

High-Pressure Oligomerization of Propene over Heteropoly Acids

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Ammonium, potassium, nickel, copper, cobalt, iron, cerium, and aluminium salts of 12-tungstophosphoric acid (HPW) as well as the ammonium and aluminium salts of 12-tungstosilicic acid have been synthesized and characterized by TG-DTA, nitrogen adsorption, XRD, electron microscopy, ammonia temperature programmed desorption, and FTIR. Consistent with the findings of other heteropolyacid (HPA) characterization studies the HPAs could be divided into two types: Type A, low surface area salts with multiple endothermic mass losses, and Type B, high surface area salts with a single endothermic mass loss. The surface acidity of some of these catalysts was evaluated using butane cracking and butene isomerization as probe reactions. These indicated that the Type B salts had strong acid sites on the surface as they were capable of cracking butane and butene. The Type A salts were inactive for these reactions. The propene oligomerization activity of the HPW salts decreased in the order: Al \gg Co > Ni, NiH, NH₄ > H, Cu > Fe, Ce > K. Premature deactivation as a result of substantial film temperature gradients occurs due to the inability to dissipate the large heat of reaction in the undiluted catalyst bed. Diluting the catalyst with acid-washed sand (1 part catalyst to 10 parts sand) dramatically increased the liquid product yield and catalyst lifetime but the activity order remained the same as the pure powder form. The pure aluminium salt of HPW, viz. AIPW, was found to be the most active, achieving 90% conversion at a WHSV of 12 h⁻¹, 230–240°C, and 5 MPa. The main product of propene oligomerization was the trimer. The sand-diluted AIPW catalyst achieved 100% conversion under identical conditions with no sign of deactivation after 150 h on stream. Pure AIPW yielded a catalyst utilization value (CUV) of 540 g · (liquid product)/g · catalyst with a distillate fraction cetane number of 40. The CUV of the diluted AIPW catalyst was in excess of 1800 g · (liquid product)/g · catalyst. The relationship between the catalytic activity, surface area, and structure of the catalysts is discussed.

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INTRODUCTION

Salts of heteropoly acids consist of heteropoly anions, counter cations, and water of hydration. The anions constitute the primary structure, and the three-dimensional structure of the polyanions, counter cations, and water of hydration is regarded as the secondary structure. The most common primary structure is that of the Keggin

anion; the 1:12 structure of a typical example, [PW₁₂O₄₀]³⁻, is shown in Fig. 1 where 12 WO₆ octahedra surround a central PO₄ tetrahedron. In the secondary structure, the Keggin units are bound to each other either by water of hydration or metals acting as counter cations typically in a *bcc*-type packing formation. The synthesis, structure, acidity, and catalytic activity of heteropoly compounds (HPC) have been extensively reported for a wide range of heterogeneous and homogeneous catalytic reactions (1–10). Typical examples of some applications include the conversion of methanol to hydrocarbons (9, 11–17), the oxidation of methacrolein to metacrylic acid (18, 19), the liquid phase isomerization of C₆–C₈ alkenes (20), and the oxidative conversion of methane to hydrocarbons (9, 21). Heteropoly acids (HPA) have been characterized by powder and single crystal XRD (6, 10, 12–15, 19, 21–31), ammonia, pyridine and water temperature programmed desorption (TPD) (22, 29, 32–34), infrared spectroscopy (6, 9, 10, 18, 19, 30, 32, 33, 35–39), as well as solid state P-, Si-, and H-NMR (10, 30, 40–44) and ESR (10, 19, 37, 40, 45).

In particular, 12-tungstosilicic acid (HSiW) has been shown to be active for the oligomerization of propene to distillate fuels (46–50). The catalytic activity was reported to be sensitive to the calcination temperature, with optimum conversion being achieved after calcination at 240°C. Bauxite-supported HSiW has been shown to coke less rapidly than the pure acid form (47). The oligomer product had a greater C₁₂⁺ fraction than in the case of the classical, phosphoric acid on keiselghur oligomerization catalyst. Conversions of up to 95% propene were achieved at 170–180°C and a pressure of 12 MPa using HSiW. Recently Ratnasamy and Sivasanker (50) claimed that, using HSiW on a silico-tungsten support, a distillate fuel, defined in their patent as the fraction boiling above 230°C, with a cetane number of 52, can be produced. The reaction conditions were 220°C and 5 MPa, and conversions were in excess of 90%. No mention was made of the lifetime properties of this catalyst.

This paper reports on the synthesis, characterization, and propene oligomerization activity of HPW, HSiW, HPMo, and a number of their salts, hereafter referred to

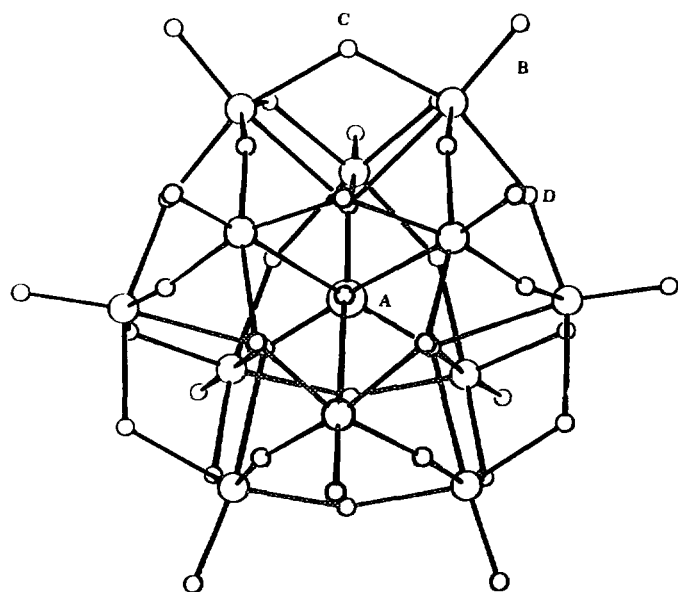


FIG. 1. Structure of 12-tungstophosphoric acid (Keggin Unit): (A) P-O, (B) $M=O$, (C) $M-O-M_{edge}$, (D) $M-O-M_{corner}$.

as *MXP*, where *M* is the counteranion, *X* the central ion, and *P* the peripheral ion. The choice of 12-tungstophosphoric acid (HPW) was based on its well-known catalytic activity and because it is known that HPW has stronger Brønsted acidity than HSiW (4). Since the salts of HPW have also been shown to have different selectivities for the conversion of methanol to hydrocarbons (13, 14, 17) the salts of the parent acids were also studied for propene oligomerization. 12-molybdophosphoric acid (HPMo) was investigated to determine the effect of the peripheral ion on the activity and selectivity. The effect of water in the propene feed stream and steaming of the AIPW catalyst have also been investigated, as has been the effect of varying the calcination temperature and medium. The effect of diluting the pure catalyst in a 1 : 10 mixture with acid-washed sand and its effect on catalyst utilization value (CUV), i.e., $g \cdot (\text{liquid product})/g \cdot \text{catalyst}$, is reported and the effect of supporting HPW and HSiW on α -alumina is also briefly examined.

EXPERIMENTAL

Catalyst Synthesis

The parent acids, HPW, HSiW, and HPMo, were obtained as analytical reagents from Merck. The following compounds were used in the synthesis of the salts: the nitrates of nickel (BDH), aluminium (Riedel-de-Haen), cerium (Mintek), iron (BDH), and cobalt (BDH), the carbonates of nickel (BDH), potassium (Merck), and ammonium (Holpro), as well as copper acetate (Merck) and

aluminium isopropoxide (Fluka). The oligomerization feed mixture (86 wt.% propene, 14 wt.% propane) was obtained from Sasol. Butane and 1-Butene were 99.4% and 99.8% pure, respectively.

The salts were prepared from an aqueous solution of the parent acid to which the required stoichiometric amount of the carbonate, nitrate, or acetate salt of the counter cation was added (3, 13, 14, 17). The aqueous salt solution was stirred and held at 80°C for 30 min. The salts were crystallized out of solution by evaporating to dryness in an air oven at 80°C. The aluminium salts were also prepared by reacting aluminium isopropoxide with the respective parent acid in diethylether (13) (referred to hereafter as AIPW : ether). These salts were either crystallized directly from the diethylether solution or recrystallized from an aqueous solution (referred to hereafter as AIPW : ether/water). The dried salts were crushed and sieved to a size fraction less than 250 μm before being stored. The sand-diluted catalysts were prepared by intimately mixing a 1 : 10 mixture of pure catalyst to sand. The α -alumina supported catalysts were prepared by the incipient wetness technique.

Catalyst Characterization

Thermogravimetric-differential thermal analysis (TG-DTA) of the freshly synthesized catalysts was carried out using a Stanton-Redcroft STA-780 thermal analyzer. Coke content of deactivated catalysts was also analyzed using TG-DTA by sequentially passing nitrogen over the sample up to 500°C, holding at that temperature for 60 min, and thereafter passing air over the catalyst for another 60 min. In this way the amounts of high boiling point hydrocarbons, or "soft" coke, and polynuclear aromatics, or "hard" coke, were determined.

X-ray diffractograms were obtained using a Philips X-ray diffractometer with $\text{CuK}\alpha$ radiation at 40 kV, 30 mA, and a 2θ range of 5–45°. The calcined samples were pretreated at 325°C in nitrogen before recording the diffractograms. Electron micrographs were obtained using a Cambridge S200 scanning electron microscope (SEM) with the accelerating voltage set at 10 keV. In the NH_3 -TPD studies the catalyst samples were calcined in air at 325°C for 4 h and then cooled to 100°C prior to the introduction of a 5% NH_3 in helium gas mixture. The detailed procedure has been described elsewhere (51). IR spectra of as-synthesized and ex-TPD HPAs were recorded on a Nicolet 5ZDX FTIR spectrometer (resolution 4 cm^{-1}) at room temperature using KBr discs. The ex-TPD HPA samples were calcined and the ammonia was adsorbed following the NH_3 -TPD procedure except that the catalysts were kept in flowing helium for 24 h as opposed to 2 h. The ex-TPD samples were then heated at 10°C min^{-1}

to 200, 300, 400, 500, and 600°C for approximately 1 h before being pressed into KBr discs and transferred to the FTIR.

Reaction Procedures

The propene oligomerization apparatus used has been described previously (52). The feed mixture (86 wt.% propene, 14 wt.% propane) was dried over 3A molecular sieves and fed via a high-pressure diaphragm pump to the reactor. The reactor pressure was 5 MPa and the weight hourly space velocity (WHSV) used was 12–14 h⁻¹ unless otherwise stated. Temperature profiles were measured by a thermocouple housed within an axially positioned thermowell at the centre of the reactor. Typically, 1 g of catalyst was used. Prior to reaction the catalysts were calcined in nitrogen at 325°C for 2–6 h. Downstream of the reactor the pressure was decreased to atmospheric via a back-pressure regulator, and phase separation of the reaction products took place in a catchpot held at 20°C. For butane cracking reactions 0.5 g of catalysts was packed into the same reactor used for oligomerization studies and calcined at reaction temperature for 6 h before butane (GHSV = 21,600 h⁻¹) was passed over the catalyst. The first gas sample was taken after 3 min on stream and analyzed by gas chromatography. Thereafter effluent samples were analyzed every half-hour. In the study of butene isomerization approximately 1 g of catalyst was packed into a quartz reactor (25 cm long and an I.D. of 10 mm) and calcined at 325°C in nitrogen for approximately 2 h before being cooled to reaction conditions (225°C). The feed mixture, consisting of a 1 : 4 mixture of 1-butene and nitrogen, was then passed over the catalyst (GHSV = 10,800 h⁻¹). The first gas sample was taken after 3 min

on stream and thereafter samples were taken at 30-min intervals.

Analysis

The vapour-phase products were analyzed by gas chromatography (GC) using a 6.35-mm O.D., 3-m long stainless steel column packed with *n*-octane/Porasil C. The liquid-phase products were analyzed using a 0.352-mm I.D., 50-m long fused silica megabore column coated with a 1.5- μ m film of DB-1 (100% methylpolysiloxane). The oligomer groupings, as shown in Table 5, were assigned on the basis of GC-MS analysis of samples. Samples of the liquid product were hydrogenated in a high-pressure autoclave at 3 MPa and 165°C for 12 h under hydrogen. Palladium on activated carbon (Aldrich, 5 wt.% Pd) was used as the hydrogenation catalyst and was added in 5 wt.% aliquots to the liquid product. H-NMR spectra of the hydrogenated unfractionated liquid product were recorded using a 90 MHz Bruker NMR spectrometer.

RESULTS

Catalyst Characterization

The surface areas of HPW and its salts were given in Table 1. With the exception of KPW and NH₄PW these were between 3 and 15 m²/g. KPW and NH₄PW had surface areas greater than HPW. The surface area values were reproducible to within 5%. The TG-DTA data are also presented in Table 1 and the TG-DTA of AIPW : nitrate is shown in Fig. 2. For the HPCs tested the results showed that KPW and NH₄PW had single endotherms and all the others multiple endotherms. All the aluminium

TABLE 1
TG-DTA and Surface Area Data of MXP(H₂O)_x

Catalyst	Formula	Type	SA (m ² /g)	Endo(1) (°C)	Endo(2) (°C)	Endo(3) (°C)	Endo(4) (°C)	Exo (°C)	H1/H2 ^a	xH ₂ O ^b
HPW	H ₃ PW ₁₂ O ₄₀	A	—	110	240	—	—	600	2.8	24
NH ₄ PW	(NH ₄) ₃ PW ₁₂ O ₄₀	B	37	110	—	—	—	600	—	6
KPW	K ₃ PW ₁₂ O ₄₀	B	140	105	—	—	—	—	—	7
CuPW	Cu _{3/2} PW ₁₂ O ₄₀	A	2	140	250	—	—	590	0.3	7
CoPW	Co _{3/2} PW ₁₂ O ₄₀	A	2	115	250	—	—	595	0.3	8
NiPW	Ni _{3/2} PW ₁₂ O ₄₀	A	6	120	250	360	—	600	0.3	8
CePW	CePW ₁₂ O ₄₀	A	6	140	230	370	—	600	0.8	11
FePW	FePW ₁₂ O ₄₀	A	11	120	230	300	—	600	0.8	9
AIPW : nitrate(2)	AIPW ₁₂ O ₄₀	A	2	130	230	280	400	570	1.3	11
AIPW : nitrate(12)	AIPW ₁₂ O ₄₀	A	12	130	230	280	400	570	1.0	10
AIPW : ether(5)	AIPW ₁₂ O ₄₀	A	5	138	—	300	410	570	1.2	11
AIPW : ether/water(9)	AIPW ₁₂ O ₄₀	A	9	140	—	300	410	570	1.3	12

^a Ratio of water of crystallization to water associated with acid sites.

^b Total amount of water molecules.

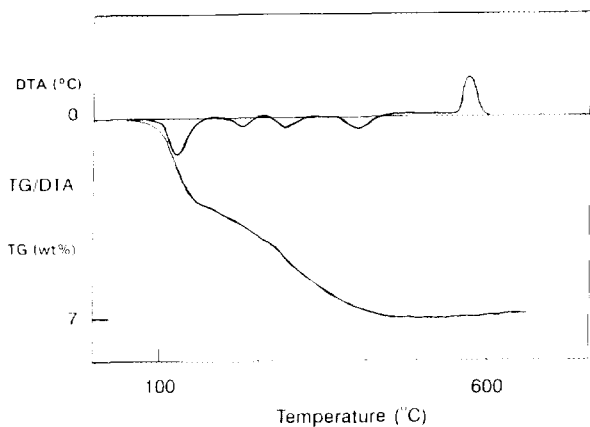


FIG. 2. TG-DTA of AlPW:nitrate.

salts decomposed at approximately 570°C, 30°C lower than the decomposition temperature of the parent acid HPW. On the basis of the TG-DTA and surface area data the HPAs were divided into two types, after Niiyama *et al.* (53), viz. Type A, which are the low surface area salts with multi-endothermic regions, and Type B, the high surface area salts with a single endotherm at 100°C. The Type A salts were water soluble and the Type B salts were water insoluble.

The X-ray diffractogram of fresh HPW is shown in Fig. 3a. After drying in flowing nitrogen at 325°C the diffractogram had fewer and broader peaks (Fig. 3b), indicating a loss of crystallinity. The Type B salts (Figs. 3c and 3d) had well-defined diffractograms that changed little upon drying at 325°C indicating greater thermal stability for this crystalline structure. The intensities of the spectra shown in Figs. 3a and 3b are on the same scale but due to the much greater intensity of the KPW spectrum the intensities in Figs. 3c and 3d have been divided by a factor of 5. Diffractograms of the aluminium salts of HPW, shown in Fig. 4, indicated a partly crystalline structure. When the AlPW: ether salt was recrystallized from water the intensity and the sharpness of the peaks increased. The appearance of new peaks at 2θ of $\sim 25^\circ$ may be indicative of the presence of a new phase.

Figure 5a shows an electronmicrograph of the parent acid, HPW. This acid consisted of irregularly shaped smooth crystallites, approximately 20 μm in diameter, as well as sponge-like crystallites. AlPW:nitrate (Fig. 5b), AlPW: ether, and AlPW: ether/water, on the other hand, consisted of irregularly shaped column-like crystallites 10–50 μm long, although the ends of these columns appeared to have the same sponge-like morphology as in HPW. NH_4PW (Fig. 5c) and KPW consisted of 50–150 μm agglomerates of well-formed 0.5–2 μm rounded cubic crystallites.

Typical ammonia TPD spectra are shown in Fig. 6.

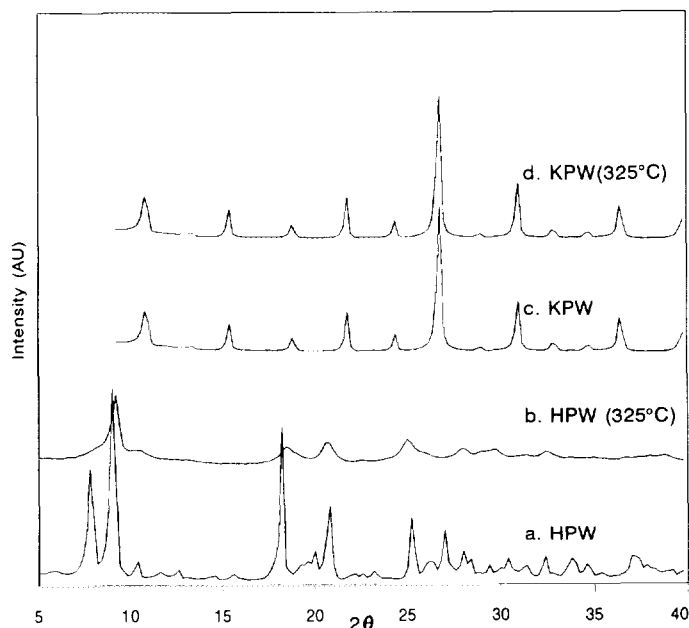


FIG. 3. XRD of HPW, HPW calcined in nitrogen at 325°C, KPW, and KPW calcined in nitrogen at 325°C.

All exhibited two temperature regions in which ammonia desorbed, viz. 100–200°C (low-temperature desorption (LTD)) and 530–600°C (high-temperature desorption (HTD)). The desorption temperatures and the respective quantities of ammonia desorbed are shown in Table 2. There was little difference between the TPD spectra of the Type A and B salts except that the Type A salts in general had two to three times the amount of acidity of the Type B salts.

The infrared spectra of HPW are shown in Fig. 7 and the Keggin unit bands (38) are well defined. The Keggin unit bands of the HPW salts used in this study are listed

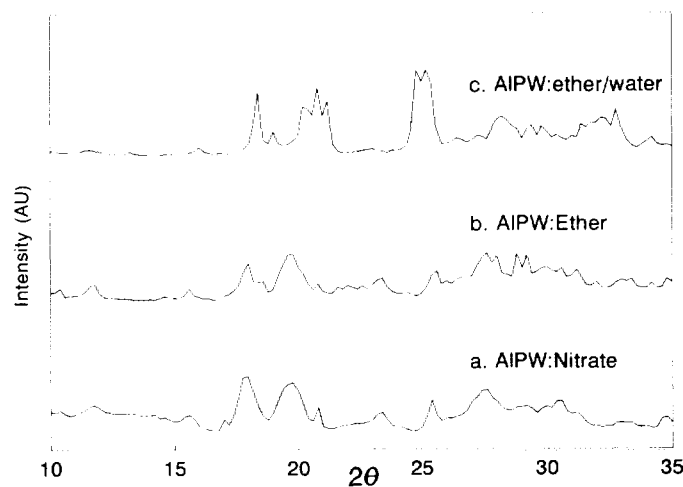


FIG. 4. XRD of the aluminium salts of HPW.

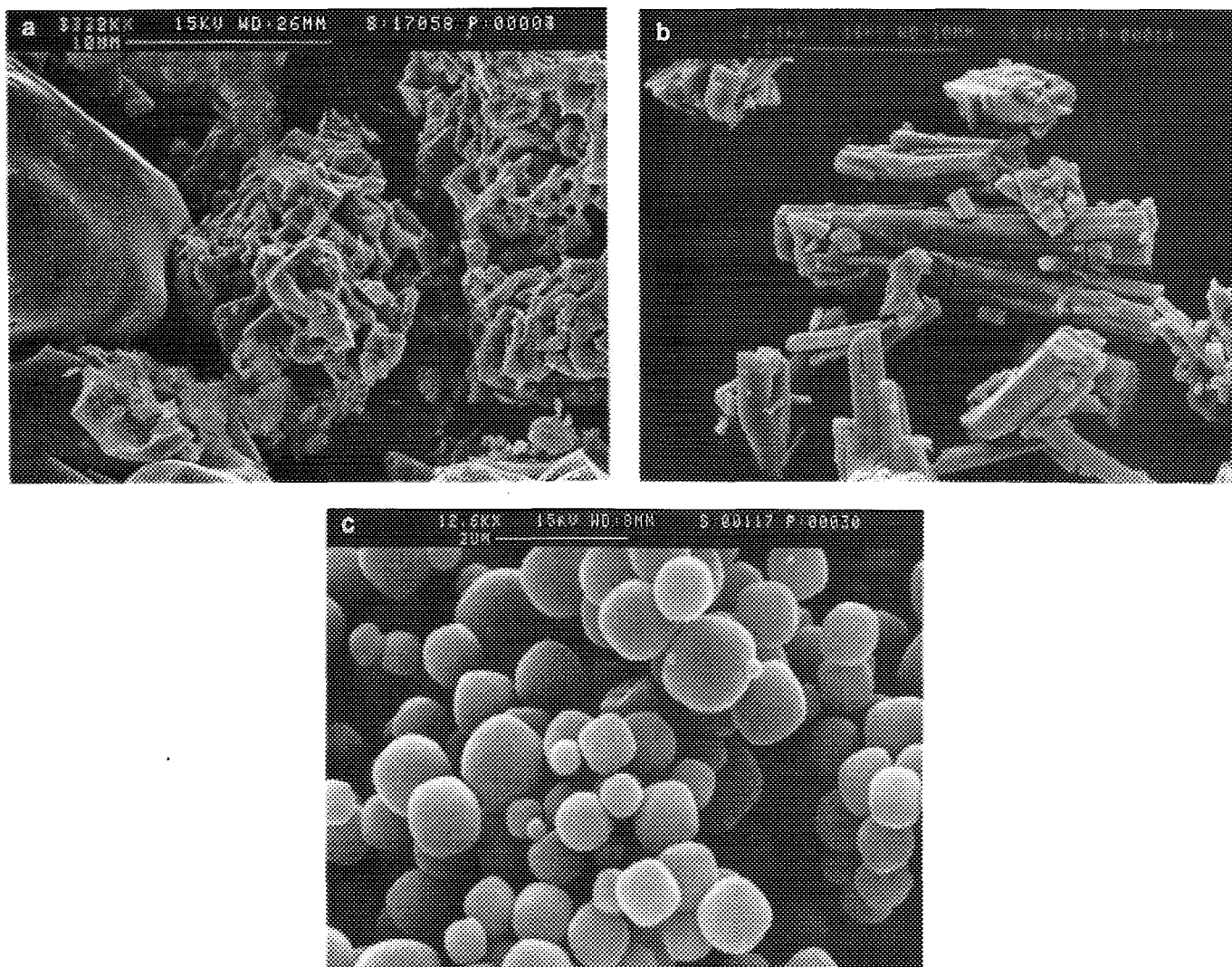


FIG. 5. Electron micrographs of (a) HPW, (b) AIPW:nitrate, and (c) NH_4PW .

in Table 3. The band most affected by the type of countercation present was the $\nu M-O-M$ (edge) band. As can be seen from Fig. 7 adsorbing ammonia on HPW resulted in the appearance of the NH_4^+ band at 1420 cm^{-1} . For AIPW, KPW, and CoPW the 1380 cm^{-1} band was also present, particularly at higher temperatures, indicating ammonia coordinatively bound with metal ions. The initial ratios of $A_{(1420)}/A_{(1080)}$ for AIPW, CoPW, KPW, and HPW are given in Table 4, and as the desorption temperature increased this ratio decreased for all catalysts. At 500°C the Keggin ions of AIPW:nitrate + NH_3 and CoPW + NH_3 began to decompose whereas the Keggin bands of HPW + NH_3 and KPW + NH_3 remained relatively intact. At 600°C the HPW + NH_3 , AIPW + NH_3 , NH_4PW + NH_3 , and CoPW + NH_3 Keggin bands were essentially nonexistent which indicated complete decomposition of

the Keggin anions had occurred. The Keggin bands of KPW + NH_3 were still intact at 600°C which indicated no collapse of the Keggin anions.

Butane Cracking, Butene Isomerization, and Propene Oligomerization Activity

HPW and AIPW:nitrate(2) (Type A) showed no activity for butane cracking between 350 and 450°C . When the catalysts were removed from the reactor, however, they were black in appearance. TG-DTA of these samples indicated that only about 0.4 to 1 wt.% "non-graphitic" or "soft" coke and no "graphitic" or "hard" coke was present. NH_4PW (Type B) was active for butane cracking, converting 1.9% at 400°C (1.4 wt.% iso-butane, 0.3 wt.% propene, 0.1 wt.% ethene, and 0.1 wt.% butenes), but

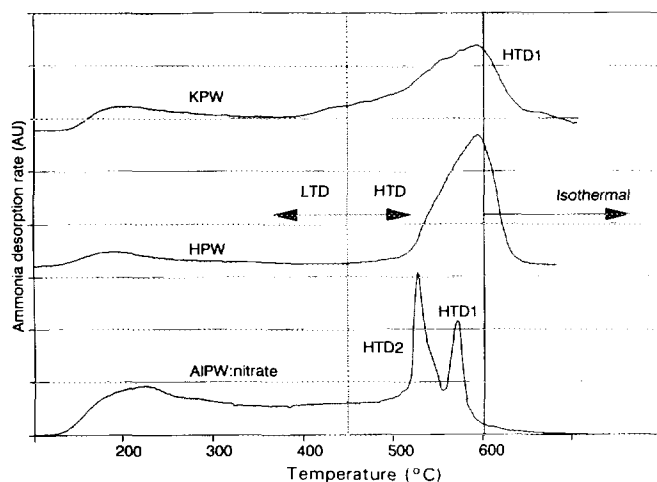


FIG. 6. NH_3 -TPD spectra of HPW, AIPW, and KPW.

the activity was far less than that of ZSM-5 at the same reaction conditions.

The butene isomerization results are given in Table 5. Both the Type A and B salts achieved similar conversion levels but their initial product selectivities differed. The Type A salts produced almost exclusively double bond shift products whereas the Type B salts initially produced reaction products typical of cracking and skeletal isomerization as well as double bond isomerization. As the reaction time increased the products became exclusively double bond isomerization products.

Table 6 shows the activities of the pure HPW and its salts calcined at 325°C for propene oligomerization. The activity is defined as fractional conversion (mass%) of propene to liquid product retained in the catchpot at 20°C.

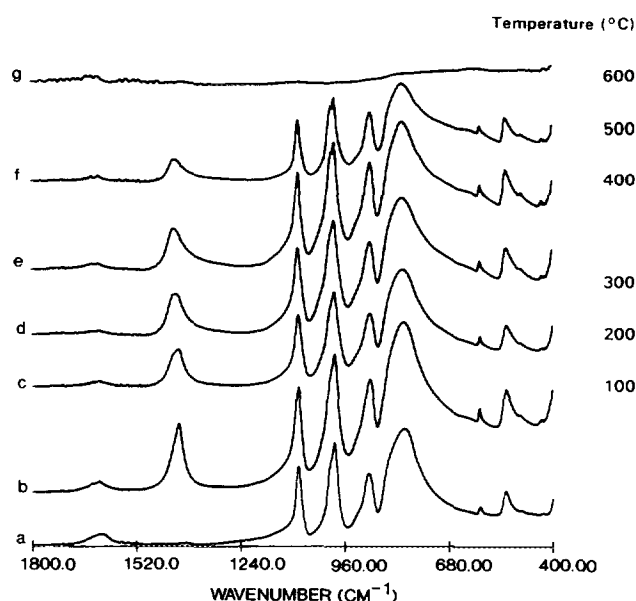


FIG. 7. FTIR spectra of (a) HPW calcined at 325°C and (b-g) HPW + NH_3 after being heated to 100, 200, 300, 400, 500, and 600°C.

HPMo, HSiW, and NH_4SiW had minimal activity when calcined at 325°C whereas AlSiW was active when calcined at this temperature. HPW and its corresponding salts were the most active. AIPW:nitrate(2) and AIPW:ether(5), which had surface areas of 2 and 5 m^2/g , respectively, had similar activities (Fig. 8). Recrystallizing AIPW:ether(5) in water increased the surface area to 9 m^2/g but surprisingly the oligomerization activity was more than halved. Similarly, the activity of the higher surface area AIPW:nitrate(12) more than halved. Simi-

TABLE 2
Ammonia TPD Data

Catalyst	LTD (°C)	HTD1 (°C)	HTD2 (°C)	LTD ^a (mmol/g)	HTD1 (mmol/g)	HTD2 (mmol/g)	Total (mmol/g)	P.Elec. ^b
HPW	170	598	—	0.20	0.92	—	1.12	2.20
NH_4PW	170	575	—	0.18	0.28	—	0.46	—
KPW	192	571	—	0.14	0.28	—	0.42	0.82
CuPW	252	568	—	0.63	1.01	—	1.64	1.90
CoPW	257	556	—	0.78	0.56	—	1.34	1.80
NiPW	230	585	—	0.35	0.45	—	0.80	1.80
CePW	193	581	564	0.51	0.20	0.31	1.02	1.10
FePW	194	583	541	0.63	0.51	0.43	1.57	1.80
AIPW:nitrate(2)	223	579	529	0.96	0.46	0.26	1.68	1.61
AIPW:nitrate(12)	283	578	534	0.80	0.53	0.26	1.59	1.61
AIPW:ether(5)	269	575	530	0.88	0.48	0.24	1.60	1.61
AIPW:ether/water(9)	260	575	528	0.83	0.54	0.27	1.64	1.61
HSiW	292	557	—	0.33	1.01	—	1.34	2.20

^a LTD (mmol/g) determined between 100 and 450°C.

^b Pauling electronegativity.

TABLE 3
Keggin Unit Bands of HPW Salts

IR Band (cm ⁻¹)	HPW	NH ₄ PW	KPW	CoPW	CuPW	NiPW	FePW	AIPW : nitrate
δO-P-O	595	596	596	595	595	594	595	594
νM-O-M(edge)	794	809	800	797	793	798	793	792
νM-O-M(corner)	892	891	891	892	893	892	891	892
νM=O	984	986	985	982	983	984	982	984
νP-O	1081	1081	1081	1081	1081	1081	1081	1081

larly, the activity of the higher surface area AIPW : nitrate(12) salt was also almost half that of the lower surface area AIPW : nitrate(2) salt.

Figure 9 illustrates that the moisture content (0.1 wt.% H₂O in feed) of the feed affected the oligomerization activity of low surface area AIPW : nitrate. In normal circumstances all oligomerization runs were completed as indicated in the experimental section, i.e., the feed was dried by passing over 3A molecular sieves. These were the "dry feed" conditions. When "wet feed" (no molecular sieves present) was used the conversion decreased by more than half compared to dry feed conversion. However, bypassing the molecular sieves after steady state dry feed conversion had been reached, and hence changing to wet feed conditions, resulted in a sudden increase in activity followed by a steady deactivation. Since the nitrate salts were crystallized out of water it does not appear that water caused the decrease in the activity of the AIPW : ether/water salt referred to above.

The effect of steam calcining the low surface area AIPW : nitrate(2) at 200°C, 70 mm Hg water pressure and a steam flow rate of 100 ml/min for 1 h after pretreating the catalyst at 325°C in nitrogen was also studied. The activity of this catalyst was between that of the dry and wet feed cases.

Calcining HPW and AIPW : nitrate(2) in nitrogen at 200°C or 425°C resulted in similar activities to those observed after calcination at 325°C. No activity was ob-

TABLE 4

Ratio of $A_{(1420)}/A_{(1080)}$ versus Temperature for HPW, NH₄PW, KPW, CoPW, and AIPW : Nitrate

Catalyst	Temperature (°C)					
	100	200	300	400	500	600
HPW	3.45	3.06	2.71	2.49	2.34	0.00
NH ₄ PW	2.82	2.60	2.50	2.27	2.27	0.00
KPW	0.69	0.57	0.52	0.42	0.24	0.09
CoPW	3.00	2.46	2.46	1.53	0.93	0.00
AIPW : nitrate	1.59	1.53	1.35	0.87	0.86	0.00

served when HSiW was calcined in nitrogen at 325 or 425°C. However, the activity of HSiW, when calcined at 200°C, was far greater than that of HPW calcined in the range 200–425°C (see Fig. 11). Calcining AIPW : nitrate(2) in air, as opposed to nitrogen, at 325°C resulted in similar conversion levels.

Propene Oligomerization over Catalysts Diluted with Sand

As propene oligomerization is an exothermic reaction, sand was added to dilute the bed and reduce the possibility of temperature runaways and hot spots, which are most likely to occur during the startup phase. Sand dilution resulted in a dramatic increase in lifetime and activity as can be seen from Fig. 10. This illustrated the need to

TABLE 5

1-Butene Isomerization over HPW, AIPW : Nitrate, and KPW
($T_{\text{reaction}} = 225^\circ\text{C}$, $P = 101 \text{ kPa}$, $\text{GHSV} = 10,800 \text{ h}^{-1}$)

Catalyst	HPW		AIPW : nitrate		KPW	
	A		A		B	
Type	A		A		B	
Run Time (min)	3	30	3	30	3	30
Product	mass %		mass %		mass %	
Methane	0.00	0.00	0.00	0.01	0.05	0.00
Ethane	0.00	0.00	0.00	0.00	0.74	0.00
Ethene	0.08	0.03	0.09	0.00	0.26	0.03
Propane	0.33	0.08	0.24	0.06	11.69	0.28
Propene	0.71	0.64	0.75	0.58	4.27	0.61
1-Butene	14.24	14.79	14.55	16.57	12.64	17.35
trans-C4	53.21	54.45	52.61	52.82	41.98	52.88
cis-C4	31.42	30.02	31.77	29.97	26.35	28.85
iso-C4	0.00	0.00	0.00	0.00	2.03	0.00
Conversion(%)	85.76	85.21	85.45	83.43	87.36	82.65
C/T	0.59	0.55	0.60	0.57	0.63	0.55
DBS	98.69	99.12	98.75	99.23	78.21	98.88
Cracking	1.31	0.88	1.26	0.77	19.47	1.12
SI	0.00	0.00	0.00	0.00	2.32	0.00

Note. C/T, ratio of cis-but-2-ene to trans-but-2-ene; DBS, selectivity to double bond shift products; cracking, selectivity to cracking products; SI, selectivity to skeletal isomerization products.

TABLE 6

Propene Oligomerization over HPA Catalysts ($T_{\text{calcination}} = 325^{\circ}\text{C}$, $T_{\text{reaction}} = 220\text{--}230^{\circ}\text{C}$, $P = 5\text{ MPa}$, $\text{WHSV} = 12\text{ h}^{-1}$)

Catalyst	Initial % conversion ^a	$\frac{1}{2}$ life (h) ^b	Trend ^c	Run length (h)	Maximum % conversion	Steady state % conversion	Coke (wt.%)	H/S Coke ^d	C_{12}^+ (wt.%) ^e
HPW	17	4	d	4	17	—	8	0.05	68
NH4PW	22	—	n	6	22	21	9	0.15	44
KPW	11	3	d	5	11	—	7	0.08	55
CuPW	15	6	d	3	15	—	17	0.13	41
CoPW	28	—	n	6	26	22	17	0.13	41
NiPW	35	—	n	6	35	20	10	0.00	41
NiHPW	24	—	n	6	24	20	13	0.38	44
FePW	11	—	n	6	11	10	20	0.01	56
CePW	9	—	n	3	9	7	—	—	51
AIPW : nitrate(2) ^f	42	—	n	33	90	87	42	0.16	36
AIPW : nitrate(12)	35	—	n	6	40	40	30	0.30	41
AIPW : ether(5)	34	—	n	8	75	75	36	0.25	37
AIPW : ether/water(9)	24	—	n	6	45	35	29	0.31	40
HPW on alumina	26	—	n	6	26	20	—	—	47
HSiW	40	—	n	25	40	25	—	—	47
AlSiW : ether	17	—	n	2	23	23	—	—	36
HsiW on alumina	10	—	n	7	40	40	—	—	36

^a Conversion of propene to liquid product after 1 h.^b Time to $\frac{1}{2}$ maximum conversion; no value indicates no loss of activity during time on stream.^c Indicates whether catalyst was deactivating(d) or not(n).^d H/S represents hard coke to soft coke ratio as determined by TG-DTA.^e Determined from GC analysis of liquid product.^f Value in parentheses is surface area of salts in m^2/g .

operate the catalysts isothermally. The catalyst utilization values, or yield trends, for the sand-diluted catalysts, however, followed the same activity trends for the pure powder results, viz. AIPW : nitrate(2) > CuPW > FePW.

Coke Analysis

TG-DTA of the ex-reactor catalysts showed that the mass% coke deposited on the catalysts increased with increasing run time. The majority of the coke was "soft"

coke and the amount of "hard" coke also increased with increasing run time. In the interpretation of this data it was noted that further polymerization of the olefinic species adsorbed on the HPA may have occurred during the TG-DTA coke analysis procedure, especially given the strongly acidic nature of these catalysts.

FTIR showed that when the reactor was operated non-isothermally the Type A salts produced mainly Type I

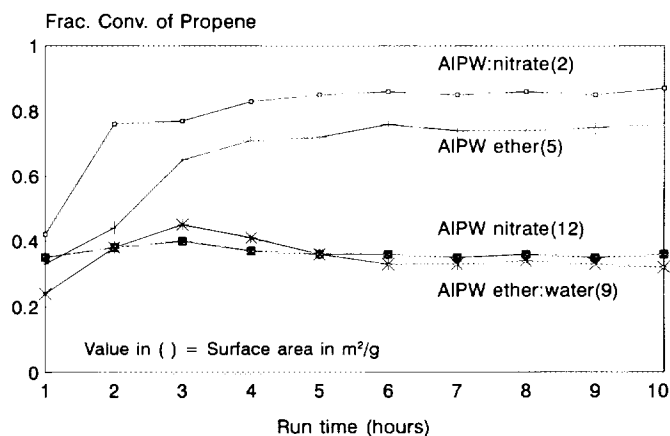


FIG. 8. The effect of surface area on the oligomerization activity of the AIPW : nitrate salts.

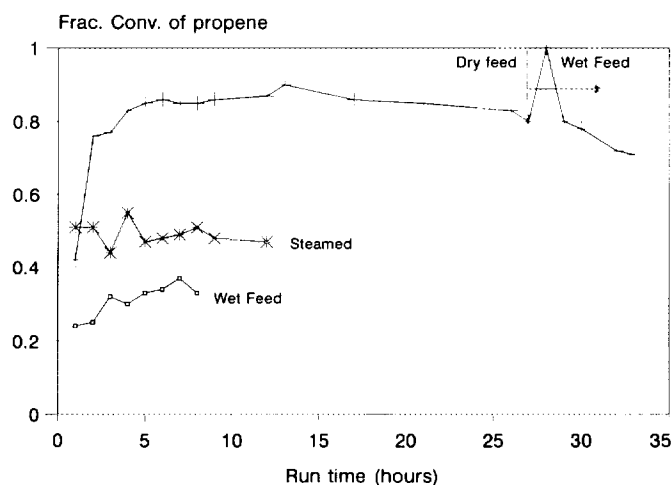


FIG. 9. The effect of water in the SASOL feed and steaming AIPW : nitrate(2) on its oligomerization activity.

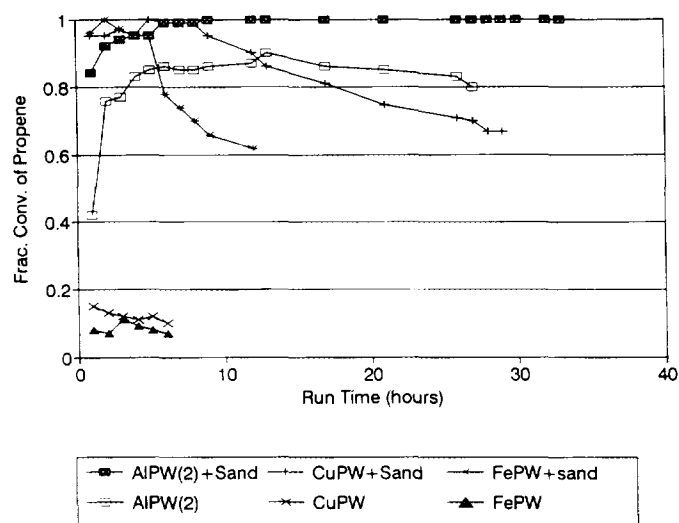


FIG. 10. The effect of sand dilution on the propene oligomerization activity of AIPW, CuPW, and FePW.

coke was well as Type II coke. As the run time was increased or when the catalysts began to deactivate, the amount of Type II coke present increased. In those cases where isothermal conditions were used Type I coke was formed selectively and after long run times or when the catalyst deactivated Type II coke was formed. The Type B salts produced both Type I and II irrespective of the run time.

Effect of α -Alumina Support

The effect of supporting HPW and HSiW on α -alumina is illustrated in Fig. 11. HPW and HSiW supported on α -alumina (25 wt.% HPA) had increased activities and lifetimes compared to their pure acid forms. Supported HSiW was more active than HPW on α -alumina. However, if the catalysts were stored for some time (three

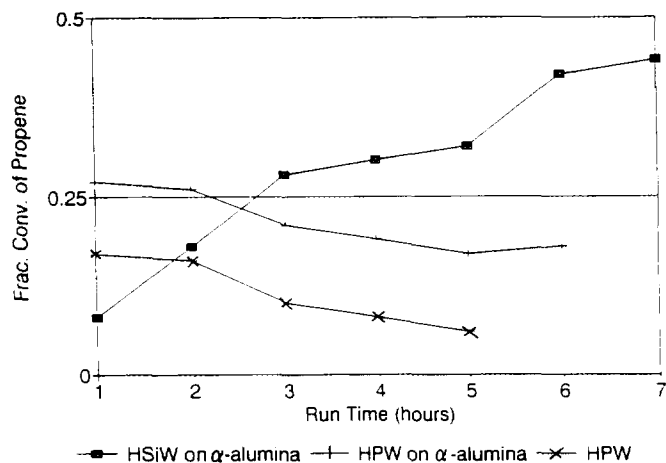


FIG. 11. The effect of α -alumina support on the propene oligomerization activity of HPW and HSiW ($T_{\text{calcination}} = 325^{\circ}\text{C}$).

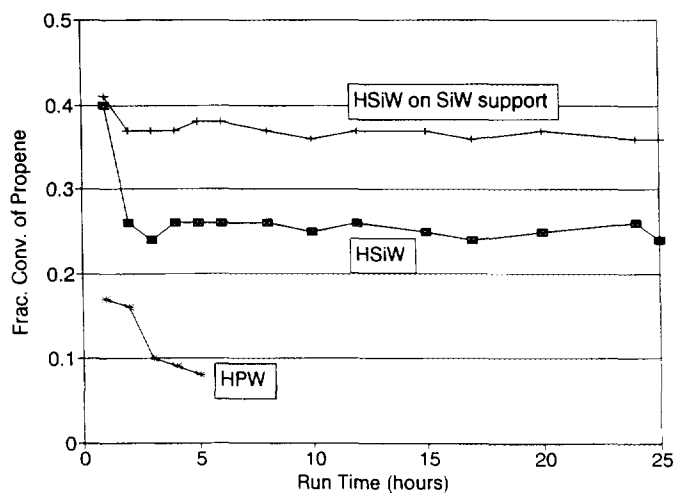


FIG. 12. The effect of a silico-tungsten support on the propene oligomerization activity of HSiW ($T_{\text{calcination}} = 200^{\circ}\text{C}$).

months) and then tested again the activity of supported HPW was significantly lower than when the catalyst was freshly prepared. Supported HSiW was not affected by storage time as much as HPW. This type of loss of activity through aging has previously been reported for HPAs supported on α -alumina (29). HSiW supported on silico-tungsten, prepared according to the procedure of Ratnasamy and Sivasanker (50), resulted in the conversion remaining constant at the initial level, whereas HSiW deactivated to a lower level before achieving steady state conversion (see Fig. 12).

Liquid Product Selectivity

Table 7 presents the GC analysis of the liquid products obtained from propene oligomerization. As selectivities can only be properly compared at similar conversion levels only limited conclusions can be made about possible shape selective effects over these different heteropoly acids. This was especially the case for this study as not only are the conversions quite dissimilar but some of the products of oligomerization do not condense out at 20°C and would thus exist in the vapour phase (up to 10 to 15 wt.% of C_6 was present in the vapour phase). Thus the salts which had very low conversion levels appeared to have liquid products with high C_{12}^+ selectivity when in actual fact a large proportion of the lighter products exited in the vapour phase. From Fig. 13 it can be seen that the C_{12}^+ yield as opposed to selectivity is a function of conversion and not type of counteraction. In all cases the trimer was the dominant oligomer present in the liquid product. The sand-diluted catalysts had similar C_{12}^+ product selectivities in the region of 40 to 43.7 wt.%.

The HPAs supported on α -alumina had liquid products with lower C_{12}^+ selectivity values compared to their respective unsupported pure acids, probably due to the differ-

TABLE 7
Liquid Product Selectivity and Cetane Number Data from Propene Oligomerization

Catalyst		HPW	NH ₄ PW	KPW	CoPW	CuPW	AIPW : nitrate(2)	AIPW : ether(5)	FePW	CePW
Dimer	C ₆ -C ₈	7.2	19.2	10.5	19.5	9.5	25.9	21.8	8.7	9.0
Trimer	C ₉ -C ₁₁	25.0	36.7	34.5	39.9	38.1	37.8	40.6	34.4	39.7
Tetramer	C ₁₂ -C ₁₄	24.2	21.6	27.1	22.8	24.5	19.5	19.9	25.1	24.2
Pentamer	C ₁₅ -C ₁₇	22.1	13.1	15.7	11.0	15.4	9.8	10.0	16.3	14.2
Hexamer	C ₁₈ -C ₂₀	12.7	5.6	7.6	4.5	7.7	4.3	4.5	9.1	7.3
C ₂₁ ⁺		8.8	3.8	4.6	2.4	4.8	2.8	3.2	6.4	5.5
C ₁₂ ⁺		67.8	44.1	55.0	40.6	40.6	36.3	37.6	56.9	51.3
Cetane no.		26.0	22.0	—	—	—	38.4	36.0	38.0	—

Catalyst		HSiW	AlSiW	HPW α-alumina	HSiW α-alumina	HSiW/ SiW	AIPW + sand	CuPW + sand	FePW + sand
Dimer	C ₆ -C ₈	19.0	25.4	12.2	17.4	17.4	11.9	10.0	14.0
Trimer	C ₉ -C ₁₁	34.3	38.6	40.6	46.3	34.6	42.7	39.3	40.0
Tetramer	C ₁₂ -C ₁₄	21.1	17.8	22.7	22.1	22.4	25.0	23.4	24.6
Pentamer	C ₁₅ -C ₁₇	13.5	10.7	12.7	9.1	14.1	13.3	12.6	13.0
Hexamer	C ₁₈ -C ₂₀	6.9	4.4	7.4	3.3	6.8	2.9	5.4	2.3
C ₂₁ ⁺		5.2	3.0	4.3	1.8	4.6	0.2	2.2	0.1
C ₁₂ ⁺		46.8	36.0	47.2	36.2	47.9	41.4	43.7	40.0
Cetane no.		31.6	—	35.8	39.9	37.0	37.0	32.6	36.6

ence in activities. They did, however, have high C₁₂⁺ yields. For HSiW on a silico-tungsten support, however, the C₁₂⁺ selectivity was similar to that of HSiW even through their respective conversions were dissimilar.

Cetane Number

Cetane numbers were calculated using an empirical correlation (54). Table 7 lists the cetane numbers of the whole liquid product fraction. The cetane number error margin has been estimated to be ±1.5 cetane units. AIPW : nitrate(2) liquid product fractionated at 180°C yielded a

slightly higher cetane number (41) than that of the cetane number of whole liquid product fraction (37) and thus the cetane numbers of the distillate fractions of the liquid products are likely to be about 4 numbers higher than the values given in Table 7.

DISCUSSION

The surface area results were similar to those reported by other workers (4, 6, 13, 14, 23). The NH₄PW salt had a lower surface area than that reported by Hayashi and Moffat (14) but was similar to that reported for NH₄PMo by Akimoto *et al.* (23). The higher surface areas of the Type B salts may be due to their smaller crystallite size (4). The electron micrographs showed clearly that the Type B crystallites were much smaller than the Type A crystallites and hence an increase in their surface areas would be expected. The higher surface areas of NH₄PW and other Type B salts may also be a result of the microporosity of these salts (7, 24-27). These micropores are not uniform as in zeolites, being between 8 and 13 Å in diameter.

The TG-DTA results were consistent with those previously reported and confirmed the validity of the synthesis procedures (3, 53). At higher calcination temperatures it is known that the XRD peaks become broader and less intense due to loss of crystallinity (10, 19) and this was shown for HPW after calcination at 325°C (Fig. 3). Since the XRD spectrum of the Type B salts did not change

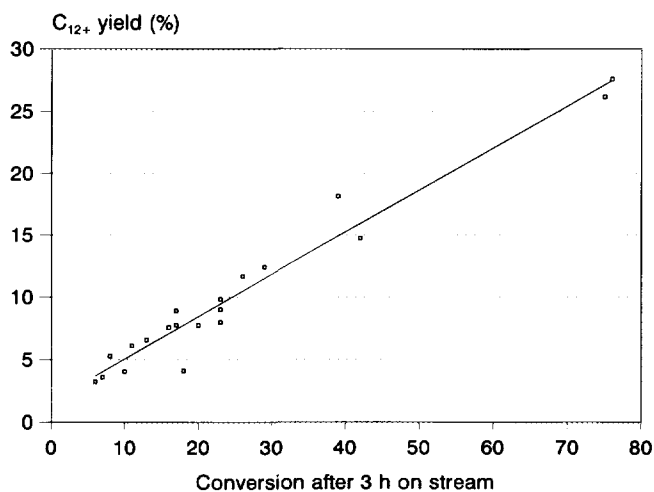


FIG. 13. C₁₂⁺ versus conversion of propene over HPA catalysts.

significantly on heating to 325°C it can be concluded that the secondary structure is thermally stable. This different thermal stability of the secondary structure of Type A and Type B salts has been reported elsewhere (4, 6, 18, 19, 34, 35, 39). In both instances, however, the primary Keggin structure remains intact at temperatures below 400°C as was evident from FTIR data for Type A salts in particular, which showed that the Keggin ion bands remained essentially unchanged (4, 18, 19, 31).

Since ammonia and other oxygen- and nitrogen-containing polar molecules are readily adsorbed into the bulk of the HPA (4, 6, 14, 18, 55–57), the ammonia TPD results are representative of the bulk as well as surface acidity. The broad LTD peak between 120 and 300°C implies that there is some weak acidity present. As can be seen from Tables 1 and 2 the HTD1 peak positions of the HPAs corresponded to within 15°C of their respective exotherms from TG–DTA. This peak is most probably due to the release of ammonia when the salt decomposes as infrared spectra of the catalysts after TPD showed that the Keggin ion bands had disappeared. The HTD2 peaks are associated with the structural decomposition.

It was clear that for both the Type A and B salts, adsorbed ammonia was held at temperatures as high as 600°C and was released only when the salts decomposed. This suggested that there were strong acid sites present. The presence of strong acid sites has been confirmed by Nowinska (58), who has shown that NH_4PW is capable of cracking cumene and of toluene disproportionation at low temperatures. Both these reactions require strong acid sites (58). As nonpolar molecules such as butane, butene, and propene are not adsorbed into the bulk of the HPA, reactions of these molecules are regarded as surface-type reactions (4) and can therefore be used to probe the surface acidity of HPAs. It was apparent from the butane cracking and butene isomerization results in this present study that few or no strong acid sites existed on the surface of the Type A salts since none of the products observed is associated with reactions on strong acid sites. The presence of a small but measurable amount of coke (<1 wt.% on the catalysts after butane cracking did indicate, however, that some reaction had occurred, but any strong acid sites on the surface must have been rapidly deactivated due to this coke formation. Thus the majority of the strong acid sites observed from ammonia TPD of the Type A salts were probably located within the bulk of the salts and were not accessible to the nonpolar hydrocarbons. There were, however, acid sites present on the surface of the Type HPAs which were capable of forming products typical of the double bond shift reaction of butene (59).

The Type B salts, which had similar butene isomerization conversion levels to the Type A salts (85%), were able to crack butane and butene, thus indicating that the

Type B salts had stronger acid sites present on the surface than the Type A salts. When butane was passed over the Type B catalysts the cracking and skeletal isomerization products decreased after 30 min on stream. As these two reactions both require strong acid sites (59) such sites may be deactivated quite rapidly due to coke formation, with the remaining weak acid sites only being capable of producing the *cis*- and *trans*-isomers. Baba *et al.* (60) have reported a similar deactivation behaviour for *o*-xylene conversion over Type A AIPW salts with the amount of disproportionation products decreasing to zero after 3.5 h on stream.

From the cracking and isomerization data it was clear that the ammonia TPD results were not a good indication of the surface acidity and there were no clear correlations between the ammonia TPD results and the propene oligomerization results. Type B salts, which butane cracking experiments had shown to have strong acid sites, had low propene oligomerization activities. It is of course possible that, as in the case of butene isomerization, the strong acid sites deactivated during propene oligomerization due to rapid coke formation.

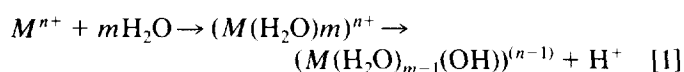
The poor oligomerization activity of the two samples which had much greater surface areas than the others, viz. NH_4PW and KPW , is difficult to explain. Compared to AIPW the former two salts had less acidity as measured by TPD. They did, however, show indications of greater acid strength in their ability to crack butane and skeletally isomerize butene, and have been shown to be able to crack cumene (58). In the propene oligomerization runs, the coke-forming capacity of all the catalyst seemed to be related only to conversion and lifetime, and in all cases the coke consisted largely of high boiling point hydrocarbons or "soft" coke. Because of the poor performance of the two high surface area catalysts no in-depth study was made of their post-reaction characteristics and hence it is only possible to speculate that their apparent poor performance for propene oligomerization is due to the site poisoning caused by carbonaceous species formed on those sites which are capable of skeletal isomerization of butene. Dilution of the catalyst with sand proved to be advantageous to the lifetime and this is discussed below.

By far the most active of the catalysts was the AIPW : nitrate(2) salt and as a result this salt was studied in more detail to determine the possible reasons for its greater activity. AIPW has also been shown to be more active than HPW and CuPW for *o*-xylene isomerization (60), and of the metal salts of HPW it produced the greatest yield of C_4 hydrocarbons for the MTO reaction (13). Several batches of AIPW were synthesized and depending on the synthesis route and crystallization time the surface areas ranged between 2 and 12 m^2/g . Previous workers have also synthesized salts with different surface areas by varying the amount of counteraction (61). Surprisingly

the activity of the AIPW salts decreased as the surface areas increased (see Fig. 8). AIPW : nitrate(2) was as active for propene oligomerization as the zeolite ZSM-5, which has an appreciably higher surface area. The turnover numbers of propene per Keggin ion on the surface for the AIPW : nitrate(2) salt were approximately 2 orders of magnitude higher than those calculated per acid site of ZSM-5. As oligomerization is an exothermic reaction it was suspected that there may be difficulties in transferring the heat from such a low surface area catalyst to the bulk. During start-up the bed temperature of the higher surface area AIPW : nitrate(12) rose faster than that of the lower surface area AIPW : nitrate(2). At no time, however, did the bed temperature increase in such a way as to indicate that temperature runaway conditions were present.

The catalyst bed was diluted with sand to act as a heat sink and to essentially eliminate temperature runaways or the formation of hot spots which have been known to be responsible for the formation of hard coke and subsequent deactivation of catalysts (47). The results shown in Fig. 10 illustrated that sand-diluted AIPW : nitrate(12) was as active as the sand-diluted AIPW : nitrate(2). The increase in activity of both salts when diluted with sand compared to their pure catalyst forms indicated clearly that there was poor heat transfer in the undiluted bed. It is thus clear that, when evaluating the catalytic activity of HPA catalysts, extreme care needs to be taken to maintain strictly isothermal conditions in the reactor. In order to determine the true catalytic activity of the salts the CUVs of the sand diluted catalysts were compared and for AIPW, CuPW and FePW they followed the trends obtained when they were undiluted, i.e., AIPW \gg CuPW $>$ FePW.

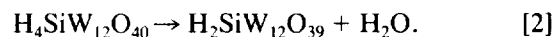
Water plays an essential role in the generation of Brønsted acidity in the metal salts of HPAs (32, 53, 60) and the generation of acid sites has been proposed as follows:



Brønsted acid sites have been shown to form when AIPW was steamed (53, 60, 62, 63) and these sites were responsible for an increase in *o*-xylene isomerization activity. Water pulsed with the *o*-xylene feed also enhanced the activity of AIPW for isomerization. For propene oligomerization steaming AIPW : nitrate(2) halved its activity. Steaming sand-diluted AIPW : nitrate(2), however, resulted in no activity loss with the catalyst remaining active for 150 h without any sign of deactivation. But by comparing this result with the pure catalyst data it seems that steaming may have enhanced the acidity, resulting in a rapid loss in activity of the steamed pure AIPW : nitrate(2) salt due to rapid coke formation because of the strong acid sites present.

The presence of water in the hydrocarbon feed mixture, either at the start of a run, or by introduction during a run, had a detrimental effect on the activity of the undiluted AIPW : nitrate(2) catalyst. The sudden increase in activity of the undiluted AIPW : nitrate(2) when the feed conditions were changed to "wet" (Fig. 9) may have been due to water interacting with aluminium to produce stronger acid sites as described above. This resulted in the sudden but temporary increase in activity since these strong acid sites deactivated due to coke formation. However, in the case of sand-diluted catalysts when wet feed was used, or the feed was changed to wet conditions during the run, there were no losses in activity.

Water plays an important role in determining the acidity of HPAs, and several studies have concentrated on determining the relationship between water loss and acidity by looking at the effect of increasing the calcination temperature (12, 32). For butene isomerization, a surface-type reaction for HPAs, increasing the calcination temperature of the catalyst did not increase the conversion but did affect the *cis-trans-isomer* ratios (32). Hayashi and Moffat (12) have shown that the yields of hydrocarbons were strongly dependent on the calcination temperatures of HPW for MTO, with the highest yields being observed after calcination at 350°C (12). The conversion of methanol remained quite similar, however, for all the catalysts. Calcining at temperatures higher than 400°C resulted in lower activities and yields, most probably due to loss of protons from HPW, via Eq. [1]. The activity of AIPW : nitrate(2) or HPW was unchanged when calcined at 200, 325, or 425°C, and hence it is unlikely that, within these temperature ranges, the strength or numbers of their acid sites changed significantly. As expected (46–50) HSiW was certainly affected by the amount of water present, as its oligomerization activity decreased markedly as the calcination temperature increased. As HSiW is thermally less stable than HPW, calcination at 325°C may have caused partial decomposition of the catalyst, resulting in lower activity due to the loss of protons:



Increasing the surface area available for reaction by supporting the HPA catalysts on suitable high surface area supports should result in increased activity for surface-type reactions (4, 64). The thermal stability of HPA catalysts has also been reported to increase (21), as well as decrease (4, 43, 44) when the catalyst is supported. The role of the support is often quite complex and the activity of the supported HPA is dependent not only on the type of support but also on the extent of loading (64). In our case the loadings were kept constant at 25 wt.%, and supported HSiW, when calcined at 325°C, was active for propene oligomerization. This activity may be due

to increased thermal stability compared to unsupported HSiW which was inactive when calcined at 325°C. The activity may also be due to the presence of an aluminated SiW phase on the surface of the α -alumina (64) since AlSiW was active when calcined at 325°C. However one cannot exclude the possibility that the increased activity may also be due to a dilution effect of the support phase.

Since it has been observed that HPAs are degraded by the presence of any basic residual material on the alumina support (29), the less acidic nature of HSiW compared to HPW may be advantageous as the extent of degradation due to any basic material present on the α -alumina would be less pronounced. This may account for the activity of α -alumina supported HSiW being greater than that of α -alumina supported HPW.

The HPAs did not have any intrinsic selectivity properties as they all produced the trimer as the major oligomer group and, as seen in Fig. 12, it was evident that the higher the conversion the greater the yield of heavier products. There were, however, quite large differences in the values of the cetane numbers of the liquid products obtained using pure powders. This suggested that the counteraction may be responsible for changes in linearity of the product. The low cetane number of the liquid product using NH_4PW may be a result of this catalyst's ability to skeletally isomerize olefins as was evident from the butene isomerization results, thus increasing the degree of branching of the liquid product. The Type A salts on the other hand are unlikely to produce skeletal isomers as they only showed double bond shift activity for butene isomerization, and hence they would be expected to yield more linear product than the Type B salts. Analysis of the liquid products using sand-diluted Type A catalysts indicated that they all had identical amounts of C_{12}^+ , and therefore the counteraction did not appear to affect the product selectivity of these catalysts.

CONCLUSIONS

Consistent with the findings of other characterization studies it has been shown that heteropoly compounds could be divided into two types characterized by low surface areas and multiple endothermic mass losses and high surface areas and a single endothermic mass loss, respectively. Ammonia TPD results of the HPAs indicated the amount of bulk acidity but gave no information about the amount or type of surface acidity and hence no correlations were found between the TPD results and the hydrocarbon reaction activities. Butane cracking and butene isomerization indicated that strong acid sites were present on the surface of the Type B HPAs but these catalysts were not as active for propene oligomerization as the Type A salts which had few if any strong acid sites on the surface.

Diluting the catalysts in a 1 : 10 mixture of sand greatly improved the CUV most probably due to increased heat transfer and consequently near-isothermal bed conditions. This reduced the formation of hot spots and temperature runaways which causes decreased activity levels due to the formation of "hard coke." The aluminium salt of HPW was the best oligomerization catalyst as it had high activity and produced an acceptable quality distillate fuel. The activity of pure powder AIPW : nitrate was sensitive to water present in the feed as well as steaming. The loss in activity of the pure catalysts upon steaming or with the introduction of water in the feed was due to the formation of hot spots as a result of increased activity and subsequent deactivation due to hard coke formation. This indicates that steamed sand-diluted AIPW : nitrate may have even greater activity than sand-diluted AIPW : nitrate. The CUV of sand-diluted AIPW : nitrate(2) salt is greater than that of ZSM-5 (52), a widely used catalyst for the oligomerization of propene. However, the liquid product obtained when using sand-diluted AIPW : nitrate(2) has less C_{12}^+ than that of ZSM-5, most probably due to the lack of shape selectivity of the HPA catalysts.

Calcination temperature plays an important role in determining the activity of the HSiW for propene oligomerization, with calcination at temperatures higher than 200°C resulting in no activity for oligomerization. Calcining in the range 200–425°C did not affect the activity of HPW and its salts for propene oligomerization as a result of its higher thermal stability compared to HSiW. The high activity of HSiW on the α -alumina support even when calcined at 325°C suggests favourable support interactions and the activity increase is most probably due to the formation of an active AlSiW phase.

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