Dehydration of 2-methylbutanal to isoprene using aluminium phosphate catalysts

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The synthesis of isoprene from the dehydration of 2-methylbutanal is described using aluminium phosphates as catalysts. Two samples of aluminium phosphate are studied prepared from the reaction of phosphoric acid with aluminium chloride or sulphate. The chloride route gives a mixed cristobalite/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 sulphate route. The $AlPO_4$ catalysts are also shown to be active catalysts for the synthesis of isoprene from 3-methylbutan-2-one, which is the major by-product formed from the reaction of 2-methylbutanal. The $AlPO_4$ catalysts are deactivated due to the deposition of coke in addition to loss of phosphorus from the surface. Catalytic activity can be totally restored by a simple calcination procedure at 800 °C.

Keywords: aluminium phosphate catalysts, aldehyde dehydration, isoprene synthesis

1. Introduction

Industrial interest in the synthesis of isoprene originated from the discovery of a process for the stereoselective polymerisation to form 1,4-*cis*-polyisoprene. This led to isoprene becoming a strategically important monomer for the production of substitutes for natural rubber. In view of this, considerable research interest has been given to identifying new catalytic routes for isoprene production. To date, however, most isoprene is produced by extraction of pyrolysis fractions that result from naphtha cracking. 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. This synthetic route has been known since 1911 when Kiselev et al. [2] and Kyriakides [3] demonstrated that aluminium silicate, TiO_2 and SiO_2 were effective catalysts. Subsequently, Fischer and Schunchel [4] 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 [5–8]. We have recently shown [9] that the deactivation of boron phosphate is due to 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 [10,11], ammonium aluminium sulphate [12] and magnesium ammonium phosphate [13] have all been shown to be active catalysts.

More recently, zeolites and other microporous materials have been investigated [14–19] and, in particular, zeolites with weak acidity can give very high selectivities to isoprene with a relatively long service time. However, in contrast, microporous phosphates demonstrate 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. For this reason, we became interested in the use of dense phase phosphates. As noted previously, boron phosphate has been extensively studied for aldehyde dehydration but other phosphates, e.g., $AlPO_4$, have not been investigated. Such phosphates have been used as catalysts for alcohol dehydration. Haber and Szybalska [20] have compared boron phosphate and aluminium phosphate catalysts for ethanol dehydration and showed that similar ethene yields could be obtained. In addition, the catalytic properties of aluminium phosphate are known to be significantly affected by the preparation method. Campelo et al. [21] have shown that the $AlPO_4$ phase that is prepared can be controlled by the selection of an appropriate aluminium salt.

In this paper we present our preliminary results for the use of $AlPO_4$ as a catalyst for the dehydration of 2-methylbutanal, and show that this catalyst can give high yields of isoprene and, although slow deactivation is observed, it is shown that the catalyst can be readily reactivated.

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2. Experimental

2.1. Catalyst preparation

Two samples of aluminium phosphate were prepared using the precipitation method of Campelo et al. [21]. 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 orthophosphoric acid (0.985 mol/l, 5 °C). The aqueous ammonia addition was continued until pH = 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 pelletted and sieved (600–1000 μm). This catalyst is denoted $AlPO_4$-Cl. Powder X-ray diffraction showed that the catalyst was a mixture of the cristobalite and tridymite phases of $AlPO_4$, and the surface area was determined to be 93 $m^2\,g^{-1}$.

The second sample was prepared using the same procedure except the aluminium source was aluminium sulphate. This sample was denoted $AlPO_4$-S. Powder X-ray diffraction showed that the catalyst comprised only the tridymite phase of $AlPO_4$, and the surface area was determined to be 50 $m^2\,g^{-1}$.

2.2. 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 N_2 (1.44 l/h) as the carrier gas. The resultant 2-methylbutanal/N_2 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 catalyst, no thermal dehydration of 2-methylbutanal was observed at the temperature used in this study. Satisfactory carbon mass balances ($\geqslant$95%) were obtained for all data presented.

3. Results

3.1. 2-methylbutanal dehydration

The dehydration of 2-methylbutanal was investigated using the two $AlPO_4$ samples at 400 °C and the results are shown in figures 1 and 2. The initial conversion for $AlPO_4$-Cl was ca. 90% but this steadily declined to ca. 75% after

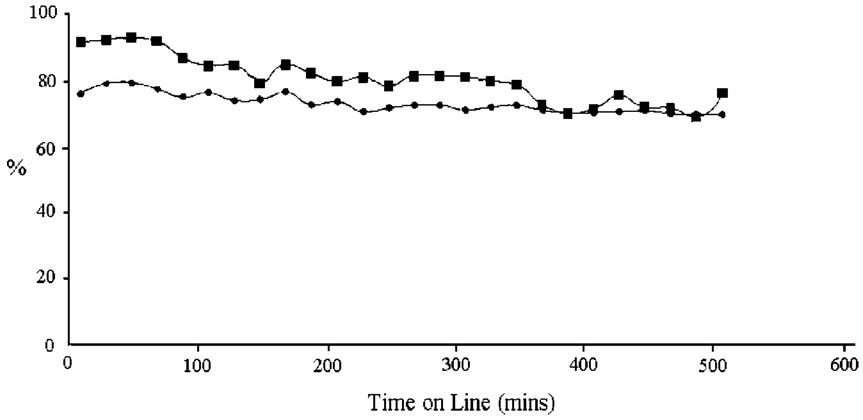

Figure 1. Reaction of 2-methylbutanal over $AlPO_4$-Cl at 400 °C as a function of time on line. (■) Conversion, (•) isoprene selectivity.

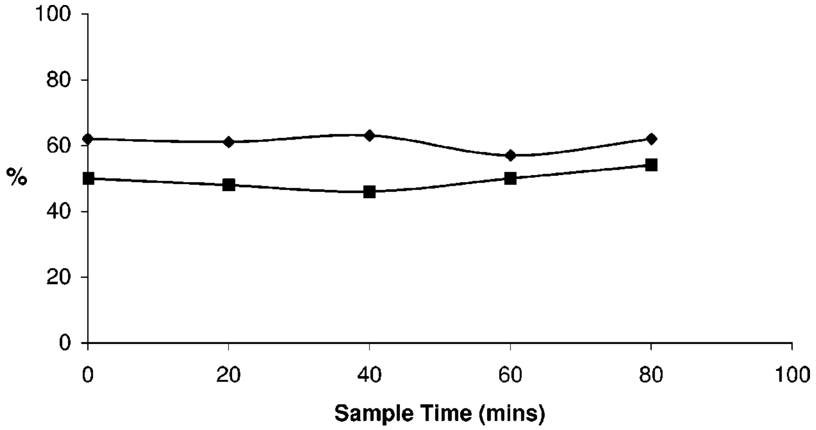

Figure 2. Reaction of 2-methylbutanal over $AlPO_4$-S at 400 °C as a function of time on line. (■) Conversion, (♦) isoprene selectivity.

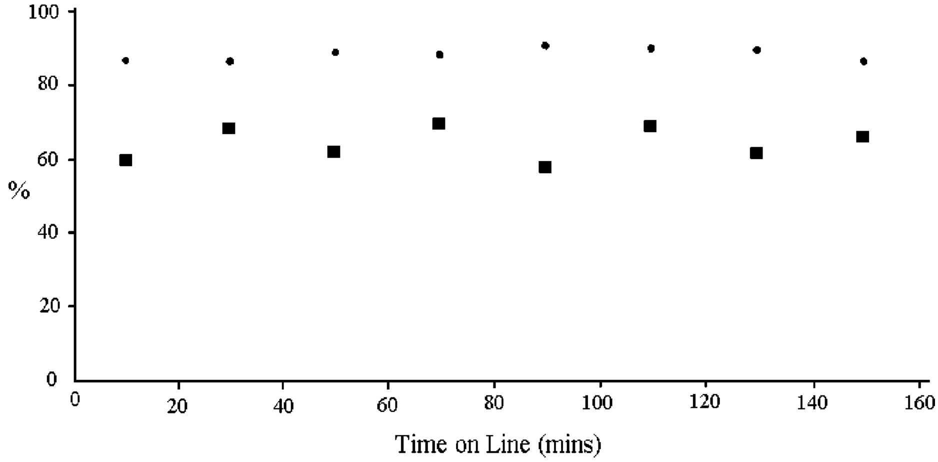

Figure 3. Reaction of 3-methylbutan-2-one over $AlPO_4$-Cl at 400 °C as a function of time on line. (■) Conversion, (•) isoprene selectivity.

500 min. The selectivity to isoprene was 70–80% throughout this testing period and the only by-product observed was 3-methylbutan-2-one. Following 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 $m^2\,g^{-1}$. The catalyst was found to contain 5 wt% carbon after reaction. In comparison, $AlPO_4$-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 observed was 3-methylbutan-2-one. Following reaction, the catalyst structure was found to be unchanged, however, the surface area had decreased to 25 $m^2\,g^{-1}$. The catalyst was typically found to contain 1–2% carbon following reaction.

3.2. Reaction of 3-methylbutan-2-one

The reaction of 3-methylbutan-2-one was investigated using $AlPO_4$-Cl at 400 °C under the same conditions used for the dehydration of 2-methylbutanal and the results are shown in figure 3. It is apparent that this catalyst is effective for the conversion of 3-methylbutan-2-one to isoprene, and conversions of ca. 65% and selectivities of ca. 85–90% are typically observed. No significant deactivation was observed over the 150 min timescale of the experiment.

3.3. Deactivation and reactivation of $AlPO_4$-Cl

As noted previously, coke is deposited on $AlPO_4$-Cl during the dehydration reaction and the catalyst shows a steady deactivation rate over the 500 min test period. TGA analysis, in an air atmosphere, showed that the coke could be removed by calcination in air at 500 °C. The catalyst obtained following reaction for 500 min was then calcined *in situ* in the reactor (500 °C, 3 h) and analysis confirmed that the carbon was removed by this treatment. The calcined catalyst was then used for the reaction of 2-methylbutanal and although some catalyst activity was restored, this improvement was relatively short lived. In particular, the selectivity to isoprene decreased rapidily following reactivation at 500 °C. This indicates that the deposition of coke is not the sole cause of deactivation for $AlPO_4$ catalysts.

Samples of $AlPO_4$-Cl before and after reaction were examined using diffuse reflectance infrared spectroscopy (DRIFTS) and the spectra are shown in figure 4. It is apparent that the IR absorption bands between 1000 and 1700 cm^{-1} are significantly decreased in intensity following reaction. In particular, the intense band at 1300 cm^{-1}, associated with the P–OH deformation [22], is absent following reaction. This indicates that there is a loss of surface P–OH groups during reaction. Subsequent analysis using X-ray photoelectron spectroscopy (XPS) confirmed that there was a loss of phosphorus from the catalyst surface during reaction. DRIFTS and XPS of the $AlPO_4$-Cl following calcination in air at 500 °C showed that the surface phosphorus was not restored by this treatment and it is for this reason that the catalyst activity is not restored by such a calcination procedure. Treatment of the reacted $AlPO_4$-Cl at a higher temperature (800 °C, 3 h) is found to restore the surface P–OH groups (figure 4) and this treatment is found to restore the catalytic performance. The results for two reactivation and three deactivation cycles are shown in figure 5 and, in particular, it is observed that selectivity to isoprene is unaffected by the treatment at 800 °C.

4. Discussion

In this study, two $AlPO_4$ catalysts have been investigated for the dehydration of 2-methylbutanal and these differ in the bulk phase composition. The sample comprising cristobalite in combination with tridymite is more active and selective than the sample containing tridymite alone. Under comparable conditions, the cristobalite-containing catalyst gave yield of isoprene of 49%, whereas the tridymite catalyst gave only 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

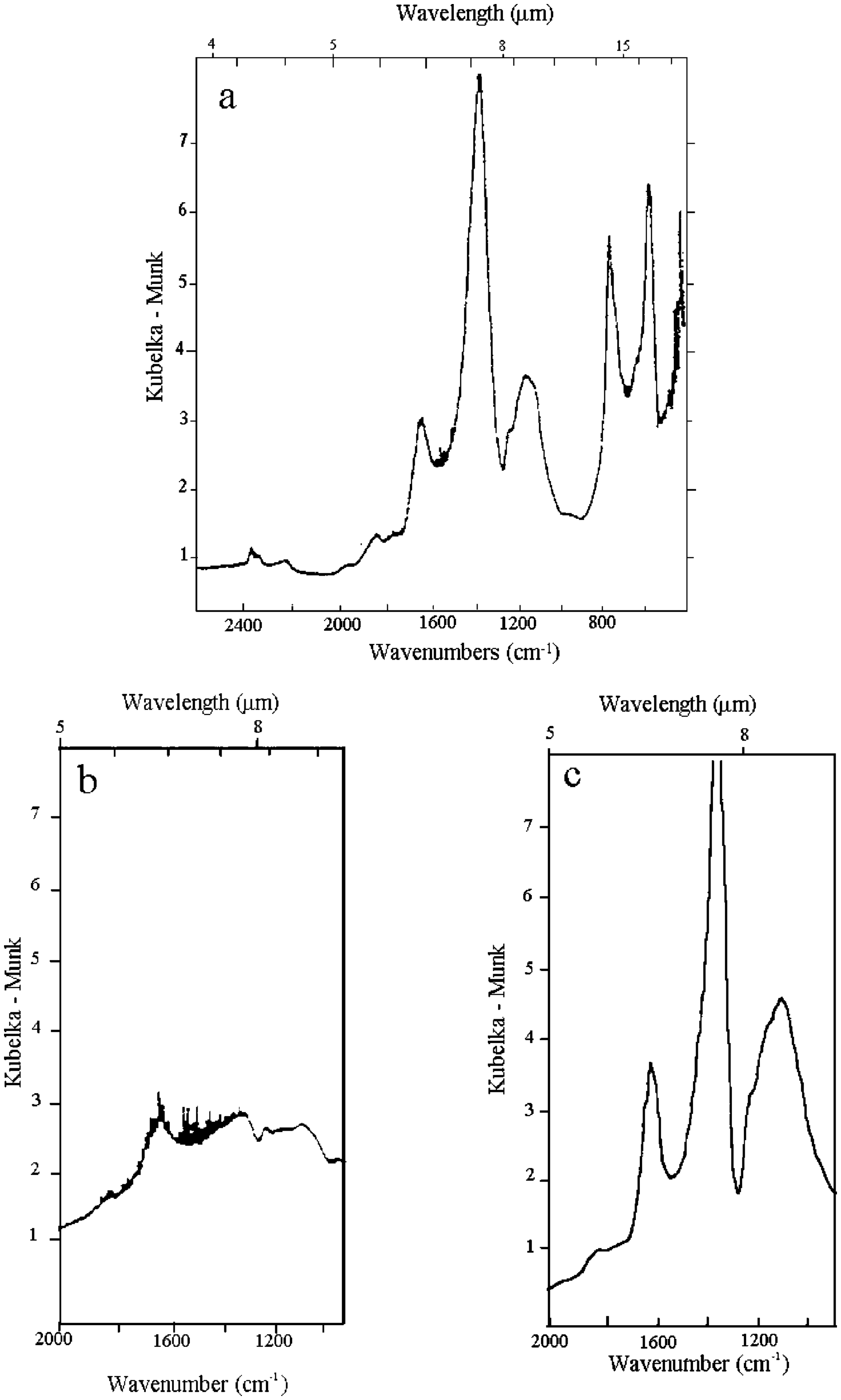

Figure 4. DRIFTS of $AlPO_4$ (a) before reaction and (b) after reaction at 400 °C for 500 min; (c) sample (b) after calcination at 800 °C for 3 h.

differences in catalytic performance are still apparent (intrinsic activity $AlPO_4$-Cl $= 2.84\times10^{-5}$ mol isoprene/(m^2 g) and intrinsic activity of $AlPO_4$-S $= 1.86 \times 10^{-5}$ mol isoprene/(m^2 g)). Hence it can be concluded that the cristobalite form of $AlPO_4$ is far more active than the tridymite form. It is interesting to note that the structure of BPO_4 catalysts that are active and selective for 2-methylbutanal dehydration is also the cristobalite phase. However, the boron phosphate catalysts are active at 325 °C, but this may be due to these catalysts comprising 100% cristo-

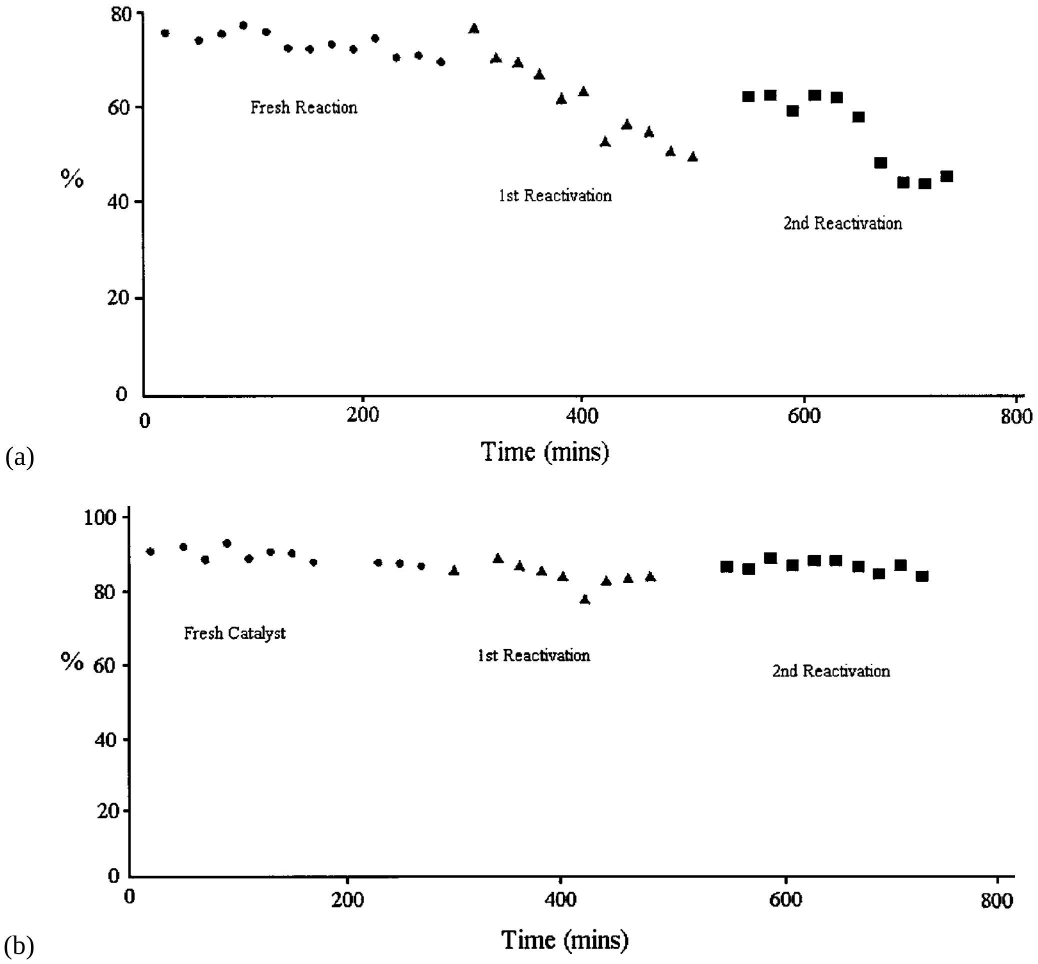

Figure 5. Reaction of 2-methylbutanal over $AlPO_4$-Cl at 400 °C as a function of time on line showing the effect of sequential deactivation and reactivation. (a) Conversion, (b) isoprene selectivity; (•) fresh catalyst, (▲) first reactivation, (■) second reactivation.

balite, whereas the $AlPO_4$-Cl catalysts only contain 20–30% cristobalite.

An interesting observation is that when 2-methylbutanal is reacted over $AlPO_4$ catalysts only isoprene and 3-methylbutan-2-one are observed as products. However, we have found that 3-methylbutan-2-one is readily reacted over the $AlPO_4$ catalysts to give isoprene. The yields of isoprene from the two reactants are very similar (at 400 °C, 49% isoprene yield from 2-methylbutanal and 54% isoprene yield from 3-methylbutan-2-one). These results indicate that there is probably a common intermediate linking isoprene and 3-methylbutan-2-one.

The $AlPO_4$ catalysts deactivate during use due to two unrelated factors. First carbonaceous deposits are formed on the catalyst surface, probably as a result of isoprene polymerisation catalysed by the surface acid P–OH sites. The present study has shown that this is not the main cause of deactivation of $AlPO_4$ 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 catalyst activity on use is due to 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 diffusion of bulk phosphorus atoms to occur, a process that typically becomes facile at the Tammann temperature [23]. Since the major cause of deactivation of $AlPO_4$ catalysts has been identified, it may be possible to design additives that stabilise the surface phosphorus and hence decrease the rate of deactivation.

The present study has demonstrated that catalysts based on the cristobalite form of $AlPO_4$ are highly active for the conversion of both 2-methylbutanal and 3-methylbutan-2-one to isoprene. Furthermore, although these catalysts slowly deactivate with time on stream, they can be readily reactivated by a simple thermal treatment.

Acknowledgement

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