

Application News

No. A489

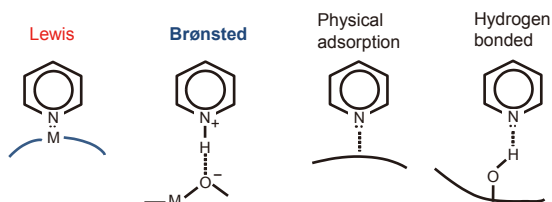
Spectrophotometric Analysis

High Speed Monitoring of Pyridine Adsorbing on Surface of TiO₂ Powder by Rapid Scan

Catalysts play an important role in promoting reactions in a wide range of industrial fields, including petroleum refining, petrochemical, gas purification, foods, fine chemicals, biochemicals, etc., and research and development of new catalysts is becoming increasingly important. Titanium oxide (TiO₂), which exists in forms that display a variety of crystalline structures, is well known as a photocatalytic substance. Here, using the rapid scan feature of the IRTracer-100 FTIR, we evaluated two types of TiO₂ powder having different crystalline structures.

■ Catalytic Characterization by Pyridine Adsorption Measurement

Solid oxides such as TiO₂ are widely used as catalysts. On the TiO₂ surface, there exist both Brønsted acid sites (B acid sites) that donate a proton to a companion molecule, and Lewis acid sites (L acid sites) that receive a pair of electrons from a companion molecule. Identification of these acid sites is possible using a basic molecule, such as pyridine, which is adsorbed on a solid oxide surface, thereby permitting measurement of the infrared spectrum. At the Lewis acid sites, the pyridine molecule bonds to the solid oxide. The presence of pyridine can be monitored by a pyridine characteristic absorption peak in the vicinity of 1440 cm⁻¹. At the Brønsted acid sites, the pyridine molecule becomes a pyridinium ion when the proton is donated. The pyridinium ion can be observed as a characteristic peak in the vicinity of 1540 cm⁻¹. In addition pyridine can bond to the substrate through physical adsorption and an H-bond. These alternative bonds give rise to IR absorption bands in the vicinities of 1585 cm⁻¹ and 1435 cm⁻¹, and their intensities are dependent on the surface properties of the catalyst. When the catalyst possesses a hydroxyl group, a characteristic peak is observed in the vicinity of 1600 cm⁻¹.¹⁾ A schematic view of these bond states are shown in Fig. 1.



Brønsted acid (B acid): Gives proton (H⁺) to companion molecule.
Lewis acid: Receives a pair of electrons from another molecule.

Fig. 1 Configuration of Pyridine Adsorbed on Metal Oxide

■ Measurement

Approximately 15 mg each of TiO₂ powder samples consisting of spindle-type and cubic-type crystalline structures, respectively, were formed into tablets. The tablets were then subjected to reduced pressure using a heat-vacuum resistant transmission cell, and heated at

200 °C for one hour. The sample tablets were allowed to cool to room temperature, and were then subjected to background measurement.

After acquisition of the background, the rapid scan measurement sequence was started, and pyridine vapor was immediately introduced. Table 1 shows the FTIR measurement conditions, and Table 2 shows the particle size and specific surface area of sample powder. In addition, the FTIR with the mounted chamber and the sample mounted in the cell are shown in the photographs of Fig. 2.

Table 1 FTIR Measurement Conditions

| | |
|----------------------|----------------------|
| Instrument | : IRTracer-100 |
| Resolution | : 4 cm ⁻¹ |
| Accumulation | : 1 |
| Apodization | : Happ-Genzel |
| Detector | : MCT |
| Measurement Interval | : 0.19 second |
| Measurement Time | : 60 seconds |

Table 2 Particle Size and Specific Surface Area of Sample Powder

| | Particle Size | Specific Surface Area |
|---------|---------------|-----------------------|
| Spindle | 205 ± 75 nm | 49 m ² /g |
| Cubic | 18 ± 5 nm | 52 m ² /g |

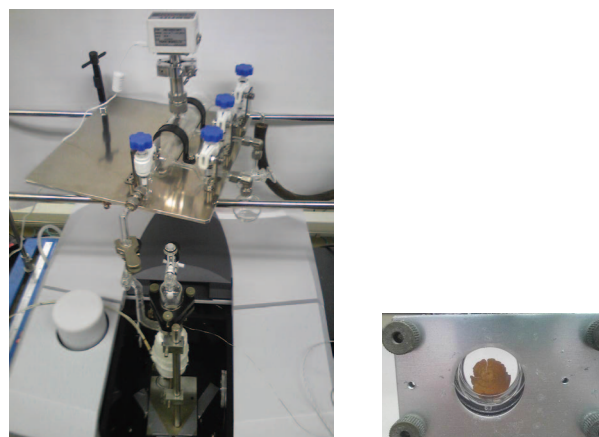


Fig. 2 Photograph of IRTracer-100 with Mounted Environmental Chamber (left) and TiO₂ Tablet in Environmental Chamber (right)

Fig. 3 shows the spectral changes that occur following introduction of the pyridine. In the case of the spindle-type TiO₂, initially, L acid type pyridine bonding increases soon after the introduction of pyridine vapor as is evident by the adsorption band at 1444 cm⁻¹. As time elapses, a peak in the physical adsorption band at 1438 cm⁻¹ increases in size. As for the cubic type TiO₂, however, the initial period of pyridine adsorption shows only minor growth of the L acid peak at 1444 cm⁻¹. As time elapses, however, a peak in the physical adsorption band at 1438 cm⁻¹ gradually exhibits increased intensity.

Although the specific surface area of both the specimens is more or less equivalent, the peak area of the L acid is greater for the spindle type than for the cubic type, indicating that there are more functional coordination deficit sites that function as an L acid. Fig. 4 shows the peak changes that occur when

pyridine is introduced, in addition to electron microscope images. A comparison of the changes that occur in the peaks at 1444 cm^{-1} and 1438 cm^{-1} suggests that adsorption occurs more quickly in the spindle type than in the cubic type. Further, the results suggest that the spindle type possesses greater catalytic activity.

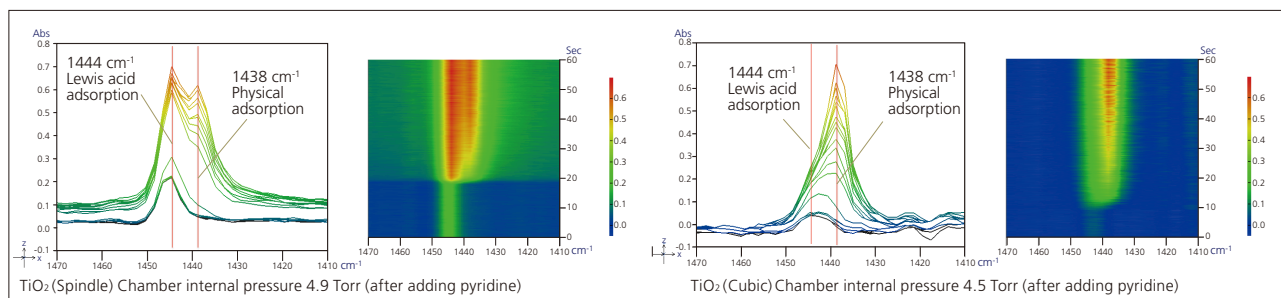


Fig. 3 Infrared Spectra (Left) and 2D Plot (Right) of Pyridine Adsorbing on Surface of TiO₂ Powder

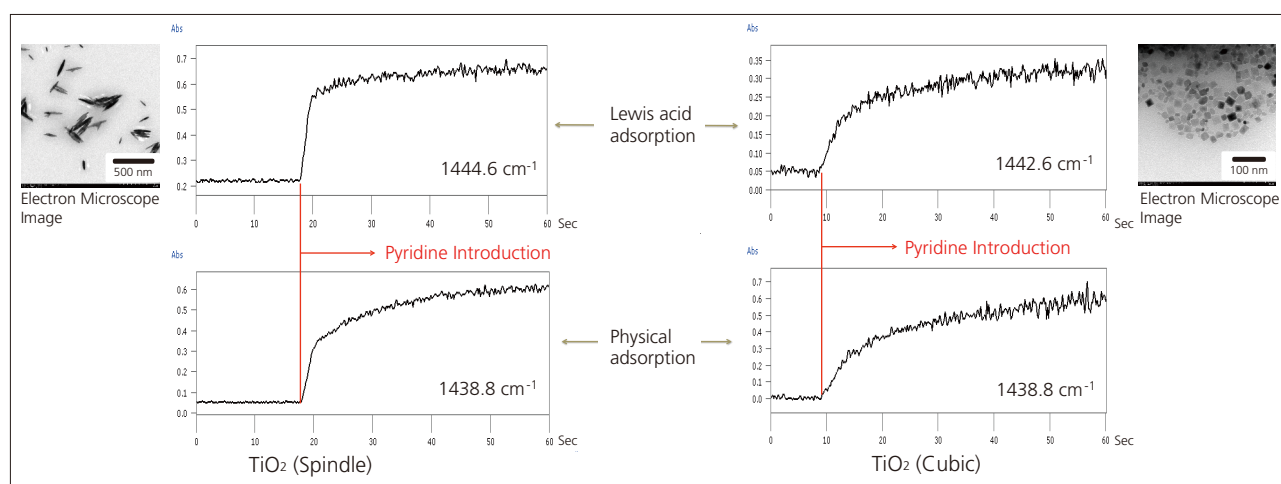


Fig. 4 Time-Course Graphs of Peak Intensity for Lewis Acid Position and Physical Adsorption and Micrographs of TiO₂ Powder

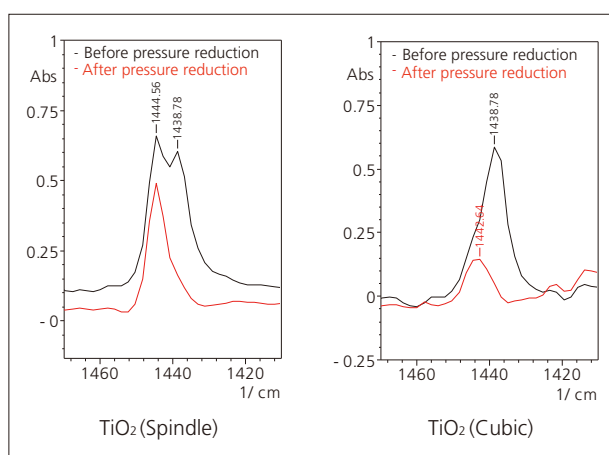


Fig. 5 Spectra Before and After Pyridine Pressure Reduction

Additionally, after permitting the pyridine to stabilize at about 5 Torr following its introduction, evacuation of the system was conducted until the system pyridine pressure was lowered to about 0.3 Torr, after which spectral measurement of the pyridine was conducted. Those results are shown in Fig. 5. The physical adsorption peak in the vicinity of 1438 cm^{-1} almost completely disappeared in both specimens.

Conclusion

Rapid scan FTIR measurement permitted quick (tens of seconds) and detailed observation of the process in which pyridine is adsorbed to a solid oxide surface. The sample used for this measurement was generously provided by Professor Atsushi Muramatsu of the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, and guidance regarding the experimental method was kindly provided by Assistant Professor Kiyotaka Nakajima of the Hara Laboratory, Materials & Structures Laboratory, Tokyo Institute of Technology.

1) (M.I. 262 Zaki et al. / Colloids and Surfaces A: Physicochem. Eng. Aspects 190 (2001) 261–274)