

Application of Sealed Type Diffuse Reflectance FTIR Method

In 1950s infrared spectrophotometry was first applied to the research of catalysts and thereafter attracted much attention. It was shortly after the spectrum of CO absorbed in metal catalysts was measured for the first time that infrared spectrophotometry became popular among researchers. Since that time, infrared spectrophotometry has become one of the most effective methods for the study of the conditions of molecules absorbed on catalysts. For the measurement of infrared absorption spectrum of catalyst samples, transmission measurement of the sample formed into a disk

and put in a heated glass vacuum cell was the most popular method. Since the introduction of the Fourier transform infrared spectrophotometer (FTIR), high sensitivity measurement has also become possible using the diffuse reflectance method. So, it is expected that a heated vacuum diffuse reflectance attachment in which the sample cup is accommodated in a heated vacuum chamber will be used widely in the research of catalysts. Introduced here are examples of measurement using the heated vacuum diffuse reflectance method.

Outline of Attachment

The heated vacuum type diffuse reflectance attachment is so constructed that the sample cup of an ordinary diffuse reflectance attachment can be accommodated in the heated vacuum chamber as is shown in Fig. 1. The heater and the thermocouples for temperature monitoring are embedded in the base supporting the sample cup. As it permits evacuation or introduction of a controlled atmosphere (gas) while the sample is being heated, it is possible to measure the infrared spectra of the sample under a variety of reaction conditions.

Temperature-programmed Measurement of Silica Gel

Figure 2 shows infrared spectra of powder sample of silica gel measured at 50°C, 100°C, 200°C, and 400°C by heating the sample gradually from room temperature. The surface of silica gel is covered with hydroxy (OH) groups covalently bound with Silicon ($\equiv\text{Si-OH}$, silanol). In fact, these silanol groups are hydrophilic and readily capture hydrogen or water at room temperature by hydrogen bonding. In Fig. 2, the desorption process at the silanol groups, which have absorbed water or are combined with hydrogen, can be observed as temperature goes up by monitoring the peak at 3740 cm^{-1} which is a characteristic absorption band of a free silanol group.

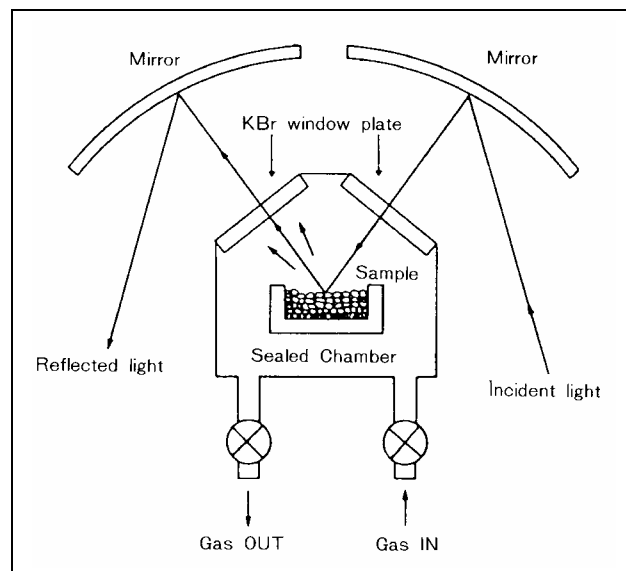


Fig. 1 Optics of Diffuse Reflectance Measurement Unit

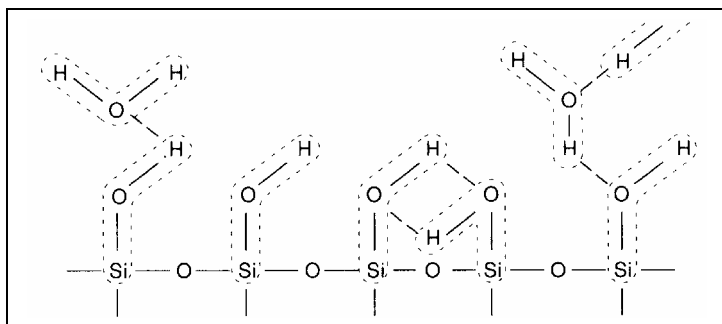


Fig. 3 Hydrogen Bonding at Surface of Silica Gel

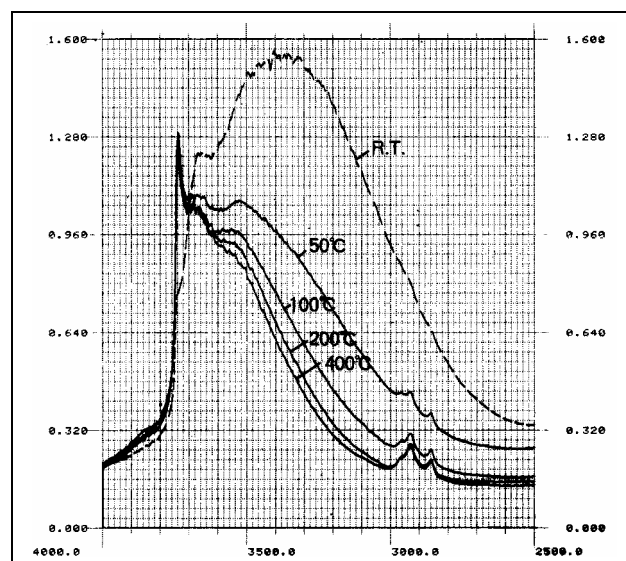


Fig. 2 Spectra of Silica Gel Showing Degrees of H₂O Adsorption at Different Temperatures.

Table 1 Analytical Conditions

Resolution: 4 cm^{-1}	Detector: MCT Detector
Apodization: Happ-Genzel	Accumulation: 200

Infrared Spectrum of Pyridine Absorbed on Zirconium Oxide

Metal oxides are used as catalysts in redox systems. In order to discriminate a catalytic Bronsted acid from a Lewis acid, the information from infrared spectrum of a reactant such as pyridium can be used; If the catalyst displays Bronsted acid, character (i.e., proton donor), the absorption bands of the pyridium ion will appear. If, however, the catalyst displays Lewis acid characteristics (i.e., electron pair acceptor.), the absorption bands of the pyridine coordination bond will be observed. Figure 4 show measurement of absorbed pyridine; ZrO₂ was left for 2 hours in a stream of helium at about 400°C, then the temperature was lowered to 100°C to allow the adsorption of pyridine on the sample. The chamber was evacuated and the sample was subjected to measurement at room temperature. The dotted line shows the spectrum measured before the adsorption. As there is an absorption band at around 1445 cm⁻¹ attributable to the pyridine coordination bond, it is perceived that ZrO₂ is mainly a Lewis acid.

Table 1 Analytical Conditions

Resolution: 4cm ⁻¹
Apodization: Happ-Genzel
Detector: MCT Detector
Accumulation: 200

Infrared Spectrum of Furosemide

Furosemide, a medicine which is often used lowering blood pressure and as a diuretic, has the structure shown below. figure 5 shows measurement Furosemide II, one of the metastable crystalline forms Furosemide, at room temperature. Figure 6 shows the result of measurement with the temperature raised 180°C. When heated to 180°C, Furosemide II will make transition to Furosemide VII which is stable at high temperature. It is clearly observed that at various wavenumbers there are differences between the spectra. Particularly, at around 3300 cm⁻¹, the difference in the absorption band of N-H is clearly recognized. The samples used for the measurements were courtesy of Professor Matsuda, Kobe Women's College Pharmacy.

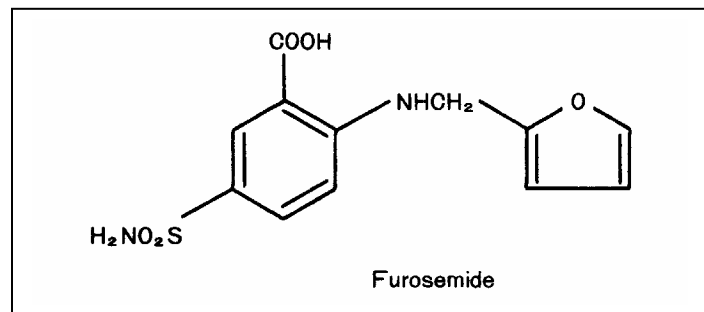


Table 3 Analytical Conditions

Resolution: 2cm ⁻¹
Apodization: Triangular
Detector: MCT Detector
Accumulation: 200

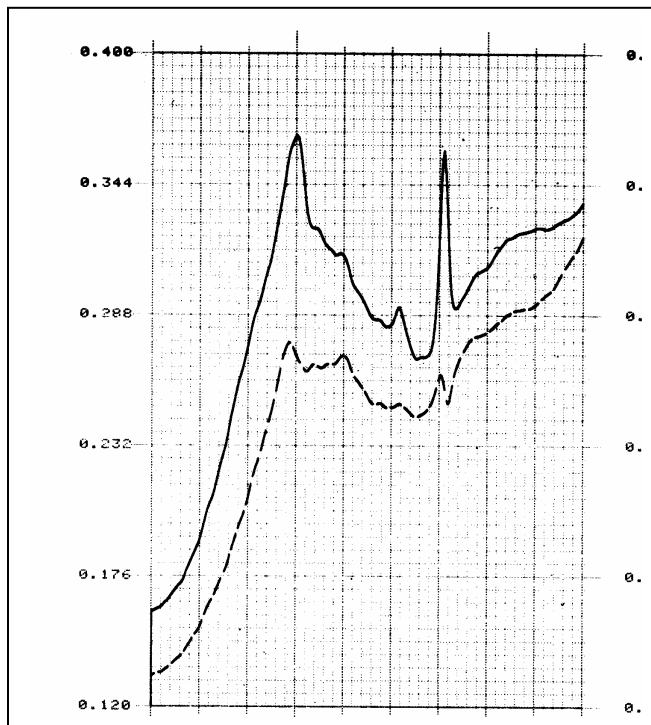


Fig. 4 Infrared Spectrum of Pyridine Absorbed on Zirconium Oxide

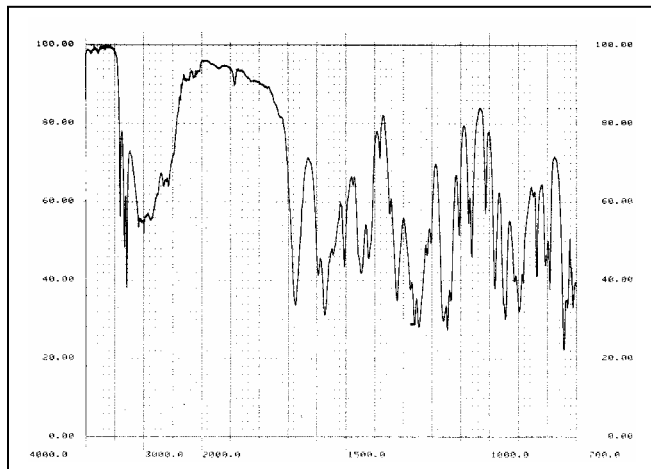


Fig. 5 Infrared Spectrum of Furosemide II

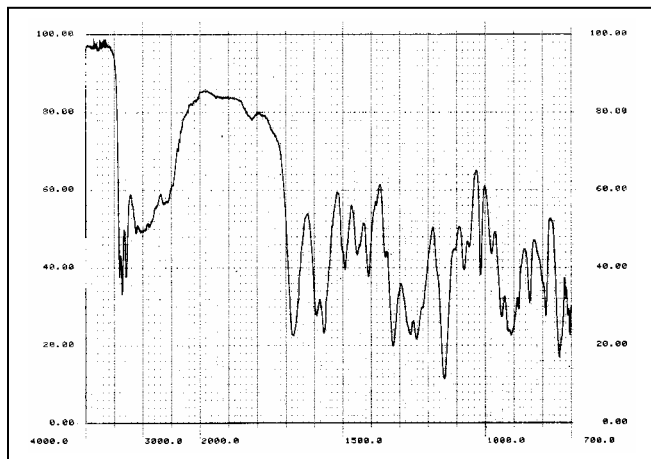


Fig. 6 Infrared Spectrum of Furosemide VII