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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: $Au/CeO_2 \geq Ag/CeO_2 > Cu/CeO_2 \gg CeO_2$. The same trend was also found in the PROX reaction in terms of total conversion of O_2, which includes O_2 consumed both for CO and H_2 oxidation. A different behaviour was observed in the CO conversion to CO_2, that is the desired PROX reaction. For this reaction, in fact, Au and Cu catalysts gave high CO conversions, Au/CeO_2 at low temperature (maximum of 84.3% for AuDP at 70 °C) and Cu/CeO_2 at higher temperature (maximum of 96.8% for CuCP at 150 °C), whereas Ag catalysts always exhibited very low CO conversions (maximum of 16.7% for AgCP 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, H_2-TPR, surface area measurements, H_2–D_2 isotopic exchange, N_2O and H_2–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 CO molecule.

1. Introduction

Ceria (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 $Au/Fe_2O_3 > Ag/Fe_2O_3 > Cu/Fe_2O_3 > Fe_2O_3$. 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 chemico-physical properties and therefore the performance of the catalytic system.

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Table 1
Code and chemico-physical properties of IB metal/ceria catalysts.

Code	IB metal content (%)	BET surface area ($m^2 g^{-1}$)	IB metal dispersion (%)	Average IB metal diameter (nm)	Average CeO_2 diameter[a] (nm)
AuDP	4.3	118	>30[a]	<4[a]	9.9
AuCP	4.6	127	19.5[a]	6.1[a]	8.7
AgDP	4.8	112	16.9[b]	7.1[a]–6.7[b]	9.0
AgCP	4.7	130	33.7[b]	<4[a]–3.3[b]	6.9
CuDP	4.5	116	32.6[c]	<4[a]–3.1[c]	9.2
CuCP	4.7	125	62.4[c]	<4[a]–1.6[c]	6.4
CeO_2	–	110	–	–	10.0

[a] Estimated by XRD.
[b] Estimated by H_2–O_2 titration.
[c] Estimated by N_2O dissociative chemisorption.

2. Experimental

2.1. Catalyst preparation and testing

IB/cerium oxide catalysts were prepared by coprecipitation (CP) or deposition–precipitation (DP), using $Ce(NO_3)_3·6H_2O$ (Aldrich) and the precursor of the IB metal ($HAuCl_4$, $AgNO_3$ and $Cu(NO_3)_2·6H_2O$ 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 °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 °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 °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, and CuCP). The IB metal content of investigated catalysts, measured by atomic absorption spectrophotometry, is reported in Table 1.

The cerium oxide, used as support, was prepared by precipitation from $Ce(NO_3)_3·6H_2O$ following preparation conditions similar to those employed in the CP method, and then was calcined in air at 450 °C for 2 h. The surface area of the obtained ceria was 110 $m^2 g^{-1}$. The pure cerium oxide sample was coded as CeO_2.

Catalytic tests were carried out in the gas phase at atmospheric pressure in a continuous-flow reactor filled with the catalyst (5–100 mg, 80–140 mesh) diluted with an inert glass powder. For each experiment the reactor temperature was ramped at a rate of 5 °C min^{-1} up to the chosen reaction temperature. Then the reactant mixture was passed over the catalyst for 15 min (to reach a steady-state) before sampling the products for analysis. By using the above procedure, conversion and selectivities were reproducible within 3–5%.

Preliminary runs carried out at different flow-rates (ranging from 25 to 100 ml min^{-1}) showed the absence of external diffusional limitations. The absence of internal diffusion limitations was verified by running experiments with different grain size powders (60–80, 80–140 and 140–200 mesh). We excluded the occurrence of heat transfer limitations, because we found that the temperature of the reactor at different heights was substantially the same, reasonably due to the low concentration of the reactants used in the catalytic tests.

For VOC oxidation the reactant mixture (0.7 vol.% VOC, 10 vol.% O_2, balance in helium) was fed to the reactor by flowing a part of the He stream through a saturator containing the VOC and then mixing with O_2 and He before reaching the catalyst. Used VOCs were methanol (Fluka, >99.5%), acetone (Carlo Erba, 99.7%) and toluene (Fluka, 99.5%). A space velocity (GHSV) of 7.6×10^{-3} mol_{VOC} h^{-1} g_{cat}^{-1} was used. The effluent gases were analysed on-line by a gas chromatograph, equipped with a packed column with 10% FFAP on Chromosorb W and FID detector, and by a quadrupole mass spectrometer (VG quadrupoles). The carbon balance was always higher than 95%. Before VOC oxidation activity tests samples were calcined in air at 300 °C. It must be underlined that 300 °C was chosen as calcination temperature as we verified that a higher temperature leads to an evident sintering of the IB metal with detrimental effect on the activity.

In the case of PROX reaction the gas composition (flow rate: 80 ml min^{-1}) was 1% CO, 1% O_2, balance in H_2. A space velocity (GHSV) of 3.92×10^{-2} mol_{CO} h^{-1} g_{cat}^{-1} was used. The effluent gases were analysed on-line by a gas chromatograph, equipped with a packed column (Carboxen 1000) and TCD detector. Before PROX activity tests samples were calcined in air at 300 °C and then reduced in H_2 at 150 °C.

For both reactions no significant catalysts deactivation was observed under reaction conditions used, at least during the maximum time of stream tested in this work (8 h).

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 °C min^{-1} using 5 vol.% H_2 in Ar. Before TPR tests samples were calcined in air at 300 °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 °C, reduced in H_2 at 150 °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 °C and then outgassed (10^{-3} Torr) at 120 °C.

The silver dispersion of Ag/CeO_2 catalysts was calculated by H_2–O_2 titration pulse method at 170 °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_2O adsorption at 60 °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_2O consumed. The specific area of metallic copper was calculated assuming a reaction stoichiometry $N_2O/Cu = 0.5$ and a Cu surface density of 1.46×10^{19} atoms/m^2