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Infrared Spectra of Ammonia Adsorbed on Titanium Dioxide

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Synopsis. IR spectra of ammonia adsorbed on titanium dioxide were measured including those of partially deuterated ammonia. The results were compared with spectra reported in the literature.

A few papers have been published on IR spectra of ammonia adsorbed on TiO_2 studied with object of surface characterization.[1-3] Parfitt *et al.*[2] observed the spectra on a rutile surface and Primet *et al.*[3] on anatase including 10—15% of rutile. A good agreement is seen between the spectra observed by them. They attributed the observed bands to the two types of ammonia adsorbed on different Lewis acid sites. However, some differences are seen in the details of their assignments (Table 1, Assignments 1 and 2). The purpose of the present paper is to resolve the confusion in the assignments by the use of partially deuterated ammonia.

Experimental

Degussa Titanium dioxide p-25 (60% anatase, 40% rutile) was used as the sample. The self-supporting disk samples were initially heated at 450 °C for 5 h and cooled to room temperature in flowing oxygen, then evacuated in situ at 350 °C for 2 h, exposed to 40 Torr (1 Torr≈133.322 Pa) of oxygen at the same temperature for 0.5 h, and finally again evacuated at the same temperature for 0.5 h. Standard ammonia (Takachiho Co. Ltd.) was dried with sodium metal at a low temperature. Deuterated ammonia was distilled from a D_2O solution of ammonia-d_3 (99 atom%, E. Merck Darmstadt), and then dried in the same manner as for the ammonia. All the spectra were measured at room temperature. The IR cell was similar to that previously described,[4] and a JASCO-Model 402G spectrophotometer was used for the measurements.

Results and Discussion

The NH_3–TiO_2 adsorption system showed almost the same spectra as those reported by the previous authors.[2,3] Five absorption bands in the NH stretching region, and two bands in the deformation region were observed after pumping at room temperature (Table 1). Elevation of the evacuation temperature gave rise to the appearance of a new band around 1230 cm^{-1}. As a result of evacuation at 350 °C, all the above bands disappeared. After the surface OH groups were exchanged for OD groups by repetition of the introduction of ND_3 followed by evacuation

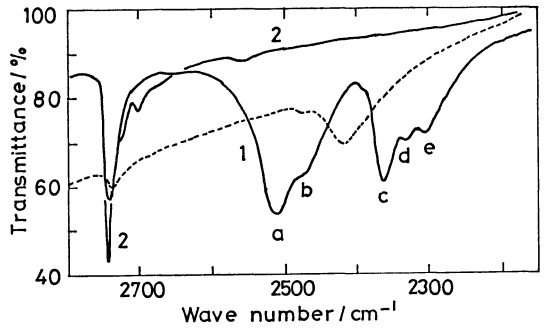

Fig. 1. Spectra of ammonia adsorbed on TiO_2 in the ND stretching region.
Full line: TiO_2–ND_3 system; evacuated at room temperature for 20 min (1), and at 350 °C for 3 h (2) after saturated with ND_3 gas at room temperature. Sample disk thickness was 40 mg/cm². Broken line: TiO_2–NH_2D system; evacuated at room temperature for 20 min after saturated with NH_3–ND_3 10.1 to 1.0 mixed gas at room temperature. Sample disk thickness was 140 mg/cm².

TABLE 1. IR BANDS OF AMMONIA ADSORBED ON TITANIUM DIOXIDE (STRETCHING REGION)

Band sign	νNH/cm^{-1}		νND/cm^{-1}		Assignment		
	NH_3	NHD_2	ND_3	NH_2D	(1)	(2)	(3)
a	3395		2520		ν_3	ν_3	ν_3
b	3345		2476		ν_1	ν_3	ν_3
		3285		2423			
c	3251		2372		ν_3	ν_1	ν_1
d	3188		2340		ν_1		$2\delta_4$
e	3151		2310			ν_1	ν_1

(1) Ref. 2, (2) Ref. 3, (3) this paper. Bands coupled with a L-shaped line mean that they are the pair of ν_3 and ν_1 of one type of the adsorbed ammonia.

at 350 °C, the spectra of ND_3 adsorbed on TiO_2 were measured (Fig. 1). The stretching bands correspond well to those of NH_3 adsorbed on TiO_2 (Table 1). Besides the D-shift, a small hump attributable to a combination band of ND_3 was detected at 3400 cm^{-1}. The bands at 2745, 2730, 2700, and 2675 cm^{-1} in Fig. 1 may be assigned to the surface OD groups on TiO_2.

Spectra of ammonia adsorbed on TiO_2 were measured for various H/D ratios. A typical result is shown in Fig. 1, using NH_3: $ND_3 \approx 10:1$ gas mixture, where NH_3: NH_2D: NHD_2: $ND_3 \approx 1000:300:30:1$. Hence, the bands in the νND region of the observed spectra are mainly due to adsorbed NH_2D. The result shows only a strong main band at 2423 cm^{-1} with a very small shoulder at 2482 cm^{-1} in the ND stretching region. The band at 2423 cm^{-1} is safely assigned to the νND of the adsorbed NH_2D; neither the NH_3-adsorbent system nor the ND_3-adsorbent system showed any band at this frequency (Fig. 1). For the NHD_2–TiO_2 system, the νNH band of the adsorbed NHD_2, which corresponds to the band at 2423 cm^{-1} for the NH_2D–TiO_2 system, was observed at 3285 cm^{-1}.

The fundamental νNH band of NHD_2 appears approximately at the mean frequency of ν_3 and ν_1 of NH_3, and the νND band of NH_2D appears between ν_3 and ν_1 of ND_3.

On the basis of these observations, the tentative assignments shown as "Assignment (3)" in Table 1 were made for the bands a—e. It is seen from the table that the proposed assignments are more consistent with those made by Primet *et al.*[3] than with those of Parfitt *et al.*[2] However, to confirm the assignments further experimental studies including considerations of hydrogen-bonding effect are necessary. The small shoulder at 2482 cm^{-1} may be attributed to the adsorbed species of NHD_2 which coexists in the mixed sample gas, or may suggest the existence of a small amount of another adsorbed species such as $-NH_2$ proposed by Parfitt *et al.*[2] near the frequencies of the bands a and b.

References

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