JOURNAL OF CATALYSIS 153, 293–303 (1995)

Infrared and Thermal Analysis Studies of Heteropoly Acids

B. W. L. Southward, J. S. Vaughan, and C. T. O'Connor

Catalysis Research Unit, Department of Chemical Engineering, University of Cape Town, Private Bag, Rondebosch 7700, South Africa

Received November 16, 1993; revised September 12, 1994

The thermal stability and acidity of 12-tungstophosphoric acid (HPW) and its salts, both fresh and postreaction, have been studied by *in situ* and *ex situ* infrared and thermal analytical methods. The relationship between acidity and the lifetime and deactivation behavior in the high-pressure oligomerization of propene has also been investigated as has been the location of the active sites in heteropoly anions. These studies have confirmed a correlation between structural stability and the salt cation, with the potassium salt of HPW being the most thermally stable. A correlation has also been established between salt Type (A or B) and the nature of coke deposits formed during reaction. Type A salts produced only Type I (aliphatic) coke during butene isomerisation, butane cracking and short time-on-stream isothermal propene oligomerisation reactions but both Type I and Type II (aromatic) coke in long time-on-stream and/or nonisothermal oligomerisation operation. Type B (high surface area) salts always formed both Type I and Type II coke. In all cases the formation of Type II coke was responsible for catalyst deactivation. This coke blocking of acidic sites was confirmed by NH_3 adsorption/desorption studies of postreaction heteropoly anions. On the basis of shifts in IR bands, it is proposed that the coke deposits responsible for deactivation are formed in the so-called cup *M–O–M* edge sites of the Keggin Unit. A mechanism is proposed to describe the thermal decomposition of HPW.

INTRODUCTION

In recent years there has been much interest in the synthesis, characterization and catalytic properties of heteropoly compounds. In particular, the bifunctional acidic and redox properties of heteropoly anions based upon the Keggin unit structure (1) (Fig. 1) have been utilized in many heterogeneous and homogeneous catalytic reactions (2–17). Consequently there have been numerous attempts to characterize the structural, physical and chemical properties of these materials using techniques such as XRD (1, 4, 7, 9, 18–22), IR spectroscopy (3, 5, 7, 10, 11, 16, 21–34), temperature programmed methods (5, 10, 21, 27, 28, 30, 31, 33–36), electron microscopy (21, 22). ESCA (21, 28), NMR (21, 27, 29, 38–42) and ESR (3, 11, 21, 32, 34, 38, 43, 44). This research has been reviewed by various authors (45–47).

There is however no general consensus on the mechanism of structural collapse and both single and multiple step decomposition mechanisms have been proposed (28, 33–36). Moreover, although it has recently been shown that heteropoly acids (HPAs), in particular the aluminium substituted HPW, are very good catalysts for propene oligomerization (50) there has been little reported on the properties of these catalysts and the reasons for their deactivation. The present paper presents the results of *in situ* and *ex situ* infrared and thermal analysis studies aimed at investigating the thermal stability and acidity of HPW and its salts as well as the nature of carbonaceous deposits and the effect on the acidity of the salts resulting from extended high pressure propene oligomerization reactions over these catalysts (50).

EXPERIMENTAL METHODS

The salts were prepared from an aqueous reaction of the parent acid, HPW (A. R. Merck), to which the required stoichiometric quantity of counter cation salt was added, as described by Tsigdnos (46) and Hyashi (4, 49). The resulting solutions were stirred at 80°C for 30 min to ensure complete reaction. The salts were crystallized out of solution by evaporating to dryness in air at 80°C. All salts are denoted XPW, where X represents the charge balancing cation. On the basis of the TG-DTA and surface area measurements Type A salts are characterized by low surface areas with multiendothermic regions and Type B salts are high surface area salts with a single endotherm (50).

Infra-red spectra from 4000 to 400 cm^{-1} (4000 to 950 cm^{-1}, *in situ*) were recorded at 4 cm^{-1} resolution on a Nicolet 5ZDX Fourier transform spectrometer. Samples were mixed with dried KBr (1 : 100 ratio, unless otherwise stated) and pressed into discs of 0.6–1.2 mg cm^{-2} thickness. Special care was taken to maintain the dryness of samples throughout the experiments. *Ex situ* samples were dried at 110°C for 2 hours prior to analysis. In situ analyses were carried out using the pretreatment cell described previously (48), using 5% sample : KBr discs.

0021-9517/95 $6.00

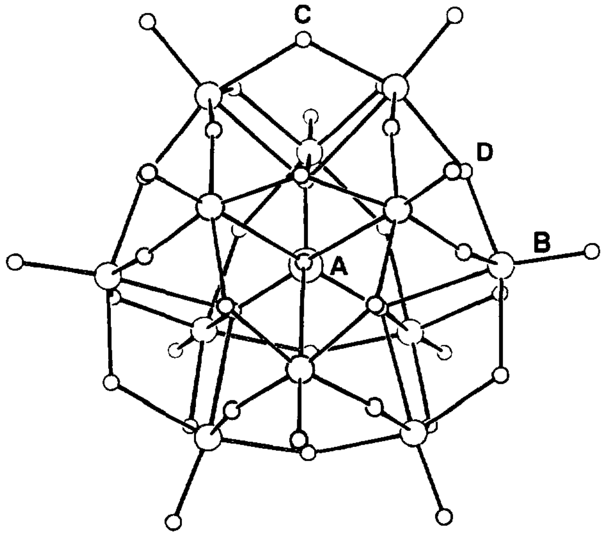

FIG. 1. Structure of 12-tungstophosphoric acid (Keggin Unit): (A) P–O, (B) $M = O_{+}$ (C) M–O–M_{edge}, (D) M–O–M_{corner}.

Ex situ ammonia TPD analysis was performed using apparatus described previously (50). In all cases the sample was calcined for 4 hr at 320°C then dosed with excess NH_3 (5% in He) at 100°C. The sample was then purged for 24 hr at 100°C to remove physisorbed species and a sample taken. The temperature was then raised in 100°C increments ($T_{\max} = 600°C$) and maintained at each temperature for 1 hr prior to sampling. *In situ* analyses were performed by calcining the sample at 120°C for 24 hr and dosing with excess NH_3. The sample was then purged in dry flowing He for 2 hr at 100°C and the spectra recorded. Further spectra were taken after heating *in situ* at 100°C increments. Infrared studies of HPAs used in butane cracking, butene isomerisation, and propene oligomerisation reactions were performed. The apparatus used and results obtained have been described in a previous paper (50). The NH_3 adsorption properties of *ex*reactor catalysts were analyzed by purging a disc in dry flowing He at 100°C for 4 hr, then dosing NH_3 and purging in He (1 hr each at 100°C) and recording the spectrum. A further spectrum was taken after purging for 24 hr at 100°C and the difference spectra determined. TG-DTA studies of prereactor HPAs were performed in a Standton Redcroft STA-780 thermal analyzer, with 15-mg samples being heated in dry flowing N_2 from 20 to 700°C, at 20°C min^{-1}.

RESULTS

Thermal Stability of $H_3PW_{12}O_{40}$ and $(NH_4)_3PW_{12}O_{40}$

Infrared analysis of the thermal stability of HPW and NH_4PW (Fig. 2) indicated that both materials were stable up to 400°C, as confirmed by the presence of the fingerprint bands below 1100 cm^{-1} which are characteristic of the $PW_{12}O_{40}^{3-}$ ion, i.e., the Keggin Unit (23). As has been previously noted (50), there was a shift of the Keggin Unit bands in NH_4PW and in particular the M–O–M edge band (hereafter referred to tM–O–M_e) shifted to 809 cm^{-1} compared to 794 cm^{-1} in HPW. It was found that after pretreatment at 500°C; however, both samples exhibited a loss in the intensities of these bands, particularly HPW which also showed secondary features for the tP–O band. The latter phenomenon is in agreement with previous findings and has been attributed to symmetry loss within the Keggin Unit (25). Further pretreatment at 600°C resulted in complete loss of the Keggin Unit bands, indicative of structural collapse. The presence of hydroxonium ($H(H_2O)_n^+$) and NH_4^+ ions were confirmed in HPW (band at 1715 cm^{-1}—Fig. 2 (inset)) and NH_4PW (bands at 3200 and 1405 cm^{-1}) respectively. This is in agreement with previous findings (24, 25, 51). Both of these features were sensitive to temperature with the former being removed by pretreatment at 200°C, while the latter developed multiple features and shifted to higher wavenumbers at higher temperatures.

Acidity of HPW and Its Salts

The infrared spectra of samples onto which ammonia had been adsorbed was used to characterize the acidity of the salts (Table 1; Figs. 3 and 4). All of the materials contained Bronsted acidity due to the presence of residual HPW. Moreover, analysis of the stoichiometries obtained from NH_3 uptake (Table 2) reflected the ease with which protons were substituted by the various ions. This analysis also indicates adsorption of 3 NH_4^+ ions per Keggin Unit for HPW, consistent with the known stoichiometry. Moreover these results showed that the AlPW consisted of salt and acid rich domains. It is not possible to distinguish the salt-rich and acid-rich domains. Nevertheless this sample was shown previously to have remarkably good catalytic activity far superior to that of pure

TABLE 1

Variation of NH_4^+: Keggin Unit Ratio for Various Heteropoly Acids

Temperature (°C)	HPW	NH_4PW[a]	NH_4PW	AlPW	KPW
200	3.1	2.2	2.6	1.5	0.6
300	2.7	2.3	2.5	1.4	0.5
400	2.5	2.3	2.3	0.9	0.4
500	2.3	2.4	2.3	0.6	0.2
[b]	−24	NA	−65[c]	−46	−65

[a] NH_4PW not dosed with NH_3.
[b] Percentage change in NH_4^+: KU for samples at 200 and 500°C.
[c] Percentage change in NH_3 uptake only.

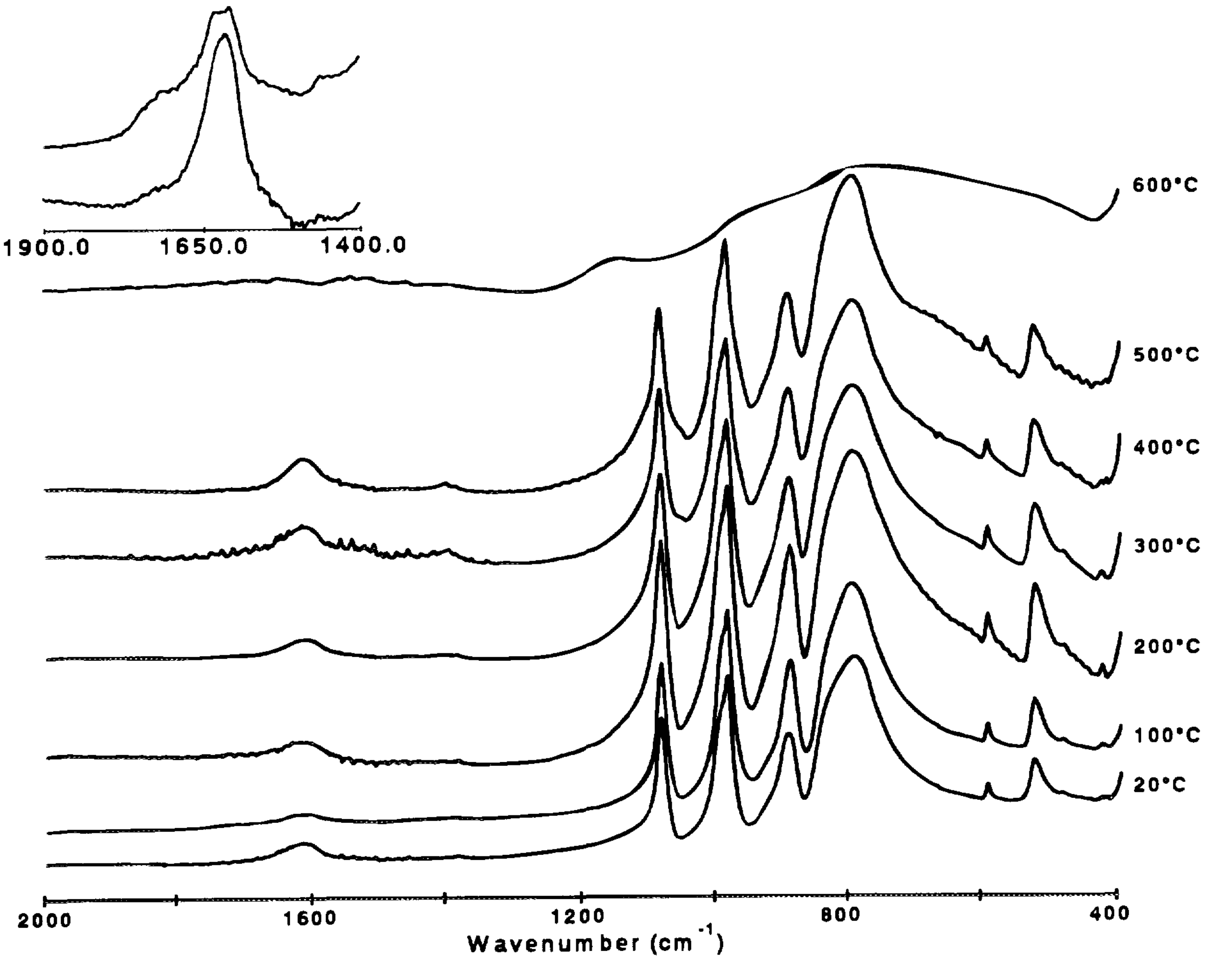

FIG. 2. FTIR spectra of HPW heated to 100, 200, 300, 400, 500, and 600°C.

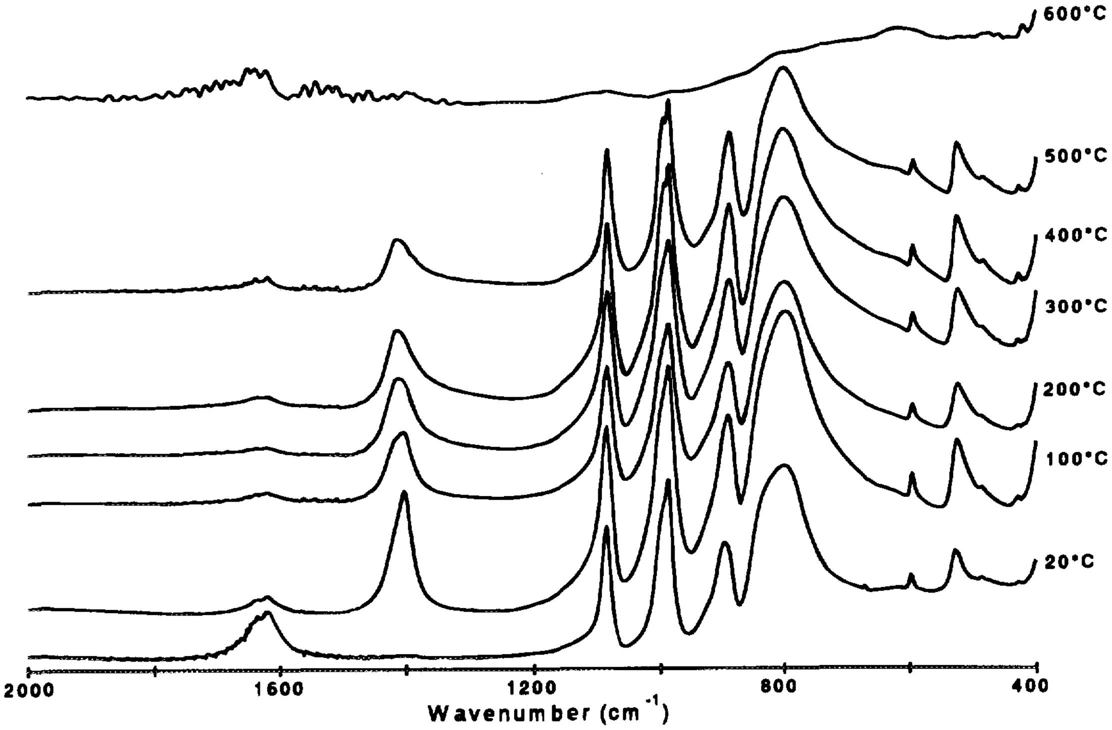

FIG. 3. FTIR spectra of HPW calcined at 300°C (spectrum at 20°C) and HPW + NH_3 after being heated to 100, 200, 300, 400, 500, and 600°C.

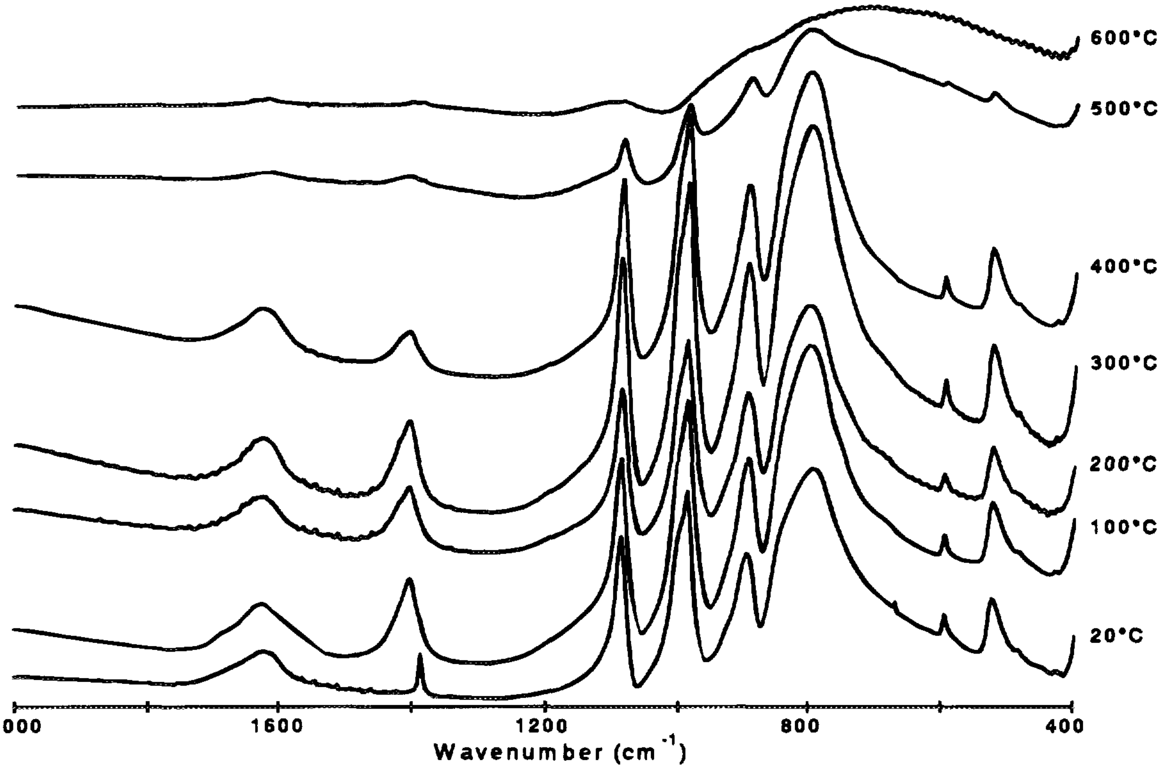

FIG. 4. FTIR spectra of AlPW calcined at 300°C (spectrum at 20°C) and AlPW + NH_3 after being heated to 100, 200, 300, 400, 500, and 600°C.

samples of other salts (50). The presence of Lewis acidity was also recorded for AlPW and KPW (band at 1386 cm^{-1} in Fig. 4). All of these findings are in agreement with previous findings (25).

All materials showed a loss of acidity upon heating, as indicated by the decrease in the NH_4^+: Keggin Unit ratio (Fig. 5; Table 1). Furthermore after pretreatment at higher temperatures all spectra showed shifts in the peak maxima of the $NH4^+$ band (Fig. 6), indicative of increasing proton bond and hence acid strength.

A qualitative analysis of the water content of the HPAs was made assuming that the due care taken during the experimental procedure would not have allowed any changes in the water content (Fig. 7). These results indicated that there was a gradual loss of physically bound water up to 300°C. However, after pretreatment at 400°C, all samples showed an increase in water content and, as discussed later, this phenomenon appeared to be linked to the onset of structural collapse.

An analysis of the fingerprint bands of the salts again showed a variation of band maxima with counter cation. Moreover, examination of the AlPW spectra showed the

TABLE 2

Substoichiometry of Three XPW Salts

Salt	NH_3 : KU	Stoichiometry
NH_4PW	0.51	$(NH_4)_{2.3}H_{0.7}PW_{12}O_{40}$
KPW	0.57	$K_{2.4}H_{0.6}PW_{12}O_{40}$
AlPW	1.53	$Al_{0.5}H_{1.5}PW_{12}O_{40}$

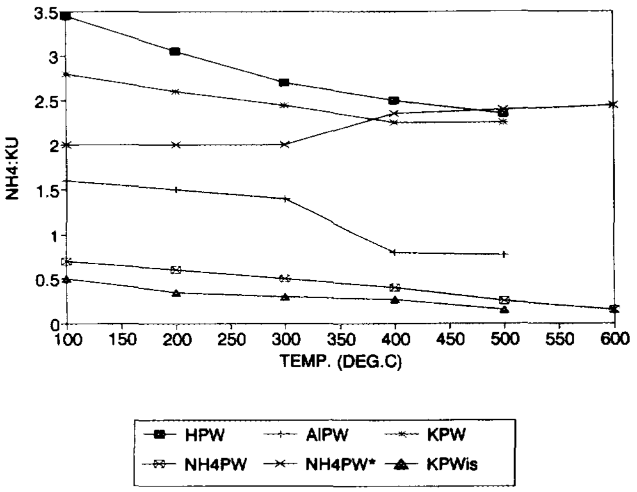

FIG. 5. Variations in the NH_4^+: Keggin Unit ratio at different temperatures.

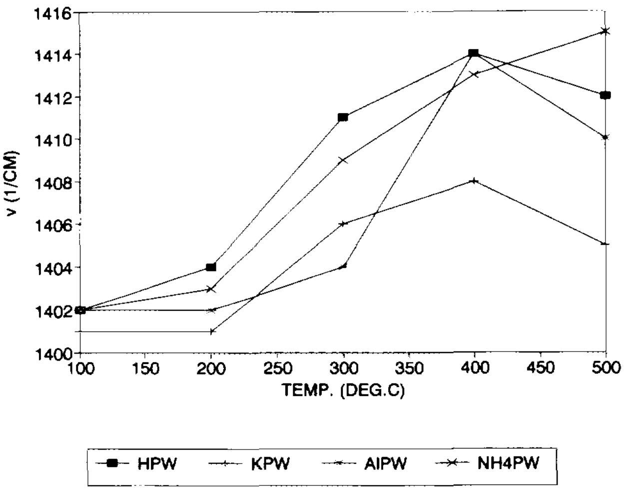

FIG. 6. Variations in the νN–H band at different temperatures.

presence of secondary structural features on the Keggin Unit bands. This is probably indicative of some degree of structural disorder consistent with the presence of salt and acid domains as suggested from the stoichiometric considerations referred to above. The response of the Keggin Unit bands to temperature was also monitored and reflected the trends seen previously. There was little change in the fingerprint bands up to 400°C. At higher temperatures, however, secondary features became apparent and this was followed eventually by complete loss of structure. In particular, the spectra obtained for AlPW indicated considerable thermal instability, clearly visible at 500°C (Fig. 4). Highfield and Moffat (25) have indicated that AlPW is stable at these temperatures and this apparent discrepancy may be due to differences in the bulk distribution of Al^{3+} or to the fact that their sample was much purer than the present. However the clearest exception to this trend was KPW which was found to thermally stable over the entire temperature range studied with no loss of spectral features recorded. It has been shown previously that the AlPW had about 5% of the surface area of the KPW but considerably more acidity. The reduced surface area may be ascribed to the impurity of the sample but it is noteworthy nevertheless that the AlPW was the far superior catalyst (55).

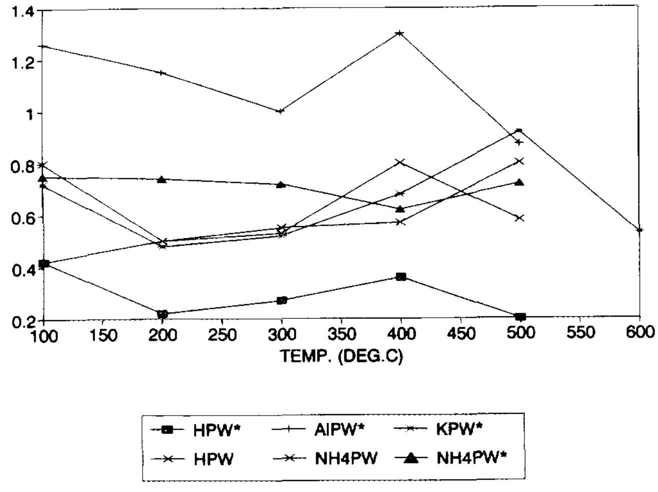

FIG. 7. Variations in the lattice water: Keggin Unit at different temperatures.

Analysis of HPA Sample Studied after Reaction

An infrared analysis of the coke deposits formed during hydrocarbon conversion reactions, using the method of Karge (53), gave the results shown in Table 3. The effects of coking on band structure and intensities were also examined and these results are shown in Table 4.

These results suggest that there is a relationship between the salt type and coke formation. The Type A salts (HPW, AlPW) generally formed only Type I aliphatic coke (53) except in those cases where the reaction conditions were nonisothermal or for long time-on-stream high pressure oligomerization runs. In contrast the Type B (KPW, NH_4PW) salts contain both Type I and Type II aromatic coke (53). With increased coking there was also a correlation between extent of coking and Keggin unit band shifts, particularly the tM–O–M_e band, resulting in larger peak shifts. The variation of peak intensities also appeared to be linked to the degree of coking. In particular, all spent oligomerisation catalysts showed significant losses in band intensities in a manner analogous to that observed prior to structural collapse. Such losses in intensity followed the trend:

$$\text{AlPW3} > \text{AlPW2} > \text{FePW} > \text{AlPW1} > \text{NH}_4\text{PW}.$$

This trend followed that of observed band shifts and also agreed with coke deposition as determined by TG-DTA (50). These results are indicative of a high degree of structural distortion of the Keggin Unit due to the buildup on the HPA of carbonaceous deposits, in particular aromatic and polyaromatic species.

The acidity of three spent AlPW oligomerisation catalysts was characterized by *in situ* NH_3 adsorption. The difference spectra are shown in Fig. 8. It is clear that the HPAs retained some acidity, the degree of which was dependent upon the reaction conditions used. In the case of the short time-on-stream catalyst, viz. AlPW1 (spectrum a), there were still a significant number of Bronsted sites present as evidenced by the large irreversible uptake of NH_3. The long time-on-stream catalysts and those used in cases where the reaction conditions were nonisothermal, viz. AlPW2 and AlPW3 (spectra b and c, re-

TABLE 3

FTIR Analysis of Carbon Deposits on Spent XPW Catalysts after High-Pressure Propene Oligomerization

Catalyst/reaction	Coke I	CH		Peaks		Coke	Coke II	C–H	Arom.	Coke	
HPW											
Postisomerization	Y	2965	2924	2864w	2852w	—	N	—	—		
Postcracking	Y	2965	2925	2864	2853	—	N	—	—		
AlPW											
Postisomerization	Y	—	2924w	—	2852w	—	N	—	—		
Postcracking	Y	2965	2928	—	2852	—	N	—	—		
AlPW1	Y	2960s	2926s	2870s	2855s	—	N	—	—		
AlPW2	Y	2957v	2924v	2868v	2854v	1638	Y	3005	3095	1588	1547
AlPW3	Y	2958v	2926v	2870v	2856v	1635	Y	3070w	3092w	1597	1545
KPW											
Postisomerization	Y	2966	2928	2865w	2852w	—	Y	3061	3098	—	1545w
NH4PW											
Postcracking	Y	2968w	2928w	—	2854	—	Y	3026	1605		
Postisomerization	Y	2963	2926	2868	2853	1637	Y	3008	3070d	1595	
FePW											
Postoligomerization	Y	2957	2926	2867	2855	1630	Y	3004	3070d	1600	1550

Note. (See Ref. 54 for peak assignments.) Type I Coke is defined as "paraffinic and, to a lesser extent olefinic/polyolefinic species." Type II Coke is defined as "polyalkanes, but predominantly alkylaromatics and polyaromatics" see Karge (54).

TABLE 4

Effect of Coking on Fingerprint Bands in Various XPW Salts

	UA (m)	OPO (w)	*MOMe* (v)	*MOMc* (m)	*M* = O(s)	P–O(m)
Catalyst/reaction						
HPW	525	595	794	892	984	1081
Postisomerization	0	0	4	−2	−1	0
Postcracking	−1	−1	2	−1	0	0
AlPW	523	594	792	892	984	1081
Postisomerization	1	1	2	1	−1	0
Postcracking	2	0	4	−2	−2	0
AlPW1	1	2	10	0(mw)	0	0
AlPW2	−9(w)	2(vw)	27	4(w)	−5	−1(mw)
AlPW3	−9(w)	1(vw)	27	5(w)	−1	0(mw)
AlPW1 ex-NH3	1	2	6	−2	−1	0
AlPW2 ex-NH3	0	2	24	3	−1	−1
AlPW3 ex-NH3	0	2	24	1	−1	0
KPW	525	596	801	890	983	1081
Postisomerization	1	0	1	−1	−2	0
NH$_4$PW	526	596	809	891	986	1018
Postcracking	0	0	−3	−1	−1	0
Postoligomerization	−1	0(vw)	6	−2	−1	−1
FePW	525	595	793	891	982	1081
Postoligomerization	−4	0(vw)	21	4(mw)	0(mw)	−1(mw)

Note. V = very strong, s = strong, m = medium, mw = medium weak, w = weak, vw = very weak.

TABLE 5

TG–DTA Data for Various XPW Salts (°C)

	Endo 1	Endo 2	Endo 3	Endo 4	Exo 1	Exo 2	Exo 3
HPW	110	—	300	—	—	625	—
NH_4PW	110	—	—	—	—	625	650
AlPW	120	235	285	400	570	625	—
KPW	105	—	—	—	—	—	—

spectively) showed significant loss of acidity. Within experimental error their uptake of NH_3 per Keggin Unit was respectively equal to and about half of that of AlPW1 (ca. 0.4 NH_4 : KU for AlPW2 and AlPW3 vs 0.75 NH_4 : KU for AlPW1). Furthermore the adsorption of ammonia coincided with the desorption of Type I coke species, as shown by the negative features in the difference spectra. Analysis of the fingerprint bands, after NH_3 adsorption, was performed *ex situ* (Table 3). These showed further shifts of the Keggin Unit bands, with the tM–O–M_e peak decreasing in frequency compared to that of an undosed sample out of the reactor.

Further heating of the AlPW3 to 300°C in order to regenerate the catalyst *in situ* was attempted. However, while this showed losses in peak intensities indicative of loss of water (3400 and 1620 cm^{-1}), Type I coke (2900, 1380 cm^{-1}) and NH_4^+ (1400 cm^{-1}) respectively, there was also a minor increase in the Type II coke bands. This is consistent with the ageing of the light hydrocarbons via hydrogen loss and aromatization to give an increase in aromatic deposits (54).

DISCUSSION

The aims of this investigation were to study the thermal stability and acidity of the heteropoly acids and to attempt to analyze the cause of deactivation after high pressure propene oligomerization viz. coking or loss of acidity.

Thermal Stability

On the basis of the infra-red and thermal analysis studies (Table 5) it has been shown that the thermal stabilities of the acids decreased in the following order:

$$\begin{aligned} \mathrm{KPW}^* &> \mathrm{NH_4PW} = \mathrm{NH_4PW}^* \\ &> \mathrm{HPW}^* > \mathrm{HPW} > \mathrm{AlPW}^* \end{aligned}$$

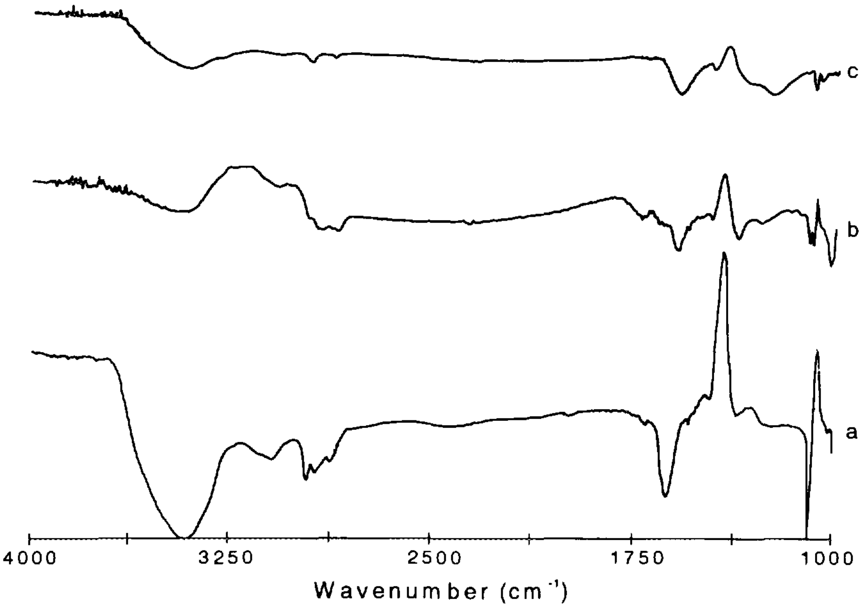

FIG. 8. Difference spectra of NH_3 dosed oligomerization catalysts. (a) AlPW1 (short time-on-stream catalyst). (b) AlPW2 (long time-on-stream catalyst). (c) AlPW 3 (nonisothermal reaction conditions).

where * denotes that the sample was dosed with NH_3. This confirms the stability of KPW as has been reported previously (31). The lower stability AlPW is consistent with the structural disorders evident in the samples.

In considering the thermal stability of HPW Hodnett and Moffat (35, 36) have proposed the following decomposition mechanism:

$$H_3PW_{12}O_{40} \rightarrow PW_{12}O_{38.5} + 1.5H_2O \quad (2a)$$

$$PW_{12}O_{38.5} \rightarrow 12WO_3 + PO_x \quad (2b)$$

In this mechanism there is a single dehydration step followed by the collapse of an anhydrous anion. They postulate that after dehydration no acidic protons remain.

Alternatively the mechanism may be proposed to account for the thermal stabilities of the HPW (see Fig. 9). This mechanism accounts for the increase in lattice water at 400°C, due to interaction of the protons in HPW (or the residual HPW phase in the HPA salt) with anionic oxygen atoms, prior to dehydration (step 1a). It is also consistent with the reduction mechanism proposed for 12-molybdophosphate (5, 34). Furthermore, in agreement with Eguchi *et al.* (28), the mechanism is consistent with the observed fine structure and losses in band intensities which arise from structural perturbations occurring in the partial reduction of the anion (step 1b). Structural collapse via reduction/dehydration (step 1c), is also in agreement with the NH_3 temperature programmed desorption results reported in Ref. (55) which showed loss of both NH_3 and H_2O to occur concomitantly with structural collapse.

It is proposed that this mechanism is not followed in the case of NH_3-dosed HPW (or NH_4PW) due to the interaction between NH_3 and the proton which forms bulk NH_4PW (25). This essentially "fixes" the H^+ moiety thus inhibiting step (1a) and resulting in greater thermal stability and absence of the observed increase in lattice water (Fig. 7). However, at higher temperatures, this stability is lost due to the dissociation of NH_4^+. In agreement with previous findings the desorbed proton thus formed then reacts rapidly with the anionic oxygen (55). This reaction would occur at a critical temperature (i.e., a desorption/NH_4^+ dissociation temperature) and result in the rapid collapse of the anion rather than the gradual process observed in the case of HPW.

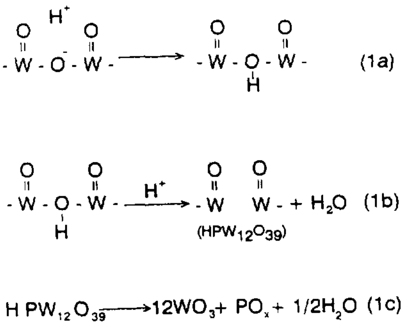

FIG. 9. Proposed mechanism for the thermal decomposition of HPW.

Finally the stability of KPW is ascribed to the substitution of protons by K^+. In the case of AlPW, structural collapse occurs in two stages, firstly, decomposition of salt (570°C) and, secondly, HPW (625°C) as indicated by TG-DTA.

Evidence in favour of the proposed mechanism was derived from water TPD, TPR and acidity measurements (35, 36) and in all cases the results are consistent with the mechanism proposed herein. Firstly, whereas water TPD of HPW did not show that the production of water coincided with structural collapse (step 1c), this was probably due to the temperature limit of the study being below 600°C (the decomposition temperature of HPW is ca. 620°C). Hence no relevant information could be obtained. In contrast, water TPD of both HSiW and HPMo showed sharp peaks of water production coinciding with the measured DTA decomposition temperatures. Hodnett and Moffat (35) attribute this to the accelerated desorption expulsion of proton related water. However, these observations are also consistent with dehydrational collapse (step 1c). In the TPR study of HPW (36), there was again no direct evidence that water evolution coincided with structural collapse, due to the increasing water background. However, TPR of HPMo, NaPW, and MgPW all exhibited high temperature water evolution at temperatures close to their DTA decomposition temperatures, consistent with step 1c. Secondly, analysis of HPA acidity via pyridine adsorption (35) has shown that HPW, pretreated at 450°C to remove acidic protons (2a), adsorbed less base than untreated HPW thus indicating low acidity. However, this sample irreversibly adsorbed ca. $\frac{1}{3}$ of the pyridine adsorbed by untreated HPW, consistent with the presence of $HPW_{12}O_{39}$ as shown in step (1b).

It is thus proposed that the above mechanism may be more consistent than those suggested previously in explaining the results obtained in those studies. At the same time they also account for the results obtained in this work. It is also consistent with the models proposed for Mo and Si containing HPAs and may represent a more accurate model of the decomposition mechanism.

Acidity of As-Synthesised HPAs

NH_3 adsorption results indicated that the number of acid sites present on the HPAs decreased in the order:

$$HPW > AlPW > NH_4PW, KPW$$

This trend does not reflect acid site strength since NH_3 cannot differentiate between sites of different strengths (56). However NH_3 attains adsorption–desorption equilibrium rapidly and, as has been shown in previous studies, it provides more accurate information on the bulk acidity of HPAs (25). NH_3 adsorption also reflected the presence of the large residual HPW phase in AlPW (which gives rise to a comparatively high number of acid sites) consistent with the observations of multiple nondegenerate features in the fingerprint bands of these salts. As stated above, these probably are caused by the presence of salt-rich and acid-rich domains, arising out the improper substitution of Al^{3+} for the proton. These domains give rise to both the high NH_3 uptake and the spectral features caused by the two phases, which would be of similar (but not identical) frequencies.

As expected the desorption profiles obtained (Fig. 5) were similar, due to the common identity of the acidic phase. Further analysis (Table I) indicated that, after heating to 500°C, all HPAs retained ca. $\frac{1}{3}$ of the initial uptake of NH_3. This is consistent with the proposed mechanism of structural collapse, (step 1b with dehydration and loss of $\frac{2}{3}$ of the acid sites). The response of HPW was different, however, due to the formation of bulk NH_4PW, as noted earlier. This is reflected in the NH_4^+ : Keggin Unit ratio of HPW at 500°C, which was identical to that of NH_4PW and NH_4PW^*. The shifting of the NH_4^+ adsorption bands (Fig. 6) was indicative of the presence of stronger acid sites, due to the formation of $H^+ \ PW_{12}O_{39}^-$, which contains a hard acid (H^+) and a soft base (the large and polarizable $PW_{12}O_{39}^-$). The presence of this strong acid site is in agreement with the findings of Nowinska *et al.* (9, 54) who found that although NH_4PW contained $\frac{1}{3}$ of the number acid sites of HPW, the sites present were strong enough to crack cumene.

Postreactor Catalysts

An analysis of the coke formation on samples of heteropoly acids after they had been used for propene oligomerization provided by inference a further indication of the acidity of the various HPAs. Indeed, in this way it was possible to obtain information on the strength of the acidic sites accessible to the various hydrocarbon reactants and this was compared with the analysis of bulk acidity results as obtained by NH_3 adsorption.

The formation of Type I coke on Type A salts and Type I and II coke on Type B heteropoly compounds was consistent with the determined acidities of these samples (45, 46). These results were also in agreement with the results of the butene isomerisation reaction (50) where Type B salts were shown to catalyze both skeletal and double bond shift reactions while Type A only catalyzed the latter (50). The presence of coke alone, however, is not a reflection of acid site strength unless the coke type is considered although it is generally accepted that Type A salts contain weaker acidic sites than Type B (9, 54) and it is the strong acid sites on the latter type which are responsible for the formation of aromatic Type II coke. The presence of Type II coke on AlPW2 and AlPW3 did not represent any anomaly since it was a result of the different process conditions used in those studies (50). For AlPW2, viz. nonisothermal operation, the catalyst bed experienced displayed hot-spots due to a combination of high activity and the poor heat transfer characteristics of the catalyst bed (50, 55). This resulted in the formation of the aromatic coke deposits observed. In the case of AlPW3, the presence of aromatics is attributed to the ageing of Type I coke as suggested by Karge (57).

The presence of coke, and in particular Type II coke, is also associated with the changes in the infrared spectra. Keggin Unit band shifts were observed for samples of spent catalyst, indicative of interactions between coke species and the anion. Furthermore the reduction in intensities of fingerprint bands at high coke levels was indicative of severe structural perturbation similar to that observed during structural collapse. The degree of these perturbations increased as coking increased, implying that the build up of coke deposits on the active sites of the Keggin Unit led to a physical distortion of the anion structure. This is consistent with acidity measurements which showed marked increases in the acidity of AlPW2 and AlPW3 compared to AlPW1 and prereactor AlPW. This indicated that acid sites are lost by the build up of aromatic coke species on the $tM–O–M_e$, so-called, cup site, which showed the greatest changes with respect to coke deposition. This is also consistent with the proposed location of the proton or other counter cation based upon Keggin Unit peak variations with counter cation (50). Based upon these observations it is proposed that the active site in the acid catalyzed oligomerisation of propene over heteropoly acids is a proton located within the $tM–O–M_e$ site of the Keggin Unit. Further evidence or this postulate can be seen in the displacement of Type I coke by NH_3, which clearly indicates that coke deposition occurs on the acid sites of the Keggin Unit. This suggests that the presence of high concentrations of Type I coke is not detrimental to catalytic activity (50). These species are presumably precursors to oligomerisation products and are strongly chemisorbed on the active sites of the HPA. Their conversion to Type II coke species, after *in situ* heating, also indicates that these species may serve as precursors to the formation of aromatic hydrocarbons. The production of Type II coke species may also be facilitated by strong acid sites, as evidenced by the performance of NH_4PW in propene oligomerisation (50). This salt was found to deactivate rapidly due to the formation of Type II coke adsorbed on the strong acid sites of the salt. Clearly the nature and number of the acid sites on the heteropoly acids are crucial to their activity with the presence of a large number of acid sites resulting in a high probability of undesired cracking reactions, and the presence of strong acid sites resulting in deactivation due to the formation of aromatics. This is consistent with the high activity of the AlPW synthesized in this study for propene oligomerisation. It had a moderate number of intermediate strength acid sites and displayed both high activity and long lifetime.

CONCLUSIONS

The thermal stability and acidity of 12-tungstophosphoric acid (HPW) and its salts before and after being used for the high pressure oligomerization of propene have been determined using infrared spectroscopy and thermal analysis. The relationship between acidity and reactivity in hydrocarbon conversion reactions has been investigated and also the location of the active sites in heteropoly anions. These studies have confirmed that there is a correlation between the structural stability and salt cation, with the potassium salt of HPW being the most thermally stable. The AlPW salt used in this study, however, although having a very high catalytic activity was not pure and did not have a relatively high thermal stability. A correlation has been established between the salt Type (A—low surface area, or B—high surface area) and the nature of coke deposits formed during reaction. Type A salts produced only Type I (aliphatic) coke when catalyzing butene isomerization, butane cracking and short time-on-stream high-pressure isothermal propene oligomerisation reactions. On the other hand, both Type I and Type II (aromatic) coke formed after long time-on-stream and/or non-isothermal high-pressure propene oligomerization. Type B salts always formed both Type I and Type II coke. In all cases the formation of Type II coke was responsible for catalyst deactivation. This coke blocked acidic sites as was confirmed by NH_3 adsorption studies of samples analyzed after reaction. On the basis of the shift in the IR bands, it is proposed that the coke deposits responsible for deactivation are formed in the *M*–O–*M* edge sites or so-called cup sites of the Keggin Unit. The strength of these sites may be influenced by the presence of secondary counter cations. Cation substitution leads to a decrease in number of acid sites but an increase in strength of residual sites, with the strong acidic sites formed exhibiting rapid deactivation due to their tendency to form site blocking aromatics.

ACKNOWLEDGMENTS

The financial support of the FRD, SASOL, and AECI are gratefully acknowledged.

REFERENCES

1. Keggin, J. F., *Proc. Royal Soc. A* **144,** 75 (1934).
2. Black, J. B., Scott, J. D., Serwicka, E. M., and Goodenough, J. B., *J. Catal.* **106,** 16 (1987).
3. Serwicka, E. M., Black, J. B., and Goodenough, J. B., *J. Catal.* **106,** 23 (1987).
4. Hayashi, H., and Moffat, J. B., *J. Catal.* **81,** 61 (1983).
5. Qinwei, Z., and Jingfa, D., *J. Catal.* **116,** 298 (1989).
6. Kozhevnikov, I. V., and Matveev, K. I., *Appl. Catal.* **5,** 135 (1983).
7. Moffat, J. B., *in* "Methane Conversion, Auckland, 1987" (D. M. Bibby, C. D. Chang, R. F. Howe and S. Yurchak, Eds.) p. 563. Elsevier, Amsterdam, 1988.
8. Kasztelan, S., and Moffat, J. B., *J. Catal.* **116,** 82 (1989).
9. Nowinska, K., *Chem. Soc. Chem. Commun.* 44 (1980).
10. Bruckman, K., Haber, J., Lalik, E. and Serwicka, E. M., *Catal. Lett.* **1,** 35 (1988).
11. Okuhara, T. Hasmoto, T., Hibi, T., and Misono, M., *J. Catal.* **93,** 224, (1985).
12. McGarvey, G. B., McMonagle, J. B., Nyak, V. S., Taylor, D., and Moffat, J. B., *in* "Proceedings of the 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.) p. 1804. Chem. Institute of Canada, Ottawa, 1988.
13. Misono, M., Okuhara, T., and Mizuno, N., *in* "Successful Design of Catalysts" (T. Inui, Ed.) p. 267. Elsevier, Amsterdam, 1988.
14. Tsigdnos, G. A., *Ind. Eng. Chem. Prod. Res. Develop.* **13,** 267 (1974).
15. Nayak, V. S., and Moffat, J. B., *Appl. Catal.* **36,** 127 (1988).
16. Misono, M., Sakata, K., and Yoneda, Y., Studies in Surface Science and Catalysis, in "Proceedings of the 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe. Eds.), p. 1047. Kodansha–Elsevier, Tokyo Amsterdam, 1981.
17. Konishi, Y., Sakata, K., Misono, M., and Yoneda, Y., *J. Catal.* **77,** 169 (1982).
18. Brown, G. M., Noe-Spirlet, M. R., Busing, W. R., and Levy, H. A., *Acta. Crystallogr. Sect. B* **33,** 1038 (1977).
19. Ichida H., Kobayashi, A., and Sasaki, Y., *Acta. Crystallogr. B* **36,** 1382 (1980).
20. Ghosh, A. K., and Moffat, J. B., *J. Catal.* **101,** 238 (1986).
21. Black, J. B., Clayden, N. J., Gai, P. L., Scott, J. D., Serwicka, E. M., and Goodenough, J. B., *J. Catal.* **106,** 1 (1987).
22. Misono, M., Mizuno, N., Katamara, K., Kasai, A., Konishi, Y., Sakata, K., Okuhara, T., Yoneda, Y., *Bull. Chem. Soc. Jpn.* **55,** 400 (1982).
23. Rocchiccioli-Deltcheff, C., Thouvenot, R., and Franck, R., *Spectrochim. Acta. Part A* **32,** 587 (1976).
24. Bielanski, A., Malecka, A., and Kubelkova, L., *J. Chem. Soc. Faraday Trans. I* **85,** 2847 (1989).
25. Highfield, J. G., and Moffat, J. B., *J. Catal.* **88,** 177 (1984).
26. Highfield, J. G., and Moffat, J. B., *J. Catal.* **89,** 189 (1984).
27. Finke, R. G., Rapko, B., Saxton, R. J., and Domaille, P. J., *J. Am. Chem. Soc.* **108,** 2947 (1986).
28. Eguchi, K., Toyozawa, Y., Yamazoe, N., and Seiyama, T., *J. Catal.* **83,** 32 (1983).
29. Baba, T., Nomura, M., Ono. Y., and Kansaki, Y., *J. Chem. Soc. Faraday Trans. I* **88,** 71 (1992).
30. Matsuda, T., Sato, M., Kanno, T., Miura, H., and Sugiyama, K., *J. Chem. Soc. Faraday Trans. I* **77,** 3107 (1981).
31. Serwicka, E. M., Bruckman, K., and Haber J., *Appl. Catal.* **73,** 153 (1991).
32. Centi, G., Lopez Nieto, J., Ipalucci, C., Bruckman, K., and Serwicka, E. M., *Appl. Catal.* **46,** 197 (1989).
33. Katamura, K., Nakamura, T., Sakata, K., Mison, M., and Yoneda, Y., *Chem. Soc. Jpn. Chem. Lett.* 89 (1981).

34. Mizuno, N., Katamura, K., Yoneda, Y., and Misono, M., *J. Catal.* **83,** 384 (1983).
35. Hodnett, B. K., and Moffat, J. B., *J. Catal.* **88,** 253 (1984).
36. Hodnett, B. K., and Moffat, J. B., *J. Catal.* **91,** 93 (1985).
37. Izumi, Y., Hasebe, R., and Urabe, K., *J. Catal.* **84,** 402 (1983).
38. Serwicka, E. M., and Grey, C. P., *Colloids Surf.* **45,** 69 (1990).
39. Mastikhin, V. M., Kulilov, S. M., Nosov, A. V., Kozhevnikov, I. V., Mudrakovsky, I. L., and Timofeeva, M. N., *J. Molec. Catal.* **60,** 65 (1990).
40. Thouvenot, R., Rocchioccioli-Deltchcheff, C. and Fournier, M., *J. Chem. Soc. Chem. Commun.,* 1352 (1991).
41. Thouvenot, R., Fournier M., and Rocchioccioli-Deltcheff, C., *J. Chem. Soc. Faraday Trans. 1* **87,** 2829 (1991).
42. Chidichimo, G., Golemme, A., Imbardelli, D., and Santoro, E., *J. Phys. Chem.* **94,** 6830 (1990).
43. Konishi, Y., Sakata, K., Misono, M., and Yoneda, Y., *J. Catal.* **77,** 169 (1982).
44. Serwicka, E. M., *Z. Phys. Chem. N. F.* **152,** 105 (1987).
45. Misono, M., Catal. Rev. Sci. Eng. **29,** 269 (1987).
46. Tsigdnos, G. A., *Method. Chim.* **8** *in* "Preparations of Transition Metal Derivatives" (K. Niedenzu and H. Zimmer Eds.) p. 553. Academic Press, New York, 1976.
47. Tsignos, G. A., *Top. Curr. Chem.* **76,** 1 (1978).
48. O'Connor, C. T., Fletcher, J. C. Q. and Rautenbach, M. W., *J. Phys. E Sci. Inst.* **19,** 367 (1986).
49. Hayashi, H., and Moffat, J. B., *J. Catal.* **83,** 192 (1983).
50. Vaughan, J. S., O'Connor, C. T., and Fletcher, J. C. Q., *J. Catal.* **147,** 441–454 (1994).
51. Wagner, E. L., and Hornig, D. F., *J. Chem. Phys.* **18,** 296 (1950).
52. Papaconstantinou, E., *Chem. Soc. Rev.* **18,** 1 (1989).
53. Karge, H. G., and Klose, K., *Z. Phys. Chem. N.F.* **83,** 100 (1973).
54. Nowinska, K., Fiedorow, R., and Adamiec, J., *J. Chem. Soc. Faraday Trans.* **87,** 749 (1991).
55. Vaughan, J. S., PhD Thesis, University of Cape Town, 1993.
56. Knozinger, H., *in* "Advances in Catalysis" Vol. 25, p. 184. Academic Press, New York, 1976.
57. Karge, H. G., *in* "Introduction To Zeolite Science and Technology" (H. van Bekkum, E. M. Flanigen and J. C. Jansen Eds.) Chap. 14, p. 531. Elsevier, Amsterdam, 1991.