Dynamical Light Scattering Method For Particle Size Determination Using Optical Fibres

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Abstract

Dynamic light scattering (DLS) method is widely used for particle size determination in stagnant solutions. By measuring the autocorrelation function of particles under Brownian movement, their size as small as 2R=2 nm can be found [1-3]. In contrast to a cell of a granulometer, industrial reactors are often stirred and their walls are not transparent. In these conditions the laser beam may be strongly perturbed on the way through the reactor. We developed a optical fibre probe, which was tested in different operational conditions and used in a new sol-gel reactor for the kinetics control of titanium oxide nanometric sols. Complex surface coverage applications are considered.

Optical fibre probe

DLS could be useful tool for in-situ size control of the smallest submicronic particles, whereas on-line light diffraction appeared efficient for a control of larger particles. We prepared the optical fibre probes made of multimode (D=100 μm, numerical aperture α=0.3) and monomode (D= 5 μm, α=0.1, *SEDI*) optical fibre probes and compared their performances. Each probe is made of two optical fibres, which ends are fixed at a short distance (adjusted, $\leq$1 mm) and at a right angle between the optical axes. A radiation from He-Ne laser (*Spectra Physics*, P=20 mW, λ=632.8 nm) was coupled to one fibre by using an optical adapter (*Newport*). The second fibre captures and conducts the scattered light to the photo-multiplier. The measurements were made in the homodyne technique of photon-correlation spectroscopy by using a 16-bit, 72 channels PC board plugged digital correlator (*PhotoCor Instruments*). Suspensions of particles of different sizes were used to test the probe: latex particles (by *SIGMA*) of 100 and 330 nm in water and titanium oxide particles of 18 nm in 2-propanol prepared in the laboratory. Equations are set-up and checked for measurements achieved under mechanical stirring [4]. Moreover, the 150-μm (D) capillary TEFLON AF 2400 (*Biomed Inc., CA*) was tested for a rapid sampling of reactor colloids. We have also tested another arrangement using a fibre-capillary coupling. The turbulence is strongly reduced inside this capillary (Re$\propto$d), which enables precise particle size measurements. Because of a low refraction index of the capillary walls (n_c=1.29), the injected liquid (n_l>n_c) serves to be a waveguide for laser radiation, which is axially introduced by a monomode optical fibre. The light scattered by particles inside the capillary is collected by another monomode fibre in the normal geometry. Despite of a lower coupling efficiency with the laser beam, use of the

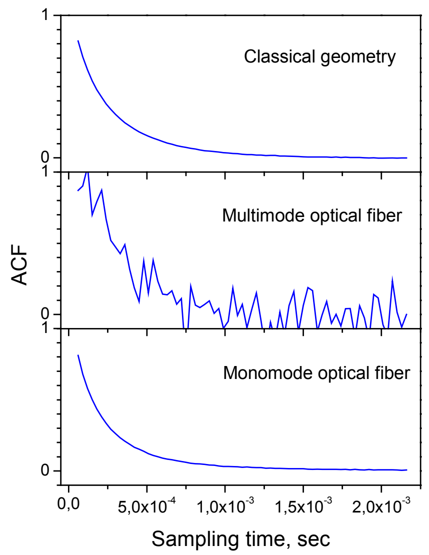

Fig.1 ACF's measured in different experimental geometries

monomode optical fibre results in higher contrast of the autocorrelation function and shorter accumulation time, which guarantees desirable precision of measurements [5].

Sol-gel reactor

We used the optical fibre probe to control of the growth kinetics of nanoparticles in the sol-gel reactor [6]. Its principal parts are shown in fig.2. Two stock solutions A (titanium tetra- isopropoxide/2-propanol) and B (water/2-propanol) are sinchroneously injected into the receiver (1) by the pressure of dry nitrogen gas through the static Hartridge-Roughton type mixer (2). It assures a perfect reagent mixing on the timescale of t<10 ms, before the reactions begin, which guarantees creation of monodispersed nuclei. The temperature of the reactor is stabilized within ±0.5 °C in the range of -20/+40°C. To measure the kinetics of particle size increase within the reactor, the monomode optical fibre probe (3), made in the laboratory, was used allowing an access with a laser beam to bulk reactor points. This probe is essential in the reactor control because direct measurements using classical experimental arrangement (tracing the beam with lenses) are strongly influenced by the macroscopic movement of the reactor fluid and require optical quality reactor walls.

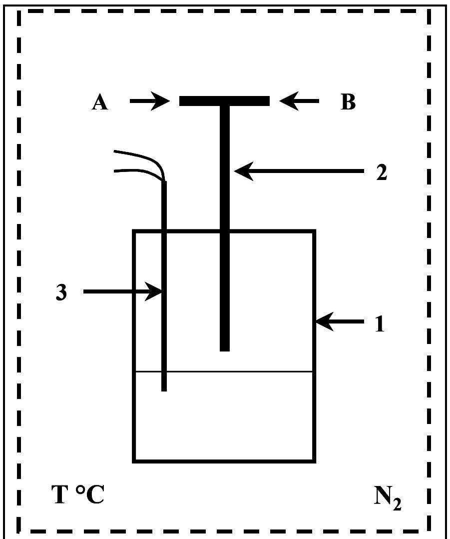

Fig.2 Schema of the sol-gel reactor:

The use of the reactor allowed a good experimental kinetics reproductibility (<2%). An example of measurement of series of kinetic curves ([Ti]=0.146M and H varyes) $\mu_2=\int mF(m)dm$ (where *m* stands for a particle size and *F(m)* is the particle mass distribution function) is shown in fig.3. During the considered delay time before precipitation (called the induction time of the sol-gel process) the hydrodynamic particle size increases from 2.0 nm to ~10 nm. Actually the reactor performance was tested at different operation conditions of [Ti], H, T°C, injection rate, extra agitation in (1), etc. The optical fibre probe allowed sensitive and accurate control. Moreover, new data about the reaction activation energy and fractal dimention of the growing nano-sized objects were obtained [7].

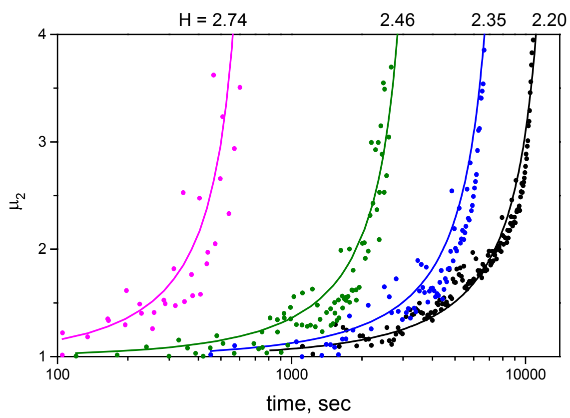

Fig.3. Kinetic curves of the growing particles for different hydrolysis ratio H=[H_2O]/[Ti].

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