A new method to graft titania using Grignard reagents

Supplementary information

Pore Size Distribution

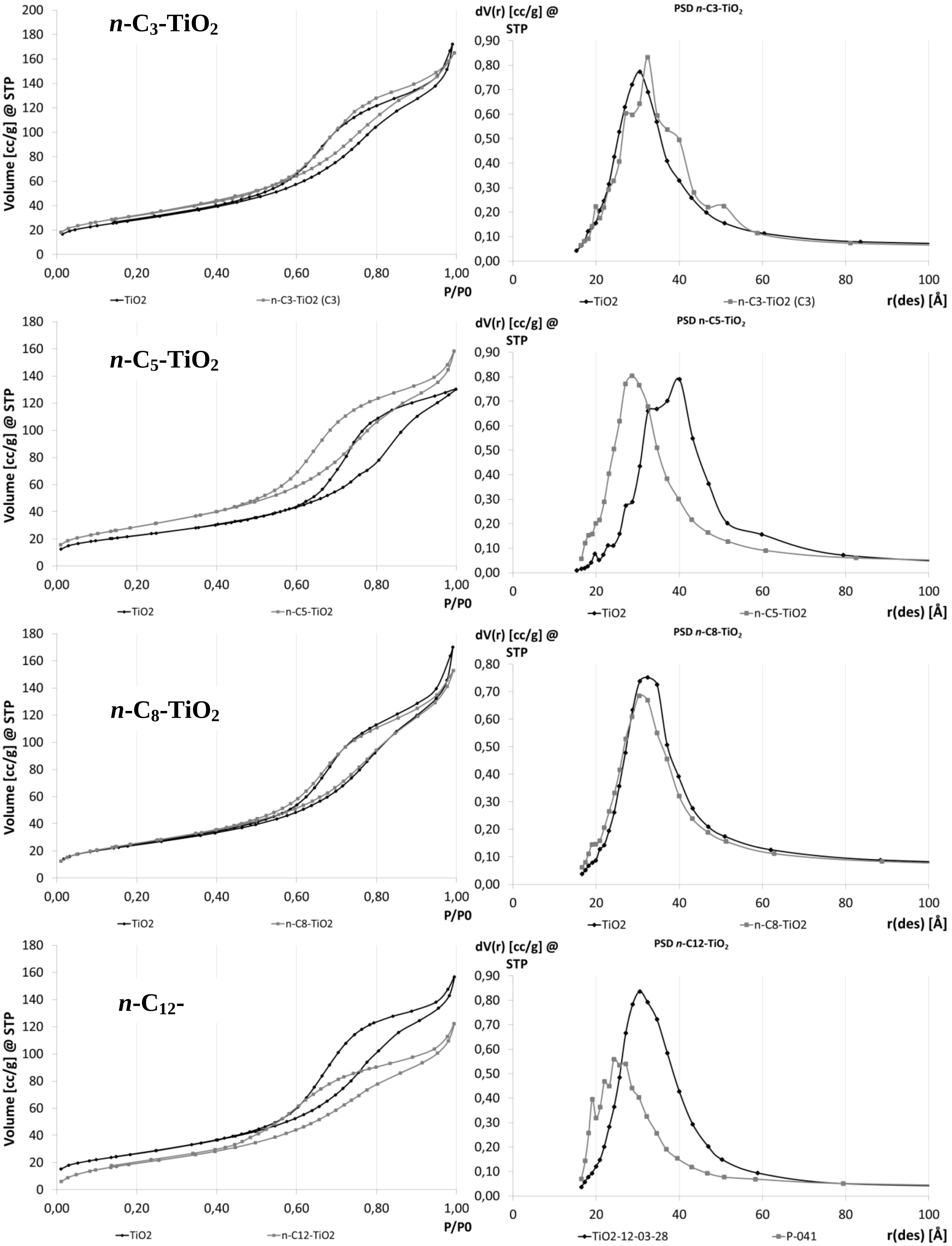

Fig. A1 Pore Size Distribution of *n*-C3-TiO_2, *n*-C5-TiO_2, *n*-C8-TiO2 and *n*-C12-TiO_2

Although there is no straight correlation between chain length and pore size distributions, according these N_2 sorption isotherms and pore size distributions, lower pore sizes of pentyl and dodecyl chains suggest already the presence of a grafted (incomplete) monolayer. Due to the observed submonolayer coverage, there is no formation of a closely packed dense monolayer that causes a vertical alignment effect of the chains to the surface in function of their chain length. However, depending on the chain length, a horizontal (parallel) alignment might occur. Assuming a homogenous distribution at a density of 1group/nm^2 (deduced from TGA Fig. 3), this effect of parallel alignment cannot be present for chains shorter than at least half of the distance where bonded. On the other hand, longer chains like octyl chains can lie down and align parallel at the surface to minimize the surface energy as suggested by the work of Lassiaz et al. for organophosphonate grafted alumina surfaces with a comparable grafting density of 1 group/nm^2 [1]. Therefore, almost no narrowing of the pores can be observed in this pore size distribution as well as the BET surface area. Longer groups (e.g. C12) can also have this effect, but a larger volume of organic material covering the surface, causes the pores to narrow along with a lower BET surface area. Analogue to propyl chains, pentyl chains are too short for this density and doesn't have the tendency to lie down (parallel alignment) but can freely rotate more perpendicular to the surface causing the pore size distribution to narrow. In addition, also the BET surface area can increase. Because no dense monolayer has been formed, N_2 molecules will also undergo lateral interactions with the upright chains causing an enhanced uptake of nitrogen in the low relative pressure range (BET range). As the pentyl chains are too short for the parallel alignment, they are expected to be freely rotating more perpendicular to the surface, allowing for lateral interactions with nitrogen. In contrast, the longer dodecyl chains, are expected to be lying parallel to the surface with explaining the lower BET surface area (table 1) in combination with the narrowed pore size distribution to the volume that is taken by these long chains. For the shortest propyl chains at this density, no visible effect on the pore sizes can be observed because of insufficient organic volume covering the surface. On the other hand, the BET surface area is also slightly higher as expected by the previous described effect.

1. S. Lassiaz, A. Galarneau, P. Trens, D. Labarre, H. Mutin, and D. Brunel, *New Journal of Chemistry*, 2010, **34**, 1424.

Experimental conditions ^{13}C-CP/MAS NMR experiment

Synthesis

For both ^{13}C enriched and natural abundance grafting, 1g of TiO_2 was pre-treated with 60ml methanol under reflux conditions for 2days, then filtered and vacuum dried (<5.10-4mbar) overnight at 60°C. The dried material was grafted by an in situ made Grignard reagent. For this, 0.8ml of respectively $CH_3{}^{13}CH_2Br$ and CH_3CH_2Br was added to 0.4g of fine Mg powder in 40mL dry Et_2O under Argon atmosphere and kept in an ultrasonic bath for 30min. After 4h stirring, 17mL of the Grignard reagent was added to TiO_2 in 40mL dry Et_2O, stirred for 3 days and kept under constant Argon atmosphere. After reaction the samples were washed successively with 3 x 25ml Et_2O, 3 x 25ml of 1M HCl and 3 x 25ml of H_2O. Finally, the samples were vacuum dried again overnight at 60°C.

Measurement conditions

The ^{13}C-CP/MAS NMR experiments were acquired on an Agilent Inova 400 spectrometer (9.4 T wide bore magnet) in 7 mm ceramic Si_3N_4 rotors. Magic angle spinning (MAS) was performed at 5 kHz. The aromatic signal of hexamethylbenzene was used to determine the Hartmann-Hahn condition for cross-polarization (CP) and to calibrate the carbon chemical shift scale (132.1 ppm). Acquisition parameters used were: a spectral width of 50 kHz, a 90° pulse length of 5.0 µs, a spin-lock field for CP of 50 kHz, a contact time for CP of 1 ms, an acquisition time of 25 ms, a recycle delay time of 5 s and 10.000 (^{13}C-labeled product) or 50.000 (non ^{13}C-labeled product) accumulations. High power proton dipolar decoupling during the acquisition time was set to 65 kHz.