Solid-state NMR investigation of the $^{16/17}$O isotope exchange of oxygen species in pure-anatase and mixed-phase TiO$_2$

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Abstract

Quantitative $^{17}$O MAS NMR investigation of the $^{16/17}$O isotope exchange on pure-anatase TiO$_2$/A and mixed-phase TiO$_2$/A + R with an anatase to rutile ratio of 1:1 has been performed. Evaluation of the exchange kinetics hints to a strong decrease of the activation energy of this reaction on mixed-phase TiO$_2$/A + R material (61 (A) and 70 kJ/mol (R)) compared with pure-anatase TiO$_2$/A (105 kJ/mol). Furthermore, a very rapid increase of the $^{17}$O MAS NMR signals of surface oxygen species indicates a preferred $^{16/17}$O isotope exchange at these sites and a subsequently exchange with $^{16}$O framework atoms in the anatase and rutile domains.

1. Introduction

Heterogeneous photocatalysis has been attracting researchers' attention since the water splitting on photoexcited TiO$_2$ was discovered by Fujishima and Honda in 1972 [1], due to its potential for applications in solar energy conversion. TiO$_2$ is still one of the most extensively studied materials because of its superior photocatalytic activity, high resistance to photocorrosion, and nontoxicity [2]. Furthermore, TiO$_2$ is widely employed as conventional catalyst support [3], pigment [4], photocatalysts [5,6], and components of solar cells [7,8]. As often described, the two common phases, which are applied for photocatalysis, are anatase and rutile. The rutile phase is the most stable structure of TiO$_2$, while the anatase phase can transform to rutile at high temperatures [9]. Both anatase and rutile consist of TiO$_6$ groups, which are joined together by sharing different numbers of edges – two in rutile and four in anatase. The single oxygen site in each phase is trigonally coordinated (OTi$_3$) with average bond lengths of 0.1959 nm for rutile and 0.1946 nm for anatase [10].

Zhang et al. [11,12] studied the phase transition from anatase to rutile by Raman spectroscopy and X-ray diffraction and found that the photocatalytic activity of TiO$_2$ is related to specific surface species. They observed that phase junctions formed between the anatase and rutile domains enhance the hydrogen production in the photocatalytic water splitting.

Generally, the study of the oxygen isotope exchange is an effective way for understanding the reactivity of oxygen species on oxide surfaces. A number of oxygen isotope exchange (OIE) investigations performed by Boreskov, Winter, Novakova, and others have been performed by using $^{18}$O-enriched oxygen gas and mass spectroscopy of the gas phase to obtain insights into the mechanisms of OIE on various oxides [13–15]. Generally, an exchange of the surface oxygen atoms $^{16}$O on solid oxides with $^{18}$O atoms of $^{18}$O$_2$(g) gas occurs via the reactions $R_1$ and $R_2$ in Eqs. (1) and (2), respectively [13–15]:

$^{18}$O$_2$(g) + $^{16}$O —— $^{18}$O$^{18}$O(g) + $^{16}$O (1)

$^{18}$O$_2$(g) + $^{16}$O —— $^{16}$O$^{18}$O(g) + $^{16}$O$_2$ (2)

This OIE can be induced by thermal treatment [13–15,16] or UV/Vis irradiation [17,18]. The same is valid for an exchange of oxygen in solid oxides with $^{17}$O$_2$ gas. By measuring the OIE via mass spectrometry, the activation energy for this reaction on V$_2$O$_5$, Cr$_2$O$_3$, MnO$_2$, Fe$_2$O$_3$, Co$_3$O$_4$, NiO, CuO, and ZnO vary from $E_a = 103$ to 258 kJ/mol in the case of an $R_1$ mechanism and from $E_a = 83$ to 211 kJ/mol for the $R_2$ mechanism [16]. Winter and Sturge [14] found that the oxygen isotope exchange reactions on pure-anatase and pure-rutile TiO$_2$ occurs via the $R_1$ mechanism with activation energies of $E_a = 134$ and 144 kJ/mol, respectively. Pichat et al. [18] considered the lability of surface oxygen atoms as a reason of the UV/Vis-induced oxygen isotope exchange properties of TiO$_2$ [18]. Sato et al. [17] could show that the oxygen isotope exchange capacity of TiO$_2$, induced by UV/Vis irradiation, correlates well with the activity in the photocatalytic oxidation of ethane.

$^{17}$O solid-state nuclear magnetic resonance (SSNMR) spectroscopy with rapid spinning of the powder samples around an axis
in the magic angle (MAS: magic angle spinning) to the direction of the magnetic field $B_0$ is a powerful method for investigating and distinguishing the various local structures of oxygen atoms in TiO₂ materials [19–22]. As a specific property, $^{17}$O nuclei have the nuclear spin $I = \frac{5}{2}$ and are, therefore, quadrupole nuclei. In this case, the position and shape of their $^{17}$O MAS NMR signals are strongly affected by the quadrupolar interaction of the electric quadrupole moment ($eQ$) of the $^{17}$O nuclei and the electric field gradient ($V_{zz}$) at the position of the resonating nuclei. The most important SSNMR parameters describing quadrupolar interactions are the quadrupole coupling constant $C_q = e^2Q/h$ (h: Planck constant) and the asymmetry parameter $\eta_q = (V_{yy} - V_{xx})/V_{zz}$, which depends on the principal axes values of the electric field gradient $V_{ii}$ ($i = xx, yy, zz$) [23,24].

The present work focuses on the study of the $^{16/17}$O isotope exchange on pure anatase in comparison with a mixed-phase TiO₂ material containing anatase and rutile domains as well as various surface oxygen species and phase conjugations on the anatase and rutile domains. $^1$H and $^{17}$O MAS NMR spectroscopy were utilized for studying the type as well as density of surface TiOH groups and the $^{17}$O atoms in TiO₂ materials, respectively, upon a thermally induced $^{16/17}$O isotope exchange with $^{17}$O₂ gas. Furthermore, the activation energies of the OIE were determined. To the best of our knowledge, this is the first quantitative $^{17}$O solid-state NMR investigation of the $^{16/17}$O isotope exchange of oxygen species on pure and mixed-phase TiO₂ materials.

2. Experimental section

2.1. Preparation of the TiO₂ materials

All chemicals used for the TiO₂ synthesis were of analytical grade, purchased from Alfa Aesar Chemical Co., and used as received without further purification. The TiO₂ materials were prepared via an ionic liquid (IL) assisted hydrothermal method according to a modified procedure described in literature [25].

For the synthesis of the $^{17}$O-enriched reference material consisting of pure anatase (TiO₂/Reference), 10 g of $^{17}$O-enriched H₃O₂ ($^{17}$O-enrichment of 20%, Cambridge Isotope Lab., Inc., USA) and 1 ml of 48% aqueous solution of H₂SO₄ were added successively to 92 g of 1-butyl-3-methylimidazolium chloride (bmim+Cl⁻) in a 250 ml Teflon liner inside an ice-water bath. H₂SO₄ was used for inhibiting the anatase to undergo phase transformation to rutile [26]. This mixture was stirred until a clear yellow liquid was formed. Then, 50 g of TiCl₄ was slowly added. During the mixing process, HCl gas was released as a product of the hydrolysis of TiCl₄ with the water in the solution. At the same time, a yellow solid was formed gradually in the mixture, which was purged by dry N₂ gas to remove the HCl gas. Afterwards, the Teflon liner was put into a stainless steel autoclave heated at 140 °C for 1 h. During this time, the yellow solid became melted and stirred to be homogenous and fully converted. Finally, the mixture was maintained at 150 °C for 2 days for crystallization. After cooling down to room temperature, the product was washed five times by centrifugation and redispersion in ethanol, followed by drying in air at 80 °C for 24 h. The obtained TiO₂/Reference material has a molar $^{17}$O-content of 17.8% corresponding to 2.22 mmol/g.

For the synthesis of the non-enriched pure-anatase material (TiO₂/A), the procedure was the same as described before, but distilled conventional water was used instead of $^{17}$O-enriched water. The obtained material was calcined at 400 °C for 4 h to remove all organic compounds.

The mixed-phase TiO₂/A+R material was obtained by calcination of the non-enriched TiO₂/A material at 750 °C for 6 h in synthetic air. The phase composition was determined via X-ray diffraction according to $R = I_R/(I_R + 0.8I_A)$, in which $R$ is the weight fraction of rutile and $I_R$ and $I_A$ are the peak intensities of the anatase (101) and rutile (110) reflections, respectively [27].

2.2. Characterization methods

X-ray diffraction (XRD) patterns of the calcined samples were recorded on a Bruker D8 diffractometer with CuKα radiation. Transmission electron microscopy (TEM) images of the samples were acquired on a Philips Tecnai G2 20 S-TWIN electron microscope. The specific surface areas of the samples were determined via N₂ adsorption/desorption isotherms collected on a Quantachrome IQ-MP gas adsorption analyzer.

Solid-state NMR investigations were performed on a Bruker Avance III 400WB spectrometer at resonance frequencies of 54.2 MHz for $^{17}$O nuclei and 400.1 MHz for $^1$H nuclei. The spectra were recorded upon single pulse excitation of $\pi/8$ and $\pi/2$, with repetition times of 0.5 s and 10 s, and sample spinning rates of 20 kHz and 8 kHz using a 2.5 mm and a 4 mm MAS NMR probe for $^{17}$O and $^1$H MAS NMR spectroscopy, respectively. Before the $^1$H MAS NMR studies, the TiO₂ samples were dehydrated in vacuum at 400 °C for 4 h and subsequently sealed in glass tubes until their use. The dehydrated TiO₂ samples were transferred into 4 mm MAS rotors inside a glove box purged with dry nitrogen gas. The TiOH density on the dehydrated TiO₂ materials was determined by comparing the $^1$H MAS NMR intensities with that of an external standard consisting of zeolite Na, H-Y, which was obtained by exchange of 35% of the sodium cations by ammonium ions and calcination at 673 K. The simulation and deconvolution of the $^{17}$O MAS NMR spectra was performed utilizing the SOLA module of the Bruker BioSpin software TopSpin 3.0, patch level b.58.

2.3. Oxygen isotope exchange experiments

For a typical $^{16/17}$O isotope exchange experiment, 20.0 ± 0.2 mg of the TiO₂ materials under study filled into a quartz glass tube were evacuated at 673 K in vacuum (pressure below 10⁻² Pa) for 4 h to remove physisorbed water. Subsequently, 500 mbar of $^{17}$O-enriched oxygen gas with an enrichment degree of 85% (ISOTEC, Miamisburg, USA) were loaded on the dehydrated powder sample inside the quartz glass tube (volume of 1 ml) and, then, sealed. Samples with different $^{16/17}$O-exchange degrees were obtained by thermal treatments of the sealed and $^{17}$O-loaded TiO₂ samples at 450, 500 or 550 °C for durations up to 100 h.

![Figure 1. XRD patterns of TiO₂/Reference (a), TiO₂/A (b), and TiO₂/A + R (c).](image-url)
3. Results and discussion

3.1. Characterization of the catalyst materials

The X-ray patterns of the as-synthesized TiO$_2$/Reference and TiO$_2$/A materials in Figure 1a and b reveal the typical diffraction lines of anatase (A). In the X-ray patterns of TiO$_2$/A + R depicted in Figure 1c, additional reflections of rutile (R) occur, which was formed after calcination at 750 °C. Based on the peak intensities of the anatase (101) and rutile (110) reflections, an A:R ratio of 0.53:0.47, i.e. ca. 1:1, was calculated.

The TEM images show that on the one hand the particle size increases from 35 nm to 77 nm (Table 1) upon transformation of pure-anatase TiO$_2$/A (Figure 2a) to mixed-phase TiO$_2$/A + R (Figure 2b), respectively. On the other hand, the particle surfaces of the mixed-phase TiO$_2$/A + R (Figure 2d) are covered by a thick layer of non-ordered material, while the pure-anatase TiO$_2$/A (Figure 2c) shows a very thin surface layer only. The above-mentioned increase of the particle size due to phase transformation agrees with the finding of Yan et al. [28], while the non-ordered surface layers of TiO$_2$/A + R are very similar to the phase junctions described by Zhang et al. [11,12]. Considering the BET areas of 43 m$^2$/g for TiO$_2$/A, the value of 30 m$^2$/g for mixed-phase TiO$_2$/A + R can be explained by the growing particle size due to the phase transformation (Table 1). For further characterization of sample TiO$_2$/Reference, see Supporting information.

3.2. Assignment of the $^{17}$O MAS NMR signals of pure-anatase TiO$_2$/A and mixed-phase TiO$_2$/A + R

For studying the various types of oxygen species in pure-anatase TiO$_2$/A and mixed-phase TiO$_2$/A + R, dehydrated samples of these materials were treated with $^{17}$O$_2$ gas at 500 °C for 60 h. The $^{17}$O MAS NMR spectra of these materials are shown in Figure 3a and b, respectively. In agreement with literature [15], the $^{17}$O MAS NMR spectrum of TiO$_2$/A (Figure 3a) consists of a single signal at 562 ppm with a shape and broadening according to the quadrupole coupling constant of $C_q = 1.2$ MHz and an asymmetry parameter of $g_q = 0.6$ (Table 2) corresponding to OTi$_3$ oxygen species in anatase [19]. In contrast, the spectrum of TiO$_2$/A + R material contains at least five signals at chemical shifts of 516, 543, 562, 572, and 596 ppm (Figure 3b). Simulation of the spectrum led to the $C_q$ and $g_q$ values summarized in Table 2.

According to Bastow et al. [19], $^{17}$O MAS NMR signals at 562 and 596 ppm are caused by OTi$_3$ species in anatase and rutile domains, respectively. In an earlier $^{17}$O MAS NMR study of the commercial mixed-phase TiO$_2$ photocatalyst P25, signals at 516 and 543 ppm were assigned to distorted OTi$_3$ and/or tetrahedral oxygen sites (OTi$_4$) near the surface of anatase [22]. For TiO$_2$ precursors, Rao et al. [29] observed a $^{17}$O MAS NMR signal at 574 ppm assigned to OTi$_3$ species in low-ordered TiO$_2$. Therefore, also the signal at 572 ppm observed in the present study is assigned to oxygen species in low-ordered TiO$_2$ or phase junctions on anatase and rutile domains. In Table 3, the densities of OTi$_3$ species in anatase (562 ppm) and rutile (596 ppm) domains as well as of surface oxygen species (516, 543, and 572 ppm) in TiO$_2$/A + R, observed upon $^{16/17}$O isotope exchange at 550 °C for 60 h are given. These values were determined by comparing the corresponding $^{17}$O MAS NMR intensities with that of TiO$_2$/Reference.

Table 1. Physico-chemical properties of the TiO$_2$ materials under study.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Structure</th>
<th>Crystal size$^a$ (nm)</th>
<th>S$_{BET}$$^b$ (m$^2$/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiO$_2$/Reference</td>
<td>Anatase</td>
<td>48</td>
<td>27</td>
</tr>
<tr>
<td>TiO$_2$/A</td>
<td>Anatase</td>
<td>35</td>
<td>43</td>
</tr>
<tr>
<td>TiO$_2$/A + R</td>
<td>Anatase + rutile</td>
<td>77</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$ Estimated by TEM, accuracy ±10%.

$^b$ Specific surface area determined by nitrogen adsorption.
gas and thermal treatment at 450, 500, and 562 ppm was evaluated. For characterizing TiOH groups on dehydrated pure-anatase TiO2, their chemical shifts, quadrupole coupling constants, asymmetry parameters, and assignments according to literature (last column).

<table>
<thead>
<tr>
<th>δTiO2 (ppm)</th>
<th>CP (MHz)</th>
<th>Assignment</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>516</td>
<td>1.8</td>
<td>0.8</td>
<td>Distorted OTi3 or OTi4 near the surface</td>
</tr>
<tr>
<td>543</td>
<td>1.6</td>
<td>0.6</td>
<td>Distorted OTi3 or OTi4 near the surface</td>
</tr>
<tr>
<td>562</td>
<td>1.2</td>
<td>0.6</td>
<td>OTi3 in anatase</td>
</tr>
<tr>
<td>572</td>
<td>2.0</td>
<td>0.1</td>
<td>OTi3 in low-ordered TiO2</td>
</tr>
<tr>
<td>596</td>
<td>1.8</td>
<td>0.6</td>
<td>OTi4 in rutile</td>
</tr>
</tbody>
</table>

Table 3

Densities of TiOH groups and surface oxygen species of different nature (see Table 2) on pure-anatase TiO2/A (A) and mixed-phase TiO2/A + R (A + R), determined by quantitative 1H and 17O MAS NMR spectroscopy, respectively, upon 16/17O isotope exchange at 500 °C for 60 h.

<table>
<thead>
<tr>
<th>Surface species</th>
<th>Chemical shift/method</th>
<th>Site density (mmol/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiOH (A)</td>
<td>1.9 ppm/1H MAS NMR</td>
<td>0.0242</td>
</tr>
<tr>
<td>TiOH (A)</td>
<td>6.8 ppm/1H MAS NMR</td>
<td>0.0277</td>
</tr>
<tr>
<td>TiOH (A + R)</td>
<td>11.5 ppm/1H MAS NMR</td>
<td>0.0187</td>
</tr>
<tr>
<td>TiOH (A + R)</td>
<td>1.7 ppm/1H MAS NMR</td>
<td>0.0097</td>
</tr>
<tr>
<td>TiOH (A + R)</td>
<td>5.1 ppm/1H MAS NMR</td>
<td>0.0497</td>
</tr>
<tr>
<td>Surface oxygen (A + R)</td>
<td>516 ppm/17O MAS NMR</td>
<td>0.0069</td>
</tr>
<tr>
<td>Surface oxygen (A + R)</td>
<td>543 ppm/17O MAS NMR</td>
<td>0.0207</td>
</tr>
<tr>
<td>Surface oxygen (A + R)</td>
<td>572 ppm/17O MAS NMR</td>
<td>0.0109</td>
</tr>
<tr>
<td>Oxygen in (A + R)</td>
<td>562 ppm/17O MAS NMR</td>
<td>0.1330</td>
</tr>
<tr>
<td>Oxygen in (A + R)</td>
<td>596 ppm/17O MAS NMR</td>
<td>0.0380</td>
</tr>
</tbody>
</table>

Summary of the 17O MAS NMR signals occurring in the spectra of TiO2/A and TiO2/A + R, their chemical shifts, quadrupole coupling constants, asymmetry parameters, and assignments according to literature (last column).

The evaluation of the signals and assignments according to literature (last column).

Experimental accuracy ±10%.

The TiOH signals in the spectrum of TiO2/A and TiO2/A + R, their chemical shifts, quadrupole coupling constants, asymmetry parameters, and assignments according to literature (last column).

3.3. SSNMR investigation of TiOH groups of pure-anatase TiO2/A and mixed-phase TiO2/A + R

Studying titanium oxopolymers with static 1H/17O CP NMR spectroscopy (no MAS), a broad 17O solid-state NMR signal extending between –200 and 400 ppm was observed and assigned to oxygen atoms of TiOH groups on TiO2 [30]. For TiO2/A and TiO2/A + R materials investigated in the present work, however, no 17O MAS NMR signal of TiOH groups could be observed in the above-mentioned shift range. Hence, no thermally induced 16/17O isotope exchange between 16O atoms of TiOH groups with 17O atoms of the 17O2 gas occurred. For characterizing TiOH groups on dehydrated TiO2/A and TiO2/A + R materials, therefore, 1H MAS NMR spectroscopy was utilized.

The spectrum of dehydrated TiO2/A in Figure 4a consists of three well-resolved signals of TiOH groups at 1.9, 6.8, and 11.5 ppm, which agrees well with the observation of Mastikhin et al. [31]. As for many other oxides [31], the high-field signal at 1.9 ppm is caused by OH groups at the outer particle surface, while the signals at 6.8 and 11.5 ppm are low-field shifted due to internal interactions. Probably, the TiOH groups involved in these internal interactions are located in internal phase conjugations visible in the TEM images of the sample TiO2/A + R (see Figure 2b and d). The TiOH signals in the spectrum of TiO2/A + R (Figure 4b) show a strong broadening probably due to a distribution of chemical shift caused by low-ordered TiO2 and internal interactions. The evaluation of the 1H MAS NMR spectra in Figure 4 gave the TiOH densities summarized in Table 3. According to these values, the transformation of the pure-anatase TiO2/A to the mixed-phase TiO2/A + R is accompanied by a small decrease of the TiOH density and a slight change of the resonance position of the TiOH groups involved in internal interactions.

3.4. 17O isotope exchange experiments on pure-anatase TiO2/A and mixed-phase TiO2/A + R

The OIE kinetics were investigated by recording the 17O MAS NMR spectra of dehydrated TiO2/A and TiO2/A + R upon loading with 500 mbar 17O2 gas and thermal treatment at 450, 500, and 550 °C for durations up to 100 h. As an example, Figure 5a and b show the stack plots of the 17O MAS NMR spectra of TiO2/A and TiO2/A + R, respectively, recorded upon OIE at 500 °C. For TiO2/A, the total intensity of the OTi3 species at 562 ppm was evaluated to determine 16/17O isotope exchange rates k (see, e.g., Figure 6) according to [32]:

\[ I(t) = I(\infty) \left[ 1 - b \cdot \exp \left( -k \cdot t \right) \right] \]

where \( I(t) \) and \( I(\infty) \) denote the intensity of the 17O MAS NMR signals at time \( t \) and in the equilibrium state, respectively, while the value \( b \) describes the exchange at \( t = 0 \). The obtained isotope exchange rates \( k \) are utilized for an Arrhenius plot allowing the determination of the OIE activation energy \( E_a \) via [14]:

\[ k = A_0 \cdot \exp \left( -E_a / R \cdot T \right) \]

with the gas constant \( R \), the isotope exchange temperature \( T \), and the pre-exponential factor \( A_0 \).

The Arrhenius plot of the rates \( k \) obtained by evaluating the 17O MAS NMR signal at 562 ppm in the spectra of pure-anatase TiO2/A gives an activation energy of \( E_a = 105 \pm 10 \) kJ/mol (Figure 7 and Table 4). The plots of the 17O MAS NMR intensities of the anatase and rutile signals at 562 and 596 ppm, respectively, in the spectra of TiO2/A + R are shown in Figure 6a–c, closed symbols. Interestingly, activation energies of \( E_a = 61 \pm 10 \) kJ/mol and \( 70 \pm 10 \) kJ/mol (Table 4) were obtained for the OIE with the anatase and rutile domains of TiO2/A + R. For comparison, activation energies of
$E_a = 134$ and $144$ kJ/mol were determined by Winter and Sturge [14] for the oxygen isotope exchange on pure-anatase and pure-rutile TiO$_2$, respectively, and of $E_a = 105$ kJ/mol for pure-anatase TiO$_2$ in the present work. Hence, the activation energies for the OIE with anatase as well as rutile domains in the mixed-phase TiO$_2$ are decreased by ca. 30% in comparison with that of the corresponding pure-phase materials.

Based on Pichat et al. [18], the above-mentioned strong decrease of the activation energy for the $^{16/17}$O isotope exchange could be explained by the lability of surface oxygen atoms formed by the transformation of pure-anatase TiO$_2$/A into the mixed-phase TiO$_2$/A + R material. As demonstrated by the occurrence of $^{17}$O MAS NMR signals at 516, 543, and 572 ppm in Figure 3b, surface oxygen species have a significant higher densities in mixed-phase TiO$_2$/A + R in comparison with pure-phase TiO$_2$/A.

In Figure 6a–c, open symbols, the intensities of the $^{17}$O MAS NMR signals are plotted as a function of the oxygen isotope exchange time. Due to their much lower intensities in comparison with the $^{17}$O MAS NMR signals of oxygen atoms in the anatase and rutile domains, no evaluation of the exchange kinetics for the surface oxygen sites is possible. However, an important characteristic of the $^{17}$O MAS NMR signals at 516, 543, and 572 ppm is their very rapid increase, i.e. these signals increase in a much shorter time due to the $^{16/17}$O isotope exchange compared with the anatase (562 ppm) and rutile (596 ppm) signals of the mixed-phase TiO$_2$/A + R. This observation indicates that the OIE in mixed-phase TiO$_2$/A + R starts at surface oxygen sites causing the $^{17}$O MAS NMR signals at 516, 543, and 572 ppm. These surface oxygen species, on the other hand, cover the anatase and rutile domains or contribute to phase junctions between anatase and rutile domains. Therefore, a subsequent OIE between $^{17}$O-enriched surface oxygen species and $^{16}$O atoms in the anatase and rutile domains occurs. The OIE via surface oxygen species in low-order TiO$_2$ layers may be the reason for the significantly lower activation energy of the OIE with anatase and rutile domains of TiO$_2$/A + R compared with that on pure-phase TiO$_2$/A materials characterized by a negligible low number of surface oxygen species.

According to the evaluation of the X-ray pattern of TiO$_2$/A + R (see Figure 1c), the anatase and rutile domains in this material have a ratio of ca. 1:1. However, a much lower relative intensity
of the $^{17}$O MAS NMR signal of oxygen atoms in the rutile domains (596 ppm) in comparison with those in anatase domains (562 ppm) in TiO$_2$/A + R was found in the equilibrium state, as indicated by the arrows in Figure 6 and the corresponding OTi$_3$ densities summarized in Table 3. Assuming that the $^{16/17}$O isotope exchange occurs via surface oxygen species, which are responsible for the significant decrease of the activation energy of this exchange reaction, a higher content of rutile domains compared to anatase domains in the mixed-phase TiO$_2$/A + R must be formed inside the TiO$_2$ particles without having contact with surface oxygen species performing and accelerating the $^{16/17}$O isotope exchange.

4. Conclusions

In this work, first quantitative $^{17}$O MAS NMR investigation of the $^{16/17}$O isotope exchange of oxygen atoms in the framework of pure-anatase and mixed-phase TiO$_2$ has been performed. For this purpose, a pure-anatase TiO$_2$/A material was synthesized via hydrolysis of TiCl$_4$, which was subsequently calcined to obtain a mixed-phase TiO$_2$/A + R material with anatase and rutile domains in the ratio of ca. 1:1 as determined by XRD. TEM images of TiO$_2$/A and TiO$_2$/A + R indicate that especially the latter material is covered by low-ordered TiO$_2$. On the other hand, a slightly lower TiOH density was found by $^1$H MAS NMR spectroscopy for mixed-phase TiO$_2$/A + R compared with pure-phase TiO$_2$/A.

In the $^{17}$O MAS NMR spectra of the mixed-phase TiO$_2$/A + R material, signals of OTi$_3$ oxygen species in anatase and rutile domains at 562 and 596 ppm, respectively, and of surface oxygen species at 516, 543, and 596 ppm were observed. In contrast, the spectrum of the pure-anatase TiO$_2$/A consists of a single signal at 562 ppm only, which is due to OTi$_3$ oxygen species of anatase. Interestingly, no $^{17}$O MAS NMR signals were found in the spectral range described in literature for TiOH groups (200 to 400 ppm). Hence, TiOH groups are not involved in the $^{16/17}$O isotope exchange of dehydrated TiO$_2$ with $^{17}$O gas. On the other hand, a significantly higher density of surface oxygen species in the mixed-phase TiO$_2$/A + R material compared to the pure-anatase TiO$_2$/A was found by $^{17}$O MAS NMR spectroscopy.

As the most important result of the $^{16/17}$O isotope exchange studies, a strong decrease of the activation energy of this exchange reaction on the mixed-phase TiO$_2$/A + R material ($E_a = 61$ (A) and 70 kJ/mol (R)) compared with the pure-anatase TiO$_2$/A ($E_a = 105$ kJ/mol) was determined. Furthermore, the very rapid increase of the $^{17}$O MAS NMR signal of surface oxygen species in the TiO$_2$/A + R material indicates that the $^{16/17}$O isotope exchange reaction starts at these surface sites, which subsequently exchange with $^{16}$O framework atoms in the anatase and rutile domains. By this way, the presence of a large density of surface oxygen species accelerates the $^{16/17}$O isotope exchange in mixed-phase TiO$_2$. The much weaker content of $^{17}$O-exchanged framework atoms in rutile domains compared with those in anatase domains of the mixed-phase TiO$_2$/A + R is explained by the formation of a significant content of rutile domains inside the mixed-phase TiO$_2$/A + R particles having no contact to surface oxygen species.

Acknowledgments

This work was supported by the Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), 111 Project (B12015), MOE Innovation Team (IRT 13022), and the Ministry of Education of China (NCET-11-0251). Furthermore, M.H. wants to thank for financial support by Deutsche Forschungsgemeinschaft.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.cplett.2014.01.014.

References
