



Full paper / Mémoire

Influence of the nature of the lanthanide element of Ln_2CuO_4 precursors on the catalytic activity obtained after activation in the CO + NO reaction

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Abstract

Three lanthanide cuprates Ln_2CuO_4 ($\text{Ln} = \text{La}, \text{Pr}$ and Nd) have been studied in the CO + NO reaction. Under reaction conditions, a reduction of the cuprate was observed, with formation of metallic copper, which constitutes the active species in the reaction. After stabilisation, the resulting activity is lower when La in La_2CuO_4 is replaced by Pr or Nd. This decrease in activity has been related to a different reducibility of the cuprates, as shown by TPR under H_2 . When La is substituted by Pr or Nd, a higher temperature of formation of the copper active sites should induce the growth of bigger copper particles, which could be at the origin of the observed difference in activity. **To cite this article:** S.D. Peter et al., C. R. Chimie 7 (2004).

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Résumé

Trois cuprates de lanthanide Ln_2CuO_4 ($\text{Ln} = \text{La}, \text{Pr}$ et Nd), synthétisés à 1000 °C, ont été étudiés dans la réaction CO + NO entre 150 et 650 °C. Les catalyseurs s'activent sous réactifs et, dans les trois cas, on observe la réduction du cuprate, avec formation de cuivre métallique. La comparaison des activités après stabilisation montre que le remplacement du lanthane dans La_2CuO_4 par Pr ou Nd conduit à des systèmes moins actifs. Ces différences d'activité ont été reliées aux réductibilités différentes de ces oxydes binaires observées par RTP sous H_2 . Quand le rayon ionique du lanthanide diminue de La à Nd, la structure cristalline de l'oxyde devient plus stable et la température moyenne de réduction augmente d'environ 200 °C. Cette température plus élevée de formation des espèces actives de cuivre doit conduire à des particules plus grosses, ce qui pourrait être à l'origine de la différence d'activité observée. **Pour citer cet article :** S.D. Peter et al., C. R. Chimie 7 (2004).

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Keywords: La_2CuO_4 ; Lanthanide cuprate; Praseodymium; Neodymium; CO + NO reaction

Mots clés : La_2CuO_4 ; Cuprate de lanthanide ; Praséodyme ; Néodyme ; Réaction CO + NO

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1. Introduction

Perovskite-type ABO_3 mixed oxides [1–3] and related A_2BO_4 structures [4–7] had been investigated as catalysts for the exhaust gas after-treatment of automobiles since around 30 years. Their interest is still under study [8–11] and, recently, their introduction to automotive series application, in combination with precious metals, was announced by a car manufacturer [12]. Perovskites are of high thermal stability in oxidation reactions and allow the incorporation of a large number of different metal ions [13]. In this context, we have shown that the partial substitution of copper in La_2CuO_4 by small quantities of palladium [4] or iron [7] leads to an activity enhancement in the CO + NO reaction. In the present paper, we investigate the influence of the Ln^{3+} rare-earth ion in the Ln_2CuO_4 binary oxide. Therefore we replaced La by its homologues Pr and Nd, leading to Pr_2CuO_4 and Nd_2CuO_4 . As described in former publications, the catalysts were tested in the CO + NO reaction.

2. Experimental

The catalysts were prepared by the so-called evaporation–decomposition method, as exactly described in a former work [5]. Starting from the corresponding nitrates and passing by an intermediate decomposition at 500 °C, the final calcination temperature was 1000 °C.

For chemical analysis, solids were dissolved in a mixture HF/HCl/HNO₃. The quantification of Cu was done by AAS on a Perkin Elmer AAS 1100 using an air/C₂H₂ flame. For the lanthanides, the apparatus used was a Spectroflame D with an Argon-ICP.

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

BET area was measured on 1 g of sample by adsorption of N₂ at –196 °C. Previously, a desorption treatment was carried out under a vacuum of 10^{–2} Pa for 2 h at 500 °C.

Temperature programmed reduction (TPR) experiments under 1% H₂/Ar (1.2 l h^{–1}) were performed up to 900 °C with 50 mg of non pre-treated sample, diluted in 150 mg of SiC. The heating rate was 5 °C min^{–1} and the H₂ uptake was detected by thermal conductivity.

The catalytic test was carried out between 150 and 650 °C on 200 mg of catalyst, with a reaction mixture of 2000 ppm CO and 2000 ppm NO diluted in He. Conditions were previously described in full detail [5]. It is important to note here that the temperatures corresponding to 50 and 80% conversion (T50, T80) and the activity values given in this paper were obtained after preconditioning the catalyst under reaction conditions, i.e. in the so-called stabilised state [5].

3. Results and discussion

3.1. Characterisation of the fresh solids

Chemical analysis of the prepared solids shows that the expected Ln/Cu atomic ratios were obtained within a tolerance below 10% in all cases (Table 1). However, a slight excess of copper with respect to the lanthanide stoichiometry can be noticed. Probably the rare earth salts used suffered from hydration, giving rise to a lack of the Ln-component. The specific surface areas of the Ln_2CuO_4 mixed solids were found to be very close to that of La_2CuO_4 , about 0.5 m² g^{–1}. The observed phases are the so-called K₂NiF₄-type structures, La_2CuO_4 , Pr_2CuO_4 and Nd_2CuO_4 . Besides very weak diffraction lines characteristic of compounds originating from the corresponding lanthanide precursors, La_2O_3 , PrO₂ and Nd(OH)₃, were identified.

The TPR profiles of the three Ln_2CuO_4 are given in Fig. 1. The mixed oxides are reduced within the temperature range 350–750 °C, but with marked differ-

Table 1
Characteristics of the Ln_2CuO_4 catalysts

Catalyst	BET area (m ² g ^{–1})	Analysis	XRD
La_2CuO_4	0.6	La 68.1% (68.5) ^a	La_2CuO_4 s ^b
		Cu 15.8% (15.7)	La_2O_3 ? vw
		$[La_2Cu_{1.02}O_4]$ ^c	
Pr_2CuO_4	0.4	Pr 64.9% (68.8)	Pr_2CuO_4 s
		Cu 15.8% (15.5)	PrO ₂ vw
		$[Pr_2Cu_{1.08}O_4]$	
Nd_2CuO_4	0.5	Nd 65.7% (69.3)	Nd_2CuO_4 s
		Cu 15.2% (15.3)	Nd(OH) ₃ vw
		$[Nd_2Cu_{1.05}O_4]$	

^a Theoretical values for ideal stoichiometry.

^b Intensity of the diffraction peaks: s: strong, vw: very weak.

^c Formula calculated from chemical analysis.

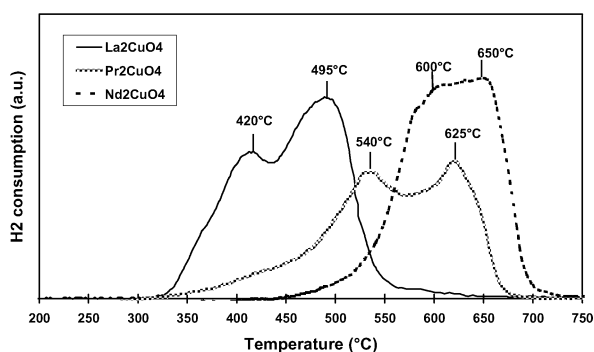


Fig. 1. TPR profiles of the three Ln_2CuO_4 mixed oxides.

ences between each other. La_2CuO_4 exhibits two main peaks at 420 and 495 °C, which may be attributed to reduction of Cu^{2+} to Cu^0 via the intermediate formation of Cu^+ [14]. When Pr or Nd substitutes for La, the reduction occurs at higher temperature, with maxima at 540–625 °C for Pr_2CuO_4 and 600–650 °C for Nd_2CuO_4 . The calculation of the H_2 consumption up to 750 °C shows an almost complete reduction of Ln_2CuO_4 in Cu^0 and Ln_2O_3 , the reduction percentage in metallic copper being 104, 95 and 97%, respectively, for La_2CuO_4 , Pr_2CuO_4 and Nd_2CuO_4 .

3.2. Catalytic activity of Ln_2CuO_4

The T80 and T50 temperatures for the NO conversion are plotted in Fig. 2 as a function of the ionic radius of the rare earth ion. The dashed lines represent the

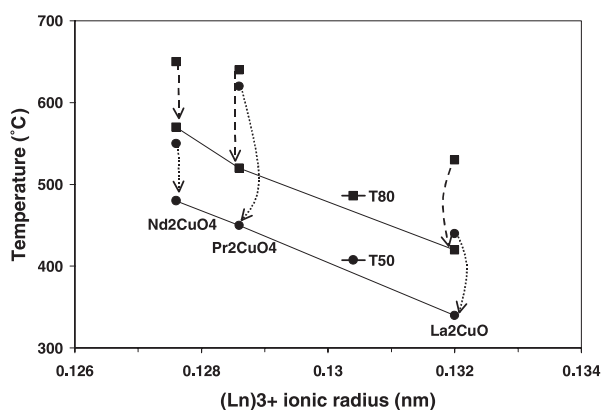


Fig. 2. Light-off temperatures for 50 and 80% conversion in the CO + NO reaction as a function of the lanthanide ionic radius. The upper points correspond to the first run, whereas the lower points are those obtained after stabilisation of the activity. The points are connected by dashed arrows in order to show the activation of the catalysts under reaction conditions (decrease of T50 and T80).

activation observed between the first temperature rise of the test and after catalytic stabilisation, i.e. when two complete cycles of heating and cooling under reaction conditions had been run. This phenomenon of catalytic activation under reaction conditions had already been described in previous work [5]. The values plotted here are those after stabilisation of the catalysts. The T80 and T50 values for Nd_2CuO_4 and Pr_2CuO_4 are by around 100–140 K higher than for La_2CuO_4 , which therefore is the most active of the three catalysts.

In addition to N_2 , some N_2O is formed. The selectivity to N_2O is close to 100% at low temperature (200 °C) and then decreases with temperature. It is about 10% at 450 °C. However, the maximum N_2O production (≈ 100 ppm) was observed at around 400 °C for Pr_2CuO_4 and Nd_2CuO_4 , as it is observed for this type of solids [6].

After stabilisation of the activity, the apparent activation energies given in Table 2 are equal with values around 45 kJ mol^{-1} for the three Ln_2CuO_4 oxides, whatever the lanthanide ion is. Before activation under reaction conditions the values differ between the catalysts, 103 kJ mol^{-1} for Pr_2CuO_4 , 88 kJ mol^{-1} for Nd_2CuO_4 and 31 kJ mol^{-1} for La_2CuO_4 . However, in the latter case, the Arrhenius plot varies strongly during the temperature rise and is not really reliable. In the low temperature domain, it is higher than 150 kJ mol^{-1} .

The activity per gram of La_2CuO_4 shown in Fig. 3 was found to be 4 times higher than for the oxide containing Nd and still 2–3 times higher than for the Pr-based oxide, depending on the temperature at which the activity was measured. Thus, as seen in Fig. 3, the catalytic activity seems to increase almost linearly with the ionic radius of the rare-earth element.

Table 2
Apparent activation energies of the Ln_2CuO_4 oxides before and after activation under CO + NO reaction conditions

catalyst	Apparent activation energies E_a^a (kJ mol^{-1})	
	before	after
La_2CuO_4	(31) ^b	45
Pr_2CuO_4	103	46
Nd_2CuO_4	88	44

^a All values with an uncertainty of ± 5 kJ mol^{-1} .

^b Questionable value given in brackets, energy variable during the temperature rise.

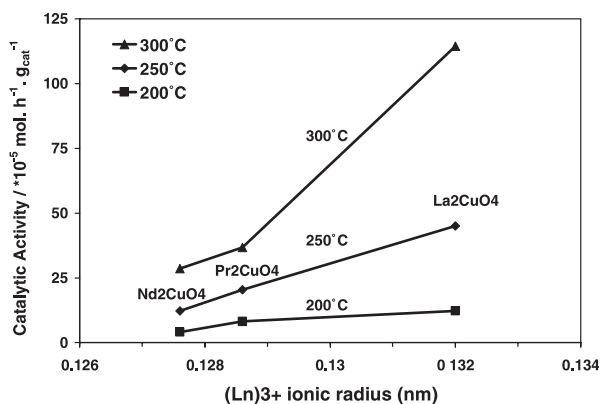


Fig. 3. Specific catalytic activity in the CO + NO reaction plotted as a function of the lanthanide ionic radius.

3.3. Modifications of Ln_2CuO_4 under reaction conditions

We had previously found [5] that La_2CuO_4 is subject to modifications under CO + NO reaction conditions, leading to the formation of metallic copper and lanthanum hydroxide resulting from hydration of the oxide after exposure to air. In order to check whether this reduction is restricted to lanthanates or is also possible for other rare earth oxides, we recorded X-ray diffraction patterns of the Pr_2CuO_4 and Nd_2CuO_4 samples issued from the catalytic test. In Table 3, their phase composition is compared to La_2CuO_4 in the same state.

We can state that the initial Ln_2CuO_4 binary oxide has been completely transformed during the activation

Table 3

Phase identification of the Ln_2CuO_4 catalysts before and after CO + NO testing

Catalyst	XRD		XRD	
	before CO + NO test		after CO + NO test	
La_2CuO_4	La_2CuO_4	s ^a	$\text{La}(\text{OH})_3$	s
			metallic	m
			Cu	
Pr_2CuO_4	La_2O_3 ?	vw	La_2CuO_4	vw
	Pr_2CuO_4	s	$\text{Pr}(\text{OH})_3$	s
	PrO_2	vw	metallic	m
Nd_2CuO_4			Cu	
	Nd_2CuO_4	s	$\text{Nd}(\text{OH})_3$	s
	$\text{Nd}(\text{OH})_3$	vw	metallic	m
			Cu	
		NdCuO_2 ?	w	

^a Intensity of the diffraction peaks: **s**: strong, **m**: middle, **w**: weak, **vw**: very weak, (?) phase attribution questionable.

under the CO + NO mixture. As previously observed for La_2CuO_4 [5], the principal phases after reaction and exposition to air are the corresponding rare earth hydroxides $\text{Ln}(\text{OH})_3$ and metallic copper. The observed activation under reaction conditions thus corresponds to a reduction of the initial cuprate.

3.4. Discussion

The active sites for the CO + NO reaction should be the same for La_2CuO_4 , Pr_2CuO_4 and Nd_2CuO_4 . In fact, we found the same apparent activation energy for the three solids after the catalysts had reached their activated state under reaction conditions. We attribute this coincidence to the presence of metallic copper, the common component of the three samples. Indeed for La_2CuO_4 [7], the surface concentration of metallic copper was found to be related to the catalytic activity, and it was concluded that copper could be considered as the main active species in the reaction. It can be remarked that the presence of metallic copper does not exclude redox mechanisms involving copper in different valence states and occurring at the surface or at the interface with the lanthanide oxide. In the present work, the catalytic activities of the three solids after stabilisation are different and related to the ionic radius of the lanthanide. It suggests that the number of active copper sites should be different for the three solids, which implies some differences in the reduction steps of the original cuprates and in the formation of the copper particles. If we consider the ionic radii of the rare earth element with a coordination number of 12, they are of 0.1286 nm for Pr^{3+} and 0.1276 nm for Nd^{3+} compared to 0.1320 nm for La^{3+} [15]. These differences in ionic radii are small, but they correspond to different energetics of the cuprates crystal lattice. The smaller ionic radii for the Pr- and Nd-based catalysts result in a more compact structure, which makes the oxygen less labile and consequently the reduction of the oxide more difficult. This is evidenced by the TPR study under hydrogen, which clearly shows that the smaller the ionic radius, the higher the reduction temperature. Cu^0 is formed less easily when La is substituted by Pr or Nd. However, the link between this difference in reducibility observed by TPR and the changes in catalytic activity requires further discussion. In TPR processes, both thermodynamic and kinetic factors are important to control the initial forma-

tion of copper nuclei and then the interface propagation inside the bulk [16]. However, in the present catalytic study, the differences of activities in the CO + NO reaction cannot be related directly to a variation in the reduction rate constants of the cuprates, because the activities were measured on solids after stabilisation, i.e. after formation of the copper particles. In these conditions, the decrease in activity from La to Nd should be related to an increase in the copper particle sizes, which means a lower number of active sites. Indeed, the easier reducibility of La_2CuO_4 at low temperature favours the formation of a high number of copper nuclei thus inducing the formation of a dispersed copper phase. On the other hand, for the less reducible oxide (Nd_2CuO_4), the reduction proceeds at higher temperature. There are a smaller number of nuclei and the reduction therefore results in the growth of large particles, all the bigger as the high temperature favours their sintering. Consequently, the number of active sites is decreased and thus the catalytic activity.

4. Conclusion

The replacement of lanthanum in La_2CuO_4 mixed oxides by praseodymium or neodymium leads to less active catalysts for the CO + NO reaction. As already found for La_2CuO_4 [5], a reduction under reaction conditions to metallic copper was observed also for Pr_2CuO_4 and Nd_2CuO_4 . Since Cu^0 sites are the active species in the three cases, the increase in the reduction temperatures of the mixed oxides, related to the change in ionic radii of the rare earth element, seems to be at the origin of this decrease in activity, because it results in copper particles with higher particle sizes.

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