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### Fast determination of metal nanosize for catalytic applications

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Catalysts represent probably the oldest application of nanotechnology. In particular, nanoparticles are typically present in supported metal catalysts, where metal particles having size usually in the range 1-10 nm are deposited on the external surface and/or in the porous texture of inert materials. Metal particle nanosize is a critical factor for several catalytic reactions (the so-called structure-sensitive or demanding reactions), in which the surface density of the active sites depends on such particle nanosize. Therefore metal particle nanosize is a key point in catalysis by supported metals and must be known with as high as possible accuracy.

The method traditionally used by the scientific community for measuring the metal particle size is certainly chemisorption. In this presentation we would like to discuss problems, merits and applicability of the technique. In particular, different examples of our recent experiences, such as Pd supported samples for applications in the PET (polyethyleneterephthalate) manufacturing, and gold based catalysts for hydrogen production and fuel cells, will be presented.

First of all, it must be stressed that the measure of metal nanosize by chemisorption requires that chemisorption stoichiometry and degree of surface coverage are known. Unfortunately both of them are usually arbitrarily assumed (in most cases taken as 1, probably for the sake of simplicity), with consequent errors that can be as high as 100%. In fact what is required for calculating the metal particle size from chemisorption data is the ratio between the amount of surface metal atoms and that of chemisorbed probe molecules in the chosen experimental conditions. This ratio has been called "average chemisorption stoichiometry" ( $S_{av}$ ) and clearly includes the degree of surface coverage.

The idea of our work is to determine the average metal particle nanosize by physical techniques like WAXS, SAXS or TEM, and then to calculate  $S_{av}$  from the experimental chemisorbed volume. The choice of the physical technique to be employed must be carefully done case by case, according to the characteristics of the specific catalysts.

In such a way we have been experimentally determined  $S_{av}$  for Pd/C, Pd/Al<sub>2</sub>O<sub>3</sub>, Pd/SiO<sub>2</sub> catalysts [1-2], using CO as probe molecule, finding an experimental value of chemisorption stoichiometry Pd/CO = 2 for samples supported on various support and with different Pd nanosize. So chemisorption, which is easier, faster and less expensive than TEM, can be proposed as routine test for the determination of Pd nanosize on different

carriers. Supported Pd catalysts find widespread use in both petrochemical and fine chemical industries for many chemical reactions, frequently having selectivity problems. Pd is a very effective metal for catalysing hydrogenation of aromatic aldehydes to alcohols and of the latter ones to hydrocarbons.

For example, the purification of terephthalic acid, one of the most important petrochemical intermediates, is carried out by hydrogenation on a granular 0.5% Pd/C catalyst. The worldwide consumption of this catalyst is now estimated about 1500 tons/year with a turnover of more than 50 millions USD/year. Many problems are usually encountered during catalyst manufacture and use in the industrial plants. The catalyst performances strongly depend on the nature of carbon support and on the manufacturing technology. In particular, we have demonstrated that the catalytic activity is directly proportional to the size of Pd nanoparticles [3]. Poor manufacturing technologies are not unusual, therefore extensive quality controls before catalyst loading in the plant are mandatory. We are able to propose the use of the chemisorption test as a preliminary routine measurement of the catalyst performance.

Chemisorption can be proposed as routine test also for the innovative gold-based samples. Gold supported on oxides or carbon, once considered catalytically inert, is now firmly established as an effective catalyst and the repertoire of reactions that it can catalyze is really wide. Gold catalysts already have done it out of the lab and into commercial use. Bulk gold itself is an inert material and the reasons for small gold particles activity are still a matter of debate. It has been shown that the catalytic activity of gold critically depends on the preparation method, on the support type and on the pretreatment procedure. The most widely diffuse explanation for the variability of the catalytic properties of gold catalysts, is focused on the size of the gold particles and on the amount of low coordinated gold sites. Also for these catalytic systems, well defined and widely accessible procedures of characterization are needed in order to understand the origin of the differences in the activity observed for the samples. The size of gold metallic particles is, in most of the works, determined by TEM. However TEM, when performed accurately, provides a particle size distribution from which a mean size can be derived, but the very small metallic particles (<1 nm) are hardly detectable, so the method is applicable with difficulty for samples with highly dispersed gold. In these cases, other techniques as EXAFS and XANES can be employed, from which

information on the coordination number of gold can be deduced. However, these measurements are not so widely diffuse and cannot be proposed as routine tests. On the other hand, we stress that chemisorption is a widely used technique, especially in industrial laboratories, for measuring metal particle size in supported catalysts, because it is easier, faster and less expensive than TEM. In spite of the great attention that gold-based catalysts have received in the past 15 years, characterization of supported gold by chemisorption methods has not been widely investigated if compared to common applications of H<sub>2</sub>, O<sub>2</sub>, CO and N<sub>2</sub>O chemisorption to characterize other metals. In fact, gold surfaces do not chemisorb many molecules easily. For determining the concentration of gold active sites and comparing different samples, we propose CO chemisorption by a pulse flow technique and Fourier transform infrared measurements of adsorbed CO in well defined and controlled conditions of temperature and pressure.

Au/TiO<sub>2</sub> and Au/Fe<sub>2</sub>O<sub>3</sub> Reference Catalysts provided by the World Gold Council were examined in this study, together with different Au/CeO<sub>2</sub> and Au/ZrO<sub>2</sub> catalysts prepared by deposition – precipitation (dp) in our lab. Volumetric measurements of CO chemisorption were performed on mildly reduced catalysts and after saturation of the surface with water, in order to avoid CO chemisorption on uncoordinated support ions [4]. In the present work we have chosen to perform pulse flow CO chemisorption measurements at the temperature of 157K. Values obtained performing chemisorption measurements at a lower temperature (140K) are slightly higher and present broad peaks, indicating that under these experimental conditions part of CO chemisorbs on support ions. On the contrary, measurements carried on at higher temperature (180K) are, under the experimental error, identical to the ones obtained at 157K. However, since the latter is a temperature which is easier to attain, we suggest to use it for the routine analyses. Preliminary runs carried out on the bare supports have shown the absence of CO chemisorption on uncoordinated support ions. On the contrary, as a proof of the reliability of the selected experimental conditions, measurements on the same blank sample (c) without performing the hydrating pretreatment, have shown that a fraction of CO has been chemisorbed on the support. So chemisorption test, which is a technique widely diffuse both in academic and industrial laboratories, economic, fast and, if performed under proper conditions, reproducible and reliable, can be used also for gold based samples.

This provides a prompt spin-off for academic and industrial laboratories. For example, there has been a renewed interest in the low temperature water gas shift (WGS) reaction on gold nanoparticles 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. We have recently investigated

gold nanoparticles over zirconia and sulfated zirconia catalysts for the low-temperature water-gas shift reaction, in particular investigating the possible correlation between gold dispersion and catalytic activity. It was pointed out that the samples with higher CO/Au molar ratio were the most active in the water-gas shift reaction. 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. Therefore a chemisorption test is suitable and very useful for a preliminary evaluation of these Au/ZrO<sub>2</sub> systems used for the LT-WGSR, in particular on Au/ZrO<sub>2</sub> catalysts, where gold particles cannot be detected by TEM [5].

## 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 60 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 in Chemistry 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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