

REACTIVITY OF PEROVSKITES AS AUTOMOTIVE CONVERTERS

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ABSTRACT

The reactivity of three perovskites containing cobalt in three different oxidation states, Co(II), Co(III) and Co (IV) has been studied under two types of gas flow composition : i) binary mixtures containing either CO + O₂, CO + NO or C₃H₈ + O₂ . ii) a complete gas mixture with CO + C₃H₈ + NO + O₂ . In both cases nitrogen was the balance gas. The reactivity order is found always to be the same, whatever the reaction : Co₃O₄ > LaCoO₃/Co₃O₄ ≈ LaCoO₃ > BaCoO_{2-x} > Ba₂CoWO₆ , and is correlated to the reducibility of the samples followed by TPR. The first four catalysts exhibit the same reactivity for the CO + O₂ reaction as classical Pt-Al₂O₃ and Pt-CeO₂/Al₂O₃ catalysts, their light-off temperatures being between 430 and 500 K. These perovskites give reproducible results after the surface has been changed by the reactant gases, this phenomenon has been observed by the presence of a hysteresis, for Co₃O₄ , under the CO + O₂ gas mixture.

1. INTRODUCTION

Since 1970 perovskite-type oxides (ABO₃) have been suggested as substitutes for noble metals in automotive exhaust catalysts [1]. These oxides are efficient for oxidation reactions when for reduction the results obtained from the literature are dissimilar [2], mainly due to huge differences in the experimental conditions. The properties of perovskite-based catalysts are a function of the spin and the valence state of the metal in the B site cation, which is surrounded octahedrally by oxygen. The A site cation is located in the cavity made by these octahedra. For some perovskite-type oxides, their electronic structures have been pointed out to be similar to those of transition metals on the basis of theoretical

calculations and valence band structures [3-6]. Thus one of the catalytic features of these systems is to be active for hydrogen-involving reactions such as, for example, the hydrogenolysis of hydrocarbons [7].

As correlations have been observed, for catalytic oxidation reactions, between the activity and the electronic state of the transition metal [8], or the non stoichiometry of the perovskite [9], we have chosen, in our study, three perovskites containing cobalt in three different oxidation states, i) Co (II) in Ba_2CoWO_6 , ii) Co (III) in LaCoO_3 , iii) Co (IV) in BaCoO_3 , and we have compared their reactivity with the spinel Co_3O_4 .

The aim of this study is to assess the catalytic behaviour of these perovskites as automotive converters.

2. EXPERIMENTAL

2. 1. Preparation of the catalysts

All the catalysts have been prepared by a sol-gel method, starting from the oxide, acetylacetonate and carbonates : La_2O_3 , $\text{Co}(\text{CH}_3\text{COCHCOCH}_3)_3$, BaCO_3 , $\text{Co}(\text{CO}_3)$. Each precursor was dissolved in propionic acid, in such a way to get a concentration of 0.1 mol.dm^{-3} , and mixed together in the desired proportions.

For Ba_2CoWO_6 , the ammonium metatungstate could not be dissolved in the propionic acid, and was thus suspended in this acid before mixing.

After evaporation of the acid, the gel obtained was frozen, ground and calcined. All the calcinations were performed under air, with two temperature rates : one of 2 Kmin^{-1} up to 525 K, and the other of 3 Kmin^{-1} up to the final temperature, except for Ba_2CoWO_6 which was put directly in the furnace at 1225 K. Temperature and time of calcination are listed in Table 1.

2. 2. Characterization

BET : the measurements were performed by the use of krypton at a temperature of 77 K with a $P_0 = 3.276 \text{ mBar}$, the cross sectional area of krypton was taken equal to 19.5 \AA^2 . All the results are listed Table 1.

SEM : The average of the measured diameters of the particles are from 0.1 to 0.2 μm .

TPR/TPO measurements were obtained under 1.5% CO/He and 1% O₂/He respectively. Oxygen was analysed by thermal conductivity detectors (TCD), CO and CO₂ by IR.

About 0.015 g of the catalyst was placed in a U-shaped reactor, and was heated at a constant rate of 5 Kmin⁻¹ under a gas flow of 40 cm³min⁻¹ from room temperature to 1075 K. The results are discussed in the next section.

X-RAY analysis : the identification of the catalysts by X-Ray diffraction (K_α Cr, D5000 Siemens) did not show phases other than those desired, i.e. perovskite or spinel phases. For BaCoO₃, the phase obtained is a non-stoichiometric perovskite, a mix between BaCoO_{2.8} and BaCoO_{2.x}.

MICROANALYSIS was performed at Vernaison in the CNRS laboratory. The results obtained (table 1) showed a good stoichiometry in the perovskite phase between the ions in A and B sites, and gave us exactly the ratio between LaCoO₃ and Co₃O₄ in the sample containing the two oxides : this ratio is Co/La = 2.7.

Table 1 Different characteristics of the catalysts

Catalysts	Calcination		BET surface	Microanalysis
LaCoO ₃	1075 K	4 hours	3.2 m ² g ⁻¹	Co/La = 1.02
LaCoO ₃ /Co ₃ O ₄	1075 K	4 hours	3.3 m ² g ⁻¹	Co/La = 2.70
BaCoO _{2,x}	1125 K	3 hours	1.5 m ² g ⁻¹	Co/Ba = 1.03
Ba ₂ CoWO ₆	1225 K	5 hours	1 m ² g ⁻¹	Co/W = 0.92
Co ₃ O ₄	1075K	4 hours	2.6 m ² g ⁻¹	Co/O = 0.95 *

2. 3. Reactivity Testing

The catalyst powder (0.8 g) was placed in a tubular quartz reactor. The composition of the gas flow was obtained by mixing the different components (CO, O₂, NO, C₃H₈) diluted in N₂ with the use of gas flowmeters. For all experiments the ratio (oxydant species/reductive species) was taken equal to 1. Before each reaction, the reactor is bypassed in such a way as to know precisely the composition of the gas flow before reaction.

* This ratio is surprising, by the fact its value is higher than for the pure stoichiometric oxide. But the X-Ray data doesn't show any other pick as for Co₃O₄. If there is an other phase (cobalt suboxide), this phase is not crystallised.

The analysing section is composed of the following detectors: IR for CO, C₃H₈, and CO₂, chemiluminescence for NO, paramagnetism for O₂.

The experiments consist of increasing gradually the temperature with a rate of 4Kmin⁻¹ and following the concentration of the gas flow. In all experiments, *except when hysteresis reactions were performed*, the catalyst was cooled under N₂. When more information about the NO conversion was needed, we used a similar apparatus in which the analysing section is composed of three IR detectors for NO, N₂O, NO₂. The composition of the other gases was determined by gas chromatography. Two sorts of gas flow composition were used: i) a *binary mixture* containing either CO + O₂, CO + NO or C₃H₈ + O₂. ii) a *complete gas mixture* containing CO + C₃H₈ + NO + O₂. All experiments were performed four times. The first one is considered as the activation process. The results given in the tables are an average of the three last experiments.

3. RESULTS AND DISCUSSION

3.1 Temperature programmed reduction

Figure 1 shows the TPR profiles for the three following compounds : Co₃O₄, LaCoO₃ and LaCoO₃ / Co₃O₄. We can observe the presence of one broad reduction peak at 640 K for Co₃O₄, in contrast two reduction peaks appear for the two other compounds; their reduction temperatures are 640 K and 750 K for LaCoO₃ / Co₃O₄ and 720 K and 855 K for LaCoO₃. The presence of metallic cobalt at the end of the experiment was verified by X-ray diffraction. In LaCoO₃ we can observe that one cobalt species is more difficult to reduce. The last TPR peak appears at 855 K and can be attributed to an hindered reduction process of the cobalt due to the close presence of lanthanum oxide. This peak is shifted to lower temperature for LaCoO₃ / Co₃O₄ because less lanthanum oxide is present in this sample, and finally for Co₃O₄ only one peak appears shifted by 80 K towards lower temperature.

For Co₃O₄ similar results were obtained by Arnoldy and Moulijn [10]. They observed one sharp reduction peak for Co₃O₄ at 595 K, the TPR experiment was performed under hydrogen at a temperature rate of 10 Kmin⁻¹. In our case we observed one reduction peak in the same range of temperature. For the perovskite, two reduction peaks were formed corresponding to Co (III) → Co (II) and Co (II) → Co (0), as already observed by Crespin and Hall [11].

For $\text{BaCoO}_{2.x}$ TPR cannot be interpreted due to carbonation of this perovskite under CO.

For Ba_2CoWO_6 , the TPR showed a little CO consumption at 655 K and can be related to adsorption-desorption phenomena.

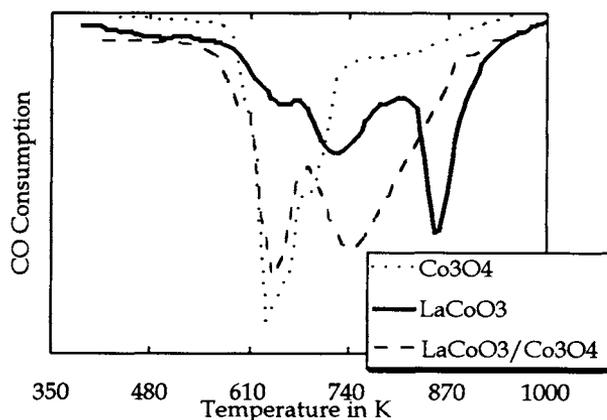


Figure 1 : CO consumption in TPR experiments as a function of the temperature in K. The scale for the consumption is related to the ppm of CO consumed per mole of cobalt in the catalyst.

3. 2 Temperature programmed oxidation

The X-ray diffractions performed in a Guinier chamber (K_{α} Fe) have shown that, in all cases, TPO experiments performed after a TPR reproduced the initial compound. Only one oxidation peak was observed at 625 K for LaCoO_3 and $\text{LaCoO}_3 / \text{Co}_3\text{O}_4$ and at 725 K for Co_3O_4 ; no significant peak was observed for Ba_2CoWO_6 .

3. 3 Catalytic activity under binary mixtures

The results are listed in Tables 2a, 2b and 2c, and illustrate the temperatures at which the conversion, calculated on the basis of the disappearance of the pollutant, is equal to 10%, 50% and 90%.

Table 2a Temperature of 10% conversion in binary mixture (K)

	CO + NO		CO + O ₂	HC + O ₂
	T ₁₀ NO	T ₁₀ CO	T ₁₀ CO	T ₁₀ HC
Co ₃ O ₄	385	415	385	490
LaCoO ₃ /Co ₃ O ₄	445	485	405	520
LaCoO ₃	445	520	410	550
BaCoO _{2.x}	495	525	425	635
Ba ₂ CoWO ₆	645	655	475	680

Table 2b Temperature of half conversion in binary mixture (K)

	CO + NO		CO + O ₂	HC + O ₂
	T ₅₀ NO	T ₅₀ CO	T ₅₀ CO	T ₅₀ HC
Co ₃ O ₄	480	545	430	550
LaCoO ₃ /Co ₃ O ₄	570	595	453	595
LaCoO ₃	615	600	440	640
BaCoO _{2.x}	660	640	475	775
Ba ₂ CoWO ₆	760	770	525	855

Table 2c Temperature of 90% in binary mixture (K)

	CO + NO		CO + O ₂	HC + O ₂ *
	T ₉₀ NO	T ₉₀ CO	T ₉₀ CO	T ₈₀ HC
Co ₃ O ₄	545	590	450	590
LaCoO ₃ /Co ₃ O ₄	745	640	470	670
LaCoO ₃	710	640	450	730
BaCoO _{2.x}	765	700	490	< 80%
Ba ₂ CoWO ₆	865	885	575	< 80%

* for HC we do not reach more than 85% conversion, the results listed are for 80% conversion, when it was reached.

From these tables we can observe the following points :

- The reactivity order is always the same, whatever the reaction and conversion, $\text{Co}_3\text{O}_4 > \text{LaCoO}_3/\text{Co}_3\text{O}_4 \approx \text{LaCoO}_3 > \text{BaCoO}_{2.x} > \text{Ba}_2\text{CoWO}_6$. The two latter compounds have very small TPR peaks, implying low oxygen mobility, which may explain in part their low reactivity.

- Concerning the two oxidation reactions i.e $\text{CO} + \text{O}_2$ and $\text{HC} + \text{O}_2$, the former occurs at the lower temperature than the latter. The $\text{CO} + \text{NO}$ reaction takes place in between these two ranges of temperature.

- In the $\text{CO} + \text{NO}$ reaction, the NO transformation is faster than the CO oxidation. To understand this point we have performed the experiments on the apparatus where IR detectors for NO , N_2O and NO_2 are present. We have noticed that the NO reduction does not give directly N_2 but rather N_2O , as can be seen in figure 2.

- When we compare the oxidation temperatures for CO in the $\text{CO} + \text{O}_2$ and $\text{CO} + \text{NO}$ reactions, we notice that the temperature is always lower in the former reaction. NO might be a poison of these catalysts, but on the other hand the apparent activation energy for $\text{CO} + \text{NO}$ is higher than for $\text{CO} + \text{O}_2$. From the work by Oh et al. [12] on rhodium catalysts they noticed that the apparent activation energy for $\text{CO} + \text{O}_2$ was equal to 14 kcal/mol and was lower by 17 kcal/mol than for $\text{CO} + \text{NO}$ reaction. Halasz et al. [13] observed an apparent activation energy of 13 kcal/mol for the catalytic oxidation of CO over Co_3O_4 . These results may suggest that the same slow step occurs on rhodium and Co_3O_4 , and it was observed that the surface oxides can be formed either on $\text{Rh}(111)$ or on supported rhodium, when they are treated under an oxidising environment [14,15].

From these results we can observe that Co_3O_4 is the more reactive system, but we notice that this oxide is the only one to be modified after the activation step. This modification was observed by XRD, and we showed the presence of two oxides : CoO and Co_3O_4 . This result led us to study this oxide more carefully.

3.4 Co_3O_4 reactivity

One question which may arise in these experiments concerns the reversibility* of these reactions. We studied the $\text{CO} + \text{O}_2$ reaction by increasing and then decreasing the temperature under the same gas mixture. In figure 3 we

* The term reversible has to be taken with care. In our case it does not imply the thermodynamic reversibility.

can see the presence of a hysteresis loop. After returning to room temperature, the next experiment follows the first curve obtained when the temperature was increased.

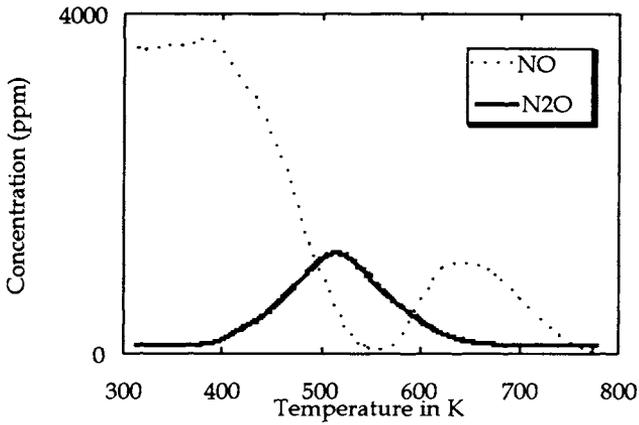


Figure 2 : $CO + NO$ reaction over $LaCoO_3/Co_3O_4$

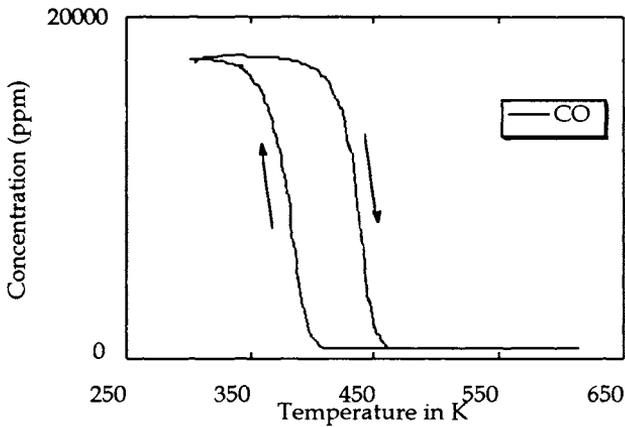


Figure 3 : Hysteresis experiment for Co_3O_4 under the binary mixture $CO + O_2$

Similar behaviour is also observed when the return to room temperature occurs under nitrogen instead of being performed under the reactive gas..

This result points out that either two different sites may exist at the surface, their presence being a function of the reaction temperature, or the nature and the amount of the adsorbed molecules are different versus the reaction temperature

This phenomenon has also been observed with alumina supported catalysts, and rules out the hypothesis that hysteresis is related to a change in the oxidation state of the cobalt

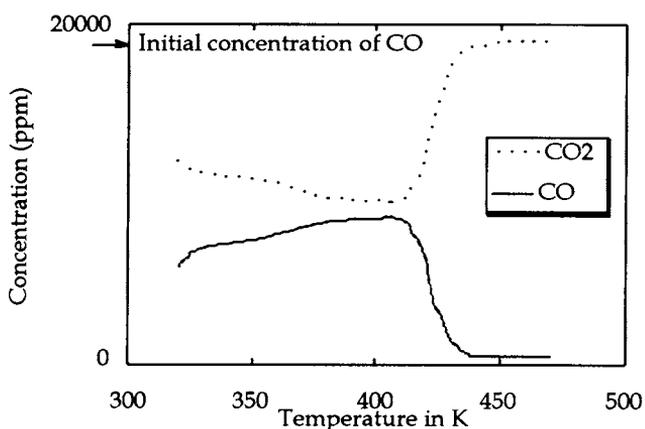


Figure 4 : The $\text{CO} + \text{O}_2$ reaction over Co_3O_4

To confirm this idea we increased the cooling rate of the catalyst. At the end of a $\text{CO} + \text{O}_2$ reaction, when the catalyst was at 573 K, it was rapidly cooled to room temperature in ten minutes under N_2 and put again in contact with $\text{CO} + \text{O}_2$, the CO concentration being 18 000 ppm. We have observed that this oxide was able to transform $\text{CO} \rightarrow \text{CO}_2$ at room temperature with a conversion of 50% as shown in figure 4.

This result may be explained by the quenching of the high temperature surface sites.

3. 5 Catalytic activity under the complete gas composition

The results are listed in table 3, and show the temperature at which the conversion is equal to 50%.

Table 3 Temperature of half conversion in complete mixture (K)

	T ₅₀ NO	T ₅₀ CO	T ₅₀ HC
Co ₃ O ₄	<50%	435	595
LaCoO ₃ /Co ₃ O ₄	<50%	440	635
LaCoO ₃	<50%	465	665
BaCoO _{2,x}	<50%	500	>520
Ba ₂ CoWO ₆	<50%	575	910

First of all we can notice that the temperatures of half conversion for NO, CO, and C₃H₈ are always higher than in the experiments performed with binary mixture. We never reach more than 15% NO conversion under a complete gas flow : conversion starts between 575 - 675 K, but in excess of this temperature the NO conversion activity is seen to decrease to zero. The small conversion of NO can be explained by the fact that the more rapid reaction CO + O₂ occurs first, then all the CO is transformed in CO₂ and NO has to react with hydrocarbon which needs very higher temperature.

CONCLUSION

These catalysts give reproducible results after the activation process which effects a change in the catalyst surface. The catalysts have been found to be very active for oxidation reactions, however NO transformation occurs only to a small extent. The cobalt oxide Co₃O₄ and the perovskite LaCoO₃/Co₃O₄ are the more reactive catalysts. They show a reversible modification of the surface when the temperature is increased, when compared to Pt-Al₂O₃ and Pt-CeO₂/Al₂O₃ catalysts [16,17] where the platinum loading is around 2%, the light-off temperatures for all the catalysts were found to be in the same range (around 500 K) for the CO + O₂ reaction, under similar experimental conditions.

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