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Important Reaction Parameters in the Synthesis of Phenylphosphonic Acid Functionalized Titania Particles by Reactive Milling

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Surface functionalized titania particles are obtained using a high energy planetary ball mill. A parameter that is often overseen applying this technique is the grinding bowl and grinding sphere material which has a crucial influence on the energy impact in the milling process. In this paper we describe the influence of the grinding bowl focusing on a zirconia ceramic material and comparing the results with experiments obtained in a WC/Co-hard metal grinding bowl. The degrees of surface coverage as well as tribochemical phase transitions are dependent on the grinding bowl material. Due to the lower density of ZrO_2-ceramic the overall energy input is lower. As a result the surface coverage and amount of phase transition decreased when using a zirconia ceramic grinding bowl instead of WC/Co-hard metal grinding bowl. Lower impurity concentration in the final material was reached due to the better abrasion behavior of the zirconia grinding bowl.

Introduction

Reactive milling is a solvent-free and therefore environmentally friendly alternative to conventional synthetic strategies. For this reason there is increasing interest for several applications.[1, 2] Reactive milling can not only be applied for inert oxide compounds but also for the synthesis of quite sensitive materials, such as metal hydrides. Here small particles show a large efficiency in the uptake and release of hydrogen, as a result these compounds got great attention in the last years for the storage of hydrogen. Ney et al. reported that it is possible to obtain calcium hydride by milling calcium and phenylphosphonic acid under inert atmosphere.[3] Furthermore, reactive milling was already used for the preparation of various alloys and a couple of organic synthesis.[1, 4, 5] Another example for the advantageous use of reactive milling is the synthesis of multicomponent oxides. Due to the strong forces which act in a ball mill the resulting products distinguish themselves through small particle sizes, inconvenient metastable phases and structure defects.[6] Many research fields are very interested in surface-functionalized (nano)particles, because they are important building blocks for various applications for example in material science[7], optics[8], electronics[9] or in the biomedical field[10]. Such materials with tunable properties are in a great demand but their preparation is still very complex. While previously most of those particles were prepared by bottom-up approaches due to the advantages of higher control of morphology and composition of the particles, we showed recently that reactive milling is suitable for the preparation and *in situ* surface functionalisation of inorganic nanoparticles. We

investigated reactive milling processes applying phenylphosphonic acid as additive and titania as inorganic pigment. It was possible to create functionalized particles using a high energy planetary ball mill and a WC/Co-hard metal grinding bowl.[11] In this study we investigate the effect of the grinding bowl on this synthesis route. The goal was to clarify the influence of the grinding bowl on the synthesis and *in situ* surface functionalization of titania with phenylphosphonic acid in a planetary ball mill.

Results and Discussion

Reactive milling was carried out using a high energy planetary ball mill with a ZrO_2-ceramic grinding bowl under varying the hours of milling time and the revolutions per minute (rpm). Titania was used as inorganic pigment and phenylphosphonic acid as surface reactive reagent. Due to the fact that titania has different crystallographic phases which are dependent on the energy put into the system, the ratio between these phases indicates the energy input to the sample during the milling process. The obtained material was thoroughly washed before it was characterized applying various techniques focusing on changes in the composition depending on the reaction parameters. FTIR-analysis showed that the phenylphosphonic acid was attached to the surface of the titania. Instead to the starting material, which reveals no absorption in the typical region for organic melecules, the samples after the milling process display such characteristic bands. There are typical bands for the aromatic C-C oscillation (1600 cm^{-1}) and the aromatic C-H deformation (3050 cm^{-1}) as well as the C-H (1440 cm^{-1}), P-phenyl(1150 cm^{-1}) and the P-O (1000 cm^{-1}) vibration. The covalent binding of the phenylphosphonic acid

to the surface of the titania particles is indicated by the broad band at approximately 1000 cm⁻¹. The different bonding types e. g. bi- and tridentate of the phenylphosphonic acid on the titania are responsible for the width of this band.[12] The different process parameters yield in a variation of the intensity of the bands (Figure 1). These results show that the synthesis of particles with *in situ* surface modification occurs not only using a WC/Co grinding bowl but also by using a ZrO$_2$ grinding bowl.
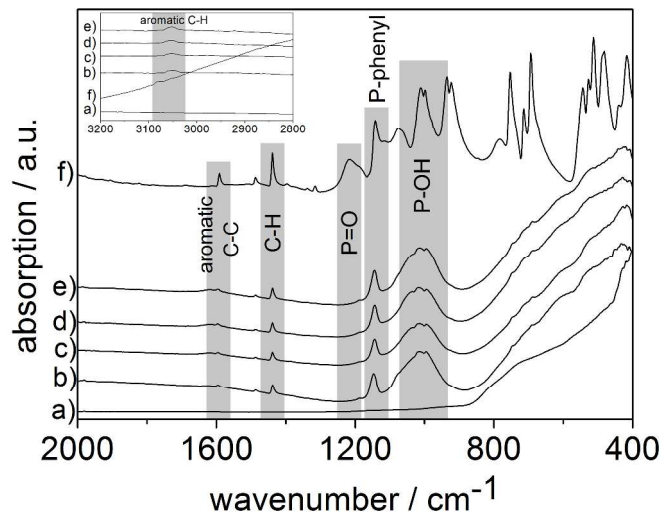

Figure 1: FTIR-spectra: a) starting material titania, f) coupling agent phenylphosphonic acid and samples after the milling process: b) 300 rpm / 12 h, c) 300 rpm / 24 h, d) 300 rpm / 36 h, e) 300 rpm / 48 h; surface modification has taken place after the milling process, which is indicated by the characteristic bands for aromatic C-C oscillation (1600 cm⁻¹), the C-H oscillation (1440 cm⁻¹), P-phenyl vibrations (1150 cm⁻¹), the wide band at 1000 cm⁻¹ (P-O region) and the aromatic C-H oscillation at 3050 cm⁻¹.

Beside the proof that organophosphorous coupling agent was attached to the surface it is important to determine the amount of surface coverage using thermal (TGA) and elemental (CHN) analysis. These methods were applied to the obtained products and the results were associated with the milling time and the rotational speed (Figure 2). With increasing values both parameters are expected to decrease the particle size as well as the number of defects on the particle surface which is accompanied by an increase of surface coverage, which was observed for the treated samples. It is noticeable that there is only a small difference between milling times of 12 h or 24 h at 200 rpm. Apart from that the increase of surface coverage correlates almost linear with milling time a. CHN analysis generally results in a slightly higher amount of surface coverage than TGA analysis which is due to experimental errors of both methods. Comparing these achievements to the outcome resulting from the experiments with the WC/Co-hard metal grinding bowl it becomes apparent that in case of using the ZrO$_2$-ceramic grinding bowl the overall surface coverage is lower. The reason for this is the difference in the density of the material of the grinding bowl. Due to the lower density of the ZrO$_2$-ceramic in comparison to the WC/Co-hard metal the overall energy input during the milling process is lower. On the average it is possible to achieve approximately 0.2 mmol per gram more surface modification with the WC/Co grinding bowl than with the ZrO$_2$ grinding bowl.
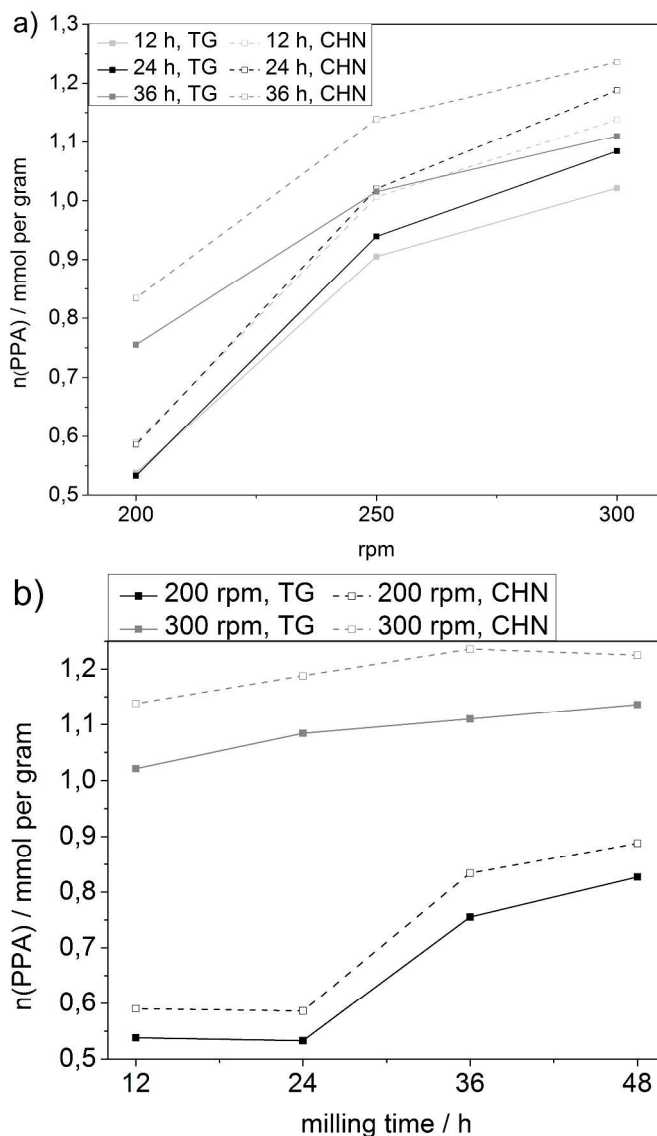

Figure 2: Surface modification in dependence of a) the rpm or b) the milling time, results calculated fom TGA analyses (straight line) and from CHN analyses (dashed line).

The so far applied characterization methods indicate that a surface modification has taken place during the milling process. Beside this fact and the information on the amount of surface coverage it would be interesting to know in which way the phenylphosphonic acid has bound on the surface of the titania. For this reason solid state NMR spectroscopy was performed. The results reveal that covalent bonding occurs. Pure phenylphosphonic acid shows a signal at $\delta = 21.8$ ppm in the solid state ^{31}P NMR spectrum. ^{31}P solid state NMR spectra of the samples after the milling process show a broad signal between $\delta = 0$ ppm and $\delta = 16$ ppm (supporting information S8 – S10) which is characteristic for covalent bonding of phosphonic acid on the surface.[13] The. The ^{13}C-solid state NMR spectra of the samples after the milling process show overlapping signals between $\delta = 121$ ppm and $\delta = 125$ ppm which indicates that a phenyl ring is present.

X-ray powder diffraction show that the milling process was accompanied by a tribochemical phase transition which occurs from the starting material anatase to the thermodynamically more stable rutile and a high pressure modification of titania (Figure 3). The difference between rutile and the high pressure titania appear in the orientation of the vertex-connected TiO_6-octrahedra along the c-axis. In case of the rutile phase they form straight lines but in case of high pressure titania they build zigzag chains. Such a phase formation was observed when using the WC/Co grinding bowl as well. In both cases the reflections for high pressure TiO_2 ($2\theta = 31°$, $42°$and $66°$) and rutile ($2\theta = 27°$) becomes more intensive when the milling time or the rotational speed are enhanced.

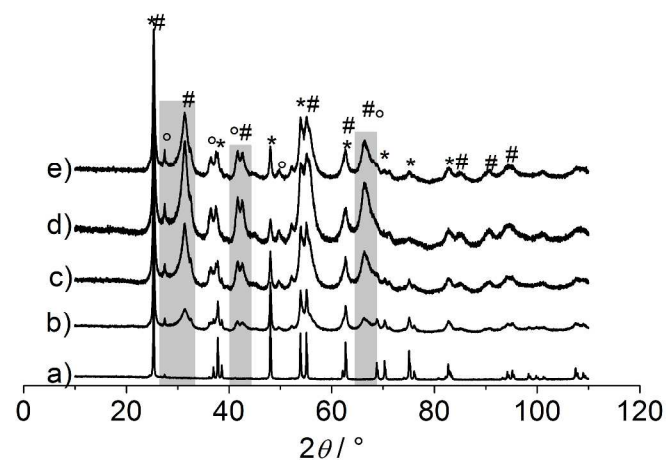

Figure 3: XRD patterns of a) the starting material anatase (*) and some samples after the milling process titania with phenylphosphonic acid: b) 300 rpm / 12 h, c) 300 rpm / 24 h, d) 300 rpm / 36 h, e) 300 rpm / 48 h. The selection indicates the main differences in the reflections: The presence of high pressure TiO_2 (#) ($2\theta = 31°$, 42° and 66°) and rutile (°) ($2\theta = 27°$) is indicated by additional reflections.

In addition to the qualitatively visible change in the reflection intensity a quantitative Rietveld phase analysis was performed. The presence of an amorphous phase cannot be excluded but the development of the background gives no evidence for it. In case that an amorphous phase is present its proportion is estimated to be less than 5%. The summarized results are presented in Figure 4 and some results are listed in Table 1. These results confirm the assumption established based on the reflection intensity which revealed that there is increase in the amount of rutile and high pressure TiO_2 in the samples with increasing milling time and rpm.

Table 1: Titania milled with phenylphosphonic acid, phase composition of some selected samples

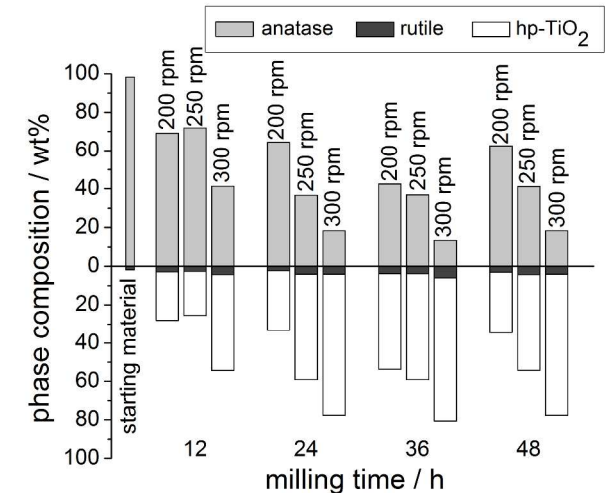| Process parameter	Anatase / wt%	Rutile / wt%	hp-TiO$_2$ / wt%
0 h / 0 rpm	98.2 ± 0.1	1.8 ± 0.1	0
12 h / 200 rpm	69.1 ± 0.2	2.9 ± 0.1	28.0 ± 0.2
48 h / 200 rpm	62.4 ± 0.2	3.0 ± 0.1	34.6 ± 0.2
12 h / 300 rpm	41.3 ± 0.2	4.3 ± 0.2	54.4 ± 0.2
48 h / 300 rpm	18.3 ± 0.2	4.1 ± 0.1	77.6 ± 0.2

Figure 4: Titania milled with phenylphosphonic acid: Phase composition of the samples after the milling process determined by X-ray powder diffraction. Phase composition occurs from the starting material anatase to rutile and high pressure (hp) TiO_2.

Comparing these results with the findings of the WC/Co grinding bowl it is apparent that there is less phase transition during the milling process in the ZrO_2 grinding bowl. This confirms the assumption that the overall energy input into the system is lower if a ZrO_2 grinding bowl is used (Table 2).

Table 2: Overall phase transition of titania particles milled with phenylphosphonic acid at various process parameters in different grinding bowls

	WC/Co-hard metal grinding bowl	ZrO$_2$-ceramic grinding bowl
Process parameters	anatase / wt%	anatase / wt%
12 h / 200 rpm	73.0 ± 0.2	69.1 ± 0.2
48 h / 200 rpm	49.3 ± 0.2	62.4 ± 0.2
12 h / 300 rpm	32.6 ± 0.3	41.3 ± 0.2
48 h / 300 rpm	7.6 ± 0.1	18.3 ± 0.2

The influence of the coupling agent on the tribochemical phase transition was discovered by milling titania without any addition. Some results are listed in Table 3 and Figure 5 gives an overview on all results.

Table 3: Titania milled without any additives, phase composition of some selected samples

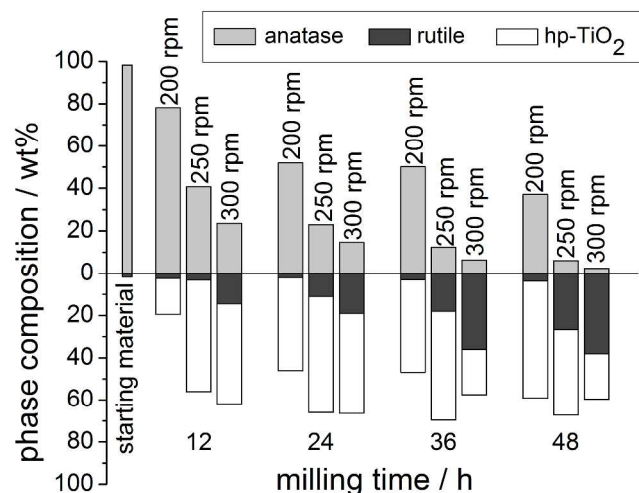| Process parameter	Anatase / wt%	Rutile / wt%	hp-TiO$_2$ / wt%
0 h / 0 rpm	98.2 ± 0.1	1.8 ± 0.1	0
12 h / 200 rpm	78.1 ± 0.3	2.4 ± 0.2	19.5 ± 0.3
48 h / 200 rpm	37.1 ± 0.4	3.8 ± 0.2	59.1 ± 0.4
12 h / 300 rpm	23.6 ± 0.2	14.5 ± 0.4	61.9 ± 0.4
48 h / 300 rpm	2.4 ± 0.1	38.0 ± 0.6	59.6 ± 0.6

Figure 5: Titania milled without any additives: Phase composition of the samples after the milling process determined by X-ray powder diffraction. Phase composition occurs from the starting material anatase to rutile and high pressure (hp) TiO$_2$.

It turned out that the phase transition behaves differently when titania was milled without an additive. In case of milling titania without the addition of the coupling agent phenylphosphonic acid the overall phase transition is higher and more rutile is generated. This behavior was also found when the experiments were performed in the WC/Co grinding bowl. Hence, the phenylphosphonic acid inhibits the phase transformation of anatase; a reason for this could be that anatase becomes more stable against phase transition due to the surface modification. Concurrently the phenylphosphonic acid enhances the formation of high pressure TiO$_2$ which could be explained by the assumption that the phenylphosphonic acid favors the surface of the high pressure titania for functionalization which consequently stabilizes this modification in comparison to rutile. Also in case of milling titania without any additive the overall phase transition is higher when milling in a WC/Co than in a ZrO$_2$ grinding bowl (Table 4).

Table 4: Overall phase transition of titania particles milled without any additive at various process parameters in different grinding bowls

	WC/Co-hard metal grinding bowl	ZrO$_2$-ceramic grinding bowl
process parameters	anatase / wt%	anatase / wt%
12 h / 200 rpm	39.8 ± 0.3	78.1 ± 0.3
48 h / 200 rpm	31.3 ± 0.3	37.1 ± 0.4
12 h / 300 rpm	6.1 ± 0.1	23.6 ± 0.2
48 h / 300 rpm	4.2 ± 0.1	2.4 ± 0.1

An important characteristic of the obtained samples beside the surface functionalization and phase transition are the crystallite as well as the particle sizes. The crystallite sizes were derived from XRD pattern applying the Pawley method. The results show that the milling process yields in a slightly decrease of the crystallite size. As

starting material granular crystalline anatase with crystallite sizes above 300 nm was used. In contrast the resulting high pressure TiO$_2$ has sizes around 5 nm to 6 nm. The residual anatase phase remains in the granular crystalline dimension, there is only a reduction of about 100 nm compared to the starting material. The milling time and the rotational speed mostly influence the phase transition but not the particle size. Independent of these parameters the resulting high pressure TiO$_2$ is nano crystalline but the residual anatase remains granular crystalline. SEM images of the obtained powders show that the samples are not uniformly shaped and agglomerated (Figure 6). Particle sizes are in a range of 100 nm to 300 nm and decreases with increasing milling time.
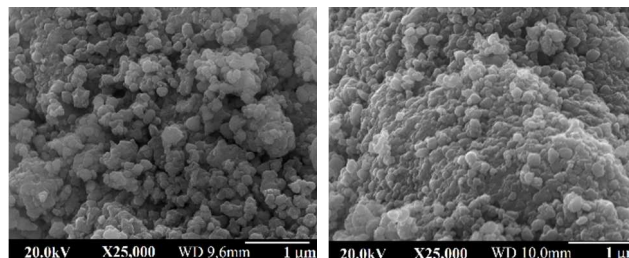

Figure 6: SEM images of two selected samples: titania milled with phenylphosphonic acid at 300 rpm for 12 h (left) and for 48 h (right). Both samples are agglomerated and not uniformly shaped, the size of the particles decreases with increasing milling time.

The radius of the particles was determined by dynamic light scattering (DLS) (Figure 7 and Figure 8). The surface functionalized particles can be directly dispersed in cyclohexane by the exposition of ultrasound for 30 minutes. The starting material and the unmodified samples can be dispersed in water. The starting material has sizes of 500 nm or larger but it is apparent that after the milling process there is a significant reduction of the particle size. The samples after the milling process exhibit two distinctly sized particle fractions which is in accord to the results of XRD that there are different phases of titania. Firstly there are particles with sizes about 400 nm and secondly there are some which show sizes around 140 nm (300 rpm, 48 h) and 200 nm (200 rpm and 12 h). In case of milling titania without any additive the reduction of the particle size due to the milling process is advanced. There are two different fractions as well but the smaller one show sizes about 110 nm and 160 nm. In addition the fraction with particle sizes around 400 nm is smaller.
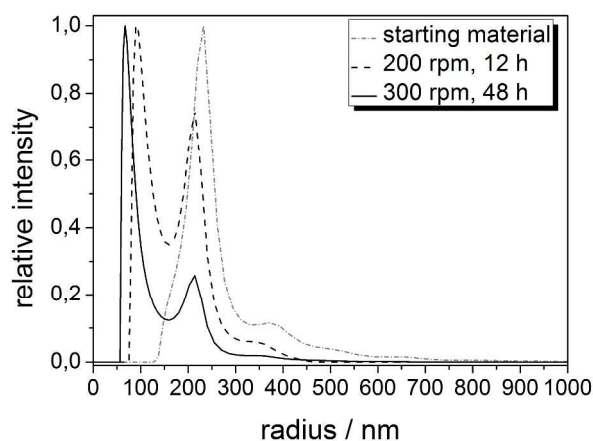
Figure 7: Particle size determination by dynamic light scattering, titania milled with phenylphosphonic acid. The starting material was dispersed in water while the functionalized particles were dispersed in cyclohexane, both by the exposition to ultrasound for 30 minutes. Particle size decreases slightly with increasing milling time and increasing rpm.
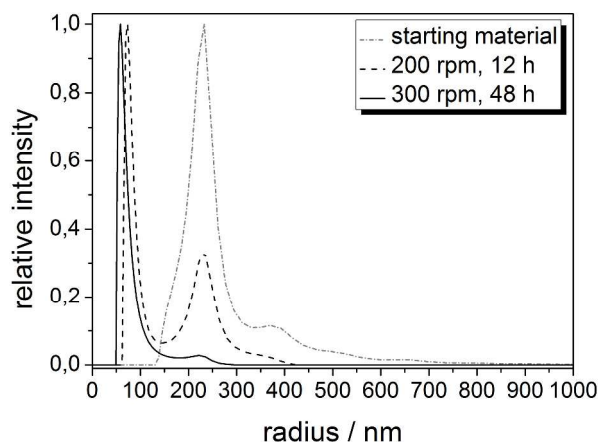

Figure 8: Particle size determination by dynamic light scattering, titania milled without any additive. All samples were dispersed in water by the exposition to ultrasound for 30 minutes. Particle size decreases slightly with increasing milling time and increasing rpm.

The contamination of the samples due to abrasion of the grinding bowl was analyzed by applying X-ray fluorescence spectroscopy (Figure 9). As expected there is more contamination with increasing milling time and rotational speed. Compared to the results obtained by using the WC/Co grinding bowl the impurities are smaller. In case of the WC/Co grinding bowl impurities of 0.05 wt/% up to 0.28 wt/% tungsten were found. Milling in the ZrO_2 grinding bowl results in impurities between only 0.03 wt/% and 0.15 wt/% Zr.
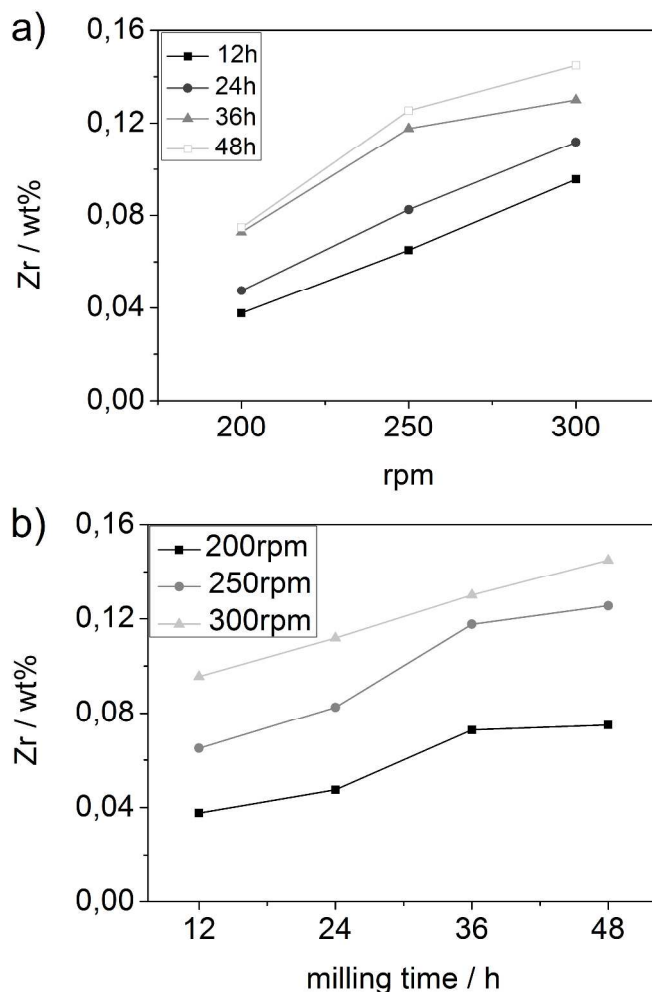

Figure 9: Impurities by the grinding bowl according to a) the rpm or b) the milling time determined by X-ray fluorescence spectroscopy, titania milled with the coupling agent.

Whereas the starting materials TiO_2 and PPA are white the samples after the milling process show a grey discoloration which becomes more intensive with increasing milling time and speed (Figure 10). This discoloration was observed as well when a WC/Co-hard metal grinding bowl was used. We assumed that this discoloration has its origin in impurities due to the abrasion of the grinding bowl which is likely to be grey in case of tungsten. The experiments with the zirconia grinding bowl results in a grey discoloration as well. Here it is unlikely that the zirconia impurities lead to a grey discoloration because it is white as well. An explanation for the change in color beside the contamination with impurities could be the presence of subvalent Ti species which could be formed during the milling process due to reduction of Ti^{4+} to Ti^{3+}. To clarify the reason for this aspect electron paramagnetic resonance was applied. The results confirm the presence of Ti^{3+} in the samples where titania was milled with a coupling agent. These samples show the characteristic ESR signal for Ti^{3+}.[14] In case of milling titania without any additive there was no signal associated with Ti^{3+} (supporting information S11). In this case the grey discoloration has its origin in the contamination with tungsten if a WC/Co-grinding bowl was used. When a zirconia grinding bowl was used the samples milled without any additive show nearly no discoloration (Figure 11). Consequently, in case of using a WC/Co-hard metal grinding

bowl the grey discoloration has two origins. On the one hand the impurities due to abrasion and on the other hand the presence of subvalent Ti species which lead to a darkening of the samples. When a zirconia grinding bowl is used the grey discoloration is attributed only to the presence of subvalent Ti ions. The presence of Ti^{3+} is only appropriate in case of milling titania with a coupling agent because it act as a reducing agent as well.
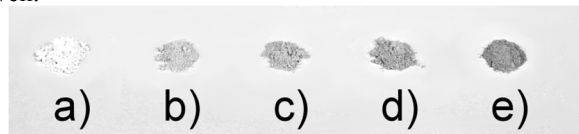

Figure 10: Images of some selected samples titania milled with the coupling agnet: a) TiO_2 b) 200 rpm / 12 h c) 200 rpm / 48 h d) 300 rpm / 12 h e) 300 rpm / 48 h The contamination due to abrasion of the grinding bowl is visible to the naked eye. With increasing revolutions per minute as well as increasing milling time the samples show an increasing grey discoloration.
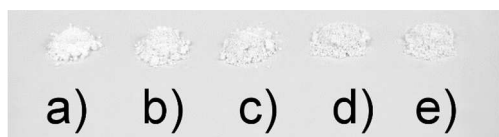

Figure 11: Images of some selected samples titania milled without any additive: a) TiO_2 b) 200 rpm / 12 h c) 200 rpm / 48 h d) 300 rpm / 12 h e) 300 rpm / 48 h

Conclusions

In summary, reactive milling exhibits to be a promising environmental friendly technique for the synthesis of particles with *in situ* surface functionalization. The systematic study on the influence of the different process parameters show that increasing milling time and increasing rotational speed results in an increasing degree of surface modification as well as an increasing phase transition of the starting material anatase to rutile and high pressure TiO_2. This observed tribochemical phase transition is not only dependent on the rpm and the milling time but also on the presence of the coupling agent. In this work we illustrate that the grinding bowl has an influence of the milling result as well. Compared to previous studies where a WC/Co hard metal grinding bowl was used it turned out that the overall phase transition is lower and there is less surface modification by using a ZrO_2 ceramic grinding bowl. Another difference is the contamination caused by the abrasion of the grinding bowl. These impurities are lower when a ZrO_2 grinding bowl is used.

Experimental Section
Materials
Titanium(IV)-oxide powder anatase (99.8%) and phenylphosphonic acid (98%) were purchased from Sigma Aldrich (Steinheim, Germany). All chemicals have been used without further purification.

Instruments and Characterization
FT-IR measurements were performed under ambient air (40 scans at a resolution of 4 cm^{-1}) in attenuated total reflectance (ATR) mode on a Bruker Vertex 70 spectrometer. X-ray powder diffraction was carried out on two different diffractometers a Panalytical X´Pert and a Bruker D8 Advance-system, Bragg-Brentano geometry and CuKα

radiation was used in both cases. The quantitatively analysis was carried out by the Rietveld-method using the program TOPAS[15] and crystallographic data for the modifications of titania (anatase[16], rutile[17], high pressure TiO_2[18]). The same program package was used for the determination of the crystallite sizes applying the Pawley-method. X-ray fluorescence spectroscopy measurements were performed on an Eagle EDAX and EDAX II instrument. Thermogravimetric analysis (TGA) was carried out on a Netzsch Iris TG 209. The sample was placed in an alumina crucible which was then heated from room temperature to 700 °C under nitrogen atmosphere followed by heating to 800 °C under oxygen atmosphere with a rate of 20 K min^{-1}. The mass loss during the thermal analysis was used to calculate the amount of coupling agent on the surface of the titania particles. Here one has to consider that the residue is not only titania because the phosphonate groups are oxidized to phosphonate which remains on the surface of the particles. Equation 1 gives the molar amount of coupling agent per gram particles.

$$c_{CA} = \frac{\Delta m \cdot 10}{M_{\Delta m}} \qquad (1)$$

c_{CA}: molar concentration of coupling agent per gram [mmol g^{-1}]
Δm: mass loss during thermal analysis [%]
$M_{\Delta m}$: molar mass of the molecule which leave during thermal analysis [g mol^{-1}]

Elemental analysis was carried out on a Leco CHN-900 analyzer. The amount of coupling agent on the surface of the titania particles was calculated by using the percentage of carbon from elemental analysis. The molar amount of coupling agent per gram of particles can be calculated by using Equation 2.

$$c_{CA} = \frac{m_C \cdot 10}{M_C \cdot N_C} \qquad (2)$$

c_{CA}: molar concentration of coupling agent per gram [mmol g^{-1}]
m_C: mass of carbon from elemental analysis [%]
M_C: molar mass of carbon [g mol^{-1}]
N_C: number of carbon atoms per coupling agent

Solid state NMR spectroscopy was carried out on a Bruker Avance DPX 300 instrument equipped with a 4 mm broad band cross-polarization Magic Angle Spinning probe head operating at 75.40 MHz for ^{13}C and 121.39 MHz for ^{31}P. The spinning rate was 3976 Hz for ^{13}C spectra and 2040 Hz for ^{31}P spectra. Scanning electron microscopy (SEM) images were recorded on a JEOL SEM-7000 microscope. The SEM samples were prepared by placing some grains on a specimen stub with attached carbon adhesive foil followed by deposition of a gold layer. Dynamic light scattering (DLS) measurements were carried out on an ALV/CGS-3 compact goniometer system with an ALV/LSE-5003 multiple τ correlator at a wavelength of 632.8 nm (He-Ne Laser) and at a 90° goniometer angle. The particle radius was then determined by the analysis of the correlation-function via the g2(t) method followed by a logarithmic number-weighting (n.w.) of the distribution function.

Synthesis
The following experiments were performed in a high energy planetary ball mill Retsch PM 100. The material of the grinding

bowl was a ZrO_2-ceramic. We used a 50 mL grinding bowl and 200 corresponding milling balls with a diameter of 5 mm. Systematic studies on the effect of the milling time and the rpm on the result of the milling process were carried out. The milling time was varied between 12 h and 48 h and the rpm had values of 200 rpm, 250 rpm and 300 rpm.

In each case 4 g of titana (anatase) and 1 g of the respective coupling agent (phenylphosphonic acid) were placed in the grinding bowl and milled at specific parameters.

After the milling process the product was washed with ethanol (three times) and distilled water (three times). Finally, the functionalized particles were separated by centrifugation (13000 rpm) and dried at 100°C.

Acknowledgements

Notes and references

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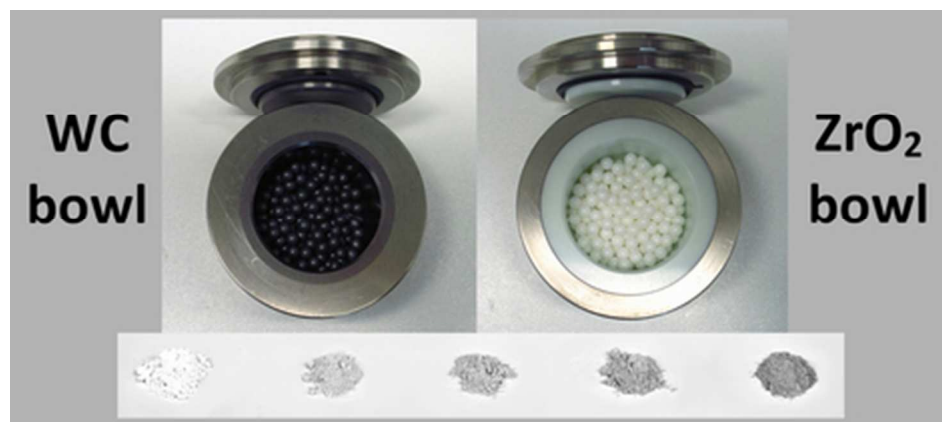http://www.uni-saarland.de/lehrstuhl/kickelbick.html

† Supporting Information contains IR spectra and XRD patterns of all samples, tables summarizing the phase composition of all samples and solid state NMR as well as ESR spectra.

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