High-temperature growth of anatase on kaolinite substrate

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When a fine fraction of kaolinite (less than 2 μm) is mixed with titanyl sulphate (weight ratio approx. 1:7), hydrolysed, washed, dried and heated to temperatures between 750 and 900°C, it transforms into metakaolin, and titania crystallizes as anatase with a small particle size (approx. 20–30 nm). In parallel experiments with plain titania (without kaolinite), rutile is the sole product phase at 850 and 900°C and the dominant phase in a mixture with anatase at 750°C. The particle sizes are much larger (approx. 400–1100 nm). It appears that kaolinite is instrumental in preserving titania in the anatase form and with a small particle size even at fairly high temperatures and hindering its transformation to rutile. However, this anatase exhibits poor photocatalytic activity.

Keywords: TiO2; kaolinite; metastability; photocatalytic activity; X-ray powder diffraction

1. Introduction

Titania has recently received considerable attention as a nanocrystalline material with a multitude of applications ranging from photocatalysis all the way to medicinal uses (e.g. Stir et al. 2006). A related research direction is using titania for pillaring clay minerals in order to open up their interlayer spaces and thus increase their surface area (Yamanaka et al. 1987). The growth of composites of titania with clay minerals for the purpose of photocatalytic performance is another frequent research topic (e.g. Valášková et al. 2006; Belessi et al. 2007).

Among the known modifications of TiO2, only rutile and the high-pressure form TiO2-II are believed to have fields of stability in the classic thermodynamic sense (DeVries & Roy 1954; Lindsley 1976), whereas anatase and brookite are considered to be metastable. Their behaviour with each other and with rutile may be viewed as a matter of kinetics rather than equilibrium. An alternative approach is to treat their behaviour as a function of particle size, thereby adding one more dimension to the phase diagram (Mayo et al. 2003). Consequently, all researchers dealing with titania should also pay attention to the phase relations.

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The present study was performed within a programme aimed at narrowing the conditions for synthesizing anatase with optimum photocatalytic properties. In this paper, we report the results of a study of anatase grown in a mixture with natural kaolinite.

2. Experimental

Kaolinite from the now abandoned classic deposit at Sedlec (Zettelitz) near Karlovy Vary, Czech Republic, was finely ground under acetone in a ball mill. The less than 2 μm fraction was obtained by sedimentation from an aqueous suspension and checked by X-ray diffraction. This fraction was mixed with titanyl sulphate (TiOSO₄, manufactured by Precheza a.s., Czech Republic) in the weight ratio of approximately 1:7, and the resulting suspension was hydrolysed in distilled water. The supernatant liquid was removed by centrifugation (3000 rpm, 30 min), which was followed by five cycles of washing in deionized water and a final centrifugation. The washed material was dried for several hours at 60°C. In a set of reference experiments, pure TiO₂ was prepared from TiOSO₄ by the same process.

Products prepared in these two sets of experiments were divided into batches that were annealed at, respectively, 750, 850 and 900°C, for 60 min each. The corresponding samples are referred to as a750, a850 and a900 (kaolinite plus titania) and s750, s850 and s900 (titania only). The temperatures and the time of annealing were chosen so that kaolinite would already be converted to metakaolin, but the formation of the spinel phase would not have started yet (McConville et al. 1998). Unfortunately, the quantities of products grown in experiments a750–a900 did not suffice for the measurements of the photocatalytic effect, so larger quantities using the same starting materials were grown in analogous experiments aa750–aa900 performed under the same conditions as a750–a900. The only difference was Riedel de-Haën’s titanyl sulphate that was used as the source of Ti.

As a standard in structure refinements, we used anatase manufactured at Precheza in the 1970s, ground to a grain size of approximately 5 μm. This material is labelled TiO₂-5. The anatase standard used in evaluating the photocatalytic effect was obtained from BDH Ltd., Dorset, UK.

X-ray data were recorded using CoKα radiation (40 kV, 30 mA) on a Bruker D8 powder diffractometer equipped with a diffracted-beam graphite monochromator. Each sample was gently crushed in ethanol, and the suspension was poured on a silicon wafer and allowed to dry. The data were collected in the range 27.0–148.0° 2θ, with a step size of 0.02° 2θ and an exposure time of 8 s per step. Additional scans in the range 13.0–25.0° 2θ were recorded to check for the possible presence of kaolinite or other phyllosilicates.

For the calculation of particle size, the diffractometer was calibrated with Si and LaB₆ standards. The peaks were α₂-stripped using program RACHRACH that employs the technique of Ladell et al. (1975), and the full width at half maximum (FWHM) of the profiles was determined using the Origin’s Peak Fitting Module (Origin Scientific Graphing and Analysis Software 2003); the best fit was obtained for the pseudo-Voigt function type 2. The FWHM for the Si and LaB₆ standards is at least a second-order function of 2θ, but in
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the angular range of interest, it can be faithfully approximated with a linear regression $\text{FWHM} = 0.000128 \times (2\theta) + 0.103$. For the specimens studied, we used the Scherrer equation and followed the procedure outlined by Allmann (1994).

The Rietveld refinement calculations were performed with program GSAS (Larson & Von Dreele 1994). The input data were treated with the program KORHLA that includes smoothing with equal-weight nine-point parabolas and a correction for what can be termed ‘instrument function’ based on a calibration of the diffractometer with Si and LaB₆. The profile function used was a pseudo-Voigt with Stephens’ (1999) model for peak broadening, which yields Gaussian and Lorentzian contributions. The programs KORHLA and RACHRACH (Fortran) were written by one of the authors (M.R.) for this and related applications.

Transmission electron microscopy (TEM) was carried out on a JEOL JEM 3010 microscope operated at 300 kV (LaB₆ cathode, point resolution 1.7 Å) with an energy dispersive X-ray detector attached. Images were recorded on a charge-coupled device camera with a resolution of 1024 × 1024 pixels using the Digital Micrograph software package. Powder samples for TEM work were dispersed in ethanol, and the suspension was treated in ultrasound for 10 min. A drop of a very dilute suspension was placed on a carbon-coated copper grid and allowed to dry at ambient temperature.

To evaluate the photocatalytic activity of the samples, the kinetics of 4-chlorophenol (4-CP) decay were measured. Laboratory irradiation experiments were performed in a photoreactor (Lukác et al. 2007). The aqueous suspension (60 ml) containing 4-CP (0.14 mM) with 60 mg of the studied sample was kept in darkness for approximately 1 h to achieve adsorption equilibrium, and irradiated thereafter. Probes of irradiated suspension (1 ml) were drawn off at desired irradiation times and analysed by high performance liquid chromatography (HPLC), employing filtration by a Millipore syringe adapter with filter #408, which has a 0.45 mm porosity. The HPLC experiments were run on a Merck device with a L-6200 Intelligent Pump, L-3000 Photo Diode Array Detector and D-2500 Chromato-Integrator. Mobile phase methanol/water (2:3, v/v) and a Merck column LiChro-CART 125-4 filled with LiChrosphere 100 RP-18 (5 mm) were used. The injection loop was 20 ml, the flow rate was 1 ml min⁻¹, and a detection wavelength of 280 nm was applied.

3. Results and discussion

All X-ray patterns recorded contain only peaks of anatase (a750, a850, a900, s750, TiO2-5) and rutile (s750, s850, s900). No peaks of kaolinite were detected and no other impurities were identified (figure 1). This is in agreement with the reported decomposition of kaolinite by heating for several hours at 550°C (Brindley & Brown 1980; McConville et al. 1998). It has long been known (Grim & Bradley 1948; Grim 1953) that the loss of OH in well-crystallized kaolinite is accompanied by a ‘fairly complete loss of structure’. The corresponding dynamic thermal analysis peak lies at about 600°C, which is below the temperatures used in our experiments.

However, under the TEM, relics of metakaolin can be observed in all samples (a750, a850, a900), and they yield good quality electron-diffraction patterns that do not betray defects such as bending of flakes. Figure 2a shows micrometre-size
metakaolin crystals covered with nanocrystals of anatase. The corresponding
diffraction pattern (figure 2b) is a combination of a spot pattern originating
from a single crystal of metakaolin and a ring pattern originating from anatase
nanocrystals.

The summary of X-ray results appears in table 1. Usual quality Rietveld
refinements were obtained for anatase standard TiO$_2$-5 and anatase s750 as well
as for rutile from experiments s750, s850 and s900. Each of these structures has
one refineable atomic parameter, but in addition to unit-cell data and the usual
general and instrumental parameters, the calculations also yielded anisotropic
displacement factors, a March-Dollase preferred orientation coefficient, and the
effective $\alpha_2/\alpha_1$ wavelength ratio. Also, a two-term correction for surface roughness
(Pitschke et al. 1993) improved the fit. The $R_{\text{calc}}$ values for these refinements vary
between 6.7 and 8.9 per cent. The results agree well with recent entries in the
ICSD database.

On the contrary, the number of variables refined for anatase from experiments
a750, a850 and a900 is limited. Among the potentially important variables that
could be refined are unit-cell parameters, but they show no systematic variation
with temperature or particle size. Also, they do not differ from those obtained
in experiments without the presence of kaolinite. Only isotropic displacement
factors could be calculated, the $\alpha_2/\alpha_1$ ratio could not be varied (was kept constant
at 0.535), and attempts to calculate surface roughness resulted in divergence.
The $R_{\text{calc}}$ values are correspondingly poor (27–34%).
Figure 2. TEM observations on sample a850. (a) Low-magnification image showing anatase nanocrystals (small black grains) grown on metakaolin (medium grey; scale bar, 0.5 μm), (b) Electron diffraction from the particle shown in (a). Sharp diffraction spots correspond to metakaolin (along the [001] direction), the rings are due to anatase. (c) High-resolution image of several anatase nanocrystals on metakaolin crystals viewed along the [001] direction of metakaolin (‘face-on’). The approximately SW-NE lattice fringes on metakaolin correspond to a periodicity of approximately 4.46 Å (scale bar, 10 nm). (d) High-resolution image of anatase nanocrystals grown on metakaolin, viewed in a section perpendicular to the layers of metakaolin (‘edge-on’). A Fourier transform of the metakaolin indicates a periodicity of approximately 10.05 Å. Note that between metakaolin and anatase, there is an amorphous layer fringing metakaolin particles (scale bar, 10 nm).

Nonetheless, all data obtained agree with an internally consistent picture. The FWHM correlates strongly not only with the Gaussian (GP, $r = 0.98$) and Lorentzian (LX, $r = 0.98$) components of the profile, but, interestingly, also with the ratio $\frac{\text{GP}}{\text{GP} + \text{LX}}$ ($r = 0.91$). The peaks are rather broad for anatase from experiments a750 and a850 and less so for anatase grown at a higher temperature (a900). In contrast, titanium dioxide grown without the presence of kaolinite (s750) has considerably narrower peaks, reflecting a better crystallinity. Even narrower peaks are observed in anatase standard (TiO$_2$-5) and in all rutile samples (s750, s850 and s900).

High-resolution images (figure 2c,d) show anatase nanocrystals grown on the surface of a metakaolin single crystal. It is interesting to note that the anatase crystals, around 20 nm in size, do not lie directly on the surface of the metakaolin crystal but appear to be separated by an amorphous layer (figure 2d).
Table 1. Rietveld refinements of anatase and rutile accompanied by FWHM obtained by profile fitting and particle size obtained from the Scherrer equation. (Parenthesized estimated standard errors are given in units of the last decimal place. Values without errors were not varied in the final cycles or were not varied at all.)

<table>
<thead>
<tr>
<th>sample</th>
<th>TiO$_2$</th>
<th>a750</th>
<th>a850</th>
<th>a900</th>
<th>s750</th>
<th>s850</th>
<th>s900</th>
</tr>
</thead>
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<tr>
<td>phase</td>
<td>anatase</td>
<td>anatase</td>
<td>anatase</td>
<td>anatase</td>
<td>anatase</td>
<td>rutile</td>
<td>rutile</td>
</tr>
<tr>
<td>space group</td>
<td>$I4_1$/amd</td>
<td>$I4_1$/amd</td>
<td>$I4_1$/amd</td>
<td>$I4_1$/amd</td>
<td>$I4_1$/amd</td>
<td>$P4_2mm$</td>
<td>$P4_2mm$</td>
</tr>
<tr>
<td>a (Å)</td>
<td>3.78476 (4)</td>
<td>3.7826 (7)</td>
<td>3.7843 (7)</td>
<td>3.7835 (6)</td>
<td>3.78273 (8)</td>
<td>4.59311 (7)</td>
<td>4.59224 (4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>9.51214 (15)</td>
<td>9.511 (2)</td>
<td>9.523 (2)</td>
<td>9.517 (2)</td>
<td>9.5224 (3)</td>
<td>2.96016 (6)</td>
<td>2.96003 (3)</td>
</tr>
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<td>Ti: x</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0.75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ti: z</td>
<td>0.125</td>
<td>0.125</td>
<td>0.125</td>
<td>0.125</td>
<td>0.125</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Ti: 100 × U$_{11}$</td>
<td>2.35 (9)</td>
<td>12.5 (3)</td>
<td>10.5 (3)</td>
<td>13.4 (3)</td>
<td>3.0 (1)</td>
<td>4.0 (1)</td>
<td>2.73 (5)</td>
</tr>
<tr>
<td>Ti: 100 × U$_{22}$</td>
<td>2.35 (9)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>3.0 (1)</td>
<td>4.0 (1)</td>
<td>2.73 (5)</td>
</tr>
<tr>
<td>Ti: 100 × U$_{33}$</td>
<td>3.4 (1)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4.4 (1)</td>
<td>3.5 (2)</td>
<td>2.08 (9)</td>
</tr>
<tr>
<td>Ti: 100 × U$_{12}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.24 (16)</td>
<td>0.08 (8)</td>
</tr>
<tr>
<td>O: x</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.25</td>
<td>0.3029 (8)</td>
<td>0.3035 (4)</td>
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<tr>
<td>O: z</td>
<td>0.0823 (3)</td>
<td>0.074 (1)</td>
<td>0.078 (1)</td>
<td>0.080 (1)</td>
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<td>0</td>
<td>0</td>
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<tr>
<td>O: 100 × U$_{11}$</td>
<td>1.0 (2)</td>
<td>8.4 (3)</td>
<td>8.1 (3)</td>
<td>11.9 (3)</td>
<td>2.6 (3)</td>
<td>4.9 (2)</td>
<td>2.7 (1)</td>
</tr>
<tr>
<td>O: 100 × U$_{22}$</td>
<td>5.5 (4)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>4.1 (3)</td>
<td>4.9 (2)</td>
<td>2.7 (1)</td>
</tr>
<tr>
<td>O: 100 × U$_{33}$</td>
<td>3.7 (3)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>5.5 (3)</td>
<td>3.1 (3)</td>
<td>2.6 (2)</td>
</tr>
<tr>
<td>O: 100 × U$_{12}$</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.09 (13)</td>
<td>0.10 (13)</td>
</tr>
<tr>
<td>Pitschke A$_{B1}$</td>
<td>0.48</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.40</td>
<td>0.40</td>
<td>0.37</td>
</tr>
<tr>
<td>Pitschke A$_{B2}$</td>
<td>0.19</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>$\alpha_2/\alpha_1$</td>
<td>0.520 (1)</td>
<td>0.535</td>
<td>0.535</td>
<td>0.535</td>
<td>0.535 (3)</td>
<td>0.535 (3)</td>
<td>0.535 (3)</td>
</tr>
<tr>
<td>March $R_\text{L}$</td>
<td></td>
<td>(101)</td>
<td>1.17 (3)</td>
<td>0.91 (2)</td>
<td>0.87 (2)</td>
<td>0.92 (2)</td>
<td>1.26 (2)</td>
</tr>
<tr>
<td>GP (Gaussian)</td>
<td>10.2 (4)</td>
<td>203 (20)</td>
<td>233 (21)</td>
<td>84 (11)</td>
<td>29.5 (1.6)</td>
<td>8.7 (6)</td>
<td>8.5 (3)</td>
</tr>
<tr>
<td>LX (Lorentzian)</td>
<td>5.5 (1)</td>
<td>34 (1)</td>
<td>33 (1)</td>
<td>30 (1)</td>
<td>10.7 (2)</td>
<td>6.6 (2)</td>
<td>5.03 (8)</td>
</tr>
<tr>
<td>shift</td>
<td>$-3.12$ (6)</td>
<td>$-1.5$ (6)</td>
<td>$-3.9$ (6)</td>
<td>$-1.2$ (5)</td>
<td>$-5.49$ (8)</td>
<td>$-5.49$ (8)</td>
<td>$-3.67$ (5)</td>
</tr>
<tr>
<td>$R_\text{calc}$</td>
<td>7.9</td>
<td>34.9</td>
<td>27.1</td>
<td>33.8</td>
<td>8.9</td>
<td>6.9</td>
<td>6.7</td>
</tr>
<tr>
<td>vol. %</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>35.3 (3)</td>
<td>64.7 (3)</td>
<td>—</td>
</tr>
<tr>
<td>FWHM 101 (°)</td>
<td>0.126</td>
<td>0.538</td>
<td>0.572</td>
<td>0.383</td>
<td>0.194</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>FWHM 110 (°)</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.119</td>
<td>0.111</td>
<td>0.112</td>
</tr>
<tr>
<td>particle size (nm)</td>
<td>270 (180)</td>
<td>19 (1)</td>
<td>18 (1)</td>
<td>29 (4)</td>
<td>75 (25)</td>
<td>460 (310)</td>
<td>1100 (1000)</td>
</tr>
</tbody>
</table>
An interesting hint is offered by the March coefficient $R_0$ for preferred orientation (Dollase 1986). For rutile, this coefficient calculation yields 1 (within error) for all probable crystallographic planes, thus indicating no preferred orientation. Anatase grown on the kaolinite-turned-metakaolin substrate yields $R_0$ of about 0.9, which corresponds to a weak preferred orientation of anatase tabular on \{101\}. In contrast, anatase grown in experiment s750 (without the presence of kaolinite) and anatase standard TiO$_2$-5 both yielded an $R_0$ of approximately 1.2, a value corresponding to a moderate preferred orientation of columnar particles. The particle size and morphology of anatase from experiments a750–a900 does not make it probable that anatase itself would be prone to preferred orientation to any detectable extent. However, if anatase grows with its (101) planes on (001) of kaolinite platelets and if these platelets (or whatever becomes of them after thermal treatment) tend to orient themselves in the powder mount, the effect would be similar to the observations. We did not notice any of these effects under the TEM, but (i) the preferred orientations are weak and would not be easy to diagnose, and (ii) the strength of the TEM is in showing details rather than such larger scale effects, particularly in powder samples.

It is not known at which temperature anatase nucleates, and it is unknown whether at that temperature the clay mineral phase still retains the kaolinite structure. However, if we compare the geometry of the atomic arrangement in the (001) plane of kaolinite (Bish 1993) with that in the (101) plane of anatase (Howard et al. 1991) and try to match the oxygen triangles in the plane (101) of anatase with oxygen triangles in the plane of basal tetrahedral oxygens in kaolinite, we find no metric similarities. The match is better in the plane of oxygens/hydroxyls of the octahedral sheet of kaolinite, particularly with the triangle of hydroxyls belonging to the vacant octahedron. At this point, it is a speculation, but some such mechanism might be at work in producing an oriented overgrowth of anatase on the kaolinite substrate.

Titania grown plain (without kaolinite) at 750°C crystallizes as a mixture of anatase and rutile, whereas at 850 and 900°C, the run products are rutile only. Our experiments were not aimed at pinpointing fields of stability of the TiO$_2$ phases, and they essentially agree with what the phase diagram for nanocrystalline TiO$_2$ predicts for ambient pressure (Stir et al. 2006), but shifted to higher temperatures by several tens of degrees.

It has been observed that decreasing particle size in zirconia is associated with a lowering of the temperatures of phase transitions, and a thermodynamic model for the effect was developed by Mayo et al. (2003). Analogously, a lower temperature is shown in the phase diagram for nanocrystalline titania (average particle size approx. 80 nm; Stir et al. 2006), whereas in runs s750, s850, s900 we observed a significantly coarser particle size (approx. 400–1100 nm) and noticed that the temperature of transition to rutile appears to be higher. Thus, the thermodynamic model of Mayo et al. (2003) helps to reconcile the results obtained on nanocrystalline titania (Stir et al. 2006) with ours.

To evaluate the photocatalytic activity of the samples, the kinetics of 4-CP decay were measured. For each sample, the concentration of the 4-CP was plotted as a function of irradiation time (figure 3). As a standard, pure anatase from BDH Ltd. was included. The obtained kinetic data were treated as a
first-order reaction with a constant experimental rate. Kinetic curves were fitted to the experimental points, and the experimental rate constants for photodegradation of 4-CP were calculated (table 2). From the results in figure 3 it is seen that sample aa750 has the highest photocatalytic activity, and the corresponding experimental rate constant is $8.8 \times 10^{-4}$ per minute. Let us note that the photocatalytic activity of all samples is substantially lower compared to the activity of pure BDH anatase. Also, the photocatalytic activity is expected to generally increase with temperature and particle size (Bakardjieva et al. 2005), but the present data show the opposite: The effect is more pronounced for aa750 than for the samples prepared at higher temperatures. However, our samples are not pure anatase, and the nature and extent of a probable interference of metakaolin is unknown. Apparently, several independent variables are involved, and future research will hopefully single out the dominant ones.
4. Conclusions

The behaviour of titania grown in the presence of kaolinite is considerably different from that of plain titania. In experiments with kaolinite, titania retains the form of metastable anatase at all temperatures (750, 850 and 900°C) and has a rather small particle size, 18–29 nm. Besides, this anatase has a mild preferred orientation with its (101) planes parallel to (001) of metakaolin. Growing titania in the presence of kaolinite apparently represents a means for keeping titania as anatase (with a small particle size) at elevated temperatures and for hindering its transformation to rutile. However, this form of anatase displays low photocatalytic activity.

We are grateful to V. Matějka (Nanotechnology Centre, VŠB-TU Ostrava) for the preparation of samples a750–a900 and s750–s900 and to M. Drábek (Czech Geological Survey) for the synthesis of additional samples aa750–aa900. M. Valášková-Chmielevá (Nanotechnology Centre, VŠB-TU Ostrava) made available the anatase standard. Robert Von Dreele offered valuable advice related to some aspects of data treatment. This research was partly supported by grants 205/04/0600 and 205/05/0459 from the Czech Grant Agency.

References