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Exchange and oxidation of $C^{16}O$ on ^{18}O-predosed Rh–Al_2O_3 and Rh–CeO_2 catalysts

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Abstract

Exchange and oxidation of $C^{16}O$ were investigated at 450°C on ^{18}O-predosed Rh and Pt catalysts supported on Al_2O_3, CeO_2 and CeO_2–Al_2O_3. In all cases, a rapid exchange of $C^{16}O$ with the surface can be observed. CO oxidation leads to $C^{16}O_2$, $C^{16}O^{18}O$ and $C^{18}O_2$. Significant formation of $C^{16}O_2$ is due to the relatively high ^{16}O coverage in reaction resulting from the $C^{16}O$ exchange and from an exchange between ^{18}O surface species and ^{16}O internal atoms. Hydrogen is also formed via a water–gas shift reaction (CO + surface OH) in higher proportion on CeO_2-containing catalysts than on Al_2O_3. Chlorine inhibits all the reactions (exchange, oxidation and WGS) and particularly the internal exchange.

Keywords: Exchange of $C^{16}O$; Oxidation of $C^{16}O$; Rh/Al_2O_3; Rh/CeO_2

1. Introduction

Carbon monoxide can be oxidised into CO_2 over pre-oxidised Pt–Rh/CeO_2–Al_2O_3 catalysts in the absence of gas phase O_2. This property is used for the measurement of the oxygen storage capacity (OSC) in three-way catalysts [1–7]. In the most convenient technique, pulses of CO are injected on the pre-oxidised catalyst sample: the amount of CO_2 produced from the first pulse corresponds to the most active oxygen, which is available for CO oxidation while the total amount of CO_2 produced from several pulses gives an evaluation of the whole oxygen ('fast' + 'slow') available in the oxidation reaction [7]. In the nomenclature of Yu Yao, the 'fast' oxygen is referred to as the OSC of the catalyst while the total oxygen ('fast' + 'slow') is referred to as OSCC (OSC Complete).

In this study, the exchange and oxidation of $C^{16}O$ on Rh/Al_2O_3 and Rh/CeO_2 catalysts pre-oxidised with $^{18}O_2$ were investigated, with the aim of obtaining information for the CO_g + O_s reaction used in OSC measurements. The role of chlorine was studied particularly for alumina supported catalysts. The behaviour of Rh and Pt catalysts supported on CeO_2–Al_2O_3 was also examined in terms of the exchange and the oxidation of carbon monoxide in the absence of gas phase oxygen.

In the second part of this paper, these results are discussed on the basis of recent data obtained in the domain of surface and bulk mobil-

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ity of oxygen by mean of isotopic oxygen ($^{18}O_{2\,g}/^{16}O_{s\,sup.}$) exchange.

2. Experimental

A γ-alumina (120 m^2 g^{-1}, code: A), a ceria (LSA Rhône–Poulenc, 16 m^2 g^{-1}, code: Ce) and a 12 wt.-% CeO_2–Al_2O_3 (100 m^2 g^{-1} prepared from cerium nitrate impregnated on the γ-alumina, code: CeA) were used as supports. The catalysts were prepared by the impregnation of these supports with an aqueous solution of rhodium chloride (code: Cl), rhodium nitrate (code: N) or dinitrodiamino platinum (code: N). The solids were dried at 120°C and calcined at 450°C. Having shown that OSC values of Al_2O_3 supported catalysts depended strongly on the Cl content, the RhACl catalyst was dechlorinated in a stream of $H_2 + H_2O$ at 450°C. This treatment allowed us to reduce the Cl content from 0.6% in RhACl to 0.12% in RhADCl. These catalysts were characterised by H_2 chemisorption and oxygen titration's and by their oxygen storage capacities (OSC pulse). These measurements were carried out in a pulse chromatographic apparatus described previously [7,8].

The exchange and oxidation of $C^{16}O$ on ^{18}O-pre-oxidised catalysts were carried out in a recycle microreactor coupled with a mass spectrometer (QMG Balzers). The oxygen of the catalysts was first exchanged with $^{18}O_2$ (100 mbar) at 450°C during 1 h. After evacuation at 450°C for 1 h, the catalyst sample was reacted with $C^{16}O$. The evolution of the different isotopomers of CO, CO_2, H_2O as well as the formation of H_2 was recorded between CO admission and 1 h-on-stream. This allowed the determination of the relative rates of exchange and of oxidation.

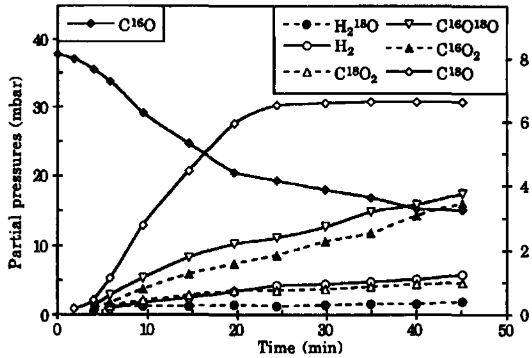

Fig. 1. Exchange and oxidation of $C^{16}O$ on 10 mg of Rh–CeO_2 (RhCeCl) $^{18}O_2$-predosed.

Oxygen mobility was determined by means of isotopic exchange experiments carried out in a recycle reactor coupled to a mass-spectrometer [9,10]. 'In situ' pretreaments were: $^{16}O_2$ at 450°C for 0.25 h, H_2 at 450°C for 0.25 h, outgassing at 450°C for 0.5 h and cooling down to the temperature of exchange before admission of $^{18}O_2$. Mass spectra ($^{18}O_2$, $^{18}O^{16}O$ and $^{16}O_2$, plus mass 18, 28 and 44 to detect possible leaks) were recorded every 9 s, which allowed us to determine the coefficients of surface (D_s) and bulk (D_r) diffusion [10].

3. Results and discussions

3.1. Oxygen storage measurements

The evolution of the partial pressures of the reactant ($C^{16}O$) and of the different products with respect to time are shown for four representative catalysts (RhCeCl, RhADCL, RhAN and RhCeAN) in Fig. 1, Fig. 2, Figs. 3 and 4.

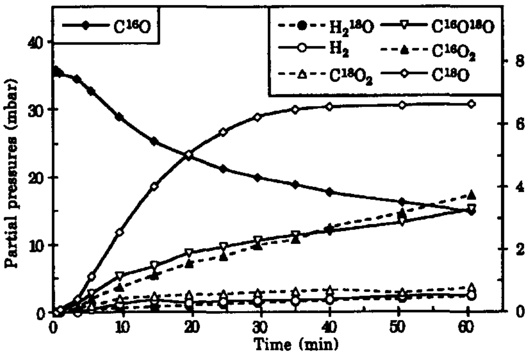

Fig. 2. Exchange and oxidation of $C^{16}O$ on 50 mg of Rh–Al_2O_3 (RhADCl) $^{18}O_2$-predosed.

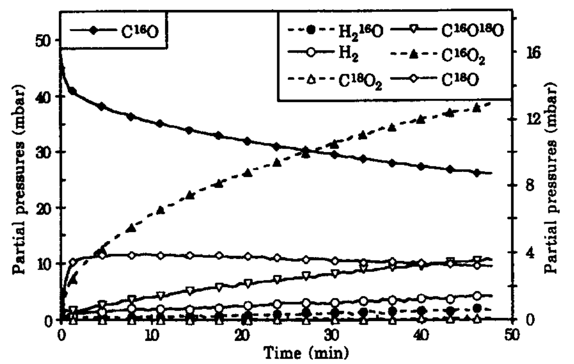

Fig. 3. Exchange and oxidation of $C^{16}O$ on 20 mg of $Rh-Al_2O_3$ (RhAN) $^{18}O_2$-predosed.

Clearly, on all catalysts, the exchange is the fastest reaction (1):

$$C^{16}O + {}^{18}O_s \rightarrow C^{18}O + {}^{16}O_s \qquad (1)$$

CO oxidation was characterized by the rapid appearance of $C^{16}O_2$ and of $C^{16}O^{18}O$ while a slow formation of $C^{18}O_2$ is always observed.

On Al_2O_3, compare Figs. 2 and 3, chlorine inhibits both CO exchange ($C^{18}O$ formation) and oxidation ($C^{16}O_2$, $C^{16}O^{18}O$ and $C^{16}O_2$ formations). On the chlorine free alumina sample (Fig. 3), the amount of CO oxidised into CO_2 indicates that not only surface oxygen but also bulk oxygen atoms participate in the oxidation process. In fact, the large amount of CO oxidised into $C^{16}O_2$ could only be explained by a re-equilibration of the alumina surface between ^{18}O and ^{16}O during the evacuation period. This change in the surface composition is due to a bulk migration of oxygen in alumina. There is evidence that chlorine has a marked influence on the surface and bulk mobility of oxygen, as we will see in Section 3.2.

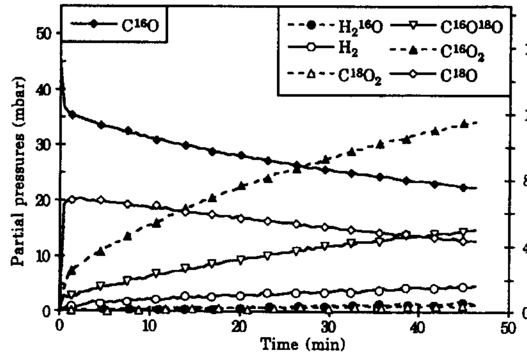

Fig. 4. Exchange and oxidation of $C^{16}O$ on 20 mg of $Rh/CeO_2-Al_2O_3$ (RhCeAN) $^{18}O_2$-predosed.

Table 1
CO_2 (μmol g^{-1}) formed by WGS like reaction (= $2H_2$, See reaction (2)) and by direct oxidation (= $C^{16}O_2 + C^{16}O^{18}O + C^{18}O_2 - 2H_2$, by comparison)

Catalysts	CO_2 from oxidation	CO_2 from WGS
RhAN	1211	279
PtAN	795	156
RhCeAN	1180	334
PtCeAN	1359	292
RhADCl	345	53
RhCeCl	1740	540

H_2 formed during the oxidation (see Fig. 1, Fig. 2, Figs. 3 and 4) is indicative of a water gas shift (WGS) like in reaction (2):

$$CO + OH_s \rightarrow CO_2 + \tfrac{1}{2}H_2 \qquad (2)$$

In Table 1, the amounts of CO_2 formed by direct oxidation and by the WGS-like reaction on alumina and ceria/alumina are compared for Rh and Pt. The amounts of CO_2 formed with the two Rh catalysts containing chlorine are also given. CeO_2 improves CO oxidation, independently of the metal used (Rh or Pt), particularly by WGS.

3.2. Correlation with oxygen mobility

Independently of these OSCC measurements, we could determine surface and bulk oxygen mobility by isotopic oxygen exchange on rhodium catalysts [9,10]. Tables 2 and 3 sum-

Table 2
Relative oxygen surface mobility (based on 100 for RhAN) and the number of exchangeable oxygen species at 400°C

Catalysts	Relative mobility	Exchangeable Oxygen (at nm^{-2})
RhCeN	28100	100
RhAN	100	15
RhAN + 0.1% Cl	40	10
RhCeAN	180	20

Table 3
Oxygen bulk mobility at different temperatures

Catalysts	T (°C)	Bulk mobility (E-23 m^{-2} s^{-1})
RhCeN	350	50
RhAN	450	7
RhAN + 0.1% Cl	450	no bulk diffusion
RhCeAN	300	10

marise the relative oxygen surface mobilities, the number of exchangeable oxygen species and the bulk mobilities on different rhodium catalysts.

On alumina, chlorine is a poison of surface and bulk oxygen mobility (Tables 2 and 3). So on chlorine containing catalyst (Figs. 1 and 2), the exchange of $C^{16}O$ into $C^{18}O$ is the principal reaction during all the period of reaction. In contrast (compare Figs. 2 and 3), for alumina (Fig. 3) and ceria–alumina (Fig. 4) chlorine free catalysts, if exchange is the fastest process at the beginning of the reaction, after a few minutes, oxidation is the main reaction. Twice the amount of CO is exchanged on ceria–alumina than on alumina which is due to a double phenomenon: the increased surface mobility of oxygen and the higher number of exchangeable oxygen species on ceria–alumina.

Within the same period (40 min), the amount of CO oxidised to CO_2 is the same for alumina and ceria–alumina catalysts (see Figs. 3 and 4). This observation confirms the supposition that this product is due to bulk oxygen atoms from alumina which migrate during evacuation at a very slow rate on each sample compared to surface mobility.

4. Conclusion

Two main reactions can be observed during interaction of $C^{16}O$ with ^{18}O-predosed Rh and Pt catalysts: exchange ($C^{16}O \rightarrow C^{18}O$) and oxidation ($C^{16}O \rightarrow C^{16}O_2 + C^{18}O^{16}O + C^{18}O_2$). Water gas shift yielding H_2 ($CO + OH \rightarrow CO_2 + \frac{1}{2}H_2$) can also be observed, particularly on CeO_2 catalysts.

The exchange of gaseous $C^{16}O$ with surface ^{18}O, extremely rapid, leads to an enrichment of the surface in ^{16}O. This process is reinforced by an exchange between the surface ^{18}O species and the internal ^{16}O atoms, which explains why $C^{16}O_2$ is obtained in significant proportion. Chlorine is a severe inhibitor of all the reactions and particularly the internal exchange: a great proportion of ^{18}O-labelled CO_2 is obtained with Cl-containing catalysts.

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