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Infrared and ESR Spectra of Reaction Intermediates Formed from 1,1-Diphenylethylene Adsorbed on Oxides

Noriko TANI, Asako KAWAMORI, and Haruka YAMADA*

Faculty of Science, Kwansei Gakuin University, Nishinomiya, Hyogo 662

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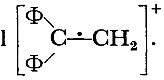
When 1,1-diphenylethylene (DPE) was adsorbed on porous Vycor glass (PVG) or silica–alumina, some unstable reaction intermediates, blue, green, and yellow species, were formed. The blue species produced on the silica–alumina showed a characteristic band at 1525 cm^{-1}, assigned to the shifted C=C stretching band, which disappeared in the green and yellow samples; it also showed an ESR signal. This indicates that the unstable blue species is probably a cation radical  $\left[\begin{array}{l}\Phi\diagdown \\ \quad C\overset{\cdot}{-}CH_2 \\ \Phi\diagup\end{array}\right]^{+}$. The infrared spectra of the green and yellow species on the silica–alumina showed new bands, ascribed to the $-CH_3$ and $-CH_2-$ vibrations, which were in good agreement with the resonance Raman bands of the carbonium ions formed on the PVG. The green and yellow intermediates, therefore, should be two kinds of carbonium ions. The structures, formation mechanisms, and surface coverages of these intermediates are discussed.

We first applied the resonance Raman technique to the study of a small amount of surface species; the resonance Raman spectra could be successfully obtained for halogens adsorbed on silicas,[1] reaction intermediates on porous Vycor glass,[2] dye adsorbed on a working ZnO electrode[3] and pyridines adsorbed on various oxides.[4]

When 1,1-diphenylethylene (DPE) was adsorbed on porous Vycor glass (PVG) treated at 500 °C, two carbonium ions, reaction intermediates, were detected by means of the resonance Raman spectra.[2] In the present work, the infrared and ESR spectra of the reaction intermediates formed from DPE adsorbed on oxides have been studied in order to obtain more precise information about the vibrational spectra of the reaction intermediates and also about the adsorption mechanism. As adsorbents PVG treated at a higher temperature (800 °C) and silica–alumina were used in this study; they had more Lewis or Brönsted acid sites than the PVG treated at 500 °C.

On the other hand, reaction intermediates produced by the adsorption of DPE on silica–alumina were studied by measuring the ESR and electronic spectra.[5–10] The structures of the intermediates, however, are still in question. Some radical species were really found on silica–alumina by observing the ESR signal. However, it is uncertain whether the radical is produced directly from the DPE adsorbed or whether it is concerned with any impurity involved.

Experimental

The porous Vycor glass used was obtained from Corning Glass Works, No. 7930; 1 mm thick transparent sheet, containing 96.3% SiO_2 and 2.9% B_2O_3. It was cut into 20×10 mm sections. Then it was pretreated in the same way as that for the resonance Raman measurements;[2] it was heated at 500 °C in 500 Torr** oxygen for 4 h and then degassed at 800 °C for 10 h. The surface area was 130 m^2/g,[11] compared with 170 m^2/g[1] for the PVG treated at 500 °C.

The silica–alumina was obtained from the Catalysts and Chemicals Ind. Co.; it was 13.8% Al_2O_3 and 85.9% SiO_2 and consisted of particles 60 μm in diameter. It was pressed into disks (10 or 20 mm in diameter) whose optical thickness was about 10 mg/cm^2. This was heated at 500 °C in 500 Torr** oxygen and then degassed at 400 °C (or 500 °C) for 3 h.

The 1,1-diphenylethylene used was obtained from Nakarai Chemicals (99.8%) and also from Wako Chemicals and Tokyo Chemicals (99%). This DPE was used after having been degassed by alternate freezing and thawing. The infrared spectra of these three DPE's did not show any difference from one another, and the 99% DPE did not show any appreciable OH stretching band.

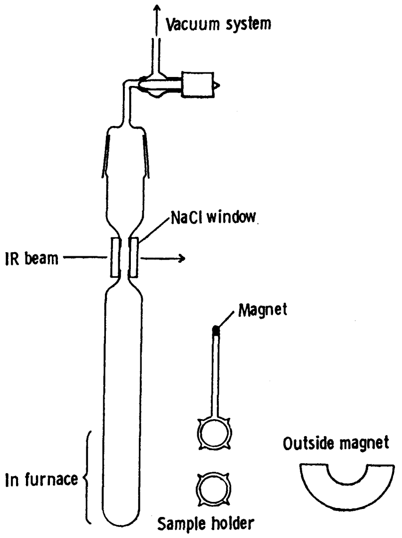


Fig. 1. Infrared absorption cell made of quartz. Sample was fixed in the holder with platinum wire and placed into the cell tube.

An infrared cell made of quartz was specially designed, as is shown in Fig. 1; it consisted of a tube and a sample holder. There were NaCl windows where infrared light passed through. The distance between these two plates was only 5 mm, so that atmospheric vapors could hardly interfere at all with the spectra obtained. A small magnet was enclosed in the tip of the holder, so a sample fixed in the holder could be moved up to the window for the infrared measurement. Greaseless stopcocks and a connector were used.

The infrared spectra were measured with a JASCO DS-402

** 1 Torr≃133.3 Pa.

G infrared spectrophotometer and a modified JASCO DS-301 infrared spectrophotometer especially designed for the use with small samples.[12] The ESR measurements were carried out with a JEOL-JES 3B-type X-band spectrometer using 100 kHz modulation.

Results and Discussion

PVG. When the vapor of DPE was adsorbed onto PVG, some unstable intermediates were produced. First, a blue species was found, and then it gradually changed to a green species and then to a yellow species. Finally, the sample became reddish brown. The blue, green, and yellow species, therefore, might be reaction intermediates. The color development observed was the same for both DPE's; 99.8% and 99%. Since the PVG (1 mm) absorbed infrared light strongly in the region below 2000 cm^{-1}, only the >2000 cm^{-1} region could be used for the measurements of the reaction intermediates. When a disk (*ca.* 0.1 mm thick) made of PVG powder was used instead of 1 mm PVG, it was fairly transparent in the <2000 cm^{-1} region. However, no band assigned to the unstable species adsorbed on that disk could be detected, so the number of surface species adsorbed on it must be quite small.

The infrared spectra for the blue, green, and yellow samples are shown in Fig. 2. (a) shows the spectrum of PVG pretreated at 800 °C as a background. The two bands at 3747 and 3703 cm^{-1} are assigned to the free surface OH groups.[13] The spectra for the colored samples are shown in (b), (c), and (d). For comparison, the liquid spectrum of DPE is also given in Fig. 2.

A new OH band at 3610 cm^{-1} appeared in these (b), (c), and (d) spectra. This is a shifted OH band due to the interaction of surface OH groups with the π-electrons of DPE. Further, these spectra showed new bands at 2966 and 2926 cm^{-1}; these bands increased in intensity in the order of (b), (c), and (d). An additional band at 2865 cm^{-1} appeared in the (c) and (d) spectra. These three new bands can be assigned to the CH stretching vibrations of $-CH_3$ and $-CH_2-$ groups. On the other hand, the olefinic band at 3083 cm^{-1} decreased. That is to say, the bond order of the olefinic C=C decreased upon adsorption, while new surface species with aliphatic $-CH_3$ and $-CH_2-$ groups were formed on the PVG. In Table 1 the absorption peak frequencies observed for the DPE adsorbed on PVG are listed, with the relative intensities in parentheses. The amounts of the intermediates produced on the PVG are rather small, so only the bands in the 3 μm region can be detected by using the 1 mm thick PVG. The blue species is probably a kind of radical, because the ESR signal was observed for the blue sample.[2]

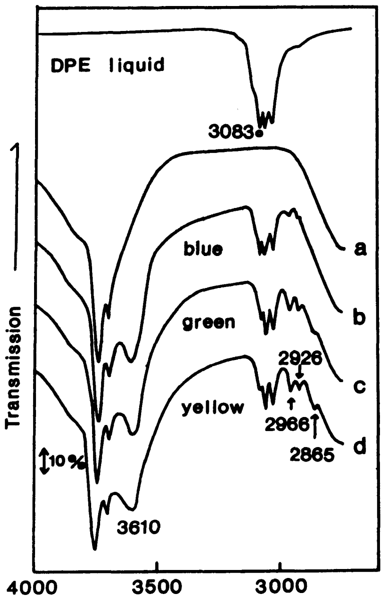


Fig. 2. Infrared spectra of DPE adsorbed on PVG pretreated at 800 °C for 10 h; (a) background, (b) blue, (c) green, and (d) yellow samples.

Silica–Alumina. When the 99.8% DPE was adsorbed on the silica–alumina pretreated at 400 °C for 3 h, the sample appeared blue or blue-green immediately and then changed to a deeper color as the amount of adsorbed species increased. After the sample had been kept at 80 °C for 20 h, it turned green and then to yellow (after several days), and finally it became brown. Much more reaction intermediates were produced on the silica–alumina than on the PVG. When the 99.8% DPE was adsorbed on the silica–alumina pretreated at 500 °C for 3 h, the sample showed a rather green color at first, while when the 99% DPE was used instead of the 99.8% DPE on the silica–alumina pretreated at 500 °C, the sample appeared rather blue at first. All the blue samples gradually changed in

TABLE 1. PEAK FREQUENCIES OF ABSORPTION BANDS OF DPE ADSORBED ON PVG (cm^{-1})

Sample adsorbed			Liquid	Assignment
Blue	Green	Yellow		
≈3610	≈3610	≈3610		OH···π
			3100 sh	
3083 (78)	3083 (53)	3086 (48)	3083 (101)	$=CH_2$ ν_{CH}
3062 (100)	3063 (100)	3064 (100)	3061 (100)	Φ ν_{CH}
3028 (82)	3029 (82)	3028 (77)	3029 (90)	Φ ν_{CH}
2967[i] (13)	2965[i] (63)	2966[i] (86)	2932 (4)	$-CH_3$ ν_{CH}
2927[i] (6)	2927[i] (15)	2926[i] (26)		$-CH_2-$ ν_{CH}
	2862[i] (26)	2865[i] (33)		$-CH_3$, $-CH_2-$ ν_{CH}

[i] Band ascribed to an intermediate or a product.

color in the order of green, yellow, and brown when they were kept at room or a higher temperature. Thus, the blue, green, and yellow species formed on the silica–alumina must be reaction intermediates, though there was a little difference in the color development of the samples. Dollish and Hall[10] reported that lemon yellow appeared on the silica–alumina pretreated at 540 °C for 24 h; they pretreated the silica–alumina at a higher

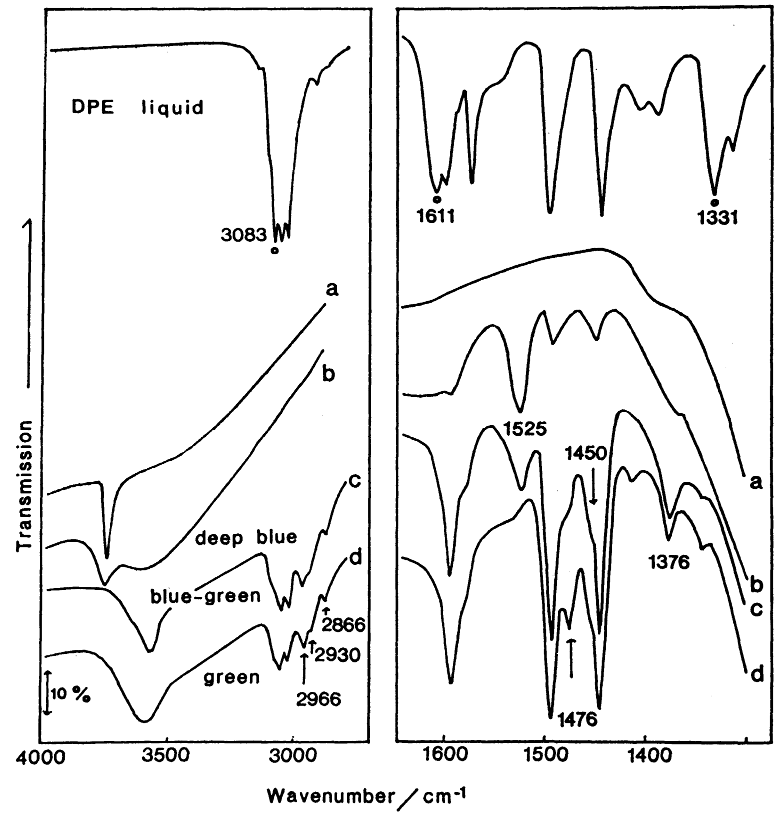


Fig. 3. Infrared spectra of DPE adsorbed on silica–alumina pretreated at 500 °C for 3 h; (a) background, (b) deep blue, (c) blue-green, and (d) green samples.

Table 2. Peak frequencies of absorption bands of DPE adsorbed on silica–alumina (cm^{-1})

Sample adsorbed				Liquid	Assignment
Deep blue	Blue-green	Green	Yellow		
	≈3570	≈3580			OH···π
			3000—3600		
				3100 sh	
	3082 (82)	3080 sh		3083 (101)	$=CH_2$ ν_{CH}
≈3058	3060 (100)	3058 (100)		3061 (100)	Φ ν_{CH}
≈3035	3025 (100)	3026 (98)		3029 (90)	Φ ν_{CH}
≈2983[i]	2963[i] (83)	2966[i] (88)	2963[i]	2932 (4)	$-CH_3$ ν_{CH}
	2930[i] sh	2930[i] sh	2933[i]		$-CH_2-$ ν_{CH}
	2873[i] (27)	2866[i] (38)	2870[i]		$-CH_3$, $-CH_2-$ ν_{CH}
				1611 (47)	$C{=}CH_2$ ν_{CC}
1595	1594 (54)	1596 (56)	1596 (30)	1602 (38)	Φ
	1577 sh	1580 sh	1580 sh	1575 (34)	Φ
1525[i] (100)	1525[i] (23)	1540[i] sh			radical ν_{CC}
1492 (32)	1492 (116)	1494 (117)	1494 (117)	1494 (110)	Φ
1476[i] sh	1480[i] sh	1476[i] (14)	1476[i] (17)		$-CH_2-$ δ_{CH}
1450[i] (32)	1450[i] sh	1450[i] sh	1450[i] sh		$-CH_3$ δ_{CH}
	1444 (100)	1446 (100)	1445 (100)	1445 (100)	Φ
		1414[i] (3)			
1366[i] (8)	1376[i] (26)	1376[i] (14)	1374[i] (13)		$-CH_3$ δ_{CH}
	1343[i] (4)	1344[i] (7)			
				1331 (49)	$=CH_2$ δ_{CH}

[i] Band ascribed to an intermediate or a product.

temperature and for a longer period than in the present work.

Figure 3 shows the observed spectra for the colored samples on the silica–alumina pretreated at 500 °C. The spectrum of the yellow sample was similar to (d). The spectra observed for the adsorbed species differed from that of liquid DPE as follows: Three new bands appeared at 2966, 2930, and 2866 cm^{-1}; they were assigned to the aliphatic CH stretching bands. On the other hand, the olefinic CH band of DPE at 3083 cm^{-1} decreased in intensity in the 3 μm region. In the region below 1700 cm^{-1} the blue sample showed a characteristic new band at 1525 cm^{-1} (b). This band was also found for the blue-green sample (c), but it disappeared for the green sample (d). The (c) and (d) spectra showed distinct bands at 1476 and 1376 cm^{-1} which could be assigned to the aliphatic CH bending vibrations. On the other hand, the 1611 and 1331 cm^{-1} bands of DPE almost disappeared for the adsorbed species. The 1611 and 1331 cm^{-1} bands can be assigned to the olefinic C=C stretching and CH deformation vibrations respectively. Since these bands disappear in (b), (c), and (d), it follows that the double bond might vanish for the adsorbed species. In Table 2 the absorption peak frequencies observed for the DPE adsorbed on the silica–alumina are listed, with the relative intensities in parentheses.

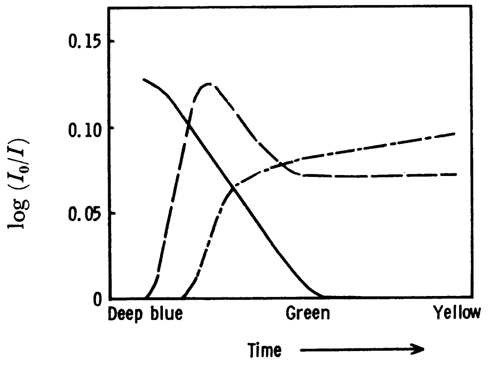
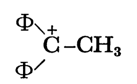
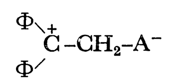


Fig. 4. Intensity changes accompanied with color development; (——) 1525 cm^{-1} band ascribed to radical species, (-•-•-) 1476 cm^{-1} band assigned to $-CH_2-$ bending vibration and (– – – –) 1376 cm^{-1} band assigned to $-CH_3$ bending vibration.

The relationship between the color development of the sample and the infrared band intensities can be seen in Fig. 4. The abscissa shows the color change with the time after the DPE has been adsorbed, while the ordinate shows the relative peak height of each band. As the blue species decreased, the 1525 cm^{-1} band rapidly dropped, while the 1476 cm^{-1} band increased in intensity. The 1476 cm^{-1} band could be assigned to the $-CH_2-$ deformation, and the 1376 cm^{-1} band, to the $-CH_3$ deformation. These two bands (1476 and 1376 cm^{-1}) must be ascribed to the unstable reaction intermediates. The present infrared spectra observed for the blue-green, green, and yellow samples are in good harmony with the results of the resonance Raman spectra for DPE adsorbed on the PVG. The reaction intermediates, therefore, must be the carbonium ions;[2]



$$\begin{array}{l}\Phi\diagdown_{+}\\ \quad C\text{-}CH_3\\ \Phi\diagup\end{array}$$



$$\begin{array}{l}\Phi\diagdown_{+}\\ \quad C\text{-}CH_2\text{-}A^-\\ \Phi\diagup\end{array}$$

where A represents the adsorbent.

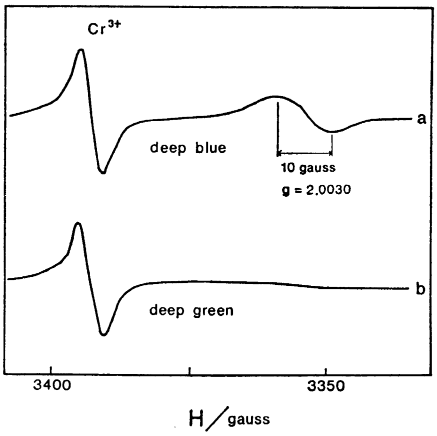
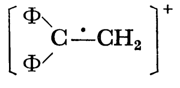


Fig. 5. ESR spectra of DPE adsorbed on silica–alumina pretreated at 500 °C for 3 h (9 GHz); (a) deep blue and (b) deep green samples.

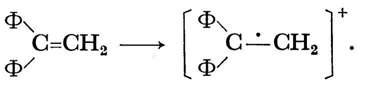
In order to ascertain whether the reaction intermediates were paramagnetic or not, we measured the ESR spectra for these samples. Figure 5 shows the ESR spectra obtained for the blue and green samples with the signal belonging to the Cr^{3+} ion (g=1.9800) doped in MgO added as a standard material. The blue sample had a broad signal centered at g=2.0030, whose half-width was about 10 G,*** while the green sample did not show any ESR signal. Consequently, it is found that the blue sample certainly included some radical. The ESR signal observed for the blue sample was also observed for the deep blue or blue-green samples, but not for the green sample. This ESR signal coincides well with that observed by Leftin *et al.* for the blue sample on silica–alumina.[7]

Since the infrared 1525 cm^{-1} band characteristic of the blue species was observed, the 1525 cm^{-1} band must be ascribed to a radical which showed the ESR signal. For this radical the following structure must be considered;



$$\left[\begin{array}{l}\Phi\diagdown\\ \quad C\overset{\cdot}{-}CH_2\\ \Phi\diagup\end{array}\right]^{+}$$

which is consistent with the results of the observed infrared and ESR spectra. When the DPE changes to this radical, the C=C band has to shift to the lower-frequency side. The band observed at 1525 cm^{-1} is lower than the 1611 cm^{-1} band by 90 cm^{-1}; this shift corresponds well to this change:



$$\begin{array}{l}\Phi\diagdown\\ \quad C{=}CH_2\\ \Phi\diagup\end{array} \longrightarrow \left[\begin{array}{l}\Phi\diagdown\\ \quad C\overset{\cdot}{-}CH_2\\ \Phi\diagup\end{array}\right]^{+}.$$

It is the first time that the vibrational spectrum of this unstable radical has been detected.

Now we have actually found these three reaction intermediates formed on the silica–alumina, a cation

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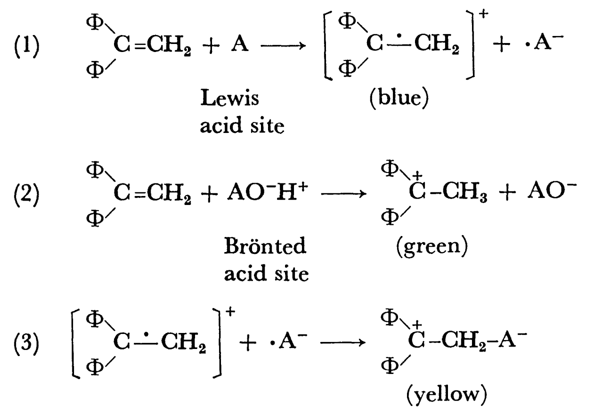
*** 1 G=10^{-4} T.

radical, and two carbonium ions. We shall now proceed to consider the formation mechanism of these reaction intermediates. When DPE was adsorbed on the Lewis acid site, the cation radical could be formed. If the proton was accepted by the DPE on the Brönsted acid site, the carbonium ion, $\Phi_2C^+\text{-}CH_3$, could be formed. The cation radical combined with the Lewis acid site changes to the carbonium ion, $\Phi_2C^+\text{-}CH_2\text{-}A$. More



$$(1)\quad \Phi_2C{=}CH_2 + A \longrightarrow \left[\Phi_2C\dot{-}CH_2\right]^+ + \cdot A^-$$

$$(2)\quad \Phi_2C{=}CH_2 + AO^-H^+ \longrightarrow \Phi_2\overset{+}{C}\text{-}CH_3 + AO^-$$

$$(3)\quad \left[\Phi_2C\dot{-}CH_2\right]^+ + \cdot A^- \longrightarrow \Phi_2\overset{+}{C}\text{-}CH_2\text{-}A^-$$

blue species were formed when the silica–alumina was pretreated at a lower temperature or for a shorter period. Therefore, it seems likely that the surface OH groups play an important role in the formation of the blue species. However, it is not clear whether or not this role of the OH groups is catalytic. For the cation radical, a modified C=C stretching vibration was observed, while for the carbonium ions, $-CH_3$ and $-CH_2-$ stretching and deformation vibrations were observed. The CH stretching bands for the carbonium ions are in good agreement with those of the resonance Raman spectra of the carbonium ions formed on the PVG.

Now we would like to consider the coverage of the intermediates. When DPE was adsorbed on PVG or silica–alumina, the reaction intermediates with physically adsorbed DPE were formed. The CH stretching vibration of the phenyl group at 3061 cm^{-1} is supposed to be hardly changed when the DPE is changed to the three intermediates described above or a physically adsorbed species. Therefore, if the absorption intensities of the 3061 cm^{-1} bands for all the adsorbed species are the same as that of the liquid DPE, the total amount of the adsorbed species can be estimated from the observed intensities; 0.05 molecule/nm^2 for the PVG treated at 800 °C and $\approx$1.4 molecule/nm^2 for the silica–alumina treated at 500 °C. The intensity decrease of the olefinic band at 3083 cm^{-1} may be proportional to the amount of the intermediates. For the DPE on the PVG, this decrease was $\approx$10% for the blue sample, $\approx$20% for the blue-green sample, and 30—40% for the green or yellow sample. The intensity of the 3061 cm^{-1} band was almost constant during this color changing of the sample. For the DPE on the silica–alumina, the intensity decrease of the 3083 cm^{-1} band was found to be $\approx$70% for all the samples (blue to yellow). Therefore, the coverage of the intermediates and products should be 0.005—0.02 molecule/nm^2 on the PVG and $\approx$1 molecule/nm^2 on the silica–alumina in Table 3, judging from the surface areas of 130 m^2/g on the PVG and $\approx$500 m^2/g on the silica–alumina.[14)]

Table 3. Coverage of surface intermediates formed from DPE

(molecules/nm^2)

Adsorbent	θ (total)	θ (intermediates and products)
PVG(800 °C)	0.05	0.005—0.02
Silica–alumina (500 °C)	$\approx$1.4	$\approx$1

Table 4. Numbers of Lewis and Brönsted acid sites obtained from the adsorbed pyridine

(molecules/nm^2)

Adsorbent	Lewis acid site	Brönsted acid site
PVG (800 °C)	0.05	Not observed
Silica–alumina (500 °C)	0.2	0.04

Let us now compare these coverages with the numbers of Lewis and Brönsted acid sites[15)] which could be found from the experiments on adsorbed pyridines (Table 4). The numbers of Lewis acid sites were estimated by comparing the intensities of the 1629 cm^{-1} (on the PVG) and 1452 cm^{-1} (on the silica–alumina) bands with those of the 1610 cm^{-1} (ν_{8a}) and 1450 cm^{-1} (ν_{19a}) bands[16)] of pyridine respectively in the $(\text{pyridine})_2\text{–}ZnCl_2$ complex. Also, the number of Brönsted acid sites on the silica–alumina was obtained by comparing the intensity of the 1545 cm^{-1} band of adsorbed pyridine with that of the 1528 cm^{-1} (ν_{19b}) band[16)] of pyridine in the pyridine–HCl complex. The coverage of the intermediates on the PVG is comparable to the number of Lewis acid sites, while the coverage on the silica–alumina seems much more than that of the Lewis or Brönsted acid sites.

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