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Low-temperature water-gas shift reaction over Au/CeO_2 catalysts

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Abstract

A high and stable activity for gold/ceria catalyts has been established for the water-gas shift reaction. The relationship between gold loading and catalytic activity was studied over a wide temperature range. The influence of space velocity and H_2O/CO ratio at different temperatures on the catalytic activity and stability was also investigated. The reduction/oxidation processes of ceria in the presence of gold was readily followed by TPR measurements. It was shown that ceria plays the role of an active support capable of producing oxygen. The high and stable activity of gold/ceria catalysts could arise from the high and stable gold dispersion present during the catalytic operation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Water-gas shift; Gold; Ceria

1. Introduction

Recently, a renewed interest in the water-gas shift (WGS) reaction has occurred, arising from the need for pure hydrogen production in conjunction with the development of fuel-cell power systems. Moreover, the WGS reaction is also one of the key steps involved in automobile exhaust processes, since the hydrogen produced is a very effective reductant for NO_x removal. Studies on ceria-supported precious metals (Me = Pd, Pt, Rh) have revealed these materials as effective catalyst for CO oxidation and the WGS reaction [1]. A number of gold-based catalysts on different supports have been successfully used in these reactions at low temperatures [2–5].

Ceria is a crucial component of emission control catalysts, mainly on account of its role in oxygen storage. A correlation between the oxygen storage capacity of commercial three-way catalysts and their catalytic activity has been proposed [6]. The facile Ce^{4+}/Ce^{3+} redox reaction is believed to be the driving force leading to this behavior. The oxygen produced via the redox process $2CeO_2 \leftrightarrow Ce_2O_3 + 1/2O_2$ can be utilized under reduction conditions. However, the role of ceria as a support for noble metal-based catalyst is not only related to its high oxygen storage capacity but also to the improved dispersion of the noble metal and the promotion of the WGS reaction [7,8].

In this paper, new results on the activity of Au/CeO_2 catalysts in the WGS reaction are reported. The prerequisite for the synthesis of a highly active gold supported catalyst is not only to obtain a high dispersion of gold particles but also to choose an appropriate support for the reactions. The activity and especially the stability of the gold catalysts depend on both the state and structure of the support and the specific interaction between gold and the support.

The present study focuses on determining the role of ceria as a support for the preparation of highly active

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and stable gold catalysts for the WGS reaction. The effects of the gold content, space velocity and vapor/CO ratio were studied. The reduction behavior of the samples was determined in relation to the gold loading and the reoxidation at room or operating temperature.

2. Experimental

2.1. Catalyst preparation

A series of three samples were prepared with different gold loadings, i.e. 1, 3 and 5 wt.% gold content, denoted as $1Au/CeO_2$, $3Au/CeO_2$ and $5Au/CeO_2$. The samples were synthesized in a "Contalab" laboratory reactor enabling careful control of all the variables, i.e. pH, temperature, stirrer speed, reactant feed flow, etc. The deposition–precipitation method was used. The gold hydroxide was deposited onto suspended ceria in water by ultrasound via the chemical reaction between $HAuCl_4 \cdot 3H_2O$ and Na_2CO_3 in aqueous solution. "Analytical grade" chemicals were used throughout.

2.2. Sample characterization

X-ray diffraction patterns were obtained on a Siemens D-500 X-ray diffractometer using Cu Kα ($\lambda = 1.54050$ Å) with a secondary graphite monochromator. HRTEM analysis was performed using a Philips CM 20 (200 kV) microscope. TPR measurements were carried out using the apparatus described in detail in Ref. [9], under the following conditions: gas mixture—hydrogen–argon (10% H_2); flow rate—24 ml min^{-1}; temperature rise—15 °C min^{-1}; sample amount—0.100 g. After the first temperature programed reduction (TPR) peak was recorded for the gold-containing samples, additional experiments including reoxidation with purified air were performed. The reoxidation was performed at two different temperatures. In the first case, the H_2–Ar flow was switched over to air flow at 200 °C and the sample was kept at this temperature for 15 min. After cooling to room temperature, the TPR measurement was made. In the second case, after the first TPR peak was registered, the sample was cooled to room temperature in an inert atmosphere and reoxidized in air for 15 min at this temperature, after which the TPR spectrum was recorded.

2.3. Catalytic activity measurements

The catalytic activity of the samples towards the WGS reaction, expressed as the degree of CO conversion, was evaluated over a wide temperature range (140–350 °C). The activity was measured in a flow reactor at atmospheric pressure. A gas mixture of initial composition 4.498 vol.% CO in argon was used. The following experimental conditions were applied: catalyst bed volume—0.5 cm^3 (0.63–0.80 mm sieve fraction), space velocity of the dry gas—4000 h^{-1}, partial pressure of water vapor—31.1 kPa. The CO and CO_2 contents at the reactor outlet were determined on an "Infralit" gas analyzer. Before the catalytic tests, preliminary reduction of the samples was conducted at 100 °C for 1 h in a hydrogen–argon mixture (1% H_2). The stability of the catalysts was studied under different space velocities (4000, 8000 and 12,000 h^{-1}) and different water vapor partial pressures (10–50 kPa).

3. Results and discussion

3.1. Effect of gold loading on the catalytic activity

The catalytic activity of the samples with different gold loading, measured in the temperature range 140–350 °C is presented in Fig. 1. As can be seen, the

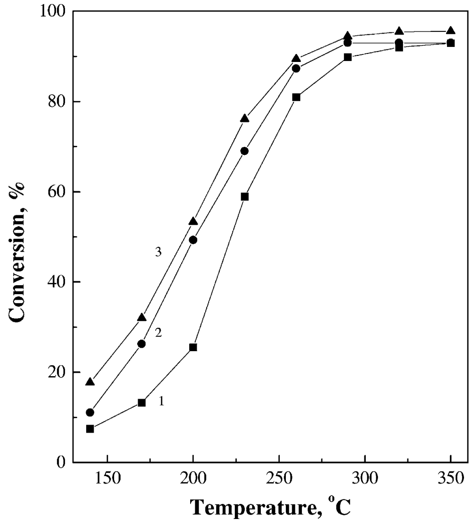

Fig. 1. Effect of gold loading on the WGS activity: (1) $1Au/CeO_2$; (2) $3Au/CeO_2$; (3) $5Au/CeO_2$.

sample with the highest gold loading ($5Au/CeO_2$) exhibits the highest CO conversion. It should be noted, however, that the activity of the $3Au/CeO_2$ sample is comparable with that of $5Au/CeO_2$. The activity of pure ceria in the WGS reaction becomes significant only at temperatures above 300 °C [1]. The catalytic activity of the samples in the WGS reaction was tested over a course of 3 weeks. During this long period, very high and stable activity was recorded. It would be of interest to compare the observed catalytic activity in terms of the physical and structural properties of the samples. The data obtained from the catalytic activity tests with different contact times and different H_2O/CO ratios at different temperatures will be shown below and the results will be related to the structure and properties of the catalysts.

3.2. Characterization

3.2.1. Gold dispersion, state and structure of the support

The X-ray analysis of the fresh samples shows the diffraction lines of CeO_2 typical for the cubic crystal structure of fluorite-type oxides. After the catalytic operation, the X-ray lines are noticeably sharpened, and this is indicative of crystallization processes taking place during the catalytic work.

The average size of the gold particles was estimated by TEM techniques. As an illustration Fig. 2 presents the TEM pictures of the fresh and spent $3Au/CeO_2$ sample. The spherical gold particles are homogeneously distributed on the ceria surface. The TEM results indicate an average size of the gold particles in fresh $3Au/CeO_2$ of about 5.5 nm and in fresh $5Au/CeO_2$ 4.0 nm. The average size of the gold particles in spent $3Au/CeO_2$ is about 4.5 nm and in spent $5Au/CeO_2$ 3.5 nm. The lower average size of the gold particles after operation was rather unexpected because gold particles usually agglomerate into bigger ones after catalytic work, and this is usually considered to be the main reason for the deactivation of gold catalysts. In the case of gold–ceria samples on the contrary, the size of the gold particles was not only preserved after operation, but even tended to decrease. This is the first time that this kind of behavior has been observed for gold on inorganic supports. This effect could be connected with the strong interaction between the gold particles and the ceria surface. The improved catalytic performance of these systems can be related to the high and stable dispersion of gold on ceria.

3.2.2. TPR

Ceria is considered to be an oxygen storage component in ceria-based catalysts, so by definition, it should be capable of being readily reduced and reoxidized. TPR was used to study the influence of gold on ceria reducibility.

Two reduction peaks are registered in the TPR spectra of pure ceria. The low-temperature peak at about 500 °C is assigned to the reduction of surface oxygen species. The size of this peak appears to be dependent on the method of preparation and on the amount of surface oxygen anions attached to surface Ce^{4+} ions [7]. The high-temperature peak (>800 °C) corresponds to the reduction of bulk oxygen and the formation of lower oxides of cerium. For all the samples examined, these two characteristic peaks were observed, the first one being shifted significantly to the lower temperatures in the presence of gold. Such enhanced reduction behavior has been observed in the case of other noble metals supported on ceria [7,10,11]. The TPR profiles of gold-promoted ceria in the low-temperature range are shown in Fig. 3A. The high-temperature range is not shown in Fig. 3 because: (i) the low-temperature WGS reaction is of predominant interest in this work and (ii) the presence of gold has no effect the reduction of bulk ceria. It can be seen that the first reduction peak of the gold-promoted ceria consists of two overlapping peaks. We assume that the hydrogen consumption is due to two processes, one of which could be connected with the reduction of the oxygen species on the fine gold particles and the second one with the surface ceria reduction. The differences in peak shape and position depending on the gold content of the samples are clearly seen. For the sample with the highest gold content ($5Au/CeO_2$), there is a peak with a maximum at 110 °C and a shoulder at about 135 °C. For the sample with the lowest concentration of gold ($1Au/CeO_2$), the peak is asymmetric with a maximum at 135 °C. For the $3Au/CeO_2$ sample, a broad peak is recorded with T_{max} at about 120 °C. Taking into account the different amounts of gold in the samples, one may assume that the low-temperature part of the peaks is connected with the oxygen species on the gold particles. The high-temperature part is due to the reduction

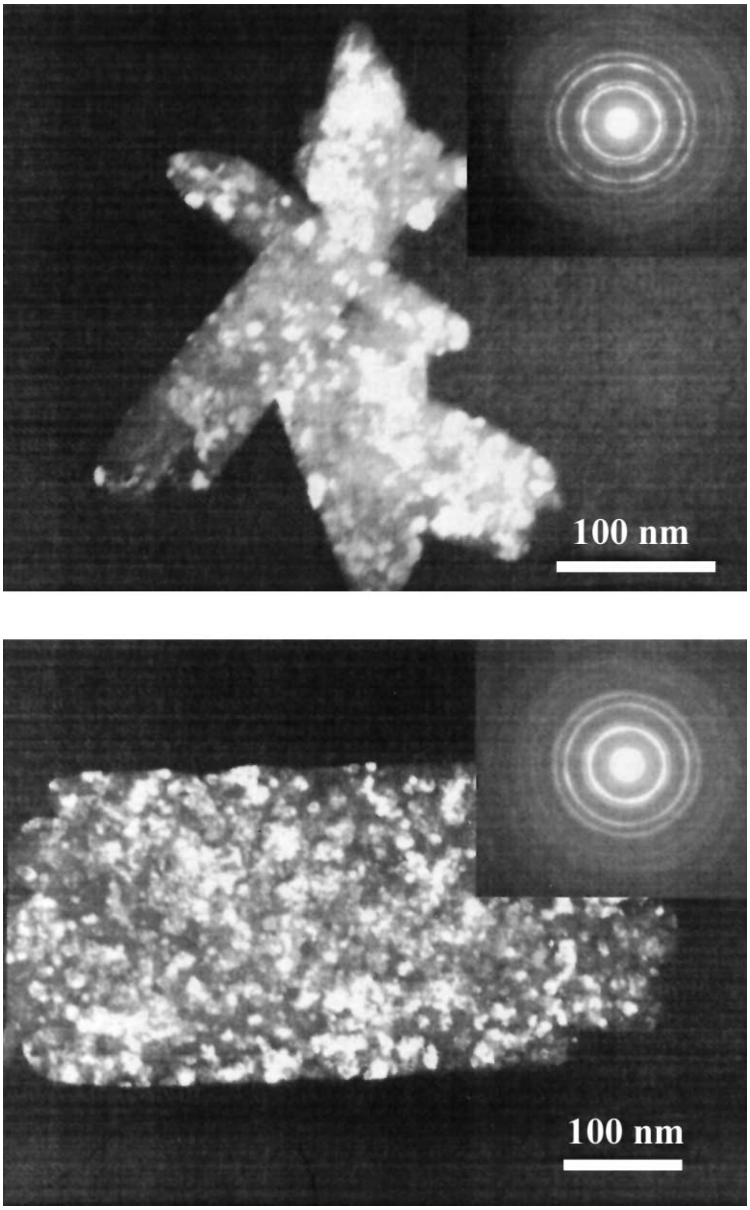

Fig. 2. TEM picture of the 3Au/CeO_2 sample: fresh—top and spent—down.

of the surface ceria. In our preliminary studies with gold-promoted titania and zirconia, a peak also appeared at temperatures around 100 °C. This peak was assigned to the reduction of oxygen species on the fine gold particles and eventually to the reduction of the support surface on the border with gold [12].

In order to explain the high activity of this catalyst system in the WGS reaction, it was necessary to throw light on the ease of performing reduction/oxidation processes on the catalyst surface, and some additional experiments were consequently carried out, as follows. After the first reduction peak, the sample was

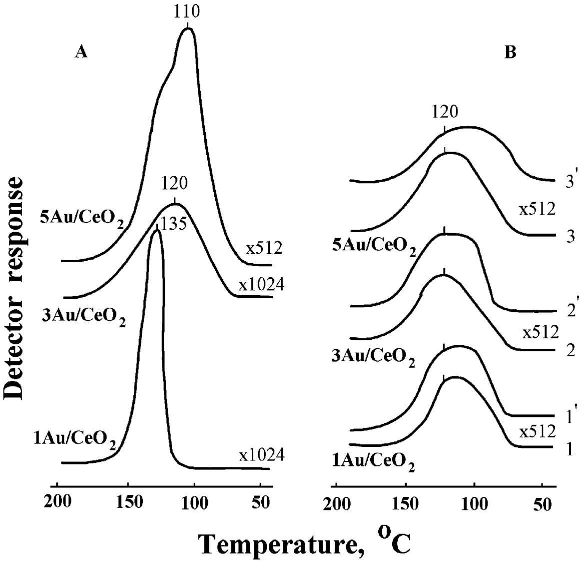

Fig. 3. TPR spectra: (A) fresh samples; (B) reoxidation after first reduction peak: at room temperature (1, 2 and 3 curves) and at 200 °C (1′, 2′ and 3′).

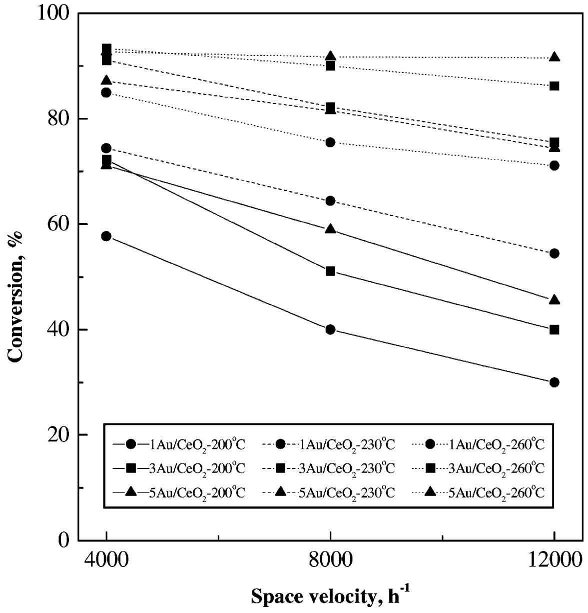

Fig. 4. Effect of contact time on the CO conversion at different temperatures: 200 °C (—); 230 °C (- - -); 260 °C (· · ·).

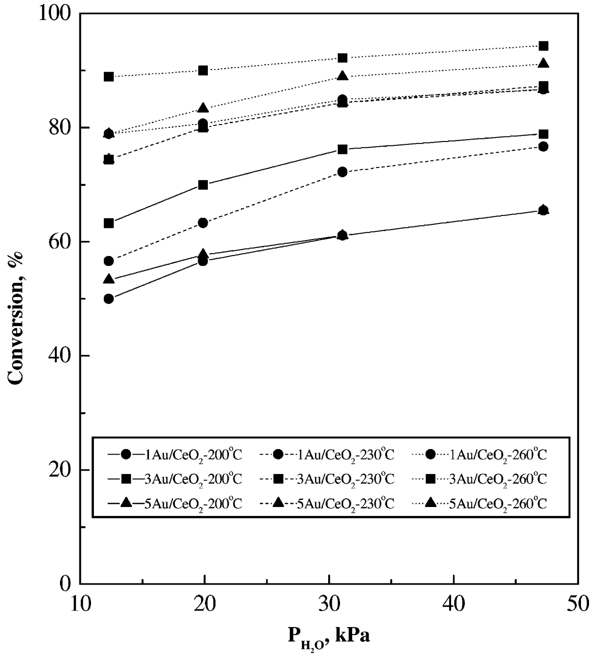

Fig. 5. Effect of H_2O/CO ratio on the CO conversion at different temperatures: 200 °C (—); 230 °C (- - -); 260 °C (· · ·).

cooled to room temperature (RT) in pure argon, then reoxidized in air at RT. The TPR spectra obtained after this treatment are shown in Fig. 3B (1, 2 and 3). Reoxidation in air at 200 °C was also done and the TPR spectra are presented in Fig. 3B, denoted with 1′, 2′ and 3′. All TPR peaks are broad and composite and their position depends on the gold content. It should be noted that in both the cases of reoxidation, a high oxygen storage capacity is manifested. There are literature data about the reduction/oxidation capacity of noble metals supported on ceria where only high-temperature reoxidation has been carried out [7]. The results obtained in this study give evidence for reduction/oxidation processes taking place at significantly lower temperatures, even at RT in the presence of gold. In our opinion, this could be connected with the high activity of the gold/ceria catalytic systems in the low-temperature WGS reaction.

3.3. Effect of contact time on the catalytic activity

Fig. 4 shows the effect of the contact time on the degree of CO conversion at three different temperatures (200, 230 and 260 °C) over the studied gold–ceria catalysts. The tests were performed with space velocities of 4000, 8000 and 12,000 h^{-1}. The sample with the lowest gold amount (1Au/CeO_2) demonstrates a noticeable decrease in CO conversion when the space velocity was increased. The effect of contact time on the degree of CO conversion for 3Au/CeO_2 and 5Au/CeO_2 samples is negligible, especially at higher temperatures.

3.4. Effect of H_2O/CO ratio

Fig. 5 presents the data for the catalytic activity of the samples at four different H_2O/CO ratios at the above chosen temperatures. As can be seen, the catalytic activity slightly increases as a function of the H_2O/CO ratio. Comparing the data obtained for the samples 3Au/CeO_2 and 5Au/CeO_2, it was unexpected

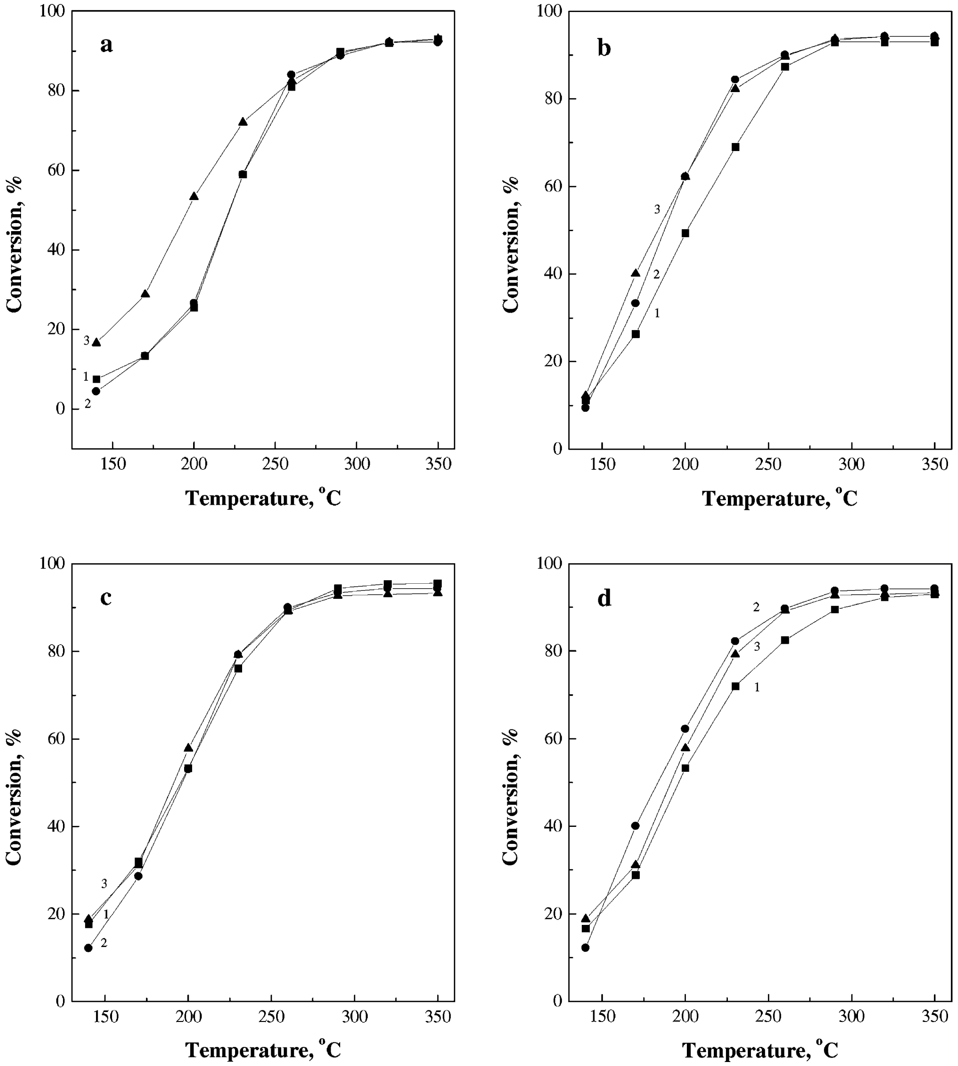

Fig. 6. Catalysts stability test: (a) 1Au/CeO_2 sample: (1) after reduction pretreatment; (2) after different space velocity test; (3) after different H_2O/CO ratio test; (b) the same for 3Au/CeO_2 sample; and (c) for 5Au/CeO_2 sample, respectively; (d) temperature dependence of the degree of CO conversion after catalytic stability test for the studied catalysts: (1) 1Au/CeO_2; (2) 3Au/CeO_2; (3) 5Au/CeO_2.

that the sample with lower gold loading exhibits even higher CO conversion than the sample with higher gold content.

3.5. Catalyst stability

Fig. 6 illustrates the temperature dependence of the CO conversion over the samples studied after different treatments. Fig. 6a shows the catalytic activity of the sample 1Au/CeO_2 after reduction—curve 1; after the space velocity tests—curve 2 and after the H_2O/CO ratio tests—curve 3. Fig. 6b and c correspond to the samples 3Au/CeO_2 and 5Au/CeO_2, respectively. The 5Au/CeO_2 sample manifests stable operation after the different treatments. 1Au/CeO_2 shows constant activity after the space velocity tests and even higher activity after the H_2O/CO ratio tests. Most interesting is the behavior of 3Au/CeO_2. Not only after the H_2O/CO ratio tests but also after the space velocity tests, this sample exhibits a higher activity compared with the initial one, just after the reduction pretreatment of the sample (curve 1). In Fig. 6d the dependence of CO conversion versus temperature over all the samples studied after 3 weeks of catalytic work is presented, including the above described treatments (space velocity and H_2O/CO ratio tests). It should be stressed that the activity of the 3Au/CeO_2 sample is higher than that of 5Au/CeO_2 (cf. Fig. 1) and it is stable over a long period of operation.

4. Conclusions

The results obtained can be summarized as follows:

- A high and stable activity for gold–ceria catalytic systems over a wide temperature range and at different space velocities and H_2O/CO ratios was established. The 3Au/CeO_2 and 5Au/CeO_2 samples manifest comparable activity and stability in the WGS reaction which are higher than those of the 1Au/CeO_2 sample. The 3Au/CeO_2 sample exhibits the highest stability. After 3 weeks of operation, the final activity of this sample exceeds the initial one, remaining stable during the whole test period.
- The high and stable activity of the gold/ceria catalysts could be related to the high stability of the gold dispersion. Moreover, a tendency for the gold particles to decrease in size under the reaction conditions was observed.
- The TPR results indicate that the reduction/oxidation processes take place readily in the presence of gold. Evidently, the sample 3Au/CeO_2 has the optimal ratio between surface gold active centers and free ceria surface being capable to produce oxygen.

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