Comparison between turnover rates of CO oxidation over Rh^0 or Rh^{x+} supported on model three-way catalysts

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The kinetics of CO oxidation over two catalytic sites, either 100% zero-valent or 100% oxidised rhodium atoms, were studied. It was shown that an oxidised rhodium species exhibits a significant higher turnover rate in CO oxidation (factor 25) than the corresponding zero-valent one. This noticeable difference, interpreted with respect to mechanistic considerations, led us to conclude that one of the promoting effects of ceria–zirconia is to stabilise rhodium atoms as oxidised species.

KEY WORDS: kinetics; turnover rate; CO oxidation; zero-valent or oxidised rhodium species; ceria–zirconia support

1. Introduction

The kinetics of CO oxidation reaction have been intensively studied over noble-metal-based catalysts because of their well known importance in the field of automotive gas exhaust purification. A general agreement has been found for the kinetic parameters of this reaction, such as reaction orders and apparent activation energy, over either rhodium single crystals or silica- and alumina-supported rhodium catalysts [1–4], whereas more controversial values have been reported over ceria-promoted noble metal catalysts [4–6]. Nevertheless, in these latter studies, a significant enhancement of the CO oxidation reaction rate has been pointed out in the presence of ceria. Indeed, ceria is an essential additive of three-way catalysts which leads to major modifications of the kinetic parameters as compared to those found over non-promoted catalysts [4–6].

Several assumptions have been made to explain the ceria promoting effect on the CO oxidation reaction rate. Both a new mechanism [5,6], involving the occurrence of the oxidation of CO at the interface between Rh and the ceria support, and a new catalytic site [4] were proposed. In this latter case, the nature of the catalytic site was assumed to be an oxidised noble metal species [4]. To explain the observed higher turnover rate in the CO–NO reactions after preoxidation of a silica-supported rhodium catalyst, Hecker and Bell also suggested the presence of oxidised rhodium species [7]. More recently, Djéga-Mariadassou *et al.* [8] and Bera *et al.* [10] pointed out the presence of noble metal oxidised species over ceria-based supported catalysts. From a kinetic point of view, this finding is of particular importance when measuring the turnover rate of a given reaction since this intrinsic rate depends both on the nature as well as the number of catalytic sites.

The aim of this work was to study the kinetics of the carbon monoxide oxidation by molecular oxygen over the two possible catalytic sites, either zero-valent or oxidised noble metal atoms. For this purpose, the reaction was carried out over rhodium-based model catalysts synthesised on the appropriate supports. Silica support was chosen for its ability of stabilising zero-valent rhodium species (Rh^0) whereas ceria–zirconia support was chosen to stabilise oxidised rhodium species (Rh^{x+}) [8].

2. Experimental

The silica (Degussa, Aerosil 50)-supported rhodium catalyst (0.66 wt% Rh) was prepared by incipient wetness impregnation of the support by an aqueous solution of $RhCl_3 \cdot 3H_2O$ (Johnson Matthey). The ceria–zirconia (Rhodia, 25 wt% ZrO_2)-supported rhodium catalyst (0.29 wt% Rh) was prepared by anionic exchange from an acidic solution of $RhCl_3 \cdot 3H_2O$ with the support [8]. After drying in air at room temperature, the materials were dried at 393 K for 3 h. Finally, the catalysts were crushed and sieved to the desired particle size (0.125–0.200 mm).

The exposed zero-valent rhodium atoms of both catalysts were titrated through benzene hydrogenation reaction [11].

Before testing, the catalyst samples (0.1–0.2 g) were submitted to a temperature-programmed pretreatment from 298 to 773 K (3 $K\,min^{-1}$). The temperature was then kept constant at 773 K for 2 h. Silica- and ceria–zirconia-supported catalysts were submitted to either a pretreatment under pure hydrogen (Air Liquide, 100 STP $cm^3\,min^{-1}$) or in flowing

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Table 1
Kinetic parameters associated to the CO–O_2 rate equation $r = k_0 \times \exp(-E_a/RT)P_{CO}^{\alpha}P_{O_2}^{\beta}$ over zero-valent and oxidised rhodium species.

Catalyst sample	Catalytic site	T (K)	α	β	E_a (kJ mol^{-1})	TOR[a] (10^{-4} s^{-1})
Rh/SiO_2	Rh^0	428	−1.2	1.1	131	54[b]
Rh/$Ce_{0.75}$–$Zr_{0.25}O_2$	Rh^{x+}	403	0.4	0.1	117	172[b]
Rh/$Ce_{0.75}$–$Zr_{0.25}O_2$	Rh^{x+}	428				1320[c]

[a] Mol of CO_2 formed per mol of either Rh^0 or Rh^{x+} (10^{-4} s^{-1}).
[b] Experimental values determined at the mentioned temperature (T).
[c] Extrapolated value at a temperature of 428 K from α, β and E_a determined at a temperature of 403 K.

a CO–NO–O_2 stoichiometric mixture in helium [8] (1.5%–0.2%–0.65%, hour space velocity = 100 000 h^{-1}), respectively. After being pretreated, the catalysts were flushed at 773 K for 15 min under helium (230 STP cm^3 min^{-1}) and the catalyst temperature was decreased to 298 K. Before carrying out kinetic measurements, two subsequent and reproducible CO–O_2 (0.4%–0.2% in He, 230 STP cm^3 min^{-1} total flow rate) temperature-programmed reactions were carried out from 298 to 773 K with a heating rate of 3 K min^{-1} to ensure the reliability of the activation procedure.

The kinetic study was carried out in a U-type quartz reactor (8 mm internal diameter) where reactant gases were fed from independent mass flow controllers. The reactor outflow was analysed using both a CO infrared detector (Maihak, Finor F) and a gas chromatograph (HP 5890) equipped with a two packed-column system (Porapak Q and Gas chrom MP-1) and a thermal conductivity detector.

The kinetic parameters reported here were obtained at steady state conditions (from reducing to oxidising mixtures) whilst operating the reactor isothermally and as close to differential reactor as possible by limiting the conversion to less than 10%.

3. Results and discussion

It was first shown that 97 and 0 mol% of the rhodium content was exposed as zero-valent metal atoms on SiO_2 and CeO_2–ZrO_2, respectively. According to a previous paper, the latter catalyst was not found to be active in benzene hydrogenation (no Rh^0 species) and presented only Rh^{x+} species [8].

Table 1 reports the kinetic parameters as well as the turnover rates related to both zero-valent and oxidised rhodium catalytic sites. On the one hand, one can see that the kinetic parameters obtained for the zero-valent active species are in fairly good agreement with those already reported in previous studies [1–4]. Indeed, a negative order with respect to CO, a positive one with respect to O_2 and an activation energy of 131 kJ mol^{-1} were found. On the other hand, the oxidised rhodium catalytic site displays remarkably different reaction orders, since the CO order becomes positive and a near-zero order with respect to O_2 is observed, which nevertheless fall in the quite confusing broad range of values reported over ceria-promoted catalysts [4–6]. Moreover, the activation energy of the reaction is a little lower than that observed over the zero-valent catalytic site which is fully consistent with the studies performed by Yu Yao [4] and Bunluesin *et al.* [5] over ceria-promoted rhodium catalysts.

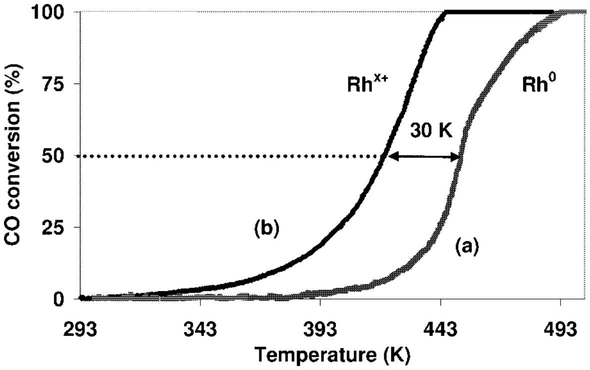
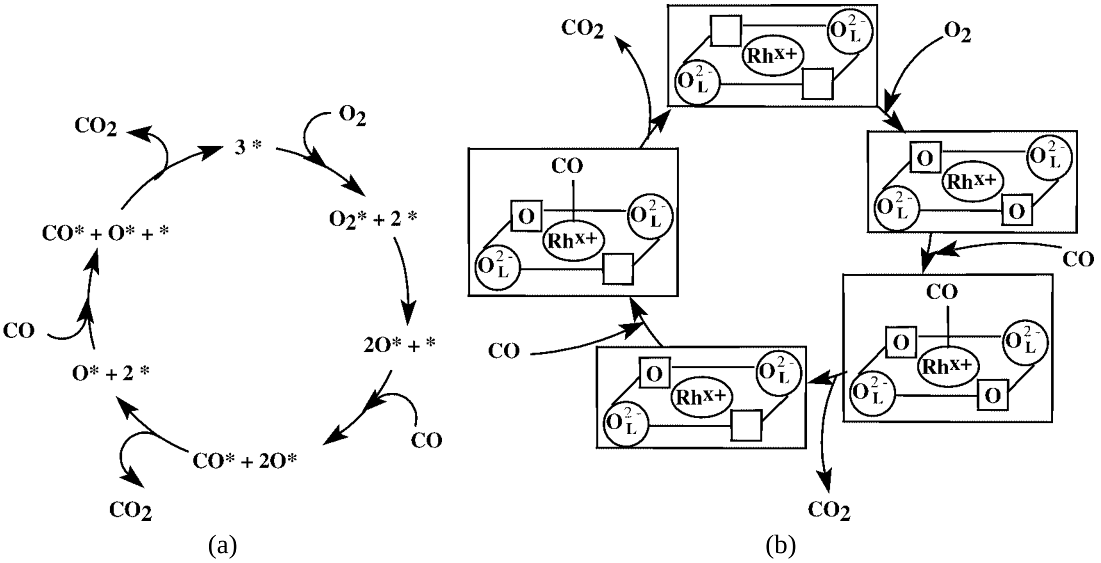


Figure 1. CO–O_2 (0.4%–0.2% in He) temperature-programmed reaction (3 K min^{-1}) over zero-valent and oxidised rhodium catalytic sites: (a) Rh^0 and (b) Rh^{x+}.

The turnover rates were then estimated for both catalytic sites at a temperature of 428 K (table 1). It is worth noting that the turnover rate of the CO oxidation reaction is more than one order of magnitude higher (factor 25) for the oxidised rhodium species than for the zero-valent one. Such a trend has already been reported in the case of platinum and palladium catalytic sites [10]. However, in this latter study, the authors were not able to compare the turnover rates of the two catalytic sites for a given reaction temperature, as we did, since they did not perform a complete kinetic study.

In addition, a CO–O_2 stoichiometric mixture temperature-programmed reaction was carried out on both catalysts (figure 1). Although the catalyst sample weights were chosen so that a similar number of either zero-valent or oxidised active sites were present on both samples, the light-off temperature (50% conversion) of CO was about 30 K higher over Rh^0/SiO_2 than over Rh^{x+}/$Ce_{0.75}$–$Zr_{0.25}O_2$. This result is consistent with the estimated turnover rates and the higher intrinsic activity exhibited by the oxidised rhodium catalytic species (table 1).

This noticeable difference between the turnover rates, which has not been reported up to now, as well as the obtained reaction orders can be explained with respect to mechanistic considerations. The CO oxidation reaction over both a zero-valent and an oxidised rhodium active site, as suggested in [9], is shown in scheme 1. From this scheme, the observed difference in turnover rates for the two catalytic sites becomes obvious. Indeed, over the former active site, it can be seen that at least three zero-valent atoms in close proximity are needed to complete the CO oxidation reaction (scheme 1(a)). Moreover, this catalytic cycle stresses the competitive adsorption of the two reactants [1,3,4] on the same catalytic sites. This latter proposal is supported by the negative order obtained with respect to CO which suggests



Scheme 1. Catalytic cycles for the CO–O$_2$ reaction over zero-valent and oxidised rhodium catalytic sites: (a) Rh^0, $*$ representing a zero-valent rhodium atom; (b) Rh^{x+}, O_L^{2-} and (□) representing a ceria–zirconia lattice oxygen anion and an oxygen vacancy, respectively.

that CO is the most abundant adsorbed species at the surface of the catalyst in our reaction conditions.

In contrast, it can be seen that only one oxidised rhodium atom is needed over the Rh^{x+}/Ce$_{0.75}$–Zr$_{0.25}$O$_2$ catalyst for CO oxidation (scheme 1(b)). In addition, the proximity between CO$_{\text{“ads”}}$ and O$_{\text{“ads”}}$ in the rhodium coordinative sphere, required to achieve the elementary reaction step leading to CO$_2$, is intrinsic to the oxidised active site (supported homogeneous catalysis). Isolated oxidised catalytic species should therefore be able to carry out the CO oxidation reaction. The absence of negative order with respect to both reactants clearly indicates that there is no more competition of both reactants for the same catalytic centre. Moreover, the obtained near-zero order with respect to O$_2$ shows that the vacancies associated to the oxidised species are always occupied by dissociated oxygen under our experimental conditions.

Finally, this work also stresses one of the promoting effects of ceria by stabilising oxidised noble metal species which, due to intrinsic properties of this type of catalytic site, exhibits a higher turnover rate in CO oxidation reaction [4,10]. Moreover, the proposed mechanism over the Rh^{x+}/Ce$_{0.75}$–Zr$_{0.25}$O$_2$ unifies the two above mentioned assumptions (both a new catalytic site [4] and a new mechanism [5,6], involving the occurrence of the oxidation of CO at the interface between Rh and the ceria support) to explain the higher activity of ceria-promoted catalysts in the oxidation of CO.

4. Conclusion

In summary, it was shown that an oxidised rhodium species exhibits a significant higher turnover rate in CO oxidation (factor 25) than the corresponding zero-valent one. Moreover, it was found that the reaction orders with respect to both reactants were strikingly different over the two catalytic species. These noticeable differences could be explained with respect to mechanistic considerations and led us to conclude that one of the promoting effects of ceria–zirconia, and thus ceria, is to stabilise the rhodium atoms as oxidised species.

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