

## MONITORING THE THERMAL STABILITY OF THE POROUS STRUCTURE OF HYBRID SiO<sub>2</sub>-TiO<sub>2</sub> MATERIALS BY MEANS OF MASS TRANSPORT COEFFICIENT CALCULATIONS

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### Abstract

The physical characterization of solids, mainly the surface area measurement and the pore size distribution determination by means of nitrogen adsorption and mercury porosimetry, respectively, might be a matter of controversy in the case of materials that can suffer important structural changes between 77K and their operation temperatures (room or higher), or whose pore structure may be damaged due to the mercury intrusion.

The goal of this work is to identify changes in the physical structure of solids when they are exposed to temperatures similar to those used in conventional thermal pretreatments, when they are used as catalysts, by means of mass transfer coefficient measurements. Our working hypothesis is that, if structural changes occur, these should be easily detected via noticeable changes in the mass transfer coefficient for a selected adsorbate.

The calculation of relaxation constants, which characterize the transport of cyclohexane through the hybrid materials is carried out by modeling the experimental data corresponding to the transient state of the adsorption tests.

**Keywords:** Hybrid materials, Structural changes, Mass transfer coefficients, Oscillating Microbalance.

### 1. Introduction

Among the novel materials with desired properties (thermal and electrical conductivity, effective diffusivity, mechanical strength, transparency, etc.), required for many fields related to science and technology, the inorganic/organic gels, obtained by hydrolysis and condensation of organic and inorganic precursors, can combine some of the properties that define organic polymers (e.g. flexibility), with the mechanical strength that is typical of inorganic materials. The physical properties of the final product, depend on the way in which molecules or particles are linked to form the hybrid structure (Ballard *et al.*, 1999). Adsorption experiments is the most frequent technique

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used to describe the porous structure of solids. Nitrogen, helium and recently neopentane (Larsen *et al.*, 2000a), are the most popular adsorbates to carry out physisorption tests. An adequate characterization of the porous structure is a central issue in order to predict the behavior of the material with regard to the mass and energy transport. When a solid structure is characterized by means of an adsorption test, an important point must be taken into account. Some solids have a porous structure that changes substantially with temperature. For these solids, the information gathered from an experimental adsorption test at 77K is virtually useless. In these cases, adsorption tests at higher temperatures should yield useful information about the actual physical structure of the solid at temperatures similar to those of its practical applications (Larsen *et al.*, 2000b).

In this work, the evaluation of the thermal stability of hybrid SiO<sub>2</sub>-TiO<sub>2</sub>, is carried out. These materials which are proposed as catalysts for C<sub>5</sub>-C<sub>8</sub> olefine epoxidations (Larsen *et al.*, 1999; Muller *et al.*, 2000a,b), are thermally pretreated before their use. From adsorption tests of cyclohexane over the hybrid materials obtained from different organic precursors, the calculation of the coefficients that characterize mass transport, is carried out. These experiments are performed in a oscillating microbalance.

### 2. Experimental

#### 2.1 – Sample preparation

The hybrid SiO<sub>2</sub>-TiO<sub>2</sub> gels were prepared by the hydrolysis and condensation of silicon precursors according to the protocol recently described (Larsen *et al.*, 1998). Basically, two-thirds of the total amount of moles of silicon was added in the form of tetraethylortosilicate (inorganic silicon precursor) and one-third in the form of the organic precursor (hexamethylcyclotrisiloxane, for the hybrid labeled as SiO<sub>3</sub>-Ti and decamethylcyclopentasiloxane for the hybrid labeled as SiO<sub>5</sub>-Ti). The mixture was prehydrolyzed for 5 hours at 338 K, before the