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NO reduction by CO over aluminate-supported perovskites

S.D. Peter [*], E. Garbowski [**], V. Perrichon and M. Primet

LACE, UMR CNRS 5634, Université Claude Bernard Lyon 1, 43, Boulevard du 11 Novembre 1918, 69622 Villeurbanne Cedex, France
E-mail: Edouard.Garbowski@univ-lyon1.fr

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Well crystallised La_2CuO_4 and $LaMO_3$ perovskites were studied in the CO + NO reaction. Whereas for $LaMO_3$ solids (M = Cr, Mn, Co and Ni) the activity decreased after reaction at 650 °C, the opposite was observed for $LaFeO_3$ and La_2CuO_4 leading to the most active catalysts. Their activity was even more enhanced when supported onto magnesium aluminate of 60 $m^2\,g^{-1}$.

Keywords: carbon monoxide, nitrogen monoxide, perovskite, spinel support, NO + CO reaction, three-way catalyst

1. Introduction

Nowadays three-way automotive catalysts (TWC) contain noble metals supported on modified ceria–alumina [1]. Up to now, only noble metals, and amongst them rhodium, are sufficiently active at low temperature for NO removal [2]. As a consequence, 80% of the use of rhodium is devoted to autocatalysts [3]. Due to more severe legislation and to the probable need of large-scale exhaust gas aftertreatment systems consisting of close-coupled PdRh precatalysis plus underfloor PtRh main catalysis, one can expect a strongly increasing demand of such precious metals. Shortage of the world-wide resources and high prices are the likely consequences. Therefore, it has been thought to replace them by other less expensive active phases. However, the presence of water wapor and carbon dioxide in the exhaust gas, along with high temperature encountered sometimes due to excessive overheating, lead essentially to the use of mixed oxides. Amongst them, perovskites appear to be quite attractive: numerous studies have been dedicated to such solids concerning either chemical properties like catalysis [4,5] or physical properties like ionic conductivity [6]. However, despite numerous properties of perovskites, they suffer from low specific surface area (SSA) when prepared as bulk catalysts. Due to the high calcination temperature needed for the solid state reaction to form the mixed oxide only values of SSA as low as 1 $m^2\,g^{-1}$ or even lower are generally obtained [7]. Other preparation methods starting from costly precursors, complicated synthesis [8] or low calcination temperature are not suitable for automotive application [9]. However, to increase surface area it is possible to support perovskites on another oxide like alumina for which area is well developed. It has been also shown previously that for $LaCrO_3$ perovskite [10], a support like aluminate is preferable to alumina because solid state reaction between support and oxide may be avoided. In the present work reported here, a magnesium spinel having a fairly well developed SSA has been used for supporting $LaMO_3$ where M stands for Cr, Mn, Fe, Co and Cu. Such solids have been characterised and tested in the most difficult reaction for TWC, which is the NO reduction by CO. The bulk La_2CuO_4 catalytic properties were already presented [11] and could be considered here as a reference.

2. Experimental

2.1. Preparation of catalyst

2.1.1. Bulk perovskites

Stoichiometric ratios of nitrates salts were dissolved in boiling deionized water. After drying at 80 °C, salts mixtures were crushed and then calcined in air in a muffle furnace at 500 °C for 12 h in order to decompose nitrates into oxides. After cooling to room temperature, solids were crushed again and put into a quartz cylindrical cell. A second calcination under flowing oxygen was carried at 1000 °C during 6 h in order to perform the solid state reaction.

2.1.2. Support

The support used here is the $MgAl_2O_4$ spinel. It has been prepared from alumina and magnesium nitrate according to a procedure already published [12]. After impregnation of alumina oxide C from Degussa (∼100 $m^2\,g^{-1}$) with an aqueous solution of magnesium nitrate, water removal and decomposition at 500 °C, calcination at 1000 °C in oxygen induced a solid state reaction and allowed a solid having a SSA of 59 $m^2\,g^{-1}$ to be obtained. Due to the presence of unreacted MgO, a second calcination at 1000 °C during 24 h in oxygen was performed. No disappearance of MgO occurred. Solid issued from the second oxygen calcination was percolated in boiling water for 24 h. Then

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[*] Present address: AUDI AG, Vorentwicklung Dieselmotoren (N/EA-35), Postfach 1144, D-74148 Neckarsulm, Germany.

[**] To whom correspondence should be addressed.

it was calcined again at 1000 °C during 48 h. After these treatments MgO had almost disappeared. The remaining surface area after almost 100 h calcination was not changed (58 $m^2\,g^{-1}$).

2.1.3. Supported perovskites preparation

In order to obtain a $LaMO_3/MgAl_2O_4$ supported catalyst with a perovskite layer consisting of two elementary cells, the weight of precursors was calculated according to the BET area of the support. At first, spinel (7 g) has been contacted with 200 ml of a hot aqueous solution containing 4.9 g of lanthanum nitrate. After water removal at 50 °C under reduced pressure, drying at 80 °C, the solid was calcined at 500 °C in a muffle furnace during 12 h in order to obtain a layer of lanthanum oxide supported onto the spinel surface. After cooling to room temperature, the procedure was repeated with metal nitrate in order to obtain a second layer of metallic oxide. The resulting product consisted of M_xO_y supported onto $La_2O_3/MgAl_2O_4$. The ultimate calcination occurred at 1000 °C during 6 h under flowing oxygen in a quartz cell in order to ensure the solid state reaction between M_xO_y and La_2O_3 leading to $LaMO_3$ assuming that the supporting spinel was not modified.

2.2. Physicochemical characterisation

2.2.1. Chemical analysis

The solids were analysed by AAS. After chemical attack with hot concentrated $HF+HNO_3+HCl$ acids, the solutions were evaporated to dryness and then put again in a HCl solution. Drying and dissolving was repeated twice before injecting solution to the flame of a Perkin–Elmer AAS 1100 spectrometer. For some refractory elements (Cr, Al and Mg) a hotter $N_2O+C_2H_2$ flame was necessary. Results are reported in tables 1 and 2.

2.2.2. BET surface area

BET specific surface areas were measured for support, bulk and supported perovskites. Measurements were carried out with nitrogen adsorption at 77 K with a fully computerised laboratory made apparatus. Determinations were performed with six to eight adsorption points: the values reported in tables 1 and 2 are reliable within 0.1 $m^2\,g^{-1}$.

2.2.3. X-ray diffraction (XRD)

X-ray diffraction was performed with a Siemens D500 counter tube diffractometer using Ni-filtered Cu Kα wavelength at 1.5404 Å. Data were digitally processed from 5° to 80° (2θ), and for each step (0.02°) accumulation time was 1 s. The resulting diffraction diagram was mathematically treated and compared to the JCPDS-ICDD data file in order to ensure that the wanted structure was obtained.

Table 1
Structural properties of perovskites.

Solid	Calcination time at 1000 °C (h)	Observed XRD structure[a]	BET area ($m^2\,g^{-1}$)	Analysis[b]
$LaCrO_3$	24	$LaCrO_3$ (s)	2.5	$LaCr_{0.97}O_z$
$LaMnO_3$	48	$LaMnO_{3.15}$ (s) La_2O_3 (w)	3.4	$LaMn_{0.98}O_z$
$LaFeO_3$	48	$LaFeO_3$ (s) La_2O_3 (vw)	2.5	$LaFe_{0.98}O_z$
$LaCoO_3$	48	$LaCoO_3$ (s) La_2O_3 (vw) Co_3O_4 (vw)	0.9	$LaCo_{0.95}O_z$
$LaNiO_3$	48	$LaNiO_3$ (s) $LaNiO_3$[c] (s) NiO (w)	2.2	$LaNi_{0.95}O_z$
La_2NiO_4	48	La_2NiO_4 (s) $LaNiO_3$[c] (s) $La(OH)_3$ (m) La_2NiO_7[d] (vw)	3.2	$La_2Ni_{0.98}O_z$
La_2CuO_4	48	La_2CuO_4 (s) La_2O_3 (vw)	0.6	$La_2Cu_{1.01}O_z$

[a] s, m, w and vw stand for strong, medium, weak and very weak.
[b] Formula deduced from chemical analysis (oxygen was never analysed).
[c] High temperature form.
[d] Questionable structure.

Table 2
Structural properties of supported solids [16].

Solid	Calcination time at 1000 °C (h)	XRD phases observed[a]	BET area ($m^2\,g^{-1}$)	Formula[b]
$LaFeO_3$ (24.3%) $/MgAl_2O_4$	6	$LaFeO_3$ (s) $MgAl_2O_4$ (s) $LaAlO_3$ (s) MgO (vw)	38.4 (60.3)[c]	$La_{0.99}FeO_z$ 24.6 wt% on $MgAl_{2.08}O_z$
La_2CuO_4 (24.3%) $/MgAl_2O_4$	6	$MgAl_2O_4$ (m) $LaAlO_3$ (s) MgO (vw)	30.5 (60.3)[c]	$La_{1.72}CuO_z$ 23.5 wt% on $MgAl_{2.12}O_z$

[a] s, m, w and vw stand for strong, medium, weak and very weak.
[b] Formula deduced from chemical analysis (oxygen was never analysed) and % is related to support element percentages.
[c] The BET specific surface area value for the support.

Table 3

(a) Catalytic activity of solids expressed as 10^{-5} moles CO converted per hour and per solid weight (g), (b) catalytic activity of solids expressed as 10^{-5} moles CO converted per hour and per area unit (m^2).[a]

θ (°C)	Cr	Mn	Fe	Co	Ni	Ni	Cu
			(a)				
200	∼0	6	8	∼0	8	∼0	11
250	2	10	46	2	16	4	44
300	6	22	139	10	33	12	114
			(b)				
200	∼0	1	3	∼0	5	∼0	18
250	1	3	18	2	6	1.5	73
300	2.4	6.6	42	11	15	4	190

[a] Cr, Mn, Fe, Co and Ni correspond to $LaMO_3$ perovskites. Ni and Cu correspond to La_2NiO_4 and La_2CuO_4, respectively.

2.2.4. Electron microscopy

For the support and some copper-based perovskites, TEM was used combined with EDX analysis. A VG-HB 501 microscope used a 100 kV tension for accelerating electrons. This allowed also analysis of a circular area of a few nm in diameter.

2.3. Catalytic activity measurement in the CO + NO reaction

A gaseous mixture consisting of helium and 2000 ppmv of each reactant was allowed to flow through a U-shaped quartz reactor. 200 mg of catalysts were used either for bulk solid or supported ones. Analyses were done by GC using a catharometer detector. A double column (molecular sieve and Porapak Q) allowed separation of CO, NO, CO_2, N_2O and N_2. However, due to lack of sensitivity for NO detection, an infrared NO analyser (Beckman IA 865) was used also downstream the chromatographic line. Before each test, samples were activated in flowing helium at 150 °C during $\frac{3}{4}$ h, then contacted with the reactants mixture with a flow of 10 $l\,h^{-1}$ leading to a GHSV of ca. 50 000 h^{-1}. Analyses were carried out every 10 min whereas temperature increased at a rate of 2 $°C\,min^{-1}$ from 150 to 650 °C. Then cooling to 150 °C under reactants (same rate of temperature decrease) occurred, followed by a second increase at 650 °C, in order to ensure complete conversion again. So tests were not performed in isothermal conditions. Activity was finally calculated either per mass of perovskite or per area unit when it was known (table 3).

3. Results

3.1. Physicochemical characterisation

3.1.1. Bulk perovskites

Main characteristics of the bulk solids are given in table 1. After calcination at 1000 °C the right ABO_3 structure was obtained in every case. Copper induces a derived structure called K_2NiF_4-type. On the other hand, due to the conditions used for synthesis neither amorphous La_2O_3 nor amorphous MO_x (M = Cr, Mn, Fe, Co and Cu) are likely to exist. This means that the solid state reaction had effectively occurred within 6 h calcination only. Indeed parent oxides were hardly observed by XRD (extremely low diffraction peaks assigned to either La_2O_3 or MO_x) meaning an almost fully complete solid state reaction.

Globally, the BET areas are very low (a few $m^2\,g^{-1}$) but typical for bulk perovskites obtained after high-temperature calcination. $LaFeO_3$ has an SSA of 2.5 $m^2\,g^{-1}$ and La_2CuO_4 has a value of 0.6 $m^2\,g^{-1}$ only.

3.1.2. Support

$MgAl_2O_4$ or $ZnAl_2O_4$ synthesis via coprecipitation of a magnesium (zinc) and aluminium nitrates solution leads to the right spinel structure after calcination of hydroxide at 1000 °C [13]. However, the obtained SSA are rather low, close to 4–6 $m^2\,g^{-1}$, which is comparable to those for bulk perovskites. In contrast, synthesis via impregnation of alumina having already a high SSA is a more valuable method.

After impregnation and two calcinations at 1000 °C, XRD shows that some MgO is still present. Percolation in boiling water leads to redispersion of MgO into $Mg(OH)_2$, which disappears after two subsequent calcinations at 1000 °C during 24 h. XRD reveals only one structure crystallised whereas the chemical analysis performed on this solid revealed that the right stoichiometry of the solid was almost obtained (Al/Mg = 2.08).

Characterisation of the final support has been done by electron microscopy. The TEM photograph reveals that spinel crystallites are homogeneous in size (roughly 10–50 nm) with a 30–40 nm mean average size, which is close to the value of the parent amorphous alumina [14]. Moreover, a careful examination of the photographs with the help of a magnifying glass reveals the fringes pattern of a crystallised phase with a spacing of ca. 4 Å, which is the unit cell parameter [15]. The analysis of some crystallites by EDX reveals that no zone is enriched in either Mg or Al. The absence of an aluminium-rich zone indicates the absence of residual starting alumina which had to be amorphous and could have been escaped XRD analysis.

3.1.3. $LaFeO_3/MgAl_2O_4$ and $La_2CuO_4/MgAl_2O_4$

The preparation of supported perovskites has been limited to the case of $LaFeO_3$ and La_2CuO_4, which were found very active when supported and exhibited activity enhancement under reactants (see section 3.2.1).

Concerning the phases observed by XRD, table 2 shows that spinel support and perovskite are not the only ones observed. As reported elsewhere [16], some new strong diffraction peaks pertaining unambiguously to $LaAlO_3$ are observed as well as some MgO traces. Clearly, during the supported mixed oxide synthesis, there was a solid state reaction between support and lanthanum oxide precursors.

The BET areas strongly decrease (31 and 38 $m^2\,g^{-1}$) by comparison with the initial support (60 $m^2\,g^{-1}$). However, it should be remembered that the support is now only 75% in weight and thus global BET should be that of the supported mixed oxide (almost nil) and $0.75 \times 60 = 45\ m^2\,g^{-1}$. Values experimentally obtained are sufficiently low to think that the second calcination at 1000 °C for solid state reaction between La_2O_3 and Fe_2O_3 or CuO has induced some sintering.

Electron microscopy has been performed onto the $La_2CuO_4/MgAl_2O_4$ catalyst only. The electron micrograph shows a great deal of particles having 20–60 nm in diameter. The EDX analysis gives a mean value of La/Cu = 2/1 and Mg/Al = 1/2.5. The total atomic copper content is 4%, which is close to the value deduced from chemical analysis. However, a careful examination shows two types of particles:

(a) Some particles being rather clear where Mg/Al = 1/(2.5–3) correspond to the support alone. For Cu and La it is observed mean values of 4 and 7% in atoms which correspond to chemical analysis. However some zones were almost free of copper or lanthanum, whereas other ones were enriched in both metals.

(b) Some particles appear darker for which mean sizes are larger (50–150 nm) and La/Al ratio is close to 1 ascribable to $LaAlO_3$ evidenced by XRD. Moreover, for them, magnesium is mostly absent whereas they contain more copper (from 5 to 10 mol%).

3.2. Catalytic activity

3.2.1. Bulk perovskites

Concerning the catalytic activity, big differences are observed for $LaMO_3$ on the one hand depending upon the M metal, and for La_2CuO_4 on the other hand when compared to other $LaMO_3$ compounds. Moreover, the catalytic activity is not stable, and either increases or decreases between the first and the second runs.

Two solids show higher activities as compared to the others, namely $LaFeO_3$ and La_2CuO_4, as already reported [11]. They show light-off temperatures (T_{50}, corresponding to 50% conversion) close to 340 °C whereas the other solids have conversion of only 10% at this temperature. Moreover, for these two solids it is observed that during the decrease of the temperature (first testing curve) after full conversion at 650 °C, activity is systematically higher. An activation occurred. On the other hand, for the second test performed directly after, when temperature increases almost no more modification occurs. The same values of conversion were observed as for the first decrease of temperature. Globally for both solids the T_{50} and T_{80} values concerning the second run are roughly 100 °C lower. There is some activation process of the catalysts during the first test which seems to modify themselves under reactants [11].

The other $LaMO_3$ solids (M = Cr, Mn, Co and Ni) behave differently: they have lower activities than $LaFeO_3$ and La_2CuO_4. For $LaCrO_3$ and $LaNiO_3$ no modification of activity occurs between the first and second run, and for both $LaMnO_3$ and $LaCoO_3$, in contrast a deactivation is observed after the second run (stabilisation of activity). Figure 3 summarises all these variations in activity during cycling tests by indicating bar graph heights for the T_{50} and T_{80} temperatures for the first cycle and after the second test (stabilisation of activity): T_{50} and T_{80} represent temperatures for which 50 and 80% of CO + NO conversions are obtained. Moreover, for all perovskites, values of activity have been calculated at 200, 250 and 300 °C and are illustrated in table 3, part (a) where values are expressed in mole converted per mass unit ($mol\,h^{-1}\,g^{-1}$). A quite similar trend can be obtained if the activity values are expressed in mole converted per area unit ($mol\,h^{-1}\,m^{-2}$) (table 3, part (b)). Since all solids have similar BET areas, $LaFeO_3$ and La_2CuO_4 behave quite differently from the others: ac-

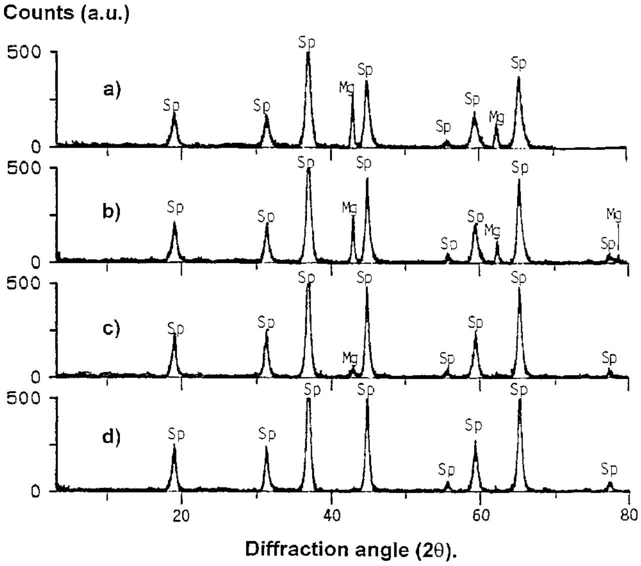

Figure 1. X-ray diffraction of the $MgAl_2O_4$ support according to different treatments: (a) synthesis at 1000 °C during 24 h, (b) synthesis at 1000 °C during 48 h, (c) after the first percolation treatment, (d) after the second percolation treatment. Sp – $MgAl_2O_4$ (spinel) and Mg – MgO.

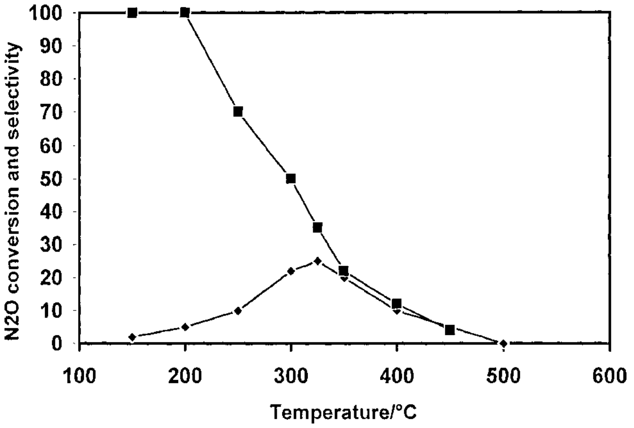

Figure 2. Catalytic activity of bulk $LaFeO_3$. (♦) Conversion and (■) selectivity into N_2O.

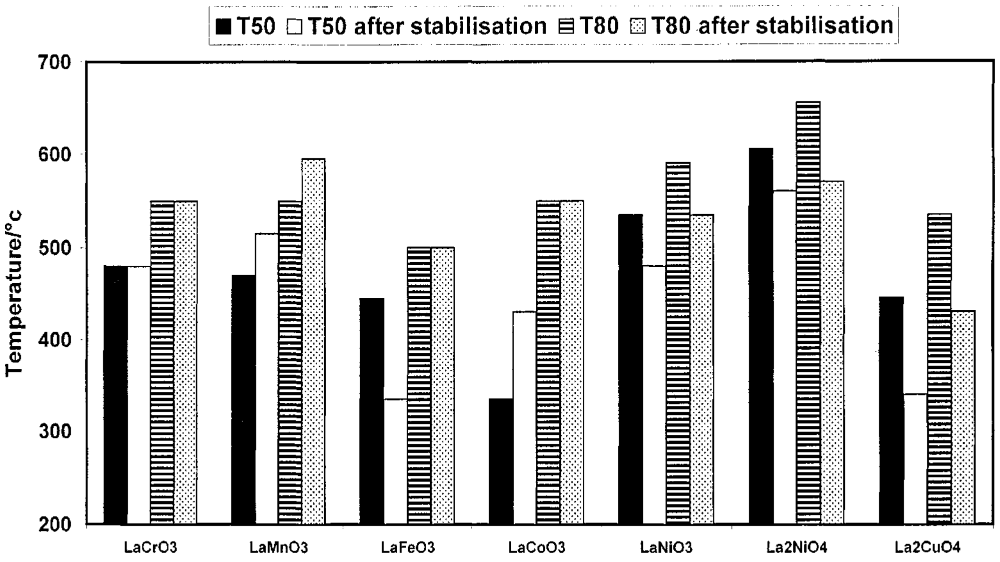

Figure 3. Light-off temperatures for 50 and 80% conversion for the first run and the second run (stabilisation of the activity).

Table 4
Apparent activation energy (values in kJ/mol within ±5 kJ/mol) for the CO + NO reaction on bulk perovskites (values in parentheses are for supported perovskites).

Solid	E_a (kJ mol^{-1})	
	First run	Second run
$LaCrO_3$	61	62
$LaMnO_3$	53	55
$LaFeO_3$	68 (65)	68 (67)
$LaCoO_3$	43	76
$LaNiO_3$	106	35
La_2NiO_4	78	35
La_2CuO_4	31[a] (33[a])	45 (46)

[a] Questionable value due to variation of E_a during test.

tivities are roughly higher by one order of magnitude. For the bulk catalysts the rank of activity at 300 °C then is the following:

$$La_2CuO_4 \approx LaFeO_3 \gg LaNiO_3 \approx LaMnO_3 \approx LaCoO_3 > LaCrO_3.$$

At low temperature, some N_2O is formed, and the lower the temperature and the lower the activity of course, the higher is the selectivity to N_2O. For almost all solids N_2O appears with a maximum concentration of about 50–100 ppm, except for $LaFeO_3$ where up to 250 ppm of N_2O were observed. Due to the high partial pressure observed and low conversion encountered, selectivity into N_2O was as high as 100% when conversion did not exceed 5%. For all solids the N_2O maximum occurred between 350 and 450 °C, with variable partial pressure and depending on activity.

For all runs apparent activation energy has been calculated for conversion lower than 20%. Values reported in table 4 are either for the first or for the second run. It should be noted that values are somehow dispersed, especially for the first run.

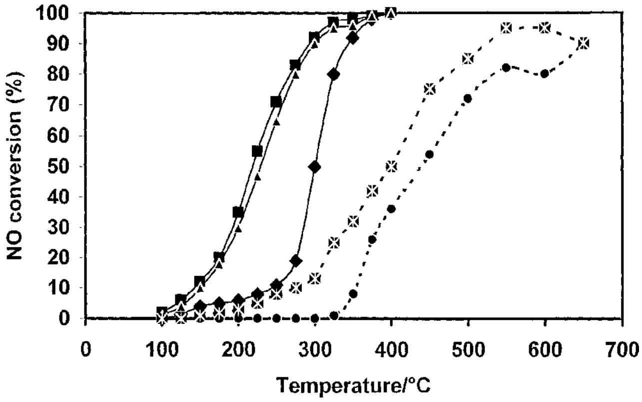

Figure 4. Conversion of NO on La_2CuO_4 and on $La_2CuO_4/MgAl_2O_4$. $La_2CuO_4/MgAl_2O_4$ first run with (♦) increasing and (■) decreasing temperature, (▲) $La_2CuO_4/MgAl_2O_4$ second run with increasing (decreasing) temperature, bulk La_2CuO_4 first run with (•) increasing and (∗) decreasing temperature.

3.2.2. $LaFeO_3/MgAl_2O_4$ and $La_2CuO_4/MgAl_2O_4$

Before performing any test on supported perovskites the $MgAl_2O_4$ support alone was tested: no conversion was observed at 450 °C, and at 650 °C a conversion of 5% was observed.

For the iron-containing solid the effect of support is evidenced by a lowering of 20 °C for T_{50} (330 °C) and 110 °C for T_{80} (380 °C) when compared to the performance of bulk $LaFeO_3$ perovskite. Besides the supported perovskite (like the bulk one) showed an increase of activity under reactants indicating that modifications of the catalytic surface may have happened under the reaction conditions.

Concerning $La_2CuO_4/MgAl_2O_4$, we observed, at first, that the supported active phase behaves exactly as the bulk one [11]. As obvious in figure 4, an activation process takes place between the first and second runs. Secondly, one can state a strong beneficial effect of the support because both T_{50} and T_{80} are lowered by ca. 100 °C close to 220 and

270 °C, respectively. $La_2CuO_4/MgAl_2O_4$ appears here as one the most efficient solids for CO oxidation by NO. It should be remembered that the latter contains only 25% by weight of active phase when compared with the bulk one. Activation energies are very close to those observed for bulk solids.

4. Discussion

All prepared bulk perovskites were active in the CO + NO reaction, but among them only $LaFeO_3$ and La_2CuO_4 showed sufficiently high activity at moderate temperature. Thus for any application in TWC only Fe and Cu may be considered as base metals in perovskite-based catalysts. The other metals (Cr, Mn, Co or Ni) give too low conversions and also loose activity under reaction conditions during run. Additionally, they may pose environmental problems due to their own toxicity (Cr, Ni).

The behaviour of the solids containing Cu^{2+} or Fe^{3+} may be explained by the ease for both cations Fe^{3+} and Cu^{2+} to switch their oxidation state in the reaction conditions into Fe^{2+} and Cu^{+}, or even to the metallic state, as it has been evidenced in the case of copper [11]. In fact, the simple copper or iron oxides are good catalysts for total oxidation either for CO [17] or for hydrocarbons like methane [18]. For the other perovskites their low activity may be ascribed to the impossible reduction of M^{3+} (Cr^{3+}) or impossible oxidation of reduced M^{n+} species (Ni^{2+}). For cobalt- or manganese-containing solids, oxidation of reduced species requires both a stronger oxidiser and a high temperature like for perovskites synthesis.

For the two solids containing iron or copper, an activation has been observed. The light-off temperatures decrease from 440 to 330 °C for both $LaFeO_3$ and La_2CuO_4 between the first and second tests indicating important surface modifications. However, the apparent activation energies remain the same after activation meaning that only the number of sites, and not their quality, has increased. This can be explained by a reconstruction under reactants leading to a more active surface. Indeed, the formation of metallic copper has been clearly correlated to the catalytic activity of La_2CuO_4-based catalysts [11,16].

One aim of this work was to enhance accessible surface catalytic sites of $LaMO_3$ in order to improve the catalytic activity. This goal was previously achieved for $LaCrO_3$/support in a former work on methane combustion [10]. In this case, it has been demonstrated that the perovskite may cover the support uniformly as a thin layer and that the activities ratio between bulk and supported oxides was exactly the BET areas ratio. In the present case for the CO + NO reaction it seems that there is some constraint in developing the area of perovskites. Tests with supported $LaFeO_3$ or La_2CuO_4 showed a lot of modifications in structure and catalytic properties along with lowered BET areas. XRD revealed without ambiguity that $LaFeO_3$ has crystallised out of the spinel surface, contrary to La_2CuO_4, probably well dispersed, which is not observed by XRD.

For both cases, the reduced BET areas are certainly due to the appearance of a new perovskite $LaAlO_3$ which has been synthesised at the expense of magnesium spinel (lowered intensities on XRD diagram lines) according to the following reaction:

$$La_2O_3 + MgAl_2O_4 \rightarrow 2LaAlO_3 + MgO$$

The presence of $LaAlO_3$ is a proof that there is a phase segregation: aluminium ions escape the spinel structure, induces MgO appearance, enters perovskite and dislodges the transition metal ion.

For $LaFeO_3/MgAl_2O_4$ both spinel and perovskite patterns appear almost unchanged because peaks due to $LaAlO_3$ are relatively low. According to the temperature used for the synthesis there should be some solid state reaction like

$$LaFeO_3 + MgAl_2O_4 \rightarrow LaAlO_3 + MgFeAlO_4$$

which explains the appearance of $LaAlO_3$ and the area loss.

For $La_2CuO_4/MgAl_2O_4$ things are completely different and one remarks that $LaAlO_3$ peaks appear with an intensity stronger than that due to spinel. The reaction that occurs partially may be the following:

$$La_2CuO_4 + MgAl_2O_4 \rightarrow 2LaAlO_3 + MgO + CuO$$

This explains the appearance of strong $LaAlO_3$ peaks and the decrease of the XRD peaks of $MgAl_2O_4$. But one should have obtained MgO and CuO also. However, the low copper content (4.1 wt%, 6 at%) may explain that CuO escapes XRD.

In the case of supported La_2CuO_4 there is a strong activation during the first test like for bulk La_2CuO_4, but the main effect is that activity is much higher in that case. T_{50} and T_{80} are lowered by 100 °C when compared to the value of unsupported catalyst. Taking into account that only 25 wt% of La_2CuO_4 are present one can calculate the specific activity, which is multiplied by a factor of 100. This has to be connected with the BET area, which is multiplied by a factor 50. Both values, if not equal, are however comparable: support effect seems to be only geometrical here. For the supported $LaFeO_3$ solid the same effect is observed although it is less marked. When comparing activities at 300 °C one observes that for supported perovskite, specific activity is reduced roughly by a factor 5. This is due to the fact that $LaFeO_3$ is not so well dispersed as obvious from XRD and that perovskite may have crystallised apart from the spinel surface.

A catalyst for automotive exhaust gas has to be active at low temperature. $LaFeO_3/MgAl_2O_4$ and $La_2CuO_4/MgAl_2O_4$ have been found to be efficient for simultaneous elimination of both CO and NO (330 and 230 °C for T_{50}, respectively), which at least for supported La_2CuO_4 are comparable to classical noble metal catalysts. Such results are also similar to that found by Misono et al., who showed the solid very efficient for removing both CO and NO when supporting it on zirconia [19].

5. Conclusion

The aim of this work was to prepare supported perovskites in order to improve their catalytic activity in the CO + NO reaction. The support was a high specific area and thermally stable $MgAl_2O_4$ spinel synthesised from highly divided alumina impregnated with magnesium nitrate. Synthesis of several bulk $LaMO_3$ perovskites (M = Cr, Mn, Fe, Co and Ni) and La_2CuO_4 via a decomposition of nitrate mixture is very easy, and leads to crystallised solids, having however low BET area for this kind of solid. Two binary oxides ($LaFeO_3$ and La_2CuO_4) appear attractive because their activity increases during the catalytic test, and after a full conversion at 650 °C they develop excellent catalytic properties for the reduction of NO by CO. Their synthesis on a $MgAl_2O_4$ support was performed from a mixture of nitrate salts as precursors. It was effective for the $LaFeO_3$ supported perovskite within a few hours calcination at 1000 °C.

Globally, the supported oxides show an enhanced activity in the CO + NO reaction as compared to the bulk ones. This effect is especially observed for $La_2CuO_4/MgAl_2O_4$ where surface of the support seems to enlarge the oxides surface. For $LaFeO_3$ the effect of the support is limited because of the separation of precursors, but finally a better dispersion of perovskite could be obtained. However, in both cases there is a solid state reaction between spinel support and lanthanum oxide.

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