

MONITORING THE THERMAL STABILITY OF THE POROUS STRUCTURE OF HYBRID SiO₂-TiO₂ 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 SiO₂-TiO₂, is carried out. These materials which are proposed as catalysts for C₅-C₈ 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 SiO₂-TiO₂ 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 SiO₃-Ti and decamethylcyclopentasiloxane for the hybrid labeled as SiO₅-Ti). The mixture was prehydrolyzed for 5 hours at 338 K, before the

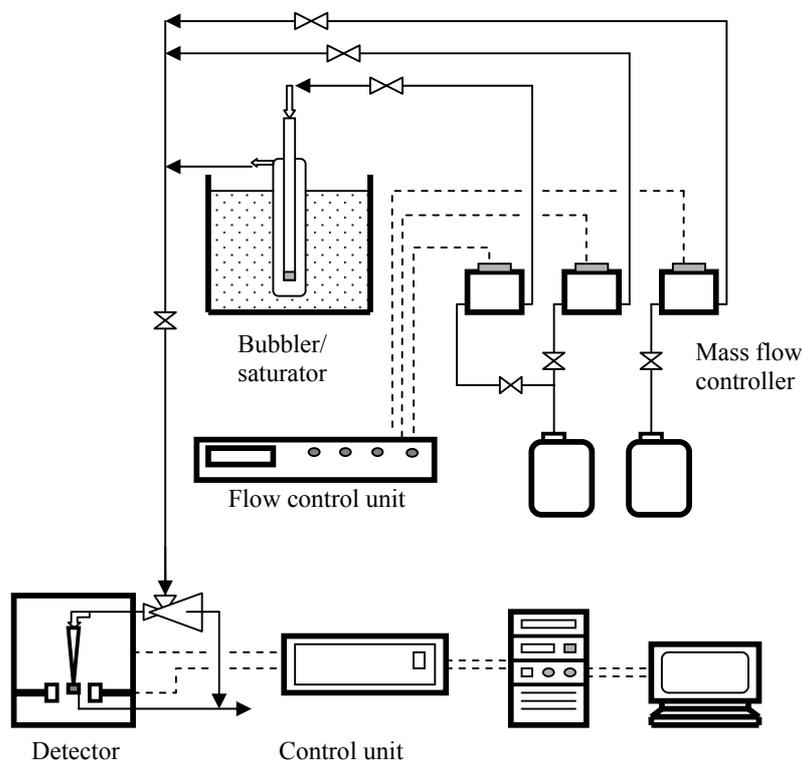


Fig. 1- Experimental arrangement for the adsorption tests

addition of the precursor of titanium. The samples were placed in open containers, in an oven at 338 K, with no forced air circulation, for slow gel and evaporation. Although the samples gelled in less than 24 hours, all the samples were removed from the oven after 60 hours.

2.2 – Adsorption studies

The adsorption experiments were carried out with the aid of an oscillating balance reactor (Fig. 1), which was initially developed for quantification of particulate in air (Patashnik *et al.*, 1992). Recently this device was adapted for in situ catalysis research (De Chen *et al.*, 1996; Liu *et al.*, 1997) or for adsorption studies (Hershkowitz and Madiara, 1993) It consists of a detector unit which behaves as a physical pendulum, a control unit which fixes the experimental parameters (basically the temperature program) and a PC as the input/output data unit. The oscillating element is a quartz tube and the solid is placed as a packed bed at its end (Fig. 2). The basic idea is that the solid packed bed is made to oscillate at its natural frequency by means of an electronic device and instantaneous mass changes are detected and processed by a computer.

A commercial unit from Ruppert & Patashnik Company was used. The main feature of this form of microbalance is that it has the ability to detect minute weight changes with excellent mass-time resolution,

and the flow profile is much better defined compared with those which take place in conventional

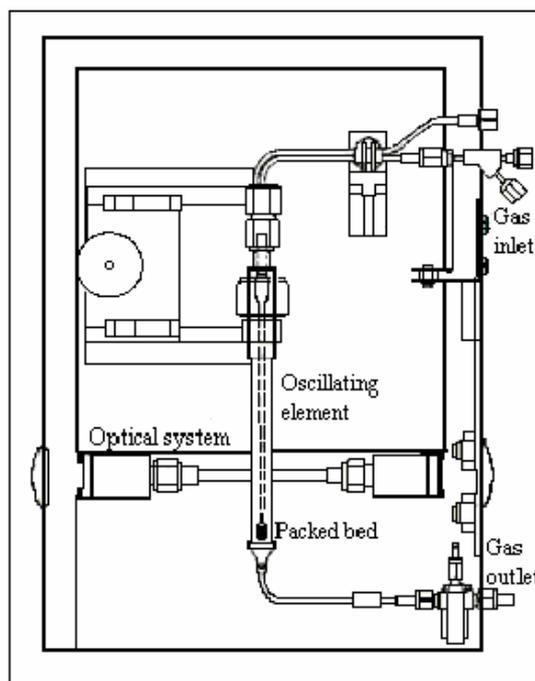


Fig. 2 – Oscillating packed-bed detector

microbalances, given its packed-bed geometry.

The experimental arrangement includes a bubbler/saturator assembly, where a constant flow of a carrier (helium), measured with a 5850 Brooks mass flow controller, is saturated with cyclohexane at 280 K. The hybrid solids were dried in situ in the microbalance at 383 K, for 1 hour under a constant flow of nitrogen. The temperature was then stabilized at 313 K, under a helium flow. The helium flow was then switched to helium saturated with cyclohexane. This flow passes through the oscillating element of the microbalance and the adsorption of cyclohexane takes place. The same protocol is used for the adsorption of cyclohexane on hybrid materials pretreated at 423 K, 463 K and 543 K.

3. Results and Discussion

Figures 3 and 4 show the cyclohexane dynamic adsorption results over the two hybrid materials.

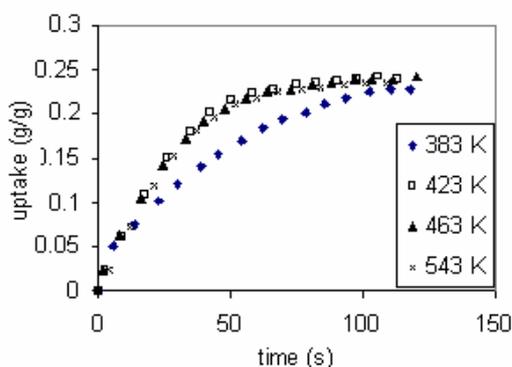


Fig. 3- Cyclohexane dynamic adsorption over SiO₃-Ti pretreated at different temperatures

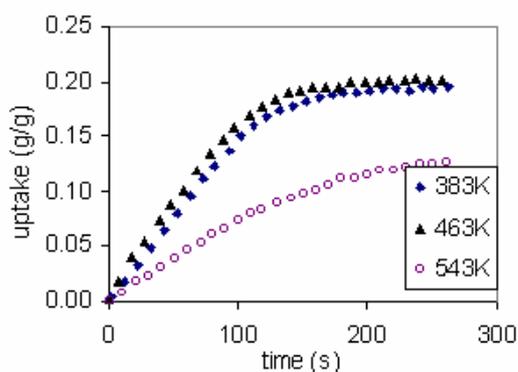


Fig. 4- Dynamic cyclohexane adsorption over SiO₅-Ti pretreated at different temperatures

When the transport of a fluid in spheroidal heterogeneous catalyst pellets (radius R_c), is considered, Fickian diffusion is assumed. Then, the porous structure is considered a rigid one, and the expected concentration profile for a fluid within the particle,

shown in Fig. 5, basically depends on the mass transport coefficient value (i.e., the effective diffusivity, D_{eff}).

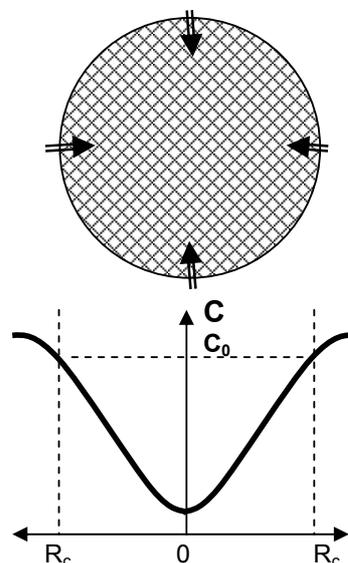


Fig. 5 - Concentration profile for a fluid transported within a rigid porous solid

In this case the time dependant uptake $M(t)$ of the adsorption test, relative to the total uptake M_∞ ($t \rightarrow \infty$), that is, the relative uptake, can be calculated from

$$\frac{M(t)}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(\frac{-D_{eff} n^2 \pi^2 t}{R_c^2}\right) \quad (1)$$

For relative uptakes < 0.3 , an approximate form of Eqn. (1) is generally adopted (Crank, 1976)

$$\frac{M(t)}{M_\infty} = \frac{6}{\pi^{1/2} R_c} D_{eff}^{1/2} t^{1/2} \quad (2)$$

In polymer research it is usual to deal with swellable materials instead of rigid porous matter. Mass transport phenomena in those solids have been loosely defined as “anomalous” or non-Fickian diffusion, which is characterized by the following features: a) As the fluid penetrates into the porous structure, a sharp advancing boundary separates the inner non swollen core from the swollen shell. b) The boundary between the swollen porous structure and the non swollen core advances to the center of the spherical particle with constant velocity. c) The swollen gel behind the advancing boundary is at uniform state of swelling. According to this, the concentration profile for a penetrant within the particle is the one shown in Fig. 6.

In the region $R(t) \geq r \geq 0$, there is basically no penetrant. C_0 is the penetrant equilibrium concentration

in the already swollen shell (i.e., the equilibrium concentration of penetrant at $R(t) < r < R_c$).

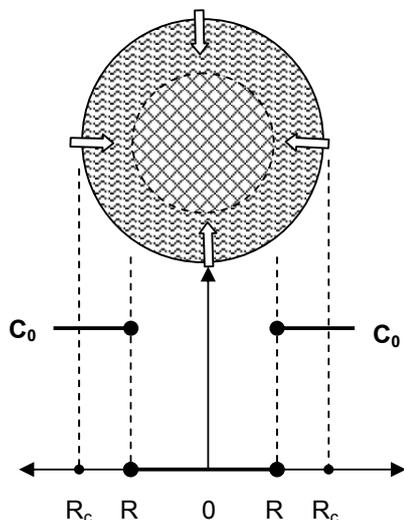


Fig. 6– Concentration profile for a fluid which is transported in a swellable solid structure.

⊗ Non swollen solid ⊞ Swollen solid

If k_0 , the relaxation constant ($\text{mol m}^{-2} \text{s}^{-1}$), is defined as the parameter that characterizes the non Fickian mass transport and is assumed to be constant, the kinetic equation that describes the mass transport through the outer surface on $N(R)$ spherical particles of radius R is

$$\frac{dM(t)}{dt} = N(R) k_0 4 \pi R^2 \quad (3)$$

The amount of penetrant $M(t)$ absorbed in an array of uniform spheres in a time t (i.e., the uptake measured in a typical test carried out in the oscillating microbalance) will be:

$$M(t) = \frac{4\pi}{3} C_0 N(R) (R^3 - R_c^3) \quad (4)$$

From this conceptual model, Enscore *et al.* (1977), derived the following formula for diffusion of penetrants in glassy and swellable materials:

$$\frac{M(t)}{M_\infty} = 1 - \left(1 - \frac{\alpha_0 t}{R_c}\right)^n \quad (5)$$

where α_0 is k_0/C_0

The power n adopts the value 1 for films, 2 for cylinders and 3 for spheres. Equations 2 and 5 provide a quick test to determine whether mass transport is either non-Fickian or Fickian, since only the latter produces $M(t)/M_\infty$ vs. $t^{1/2}$ linear plots. Figures 7 and 8 show these

plots for the hybrid materials, which have in fact been wetted (organic polymer style) by cyclohexane. No linearity is observed over the whole range of time.

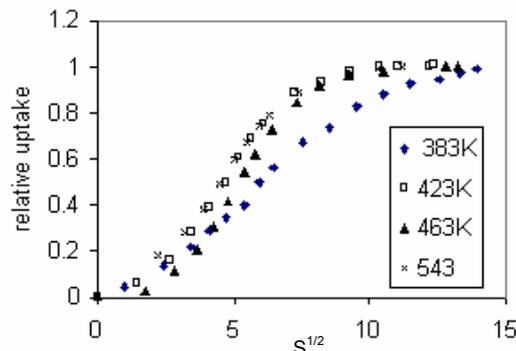


Fig. 7 - Relative uptake vs. square root of time correlation for SiO_3 -Ti material

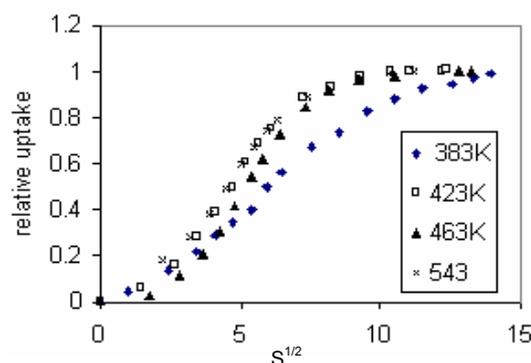


Fig. 8 - Relative uptake vs. square root of time correlation for SiO_5 -Ti material

To better understand the transport data, we point to the deviations of the adsorption curves from linearity. The sigmoid shape of the curves can either be due to pure non-Fickian transport or a combination of Fickian and non-Fickian behavior. In the last case, the total uptake could be calculated from the fractional contribution due to the Fickian transport (F_F) and that from the non-Fickian transport (F_{NF}). This yields:

$$\frac{M(t)}{M_\infty} = F_{NF} \left[1 - \left(1 - \frac{\alpha_0 t}{R_c}\right)^3 \right] + F_F \left(\frac{6}{\pi^{1/2} R_c} \right) D_{\text{eff}}^{1/2} t^{1/2} \quad (6)$$

Two competing factors have to be considered to analyze the cyclohexane diffusion in these hybrid materials. Removal of unreacted (pendant) alkoxi groups tends to open up the structure only if their elimination does not produce cross-linking of the polymer chains. The saturation uptakes for the SiO_3 -Ti samples pretreated at different temperatures are practically identical (0.242 at

383 K, 0.243 at 423 K, 0.245 at 463 K, 0.239 at 503K and 0.240 g/g at 543 K), which indicates that the pore volume stays essentially unchanged. A similar behavior is observed for the SiO₅-Ti hybrid until 503K, but the final uptake for the hybrid pretreated at 543K decreases markedly, which indicates that the pore volume has changed substantially.

The stiffening of the porous structure is monitored by the transient adsorption data. The analysis indicates that the porous structure of the SiO₃-Ti hybrid relaxes more rapidly as the preheating temperature increases but the opposite holds true for the SiO₅-Ti material.

To determine whether the mass transport is controlled by either a single mechanism or a combination of both (Eqn. 6), some information about the texture of the material is necessary. An average particle size of 31 nm has been determined by scanning electron microscopy (SEM) for the oven dried materials. They are composed of largely irregular particles with aspect ratios comparable to those of a sphere.

The C₀ value is determined from the vapor pressure of cyclohexane corresponding to the bubbler /saturator temperature using the ideal gas law.

An empirical first order non-Fickian term for long adsorption times, was proposed as a preliminary test. According to this, Eqn. (6) can be written:

$$1 - \frac{M(t)}{M_\infty} = (1 - F_F) \exp(-kt) + F_F \frac{6}{\pi^2} \exp\left(\frac{-t\pi^2 D_{eff}}{R_c^2}\right) \quad (7)$$

If $\ln[1 - M(t)/M_\infty]$ is plotted against time, the intercept value will allow for the determination of the controlling mechanism in the event it would exist. If the Fickian transport controls ($F_F \sim 1$), $\ln[(6/\pi^2)F_F]$ must be bound between $[-\infty, -0.5]$.

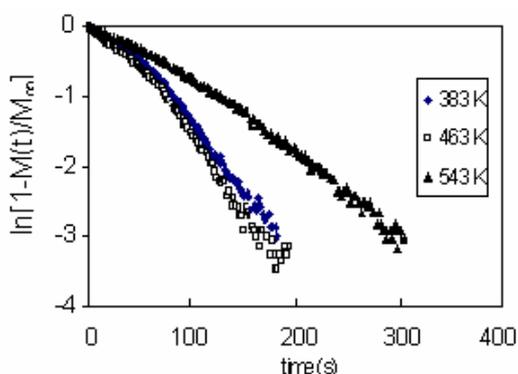


Fig. 9 - $\ln[1 - M(t)/M_\infty]$ vs. time correlation for SiO₃-Ti material

In case the non-Fickian transport is the controlling mechanism ($F_F \sim 0$), the intercept must lie between $[-\infty, 0]$. Figures 9 and 10 show, by back-extrapolation to $t=0$, that a non-Fickian controlling transport can be predicted.

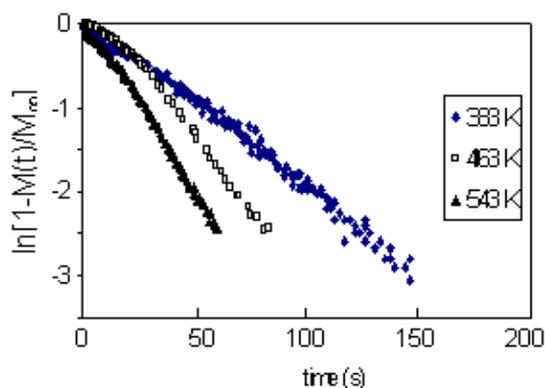


Fig. 10 - $\ln[1 - M(t)/M_\infty]$ vs. time correlation for SiO₅-Ti material

The intercept obtained by linear regression of the $t > 0.7$ regions for all adsorption tests, converge to zero or to a value slightly above 0. Values slightly above zero are accepted. Within scattering of data, we take this as an indication that these hybrid solids have $F_{NF} \approx 1$, and it should therefore be modeled by Eqn. (3).

The results of such modeling are summarized in Table 1. The relaxation constant values indicate that thermally induced transport changes in these two solids do not follow the same trend.

Despite the fact that ²⁹Si MAS-NMR, conventional nitrogen adsorption, temperature programmed decomposition techniques and DRIFTS had been unable to detect important differences between these two solids, it is clear that the ring size of the organic Si precursor determines, in a subtle way, the residual reactivity (cross-linking) and permeability of these porous matrices.

Table 1. Relaxation constant

Temperature [k]	SiO ₃ -Ti k ₀ [mol/m ² s]	SiO ₅ -Ti k ₀ [mol/m ² s]
383	3.22 10 ⁻¹⁵	2.79 10 ⁻¹⁵
423	7.03 10 ⁻¹⁵	2.79 10 ⁻¹⁵
463	6.52 10 ⁻¹⁵	2.94 10 ⁻¹⁵
503	6.61 10 ⁻¹⁵	3.01 10 ⁻¹⁵
543	6.7 10 ⁻¹⁵	1.64 10 ⁻¹⁵

4. Conclusions

The two hybrid materials studied here show different behavior when they are thermally pretreated in the same temperature range. While that made from the cyclic trimer (SiO₃-Ti) improves the mass transfer coefficient

as the pretreatment temperature increases, the opposite holds true for the SiO₂-Ti hybrid. It seems that the key factor is the ability of the structure to eliminate unreacted alkoxide groups without concerted cross-linking. This is one of the central features that have to be considered when these materials are proposed in some industrial uses (e.g., catalysts).

In conclusion, flow-through vibrational microbalances can be used to monitor subtle changes in the transport properties, due to mild thermal treatments, of hybrid porous glasses. With the right design of gas supply manifold, the technique is useful and reliable to measure diffusion processes in the order of seconds. This is a key information in order to predict the behavior of these materials respect of the mass transfer of a defined fluid, under operating conditions similar to those used in their industrial applications.

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