

Infrared Study of the Adsorption of But-1-ene, Buta-1,3-diene, Furan and Maleic Anhydride on the Surface of Anhydrous Vanadyl Pyrophosphate

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Brønsted-acidic hydroxy groups on the surface of vanadyl pyrophosphate act as catalytically active sites for the isomerisation of but-1-ene to but-2-enes. Progressive poisoning of the reaction is attributed to the formation of alkyl species, possibly alkoxy groups, on the $(VO)_2P_2O_7$ surface. Adsorbed alkyl groups also result from buta-1,3-diene adsorption. Furan adsorbs on $(VO)_2P_2O_7$ through coordinative interactions with Lewis-acidic surface sites. The presence of oxygen promotes the oxidation of furan to maleic anhydride.

The importance has been established of vanadyl pyrophosphate as a component of vanadium–phosphorus mixed-oxide catalysts for the oxidation of butane or but-1-ene to maleic anhydride.^{1–3} The surface character of $(VO)_2P_2O_7$ has been partly established by infrared studies of the adsorption of water, pyridine, CO, CO₂, acetic acid and acetic anhydride.^{4,5} The present paper reports an infrared study of the adsorption on $(VO)_2P_2O_7$ of the species (butane, but-1-ene, buta-1,3-diene, furan and maleic anhydride) involved as reactants, intermediates or product in the oxidation reactions.

Experimental

Vanadyl pyrophosphate (surface area 11 m² g⁻¹) was prepared by reacting orthophosphoric acid and vanadium pentoxide in strongly acidic solution and decomposing the reaction product by thermal activation in vacuum. The purity of the final product was confirmed by infrared spectroscopy and X-ray powder diffraction.¹ Compressed (3.3 ton) self-supporting discs (25 mm diameter) of $(VO)_2P_2O_7$ (*ca.* 55 mg) were mounted in an evacuable infrared cell with fluorite windows and an external furnace and were heated at 673 K (17 h) in vacuum before the admission of adsorbate gases. Spectra of discs at *ca.* 300 K were recorded using a Perkin-Elmer 580A spectrophotometer. High-purity commercial samples of butane, but-1-ene, buta-1,3-diene and furan were freed from permanent gases by a series of freeze–thaw cycles. Maleic anhydride was purified by sublimation under reduced pressure to remove maleic acid.

Results

Contact between butane vapour (1.3 kN m⁻²) and $(VO)_2P_2O_7$ at temperatures in the range 293–723 K gave no detectable change in the infrared spectrum of the gas phase and no infrared bands due to adsorbed species. However, at elevated temperatures the disc turned black, implying that carbon deposition had occurred.

Exposure of $(VO)_2P_2O_7$ at the ambient temperature in the sample beam of the spectrophotometer (*ca.* 300 K) to but-1-ene (2.5 kN m⁻²) gave spectra [fig. 1(b)] in which the observed bands could primarily be attributed to but-1-ene in the gas phase. The spectra did not vary with time but removal of the gas phase by evacuation left residual

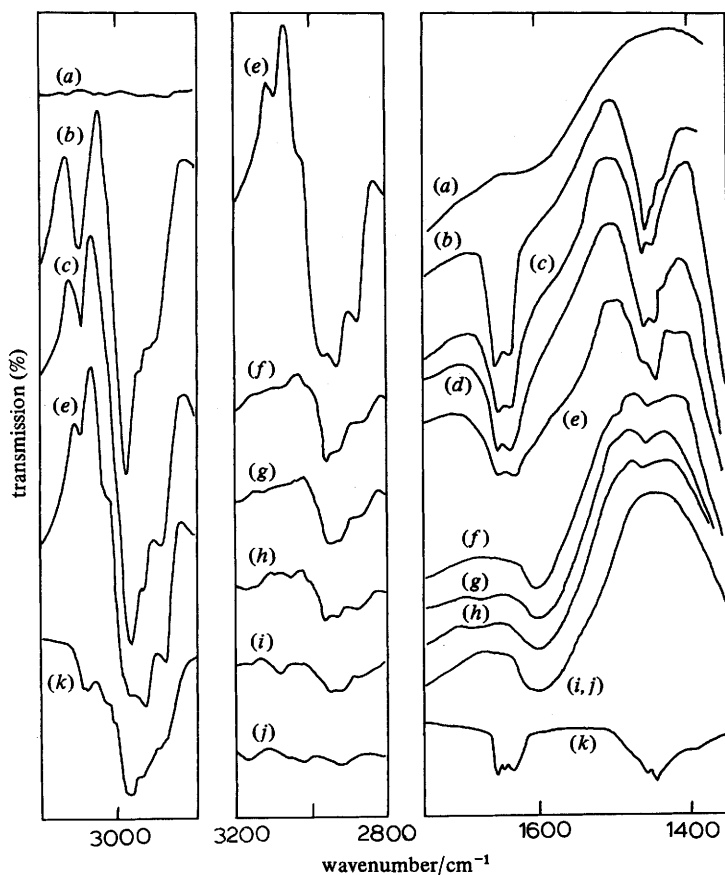


Fig. 1. Spectra of $(VO)_2P_2O_7$, after (a) evacuation (17 h, 673 K), (b) contact with but-1-ene (2.5 kN m^{-2}) at ca. 300 K, (c)–(e) heat treatment (473 K) in but-1-ene (2.5 kN m^{-2}) for (c) 1 h, (d) 3 h, (e) 15 h, (f)–(j) subsequent evacuation (1 h) at (f) ca. 300 K, (g) 373 K (h) 473 K, (i) 553 K and (j) 623 K. (k) Spectrum of vapour phase after 15 h contact between but-1-ene (2.5 kN m^{-2}) and $(VO)_2P_2O_7$, at 473 K.

bands at 2960, 2930 and 2880 cm^{-1} which are assigned to vibrations of saturated hydrocarbon species adsorbed on the $(VO)_2P_2O_7$ surface. Contact between but-1-ene and $(VO)_2P_2O_7$ at 473 K resulted in changes in the spectrum as a function of time over several hours [fig. 1(c)–(e)]. A dominant factor contributing to the changes was the slow $(VO)_2P_2O_7$ catalysed isomerisation reaction of but-1-ene to a mixture of but-1-ene and *cis*- and *trans*-but-2-enes.⁶ The isomerisation reaction was separately monitored by recording spectra of the gas phase alone and it was confirmed that the spectra of $(VO)_2P_2O_7$ in contact with gas largely reflected the changing composition of the gaseous mixture. However, removal of the gas phase revealed residual bands at 2960, 2930(sh), 2880(sh), 1600 and 1465 cm^{-1} [fig. 1(f)]. The species responsible for these bands were resistant to removal by evacuation at elevated temperatures, suggesting they were chemisorbed at the $(VO)_2P_2O_7$ surface [fig. 1(g) and (h)]. The maximum at 1600 cm^{-1} was still present in spectra after heat treatment at 623 K, by which temperature the other four bands, ascribed to saturated hydrocarbon groups, had disappeared [fig. 1(j)]. A weak band in spectra at 3080 cm^{-1} after heat treatment at 553 K [fig. 1(i)] suggested that partial decomposition of chemisorbed alkyl species to adsorbed alkenyl groups preceded desorption.

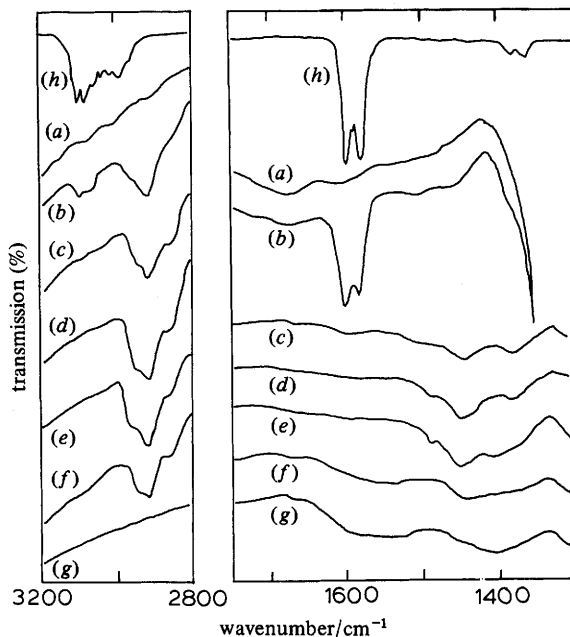


Fig. 2. Spectra of $(\text{VO})_2\text{P}_2\text{O}_7$ after (a) evacuation (17 h, 673 K), (b) contact with buta-1,3-diene (0.93 kN m^{-2}) at *ca.* 300 K, (c)–(g) subsequent evacuation at (c) *ca.* 300 K (1 h) (d) *ca.* 293 K (5 h), (e) 373 K (1 h), (f) 473 K (1 h) and (g) 673 K (1 h). (h) Spectrum of buta-1,3-diene vapour. Spectra (c)–(g) are presented after subtraction of the baseline (a).

The isomerisation reaction of but-1-ene over $(\text{VO})_2\text{P}_2\text{O}_7$ was briefly investigated by g.l.c. analyses as a function of time of the gas phase in contact with powdered $(\text{VO})_2\text{P}_2\text{O}_7$ at 423 K. The initial rate of isomerisation, $-\text{d}(\text{but-1-ene})/\text{d}t$, over 0.5 g of $(\text{VO})_2\text{P}_2\text{O}_7$ was $1.26 \times 10^{-7} \text{ mol s}^{-1}$ at a but-1-ene pressure of 5.3 kN m^{-2} . The product contained more *cis*-but-2-ene than *trans*-but-2-ene [ratio (*cis/trans*) = (1.35/1)] and the reaction was largely poisoned after *ca.* 25 min when the pressure of but-1-ene had fallen to 1.6 kN m^{-2} . Reaction subsequently proceeded slowly, the pressure of *cis*-but-2-ene also decreasing with time as the relative pressures of the three isomers tended towards the thermodynamic equilibrium values. The effects of preadsorbed pyridine, acetic acid and water on the activity of $(\text{VO})_2\text{P}_2\text{O}_7$ as a catalyst for but-1-ene isomerisation were tested. Exposure of $(\text{VO})_2\text{P}_2\text{O}_7$ to an excess of pyridine vapour for 30 min at 293 K followed by evacuation at 293 K (1 h) and 423 K (1 h) completely destroyed the activity of $(\text{VO})_2\text{P}_2\text{O}_7$ at 423 K. A similar experiment involving acetic acid only resulted in a 9.4% reduction in catalytic activity to $1.12 \times 10^{-7} \text{ mol s}^{-1}$. In contrast equilibration of $(\text{VO})_2\text{P}_2\text{O}_7$ with water vapour at 293 K followed by evacuation at 423 K (1 h) resulted in a 15.9% increase in activity.

Spectra of $(\text{VO})_2\text{P}_2\text{O}_7$ in contact with buta-1,3-diene [fig. 2(b)] exhibited bands characteristic of buta-1,3-diene in the gas phase [fig. 1(h)] together with additional bands in the range 2800–3000 cm^{-1} due to CH-stretching vibrations of alkyl groups. These groups were contained in adsorbed species since bands at 2950(sh), 2920 and 2860 cm^{-1} remained in spectra after removal of the gas phase [fig. 2(c)]. Weak bands in the spectra at 1450 and 1380 cm^{-1} can be assigned to deformation vibrations of alkyl groups. Adsorbed alkyl groups were not desorbed by evacuation at temperatures up to 373 K [fig. 2(e)], were partially desorbed at 473 K [fig. 2(f)] and completely desorbed at 673 K [fig. 2(g)]. Two residual broad infrared bands at 1560 and 1410 cm^{-1} suggested

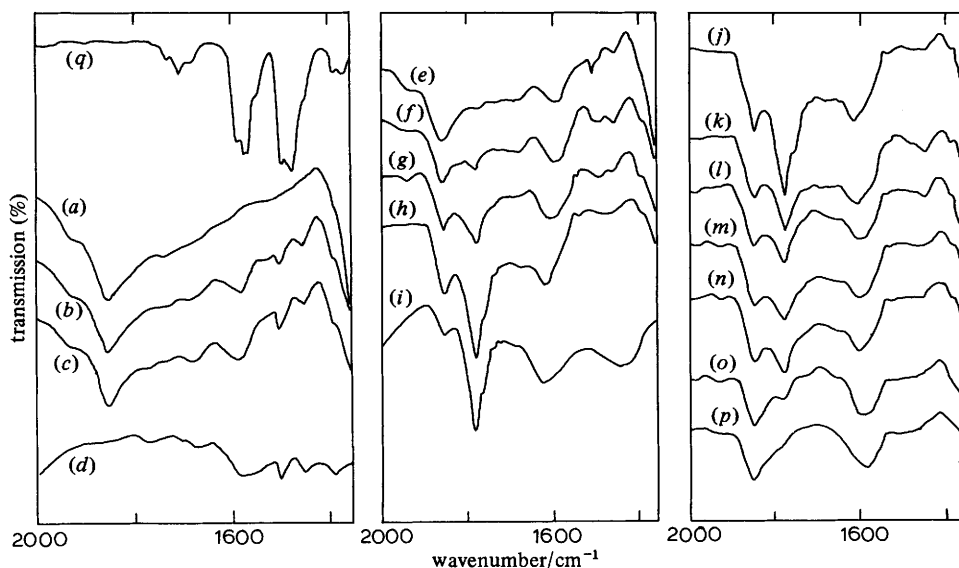


Fig. 3. Spectra of $(VO)_2P_2O_7$, after (a) evacuation (17 h, 673 K), (b) contact with furan (1.7 kN m^{-2}) and evacuation (5 min, *ca.* 300 K), (c) and (d) contact with furan (4.5 kN m^{-2}) and evacuation (5 min, *ca.* 300 K), [spectrum (d) = (c) – (a)], (e) subsequent evacuation (1 h, *ca.* 300 K), (f)–(j) subsequent heat treatment in oxygen (0.67 kN m^{-2}) at (f) 473 K (0.5 h), (g) 473 K (2 h), (h)–(j) 573 K (0.5 h) [spectrum (i) = (h) – (a)], (k)–(p) subsequent evacuation at (k) *ca.* 300 K (1 h), (l) 373 K (2 h), (m) 473 K (0.75 h), (n) 553 K (0.75 h), (o) 623 K (0.75 h) and (p) 723 K (17 h). (q) Spectrum of furan vapour.

that partial oxidation of adsorbed species to carboxylate anions had occurred at high temperature.⁵

Adsorption of furan on $(VO)_2P_2O_7$, followed by evacuation at *ca.* 300 K resulted in spectra with weak bands at 1770, 1720 and 1675 cm^{-1} and stronger bands at 1580, 1500, 1450 and 1390 cm^{-1} [fig. 3(a)–(d)]. Comparison with spectra of furan vapour [fig. 3(q)] and liquid⁷ suggest that all these bands except that at 1770 cm^{-1} could be assigned, at least in part, to vibrations of associatively adsorbed furan molecules. The band at 1770 cm^{-1} is ascribed to a low surface concentration of maleic anhydride formed by the oxidation of furan. The oxidation process was enhanced by heat treatment of $(VO)_2P_2O_7$, with adsorbed furan in oxygen [fig. 3(f)–(j)]. The appearance of a strong maximum at 1776 cm^{-1} and a weaker maximum at 1850 cm^{-1} [fig. 3(i)] is characteristic of adsorbed maleic anhydride (fig. 4). Broader bands at 1615 and 1430 cm^{-1} resembled maxima assigned to surface carboxylate anions in spectra of acetic acid adsorbed on $(VO)_2P_2O_7$.⁵ Maleic anhydride was progressively desorbed by evacuation at increasing temperatures but carboxylate species were more resistant to desorption [fig. 3(k)–(p)]. A residual maximum at 1855 cm^{-1} [fig. 3(p)] was due to vibrations of bulk $(VO)_2P_2O_7$, [fig. 3(a)].

Spectra of maleic anhydride on $(VO)_2P_2O_7$, contained bands at 1850, 1776 and $1760(\text{sh}) \text{ cm}^{-1}$ [fig. 4(d)] which resembled corresponding bands in spectra of maleic anhydride in carbon tetrachloride [fig. 4(k)]. Maleic anhydride was primarily non-dissociatively adsorbed on $(VO)_2P_2O_7$. Two further bands at 1560 and 1450 cm^{-1} were probably due to carboxylate anions formed by oxidation of maleic anhydride on the $(VO)_2P_2O_7$ surface. The desorption behaviour of maleic anhydride on evacuation [fig. 4(c)–(j)] resembled the behaviour of adsorbed maleic anhydride formed by the oxidation of furan. Carboxylate species were again more resistant to desorption than maleic anhydride, although carboxylate formed from maleic anhydride was more readily desorbed than carboxylate generated by the oxidation of furan.

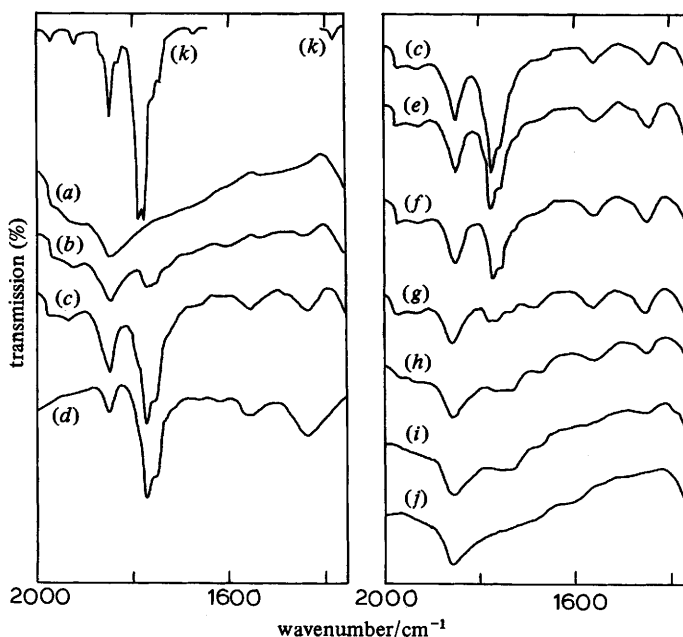


Fig. 4. Spectra of $(\text{VO})_2\text{P}_2\text{O}_7$, after (a) evacuation (17 h, 673 K), (b)–(d) contact with increasing amounts of maleic anhydride [spectrum (d) = (c) – (a)], (e)–(j) subsequent evacuation at (e) ca. 300 K (1 h), (f) ca. 300 K (5 h), (g) ca. 300 K (16 h), (h) 383 K (1 h), (i) 473 K (0.5 h) and (j) 673 K (0.5 h). (k) Spectrum of maleic anhydride in carbon tetrachloride solution.

Discussion

Infrared bands due to adsorbed alkyl groups resulting from contact between $(\text{VO})_2\text{P}_2\text{O}_7$ and but-1-ene were closely similar to previously recorded bands for 'a V–P catalyst' exposed to butenes.⁸ Two possible explanations of the results are either that oligomerisation or polymerisation of butene is catalysed by surface sites or that interaction between butene and surface oxide anions of hydroxy groups⁴ result in the complete or partial breaking of alkenyl bonds with the formation of surface alkoxy groups. The involvement of hydroxy groups in an irreversible reaction leading to alkoxy groups appears possible in view of the results of the kinetic study of but-1-ene isomerisation. Pyridine interacts with both Lewis- and Brønsted-acidic sites on the surface of $(\text{VO})_2\text{P}_2\text{O}_7$.⁴ Lewis sites are converted to Brønsted sites by the adsorption of water.⁴ The poisoning effect of adsorbed pyridine and the promoting effect of adsorbed water on the rate of but-1-ene isomerisation therefore suggest that Brønsted-acidic surface hydroxy groups are involved in the catalytic reaction. An adsorption process which gradually converts hydroxy groups to alkoxy groups would hence account for the progressive poisoning of the isomerisation reaction during contact between butenes and $(\text{VO})_2\text{P}_2\text{O}_7$. However, the formation of oligomers or polymers from butenes could also be held responsible for isomerisation deactivation.⁹

The band at 1600 cm^{-1} in spectra of but-1-ene on $(\text{VO})_2\text{P}_2\text{O}_7$, was also present in spectra of butenes on a V–P catalyst and was attributed to surface carbonate.⁸ Carbon dioxide is adsorbed on $(\text{VO})_2\text{P}_2\text{O}_7$, to give carbonate or bicarbonate species with an infrared band at 1620 cm^{-1} .⁵ However, the product of adsorption of carbon dioxide was more easily desorbed by thermal treatment than the species giving the band at 1600 cm^{-1} in spectra of adsorbed butenes. A temperature programmed desorption study of the products of adsorption of but-1-ene on a V–P mixed oxide of composition $(\text{VO})_2\text{P}_2\text{O}_7$,

established the occurrence of isomerisation, in accordance with the present data, and showed that furan was a dominant desorption product following butene adsorption at 473 K.³ The present infrared band at 1600 cm^{-1} after butene adsorption at 473 K resembles a similar maximum in spectra of $(VO)_2P_2O_7$ after the adsorption of furan (fig. 3) and could well be attributable to the same species, probably surface carboxylate.⁵

Either 1,4-polymerisation or 1,2-polymerisation of buta-1,3-diene leads to macromolecules with a high degree of alkenyl unsaturation and therefore the absence of infrared bands in the $3000\text{--}3200\text{ cm}^{-1}$ spectral region after the adsorption of buta-1,3-diene on $(VO)_2P_2O_7$ suggests that oligomerisation or polymerisation had not occurred. The relative intensities of the bands due to CH-stretching vibrations of alkyl species (fig. 2) showed that the alkyl species contained a high proportion of CH_2 groups rather than CH_3 groups. Partial or complete cleavage of alkene bonds by reaction with surface oxide ions or hydroxy groups probably occurred and led to the formation of alkoxy groups. Surface hydroxy groups would contribute hydrogen atoms to assist the conversion of unsaturated to saturated hydrocarbon groups.¹⁰ The bands assigned to surface carboxylate after heat treatment of buta-1,3-diene on $(VO)_2P_2O_7$ at $\geq 473\text{ K}$ [fig. 2(f) and (g)] were similar to maxima due to acetate anions in spectra of acetic acid adsorbed on $(VO)_2P_2O_7$.⁵ Acetic acid has been reported as a product of adsorption of but-1-ene on $(VO)_2P_2O_7$ at $\geq 423\text{ K}$ followed by desorption at *ca.* 610 K.³

The present results for furan adsorption show that only slight oxidation of furan to maleic anhydride occurred over $(VO)_2P_2O_7$ in the absence of oxygen but that the presence of oxygen promoted maleic anhydride formation. A t.p.d. study of but-1-ene adsorption on $(VO)_2P_2O_7$ similarly established that conversion to maleic anhydride was low in the absence of oxygen but was high in the presence of air.³ An infrared study of interactions between furan and V_2O_5 supported on MgO gave results which were essentially similar to those reported here.¹¹ Furan was physically adsorbed on the V_2O_5 surface but oxidation to maleic anhydride also occurred apparently to a greater extent on V_2O_5 than on $(VO)_2P_2O_7$. Maleic anhydride is similarly more readily generated as a result of but-1-ene adsorption on V_2O_5 than on $(VO)_2P_2O_7$.³ Bands at 1610 and 1435 cm^{-1} in spectra of furan on V_2O_5 were ascribed to carboxylate species¹¹ and compare with the corresponding bands at 1615 and 1430 cm^{-1} for furan on $(VO)_2P_2O_7$.

The primary interaction between furan and the $(VO)_2P_2O_7$ surface probably involves coordination between the oxygen atoms of associatively adsorbed furan molecules and coordinatively unsaturated exposed vanadium cations,¹² which are known to behave as Lewis-acidic sites for the adsorption of pyridine.⁴ Subsequent oxidation to maleic anhydride in the absence of air or oxygen gas must rely upon the availability of lattice oxygen in the catalyst surface. Yoshida *et al.*¹³ concluded that VO^{2+} ions in vanadyl phosphate were less active for CO oxidation than $V=O$ groups in V_2O_5 in accordance with the present comparison of the ease of oxidation of furan to maleic anhydride over $(VO)_2P_2O_7$ and V_2O_5 .¹¹ However, it is probable that the active sites for the oxidative reaction over $(VO)_2P_2O_7$ which had been heated at 673 K for 17 h were oxygen-deficient and existed as coordinatively unsaturated V^{4+} cations.¹⁴ These cations constitute the Lewis acidic sites for pyridine⁴ or furan adsorption. Oxidation over $(VO)_2P_2O_7$ in the absence of oxygen gas was therefore slight through lack of an appropriate form of available lattice or surface oxygen. Addition of oxygen gas led to a chemisorptive reaction in which V^{4+} sites were converted to $(V=O)$ ¹⁴ or $(V-O=O)$ ¹⁵ species which were actively involved as providers of oxygen in the catalytic reaction.

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