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Full Length Article

Atomistic investigation on the detachment of oil molecules from defective alumina surface

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ABSTRACT

The mechanism of oil detachment from defective alumina surface in aqueous solution was investigated *via* atomistic molecular dynamics (MD) simulations. Special attention was focused on the effect of surface defect on the oil detachment. Our simulation results suggest that compared with perfect Al_2O_3 surface, defective substrate surface provides much more sites for the adsorption of oil molecules, thus it has higher oil adsorption energy. However, higher oil-solid adsorption energy does not mean that oil contaminants are much more difficult to be detached. It is found that surface defect could induce the spontaneous imbibition of water molecules, effectively promoting the detachment of oil molecules. Thus, compared with perfect alumina surface, the detachment of oil molecules from defective alumina surface tends to be much easier. Moreover, surface defect could lead to the oil residues inside surface defect. In water solution, the entire detachment process of oil molecules on defective surface consists of following stages, including the early detachment of oil molecules inside surface defect induced by capillary-driven spontaneous imbibition of water molecules, the following conformational change of oil molecules on topmost surface and the final migration of detached oil molecules from solid surface. These findings may help to sufficiently enrich the removal mechanism of oil molecules adhered onto defective solid surface.

1. Introduction

Detachment mechanism of oil molecules from solid surface is of significance in many application fields, such as detergency [1], enhanced oil recovery(EOR) [2], high-power laser facility [3,4]. Deeply understanding the microscopic detachment process of oil molecules occurring at the oil/water/solid interface is often key in further improving these important industrial processes and providing fundamental physical insights into detachment mechanism of oil molecules in aqueous solution. An important feature of solid substrate surface should be further considered. That is, the machined solid surfaces obtained by various kinds of machining methods, such as precision milling [5], laser machining [6], and polishing, et al. are rarely perfect and defect-free.

It has been extensively observed in many investigations that surface defect has evident influence on the adsorption behavior of various molecules on different solid surfaces [7–12]. For instance, by using QCM technology, Wu et al. experimentally found that surface roughness greatly affected the total adsorption amount and the adsorption kinetics of CTAB molecules [7]. From the theory and simulation point of view, Maria et al. investigated the effect of point and line defects on the structure and aggregation kinetics of SDS and dodecane molecules on a graphite surface [8,9]. It was demonstrated that vacancies on substrate surface could interface with the aggregation formation of SDS and dodecane molecules, while line defects are capable of localizing and orienting the aggregates of surfactant molecules. Wu and Song et al. studied the effect of various surface structures, including reduced groove, pit, and step et al. on the adsorption behavior and dynamics of RGD tripeptides onto the rutile TiO_2 (110) surface in aqueous solution [10,11]. They noted that all of these surface defects could provide more sites for the adsorption of RGD molecules. Claudio Melis et al. found that the adhesion of poly(3-hexylthiophene) on nanostructure titanium surface is easily affected by the local morphology and surface curvature of substrate surface [12]. All of these researches clearly indicate that taking the effect of surface defects on solid surface into account is of significance for deeply revealing the interfacial interactions at aqueous/solid interface.

Thus, the presence of surface defect on solid surface is believed to have great effect on the detachment of oil molecules. Better understanding the effect of surface defect on the detachment of oil molecules is important for many practical applications. Moreover, most of surface defects on the processed surface are micro-scale and even nano-scale. Owing to the restriction of experimental

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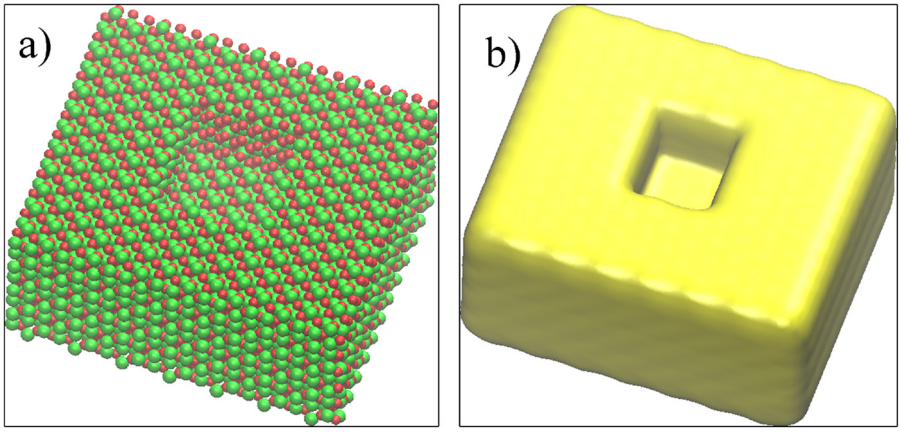

Fig. 1. Surface topographies of defective alumina surface using vdw spheres (a) and quick surface styles (b).

methods, it remains to be a challenge to directly observe the effect of surface defect, particularly those nanoscale defects, on the dynamic detachment process of oil molecules from defective surface.

Computational simulations, including molecular dynamics (MD), Monte calro (MC) and dissipative particle dynamics (DPD) simulations, have become powerful tool to analyze the microscopic dynamics of oil molecules adsorbed to solid surface in aqueous solution environment has been the subject of many studies [13–15]. For instance, in Wang and co-authors' MD study on the oil detachment from solid surfaces immersed in the charged nanoparticle suspensions, it was found that the removal efficiency of oil molecules could be evidently enhanced by using nanofluids of charged nanoparticles [16]. And Zhang et al. studied the effect of substrate surface wettability on the detachment of oil droplet in water solution [17].

For these reasons, we report the MD study of the dynamic conformational change process of oil molecules on defective α-Al_2O_3 surface in the aqueous solution and the effects of closed-end surface defect are mainly focused. To solve these problems, the present paper is organized in the following sections: The Section 2 briefly introduces the simulation models and protocols used in this study. In Section 3, the main findings and results are presented and discussed. And our conclusions are summarized in section IV.

2. Simulation details

2.1. Simulation model

In this work, aluminum oxide surface was selected as the substrate surface. As is known, the oxide layer on aluminum alloy surface has evident effect the interfacial properties of aluminum surface [18,19]. To obtain the precision processed aluminum surface with high surface cleanliness, we investigate the microscopic removal detachment of those oil molecules adsorbed to defective Al_2O_3 surface. Al_2O_3 substrate surface was simulated by using the (0001) crystallographic face of α-Al_2O_3 (space group). Many studies have been conducted to analyze the interfacial issues occurring at α-Al_2O_3 (0001) surface, such as interfacial water, adsorption of phenolic compounds [20,21]. In the present simulations, the α-Al_2O_3 (0001) substrate surface was placed in *x*-*y* plane and its *xy*-size is 5.7701 × 5.7108 nm^2. Meanwhile, the defective α-Al_2O_3 (0001) surface was constructed *via* building surface defects on perfect solid surface. The rectangular pit was adopted to represent surface defect. The surface topography of defective alumina surface is shown in Fig. 1. As for oil molecules, similar to our previous work [22], they are simulated by hexadecane molecules (C16).

To clearly elucidate the effect of surface defect on detachment process of oil molecules in the water solution, two groups of simulation systems consisting of oil/solid and oil/water/solid systems were established. Group I was designed to indicate the reproducibility of MD simulation results. A defective Al_2O_3 surface with a rectangular pit defect of the size 20.2 × 24.2 × 6.485 $Å^3$ was established by removing 140 Al atoms and 210O atoms from perfect Al-terminated Al_2O_3 (0001) surface. Then the defective Al_2O_3 surfaces contaminated by 40, 60 and 80 C16 molecules were respectively prepared, according to Liu's method [23]. Further, the oil/water/solid systems, which were applied to visualize the microscopic details in the detachment process of oil molecules, were obtained by adding 5508 water molecules over those contaminated defective surfaces and they are labelled to C16-40-groove2, C16-60-groove2 and C16-80-groove2, respectively. The construction procedure of simulation systems in Group I was also adopted to prepare other systems, which were involved in our present work. Group II was used to analyze the effect of geometry parameters, such as defect depth and cross-sectional area, on the spontaneous conformational dynamics of oil molecules. More details of the established oil/water/α-Al_2O_3 systems are listed in Table 1.

2.2. Simulation protocol

In simulations, CHARMM [24] force field was adopted to adequately model the oil molecules and the CLAY [25] force field was applied to describe the interactions involving the Al_2O_3 atoms. Sim-

Table 1
Model parameters of oil/water/α-Al_2O_3 systems.

	ID	Dimension/$Å^3$	Groove/$Å^3$	Oil	Water
Group I	C16-40-groove2	57.687 × 57.108 × 26.50	24.2 × 20.17 × 12.970	40	5504
	C16-60-groove2			60	
	C16-80-groove2			80	
	C16-80-groove1		24.2 × 20.17 × 6.4850		
Group II	C16-80-groove3		24.2 × 20.17 × 19.455		
	C16-80-groove4	57.687 × 57.108 × 31.993	24.2 × 20.17 × 25.940		
	C16-80-groove5	57.687 × 57.108 × 51.480	24.2 × 20.17 × 32.425		