

³¹P solid state NMR for the quantitative characterization of TiO₂ nanopowders modified with phosphonic acids

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The reaction mechanism of the reaction between titanium dioxide (P25 TiO₂) nanopowder and phenyl phosphonic acid (PPA) is explored thoroughly and the influence of the reaction conditions on the formed products is presented. This modification can result in grafting of the phosphonic acid at the nanocrystal surface as well as in the formation of titaniumphenylphosphonate lamellar structures. The formation of titaniumphenylphosphonate is favored at increasing reaction temperatures¹. Calcination experiments (at 600 and 1000 °C) elucidated that the presence of amorphous TiO₂² is a crucial factor in the formation of titaniumphosphonate. It was established that in water and at temperatures above 45°C, the dissolution of amorphous TiO₂ leads to the formation of these lamellar structures. This in contrast to the grafting of phosphonic acids at the TiO₂ surface which is independent of the reaction temperature. The grafting mechanism involves the protonation of the surface hydroxyl groups, followed by the nucleophilic attack of the phosphonic acid and simultaneous release of water. The formation of covalent bonds between titanium and the phosphonic group (P-O-Ti bonds) and the amounts of surface grafting and titaniumphosphonate formation are quantitatively determined, using an internal standard, with ³¹P MAS SS-NMR^{3,4}. The broad signal situated at between 0-20 ppm results from the phosphonic acid grafting, while the signal around -8 ppm originates from titaniumphosphonate. TEM images and spin-diffusion path lengths indicate titaniumphosphonate crystal dimensions between 25 and 550 nm depending on the reaction conditions. The results indicate that the amount of PPA involved in titaniumphenylphosphonate crystals increases for higher reaction temperatures while the amount of phosphonic acid grafting remains constant.

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