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A Convenient Determination of Surface Hydroxyl Group on Silica Gel by FT-IR Spectroscopy

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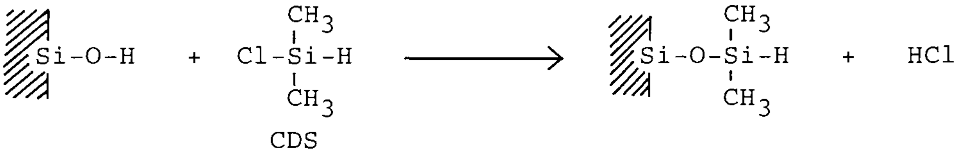
The dimethylsilyl(-Si(CH_3)$_2$H) substitution of hydroxyl hydrogen led to a convenient determination of surface silanol group on silica gels by Si-H bond stretching vibrational absorption analysis. The proposed procedure can be freed from influences of adsorbed water and moisture through the measurement process.

Polymer-modified metal oxide super-fine particles or colloids recently become of much interest as a new kinds of functional composite materials. There are many determination methods for surface hydroxyl groups on metal oxide gels, mainly silica gels, by means of thermal gravimetric analysis,$^{1)}$ active hydrogen measurement using organometallic compounds,$^{2)}$ O-H bond vibrational absorption analysis on IR spectrum,$^{3)}$ and so on.$^{4)}$ Most of these methods, however, are generally influenced by adsorbed water or moisture during operational processes, and also some procedures are inadequate for the determination of hydroxyl group on polymer or organic compounds-modified gels.

Now we wish to propose here a new and convenient method for the deter



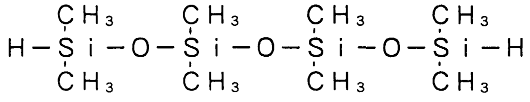
$$\text{Si-O-H} + \underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{\text{Cl-Si-H}}} \longrightarrow \text{Si-O-}\underset{\substack{|\\ CH_3}}{\overset{\substack{CH_3\\ |}}{\text{Si-H}}} + \text{HCl} \qquad (1)$$

CDS

$$2\ \text{CDS} + H_2O \longrightarrow \text{H-Si}(CH_3)_2\text{-O-Si}(CH_3)_2\text{H} + 2\ \text{HCl} \qquad (2)$$

mination, which can avoid awkward problems of the adsorbed water or moisture, based on IR spectroscopic absorption measurement due to the stretching vibration of Si-H bond, formed by the reaction (Eq. 1) of silanol group with chlorodimethylsilane (CDS). Principally, the present method can ignore water adsorbed or freely existed in the system, because the water molecules immediately react with CDS to produce volatile tetramethyldisiloxane (Eq. 2), which can be easily removed by washing and drying under vacuum.

We have examined the present method using four kinds of commercially available silica gels (Merck Silica Gel-40, -60 and Aerosil-200, -380). The reaction of silica gel (0.1 g), dried at 120 °C for 2 h under vacuum, with CDS (1 g, 9 mmol) was carried out in $CHCl_3$ solution (10 ml) containing Et_3N (1 ml) in N_2 atmosphere at room temperature. After the mixture was kept stirring for 24 h, the resulting gel was filtered and thoroughly washed with $CHCl_3$, and then dried in vacuo for 24 h. A mixture of dimethylsilyl-substituted gel (50 mg), KBr (0.200 g) and 10 mg of cyanoacetamide as an internal standard was ground on a mortar and subjected to measurement of IR spectrum, which was recorded on JEOL JIR-5500 with the diffuse reflectance technique. The K-M function due to Si-H bond stretching vibrational absorption was calibrated employing octamethyltetrasiloxane (OMTS) as a dummy compound. Various amounts (0.04-0.20 g) of OMTS were impregnated on 0.1 g of silica gel (460 m^2/g) from $CHCl_3$ solution, and then the mixture of each resulting $OMTS/SiO_2$ (50 mg), cyanoacetamide (10 mg) and KBr (0.20 g) was supplied to the spectroscopic measurement. The calibration was obtained by a linear relationship of molar ratio (Si-H to C≡N) to peak area ratio of Si-H bond absorption bands at 2144 cm^{-1} to C≡N bond absorption bands at 2269 cm^{-1} (Fig. 1).



$$H-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-O-\underset{CH_3}{\overset{CH_3}{Si}}-H$$

OMTS

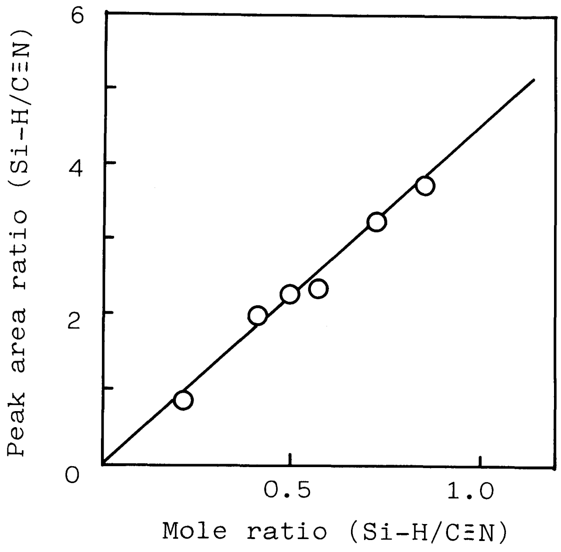


Fig. 1. Calibration of K-M function peak area for Si-H bond absorption with that for C≡N bond.

Stoichiometric dimethylsilyl substitution of hydroxyl hydrogen on silica gel was observed by appearance of an absorption peak at 2148 cm^{-1}, assigned to Si-H bond stretching vibration, and by disappearance of peaks at 3741 and 975 cm^{-1}, assignable to SiO-H bond stretching and bending vibrations, respectively (Fig. 2). It was also confirmed that the dimethylsilyl group on silica gel was stable to moisture and air, from the fact that intensity of the Si-H bond absorption bands was unchanged after exposure of the substituted gel to the atmosphere for a week.

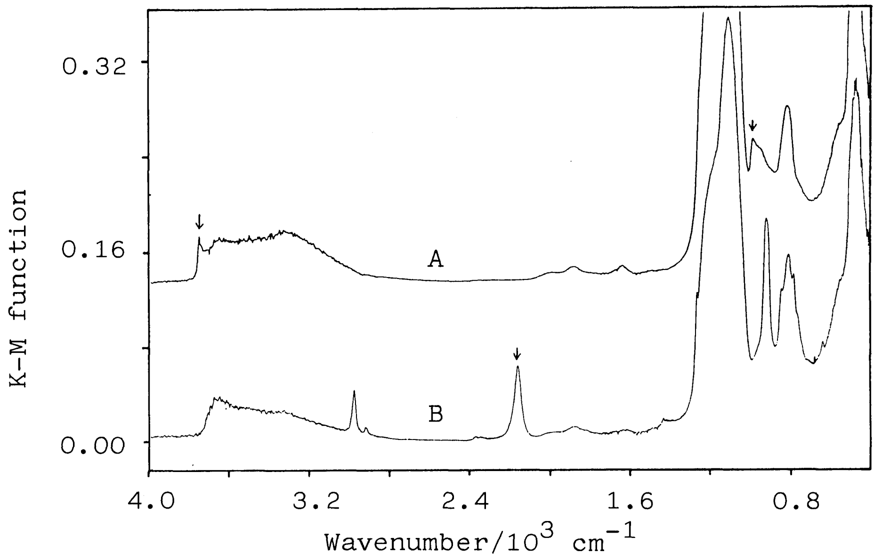


Fig. 2. IR spectra of unmodified (A) and dimethylsilyl-substituted (B) Silica gel-60.

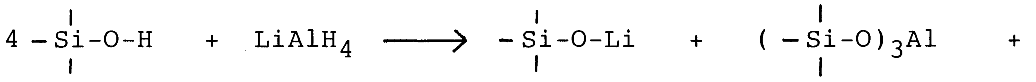
In Table 1, results of hydroxyl group determination by the present method are listed. Values obtained were reproducible in the range of ±5% error. In order to verify propriety of our procedure, we have also deter-

Table 1. Determination of hydroxyl group on silica gels[a)]

Silica	Surface area[b)] m^2 g^{-1}	Si-O-H/mmol g^{-1} Present method[c)]	Si-O-H/mmol g^{-1} $LiAlH_4$ method	Si-O-H 100 $Å^2$
Aerosil-200	200	1.19 ± 0.02 (1.23 ± 0.04)	1.80 ± 0.11	3.6
Aerosil-380	380	2.16 ± 0.04 (2.31 ± 0.04)	2.61 ± 0.05	3.4
Silica gel -60	460	2.54 ± 0.08 (3.24 ± 0.13)	2.98 ± 0.02	3.3
Silica gel -40	570	2.96 ± 0.14 (2.84 ± 0.10)	4.12 ± 0.01	3.1

a) All measurements with each method were carried out four times.
b) The areas were determined within ±10% error by BET method based on N_2 adsorption at -196 °C.
c) Values in parentheses are obtained using silica gels without drying at 120 °C under vacuum.

mined hydroxyl group by a typical usual method, active hydrogen measurement accompanied by H_2 evolution,5) based on the following reaction;



$$4\ -\mathrm{Si{-}O{-}H}\ +\ \mathrm{LiAlH_4}\ \longrightarrow\ -\mathrm{Si{-}O{-}Li}\ +\ (-\mathrm{Si{-}O})_3\mathrm{Al}\ +\ 4\ \mathrm{H_2}. \qquad (3)$$

The $LiAlH_4$ method gave about 0.5 mmol/g higher values than the present method, except for Silica gel-40. The differences between these methods probably comes from the adsorbed and/or liganded water which can not be eliminated under the pretreatment condition.3a) Since the present method principally does not count water adsorbed and/or existed in the system, values by the FT-IR method seem to show precise contents of surface hydroxyl group. Indeed, silica gels without the pretreatment brought about almost same contents of hydroxyl group as pretreated ones. Also, surface hydroxyl concentrations (3.1-3.6 Si-OH/100 $Å^2$) are considered to be reasonable according to the estimations (less than 5.0 Si-OH/100 $Å^2$) in the literatures.1,4a,6) However, Silica Gel-40, having higher surface area of 570 m^2/g and mean pore size of 40 Å, gave larger difference (1.0-1.3 mmol/g) between values by the two methods, as compared with relatively low porous silica gels. Probably, adsorbed water in very small size pores (less than 40 Å), which has been reported to remain even after evacuation at 100-120 °C,4a) brings about a higher value by the $LiAlH_4$ method than that by the present method.

Further investigations of versatility for polymer or organic compound-modified silica gels and for another metal oxide gels are now in progress.

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