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Polymer-Anchored Vanadyl Catalysts for the Oxidation of Cyclohexene

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Oxovanadium(IV) ion was incorporated onto several insoluble polymers containing ligand groups such as acetylacetonate, ethylenediamine, and pyridine. The general approach to the synthesis of the catalysts was to attach the ligand to a polymerizable monomer, carry out suspension polymerizations to form beads, and incorporate the metal ion, in that order. The catalysts thus formed were used for the epoxidation of cyclohexene with *t*-butyl hydroperoxide. The catalysts were generally more active than the homogeneous model, $VO(acac)_2$, and the nitrogen-donor polymers could be recycled many times before gradual leaching of vanadyl ion caused a significant decrease in activity.

INTRODUCTION

In the attachment of homogeneous catalysts to immobile polymer supports, functionalized polystyrene copolymers have received the most study. Examples of ligands bonded to cross-linked polystyrene are phosphines (*1*), amines (*2*), and cyclopentadienyl rings (*3*). Recent reviews have appeared in which a variety of ligands and supports as well as comparisons of the activities of polymer-anchored catalysts with their corresponding homogeneous counterparts are discussed (*4–7*).

The classical uncatalyzed preparation of epoxides is accomplished by the reaction of olefins with a peracid, producing the epoxide and the carboxylic acid. Inherent disadvantages exist in this method, because the epoxide is unstable in the presence of acids, and by-products, such as ketones, are also formed in the oxidation of the olefin.

The disadvantages may be eliminated, however, if a hydroperoxide is used as the oxidant in the presence of a suitable transition-metal catalyst. Several acetylacetonate (acac) complexes of transition metals were studied as catalysts for the oxidation of cyclohexene and other cyclic olefins by Gould and co-workers (*8–12*). In these papers, vanadyl ion was of primary interest as the catalytic species.

The purpose of this research was to develop several new and effective methods of synthesis of ligands on a polymer backbone and to incorporate vanadyl ion as a heterogenized homogeneous catalyst. It was also of interest to compare relative activities of the immobile catalysts with the model homogeneous counterpart, $VO(acac)_2$.

METHODS

Starting Materials

Vanadyl sulfate was purchased from Alfa and was used as received. Cyclohexene, 4-vinylpyridine, and 2,4-pentanedione were supplied by Eastman Kodak and were used without further purification. Dibenzoyl

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peroxide and bis(acetylacetonate)oxovanadium(IV), VO(acac)$_2$, were obtained from J. T. Baker, while *t*-butyl hydroperoxide was purchased from Aldrich and was dried over 4A molecular sieves before use. Pfaltz and Bauer supplied divinylbenzene, which was vacuum distilled and stored in the cold. Vinylbenzyl chloride (VBC), obtained from Dow as a mixture of 65% *meta* and 35% *para* isomers, was used as received. Ethylenediamine was purchased from Matheson, Coleman and Bell and was used without further purification.

Physical Methods

Infrared spectra were recorded on a Perkin–Elmer Model 337 grating infrared spectrophotometer. Viscous liquid samples were recorded neat between KBr plates, and spectra of solids were obtained as Nujol mulls or KBr pellets. Polymer beads were ground to a powder and run as either a neat or a KBr pellet.

Nuclear magnetic resonance spectra were recorded on a Varian A-60 spectrometer in deuterioacetone solvent; tetramethylsilane (TMS) was used as an internal standard. Electron spin resonance spectra were obtained on a Strand–Magnion–Varian hybrid instrument.

Gas chromatography was performed on a Hewlett–Packard Model 5750-B instrument equipped with a thermal conductivity detector. Helium was used as the carrier gas, and the columns (10 ft × $\frac{1}{8}$ in.) were packed with 5% silicone rubber Type UCC-982 (methylvinyl) on 80- to 100-mesh Chromasorb G support. Durene was employed as an internal standard for the gas chromatography measurements.

Elemental Analyses

Elemental analyses were conducted by Galbraith Laboratories Inc., Knoxville, Tenn. The authors determined concentrations of hydroperoxide by pipetting samples into an acidified KI solution and then titrating the liberated iodine with a standard $Na_2S_2O_3$ solution.

Preparation of the Catalysts

The preparations of the polymer-anchored catalysts all involved the same approach, in which operations were carried out in the order: (i) reactions to attach the ligand to a polymerizable monomer, (ii) suspension polymerization of the functionalized monomer to beads of 20–100 mesh, and (iii) incorporation of vanadyl ion onto the polymer. Therefore, only the preparation of one of the catalysts will be given in detail.

1. Preparation of Poly(vinylbenzylacetylacetonate) oxovanadium(IV) Sulfate, P-CH$_2$-acac(VO)SO$_4$-Na$^+$

a. Functionalization of monomer. To incorporate acetylacetone onto vinylbenzyl chloride, reactions were carried out according to procedures described in the literature (*13–16*). To 141 ml (1 mol) of vinylbenzyl chloride in a 1500-ml Erlenmeyer flask, 154 g (1.1 mol) of sodium acetylacetonate monohydrate and 15 g (0.1 mol) of sodium iodide were added at room temperature. Acetone (600 ml) was then added, and the mixture was stirred until a homogeneous solution was obtained. The mixture was warmed to 40–50°C until reaction commenced and then was cooled by means of an ice bath to prevent overheating. After 1 hr of reaction time, the sodium chloride formed was filtered off, and most of the acetone was removed by heating and stirring under an aspirator vacuum. The residue was then washed with 5 vol of 5% HCl solution (2 liter, total volume) and was extracted with benzene in a separatory funnel. The benzene extracts were concentrated on a rotary evaporator, yielding about 50 ml of an oily residue. *Anal.* Calcd for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46; O, 14.79; MW 216.3. Found: C, 77.62; H, 7.38; O, 14.46; MW 230.

The functionalized monomer was characterized further by infrared and NMR analyses; the spectra were compared to those of an authentic sample of 3-benzylacetylacetone. The infrared spectrum of 3-vinylbenzylacetylacetone shows aromatic and olefinic CH stretching frequencies in the 3000- to 3100-cm^{-1} region, and the CO stretching frequency at 1700 cm^{-1}. The spectrum of 3-benzylacetylacetone shows corresponding bands at the same frequencies.

The NMR spectrum of 3-vinylbenzylacetylacetone is nearly identical to that of 3-benzylacetylacetone, except for the olefinic resonances in the δ 5–6 region. Other signals characteristic of the compound are aromatic protons (δ 6.5–7.5), methine triplet at δ 4.2, methylene doublet at δ 3.2, and methyl signals δ 2.0–2.1. All resonances are reported as downfield from TMS.

b. Polymerization of monomer. The monomer was polymerized according to methods outlined in the literature (*17–22*). Since most of these references are not readily available, the method is described in some detail.

In a 500-ml resin kettle flushed with N_2 were mixed 150 ml of distilled water, 30 ml (0.15 mol) of the monomer, 3 ml (0.03 mol) of divinylbenzene, 2 g of bentonite (clay), 1 g (1 mol%, based on monomer) of benzoyl peroxide, and 0.2 g of polyvinyl alcohol. The mixture was heated at reflux for 2 hr with mechanical stirring at a moderate rate. The resulting polymer beads were suction filtered from solution, washed with water (5 × 100 ml) on a Buchner funnel, and dried for 8 hr in an oven at 50°C. The low molecular weight materials were extracted with benzene in a Soxhlet extractor overnight.

It was found that the size of the beads produced is a function of the stirring rate; faster stirring produces smaller beads. In these preparations, the stirring rate was adjusted to give a product which was between 20 and 100 mesh in size.

In a separate experiment, the beads were investigated with respect to their tendency to swell in cyclohexene, which was the olefin used in the reactions (see below). No swelling of the beads was observed after 6 hr of standing in cyclohexene at 50°C.

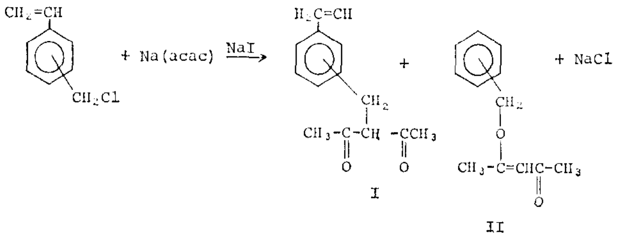
c. Catalyst incorporation. The poly(vinylbenzylacac) beads were placed in a chromatography column and were washed with dilute (5%) NaOH solution until the effluent stream was basic to pH indicator paper. The material in the column was then washed with distilled water until the washings were neutral. The beads were then treated with vanadyl sulfate solution until the effluent was deep blue in color, and excess $VOSO_4$ was washed from the beads with distilled water until the washings showed no white precipitate when tested with a $BaCl_2$ solution. The beads were taken from the column and dried in an oven at 50°C for 8 hr. The dried beads showed an analysis of 10.09% V and 3.37% Na.

2. Preparation of Poly(vinylbenzylacetylacetonato) (acetylacetonato)oxovanadium(IV), P-CH$_2$-acacVOacac

The preparation of the beads was identical to that described above in Sections 1a and b. To attach the metal ion onto the polymer, the beads (H^+ form) were treated for 15 hr at room temperature with bis(acetylacetonato)oxovanadium(IV) (5 g, 0.019 mol) dissolved in 100 ml of acetone. After that time, the beads were filtered from solution and dried in an oven at 50°C for 4 hr. The resulting beads were bluish-green in color which could not be removed by acetone extraction. Analysis of this material showed it to contain 9.03% V.

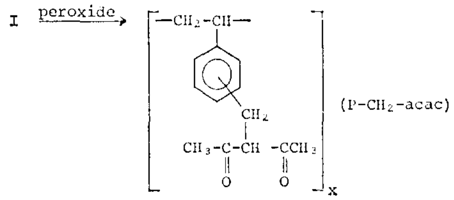
The chemistry involved in the preparation of acetylacetonate catalysts is outlined below.

a. Functionalization of polymerizable monomer.



$$I + II \xrightarrow{5\%\ HCl} I + CH_2{=}CH\text{-}C_6H_5CH_2OH + Hacac$$

b. Suspension polymerication.



c. Incorporation of metal ion.

$$\text{P-CH}_2\text{-acac} \xrightarrow[\text{VOSO}_4]{\text{NaOH}} \text{P-CH}_2\text{-acac-VOSO}_4^-\text{Na}^+.$$

$$\text{PCH}_2\text{-acac} \xrightarrow{\text{VO(acac)}_2} \text{P-CH}_2\text{-acac-VO-acac}.$$

3. Preparation of Poly(vinylbenzylethylenediamine)oxovanadium(IV) Sulfate, P-CH$_2$-enVOSO$_4$

Ethylenediamine (600 ml, 10 mol) in a 1000-ml Erlenmeyer flask was alkylated to the hydrochloride by dropwise addition of vinylbenzyl chloride (141 ml, 1 mol). The solution was then washed with three 500-ml volumes of 20% NaOH solution, followed by three 500-ml washings of the organic phase with distilled water. Approximately 100 ml of an oily organic compound was obtained which had to be used immediately, since it was found to set to a gel within 1 hr.

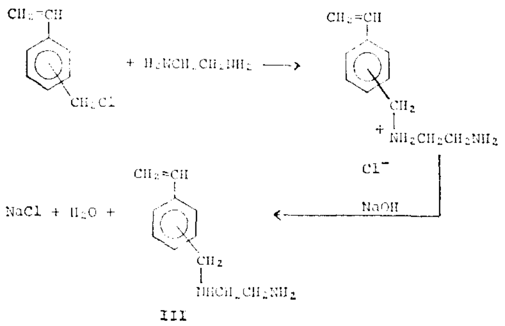
The monomer (*N*-vinylbenzylethylenediamine) was suspension polymerized to 20- to 100-mesh beads by the methods described above. The polymer–ligand was then treated with VOSO$_4$ as above, yielding a polymer-bound catalyst that showed the analysis: 5.11% V, 7.50% N.

The *N*-vinylbenzylethylenediamine monomer was characterized by its infrared and NMR spectra with those of an authentic sample of *N*-benzylethylenediamine. The former exhibited NH stretching bands at 3200 cm^{-1}, vinyl and aromatic bands at 3000 cm^{-1}, aliphatic CH modes in the 2800- to 2900-cm^{-1} region, a C=C stretching frequency at 1630 cm^{-1}, and the CH$_2$ deformation at 1470 cm^{-1}.

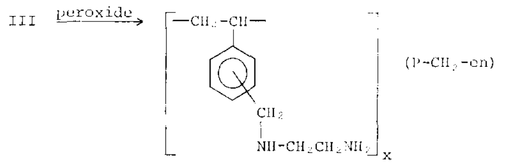
The NMR spectrum of *N*-vinylbenzylethylenediamine is nearly identical to that of *N*-benzylethylenediamine, except for the vinyl proton resonances in the δ 5.0–6.0 region for the former. Other signals supporting the proposed structure are the aromatic protons in the δ 6.5–7.5 region, and amino and methylene protons in the δ 1.1–3.6 region.

The chemistry in the preparation of the ethylenediamine catalysts is shown below.

a. Functionalization of polymerizable monomer.



b. Suspension polymerization.



c. Incorporation of metal ion.

$$\text{P-CH}_2\text{-en} + \text{VOSO}_4 \rightarrow \text{P-CH}_2\text{-enVOSO}_4.$$

4. Preparation of Poly(vinylbenzylethylenediamine)acetylacetonatooxovanadium(IV) Acetylacetonate, P-CH_2-enVO(acac)$_2$

After polymerization of *N*-vinylbenzylethylenediamine was accomplished, the resulting beads were treated with VO(acac)$_2$ in acetone solution. The resulting polymer-anchored catalyst showed the following analysis: 8.37% V, 8.02% N.

The incorporation of the metal was by ligand exchange, acac for en:

$$\text{P-CH}_2\text{-en} + \text{VO(acac)}_2 \rightarrow \text{P-CH}_2\text{-enVO(acac)}_2.$$

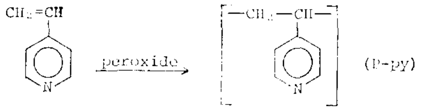
Because of charge considerations, one of the acac's functions is simply as a counterion.

5. Preparation of Poly(vinylpyridine)oxovanadium(IV) Sulfate, P-py-VOSO$_4$

A sample of vinylpyridine was suspension polymerized, but the resulting solid turned out as a chunky mass, rather than discrete spheres. The polymer was ground in a blender to a powder and was then treated with VOSO$_4$ solution as described earlier. The final polymer-bound catalyst showed the following analysis: V, 6.79; N, 6.58; S, 7.78%. It should be noted that the polymerization of this molecule is linear; no divinylbenzene was employed as a co-monomer.

The chemistry in the preparation of the polyvinylpyridine catalysts is shown below.

a. Suspension polymerization.



b. Incorporation of metal ion.

$$\text{P-py} + \text{VOSO}_4 \rightarrow \text{P-py-VOSO}_4.$$

Additional Studies on the Catalysts

After the metal ion was incorporated in the above systems, the final catalyst was characterized by: analysis of the vanadium content; infrared spectroscopy of the vanadyl ion which, in each case, showed a characteristic VO stretching band in the 900- to 1000-cm^{-1} region; and ESR spectrometry (first derivative spectrum) to observed the d^1 configuration of the vanadyl ion.

Epoxidation of Cyclohexene

The epoxidation of cyclohexene using the catalysts described above was carried out in a similar manner. Therefore, only a general description of the experiments will be given in detail. A 25-ml three-neck flask was fitted with a condenser, a thermometer, and a serum cap. The top of the condenser was fitted with a gas adaptor, which was in turn connected to an oil bubbler. Into the flask was placed an amount of polymer-supported catalyst containing 1.2×10^{-4} mol of V, a stirring bar, 10 ml of cyclohexene which also served as the solvent, and 2 ml (0.02 mol) of *t*-butyl hydroperoxide. After the flask was flushed with N_2, the serum cap was fitted, and the reaction mixture was heated at 80°C by means of an oil bath controlled by a thermoregulator. The temperature was maintained for 6 hr, whereupon a 3-ml aliquot was removed and divided into three equal portions. One milliliter was analyzed for peroxide remaining in the solution, and the other portions were used to determine the yield of cyclohexene oxide formed. This was carried out by gas chromatography after the aliquot was treated with triphenylphosphine (5.0 g, 0.12 mol) in acetone to remove the unreacted hydroperoxide.

RESULTS AND DISCUSSION

Expression of Yield

Before presenting the results of the oxidation of olefins, it is necessary to define the methods by which the yields of products were calculated. Since the olefin is added in excess and is also used as the solvent, the yield must be based on the amount of t-butyl hydroperoxide added or consumed. Yields based on oxidant added initially can be misleading, since it was found that some oxidant decomposition occurred in competition with the epoxidation reactions. Therefore, the yields in the reactions are expressed in two ways: on the basis of oxidant added initially (o.i.), and on the basis of oxidant consumed (o.c.). These are defined as follows.

$$\text{Yield of (oxidant added initially)} = \text{o.i.} = \frac{\text{moles of product formed}}{\text{moles of oxidant (initial)}} \times 100;$$

$$\text{Yield of (oxidant consumed)} = \text{o.c.}$$

$$= \frac{\text{moles of product formed}}{[\text{moles of oxidant (initial)} - \text{moles of oxidant (final)}]} \times 100.$$

Epoxidation Reactions

The epoxidation of cyclohexene was carried out according to the equation below, and, in order to determine relative activities of the various catalysts, an amount of beads containing 1.2×10^{-4} mol of vanadium was placed in the reaction flask. Also held constant in all reactions were the amounts of cyclohexene (10 ml) and *t*-butyl hydroperoxide (2 ml). No solvents were employed in these reactions.

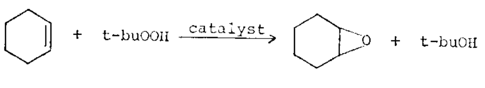


Table 1 shows the yields of cyclohexene oxide after a 6-hr reaction time with respect to each catalyst; included for comparison is the yield obtained from the VO(acac)$_2$ catalyst, the homogeneous standard.

With the exception of the polymer-bound catalysts, P-pyVOSO$_4$ and P-CH$_2$-acac-VOSO$_4$, which are about comparable in promoting yields of cyclohexene oxide to that of the homogeneous catalyst VO(acac)$_2$, the other heterogenized systems promote yields of product at least double that of VO(acac)$_2$ after 6 hr of reaction.

The principal advantage of a heterogenized homogeneous catalyst is that the high reactivity of the homogeneous catalyst is retained and, in some cases, might be recycled for use several times. If no leaching of the metal ion or decomposition of the catalyst occurs, then the catalyst should be active indefinitely. The advantage of high reactivity is shown in Table 1; it was then of interest to determine the longevity of the catalysts in a series of reactions.

To determine the lifetime of the catalysts, reactions were carried out under the conditions described earlier, the yield of cyclohexene oxide was determined, and the catalyst was removed from the reaction mixture and placed in a vessel with fresh reactants. This process was repeated several times, and the vanadium content was determined from time to time until the catalyst was spent.

TABLE 1

Yields of Product with Various Vanadyl Catalysts[a]

Catalyst	Yield of Cyclohexene Oxide (%)	
	o.i.	o.c.
VO(acac)$_2$ (homogeneous)	10.21	12.33
P-CH$_2$-acac-VOSO$_4$	11.58	14.64
P-CH$_2$-acac-VOacac	20.16	20.78
P-CH$_2$-en-VOSO$_4$	22.02	26.20
P-CH$_2$-en-VO(acac)$_2$	20.16	20.78
P-py-VOSO$_4$	6.51	14.79

[a] All catalysts were in amounts containing 1.2 × 10^{-4} mol of V, 10 ml of cyclohexene , and 2 ml of *t*-butyl hydroperoxide; the temperature was 80°C, and the reaction time was 6 hr.

The acetylacetonate systems proved to be too labile for recycling of the catalyst. The P-CH$_2$-acacVOSO$_4$ system was particularly susceptible to leaching. The initial activity of the catalyst is about comparable to the homogeneous system; after one run, analysis showed that essentially no vanadium remained on the beads. The P-CH$_2$-acac-VO-acac system was somewhat longer-lived. After the first run, the amount of vanadium remaining on the catalyst was about 74% of the starting amount. The yield (o.i.) was approximately 50% of that of the first run. After the third run, only about 2% of the initial amount of vanadium was still incorporated onto the beads.

These studies prompted the use of a stronger-field ligand, and the ethylenediamine and pyridine systems were synthesized and investigated. Both of these systems were particularly effective over several runs.

For the P-CH$_2$-enVOSO$_4$ system, yields (o.i.) of cyclohexene oxide slowly decreased over six runs from 22.02 to 9.98%, while the percentage of vanadium on the beads decreased by about 50% over the six runs. The activity after six runs was about equal to that of the homogeneous catalyst.

The P-py-VOSO$_4$ catalyst appears to be the longest-lived species investigated in this study. The yield (o.i.) of the epoxide in the first run was 6.51%, and the initial analysis of vanadium on the beads was 6.79%. After six runs, the yield was 5.64%, about 86% of the initial run. Furthermore, the amount of vanadium decreased by a similar percentage, from 6.79 to 6.01%, about 88% of the original vanadium content still remaining on the beads after six runs. Whereas this catalyst may be less active than the homogeneous one, it can be recycled many times before it becomes inactive.

Several qualitative experiments were performed to decide if the mechanism of Gould and co-workers (*8*, *9*) applied to these studies. One of the features of this mechanism was the inhibition of the reaction caused by the by-product of the reaction, *t*-butanol. We carried out reactions using the polymer-bound catalysts in the presence of *t*-butanol, which was added at the beginning of the reactions. The amounts added varied between 1 and 10 ml; in all cases, no product was detected at reaction times up to 24 hr in those systems to which *t*-butanol was added.

Another feature of the mechanism proposed by Gould and co-workers (*8*, *9*) is the oxidation of V(IV) to V(V) as the first step in the reaction. We followed the oxidation reactions in the homogeneous system by ESR spectrometry. Whereas the paramagnetism of VO(acac)$_2$ was revealed at the start, upon addition of *t*-butyl hydroperoxide to begin the reaction, the solution became diamagnetic within minutes after addition of the oxidant.

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