

# Three-way catalytic activity of alumina-supported copper catalysts modified by rhodium

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**Abstract** – The three-way catalytic activity of a 4.7% Cu/Al<sub>2</sub>O<sub>3</sub> catalyst modified by addition of small amounts of rhodium (from 100 to 2 000 ppm) was measured up to 550 °C, in steady state or oscillatory conditions (0.1 Hz), using a synthetic gas containing N<sub>2</sub>, O<sub>2</sub>, CO, C<sub>3</sub>H<sub>6</sub> and NO. No synergetic effect in the catalytic properties has been observed between Cu and Rh, as the CO, NO and C<sub>3</sub>H<sub>6</sub> conversions at low temperature increase with rhodium concentration. At high temperature, the use of copper which exhibits oxygen storage properties improves the CO and NO conversion by moving up the limitations observed in the conversion under oscillatory conditions. © 2000 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

**rhodium / copper / three-way catalysts / oscillatory conditions / Cu/Al<sub>2</sub>O<sub>3</sub> / CuRh/Al<sub>2</sub>O<sub>3</sub> / oxygen storage**

**Version française abrégée — Activité en catalyse trois-voies de catalyseurs au cuivre supportés sur alumine modifiés par ajout de rhodium.** L'influence de faibles ajouts de rhodium sur l'activité en catalyse trois-voies d'un catalyseur 4.7% Cu/Al<sub>2</sub>O<sub>3</sub> avec des teneurs en rhodium de 100, 500, 1 000 et 2 000 ppm a été étudiée. L'activité catalytique a été mesurée entre 50 et 550 °C, en régime stationnaire et transitoire (0,1 Hz), sur un mélange synthétique contenant N<sub>2</sub>, O<sub>2</sub>, CO, C<sub>3</sub>H<sub>6</sub> et NO. Aucun effet de synergie entre le cuivre et le rhodium n'a été observé sur les propriétés catalytiques. En régime stationnaire et à basse température, la conversion de NO augmente avec la concentration en Rh. On observe en parallèle une légère amélioration de la conversion en oxydation de C<sub>3</sub>H<sub>6</sub> et CO. Comparé au rhodium, le cuivre améliore l'oxydation de CO à basse température. À température plus élevée, C<sub>3</sub>H<sub>6</sub> est oxydé préférentiellement à CO, jusqu'à conversion totale. En régime transitoire, CO et NO ont des conversions limitées, par suite de l'épuisement temporaire de l'un des réactifs durant les oscillations de composition « mélange riche–mélange pauvre ». La présence de cuivre, élément qui présente des propriétés de stockage d'oxygène, permet d'augmenter la conversion de CO et NO à haute température. © 2000 Académie des sciences / Éditions scientifiques et médicales Elsevier SAS

**rhodium / cuivre / catalyseurs trois voies / régime transitoire / Cu/Al<sub>2</sub>O<sub>3</sub> / CuRh/Al<sub>2</sub>O<sub>3</sub> / stockage d'oxygène**

## 1. Introduction

The precious metals (Pt, Rh, Pd) constitute the active phase of the current three-way catalysts used for the automotive exhaust gas treatment. Their cost and their availability in the future constitute a revolving

problem and it would be highly valuable to find substitutes of lower costs. Recently, it was shown that a perovskite type mixed oxide such as La<sub>2</sub>CuO<sub>4</sub> was active in the CO + NO reaction [1, 2]. Under reaction conditions, there was an activation and it was deduced that metallic copper species were the

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active sites for the reaction [2]. However, copper seems not active enough to be used alone for real applications without promoter addition. Therefore, looking for new types of three-way catalysts, we have investigated in this study how the addition of rhodium which is known to be a key component in the NO<sub>x</sub> conversion can influence the catalytic properties of copper in alumina-supported catalysts. Conversely, copper was found to be an excellent promoter of the oxygen storage capacity (OSC) of a Rh/CeO<sub>2</sub> catalyst [3]. In this work, the catalytic data obtained with the CuRh/Al<sub>2</sub>O<sub>3</sub> systems in steady state or cycled feed stream are presented and discussed.

## 2. Experimental

The alumina support (Rhodia 531P) had a BET surface area of 115 m<sup>2</sup>·g<sup>-1</sup>. It was co-impregnated with copper and rhodium nitrate solutions in order to obtain catalysts with a 4.7 wt% copper content and 0, 100, 500, 1 000 and 2 000 ppm rhodium content. A monometallic catalyst with 1 000 ppm Rh was also prepared. After drying under air for one night at 110 °C, the solids were ground and calcinated for 6 h at 400 °C under a 6 L·h<sup>-1</sup> O<sub>2</sub> flow (1 °C min<sup>-1</sup> heating rate). Finally, the catalysts were reduced at 500 °C under hydrogen (7 L·h<sup>-1</sup>) for 6 h. After cooling under H<sub>2</sub> to room temperature, the samples were put under nitrogen and then slowly under air. The samples are referred as CuRh<sub>x</sub>/Al, where *x* indicates the Rh content in ppm.

The three-way catalytic activity was measured in the simultaneous conversion of CO, NO<sub>x</sub> and C<sub>3</sub>H<sub>6</sub>. The experimental device [4, 5] is constituted of two independent ramps in which mixtures of different compositions can be prepared using mass controllers

for each gas diluted in nitrogen (CO, NO, C<sub>3</sub>H<sub>6</sub>, O<sub>2</sub>). Thus, it is possible to work either with only one ramp in steady state conditions, i.e. with a unique composition mixture, or in oscillatory conditions, using the two ramps with two mixtures of different composition. In the latter case, each mixture goes alternately through the catalytic bed. This allows to simulate the rich/lean oscillations of the mixture occurring in the real conditions of a catalytic converter. A by-pass system allows to verify the composition of the initial mixture before the catalytic test. At the exhaust of the reactor, the gases are cooled and then analysed in series by paramagnetism for O<sub>2</sub> and by infrared spectrometry for CO, CO<sub>2</sub>, NO, N<sub>2</sub>O and C<sub>3</sub>H<sub>6</sub>.

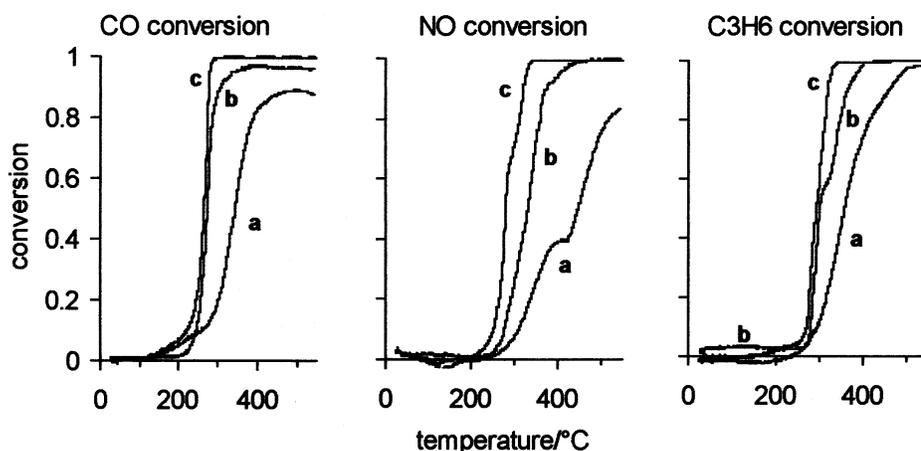
The tests were performed on 20 mg catalyst diluted in 180 mg SiC, in order to limit the possible temperature increase due to highly exothermic reactions, like propene combustion. It was verified that SiC alone was not active. Before the measurement of the activity itself, the catalyst was first activated in steady-state operation under a stoichiometric mixture having the composition given in *table I*. The solid was heated at 10 °C·min<sup>-1</sup> under this mixture up to 550 °C, kept 1 h at this temperature and cooled to room temperature under N<sub>2</sub> flow. At this stage, the state of the metals was undetermined, even if we can assume that it was metallic, in accordance with the results obtained with La<sub>2</sub>CuO<sub>4</sub> [2]. Then the reaction mixture was introduced and one can think that the metals were partially oxidised by O<sub>2</sub> and NO present in the mixture, at least during the first heating minutes. The catalytic activity test was performed up to 550 °C (heating rate: 5 °C·min<sup>-1</sup>), either under stoichiometric or oscillating mixture (compositions in *table D*). The cycling frequency between the two ramps was low (0.1 Hz) to insure at the catalytic bed

**Table I.** Composition of the gaseous mixtures used in steady state and oscillatory conditions<sup>a</sup>.

	Steady state	Oscillatory		
		Lean mixture	Rich mixture	Variation
O <sub>2</sub> (ppm)	5 600	7 820	3 380	±2 220
CO (ppm)	6 200	1 620	10 780	±4 580
NO (ppm)	1 000	1 000	1 000	0
C <sub>3</sub> H <sub>6</sub> (ppm)	667	667	667	0
<i>s</i>	1	2,18	0,46	

<sup>a</sup> All the gases are used diluted in nitrogen. *s* represents the oxidant/reductant ratio. It is calculated from the concentrations of each component by the expression:

$$s = \frac{2[\text{O}_2] + [\text{NO}]}{[\text{CO}] + 9[\text{C}_3\text{H}_6]}$$



**Figure 1.** Activity in steady state conditions for CO, NO and C<sub>3</sub>H<sub>6</sub> and for (a) Cu/Al, (b) Rh1000/Al and (c) CuRh2000/Al catalysts.

the effective variation of composition programmed in each ramp in spite of the mixing of the gaseous front. In both conditions (steady state or oscillatory) the flow rate was 12 L·h<sup>-1</sup>, which corresponded approximately to a SV of 500 000 h<sup>-1</sup>. It must be remarked that, due to the mixing of the gaseous fronts before and after the catalytic bed, the amplitude of the variations of composition was lower at the level of the analysers than that imposed initially in the ramps. However, it has been verified that with this frequency, the catalyst sees effectively the nominal changes in composition [4].

### 3. Results

#### 3.1. Catalytic activity in steady state conditions

The two monometallic catalysts, Cu/Al and Rh1000/Al, were compared to the CuRh2000/Al sample. The alumina support alone was inactive in our conditions. *Figure 1* gives the conversions for each reactant between 50 and 550 °C. In a general description, all the catalysts exhibit a sigmoidal activity profile. In the case of Rh1000/Al, the CO, NO and propene conversions begin at 215, 240 and 270 °C, respectively. For  $T > 400$  °C, the three pollutants are fully converted. Cu/Al is always less active, except for the CO oxidation which starts at lower temperature, at around 120 °C. CuRh2000/Al is a little more active than Rh1000/Al and, as for Cu/Al, its activity in CO oxidation starts at around 120 °C.

It must be noted that the NO conversion at low temperature does not produce only nitrogen. There is also formation of N<sub>2</sub>O, which is also a pollutant. For Rh1000/Al and below 300 °C, the N<sub>2</sub>O selectivity is 100 %. Then the selectivity drops quickly and for

$T > 400$  °C, N<sub>2</sub>O is practically not observed. In the case of Cu/Al, the NO conversion occurs at higher temperature and the maximum selectivity in N<sub>2</sub>O is only 6 % at 470 °C. For CuRh2000/Al, the maximum N<sub>2</sub>O selectivity is 37 % at 292 °C.

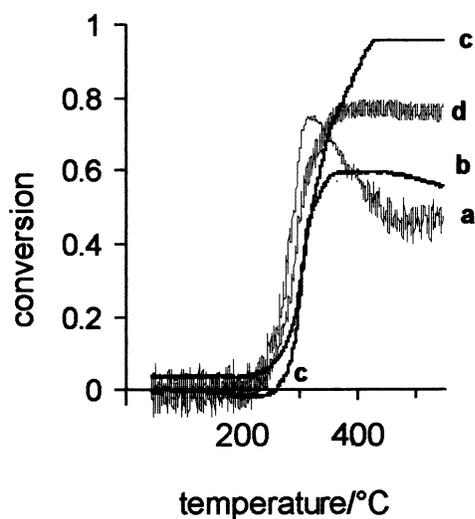
#### 3.2. Catalytic activity in oscillatory conditions

The influence of the Cu/Rh ratio was studied in more details in oscillatory conditions. Since strong differences appear between Rh and the other copper based catalysts for the CO and NO conversion curves, we examine first the case of the Rh sample and then the copper and bimetallic catalysts. Because of the fluctuations in the concentration of CO and O<sub>2</sub> at the reactor inlet, the actual conversions given in the figures were calculated on a mean concentration basis, i.e. with the steady state composition (see *table 1*).

##### 3.2.1. Rh1000/Al<sub>2</sub>O<sub>3</sub> catalyst

*Figure 2* gives the conversion curves in oscillatory conditions. The comparison with the steady-state data shows that the conversions are similar at low temperature but differ greatly at high temperature for CO and NO. The CO conversion begins near 170 °C, goes through a maximum at 315 °C where 75 % CO is oxidised, and then drops down and stabilises at 47 % for  $T > 450$  °C. In this temperature domain, the oscillations between the rich and lean composition ( $\Delta\text{comp.}$ ) are then scarcely attenuated ( $\Delta\text{comp.} = 925$  ppm at room temperature,  $\Delta\text{comp.} = 780$  ppm at 450–550 °C).

The NO conversion starts at 220 °C. For  $T > 350$  °C, the NO conversion remains limited to about 60 % and even decreases at the end of the test to 56 %. The N<sub>2</sub>O selectivity goes through a maximum (80 %) at 297 °C, the maximum N<sub>2</sub>O concentration



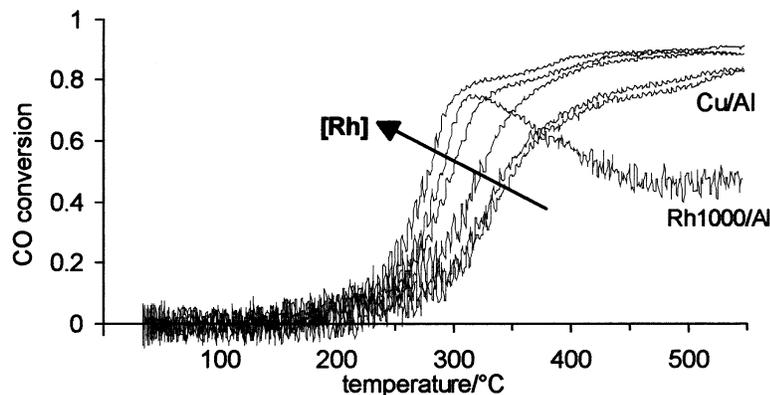
**Figure 2.** Activity in oscillatory conditions for Rh1000/Al. (a) CO, (b) NO, (c) C<sub>3</sub>H<sub>6</sub> and (d) O<sub>2</sub>.

(150 ppm) being obtained at about 315 °C. For higher temperatures, the N<sub>2</sub>O production decreases to zero.

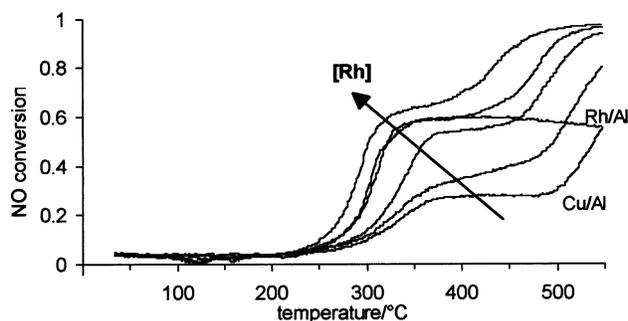
The propene conversion starts only at around 260 °C, but with a higher activation energy than for CO or NO ( $E_a = 204 \text{ kJ}\cdot\text{mol}^{-1}$ ). When the conversion is higher than 50 %, the increase in activity slows down, but the propene is entirely eliminated for  $T > 430 \text{ °C}$ .

### 3.2.2. CuRh/Al<sub>2</sub>O<sub>3</sub> catalysts

As shown in *figure 3*, the CO conversion is favoured upon addition of rhodium to copper. The temperature of the beginning of reaction slightly decreases. The light off temperature ( $T_{50}$ ), temperature for which 50 % of the pollutants are converted, decreases from 350 °C for Cu/Al to 275 °C for CuRh2000/Al. Also, at high temperature, the maximum of conversion increases with rhodium but is



**Figure 3.** Conversion of CO in oscillatory conditions on monometallic Cu/Al, Rh1000/Al and bimetallic CuRh100/Al, CuRh500/Al, CuRh1000/Al and CuRh2000/Al catalysts.



**Figure 4.** Conversion of NO in oscillatory conditions on monometallic Cu/Al, Rh1000/Al and bimetallic CuRh100/Al, CuRh500/Al, CuRh1000/Al and CuRh2000/Al catalysts.

always much higher than that obtained with Rh1000/Al alone.

The NO conversion curves are more complex since they present like an intermediate plateau in the sigmoidal profile. This peculiar shape will be discussed below. However, it is evident from *figure 4* that the higher the rhodium content, the more active the catalyst. More than 200 °C difference is obtained for  $T_{50}$  between Cu/Al and CuRh2000/Al. At 550 °C, all the bimetallic catalysts are more active than Rh1000/Al.

The propene conversion curves are given in *figure 5*. They are almost sigmoidal but rather close between each other (difference in  $T_{50}$  lower than 50 °C for the extreme curves). Nevertheless the increase in the activity upon addition of Rh is clearly evidenced.

## 4. Discussion

### 4.1. Influence of rhodium in the bimetallic CuRh catalysts

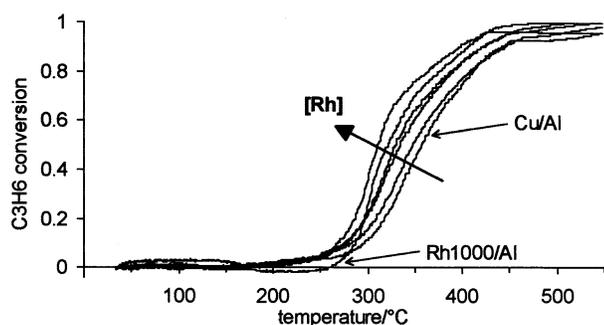
The copper-alumina catalyst exhibits some three-way catalytic activity. However, as evidenced in

figures 3–5, it is clear that this activity is improved upon addition of small amounts of rhodium. Rhodium itself is very active in the three reactions, and it must be noted that there is no great difference in the activity curves between Rh1000/Al and CuRh1000/Al, mainly for conversions  $< 50\%$ . Thus, an addition of the properties of each metal is sufficient to explain the obtained conversions and no synergetic effect is deduced, which would have strongly increased the activity of both metals.

Conversely, because of the addition of the properties of each metal, the CuRh/Al bimetallic catalysts exhibit slight improvements in the catalytic properties compared to Rh1000/Al. It is well shown in figure 1 for the CO and  $C_3H_6$  conversions at low temperature (steady state conditions) and also in figures 3–4 for the CO and NO transformation at high conversions (oscillatory conditions). This can be attributed to the redox properties of copper. Indeed, copper is an oxidation catalyst which favours the beginning of the CO and propene oxidation at lower temperature than rhodium. Concerning the improvement at high conversion, it involves the property of copper to store oxygen. The relation of this oxygen storage capacity (OSC) with the CO and NO conversion is explained hereafter.

#### 4.2. Effect of OSC on the catalytic activity in oscillatory conditions

In order to explain the limitations observed in oscillatory conditions for Rh1000/Al in the CO and NO conversion curves at high temperatures, we have to consider that in our working conditions, a very low cycling frequency and a large cycling amplitude may result in the succession of incomplete conversions either of the oxidants or the reduc-



**Figure 5.** Conversion of  $C_3H_6$  in oscillatory conditions on monometallic Cu/Al, Rh1000/Al and bimetallic CuRh100/Al, CuRh500/Al, CuRh1000/Al and CuRh2000/Al catalysts.

tants. For example, if the propene oxidation is complete as it is observed, the conversion for CO will be limited during the rich half-cycle, because there will not be enough oxygen. Thus, we have calculated for each mixture, rich or lean, what is the maximum possible conversion for each pollutant. However, for the calculation, it is necessary to define a hierarchical order in the competitive reactions. Considering the experimental results (figure 2), it is clear that at high conversion, propene oxidation is favoured compared to CO oxidation. Moreover, the reduction of NO by CO is strongly inhibited by oxygen [6]. Consequently, we have assumed the following decreasing reactivity sequence:  $C_3H_6 + O_2 > CO + O_2 > CO + NO$ . The oxidation of CO and  $C_3H_6$  by NO as oxidant was not considered for simplification. Indeed, the total conversion of NO would allow to oxidise only 11% of propene in  $CO_2$  and the reduction of CO by NO would be limited to 16%. Finally, in the present case (Rh1000/Al), the OSC is very low and was neglected. Therefore, the succession of the reactions is as following.

In lean mixtures:

$C_3H_6 + 9/2 O_2 \rightarrow 3 CO_2 + 3 H_2O$ : the hydrocarbon conversion is total, and  $O_2$  ( $\approx 4800$  ppm) is available for the CO oxidation.

$CO + \frac{1}{2} O_2 \rightarrow CO_2$ : the CO conversion is total, and it still remains  $\approx 4000$  ppm  $O_2$ .

$CO + NO \rightarrow CO_2 + \frac{1}{2} N_2$ : the reaction is not possible, because there is no more CO.

In rich mixture:

$C_3H_6 + 9/2 O_2 \rightarrow 3 CO_2 + 3 H_2O$ : the hydrocarbon conversion is again complete and it remains  $\approx 380$  ppm  $O_2$  for the CO oxidation.

$CO + 1/2 O_2 \rightarrow CO_2$ : the conversion of  $O_2$  is total, and this time, it remains  $\approx 10000$  ppm CO.

$CO + NO \rightarrow CO_2 + 1/2 N_2$ : the NO conversion is complete, it remains  $\approx 9000$  ppm CO.

Table II gives the theoretical maximum conversions and their average obtained in oscillatory conditions for each mixture and with each pollutant. For CO, NO,  $C_3H_6$  and  $O_2$ , the mean maximum conversions are 27, 50, 100 and 64%, respectively. These values are in agreement with the experimental results, the observed differences being explained by the unavoidable mixing of the gaseous fronts before passing through the catalytic bed. Therefore, these results clearly show that the rich-lean oscillations are the reason of the limitations of the conversions in CO and NO for the Rh1000/Al catalyst. They are in agreement with previous transient CO and NO experiments performed with different frequencies on a Rh/Al solid [7].

**Table II.** Remaining compositions and theoretical conversions for each mixture, calculated assuming the following reactivity order:  $C_3H_6 + O_2 > CO + O_2 > CO + NO$ . Comparison with the experimental results.

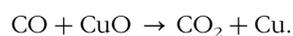
	Lean mixture		Rich mixture		Average rich-lean		Experimental results	
	remaining concentration (ppm)	conversion (%)	Remaining concentration (ppm)	conversion (%)	Remaining concentration (ppm)	conversion (%)	conversion (%)	conversion (%)
CO	0	100	9 026	16	4 513	27	47	47
NO	1 000	0	0	100	500	50	56	56
$C_3H_6$	0	100	0	100	0	100	100	100
$O_2$	4 008	49	0	100	2 004	64	76	76

Consequently, the catalytic activity at high conversion must be strongly influenced by the oxygen storage capacity of the solids. It must be underlined that in steady state operation there is no excess of oxidant or reductant, and that the conversions are total at high temperature for the three reactants. In oscillatory operation, a component having an OSC is able to store and release oxygen during the oscillations and thus allows to attenuate the amplitude of the oscillations responsible for the CO and NO conversion limitations. Copper is present at a relatively high content ( $0.74 \text{ mmol}\cdot\text{g}^{-1}$ ). Therefore it may act as an OSC component, and effectively it moves up the conversion limits, as it is evidenced in *figures 3* and *4*. This positive effect of OSC components under transient feed stream conditions is well documented in the literature [8].

The  $\text{C}_3\text{H}_6$  conversion is little influenced by the presence of copper and the testing conditions. This appears quite normal, since the oxidation of  $\text{C}_3\text{H}_6$  by  $\text{O}_2$  is the most favoured reaction as it was shown above, in agreement with literature [9]. As long as there is enough oxygen to oxidise the hydrocarbon, there will be no influence of the mixture composition.

#### 4.3. Effect of copper on the NO conversion curves in the bimetallic CuRh catalysts

In steady state conditions, the NO conversion curve vs. temperature for Cu/Al exhibits a temporary constant level at around  $400^\circ\text{C}$  (*figure 1*). A more pronounced intermediate plateau is observed for CuRh/Al in oscillatory conditions, with conversion percentage and temperature range depending on the Rh content (*figure 4*). For Rh1000/Al, the plateau at 56% was explained above by the limitations resulting from the rich-lean oscillations. For the CuRh/Al, the presence of copper attenuates the amplitude of the oscillations and thus favours the conversion at high temperature. The copper oxygen storage capacity may also account for the existence of the plateau at lower conversion, i.e. for  $\text{C}_3\text{H}_6$  and CO partial conversion. For  $T > 300^\circ\text{C}$ , the oxidation of copper by gaseous  $\text{O}_2$  is a fast reaction involving both the surface and the bulk of copper particles. Then the formed copper oxide constitutes an oxygen reservoir, which participates to the CO and  $\text{C}_3\text{H}_6$  oxidation according to the reactions:



Therefore, during a cycle, as long as there is oxygen left in the reactor or stored by copper, unreacted CO

and  $\text{C}_3\text{H}_6$  react preferentially with this oxygen rather than with NO, and the NO conversion remains nearly constant. In parallel, the conversions for CO and  $\text{C}_3\text{H}_6$  increase and the curves effectively exhibit inflexion points, which corresponds to the intervention of this stored oxygen in the oxidation reactions. It is important to note that, at higher temperature, the conversion of NO with the residual CO increases again precisely when oxygen becomes depleted, i.e. when the  $\text{O}_2$  conversion is nearly complete (not shown). The fact that the NO conversion at the plateau increases with Rh content must be attributed to the own activity of rhodium.

## 5. Conclusion

The study of CuRh/alumina catalysts has evidenced no synergetic effect between Cu and Rh for the activity in three-way catalysis. For each reaction, the conversion at low temperature increases with the rhodium concentration. However, compared to rhodium alone, the CO and  $\text{C}_3\text{H}_6$  oxidation begins at lower temperature in presence of copper.

When the catalytic tests are performed under oscillatory conditions, differences are observed at high conversions between the catalysts of different composition. The analysis of the conversion curves as resulting from the succession of competitive reactions in reducing and oxidising mixtures easily explains the incomplete CO and NO conversions at high temperature by the alternate depletion of one of the reactants during the oscillations 'rich mixture–lean mixture'. However, in presence of copper, which alternately is able to adsorb and release oxygen, the regular fluctuations of the mixture composition are attenuated at the catalyst level and the NO and CO conversions become less limited. The propene oxidation is much less sensible to the composition fluctuations because, under oxygen deficient mixture, the hydrocarbon is preferentially oxidised compared to CO at high temperature. It may be concluded that, in this bimetallic catalyst, the important role of copper appears more related to its oxygen storage capacity than its own catalytic properties.

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