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## **Distinct roles of copper in bimetallic copper-rhodium Three-Way-Catalysts deposited on redox supports.**

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### **ABSTRACT**

Copper(4.7%)-rhodium(0-2000ppm) catalysts deposited on three supports with different oxygen storage capacity (OSC) were tested under three-way catalytic cycling conditions using a low frequency and large composition fluctuations. The reducibility by hydrogen was also studied for all the catalysts in order to assess their OSC. Alumina (Al), ceria-alumina (CeAl) and ceria-zirconia (CeZr) were selected as supports. Both copper and rhodium metals favour the reduction of CeAl and CeZr at low temperature. The catalytic activity of rhodium in CO, NO and C<sub>3</sub>H<sub>6</sub> conversion in presence of oxygen is little influenced by the oxygen mobility of the support. However the OSC of the supports allow to attenuate or even suppress the effects of the composition fluctuations and thus improves the conversion at high temperatures. For monometallic copper catalysts, copper participates to the regulation of the oxidant/reducer ratio and is determinant if the support OSC is insufficient. Moreover, the interaction between copper and the mobile oxygen of the support greatly favours the CO oxidation at low temperature, whereas it has little influence on C<sub>3</sub>H<sub>6</sub> oxidation and disfavours the NO reduction at low temperature. No synergetic effect was observed for the bimetallic CuRh catalysts. In this case, the activity is ruled by the metal or the association metal-support which is the most active in each temperature range. The association "copper-support exhibiting mobile oxygen" is the most active for CO conversion. NO reduction depends mainly on the rhodium content, especially at low temperature, and C<sub>3</sub>H<sub>6</sub> conversion is a little improved by rhodium addition.

## 1. INTRODUCTION

The automotive three way catalysts (TWC) exhibit an optimum activity when the redox gas composition is stoichiometric. In spite of large improvements in the engine regulation with the use of electronic injection, it is impossible during the driving to avoid some fluctuations around the stoichiometry. To compensate this phenomenon, the catalysts are modified by addition of components exhibiting a high Oxygen Storage Capacity (OSC), such as ceria or ceria-zirconia [1,2]. These compounds are oxidised during the lean periods and thus store some oxygen. On the opposite, in the rich periods, they are reduced and thus release their stored oxygen. [3,4]. In that way, they damp the composition fluctuations around the stoichiometry. In the recent years, efforts have been made to develop new materials still having high OSC but if possible less expensive, i.e. being less loaded in expensive metals. With this objective, we have studied in a previous work the TWC activity of a model substitute catalyst, in which a 4.7 % Cu/Al<sub>2</sub>O<sub>3</sub> catalyst was modified by addition of rhodium (from 100 to 2000 ppm) [5]. Under cycling condition and in absence of OSC, i.e. with a rhodium on alumina catalyst, the CO and NO conversion curves exhibited limitations at high temperature due to a low cycling frequency and a large cycling amplitude, whereas the conversion of C<sub>3</sub>H<sub>6</sub> was achieved. However, the presence of copper, which exhibits oxygen storage properties, has attenuated the composition oscillations and has markedly improved the CO and NO conversions at high temperature. There was no synergetic effect between copper and rhodium on the catalytic activity, but the presence of copper slightly improved the oxidation of CO and C<sub>3</sub>H<sub>6</sub> at low temperature.

In this paper, we have examined if the copper OSC is still an important parameter in presence of a redox support. The objective was also to precise if copper associated with rhodium acted only as an OSC provider or if it could have also a specific role in the three-way-catalytic activity. Thus, the same type of CuRh bimetallic composition was studied after deposition on two redox supports with different OSC, i.e. a ceria-alumina support and a ceria-zirconia support. A copper on ceria support has also been studied. Their properties were compared to those of alumina-supported CuRh catalysts chosen as references.

## 2. EXPERIMENTAL

### 2.1. Preparation of the catalysts

The alumina (Al) support (Rhodia 531P) has a BET surface area of 115 m<sup>2</sup>.g<sup>-1</sup>. It has been used to prepare a ceria-alumina (CeAl) support with a 20wt.% CeO<sub>2</sub> content and a BET surface area of 95 m<sup>2</sup>.g<sup>-1</sup> (Rhodia 531P2). The CeO<sub>2</sub> mean crystallite size estimated from X ray diffraction was about 11 nm.

To obtain a support with a very high OSC, a ceria-zirconia mixed oxide have been prepared. The addition of zirconia to ceria to obtain a solid solution is well known to improve the ceria OSC, because not only the surface can be reduced at low temperature, but a contribution of the bulk is also observed [3,4,6-7]. A high cerium loading is needed to have a high OSC because only the cerium is reducible [8-10]. The Ce<sub>0.68</sub>Zr<sub>0.32</sub>O<sub>2</sub> composition has been reached because this composition allow to obtain of a high surface area with a good thermal stability [11,12]. To prepare this support (CeZr), a mixture of the cerium and zirconium nitrate

solutions ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  Prolabo, and  $\text{ZrO}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ , Strem Chemical) in the desired proportion have been prepared. The co-precipitated hydroxide was obtained by slow addition of this solution to concentrated ammonia (28%), under vigorous agitation. After a thorough washing, the precipitate was dried at  $110^\circ\text{C}$  under  $\text{N}_2$  for 2 days. The solid was then ground and calcined under oxygen flow ( $6 \text{ L}\cdot\text{h}^{-1}$ ) for 6 h at  $650^\circ\text{C}$  (heating ramp  $1^\circ\text{C}\cdot\text{min}^{-1}$ ). The chemical analysis (57.3 wt % Ce and 17.4 wt % Zr) and the mean composition derived from XRD [13] were consistent with the theoretical composition. The resulting BET surface area was  $86 \text{ m}^2\cdot\text{g}^{-1}$  which gives an equivalent mean size of about 10 nm. It is slightly higher than that obtained from XRD (about 5 nm) by the half height width method. This difference can be due to a broadening of the XRD peaks because of a slight distribution of composition around the nominal 68/32 composition.

These three supports were co-impregnated with copper and rhodium nitrate solutions in order to obtain catalysts with 4.7 wt % Cu and variable rhodium contents between 0 and 2000 ppm. After impregnation, the solids were dried under air for one night at  $110^\circ\text{C}$ . Then, they were ground and calcined for 6 h at  $400^\circ\text{C}$  in flowing air with a  $1^\circ\text{C}\cdot\text{min}^{-1}$  heating rate. Finally, the three series of catalysts were reduced at  $500^\circ\text{C}$  in flowing hydrogen for 6 h. After cooling under  $\text{H}_2$  to room temperature, the samples were put under nitrogen and then slowly oxidized under air.

These three series of samples are referred as  $\text{CuRh}_x/\text{Al}$ ,  $\text{CuRh}_x/\text{CeAl}$  and  $\text{CuRh}_x/\text{CeZr}$ , depending on whether copper and rhodium are deposited on alumina, ceria-alumina or ceria-zirconia, where  $x$  specifies the rhodium content in ppm. The rhodium contents were verified by chemical analysis to be within 10% the nominal composition. A monometallic rhodium catalyst with 1000 ppm rhodium concentration and a copper on ceria support was also prepared by the same method (HSA ceria from Rhodia,  $S_{\text{BET}}=115 \text{ m}^2\cdot\text{g}^{-1}$ )

The dispersion of the reduced  $\text{Cu}/\text{Al}$  catalyst was determined via dissociative  $\text{N}_2\text{O}$  adsorption [14] ( $\text{N}_2\text{O}_{(\text{g})} + 2\text{Cu}_s \rightarrow \text{N}_{2(\text{g})} + (\text{Cu}_2\text{O})_s$ ) at  $90^\circ\text{C}$  measuring the amounts of  $\text{N}_2\text{O}$  consumption and  $\text{N}_2$  production in the course of the adsorption using an analytical system for transient experiments with a mass spectrometer as detector [15]. A 0.8%  $\text{N}_2\text{O}/2\%$   $\text{Ar}/\text{He}$  mixture was used and the amount of  $\text{N}_2$  formed indicates a dispersion of 0.11 for the fresh reduced catalyst assuming a ratio  $\text{Cu}/\text{N}_2 = 2$  [14]. This value is lower than that determined by Dandekar and Vannice [14] (range  $\approx 0.2-0.5$ ) on 5.1%  $\text{Cu}/\text{SiO}_2$  and 4.9%  $\text{Cu}/\text{Al}_2\text{O}_3$ , but the solids were pretreated and reduced at lower temperatures ( $200^\circ\text{C}$  and  $300^\circ\text{C}$ ) compared to the present study ( $500^\circ\text{C}$ ). Unfortunately, this method can not be used to estimate the dispersion of copper in presence of ceria/ceria-zirconia and/or rhodium, because of their contribution to  $\text{N}_2\text{O}$  decomposition. The low loading of rhodium (0.2wt% max) do not allow to obtain a representative dispersion by conventional chemisorption techniques. However, CO adsorption at  $25^\circ\text{C}$  on in-situ reduced  $\text{Cu}-\text{Rh}/\text{Al}$  samples ( $\text{H}_2$ ,  $500^\circ\text{C}$ ) and followed by FTIR shows a linear relationship between the Rh content and the "CO-Rh" peaks areas [16], indicating that the rhodium dispersion should be similar for each  $\text{CuRh}$  catalyst.

Table 1 gives the list of the different preparations with the corresponding BET surface area obtained after the reduction treatment.

Table 1: BET surface areas ( $\text{m}^2.\text{g}^{-1}$ ) of the studied catalysts.

Catalyst	Support	$\text{Al}_2\text{O}_3$	$\text{CeO}_2\text{-Al}_2\text{O}_3$	$\text{Ce}_{0.68}\text{Zr}_{0.32}\text{O}_2$
Rh		113	97	82
Cu		105	85	74
CuRh100		104	86	75
CuRh500		103	86	75
CuRh1000		103	85	75
CuRh2000		100	83	73

## 2.2. Experimental techniques

The OSC of supports and catalysts was determined by temperature programmed reduction (TPR) under hydrogen. 30-50 mg of calcined sample were pretreated in situ under oxygen at  $400^\circ\text{C}$  for 1 h and then under argon at  $500^\circ\text{C}$  for 1h30 in order to eliminate most of the adsorbed species ( $\text{H}_2\text{O}$ ,  $\text{CO}_2\dots$ ). After cooling at room temperature under argon, the reduction was then carried out under a 1%  $\text{H}_2/\text{Ar}$  mixture up to 800 or  $1000^\circ\text{C}$ , with a  $20^\circ\text{C}.\text{min}^{-1}$  heating rate. The hydrogen consumption was followed by thermal conductivity.

The three-way catalytic activity was measured in the simultaneous conversion of  $\text{CO}$ ,  $\text{NO}_x$  and  $\text{C}_3\text{H}_6$ . The experimental device was developed by Weibel [17,18]. It allowed to work in cycling conditions, using two mixtures of different composition in order to simulate the rich/lean oscillations of the mixture occurring under real conditions of use of the catalytic converter. At the outlet of the reactor, the gases were cooled and then analysed in series by specific analysers (paramagnetism for  $\text{O}_2$  (Siemens Oxymat 5E) and infrared for  $\text{CO}$ ,  $\text{CO}_2$ ,  $\text{NO}$ ,  $\text{N}_2\text{O}$  and  $\text{C}_3\text{H}_6$  (Siemens Ultramat 5E-2R or 5E)) with a frequency of one measure per second. The tests were performed on 20 mg catalysts diluted in 180 mg SiC because of the exothermicity of the oxidation reactions. The protocol was the same as that used for the series on alumina [5]. Before the test, the catalyst was first activated in stationary regime under a stoichiometric mixture having the composition given in Table 2. The solid was heated at  $10^\circ\text{C}.\text{min}^{-1}$  under this mixture up to  $550^\circ\text{C}$ , kept 1 h at this temperature and cooled down to room temperature under nitrogen flow. Then, the catalytic activity test was performed up to  $550^\circ\text{C}$  (heating rate  $5^\circ\text{C}.\text{min}^{-1}$ ) in cycling conditions, with the two mixtures having the compositions given in Table 2. The redox state of the catalyst after the activation treatment was unknown but, as the catalytic test in cycling condition was starting at room temperature, it can be supposed that redox support and almost the metallic surface were then in an oxidised state before any conversion. The switching period between the two mixtures was 5 seconds. Although these conditions (low frequency of oscillation and broad variations in composition) are not representative of those occurring in a TWC converter, they should facilitate the study of the OSC and catalytic

properties of each catalyst. In both regimes (stationary or transitory) the flow rate was 12 L.h<sup>-1</sup>. Taking into account the SiC, it corresponds to a space velocity near 25000 h<sup>-1</sup>. The conversion for each reactant was calculated every seconds on the average inlet concentration during one rich/lean cycle, i.e. with concentrations corresponding to the stoichiometry. T50 is the temperature for 50% conversion.

Table 2: Composition of the gaseous mixtures used in stationary and transitory regimes.

	Stationary regime		transitory regime	
	(stoichiometry)	lean mixture	rich mixture	variation
O <sub>2</sub> / ppm	5600	7820	3380	± 2220
CO / ppm	6200	1620	10780	± 4580
NO / ppm	1000	1000	1000	0
C <sub>3</sub> H <sub>6</sub> / ppm	667	667	667	0
r <sup>a</sup>	1	2.18	0.46	

All the gases are used diluted in nitrogen. The total flow rate is 12 L.h<sup>-1</sup>.

<sup>a</sup> "r" represents the oxidising gas/reducing gas ratio. It is calculated from the concentrations of each component by the expression:  $r = \{ 2[\text{O}_2] + [\text{NO}] \} / \{ [\text{CO}] + 9[\text{C}_3\text{H}_6] \}$

### 3. RESULTS

In order to discriminate the effects of the OSC and the specific catalytic activity of copper, the OSC properties of the different catalysts have been studied first and then their catalytic properties have been evaluated.

#### 3.1. OSC measurements from TPR under hydrogen

The OSC of the catalysts was calculated by integration of the H<sub>2</sub> uptake profile obtained by TPR. Figure 1 gives the corresponding cumulative hydrogen consumption curves up to 800°C for the CeAl and CeZr supports, and for the copper catalysts deposited on the different supports. On each curve, the various inflection points correspond to the maximum of the peaks in the classical representation of the TPR curves. Then, they also correspond to the maximum reduction rate and are characteristic of the different reduction steps. The hydrogen uptake of the alumina support (not shown) is very small and starts only for temperature higher than 750°C. For the CeAl support (curve a), the reduction starts at about 450°C with an inflection point at 635°C. In agreement with literature [19,20], this first step is attributed to the ceria surface reduction. The reduction of bulk ceria occurs for T > 800°C. The OSC of the CeZr support is significantly higher (curve b). The hydrogen consumption starts at around 350°C and gives a broad peak with a maximum rate at 640°C. At 800°C, the reduction is not total, but with an OSC of almost 1 mmol.g<sup>-1</sup>, the equivalent of several layers has been already reduced [4,6,21].

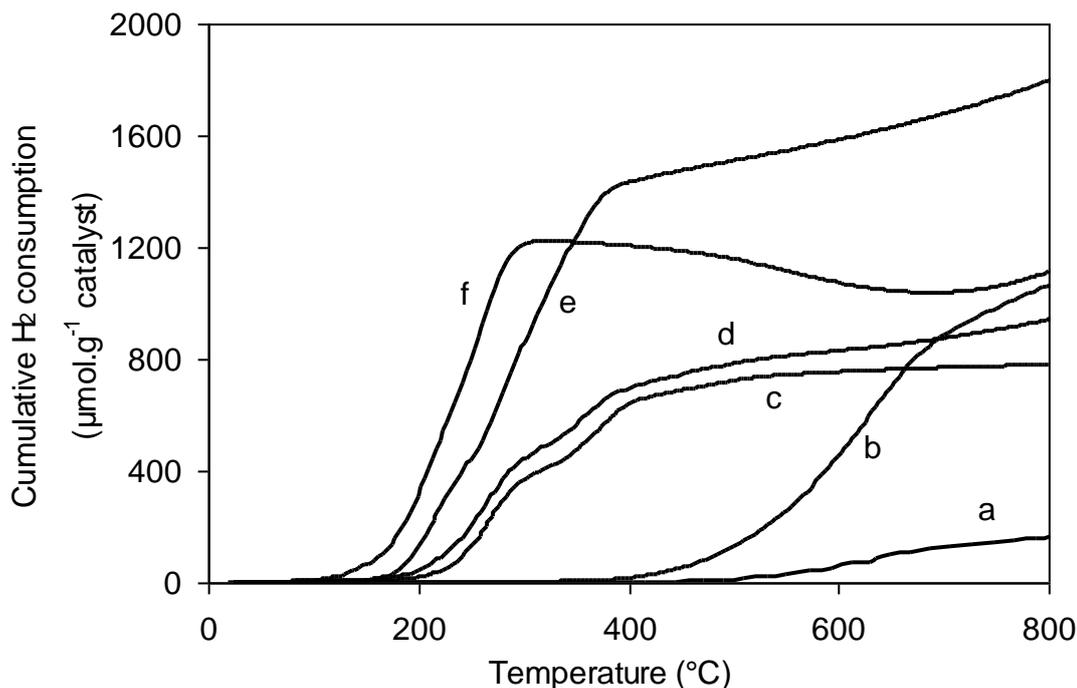


Figure 1: Cumulative hydrogen consumption during the TPR: (a) CeAl support, (b) CeZr support, (c) Cu/Al, (d) Cu/CeAl, (e) Cu/CeZr and (f) Cu/Ce.

Table 3: Variation of the hydrogen consumption ( $\mu\text{mol H}_2\cdot\text{g}^{-1}$ ) corresponding to the low temperature TPR peak ( $T < 350^\circ\text{C}$ ) as a function of the rhodium content in the bimetallic CuRh catalysts.

Catalyst	Support	$\text{Al}_2\text{O}_3$	$\text{CeO}_2\text{-Al}_2\text{O}_3$
Cu		365	491
CuRh100		377	485
CuRh500		535	648
CuRh1000		585	
CuRh2000		644	676

The presence of copper strongly modifies the shape of the curves. As already reported [22], the Cu/Al and Cu/CeAl catalysts are reduced at much lower temperature. The corresponding curves c and d are very similar and exhibit two maximum rates at about  $270^\circ\text{C}$  and  $375^\circ\text{C}$  corresponding to the successive reduction in metallic copper of i) isolated ions and small clusters and ii) bulk copper oxide [22-27]. Note that the  $\text{H}_2$  uptake at  $650^\circ\text{C}$  for the Cu/Al catalyst corresponds to the total copper reduction assuming  $\text{CuO} + \text{H}_2 \rightarrow \text{Cu} + \text{H}_2\text{O}$ . However, in agreement with literature [28,29], the ceria in contact with copper is reduced simultaneously at low temperature. It explains the increase in the  $\text{H}_2$  uptake at low temperature observed with Cu/CeAl in comparison with Cu/Al ( $+ 126 \mu\text{mol H}_2\cdot\text{g}^{-1}$ , see table 3). The two other curves (e and f) are related to copper supported on ceria-zirconia and ceria. The  $\text{H}_2$  consumption at low temperature is much more important and the increase of the OSC is very significant in the whole

temperature range. The higher H<sub>2</sub> consumption obtained at low temperature with the Cu/Ce catalyst can be attributed to a higher cerium surface concentration, a higher specific area (115 m<sup>2</sup>.g<sup>-1</sup> for the Ce support and 86 m<sup>2</sup>.g<sup>-1</sup> for CeZr support) and probably to a higher copper dispersion. The negative drift observed with the Cu/Ce catalyst above about 400°C corresponds to the elimination of some carbonate species present in the oxide which leads to CO<sub>2</sub> formation responsible for the negative signal of the conductivity detector [30] (TCD signal superior to the 1% H<sub>2</sub>/Ar signal).

In the case of alumina and ceria-alumina support, it has already been reported [22] that the addition of small amounts of rhodium during the preparation of the copper catalyst does not really modify the reduction mechanism of copper. The main point was that the distribution of copper phases is modified, with an increase of the relative importance of small copper clusters with the rhodium content. Thus, the reducibility (and the OSC) at low temperature (T<350°C) of these catalysts corresponding to the reduction of these clusters slightly increases with the rhodium content (see Table 3).

When ceria-zirconia is used as support, rhodium also favours the formation of small copper clusters at the expense of bigger particles, as it can be deduced from the hardly detectable main copper diffraction line ( $2\theta = 43.3^\circ$ ) in the diffraction diagrams (not shown), whereas it was clearly evidenced for low rhodium concentrations in the alumina and ceria-alumina supported catalysts [22]. Consequently, a slight improvement of the reduction of the support was also observed at lower temperature, but the cumulative OSC is basically not very different from that of Cu/CeZr, as shown on Figure 2. At 450°C, the OSC is about 1.5 mmol H<sub>2</sub>.g<sup>-1</sup>. In addition to the total copper oxide reduction, the H<sub>2</sub> consumption below 450°C indicates that about 30% of the cerium ions are reduced. It corresponds to nearly three times the surface cerium ions reduction. Compared to CeO<sub>2</sub>, not only the surface is reduced in this temperature range, the reduction is deeper, as observed with other metals [3-4,6-7]. It must be remarked that the contribution of rhodium to OSC is almost negligible. With the hypothesis of a total rhodium reduction according to  $1/2\text{Rh}_2\text{O}_3 + 3/2\text{H}_2 \rightarrow \text{Rh} + 3/2\text{H}_2\text{O}$ , it is only 29 μmol H<sub>2</sub>.g<sup>-1</sup> for 2000 ppm Rh.

It should be noted that on Rh/CeZr as for the two other rhodium catalysts, Rh/Al and Rh/CeAl, no hydrogen consumption was observed at room temperature. This is in opposition with some results obtained with Rh/CeO<sub>2</sub> or Rh/CeO<sub>2</sub>-ZrO<sub>2</sub> catalysts, with the occurrence of hydrogen spill-over on the support [31-34]. For our samples, the absence of H<sub>2</sub> spill-over at 25°C can be ascribed to the fact that the rhodium ions are well dispersed and in strong interaction with the support, making their reduction more difficult. The spill-over occurs only when some metallic rhodium atoms are formed, i.e. at about 100-150°C in the present study as indicated by the shoulder obtained on the TPR profile (see Fig.3).

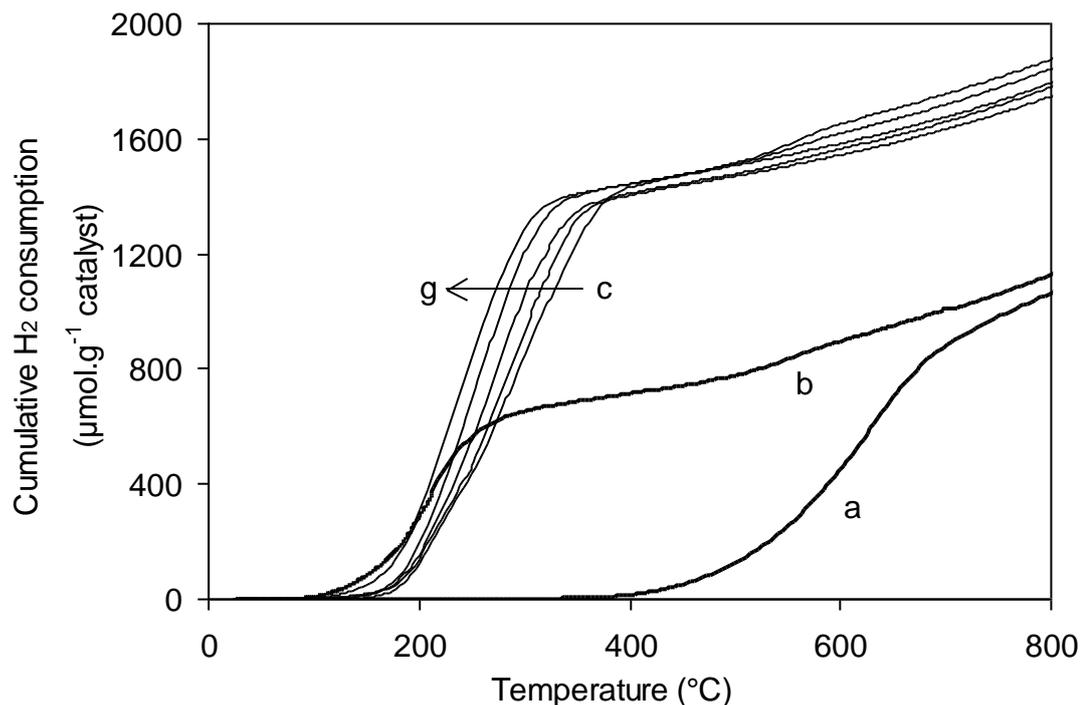


Figure 2: Cumulative hydrogen consumption during the TPR for the series of CuRh/CeZr catalysts: (a) CeZr support, (b) Rh/CeZr, (c) Cu/CeZr, (d) CuRh100/CeZr, (e) CuRh500/CeZr, (f) CuRh1000/CeZr and (g) CuRh2000/CeZr.

More important is the observation on Fig.2 of a small H<sub>2</sub> uptake increase at about 550°C on the curves b to f. It is more obvious in Fig.3 where a new peak increasing with rhodium content is observed. It can be also observed on the TPR curves at about the same temperature with the Rh1000/CeAl and the bimetallic CuRh/CeAl samples (Fig.3). This hydrogen consumption can be tentatively attributed to a reduction process involving both cerium and rhodium. Moreover, it increases linearly with the rhodium content of the bimetallic CuRh/CeZr catalysts (Fig.4) with an average slope H<sub>2</sub>/Rh = 3. Thus, a well defined reaction between metallic rhodium and Ce<sup>3+</sup> ions can be supposed, leading to a cerium sub-oxide or more probably to a Rh-Ce alloy, according to the following global reaction:



The formation of a well defined CePt<sub>5</sub> intermetallic compound has been already observed in Pt/CeO<sub>2</sub> and Pt/Ce<sub>0.80</sub>Tb<sub>0.20</sub>O<sub>2-x</sub> catalysts reduced at 900°C [35-37]. However, regarding ceria-supported rhodium catalysts, alloying effects have never been reported to occur [38]. It can be supposed that in this case, the high specific surface area of the support greatly favours the interaction between the cerium ions and the rhodium atoms and consequently the complete reduction of the cerium ions.

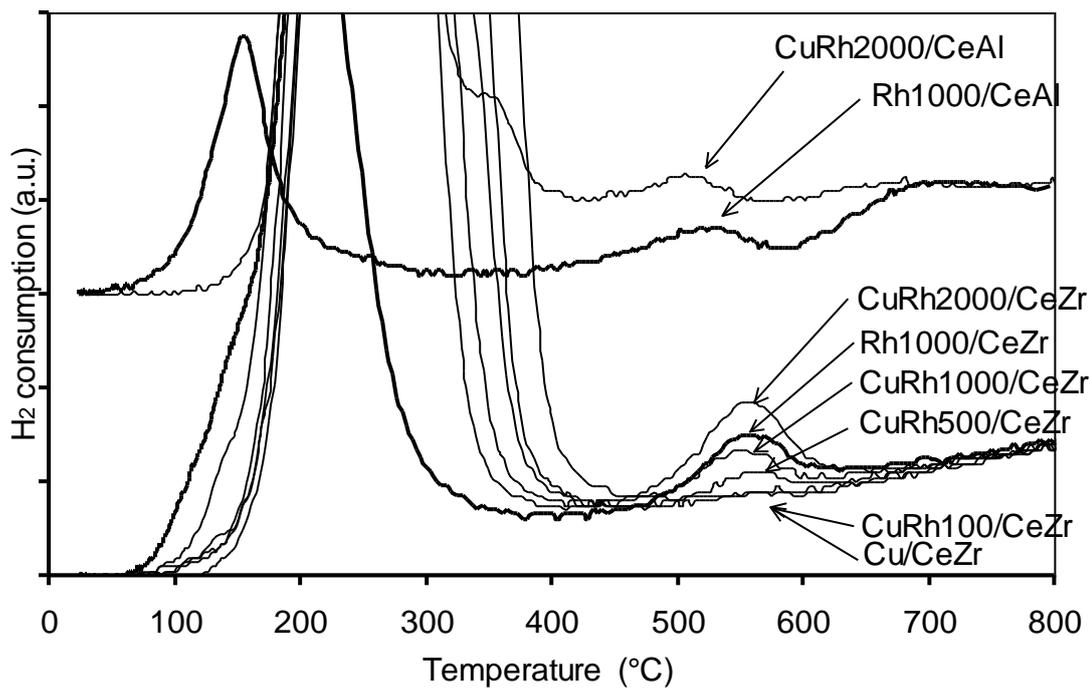


Figure 3: CuRh/CeZr and CuRh/CeAl catalysts: Evolution of the TPR peak at 550°C as a function of the rhodium content.

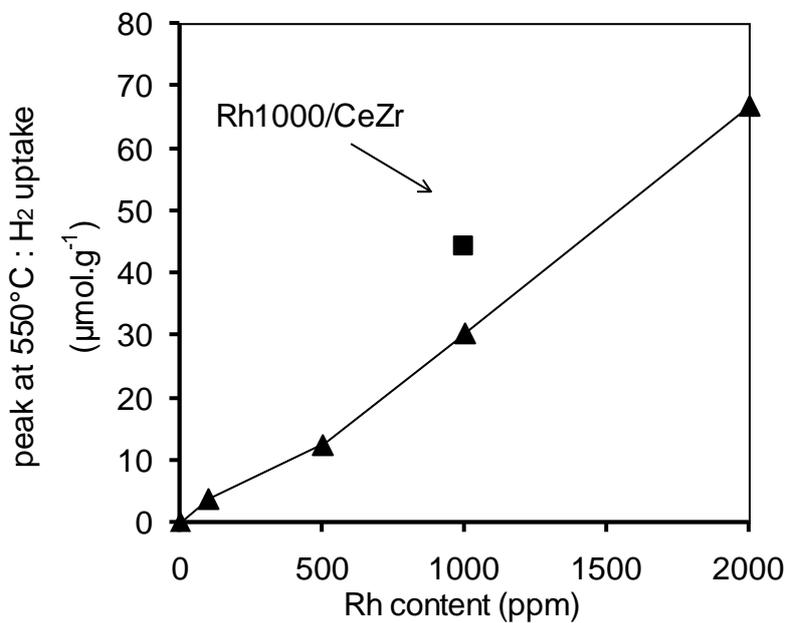


Figure 4: CuRh/CeZr catalysts: Relationship between hydrogen uptake of the TPR peak at 550°C and the rhodium content.

## 3.2 Catalytic activity in transitory conditions

All the catalysts were tested in cycling condition after 1 hour activation under the stoichiometric reaction mixture. Basically, all the activity profiles exhibit a sigmoid shape.

### 3.2.1. Activity of supports

The alumina support was found inactive in our conditions. Ceria-alumina has a low activity, with a beginning of conversion at around 350°C. At 550°C, the maximum temperature of the test, the conversions were 18%, 7% and 29% for CO, NO and C<sub>3</sub>H<sub>6</sub> respectively. In the case of ceria-zirconia solid solutions, no activity (<5%) was found for the conversion of NO in the whole temperature range studied. However the oxidation reactions of CO and C<sub>3</sub>H<sub>6</sub> started at around 300°C and the conversions at 550°C were 70 % for CO and 63 % for C<sub>3</sub>H<sub>6</sub>. Then the increase of the OSC of the supports favours only the oxidation reactions.

### 3.2.2. Activity of supported rhodium catalysts.

The conversion curves for each pollutant are given in Fig.5 for the three rhodium monometallic catalysts containing 1000 ppm Rh. They present the same type of evolution up to 50% conversion. The curves are close with a T50 rather constant whatever the support, near 280°C for CO, 320°C for NO and 322°C for C<sub>3</sub>H<sub>6</sub>. The maximum difference in T50 is 21°C, obtained for CO conversion between Rh/Al and Rh/CeZr. For higher temperature, big differences appear between the catalysts in the conversion achievement, mainly for CO and NO. From 450°C to 550°C, CO conversion is limited at 47% for Rh/Al, 74% for Rh/CeAl and is total for Rh/CeZr. Similar evolutions are obtained with NO, the conversion rates are 58%, 75% and 100%, respectively. Some N<sub>2</sub>O is formed at low temperature with a maximum concentration at about 310-320°C corresponding to NO conversions of 46-52%. These maximal N<sub>2</sub>O concentrations are 150 ppm, 81 ppm and 34 ppm, for Rh/Al, Rh/CeAl and Rh/CeZr, respectively. Finally, the support has little influence for the C<sub>3</sub>H<sub>6</sub> conversion. The curves are nearly the same with however a slower reaction rate for Rh/Al when the conversion becomes higher than 50%.

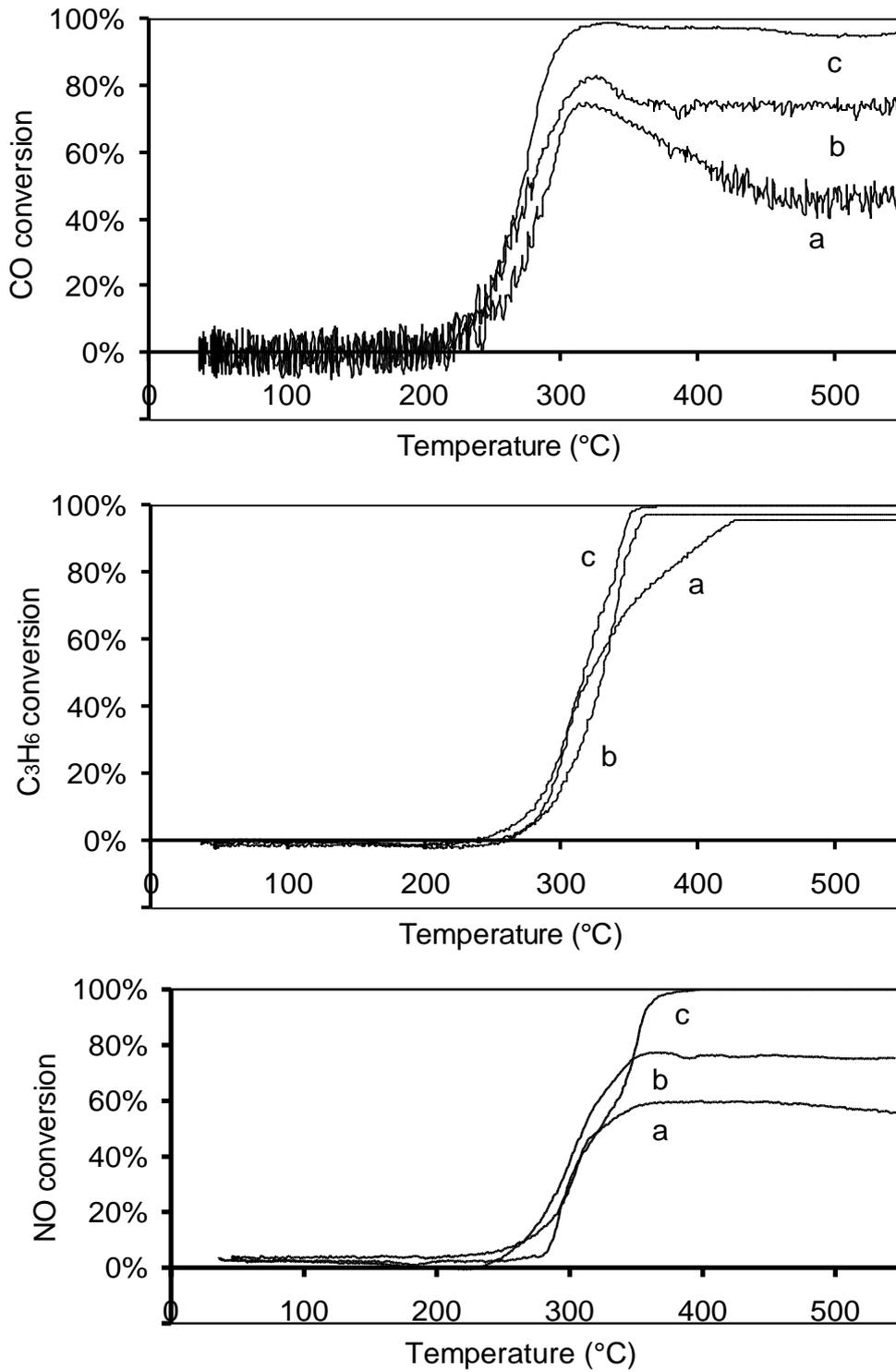


Figure 5: Conversion of CO, C<sub>3</sub>H<sub>6</sub> and NO in cycling conditions on rhodium supported on alumina, ceria-alumina and ceria-zirconia: (a) Rh/Al, (b) Rh/CeAl, (c) Rh/CeZr.

### 3.2.3. Activity of supported copper catalysts.

The results are summarised in Fig.6 for the monometallic copper catalysts, including copper on ceria. As shown on this figure, the activity in CO conversion strongly depends on the nature of the support. The T50 decreases from 356°C for Cu/Al to 158°C for Cu/Ce, the best catalyst of the series.

C<sub>3</sub>H<sub>6</sub> conversion curves exhibit a limited influence of the support. The beginning of activity is observed at about 250°C and there is only 40°C difference in T50 (340-380°C) between the more active (Cu/Ce and Cu/CeZr) and the less active catalysts (Cu/CeAl and Cu/Al).

The activity for NO reduction is low for the four catalysts. Again, as for C<sub>3</sub>H<sub>6</sub>, there are the same two groups of catalysts. The curves are more complex, with an intermediate plateau at about 20-25% conversion at around 400°C for Cu/Al and Cu/CeAl. For Cu/CeZr and Cu/Ce which are the most active catalysts of the series in CO and C<sub>3</sub>H<sub>6</sub> conversion, there is practically no activity below 400°C, but at 550°C, the NO conversion reaches nearly 75 %. In addition, for these two catalysts, a small deviation is observed at about 100°C, corresponding to the desorption of NO from the support. Thus, it is clear that copper is poorly active in the NO reduction.

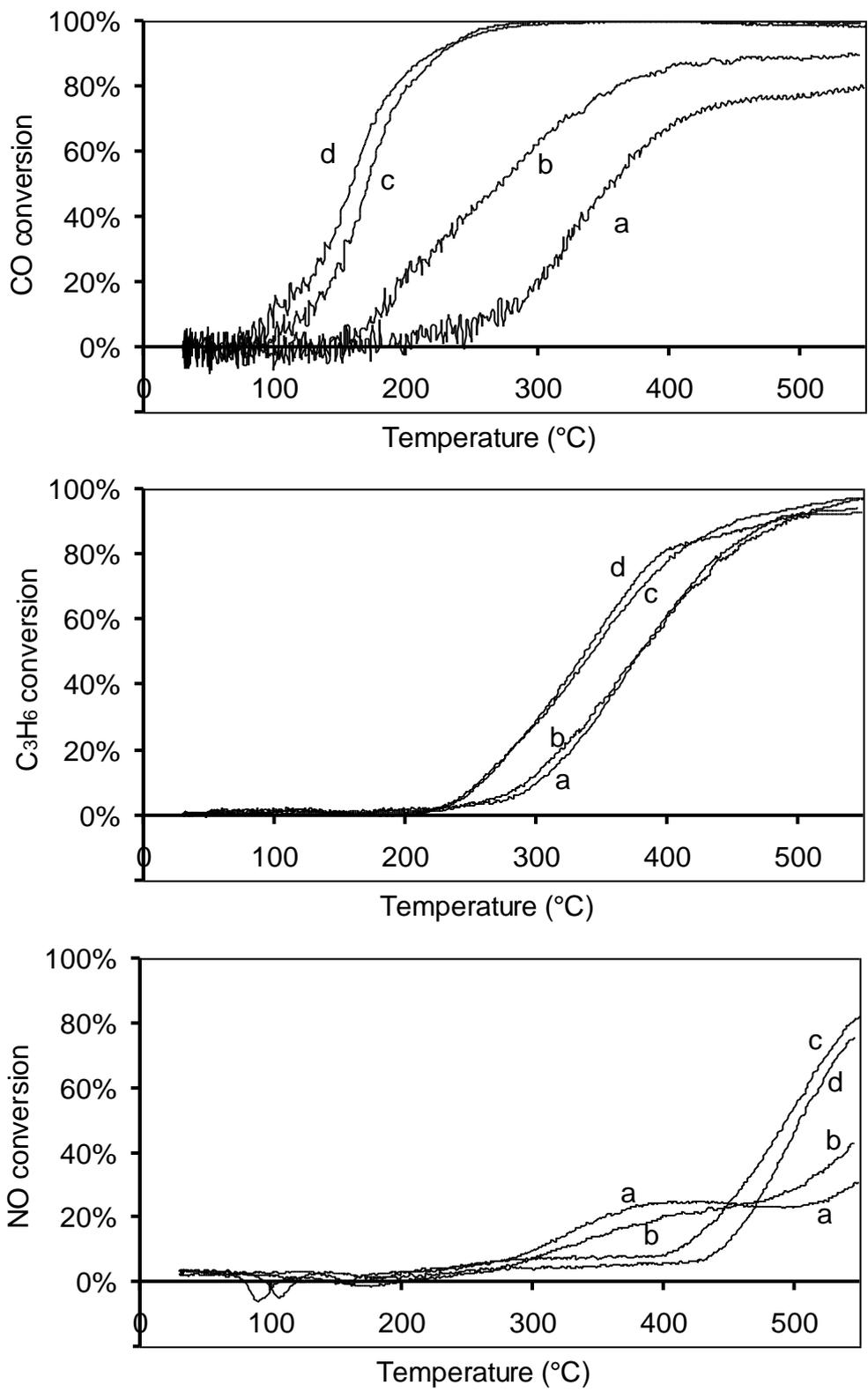


Figure 6: Conversion of CO, C<sub>3</sub>H<sub>6</sub> and NO in oscillatory conditions on copper supported on various supports : (a) Cu/Al, (b) Cu/CeAl, (c) Cu/CeZr (d) Cu/Ce.

### 3.2.3. Influence of rhodium addition on the activity of copper catalysts.

The results are summarised schematically on Figure 7 by using for each reaction the light-off temperature (T50) obtained for the series of bimetallic catalysts prepared on the three supports, CeAl, CeAl and CeZr. The results for the series supported on alumina have been already published [5] and are included for comparison.

#### *CO conversion.*

We have previously shown that in the case of the alumina supported series, the CO conversion was favoured by addition of rhodium to copper. The T50 decreased from about 350°C for Cu/Al to 275°C for CuRh2000/Al. With the catalysts supported on ceria-alumina, the CO conversion occurs at lower temperature for the monometallic copper catalysts and there is practically no influence of rhodium. However, for  $T > 275^{\circ}\text{C}$ , the rhodium addition slightly favours the activity (not shown), but this increase is ascribable to the CO+NO reaction. It must be also remarked that up to 50% conversion, all the bimetallic catalysts are more active than the monometallic Rh/CeAl, which puts in evidence the role of copper in CO oxidation. Finally, for the catalysts deposited on ceria-zirconia, there is absolutely no effect of the addition of rhodium on the CO conversion (T50 = 170°C), certainly because the solids containing copper are much more active than the rhodium monometallic Rh/CeZr (T50 = 271°C).

Thus, the activity of copper in CO oxidation is modified by the addition of rhodium, only in the case of the alumina support.

#### *C<sub>3</sub>H<sub>6</sub> conversion.*

For the three series of catalysts, C<sub>3</sub>H<sub>6</sub> conversion is slightly improved by rhodium addition. On ceria-zirconia, the CuRh/CeZr catalysts are more active, with an average decrease of 20°C and 40°C in the T50 compared to the alumina and ceria-alumina series, respectively.

#### *NO conversion.*

The T50 are decreased by about 200-250°C for the three series of catalysts when 2000 ppm rhodium are added to the copper catalysts (Fig.7). This great difference results from the high activity of rhodium towards the NO reduction whereas copper alone is a poor catalyst. The influence of ceria-zirconia support proves to be positive for very low rhodium content ( $\leq 100$  ppm) but negative for higher contents. However the NO conversion curves are complex as illustrates the figure 8 which shows the curves obtained with the Cu and CuRh2000 catalysts on the three supports. When the temperature increases, an intermediate plateau is observed in the NO conversion. Within each series, i.e. with or without rhodium, the limited conversion at the plateau is lower as the OSC increases. At higher temperature, the NO conversion increases again and the OSC of the catalyst has now a positive influence by lowering the temperature of activity revival and favouring the total conversion. Note that some N<sub>2</sub>O is formed at low temperature. For example, for the CuRh2000/Al, CuRh2000/CeAl and CuRh2000/CeZr catalysts, the maximum concentration is obtained in the temperature range of 306-314°C corresponding to a NO conversion of approximately 50%. The N<sub>2</sub>O concentrations are respectively 110 ppm, 68 ppm and 58 ppm.

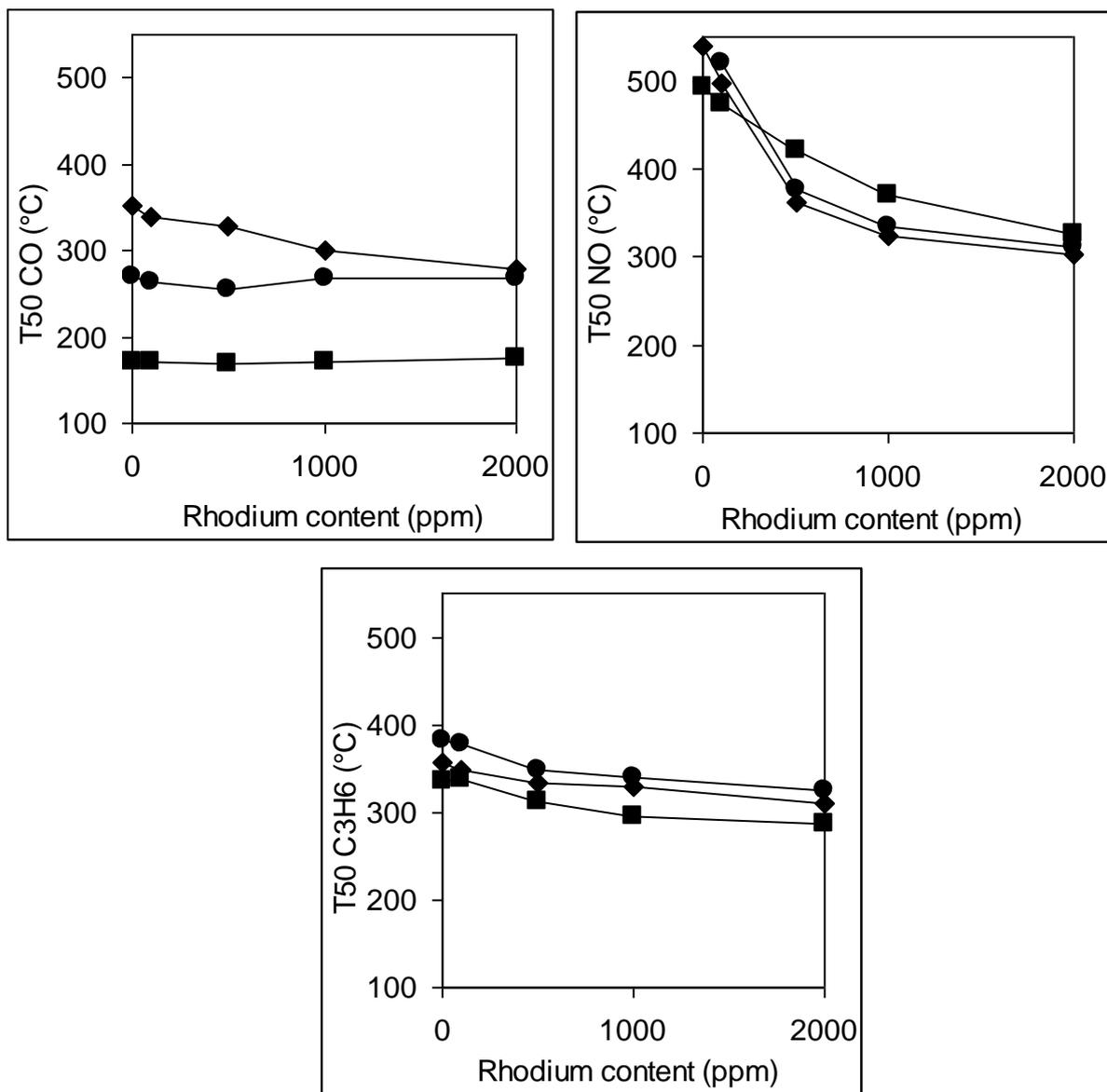


Figure 7: Evolution of the light off temperatures (T50) for CO, C<sub>3</sub>H<sub>6</sub> and NO as a function of the rhodium content for CuRh catalysts supported on alumina (▲), ceria-alumina (●) and ceria-zirconia (■).

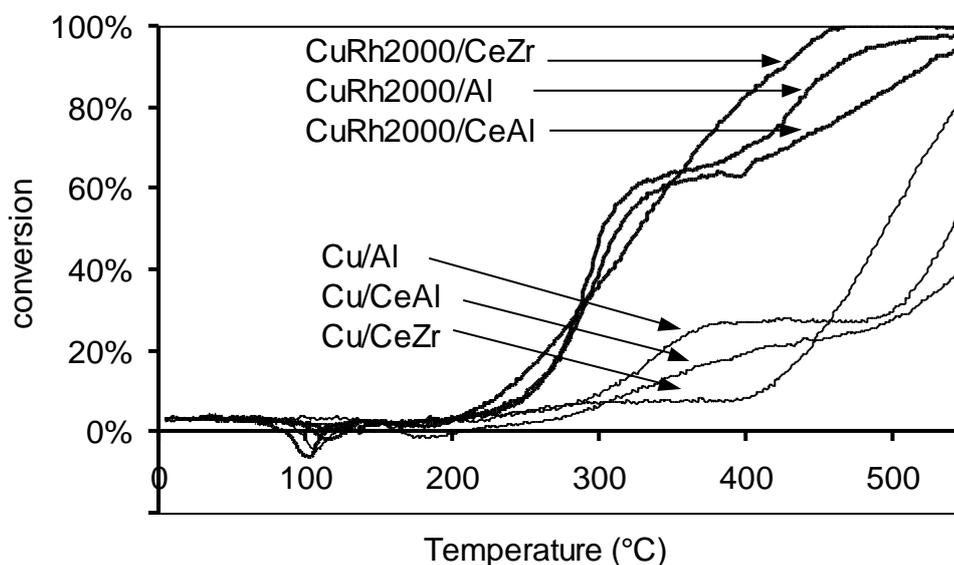


Figure 8: Conversion of NO in oscillatory conditions on monometallic Cu/support and bimetallic CuRh2000/support catalysts.

#### 4. DISCUSSION

By using H<sub>2</sub>-TPR, the different reduction steps were described and the reducibility behaviour of the catalysts was obtained. The OSC values of the solids at different temperatures are assessed on the basis of the data presented in Fig.1 and 2. The temperature of 550°C which is the highest temperature of the test could be chosen to obtain quantitative estimations of OSC. However, the catalytic results were obtained in the whole temperature range between 25°C and 550°C and the conversion is total for most of the solids at 550°C. Consequently, to discuss the catalytic results in relation to OSC, we will focus mainly on the qualitative variation of the OSC. We will examine how the OSC of the support and that of copper contribute to the catalytic activity. The monometallic rhodium catalyst will be considered first because the contribution of the rhodium to the OSC is negligible and the role of the support OSC can be easily put in evidence. Then we will discuss the roles of copper in the activity of Cu and Cu-Rh catalysts.

##### 4.1. Contribution of support OSC to the catalytic behaviour of Rh catalysts.

When increasing the support OSC from alumina to ceria-zirconia, the main change appears for  $T > 300^\circ\text{C}$  (Fig.5), where the limitations in CO and NO conversions decrease with ceria-alumina and are even suppressed with ceria-zirconia. These results can be explained on the basis of the interpretation developed in the case of the Rh/Al catalyst [5]. Such a solid has no significant OSC. During the rich period, there is not enough oxidizing agents in the gas phase to totally oxidise CO and C<sub>3</sub>H<sub>6</sub>. It is then observed that the C<sub>3</sub>H<sub>6</sub> oxidation is favoured and the

CO conversion is limited. Conversely, during the lean period, the NO reduction is inhibited. Thus, in absence of available material in the catalyst to attenuate the effect of these oscillations, the conversions of both CO and NO reach a limit. The different behaviours between Rh/Al and the two other catalysts is ascribed to the mobile oxygen present on ceria-alumina and ceria-zirconia and not on alumina. During the rich period, CO and C<sub>3</sub>H<sub>6</sub> react with O<sub>2</sub> and NO, but also with the support oxygen species. Conversely, in the following step in the lean mixture, the oxygen vacancies are filled by the excess of oxygen (from O<sub>2</sub> and/or NO dissociation). These two processes result in an attenuation of the effect of the mixture composition fluctuations and the NO and CO conversion are less limited. Supposing that C<sub>3</sub>H<sub>6</sub> oxidation occurs preferentially to CO oxidation which is experimentally observed at high temperature, the theoretical maximum conversions in absence of OSC and conversely the theoretical OSC needed to obtain the total conversions in CO and NO can be calculated. Table 4 gives these values and the experimental data obtained for the three catalysts. The OSC values were deduced from the integrated uptake during the first TPR peak up to about 400°C. The experimental results clearly show the correlation between the OSC of the catalyst and the CO and NO conversions. The OSC of Rh/CeZr is much higher than the theoretical value to obtain a complete conversion, whereas that of Rh/CeAl is intermediate.

The OSC influences also the N<sub>2</sub>O production. As shown in Table 4, the higher is the OSC, the lower is the maximum N<sub>2</sub>O concentration. Note that this maximum is observed near the same temperature (310-320°C) for approximately the same NO conversion (50%) with the three catalysts. For conversion levels inferior or equal at 50%, we can assume that the NO reduction occurs only during the rich periods. The first steps of the NO reduction with rhodium is assumed to be the NO adsorption followed by its dissociation [39], which is inhibited in presence of oxygen [18]. The N<sub>2</sub>O formation is due to the reaction of adsorbed NO (not yet dissociated) with adsorbed atomic nitrogen [40-42] or with another adsorbed NO species [43]. Whatever the mechanism, the decrease of the N<sub>2</sub>O formation can be ascribed to better properties for NO dissociation when using reducible supports. In rich conditions, the redox supports can act as an oxygen pump, leading to a decrease of the oxygen concentration on the rhodium surface. Then, the NO dissociation can be favoured, and the N<sub>2</sub>O formation is limited.

Table 4: Monometallic rhodium catalysts: Comparison between the catalyst OSC (1<sup>st</sup> TPR peak) and the experimental catalytic data (CO, NO maximum conversions and maximum N<sub>2</sub>O concentration).

Catalyst	OSC (μmol.g <sup>-1</sup> ) TPR 1 <sup>st</sup> peak	CO conversion (upper limit in %)	NO conversion (upper limit in %)	N <sub>2</sub> O maximum concentration (ppm)
-	-	27	50	
Rh/Al	≈0	47	57	150
Rh/CeAl	50	75	75	81
*	154	100	100	
Rh/CeZr	325	100	100	34

\* : Theoretical OSC value to obtain total CO and NO conversions.

The redox supports have few influence on the C<sub>3</sub>H<sub>6</sub> oxidation. The conversion curves for the three solids are close and the conversion reaches 100%. In fact, C<sub>3</sub>H<sub>6</sub> oxidation is much less sensitive to the mixture composition fluctuations, because, as observed in the case of alumina [5], the hydrocarbon is oxidised preferentially to CO at high temperature.

In summary, for the rhodium catalysts, the activity obtained in transitory regime is little sensitive to the support until the conversions remain inferior to 50 %, where no OSC is necessary. For higher conversions and especially in the case of CO and NO, the support OSC influences directly the activity by attenuating the composition variations and then suppressing the limitation of conversion.

#### **4.2. Case of copper catalysts, copper being itself an OSC component.**

The role of the copper OSC have been already put in evidence for the Al<sub>2</sub>O<sub>3</sub> supported catalysts [5]. Total oxygen conversion was observed with the Cu/Al catalyst at the end of the activity test in cycling conditions (some NO and CO were remaining), showing that around 150 μmol"O" species.g<sup>-1</sup> can be stored. Note that the OSC estimated from the TPR experiments is higher, near 365μmol"O" species.g<sup>-1</sup> (table 3). As shown on Fig.6, the influence of the support with the copper catalysts is not found only at high conversions. Great differences are also observed at low temperature in the CO oxidation, with 200°C difference in the light off temperatures. On alumina which has no OSC available, copper itself is active. On ceria-alumina, ceria-zirconia and ceria, the more the OSC is available at low temperature, the more active is the catalyst (see figs.1 and 6). Such an effect was not observed with rhodium, for which only the high conversion region was modified by OSC. It means that the association between copper and the redox support greatly improves the activity. Park et al [44] and Martinez Arias et al. [45] have already shown that addition of ceria to copper on alumina catalysts largely increases the activity in CO oxidation. This synergetic effect is not directly related to the OSC of the copper oxide (nearly the same for Cu/Al and Cu/CeAl catalysts), but must be ascribed to the interaction between copper and redox support, via its mobile oxygen. This activation of the support oxygen by copper to oxidise CO has already been proposed by Liu et al [46] or Skarman et al. [47], the behaviour of copper being similar to that of the noble metals [48-53].

The different behaviours observed in the NO conversion curves from Cu/Al to Cu/Ce have to be related to the actual composition of the reaction mixture during the oscillatory regime and the low temperature OSC.

The NO reduction curves are linked to the oxygen conversion (not shown) and can be divided in two parts, according as oxygen is still detected in the gas phase or not. During the first part, i.e until 500°C for Cu/Al and Cu/CeAl, and until 400°C-430°C for Cu/Ce and Cu/CeZr, the more the OSC is important, the more the NO conversion is low. Then, in this condition, the mobile oxygen of the support plays an inhibitor role. The main idea to explain these curves is that the catalysts have to be in a reduced state to allow the NO reduction. If not, the reducing agents react first with oxygen, from gas phase and/or from the catalyst (copper and support). We can assume that there is no significant NO conversion during the lean periods during this first part. Then, for the Cu/Al catalyst, the NO reduction occurs first during the rich periods, only after reduction of the copper. It explains the limitation of the conversion at only 25%,

against 50% for the theoretical value, (total NO reduction during the rich periods), also obtained with Rh/Al (no OSC). With increasing the OSC, the reduction of the catalysts need more reducing agents and the NO conversion is disfavoured, reaching less than 10% with Cu/Ce and Cu/CeZr.

Moreover, the supports with OSC damp the variation of the composition mixture and especially favour the oxidation reactions. It leads to a decrease of the temperature of the total oxygen consumption. Then, NO conversion re-increases at lower temperature with the increase of the OSC, and high conversion rate can be reached at high temperature (second part of the curves).

#### **4.3. Roles of Cu and Rh in bimetallic copper-rhodium catalysts.**

On alumina support which exhibits no OSC, the activity of copper is clearly improved upon addition of rhodium. This is particularly evident for CO and NO conversions, much less for propene oxidation. It was ascribed to the better reactivity of Rh at low temperature compared to that of copper [5]. In fact, there is no synergetic effect and practically no additive effect between copper and rhodium. The activity is directly linked to the best metal for each temperature range. The only additive effect is observed for CO conversion with a small increase for  $T > 350^{\circ}\text{C}$ . It can be related to the CO+NO reaction which is favoured by Rh. In these bimetallic catalysts on alumina, the main role of copper appears more related to its oxygen storage capacity, which allows high conversion rates at high temperature, than to its own catalytic properties.

In presence of a redox support, rhodium does not deeply modify the activity for CO conversion when added to Cu/CeAl and has no influence with Cu/CeZr (fig. 7). In this case, it is due to the better activity of the monometallic copper catalysts observed at low temperature and attributed to the association “copper-mobile oxygen”. Consequently, this effect is determining for the activity and the addition of rhodium has no additional influence for CO conversion. For the NO conversion (Fig. 7 and 8), the activity of the bimetallic catalysts increases continuously with the rhodium content and the influence of the redox support is very limited. At low conversion, i.e. as long as oxygen is present in the reaction mixture, the rhodium phase is much more active than copper for NO reduction and therefore the conversion is not affected neither by copper nor by the support OSC. The activity basically depends on the rhodium content. At higher conversion, the support OSC modifies the conversion by attenuating the fluctuations of composition and there is less or no limitation of the conversion depending on the rhodium content and the support OSC. As for the monometallic rhodium catalysts, the formation of  $\text{N}_2\text{O}$  with the bimetallic catalysts decreases with increasing the OSC of the support. Finally, rhodium presents the same properties in Cu-Rh bimetallic than in Rh monometallic catalysts. For propene oxidation, the conversion is slightly increased by rhodium addition to copper. It is also a little improved by the redox properties of the support, mainly when supported on ceria-zirconia. This shows again that rhodium is active for propene oxidation and that it is less sensitive than copper to the presence of support mobile oxygen species.

## 5. CONCLUSION

The objective of this work was to study if copper used in the three way catalytic reactions acted only as OSC provider or if, deposited on a redox support like ceria-alumina or ceria-zirconia and/or associated with rhodium, it could have also a specific role in the catalytic activity.

In the three way catalysis, the influence of the OSC is well established and the catalytic tests on the various supported CuRh catalysts have confirmed the essential function of the OSC.

Regarding the specific properties of each metal, rhodium alone is active for the conversion of the three pollutants from 200°C. In itself, it is little sensitive to the mobility of the support oxygen species. The OSC of the supports play a role only at high temperature for CO and NO conversions. There is less or even no limitation of the conversion when the support can attenuate (CeAl) or even suppress (CeZr) the effects of the composition oscillations. However, these effects are not operative in propene oxidation, because C<sub>3</sub>H<sub>6</sub> is oxidised preferentially to CO, whatever the support OSC.

Copper is also active although much less than rhodium to transform the three reactants, especially for the oxidation reactions. At low temperature, the order of reaction is the following: CO oxidation > C<sub>3</sub>H<sub>6</sub> oxidation > NO reduction. As already mentioned, copper participates to the regulation of the mixture composition. Then, it could have been supposed that a redox support has a limited influence because copper itself largely contributes to the catalyst OSC. If there is only a very limited effect for propene oxidation, it is different for CO and NO conversions. The copper activity is deeply influenced by the support redox properties, showing an interaction between the copper phase and the mobile oxygen species of the support. More positive is the consequence for CO conversion. The association of copper with some mobile oxygen species of the support leads to a very significant synergetic effect for CO conversion: T50 decreases from 356°C for Cu/Al to 158°C for Cu/Ce. On the contrary, the mobile oxygen of the support is unfavourable for the NO reduction at low temperature. Copper has to be in a reduced state to allow the NO reduction and the oxygen stored in the support during the lean periods acts as a reserve, also showing the strong mobility between the stored oxygen and copper. Note that at higher temperature, the support OSC, by favouring the oxidation reactions, allows the NO conversion to resume more easily.

Concerning the competition between CO and C<sub>3</sub>H<sub>6</sub> for the oxidation reactions, C<sub>3</sub>H<sub>6</sub> oxidation is favoured when the OSC is limited (support Al or CeAl). With a support exhibiting an OSC higher than that required to regulate the reducer/oxidant ratio (case of CeZr), the CO oxidation is predominant.

The association of copper with rhodium in the bimetallic catalysts did not result in a synergetic effect. The most active metal for one reaction or the most active metal-support association determines the activity. Thus for CO conversion, the association copper-support exhibiting mobile oxygen is the most active. For the NO reduction, the activity essentially depends on rhodium, mainly at low temperature (200-400°C). Finally, copper and rhodium catalyse C<sub>3</sub>H<sub>6</sub> conversion practically in the same temperature domain, with a slightly higher activity for rhodium.

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