Investigation on gold dispersion of Au/ZrO$_2$ catalysts and activity in the low-temperature WGS reaction

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Gold over zirconia and sulfated zirconia catalysts were tested in the water–gas shift (WGS) reaction at temperatures between 423 and 453 K. Samples were characterized by N$_2$ adsorption analysis, XRD, TPO, TG-DTA and pulse-flow CO chemisorption. A very good linear relationship between catalytic activity and dispersion determinated by chemisorption has been evidenced. Sulfated catalysts showed higher activities than samples over plain zirconia. SO$_4^=$ do not behave as promoters of the gold active phase, but they yield a larger specific surface area of the zirconia, thus favouring a better dispersion of gold nanoparticles on the support. CO amount at the reactor outlet has been checked and will be discussed.

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1. Introduction

The conversion of hydrocarbons through hydrodesulfurization, steam reforming, water–gas shift (WGS) and preferential oxidation processes is the most common way to produce clean hydrogen for different applications. Aim of the water–gas shift reaction:

$$CO + H_2O = CO_2 + H_2, \quad \Delta H = -41\,kJ/mol, \quad \Delta G = -28.6\,kJ/mol$$
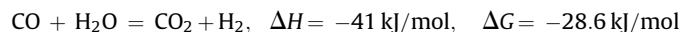
is to reduce the CO concentration coming from the steam reforming reactor, producing at the same time hydrogen, thus improving the global efficiency of the process. Commercial reaction usually proceeds in two different steps with two types of catalyst: an high temperature (HT) stage over an iron oxide promoted with chromium oxide catalyst, and a low temperature (LT) stage, on a catalyst composed of copper, zinc oxide and alumina [1]. Recently there has been a renewed interest in WGSR as a key step in the conversion of fuel to hydrogen, to be used in proton exchange membrane fuel cells to generate electricity. The development of a new generation of catalysts, showing high activity towards the conversion of CO at low temperatures, easy to activate and with good stability to air and liquid water, is highly desirable, since commercially available LT-WGS catalysts do not meet these requirements [2].

By now it is ascertained that gold becomes a catalyst when supported on a metal oxide, in the form of nanoparticles strongly bound to the oxide surface [3]. Gold catalysts show high activity in some important industrial reactions, such as CO oxidation [4], low-temperature WGS [5], hydrogen peroxide production from H$_2$ and O$_2$ [6], selective epoxidation [7]. In particular the catalysis of the WGS reaction by gold nanoparticles supported over metal oxides has recently been the subject of numerous investigations [8,9]. It has been shown that the nature and the structure of the support and the preparation conditions strongly influence the catalytic activity and selectivity of gold-based samples. Gold catalysts supported on Fe$_2$O$_3$ [10], TiO$_2$ [11], ZnO [12], CeO$_2$ [13] and ThO$_2$ [12] showed good catalytic activity in the water–gas shift reaction. Recently gold samples supported on mesoporous zirconia have also been studied [14–16]. The opportunity of use ZrO$_2$ as support is due to its intrinsic characteristics: chemical and surface features of zirconia, as surface acidity, redox properties, porosity and surface area, can be adjusted by choosing different precursors and synthesis conditions and by dopants addition. In particular sulfates increase surface acidity, retard crystallization and enhance the surface area and the pore size distribution [17].

The goal of the present work is to investigate the possible correlation between gold dispersion and catalytic activity in the LT-WGSR. Besides the effects of sulfates addition on the support and its effect on the activity and the properties of gold on zirconia catalysts for the low-temperature water–gas shift reaction have been studied. Other aspects, such as the effect of gold content, the

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use of different bases for the deposition-precipitation procedure (dp) (Na_2CO_3 and NaOH), and the applicability of the newly prepared samples in the fuel processing systems for fuel cells have been examined too.

2. Experimental

2.1. Catalyst preparation

Zirconia was prepared by a two-step synthesis technique. $Zr(OH)_4$ was prepared from $ZrOCl_2 \cdot 8H_2O$ by precipitation in water at constant pH (pH 8.6) by continuous addition of aqueous ammonia 5 M, aged under reflux conditions for 20 h at 363 K, washed free from chloride ($AgNO_3$ test) and dried at 383 K overnight. Part of the hydroxide was then sulfated with $(NH_4)_2SO_4$ (Merck) by incipient wetness impregnation, in order to obtain a 2 wt% amount of sulfates on the final support. Sulfated (ZS) and non-sulfated zirconium hydroxides (Z) were then calcined in air (30 mL/min STP), by slowly heating up from room temperature to 923 K over 7 h, and keeping this temperature for 6 h. Various gold amounts (0.5, 0.8 and 1 wt%) were added by deposition-precipitation at pH 8.6: the oxide support was suspended in an aqueous solution of $HAuCl_4 \cdot 3H_2O$, then the pH was controlled by the addition of either Na_2CO_3 (1 M) (samples denoted with a final c) or NaOH (0.5 M) (samples denoted with a final n) for 3 h. After filtrations the samples were finally dried at 308 K overnight.

2.2. Methods

Surface area and pore size distributions were obtained from N_2 adsorption/desorption isotherm at 77 K, using a Micromeritics ASAP 2000 Analyser. Non-sulfated and sulfated zirconia supports (400 mg) were pre-treated at 570 K for 2 h under vacuum, while finished catalysts (300 mg) were pre-treated at room temperature for 6 h under vacuum. Surface area was calculated from the N_2 adsorption isotherm by the BET equation [18], and pore size distribution was determined by the BJH method also applied on the adsorption branch [19]. Total pore volume was taken at $p/p_0 = 0.99$.

Sulfate amount was determined by ion chromatography (IEC). Samples were dissolved following a previously reported procedure [20]. Sulfate concentration was calculated as the average of two independent analyses, each including two chromatographic determinations.

Gold amount was determined by atomic adsorption spectroscopy, after microwave disgregation of the samples (100 mg).

X-ray powder diffraction (XRD) patterns were measured by a Bruker D8 Advance diffractometer equipped with a Si(Li) solid state detector (SOL-X) and a sealed tube providing Cu Kα radiation. Measuring conditions were 40 kV × 40 mA. Apertures of divergence, receiving and detector slits were 1°, 1°, and 0.3° respectively. Data scans were performed in the 2θ ranges 15–55° and 35–40° with 0.02° stepsize and counting times of 3 and 10 s/step, respectively.

CO pulse chemisorption measurements were performed at 157 K in a home-made equipment. Before the analysis the following pre-treatment was applied: the sample (200 mg) was reduced in H_2 flow (40 mL/min) at 423 K for 60 min, cooled in H_2 to ambient temperature, purged in He flow and finally hydrated at ambient temperature. The hydration treatment was performed by contacting the sample with a He flow (10 mL/min) saturated with a proper amount of water. The sample was then cooled in He flow to the temperature chosen for CO chemisorption (157 K) [21].

Thermal analyses (TG/DTA) were performed on a NETZSCH STA 409 PC/PG instrument in flowing air (20 mL/min) with temperature rate set at 5 K/min in the 300–1300 K temperature range.

TPO measurements were carried out to determine the substances released during the TG/DTA thermal treatment, in a home-made equipment: samples (100 mg) were heated with a temperature ret of 10 K/min from 300 to 1300 K in air (40 mL/min). The effluent gases were analysed by a Genesys 422 quadrupole mass analyzer (QMS). The signals for masses 18, 28, 44, 48 and 64 were recorded.

2.3. Catalytic activity measurement

WGSR was performed in a fixed-bed flow reactor at atmospheric pressure and in the temperature range from 423 to 453 K. The following conditions were applied: space velocity = 9400 h^{-1}; catalyst volume = 0.5 cm^3 (35–50 mesh) diluted to 1.5 cm^3 with quartz sand (Carlo Erba; 35–50 mesh); the feed mixture contained 1.9 vol.% CO, 39.7 vol.% H_2, 9.5 vol.% CO_2, 11.4 vol.% N_2 and 37.5 vol.% H_2O. Gold supported samples were previously subjected to a slow (60 K/h) thermal activation in air (50 mL/min) from room temperature to 453 K, kept at this temperature for 1 h in the same air flow and then cooled in N_2 (50 mL/min). Then the catalysts were heated again (180 K/h) in a 2% hydrogen/nitrogen mixture (50 mL/min) up to 453 K; once this temperature was reached, the gas feed composition was slowly changed to pure hydrogen (50 mL/min) and these conditions were kept for 1 h. Commercial 30% $Cu/ZnO/Al_2O_3$ sample was activated with a careful reducing treatment to avoid copper sintering. A 1.0% H_2 in N_2 mixture was first introduced at room temperature, then the temperature and H_2 concentration were gradually increased to complete Cu reduction. The progress of the reaction was followed by gas-chromatographic analysis of the converted mixture at the reactor outlet.
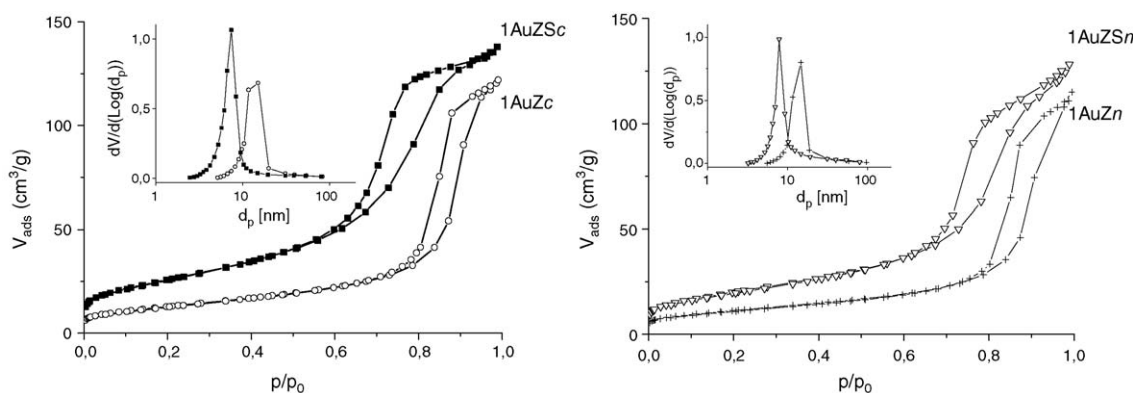

Fig. 1. N_2 physisorption isotherms and BJH pore size distributions of catalysts containing 1 wt% of gold.

Table 1
Surface features of the samples.

Sample	Preparation method	Surface area (m²/g)	Pore volume (cm³/g)	Pore diameter (nm)
1AuZSc	dp with Na₂CO₃	94	0.21	7.2
1AuZc	dp with Na₂CO₃	47	0.19	13.4
1AuZSn	dp with NaOH	74	0.20	8.7
1AZn	dp with NaOH	41	0.18	14.1

3. Results and discussion

3.1. Catalyst characterization

The choice of the materials is very important in this investigation, since a low surface area of the support would not allow a good dispersion of the gold active phase. So N_2 physisorption analyses were carried out in order to determine surface areas and pore size distributions of the samples. As example, physisorption isotherms and pore diameter distributions of catalysts containing 1 wt% of gold are shown in Fig. 1, and the corresponding data are summarized in Table 1. All samples show type IV isotherms with hysteresis loop typical of mesoporous materials. Sulfated zirconia catalysts show higher specific surface area values than the non-sulfated ones; besides the pore size distribution curves of samples over sulfated zirconia are narrower and shifted towards smaller diameters. This result matches literature data: it is well known [22] that the effect of sulfates on zirconium oxide is to increase its surface area, shifting crystallization processes towards higher temperatures during calcination treatment.

Sulfated zirconia support and samples prepared over it were analysed by ion exchange chromatography to determine the amount of sulfate groups. It was found that the $ZrO_2/SO_4^=$ support after calcination contains a 2 wt% of sulfates. On the contrary, as previously reported [16,21], tests of sulfates carried out on the samples after deposition of gold, evidence that no sulfates are present in the final catalysts anymore. This is not unexpected, pointing out that the detachment of sulfate groups occurs during the deposition-precipitation, as a consequence of the basic conditions. In fact the methodology of gold deposition-precipitation on the support is carried out at a basic pH (pH 8.6) for the synthesis with both Na_2CO_3 and NaOH, leading to the disappearance of sulfates from the catalysts. So $SO_4^=$ do not behave as promoters of the gold active phase in the final catalysts, but they only modify structural properties of the support as shown in the surface analyses results. For this reason we refer to catalysts object of this work as Au/ZrO_2 samples.

The results of gold amount determination by atomic adsorption spectroscopy and the relative percentage of gold lost during the deposition-precipitation step are reported in Table 2, since they are a critical parameter in the volumetric CO chemisorption determinations. The analyses reveal that the amount of gold deposited on the catalysts surface is generally lower than the nominal value. In particular for the samples prepared with Na_2CO_3 the average loss of gold is higher than for the samples prepared with NaOH. This result can be explained considering that the pH control during the dp differs using different bases. In fact after dp with Na_2CO_3 the pH value was higher than expected (about 9.0), favouring the detachment of gold anionic species from the negative charged support surface, thus limiting the maximum amount of gold that can be introduced with this technique.

X-ray diffraction patterns for the gold-based samples in the range of 2θ between 32° and 50° are reported in Fig. 2. No significant difference is observed between sulfated and non-sulfated samples, for all the peaks appearing in the diffractograms are related to the monoclinic phase of zirconia. 1AuZc and 1AuZn diffractograms show a better resolution, and this means that the addition of sulfates lead to the formation of a support with a lower degree of crystallization. It is interesting to notice that no peak related to the presence of gold crystallites is observable, suggesting a high dispersion of gold particles on the support surface.

3.2. Kinetic data and chemisorption results

The effects of sulfates addition on the support and its consequences on the properties of gold on zirconia catalysts and activity for the low-temperature water–gas shift reaction have been firstly investigated. In Fig. 3 there are reported conversions obtained with the 1 wt% gold-loaded catalysts. It is evident that the use of a sulfated support led to an enhancement of the catalytic activity for both sets of catalysts. For a better comprehension of this experimental evidence, this results have been compared with those deriving from CO chemisorption analysis (Table 2). It has been found that the CO/Au molar ratio has a similar trend to the 453 K conversion values, and for sample 1AuZSn both these techniques gave the highest value. As stated above, the final catalysts do not contain sulfates anymore. However, their effects are evident in both catalytic activity and gold dispersion. $SO_4^=$ do not behave as promoters of the gold active phase in the final samples, but they yield a larger specific surface area of the zirconia, thus favouring a better dispersion of gold particles on the support surface. This is the obvious conclusion of the positive role of sulfates over zirconia. Nevertheless an active role of sulfates during the deposition-precipitation phase should not be excluded, even if not proved at the moment, and it is currently under investigation. In fact, it would be very interesting to prove an active role of $SO_4^=$ in the delicate phase of gold deposition on the support, and subsequently on Au dispersion and catalytic activity. In theory, $SO_4^=$ groups could have a positive role addressing the deposition of Au nanoparticles to suitable sites, or altering the local pH, but other hypotheses cannot even be excluded.

Besides from Fig. 2 and Table 2 it is important to underline that samples with similar amounts of gold synthesized by the NaOH deposition-precipitation method show higher activities in the water–gas shift reaction. Results of the thermal analyses on 1AuZSc and 1AuZSn are reported in Fig. 4. Both samples shows a mass loss of about 3% between 300 and 400 K, in correspondence to large

Table 2
Gold amounts, CO chemisorption and conversion at 453 K for the catalysts.

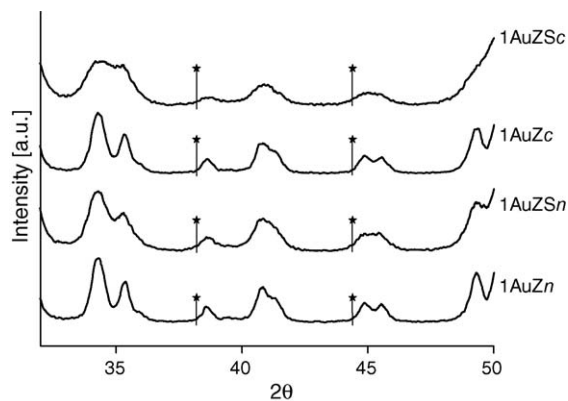| Sample	Preparation method	Au loaded (wt%)	Au found (wt%)	Au loss (rel%)	mol$_{CO}$/mol$_{Au}$	Conversion at 453 K (%)
1AuZc	dp with Na₂CO₃	1.0	0.76	24	0.07	64
1AuZSc	dp with Na₂CO₃	1.0	0.80	20	0.17	86
0.5AuZSc	dp with Na₂CO₃	0.5	0.43	14	0.07	61
1AuZn	dp with NaOH	1.0	0.93	7	0.14	78
1AuZSn	dp with NaOH	1.0	1.00	0	0.19	92
0.8AuZSn	dp with NaOH	0.8	0.71	11	0.18	88
0.5AuZSn	dp with NaOH	0.5	0.47	6	0.13	79
1.5AuTiO₂	(WGC)		1.51		0.03	10

Fig. 2. XRD patterns of catalysts containing 1 wt% of gold. Star symbols (★) indicate the positions where peaks related to gold crystallites should appear.
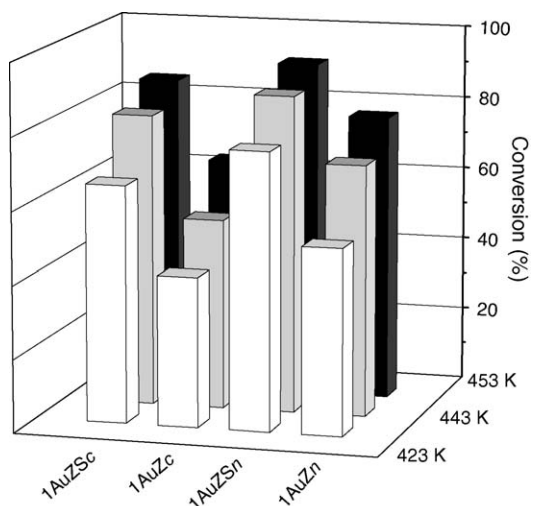

Fig. 3. LT-WGSR conversions obtained over 1 wt% gold–zirconia catalysts at different temperatures.

Fig. 4. TPO, DTA and DTG curves for 1AuZSc and 1AuZSn samples.

endothermic peaks in the DTA curve, due to the release of water from the surface of the catalysts. Another transformation occurs on 1AuZSc at temperatures between 750 and 800 K: a mass loss of 0.4% can be observed, associated with an exothermic peak in the DTA curve, while for 1AuZSn this features were not seen. The results of TPO analysis, reported in the upper section of the same figure, reveal that the mass loss is due to the release of CO_2. This evidence lead to the conclusion that formate or carbonate groups are bound on the support and on the gold particles of 1AuZSc. These species coming from the Na_2CO_3 used for the deposition-precipitation can occupy active sites on gold particles, thus worsening their ability to chemisorb CO molecules and their activities.

Further catalytic tests have been performed on these catalysts to evaluate the stability of the Au/ZrO_2 system in the water–gas shift reaction: CO conversion was measured at the beginning and after 21 h of time on stream at 453 K. As previously reported [16] samples prepared on sulfated zirconia are more stable than the corresponding catalysts on plain zirconia. For example the 1AuZSn catalyst preserves a conversion of 87% after 21 h of reaction at 453 K.

Afterwards we have investigated the effect of gold amount on the catalytic activity, as reported in Fig. 5. It is evident for both samples prepared by $NaCO_3$ and by NaOH that a decrease of the quantity of the active species implies a diminution of the catalytic activity. This effect is easily observable from the results obtained
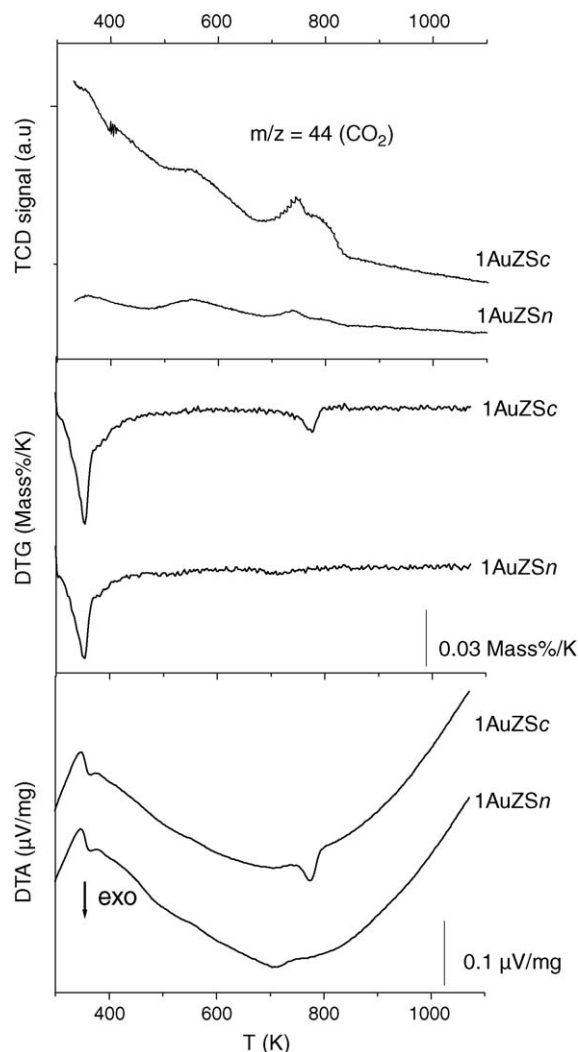
with the catalysts prepared with Na_2CO_3, since using 1AuZSc a conversion of 86% at 453 K was achieved, while with 0.5AuZSc it got only a 61% conversion. A similar trend is visible also for the set of catalysts prepared by NaOH, but with a less drastic decrease of
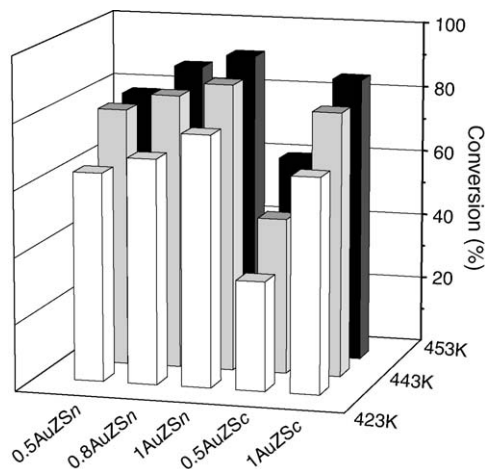

Fig. 5. Water–gas shift reaction conversions obtained over sulfated zirconia catalysts with different loadings of gold at different temperatures.
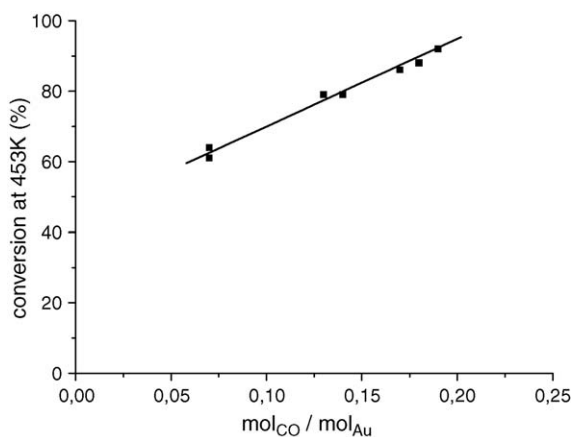
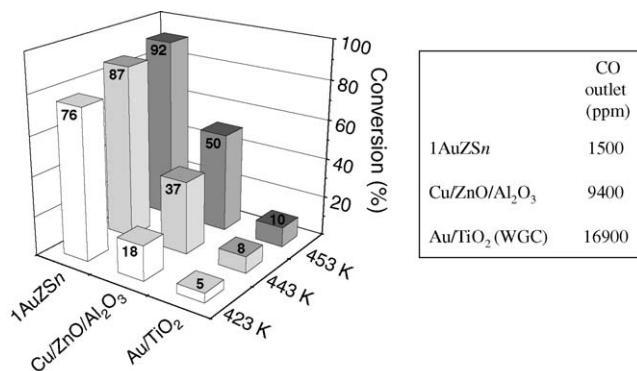Fig. 6. LT-WGSR conversions at 453 K vs. chemisorption results.

Fig. 7. Comparison of catalytic activity in the LT-water–gas shift reaction obtained over various samples at different temperatures and the corresponding CO amount at the exit of reaction (453 K).

the catalytic activity. These results are summarized in Table 2, in comparison with CO chemisorption data. Again it was pointed out that the samples with higher CO/Au molar ratio were the most active in the water–gas shift reaction, thus suggesting a strong correlation between catalytic activity and gold particles dispersion. For sake of clarity, in Fig. 6 LT-WGSR conversions at 453 K vs. chemisorption results have been plotted. It is evident that inside the considered ranges of gold concentration and dispersion there is a linear relationship between the two parameters. We have recently demonstrated that CO chemisorption performed by a pulse flow system at 157 K on mildly reduced and prehydrated samples can be taken as a method for the quantitative determination of the gold sites on Au/ZrO$_2$ catalysts [21]. The close correlation between chemisorption data and catalytic results that we have reported in Fig. 6 indicates that Au dispersion in zirconia LT-WGS catalysts is a very important parameter for their evaluation, even if other factors are certainly relevant to catalytic activity. Chemisorption test is a technique widely diffuse both in academic and industrial laboratories, it is economic and fast and, if performed under proper conditions, it is reproducible and reliable. Therefore it can be concluded that a chemisorption test should be very useful for a preliminary evaluation of these Au/ZrO$_2$ systems used for the LT-WGSR. On the other hand, the effect of gold loading was previously investigated on samples supported over TiO$_2$ and CeO$_2$ [23–25]. The higher activity with respect to Au content of the samples with lower gold loading was related above all to the size of Au particles. In fact, as was observed for other reactions, the WGS activity of gold-based catalysts is closely connected to the size of the gold particles [26]. A recent work on ceria modified mesoporous titania [27], have reported that different gold loadings strongly influence the WGS catalytic activity, showing that, on the analogy of our results, the degree of CO conversion increases with the gold amount.

Finally a comparison between the gold on zirconia sample with the best activity (1AuZSn), a commercially available Cu/ZnO/Al$_2$O$_3$ catalyst and a Au/TiO$_2$ World Gold Council reference has been performed, and results are reported in Fig. 7. Au/ZrO$_2$ catalyst gave the highest conversions in the studied range of temperatures and under the adopted experimental conditions. In the same figure it has also been reported the amount of CO at the exit of the reactor. It is important to underline that for the Au/ZrO$_2$ catalyst such concentration is 1500 ppm, while using copper and gold–titania it is much higher. The attained value is still far from the suggested concentration for application in the fuel processing systems for fuel cells [28]. Nevertheless such very low CO value is a big improvement with respect other catalytic systems analysed under the same experimental conditions.

4. Conclusions

Gold over zirconia and sulfated zirconia catalysts were tested in the low-temperature water–gas shift reaction. Sulfated catalysts showed higher activities than samples on plain zirconia, due to the promotion of zirconia to a higher specific surface area that leads to a better dispersion of gold nanoparticles on the surface. In fact a very good relationship between catalytic activity and chemisorption data has been evidenced. Such close correlation indicates that the chemisorption test is suitable for a preliminary evaluation of these Au/ZrO$_2$ systems used for the LT-WGSR. The possible role of sulfates during the Au deposition-precipitation phase cannot be excluded and it is currently under investigation.

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