

Water-mediated assemblies and processes in the synthesis of oxide-supported catalysts

Michel Che

Institut Universitaire de France and
Laboratoire de Réactivité de Surface, UMR 7609 - CNRS,
Université Pierre et Marie Curie-Paris 6, 4, Place Jussieu 75252 Paris Cedex 05
e-mail: che@ccr.jussieu.fr

Hundred years ago, in the single and miraculous year 1905, Einstein wrote five papers [1] that shook the world and changed the face of physics. They are at the origin of the World Year of Physics 2005 (Einstein in the 21st Century) [2], which lead the CNRS to publish a special issue [3], in which the 10 great enigma of Physics are identified. It is striking that the first one, expressed as "the mysteries of water", could be ranked also as N°1 for biology and chemistry, so overwhelming is the role of water in life processes and in the genesis of intelligent materials, amongst which catalytic systems can be included.

Numerous strategies exist to design and synthesize catalysts but when large quantities are needed, some strategies no longer apply. The lecture will focus on catalytic systems, particularly oxide-supported ones, produced at the industrial scale from conventional oxides (alumina, silica, zeolites, etc...) and water-soluble transition metal complexes as precursors of the catalytically active phase.

The preparation of catalysts [4] involves several stages called unit operations in the industry [5] or preparation steps in the laboratory. A typical sequence involves: deposition on the support of the precursor complex in aqueous medium, elimination of the solvent, drying, calcination, and reduction. Industry and laboratory procedures are the same and only differ by the quantities of catalysts prepared, typically of the order of the ton and gram respectively.

In recent years, major advances have been made in physical techniques [6] particularly for the *in situ* characterization of catalysts, either during preparation or in working conditions [7-9]. A molecular approach based on the use of such techniques and of transition metal elements has been developed in our laboratory and applied to the study of oxide-supported catalysts [10]. The role of transition metal complexes is threefold [10]: i) transition elements generally have remarkable catalytic properties, ii) their partly filled *d* orbitals provide them also with unique optical and magnetic properties, iii) such properties followed by suitable spectroscopies strongly depend upon the immediate environment of the transition metal elements which can thus function as *probes* of their own interactions with the oxide support in the course of preparation, thus providing very valuable information on the role played by the support.

The lecture will consider the deposition methods most frequently used in the industry, i.e., impregnation and equilibrium adsorption. The catalysts obtained are characterized both at the molecular level by spectroscopies such as diffuse reflectance UV-Visible, NMR, and EXAFS, and at the macroscopic level by techniques such as TEM, TPR and XRD.

Within this context, the lecture will try to evidence the role of the oxide support and particularly that of water all too often considered as a simple solvent. It will be shown that it is possible, by a careful control of the experimental conditions, to promote specific "precursor complex - support" interactions and to describe them in molecular terms within the conceptual framework of various types of chemistry (colloidal chemistry, electrochemistry, supramolecular chemistry, coordination chemistry, geochemistry). While the oxide support is found to be a very versatile entity (counter ion [10,11], receptor [10,12,13], ligand [10,14], or reactant [10,15-17]), the role of water is even more fascinating. Apart from its classical role of ionizing and dissociating solvent and of acid and base, water can exhibit new properties in presence of both the precursor complex and the oxide support. Water can act as a viscous solvent [18], a s and p donor weak and labile ligand [10,14,19,20,21], a H-bond intermediate [22,23], a transport agent [16], and finally a reactant [10].

References

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