

DYNAMICS OF TWO-Dimensionally CONDENSED WATER ON HYDROXYLATED CHROMIUM (III) OXIDE SURFACE

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The dynamic properties of water molecules adsorbed on the hydroxylated chromium (III) oxide surface were investigated around the two-dimensional critical temperature (303 K) by FT-IR, quasielastic neutron scattering and dielectric relaxation techniques. The Cr₂O₃ sample covered with a water monolayer gives a broad band at 3400 cm⁻¹ due to the mutual hydrogen bonding between the adsorbed water molecules. The quasielastic neutron scattering data have revealed that when crossing the two-dimensional critical temperature, the motion of the adsorbed water molecules changes from that of a supercritical fluid to that of a solidified phase. The dielectric spectra observed at 298 K have been interpreted in terms of two relaxations due respectively to interfacial and orientational polarizations. The interfacial polarization was explained in terms of a hopping model of protons of adsorbed molecules. As a result, from the behaviour of conductivity, one concludes that below the monolayer coverage, small clusters are formed on the Cr₂O₃ surface.

The knowledge of interactions of water molecules with metal oxide surface is of essential interest. In effect, metal oxide surface is covered with hydroxyls carrying various physico-chemical properties such as heterogeneity, acidity, hydrophilicity. Among metal oxide surfaces, hydroxylated chromium oxide (Cr₂O₃) surface is specifically characteristic because of its exceptionally high homogeneity. As a result, adsorbed water molecules are considered to perform some uniform two-dimensional (2D) phase. Figure 1 shows the phase diagram of a water monolayer on the hydroxylated Cr₂O₃. A 2D critical temperature has been determined to be 303 K, but the triple point has not been observed. Thus, the question is raised if the condensed phase is either liquid or solid on the basis of physico-chemical point of view. Dynamic properties of water molecules in this system was investigated by using FT-IR, quasi-elastic neutron scattering, and dielectric techniques.

Results and Discussion

In a previous work (1), a broadening of OH stretching band of monolayer water at ~3400 cm⁻¹

was observed above 2D critical temperature, suggesting the easing of the lateral bonding of monolayer water. FT-IR measurements of the surface hydroxyls and monolayer water at low temperatures suggested that there were no definite phase changes below the 2D critical temperature.

Quasielastic neutron scattering experiments were realized on a water monolayer as a function of temperature using the cold neutron beam of MIBEMOL. The obtained spectra were fitted with one delta function and one Lorentzian function. Fig. 2 represents the half-width at half maximum (Γ) of the quasielastic part of the spectra as a function of the momentum transfer Q . Below the 2D critical temperature, Γ values are independent on Q , while above this temperature, Γ exhibits some increase at large Q values. The latter tendency becomes marked as temperature increases. This change in Γ - Q relation above 297 K suggests some change in rotational motion from three sites to higher sites model: this suggests that the environment of the water molecule evolves from some ice-like water to some hypercritical liquid (2).

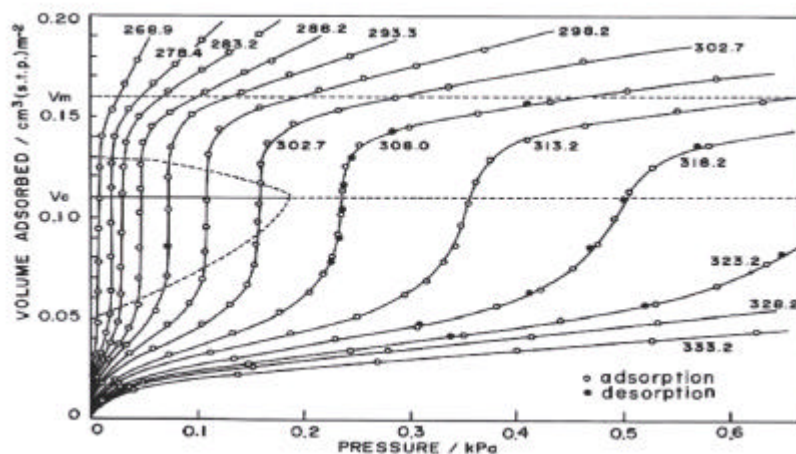


Figure 1. Adsorption isotherms of water on hydroxylated Cr_2O_3 surface at various temperatures.

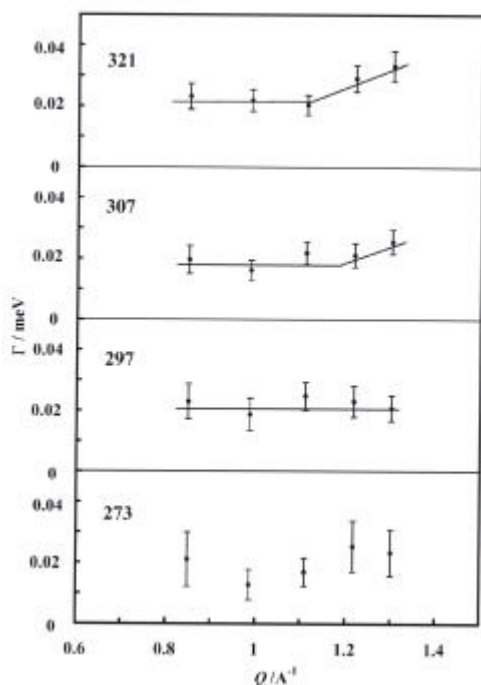


Figure 2. HWHM-Q relation for the adsorbed water on the hydroxylated Cr_2O_3 surface.

The structure and dynamic properties of adsorbed water below the critical temperature were inferred, into details, from dielectric measurements. Figure 3 shows the effect of coverage on the dielectric permittivity (ϵ') of the system determined at various frequencies (numbers in Hz in figure 3). Constancy of values of dielectric permittivity at the 2D condensation region shows that the increase in adsorbed water molecules does not directly lead to an electric conductivity increase and thus the relaxation is not of Onsager type (3). In other words, we may say that the 2D condensed phase is composed of monolayer patches on the hydroxylated Cr_2O_3 surface.

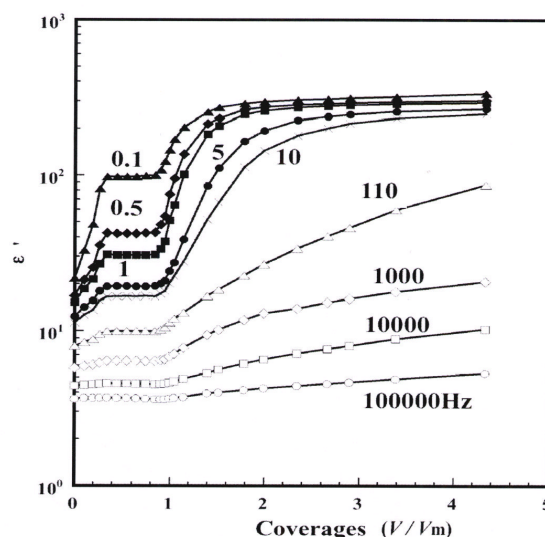


Figure 3. Dependence of dielectric permittivity, ϵ' , versus coverage of H_2O adsorbed on Cr_2O_3 at 288 K for various frequencies.

Figure 4 shows one example of Cole-Cole plots of relaxation for the system including water monolayer (coverage 1.1) at 298 K. The inset is an expanded figure of the smaller part of the full plot, corresponding to the contribution of dipolar polarization relaxation. The characteristic frequency (peak point of dielectric loss curve) for this relaxation is about 300 Hz, which is much smaller than 2.5 kHz for ice at 273 K and 18 GHz for liquid water at 293 K (4,5). Furthermore, this is smaller than 33 kHz for a water monolayer on SrF_2 at 159 kHz (6), as shown by a neutron study which will soon be reported. It is clear that water on the hydroxylated Cr_2O_3 has strongly hindered rotational motion below the 2D critical temperature due to ice-like structure originating from commensurating structure with (001) Cr_2O_3 surface.

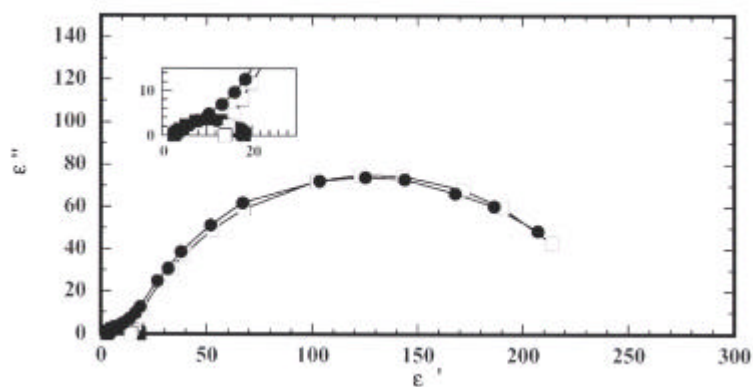


Figure 4. Cole-Cole plot (●) for the relaxations observed at 298 K and the coverage of 1.1. Interfacial (◻) and dipolar (■) polarizations.

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