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Infrared Spectroscopic Studies of Boron Phosphate and Adsorbed Species

II. Adsorption of Ammonia

J. B. MOFFAT AND J. F. NEELEMAN

Department of Chemistry, University of Waterloo,
Waterloo, Ontario, Canada

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The adsorption of ammonia on boron phosphate has been studied by infrared spectroscopy. Dissociation of ammonia appears to occur and bands assignable to coordinately bonded ammonia and to NH_4^+ were observed. Heating of the catalyst prior to adsorption decreases the amount of NH_4^+ produced. Samples of boron phosphate with excess boron display coordinately bonded ammonia and the frequencies of these bands suggest a similarity to those found for ammonia adsorption on porous glass and silica impregnated with boron oxide. In contrast, the bands found with the samples of boron phosphate containing excess phosphorus are similar to those found for ammonia on alumina and silica–alumina.

INTRODUCTION

The first paper in this series (*1*) reported on an infrared spectroscopic study of changes produced in boron phosphate on heating and on adsorption or desorption of water. It was shown that water adsorbed on dehydrated boron phosphate was, at least, partially dissociated, and bands assignable to hydroxyl groups in a variety of configurations attached to boron or phosphorus were found to be present. This work (*1*) and previous work cited therein has demonstrated the presence of acidic sites on the surface of boron phosphate. Infrared spectroscopic investigation of the adsorption of a weak base, such as ammonia, can be used to provide information concerning the type, relative strength and relative concentration of these acidic sites on the surface of a solid. No earlier studies of the infrared spectroscopy of adsorbed ammonia on boron phosphate have been reported in the literature.

EXPERIMENTAL METHODS

The preparation of boron phosphate of both high surface area (50–200 $m^2\,g^{-1}$) and low surface area (less than 50 $m^2\,g^{-1}$) has been described earlier (*1–3*), the former being prepared from tri-*n*-propyl borate and orthophosphoric acid and the latter from this acid and boric acid. Further details concerning the treatment of samples, the preparation of self-supported pellets of the solid and the apparatus employed have been given previously (*1*).

Anhydrous ammonia (99.99%, Matheson) was subjected to a trap-to-trap distillation before use and was stored at liquid nitrogen temperature.

Table 1 summarizes information concerning the samples employed.

RESULTS AND DISCUSSION

Figures 1A, B, C and 2, display the spectra for ammonia adsorbed at 30°C on BP(TB-9, 10α), a sample prepared with equal molar ratios of P_2O_5 and B_2O_3, and which has been pretreated at one of 300, 500 and 700°C. For comparison, Figs. 3, 4 and 5 show the same information for three additional samples, BP(TB-11), BP(TB-12) and BP(RS-2,3α) of P_2O_5/B_2O_3 ratios 1.2, 0.8 and 1.15, respectively, each

TABLE 1
INITIAL SURFACE AREAS AND PHOSPHORUS/BORON RATIOS OF SAMPLES OF BORON PHOSPHATE

Sample no.	P_2O_5/B_2O_3 (*M*)	Surface area (m^2/g)
TB-9,10α	1.00	118
TB-11	1.2	69
TB-12	0.8	138
RS-2,3α	1.15	20

of which was pretreated at 700°C. Finally, Fig. 6 applies to BP(TB-9, 10α), preheated at 500°C, on which ammonia had been adsorbed at 30°C, followed by adsorption of water. Table 2 summarizes the band assignments for ammonia adsorbed on boron phosphate. Justifications for such assignments are discussed below.

Ammonia appears to be readily adsorbed on boron phosphate evacuated at elevated temperatures, and strong broad bands in the region 3300–2700 cm^{-1}, with weaker and sharper bands in the 3600–3300 cm^{-1} region are evident. Some of these bands are not eliminated by prolonged evacuation at 150°C, indicating that a portion of the ammonia is chemisorbed. Some of the adsorbed ammonia is dissociated, since bands assignable to surface hydroxyl groups are formed.

For BP(TB-9,10α) evacuated at 700°C, ammonia adsorbed at 30°C (Figs. 1A, B and C), bands appeared initially at 3493 I, 3402 II, ca. 3290 III, 3230 IV; a strong broad band near 3020 V, a weak band at 2915 VI and a shoulder at 2775 VII. The weak band near 3630 VIII decreased on ammonia adsorption. In the NH bend region, bands appeared at 1660 IX, 1620 X; a sharp peak at 1557 XI, and a band near 1440 XII increased. The band at 1640 has decreased or else overlaps with the bands at 1660 and 1620 cm^{-1}. The band at 1532 almost completely disappeared. Also, a band below 1400 cm^{-1}, decreased on adsorption. Possibly, weak bands appeared near 1600 and 1490 cm^{-1},

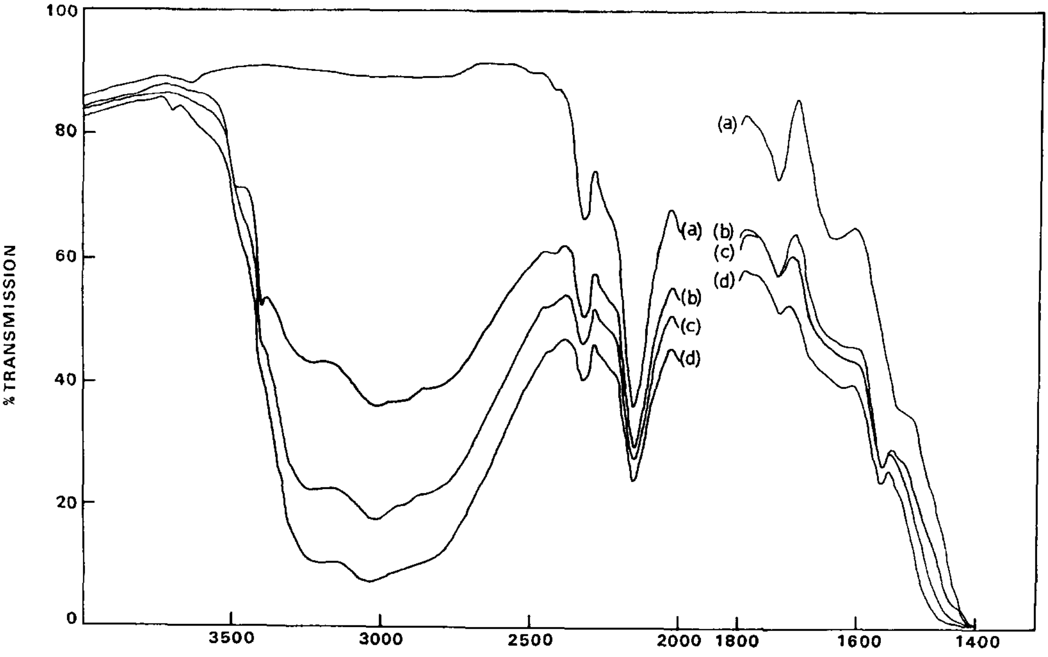


FIG. 1A. Infrared spectra of BP(TB-9,10α)-11 evacuated at 700°C; ammonia adsorbed at 30°C: (a) evacuated 150°C, 24 hr; 700°C, 12 hr; (b) ammonia adsorbed 30°C, 0.6 Torr, 2 min; evacuated 10 min, 30°C; (c) ammonia adsorbed 30°C, 1.6 Torr, 1 hr; no evacuation; (d) ammonia adsorbed 30°C, 5.9 Torr, 12 hr; no evacuation.

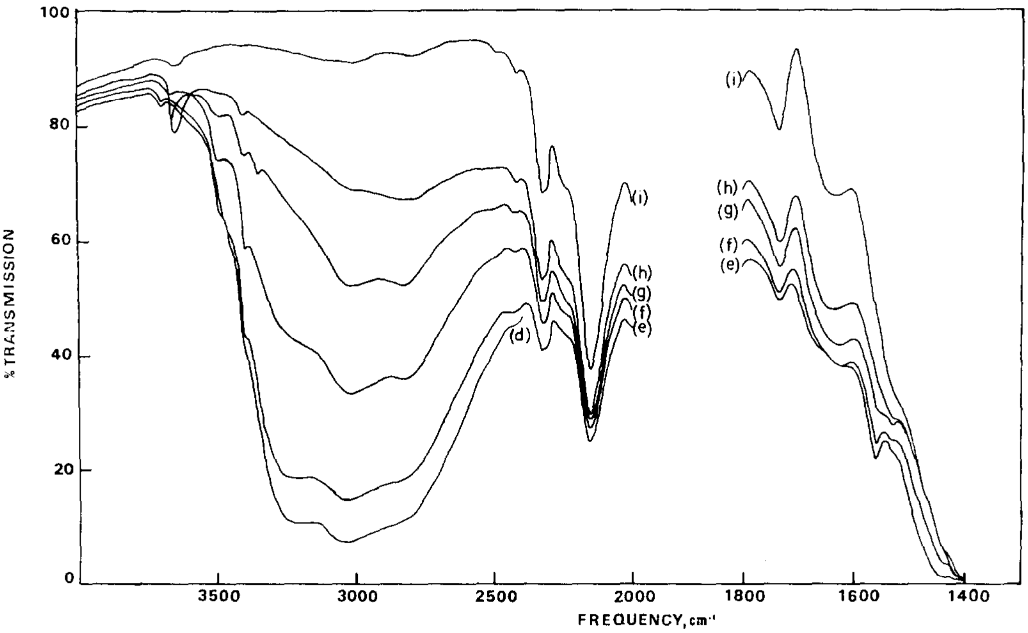


FIG. 1B. Infrared spectra of BP(TB-9,10α)-11 evacuated at 700°C; ammonia adsorbed 30°C, desorbed at progressively increasing temperatures: (d) ammonia adsorbed 30°C, 5.9 Torr, 12 hr; no evacuation; evacuated: (e) 30°C, 8 hr; (f) 150°C, 8 hr; (g) 300°C, 4 hr; (h) 450°C, 4 hr; (i) 700°C, 12 hr.

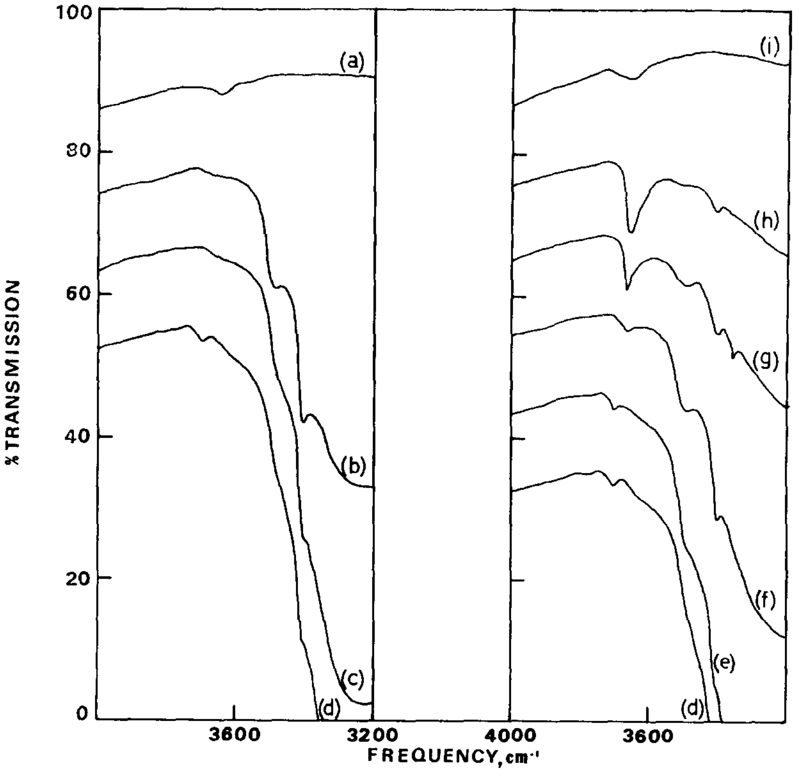


FIG. 1C. Infrared spectra of BP(TB-9,10α)-11 (same spectra as 1A and B, only separated by 10% T to prevent overlapping): (a) evacuated 700°C; 12 hr; (b) exposed to ammonia: 2 min, 0.6 Torr; (c) 1 hr, 1.6 Torr; (d) 12 hr, 5.9 Torr; (e) evacuated: 8 hr, 30°C; (f) 8 hr, 150°C; (g) 4 hr, 300°C; (h) 4 hr, 450°C; (i) 12 hr, 700°C.

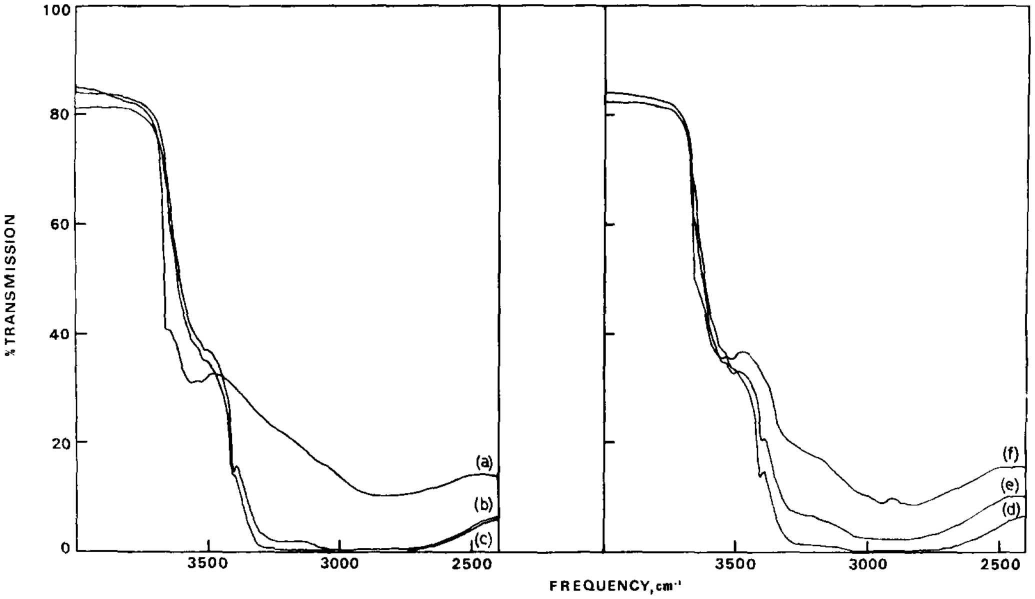


FIG. 2. Infrared spectra of BP(TB-9,10α)-12 evacuated at 300°C; ammonia adsorbed 30°C; desorbed 30, 150, 300°C: (a) evacuated 300°C, 12 hr; (b) ammonia, 2.0 Torr, 30°C, 1 hr; no evacuation; (c) ammonia, 5.3 Torr, 30°C, 12 hr; no evacuation; (d) evacuated 30°C, 8 hr; (e) evacuated 150°C, 8 hr; (f) evacuated 300°C, 5 hr.

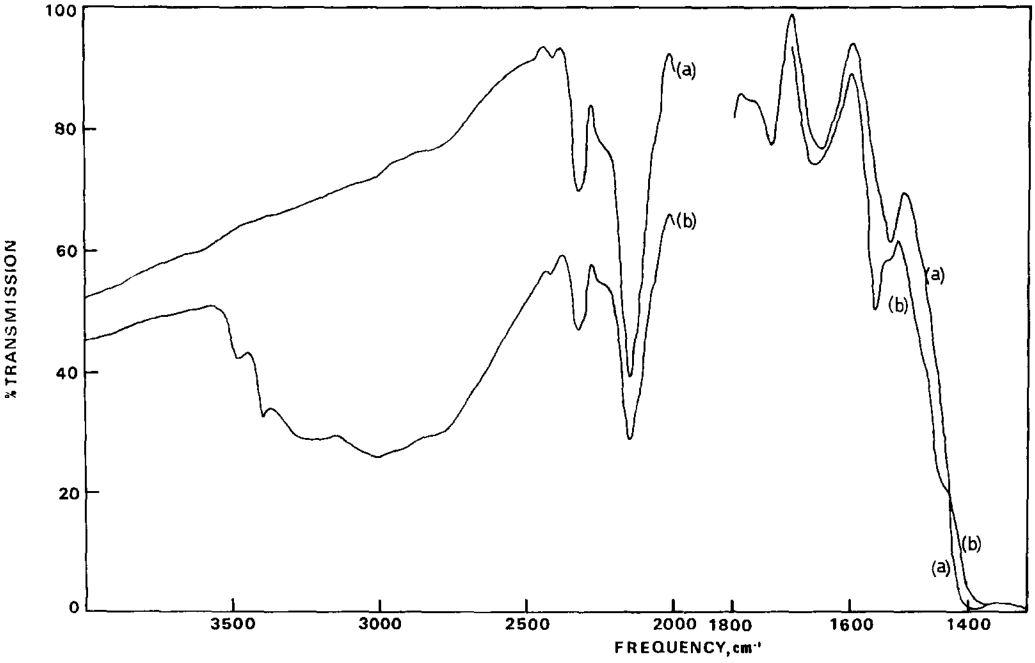


FIG. 3. Infrared spectra of BP(TB-11)-1 evacuated at 700°C; ammonia adsorbed 30°C: (a) evacuated 700°C, 2 hr; (b) ammonia, 0.4 Torr, 30°C, 2 min; evacuated 30°C, 10 min.

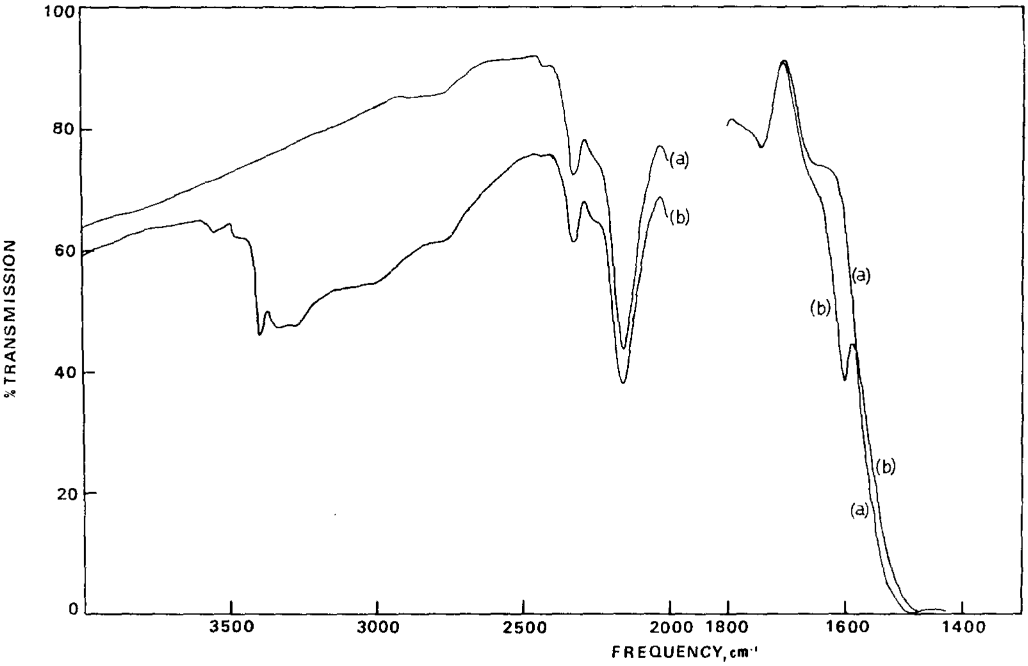


FIG. 4. Infrared spectra of BP(TB-12)-1 evacuated at 700°C; ammonia adsorbed at 30°C: (a) evacuated 700°C, 2 hr; (b) ammonia, 0.44 Torr, 30°C, 2 min; evacuated 30°C, 10 min.

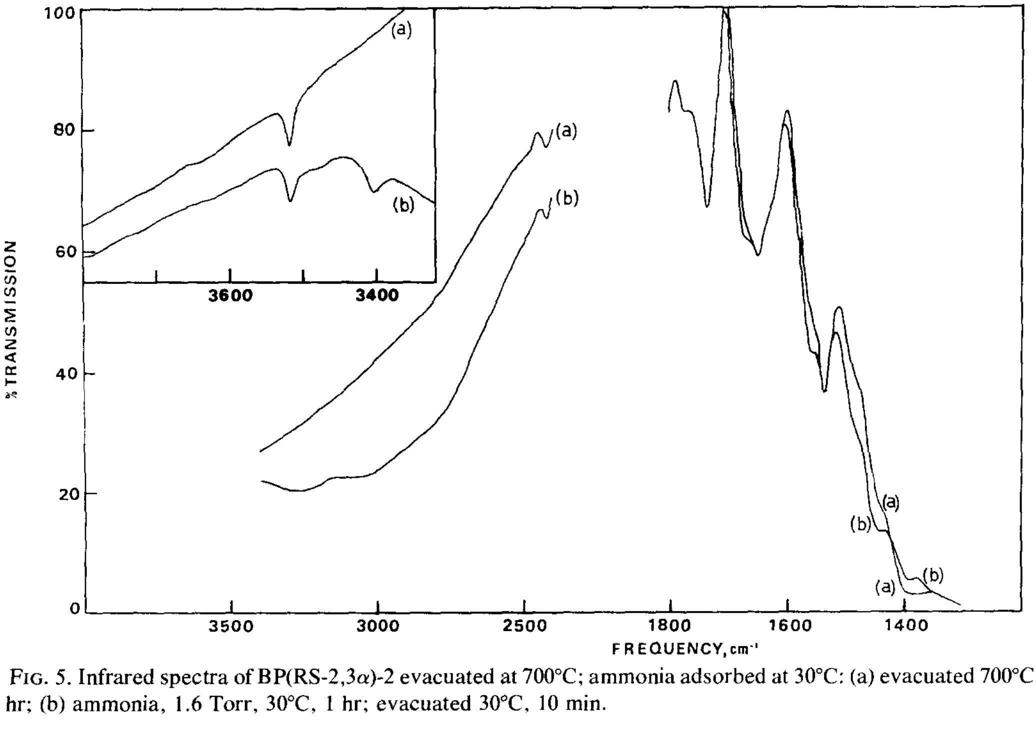


FIG. 5. Infrared spectra of BP(RS-2,3α)-2 evacuated at 700°C; ammonia adsorbed at 30°C: (a) evacuated 700°C, 2 hr; (b) ammonia, 1.6 Torr, 30°C, 1 hr; evacuated 30°C, 10 min.

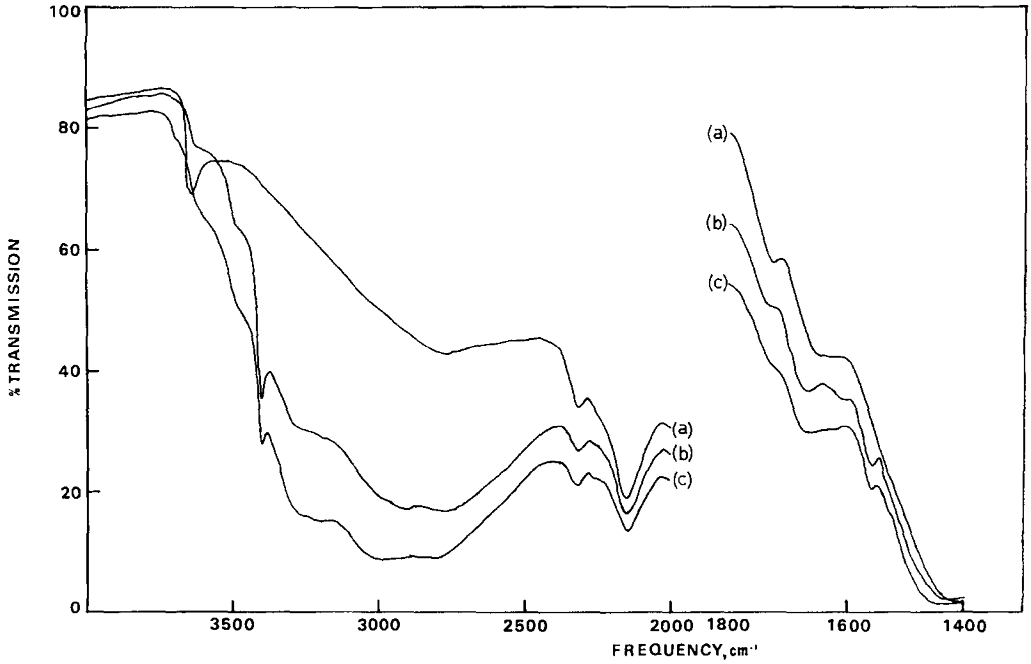


FIG. 6. Infrared spectra of BP(TB-9,10α)-13 evacuated 500°C; ammonia adsorbed 30°C, followed by water adsorption at 30°C: (a) evacuated 500°C, 4 hr; (b) ammonia, 1.05 Torr, 30°C, 2 min; evacuated 30°C, 10 min; (c) water, 1.25 Torr, 30°C, 2 min; evacuated 30°C, 10 min.

but this was uncertain. With increasing coverage, a weak band appeared at 3700 cm^{-1}; the bands at 3493 I and 3402 II decreased and may have shifted slightly. The bands in the 3300–3200 cm^{-1} range increased; V increased and shifted to 3040 cm^{-1}; also the 2775 cm^{-1} shoulder increased. In the low frequency range, the

TABLE 2
BAND ASSIGNMENTS FOR AMMONIA ADSORBED ON BORON PHOSPHATE

Frequency (cm^{-1})	Assignment	Refs.
BP(TB-9,10α), BP(TB-11), BP(RS-2,3α)		
3400; 1558	Non-H-bonded PNH_2	*(20,21)*
3491	PNH_2 or PNHP	*(16,18)*
3350	PNHB?	
3280; (1620?)	$NH_3 \rightarrow B$	*(16,12,13)*
3220; 1445	NH_4^+	*(18,22)*
ca. 3000; (1665?)	H-bonded N-H	*(20,21)*
2915	POH---NH_3? or BOH---NH_3? (OH)	
3700	BOH	
3665–3630	POH	(*1*, Table 4)
2800	(P=O) OH	
BP(TB-12)		
3335; 3258; 1598	$B \leftarrow NH_3$	
3540; 3452	BNH_2	
ca. 3000	BOH---NH_3? or H-bonded NH?	*(10,9)*
3396; 3474	PNH_2? or BNHB?	

bands at 1660, 1620, 1440 cm^{-1} increased, while the band at 1558 decreased slightly. Possibly, 1733 decreased also.

Evacuation at 30°C caused a large decrease in the intensity of the bands in the 3300–2700 cm^{-1} range, while I and II increased and shifted to 3492 and 3403 cm^{-1}. In low frequency range, IX decreased and shifted to 1670 cm^{-1}; the other bands were only slightly changed. Evacuation at 150°C caused the band near 3695 cm^{-1} to disappear, while a weak band appeared near 3662 XIII. Bands I and II increased and shifted to 3490 and 3398, and a weak peak appeared at 3350. The band near 3220 IV appeared to be completely removed. The strong broad band V decreased and shifted to 3030 cm^{-1} while VII shifted to 2805 cm^{-1}. In the low frequency range, the bands at 1670, 1620, 1558, and 1445 cm^{-1} have decreased, while bands appeared at 1640 and 1532 cm^{-1}.

On 300°C evacuation, XIII increased and shifted to 3660 cm^{-1}, I and II decreased slightly. The band at 3550 cm^{-1} increased slightly, III shifted to 3280 cm^{-1} and about completely disappeared. V and VII decreased and shifted to 3020 and 2825 cm^{-1}. In the lower frequency range, IX was completely removed, 1620, 1558, and 1445 cm^{-1} were reduced, while the bands at 1733, 1532 and 1650 cm^{-1} increased. On 450°C evacuation XIII had shifted to 3650 cm^{-1} and broadened, and a shoulder appeared at 3630 cm^{-1}; the bands I and II at 3490 and 3402 cm^{-1} were greatly reduced and the band at 3350 cm^{-1} was removed. V and VI were greatly reduced. In the lower frequency range, the 1620 and 1560 cm^{-1} bands were about completely removed, while the band at 1650 and 1532 increased.

On 700°C evacuation, most of the bands between 3700–2700 cm^{-1} were removed, possibly a weak band remained at 3020. In the low frequency range, the bands produced by the ammonia adsorption were also removed. The percentage transmittance past 1400 cm^{-1} decreased.

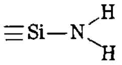
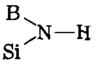
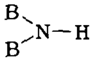
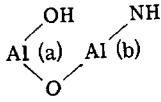
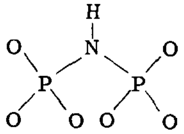
The results obtained for ammonia adsorption on BP(TB-9,10α) evacuated 500°C were similar to the previous results for 700°C evacuation. On adsorption at 30°C, the band at 3636 cm^{-1} decreased and broadened, and shifted to 3626 cm^{-1}. Possibly, the band at 1670 cm^{-1} was relatively larger than for 700°C preheat. When the sample was again evacuated at 500°C, most of the ammonia appeared to have been desorbed; the spectrum was almost identical to that before ammonia adsorption.

For BP(TB-9,10α) evacuated at 300°C (Fig. 2), the bands formed on ammonia adsorption are harder to classify because of the low percentage transmission and the sloping background. On ammonia adsorption, the bands at 3657 and 3560 disappeared, bands appeared near 3600 and 3404 cm^{-1}. A broad strong band formed at 3010 cm^{-1}, and a medium band centered near 3300–3250 cm^{-1}. On desorption at 300°C the bands at 3657 and 3560 reappeared, the bands near 3590 decreased, and the 3404 band disappeared. A medium broad band remained, centered near 3300 cm^{-1}, while the band at 3020 was reduced.

The adsorption of ammonia at 30°C on high boron [BP(TB-12)] and high phosphorous BPO_4 [BP(TB-11)] and low surface area BPO_4 [BP(RS-2,3α)], all preheated 700°C, was also investigated (Figs. 3, 4 and 5, respectively). High P BPO_4 appeared to be similar to BP(TB-9,10α), however, the bands at 3486, 3400 and 1558 cm^{-1} appeared to be larger than for BP(TB-9,10α). Possibly the 3295 band was smaller, while the 3240 cm^{-1} was larger than for BP(TB-9,10α). A medium band was also noted at 1665 cm^{-1}. If a 1620 cm^{-1} is present it is rather weak. Also a weak band near 1445 cm^{-1} was noted. As in the case of BP(TB-9,10α) bands near 1650, 1534 and 1390 cm^{-1} decreased on adsorption.

TABLE 3

Infrared Band Assignments for Ammonia Adsorbed on Oxides and Phosphates

Oxide	Frequency (cm^{-1})	Assignment	Refs.
Silica gel	3400, 3320, 1630	Phys. ads. NH_3	(*4–6*)
	2800	OH: ≡Si—OH---NH_3	
Aerosil Cab-O-Sil	3526, 3446 (weak)		(*8*)
Porous glass	3409, 3320	SiOH---NH_3	(*5–9*)
	3350, 3308	B—OH---NH_3	
	3365, 3280	B ← NH_3	
	3543, 3459	$SiNH_2$	
	3569, 3479	BNH_2	
	3373	$(Si)_2NH$	
	3455	$(B)_2NH$	
B_2O_3 on Aerosil	3365, 3280, 1595	B ← NH_3	(*10*)
	3450	 or 	(*9*)
		(no evidence of ═B—NH_2)	
Alumina Aerogel	3400, 3355, 1620	≡Al ← NH_3	(*11*)
	3335, 3200, 1560–1510(b) 3725(a)		(*10*)
Silica-alumina	3341, 1620	Phys. adsorbed NH_3	(*12–14*)
	3335, 3280, 1610	≡Al ← NH_3	
	3270, 1440	NH_4^+	
P_2O_5 on silica gel	3400, 3320, 1620	Phys. ads. NH_3	(*15*)
	3400, 1450	NH_4^+?	
	3450, 1549	PNHP tentative	
	3500, 1480 (~3411)	PNH_2	
$Ca_{10}(PO_4)_6(OH)_2$	3420		(*16,17*) (*11*)
	3385, 3280	Ca ← NH_3?	
$AlPO_4$ gel	3300, 3400, 1625	Al ← NH_3	(*18*)
	3200–3450 (1625)	Phys. ads. NH_3?	
	1450	NH_4^+	
	3530, 3440, 1570	P-NH_2	
	3780	Al-OH?	
		(no Al-NH_2 noted)	
TiO_2	3250	Ti-OH bands	(*19*)
	Ca. 1400	NH_4^+	
	3385, 3245, 1190 3330, 3140, 1220	Ti-NH_2	

Ammonia adsorption on BP(RS-2,3α) or low surface area BPO_4 appeared to be similar to BP(TB-9,10α). The band at 3518 cm^{-1} appeared to remain unchanged; bands appeared at 3480, 3404, 3290, 3020 and 1800 cm^{-1}. Weak bands appeared at 1668, 1558 and 1445 cm^{-1}. A band at 1390 cm^{-1} was seen to decrease on ammonia adsorption. Unlike BP(TB-9,10α), the bands at 1648 and 1536 cm^{-1} appeared to be only slightly affected.

BP(TB-12) or high B BPO_4 behaved differently for ammonia adsorption. On adsorption at 30°C, bands appeared at 3540, 3474, 3452, 3396, 3335, and 3258 cm^{-1}. Bands also appeared at 3010 and 2770 cm^{-1} but these were a great deal weaker than for the other BPO_4 samples. Possibly, a band appeared at 1675 and 1620 cm^{-1} while a sharper peak appeared near 1598 cm^{-1}. The band near 1650, and the strong broad band near 1400 cm^{-1} (or a shoulder near 1530–1540 cm^{-1}) appeared to decrease.

The band assignments for ammonia adsorption were made by comparison with similar investigations for other oxides, and the relative rates of desorption on heating. For purposes of comparison, infrared band assignments for ammonia adsorbed on a variety of oxides and phsophates are summarized in Table 3.

In general, physically adsorbed ammonia can be largely removed by evacuation at room temperature, and completely by evacuation at 150°C. Ammonium ion and coordinately bound ammonia can be removed by evacuation at 300°C, and amine groups by evacuation at 500°C.

The bands appearing near 3020 and 1670 cm^{-1} have been assigned to some form of H-bonded ammonia. For other oxides, bands near 3000 cm^{-1} have been assigned to surface OH groups hydrogen bonded to ammonia (*23*). However, these bands can be almost completely removed by evacuation at room temperature. In the case of BPO_4, the bands near 3020 cm^{-1} are reduced but not completely removed even by 300°C evacuation. This suggests that there are several overlapping bands in this region. A band appearing near 2915 cm^{-1} may be due to surface hydroxyls perturbed by ammonia adsorption (*23*). The band remaining after 300°C evacuation appears similar to a band noted by Peri (*11*) for ammonia on alumina, assigned to $Al–NH_2$.

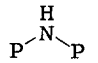
Bands appearing near 3220–3230 and 1445 cm^{-1} are greatly reduced by evacuation at 150°C, and removed by 300°C evacuation. This band is assigned to NH_4^+. Broad bands near 3290 and 1620 cm^{-1} are slightly reduced by 150°C evacuation, and removed at 300°C. These bands were assigned to coordinately bonded ammonia. In some respects, the frequency and desorption properties are similar to bands noted for silica–alumina by Basila and Kantner (*14*), with bands at 3335, 3280 and 1610 cm^{-1} assigned to coordinated ammonia, and bands at 3270 and 1440 cm^{-1} to ammonium ion. This indicates that both Lewis and Brünsted acid sites are present on BPO_4.

On ammonia adsorption on BP(TP9,10α) preheated 500°C followed by water adsorption (Fig. 6), the bands at 3320 and 1440 cm^{-1} increase as would be expected if these bands are due to NH_4^+, since the water can convert physically adsorbed ammonia, amines and coordinately bonded ammonia to produce NH_4^+. In this case, the reaction appears to involve physically adsorbed ammonia, there being no conclusive evidence for conversion of coordinately bonded NH_3 to NH_4^+. An increase in intensity of the bands near 3000 cm^{-1} suggests this band may be partly due to NH_4^+. It is interesting to note that this spectrum bears a superficial resemblance to $NH_4H_2PO_4$ and $(NH_4)_2HPO_4$, whose spectra have three broad bands near 3200, 3000 and 2800 cm^{-1}, with the 3000 cm^{-1} band the largest (*24*).

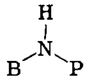
The boron phosphate surface appears to

be able to dissociate ammonia to form surface hydroxyl groups and surface amines. For BP(TB-9,10α) the bands near 3490, 3400, 3020 and 1558 cm^{-1} are stable to evacuation at 300°C, and not completely removed even by evacuation at 500°C.

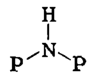
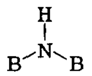
Corbridge (*20*) and Bellamy (*21*) indicate that the range for P–NH_2 is 3425–3012 cm^{-1} with generally 2 or 3 bands, and 1545–1578 cm^{-1}. In dilute solution, with no hydrogen bonding interaction, a sharp peak appears near 3400 cm^{-1}. From a comparison of bands assigned to P–NH_2 for P_2O_5–SiO_2 (*15*), hydroxyapatite (*16*), aluminum phosphate (*18*), the bands at 3490, 3404 and 1558 cm^{-1} were assigned to P–NH_2. The 3490 cm^{-1} band could also be due to



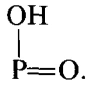
although this is less likely. The 3020 cm^{-1} band remaining after 300°C evacuation was assigned to an H-bonded P–NH_2. The weak band appearing at 3355 cm^{-1} after heating at 300°C was assigned to



although there is no supporting evidence for this assignment. 3355 cm^{-1} is lower than reported for

 (15) or  (9).

Apparently, no bands assignable to B–NH_2 appear for BP(TB-9,10α), BP(TB-11) and BP(RS-2,3α). For high B BPO_4 comparison with ammonia adsorbed on B_2O_3–SiO_2 (*10*) or porous glass (*9*) suggests the bands at 3540 and 3452 cm^{-1} are due to B–NH_2; while the bands at 3335, 3258 and 1598 cm^{-1} are due to ammonia coordinated to boron. The band near 3400 cm^{-1} is larger than found for the other BPO_4 samples. Since no desorption experiments were performed on BP(TB-12), the assignment of this band cannot be certain, and may be due to physically adsorbed ammonia.

Additional proof of surface amines is provided by the formation of bands assignable to surface hydroxyl groups. The band appearing near 2800 cm^{-1} was assigned to surface  $\overset{\mathrm{OH}}{\overset{|}{\mathrm{P}}}\mathrm{=O}$. A weak band appearing at 3700 cm^{-1} was assigned to B–OH. On evacuation at 150°C, a band appeared at 3662 cm^{-1}, and increased on 300°C evacuation. This band was assigned to P–OH. In one experiment, BP(TB-9,10α) was evacuated at 700°C, water adsorbed at 30°C, followed by ammonia adsorption. The band at 3662 cm^{-1} disappeared on ammonia adsorption. Thus, in the case of ammonia adsorption, even if the 3662 cm^{-1} band is produced initially, it may not be visible until some of the ammonia is removed by evacuation at higher temperatures. The disappearance of the 3662 cm^{-1} band may be due to the reaction of ammonia with the P–OH to form P–NH_4^+.

Mechanism of Water and Ammonia Adsorption

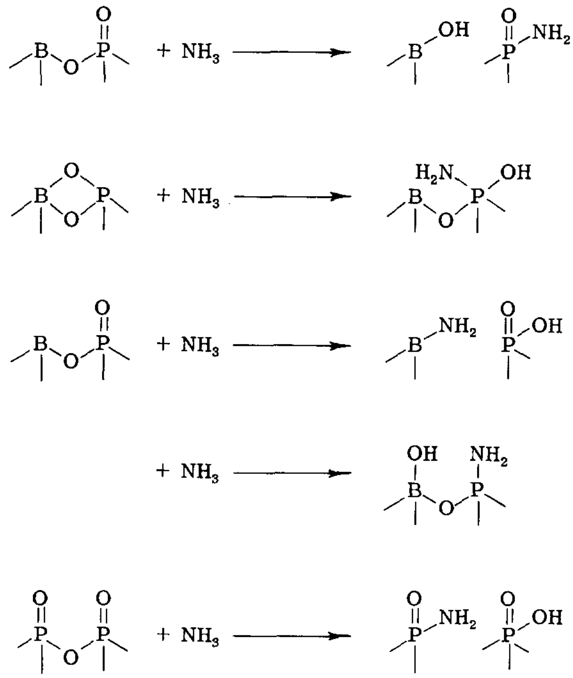
Since BPO_4 can be considered as a mixed oxide, many different sites involving P or B or both can be postulated to explain the reactivity and catalytic properties of boron phosphate. Boron phosphate used as catalyst, such as BP(RS-2,3α) is prepared with an excess of phosphoric acid, causing further complication. Also, the nominal P/B ratios for the high surface BPO_4 are based on the initial amounts of reactants used in the preparation, and an incomplete reaction may result in an excess of phosphorus since the more volatile tri-*n*-propyl borate will be more easily removed by evacuation. Previous experiments indicate that evacuation at 700°C causes removal of some excess phosphorus, probably in the form of phosphoric acid. Thus BP(TB-9,10α) with a nominal P/B ratio of

1.00 probably has an excess of P after evacuation at 300°C while the phosphorus decreases after 700°C evacuation.

From the spectroscopic data, BP(TB-9,10α), BP(TB-11) and BP(RS-2,3α) appear to have a greater amount of phosphorus than boron on the surface. This phosphorus is likely in the form of a sheet-like $(PO_4)_n$ polymer, as suggested by Low and Ramamurthy (*15*) for phosphoric acid impregnated silica. The high boron BPO_4 appears to have an excess of boron on the surface, similar in properties to B_2O_3 on silica or porous glass (*7,10*).

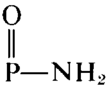
When freshly prepared, the high surface area BPO_4 samples are probably amorphous, as indicated by X-ray diffraction and the broadness of infrared bands assigned to lattice vibrations. Narrowing of the bands on evacuation indicates that the boron phosphate becomes more crystalline when heated to higher temperatures. The changes in the structure also cause corresponding changes in the surface. Some infrared bands appearing on BPO_4 evacuated at 300°C cannot be regenerated by water adsorption on samples evacuated at 500 and 700°C. The surface area of BPO_4 reaches a maximum at about 350°C evacuation. This increase is probably caused by pores formed by escaping water. Probably, the BPO_4 contains a large number of internal OH's, condensed by evacuation about 300°C, this desorption being irreversible. Evacuation at 700°C results in another rearrangement, as the excess phosphorus desorbs as phosphoric acid.

Ammonia, like water, appears to dissociate to some extent on the BPO_4 surface. Assuming that ammonia reacts with the same sites as water, the following reactions are postulated.


(1)
(2)
(3)
(4)
(5)

For high phosphorus BPO_4, bands assignable to B–NH_2 do not seem to appear. For high B BPO_4, the reaction

is probably responsible for the formation of B–NH_2. Thus, reactions (1) and (4) can explain the formation of bands assignable to B–OH on ammonia adsorption. The B–OH for (1) may be hydrogen bonded, producing a band near 3300 cm^{-1} while the



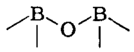
$\overset{\text{O}}{\overset{\|}{\text{P}}}\text{—NH}_2$

may result in the band near 3000 cm^{-1} remaining after evacuation at 300°C. Hydrogen bonded B–NH_2 could also result in a band in this region, by analogy with the spectra found for ammonia on alumina (*11*). The two bands near 3490 and 3400 cm^{-1} are most likely due to "free" or non-hydrogen bonded P–NH_2. As in the case of water, a large amount of the adsorbed ammonia appears to be hydrogen bonded to surface oxygen, as has been suggested in previous work (*25*). In the spectroscopic investigations, the band near 3020 cm^{-1} appearing for ammonia adsorption decreases greatly on desorption at room temperature, and thus may be in part due to physically adsorbed ammonia. A band appearing near 1670 cm^{-1} can also be assigned to ammonia hydrogen-bonded to the surface.

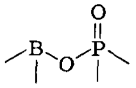
No conclusive statement about the presence of Lewis and Brönsted acid sites can be made from the ammonia adsorption results. Dissociation appears to take place, and the hydroxyl groups formed could react with dry ammonia to form ammonium ion. Thus the presence of NH_4^+ does not necessarily indicate that Brönsted sites are present initially on the BPO_4 surface.

Despite this limitation, some conclusions can still be drawn. For BP(TB-9,10α), BP(TB-11) and BP(RS-2,3α) bands assignable to coordinately bonded ammonia and to NH_4^+ were noted after ammonia adsorption, the amount of NH_4^+ appearing to be less for higher pretreatment temperatures. Thus, it would appear that both Lewis and Brönsted sites are present on the three mentioned samples, with the condition that some of the Brönsted sites could be generated by dissociation reactions. For the high boron BPO_4 BP(TB-12), coordinately bonded ammonia could be detected. The frequencies of these bands suggests a similarity with bands found for ammonia adsorption on porous glass and boron oxide impregnated silica. However, the bands for the high phosphorus samples, BP(TB-9,10α) included, are similar to alumina and silica–alumina, as indicated in Table 3.

Thus, the Lewis sites for high boron BPO_4 are probably different than found on the high phosphorus samples. For high B, sites of the type



are postulated, while for high P,



may be possible.

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