Catalysis Letters 54 (1998) 79–84

Catalytic properties of La_2CuO_4 in the CO + NO reaction

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Received 18 March 1998; accepted 5 June 1998

La_2CuO_4 is an active catalyst for the reduction of NO by CO. Under reaction conditions, the catalyst exhibits an activation which results in a lowering of the light-off temperature by 80 °C. XRD, TEM and EDX analysis carried out after the catalytic test indicate that the mixed oxide has been reduced to form a La_2O_3, Cu binary system. It seems that metallic copper species are the most active sites in the CO + NO reaction.

Keywords: La_2CuO_4, CO + NO reaction, perovskites, copper, catalyst, nitrogen oxide, carbon monoxide

1. Introduction

Perovskite type mixed oxides are known as active catalysts for the automobile exhaust gas after-treatment [1–3]. Their high thermal stability up to more than 1000 °C and the large number of possible metal ions to be incorporated in the ABO_3 structure qualify them as tailor made catalysts for this application. In a recent work [4], La_2CuO_4, a mixed oxide with a related structure called K_2NiF_4-type [5], has also been described as a potential three-way catalyst after partial substitution of copper by palladium. Our investigations focus on the catalytic properties of the pure La_2CuO_4 solid in the most difficult reaction to be realised in a catalytic converter, i.e., the reduction of NO. As reducer, the use of CO is advantageous, as it is available in the exhaust gas of an internal combustion engine. Our particular interest in the present work is to study the transformations of the lanthanum copper oxide under reaction conditions and to identify the active sites of the catalyst. Physicochemical characterisations performed before and after testing have been used as a systematic approach to follow the changes taking place in the solid during catalysis.

2. Experimental

2.1. Catalyst preparation

The catalyst was prepared by the so called evaporation-decomposition method: lanthanum and copper nitrates, in a molar ratio of 2 : 1, were dissolved in water and the solution maintained at 90 °C for 1 h. The water was then removed at 50 °C under reduced pressure using a rotary evaporator. Then, in order to decompose the nitrates into the corresponding oxides, the obtained intimate mixture of the two nitrates was heated 12 h in air at 500 °C (heating rate 1 °C min^{-1}). Finally, after grinding, the solid state reaction between the two oxides, La_2O_3 and CuO, in order to form La_2CuO_4, was realised during 48 h at 1000 °C, in oxygen atmosphere (heating ramp 2 °C min^{-1}).

2.2. Physicochemical characterisation

The copper analysis was done by atomic absorption spectroscopy on a Perkin Elmer AAS 1100 using an air/C_2H_2 flame. For lanthanum, a Spectroflame D was used with an Argon-ICP.

XRD measurements were carried out on a Siemens D500 diffractometer using a copper anticathode. The spectra were recorded in air, at room temperature, from 3 to 80° (2θ) with a resolution of 0.02° (2θ).

BET specific areas were measured on 1 g of sample by N_2 adsorption at 77 K. The catalysts were previously desorbed under a vacuum ($<10^{-2}$ Pa) for 2 h at 500 °C.

The examination of the catalyst by TEM was done by means of a JEOL 100 CX with an acceleration voltage of 100 kV. The resolution power was 0.3 nm. EDX microanalyses were also performed on a STEM VG – HB 501 working at 100 kV.

2.3. Catalytic activity measurements

Catalytic activity measurements were carried out on 200 mg powder put in a U-shaped microreactor. The catalyst was put onto a quartz wool layer and the bed dimensions were approximately: diameter = 10 mm and height = 2.5 mm. Prior to the test, the sample was pretreated at 150 °C under He to eliminate adsorbed water. The CO + NO reaction was performed between 150 and 650 °C, and then between 650 and 150 °C, with a heating or cooling rate of 2 °C min^{-1}. The reaction gas contained 2000 ppm CO, 2000 ppm NO and He as a balance, the total flow rate being 10 l h^{-1} (VVH 50,000 h^{-1}). The activity

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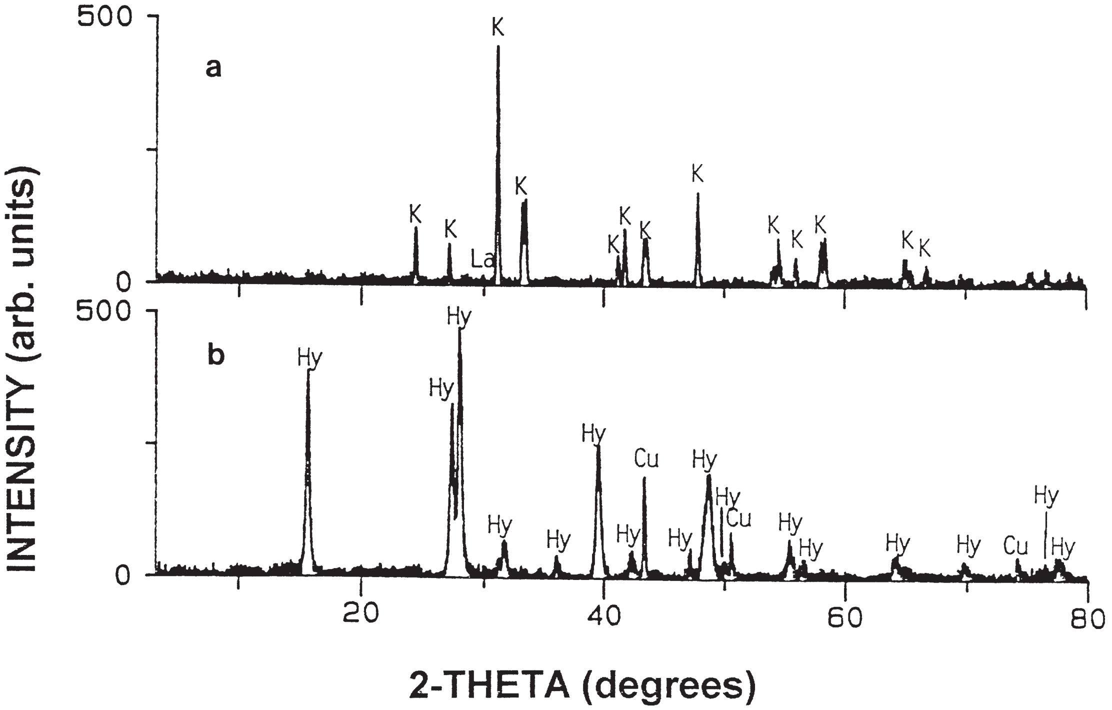

Figure 1. XRD patterns of the catalyst La_2CuO_4 before (a) and after (b) CO + NO test; four cycles 150 → 650 → 150 °C were performed under 2000 ppm CO + 2000 ppm NO. K: La_2CuO_4 (K_2NiO_4-type structure); Hy: $La(OH)_3$; La: La_2O_3; Cu: metallic Cu.

Table 1
Characteristics of the catalyst before and after the catalytic activity measurements.

Catalyst	BET surface area	Analysis	XRD[c]	
La_2CuO_4 fresh	0.6 $m^2\,g^{-1}$	La 68.1% (68.5)[a] Cu 15.8% (15.7)[a] $[La_2Cu_{1.01}O_z]$[b]	La_2CuO_4 La_2O_3?	S w
La_2CuO_4 after test	4.5 $m^2\,g^{-1}$	not analysed	$La(OH)_3$ Cu metal La_2CuO_4	S M w

[a] Theoretical values for ideal stoichiometry. [b] Formula calculated from chemical analysis. [c] Intensity of the diffraction peaks: S: strong, M: medium, W: weak, w: very weak, (?) phase attribution questionable.

changes were monitored by successive cycles of upward and downward temperature, up to the stabilisation of the catalytic activity. Analyses were performed every 10 min. The concentrations of CO, CO_2 and N_2 were determined by gas chromatography with a catharometer detector. In addition, due to lack of sensitivity, NO and N_2O concentrations were followed by an infrared analyser (IR Beckmann 865). NO_2 was not analysed.

NO conversions were calculated on the basis of the non-converted NO. To control the carbon and oxygen balance, the conversion was also calculated from the quantity of CO transformed into CO_2. When the catalyst was stabilised, the NO and CO conversions at high temperatures were almost identical in both calculation modes. However, discrepancies were observed at lower temperature because of the formation of N_2O, and also in the first activation cycles where CO_2 was formed in excess to the reaction $CO + NO \rightarrow CO_2 + (1/2)N_2$. Nitrogen balance decreased with conversion and was close to 85% for a complete NO conversion. This discrepancy must be attributed to a non-linear response of the TCD chromatographic peak. No NO_2 formation was expected under our experimental conditions.

3. Results and discussion

3.1. Solid characteristics of the fresh catalyst

Chemical analyses of the solid before testing indicate that the atomic ratio of La to Cu corresponds almost precisely to the expected 2 : 1 stoichiometry (table 1). XRD patterns exhibit narrow peaks (figure 1(a)) and confirm the formation of the desired phase La_2CuO_4. No other phase containing either La or Cu has been detected, if we except some questionable traces of lanthanum oxide La_2O_3.

The very low BET surface area (0.6 $m^2\,g^{-1}$) is in agreement with the high calcination temperature. In accordance

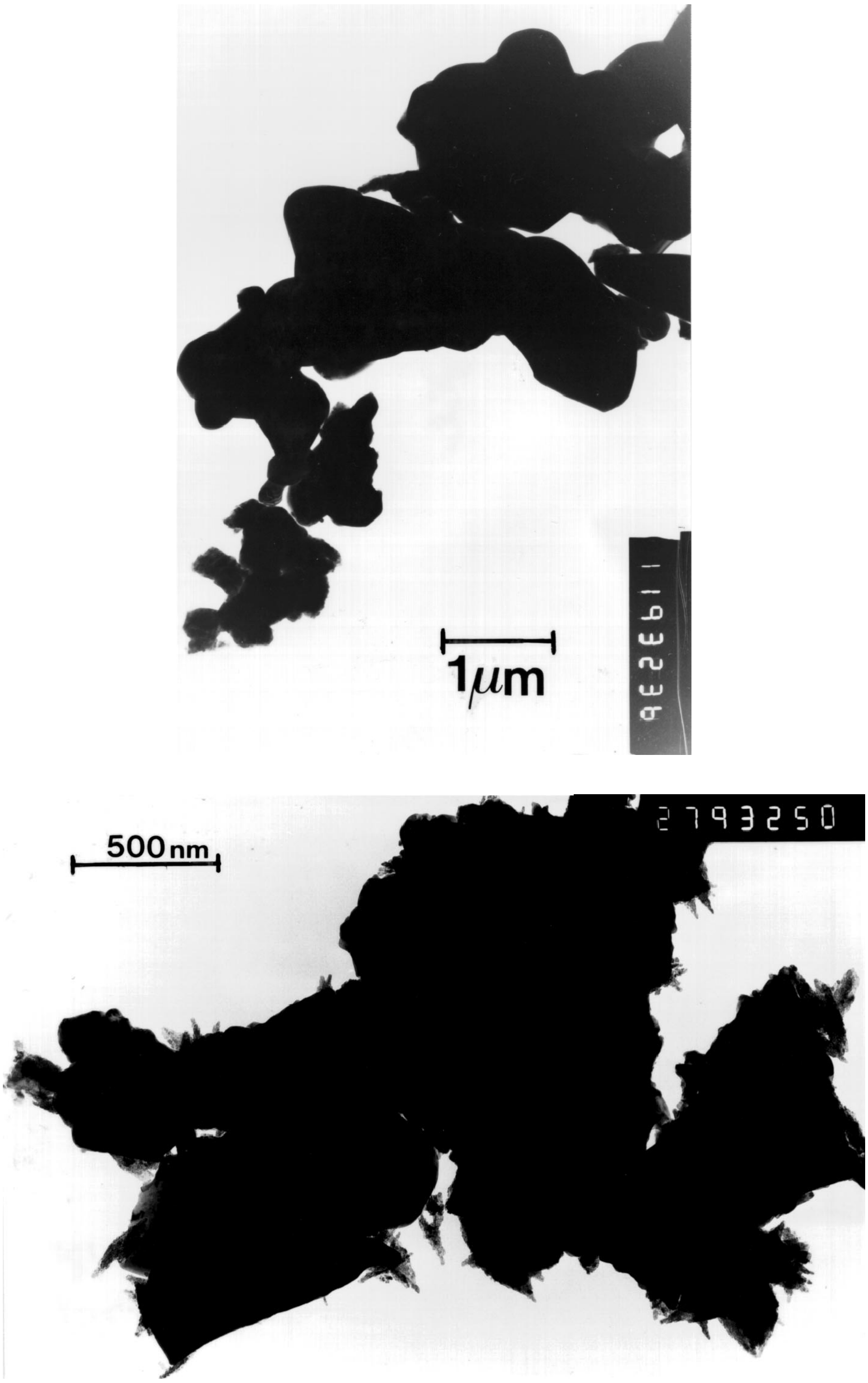

Figure 2. Electron micrograph of the catalyst La_2CuO_4 before (top) and after (bottom) CO + NO test: four cycles 150 → 650 → 150 °C were performed under 2000 ppm CO + 2000 ppm NO.

with this, the TEM micrographs show large particles of 150–1500 nm in size with a smooth shape (figure 2, top). EDX microanalysis performed on these particles issues in a La/Cu ratio varying in the range of 2 ± 0.3. Within some uncertainty, this is in good agreement with the results of the chemical analysis. A few particles of pure lanthanum oxide have also been evidenced whereas isolated copper oxide particles were not detected.

3.2. Catalytic activity of La_2CuO_4

During the first cycles, for a given temperature, the CO conversion and the parallel formation of CO_2 take place with a higher percentage than the NO conversion. For example, in the first cycle, the CO conversion is complete whereas that of NO never reaches 100%. As discussed below, a part of CO reacts with the lattice oxygen of the

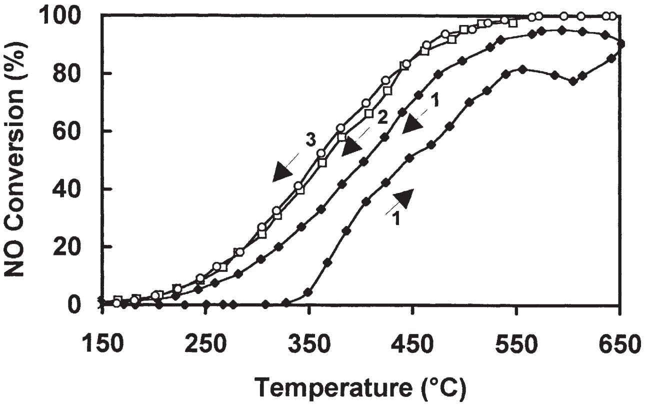

Figure 3. NO conversion curve as a function of temperature in the 2000 ppm $CO + 2000$ ppm NO reaction. La_2CuO_4 shows an activation under reaction conditions. (↑1↓1) 1st cycle, heating and cooling; (↓2) 2nd cycle, cooling; (↓3) 3rd cycle, cooling.

catalyst, which reduces the mixed oxide phase. Therefore, in the following, we concentrate only on the transformation of NO, which reflects more the real catalytic activity of the solid.

The NO-conversion curve of La_2CuO_4 as a function of temperature is reported in figure 3. A positive hysteresis is observed in the 1st and 2nd runs, i.e., the catalyst becomes more active under reactants. For the $CO + NO$ test performed during the first temperature rise, the light-off temperature T_{50}, corresponding to 50% conversion, is observed at 430 °C, whereas, during the cooling-down step, the value of T_{50} decreases to 400 °C. After two reaction cycles of heating and cooling, the catalyst reaches a stabilised state, and the final T_{50} is 340 °C. Therefore, the activated solid achieves the same 50% conversion level at a temperature 90 °C lower than in its initial state. After the third reaction cycle, no more hysteresis is observed, i.e., a fourth cycle gives the same result. After the stabilisation, the beginning of the $CO + NO$ conversion occurs at low temperatures, between 150 and 200 °C.

In this domain of low temperatures, N_2O is formed. This compound results from an incomplete NO reduction and is undesirable in atmosphere because of its high contribution to the greenhouse effect. Its concentration increases with temperature, up to a maximum quantity (100–120 ppm) measured at roughly 380–440 °C. However, the corresponding selectivity which is initially 100% decreases rapidly with the NO conversion. It is about 20% at the maximum of N_2O formation. It results that for temperatures higher than 450 °C, the selectivity of the reaction towards N_2 is always higher than 80%.

The apparent activation energy calculated after the activation (from the 2nd cycle and after) for conversion lower than 20% is equal to 45 ± 5 kJ mol^{-1}.

3.3. Modification of the catalyst under reaction conditions

Physicochemical characterisations were performed on the solid after the four cycles of the $CO + NO$ catalytic test. They show that the catalyst had been strongly modified under the reaction conditions. In its activated state, the specific area increased from initially 0.6 to 4.5 m^2 g^{-1} (table 1). Instead of the La_2CuO_4 phase, the solid contains mainly lanthanum hydroxide and metallic copper, as shown by the XRD patterns (figure 1(b) and table 1). The presence of $La(OH)_3$ rather than that of La_2O_3 can be explained by the easiness of the oxide to be transformed into hydroxide when exposed to ambient air [6]. Also, although surface carbonation can easily occur [6], no lanthanum carbonate was evidenced. This transformation of the lanthanum oxide into the trihydroxide phase underlines, by contrast, the good stability of the metallic copper particles exposed to air at room temperature. In accordance with this, the size of the copper particles calculated by means of the Debye–Sherrer relation is rather large (50–100 nm).

The electron micrographs (figure 2, bottom) exhibit large particles surrounded by needles of about 20–100 nm in sizes which are well evidenced by their different shape at the border of these particles. EDX microanalysis demonstrates that the outer needles are composed of copper exclusively, whereas the inner parts contain primarily lanthanum, the average La/Cu ratio being 10/1. In conclusion, the detailed examination by electron microscopy and microanalysis confirms the results of the global examination done by XRD.

3.4. Identification of the active sites

Under the reaction conditions of the $CO + NO$ catalytic test, the La_2CuO_4 catalyst undergoes activation. This enhancement of the catalytic activity goes along with a modification of the solid. A reduction takes place, leading to the complete transformation of the La_2CuO_4 mixed oxide into copper and lanthanum oxide. This new solid containing these metallic copper particles obviously has a much higher catalytic activity in the $CO + NO$ reaction than the initial binary oxide.

Supposition can be done that the reduction of La_2CuO_4 in the stoichiometric $CO + NO$ mixture may be due to a slight excess of reducing CO in the mixture. Indeed, an excess of 50–100 ppm of CO in the mixture is within the error of the catharometer detection. In order to clarify this question, a catalytic test was performed with a markedly oxidising mixture containing only 1000 ppm CO but still 2000 ppm NO. In spite of these oxidising conditions, a slight activation was also observed during the first cycle, and 40–45% NO conversions could be obtained for $T > 550$ °C, instead of 50% theoretically. The important fact is that the XRD diagram obtained after the test (two cycles) again evidences the presence of metallic copper and lanthanum oxide in addition to La_2CuO_4, which, however, remains the main phase (figure 4). We can conclude that, even in excess of NO and even if it is incomplete, the reduction of the catalyst takes place. Thus, the reaction of carbon monoxide with the oxygen of the catalyst obviously is easier than the reduction of the gaseous NO. On perovskites, it is usually admitted that NO is dissociatively adsorbed

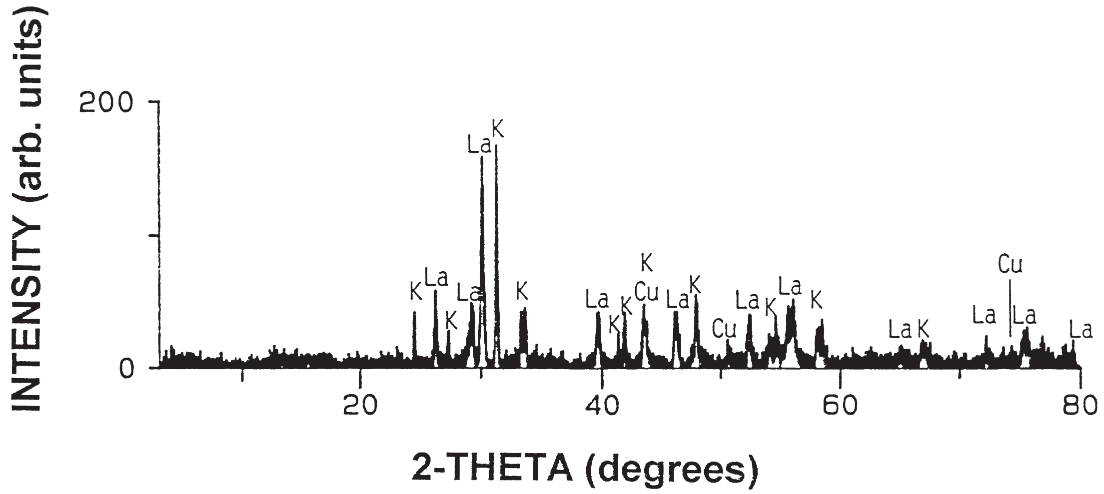

Figure 4. XRD patterns of the catalyst La_2CuO_4 after two catalytic cycles 150 → 650 → 150 °C performed under oxidising conditions (1000 ppm CO + 2000 ppm NO). K: La_2CuO_4 (K_2NiO_4-type structure); La: La_2O_3; Cu: metallic Cu.

on an oxygen vacancy, and then the adsorbed nitrogen atoms recombine and desorb as N_2. To regenerate the active surface of the catalyst, CO is necessary to eliminate some oxygen with CO_2 formation. In fact, there is probably a competition of adsorption of CO and NO on the same sites, and the reduction of the surface occurs at a higher rate.

The easy reducibility of perovskites under hydrogen or reducing CO + NO mixture has already been observed [7–9]. The important point to stress in the present study is that the La_2CuO_4 reduction leads to an improvement of the catalytic activity. This means that reduced copper species take part in the CO + NO reaction. Former results obtained in three-way catalysis with $La_2Cu_{1-x}Pd_xO_4$ solids have also shown a slow activation of the catalysts in the reaction conditions concomitant with a destruction of the initial mixed oxide structure. However, the copper reduced state has been ascribed to Cu_2O or Cu^+ species and metallic copper was never evidenced [4]. However, other groups found for different mixed oxides of the K_2NiF_4 type that the catalysts having an average oxidation number of copper close to 2 were most active for the NO reduction by CO [10,11].

To elucidate this point, we can postulate that if a reduced state of La_2CuO_4 is responsible for the higher activity, it should be possible to obtain directly this activated state by reducing the catalyst prior to the test. We have therefore carried out a prereduction of La_2CuO_4 by heating the solid at 650 °C under 2000 ppm CO in helium, with a 2 °C min^{-1} heating rate. According to the quantity of CO_2 formed during the TPR, the copper species in La_2CuO_4 are entirely reduced into metallic copper at the end of this pretreatment. The catalytic activity cycle of the solid issued from this pretreatment is shown in figure 5 and compared with that obtained on the initial La_2CuO_4 (first cycle-heating and fourth cycle-cooling). The activity of the prereduced sample is even improved compared with the stabilised activated state observed previously under CO + NO. The small irregularity at low temperature can be ascribed to a transitory NO desorption process. Consequently, it can be concluded from figure 5 that the formation of large copper particles is associated with a strong increase in the catalytic activity. Nevertheless, we have no experimental evidence that metallic copper atomss are the active sites. As a matter of fact, oxidised copper species might be present at the surface of the copper particles during the NO + CO reaction.

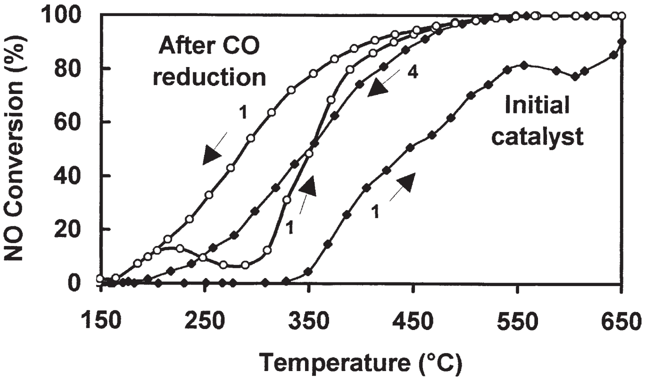

Figure 5. Comparison of the NO conversion curves as a function of temperature in the 2000 ppm CO + 2000 ppm NO reaction for La_2CuO_4 as prepared and after a TPR treatment under CO. For the initial catalyst (♦), ↑1 and ↓4 refer to the catalytic activity during the 1st cycle (heating) and 4th cycle (cooling) respectively. For the catalyst pretreated under CO (○), the two curves ↑1and ↓1 refer to the 1st cycle, heating and cooling respectively.

4. Conclusion

La_2CuO_4 is an active catalyst for the reduction of NO by CO. During the catalytic test, its activity increases up to a stabilised level. In this activated state, the solid is found to be reduced with the formation of metallic copper and lanthanum oxide. The results seem to indicate that metallic copper species are the most active sites for the CO + NO reaction. Finally, this reduction and the resulting activation are not determined by the stoichiometry of the reaction mixture. They can occur also under oxidative reaction conditions, when NO is present in large excess compared to CO.

Acknowledgement

The authors want to express their gratefulness to Renault SA, which has enabled LACE by their financial support to carry out this study. They are indebted to Mr. B. Pommier for his help in the catalytic activity measurements.

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