Complexation and Chemisorption of Trimethylphosphine on Ni Zeolites

BY ROBERT A. SCHOONHEYDT,* DIRK VAN WOUWE AND HUGO LEEMAN Centrum voor Oppervlaktescheikunde en Colloïdale Scheikunde, De Croylaan 42, B-3030 Leuven (Heverlee), Belgium

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After room temperature saturation of dehydrated NiY with trimethylphosphine two complexes are formed in the supercages. They are identified and quantified by reflectance spectroscopy as $0.9[\text{Ni}(\text{PMe}_3)_5]^{2+}$ per unit cell and $6-8[(O_1)_3-\text{Ni}-\text{PMe}_3]^{2+}$ per unit cell $(O_1$ is a lattice oxygen). The former is diamagnetic and trigonal bipyramidal, the latter is paramagnetic and compressed tetrahedral. $[\text{Ni}(\text{PMe}_3)_5]^{2+}$ is only stable in excess PMe₃, while the mono-phosphine complex is stable to ≈ 383 K *in vacuo.* On NiX only the paramagnetic compressed tetrahedral complex is formed. The ligand field parameters of this complex were calculated.

Chemisorption on lattice and extralattice oxygens gives strongly held $O=PMe_3$, $O=P(OMe_3)_3$ and a range of decomposition products such as CO, CO₂, H₂O, hydrocarbons and oxygenated P on the surface. These products were qualitatively identified by i.r. and mass spectrometry.

The coordination of 3d transition metal ions in the zeolite cavities primarily depends on the ligand field strength of surface oxygens relative to that of the adsorbed coordinating molecules. With ligands such as H₂O, NH₃, ethylenediammine and methylisocyanide the zeolite acts as a solvent. With ligands such as NO, CO, acetylene and olefins zeolitic oxygens remain in the coordination sphere. In this way unusual complexes can be stabilized on the surface.^{1,2} The ultimate goal of these studies is not only to characterize these complexes but also to apply this knowledge to develop so-called "heterogenized homogeneous catalysts".^{3,4}

Usually, these catalysts are phosphine-based. On zeolites, only the smallest tertiary phosphines can be adsorbed. Recently it was reported that PMe₃ reduced Cu^{2+} to Cu^+ in zeolite Y, whereas on CoY the formation of a low spin complex, formulated as lattice-bonded $[Co(PMe_3)_3]^{2+}$, was evidenced by reflectance spectroscopy and e.s.r.^{5,6} These data illustrate the versatility of transition metal ion zeolites towards PMe₃. In this paper we present our results on the interaction of PMe₃ with NiX and NiY zeolites. Ni²⁺ is an interesting cation because the electronic spectra of Ni(PMe₃)_xX₂ (x = 2-4) and of $[Ni(PMe_3)_5]^{2+}$ are well described in the literature.⁷

EXPERIMENTAL

SAMPLES

Linde NaY and NaX were stirred for 1.728×10^6 s in 0.1 mol dm⁻³ solutions of NaCl, washed until Cl⁻-free, air-dried and stored in a desiccator over saturated NH₄Cl. NiX and NiY were prepared from these stock samples by ion-exchange at room temperature for 8.64×10^5 s in 0.01 mol dm⁻³ NiCl₂ solutions at a solid: liquid ratio of 1 g dm⁻³. After exchange, the

$Ni^{2+} - PMe_3$ complexes on zeolites

samples were washed until Cl⁻-free, air-dried and stored over saturated NH₄Cl solution in a dessicator prior to analysis. Chemical analysis for the exchangeable cation content yielded for NiY17:1.33 meq Na⁺ g⁻¹, 2.66 meq Ni²⁺ g⁻¹ and 0.3 meq H⁺ g⁻¹; for NiX28:4.17 meq Ni²⁺ g⁻¹ and 2.04 meq Na⁺ g⁻¹. The numbers following the sample symbols are the number of Ni²⁺ per unit cell.

TRIMETHYLPHOSPHINE

An ampoule of PMe_3 from Strem Chemicals was connected to a vacuum line and frozen in liquid air. PMe_3 was purified by evacuation at liquid air temperature and then at slightly below its freezing point. The mass spectrum after these treatments gave no indication of components other than PMe_3 .

PROCEDURES AND TECHNIQUES

REFLECTANCE SPECTROSCOPY

The samples were treated simultaneously in the reflectance cells and the McBain balances, both connected to the same vacuum line, in order to attribute specific weight changes to spectral variations. Prior to adsorption of PMe_3 two pretreatments were performed. The first one consisted of heating NiY17 and NiX28 *in vacuo* at 713 and 733 K, respectively, until constant weight. In the second pretreatment both samples were similarly dehydrated, O₂ was allowed to adsorb at room temperature and it was then desorbed at 373 K until constant weight.

Reflectance spectra of the pretreated samples were recorded before and after O_2 adsorption and after O_2 removal. PMe₃ was allowed to adsorb at room temperature. During adsorption the samples were kept at ambient temperature with a water jacket around the reflectance cells. Reflectance spectra of the samples saturated with PMe₃ and after evacuation of PMe₃ were recorded at several temperatures between 293 and 573 K. Spectra were recorded on a Cary 17 instrument in the type I reflectance mode. The reference was BaSO₄. The spectra were taperecorded, computer-processed and plotted as $F(R_{\infty})$ against wavenumber (5000–50000 cm⁻¹) after subtraction of the baseline.

INFRARED SPECTROSCOPY AND MASS SPECTROMETRY

Thin self-supporting zeolite wafers (5–10 mg cm⁻²) were dehydrated *in vacuo* at 683 K for 3600 s prior to saturation with PMe₃. I.r. spectra were recorded after the pretreatment, after saturation with PMe₃ and after evacuation up to 573 K on a Beckman IR12 double beam grating instrument in the range 1200–3800 cm⁻¹. For the analysis of the desorption products ≈ 2 g zeolite were connected to the empty i.r. cell through a side arm, pretreated as described for the reflectance measurements and saturated with PMe₃. The gaseous desorption products were collected in the i.r. cell and their spectra recorded in the range 1000–3800 cm⁻¹. For the mass spectrometric analysis of the desorption products ≈ 500 mg zeolite were loaded in a U-shaped quartz reactor, dehydrated and saturated with PMe₃ as described for the reflectance measurements. During desorption the gaseous desorption products circulated through the zeolite bed in a closed circuit. Aliquots of gases were conducted to the Balzers quadrupole mass spectrometer QMG 101 A for analysis. The mass range analysed was 0–100.

RESULTS

Pretreatment results in a weight loss which corresponds to 295 and 256 H_2O UC^{-1} for NiX28 and NiY17, respectively. At room temperature NiX28 adsorbs 9–8 O_2 molecules per unit cell and NiY17 8.4. In both cases 5 O_2 UC^{-1} remain adsorbed after desorption at 373 K.

The reflectance spectra obtained are identical to published spectra and are not reproduced here.^{8,9} O_2 has no effect on the spectrum of dehydrated NiX28 but

eliminates the 14100 cm⁻¹ band in the reflectance spectrum of NiY17. This band was previously ascribed to Ni⁺.^{8,9}

The adsorption of PMe_3 is a fast, exothermic process. The zeolites in the reflectance cells must be kept in a constant temperature water bath to avoid excessive heating. Table 1 gives the amount adsorbed after saturation and desorption at different temperatures in vacuum. Only a minor fraction can be desorbed, even at 473 K. This is indicative of chemisorption, while the colour changes accompanying adsorption are in indirect proof of complexation of Ni²⁺. The numbers in table 1

saturation with $P(CH_3)_3$	47.5	42.3	
desorption of $P(CH_3)_3$			
at 323 K	43.4	37.9	
at 373 K	36.7	34.6	
at 418 K	36.7	31.5	
at 473 K	31.7	27.8	

TABLE 1.—AMOUNTS OF PMe3 ADSORBED (MOLECULES PER UNIT CELL)

are calculated as if the residual molecules on the surface are PMe_3 . Experiments to be described below indicate that this is not the case due to chemisorption and decomposition of PMe_3 upon high temperature evacuation. The adsorption of O_2 in the pretreatment step had no effect on the subsequent PMe_3 adsorption.

REFLECTANCE SPECTROSCOPY

Two types of complexes are formed as evidenced by the reflectance spectra of fig. 1 and 2. One complex (I), only formed on NiY17, is characterized by absorption bands at 18300 and 34250 cm⁻¹. These bands are removed by room temperature evacuation of excess PMe₃. The second complex (II) is formed on NiX28 and on NiY17 and is thermally stable up to 381 K. It is characterized by 3 bands in the n.i.r.-visible region. The position of these band maxima are:8600–8800, 22000 and 26000 cm⁻¹ for NiX28; 8000–8400, 21 000 and 26500 cm⁻¹ for NiY17. While the first two bands are broad and asymmetric, the third is sharp. A broad absorption encompasses the u.v. region, from which 3 bands are resolved upon desorption of PMe₃ above 381 K. They are located at 33500, 38000 and 45000 cm⁻¹. Above 381 K the spectra of the dehydrated Ni-zeolites are almost completely recovered, although in the u.v. region the 33500 cm⁻¹ band remains very pronounced.

The disappearance of complex (I) on NiY17 is accompanied by an increase in the 8400 and 26500 cm^{-1} bands of complex (II). These bands further increase with heating *in vacuo* up to 381 K. This increase in the intensity of the band with temperature also occurs on NiX28. These phenomena are indicative of the fact that complex (I) is transformed to complex (II) and that not all the Ni²⁺ is complexed after saturation at room temperature.

INFRARED SPECTROSCOPY AND MASS SPECTROMETRY

The regeneration of lattice-bonded Ni^{2+} , as evidenced by reflectance spectroscopy, is in contrast to the large amounts of residual PMe₃ on the surface. Chemisorption on lattice oxygens was suspected and this is shown by the i.r. spectra of fig. 3. Intense absorptions are found in the regions were gaseous PMe₃ absorbs



FIG. 1.—Reflectance spectra of PMe₃ adsorbed on NiY17: (1) saturated at room temperature; (2) evacuated at 323 K for 6.05×10^5 s; (3) evacuated at 381 K for 3.24×10^5 s.



FIG. 2.—Reflectance spectra of PMe₃ adsorbed on NiX28: (1) saturated; (2) evacuated at 323 K for 6.05×10^5 s; (3) evacuated at 381 K for 3.24×10^5 s.



FIG. 3.—I.r. spectra of PMe₃ on NiY17: (1) evacuated at 683 K for 2700 s; (2) saturated with PMe₃; (3) evacuated at room temperature; (4) evacuated at 593 K for 7200 s.

 $(1282-1348, 1417-1440 \text{ and } 2850-2970 \text{ cm}^{-1})$. However, the forms of the band systems are distorted with respect to those of gaseous PMe_3 (see fig. 4). Additionally, a broad asymmetric band around 1660 cm⁻¹ is generated which intensifies with time of contact. This band can be removed by evacuation at 373 K but for the elimination of the low frequency shoulder at 1605 cm⁻¹ temperatures above 573 K are necessary. This evacuation procedure leads to 3 groups of bands: a triplet with absorption maxima at 1305, 1318 and 1345 cm⁻¹, a doublet with maxima at 1422 and 1432 cm⁻¹ and a doublet with bands centered at 2922 and 2998 cm⁻¹. The latter is broader than the former due to a low frequency shoulder. The i.r. spectra of the gaseous desorption products are shown in fig. 4. PMe_3 is the only desorption product at 383 K (spectrum 1). At 438 K supplementary bands are revealed at 1080 cm^{-1} (a weak broad band at 1140 cm^{-1} accompanies the 1080 cm^{-1} band) and in the CH stretching region, but only a band at 2885 cm⁻¹ is clearly resolved from the C---H stretchings of PMe₃. Above 473 K the rotation-vibration spectrum of CH_4 is superposed on the PMe₃ spectrum. The band centres of the CH_4 spectrum are at 3010 and 1310 cm^{-1} .

The mass spectral analysis (fig. 5) of the gaseous desorption products confirms and complements the i.r. data in that PMe_3 is the main detectable desorption product below 423 K, but it remains visible in the gas phase at all desorption temperatures. At $\approx 500 \text{ K CH}_4$ is detected, also in agreement with the i.r. data. Not detectable by i.r. spectroscopy but clearly visible in the mass spectra are (i) H₂ which starts to desorb at $\approx 453 \text{ K}$ and (ii) a range of products, all of which are desorbed above $\approx 450 \text{ K}$. They have characteristic masses at 27, 28, 29, 30 and 32, Ni^{2+} — PMe_3 complexes on zeolites



FIG. 4.—I.r. spectra of gaseous desorption products of PMe₃-saturated NiY17: (1) after desorption at 383 K, p = 20.79 Pa; (2) after desorption at 438 K, p = 48.52 Pa; (3) after desorption at 483 K, p = 138.63 Pa; (4) after desorption at 553 K, p = 97.04 Pa.

at 41, 42, 43, 44 and at 71, 72 and 73. There is considerable overlap with the PMe₃ spectrum, but at the highest temperatures (spectra 4 and 5) these masses are clearly visible. There is also an effect due to the pretreatment: NiY17 pretreated in O_2 gives greater quantities of masses 43 and 44 than 41 and 42. The reverse holds for pretreatment *in vacuo*. Desorption from NiX28 gives the same products but the amount of PMe₃ with respect to the other products is higher than for NiY17.



FIG. 5.—Mass spectra of PMe₃ and of products desorbed from NiY17 after saturated with PMe₃: (1) PMe₃; (2) desorption at 453 K; (3) desorption at 473 K; (4) desorption at 507 K; (5) desorption at 638 K.

DISCUSSION

The reflectance spectra of Ni-zeolites saturated with PMe₃ can be interpreted in terms of 2 Ni²⁺—PMe₃ complexes without recourse to reduction of Ni²⁺ as in the case of Cu^{2+,5} This is in agreement with the fact that in dehydrated faujasite-type zeolites Cu²⁺ is more easily reducible than Ni²⁺, not only by H₂ but also by other molecules such as CO, NH₃ and ethylenediammine.^{10–13} This difference in behavior conforms with the difference in electrochemical potentials¹⁴ and with ligand field calculations.¹⁵

The spectrum of complex (I) is interpreted as that of a spin-paired $[Ni(PMe_3)_5]^{2+}$ complex. The spectrum of complex (II) is ascribed to a high spin pseudotetrahedral species $[(O_1)_3Ni-PMe_3]^{2+}$ where O_1 stands for lattice oxygen. Evidence for these interpretations is given below.

The known complexes of Ni²⁺ with PMe₃, Ni(PMe₃)_xX₂ (x = 2, 3, 4) and [Ni(PMe₃)₅]²⁺, are diamagnetic. In solution *bis* complexes are the most stable and excess phosphine is necessary to incorporate more than 2 PMe₃ molecules in the coordination sphere of Ni²⁺.^{7,16} A similar situation exists in the supercages of the zeolites where an equilibrium is established between the surface complexes and uncoordinated PMe₃:

$$(ZO^{-})_{3}Ni^{2+} \xrightarrow{PMe_{3}} (ZO^{-})_{3}Ni^{2+} \xrightarrow{PMe_{3}} PMe_{3} \stackrel{PMe_{3}}{\rightleftharpoons} [Ni(PMe_{3})_{5}]^{2+} + 3ZO^{-}.$$
(1)
(II) (I)

The reaction is driven to the right on NiY17 but stops at the pseudotetrahedral complex formation on NiX28. This is due to the larger Ni²⁺ content and thus lower PMe₃:Ni²⁺ ratio in the supercages of NiX28. Other factors affecting the coordination are the chemisorption of PMe₃ on surface oxygens and the difference in lattice negative charge density between X and Y.

The diamagnetic trigonal bipyramidal complex $[Ni(PMe_3)_5]^{2^+}$ is proposed on the basis of the similarity of its spectrum with that of the same complex in solution.¹⁶ In the latter case the ${}^{1}A'_{1} \rightarrow {}^{1}E'(e''^{4}e'^{4} \rightarrow e''^{4}e'^{3}a'_{1})$ transition is at 19 200 cm⁻¹ with a band width of 5000 cm⁻¹. The symmetry forbidden and therefore weak transition ${}^{1}A'_{1} \rightarrow {}^{1}E''(e''^{4}e'^{4} \rightarrow e''^{3}e'^{4}a'_{1})$ is at 27 800 cm⁻¹ and the $\sigma(PMe_3) \rightarrow d(Ni)$ charge transfer band is around 38 000 cm⁻¹. We have ${}^{1}A'_{1} \rightarrow {}^{1}E'$ at 18 300 cm⁻¹ with a bandwidth of 5000 cm⁻¹ and $\sigma(PMe_3) \rightarrow d(Ni)$ at 34250 cm⁻¹. The weak ${}^{1}A'_{1} \rightarrow {}^{1}E''$ transition is not seen and is probably hidden by the 26 500 cm⁻¹ band of the pseudotetrahedral complex. We have eliminated $[Ni(PMe_3)_2]^{2^+}$, $[Ni(PMe_3)_3]^{2^+}$ and $[Ni(PMe_3)_4]^{2^+}$ as possibilities. Indeed, the first 2 cases have, in the homogeneous phase, approximate C_{2v} symmetry and therefore a system of 3 d-d absorption bands. $[Ni(PMe_3)_4]^{2^+}$ is planar with a very broad absorption (half band width = 10000 cm⁻¹) encompassing 3 components.⁷ None of these features is seen in our spectrum.

The change of environment from EPA solution (5:5:2 mixture of diethyl ether, isopentane and ethanol) to the zeolitic supercage slightly affects the ${}^{1}A'_{1} \rightarrow {}^{1}E'$ transition (red shift of 900 cm⁻¹) but effects the L.M.C.T. much more, as evidenced by the 3750 cm⁻¹ red shift. This is a solution effect, the zeolite acting as a non-coordinating, anionic solvent. We now analyse the effect in terms of the optical electronegativity parameters.¹⁷ The change in spin pairing energy, Δ SPE, in going from d^{8} to d^{9} during the charge transfer transition is -4/3 D with D = 7B. Then, for the L.M.C.T. transition we have:

$$v_{\rm ct}^* = v_{\rm ct} - \Delta \text{SPE} = 30000 \left[\chi_{\rm opt}(\text{Ni}) - \chi_{\rm opt}(\text{PMe}_3) \right] = 30000 \,\Delta \chi_{\rm opt}.$$

For $B = 500 \text{ cm}^{-1}$, $\Delta \chi_{opt} = 1.3$ and 1.4 in the supercages and in EPA solution, respectively. With $\chi_{opt}(Ni) = 2.0-2.1$ this gives $\chi_{opt}(PMe_3) = 0.7-0.8$ and 0.6-0.7, respectively. There is therefore a slight increase, of 0.1, in optical electronegativity of PMe₃ in the zeolite. This means more electron-attracting power or less basic character. In other words one could speak of less σ -donor capacity in the zeolite. This should also be reflected in the redox potential for these complexes. The effect is too small and hardly out of the experimental accuracy range to attempt a measurement or a calculation. Note, however, that this red shift of L.M.C.T. bands for immobilized complexes appears to be a general phenomenon, as we have described a similar situation for Cu(en)₂²⁺(en = ethylenediammine) on the surface of clay minerals.¹⁸

The spectrum of complex (II) with one band in the range 5000–10000 cm⁻¹ is characteristic of a high spin complex. As all the complexes Ni(PMe₃)_xX₂ with x = 2-5 are diamagnetic,⁷ the only possibility is that our spectrum is that of a pseudotetrahedral complex with 1 PMe₃ and 3 lattice oxygens in the coordination sphere of Ni²⁺. PMe₃ is a stronger ligand than the lattice oxygens. The complex is then compressed tetrahedral with an idealized C_{3v} symmetry. The general C_{3v} case was treated by Klier *et al.*¹⁵ We have applied their general ligand field potential to our case with the following 2 assumptions: (i) the angle β , O—Ni—P, equals 100°; (ii) $G_2^P/G_4^P = G_2^O/G_4^O = 10$, where P and O refer to PMe₃ and lattice oxygens, respectively. G_2 and G_4 denote the radial integrals:

$$G_{2} = \frac{5}{4\pi} \gamma_{20} \langle r^{2} \rangle_{\text{ion}} \quad \text{with} \quad \gamma_{20} = \frac{-Ze^{2}}{R^{3}} \frac{4\pi}{5} \quad \text{for point charges}$$
$$G_{4} = \frac{9}{4\pi} \gamma_{40} \langle r^{4} \rangle_{\text{ion}} \quad \text{with} \quad \gamma_{40} = \frac{-Ze^{2}}{R^{5}} \frac{4\pi}{9} \quad \text{for point charges}.$$

The ligand field energy diagrams with which we were able to fit the experimental band maxima are shown in fig. 6. The following assignments are made:

$${}^{3}E({}^{3}F) \rightarrow {}^{3}E({}^{3}F), {}^{3}A_{2}({}^{3}F): 8000-8800 \text{ cm}^{-1}$$

 ${}^{3}E({}^{3}F) \rightarrow {}^{3}A_{1}({}^{3}F), {}^{3}A_{2}({}^{3}F): 21\,000-22\,000 \text{ cm}^{-1}$
 ${}^{3}E({}^{3}F) \rightarrow {}^{3}E({}^{3}P): 26\,500 \text{ cm}^{-1}.$

Calculations of the ligand field and interelectronic repulsion parameters, based on these assignments, give physically meaningful values which are summarized in table 2. Thus, PMe_3 is 2.1–2.3 times stronger a ligand than the lattice oxygens and the orbital reduction factor is in the range 0.88–0.57. This indicates appreciable deviation from the ionic bonding model but this is expected with a strong electronrich ligand such as PMe_3 in the coordination sphere. The absorptions in the u.v. region cannot assist our interpretation. In the temperature range of the thermal stability of the complexes there is only one broad and unresolved band. Above 381 K, the complexes are destroyed and the u.v. absorption must be ascribed to charge transfer bands from the modified surface (modified by chemisorption) to bare Ni² ions.

Before adsorption of PMe₃ all the Ni²⁺ is in the small cavities, at least for NiY17.¹⁹ Adsorption of PMe₃ induces migration of Ni²⁺ to the supercages, until a new equilibrium is attained with complexed Ni²⁺ in the supercages and residual, uncomplexed Ni²⁺ in the small cavities. An upper limit to the number of $[Ni(PMe_3)_5]^{2+}$ complexes can be estimated from the intensity changes of the 8000



FIG. 6.—Energy level diagram of *d*-orbitals of Ni²⁺ in compressed tetrahedral configuration $[(O_l)_3 \text{NiPMe}_3]^{2+}$; right hand side $G_4^P/G_4^O = 2.1$; left hand side $G_4^P/G_4^O = 2.3$.

and 26500 cm⁻¹ bands of complex (II) upon evacuation (fig. 1). The assumptions are (i) equal scattering coefficients for all the spectra of fig. 1; (ii) all the Ni²⁺ of NiY17 is in the form of complex (II) after evacuation at 381 K. The fact that the band intensity of complex (II) was increased by the 381 K evacuation with respect

TABLE 2.—RANGE OF	⁷ Racah's parameter	$A B (cm^{-1}) A$	ND LIGAND	FIELD	PARAMETERS ((cm^{-1})) FOR
	$(O_1)_3$ —Ni—P	Me ₃ on NiX	(28 and Ni	Y17			

G_4^{P}/G_4^{O}	2.3	2.1	
$G_4^{\rm O}/B$	5.5–7.7	6–8	
B	872-590	918-653	
G_{4}^{O}	4360-4131	5508-5224	
$G_{4}^{\mathbf{p}}$	100289501	11567-10970	
$10 Dq_{\rm int}^{\rm O}$	3230-3111	4080-3870	
10 Dq_{tet}^{P}	7428-7038	8568-8126	

Ni²⁺—PMe₃ COMPLEXES ON ZEOLITES 2528

to the room temperature evacuation favours this assumption; (iii) $[Ni(PMe_3)_5]^{2+}$ is completely converted to $[(O_1)_3 - Ni - PMe_3]^{2+}$ upon room temperature evacuation. The increase in the bands of the latter complex favours this assumption.

We have after saturation with PMe₃ $0.9[Ni(PMe_3)_5]^{2+}$ and 6–8 pseudotetrahedral complexes. In this way only 10.5–12.5 PMe₃ molecules are complexed to Ni^{2+} going up to 17 at 381 K. Most of the adsorbed PMe₃ is then available for chemisorption as shown by the desorption data in table 1. The same holds for NiX28 but not all the Ni^{2+} can be transformed into the pseudotetrahedral complex even at 381 K and an estimate of the number of complexes present in the supercages after saturation is not possible.

CHEMISORPTION OF PMe₃

The low temperature desorption of PMe₃ covers the decomposition temperature of the complexes and is therefore due to desorption of physisorbed and coordinated PMe_3 . The species remaining on the surface can be divided in 2 groups: (i) chemisorbed species absorbing at 1305-1345, 1422-1432 and 2910-3000 cm⁻¹ (spectrum 4 of fig. 4). The latter spectrum is in very good agreement with that of $O=PMe_3$ (1292–1305–1340; 1420–1437; 2923–2999 cm⁻¹).²⁰ Therefore it represents strongly adsorbed O=PMe₃ molecules according to the reaction

$$Z - O + PMe_3 - Z - O = PMe_3.$$
(2)

Additional evidence for the formation of chemisorbed $O=PMe_3$ comes from the average bond energies M-C and M-O with M = Si, Al and P.²¹⁻²³ These are summarized in table 3. It shows that P has a stronger affinity for O than Si and Al and that the Si—C and Al—C bonds are stronger than the P—C bonds. However, the fact that PMe₃ is found in the gas phase even after high temperature desorption indicates that at least on some lattice oxygens reaction (2) is reversible. The presence of the 1600–1660 cm^{-1} band system is indicative of a strong chemisorption process resulting in destruction of PMe₃ molecules. This band was not found in the gas phase spectra. Therefore, either the partial pressure of the components was too low or these species react upon desorption. Note that the gas phase spectra obtained after desorption in the range 423–483 K contain, besides the PMe₃ bands, the 1080, 1140 and 2885 cm⁻¹ bands. We suggest that these bands are due to the phosphorester $O = P(PCH_3)_3$. Indeed, 1080 and 1140 cm⁻¹ are in the range of frequencies for a P-O-CH₃ vibration (1010-1088 cm⁻¹) and a H₃C-O-P vibration (1168-1200 cm⁻¹), respectively.^{24,25} Secondly, its boiling point under atmospheric pressure is 470.4 K but is 358 K at 319.97. Pa.²¹ This range includes the desorption temperature of our experiments. Therefore, in the presence of "reactive" oxygens, reaction (2) proceeds further:



and eventually complete oxydation occurs to CO₂, H₂O and oxygenated P. The 1600-1660 cm⁻¹ band includes the deformation band of water, which can subsequently be incorporated in PMe_3 following reaction (3). We have not detected CO_2 on the solid phase, but according to the mass spectra CO_2 is desorbed at high temperatures. It can result from a thermal decomposition of PMe₃ analogous to

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TABLE 3.—AVERAGE BOND ENERGIES (kJ mol⁻¹) of M—C and M—O (M = P, Si, Al)

P-C in P(CH ₃) ₃ :263	P	P==0:585
Si—C in Si(CH ₃) ₄ :301	Si-O:207	
Al—C in Al(CH ₃) ₃ :255	Al	

NMe₃ or from a carbonate- or formate-like material, formed together with H_2O and absorbing in the 1600–1660 cm⁻¹ range.^{26–29} The thermal decomposition of the phosphine molecules also accounts for the presence of H_2 , CH₄, CO, ethylene, ethane, propane, n-pentane, acetone and propanol, all characterized by peaks in mass spectra in the ranges 26–30 and 39–43.

CONCLUSIONS

This report shows that zeolites are versatile supports for the synthesis of phosphine complexes. Thus, we have synthesized $[Ni(PMe_3)_5]^{2+}$ and $[Ni(O_1)_3PMe_3]^{2+}$ by simple gas phase adsorption of PMe₃ an dehydrated NiX28 and NiY17 zeolites. $[Ni(PMe_3)_5]^{2+}$ is only stable in excess PMe₃ and is converted to $[Ni(O_1)_3PMe_3]^{2+}$ by room temperature evacuation of PMe₃. $[Ni(O_1)_3PMe_3]^{2+}$ is stable to evacuation up to ≈ 381 K. It is a compressed tetrahedral, paramagnetic complex, whose spectral properties can be explained in C_{3v} symmetry. A similar complex has not yet been found in solution chemistry. The spectrum of $[Ni(PMe_3)_5]^{2+}$ agrees with that of a diamagnetic, trigonal bipyramidal complex. The fact that it is only formed in the supercages of zeolite Y shows that the PMe₃:Ni ratio in the supercages is critical. However, extensive chemisorption occurs which hampers the complexation. Additional experiments at low Ni-levels are necessary in order to separate the influence of the Ni-content and the chemisorption on the complexation of Ni by PMe₃ in the supercages.

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(PAPER 0/232)