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Original Research Paper

A novel approach to rapid sizing of nanoparticles by using optical calorimetry

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ABSTRACT

Optical calorimetry was recently presented to be a versatile screening technique for a rapid and simple evaluation of adsorption properties (e.g. specific surface area, adsorption capacity) of porous materials. In this study, optical calorimetry is introduced for the sizing of nanoparticle powders. For this purpose, the sizing is done with various pyrogenic nanoparticles (SiO_2, TiO_2, Al_2O_3, ZnO, WC) in a diameter range of 6–100 nm. By comparing the results of optical calorimetry to reference physisorption measurements as standard nanoparticle sizing technique, an excellent correlation is demonstrated. In contrast to the standard physisorption method, the optical calorimetry allows a simple and rapid screening (only 5 min per sample) of nanoparticles and therefore is well suited in fields with high sample numbers such as high-throughput synthesis or process control.

1. Introduction

Nanoparticles are of major interest in research and industry for optic, magnetic, catalytic, electronic and sensor applications [1–9]. Therefore, the knowledge of the nanoparticle size is very important. Several techniques are established for nanoparticle sizing, including dynamic light scattering (DLS), X-ray diffraction (XRD), transmission electron microscopy (TEM) and nitrogen physisorption [10–12]. Especially in industry, where nanoparticles are mostly produced by pyrogenic processes, the specific surface area analysis by adsorption measurements is the commonly used sizing technique.

Assuming spherical, smooth and monodisperse particles without agglomeration, the particle size of a nanoparticle is inversely proportional to its specific surface area [10–12]:

$$d = \frac{6000}{\rho \cdot S_{BET}} \quad (1)$$

The value S_{BET} [m^2/g] is the specific surface area, which is usually obtained from the analysis of the adsorption isotherm of a N_2 physisorption measurement at 77 K by using the BET equation. The value ρ [g/cm^3] is the density of the bulk material and d [nm] is the average diameter of the nanoparticle. According to Eq. (1), a particle size can be determined by all methods for surface area analysis basically. An alternative technique for surface area determination is the immersion calorimetry. The surface area of a solid is proportional to the immersion enthalpy which is released during the wetting of the solid in a liquid. To reduce the influence of different surface chemistry on the heat effect, the sample is covered with a liquid film prior to the immersion within the so called Harkins–Jura method [13,14].

Besides the cost aspect for purchase and maintenance and the huge measurement effort (e.g. need of liquid nitrogen temperature (77 K) for N_2 physisorption), the long measuring time limits the sample number for surface area analysis by the N_2 physisorption as well as immersion calorimetry significantly. Especially for high-throughput synthesis, quality assurance or process control, a cost-effective, rapid and simple screening method is required to ensure an efficient developing process or workflow.

For this purpose, a novel adsorption screening technique is introduced for sizing nanoparticles within this article. It is based on the optical measurement of a temperature change of a sample due to the released heat of adsorption when it is exposed to a test

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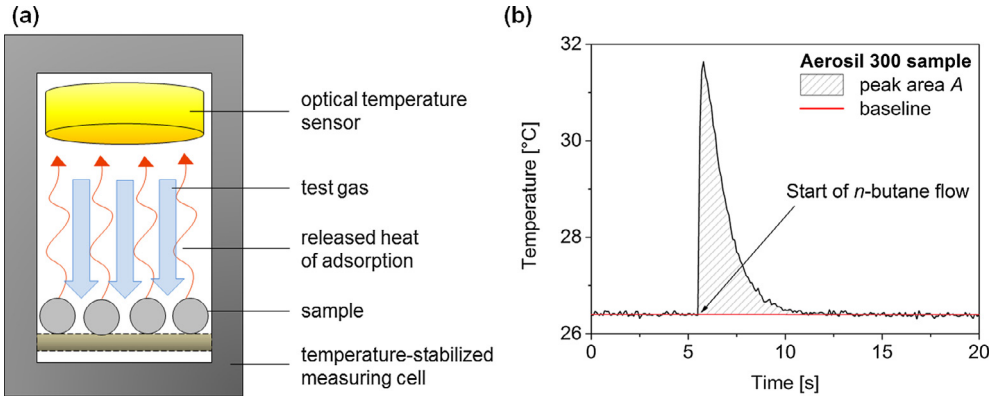

Fig. 1. (a) Experimental scheme of the optical calorimetric measurement and (b) thermal response signal of a nanoparticle material (Aerosil® 300), which is exposed to a gas flow of 70 cm^3/min *n*-butane at 299 K and 1 atm.

gas flow at ambient conditions. The experimental setup of the optical calorimeter *InfraSORP*^{one} is depicted in Fig. 1a. As a result of an optical calorimetric measurement, a time-resolved temperature change (further referred to thermal response, Fig. 1b) is obtained within only 5 min. The characteristic value is the specific peak area A/m (peak area divided by the sample mass) which can be extracted out of the thermal response. It contains information about the adsorption capacity, adsorption enthalpy as well as the heat capacity of the sample. It was previously shown that the specific peak area can be used to rapidly estimate the specific surface area of porous materials [15–17]. But so far, these measurements were predominately applied for microporous materials. Earlier studies on thermal response measurements of ethanol and acetone vapor adsorption at Bi_2MoO_6 and Bi_2WO_6 nanoparticles indicated the principal suitability of nanoparticle analysis [18].

However, an examination and evaluation of the correlation between the nanoparticle diameter and the specific peak area is addressed in this work to prove the appropriation of optical calorimetry in sizing nanoparticles. Therefore, the average diameter of various nanoparticles (SiO_2, TiO_2, Al_2O_3, ZnO, WC) has been estimated by using the optical calorimetry and compared to the results of established volumetric physisorption measurements and manufacturer specifications.

2. Material and methods

For the experiments nanoparticles of SiO_2 (AEROSIL®, Evonik), TiO_2 (AEROXIDE®, Evonik), Al_2O_3 (AEROXIDE®, Evonik), ZnO (Evonik) and WC (HC Starck GmbH) are used [19,20].

The specific surface areas are determined by nitrogen physisorption experiments at 77 K using a constant volume adsorption device (BELSORP-max, Bel. Jap. Inc.). The specific surface areas are obtained from the nitrogen physisorption isotherms using the single point BET method (SP-BET) at a relative pressure $p/p_0 = 0.3$ [21].

The optical calorimetric measurement is realized in a single cell setup (*InfraSORP*^{one}) at 299 K and ambient pressure (1 atm). About 5 mg of the sample is filled in the sample holder, weighed and placed in the *InfraSORP*^{one} device. Before starting the measurement, the sample is purged with a nitrogen flow of 242 cm^3/min until a constant temperature is observed. This purging process takes 5–10 min. The measurement is performed by using a gas flow of 70 cm^3/min *n*-butane (Linde Butan 2.5). The measurement of one sample is repeated four times (TiO_2, ZnO, Al_2O_3, WC) and eight times (SiO_2). The peak area A is determined by integration of the thermal response over a linear base line (see Fig. 1b). For the interpretation of the optical calorimetric measurement, the specific peak area A/m (peak area A divided by the sample mass m) is used [K s/mg].

3. Results and discussion

The measured specific surface areas S_{BET} (N_2 physisorption at 77 K, SP-BET $p/p_0 = 0.3$) of the used nanoparticles, the manufacturers tolerances of S_{BET}, the diameters d which are calculated by using Eq. (1) and the diameter tolerances Δd from the manufacture are listed in Table 1.

Except for AEROSIL® 200, the experimentally determined specific surface areas and consequently the diameters of all nanoparticle samples are in a good agreement with the tolerance range which is given by the manufacturer. The deviating values of AEROSIL® 200 are possibly caused by agglomeration of the nanoparticles. However, the deviating surface area does not matter since this article is focused on the validation of optical calorimetry for sizing nanoparticles in terms of obtaining adequate results like common N_2 physisorption experiments.

Recently, the direct correlation between the specific peak area A/m and the specific surface area S_{BET} was demonstrated for microporous materials [15–17]. These results can be transferred for sizing of nanoparticles by using optical calorimetry. As it is visible clearly in Fig. 2a, the plot of A/m versus S_{BET} also results in a linear correlation for nanoparticulate materials. According to Eq. (1), the nanoparticle size is inversely proportional to the specific surface area, thus the reciprocal nanoparticle diameter $1/d$ should correlate directly with the specific peak area A/m of the thermal response. As it is shown in Fig. 2b, a satisfactory linear fit between $1/d$ and A/m (Eq. (2)) is observed, where all data points match the calibration line within their respective limit (horizontal error bars from manufacturer's data (Table 1), vertical error bars from experimental standard deviation of A/m).

$$y = 30.44x - 0.01, \quad R^2 = 0.98 \tag{2}$$

Because all data points fit to the calibration curve, one can assume that the correlation is independent from the surface chemistry and hence the type of material. This fact was also demonstrated in previous publications [15–17] for different porous materials, e.g. activated carbons, metal-organic frameworks and zeolites. Nevertheless, further tests are performed to clarify the influence of hydrophilicity. Therefore, hydrophobic SiO_2 nanoparticles (AEROSIL® R812 and AEROSIL® R974, manufacturer specifications in Table 1) are measured in the optical calorimeter and compared to the even measured hydrophilic AEROSIL® samples

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