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New spinel materials for catalytic NO–CO reaction: nonstoichiometric nickel–copper manganites

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Abstract

Nonstoichiometric nickel–copper spinel manganites were found to be highly active for the reduction of nitric oxide by carbon monoxide at low temperature (300°C). The activity increases with the level of nonstoichiometry of the oxides and almost linearly with their specific surface area. Moreover, this activity was found to depend strongly on the copper content, nickel manganites being almost inactive. The influence of the surface state of the oxides was also investigated. Cuprous cations are thought to play the determining role in the catalytic cycle.

Keywords: Manganite (nickel–copper); Spinel; deNO_x; Nitric oxide; Carbon monoxide

1. Introduction

Previous works have shown the high surface reactivity of spinel oxides (such as copper cobaltites or nickel manganites) as well as their catalytic properties towards carbon monoxide and hydrocarbons oxidation [1–5]. Besides, numerous studies [6–10] have revealed that copper-containing materials such as copper-exchanged zeolites or supported copper oxide were among the most active catalysts known up to now for the reduction of nitrogen oxides. However, these compounds generally have a limited thermal stability and appear to be active only for significant contact times (typically 0.3–3 g s cm⁻³).

The aim of this paper is to report the activity for the NO–CO reaction of new spinel materials: nonstoichiometric nickel–copper manganites, that associate the great surface reactivity of nickel manganites [5]

and the presence of copper. These oxides are highly divided and cation-deficient materials (Table 1). This nonstoichiometry can be explained by the presence in the spinel structure of cations with oxidation states higher than in stoichiometric oxides; hence cationic vacancies are required for the conservation of the crystal neutrality.

2. Experimental

2.1. Oxide catalysts

The nonstoichiometric nickel–copper manganites studied herein correspond to the general formula Ni_xCu_yMn_(3-x-y)□_{3δ/4}O_{4+δ}. These compounds were synthesised at 350°C for 6 h by thermal decomposition in air of mixed nickel–copper–manganese oxalates coprecipitated by introduction of an aqueous solution of ammonium oxalate (0.2 mol l⁻¹) into an aqueous solution of nickel, copper and manganese

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Table 1
Specific surface area (Sp) and level of nonstoichiometry (δ) of various nickel and nickel-copper manganites synthesised in air at 350°C for 6 h

Oxide composition			Sp (m ² g ⁻¹)	δ
x _{Ni}	y _{Cu}	Mn		
Nickel manganites				
0.30	0	2.70	165	0.48 ± 0.03
0.45	0	2.55	170	0.51 ± 0.03
0.84	0	2.16	250	0.60 ± 0.03
1.05	0	1.95	250	0.43 ± 0.03
Nickel copper manganites				
0.25	0	2.75	165	0.45 ± 0.03
0.25	0.25	2.50	160	
0.30	0.30	2.40	160	0.47 ± 0.03
0.30	0.33	2.37	155	
0.25	0.38	2.37	155	0.37 ± 0.02
0.22	0.57	2.21	150	
0.25	0.80	1.95	150	0.66 ± 0.03
0.70	0	2.30	185	
0.70	0.26	2.04	180	0.51 ± 0.03
0.70	0.65	1.65	160	
0.70	0.75	1.55	155	0.27 ± 0.02
0.70	0.91	1.39	140	
0.77	0.35	1.88	110	0.20 ± 0.02

nitrates (0.2 mol l⁻¹) at room temperature. The detailed synthesis process is described elsewhere [11].

2.2. Catalytic tests

The total conversion rate of NO, τ_{NO} , was determined through the formula

$$\tau_{\text{NO}} = 100 \left(1 - \frac{[\text{NO}]_f}{[\text{NO}]_i} \right)$$

where the values into brackets stand for the partial pressures of the related gas. The subscript “i” refers to initial values (before the catalyst) whereas “f” means after conversion. On the other hand, specific and intrinsic activities, respectively noted A_{Sp} and A_i , were also defined as follows:

$$A_{\text{Sp}} = \frac{\tau_{\text{NO}}[\text{NO}]_i F}{m} \text{ and } A_i = \frac{A_{\text{Sp}}}{\text{Sp}}$$

where “m” is the weight of the catalyst sample, “Sp” its specific surface area and “F” the gas flow. A_i is expressed in mol s⁻¹ m⁻² and A_{Sp} in mol s⁻¹ g⁻¹.

The inlet gas composition was either 1% NO + 1% CO + Ar or 1% NO + 2% CO + 0.5% O₂ + Ar. The gas phase composition during the tests was determined by infrared spectroscopy (see [12]) using a NICOLET 510P FT-IR spectrometer. For some experiments, the concentration in nitrogen was followed by gas chromatography (molecular sieve 13×), helium being then taken as the gas vector. At no time was nitrogen dioxide observed during the tests, and the balance in nitrogen was checked in all cases.

The whole set of catalytic tests was run with a contact time close to 0.015 g s cm⁻³, using ca. 20 mg of catalyst and a gas flow of 80 cm³ min⁻¹ (atmospheric pressure). Unless otherwise specified, the oxides were first pretreated in 20% O₂ + 80% Ar at 300°C for 1 h. Such a pretreatment was used in order to clean the surface.

3. Results

The catalytic reaction studied in this work is the reduction of nitric oxide by carbon monoxide, according to the equation: NO + CO → CO₂ + 1/2N₂.

The inlet gas composition was first set to stoichiometry with 1% NO + 1% CO + Ar. In the case of the oxide Ni_{0.77}Cu_{0.35}Mn_{1.88}□_{3δ/4}O_{4+δ}, the conversion of nitric oxide began at ca. 150°C (Fig. 1). Up to ca. 250°C, nitrous oxide was the only product of the

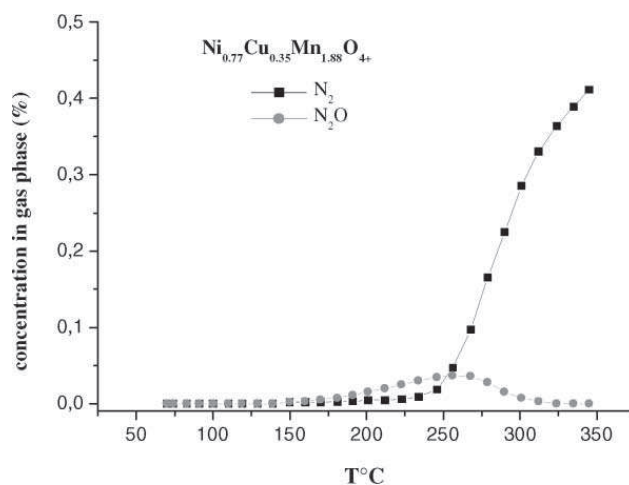


Fig. 1. Evolution of the concentrations of nitrogen and nitrous oxide during the conversion of NO with Ni_{0.77}Cu_{0.35}Mn_{1.88}□_{3δ/4}O_{4+δ} (Sp = 110 m² g⁻¹).

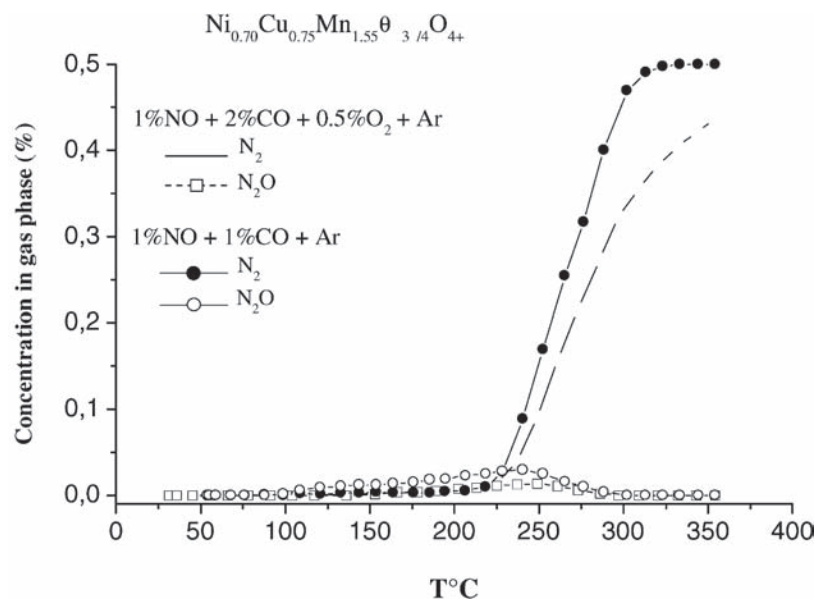


Fig. 2. Effect of the presence of oxygen on the conversion of NO to N_2 and N_2O with $\text{Ni}_{0.70}\text{Cu}_{0.75}\text{Mn}_{1.55}\square_{3\delta/4}\text{O}_{4+\delta}$.

reaction. Indeed, the analysis by gas chromatography only showed traces of nitrogen (less than 0.01%). Above 260°C, the concentration of nitrous oxide in the gas phase rapidly decreased with increasing temperature, simultaneously with the appearance of nitrogen in the gas phase, and N_2O was no more observed beyond 310°C. It should be noted that, despite the high surface area of these oxides, only a weak sorption phenomenon was detected at the very beginning of the experiment. This is probably due to the low amount of catalyst used.

On the other hand, successive tests carried out in the same conditions and on the same sample, have given similar conversion profiles, provided that temperature should not exceed 320°C; in other words, no noticeable deactivation was detected under this temperature.

In order to determine the influence of the presence of oxygen in the gas phase, we followed the conversion of nitric oxide for both stoichiometric gas mixtures: 1% NO + 1% CO + Ar and 1% NO + 2% CO + 0.5% O_2 + Ar in the case of the oxide $\text{Ni}_{0.70}\text{Cu}_{0.75}\text{Mn}_{1.55}\square_{3\delta/4}\text{O}_{4+\delta}$ (Fig. 2). As can be seen, the same profile is obtained in both cases, and nitrous oxide is observed at low temperature (from 150 to 290°C in the presence of oxygen and from 100 to 290°C without oxygen) whereas nitrogen is formed at higher temperature. However, the nitric oxide

conversion rate reached at a given temperature is always lower in the presence of oxygen. Unfortunately if the catalytic test is performed with the oxidising inlet gas composition: 1% NO + 1% CO + 0.5% O_2 + Ar, then the conversion of nitric oxide is close to zero whatever the temperature. The catalytic tests reported hereafter were carried out in the presence of oxygen, with the composition 1% NO + 2% CO + 0.5% O_2 + Ar.

The effect of the chemical composition of the oxides $\text{Ni}_x\text{Cu}_y\text{Mn}_{(3-x-y)}\square_{3\delta/4}\text{O}_{4+\delta}$ was also determined. For a fixed nickel content x_{Ni} , the catalytic activity increased with y_{Cu} (Fig. 3a) but, beyond a limit copper content, the activity tended to decrease again (Fig. 3b). For a fixed value of y_{Cu} , the influence of x_{Ni} on the activity of the oxides was less clear (Fig. 4). Indeed, a slight increase of the activity was evidenced when x_{Ni} increases, but only below 300°C.

As was said before, such nickel-copper manganites synthesised at low temperature (300–400°C) are highly divided materials, and have large specific surface areas S_p (Table 1). However, when the oxalate precursors are decomposed at higher temperatures, S_p drops down (Table 2). Hence, the nitric oxide conversion rate could be measured (Fig. 5) as a function of S_p , and a linear relationship between the specific surface area of the catalyst and the conversion rate was observed.

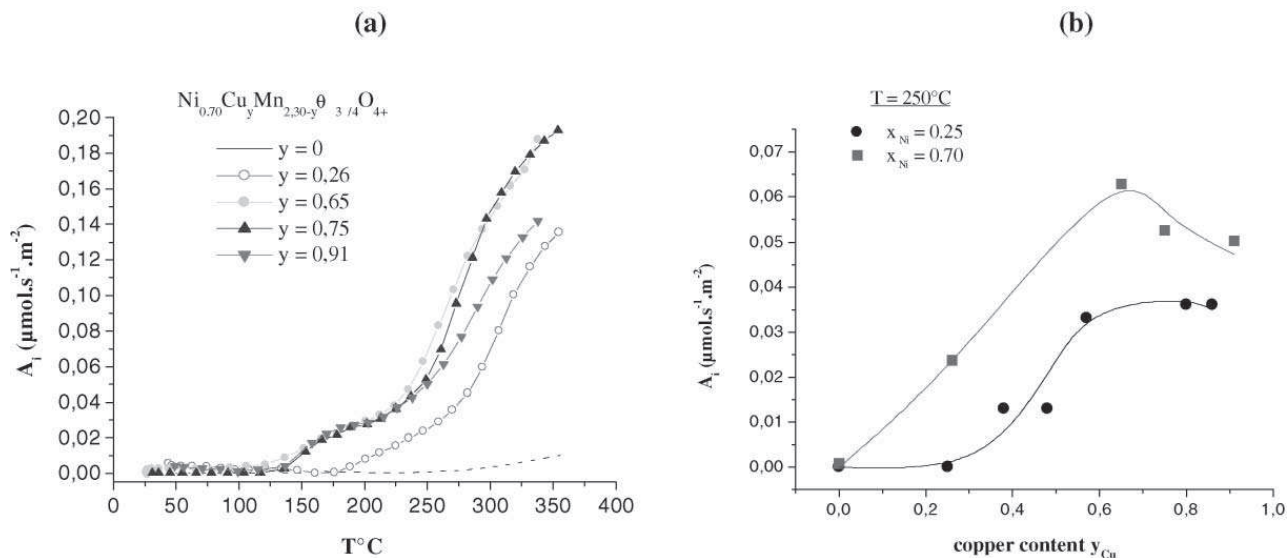


Fig. 3. Effect of the copper content of the oxides on the intrinsic activity (inlet composition: 1% NO + 2% CO + 0.5% O₂ + Ar) for $x_{\text{Ni}} = 0.70$.

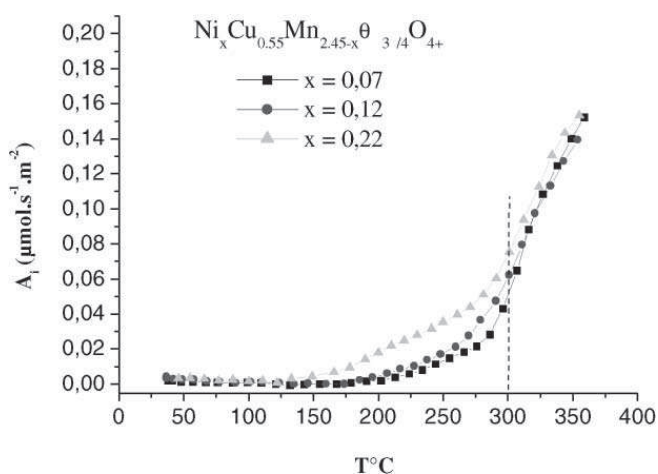


Fig. 4. Effect of the nickel content of the oxides on the intrinsic activity (inlet composition: 1% NO + 2% CO + 0.5% O₂ + Ar) for $y_{\text{Cu}} = 0.55$.

Table 2

Evolution of the specific surface area (Sp) and the level of nonstoichiometry (δ) of $\text{Ni}_{0.28}\text{Cu}_{0.80}\text{Mn}_{1.92}\square_{3\delta/4}\text{O}_{4+\delta}$ as a function of the synthesis temperature

$T_{\text{decomp.}}$ ($^{\circ}\text{C}$)	Sp ($\text{m}^2 \text{g}^{-1}$)	$\delta \pm 0.02$
400	135	0.36
425	65	0.30
470	45	0.15
700	3	0

The influence of the level of nonstoichiometry (δ) of the oxides on the activity was more difficult to determine because of the close relationship existing between Sp and δ (Table 2). However, the heating of nonstoichiometric manganites in an inert atmosphere (which is accompanied by the release of gaseous oxygen [11]) decreases their level of nonstoichiometry without affecting Sp if the temperature is lower than the synthesis temperature of the oxide. Hence, the influence of δ could be determined comparing

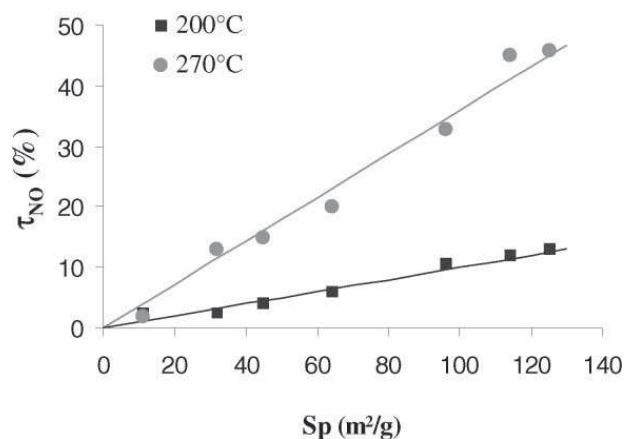


Fig. 5. Effect of the specific surface area on the conversion rate of NO (inlet composition: 1% NO + 2% CO + 0.5% O₂ + Ar) for $\text{Ni}_{0.70}\text{Cu}_{0.65}\text{Mn}_{1.65}\square_{3\delta/4}\text{O}_{4+\delta}$.

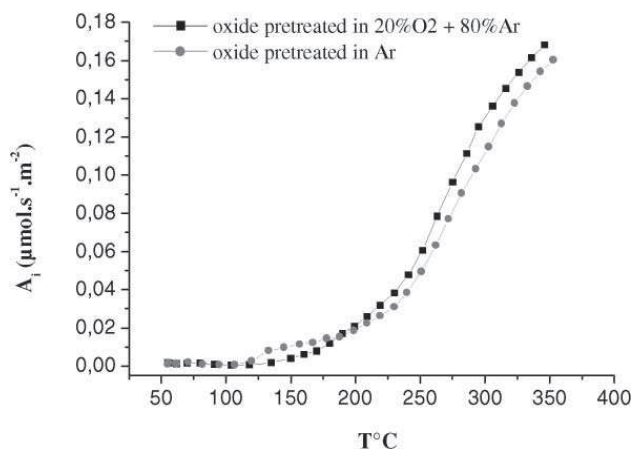


Fig. 6. Effect of the pretreatment of the oxides on the intrinsic activity (inlet composition: 1% NO + 2% CO + 0.5% O₂ + Ar) for Ni_{0.70}Cu_{0.65}Mn_{1.65}□_{3δ/4}O_{4+δ}.

the activity reached in the case of an oxide pretreated at 300 °C for 1 h either in 20% O₂ + 80% Ar or in pure argon. For example, in the case of the oxide Ni_{0.70}Cu_{0.65}Mn_{1.65}□_{3δ/4}O_{4+δ}, a pretreatment in O₂ + Ar conducted to δ = 0.27 whereas, for the argon-pretreated oxide, δ was close to 0.20. The conversion of nitric oxide to N₂O began near 120 °C (Fig. 6) for the argon-pretreated whereas it only started at 150 °C for the oxide pretreated in O₂ + Ar. However, the activity above 200 °C was higher in the case of the oxide pretreated in O₂ + Ar.

As stated above, several authors have already pointed out the good activity of copper-containing catalysts for the reduction of nitrogen oxides [6–10]. Therefore, it was interesting to compare the specific activity of the manganite Ni_{0.70}Cu_{0.65}Mn_{1.65}□_{3δ/4}O_{4+δ} to that obtained with Cu/Al₂O₃ containing 3 and 18% of copper (Fig. 7). It is clear that the nickel–copper manganite was a far better catalyst than supported copper oxide.

The partial orders for NO and CO were first determined in the temperature range 120–200 °C with the inlet gas composition 1% NO + 1% CO + Ar. In this region, nitrous oxide was the unique product of the reaction, and the reactor worked in differential conditions (conversion rate inferior to 10%). As can be seen (see Table 3), the partial order for nitric oxide was in all cases of 0.7, whatever the chemical composition of the oxide. On the contrary, the order corresponding to carbon monoxide was in the range 0.8–0.9 for

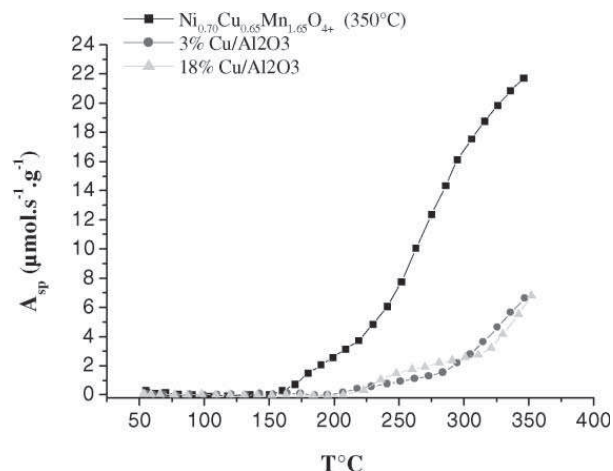


Fig. 7. Comparison of the specific activity of Ni_{0.70}Cu_{0.65}Mn_{1.65}□_{3δ/4}O_{4+δ} to that of Cu/Al₂O₃ (3 and 18% Cu), inlet composition: 1% NO + 1% CO + Ar.

the oxides (1), (2) and (3) but ca. 0.4 in the case of the oxides (4) and (5). When the order determination was performed at 300 °C, that is where nitrogen was the dominant product, the same values as before were found.

The activation energy (E_A) of the reaction was determined from the slope of the corresponding Arrhenius plots (Fig. 8). E_A can be considered, in first approximation, as constant in the temperature range 120–300 °C, and was found to be very similar (in the range 35–45 kJ mol⁻¹) for all oxides (Table 4). Since these values are rather low, it is important to note here that the experimental conditions used (catalyst weight: $m = 20$ mg, gas flow: $F = 80$ cm³ min⁻¹) were chosen so as to avoid external mass transfer limitations, as shown by the linearity of the plots $\tau_{NO} = f(m)$ and $\tau_{NO} = f(1/F)$ (Fig. 9).

In order to determine the influence of the oxidation state of the surface cations, several tests were carried

Table 3
Partial orders for the catalytic reduction of nitric oxide by carbon monoxide on nickel–copper manganites

	Ni _x Cu _y Mn _(3-x-y) □ _{3δ/4} O _{4+δ}		Partial orders	
	xNi	yCu	NO	CO
1	0.25	0.25	0.65	0.85
2	0.21	0.48	0.67	0.83
3	0.70	0.26	0.69	0.87
4	0.70	0.65	0.70	0.45
5	0.70	0.91	0.70	0.35

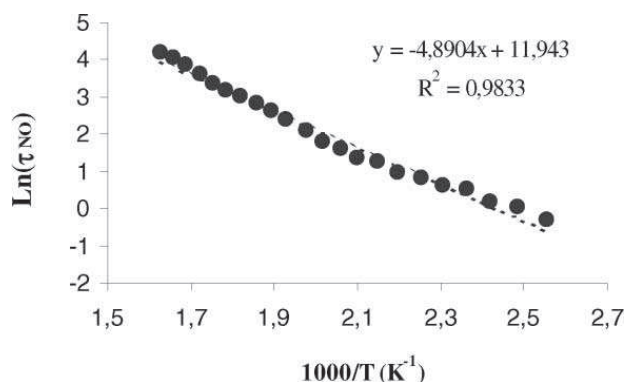


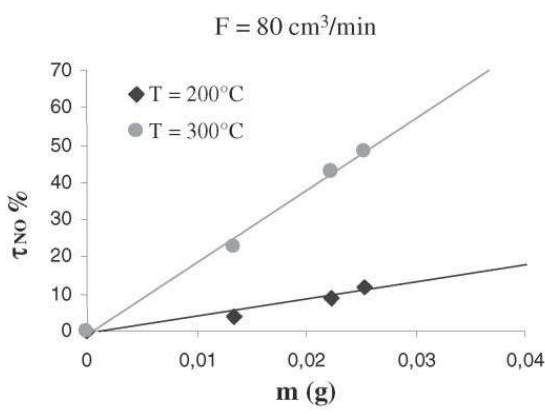
Fig. 8. Arrhenius plot $\ln(\tau_{\text{NO}}) = f(1000/T)$ for $\text{Ni}_{0.25}\text{Cu}_{0.25}\text{Mn}_{2.50}\square_{3\delta/4}\text{O}_{4+\delta}$ (inlet composition: 1% NO + 1% CO + Ar).

Table 4

Activation energy (E_A) for the catalytic reduction of nitric oxide by carbon monoxide on nickel–copper manganites

	$\text{Ni}_x\text{Cu}_y\text{Mn}_{(3-x-y)}\square_{3\delta/4}\text{O}_{4+\delta}$		E_A (kJ mol ⁻¹)
	x_{Ni}	y_{Cu}	
1	0.25	0.25	46
2	0.25	0.57	40
3	0.70	0.26	45
4	0.70	0.65	31
5	0.70	0.91	35

out at constant temperature (300°C) with oxides pretreated at 300°C for 30 min in different atmospheres. Two distinct profiles of the conversion rate versus temperature plots could be discerned (Fig. 10a and b) depending on the kind of pretreating atmosphere



(reducing or inert/oxidising). For example, the conversion rate of NO (τ_{NO}) initially attained with the oxide $\text{Ni}_{0.70}\text{Cu}_{0.65}\text{Mn}_{1.65}\square_{3\delta/4}\text{O}_{4+\delta}$ pretreated in 1% CO/Ar (Fig. 10a) was 100%. From $t \approx 200$ s, τ_{NO} slightly decreased up to its stabilised value (ca. 90%). The conversion of CO rapidly increased from the introduction of the NO + CO gas mixture, and stabilised at 90% meeting up τ_{NO} from $t \approx 300$ s. On the contrary, when the oxide was pretreated in argon (Fig. 10b), the conversion rate of CO first attained 100% and stabilised at 80% from $t \approx 100$ s. On the other hand, the initial conversion rate of NO was close to 5% (after a rapid adsorption step). Then, it increased slowly up to 80% (from $t \approx 800$ s). A such kind of profile was also observed in the case of a pretreatment in air or in 1% NO/Ar. For a comparative overview, the evolution of the initial conversion rate of NO as a function of the pretreatment atmosphere was reported in Fig. 11 in the case of the oxides CuO (prepared by thermal decomposition at 500°C of copper oxalate, $m = 40$ mg, $\text{Sp} = 12$ m² g⁻¹) and $\text{Ni}_{0.70}\text{Cu}_{0.65}\text{Mn}_{1.65}\square_{3\delta/4}\text{O}_{4+\delta}$ ($m = 20$ mg). For both oxides, the higher conversion was obtained for reducing pretreatments (it might be added that without a reducing pretreatment copper oxide had a poor activity).

4. Discussion

The nonstoichiometric nickel–copper manganites associate the high surface reactivity of spinel oxides, already pointed out by several authors [1–5], and the

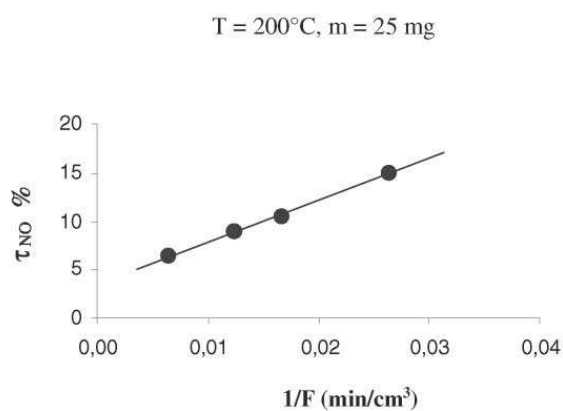


Fig. 9. Evolution of the conversion rate of NO as a function of the catalyst weight (m) and the reciprocal of the gas flow ($1/F$) for $\text{Ni}_{0.70}\text{Cu}_{0.91}\text{Mn}_{1.39}\square_{3\delta/4}\text{O}_{4+\delta}$ (inlet composition: 1% NO + 1% CO + Ar).

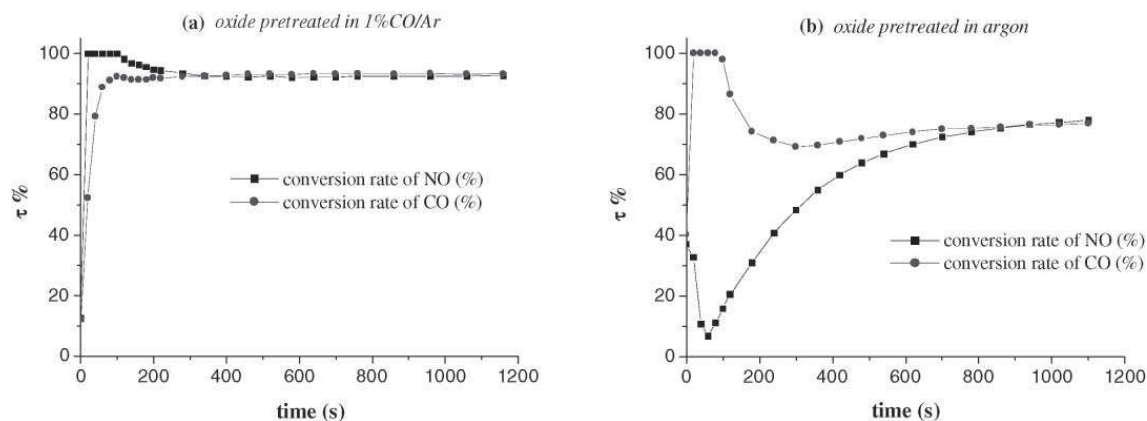


Fig. 10. Evolution with time of the conversion rate of NO at 300°C for $\text{Ni}_{0.70}\text{Cu}_{0.65}\text{Mn}_{1.65}\square_{3\delta/4}\text{O}_{4+\delta}$ pretreated in 1% CO/Ar (a) or in argon (b) (inlet composition: 1% NO + 1% CO + Ar).

presence of copper known to play an important role in the catalytic reduction of nitrogen oxides. This paper shows that such manganites are highly active in the reduction of nitric oxide by carbon monoxide. Indeed, for the most active catalysts, almost total conversion of nitric oxide can be obtained at temperatures as low as 300°C at short contact time (ca. $0.015 \text{ g s cm}^{-3}$). This activity increases with the surface area of the oxide and with its level of nonstoichiometry (probably due to the higher mobility of nonstoichiometric surface oxygen). These results underline the interest to synthesise these oxides at low temperature (300–400°C). The presence of oxygen in the gas phase inhibits the

reduction of NO by CO (Fig. 2). Hence, there is a high selectivity of the CO/O₂ reaction compared to CO/NO, as already reported [13]. The catalytic activity is closely related to the copper content of the oxides, nickel manganites being considered as almost inactive (see Fig. 3). The increase of nickel content only enhances the activity when copper is also present in the structure (Fig. 4). Thus, copper plays the central role in the catalytic mechanism. However, the activity tends to decrease slightly above a maximum limit of copper content (Fig. 3b), this maximum decreasing with increasing x_{Ni} . This point could be related to the presence of a second phase (such as CuO) highly dispersed on the surface of these oxides, as already assumed from X-ray photoelectron spectroscopy [14], arising from the difficulty to accommodate at the same time high copper and nickel contents within the spinel structure. This could also explain the lower values of the partial order of CO observed for manganites for which $x_{\text{Ni}} + y_{\text{Cu}} > 1$ (oxides (4) and (5), Tables 3 and 4) Indeed, the partial order for CO in the NO/CO reaction has been found close to zero for CuO [7].

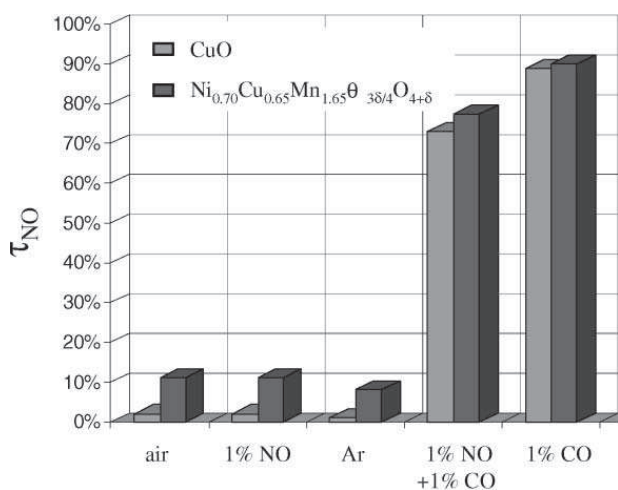
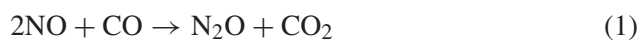


Fig. 11. Initial conversion rate of NO for $\text{Ni}_{0.70}\text{Cu}_{0.65}\text{Mn}_{1.65}\square_{3\delta/4}\text{O}_{4+\delta}$ pretreated at 300°C in different atmospheres (inlet composition: 1% NO + 1% CO + Ar).

Taking into account the nature of the reaction products (N_2 or N_2O), Shelef and Kummer [15] underlined that the reduction of nitric oxide had obviously to be accompanied by the formation of a nitrogen–nitrogen bond. Thus, the catalytic mechanism must explain the formation of such bonds. In this way, in the case of copper oxide, Davydov [16] appealed to Cu^+Cu^+ pairs involving cuprous cations in close proximity. On the contrary, Winter [17] studied the decomposition of nitric oxide over different metal oxide catalysts and

proposed a mechanism based upon pairs of anionic vacancies. Moreover, these authors also reported that the reduction of two molecules of nitric oxide not always leads to the simultaneous release of the two oxygen atoms. This point is in accordance with the works evidencing the formation of nitrous oxide as a reaction intermediate [15,16,18]. In all cases, the quantity of nitrous oxide formed reaches a maximum as a function of the temperature, because this compound is not stable at high temperature and decomposes to oxygen and nitrogen. Otto and Shelef [18] reported that nitrous oxide was the unique product of the reduction of NO by CO at $T < 200^\circ\text{C}$ in the case of the oxides NiO and $\alpha\text{Fe}_2\text{O}_3$, whereas nitrogen was the only product observed at higher temperature. In the present study, nitrous oxide was also found to be the only product of the reaction at temperatures lower than 250°C (Fig. 1) and nitrogen was the exclusive product of the reaction above 300°C . Thus, the reduction of nitric oxide by carbon monoxide on our catalysts could be a two-step process, involving the formation of nitrous oxide as an intermediate



Since the activation energy remains globally the same (Fig. 8) in the whole temperature range, we can assume that the reaction mechanism remains the same as well. Reaction (2), corresponding to the decomposition of nitrous oxide, is generally considered as a fast process compared to reaction (1). In particular, Davydov et al. [16] reported that the decomposition of nitrous oxide could be assimilated to an impact mechanism on a surface. The similarity of the reaction orders found at $120\text{--}200^\circ\text{C}$ and 300°C tends effectively to show that the decomposition of N_2O is rapid and does not influence the global kinetics of the reaction. In order to check this point, the conversion of nitrous oxide (catalyst: $\text{Ni}_{0.30}\text{Cu}_{0.30}\text{Mn}_{2.40}\square_{3\delta/4}\text{O}_{4+\delta}$) was followed as a function of the temperature (Fig. 12) without carbon monoxide (inlet composition: 0.5% $\text{N}_2\text{O}/\text{Ar}$). This experiment showed that nitrous oxide was not decomposed over such catalysts, at least below 370°C (curve a). In the presence of carbon monoxide (inlet composition: 0.5% $\text{N}_2\text{O} + 0.5\% \text{CO} + \text{Ar}$), the conversion of N_2O began from 200°C (curve b). Furthermore, from the comparison of curves b and c,

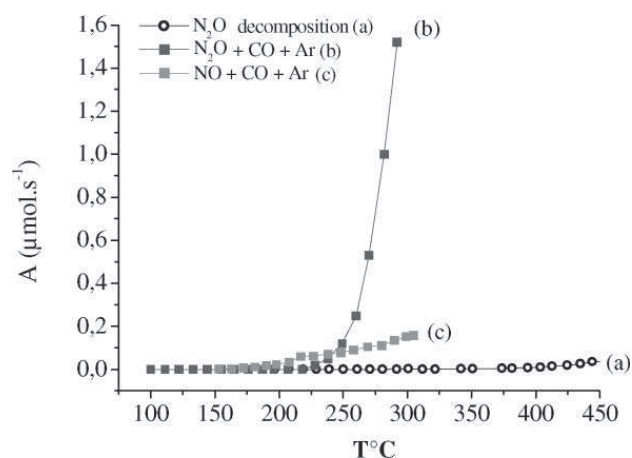


Fig. 12. (a) Decomposition of N_2O (0.5% Ar); (b) reduction of N_2O by CO (0.5% $\text{N}_2\text{O} + 0.5\% \text{CO} + \text{Ar}$); (c) reduction of NO by CO (1% NO + 1% CO + Ar) on the oxide $\text{Ni}_{0.30}\text{Cu}_{0.30}\text{Mn}_{2.40}\square_{3\delta/4}\text{O}_{4+\delta}$.

it appeared that the reduction of N_2O by CO was far faster than the reduction of NO by CO. Therefore, these results confirm that the overall reaction is not limited by the decomposition of nitrous oxide.

The determination of the initial activity of nickel–copper manganites according to the pretreating atmosphere showed that, at 300°C , more than 10 min were necessary to attain the stabilised activity in the case of an oxide pretreated in an inert or oxidising atmosphere. On the contrary, the conversion rate of nitric oxide grew up to 100% in a few seconds after a reducing pretreatment. This point can be explained by the involvement of “reduced” active centres in the catalytic mechanism. The reduction of nitric oxide by carbon monoxide on a $^{18}\text{O}_2$ -exchanged manganite showed that carbon dioxide $\text{C}^{18}\text{O}^{16}\text{O}$ was formed from the first seconds after contact between NO and CO molecules and the surface of the oxide, whereas the conversion of NO only began 200 s afterwards. This evidences a surface reduction of the oxide by CO with no involvement of NO, which can be related to the formation of reduced centres active for the catalytic reaction as assumed above. Hence, the complete suppression of NO conversion in the $\text{CO} + \text{NO} + 0.5 \text{O}_2$ reaction could be explained by the fact that this oxidising medium prevents the reduction of the catalyst by CO.

As with nickel–copper manganites, a pretreatment of CuO under reducing conditions (such as 1% CO/Ar at 300°C) led to the highest activity (Fig. 11), and an X-ray diffraction analysis after such a treatment

showed that CuO had mainly been reduced to Cu₂O. On the other hand, a pretreatment of CuO in 1% CO/Ar at 450°C led to a decrease of the activity. In this last case, XRD showed that CuO had been reduced to a mixture of Cu₂O+Cu⁰. These results strongly suggest that, in all cases, cuprous cations Cu⁺ play the key role in the catalytic cycle, whereas Cu²⁺ or metallic copper are much less active.

The study of the chemisorption of CO and NO on nickel–copper manganites [19] have shown that (i) the majority of the adsorption sites are common for NO and CO; (ii) nitric oxide adsorbs in a molecular way (not dissociative) on such oxides; and (iii) NO is able to displace the majority of CO preadsorbed molecules whereas the contrary does not hold. However, the existence of some CO-specific adsorption sites was also pointed out, and the strong increase of the equilibrium coverage of CO with the copper content of the oxide [19] tends to show that these specific adsorption sites could be copper cations. Moreover, the study by infrared spectroscopy of the adsorption of carbon monoxide on the surface of nickel–copper manganites indicates the presence of an IR absorption band at 2135 cm⁻¹ (not detected for copper-free oxides) that can be attributed to carbonyls Cu⁺–CO by comparison with Davydov's results [16] obtained in the case of copper oxide. Then, cuprous cations would be the only access points for CO to the surface of nickel–copper manganites when NO is also present in the gas phase. This result is particularly important since the partial orders towards CO and NO (see Table 3) were found to be fractional, which indicates that both carbon monoxide and nitric oxide might react in their adsorbed state.

We have shown above that the catalytic activity of these Ni–Cu–Mn spinel oxides increases with increasing surface area and with δ , which can be ascribed to a higher mobility of nonstoichiometric surface oxygens. A high mobility might facilitate the reduction of surface copper cations Cu²⁺ by CO to give the active centers Cu⁺, which could explain the relationship between δ and the catalytic activity of these oxides.

5. Conclusions

This work clearly evidences the high catalytic activity of nonstoichiometric nickel–copper manganites for the reduction of nitric oxide by carbon monoxide

at low temperature and short contact time (0.015 g s cm⁻³) since, for the most active catalysts, almost total conversion of NO to N₂ can be obtained from 300°C. The activity increases with the level of nonstoichiometry of the oxides and almost linearly with their specific surface area. On the other hand, this activity was found strongly dependent on the copper content, nickel manganites being almost inactive. The nickel content had a lesser influence, and only at low temperature. Cuprous cations Cu⁺ were shown to play the key role in the catalytic process, probably because these ions would be the only access points for CO to the surface of the catalyst in the presence of NO. The reaction seems to occur via nitrous oxide as an intermediate, and the reduction of nitrous oxide by carbon monoxide appears as a fast process leading to nitrogen above 250°C.

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