Ceria supported group IB metal catalysts for the combustion of volatile organic compounds and the preferential oxidation of CO

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Abstract

Catalytic combustion of volatile organic compounds (VOC) and preferential oxidation of CO (PROX) were investigated over IB metal/ceria catalysts prepared by deposition–precipitation (DP) or coprecipitation (CP). The activity towards the deep oxidation of VOC was in the order: \( \text{Au/CeO}_2 \geq \text{Ag/CeO}_2 > \text{Cu/CeO}_2 \gg \text{CeO}_2 \). The same trend was also found in the PROX reaction in terms of total conversion of \( \text{O}_2 \), which includes \( \text{O}_2 \) consumed both for \( \text{CO} \) and \( \text{H}_2 \) oxidation. A different behaviour was observed in the \( \text{CO} \) conversion to \( \text{CO}_2 \), that is the desired PROX reaction. For this reaction, in fact, Au and Cu catalysts gave high \( \text{CO} \) conversions, \( \text{Au/DP} \) at low temperature (maximum of 84.3% for \( \text{Au/DP} \) at 70 °C) and \( \text{Cu/CP} \) at higher temperature (maximum of 96.8% for \( \text{Cu/CP} \) at 150 °C), whereas Ag catalysts always exhibited very low \( \text{CO} \) conversions (maximum of 16.7% for \( \text{Ag/CP} \) at 80 °C). Both for PROX and VOC combustion the Au sample prepared by DP was more active than the CP one, whereas a reverse behaviour was found on Ag and Cu catalysts.

On the basis of characterization data (XRD, \( \text{H}_2\)-TPR, surface area measurements, \( \text{H}_2\)–D\(_2\) isotopic exchange, \( \text{N}_2\text{O} \) and \( \text{H}_2\)–\( \text{O}_2 \) chemisorption) it was proposed that a higher atomic radius of the IB metal and the presence of smaller crystallites of both IB metal and ceria result in a larger enhancement of mobility/reactivity of surface ceria oxygens, involved in both investigated reactions through a Mars–van Krevelen mechanism. The very low PROX activity of Ag/CeO\(_2\) samples was related to the low capacity of silver to activate the \( \text{CO} \) molecule.

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1. Introduction

Ceria (\( \text{CeO}_2 \)) is a key component in the automobile three-way catalysts primarily for its role in oxygen storage, taking up oxygen under oxidising conditions and releasing it under reducing ones [1]. Nowadays, the importance of ceria and ceria-based mixed oxides in catalysis is rapidly growing up with new applications in different fields, including oxidation (e.g. soot removal from diesel engine exhausts, CO and VOC oxidation, wet-oxidation of organic pollutants in water) and hydrocarbon-reforming processes (e.g. steam reforming and water–gas-shift) [1–7].

The addition of platinum group metals (Pt, Pd, Rh) has been found to increase the oxygen storage capacity and reducibility of pure ceria, thus resulting in improved catalytic performance [1,2]. Very interesting from a practical point of view is the catalytic behaviour of IB metal-modified ceria systems (IB metal = Au, Ag and Cu). In particular, Au/CeO\(_2\) catalysts have been reported to be among the most active systems for volatile organic compounds (VOC) combustion [8–11], preferential oxidation of CO in the excess of hydrogen (PROX) [12–14] and low temperature water–gas shift reaction [14–18]. The use of Ag deposited on ceria was found to strongly increase the rate of carbon gasification with an effect higher than other noble metals [19]. Ag/CeO\(_2\) catalysts were also reported to be active in the oxidation of methane [20]. Finally, Cu/ceria catalysts were found highly promising for PROX [21] and water gas shift [18] reactions.

Some years ago we reported a comparative study on the catalytic combustion of volatile organic compounds over IB metal/iron oxide catalysts [22]. We found that the IB metal increase the oxidation activity of the iron oxide in the order \( \text{Au/Fe}_2\text{O}_3 > \text{Ag/Fe}_2\text{O}_3 > \text{Cu/Fe}_2\text{O}_3 \gg \text{Fe}_2\text{O}_3 \). The trend of activity observed was explained on the basis of the capacity of the IB metal to weaken the Fe–O bond thus increasing the mobility of the lattice oxygen, involved in the VOC oxidation through a Mars–van Krevelen reaction mechanism [22,23].

Following these considerations in this paper we investigated the use of IB metal/ceria catalysts in two reactions of high impact in the field of sustainable chemistry, namely the combustion of VOC and the PROX reaction, with the aim to enlighten the role played by both the IB metal and the ceria in affecting the chemical–physical properties and therefore the performance of the catalytic system.
2. Experimental

2.1. Catalyst preparation and testing

IB/cerium oxide catalysts were prepared by coprecipitation (CP) or deposition–precipitation (DP), using Ce(NO$_3$)$_3$·6H$_2$O (Aldrich) and the precursor of the IB metal (HAuCl$_4$, AgNO$_3$, and Cu(NO$_3$)$_2$·6H$_2$O for gold, silver and copper, respectively). In the case of the CP method, an aqueous mixture of the precursors was poured at 7.5 ml min$^{-1}$ rate into an aqueous solution of KOH (0.1 M) maintained at 70$^\circ$C under vigorous stirring (500 rpm). In the DP method, after the pH of the aqueous solution of the IB precursor was adjusted to the value of 8 using an aqueous solution of KOH (0.1 M), cerium oxide, prepared as later described, was added under vigorous stirring (500 rpm) to the solution, keeping the slurry at 70$^\circ$C for 2 h. Both in CP and DP methods the obtained slurries were kept digesting for 24 h, washed several times (until disappearance of nitrates and chlorides), then dried under vacuum at 70$^\circ$C and finally ground before use. Samples were coded with the element symbol followed by DP for the catalysts prepared by deposition–precipitation (AuDP, AgDP, CuDP) and CP for those prepared by coprecipitation (AuCP, AgCP, CuCP). The IB metal content of investigated catalysts, measured by atomic absorption spectrophotometry, is reported in Table 1.

<table>
<thead>
<tr>
<th>Code</th>
<th>IB metal content (%)</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>IB metal dispersion (%)</th>
<th>Average IB metal diameter (nm)</th>
<th>Average CeO$_2$ diameter (nm)</th>
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<tbody>
<tr>
<td>AuDP</td>
<td>4.3</td>
<td>118</td>
<td>&gt;30$^a$</td>
<td>&lt;4$^a$</td>
<td>9.9</td>
</tr>
<tr>
<td>AuCP</td>
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<td>19.5$^b$</td>
<td>6.1$^b$</td>
<td>8.7</td>
</tr>
<tr>
<td>AgDP</td>
<td>4.8</td>
<td>112</td>
<td>16.9$^{b}$</td>
<td>7.1$^b$–6.7$^{b}$</td>
<td>9.0</td>
</tr>
<tr>
<td>AgCP</td>
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<td>130</td>
<td>33.7$^{b}$</td>
<td>&lt;4$^{b}$–3.3$^{b}$</td>
<td>9.9</td>
</tr>
<tr>
<td>CuDP</td>
<td>4.5</td>
<td>116</td>
<td>32.6$^{c}$</td>
<td>&lt;4$^{c}$–3.1$^{c}$</td>
<td>9.2</td>
</tr>
<tr>
<td>CuCP</td>
<td>4.7</td>
<td>125</td>
<td>62.4$^{b}$</td>
<td>&lt;4$^{b}$–1.6$^{b}$</td>
<td>9.0</td>
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<tr>
<td>CeO$_2$</td>
<td>–</td>
<td>110</td>
<td>–</td>
<td>–</td>
<td>10.0</td>
</tr>
</tbody>
</table>

$^a$ Estimated by XRD.

$^b$ Estimated by H$_2$–O$_2$ titration.

$^c$ Estimated by N$_2$O dissociative chemisorption.

2.2. Catalyst characterization

Temperature programmed reduction (TPR) tests were carried out in a conventional flow apparatus with a TCD detector, at heating rate of 10$^\circ$C min$^{-1}$ using 5 vol.% H$_2$ in Ar. Before TPR tests samples were calcined in air at 300$^\circ$C. H$_2$–D$_2$ isotopic exchange was carried out in a continuous-flow reactor at atmospheric pressure. Before measurements catalysts were calcined in air at 300$^\circ$C, reduced in H$_2$ at 150$^\circ$C and cooled down to room temperature always in H$_2$. The sample was then flushed with Ar and thereafter submitted to an equimolar mixture of H$_2$ and D$_2$. The variation of the H$_2$ and D$_2$ composition, as a function of the temperature, was followed by a quadrupole mass spectrometer (VG quadrupoles), monitoring mass/charge ratios of 2 (H$_2$), 3 (HD) and 4 (D$_2$). A blank measurement was performed on quartz particles. Surface area measurements were carried out using the BET nitrogen adsorption method with a Sorptomatic series 1990 (ThermoQuest). Before experiments all samples were calcined in air at 300$^\circ$C and then outgassed (10$^{-3}$ Torr) at 120$^\circ$C.

The silver dispersion of Ag/CeO$_2$ catalysts was calculated by H$_2$–O$_2$ titration pulse method at 170$^\circ$C, assuming the following stoichiometries: Ag/O$_2$ = 2 and Ag/H$_2$ = 1 [24]. The copper dispersion of Cu/CeO$_2$ catalysts was estimated by means of dissociative N$_2$O adsorption at 60$^\circ$C [25,26]. The pulse titration technique was adopted in our experiments, using He as carrier gas and a thermal detector to measure the amount of N$_2$O consumed. The specific area of metallic copper was calculated assuming a reaction stoichiometry N$_2$O/Cu = 0.5 and a Cu surface density of 1.46 × 10$^{19}$ atoms/m$^2$.
Before chemisorption experiments samples were calcined in air at 300 °C and then reduced in H2 at 150 °C.

X-ray powder diffraction (XRD) analysis of the samples was performed with an APD 2000 (Italstructure) diffractometer using a Cu Kα radiation. Diffraction peaks of crystalline phases were compared with those of standard compounds reported in the JCPDS Data File. Before XRD tests samples were calcined in air at 300 °C.

The chemico-physical properties of investigated catalysts are reported in Table 1.

3. Results

3.1. VOC deep oxidation

The conversions of methanol, acetone and toluene, as a function of reaction temperatures, over investigated catalysts are reported in Figs. 1–3, respectively. No reaction was found to occur in the absence of catalysts in the examined temperature range. For all investigated catalysts (IB metal/CeO2 and bare CeO2) CO2 and water were the only product detected under the experimental conditions used. It must be underlined that the formation of intermediate oxidation products (namely formaldehyde and formic acid from methanol, benzaldehyde and benzoic acid from toluene) has been reported in the literature, chiefly on Ag catalysts [27,28]. It must be stressed that the experimental conditions, mainly the large excess of oxygen, favor “a priori” the complete oxidation of the organic compounds. Moreover, the lack of intermediate oxidation products is in accordance to results reported for oxidation reactions on high disperse supported Ag catalysts [29,30], due to the fact that small Ag clusters, such as those present in our samples (see later on), are known to favor the complete oxidation of the organic compound to CO2. The absence of partial oxidation compounds has been also reported, under the same experimental conditions of this work, in the catalytic oxidation of the same organic molecules over IB metals supported on iron oxides [22] and over gold/cerium oxide catalysts [9]. This finding was attributed to the strong interaction of the intermediate product with the support, thus promoting the further oxidation to CO2.

Data of Figs. 1–3 clearly show that the presence of IB metals improves the catalytic activity of pure cerium oxide towards the deep oxidation of the investigated VOC. In fact, for each VOC, the light-off curves of all IB metal/CeO2 catalysts were shifted to lower temperature with respect to that of the unloaded ceria sample. This behaviour is better pointed out from data of Table 2, where the $T_{50}$ values of Figs. 1–3 were extrapolated.

<table>
<thead>
<tr>
<th>Code</th>
<th>Methanol</th>
<th>Acetone</th>
<th>Toluene</th>
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<tbody>
<tr>
<td>AuDP</td>
<td>107</td>
<td>218</td>
<td>257</td>
</tr>
<tr>
<td>AuCP</td>
<td>127</td>
<td>228</td>
<td>265</td>
</tr>
<tr>
<td>AgDP</td>
<td>131</td>
<td>225</td>
<td>265</td>
</tr>
<tr>
<td>AgCP</td>
<td>113</td>
<td>220</td>
<td>260</td>
</tr>
<tr>
<td>CuDP</td>
<td>222</td>
<td>250</td>
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</tr>
<tr>
<td>CuCP</td>
<td>180</td>
<td>240</td>
<td>285</td>
</tr>
<tr>
<td>CeO2</td>
<td>294</td>
<td>299</td>
<td>425</td>
</tr>
</tbody>
</table>

*Table 2 Extrapolated $T_{50}$ values (°C) for VOC oxidation over IB/ceria catalysts.*
conversion values (i.e. the temperature at which 50% VOC conversion was reached) are compared. In particular, for all VOC, activity resulted to be in the order Au/CeO₂ > Ag/CeO₂ > Cu/CeO₂ >> CeO₂ in the DP series and Ag/CeO₂ > Au/CeO₂ > Cu/CeO₂ >> CeO₂ in the CP series. Moreover, it is noteworthy that on all catalysts the VOC reactivity order was methanol > acetone > toluene. This trend is in accordance to the results reported in the literature [9,31–33], being related to the different degree of interaction between the organic substrate and the support surface. TPD experiments of adsorbed VOC have, in fact, shown that alcohols are more strongly adsorbed on cerium oxide than ketones and aromatics [9].

Interestingly Figs. 1–3 and Table 2 point out that the preparation method of IB metal/ceria catalysts strongly affects the oxidation activity, with an effect that depends on the metal considered. Specifically, in the case of Au/CeO₂ catalysts the sample prepared by DP was sensibly more active than the CP one. Light-off curves on the AuDP sample were, in fact, shifted to lower temperature with T₅₀ values lower compared to those found on the AuCP sample. An opposite behaviour was instead observed on both Cu/CeO₂ and Ag/CeO₂ systems, where the CP samples resulted to be more active than corresponding DP ones.

3.2. PROX reaction

Fig. 4 reports catalytic activity results, in terms of conversion of CO (Fig. 4A), conversion of O₂ (Fig. 4B) and selectivity towards CO oxidation (Fig. 4C), over investigated IB metal/ceria samples. No methane was formed in all experiments. It must be also reminded that no significant CO and O₂ conversion were observed up to 250 °C on the bare support (CeO₂).

From the figure it can be seen that, on all samples, CO conversion increased with reaction temperature reaching a maximum (84.3% for AuDP at 70 °C, 64.5% for AuCP at 90 °C, 96.8% for CuDP at 150 °C, 79.1% for CuDP at 170, 16.7% for AgCP at 80 °C and 12.8% for AgDP at 80 °C) and then decreasing at higher temperature. These results point out that the CO oxidation activity of IB metal/ceria systems is strongly affected by both the IB metal and the preparation method chosen. On the other hand, on all samples, on increasing reaction temperature, O₂ conversion continuously increased up to 100%, then remaining at this value at higher temperatures. Selectivity...
towards CO oxidation, defined as the ratio of O$_2$ consumption for the CO oxidation to the total O$_2$ consumption, was always found to decrease on increasing reaction temperature. On Au/CeO$_2$ catalysts the selectivity, which was quite high at 40°C (90 and 74% for AuDP and AuCP, respectively), significantly decreased since $T > 40°C$, whereas on Cu/CeO$_2$ samples remained around 100% up to 100–110°C both on DP and CP samples, then gradually decreasing at higher temperatures. It is noteworthy that this decrease was slightly more evident for the DP sample. On Ag/CeO$_2$ catalysts the selectivity was always very low (<20%), decreasing in any case with reaction temperature. It is also important to remind that, according to results reported in the case of Au/iron oxide catalysts [34], at the same reaction temperature, selectivity was roughly independent from the level of conversion (data not shown). The drop of CO selectivity with temperature, observed on all IB metal/ceria samples, agrees with results reported in the literature and it is attributed to the fact that activation energy of H$_2$ oxidation was found to be sensibly higher than that of CO oxidation [34,35]. This behaviour is also in accordance to the finding that on gold and copper particles the ratio of surface coverage between CO and H($\theta$/H$_1$) has been found to strongly decrease as temperature increases [36]. It must be also noted that the occurrence of the reverse water gas shift (RWGS) reaction cannot be fully excluded, chiefly at the highest temperatures. However, according to the literature, the RWGS should take place only at reaction temperatures higher than those employed in our experiments. In fact, no RWGS reaction was reported to occur on copper supported on ceria catalysts by Marino et al. at temperatures lower than 200°C with a conversion to CO of only 1.1% reached at 300°C [37].

Data reported in Fig. 4 clearly point out that Au/CeO$_2$ was the most active system for CO oxidation to CO$_2$ at low temperature, whereas Cu/CeO$_2$ was the most effective at higher temperature (nearly 100% CO removal was achieved on the CuCP sample at 150°C). Ag/CeO$_2$ is not a good PROX catalyst, exhibiting a very low CO conversion at any temperature. Interestingly in terms of O$_2$ conversion the activity of IB metal/ceria samples followed the same order than that found for the catalytic oxidation of VOC, namely Au/CeO$_2$ $\gtrsim$ Ag/CeO$_2$ $\gg$ Cu/CeO$_2$. Moreover also in the case of the PROX reaction the preparation method had a strong influence on the catalytic performance of IB metal/ceria catalysts, exhibiting the same trend found for the VOC combustion, i.e. the Au sample prepared by DP was more active than the CP one, the opposite happened on Cu/CeO$_2$ and Ag/CeO$_2$ systems.

3.3. Catalysts characterization

3.3.1. XRD results

XRD spectra of IB metal/ceria samples, together with that of the metal-free ceria, are reported in Fig. 5. The XRD profile of the bare ceria sample (Fig. 5a, spectrum a) reveals the presence of diffraction peaks related to CeO$_2$ phase in the cubic crystal structure of fluorite type.

On the AuCP catalyst (Fig. 5A, spectrum c), together with the CeO$_2$ pattern, a small broad peak at about 38°, attributed to metallic gold, can be observed. The average diameter of gold particles, estimated from this peak by the Scherrer’s equation, was 6.1 nm. The AuDP sample (Fig. 5A, spectrum b) shows only the CeO$_2$ peaks. The absence of a signal for gold suggests that the particle size of Au is below the detection limit of the instrument under the experimental conditions used (around 3–4 nm). The formation of smaller gold particles by deposition–precipitation compared to coprecipitation has been reported in the literature on Au/metal oxides catalysts [17,28,39].

In the case of the Ag/CeO$_2$ series (Fig. 5B), together with peaks related to the CeO$_2$ phase, a peak at 38° is clearly visible on the DP sample (Fig. 5B, spectrum a) with two less evident features at 44° and 64°. This pattern well agrees with the presence of metallic Ag particles [20], whose average diameter can be estimated around 7.1 nm. It must be underlined that the presence of Ag$_2$O cannot be fully excluded, considering that the peak at 38° can be due to both Ag and Ag$_2$O species. However, Ag$_2$O crystallites should exhibit a three–four times more intense peak at 33.5°, which instead is not visible in the spectrum of the DP sample, thus pointing out that metallic Ag species predominate over Ag$_2$O ones. In the case of the AgCP sample (Fig. 5B, spectrum b) only peaks related to the CeO$_2$ phase were found, suggesting that, analogously to the AuDP sample, the mean size of Ag crystallites is below the detection limit of the instrument.

XRD profiles of the both Cu/CeO$_2$ catalysts (Fig. 5C) revealed peaks related only to the CeO$_2$ phase. A closer inspection of the spectrum of the DP sample (Fig. 5C, spectrum a) showed, however,
reflections at 36° and 39° ca., attributed to CuO. Therefore it can be stated that on both Cu samples copper particles are equal (CuDP) or smaller (CuCP) than the detection limit of the instrument (3–4 nm).

From XRD spectra reported in Fig. 5, the average sizes of ceria crystallites of all investigated samples were also calculated by the Scherrer’s equation (peak at 2θ = 28.68°) and data are reported in Table 1. The bare ceria and all DP samples exhibit similar ceria crystallites (diameters in the range 9.2–10.0 nm), larger than those of CP samples, which show diameters of 6.4, 6.9 and 8.7 nm, respectively, for CuCP, AgCP and AuCP samples. Interestingly BET surface area measurements (Table 1) pointed to a higher surface area of the CP samples compared to DP ones. According to the literature [17,40], the above behaviour suggest that the presence of the IB metal affects the growth of ceria, during its formation in the coprecipitation stage, leading to a more amorphous structure and smaller ceria crystallites than those formed in the absence of the metal, as in the case of the bare ceria or the DP samples, where the IB metal was added only after ceria crystallites were formed and stabilized.

3.3.2. H2–D2 isotopic exchange

Fig. 6 reports H2–D2 isotopic exchange activities of IB metal/ceria catalysts. It must be reminded that the bare CeO2 sample exhibited no exchange activity up to 200 °C. From the figure it can be observed that the H2–D2 exchange reaction starts at about 50, 100 and 140 °C for Au/CeO2 (Fig. 6A), Ag/CeO2 (Fig. 6B) and Cu/CeO2 (Fig. 6C) samples, respectively. It is also noteworthy that the preparation method affected the H2–D2 exchange activity, the Au/CeO2 sample prepared by CP being more active than the DP one, the opposite behaviour being found for Cu/CeO2 and Ag/CeO2 systems (i.e. the sample prepared by DP has a higher exchange activity than the corresponding CP one). It must be also underlined that on all investigated samples a maximum conversion of ca. 55% was reached. This value represents the approximate thermodynamic equilibrium conversion under the experimental conditions used.

3.3.3. H2–TPR results

Fig. 7 reports temperature programmed reduction (H2–TPR) profiles carried out on ceria based catalysts. In the examined temperature range (30–600 °C), the CeO2 sample showed one broad reduction peak with a maximum at 540 °C and a shoulder at lower temperature (480 °C), both attributed to the reduction of the surface capping oxygens of ceria [40,41]. The reduction of bulk oxygens of ceria does not appear in the TPR profile of the CeO2 sample shown in the figure, occurring at T > 700 °C [41,42] and not being affected by addition of noble or transition metals [1,9,18,43].

On the AuDP sample a single and quite symmetric peak centered at 95 °C is observed, while on the AuCP sample the reduction peak is broader and shifted to higher temperature with a maximum at 120 °C and an evident shoulder at about 220 °C. It is important to note that areas of these reduction peaks are comparable, also being approximately equal to that of the capping oxygens of pure ceria. Considering that gold is in the metallic state under pre-treatment conditions of TPR (treatment in air at 300 °C) [23], the above behaviour suggests the reasonable attribution of these peaks to the reduction of ceria surface oxygen species with different reactivity, probably as a consequence of their different interaction degree with gold, the higher the interaction (as in the DP sample) the lower the reduction temperature [9]. Nevertheless it must be also reminded that a recent TPR study of Au/ceria catalysts prepared by DP has reported a hydrogen consumption at low-temperature assigned to both the reduction of adsorbed oxygen species on very small gold nanoparticles and the surface reduction of ceria [15,18]. Kang and Wan attributed the peak observed at 125 °C in the TPR profile of Au/Y zeolite to the reduction of oxygen adsorbed on surface metallic gold [44]. In any case the TPR profiles of Au/ceria catalysts here investigated confirm that the preparation method has a significant influence on the reduction of surface ceria oxygens, with the sample prepared by deposition–precipitation resulting in a higher effect.

On both Ag/CeO2 catalysts TPR profiles exhibited two not well resolved peaks with maxima at around 120–130 °C (LT peak) and 160–180 °C (HT peak). Taking into account that XRD data pointed to the presence of metallic silver, the LT peak can be attributed to the reduction of oxygen species on nanodispersed silver [45,46]. The HT peak can be, instead, assigned to the reduction of surface capping oxygens of ceria interacting with silver, as already observed in the case of Au/CeO2. Therefore it can be stated that also Ag, even if at a lower extent than Au, promotes the reducibility of surface ceria oxygens. This well agrees with results reported by Kundakovic and Flytzani-Stephanopoulos, which have demonstrated, by oxygen chemisorption, that addition of Ag increases the reducibility of ceria at low temperatures [47].
was instead observed in the CO conversion to CO₂ (Fig. 4A), that is the desired PROX reaction. In this case, in fact, gold and copper catalysts gave high CO conversions, Au/Co₃O₄ at low temperature (maximum of 84.3% for AuDP at 70 °C) and Cu/Co₃O₄ at higher temperature (maximum of 96.8% for CuCP at 150 °C). On the contrary silver catalysts exhibited very low CO conversions at any investigated temperatures (maximum of 16.7% for AgCP at 80 °C). It is also important to highlight that the preparation method significantly affected the performance of IB metal/Co₃O₄ catalysts, with an analogous trend for PROX and VOC combustion, the Au sample prepared by DP being more active than the CP one, the opposite happening on Ag and Cu catalysts.

Characterization data (XRD, H₂-TPR, surface area measurements, H₂–D₂ isotopic exchange, N₂O and H₂–O₂ chemisorption) helped us to clarify how the IB metal and the preparation method affect the catalytic performance of the IB metal/ceria system towards the deep oxidation of VOC and the preferential oxidation of CO in excess of hydrogen.

Firstly we addressed the role played by the IB metal. From this point of view, H₂-TPR profiles (Fig. 5) pointed out that the IB metal promotes the reducibility of ceria lattice oxygen species in the order Au/Co₃O₄ > Ag/Co₃O₄ > Cu/Co₃O₄ > CeO₂. An analogous reducibility trend has been reported on IB metal/Fe₂O₃ catalysts (Au/Fe₂O₃ > Ag/Fe₂O₃ > Cu/Fe₂O₃ > Fe₂O₃) [22]. The enhancement in the reducibility of lattice oxygen of reducible oxides in the presence of transition metals (Pt, Rh, Pd, Au, Cu, Ni) is well documented in the literature [9,17,18,22,23,41–43]. It must be underlined that all samples investigated in this work exhibited comparable values of surface area (110–130 m² g⁻¹), ruling out that the higher reducibility can be ascribed to the higher surface area. According to the literature [17,18,22,23], it can be proposed that the enhanced reducibility is related to the ability of the IB metal to weaken the Ce–O bond located nearby the active metal atoms. This would increase the lattice oxygen mobility of ceria as a consequence of higher structural defects induced by the metal [9,23,55]. In this context it is reasonable that a larger dimension of the IB metal atom leads to a larger extent of lattice distortion [22]. The reducibility rank above reported well agrees, in fact, with the atomic radius of IB metals which is in the order: Au (1.44 Å) = Ag (1.44 Å) > Cu (1.28 Å) [56]. It is generally accepted that the reducibility of the lattice oxygen of a reducible metal oxide directly reflects the reactivity of this oxygen [23,57]. Therefore TPR data point out that the surface oxygen reactivity of IB metal/ceria catalysts follows the order: Au/Co₃O₄ > Ag/Co₃O₄ > Cu/Co₃O₂ > CeO₂. The above rank well matches the VOC combustion activity trend (Figs. 1–3 and Table 2). The VOC deep oxidation over metal catalysts supported on reducible oxides, such as cerium and iron oxides, is in fact believed to occur through a Mars–van Krevelen mechanism, involving the reaction between the VOC molecule, mostly adsorbed on the support, and reactive lattice oxygens of the oxide, which are then replaced by the gas phase O₂ of the reaction mixture [9,10,22,23,31].

The ceria lattice oxygen reducibility/reactivity trend pointed out by H₂-TPR results is also in good accordance with the results of total conversion of O₂ (O₂ consumed both for CO and H₂ oxidation) observed in the PROX reaction (Fig. 4B), which followed the same order as the VOC combustion. In this case, however, a very different behaviour was found in terms of CO oxidation activity. In fact, Ag/Co₃O₄ catalysts, despite the very high total O₂ conversion, exhibited a very low ability to oxidize CO to CO₂ at any temperature (Fig. 4A) resulting in a very low PROX selectivity (Fig. 4C). This finding supports the hypothesis that the PROX reaction on IB metal/ceria catalysts also occurs through a Mars–van Krevelen reaction mechanism, which involves, in this case, active lattice oxygen species of the ceria reacting with CO adsorbed/activated on the IB metal particles and/or at the metal-support interface. The catalytic data reported in the present paper show that the activity towards the deep oxidation of investigated VOC was in the order: Au/Co₃O₄ ≥ Ag/Co₃O₄ ≥ Cu/Co₃O₂ ≥ Co₃O₂ (Figs. 1–3 and Table 2). Interestingly, the same trend was also found in the PROX reaction in terms of total conversion of O₂ (Fig. 4B), which includes O₂ consumed both for CO and H₂ oxidation. A different behaviour
This well agrees with the very high PROX activity of gold catalysts found at low temperature, as is well known that small nanoclusters of gold present an exceptional ability to activate CO [38,60]. The oxidation of H₂, adsorbed/activated on the IB metal, is a competitive reaction, which addresses the PROX selectivity of the system. Effectively, H₂–D₂ isotopic exchange data (Fig. 6), which reflect the H₂ activation ability of catalysts, fit well the observed PROX selectivities of ceria supported gold and copper systems, confirming the competitive H₂/CO activation on the IB metal. In fact, the H₂–D₂ exchange reaction begins to occur at around 40 °C and 140 °C, respectively, for Au/CeO₂ and Cu/CeO₂ catalysts, i.e. at those temperatures at which a drop in the PROX selectivity was observed (Fig. 4C). On the basis of H₂–D₂ exchange results, one should expect a good PROX selectivity of Ag/CeO₂ samples, at least up to 100 °C. On Ag catalysts, instead, selectivity was always very low. This discrepancy can be rationalized considering that silver has been reported to be practically unable to activate the CO molecule [18].

The second important issue of this work was the comprehension of the effect of the preparation method on the catalytic performance. The results reported in this paper clearly pointed to a significant influence of the preparation method towards the performance of IB metal/ceria catalysts. Interestingly the same effect was found both for PROX and VOC oxidation, the Au/CeO₂ sample prepared by DP being more active than the CP one, the opposite happening on Cu/CeO₂ and Ag/CeO₂ systems. H₂–TPR data of investigated IB/ceria catalysts showed that the preparation method influences the reducibility of ceria surface oxygens, which follows the same oxidation activity trend above reported. In fact, within each IB metal/CeO₂ system, a higher activity always correspond to a higher reducibility of the sample. XRD and chemisorption data (N₂O and H₂–O₂) pointed to a lower IB metal particles size of the more active catalysts (AuDP, AgCP and CuCP samples) compared to the corresponding less active one (AuCP, AgDP and CuDP, respectively), thus suggesting that the size of IB metal clusters has a key role in addressing the catalytic performance. The different effect of the preparation method, found to be dependent on the IB metal considered, can be reasonably rationalized on the basis of the relative solubilities of the hydroxide species formed during the coprecipitation stage. It has been reported, in fact, that if one of the component is much less soluble than the other sequential precipitation can occur, strongly affecting the properties of the obtained catalysts [61]. In our case, on the CP gold system, as a consequence of the much lower solubility product of Au(OH)₃ (Ksp = 5 × 10⁻⁴⁶) compared to Ce(OH)₃ (Ksp = 1.6 × 10⁻²⁰), Au(OH)₃ should be formed before than Ce(OH)₃. This should lead to a less intimate mixing of the components [61], thus favoring the aggregation of gold hydroxide in larger particles, partially covered by the cerium hydroxide successively formed. Reasonably in the presence of the support (DP samples) the extremely low solubility of gold hydroxide leads to the formation of a high number of nucleation centers, which interact with the support, resulting in small gold particles well distributed on the surface. The formation of smaller gold particles by deposition–precipitation compared to coprecipitation agrees with literature data [17,38,39]. Moreover, on Au/oxide catalysts, it has been reported that deposition–precipitation has the advantage over coprecipitation of favoring the location of gold on the surface, avoiding that active species are buried within the support [9,39]. In the case of ceria supported Ag and Cu CP samples, the solubility of the hydroxide species, AgOH (Ksp = 1.2 × 10⁻⁴⁸) and Cu(OH)₂ (Ksp = 2 × 10⁻¹⁶), is higher or similar to that of Ce(OH)₃, and therefore cerium hydroxide should precipitate in advance or contemporaneously with Ag and Cu hydroxides. This should cause a better mixing of the components and consequently a higher interaction of Ag and Cu species with ceria, also resulting in smaller IB metal and ceria crystallites. This agrees with the mean size of both IB metal and CeO₂ crystallites, which were in the order CuCP < AgCP < AuCP (Table 1). In the case of Ag and Cu samples prepared by DP the higher solubility of Cu and even more of Ag hydroxides compared to Au(OH)₃ should cause the formation of a lower number of nucleation centers, which grow in the course of the precipitation process. The dependence of the clusters dimension on the ratio of the nucleation rate to the growing rate of metal particles, has been reported in the literature, an higher ratio leading to smaller particles [62–64]. On the basis of these results, it can be concluded that preparation conditions favoring the formation of smaller IB metal clusters and ceria crystallites lead to more active catalysts towards oxidation reactions to result in a higher IB metal–ceria interaction and therefore in a more efficacious activation of the ceria surface oxygens [9].

5. Conclusions

On the basis of the reported results the following conclusions can be drawn:

The presence of IB metal increases the activity of ceria towards both VOC combustion and PROX reaction. The VOC deep oxidation activity was in the order: Au/CeO₂ > Ag/CeO₂ > Cu/CeO₂ ≥ CeO₂. In the PROX reaction Au and Cu catalysts gave high CO conversions (Au/CeO₂ at low temperatures, Cu/CeO₂ at higher temperatures), whereas Ag/CeO₂ catalysts always exhibited very low CO conversion.

It was proposed that a higher atomic radius of the IB metal and the presence of smaller crystallites of both IB metal and ceria result in a larger enhancement of mobility/reactivity of surface ceria oxygens, involved in both investigated reactions through a Mars–van Krevelen mechanism. The low PROX activity of Ag/CeO₂ samples was related to the inability of Ag to activate the CO molecule. Both for PROX and VOC combustion the Au sample prepared by DP was more active than the CP one, the opposite happened on Ag and Cu catalysts. The above behaviour was rationalized suggesting that conditions which favor the formation of smaller IB metal clusters and ceria crystallites lead to more active catalysts. This study pointed out that, among IB metal/ceria catalysts, Au/ceria and Ag/ceria are the most active systems for the VOC combustion. Interestingly, the best catalysts of the two series (namely AuDP and AgCP) exhibit comparable VOC conversions (Table 2). Taking into account the much lower cost of silver compared to gold, Ag/CeO₂ undoubtedly appears the most promising catalyst for a practical application. In the case of the PROX reaction, notwithstanding Au/CeO₂ has the highest activity at low temperature, Cu/CeO₂ can be definitely considered the most proper catalyst, being sensibly more active and selective than gold under real operative conditions.

References
