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Oxygen storage capacity of promoted Rh / CeO_2 catalysts. Exceptional behavior of RhCu / CeO_2

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The effect of various additives (V, Cr, Mn, Fe, Co, Ni, Cu and Pb) on the oxygen storage capacity (OSC) of CeO_2 and Rh/CeO_2 catalysts was investigated. Copper is an excellent promoter of OSC conferring to Rh a very high resistance to sintering (900°C, 2% O_2).

Keywords: Oxygen storage capacity; Rh/CeO_2 and CuRh/CeO_2 catalysts; resistance to sintering

1. Introduction

Surface migration of oxygen can be of the utmost importance in oxidation processes in which the catalysts are submitted to repeated changes in gas composition. This is the case with post combustion catalysts which have to store oxygen during lean phases of operation conditions so as to restitute it during the rich phases when the partial pressure of O_2 in gas phase begins to decrease. One of the roles of ceria is to improve the oxygen storage capacity (OSC) of catalysts [1–5]. Noble metals, and in particular rhodium, play an active role in promoting the OSC of the support. The aim of this paper is to examine to what extent the oxygen storage capacity of a Rh/CeO_2 can be improved by different redox promoters (M = V, Cr, Mn, Fe, Co, Ni, Cu and Pb). Copper being an excellent OSC promoter, an in-depth study of RhCu/CeO_2 catalysts was carried out: temperature-programmed reduction (TPR) and resistance to sintering of the OSC properties of this bimetallic system were investigated.

2. Experimental

The support used throughout this study was a ceria provided by IFP (19 m^2 g^{-1}

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at 350°C, 16 m^2 g^{-1} at 550°C, main impurities: La, 4000 ppm; Ca, 40 ppm), simply denoted CeO$_2$. The first series of catalysts (promoter/CeO$_2$) was prepared by impregnating the support with aqueous solutions of various nitrates. The reference (pure CeO$_2$) was obtained by treating the bare support with an aqueous solution of ammonium nitrate. The second series of catalysts (promoter/Rh/CeO$_2$) was prepared by impregnating a 0.67 wt% Rh/CeO$_2$ catalyst with the same promoters as in the first series. All the catalysts were dried overnight at 120°C. The chemical composition of the catalysts is given in table 1.

OSC measurements were carried out in a pulse chromatographic system described elsewhere [6]. The catalyst sample (10–50 mg) was inserted in a U-quartz reactor, heated to 450°C (4°C min^{-1}) in a helium flow (30 cm^3 min^{-1}; less than 1 ppm impurities) and then oxidized by ten O$_2$ pulses (0.268 cm^3) injected every other minute (oxygen storage). The temperature was subsequently adjusted to the operating temperature T_R ($350 < T_R < 550$°C) at which CO pulses were injected every other minute. OSC values were determined from the amount of CO$_2$ produced at the first pulse of CO (titration of the "fast" oxygen). The same procedure was applied but with a change in the temperature T_R after a reoxidation at 450°C. The same apparatus was used for carrying out the TPR experiments (sample weight: 0.25 g; carrier gas: Ar, 20 cm^3 min^{-1}; H$_2$ pulses injected every other minute, 4°C min^{-1} from 20 to 500°C) as well as the sintering of certain catalysts in an oxygen periodic pulse flow (sample weight: 0.5 g; carrier gas: He, 30 cm^3 min^{-1}; O$_2$ pulses injected every other minute for 2 h at 900°C; cf. ref. [7]).

3. Results and discussion

3.1. FIRST SERIES (PROMOTER/CeO$_2$)

The results of the OSC measurements for this series are given in fig. 1. For Ni, Cu and Cr, separate experiments were carried out on three different samples of the same catalyst. The reproducibility was generally better than ±1.5% (see error bars in fig. 1).

The best candidates for promoting OSC in the absence of a noble metal are:

Table 1
Chemical composition of the catalysts (M = promoter)

Promoter	V	Cr	Mn	Fe	Co	Ni	Cu	Pb
first series M/CeO$_2$								
(wt%)	0.20	0.20	0.21	0.26	0.27	0.32	0.36	0.42
second series RhM/CeO$_2$ (0.67 wt% Rh)								
(wt%)	0.21	0.22	0.19	0.25	0.27	0.32	0.37	0.43
M/Rh + M (at%)	38	39	36	41	41	45	48	25

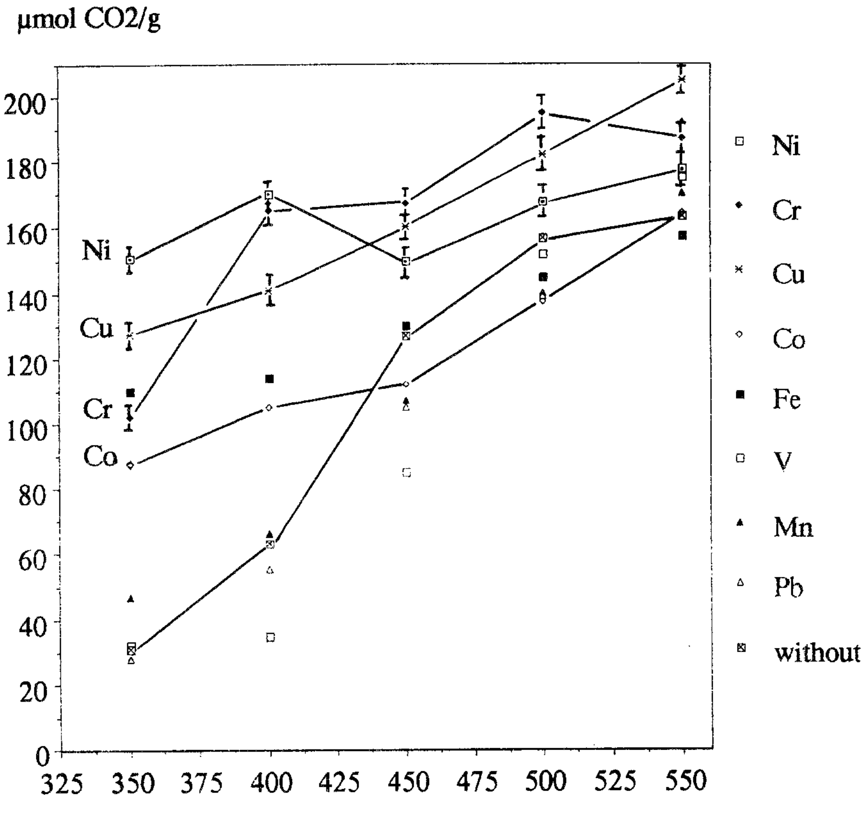

Fig. 1. OSC of promoted ceria catalysts.

Ni > Cu > Fe ≈ Cr > Co at 350°C and Cu > Cr ≈ Ni at 550°C. Mn, V and Pb are inactive and even poison the oxygen storage.

Excess values of OSC relatively to those of the bare support are given in table 2. At low temperature (350°C), the excess OSC values are higher than the – values maximal amount of oxygen stored by the promoter itself (corresponding to the reduction of M^{n+} into M^0). This means that a significant part of the oxygen is, via the promoter, stored on the support. At 550°C, the bare support is able to store directly a large amount of oxygen: at this temperature, the contributions of the promoters are well inferior to those at 350°C.

3.2. SECOND SERIES (PROMOTER/Rh/CeO_2)

The results obtained with the rhodium-containing catalysts appear in fig. 2 (error bars on Ni, Cu and Cr are deduced from triplicated experiments). The noble metal increases, in significant proportion, the OSC of ceria. This is linked to the

Table 2
Effect of the promoter on the OSC values (μmol CO_2 g^{-1}). The first line gives the absolute OSC values of the unpromoted ceria while the others indicate the additional OSC values due to the promoter. α is the theoretical amount of CO_2 formed during the reduction of M^{n+} to the metal state (n is assumed to be 2 for Cu, Co and Ni, which leads to $CO_2/M = 1$ for these promoters, while $n = 3$, or $CO_2/M = 1.5$, for Fe and Cr)

Promoter	1st series (M/ CeO_2)			2nd series (M/Rh/ CeO_2)		
	α	OSC 350°C	OSC 550°C	α	OSC 350°C	OSC 550°C
without	–	30	162	–	315	346
copper	57	+97	+42	58	+11	+37
iron	70	+80	−3	67	−35	−2
cobalt	46	+58	0	46	−7	+22
nickel	54	+121	+14	54	+32	−8
chromium	58	+72	+21	63	+15	0

high reducibility of the ceria surface in the presence of a noble metal, particularly with rhodium [4,8–10]. Moreover the number of promoters which increase the OSC values of Rh/ CeO_2 is limited: Ni, Cr, Cu at 350°C and Cu and Co at 550°C. The excess OSC values i.e., here, the differences between the OSC values of M/Rh/ CeO_2 and of Rh/ CeO_2 – are given on the right-hand side of table 2. Although nickel and copper are the best elements for promoting OSC, their excess values are always below –, the theoretical oxygen content in the promoter oxide. This means that none of the promoters is totally reduced (at least into the zero valence state) with the injection of the first pulse of CO. When rhodium is present, the contribution of the promoters to the OSC *on* CeO_2 would be nil, and even negative since the oxygen storage on the support is essentially due to the rhodium. In this case, the role of the promoter was limited to storing oxygen in its oxide. This mechanism of doping differs certainly from that proposed by Cho in the case of gadolinia-doped ceria [11]: Gd, a trivalent cation, would create new oxygen vacancies in the ceria lattice, thus increasing oxygen conductivity (and mobility). Whether or not there was rhodium in the catalyst, copper appeared as being the best promoter of the series, maintaining its performance over the whole range of temperatures. The stability of the CuRh system was then studied in more detail.

3.3. RESISTANCE TO SINTERING OF THE Cu/Rh/ CeO_2 CATALYST

The monometallics Rh/ CeO_2 and Cu/ CeO_2 as well as the bimetallics CuRh/ CeO_2 were sintered in an oxygen pulse flow (mean concentration: 2 vol% O_2) for 2 h at 900°C. Their OSC properties, compared with those of the fresh samples, are given in table 3. Monometallics' OSC decrease by ca. 45% at 350°C and by ca. 35% at 550°C. In the bimetallics, however, only a little change in the OSC values was

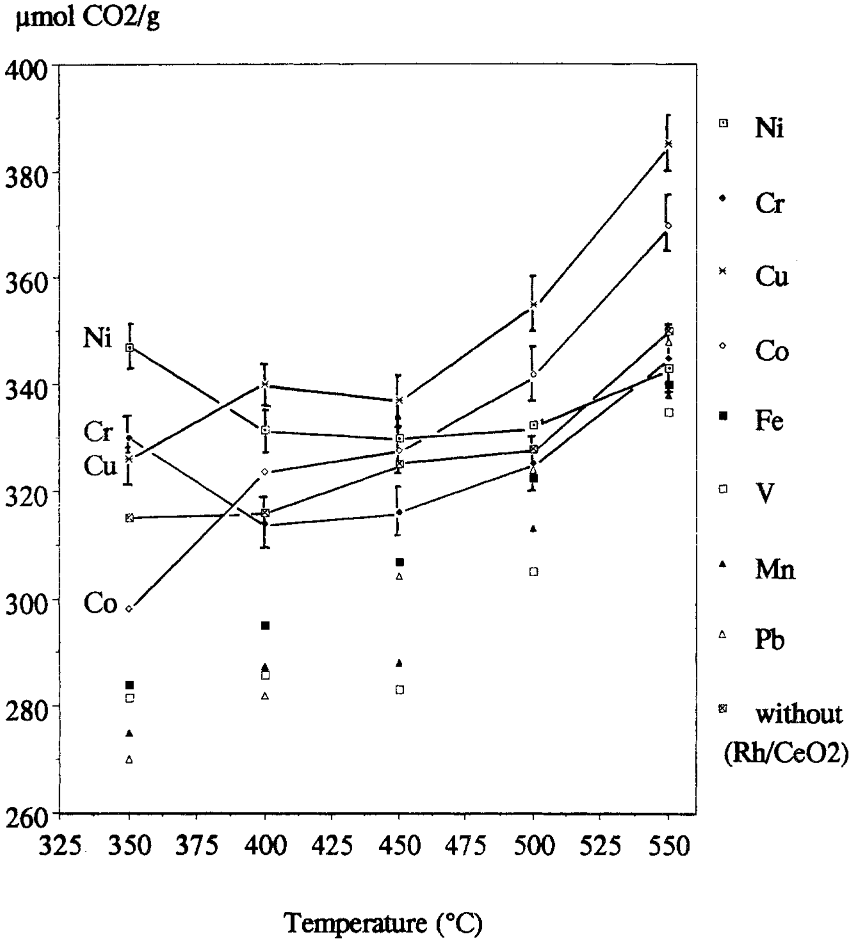

Fig. 2. OSC of promoted Rh/ CeO_2 catalysts.

recorded. To try and explain this exceptional behavior, Rh, Cu and CuRh catalysts were characterized further by chemisorption and titration as well as by TPR. H_C, O_T and H_T values are given in table 4. It is known that ceria-supported catalysts lead to very high O_T and H_T values, irrespective of the metal dispersity [10]. This was confirmed here for the Rh/ CeO_2 catalyst. It can be noted, however, that the sintered catalyst exhibited a high hydrogen uptake, quite characteristic of the formation of a new rhodium–ceria compound. For this catalyst, O_T and H_T values decreased approximately in the same proportions as those of OSC. There was no H_2 chemisorption nor H_2 titration on Cu/ CeO_2, in accordance with the usual behavior of this metal [12,13]. The behavior of the fresh CuRh bimetallics was more close to that of the rhodium (significant H_C value and large amounts of O_2 and H_2 taken in the titrations) while the sintered catalyst resembled pure copper (extremely low values for H_C and H_T). However, compared with monometallics, the CuRh catalyst conserved the highest O_T value on sintering. TPR profiles for H_2 are

Table 3
Effect of sintering in O_2 (2%) at 900°C on the OSC of copper–rhodium catalysts (f = fresh, s900 = sintered at 900°C)

Catalyst	OSC (μmol CO_2 g^{-1})		
	350°C	450°C	550°C
CeO_2 f	30	123	162
CeO_2 s900	11	49	69
Rh/CeO_2 f	315	323	346
Rh/CeO_2 s900	172	231	268
Cu/CeO_2 f	127	158	204
Cu/CeO_2 s900	68	108	148
Cu/Rh/CeO_2 f	326	337	383
Cu/Rh/CeO_2 s900	319	359	392

shown in fig. 3 while the temperatures of the peak maxima and the amounts Q_H of hydrogen consumed during the reduction are reported in table 5. In the fresh catalysts (fig. 3a) rhodium and copper reduced at 100 and 306°C respectively whereas the bimetallics reduced as a single peak at 198°C, indicating a strong interaction between the two metals. The amounts of consumed H_2 corresponded to H/metal atomic ratios close to 8 for Rh and to 12 for Cu-containing catalysts: a large part of the ceria is reduced together with the metal, this being quite in agreement with previous studies [4,8–10].

After sintering, profound changes in the TPR profiles were recorded (figs. 3b, 3c and 3d): copper lost practically all its reducing capacity while the shape and the intensity of the reduction peak of rhodium was significantly altered. The bimetallics resisted well to sintering: there was no change in the shape of the reduction peak, which seemed to show that the two metals remained in intimate contact after

Table 4
Hydrogen chemisorption (H_C) and titrations (O_T and H_T) on the rhodium–copper catalysts reduced at 450°C (f = fresh, s900 = sintered at 900°C)

Catalyst	Metal (μmol g^{-1})	H_C (μmol H g^{-1})	O_T (μmol O g^{-1})	H_T (μmol H g^{-1})
CeO_2 f	–	0	48	0
CeO_2 s900	–	0	28	0
Rh/CeO_2 f	65.1	42.1	191	394
Rh/CeO_2 s900	65.1	132	85	166
Cu/CeO_2 f	56.6	0	70	0
Cu/CeO_2 s900	56.6	0	57	0
Cu/Rh/CeO_2 f	58(Cu) + 65(Rh)	41.1	295	547
Cu/Rh/CeO_2 s900	58(Cu) + 65(Rh)	2.0	97	6

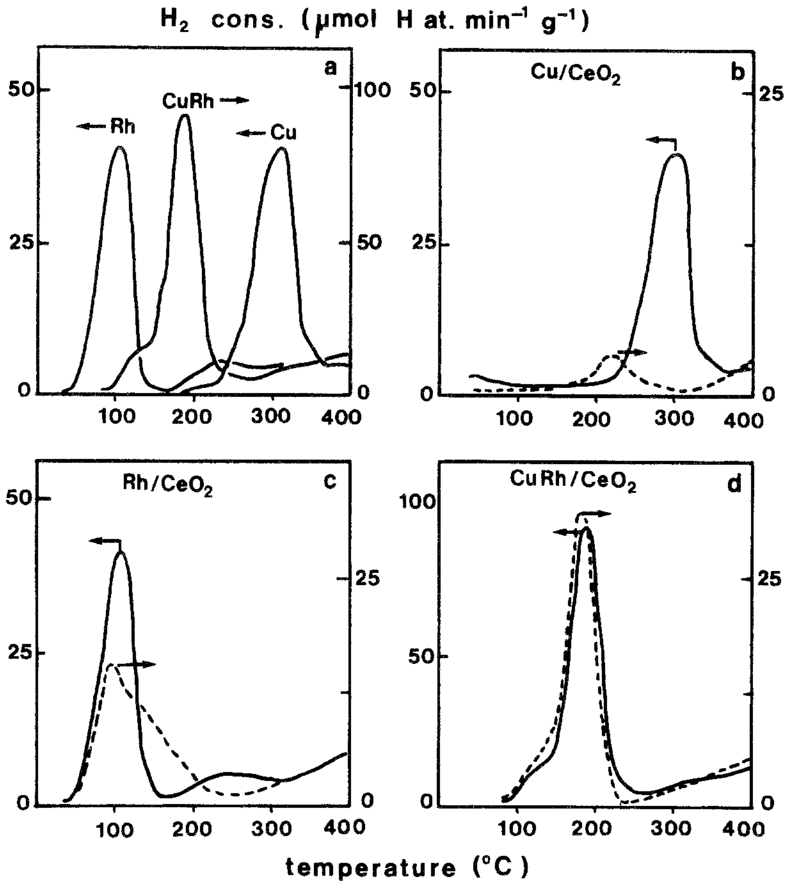

Fig. 3. TPR profiles for H_2 of Rh, Cu and CuRh/CeO$_2$ catalysts: (———) fresh catalysts; (- - -) catalysts sintered at 900°C.

the treatment at 900°C with an enrichment in copper (H_2 chemisorption being suppressed). This could explain the synergy effect observed between Rh and Cu in the sintered catalyst, the amount of hydrogen consumed in the reduction being significantly higher in the bimetallics than in the two monometallics.

Table 5
TPR of Rh, Cu and CuRh/CeO$_2$ catalysts: temperatures of the reduction peak maxima and amounts of H_2 consumed

	Rh/CeO$_2$		Cu/CeO$_2$		CuRh/CeO$_2$	
	f	s900	f	s900	f	s900
T_{max} (°C)	100	95	306	220	198	182
Q_H (μmol H g^{-1})	520	230	670	30	1490	440

4. Conclusion

Copper is a good promoter of OSC on Rh/ CeO_2 catalysts and makes this metal very resistant to sintering in an oxidizing medium. The results of chemisorption, titrations and TPR are consistent with a model in which copper and rhodium remain, during sintering, in intimate contact with an apparent enrichment in copper.

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