Reactivation of Boron Phosphate Catalysts for the Synthesis of Isoprene from 2-Methylbutanal Dehydration

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Boron phosphate catalysts, when used for the title reaction, are deactivated both by coke deposition and by loss of surface phosphorus; air reactivation at 800 °C is shown to totally restore the catalyst structure and performance.

The search for synthetic substitutes for natural rubber has led to the identification of 1,4-*cis*-polyisoprene, formed *via* the stereospecific polymerisation of isoprene, as a potential candidate. Isoprene is presently obtained from naphtha cracking but in recent years there has been continued interest in the identification of new synthesis routes. One interesting possibility is the dehydration of 2-methyl butanal which is available as a result of the commercialisation of the low pressure hydroformylation of butene.[1] It has been known for many years that at low partial pressures 2-methyl butanal can

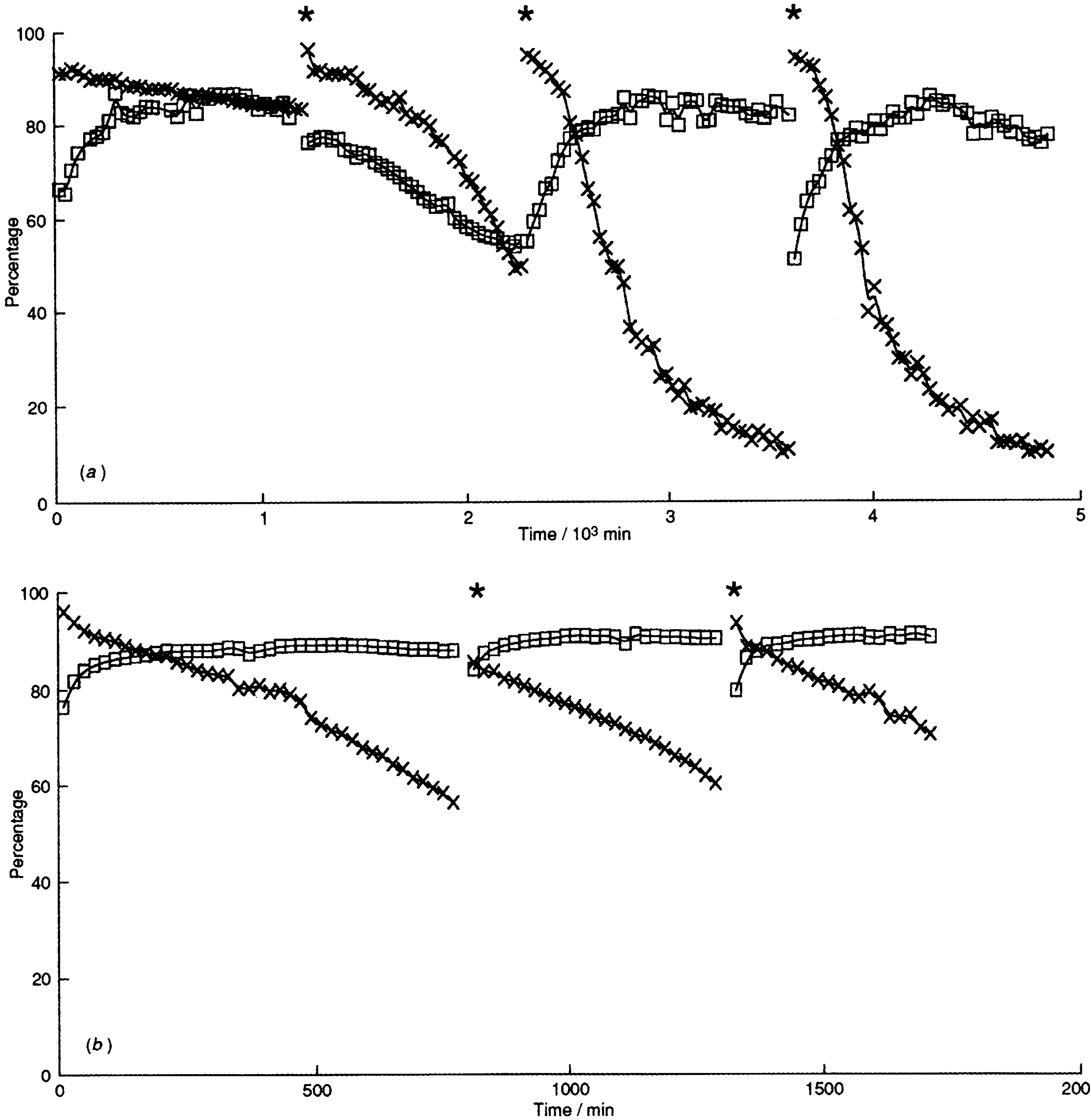

Fig. 1 Reaction of 2-methyl butanal over BPO_4 at 325 °C. (*a*) Reactivation at 500 °C (denoted*) (*b*) reactivation at 800 °C (denoted*). Key: × conversion, □ selectivity.

be dehydrated to isoprene and methyl isopropyl ketone.[2] However, the major problem associated with this reaction is that all catalysts identified to date are rapidly deactivated. No successful method of catalyst reactivation has been reported and consequently this reaction has yet to achieve commercial importance. At present, boron phosphate has been identified as the catalyst with the highest activity and isoprene selectivity.[3-5] Moffat *et al.*[4,5] have studied boron phosphate catalysts with a range of compositions for this reaction and have identified that the P/B molar ratio is an important parameter controlling catalytic performance. In particular catalysts with excess phosphorus exhibit the highest yields of isoprene but are rapidly deactivated by coke deposition.[6] The rate of deactivation has been shown to be slowed by the addition to the catalyst of ammonium bicarbonate,[6] graphite[7] and 4-*tert*-butyl catechol,[8] but the problem concerning reactivation has remained unsolved. We have now successfully addressed this problem. In this communication we demonstrate that catalyst deactivation results from both coke deposition and surface phosphorus loss, and we identify a method for the effective reactivation of boron phosphate catalysts.

Boron phosphate (P/B = 1) was prepared by heating phosphoric acid (93 ml, 85%) with boric acid (100 g) at 60 °C for 1 h. Water (100 ml) was then added and the mixture was refluxed for 5 h, dried (110 °C, 16 h) and calcined (350 °C, 4 h). The product was confirmed to be the cristobalite form of BPO_4 by X-ray diffraction. The boron phosphate (0.3 g) was investigated as a catalyst for the dehydration of 2-methyl butanal using a standard laboratory microreactor using nitrogen as a diluent (24 ml h^{-1}). Products were analysed using GC and satisfactory mass balances were obtained for all data presented.

The dehydration of 2-methyl butanal (0.67 ml^{-1} g catalyst h^{-1}) was studied at 325 °C for *ca.* 800 min. Initially the selectivity to isoprene steadily increased to a stable level of *ca.* 80% with methyl isopropyl ketone as the major by-product. The conversion, however steadily decreased from >95% to <80% throughout the reaction period although the selectivity remained unchanged. Loss of conversion without affecting reaction selectivity is indicative that the deactivation process is due to a gradual loss of active sites. Analysis of the deactivated catalyst by diffuse reflectance IR spectroscopy indicated the absence of the strong absorption bands associated with surface phosphate groups that are present in the unused catalyst. 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.*[4,5] have proposed that the Brönsted acid sites 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 apparent that the deactivation of the boron phosphate is due to a combination of (i) the loss of surface phosporus and (ii) the deposition of coke that is probably formed by the polymerisation 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 reacted *in situ* 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. 1(*a*). It is clear that this procedure did not successfully reactivate the boron phosphate 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.

We have found that air reactivation at much higher temperatures (*e.g.* 800 °C) is required to reestablish the surface phosphorus concentration to levels similar to that observed in the fresh catalyst. The results of a series of deactivation/reactivation cycles using air treatment at 800 °C for 1 h are shown in Fig. 1(*b*). 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 successive cycles thereby significantly extending the useful lifetime of the boron phosphate catalyst for the dehydration of 2-methyl butanal.

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