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Surface diffusion and entrapment of simple molecules on porous silica

Ryutaro Souda

International Center for Materials Nanoarchitectonics, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

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ABSTRACT

Interactions of simple molecules with the surface of porous silica have been investigated using time-of-flight secondary ion mass spectrometry and temperature programmed desorption. A monolayer of water diffuses into pores at temperatures higher than 110 K. Multilayers of water are also incorporated in pores via sequential surface diffusion. In contrast, a methanol monolayer tends to stay on the surface up to 150 K, and carbon dioxide diffuses into pores rather gradually. Results can be explained as the contribution of hydrogen bonds between the adsorbate–substrate and adsorbate–adsorbate interactions. The predominance of the former (latter) might be responsible for single-molecule migration of methanol and carbon-dioxide (collective diffusion of water molecules) on the surface. These molecules are entrapped at higher coordination sites in pores, as revealed from thermal desorption peaks appearing at higher temperatures than those from non-porous silica. However, no significant difference is observed in desorption kinetics of CF_2Cl_2, Kr, CH_4, and N_2 molecules between the porous and non-porous silica substrates.

1. Introduction

Porous solids are technologically important materials and have been widely applied as adsorbents, membranes, and catalysts. The specific surface area and pore size are crucial for separation techniques based on the molecular sieving effect, whereas understanding of dynamical processes on pore walls is required for modeling chemical reactions in porous catalysts. Nuclear magnetic resonance (NMR) has been used for probing details of molecular self-diffusion in porous materials under equilibrium conditions [1]. More comprehensive information about adsorption, desorption, and diffusion of molecules on well-defined solid surfaces has been gained by using field ion microscopy (FIM) [2–6], scanning tunneling microscopy (STM) [7–11], and laser-induced thermal desorption (LITD) [12–14]. Although FIM is applicable to the study of metal atoms on metal, STM and LITD have been utilized to study molecular diffusion for a wide variety of adsorbate–surface combinations. The process of surface diffusion is likely to proceed via molecular hopping between adjacent sites, but long jumps beyond the nearest-neighbor sites have also been identified [4]. The concentration of molecules (i.e., surface coverage) plays an important role in surface self-diffusion because of the different effects of adsorbate–adsorbate and adsorbate–substrate interactions. It is known that mobility of small clusters is enhanced relative to that of single particles on metal substrates [2,3,7,9].

In this paper, we report on translational diffusion and thermal desorption of some simple molecules adsorbed on a porous silica substrate using time-of-flight secondary ion mass spectroscopy (TOF-SIMS) and temperature-programmed desorption (TPD). TOF-SIMS is used for compositional analysis of molecules on the surface; diffusional information can also be obtained by studying transport of molecules from the surface into pores. The molecules are expected to be trapped by higher coordination sites; the existence of such sites might be identified from desorption kinetics of molecules.

Thin glassy films are formed when molecules are deposited at low temperatures; the occurrence of translational diffusion in them is associated with the glass-liquid transition. It is known that the glass-transition temperature, T_g, of small systems, such as thin glassy films and confined liquids in pores, is modified from the bulk value because of the nanoconfinement effect [15–21]: a large decrease in T_g was observed for supported polystyrene films with decreasing thickness [17], where the presence of a liquid-like layer near the film surface was suggested. In this respect, anomalously enhanced surface mobility was observed for vapor-deposited thin films of 3-methylpentane in the sub-T_g region [21]. The nanoconfinement effects of supported thin films can also be affected by the interaction with substrates: The lowering of T_g was observed for poly(methyl methacrylate) (PMMA)

E-mail address: SOUDA.Ryutaro@nims.go.jp.

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on gold with decreasing film thickness, whereas stiffening of the film occurs on the native oxide of silicon because of the formation of a dead layer near the interface [18]. The glassy films deposited at temperatures well below T_g are characterized by a microporous structure, which has been identified from the ability to absorb a large amount of simple molecules like N_2[22,23]. To date, mobility of molecules during the glass-liquid transition and premelting has been discussed based on permeation of liquid-like species through pores of amorphous solid water (ASW) [24,25]. For molecular diffusivity measurements, however, substrates having permanent pores are more preferable. Here we investigate how the substrate of porous silica plays a role in diffusion and desorption kinetics of simple molecules, such as H_2O, CH_3OH, CO_2, CF_2Cl_2, Kr, N_2, and O_2, to gain insights into the surface and interface effects on modification of thin films' T_g.

2. Experimental

Porous silica was prepared by photodecomposition of tetraethylorthosilicate (TEOS) in air. Droplets of TEOS were dispersed on a mirror-finished polycrystalline Ni plate; it was irradiated with a UV light (184.45 and 253.7 nm photons from a low-pressure mercury-vapor lamp) in air by keeping the substrate temperature at 80 °C. After UV irradiation for approximately 1 h, a highly cohesive film remained on the substrate. For comparison, a native oxide layer formed on a silicon wafer (referred to as non-porous silica in this paper) was also investigated after the same UV irradiation procedure. The sample was immediately introduced into an ultrahigh-vacuum (UHV) chamber with a base pressure of less than 1×10^{-8} Pa through a load-lock chamber evacuated with oil-free pumps.

The TOF-SIMS experiment was performed using a primary beam of 2-keV He^+ ions generated in an electron-impact-type ion gun (Specs, IQE 12/38) after chopping into pulses. Positive secondary ions emitted perpendicularly to the surface were detected using a microchannel plate after traveling a field-free TOF tube. To extract low-energy secondary ions efficiently, a bias voltage (125 V/mm) was applied to the sample. The compositions of the porous and non-porous silica surfaces were checked in situ by TOF-SIMS. The sample surface was contaminated with hydrocarbons, as well as alkali-metal and fluorine impurities in some cases. The former can be removed easily via slight heating (by electron bombardment from behind) but the latter is hardly removable without sputtering and higher-temperature heating. Therefore, heavily contaminated samples with nonvolatile species were not used in this study. Typical TOF-SIMS spectra for porous and non-porous silica samples after cleaning are shown in Fig. 1. The spectra consist mainly of H^+, Si^+, and $SiOH^+$ peaks for both surfaces, indicating that a hydroxide-terminated silica surface is formed. The exact temperature required for removal of hydrocarbons is unknown, but prolonged heating results in surface decomposition as revealed from reduction of the H^+ and $SiOH^+$ intensities in TOF-SIMS. A continuous film of porous silica was formed on the Ni substrate, as evidenced by the absence of sputtered Ni^+ ions. Although the composition of deep pore walls cannot be analyzed by TOF-SIMS, we assume that they are similarly terminated with the OH species because UV photons can penetrate much deeper in the film than the probing depth of TOF-SIMS.

The sample was mounted on a Cu cold finger extended from a closed-cycle helium refrigerator and was cooled to 20 K. The temperature was controlled using a cartridge heater by monitoring temperature of the cold finger close to the sample position using Au(Fe)-chromel thermocouples. The molecules were deposited onto the cooled substrate by backfilling the UHV chamber. The film thickness has been determined using a Ni(111) substrate by monitoring evolution curves of secondary-ion intensities as a function of exposure. The TPD spectrum was obtained using a quadrupole mass analyzer located in a differentially pumped housing. The temperature was ramped at a rate of 5 K min^{-1} for both TOF-SIMS and TPD measurements. The fluence of the He^+ ions in TOF-SIMS was kept below 1×10^{12} ions cm^{-2} to avoid decomposition of the film surface.

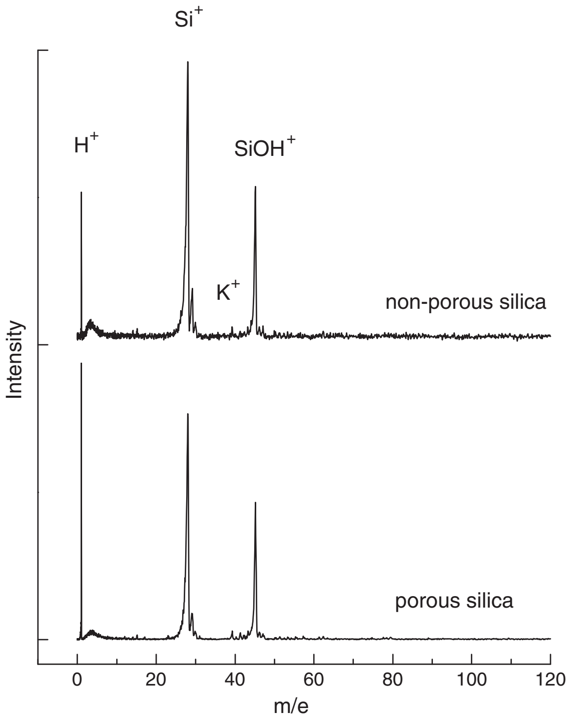

Fig. 1. TOF-SIMS spectra of positive ions sputtered from porous and non-porous silica surfaces obtained using a primary beam of 2-keV He^+ ions.

3. Results

Fig. 2 displays temperature evolutions of typical secondary-ion intensities from water molecules (1 ML) adsorbed on (a) non-porous and (b) porous silica substrates. The H_2O molecules stay on the surface of the non-porous silica up to evaporation temperature of 145–155 K, as revealed from the constant H_3O^+ and Si^+ intensities. In contrast, the H_3O^+ (Si^+) intensity from the porous silica substrate starts to decrease (increase) at 110–120 K because of molecular diffusion into the film. At around this temperature, the H^+ intensity on the non-porous silica substrate increases slightly. This behavior can be interpreted as restructuring of the molecules. Thus, the water monolayer fundamentally wets the surface without agglomeration. We have reported in a previous work [26] that the monolayer of water molecules adsorbed on graphite and a vitrified ionic liquid tends to form droplets at 120 K. Thus, surface mobility of water molecules is thought to evolve at around this temperature irrespective of the nature of substrates. In this respect, it has also been revealed using STM that the topmost surface layer of crystalline ice films becomes mobile at around 120–130 K [27].

Fig. 3(a) shows H_3O^+ intensities in TOF-SIMS from 1, 4, 8, and 40 ML H_2O films deposited on porous silica. The temperature at which the H_2O molecules disappear from the surface increases with increasing film thickness. Such a phenomenon has not been observed on the flat substrates like non-porous silica and Ni(111), so that it is ascribable to the molecular uptake into pores. Probably, the water molecules in the multilayer films are incorporated sequentially in pores at temperatures higher than 110 K, resulting in the delay of complete uptake of thicker films. The initial H_3O^+ intensity tends to decrease with increasing film thickness, and a peak appears at around the decay temperatures for multilayer films. The occurrence of a peak is indicative of the formation of a monolayer just before complete