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Structural and surface properties of heterogeneous catalysts: Nature of the oxide carrier and supported particle size effects

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ABSTRACT

Heterogeneous catalysts, investigated by several techniques, such as XRD, XPS, TEM, TPR/TPO, able to ascertain their structural, chemical, electronic and morphology properties are reviewed with respect to selected results obtained by the group during approximately the last twenty five years. The field of application covers different catalytic processes such as alkene hydrogenation over noble metal catalysts, hydrodesulfurization (HDS) and environmental catalysis. In particular the following subjects are described: the peculiarity of a support like pumice, in relation to the hydrogenation activity of the supported noble metals; supported gold and supported gold containing alloy catalysts for different types of reactions; the importance of the CoMoS precursors and the structure of bimetallic PdAu and PtAu for hydrotreating processes; the effect of a sulfatable oxide, such as TiO_2, on the CH_4 oxidation activity of supported Pd catalysts; different preparation methods influencing significantly the catalytic behavior of supported nickel catalysts for methane conversion processes. The reviewing of the different case studies illustrates the importance of the interaction between support and active metals ultimately determining the surface distribution of the active sites and their final catalytic activity.

1. Introduction

Catalysis and in particular heterogeneous catalysis, a technology devoted to the enhancement of chemical process with increased conversion and selectivity, relies very much on the structural design and the surface properties of the material used as catalyst. As commonly described in fundamental chemistry books, a catalytic process involves a sequence of elementary steps, including, adsorption, surface diffusion, chemical rearrangement of the adsorbed reaction intermediate and desorption of the products [1,2]. Each of these steps is affected by the nature of the catalyst, typically but not always, formed by an inert support and by the active species present as metallic or as oxide state usually deposited at the surface of the supports. A detailed structural and surface characterization is therefore mandatory in order to understand the behavior of a catalytic material and to be able to enhance its activity and its selectivity in a particular reaction [3].

The advancement of our scientific career in the field of catalysis has strongly relied on the knowledge of surface science and material characterization tools [4–9]. Indeed the application of X-ray photoelectron and Auger spectroscopy, using laboratory or Synchrotron facilities allowed to understand surface modification after catalytic reactions or during adsorption of molecules [10].

When considering the case of supported metal catalyst, the surface distribution of the active metal plays the main role [11]. Therefore, it is crucial to exploit synthetic routes allowing to obtain catalysts with the highest exposed surface. In other words, it is very important to achieve active site phases highly dispersed, with the highest surface to volume ratio and with the least amount of metal, saving also on the total cost of a catalyst [12]. Particles in the nano size range are suitable for heterogeneous catalysis, however it is important to keep in mind that the metallic properties and the consequent catalytic benefits, depending on the particular reaction, may be lost below a certain size [13,14]. As we are aware of, most recently, advances in syntheses and characterization techniques had allowed to demonstrate the role of even sub-nanometers particles in the enhancement of the catalytic oxidation activity [15,16].

Obviously, the design of a good catalyst takes into account the nature of the support, either “inert” e.g. carbon, SiO_2, and to a less extent Al_2O_3, or “active” such as the reducible oxides, e.g. CeO_2, TiO_2 [17,18]. In the first case the inert support acts as just a dispersing carrier, whereas in the second case, the interaction with the anchored active phase, modulated by different synthetic approaches, affects the catalytic behavior [19]. Beside the chem-

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istry, the texture and the morphology of the supports are also important. It is generally acknowledged that a high surface area support is positive for the catalyst activity, allowing for a better metal dispersion. However the use of a low surface area support, when suitable syntheses succeed in making catalysts with high metal dispersion, can improve the supported metal signal of a surface technique like XPS, therefore allowing a better understanding of the experimental results [4].

A way to enhance the catalytic behavior of a metal active species is to add a second metal producing the so called "alloying" effect [14,20]. Beside the main catalyst components, small amount of elements may be naturally present in the support or may be purposely added, acting as structural or as chemical promoter [21–23].

Since none of the above effects works independently of each other, for a better understanding of their role, we had tried to separate them by appropriate design of the catalysts. Obviously the nature of the probing reaction must govern the selection of the catalysts. The main achievements of our research activity carried out during the last 25 years are summarized in the present review article. Due to space limitations we will leave out some recent work related to biomass valorization [24–27]. Different study cases are grouped under two important types of test reactions, the catalytic hydrogenation and the catalytic oxidation. Hydrotreating reaction, hydrodesulfurization (HDS) and hydrodearomatization (HDA), although involving hydrogenation steps are treated separately because of the different target and the peculiarity of the active sites. For each typology of reaction the importance of the support nature, with and without modifiers, the structure of the active site, as single or multi-metal, will be demonstrated.

2. Experimental

2.1. Support and catalyst preparation

Different types of oxides, either commercially available either laboratory made were used as catalyst support. Sol-gel, co-precipitation or hydrothermal syntheses were employed when a particular control of the morphology, chemical and electronic properties was needed. The anchoring of the active metal was performed through a variety of procedures, depending on the final objective and application. Just to cite a few examples, in order to obtain a high dispersion of palladium particle over a low surface area support, an organometallic procedure, derived from the Yermakov's method, with the diallyl $Pd(\eta^3\text{-}C_3H_5)_2$ precursor was adopted [28,29]; gold catalysts required a carefully pH controlled deposition precipitation method [30]; solvated metal atom deposition (SMAD) procedure was modified to attain high dispersed gold particles [30,31]; CoMo catalysts were prepared by classical impregnation and also by ligand (NTA) assisted procedures [32]; the preparation of bimetallic particles with different degree of alloying and different core-shell structures involved also a preferential interaction with appropriate functional groups previously attached to the supports [33]; furthermore, microwave assisted procedures were used in the latest investigations [34].

2.2. Catalyst characterization

The catalysts, before and after the catalytic tests were characterized by several structural and surface techniques. The most commonly used ones were XRD, SAXS, XPS, TPR/TPO, TGA/DTA, SEM,TEM, FT-IR. Temperature programmed desorption of ammonia (NH_3-TPD) was used for the determination of the oxide support acidity.

Table 1
Metal loadings of different pumice supported Pd catalysts, (wt.-%), surface metal coverage (f) and diameters, d (Å) of particles as derived by SAXS.

Sample[a]	Pd (wt%)	*f*	*d*[b]
W0	0.05	0.005	18
W1	0.20	0.01	22
W2	0.11	0.006	29
W3	0.39	0.02	35
W4	0.61	0.03	35
W5	0.86	0.04	40
W6	0.37	0.01	50
W7	1.05	0.02	81

From Venezia et al. [13] with permission.

2.3. Catalytic activity

Different reactor set ups which are described in the published papers were used. Dienes hydrogenations were performed in liquid phase batch reactors, whereas gas phase reactions of CO, methane and VOC oxidation were carried out in plug –flow reactors.

3. Results and discussion

3.1. Hydrogenation

3.1.1. Monometallic catalysts

Pumice, a natural stone of volcanic origin found in the nearby island of Lipari, was used as catalyst support. Several studies related to the catalytic effects of the supported metal particle sizes and the alkali promotion have been published [13,35–40]. After a mild acid treatment, the material, an amorphous aluminosilicate, had a reproducible final composition of 85% of SiO_2, 7% of Al_2O_3 with minor amounts of Na_2O and K_2O [36]. Being characterized by a low surface area (~5 m^2/g) it was crucial to adopt metal supporting procedures able to maximize the metal dispersion. In this sense very good results were achieved using a procedure leading to an allyl intermediates with $Pd(\eta^3\text{-}C_3H_5)_2$ precursor [29]. The obtained series of pumice supported catalysts (w series) with different amounts of noble metal are listed in Table 1 along with the surface metal coverage (*f*) calculated as $f = x/(1-x)\ \rho_{pd}\ dS0_0$, where x was the palladium weight fraction in the final catalyst, ρ_{pd} the density of palladium, d the palladium particle diameter derived by SAXS measurements and S_0 the support specific surface area [13]. These catalysts were tested in the selective hydrogenation of 1,3-cyclooctadiene (1,3-COD) to mono-ene in liquid phase [29]. Surprisingly, the catalysts behaved quite differently from classical catalysts of Pd over pure alumina or silica [12]. In those cases a drastic decrease of the activity in terms of TOF was observed for metal dispersion higher than 20% (particle size smaller than 60 Å). Such behavior was explained with the rapid loss of metallic character of the palladium crystallites associated to a positive chemical shift of the Pd 3d photoelectron peaks in the X-ray photoelectron spectra (XPS). On the contrary, the pumice supported catalysts exhibited a constant turnover frequency (TOF) for metal particles larger than 30–40 Å and progressively smaller values as the dimensions of the particles decreased below 30 Å [29]. At the same time a negative Pd 3d chemical shift was observed [40]. A lowering of the binding energy with the increase of the metal dispersion suggested the presence of another effect, opposite to the loss of metallic character. XPS of the valence band and X-ray excited O KLL Auger transition revealed an interaction between pumice and metal, consistent with an electron transfer from the support to the metal [39,40]. Through the combination of core electron binding energy shifts and Auger transition shifts it was possible to calculate the Auger parameters, which, being independent on the charging and energy reference, yielded more reliable information on the charge distri-

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