Temperature-dependent Structural Properties of Water Molecules Confined in TiO₂ Nanoslits: Insights from Molecular Dynamics Simulations

Yumeng Zhang¹, Yudan Zhu^{1*}, Zirui Li², Yang Ruan¹, Licheng Li³, Linghong Lu¹, Xiaohua Lu^{1*}

¹ *College of Chemical Engineering, State Key Laboratory of Materials-oriented Chemical
Engineering, Nanjing Tech University, Nanjing 210009, P.R. China*

² *College of Mechanical and Electrical Engineering, Wenzhou University, Wenzhou 325035, P.R.
China*

³ *College of Chemical Engineering, Nanjing Forestry University, Nanjing 210037, P.R. China*

*To whom correspondence should be addressed.

Contact information:

Yudan Zhu ydzhu@njtech.edu.cn; Tel./fax: +86 25 83172287

Xiaohua Lu xhlu@njtech.edu.cn; Tel./fax: +86 25 83588063

ABSTRACT: The confinement of titanium dioxide (TiO₂) significantly affects the nanoconfined water molecules behaviors, manifested structurally as fluid layering and dynamically as slowing down of fluid mobility near the confining surface. In this work, we carried out molecular dynamics simulations to investigate temperature-dependent structural characteristics of water molecules confined in rutile (110) nanoslits. Specifically, we studied the microstructure of two layers of water molecules near TiO₂ surface under temperatures ranging from 27 to 800 °C. The simulation results showed that the mean residence time of the first layer of water molecules decreased with temperature. A dramatic decreasing rate occurred when the temperature went beyond 300 °C. Detailed microstructural investigation of confined water molecules showed that with the increase of temperature, the orientation of some water molecules changed. The possible reason is that water molecules obtained more kinetic energy due to the higher interfacial temperature, so as to increase the probability of forming hydrogen bonds between water molecules in layer I. Moreover, dimers of water molecules, which exhibit higher mobility than water monomers near TiO₂ surfaces, began to form at about 300 °C. The formation of hydrogen bonds within the first layer of water molecules is largely responsible for the reduction of mean residence time. The results of this work provide perceptive guidelines for the application of TiO₂ at high temperatures, such as TiO₂-supported catalysts.

Keywords: TiO₂; Water; Molecular Simulations; Temperature; Nanoconfinement

1. Introduction

Nanoporous titanium dioxide (TiO_2), as an important catalytic support, has attracted the attention of scholars for decades [1,2]. Porous structure of TiO_2 provides a large surface area as active sites of catalysts. In addition, nanoscale pore structure also impose nanoconfinement effects on the fluid molecules, which may promote or suppress catalytic reactions [3-5]. Recently, the role of nanoconfinement on catalytic reactions in nanopores has been reported, in terms of transport behaviors of solvent, reactant and/or product molecules [6-9]. It has been established that behaviors of nanoconfined fluid molecules differ significantly from those of their bulk counterpart due to interfacial effects at the vicinity of the solid surface [6,10]. Behaviors of the fluid molecules near TiO_2 surface play a critical role in the applications of TiO_2 nanoporous materials.

Currently, the behavior of water molecules nanoconfined on TiO_2 surface becomes one of the research focal areas since water is the most common solvent in industrial production and is widely used in many chemical reactions as a medium [11]. Molecular simulation is an effective tool for investigating clusters of nanoconfined water molecules [6]. Predota et al. [12,13], in their molecular dynamics (MD) investigations, found that there was a strong adsorption layer of water molecules existing near the TiO_2 surface, which indicates that the strong interaction between water and TiO_2 materials. Kimmel et al. [14] further found that the structures and dynamics of water adsorbed on the TiO_2 surface were closely associated with the hydrogen bonds (H-bonds) structures between water molecules on the surface. Cui et al. [15] found that the microstructures of absorption layer on solid interface was entirely different from that in bulk and confined fluids showed distinct microstructures and mean square displacements (MSD) at different solid interfaces, suggesting a strong correlation between microstructures and diffusion properties of nanofluids. With the rapid development of experimental techniques, many findings derived from molecular dynamics have been demonstrated in the experimental studies.

Li et al. [16] reported that the role of H-bonds was significant for the dynamics of molecular assembly by using the scanning tunneling microscopy (STM). Similarly, Zhu et al. [17], using ^1H solid-state nuclear magnetic resonance (^1H SSNMR), successfully monitored ligand exchange reaction between oleylamine and adsorbed water on TiO_2 nanoparticles (NPs). They classified the adsorbed water molecules into three different distinctively layers comprising strongly nanoconfined rigid water species closest to TiO_2 NPs surface, weakly nanoconfined water species on TiO_2 NPs, and water molecules with high mobility.

Most of the heterogeneous reactions using TiO_2 -supported catalysts are at elevated temperatures, such as hydrodesulfurization [9], Fischer-Tropsch synthesis (FTS) [18], denitration [19] and volatile organic compounds (VOC) oxidization [20]. Various literatures have reported the role of the temperature in determining water structure under nanoconfinement. Predota et al. [13] and Wesolowski et al. [21] studied the behaviors of water molecules under TiO_2 nanoconfinement from 25 to 250 $^\circ\text{C}$, and demonstrated that increasing temperature greatly enhanced the cation sorption affinity. Wang et al. [22] observed that the structure of interfacial water in single-walled carbon nanotubes could depend sensitively on temperature. Analogously, Striolo et al. [23] presented that the temperature could affect the microstructure of water in porous carbons. Specifically, Giraud et al. [19] investigated the adsorption of water on TiO_2 nanoparticles using the adsorption equilibrium infrared spectroscopy (AEIR) and the result indicated that the temperature could promote water desorption. Thereby, it will be very interesting to illustrate whether and how temperature affects the behaviors of water molecules nanoconfined on the TiO_2 surface via molecular dynamics simulations. On the other hand, the involvement of water in reaction activities has also been reported in many literatures [18,24-26]. Toni et al. [25] reported that traces of water reinforced the formation of a catalyst poison in CO oxidation reaction. Borg et al. [18] illustrated that water was essential for reaction activity and selectivity in FTS. However, the effects of temperature on behaviors of water molecules nanoconfined in

TiO₂ nanopores have not yet been clearly understood. Therefore, it is of great significance to investigate the temperature-dependent structural properties of water molecules confined on TiO₂ surface and find out the involved mechanisms.

In our previous works, we performed a series of simulations on the nanoconfined water near TiO₂ surface and found that the residence time of water on TiO₂ derived from MD simulations could act as an indicator to reflect the interaction between water molecules and the surface [7,27,28]. The different behaviors of confined water molecules in TiO₂ nanoslits with varying coverages of carbon were compared and the results showed that the carbon modification could break the interfacial water microstructures and then improve the mobility of water in the central region of the nanoslits [28].

In this study, effects of temperatures on the behaviors of nanoconfined water molecules confined in TiO₂ nanoslits were analyzed using MD simulations. Relationship between the microstructure of water molecules and their behaviors at the nanoscale was investigated. Physical mechanisms involved in such nanoconfinement systems were clarified and their implications in molecular transport and catalytical reactions were discussed.

2. Methodology

2.1 Simulation details

The framework of the simulation is shown in Fig. 1. A slit-shaped nanopore model was consisted of a rutile TiO₂ (110) slab in a periodic simulation box and its counterpart in another one. Rutile is the most stable one among all the TiO₂ crystal structures. Zhang et al.'s experimental results demonstrated the temperature effect on the rutile TiO₂ (110) crystal structure was slight and this structure still existed even at 800 °C [29]. Given that we focused on the influence of temperature on fluid microstructures. We adopted the rigid geometry mineral model in this work. The atom sites in the TiO₂ slab were fixed during the entire simulation process. In the initial

configuration, the unit cell parameters of rutile TiO_2 (110) were $a = b = 0.4594$ nm, and $c = 0.2959$ nm, respectively. The Ti and O coordinate sites were consistent with our previous studies [27,28]. The original size of the simulation box in the three directions was marked in Fig. 1. The thickness of the TiO_2 slab is 1.553 nm and the width of nanopore is 2.0 nm.

Fig. 1. The schematics of simulation systems. The red, white and pink spheres represent the oxygen, hydrogen and titanium atoms, respectively, and the blue rectangle frame indicates the simulation box.

MD simulations were conducted using LAMMPS [30] according to the following procedures. Firstly, 1.0 ns MD simulations were performed to obtain the equilibrium state of water molecules by applying isobaric-isothermal (NPT) ensemble only in one direction (the y direction in this work) while placing two water reservoirs (with the density of $1.0 \text{ g} \times \text{cm}^{-3}$) outside the slits in this direction (Fig. 1a). The system was maintained at a constant temperature (300K) and the pressure (p) was set to 10^6 Pa to avoid the appearance of nano bubbles. Then, another 1.0 ns MD simulations were performed with integral step of 1.0 fs by applying the canonical (NVT) ensemble without the water reservoirs (Fig. 1b) and the coordinates were saved every 0.2 ps for further analysis. Table 1 listed the total number of water molecules in the NVT environments for each temperature. The 3D-periodic Ewald method [31] was used for full electrostatic interactions at a precision of 1.0×10^{-6} with a real space cutoff of 1.0 nm and the reciprocal space vectors values of three dimensions are $k_{x\text{max}} = 9$, $k_{y\text{max}} = 10$, $k_{z\text{max}} = 9$, respectively. A cutoff distance of 1.0 nm was used to calculate the

short-range van der Waals interactions. The slabs were fixed during the entire simulation process. Periodic boundary conditions were implemented in all directions. Similar method was adopted in Wei et al.'s work [32]. Nine temperatures (27, 100, 200, 300, 400, 500, 600, 700 and 800 °C) were chosen to investigate the effects of temperature on the behaviors of water molecules confined within the TiO₂ nanoslits. The Nosé-Hoover [33] thermostat was coupled with water molecules at all temperatures. Chaban et al. [34] adopted similar method of altering temperatures to study water droplet evaporation within CNTs.

Table 1

The total number of water molecules in the NVT environments for each temperature.

Temperature/°C	Total number of water
27	831
100	815
200	811
300	812
400	803
500	790
600	782
700	780
800	764

2.2 Intermolecular potentials

Matsui–Akaogi (M-A) force field [35] was adopted to describe the rutile slabs in this work. Bandura et al. [36] compared two different force fields for hydration of TiO₂ surfaces in a vacuum and demonstrated that the parameterization in (M-A) force field was the best starting point for optimizing the force field parameters of TiO₂ surface. Later, these optimized parameters were widely adopted in the studies of the

behaviors of water molecules confined on TiO₂ surface [13,14,37]. In this study, the site-site interactions between O and Ti atoms were described by a summation of a Buckingham potential for the van der Waals interactions and the Coulombic potential for the electrostatic interactions [38]

$$U(r_{ij}) = A_{ij} \exp(-\frac{r_{ij}}{\rho_{ij}}) - \frac{C_{ij}}{r_{ij}^6} + \frac{q_i q_j}{r_{ij}} \quad (1)$$

where $U(r_{ij})$ and r_{ij} are the interaction energy and the distance between sites i and j , respectively, with parameters A_{ij} , ρ_{ij} , and C_{ij} listed in Table 2. The *ab initio*-derived interaction parameters reported by Bandura and Kubicki [36] were applied to simulate the interactions between water molecules and TiO₂. Furthermore, it should be noted that non-electrostatic interactions between oxygen atoms of rutile and water (O–O_w) were equal to those between oxygen atoms of two water molecules (O_w–O_w). The SPC/E water model [39] was chosen and interactions for water molecules have been treated as a combination of Lennard-Jones (L-J) interactions and a Coulomb term for electrostatic interactions, as follows:

$$U(r_{ij}) = 4\varepsilon_{ij}[(\frac{\sigma_{ij}}{r_{ij}})^{12} - (\frac{\sigma_{ij}}{r_{ij}})^6] + \frac{q_i q_j}{r_{ij}} \quad (2)$$

where the parameters ε_{ij} and σ_{ij} list in Table 3.

Table 2

Interaction parameters of Buckingham potential for the M-A force field [36].

$i-j$	A_{ij} , kcal mol ⁻¹	ρ_{ij} , Å	C_{ij} , kcal mol ⁻¹ Å ⁶
Ti-Ti	717647.4	0.154	121.0676
O-O	271716.3	0.234	696.8883
Ti-O	391049.1	0.194	290.3317
Ti-O _w	28593.02	0.265	148.000

Atomic charges: $q(\text{Ti}) = 2.196$ (e), $q(\text{O}) = -1.098$ (e).

Table 3

Interaction parameters [39] of L-J potential.

$i-j$	ε_{ij} , kcal mol ⁻¹	σ_{ij} , Å
O-O _w	0.15539	3.1660
O _w -O _w	0.15539	3.1660
O _w -H _w	0.000	1.5830
H _w -H _w	0.000	0.000

Atomic charges: $q(\text{O}_w) = -0.8476$ (e), $q(\text{H}_w) = 0.4238$ (e).

2.3 Analytical methods of water microstructures

2.3.1 Definition of residence time of water in a particular layer

A residence correlation function $C_R(t)$ [40] was employed to quantify how long a specific water molecule remained in a particular layer. The residence correlation function was calculated according to Eq. (3):

$$C_R(t) = \frac{\langle O_w(t)O_w(0) \rangle}{\langle O_w(0)O_w(0) \rangle} \quad (3)$$

where $O_w(t)$ describes if an oxygen atom stays on the TiO₂ surface at time t (nanoseconds, ns). The value for $O_w(t)$ equals one indicating an atom belongs to the particular layer and zero otherwise. Here, the angular brackets denote ensemble averages. $C_R(t)$ is expected to decay from 1.0 to 0.0 with time evolution, which means water molecules move into and out of a specific layer.

We further analyzed the mean residence time (MRT) of water molecules adsorbed near TiO₂ surface by calculating the average values of the residence autocorrelation functions at each temperature. The mathematical expression linking the $C_R(t)$ and the MRT was described as

$$\tau = \int_0^1 C_R(t) dt \quad (4)$$

where the range for t is from zero to one, which represented a integral of the entire 1.0 ns MD simulations.

2.3.2 Definition of hydrogen bonds of water molecules

We used geometric criteria [41] to determine the formation of H-bonds. As illustrated in Fig. 2, a H-bond is formed between two water molecules (one acts as donor and another acts as acceptor), when satisfies the following three criteria simultaneously [42]. (I) The distance between the oxygen atoms of the two molecules is smaller than a threshold distance ($R_{OO} < R_{OO}^T$). (II) The distance between the oxygen of the acceptor and the hydrogen of the donor is lower than a threshold distance ($R_{OH} < R_{OH}^T$); (III) The angle between the O-O direction and the molecular O-H direction of the donor (H means the hydrogen which forms the bond) is lower than a threshold angle ($\alpha < \alpha^T$). In general, the choice of these thresholds depends on the potential model of water. In this work, R_{OO}^T , R_{OH}^T and α^T were chosen to be 0.35 nm, 0.245 nm and 30° , respectively.

Fig. 2. Geometric criteria of H-bonds formation.

2.3.3 Definition of orientation angles of water molecules

The dipole moment orientation of a water molecule was defined by angle θ . The positive direction was along the positive z-axis (the normal vector to the pore wall). HO bonds orientations in a water molecule were defined by angle ϕ . The positive direction was also along the z-axis. Fig. 3 illustrates the orientation angle sketches of water dipole moments and HO bonds in TiO_2 nanoslits.

Fig. 3. Definition of orientation angles of water molecules (dipole angle θ and HO bonds angle ϕ).

3. Results and discussion

In this section, we first adopted the spatial distributions and residence times of interfacial water molecules to evaluate the temperature effect on their behaviors (in sections 3.1 and 3.2). Then, we analyzed the microstructures of confined water molecules in detail to shed light on the underlying mechanisms at molecular scale (in section 3.3).

3.1 Spatial distributions of the water molecules nanoconfined on TiO_2 surface

Fig. 4 shows the density profiles of the oxygen atoms in water along z -direction, which is defined as the ratio of the density $\rho(z)$ to the bulk water density ρ_0 along the z direction from surface oxygen atoms of TiO_2 (origin) up to 1.0 nm away from the surface. It could be seen that there were two distinct peaks, in all the density profiles, indicating that two layers of the water molecules were absorbed on the TiO_2 surface [12,13]. The increased local water density suggests that the distributions of these water molecules differ from those of bulk water. Hence, we divided the profiles into three regions according to their z -distance away from the surface: (i) first layers (layer I, from zero to the first valley in density profiles), (ii) second layers (layer II, from the first valley to the second valley in density profiles) and (iii) central region (water molecules beyond layers I and II). The z -ranges (distance from the mineral surface) of layer I and layer II at different temperatures was listed in Table 4.

Table 4

The z-ranges (distance from the mineral surface) of layer I and layer II at different temperatures.

Temperature/°C	Layer I		Layer II	
	z_min	z_max	z_min	z_max
27	0.0	0.16	0.16	0.29
100	0.0	0.16	0.16	0.30
200	0.0	0.16	0.16	0.31
300	0.0	0.16	0.16	0.31
400	0.0	0.17	0.17	0.31
500	0.0	0.17	0.17	0.31
600	0.0	0.17	0.17	0.31
700	0.0	0.17	0.17	0.31
800	0.0	0.17	0.17	0.32

Furthermore, we can observe two obvious changes as the temperature increases in Fig. 4. Firstly, the broadening of the peak profile indicates an increased thermal motion of water molecules suggesting that confined water molecules are more likely to get rid of the surface binding. Secondly, the minimum value between the two peaks presents stronger dependence on temperature. At relatively low temperature (below 300 °C), the minimum value remains the same and equals to zero, indicating that there was less water molecules exchange between layers I and II. On the contrary, after the temperature rose to 300 °C, the minimum value gradually becomes larger from 300 °C, indicating that more frequent exchange of water molecules between layer I and layer II. Correspondingly, the exchange of water molecules between layer II and the central region also enhanced with the increment of temperature.

Fig. 4. Density profiles of oxygen along the z -direction. The y-axis represents the density distributions of $O(\rho(z))$ along the z -direction in units of corresponding bulk density(ρ_0). The x-axis represents the distance away from the surface.

3.2 Residence time of water molecules nanoconfined on TiO_2 surface

To quantify residence time of the water molecule in a particular layer, residence autocorrelation functions $C_R(t)$ (see Eq. (3)) of water molecules for the two layers near TiO_2 surface were calculated. The faster the autocorrelation function reduces, the shorter the water molecules remain in that particular layer [40,43]. It could be seen from Fig. 5 that for both layers a higher temperature corresponds to faster decaying of $C_R(t)$, indicating a shorter residence time in their respective layers.

Fig. 5. The residence autocorrelation functions of (a) layer I and (b) layer II as a function of time.

We further analyzed the MRT of water molecules adsorbed near TiO_2 surface according to Eq. (4). The residence time is an effective indicator for investigating the behaviors of fluid molecules staying on the wall [40,42,44].

In Fig. 6, it can be observed that MRT of layer I is almost constant and close to the MD simulation time (1 ns). The extremely long residence time of water molecules of layer I near TiO_2 surfaces is also found in our previous study at room temperature [45]. On the contrary, the MRT of layer II decreased from 0.29 to 0.12 ns before 300 °C. These observations revealed that the water molecules in layer I were highly restricted whereas the water molecules in the layer II have more mobility than those in the layer I. In the other word, there is always a stable water layer until 300 °C, indicating that complete dehydration of TiO_2 surface is extremely difficult. Moreover, as shown in Fig 6, the MRT of layer I reduced dramatically after 300 °C. The pace of reduction first increased from 300 °C to 600 °C and then decreased above 600 °C. On the other hand, the MRT of layer II almost remained constant at 0.1 ns with increasing temperature. The results demonstrated that the role of confined water molecules cannot be neglected for applications of nanoporous TiO_2 below 600 °C, such as catalyst support.

Fig. 6. Mean residence time of water molecules of different layers on the TiO_2 surface as a function of temperature.

3.3 Detail microstructural analysis of water molecules nanoconfined on TiO₂ surface

In order to explain further MRT characteristics shown in Fig. 6, we analyzed the microstructures of confined water molecules by studying the orientation and H-bonds properties. Given that the spatial distribution analysis in section 3.1, we analyzed the water microstructures layer by layer.

3.3.1 Microstructures of the water molecules within the layer I

We analyzed the H-bonds distributions of the water molecules within the layer I to reflect the changes in H-bonds networks clearly [46-48]. Given that the quantities of H-bonds would scale with the surface size, we calculated the number of water molecules with i ($i = 1, \dots, 4$) H-bond per unit area (nm^{-2}) of the TiO₂ surface ($n_1, \dots, n_4$). As shown in Fig. 7a, it was found that values of n_4 were almost constant at zero under all the studied temperatures, indicating that the original hydrogen bond networks for bulk water were destroyed under this confinement of TiO₂ nanoslit. The values of n_1 , n_2 and n_3 were very small before 300 °C, but climbed abruptly above 300 °C. At room temperature (27 °C), the values of n_1 , n_2 , n_3 and n_4 were close to zero, indicating that most water molecules adopted the form of monomer on the TiO₂ surface. Moreover, n_1 , with the largest value among various H-bonds forms, grew at the fastest rate, indicating that the water molecules within the layer I had a tendency to form dimers (n_1) of water molecules with increasing temperature. The formation and diffusion of water dimers on TiO₂ surfaces was also observed by Serrano et al. [49], with the help of the high resolution STM. Matthiesen et al. [50] demonstrated that the water dimers diffused faster than the water monomers on rutile TiO₂ (110). These results agreed well with the sudden reduction of the MRT as described in Fig. 6. The increased probability of H-bonds formation of water molecules of the layer I might be responsible for the reduction in MRT.

The orientation distributions of confined water molecules within layer I from 27 to 800 °C were plotted in Fig. 7b to investigate the underlying mechanism of formation

of H-bonds within layer I. At 27 °C, there was one and two obvious peaks in dipole (θ) and HO bond (ϕ) orientations, respectively. The dipole angles were concentrated in the range from 130° to 180° at 27 °C. This observation indicated that most of the water molecules of layer I at 27 °C have a preferential orientation with an oxygen atom pointing towards the surface whereas both hydrogen atoms pointing outwards (as shown in Fig 7c), indicating water molecules were highly restricted due to the strong interactions between TiO₂ and water molecules. As shown in Fig.7b, the peaks in the distributions of θ and ϕ became less pronounced and their half-peak widths increased accordingly as the temperature increased, indicating that some water molecules in the layer I gradually deviated from their original preferential orientation at room temperature, when the temperature increased. The variations in orientation could also be found in the snapshots in Fig 7c.

We defined an “orientation factor” (F_O) to more clearly reflect this deviation in orientations of water molecules with the increase of temperature. Dipole angle distributions of water molecules at 27 °C were selected as the reference values ($F_O = 1.0$). The orientation factor was defined as the ratio of the number of water molecules, whose dipole orientation value (θ) is higher than 130° and lower than 180° to the total number of water molecules in the layer 1 for each temperature (see Eq. (5)):

$$F_O = \frac{N_{130^\circ < \theta < 180^\circ}^{\text{Layer1}}}{N_{\text{all}}^{\text{Layer1}}} \quad (5)$$

A similar approach was adopted in our previous study, when we investigated the water orientations in the first hydration shells of different ions [51,52]. The values of F_O at different temperatures were listed in Table 5. Combining the results in Fig. 7a and Table 5, it could be found that F_O decreased as the probability of forming H-bonds increased, suggesting that F_O could, to some extent, reflect the competitions between (i) the H-bonds interactions derived from water molecules and (ii) the interactions restricted by TiO₂. With the increase of temperature, some water molecules in layer I were found gradually changed their orientations. This observation could be attributed

to that water molecules obtained more kinetic energy because of the higher interfacial temperature, making the probability of forming H-bonds between water molecules in the layer I increase.

Table 5

The values of F_O at different temperatures.

$t/^{\circ}\text{C}$	27	100	200	300	400	500	600	700	800
F_O	1.0	0.99	0.97	0.95	0.92	0.89	0.85	0.82	0.79

Fig. 7. Microstructures of water molecules of layer I under different temperatures. (a) Number of water molecules with i ($i = 1, \dots, 4$) H-bond per unit area of the TiO₂ surface ($n_1, \dots, n_4$). (b) Orientation angles distributions. (c) Snapshot of MD-simulated water molecules on TiO₂ surface. Red and white balls represent oxygen and hydrogen atoms in H₂O, respectively.

3.3.2 Microstructures of the water molecules beyond layer I

Two kinds of H-bonds were discussed: type I H-bond, which was formed within water molecules in layer II, and type II H-bond, which was formed between water

molecules in and beyond layer I. According to the definitions, For the type I H-bond, all the water molecules forming H-bonds belong to the layer II. For the type II H-bond, at least one water molecule belongs to the layer I among the water molecules forming H-bonds. We calculated two kinds of H-bonds number distributions, respectively, to reflect the temperature effect on the microstructures of the water molecules beyond layer I. As shown in Fig. 8a, for type (I), the value of $n1$ was always increasing under all the temperatures. The values of $n2$, $n3$ and $n4$ first increased but then decreased with increasing temperature. Moreover, for type (II), as shown in Fig. 8b, the values of $n3$ and $n4$ were almost constant at zero and those of $n1$ and $n2$ slightly decreased with increasing temperature, indicating that H-bonds of type (II) were destroyed with increasing temperature.

In combination with the microstructural analysis in Section 3.3.1, results suggested the formation of H-bonds between water molecules within layer I is the main reason for the reduction in MRT. As shown in Fig. 7a, monomers of water molecules near TiO_2 surfaces, began to form dimers ($n1$) at about 300 °C. According to Matthiesen et al.'s investigations [50], the increased formation of dimers of water molecules with the increase of temperature suggested that the water molecules adsorbed on the TiO_2 surface had more potential to mobility at higher temperatures.

Fig. 8. The number of water molecules with i ($i = 1, \dots, 4$) H-bond per unit area of the TiO_2 surface ($n1, \dots, n4$). (a) type (I) and (b) type (II).

4. Conclusion

In this work, we carried out MD simulations to investigate the behaviors of water molecules confined in TiO_2 nanoslits under different temperatures (27 to 800 °C). Spatial distributions of interfacial water molecules and their MRT residence times were calculated to evaluate the temperature effects. Microstructures of confined water molecules were analyzed in detail to clarify on the underlying mechanisms at the molecular scale.

Spatial distribution of water molecules showed that water molecules take a layered structure at TiO_2 surface. The MRT of layer I reduced dramatically when the temperature reaches 300 °C. At this temperature, water molecules in layer I was likely to get rid of the TiO_2 surface but was still difficult to be removed TiO_2 surface. The reduction rate in MRT did not alleviate until temperature reached 600 °C. At this temperature, microstructure of water molecules near TiO_2 surface changed significantly, especially in layer I, where the water molecules obtained more kinetic energy due to the higher interfacial temperature. Structurally, water molecules in layer I were likely to form dimers with increasing temperature, which diffuses faster than the water monomers. The formation of H-bonds within layer I is largely responsible in the reduction of MRT.

These results demonstrated that the role of absorbed water nanoconfined on the TiO_2 surface could not be neglected for applications of TiO_2 at elevated temperatures. It also provided new insights into our previous experimental phenomenon. Carbon heterogeneous surface modification on a mesoporous TiO_2 -supported catalyst exhibited enhanced hydrodesulfurization performance [9]. The underlying mechanism might be that the water molecules absorbed on the TiO_2 surface were replaced by the carbon precursors with stronger molecular adsorption ability, making the modified surface more suitable for rapid removal of polarity product molecules at 300 °C.

Acknowledgements

This work was supported by the National Basic Research Program of China

[2015CB655301], National Science Foundation of China [21206070, 21490584, 21576130 and 91334202] Qing Lan Project and the State Key Laboratory of Materials-Oriented Chemical Engineering [No. KL13-18]. The authors thank Dr. Mingjie Wei in Nanjing Tech University for his constructive suggestions regarding technical details of this manuscript. We thank Prof. Hongqi Yang, Dr. Wenlong Xie and Mr. Kiros Hagos in Nanjing Tech University for their useful advice regarding the improvement of this manuscript. We would like to express our thanks to anonymous reviewers, whose careful comments on the earlier version of this paper has resulted in considerable improvement.

Nomenclature

Acronyms

1-D	one-dimensional
AEIR	adsorption equilibrium infrared spectroscopy
FTS	Fischer-Tropsch synthesis
^1H SSNMR	^1H solid-state nuclear magnetic resonance
L-J	Lennard-Jones
layer I	the first layer
layer II	the second layer
M-A	Matsui-Akaogi
MD	molecular dynamics
MRT	mean residence time
MSD	mean square displacement
NPs	nanoparticles
NPT	the isobaric-isothermal ensemble
NVT	the canonical ensemble

STM scanning tunneling microscopy

SPC/E extended simple point charge

VOC volatile organic compounds

Notation

A_{ij} potential energy parameter (see Table 1)

C_{ij} potential energy parameter (see Table 1)

$C_R(t)$ residence autocorrelation functions

$g_o(z)$ the ratio of $\rho(z)$ relative to ρ_0

Hw hydrogen of water molecules

$O_{w(t)}$ describes if an oxygen atom stay on the TiO_2 surface at time t (nanoseconds, ns).

O oxygen of rutile

Ow oxygen of water molecules

p pressure (Pa)

q_i charge of atom i

r_{ij} the distance between sites i and j (Å)

R_{OO} distance between the oxygen atoms of both molecules

R_{OH} distance between O of the acceptor molecule and the H of the donor

R_{OO}^T criterion of H-bonds: a threshold distance

R_{OH}^T criterion of H-bonds: a threshold distance

Ti titanium of rutile

$U(r_{ij})$ the interaction energy between sites i and j

α^T criterion of H-bonds: a threshold angle

ε_{ij} Lennard-Jones energy constant (kcal/mol)

θ dipole moment orientation angle

$\rho(z)$ density distributions along z -direction in confinement (nm^{-1})

ρ_{ij} potential energy parameter (see Table 1)

ρ_0	density in bulk (nm ⁻¹)
σ_{ij}	Lennard-Jones length constant (Å)
τ	mean residence time (ns)
ϕ	HO bonds orientation angle

References

- [1] X.B. Chen, A. Selloni, Introduction: titanium dioxide (TiO₂) nanomaterials, *Chem. Rev.* 114 (2014) 9281-9282.
- [2] J. Bai, B.X. Zhou, Titanium dioxide nanomaterials for sensor applications, *Chem. Rev.* 114 (2014) 10131-10176.
- [3] M. Chen, D.W. Goodman, Catalytically active gold on ordered titania supports, *Chem. Soc. Rev.* 37 (2008) 1860-1870.
- [4] J.A. Rodriguez, S.D. Senanayake, D. Stacchiola, P. Liu, J. Hrbek, The activation of gold and the water-gas shift reaction: insights from studies with model catalysts, *Acc. Chem. Res.* 47 (2014) 773-782.
- [5] K.I. Tanaka, H. He, Y. Yuan, Catalytic oxidation of CO on metals involving an ionic process in the presence of H₂O: the role of promoting materials, *RSC Adv.* 5 (2015) 949-959.
- [6] K.E. Gubbins, Y.C. Liu, J.D. Moore, J.C. Palmer, The role of molecular modeling in confined systems: impact and prospects, *Phys. Chem. Chem. Phys.* 13 (2011) 58-85.
- [7] Y.D. Zhu, J. Zhou, X.H. Lu, X.J. Guo, L.H. Lu, Molecular simulations on nanoconfined water molecule behaviors for nanoporous material applications, *Microfluid. Nanofluid.* 15 (2013) 191-205.
- [8] C. Chen, J. Xu, Q.H. Zhang, H. Ma, H. Miao, L.P. Zhou, Direct synthesis of bifunctionalized hexagonal mesoporous silicas and its catalytic performance for aerobic oxidation of cyclohexane, *J. Phys. Chem. C* 113 (2009) 2855-2860.
- [9] L.C. Li, Y.D. Zhu, X.H. Lu, M.J. Wei, W. Zhuang, Z.H. Yang, X. Feng, Carbon heterogeneous surface modification on a mesoporous TiO₂-supported catalyst and its enhanced hydrodesulfurization performance, *Chem. Commun.* 48 (2012) 11525-11527.
- [10] L. Bocquet, E. Charlaix, Nanofluidics, from bulk to interfaces, *Chem. Soc. Rev.* 39 (2010) 1073-1095.
- [11] S. Meng, L.F. Greenlee, Y.R. Shen, E. Wang, Basic science of water: challenges and current status towards a molecular picture, *Nano Res.* 8 (2015) 3085-3110.

- [12] M. Předota, A.V. Bandura, P.T. Cummings, J.D. Kubicki, D.J. Wesolowski, A.A. Chialvo, M.L. Machesky, Electric double layer at the rutile (110) surface. 1. structure of surfaces and interfacial water from molecular dynamics by use of ab initio potentials, *J. Phys. Chem. B* 108 (2004) 12049-12060.
- [13] M. Předota, M.L. Machesky, D.J. Wesolowski, P.T. Cummings, Electric double layer at the rutile (110) surface. 4. effect of temperature and pH on the adsorption and dynamics of ions, *J. Phys. Chem. C* 117 (2013) 22852-22866.
- [14] G.A. Kimmel, M. Baer, N.G. Petrik, J. VandeVondele, R. Rousseau, C.J. Mundy, Polarization- and azimuth-resolved infrared spectroscopy of water on TiO₂ (110): anisotropy and the hydrogen-bonding network, *J. Phys. Chem. Lett.* 3 (2012) 778-784.
- [15] W. Cui, Z. Shen, J. Yang, S. Wu, Molecular dynamics simulation on the microstructure of absorption layer at the liquid–solid interface in nanofluids, *Int. Commun. Heat. Mas.* 71 (2016) 75-85.
- [16] S.C. Li, L.N. Chu, X.Q. Gong, U. Diebold, Hydrogen bonding controls the dynamics of catechol adsorbed on a TiO₂ (110) surface, *Science* 328 (2010) 882-884.
- [17] L. Zhu, Q. Gu, P. Sun, W. Chen, X. Wang, G. Xue, Characterization of the mobility and reactivity of water molecules on TiO₂ nanoparticles by ¹H solid-state nuclear magnetic resonance, *ACS Appl. Mater. Inter.* 5 (2013) 10352-10356.
- [18] O. Borg, Z.X. Yu, D. Chen, E.A. Blekkan, E. Rytter, A. Holmen, The effect of water on the activity and selectivity for carbon nanofiber supported cobalt Fischer-Tropsch catalysts, *Top. Catal.* 57 (2014) 491-499.
- [19] F. Giraud, J. Couble, C. Geantet, N. Guilhaume, E. Puzenat, S. Gros, L. Porcheron, M. Kanniche, D. Bianchi, Experimental microkinetic approach of De-NO_x by NH₃ on V₂O₅/WO₃/TiO₂ catalysts. 4. individual heats of adsorption of adsorbed H₂O species on sulfate-free and sulfated TiO₂ supports, *J. Phys. Chem. C* 119 (2015) 16089-16105.
- [20] V. Idakiev, D. Dimitrov, T. Tabakova, K. Ivanov, Z.Y. Yuan, B.L. Su, Catalytic abatement of CO and volatile organic compounds in waste gases by gold catalysts supported on ceria-modified mesoporous titania and zirconia, *Chin. J. Catal.* 36 (2015) 579-587.
- [21] D.J. Wesolowski, L.M. Anovitz, P. Benezeth, A.A. Chialvo, D.A. Palmer, P. Fenter, L. Cheng, N.C. Sturchio, Z. Zhang, M.J. Bedzyk, Temperature effects and structure at the rutile-water interface, in: R. B. Wanty and R. R. Seal II (Eds.), *Water-Rock Interactions*, A. A. Balkema Publishers, 2004, pp. 775-780.
- [22] H.J. Wang, X.K. Xi, A. Kleinhammes, Y. Wu, Temperature-induced hydrophobic-hydrophilic transition observed by water adsorption, *Science* 322

(2008) 80-83.

- [23] A. Striolo, K.E. Gubbins, M.S. Gruszkiewicz, D.R. Cole, J.M. Simonson, A.A. Chialvo, P.T. Cummings, T.D. Burchell, K.L. More, Effect of temperature on the adsorption of water in porous carbons, *Langmuir* 21 (2005) 9457-9467.
- [24] A.K. Dalai, B.H. Davis, Fischer–Tropsch synthesis: a review of water effects on the performances of unsupported and supported Co catalysts, *Appl. Catal. A Gen.* 348 (2008) 1-15.
- [25] A. De Toni, H. Gies, W. Grünert, The impact of water on CO oxidation with Au/TiO₂ catalysts: poison or promotor? a study with an Au–TiO₂/MCM-48 model catalyst, *Catal. Lett.* 141 (2011) 1282-1287.
- [26] T. Fujitani, I. Nakamura, M. Haruta, Role of water in CO oxidation on gold catalysts, *Catal. Lett.* 144 (2014) 1475-1486.
- [27] M.J. Wei, J. Zhou, X.H. Lu, Y.D. Zhu, W.J. Liu, L.H. Lu, L.Z. Zhang, Diffusion of water molecules confined in slits of rutile TiO₂ (110) and graphite (0001), *Fluid Phase Equilib.* 302 (2011) 316-320.
- [28] M.J. Wei, L.Z. Zhang, L.H. Lu, Y.D. Zhu, K.E. Gubbins, X.H. Lu, Molecular behavior of water in TiO₂ nano-slits with varying coverages of carbon: a molecular dynamics simulation study, *Phys. Chem. Chem. Phys.* 14 (2012) 16536-16543.
- [29] J. Zhang, M. Li, Z. Feng, J. Chen, C. Li, UV Raman spectroscopic study on TiO₂. I. Phase transformation at the surface and in the bulk, *J. Phys. Chem. B* 110 (2006) 927-935.
- [30] S. Plimpton, Fast parallel algorithms for short-range molecular dynamics, *J Comput. Phys.* 117 (1995) 1-19.
- [31] H.G. Petersen, Accuracy and efficiency of the particle mesh Ewald method, *J. Chem. Phys.* 103 (1995) 3668.
- [32] M.J. Wei, Y. Song, Y. Wang, Heat transfer of nanofluidics in hydrophilic pores: insights from molecular dynamics simulations, *Chin. J. Chem. Eng.* (2016), <http://dx.doi.org/10.1016/j.cjche.2016.04.036>.
- [33] G.J. Martyna, D.J. Tobias, M.L. Klein, Constant pressure molecular dynamics algorithms, *J. Chem. Phys.* 101 (1994) 4177-4189.
- [34] V.V. Chaban, V.V. Prezhdo, O.V. Prezhdo, Confinement by carbon nanotubes drastically alters the boiling and critical behavior of water droplets, *ACS Nano* 6 (2012) 2766-2773.
- [35] M. Matsui, M. Akaogi, Molecular dynamics simulation of the structural and physical properties of the four polymorphs of TiO₂, *Mol. Simul.* 6 (1991) 239-244.

- [36] A.V. Bandura, J.D. Kubicki, Derivation of force field parameters for TiO₂-H₂O systems from ab initio calculations, *J. Phys. Chem. B* 107 (2003) 11072-11081.
- [37] G. Okeke, R.B. Hammond, S.J. Antony, Effects of heat treatment on the atomic structure and surface energy of rutile and anatase TiO₂ nanoparticles under vacuum and water environments, *Chem. Eng. Sci.* 146 (2016) 144-158.
- [38] P.K. Naicker, P.T. Cummings, H.Z. Zhang, J.F. Banfield, Characterization of titanium dioxide nanoparticles using molecular dynamics simulations, *J. Phys. Chem. B* 109 (2005) 15243-15249.
- [39] H.J.C. Berendsen, J.R. Grigera, T.P. Straatsma, The missing term in effective pair potentials, *J. Phys. Chem.* 91 (1987) 6269-6271.
- [40] D. Argyris, N.R. Tummala, D.R. Cole, A. Striolo, Molecular structure and dynamics in thin water films at the silica and graphite surfaces, *J. Phys. Chem. C* 112 (2008) 13587-13599.
- [41] A. Luzar, D. Chandler, Hydrogen-bond kinetics in liquid water, *Nature* 379 (1996) 55-57.
- [42] N. Zhang, Z. Shen, C. Chen, G. He, C. Hao, Effect of hydrogen bonding on self-diffusion in methanol/water liquid mixtures: A molecular dynamics simulation study, *J. Mol. Liq.* 203 (2015) 90-97.
- [43] A. Phan, T.A. Ho, D.R. Cole, A. Striolo, Molecular structure and dynamics in thin water films at metal oxide surfaces: magnesium, aluminum, and silicon oxide surfaces, *J. Phys. Chem. C* 116 (2012) 15962-15973.
- [44] Y. Shen, X. He, F.R. Hung, Structural and dynamical properties of a deep eutectic solvent confined inside a slit pore, *J. Phys. Chem. C* 119 (2015) 24489-24500.
- [45] M.J. Wei, J. Zhou, X.H. Lu, Y.D. Zhu, W.J. Liu, L.H. Lu, L.Z. Zhang, Diffusion of water molecules confined in slits of rutile TiO₂ (110) and graphite (0001), *Fluid Phase Equilib.* 302 (2011) 316-320.
- [46] Y. Ghadar, A.E. Clark, Intermolecular network analysis of the liquid and vapor interfaces of pentane and water: microsolvation does not trend with interfacial properties, *Phys. Chem. Chem. Phys.* 16 (2014) 12475-12487.
- [47] S. Calero, P. Gomez-Alvarez, Effect of the confinement and presence of cations on hydrogen bonding of water in LTA-type zeolite, *J. Phys. Chem. C* 118 (2014) 9056-9065.
- [48] J. Wang, Y.D. Zhu, J. Zhou, X.H. Lu, Diameter and helicity effects on static properties of water molecules confined in carbon nanotubes, *Phys. Chem. Chem. Phys.* 6 (2004) 829-835.
- [49] G. Serrano, B. Bonanni, M. Di Giovannantonio, T. Kosmala, M. Schmid, U. Diebold, A. Di Carlo, J. Cheng, J. VandeVondele, K. Wandelt, C. Goletti,

- Molecular ordering at the interface between liquid water and rutile $\text{TiO}_2(110)$, *Adv. Mater. Inter.* 2 (2015) 1500246 (1-6).
- [50] J. Matthiesen, J.O. Hansen, S. Wendt, E. Lira, R. Schaub, E. Laegsgaard, F. Besenbacher, B. Hammer, Formation and diffusion of water dimers on rutile $\text{TiO}_2(110)$, *Phys. Rev. Lett.* 102 (2009) 226101 (1-4).
- [51] J. Zhou, X.H. Lu, Y.R. Wang, J. Shi, Molecular dynamics study on ionic hydration, *Fluid Phase Equilib.* 194-197 (2002) 257-270.
- [52] Q. Shao, J. Zhou, L. Lu, X. Lu, Y. Zhu, S. Jiang, Anomalous hydration shell order of Na^+ and K^+ inside carbon nanotubes, *Nano Lett.* 9 (2009) 989-994.

Figure captions

Fig. 1. The schematics of simulation systems. The red, white and pink spheres represent the oxygen, hydrogen and titanium atoms, respectively, and the blue rectangle frame indicates the simulation box.

Fig. 2. Geometric criteria of H-bonds formation.

Fig. 3. Definition of orientation angles of water molecules (dipole angle θ and HO bonds angle ϕ).

Fig. 4. Density profiles of oxygen along the z -direction. The y -axis represents the density distributions of $O(\rho(z))$ along the z -direction in units of corresponding bulk density(ρ_0). The x -axis represents the distance away from the surface.

Fig. 5. The residence autocorrelation functions of (a) layer I and (b) layer II as a function of time.

Fig. 6. Mean residence time of water molecules of different layers on the TiO_2 surface as a function of temperature.

Fig.7. Microstructures of water molecules of layer I under different temperatures. (a) Number of water molecules with i ($i = 1, \dots, 4$) H-bond per unit area of the TiO_2 surface ($n_1, \dots, n_4$). (b) Orientation angles distributions. (c) Snapshot of MD-simulated water molecules on TiO_2 surface. Red and white balls represent oxygen and hydrogen atoms in H_2O , respectively.

Fig. 8. The number of water molecules with i ($i = 1, \dots, 4$) H-bond per unit area of the TiO_2 surface ($n_1, \dots, n_4$). (a) type (I) and (b) type(II).

Table captions

Table 1. The total number of water in the NVT environments for each temperature.

Table 2. Interaction parameters of Buckingham potential for the M-A force field.

Table 3. Interaction parameters of L-J potential.

Table 4. The z-ranges (distance from the mineral surface) of layer I and layer II at different temperatures.

Table 5. The values of F_O at different temperatures.

Table of Contents Graphic

Temperature-dependent Structural Properties of Water Molecules Confined in TiO₂ Nanoslits: Insights from Molecular Dynamics Simulations

Yumeng Zhang¹, Yudan Zhu^{1*}, Zirui Li², Yang Ruan¹, Licheng Li³, Linghong Lu¹, Xiaohua Lu^{1*}

For Table of Contents use only