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CO Oxidation Activity of a Au/Ceria-Zirconia Catalyst Prepared by Deposition–Precipitation with Urea

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Abstract The activation of a 2.6 wt% $Au/Ce_{0.62}Zr_{0.38}O_2$ catalyst prepared by deposition–precipitation with urea is investigated. At 298 K, the activity for CO oxidation of the as-prepared sample is very low; it is significantly increased when heated at 418 K, under the reaction mixture, and much strongly when pre-treated under flowing $O_2(5\%)/He$, at 523 K. As revealed by XPS, FTIRS, HAADF-STEM, and HRTEM studies, the activation process consists of the transformation of the initial urea-containing Au(III) precursor deposited on the support into a highly dispersed metal phase (Au nano-particle mean size: 1.8 nm).

Keywords $Au/CeZrO_2$ · Urea deposition/precipitation · Activation · CO oxidation

1 Introduction

The rather short but very intense history of gold catalysts can hardly be understood without analyzing the developments occurred in their preparation methods [1, 2]. In contrast with most of the noble metals widely used in catalysis, for which the classic impregnation techniques

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have been fruitfully applied for quite a long time, in the case of gold, these methods generally lead to catalysts with very low activity [1]. A major reason for that is the poor metal dispersion exhibited by the catalysts prepared in this way [1]. In fact, it is presently known that, for most of the reactions, highly active catalysts can only be obtained when gold nano-particles are smaller than 5 nm [3, 4]. Developments in the synthetic procedures have thus represented major breakthrough points in the recent history of the catalysis by gold. The discoveries that followed the application of the co-precipitation methods first [5–7], and of the deposition–precipitation techniques later on [8, 9], constitute good examples of the role played by the preparation procedures in the obliged revision of the classic concepts about the catalytic applications of oxide-supported gold systems.

In addition to the techniques allowing the deposition of well dispersed metal precursors, the post-synthetic treatments applied to the fresh samples may also play an important role in determining the activity of the final catalyst [10, 11]. Oxidizing pretreatments are the most common activation routines. By using CO oxidation as the reaction test for evaluating the effect of these pre-treatments, contradictory results may be found in the literature. In some cases, they enhance the activity of the gold catalysts [7, 12], whereas in some other cases they induce a negative effect [13–15]. It should be taken into account, however, that the effect of the pre-treatments may strongly depend on variables like the metal loading, the textural properties and chemical constitution of the support, the procedure followed for depositing the gold precursor, and, obviously, the specific conditions applied in the pre-treatment.

In this work, a 2.6 wt% $Au/Ce_{0.62}Zr_{0.38}O_2$ catalyst prepared by homogeneous deposition–precipitation with

urea (DPU) [16] is investigated. Because of the high activity of this relatively new family of gold catalysts for reactions like LT-WGS (low temperature-water gas shift) [17–22], oxidation of CO [23–26] and volatile organic compounds (VOCs) [27], or PROX (selective oxidation of CO in presence of an excess of H_2) [28], the interest on them is rapidly growing. However, none of the studies mentioned above have dealt with Au/CeO_2-ZrO_2 samples prepared by the homogeneous deposition–precipitation method with urea followed herein. Accordingly, it seemed interesting to explore the catalytic behavior for CO oxidation of both the as-prepared catalyst (fresh sample), and that resulting from an oxidizing pretreatment at 523 K. A dramatic difference of activity was found between them. This behavior is also compared with that exhibited by a second 2.5 wt% $Au/Ce_{0.62}Zr_{0.38}O_2$ sample prepared by deposition–precipitation with an aqueous solution of Na_2CO_3 [29]. The assayed catalysts were characterized in detail by X-ray photoelectron spectroscopy (XPS), Fourier Transform IR spectroscopy (FTIRS), as well as high resolution transmission and high angle annular dark field-scanning-transmission electron microscopies (HRTEM and HAADF-STEM). On the basis of the gathered information, an interpretation for the observed difference of catalytic behavior is proposed.

2 Experimental

The 2.6 wt% $Au/Ce_{0.62}Zr_{0.38}O_2$ (Au/CZ-DPU) catalyst, with a BET surface area of 63 m^2 g^{-1}, was prepared by homogeneous DPU. The procedure was similar to that followed by Zanella et al. [16]. The gold precursor was 99.99% $H[AuCl_4]$ from Alfa Aesar, and the support was a commercial sample kindly donated by Grace-Davison. Details of the experimental routine applied by us are reported elsewhere [30]. As deduced from the corresponding N_2 adsorption at 77 K, and X-ray diffraction studies, the deposition of the gold precursor does not significantly modify the textural and macro-structural properties of the pure support.

The catalytic assays were all carried out at atmospheric pressure under the following conditions: amount of catalyst: 25 mg (diluted with 100 mg of crushed quartz), total gas flow rate: 100 mL min^{-1}, reaction mixture: 1%CO, 0.6%O_2, and He to balance. The reactor was immersed in a bath Lauda, model Proline RP-845, filled with polymethylsiloxane, whose temperature could be varied with excellent linearity within the range 233–418 K. The assays consisted of a heating/cooling cycle. During the first step of the cycle, the catalyst was heated from 233 to 418 K, at a rate of 10 K min^{-1}; then it was kept for 30 min at 418 K

(isothermal step), and finally, the temperature was lowered from 418 to 233 K at the same cooling rate (-10 K min^{-1}). The composition of the reaction mixture was continuously monitored by means of a mass spectrometer Pfeiffer, model QME-200 D, whose capillary inset device was attached just to the way out of the reactor.

X-ray photoelectron spectroscopy studies were performed on a Kratos Axis Ultra DLD instrument equipped with a catalytic cell allowing a clean transfer of the pretreated samples to the analytical chamber. Spectra were recorded by using monochromatized AlK_α radiation (1,486.6 eV). The selected X-ray power was 72 W in the case of the fresh catalysts, and 150 W in all the other cases. The spectrometer was operated in the fixed analyzer transmission (FAT) mode, with a pass energy of 20 eV. Surface charging effects were compensated by using the Kratos coaxial neutralization system. The binding energy (BE) scale was calibrated with respect to the Zr $3d_{5/2}$ (182.64 eV) component in the mixed oxide support. Spectra processing was performed with CasaXPS software. Deconvolution studies on Au 4f core level were carried out by using Doniach-Sunjic type line shapes and Shirley-type backgrounds.

The evolution of the fresh Au/CZ-DPU catalyst under reaction conditions has also been investigated by means of FTIRS. The powdered fresh catalyst sample was used in the form of a self-supported disk (diameter: 13 mm; weight: 30 mg) pressed at 5 ton cm^{-2}, which was further transferred to a quartz cell for in situ FTIR studies developed at the Dalian Institute of Physical Chemistry (P. R. China). This cell fitted with water-cooled CaF_2 windows allowed us to record the spectra while heating the sample in flow of different gases. Prior to any experiment, the fresh catalyst was flushed with pure He at 298 K (30 min). After this purge, the gas flow was switched to the same reaction mixture used in the catalytic assays. Then, the temperature was varied in a stepwise manner from 298 to 418 K and back again to 298 K, while recording spectra at each of the steps. Isothermal steps, of 15 min duration, at 298, 323, 348, 373, 398, and 418 K were investigated. The sample resulting from this study was further heated in flow of 5%O_2/He at 523 K (60 min), then, it was flushed with pure He at 523 K (60 min), and, later on, it was cooled to 298 K, always under flowing He. Finally, the gas flow was switched to the reaction mixture, at 298 K, and a new series of spectra was recorded. The whole study was carried out on a Bruker instrument, model Vertex 70, using a DTGS detector. Typically, 100 scans at a resolution of 4 cm^{-1} were averaged.

Catalysts were also characterized by means of HRTEM and HAADF-STEM techniques. Images were recorded on a JEOL2010-F microscope with 0.19 nm spatial resolution at Scherzer defocus conditions. HAADF-STEM images were

obtained by using an electron probe of 0.5 nm of diameter at a diffraction camera length of 10 cm.

3 Results and Discussion

3.1 Catalytic Assays

We have evaluated first the activity for CO oxidation of the as-prepared (fresh) Au/CZ-DPU sample. Figure 1 shows the corresponding CO conversion–temperature curves recorded during the three steps of the assay described in the "Experimental" section. As deduced from Fig. 1a, during the heating step, the catalyst shows almost no activity up to approximately 373 K, a remarkable increase of the conversion being observed as the temperature is increased from 373 up to 418 K. Moreover, the CO conversion continues to grow during the 30 min isothermal step at 418 K, Fig. 1b. These results suggest the occurrence of a strong activation of the catalyst during the heating and isothermal steps, which is further confirmed by the evolution of the conversion during the cooling of the catalyst. In effect, as shown in Fig. 1c, the activity of the catalyst during the final (cooling) step is much higher than that exhibited throughout the first (heating) one.

Taking into account that the reaction mixture contains an excess of oxygen, it seemed reasonable to investigate the behavior of the fresh catalyst further submitted to the following treatment: heating in a flow of 5%O_2/He at 523 K (1 h), then, the catalyst was flushed with pure He, at 523 K (1 h), and, finally, it was cooled to 233 K, always

under flowing He (Routine: OE523). These experimental conditions were decided on the basis of temperature programmed oxidation-mass spectrometry (TPO-MS), under flowing 5%O_2/He, not shown for sake of brevity, and XPS studies. As will be discussed later on in this work, the XPS data clearly show that the selected oxidation temperature, 523 K, was high enough as to remove most of the surface impurities present in the fresh catalyst. Also worth of mentioning, the final step of the pre-treatment was aimed at eliminating eventual forms of adsorbed oxygen which could induce a transient increase of the catalyst activity [31]. The catalyst resulting from this pre-treatment will be hereafter referred to as Au/CZ-DPU-OE523.

Figure 1d shows the light off curve corresponding to the Au/CZ-DPU-OE523 catalyst. If compared with the trace reported in Fig. 1c, we may notice that the activity of the pretreated sample is much higher than that of the fresh catalyst heated under reaction conditions, at 418 K. Therefore temperatures higher than 418 K are required for an effective activation of the fresh catalyst.

An experiment identical to the one commented on above (Fig. 1) was also carried out on a second 2.5 wt% Au/$Ce_{0.62}Zr_{0.38}O_2$ sample. The ceria-zirconia mixed oxide support was the same in both catalysts; actually, the only major difference between them was the gold deposition method. Instead of the homogeneous DP procedure with urea applied in the case of Au/CZ-DPU, the second sample was prepared by following a DP routine in which an aqueous solution of Na_2CO_3 was used as precipitating agent [20]. Accordingly, it will be referred to as Au/CZ-DPC catalyst. Figure 2 summarizes the catalytic assay carried out on a fresh portion of Au/CZ-DPC. To make easier the comparison, data corresponding to the fresh Au/CZ-DPU sample
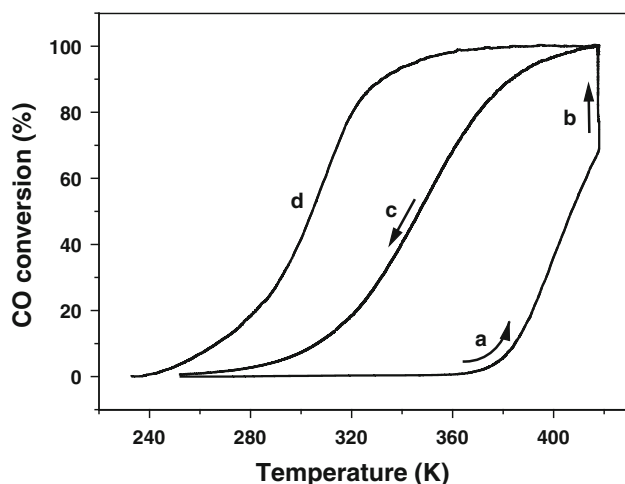

Fig. 1 Catalytic oxidation of CO. Light off curves corresponding to the heating/cooling assay carried out on the fresh Au/CZ-DPU catalyst: heating step (*a*), isothermal step (*b*), and cooling step (*c*). Also included are the light off curves (heating steps) for Au/CZ-DPU-OE523 (*d*). The reaction conditions were the same for all the assayed samples (See "Experimental" section for details)
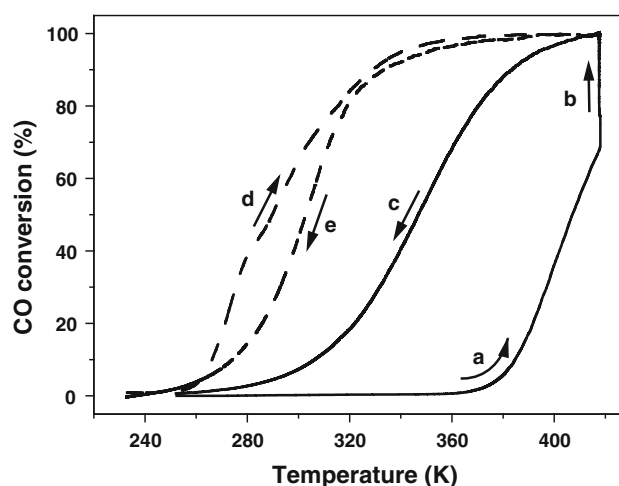

Fig. 2 Catalytic oxidation of CO. Comparison of light off curves corresponding to the assay carried out on the fresh Au/CZ-DPU: heating step (*a*), isothermal step (*b*), and cooling step (*c*); and fresh Au/CZ-DPC: heating and isothermal steps (*d*), and cooling step (*e*)

have also been included in Fig. 2. As clearly shown in Fig. 2, their catalytic behavior is dramatically different. Thus, during the initial heating step of the assay, the activity of Au/ CZ-DPC, Fig. 2d, is much higher than that of the analogous Au/CZ-DPU catalyst, Fig. 2a. Moreover, as deduced from Fig. 2e, the Au/CZ-DPC sample shows some deactivation during the cooling step of the assay. This behavior strongly contrasts with that exhibited by the fresh Au/CZ-DPU catalyst, whose activity during the cooling step, Fig. 2c, is much higher than that measured during the initial heating. This shows a very strong influence of the precipitating agent, urea or sodium carbonate, on the nature and catalytic properties of the gold precursor deposited on the surface of the CZ support. In the first case, Au/CZ-DPU sample, as already discussed, the activity of the fresh sample is very low, an activation pretreatment either under the reaction mixture at 418 K, or at a bit higher temperature, 523 K, under diluted oxygen, being required to increase its activity. By contrast, on the fresh Au/CZ-DPC sample, the highest activity is found during the initial heating, a certain deactivation being observed in the subsequent cooling step of the assay.

We have also evaluated the influence on the catalytic properties of Au/CZ-DPU-OE523 of a series of successive ageing treatments at increasing temperatures, under reaction conditions. This additional experiment had two major objectives. First, heating at increasing temperatures, under the net oxidizing conditions created by the reaction mixture, would allow us to check whether the OE523 routine leaded to the optimum activity, or treatments at higher temperatures could further improve it. Second, this study would also inform us about the behavior against thermal ageing of the Au/CZ-DPU sample. In our experiment a single portion of the catalyst was successively subjected to a series of heating/cooling cycles, in which the highest reaction temperature was progressively increased up to 523, 623, 773, and 973 K. In every case, the catalyst was kept for 1 h at the selected top limit temperature. In accordance with the investigated temperature range, a conventional electric furnace ought to be used, so that the light off curves could only be recorded from 298 K upwards. Figure 3 summarizes the results of this study. As deduced from the comparison of the reported light off curves, the applied cleaning routine, OE523, leads to the most active catalyst. Regarding the effect of the thermal ageing under reaction conditions, Fig. 3 shows that deactivation effects are rather moderate after heating at 623 K, noticeable at 773 K, and much stronger at 973 K. Even in the latter case, the activity of the catalyst is still much higher than that of the pure support, thus indicating the presence in this heavily aged sample of a significant fraction of active gold.

To gain some further understanding of the origin of the dramatic changes of catalytic behavior observed in the fresh Au/CZ-DPU, and the very remarkable difference
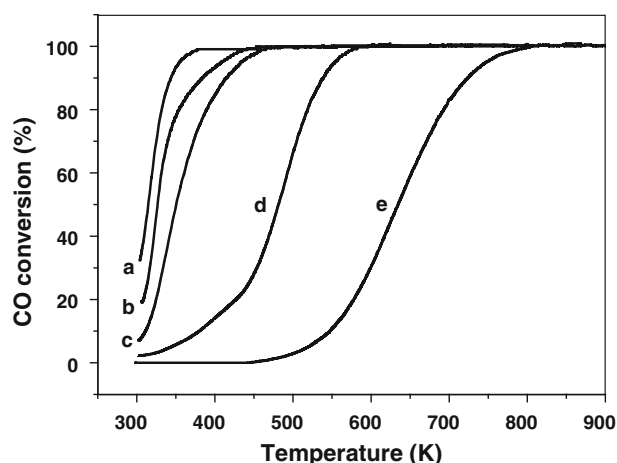

Fig. 3 Light off curves for the catalysts resulting from the application to Au/CZ-DPU-OE523 a successive series of thermal ageing cycles at 523 K (a), 623 K (b), 773 K (c), and 973 K (d), under reaction conditions. The initial assay is superimposable with the (a) one. Data for the bare support, CZ-OE523, have also been included (e), for comparison

found between Au/CZ-DPU and Au/CZ-DPC samples, we have carried out the series of XPS, FTIR spectroscopy and electron microscopy characterization studies which will be briefly commented on below.

3.2 XPS Characterization Studies

A preliminary XPS study carried out on the fresh Au/CZ-DPU showed that, at 298 K, the monochromatized AlK$_\alpha$ X-ray beam induced a noticeable decomposition of the supported gold phase. Accordingly, the usual recording conditions were modified by lowering the power in the X-ray source from 150 to 72 W, and the acquisition time from 15 to 8 min. Despite of this, remarkable changes may be observed in the Au 4f spectrum for the fresh Au/CZ-DPU sample, especially during the very first 45 min of exposure to the X-ray beam. The initial and final (after 90 min exposure) spectra are reported in Fig. 4a$_i$ and a$_f$, respectively. By analyzing these spectra, data summarized in Table 1 were obtained. In accordance with them, Au(III) and Au(0) forms coexist in the fresh sample, the percentage of the former diminishing from 68 to 24% with the exposure time. In parallel with this photo-reduction of gold a slight decrease of the Au 4f/Zr 3d intensity ratio may be noticed, from 0.16 in the initial sample, down to 0.15 in the final one.

We have also investigated the evolution under the X-ray beam of the C 1s and N 1s spectra for the fresh Au/CZ-DPU sample. These studies were performed on new portions of the fresh catalyst. The spectroscopic conditions were the same as those applied in the study of the Au 4f
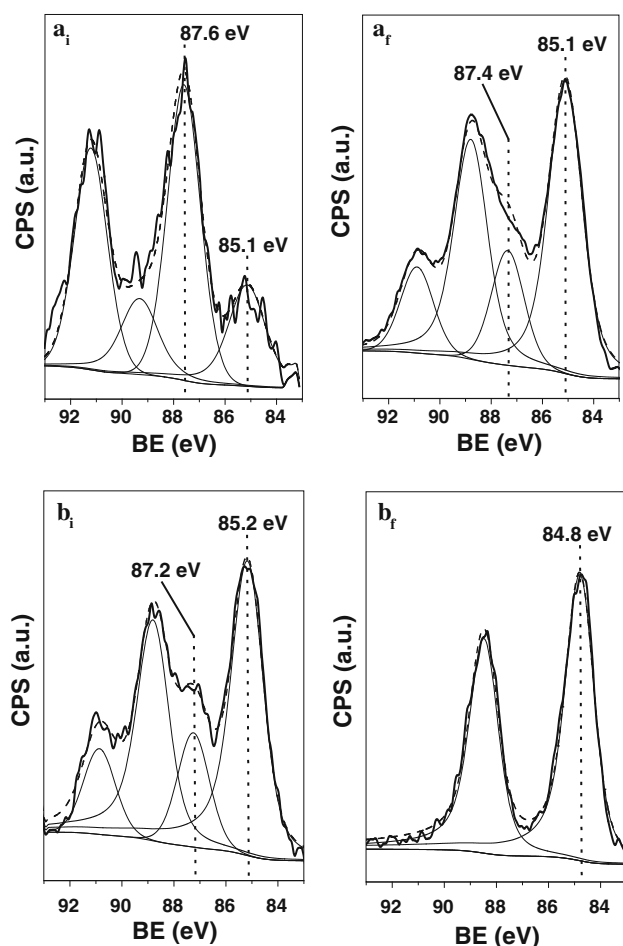
Fig. 4 Au 4f XP-spectra for the fresh catalysts: (**a**$_i$) Au/CZ-DPU and (**b**$_i$) Au/CZ-DPC, and the corresponding final samples, (**a**$_f$, **b**$_f$) resulting from their exposure to a monochromatized AlK$_\alpha$ X-ray beam (Power of the X-ray source: 72 W) for 90 min, at 298 K. Acquisition time for the spectra: 8 min

signal. Table 1 summarizes the results of the analysis made of the initial and final spectra for C 1s and N 1s signals. The presence of N-containing species in the fresh Au/CZ-DPU provides with us a first indication of the likely occurrence in the supported metal precursor phase of urea coordinated to Au(III). This proposal is further confirmed by the parallel decrease of the N 1s/Zr 3d and Au 4f/Zr 3d intensity ratios with the exposure time to the X-ray beam, which suggests that the decomposition of the gold precursor with inherent formation of metal nano-particles is coupled to the urea elimination. The effect of irradiation on the C 1s/Zr 3d intensity ratio is much less marked, thus indicating that a significant fraction of the carbon-containing species may be due to carbonate forms adsorbed on the ceria-zirconia support.

Figure 4b$_i$ and b$_f$ shows respectively the initial and final Au 4f spectra recorded for the fresh Au/CZ-DPC sample during the 90 min exposure to the monochromatized AlKα

X-ray beam. With reference to the analogous Au/CZ-DPU catalyst, remarkable differences may be noticed in both the initial and final states of the sample. As shown in Table 1, for Au/CZ-DPC, the initial percentage of Au(III), 21%, is much lower than that determined for Au/CZ-DPU, 68%. After 90 min of exposure, this percentage becomes negligible for Au/CZ-DPC, it being still very significant, 24%, for Au/CZ-DPU.

As expected, no signal for N 1s could be detected on the fresh Au/CZ-DPC catalyst. Regarding the C 1s signal, no data for its evolution under the X-ray beam are available; however, we have recorded the spectrum after 90 min irradiation at 298 K. The C1s/Zr 3d intensity ratio corresponding to this spectrum is shown in Table 1. The reported value, 0.88, is approximately one half of that determined for the final Au/CZ-DPU sample, 1.80, thus indicating a much lower surface density of carbon-containing species.

The XPS study shows no evidence of chlorine in the fresh DPU and DPC samples. In this study, instead of the most intense Cl 2p signal, Cl 2s core level ought to be analyzed because the overlap of the former with an energy loss feature corresponding to the Zr 3d component. The absence of significant amounts of chlorine was also confirmed by a parallel TPO-MS study of the fresh catalysts.

To summarize, the activity assays and XPS characterization studies carried out on the fresh Au/CZ-DPU and Au/CZ-DPC samples prove that the use of urea or sodium carbonate as precipitating agent leads to gold precursor phases of different constitution and chemical properties. By using a different experimental approach, Louis et al. [32, 33] have arrived at a similar conclusion in their comparative study of the gold precursors deposited on TiO$_2$ by DP-urea and DP-NaOH techniques. As in the present case, in effect, the studies carried out by Louis et al. on the DP-urea precursor show the presence of N and C elements in its formulation [33]. Likewise, the temperature required to fully decompose the metal precursor to Au(0) nano-particles is higher for the DP-urea sample [32]. It should be stressed, however, that both the support, TiO$_2$ or CeO$_2$-ZrO$_2$, and the alternative precipitating agent, NaOH in the case of Louis et al. studies, and Na$_2$CO$_3$ in ours, are different.

The XP-Spectroscopy has also been used to characterize the Au/CZ-DPU-OE523 catalyst, and the samples resulting from the application of the series of successive thermal ageing cycles, under reaction conditions, shown in Fig. 3. Figure 5 and Table 2 report on the corresponding results. The Au 4f spectra included in Fig. 5 are all consistent with a single contribution due to metallic nano-particles. Table 2 summarizes the Au 4f/Zr 3d intensity ratio values corresponding to the series of spectra reported in Fig. 5. The highest value, 0.09, is associated to the Au/CZ-DPU-OE523

Table 1 X-ray photoelectron spectroscopy study of the initial (Au/CZ-DPU and Au/CZ-DPC fresh catalysts) and final samples resulting from their exposure to a monochromatized AlK$_\alpha$ X-ray beam (Power of the X-ray source: 72 w) for 90 min, at 298 K

Au/CZ-DPU[a]	Au 4f/Zr 3d	%Au(III)	%Au(0)	BE (eV) Au 4f$_{7/2}$ (III)	BE (eV) Au 4f$_{7/2}$ (0)
Initial	0.16	68	32	87.6	85.1
Final	0.15	24	76	87.4	85.1
Au/CZ-DPU[a]	**C 1s/Zr 3d**	**C 1s/Au 4f**		**BE (eV) C 1s**	**BE (eV) C 1s**
Initial	2.71	16.73		285.4	289.5
Final	1.80	11.76		285.4	289.5
Au/CZ-DPU[a]	**N 1s/Zr 3d**	**N 1s/Au 4f**			**BE (eV) N 1s**
Initial	0.49	3.01			399.4
Final	0.17	1.13			399.6
Au/CZ-DPC[a]	**Au 4f/Zr 3d**	**%Au(III)**	**%Au(0)**	**BE (eV) Au 4f$_{7/2}$ (III)**	**BE (eV) Au 4f$_{7/2}$ (0)**
Initial	0.13	21	79	87.2	85.2
Final	0.13	0	100	–	84.8
Au/CZ-DPC	**C 1s/Zr 3d**	**C 1s/Au 4f**		**BE (eV) C 1s**	**BE (eV) C 1s**
Final	0.88	7.06		285.5	289.9

Acquisition time for the spectra (8 min)

[a] In every case, data were obtained from new portions of the corresponding fresh catalyst
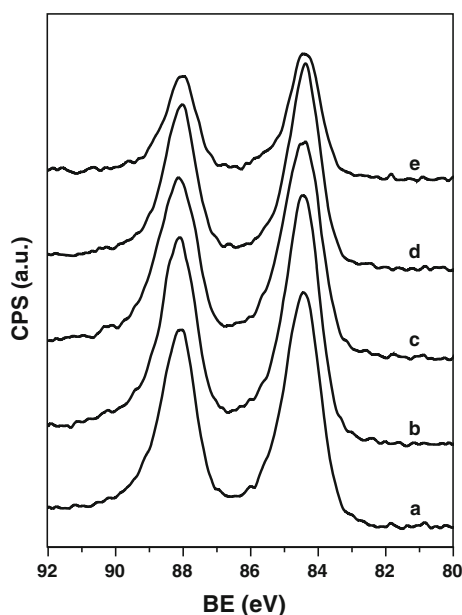
Fig. 5 Au 4f XP-spectra corresponding to Au/CZ-DPU-OE523 (*a*), and the samples resulting from its ageing under reaction conditions at 523 K (*b*), 623 K (*c*), 773 K (*d*), and 973 K (*e*). Power of the monochromatized AlK$_\alpha$ X-ray source: 150 W. Acquisition time for the spectra: 15 min

Table 2 Analysis of the Au 4f XP-spectra for Au/CZ-DPU-OE523 and the samples resulting from its ageing under reaction conditions (1 h) at the indicated temperatures

Temperature of ageing under reaction conditions (K)	BE (eV) Au 4f$_{7/2}$	Au 4f/Zr 3d intensity ratio
None (OE523 sample)	84.5	0.09
523	84.5	0.09
623	84.5	0.08
773	84.4	0.07
973	84.4	0.04

sample, before starting the ageing experiment under reaction conditions. This value is significantly lower than those reported in Table 1 for the fresh Au/CZ-DPU catalyst before (Au 4f/Zr 3d = 0.16) and after 90 min exposure to the X-ray beam (Au 4f/Zr 3d = 0.15). Also interesting, the OE523 routine eliminates the C 1s and N 1s signals observed in the fresh sample. We may conclude, accordingly, that this pretreatment temperature, 523 K, is high enough as to induce the complete decomposition of the metal precursor phase in the fresh Au/CZ-DPU sample, with inherent formation of Au(0) nano-particles. Though this decomposition process certainly implies some gold

sintering, the corresponding catalyst, Au/CZ-DPU-OE523, shows a much higher activity than the fresh Au/CZ-DPU sample, and even than that resulting from its activation under reaction conditions at 418 K, Fig. 1. To summarize, the XPS study briefly commented on above strongly suggest that the clean Au(0) nano-particles formed by the virtue of the OE523 pretreatment, rather than the Au(III) forms present in the fresh catalyst, constitute the actual active phase for the CO oxidation reaction.

The Au 4f/Zr 3d intensity ratio data reported in Table 2 also show the occurrence of a progressive decrease of this ratio as the ageing temperature under reaction conditions is increased. In effect, the Au 4f/Zr 3d value for the sample aged at 523 K, 0.09, agrees with that of the un-aged Au/CZ-DPU-OE523 catalyst, it slightly decreases to 0.08 for the sample aged at 623 K, to 0.07 after ageing at 773 K, and much strongly to 0.04 for the sample heated under reaction conditions at 973 K. This evolution of the Au 4f/Zr 3d intensity ratio, which may be interpreted as due to the progressive sintering of the metal phase, is fully consistent with the parallel shift towards higher temperatures of the (a)–(d) light off curves in Fig. 3.

3.3 FTIR Spectroscopy Studies

The evolution undergone by the fresh Au/CZ-DPU sample throughout the activation process occurring under reaction conditions has also been investigated by FTIR spectroscopy. The experiment consisted of varying the temperature of the sample in a stepwise manner from 298 to 418 K, and back again to 298 K, in flow of the reaction mixture. The results corresponding to the initial (a) and final (b) steps of the whole cycle are summarized on the part A of Fig. 6.

The spectrum recorded at 298 K, after 15 min contact with the reaction mixture of Au/CZ-DPU-OE523 is also included for comparison, Fig. 6c. As deduced from Fig. 6a, the spectrum for the fresh sample just consists of the P and Q branches of gaseous CO. We may conclude accordingly that, at 298 K, the fresh Au/CZ-DPU catalyst does not adsorb any significant amount of CO. This observation is in good agreement with the very low initial conversion deduced from the light off curve recorded for the fresh sample (heating step of the cycle), Fig. 1a. Therefore, the spectrum in Fig. 6a may be used as a reference accounting for the contribution of gaseous CO to the spectra (b) and (c) reported in Part A of Fig. 6. If so, the (b-a) and (c-a) difference spectra shown on part B of Fig. 6 would actually correspond to the adsorbed CO species. In the case of the (b-a) spectrum, that recorded on the catalyst resulting from the activation cycle under reaction conditions, bands at 2235, 2166, and 2110 cm^{-1} are observed, along with signals at ca. 2,350 cm^{-1} attributable to gaseous CO_2 (not shown). In contrast with this, the v-CO region of spectrum (c-a) is much simpler, it consisting of a single feature at 2,115 cm^{-1}.

The band at approximately 2,110–2,115 cm^{-1} is typically assigned to the stretching mode of CO, $v(CO)$, linearly chemisorbed on metallic gold sites, Au(0) [34–36], whereas those occurring in the range 2,150–2,175 cm^{-1} have been interpreted as due to CO bonded to cationic forms of gold [37, 38]. Accordingly, the band at 2,166 cm^{-1} in the spectrum (b-a), can be assigned to CO adsorbed on positively charged gold. Some contribution to this band of CO adsorbed on cations of the support cannot be excluded [29, 30]; however, the very weak nature of this adsorption, the low CO partial pressure (7.6 Torr) used in
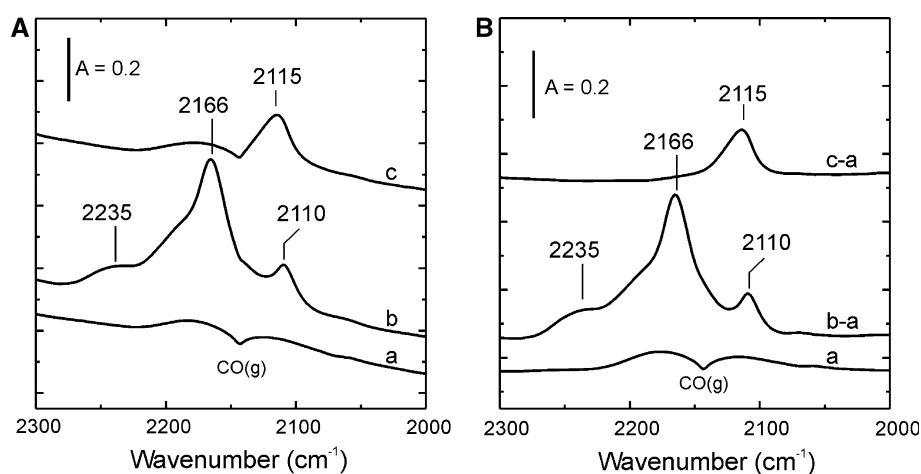

Fig. 6 FTIRS (v-CO band) study of the activation of the fresh Au/CZ-DPU catalyst sample under reaction conditions. **a** Spectra recorded after 15 min contact of the fresh sample with the reaction mixture, at 298 K (*a*); after completing a catalytic cycle in which the temperature was varied in a stepwise manner from 298 to 418 K and back again to 298 K, under the reaction mixture (*b*); and after contacting for 15 min, at 298 K, the Au/CZ-DPU-OE523 catalyst with the reaction mixture (*c*). **b** Difference spectra resulting from (*b-a*) and (*c-a*) subtractions

our experiment, and the small absorption coefficient for this band [29], make unlikely this contribution to be significant.

The assignment of the band at 2,230 cm^{-1} observed in the spectrum (b-a) of Fig. 6, remains uncertain. Some earlier studies from the literature [39, 40] suggest that it could be due to CO-Au^{3+} species.

The analysis of Fig. 6 allows us to draw a number of remarkable conclusions. The heating/cooling cycle under reaction conditions substantially modifies the nature of the supported gold phase. Initially inactive against CO adsorption, the catalytic assay induces the formation of both oxidized and metallic species which are able to chemisorb CO. This change would allow us to explain the strong activation effect induced on the fresh Au/CZ-DPU sample by the catalytic cycle, Fig. 1. Likewise, our FTIR study shows that this activated state is substantially different from that resulting from the application to the fresh catalyst the OE523 routine, which in turn would explain their different activity, much higher in the latter case. These observations, lend some further support to the proposal already advanced in this work in the sense that the metallic gold nano-particles play a key role in determining the activity for CO oxidation of our Au/CZ catalyst.

3.4 Electron Microscopy (HRTEM and HAADF-STEM) Characterization Studies

As shown in a number of recent studies [29, 41], the combination of HRTEM and HAADF-STEM techniques may provide with us rather detailed information about metal nano-particle size distributions in catalysts consisting of gold dispersed on ceria-zirconia mixed oxide supports. Because of the instability of the fresh Au/CZ-DPU sample under the electron beam, in the present case, the electron microscopy studies could only be performed on the Au/CZ-DPU-OE523. Figure 7 shows the corresponding Au nano-particle size distribution as determined from the analysis of both HRTEM and HAADF-STEM images. In accordance with Fig. 7, the distribution is rather narrow with most of the Au nano-particle ranging from 0.5 to 3.5 nm in diameter. By applying the approach developed by us [29] to this experimental size distribution, a metal dispersion (D = 100 Au$_S$/Au$_T$) of 47%, and a mean size for the Au nano-particle of 1.8 nm were determined.

In accordance with the Au 4f/Zr 3d intensity ratio data reported in Table 1 for the initial fresh Au/CZ-DPU sample, 0.16, and in Table 2 for Au/CZ-DPU-OE523, 0.09, the dispersion in the gold-containing phase in the fresh sample is significantly higher than that determined for the Au/CZ-DPU-OE523 catalyst. The actual chemical constitution of the supported gold phase rather than its dispersion has to be invoked in order to explain the much higher CO oxidation
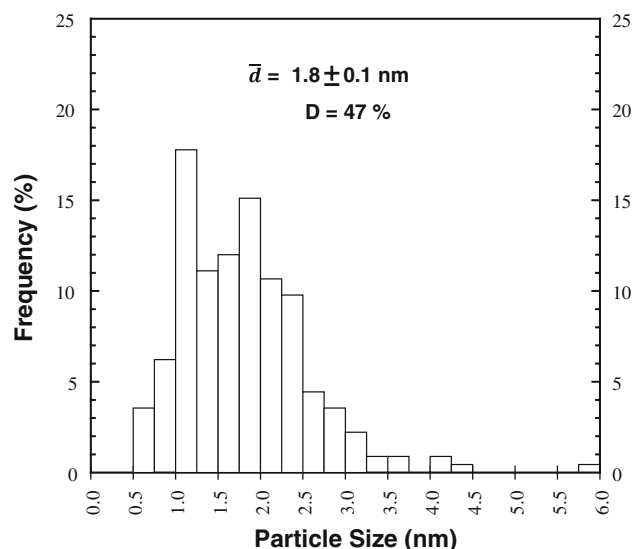

Fig. 7 Metal nano-particle size distribution for Au/CZ-DPU-OE523 as determined from the analysis of HRTEM and HAAD-STEM images. The corresponding metal dispersion (D = 100 Au$_S$/Au$_T$) and mean Au nano-particle size data were determined by applying the approach developed by us [29] to the reported experimental size distribution. Number of analyzed Au nano-particles: 226

activity of the OE523 sample. This observation is also consistent with the FTIR data, in accordance with which, the gold phase deposited on the ceria-zirconia support by application of the DPU method does not show any activity against CO adsorption.

3.5 Concluding Remarks

To summarize, in this work, we have investigated the catalytic activity of two Au/CZ samples mainly differing in the nature of the precipitating agent, urea or sodium carbonate, used in the deposition–precipitation routine applied in their synthesis. As revealed by catalytic assays carried out on the as-prepared (fresh) samples, the use of urea or carbonate as precipitating agent has a dramatic influence on their activity. As shown in Fig. 1, a strong activation of the fresh Au/CZ-DPU sample takes place during the catalytic cycle, the CO conversion being much higher during the final cooling step. This observation is further confirmed by application to this catalyst of a thermal oxidizing pretreatment at 523 K, the activity of the resulting sample, Au/CZ-DPU-OE523, being much higher than that deduced from the assay of the corresponding fresh catalyst. The effect is particularly noticeable if we take into account that, in accordance with the Au 4f/Zr 3d intensity ratio data reported in Tables 1 and 2, the OE523 activation treatment induces a significant sintering of the supported gold phase. We may conclude accordingly that, when used urea as precipitating agent, the application of an activation

protocol following the deposition–precipitation step is mandatory in order to reach the highest activity of the Au/CZ-DPU catalyst. This behavior strongly contrasts with that exhibited by the fresh Au/CZ-DPC sample used herein as a reference system. In the latter case, data reported in Fig. 2 clearly show that no oxidizing pretreatment is required to reach the highest activity level. The difference between DPU and DPC samples is particularly worth of noting if we take into account the chemical analogies that can be established between aqueous solutions of urea and Na_2CO_3, containing in both cases carbonate species at a pH close to 8. The presence in the DPU solution of an excess of urea-related species should therefore make the difference. This is confirmed by the XPS study summarized in Table 1, in accordance with which significant amounts of N and C are incorporated into the gold precursor generated by the DPU method. The presence or not of urea-related species may thus represent a key feature justifying the different chemical behavior of the fresh DPU and DPC catalysts. These observations are in fairly good qualitative agreement with some earlier studies on Au/TiO$_2$ catalysts in which the behavior of samples prepared respectively by DP-urea and DP-NaOH methods was compared [32, 33]. In effect, the chemical nature and thermal evolution of the gold-containing phase was found to depend on the precipitating agent, the behavior exhibited by their urea-containing gold precursor showing remarkable resemblances with ours.

Finally, our study has also provided with us valuable information about the thermal stability of the Au/CZ-DPU-OE523, i.e. the pre-treated sample, under reaction conditions. As deduced from the reported results, catalyst deactivation effects, though moderate, start to be noticeable upon ageing at 623 K, they becoming increasingly more important as the temperature of treatment is further increased. The XPS data reported in Table 2 suggest metal sintering effects as the most likely origin of the observed deactivation phenomena.

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