

Aldol condensation reactions of acetone and formaldehyde over vanadium phosphate catalysts: Comments on the acid–base properties

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The acid–base properties of vanadium phosphate catalysts are investigated using the aldol condensation of acetone and the reactions of 2-methylbut-3-yn-2-ol (MBOH). Three well characterised samples of VOHPO₄·0.5H₂O were prepared using the reaction of V₂O₅ and H₃PO₄ with aqueous hydrochloric acid or isobutanol as reducing agents, or from the reaction of VOPO₄·2H₂O with isobutanol. (VO)₂P₂O₇, prepared by heating VOHPO₄·0.5H₂O in He (8 h, 750 °C), before and following partial oxidation in air or butane/air, and α₁-VOPO₄ were also investigated. The reaction of MBOH was used to probe the nature of the acid–base properties of the vanadium phosphates. The V⁴⁺ phases (VOHPO₄·0.5H₂O and (VO)₂P₂O₇) exhibited only acidic active sites, whereas the V⁵⁺ phases (α₁-VOPO₄ and oxidised (VO)₂P₂O₇) exhibited some basic sites in addition to the acid sites. For the aldol condensation reactions of acetone, the V⁴⁺ phases were found to be selective for the formation of isophorone from acetone alone and methyl vinyl ketone from the reaction of acetone and formaldehyde. In contrast, vanadium phosphate catalysts containing V⁵⁺ phases are not selective to these products and only form hydrocarbons (typically isobutane and isobutene). For all these reactions, the catalyst activity is short lived and the deactivation that is observed is due to the surface becoming fouled by the adsorption of products of polymerisation of the reaction products. However, the catalyst reactivity can be restored by a simple oxidation treatment. The nature of active sites in *n*-butane oxidation to maleic anhydride is also discussed and it is concluded that basic sites are required in addition to acidic surface sites for the selective formation of maleic anhydride. For the reaction of MBOH, the data are found to give a linear relationship for a Cremer–Constable plot and this is discussed in terms of the enthalpy of adsorption of MBOH.

Introduction

Heterogeneous acid–base catalysts are extensively used in industrial processes,^{1–6} including alkylation, isomerisation, amination, cracking, aldol condensations and ether formation. A recent review by Tanabe and Hölderich⁷ has classified these industrial processes and it is noted that acid catalysed processes are predominant at the present time; since of 127 industrial processes using acid–base heterogeneous catalysts, 103 used acid catalysts. Recently, there has been considerable interest in extending the use of heterogeneous catalysis in the fine chemicals industry, and a particular reaction of interest has been aldol condensations, since these can be catalysed effectively by both acids and bases. In this respect, aldol condensation reactions using acetone as a substrate, are viewed as model reactions for the study of acid and base catalysts. These reactions have been extensively studied using base catalysts, such as MgO and alkali doped MgO,^{8–13} alkali doped silica,^{14–16} acid catalysts, such as zeolites and related microporous materials^{17–21} and layered double hydroxides,^{12,22–29} since these have acid–base properties.

Vanadium phosphate catalysts represent a class of materials that are amongst the most well studied and characterised heterogeneous catalysts. They have been extensively used for the oxidation of alkanes,^{30–34} in particular *n*-butane oxidation to maleic anhydride. Part of the research interest is due to the

observation that well defined single phase vanadium phosphates can readily be prepared, and most interest has focused on VOHPO₄·0.5H₂O, (VO)₂P₂O₇ and α₁-VOPO₄. Vanadium phosphate catalysts have also been shown by Ai³⁵ to be effective catalysts for the aldol condensation of formaldehyde with acetic acid to form methyl vinyl ketone and the aldol condensation of acetone and formaldehyde to form methyl vinyl ketone.³⁶ Ai considers this to be due to the combination of acid and base properties of vanadium phosphates.³⁷ However, the vanadium phosphate prepared by Ai comprises a complex mixture of vanadium phosphate phases, and it is possible that the catalytic activity observed in these studies was a composite of the activities of the component phases. In view of this, we have studied the self-aldol condensation of acetone and the condensation of acetone with formaldehyde over well defined vanadium phosphate catalysts. In addition, we have characterised the properties of vanadium phosphates using the reaction of 2-methylbut-3-yn-2-ol^{38–40} as a probe for acid–base sites.

Experimental

Preparation of vanadium phosphates

α₁-VOPO₄ was prepared according to a literature method⁴¹ and the structure was confirmed using powder X-ray diffrac-

tion and laser Raman spectroscopy. $(VO)_2P_2O_7$ was prepared by heating $VOHPO_4 \cdot 0.5H_2O$ in dry He at $750^\circ C$ for 8 h,⁴⁰ again the structure was confirmed using powder X-ray diffraction and laser Raman spectroscopy. A sample of a catalyst, previously prepared and described by Ai^{35–37} was prepared with a V : P atomic ratio of 1 : 1.06 according to the following procedure. V_2O_5 (15.45 g, Strem) was refluxed in benzyl alcohol (60 ml, Aldrich) and isobutanol (40 ml, Aldrich) for 2 h. H_3PO_4 (20.76 g, 85%, Aldrich) was added and the mixture was refluxed for 2 h. The solid was recovered by vacuum filtration and washed with acetone (100 ml) and water (100 ml) and dried in air (2 h, $110^\circ C$). The solid was calcined in air (6 h, $300^\circ C$; 6 h, $450^\circ C$) prior to use as a catalyst.

$VOHPO_4 \cdot 0.5H_2O$ was prepared according to the following three methods.

VPA method. V_2O_5 (7.26 g, Aldrich) was dissolved in aqueous HCl (80 ml, 37%, Aldrich), and refluxed for 3 h. H_3PO_4 (10.47 g, 85%, Aldrich) was added and the mixture refluxed for 3 h. The solvent was removed by distillation and the eventual slurry dried in air ($120^\circ C$, 16 h) to give a blue-green solid. The solid was refluxed with water (10 ml g^{-1}) for 3 h, filtered hot and the blue-green solid was dried in air ($120^\circ C$, 16 h).

VPO method. V_2O_5 (11.8 g, Aldrich) and H_3PO_4 (16.49 g, 85%, Aldrich) were refluxed in isobutanol (250 ml) for 16 h. The solid was recovered by filtration, washed with isobutanol (200 ml) and ethanol (250 ml), refluxed with water (10 ml g^{-1}) for 3 h, filtered hot and the blue solid was dried in air ($120^\circ C$, 16 h).

VPD method. V_2O_5 (11.8 g, Aldrich) was refluxed for 8 h with H_3PO_4 (115 g, 85%, Aldrich) and water (300 ml). The yellow $VOPO_4 \cdot 2H_2O$ was recovered by hot filtration, washed with water and acetone and dried in air ($110^\circ C$, 16 h). $VOPO_4 \cdot 2H_2O$ (8 g) was refluxed in isobutanol (160 ml) for 21 h. The blue solid was recovered by hot filtration, washed with isobutanol (200 ml) and ethanol (250 ml), dried in air ($110^\circ C$, 2 h) and refluxed in water (10 ml g^{-1}) for 3 h, filtered hot, washed with water and dried in air ($120^\circ C$, 16 h).

Characterisation methods

Powder X-ray diffraction was performed using an ENRAF Nonius FR590 X-ray generator with a Cu-K α source fitted with an Inel CPS 120 hemispherical detector. BET surface area measurements using nitrogen adsorption were carried out using a Micromeritics ASAP 2000 instrument. Laser Raman spectra were obtained using a Renishaw Ramascope Spectrograph fitted with a green Ar⁺ laser ($\lambda = 514.532$ nm) typically operated at 20 mW. Scanning electron microscopy (SEM) was performed using a Hitachi S-2460N SEM operating at an accelerating voltage of 25 kV.

Catalyst testing

Acetone reactions. Acetone (Fischer, 99%) was fed using a calibrated syringe pump to a vaporiser. The acetone vapour was mixed with argon as a carrier gas (30 ml min^{-1}) and fed to a laboratory microreactor and reacted with the heated catalyst (0.5 g). The acetone flow rate was 0.2 g (acetone) g^{-1} (catalyst) h^{-1} . The products were analysed using on-line gas chromatography. When acetone was reacted with formaldehyde, trioxane (Aldrich, 99%) was used as a source of formaldehyde. In this case, a mixture of acetone and trioxane was fed *via* a calibrated syringe pump, together with argon (30 ml min^{-1}), to a cracker at $380^\circ C$ where trioxane decomposed to formaldehyde. The acetone : formaldehyde molar ratio was 5 : 1. The acetone : formaldehyde vapour was cooled to the desired reaction temperature and reacted with a catalyst (0.5 g) in a

standard laboratory microreactor. The combined acetone : formaldehyde feed rate was maintained at 0.2 g g^{-1} (catalyst) h^{-1} . The products were analysed using on-line gas chromatography and the carbon mass balance was typically $97 \pm 5\%$ depending on the level of coke deposition.

Reaction of 2-methylbut-3-yn-2-ol (MBOH). MBOH (Aldrich) was fed using a calibrated syringe pump at a rate of 2.5 g h^{-1} to a vaporiser and mixed with helium (15 ml min^{-1}). The reactants were fed *via* heated lines to a laboratory microreactor containing heated catalyst (1.0 g) diluted with glass beads (Sigma, 710–1180 μm). The products were collected following cooling of the exit gases and analysed using gas chromatography and the carbon mass balance was typically $97 \pm 5\%$ depending on the level of coke deposition.

Results and discussion

Alcohol condensations of acetone over vanadium phosphate catalysts

$VOHPO_4 \cdot 0.5H_2O$ was prepared according to the VPO method. The material was then heated in helium at $750^\circ C$ for 8 h to form $(VO)_2P_2O_7$, which was confirmed by X-ray powder diffraction, laser Raman spectroscopy and electron microscopy and the material gave identical characterisation data to that we have published previously for this preparation method.³⁴ Acetone conversion was then investigated over the sample of $(VO)_2P_2O_7$ and the results are shown in Fig. 1. Below $300^\circ C$, there was very little conversion of acetone. However, above $300^\circ C$ acetone was converted primarily to isophorone and selectivities $>90\%$ were observed, but at $300^\circ C$ only isophorone was observed. Traces of mesityl oxide and light hydrocarbons, *e.g.* isobutane and isobutene, together with carbon monoxide, were also observed.

Slow deactivation of the catalyst was observed at $400^\circ C$ but, during this deactivation, the selectivity did change markedly, indicating the deactivation is due primarily to the loss of active surface/active site. Characterisation of the catalysts after reaction using powder X-ray diffraction and laser Raman spectroscopy confirmed that the material was unchanged following the reaction and was still well crystalline $(VO)_2P_2O_7$. However, analysis revealed that 2–3 wt.% carbon was present on the used catalyst. This carbonaceous material was probably the result of further reactions of acetone with the reaction products on the catalyst surface. Hence, the deactivation is considered to be the result of the surface being deactivated by reaction products. To examine this, the catalyst that had been reacted with acetone at $400^\circ C$ was treated in flowing air (30 ml

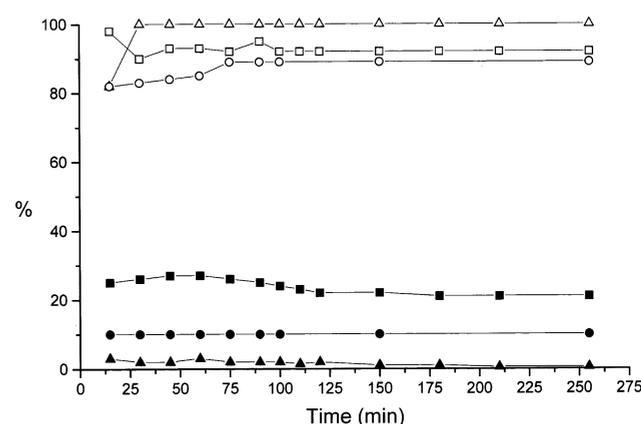


Fig. 1 Aldol condensation of acetone over $(VO)_2P_2O_7$. Key: ■ $400^\circ C$; ▲ $300^\circ C$; ● $400^\circ C$ reactivated; closed symbols = acetone conversion; open symbols = isophorone selectivity.

min^{-1}) for 16 h at 500°C , conditions which are known to remove the carbonaceous material. Analysis confirmed that the coke had been removed but laser Raman spectroscopy indicated that a small amount of oxidation had occurred and some VOPO_4 phases were also formed. The material was subsequently heated in helium at 750°C for 8 h to reform with crystalline $(\text{VO})_2\text{P}_2\text{O}_7$. When the reactivated $(\text{VO})_2\text{P}_2\text{O}_7$ was used as a catalyst for acetone conversion (Fig. 1), a lower conversion was observed compared to fresh $(\text{VO})_2\text{P}_2\text{O}_7$, however, the selectivity was very similar to that of the first material and isophorone was observed as the only major product.

$\alpha_1\text{-VOPO}_4$ was prepared and used as a catalyst for acetone conversion (Fig. 2). $\alpha_1\text{-VOPO}_4$ was found to be significantly more active for acetone conversion when compared with $(\text{VO})_2\text{P}_2\text{O}_7$, and conversions were observed initially at 150°C . However, the catalyst was not selective for isophorone formation and only traces ($<5\%$) of mesityl oxide were observed. The major products were hydrocarbons and carbon oxides. $\alpha_1\text{-VOPO}_4$ deactivated rapidly under these reaction conditions and the used catalysts were found to contain typically ≥ 5 wt.% carbon. X-ray powder diffraction and laser Raman spectroscopy confirmed that the material remained $\alpha_1\text{-VOPO}_4$ following reaction and, consequently, the rapid deactivation is again considered to be due to polymerisation of acetone with reaction products on the catalyst surface. The catalyst samples were reactivated by heating in air (30 ml min^{-1} , 16 h, 500°C) and were then re-used as catalysts for acetone conversion (Fig. 2). In this case, the catalyst activity was almost restored to the original levels, and the reaction products were also identical to those of the fresh catalysts.

A sample of a vanadium phosphate catalyst (V : P = 1 : 1.06) was prepared according to the method of Ai³⁵⁻³⁷ and calcined in air (450°C , 1.5 ml min^{-1} , 6 h) as described by Ai^{36,37} in the previous studies in which vanadium phosphorus catalysts have been investigated as catalysts for the aldol condensation of acetone. Powder X-ray diffraction of this material showed that the material comprised a mixture of phases, mainly $(\text{VO})_2\text{P}_2\text{O}_7$ and $\delta\text{-VOPO}_4$, together with amorphous material. Acetone conversion was investigated over this material (Fig. 3) and, at 400°C , acetone was converted mainly to hydrocarbons (isobutane and isobutene), and some carbon oxide. In addition, ca. 20% mesityl oxide was formed initially. The catalyst rapidly deactivated and was found to contain ca. 5% carbon following reaction.

In a subsequent set of experiments, well crystalline $(\text{VO})_2\text{P}_2\text{O}_7$, prepared using the VPO method as described earlier, was oxidised in flowing air in the reactor (30 ml min^{-1}) at 400°C for a range of times (0.5, 1, 2 and 24 h). Following

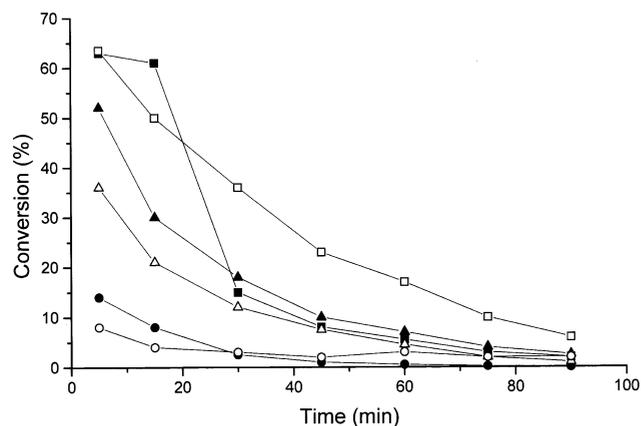


Fig. 2 Aldol condensation of acetone over $\alpha_1\text{-VOPO}_4$. Key: ■ 400°C ; ▲ 300°C ; ● 150°C ; closed symbols = fresh catalyst; open symbols = reactivated catalyst.

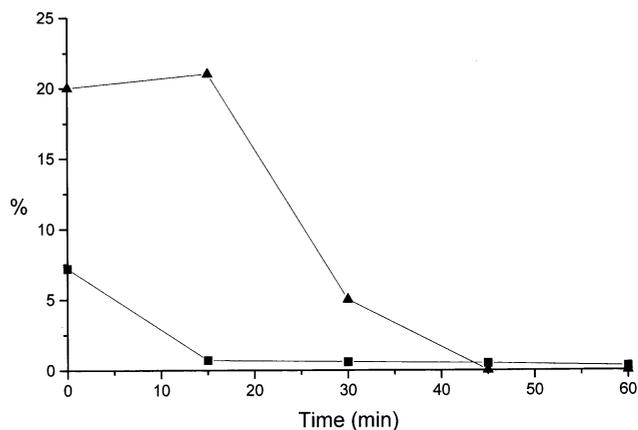


Fig. 3 Aldol condensation of acetone over vanadium phosphate (V : P = 1 : 1.06) at 400°C . Key: ■ acetone conversion; ▲ mesityl oxide selectivity.

this oxidation treatment, the catalyst was investigated for acetone conversion at 400°C and the results are given in Fig. 4. It is apparent that even a short oxidation treatment (0.5 h) of the vanadium phosphate significantly increases the catalyst activity for this reaction, when compared with the untreated $(\text{VO})_2\text{P}_2\text{O}_7$ (Fig. 1). Longer oxidation treatments of $(\text{VO})_2\text{P}_2\text{O}_7$ give more active catalysts. However, all the oxidised catalysts show a marked deactivation due to deposition of carbonaceous materials. All oxidised catalysts are initially selective only for the formation of hydrocarbons and carbon monoxide, as noted for $\alpha_1\text{-VOPO}_4$ (Fig. 2). However, as the catalysts deactivate, mesityl oxide and, subsequently,

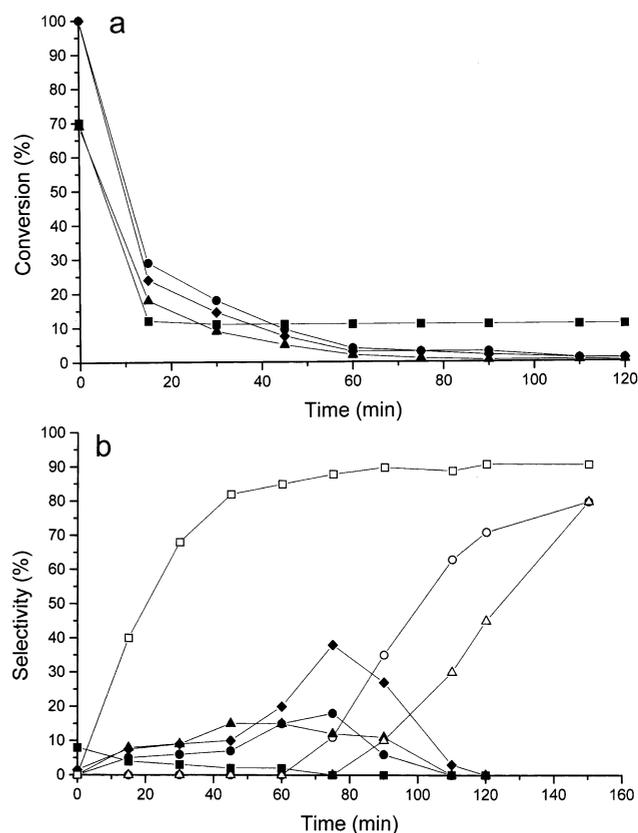


Fig. 4 Aldol condensation of acetone over $(\text{VO})_2\text{P}_2\text{O}_7$ oxidised in air at 400°C for different times, (a) acetone conversion; (b) selectivity. Key: ■ 0.5 h; ▲ 1.0 h; ● 2.0 h; ◆ 24 h. For selectivity, open symbols = isophorone selectivity; closed symbols = mesityl oxide.

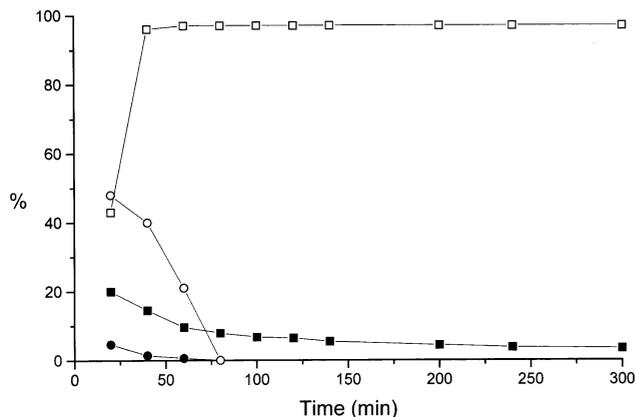


Fig. 5 Aldol condensation of acetone and formaldehyde over vanadium phosphates at 400 °C. Key: ■ $(\text{VO})_2\text{P}_2\text{O}_7$; ● $\alpha_1\text{-VOPO}_4$; closed symbols = methyl vinyl ketone selectivity.

isophorone are observed. At long reaction times, the isophorone selectivity returns to a level similar to that observed for the untreated $(\text{VO})_2\text{P}_2\text{O}_7$ for the samples oxidised for a short time (≤ 2 h). This is not observed with the catalyst subjected to the 24 h oxidation pre-treatment.

In a subsequent experiment, a sample of well crystalline $(\text{VO})_2\text{P}_2\text{O}_7$ derived from the VPO method, as described earlier, was used as a catalyst for the reaction of acetone with formaldehyde (acetone : formaldehyde = 5 : 1 mol ratio) and the results are shown in Fig. 5 for the reaction at 400 °C and, at this temperature, the formaldehyde conversion was 100%. Similar trends in conversion and selectivity are observed at 150 °C and 300 °C, although the initial acetone conversions are lower, 11% and 9% respectively. For all reaction conditions, methyl vinyl ketone was formed, almost exclusively. Interestingly, no isophorone or mesityl oxide were observed when formaldehyde was co-fed with acetone. As observed with the reaction of acetone alone over $(\text{VO})_2\text{P}_2\text{O}_7$, the catalyst activity decreased with time-on-stream. However, the deactivation rate was more marked when formaldehyde was present. Analysis of the catalyst following the reaction confirmed that carbonaceous material was formed (*ca.* 5 wt.%). Since the formaldehyde conversion remained at 100% throughout the timescale of the experiment, whereas the acetone conversion and yield of methyl vinyl ketone decreased, it is considered that the enhanced deposition of carbonaceous material results mainly from the self condensation of formaldehyde on the catalyst surface. Indeed, experiments in which formaldehyde was reacted in the

absence of acetone resulted in extremely rapid deactivation and no volatile reaction products were observed. The acetone–formaldehyde reaction was also investigated over $\alpha_1\text{-VOPO}_4$ and the results at 400 °C are also shown in Fig. 5. $\alpha_1\text{-VOPO}_4$ was much less active for this reaction, when compared with $(\text{VO})_2\text{P}_2\text{O}_7$, but methyl vinyl ketone was observed initially as the major product.

Catalyst characterisation

It is apparent that the oxidation of $(\text{VO})_2\text{P}_2\text{O}_7$, derived from the VPO method, at 400 °C significantly affected the catalyst activity and selectivity for the reaction of acetone to isophorone. The $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, $(\text{VO})_2\text{P}_2\text{O}_7$ and $(\text{VO})_2\text{P}_2\text{O}_7$ treated with air were characterised using scanning electron microscopy, powder X-ray diffraction and laser Raman spectroscopy and the results are shown in Fig. 6–8. It is apparent that the morphology of the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ precursor is retained in the $(\text{VO})_2\text{P}_2\text{O}_7$ prepared by heating the precursor in helium at 750 °C. Oxidation of the sample also does not change the morphology of the material. In addition, oxidation of the VPO-derived $(\text{VO})_2\text{P}_2\text{O}_7$ does not significantly affect the bulk structure of the material as there are no significant changes in the powder X-ray diffraction pattern or the laser Raman spectrum. In a previous study, we have shown⁴² that $(\text{VO})_2\text{P}_2\text{O}_7$ derived from the VPO method is significantly more resistant towards oxidation when compared with VPA- and VPD-derived $(\text{VO})_2\text{P}_2\text{O}_7$. It is, therefore, apparent, that the oxidation treatment must just affect the surface of the catalyst. Indeed, Volta and co-workers^{43,44} have completed a detailed study of the effects of oxidation of $(\text{VO})_2\text{P}_2\text{O}_7$ derived from the VPO preparation method. Using a range of techniques, principally UV–vis, Raman and XPS spectroscopy, they showed that oxidation of the surface occurred and $\alpha_1\text{-VOPO}_4$ was formed. Previous studies^{45,46} also confirmed that the surface of vanadium phosphate crystallites can be readily oxidised by short exposure to oxygen at elevated temperatures.

The effect of surface oxidation is further confirmed by the changes in selectivity observed for the oxidised samples for the reaction of acetone (Fig. 4). Initially, only hydrocarbons (*i.e.* isobutane and isobutene) were observed and these products are typical of $\alpha_1\text{-VOPO}_4$, a V^{5+} vanadium phosphate (Fig. 2). However, as the catalyst deactivates, the selectivity gradually becomes that expected for untreated $(\text{VO})_2\text{P}_2\text{O}_7$ and isophorone is observed as the major product. This indicates that the effect of the oxidation treatments for times ≤ 2 h are short lived for the acetone conversion reaction.

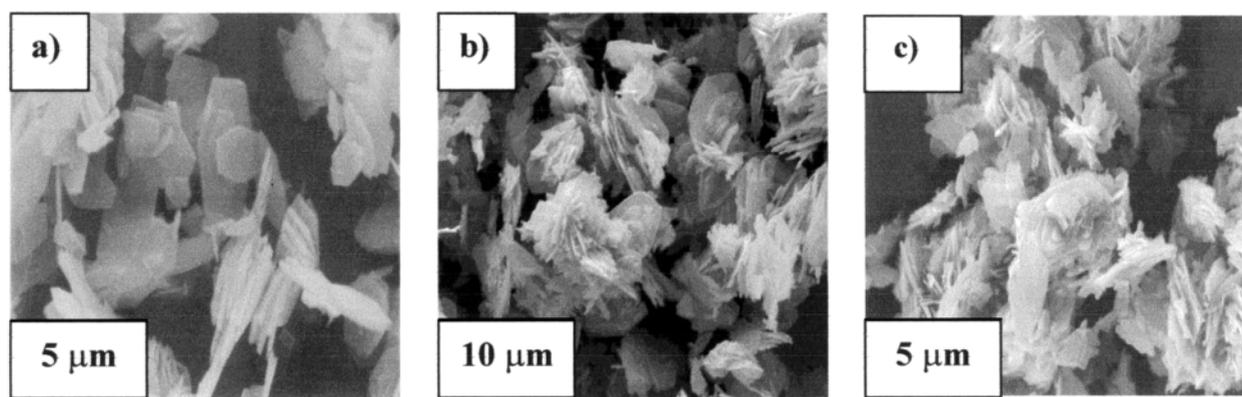


Fig. 6 Scanning electron micrographs of vanadium phosphates prepared using VPO method, (a) $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$; (b) $(\text{VO})_2\text{P}_2\text{O}_7$; (c) $(\text{VO})_2\text{P}_2\text{O}_7$ oxidised in air for 2 h at 400 °C.

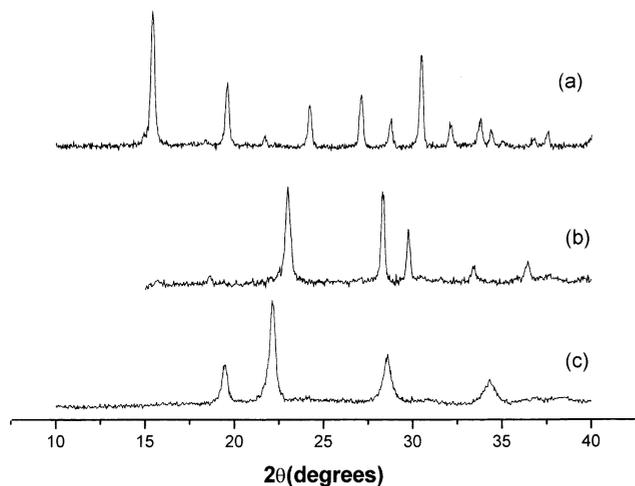


Fig. 7 Powder X-ray diffraction patterns of vanadium phosphates prepared using the VPO method, (a) $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$; (b) $(\text{VO})_2\text{P}_2\text{O}_7$; (c) $(\text{VO})_2\text{P}_2\text{O}_7$ oxidised in air for 2 h at 400°C .

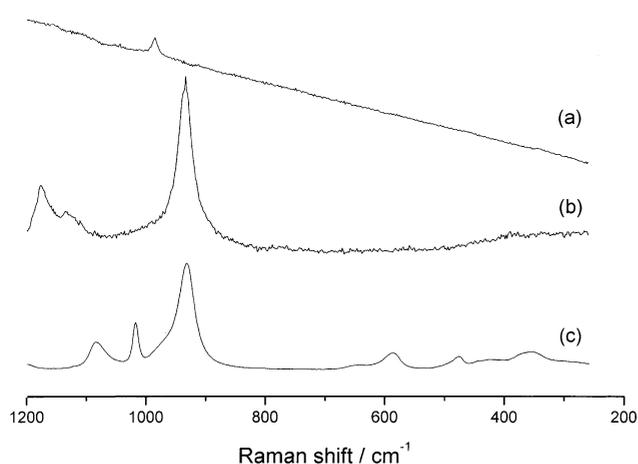
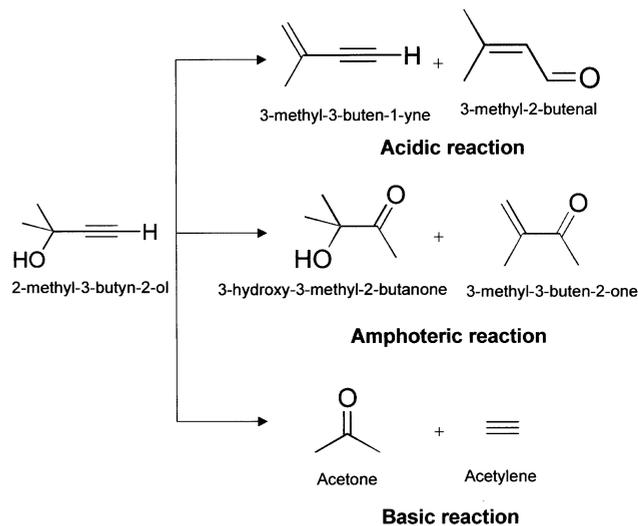


Fig. 8 Laser Raman spectra of vanadium phosphates prepared using the VPO method, (a) $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$; (b) $(\text{VO})_2\text{P}_2\text{O}_7$; (c) $(\text{VO})_2\text{P}_2\text{O}_7$ oxidised in air for 2 h at 400°C .

Characterisation of the acid–base nature of vanadium phosphate catalysts using the reaction of 2-methyl-but-3-yn-2-ol (MBOH)

Lauron-Pernot *et al.*³⁹ have shown that the reactions with MBOH can be used to characterise the acid–base sites on catalyst surfaces (Scheme 1). Interestingly, although a number of acidic and basic catalysts have been characterised using this method, vanadium phosphates have not been investigated to date. Consequently, in this study, we present the data for VPA-, VPO- and VPD-derived vanadium phosphates. In addition, the reaction profiles for the reaction of MBOH with time-on-stream has not been discussed in previous papers and this aspect is addressed in this study.

MBOH was reacted at 180°C over the three $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ samples prepared using the VPA, VPO and VPD methods and the results are shown in Fig. 9. In addition, the results for the reaction of MBOH at 180°C $(\text{VO})_2\text{P}_2\text{O}_7$ derived from $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ on heating in helium at 750°C for 8 h, are also shown in Fig. 9. Only the products characteristic of the acid catalysed decomposition of MBOH are observed. For all samples, a rapid deactivation in the MBOH conversion was observed, but this did not affect the product selectivity. Analysis of the samples following reaction confirmed that the catalyst structure, composition and morphology were unchanged for the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ and $(\text{VO})_2\text{P}_2\text{O}_7$ materials,



Scheme 1

this indicates that water formed during the dehydration of MBOH on the acidic sites has no effect on the catalyst structure during the short timescale of the experiments. It is known that, during the selective oxidation of *n*-butane to maleic anhydride, water is also formed and the catalyst structure is relatively resistant to this product.^{30–33} However, the catalysts all contained carbon (*ca.* 1–2 wt.%). Since the catalyst selectivity did not change during the deactivation, it is concluded that the deactivation is due to the deposition of carbonaceous material on the surface of the vanadium phosphate. This is probably due to acid catalysed polymerisation of the MBOH. It was subsequently shown that the carbon could be readily removed by an oxidation treatment. A sample of $(\text{VO})_2\text{P}_2\text{O}_7$ prepared using the VPO method, and deactivated by reaction with MBOH at 180°C , was oxidised in flowing air at 500°C for 2 h. Following the oxidation treatment, the material was heated in helium at 750°C for 8 h to reform $(\text{VO})_2\text{P}_2\text{O}_7$, which was confirmed by powder X-ray diffraction and laser Raman spectroscopy. When this reactivated $(\text{VO})_2\text{P}_2\text{O}_7$ was reacted with MBOH, similar results to the fresh catalyst were obtained.

In a subsequent experiment, $(\text{VO})_2\text{P}_2\text{O}_7$ derived from the VPO method was oxidised in air (400°C , 30 ml min^{-1} , 2 h), and the oxidised sample was reacted with MBOH at 180°C , and the results are shown in Fig. 10. Again, a rapid deactivation is observed but, in this case, a low selectivity is observed for base-catalysed products (acetone, acetylene) together with

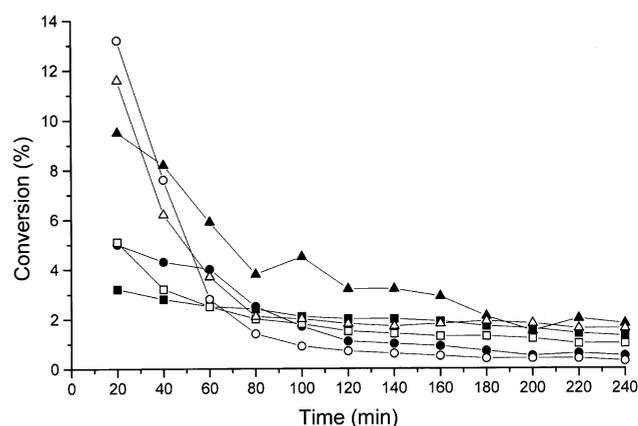


Fig. 9 Conversion of MBOH over vanadium phosphates at 180°C . Key: $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$: ■ VPA, ● VPO, ▲ VPD; $(\text{VO})_2\text{P}_2\text{O}_7$: □ VPA, ○ VPO, △ VPD.

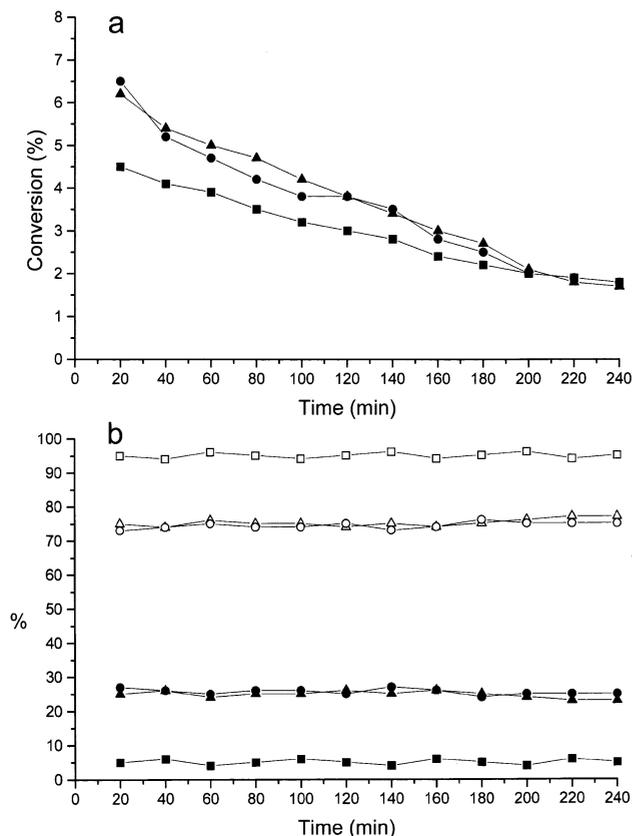


Fig. 10 Conversion of MBOH over vanadium phosphate catalysts at 180 °C, (a) conversion, (b) selectivity. Key: ■ (VO)₂P₂O₇ oxidised in air at 400 °C for 2 h; ● α_1 -VOPO₄; ▲ VOPO₄·0.5H₂O; open symbols = acid catalysed products, closed symbols = base catalysed products.

the products for the acid catalysed decomposition of MBOH. This indicates that the oxidised catalyst surface^{43,44} now contains a low concentration of basic sites, together with a higher concentration of acidic sites. These basic sites are probably associated with V⁵⁺-V⁴⁺ sites that are formed on oxidation, and are known to be present in the surface of oxidised vanadium phosphate catalysts.^{43,44,47,48}

α_1 -VOPO₄ and VOPO₄·2H₂O were reacted with MBOH at 180 °C and the results are also given in Fig. 10. Again, a rapid deactivation is observed with these V⁵⁺ vanadium phosphates. However, it is apparent that α_1 -VOPO₄ gives a significant level of product of base catalysed decomposition of MBOH, in addition to the products of the acid catalysed reaction.

From these studies, it is clear that oxidised vanadium phosphates have surfaces that comprise both acidic and basic sites; whereas V⁴⁺ vanadium phosphates (*i.e.* well crystalline VOHPO₄·0.5H₂O, (VO)₂P₂O₇) exhibit only acidic sites. Vanadium phosphate catalysts are well known for the oxidation of *n*-butane to maleic anhydride^{30–34} and, in most studies, the catalysts are stabilised and reacted in 1.5% *n*-butane in air.³³ Under these oxidising conditions, it is known that the surface becomes partially oxidised^{30,43,44,47} and, hence, we have studied the reaction of MBOH over vanadium phosphate catalysts activated in this way. Three samples of VOHPO₄·0.5H₂O prepared using the VPA, VPO and VPD methods, were pre-treated in 1.5% *n*-butane in air at 400 °C for 72 h. Under these conditions, it is known^{34,49} that VOHPO₄·0.5H₂O transforms to (VO)₂P₂O₇ and VOPO₄ phases, although the intrinsic activities (mol MA m⁻² h⁻¹) are similar for the three catalysts.⁵⁰ The activated materials were then investigated for the reaction of MBOH at 180 °C and the results are given in Fig. 11. Again, the catalysts all deactivate rapidly, but the products of both acid catalysed and base catalysed reactions are observed. For

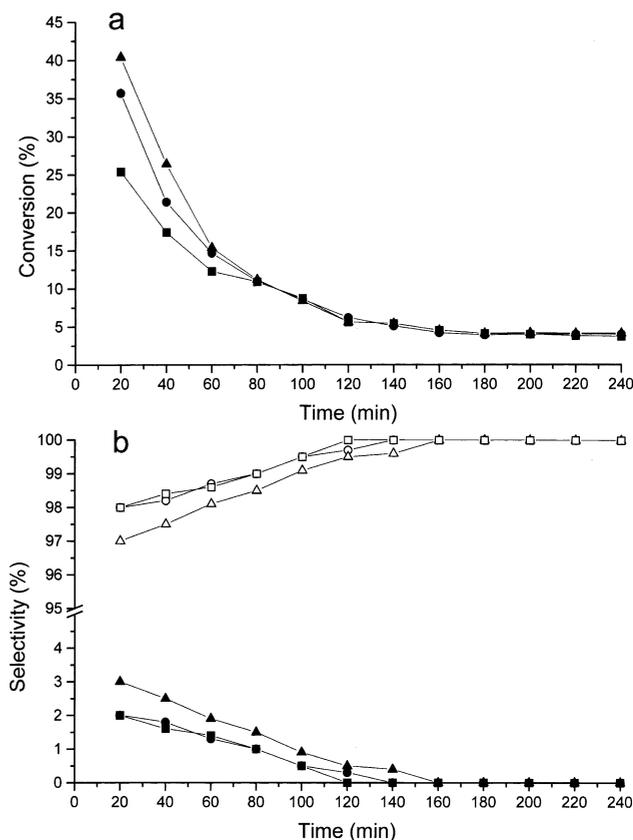


Fig. 11 Conversion of MBOH over vanadium phosphate catalysts at 180 °C pre-activated by heating in 1.5% butane/air, 400 °C, 72 h. Key: ■ VPA; ● VPO; ▲ VPD; open symbols = acid catalysed products; closed symbols = base catalysed products.

comparative purposes, the vanadium phosphate catalyst prepared by the method of Ai,^{35–37} as described earlier, was also reacted with MBOH and the results are also given in Fig. 10. Again, the products of basic, as well as acid, decomposition of MBOH are observed together with rapid deactivation.

Comments on reactivity of acid–base sites on vanadium phosphates

The reaction of MBOH over the vanadium phosphates reveals very interesting differences for catalysts that are selective for the oxidation of *n*-butane or aldol condensation reactions of acetone. For the aldol condensation of acetone to form isophorone or the reaction of acetone with formaldehyde to form methyl vinyl ketone, (VO)₂P₂O₇ is the most selective catalyst. Indeed, oxidation of (VO)₂P₂O₇ significantly decreases the selectivity initially. (VO)₂P₂O₇, when characterised by the reaction of MBOH, is found to comprise only acid sites. In contrast, α_1 -VOPO₄ or material prepared by the oxidation of (VO)₂P₂O₇, also comprise base sites in combination with the acid sites. It is clear that the basic sites are introduced on oxidation of (VO)₂P₂O₇, but these sites are totally unselective for the aldol condensation reactions. Hence, for aldol condensation reactions over vanadium phosphate catalysts, acid sites are the preferred active site. This is in contrast to the earlier studies of Ai^{36,37} in which it was concluded that a combination of acid/base sites was important for these reactions. It is interesting to comment further on the origin of the hydrocarbon products obtained from α_1 -VOPO₄ and oxidised (VO)₂P₂O₇ catalysts. Previously, we have shown⁵¹ that acetone can be converted to isobutane and isobutene, together with the formation of carbon oxides, over the acidic zeolite H- β at 400 °C. In this case, we showed that the acetone was converted

initially to phorone and isophorone, and this was the precursor for the formation of butene and isobutene. It is possible that formation of hydrocarbons from acetone over the vanadium phosphate occurs *via* a similar reaction pathway.

As stated earlier, the partial oxidation of *n*-butane to maleic anhydride is known to require vanadium phosphate catalysts that are partially oxidised.^{30–34} For example, it has been shown that oxidation of $(\text{VO})_2\text{P}_2\text{O}_7$ with air at 400 °C, in a similar manner to that carried out in this study, significantly increases the selectivity to maleic anhydride when these catalysts are subsequently studied for *n*-butane oxidation.⁴³ In addition, we have shown that combinations of α_1 - VOPO_4 and $(\text{VO})_2\text{P}_2\text{O}_7$ can give improved yields of maleic anhydride in this reaction.⁵² The *in situ* activation of $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ in *n*-butane/air transforms the material to a mixture of V^{4+} and V^{5+} phases and, during this process, the selectivity to maleic anhydride is significantly increased.⁴⁹ The reaction of MBOH over these oxidised vanadium phosphates has shown that basic sites are present, together with acidic sites, and it can be concluded that the presence of these basic sites appears to be crucial with respect to the formation of maleic anhydride on these surfaces. This is probably related to the enhanced adsorption of *n*-butane at the active site of the catalyst. On electronic grounds, V^{5+} would be expected to be more acidic than V^{4+} since it has a higher electron affinity and, consequently, a higher Lewis acidity. The basic sites must arise from combination of V^{4+} and V^{5+} and are probably associated with defect sites formed on oxidation.⁵³

Cremer–Constable relation for the reactions of MBOH

In the preceding studies of MBOH decomposition on acidic and basic materials,^{38–40} the activation energy for these reactions has not been discussed. In the present study, the activation energies were determined from the initial reaction rates for the reaction of MBOH over catalysts for a range of temperatures (160–200 °C). It is important that the initial rates are used, since the catalysts rapidly deactivate during the reaction, even at lower reaction temperatures. The activation energies for the vanadium phosphates are found to be in the range 80–200 kJ mol^{-1} . Interestingly, the plot of $\ln A$ versus the activation energy gives a linear plot (Fig. 12) for all the $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, $(\text{VO})_2\text{P}_2\text{O}_7$ and the oxidised samples, even though, in some cases, both acid- and base-catalysed reactions are observed. In view of this, the activation energies and pre-

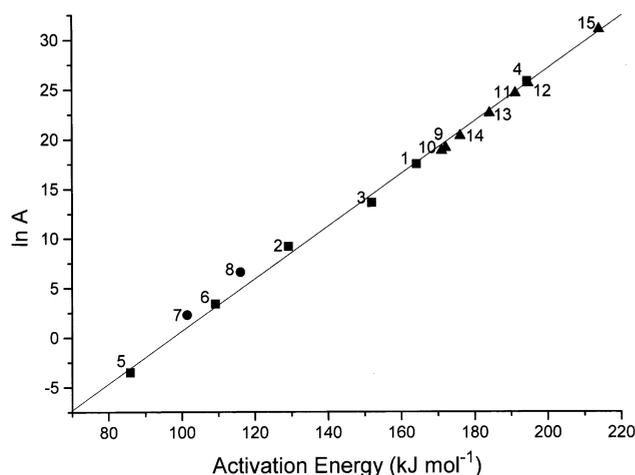


Fig. 12 Cremer–Constable plot for the reaction of MBOH over oxide and phosphate catalysts. Key: 1. $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$ VPO; 2. $(\text{VO})_2\text{P}_2\text{O}_7$, VPO; 3. $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, VPA; 4. $(\text{VO})_2\text{P}_2\text{O}_7$, VPA; 5. $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, VPD; 6. $(\text{VO})_2\text{P}_2\text{O}_7$, VPD; 7. MgO ex carbonate; 8. MgO ex hydroxide; 9. La_2O_3 ; 10. CeO_2 ; 11. Nd_2O_3 ; 12. Gd_2O_3 ; 13. Dy_2O_3 ; 14. Ho_2O_3 ; 15. Er_2O_3 .

experimental factors were determined for a range of oxides (MgO and lanthanides) which are known to give only the products associated with base-catalysed decomposition of MBOH.⁵⁴ These additional data were all found to agree with the linear plot for the vanadium phosphates (Fig. 12). The linear relationship between $\ln A$ and E_{act} is known as a Cremer–Constable relation and is sometimes referred to as a compensation effect. The Cremer–Constable relation has been the subject of intense debate since the effect was first observed in 1925⁵⁵ and the literature has recently been comprehensively reviewed by Bond.⁵⁶ The effect has been observed for the same reaction (*i.e.* conversion of a single reactant to a specific product) over a range of catalysts (*e.g.* the hydrogenolysis of ethane over various silica-supported metals,^{56–59} or the hydrogenation of CO_2 over supported metal catalysts⁵⁶). The effect has also been observed for the groups of reactants over a single catalyst, *e.g.* the hydrogenolysis of alkanes over Pt/SiO_2 .^{56,60,61} However, this is the first observation of the relationship for the more complex catalysed processes of different reactions of a substrate over a broad range of oxide and phosphate catalysts. Bond⁵⁶ indicates that a large number of explanations have been put forward to explain the origin of the Cremer–Constable relation. In the present case, the common step for the acid and base catalysed reactions is the adsorption of the MBOH molecule at the active sites. The adsorption of the large MBOH molecule probably dominates the energetics of the overall catalysed process. This is consistent with the observation of Bond, and indicates that care needs to be exercised when using the reactions of complex probe molecules to characterise heterogeneous catalyst. Indeed, the use of smaller, less complex molecules may be preferred since, for these molecules, the adsorption enthalpy may not dominate the apparent activation energy of the reactions.

Conclusion

Vanadium phosphate oxide catalysts based on $(\text{VO})_2\text{P}_2\text{O}_7$ and α_1 - VOPO_4 have been investigated for aldol condensation of acetone. In addition, the reaction of MBOH has been used to characterise the nature of the acid–base properties of the catalysts. Catalysts containing only acid sites, *i.e.* the V^{4+} phases $(\text{VO})_2\text{P}_2\text{O}_7$ and $\text{VOHPO}_4 \cdot 0.5\text{H}_2\text{O}$, were found to be selective for the formation of isophorone from acetone alone and methyl vinyl ketone from the reaction of acetone and formaldehyde. Catalysts containing V^{5+} phases exhibit basic as well as acidic sites and are not selective to these products and only form hydrocarbons. However, for the aldol condensation of acetone and the decomposition of MBOH, the catalyst activity is short lived and deactivation is observed due to coke formation on the catalyst surface. Catalyst reactivity can be readily restored by an oxidation treatment. The results observed have been used to consider the nature of the acid–base sites in the selective conversion of *n*-butane to maleic anhydride and, in this case, it is considered that a mixture of basic and acidic sites is required to observe high selectivity. Finally, for the reaction of MBOH, the data are found to give a linear relationship for a Cremer–Constable plot. It is concluded that this is caused by the high heat of adsorption of MBOH dominating the energetics of the overall catalysed reaction. This suggests that smaller, less complex, molecules may be preferred for the characterisation of acid–base properties.

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