0.75 [D]	45	$LaAl_{1-x}Cu_xO_3$, La_2CuO_4, $La_2O_3{}^{w}$	$LaAl_{1-x}Cu_xO_3$, La_2CuO_4
1.00 [E]	36	$LaAlO_3$	$LaAlO_3$

[a] A–E, as in table 1. [b] vw and w = identified by one or two weak or very weak reflections.

could be ascribed to La_2CuO_4 and La_2O_3 besides $LaAl_{1-x}Cu_xO_3$, while for samples with $z = 1.00$ the only crystalline phase present was the perovskite phase. The results of the phase analysis are summarised in table 3.

3.4. On the variation of the lattice parameters of $LaAl_{1-x}Cu_xO_3$ during the ageing procedure

The lattice parameter of $LaAl_{1-x}Cu_xO_3$ heat treated under alternating rich and lean conditions is given in fig. 5, together with those of the freshly prepared catalyst and the same catalyst conditioned in air at 600°C for 1 h after the ageing procedure. Under rich conditions the lattice parameter decreased each time the catalyst was exposed to this atmosphere, while under lean conditions an increase in the lattice parameter could be observed. The X-ray studies also revealed that after the second heat treatment Cu_2O was formed under rich conditions and seemingly increased in amount with increasing number of heat treatments. Materials heat treated three times under rich conditions contained Cu besides Cu_2O. Under lean conditions we also noticed that Cu_2O was formed but in smaller amounts. The variation of the cell parameter with the number of heat treatments suggests that $LaAl_{1-x}Cu_xO_3$ is partly decomposed into $LaAl_{1-x}Cu_xO_3$ with a lower x-value and Cu_2O under rich conditions while under lean conditions this process is partly reversed. The increased activity for oxidation of CO and C_3H_6 under subsequent lean conditions might be due to new nano-sized Cu_2O/CuO particles being formed by this process.

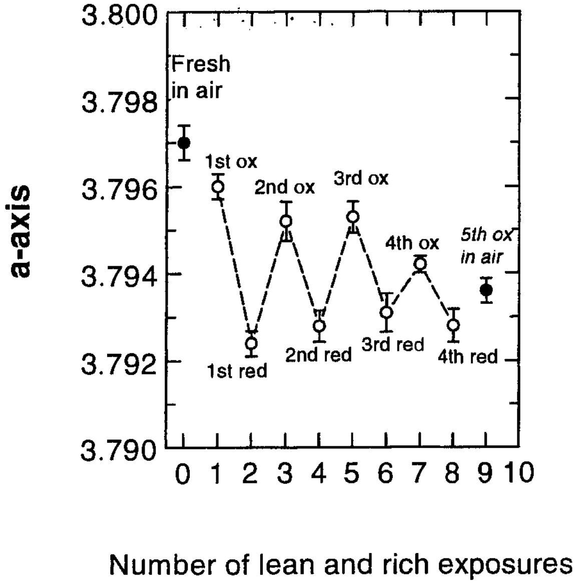

Fig. 5. Variation of the lattice parameter of $LaAl_{1-x}Cu_xO_3$ in catalyst C during the ageing procedure. The lattice parameters of a freshly prepared catalyst and the catalyst conditioned in air at 600°C for 1 h after the ageing procedure is also given for sake of comparison. The lattice parameter of $LaAlO_3$ is 3.7921(2) Å.

4. Concluding remarks

The data given above represent typical ones obtained for each catalyst. We have repeated the preparation of each catalyst several times and obtained reproducible data, i.e. T_{50}-values within ±5% and very similar degrees of conversions.

In agreement with previous findings the catalysts which predominantly contain Cu-oxides ($z = 0.0$ and 0.25) are good catalysts for oxidation of CO and C_3H_6 but their catalytic activity for reduction of NO is limited. The results given above also show that $LaAl_{1-x}Cu_xO_3$ is formed in connection with in situ preparation of $(CuO)_{1-z}(La_2O_3)_{z/2}$ catalysts with $0.25 \leqslant z \leqslant 0.75$. We have also prepared the same compound ex situ and X-ray and SEM-EDS studies have revealed that monophasic compounds are formed for $0 \leqslant x \leqslant 0.20$ at 1000°C [15]. The largest amount of this compound is found in samples with $z = 0.50$, and this composition shows the best catalytic properties. Different light-off temperatures of oxidation of CO (295°C) and C_3H_6 (299°C) and reduction of NO (405°C) were, however, observed. When this catalyst is exposed to lean conditions similar light-off temperatures are observed for these gases but the degree of conversion of NO at 450°C is less than that under rich conditions. As the pronounced conversion of NO is only observed for samples containing $LaAl_{1-x}Cu_xO_3$ in appreciable amounts, it is tempting to suggest that $LaAl_{1-x}Cu_xO_3$ in presence of Cu-oxides promotes the reduction of NO. In this connection it can

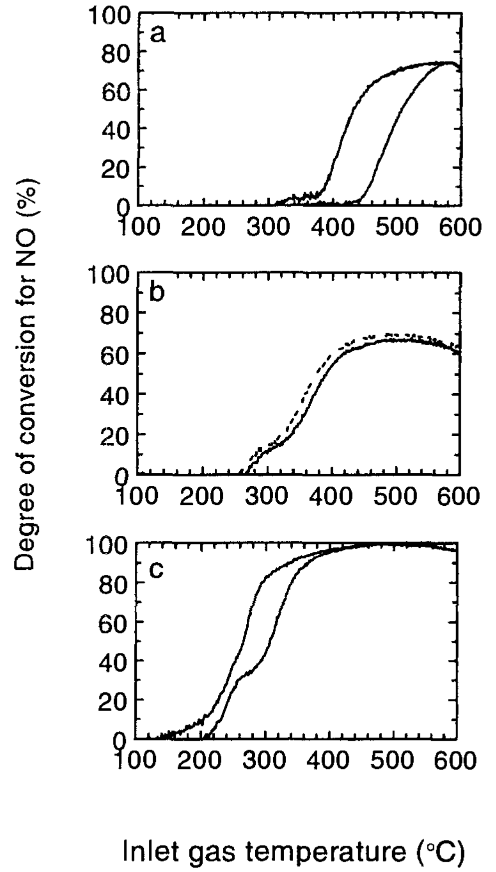

Fig. 6. Typical light-off performance of NO for catalysts of composition C (a), I (b) and H (c) recorded during the ageing procedure. The curves refer to data obtained during the first and fourth exposure to rich conditions.

also be noted that these differences in catalytic activity cannot be ascribed to different specific surface areas as the specific surface area of sample C is smaller than those of the samples B and D.

The ageing experiment also suggests that $LaAl_{1-x}Cu_xO_3$ takes an active part in the reduction of NO. We have thus interpreted the variation of the lattice parameter of $LaAl_{1-x}Cu_xO_3$ during subsequent exposure to rich and lean conditions to signify that $LaAl_{1-x}Cu_xO_3$ is decomposed under rich conditions to $LaAl_{1-x}Cu_xO_3$ with a lower x-value and Cu oxides. The nano-sized Cu-oxide particles thus formed improve the oxidative catalytic properties of the catalyst, while a decreasing Cu content in $LaAl_{1-x}Cu_xO_3$ diminishes the catalytic activity for reduction of NO. Within the framework of this interpretation it is also assumed that the decomposition of $LaAl_{1-x}Cu_xO_3$ is partially reversed under lean conditions. This interpretation is mainly based upon the observation that more Cu-oxides successively are formed during the ageing procedure. In addition, the lattice parameter of $LaAl_{1-x}Cu_xO_3$ approaches that of $LaAlO_3$ during this ageing procedure. We are aware that the oxygen content of the $LaAl_{1-x}Cu_xO_3$ phase might be different after it has been exposed to rich and lean conditions, respectively, which should also give rise to a variation of the lattice parameter of $LaAl_{1-x}Cu_xO_3$. The oxygen content of $LaAlO_3$ is not expected to vary, implying that with decreasing Cu-content in $LaAl_{1-x}Cu_xO_3$ the variation in the lattice parameter due to different oxygen content is also expected to decrease. We cannot yet say whether it is the presence of defects in the oxygen subnetwork or the presence of Cu-ions on the B position in the perovskite structure that gives rise to the catalytic activity but presumably both are of importance.

As mentioned above, Cu-containing Pd particles were formed when Pd was deposited onto the substrate via the "tetra-amine" route, but not when the "acetate" route was applied. In this connection it can be noted that the "tetra-amine" catalyst did not age while the "acetate" one did and the ageing implied that the light-off curves for conversion of NO became more and more alike that obtained for the "tetra-amine" sample, as seen in fig. 6. This behaviour suggests that Cu-containing Pd particles are formed during the ageing procedure of the "acetate" material. However, we have not been able to verify this by TEM-EDS analysis, as these particles are too small.

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