

Dehydration of 2-Methylbutanal and Methyl Isopropyl Ketone to Isoprene Using Boron and Aluminium Phosphate Catalysts

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The synthesis of isoprene from the dehydration of 2-methylbutanal is described using boron phosphate, aluminium phosphate, and mixed boron/aluminium phosphates as catalysts. Both boron phosphate and aluminium phosphate deactivate steadily with reaction time due to loss of catalyst activity but the selectivity to isoprene is not significantly affected by catalyst deactivation. Catalyst deactivation is shown to be due to two factors: (i) loss of surface phosphorus and (ii) coke formation. Reactivation of the catalysts at temperatures up to 500°C in an air atmosphere does not successfully restore the catalyst activity, although this procedure does remove all the coke. It is shown that high-temperature calcination (800°C) removes both the surface carbon and restores the surface phosphorus content, and hence this procedure is a necessary prerequisite for the successful reactivation of boron and aluminium phosphate as a catalyst for 2-methylbutanal dehydration. Two samples of aluminium phosphate were studied, prepared from the reaction of phosphoric acid with aluminium chloride or sulfate. The chloride route gives a mixed cristabolite/tridymite AlPO_4 and this is shown to be more active than a catalyst containing only the tridymite form of AlPO_4 formed from the sulfate route. However, both are less active than BPO_4 which can be readily prepared in the cristabolite structure. Mixed B/ AlPO_4 catalysts (Al : B mol ratio = 1 : 0.05 and 1 : 0.1) have also been investigated and these are shown to have a superior catalytic performance when compared with undoped AlPO_4 . ³¹P, ²⁷Al, and ¹¹B MAS NMR spectroscopy shows that B and Al are in the same lattice in these mixed phosphate catalysts. Addition of Nb is shown to stabilize the catalytic performance. The BPO_4 and AlPO_4 catalysts are also shown to be active catalysts for the synthesis of isoprene from methyl isopropyl ketone, which is the major by-product formed from the reaction of 2-methylbutanal. It is suggested that a process for the synthesis of isoprene based on the dehydration of 2-methylbutanal would involve the recycle and conversion of the by-products. The mechanism of the reaction is discussed and it is proposed that 2-methyl-but-2-en-1-ol is an intermediate central to the formation of the two major products of the dehydration reaction: isoprene and methyl isopropyl ketone.

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INTRODUCTION

Isoprene is a key intermediate and the process for the stereoselective polymerization to form 1,4-*cis*-polyisoprene is of major importance. This led to isoprene becoming a strategically important monomer for the production of substitutes for natural rubber. In view of this research interest continues to be given to identifying new catalytic routes for isoprene production. To date, however, most isoprene is produced by the extraction of pyrolysis fractions that result from naphtha cracking. The current low prices being realised for crude oil will enable this process to persist but there has always been significant interest in the identification of alternative synthetic routes. The identification of an alkene carbonylation route to 2-methylbutanal (1) has led to an interesting alternative synthesis strategy to isoprene, namely, the catalytic dehydration of 2-methylbutanal. However, this synthetic route is not new and has been known since 1911 when Kiselev *et al.* (2) and Kyriakides (3–5) demonstrated that aluminium silicate, TiO_2 , and SiO_2 were effective catalysts. Subsequently, Fischer and Schunchel (6) showed that boron phosphate was more active than the earlier oxide catalysts.

A major problem with boron phosphate concerned the rapid deactivation that is observed and many attempts were made to overcome this; however, these methods were of limited success (7–10). We have recently shown (11) that the deactivation of boron phosphate is due to the simultaneous loss of surface phosphorus and coke deposition, and that the catalysts can be successfully reactivated many times using a simple calcination procedure. Alternatives to boron phosphate have also been studied and polymer-supported mercuric phosphates (12, 13), ammonium aluminium sulfate (14), and magnesium ammonium phosphate (15) have all been shown to be active catalysts.

Alternative catalysts were investigated for this reaction, particularly during a period of increased prices for crude

oil. Zeolites and other microporous materials have been investigated (16–21). In particular, the use of microporous AlPO materials demonstrated poor activity together with rapid deactivation caused by the collapse of the microporous structure as a result of exposure to water vapour, a product of the reaction, at elevated temperatures. There have been few studies of phosphate catalysts for the dehydration of aldehydes, but the dehydration of alcohols has been investigated. Haber and Szybalska (22) have compared boron phosphate and aluminium phosphate catalysts for ethanol dehydration and showed that similar ethene yields could be obtained. Furthermore, the catalytic properties of aluminium phosphate are known to be significantly affected by the preparation method. Campelo *et al.* (23) have shown that the AlPO₄ phase that is prepared can be controlled by the selection of an appropriate aluminium salt.

In this paper we present detailed results for the use of BPO₄ and AlPO₄ as catalysts for the dehydration of 2-methylbutanal and show that these catalysts can give high yields of isoprene.

EXPERIMENTAL

Catalyst Preparation

Boron phosphate. Boron phosphate with P/B = 1.0 was prepared according to the following procedure. Phosphoric acid (93 ml, 85%) was heated with stirring at 60°C and boric acid (100 g) was added and the mixture refluxed for 1 h. Water (100 ml, deionised) was then added, the mixture refluxed for a further 5 h, and the slurry then dried (110°C, 16 h) and calcined (350°C, 4 h). The boron phosphate was characterised using x-ray fluorescence spectroscopy to confirm that P/B = 1.0. X-ray diffraction showed that the boron phosphate was well crystalline and possessed the cristabolite structure, and the surface area was determined to be 25 m² g⁻¹.

Aluminium phosphate. Two samples of aluminium phosphate were prepared using the precipitation method of Campelo *et al.* (23). The first was prepared by the slow addition of aqueous ammonia (40 vol%, 5°C), with continuous stirring, to an aqueous solution containing equimolar quantities of aluminium chloride and *o*-phosphoric acid (0.985 mol/L, 5°C). The aqueous ammonia addition was continued until a pH of 7.0 was attained. The white precipitate was aged (18 h, 20°C) and collected by filtration, washed several times with propan-2-ol, and dried (24 h, 120°C). The solid was screened (200–250 mesh), calcined (3 h, 800°C), and pelleted and sieved (600–1000 μm). This catalyst is denoted as AlPO₄-Cl. Powder x-ray diffraction showed that the catalyst was a mixture of the cristabolite and tridymite phases of AlPO₄, and the surface area was determined to be 93 m² g⁻¹.

The second sample was prepared using the same procedure except the aluminium source was aluminium sulfate. This sample was denoted AlPO₄-S. Powder x-ray diffraction showed that the catalyst comprised only the tridymite phase of AlPO₄, and the surface area was determined to be 50 m² g⁻¹.

Mixed boron/aluminium phosphate. Boron phosphate, prepared as described above, calcined at 350°C was added to an aqueous solution containing equimolar quantities of aluminium chloride and *o*-phosphoric acid (0.985 mol/L, 5°C). Aqueous ammonia (40%) was added with stirring until a pH of 7.0 was attained. The white precipitate was aged (15 h, 20°C) and collected by filtration, washed several times with propan-2-ol, and dried (16 h, 120°C). The solid was screened (200–250 mesh), calcined in static air in three portions for 3 h at 350, 500, and 800°C. The calcined materials were pelleted and sieved (600–1000 μm) for use in the catalytic tests. Two B/Al molar ratios were prepared using this methodology (B : Al = 0.05 : 0.95 and 0.10 : 0.90).

Niobium-doped mixed boron/aluminium phosphate. Niobium oxide (1.0 g) and boron phosphate (1.0 g), prepared as described above, calcined at 350°C was added to an aqueous solution containing aluminium chloride (23.4 g) and *o*-phosphoric acid (10 ml, 85%). Aqueous ammonia (40%) was added with stirring until a pH of 7.0 was attained. The white precipitate was aged (16 h, 20°C) and collected by filtration, washed several times with propan-2-ol, and dried (16 h, 120°C). The solid was screened (200–250 mesh) and calcined in static air for 3 h at 350 and 500°C. The calcined materials were pelleted and sieved (600–1000 μm) for use in the catalytic tests.

Preparation of 2-Methyl-2-buten-1-ol

Sodium borohydride (1.5 g, 10 ml) and tiglylaldehyde (10 g, 38 ml) were mixed at 0°C and then refluxed for 30 min. Following the removal of half of the methanol solvent, the pH was adjusted to 3.0 with aqueous HCl (37%) and water (100 ml) was added. The solution was extracted with ether and the extracts were washed with aqueous potassium carbonate and distilled to produce the alcohol.

Catalyst Testing

The catalysts were tested for the dehydration of 2-methylbutanal using a fixed bed microreactor. 2-Methylbutanal was fed via a syringe pump to a vaporiser at a controlled flow rate (0.2 ml/h) together with N₂ (1.44 L/h) as the carrier gas. The resultant 2-methylbutanal/N₂ was fed to the catalyst (0.3 g) contained in a fused quartz reactor tube. All reactor tubing before and after the reactor was constructed in stainless steel and was heated to ensure that no condensation of reactant or products occurred. The

reactor effluent gases were analysed using on-line gas chromatography. In the absence of a catalyst no thermal dehydration of 2-methylbutanal was observed at the temperatures used in this study. Satisfactory carbon mass balances were obtained for all data presented.

RESULTS

Reaction of 2-Methylbutanal over Boron Phosphate

The dehydration of 2-methylbutanal over boron phosphate was investigated at 325°C and the effect of increased time on-line on the catalyst performance is shown in Fig. 1. The reaction was studied for about 800 min and initially the isoprene selectivity increased during the first 200 min to >80%. After this time the selectivity was unchanged and the major by-product was methyl isopropyl ketone. It was apparent that the conversion steadily declined with increased reaction time without any observed affect on the reaction selectivity. In addition, the by-product composition was the same throughout the test period.

2-Methylbutanal Dehydration Using AlPO_4

The dehydration of 2-methylbutanal was investigated using $\text{AlPO}_4\text{-Cl}$ at 325 and 400°C and the results are shown in Figs. 2 and 3. The initial conversion observed with $\text{AlPO}_4\text{-Cl}$ was ca. 90% but this steadily declined to ca. 75% after 500 min. The selectivity to isoprene was 70–80% throughout this testing period and the only by-product observed was methyl isopropyl ketone. Following the reaction the catalyst was analysed by powder x-ray diffraction and the structure was found to be unchanged by the reaction; however, the surface area had decreased to 30 m² g⁻¹. The catalyst was found to contain 5 mass% carbon after the reaction. In comparison, $\text{AlPO}_4\text{-S}$ was significantly less active and the initial conversion at these conditions was ca. 50% and the isoprene selectivity was 60%, and the only by-product

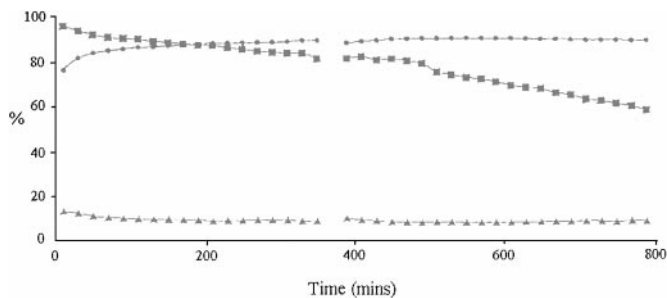


FIG. 1. Reaction of 2-methylbutanal over BPO_4 as a function of time on-line. Reaction conditions: 325°C, 0.2 ml/h 2-methylbutanal, 24 ml/h nitrogen. Key: ■ conversion, ● isoprene selectivity, ▲ methyl isopropyl ketone selectivity. After ca. 380 min of reaction time, the reactant was replaced by dry N_2 and the catalyst was cooled to room temperature for 16 h; following this, the reaction was resumed.

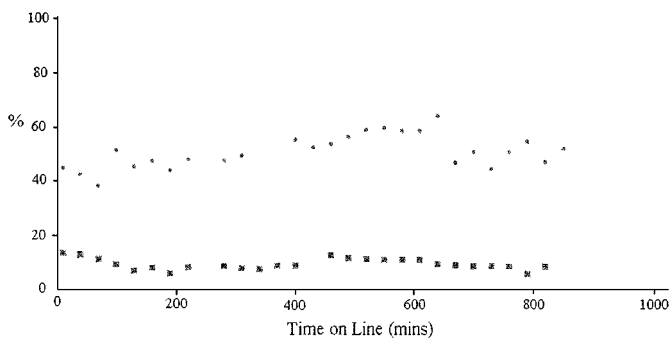


FIG. 2. Reaction of 2-methylbutanal over $\text{AlPO}_4\text{-Cl}$ as a function of time on-line. Reaction conditions: 325°C, 0.2 ml/h 2-methylbutanal, 24 ml/h nitrogen. Key: ■ conversion, ● isoprene selectivity.

observed was methyl isopropyl ketone. Following the reaction the catalyst structure was found to be unchanged but the surface area had decreased to 25 m² g⁻¹. The catalyst was typically found to contain 1–2% carbon following the reaction.

Deactivation and Reactivation of Boron Phosphate Catalysts

As noted previously, the conversion of 2-methylbutanal over boron phosphate leads to a steady loss of conversion without affecting the reaction selectivity, and this is indicative of a deactivation process that is due to a gradual loss of active sites. Characterisation of the deactivated catalyst using diffuse reflectance infrared spectroscopy indicated the absence of the strong absorption bands associated with surface phosphate groups that are present in the unused catalyst (Fig. 4). This indicates that phosphorus has been lost from the surface and this observation was confirmed by subsequent detailed x-ray photoelectron spectroscopy studies of the unused and deactivated boron phosphate. Moffat *et al.* (24, 25) have proposed that the Brønsted acid sites

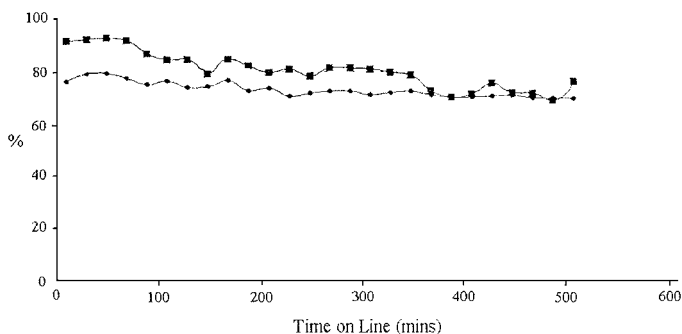


FIG. 3. Reaction of 2-methylbutanal over $\text{AlPO}_4\text{-Cl}$ as a function of time on-line. Reaction conditions: 400°C, 0.2 ml/h 2-methylbutanal, 24 ml/h nitrogen. Key: as in Fig. 2.

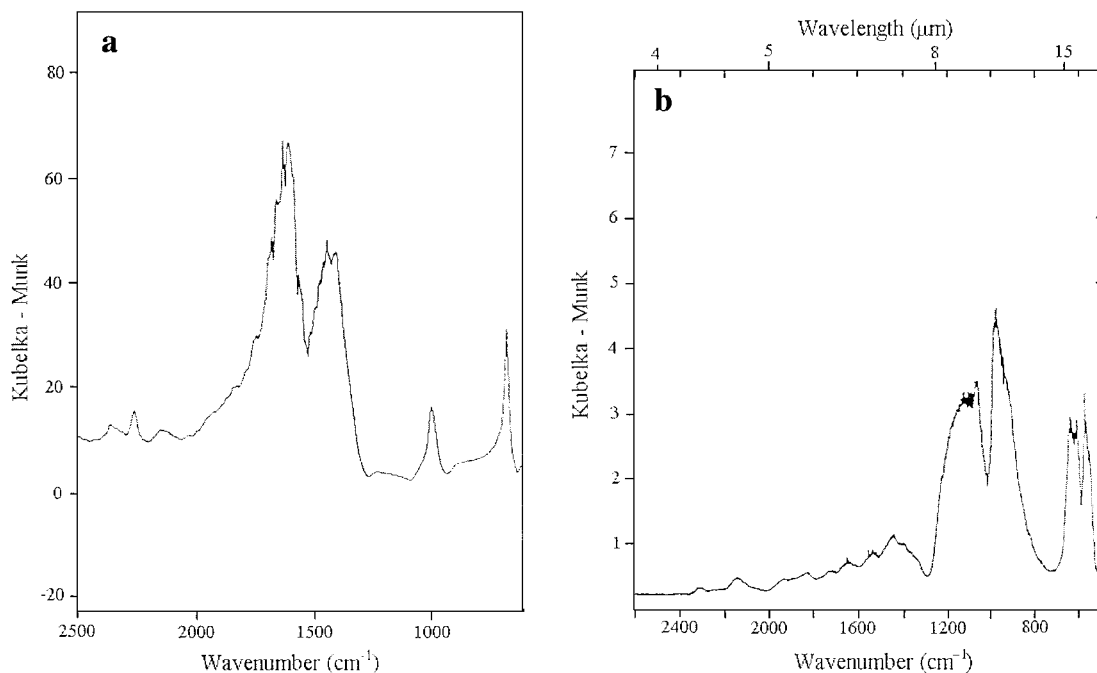


FIG. 4. Diffuse reflectance infrared spectra of BPO_4 (a) before reaction and (b) after reaction at 325°C for 500 min.

associated with the surface phosphate groups are essential for the dehydration reaction to occur. In addition to surface phosphorus loss, the x-ray photoelectron spectroscopy indicated the presence of surface carbon in the deactivated sample. Subsequent elemental analysis confirmed the presence of ca 1% by mass carbon. It is therefore proposed that the deactivation of the boron phosphate is due to a combination of (i) the loss of surface phosphorus and (ii) the deposition of coke that is probably formed by the polymerization of isoprene.

As deactivation was related to coke formation and carbonaceous residues can normally be removed by oxidation, it was decided to investigate air regeneration. The deactivated boron phosphate was treated *in situ* in the reactor with a mixture of air/nitrogen ($1:1$, 30 ml min^{-1} , 300°C for 1 h, then 500°C for 1 h). Elemental analysis confirmed that this procedure resulted in the removal of all the coke. The results for three successive deactivation/reactivation cycles are shown in Fig. 5. It is clear that this procedure did not successfully reactivate the boron phosphate, although a short-lived restoration of activity was observed after each reactivation, and in particular the rate of deactivation increases with successive reactivations; i.e., the low-temperature reactivation procedure exacerbates catalyst deactivation. Similar results were obtained in the absence of nitrogen. Detailed surface analysis of the used catalyst that had been subjected to reactivation at 500°C indicated that this procedure does not restore the surface phosphorus and it is for this reason that the catalyst activity is not restored.

It is found that air reactivation at much higher temperatures (e.g., 800°C) is required to re-establish the surface phosphorus concentration to levels similar to that observed in the fresh catalysts. The results of a series of deactivation/reactivation cycles using air treatment at 800°C for 1 h are shown in Fig. 6. It is clear that this simple procedure completely restores catalyst performance to that observed for the fresh catalyst and that the isoprene selectivity and rate of deactivation are similar for both the fresh and reactivated catalysts. This reactivation procedure was successfully carried out for a number of success cycles, thereby significantly extending the useful lifetime of the boron phosphate catalyst for the dehydration of 2-methylbutanal.

As noted previously, coke was also deposited on the AlPO_4 catalysts during the dehydration reaction. Similar

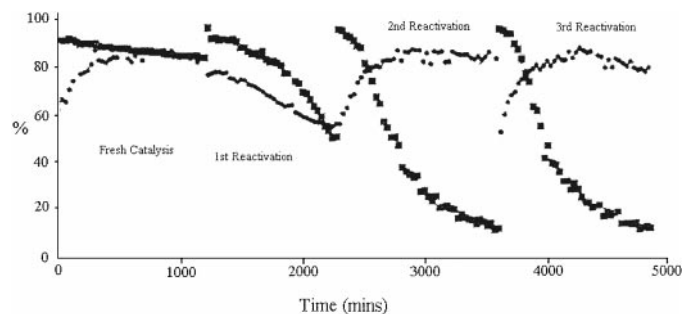


FIG. 5. Reaction of 2-methylbutanal over BPO_4 at 325°C as a function of time on-line, showing the effect of sequential deactivation and reactivation at 500°C . Reaction conditions: 0.2 ml/h 2-methylbutanal, 24 ml/h nitrogen. Key: as in Fig. 2.

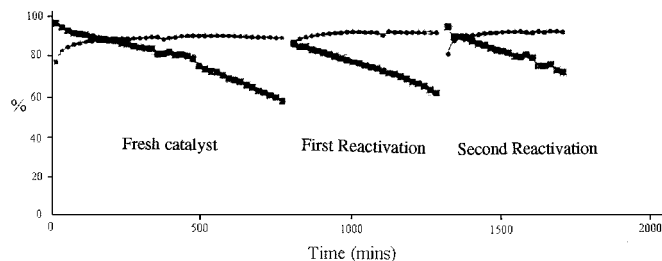


FIG. 6. Reaction of 2-methylbutanal over BPO_4 at $325^\circ C$ as a function of time on-line, showing the effect of sequential deactivation and reactivation at $800^\circ C$. Reaction conditions: 0.2 ml/h 2-methylbutanal, 24 ml/h nitrogen. Key: as in Fig. 2.

studies to those described above for the BPO_4 catalyst have shown that the $AlPO_4$ catalysts are also deactivated by the loss of surface phosphorus as well as coke deposition. Furthermore, it is found that reactivation in air at $800^\circ C$ for 3 h can restore catalyst activity; the details are described in a separate study (26).

2-Methylbutanal Dehydration Using Mixed B/ $AlPO_4$

Six mixed B/ $AlPO_4$ samples were prepared and tested as catalysts for the dehydration of 2-methylbutanal and the results are compared with undoped BPO_4 and undoped $AlPO_4$ in Table 1. These catalysts were observed to deactivate only slowly with time and representative results are given in Fig. 7. The addition of BPO_4 to $AlPO_4$ increased the catalyst activity and selectivity significantly; however, the activity was still lower than that observed for BPO_4 alone. A comparison of the catalysts prepared by calcination at $800^\circ C$ (see Table 1, experiments 2, 5, and 8) indicates that the addition of BPO_4 decreases the rate of coke deposition. However, BPO_4 gives the highest rate of coking and so the effects are not due to a simple effect of the addition of a separate phase of BPO_4 . An analysis of these catalysts after reaction for 1100 min using powder x-ray diffraction did not indicate the presence of a separate BPO_4 phase and only the cristabolite and trydimate phases of $AlPO_4$ were

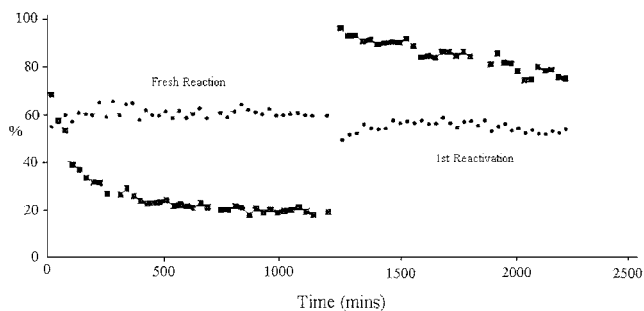


FIG. 7. Reaction of 2-methylbutanal over B/ $AlPO_4$ (B:Al=0.05:0.95) at $325^\circ C$ as a function of time on-line, showing the effect of sequential deactivation and reactivation at $500^\circ C$. Reaction conditions: 0.2 ml/h 2-methylbutanal, 24 ml/h nitrogen. Key: as in Fig. 2.

observed. The catalysts were characterised using ^{31}P , ^{27}Al , ^{11}B , and 1H MAS NMR spectroscopy and the results are given in Table 2, comparing undoped $AlPO_4$ and BPO_4 with the mixed B/Al phosphates with B:Al=0.05:0.95 molar ratio, although similar results were obtained for the samples containing higher B concentrations. ^{31}P spectra of undoped BPO_4 and $AlPO_4$ showed a single resonance at $\delta = -29.7$ ppm. The mixed B/Al samples showed two resonances. ^{27}Al spectra of the mixed B/Al systems also give two resonances, whereas the undoped $AlPO_4$ exhibits a single resonance. In addition, ^{11}B spectra of the mixed B/Al systems also gave two resonances whereas the undoped BPO_4 exhibited only a single resonance. The 1H MAS NMR spectrum of BPO_4 shows a singlet at $\delta = 7.8$ ppm, whereas $AlPO_4$ shows a singlet at $\delta = 1.2$ ppm in addition to a singlet at $\delta = 5.2$ ppm. The mixed B/Al phosphate prior to calcination has a 1H MAS NMR spectrum that is very similar to that of $AlPO_4$, but upon calcination the singlet at $\delta = 7.2$ ppm moves upfield to 5.2 ppm. This possibly indicates a change in the acidity of this proton. Characterisation of the mixed phosphates using diffuse reflectance infrared spectroscopy showed that all samples exhibited two strong absorptions at 1300 and 1410 cm^{-1} . On the basis of a comparison with infraspctra of the undoped phosphates (Fig. 4), these two strong absorptions can be assigned to the deformation of

TABLE 1

Conversion of 2-Methylbutanal over Mixed Al/B Phosphates

Experiment	Catalyst	B:Al mole ratio	Calcination temperature ($^\circ C$)	Conversion (%)	Isoprene selectivity (%)	Rate of carbon deposition (10^{-5} mol of C/h)
1	BPO_4	—	350	60	80	10.9
2	$AlPO_4-C$	—	800	10	50	4.8
3	B/ $AlPO_4$	0.05:0.95	350	15	50	10.7
4	B/ $AlPO_4$	0.05:0.95	500	20	60	1.14
5	B/ $AlPO_4$	0.05:0.95	800	30	65	4.0
6	B/ $AlPO_4$	0.10:0.90	350	25	80	6.9
7	B/ $AlPO_4$	0.10:0.90	500	28	83	3.9
8	B/ $AlPO_4$	0.10:0.90	800	30	88	1.6

Note. Reaction conditions: $325^\circ C$, 0.2 ml/h 2-methylbutanal, 24 ml/h nitrogen.

TABLE 2
MAS NMR Spectroscopic Data for Phosphate Catalysts

Catalyst	B : Al mole ratio	Calcination temperature (°C)	Chemical shift (ppm)			
			³¹ P	²⁷ Al	¹¹ B	¹ H
BPO ₄	—	350	-29.6	—	-3.6	7.8
AlPO ₄ -C	—	500	-29.9	39.0	—	7.2, 1.1
B/AlPO ₄	0.05 : 0.95	350	-29.9, — 22.3b	41.3, -10.4	-3.8, b*	5.2, 1.2
B/AlPO ₄	0.05 : 0.95	500	-29.1, — 21.7b	41.6, -12.6	-3.8, b*	—
B/AlPO ₄	0.05 : 0.95	800	-29.7, — 24.8b	39.4, -10.2	-4.6, b*	—
Nb/B/AlPO ₄ ^a	0.05 : 0 : 95	350	—	36.6, -9.6	-1.2, b*	5.0

Note. b* denotes a very broad peak upfield of the sharp singlet; b denotes a broad peak.

^a Nb : B atomic ratio 1 : 1.

P-OH bonded to B and Al (22, 27). The diffuse reflectance infrared and MAS NMR spectroscopy results taken together indicate that the mixed B/Al phosphates contain B and Al in the same phosphate lattice.

The reactivation of mixed B/Al phosphate catalysts at 500°C in air was more successful than that for the non-mixed phosphates. Reactivation at 500°C led to a significant increase in activity for the mixed catalyst system which is considered to be due to a change in the surface B/Al ratio.

2-Methylbutanal Dehydration Using Niobium-Doped Mixed B/Al Phosphates

As noted previously, one of the mechanisms by which the phosphate catalysts deactivate is by the loss of phosphorus from the surface. In an attempt to stabilize the catalyst, niobium doping was investigated. Under standard reaction conditions the conversion of 2-methylbutanal was higher than that of the undoped fresh mixed B/Al phosphate and the isoprene selectivity was also slightly higher (Fig. 8). The niobium-doped sample was characterised by MAS NMR and the results are given in Table 2; these results indicate that the niobium-doped phosphate is very similar to the undoped material. An interesting effect is observed following reactivation of the mixed B/Al phosphate catalysts. It is found that these catalysts can be reactivated at 500°C (Figs. 7 and 8). Reactivation of the niobium-doped catalyst at 500°C also leads to a significant increase in catalyst performance but now the rate of deactivation of the reactivated catalyst is much lower for the first reactivation. Clearly, the reactivation process is affecting the structure of both the undoped and doped catalysts, but analysis by MAS NMR and infrared spectroscopy did not indicate any significant changes between reactivated materials and fresh catalysts.

Reaction of Methyl Isopropyl Ketone and 2-Methyl-2-buten-1-ol

The reaction of methyl isopropyl ketone was investigated using BPO₄ at 325°C and AlPO₄-Cl at 400°C under the same conditions used for the dehydration of 2-methylbutanal and the results are shown in Table 3. It is apparent that this catalyst is effective for the conversion of methyl isopropyl ketone to isoprene, and conversions of ca. 65% and selectivities of ca. 85–95% are typically observed. A large number of by-products were observed and these included dimers due to aldol condensation and hydrocarbons, e.g., 2-methylbut-2-ene. No significant deactivation was observed over the 150-min time scale of the experiment.

The reaction of 2-methyl-2-buten-1-ol was also investigated and the results are given in Table 4. Initial

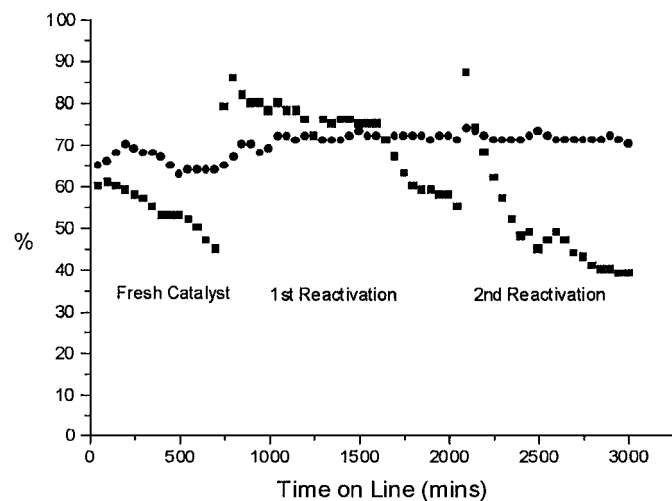


FIG. 8. Reaction of 2-methylbutanal over Nb-doped B/AlPO₄ at 400°C as a function of time on-line, showing the effect of sequential deactivation and reactivation at 500°C. Reaction conditions: 0.2 ml/h 2-methylbutanal, 24 ml/h nitrogen. Key: as in Fig. 2.

TABLE 3

Reaction of Methyl Isopropyl Ketone over BPO₄ and AlPO₄-Cl

Time on-line (min)	BPO ₄ ^a		AlPO ₄ ^b	
	Conversion (%)	Isoprene selectivity (%)	Conversion (%)	Isoprene selectivity (%)
10	41	95	60	86
30	40	95	64	84
50	42	93	60	86
100	41	95	60	86
150	40	95	61	84

Note. Reaction conditions: 0.2 ml/h methyl isopropyl ketone, 24 ml/h nitrogen.

^a 325°C.

^b 400°C.

experiments indicated that this substrate could be reacted thermally in the absence of a catalyst at temperatures as low as 110°C, and the products were isoprene, 2-methylbutanal, and 2-methylbut-2-ene. Experiments with 2-methylbutanal and methyl isopropyl ketone showed that no thermal non-catalysed reactions occurred. In the presence of BPO₄ the same products were observed at 110°C, and as the temperature was increased to 300°C, the conversion increased the product distribution in the presence of the catalyst changed to give a decrease in isoprene and an increase in 2-methylbutanal.

DISCUSSION

In this study two AlPO₄ catalysts have been investigated for the dehydration of 2-methylbutanal and these differ in the bulk phase composition. The sample comprising cristabolite in combination with tridymite is more active and selective than the sample containing tridymite alone. Under comparable conditions, the cristabolite-containing catalyst gave a yield of isoprene of 49%, whereas the tridymite catalyst gave only a 30% isoprene yield. This difference is not related to the small difference in the surface area of the active catalysts; when this factor is taken into account, the differences in catalytic performance are still apparent (intrinsic activity AlPO₄-Cl = 2.84 ×

10⁻⁵ mol of isoprene/m²/g and intrinsic activity of AlPO₄-S = 1.86 × 10⁻⁵ mol of isoprene/m²/g). Hence, it can be concluded that the cristabolite form of AlPO₄ is far more active than the tridymite form. It is interesting to note that the structure of BPO₄ catalysts that are active and selective for 2-methylbutanal dehydration also have the cristabolite phase. However, the boron phosphate catalysts are active at 325°C, but this may be due to these catalysts comprising 100% cristabolite whereas the AlPO₄-Cl catalysts only contain 20–30% cristabolite.

For BPO₄ and AlPO₄ catalysts, it was apparent that the conversion steadily declined with an increased reaction time but the by-product composition remained constant. There are a number of possible explanations for this behaviour. First, by-products and the main product, isoprene, could be formed at separate sites. It would be expected that if an indiscriminate mechanism of catalyst deactivation was in operation, this would affect both sites equally and hence the selectivity would remain the same. However, in the present case, evidence suggests that a common intermediate exists for the formation of the product and by-product and, hence, it is more probable that a single catalytic site is involved. Second, it is possible that the by-product, i.e., methyl isopropyl ketone, is formed in a consecutive reaction to the formation of isoprene. If two catalytic sites are involved, one for each step, and the concentration of the sites responsible for by-product formation increase with catalyst aging, then it is possible for catalyst selectivity to appear to remain constant. To investigate this possibility, experiments were conducted at a decreased flow rate and the selectivity was not affected by variation in the conversion for an aged catalyst. In addition, experimental evidence in the study suggests that a common intermediate is responsible for both isoprene and methyl isopropyl ketone formation. This suggests a third explanation, that the by-products and product are formed in a parallel mechanism on a single catalytic site. Hence, as the catalyst ages, the number of these sites decreases but the selectivity remains constant.

Both the BPO₄ and AlPO₄ catalysts deactivate during use due to two unrelated factors. First, carbonaceous deposits are formed on the catalyst surface, probably as a result of isoprene polymerization catalysed by the surface acid P-OH sites. The present study has shown that this is not the main cause of deactivation of AlPO₄ catalysts since the coke can be removed by treatment in air at 500°C, but this does not restore the catalytic activity. The major loss of the catalyst activity on use is due to the loss of surface P-OH groups due to a loss of phosphorus from the surface. This is a common phenomenon with phosphate catalysts and in commercial operation is sometimes overcome by the continuous addition of phosphates with the reactants. In the present case it is shown that a high-temperature treatment can restore both the surface P-OH groups and catalyst activity. The high temperature is required to enable the

TABLE 4

Reaction of 2-Methyl-2-buten-1-ol over BPO₄

Catalyst	Temperature (°C)	2MBO (%)	2MBA (%)	2MBE (%)	I (%)
None	110	13	10	40	37
BPO ₄	110	13	10	40	37
BPO ₄	300	1	25	48	10

Note. 2MBO: 2-methyl-2-buten-1-ol; 2MBA: 2-methylbutanal; 2MBE: 2-methyl-butene; I: isoprene.

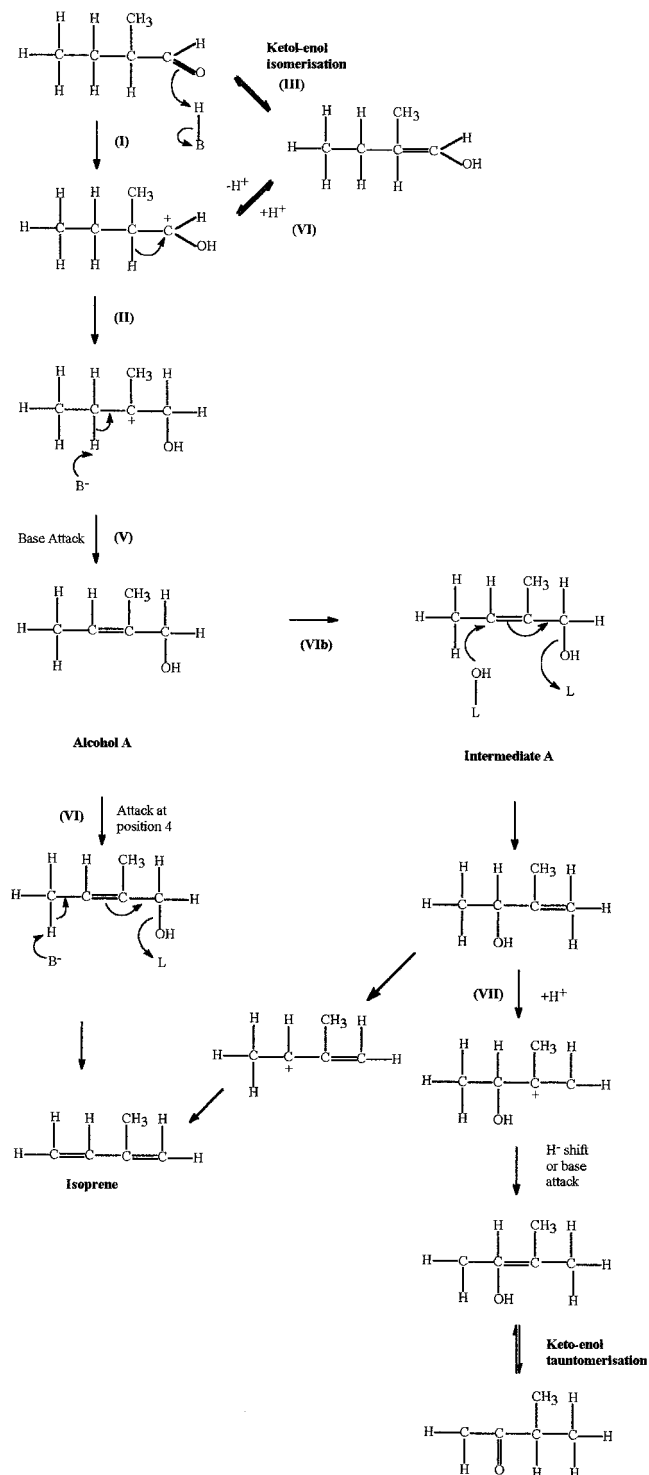


FIG. 9. Proposed reaction mechanism for the conversion of 2-methylbutanal over phosphate catalysts involving the concerted action of Lewis (L) and Brønsted (B) acid sites.

diffusion of bulk phosphorus atoms to occur, a process that typically becomes facile at the Tammann temperature. Interestingly, when mixed B/Al phosphate catalysts are used, it is found that lower temperature reactivation at 500°C is

effective, whereas reactivation at this temperature for the pure BPO₄ and AlPO₄ was ineffective. MAS NMR and infrared spectroscopy characterisation indicates that boron and aluminium are present in the same lattice. Furthermore, the catalyst containing niobium in addition to boron and aluminium exhibited an enhanced stability upon reactivation. No attempt has been made in this study to optimise the catalyst formulations, but it is apparent that there exists considerable scope to improve both the performance and lifetime of these catalysts.

An interesting observation is that when 2-methylbutanal is reacted over BPO₄ and AlPO₄ catalysts, only isoprene and methyl isopropyl ketone are observed as products. However, we have found that methyl isopropyl ketone is readily reacted over the BPO₄ at 325°C and AlPO₄ catalysts at 400°C to give isoprene. The yields of isoprene from the two reactants are very similar (e.g., for AlPO₄ at 400°C, 49% isoprene yield from 2-methylbutanal and 54% isoprene yield from methyl isopropyl ketone). These results indicate that there is probably a common intermediate linking isoprene and methyl isopropyl ketone. The observation that the ketone by-product can be converted into isoprene is significant with respect to the potential commercial operation of these catalysts since the ketone by-product can be recycled and the overall yield of isoprene can be significantly enhanced. The observation that the ketone by-product can be readily converted into isoprene over the phosphate catalysts indicates that a common intermediate may exist for the conversion of 2-methylbutanal to both isoprene and methyl isopropyl ketone. Miyata *et al.* have shown, using pyridine adsorption (24) and ammonia adsorption (25) that the surface of BPO₄ contains both Lewis and Brønsted acid sites. On the basis that the formation of isoprene and methyl isopropyl ketone involves a common intermediate and that both Lewis and Brønsted acid sites could play important roles, we propose a mechanism that involves the concerted action of Lewis and Brønsted acid sites on the phosphate surface (Fig. 9). We consider that 2-methyl-2-buten-1-ol could be the central intermediate in the formation of the products. Studies using 2-methyl-2-buten-1-ol as the reactant indicated that both isoprene and 2-methylbutanal could readily be formed and this gives some support to the proposed mechanism.

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