NOTES

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The Effect of Water Vapor on Contamination of Metallic Oxide Surfaces

Yasukatsu TAMAI, Toshiaki MATSUNAGA, and Kazutomi SUZUKI
Chemical Research Institute of Non-Aqueous Solutions, Tohoku University, Katahira, Sendai 980

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Synopsis. The contamination rates of the clean surfaces of metallic oxides by liquid-paraffin vapor are largely reduced by the coexisting water vapor. They are related to the hydrophilicity of oxides evaluated as the water-solid interaction free energy by the two-liquid-contact-angle method.

High energy surfaces such as those of metallic oxides or metals are liable to be contaminated by organic vapor in the air. The sensitive change in the contact angle of water can be utilized for the detection of organic contaminant.[1] As White[2] pointed out, organic contamination should be regarded as adsorption and not the "falling out" of materials onto a surface.

Since oxide surfaces have strong affinity to water, coexisting water vapor would have some effect on the adsorption of organic compounds on a high energy surface. In order to study the effect of coexisting water vapor on organic contamination of several metallic oxides by liquid-paraffin vapor, we have measured the contact angles of water drops. The results are discussed in relation to the affinity of oxide surfaces to water.

Experimental

A quartz glass plate for an optical cell, and five single crystal plates of oxides, rutile (TiO_2)(001), chromia (Cr_2O_3)(0001), α-alumina (Al_2O_3)(0001), nickel oxide (NiO)(100), and strontium titanate ($SrTiO_3$) were examined. The numbers in parentheses indicate the crystal planes investigated. The surface of strontium titanate was not a low index crystal plane. The purity of single crystals was 99.9—99.99%.

All the surfaces were polished up to specular surfaces with emery paper and diamond-powder paste. The surfaces were cleaned before each measurement with an ultrasonic cleaner in a detergent solution, followed by thorough washing with redistilled water. Water could perfectly wet the surfaces.

In order to detect possible impurities originating from the cleaning process, the Auger spectra for alumina samples were measured with a Physical Electronics Instruments, Type CAS 545, apparatus. Only traces of phosphorus and carbon other than aluminum and oxygen were detected. Their coverage was estimated to be smaller than 1% Carbon might have come from the contaminants in the Auger apparatus.

The oxide plate was subjected to contamination in a Petri dish containing two small vessels, one filled with liquid paraffin and the other with water for wet atmosphere and with phosphorus pentoxide for dry atmosphere. The oxide sample was picked out after a certain time and transfered to an optical cell for measurement of contact angles of water drops by means of a goniometer-telescope system at 20±0.5 °C. The points in Figs. 1 and 2 represent the average of ten to twenty advancing contact angles, the accuracy being *ca.* ±2 degrees.

Liquid paraffin (spectroscopic grade) was used as an organic contaminant. Water was redistilled from an alkaline permanganate solution in a Pyrex glass apparatus.

Results and Discussion

Changes in contact angle of water with time in dry atmosphere and in saturated water are shown in Figs. 1 and 2, respectively. The order of contamination rates is : silica<α-alumina<nickel oxide<chromia<strontium titanate<rutile. This order is the same under both conditions, regardless of the coexisting water vapor. However, water vapor supresses organic contamination of all the oxides. The tendency is larger for the surfaces which are more easily contaminated, such as rutile or strontium titanate.

Since surface contamination can be regarded as competitive adsorption of organic and water vapor, the contamination rates would be related to the affinity of

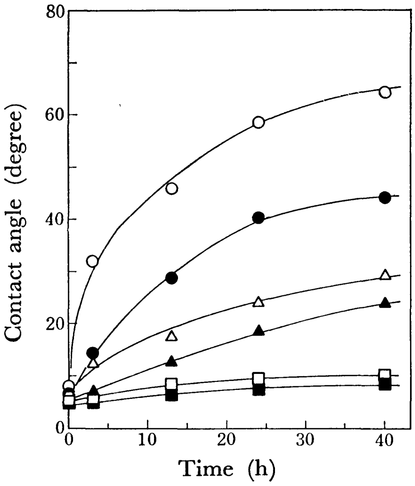

Fig. 1. Variation of contact angles under the dried atmosphere.
○: TiO_2, ●: $SrTiO_3$, △: Cr_2O_3, ▲: NiO, □: Al_2O_3, ■: SiO_2.

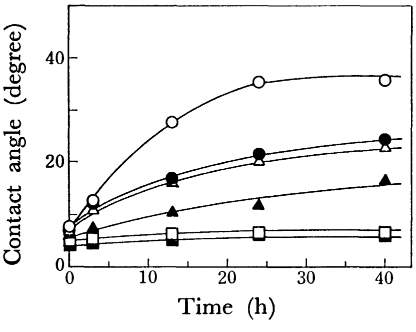

Fig. 2. Variations of contact angles under the wet atmosphere. (Symbols are the same in Fig. 1.)

oxide surface to water. Evaluation of the hydrophilicity of oxides can be carried out by such methods as adsorption of water and the heat of immersion in water, but they are restricted to powder samples.

The interaction free energy due to nondispersive forces (mainly the hydrogen bonding force) at the interface between solid and water, I^{n}_{sw}, can be obtained from the contact angles of water drops in hydrocarbon liquid. This can be defined in terms of surface tension γ by

$$I^{n}_{sw} = \gamma^{n}_{s} + \gamma^{n}_{w} - \gamma^{n}_{sw},$$

where subscripts s, w, and sw denote solid, water, and solid/water interface, respectively, and n indicates the component due to nondispersive forces. The details of the method[3,4] and the results for the oxides have been reported.[5]

The I^{n}_{sw} values obtained for the oxides are[5] as follows: TiO_2, 91.4; $SrTiO_3$, 93.2; Cr_2O_3, 93.6; NiO, 94.0; Al_2O_3, 97.6; and SiO_2, 99.2 in mJ m^{-2} at 20 °C. The accuracy is *ca.* ±0.3 mJ m^{-2}. The order of the I^{n}_{sw} values corresponds to the reverse order of the contamination rates (Figs. 1 and 2). The oxides which have smaller I^{n}_{sw} values and are thus less hydrophilic are more easily contaminated by organic vapors. This seems reasonable in view of the competitive adsorption.

It was found that the coexisting water vapor can largely reduce the contamination rates of the clean surfaces, suggesting an appropriate method for keeping the washed oxide surface clean.

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References

1) For example, J. J. Bikerman, "Physical Surfaces," Academic Press, New York (1970), p. 269.

2) M. L. White, in "Clean Surfaces," ed by G. Goldfinger, Marcel Dekker, New York (1970), p. 361.

3) Y. Tamai, K. Makuuchi, and M. Suzuki, *J. Phys. Chem.* **71**, 4176 (1967).

4) Y. Tamai and H. Kobayashi, *J. Colloid Interface Sci.* **32**, 369 (1970).

5) Y. Tamai, T. Matsunaga, and K. Suzuki, Proc. VIIth Int. Cong. Surface Active Substances at Moscow (1976), in press.