Gold nanoparticles as catalysts for low-temperature WGS reaction

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The catalysis of the low temperature water gas shift (WGS) reaction on gold nanoparticles supported on metal oxides has recently been the subject of numerous investigations [1]. In fact there has been a renewed interest in such reaction 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].

This investigation concerns Au over zirconia and sulfated zirconia catalysts for the low-temperature water-gas shift reaction. In particular the effects of sulfates addition on the support, the effects of gold content, the use of different bases for the deposition-precipitation procedure have been examined. The possible correlation between gold dispersion and catalytic activity has been investigated. Moreover the applicability of the newly prepared samples in the fuel processing systems for fuel cells will be discussed.

Zirconia has been prepared from $ZrOCl_2 8H_2O$ by precipitation in water at constant pH (pH = 8.6). Part of the material has been sulfated with $(NH_4)_2SO_4$ by incipient wetness impregnation (2wt%$SO_4^=/ZrO_2$). Various gold amounts (0.5-0.8-1wt%) have been added by deposition-precipitation (dp) either with Na_2CO_3 or NaOH on the supports previously calcined at 923K. All samples have been characterized by N_2 adsorption analysis, TPR, TPO, TG-DTA, sulfur content analysis, XRD, A.A.. Pulse-flow CO chemisorption have been performed at 157K on mildly reduced and prehydrated catalysts with a previously reported procedure [3]. WGSR has been studied in the 453-423K temperature range, with a feed mixture containing 1.9%vol. CO, 39.7% vol. H_2, 9.5% vol. CO_2, 11.4% vol. N_2, 37.5% vol. H_2O (space velocity 9400 h^{-1}). A reference 1.51%Au/TiO_2 catalyst provided by the World Gold Council and an industrial LT-WGS Cu/ZnO/Al_2O_3 sample have also been tested.

N_2 physisorption measurements have shown that sulfated zirconia catalysts possess higher specific surface area then the non-sulfated ones; besides the pore size distribution curves of samples over sulfated zirconia are narrower and shifted towards smaller diameters, according to literature data. By ion exchange chromatography it was found that the $ZrO_2/SO_4^=$ support after calcination contains a 2 %wt of sulfates. On the contrary, 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. 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.
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, favouring the detachment of gold anionic species from the negative charged support surface, thus limiting the maximum amount of gold the can be introduced with this technique.
By X-ray diffraction patterns it is interesting to notice that no peak related to the presence of gold crystallites is observable, suggesting a high dispersion of gold nanoparticles on the support surface.

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. The use of a sulfated support led to an enhancement of the catalytic activity for the two sets of catalysts, both those prepared by $NaCO_3$ and by NaOH. For a better comprehension of this experimental evidence, this results have been compared with those deriving from CO chemisorption analysis. It has been found that the CO/Au molar ratio has a similar trend to the 453 K conversion values. 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. Moreover the possible active role of sulfates during the deposition-precipitation phase will be discussed. In fact the specific positions on zirconia that $SO_4^=$ groups release during the sensitive process of gold deposition-precipitation could, theoretically, direct gold particles to specific sites. Besides it's important to underline that samples with similar amounts of gold synthetized by the NaOH deposition-precipitation method show higher activities in the water gas shift reaction. Results of the thermal analyses and of TPO have revealed that formate or carbonate groups are bound on the support and on the gold particles of catalysts prepared by Na_2CO_3. These species 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 hours of time on stream at 453K. As previously reported [4] samples prepared on sulfated zirconia are more stable than the corresponding catalysts on plain zirconia.

Afterwards we have investigated the effect of gold amount on the catalytic activity. For both samples prepared by $NaCO_3$ and by NaOH a decrease of the quantity of the active species implies a diminution of the activity. The catalytic results have been compared 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. Plotting LT-WGSR conversions at 453K vs chemisorption results it's evident a linear relationship between the two parameters. We have recently demonstrated that CO chemisorption performed by a pulse flow system at 157K 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 [3]. The close correlation between chemisorption data and catalytic results that we have evidenced 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 will be very useful for a preliminary evaluation of these Au/ZrO_2 systems used for the LT-WGSR.

Finally a comparison between the gold on zirconia sample with the best activity, a commercially available $Cu/ZnO/Al_2O_3$ catalyst and a Au/TiO_2 World Gold Council reference has been performed and results are reported in Figure 1.

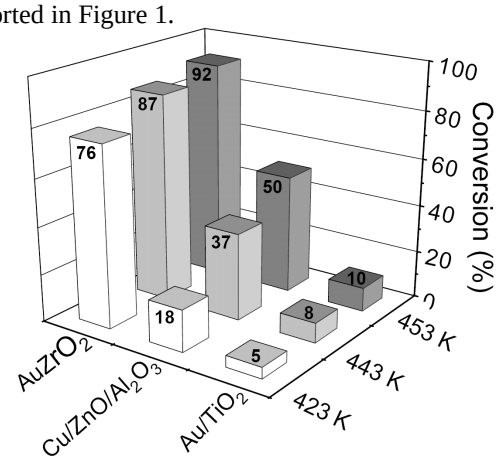

Figure 1 Comparison of catalytic activity in the LT-water-gas shift reaction

Au/ZrO_2 catalyst gave the highest conversions in the studied range of temperatures and under the adopted experimental conditions. In Table 1 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 [2]. Nevertheless such very low CO value is a big improvement with respect other catalytic systems analysed under the same experimental conditions.

	CO outlet (ppm)
Au/ZrO_2	1500
$Cu/ZnO/Al_2O_3$	9400
Au/TiO_2 (WGC)	16900

Table 1

In conclusion, these new gold based catalytic systems have shown promising results for LT-WGSR, in particular for their applicability in the fuel processing systems for fuel cells, that require hydrogen with a low CO concentration. Besides the close correlation between chemisorption data and catalytic results that we have evidenced indicates that the chemisorption test is suitable for a preliminary evaluation of these Au/ZrO_2 systems used for the LT-WGSR.

References

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Biosketch

Michela Signoretto is currently full researcher at the Chemistry Department of the University Cà Foscari of Venice. She has authored over 50 scientific publications on international journals in the field of heterogenous catalysis. Special areas of focus in Signoretto's work include nanomaterials for catalytic and pharmaceutical applications.

Federica Menegazzo graduated in Industrial Chemistry on 1998 at Cà Foscari University. Ph.D. Degree on Chemistry, at the Consortium of the Universities of Ferrara and Venice on 2003. Actually working at the Chemistry Dept., University of Venice as post-doc researcher. Her scientific interests are in the field of Catalysis with a focus on the synthesis of new nanostructured metal catalysts and their use in industrial chemistry.

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