

Polymer-Supported Molybdenum and Vanadium Catalysts for Epoxidation of Alkenes by Alkyl Hydroperoxides

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SYNOPSIS

Polymer-supported molybdenum and vanadium catalysts were synthesized using gel-type crosslinked copolymers with microheterogeneous structure. The supports were composed of inert ethylene-propylene rubber and crosslinked high molecular weight poly(ethylene oxide) matrices and polymeric ligands grafted or forming interpenetrating networks: poly(acrylic acid), poly(methacrylic acid), poly(4-vinylpyridine), and polyvinyl alcohol. Catalytic activity and selectivity of some of these complexes were tested in epoxidation of styrene by ethylbenzene hydroperoxide. Molybdenyl cations are strongly coordinated with pyridine-containing copolymers giving catalysts of high activity and selectivity. They provide conversion and selectivity above 70%. Because of the microheterogeneous mosaic-like structure of the supports, better accessibility of the active sites is achieved.

INTRODUCTION

Molybdenum (VI) and vanadium (V) complexes are efficient catalysts in the important petrochemical process of alkene epoxidation by alkyl hydroperoxides.^{1,2} Recently, polymer-supported metal complex catalysts have been receiving increasing attention.^{3,4} In many cases, the immobilization of transition metal species provides catalysts with high activity and selectivity. It offers an ease of separation of the catalyst by simple filtration, as well as permitting regeneration, recycling, and use of continuous flow reactors.

The first attempts to produce polymer-supported analogues involve the attachment of oxo-molybdenum and oxo-vanadium complexes to ion-exchange resins both of anionic and cationic types.⁵⁻⁷ In some cases high yields and selectivity for epoxide formation were reported. Polymer supports functionalized with chelating groups have also been attracting attention recently. Polymers containing acetylacetonate, ethylenediamine, and pyridine donor ligands were used to bind oxo-vanadium and oxo-

molybdenum ions.^{8,9} The oxo-vanadium (V) and oxo-molybdenum (VI) complexes were supported on polystyrene resins carrying bis(2-hydroxyethyl)amino, bis(phosphonomethyl)amino, and iminodiacetate functions.¹⁰⁻¹² The vanadium systems were the most effective with allylic alcohol substrates (conversions 100%, regioselectivity 98%). The molybdenum-based species were more effective in epoxidation of cyclohexene with conversions up to 90%, but with poorer selectivities (under 60%). Polystyrene and poly(glycidyl methacrylate)-based resins functionalized with aminoethylpyridine and pyridyl imidazole ligands have been successfully used to complex $\text{VO}(\text{acac})_2$ and $\text{MoO}_2(\text{acac})_2$.³ The resulting molybdenum catalyst was first activated by treatment with *t*-butyl hydroperoxide in the absence of alkene. Epoxidations of cyclohexene at 80°C with the activated catalyst proceed with 100% conversion and very high selectivity in short periods.

Special advantages such as catalyst supports are offered by new gel-type crosslinked grafted and block copolymers with microheterogeneous structure. The latter consists of an inert matrix swelling considerably in the reaction medium and microdomains of polymeric ligands coordinating the transition metal ions dispersed in it. Because of the readily accessible active sites, the reaction proceeds in the whole vol-

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ume of the catalyst particle. An inert matrix of non-polar elastomer may be used (e.g., ethylene-propylene rubber) and, as polymer ligands, grafted poly(vinylpyridines), polycarboxylic acids, and others. The catalytic system can be designed in the form of beads or membranes for easy separation from the reaction products. Nickel complexes immobilized on such supports have proved to be highly effective catalysts for olefin dimerization.¹³

In this paper we report on the synthesis of polymer-supported molybdenum and vanadium catalysts using supports with the previously described mosaic-like structure. Ethylene-propylene rubber and crosslinked high molecular weight poly(ethylene oxide) were used as inert matrixes. Polymeric ligands grafted or forming interpenetrating networks were poly(acrylic acid), poly(methacrylic acid), poly(4-vinylpyridine), and polyvinyl alcohol. The activity and selectivity of the catalysts in epoxidation reaction of styrene by ethylbenzene hydroperoxide were examined.

EXPERIMENTAL

Materials

All the solvents were purified by distillation. Reagent grade 4-vinylpyridine, acrylic acid, methacrylic acid, and butyl acrylate (Fluka AG) were distilled under reduced pressure before use.

Synthesis of Polymer Supports with Ethylene-Propylene Rubber (EPR)

EPR-PVP. 4-Vinylpyridine, 0.5 g (VP), and 0.075 g AIBN were added to a solution of 5.0 g EPR (Esso Chem.) in cyclohexane placed in 250 cm³ ampoule. After degassing under vacuum (10⁻³ mbar) and sealing the ampoule was heated for 10 h at 70°C. Then, 0.75 g benzoyl peroxide (BPO) were added (using breaking seal) and the ampoule was heated for another 10 h at 70°C. The polymer gel was isolated by filtration and repeatedly washed with methanol and dried under a vacuum.

EPR-PMA. The same procedure as in EPR-PVP but instead of 0.5 g VP methacrylic acid (MA) was added.

Synthesis of Polymer Supports with Polyethylene Oxide (PEO)

Crosslinked PEO (cr-PEO) was prepared by γ -irradiation of 2 wt % aqueous solution of high molec-

ular weight PEO (trade mark BADIMOL, $M_p = 2.5 \times 10^6$) with a total dose 0.85 Mrad. The gel formed was washed three times with distilled water under stirring and freeze dried.

PEO-PBuA-PAA. Five milliliters of chloroform containing 2.9 g butyl acrylate (BuA), 1.7 g acrylic acid (AA), 0.046 g AIBN, and 0.3 g tetraethyleneglycol dimethacrylate were added to 2.0 g cr-PEO placed in a 20 cm³ ampoule. After degassing and sealing the ampoule was allowed to stay 48 h in refrigerator and then copolymerization was carried out for 10 h at 70°C. The gel product was washed with chloroform and dried under vacuum.

PEO-PVA. Eight grams PEO and 8 g polyvinyl alcohol (PVA) ($M_v = 100,000$, FLUKA AG) were dissolved separately in 400 mL distilled water. The solutions were mixed by stirring 30 min, purged with argon, and irradiated with a total dose 5 Mrad. The gel was washed several times with water and freeze dried.

PEO-PVP. PEO, 8.8 g, were dissolved in 600 mL distilled water and 10.5 g VP were added. The solution was purged with argon and irradiated with a total dose 5 Mrad. The gel was washed repeatedly with alcohol and water and freeze dried.

Crosslinked PVP (cr-PVP) was prepared by suspension copolymerization of VP with 10 wt % divinylbenzene (DVB) as described in.¹⁴

Preparation of Polymer-Supported Molybdenum and Vanadium Complexes

Polymer support, 0.5 g, were shaken with 50 mL solution of the metal compound. The complexes were filtered, washed, and dried under vacuum. Preparation conditions are given in Table I.

Characterization

The IR spectra (KBr) were recorded on a UR-20 spectrophotometer (Karl Zeiss Jena). TG measurements were carried out with DTA and TG instruments (Q-Derivatograff MOM, Hungary).

Molybdenum and vanadium content was determined spectrophotometrically with a UV-VIS spectrophotometer, "Specord" (Carl Zeiss Jena). Rhodium complex of Mo and peroxide complex of V were used.^{15,16} Nitrogen elemental analysis was performed on a Karlo Erba apparatus.

Epoxydation Reaction

Epoxydation reactions were carried out in a thermostated glass reactors of batch and flowing-type loaded with catalyst (Fig. 1). Air was passed through the vessels in the course of the reaction to inhibit the polymerization of styrene. The process was carried out until the yield of styrene oxide reached a constant level. The ethylbenzene hydroperoxide concentration was then determined.¹⁷

RESULTS AND DISCUSSION

Choice of Polymer Support

The reactivity of polymer-supported systems is greatly influenced by the physical properties of the polymer backbone: the "effective polarity" of the polymer microenvironment, the flexibility of the chain segments and the rate at which reagents move in and out of a polymer domain. For this purpose, several types of polymeric supports with mosaic-like structure were synthesized. Molybdenum and vanadium complexes of the supports were prepared and characterized by metal content, IR spectra, and thermal stability. The results are summarized in Table II.

The first type of support is built up from the ethylene-propylene elastomeric matrix swellable in styrene, ethylbenzene, and other aromatic solvents used in the epoxydation reaction of olefins (Tables II, no. I). Polymeric ligands PVP and PMA were incorporated by grafting to the rubber macromolecules which subsequently were crosslinked. SEM studies of the morphology have shown that the grafted component is dispersed in the matrix of synthetic rubber, the size of the inclusions being 1000–2000 Å.¹⁸ The complexing metal is sorbed by the inclusions of the grafted phase.

The second type of support contains, as the main component of the matrix, crosslinked PEO. The latter possesses well-balanced lipophilic and hydrophilic properties and is suitable for carrying out chemical reactions in water or in organic media as well as in aqueous-organic heterogeneous systems. This property of cr-PEO enables preparation of polymer-metal complexes in aqueous solution (Table I). In our earlier study it was found that linear and crosslinked PEO form donor-acceptor complexes with molybdenyl cation.¹⁹ Hence, PEO cannot be regarded as an entirely inert matrix. In order to improve the mechanical strength of the PEO network, inert elastomeric poly (butyl acrylate) was inserted into the matrix (Tables II, no. IV). This sup-

Table I Preparation of Polymer-Supported Molybdenyl and Vanadyl Complexes

No.	Polymer Support	Metal Compound	Solvent	Concentration (mol/L)	Temperature (°C)	Time (h)	Designation
1	EPR-PVP	MoO ₂ Cl ₂	Dichlorethane	1.5 × 10 ⁻²	80	4	EPR-PVP-Mo
2	EPR-PMA	MoO ₂ Cl ₂	Dichlorethane	1.5 × 10 ⁻²	80	4	EPR-PVP-Mo
3	cr-PEO	MoO ₂ Cl ₂	Dichlorethane	1.5 × 10 ⁻²	80	4	PEO-Mo-1
4	cr-PEO	(NH ₄) ₆ Mo ₇ O ₂₄	Aqu., pH = 2	0.8 × 10 ⁻²	25	5	PEO-Mo-2
5	cr-PVP	MoO ₂ Cl ₂	Dichlorethane	1.5 × 10 ⁻²	80	4	PVP-Mo-1
6	cr-PVP	(NH ₄) ₆ Mo ₇ O ₂₄	Aqu., pH = 2	0.8 × 10 ⁻²	25	5	PVP-Mo-2
7	PEO-PVP	MoO ₂ Cl ₂	Dichlorethane	1.5 × 10 ⁻²	80	4	PEO-PVP-Mo-1
8	PEO-PVP	(NH ₄) ₆ Mo ₇ O ₂₄	Aqu., pH = 2	0.8 × 10 ⁻²	25	5	PEO-PVP-Mo-2
9	PEO-PBuA-PAA	MoO ₂ Cl ₂	Dichlorethane : toluene (1 : 1)	2.0 × 10 ⁻²	70	4	PEO-PBuA-PAA-Mo-1
10	PEO-PBuA-PAA	(NH ₄) ₆ Mo ₇ O ₂₄	Aqu., pH = 2	0.8 × 10 ⁻²	25	5	PEO-PBuA-PAA-Mo-2
11	PEO-PVA	MoO ₂ Cl ₂	Dichlorethane : toluene (1 : 1)	2.0 × 10 ⁻²	70	4	PEO-PVA-Mo-1
12	PEO-PVA	MoO ₂ Cl ₂	Isobutanol	2.0 × 10 ⁻²	70	4	PEO-PVA-Mo-2
13	EPR-PVP	VO(acac) ₂	Dichlorethane	1.9 × 10 ⁻²	60	5	EPR-PVP-V
14	PEO-PVP	VO(acac) ₂	Dichlorethane	1.9 × 10 ⁻²	60	5	PEO-PVP-V
15	PEO-PBuA-PAA	VO(acac) ₂	Dichlorethane	1.9 × 10 ⁻²	60	5	PEO-PBuA-PAA-V
16	PEO-PVA	VO(acac) ₂	Dichlorethane	1.9 × 10 ⁻²	60	5	PEO-PVA-V

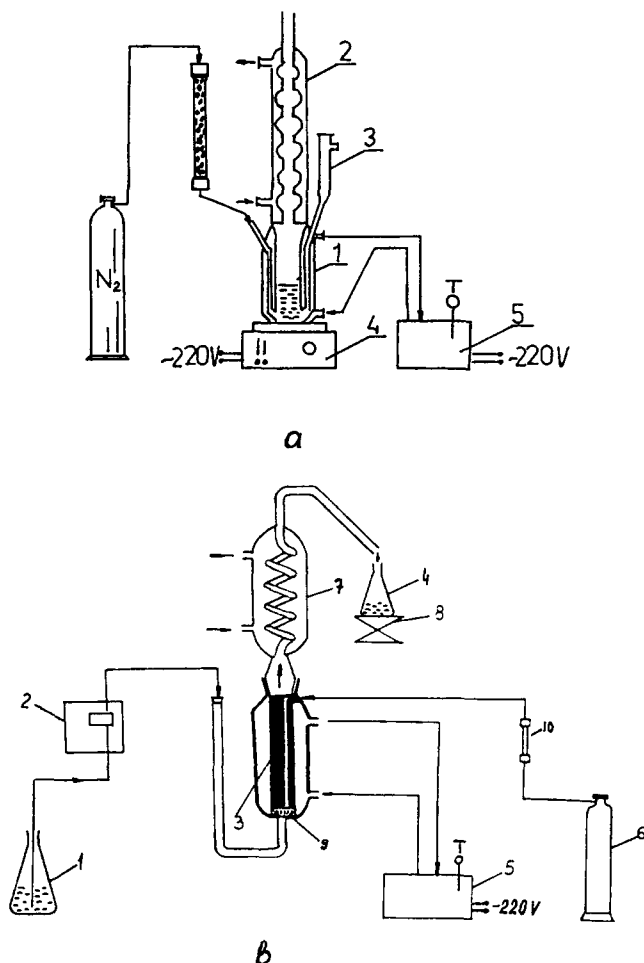


Figure 1 Equipment for epoxidation of styrene with ethylbenzene hydroperoxide. (a) batch process: 1, reaction vessel; 2, condenser; 3, sample-taking device; 4, magnetic stirrer; 5, thermostat. (b) continuous process: 1, mixer; 2, pump; 3, reaction vessel; 4, receiver; 5, thermostat; 6, air cylinder; 7, condenser; 8, support; 9, frit; 10, dryer.

port is a kind of sequential interpenetrating network (IPN) meaning that the butyl acrylate and vinylpyridine are polymerized in the presence of a preformed PEO network. Supports nos. III and V of Table II are obtained by simultaneous polymerization of both networks. The polymer ligands PVP and PVA strongly bind Mo and V and also enhance the mechanical stability of the network. For comparison cr-PEO and cr-PVP were also used as supports.

Binding of Mo and V Oxo-Cations to Polymer Supports

As seen from Table II all supports bind significant amounts of molybdenum and vanadium. The support of ethylene-propylene rubber with grafted PVP

forms 1 : 1 complexes since the molar ratio of pyridine moiety to metal atom is about one. PEO-based supports with PVP, PAA, and PVA ligands have a molar ratio of about 2 in the resulting complexes.

Crosslinked PEO exhibits the lowest binding capacity. Its uptake of MoO_2^{2+} is 0.90 meq/g corresponding to one metal atom for about 20 $-\text{CH}_2-\text{CH}_2-\text{O}-$ units. Macroporous cr-PVP binds much less metal than the new types of support nos. I and III (Table II) in which PVP forms microdomains in the matrix of the rubber or PEO. The apparent reason for this is the unaccessibility of the pyridine ligands in the bulk of the particles.

In the IR spectra of the polymer-supported metal complexes appear characteristic bands for metal oxo-cations. The stretching vibrations of the molybdenyl cation, MoO_2^{2+} , are observed at 920 cm^{-1} and 960 cm^{-1} . For vanadyl cation, VO^+ , they appear normally at 480 cm^{-1} and 1005 cm^{-1} with the exception of supports with pyridine ligands (nos. I and III), where they are shifted to 460 cm^{-1} and 965 cm^{-1} .²⁰ A strong shift from 1600 cm^{-1} to 1640 cm^{-1} is observed for the skeletal vibrations of the pyridine ring when it is coordinated to the molybdenyl or vanadium oxo-cations.

The supports and their metal complexes show good thermal stability up to 150°C . As seen from Table II the weight losses of EPR-based supports, PEO-PBuA-PAA and PEO-PVP and their molybdenum or vanadium complexes are smaller than 5%. PEO-PVA and its metal complexes reveal greater instability, especially the vanadium complex, by reason of PVA which starts to decompose above 100°C .²¹

Epoxidation Activity of Polymer-Supported Mo and V Catalysts

Some of the supported molybdenum and vanadium catalysts from Table II were tested for epoxidation reaction of styrene with ethylbenzene hydroperoxide (Table III). It is seen that molybdenum catalysts give higher conversion than vanadium ones and higher selectivity. Molybdenyl complexes of PEO reach almost 100% selectivity. This may be attributed to specific influence of the macromolecule chains on the geometry of the metal complex and its immediate surrounding. Upon reuse, the PEO-Mo catalyst rapidly decreases its activity because of leaching of the metal.²² In contrast with the ether oxygen, ligand pyridine moiety of the support nos. I and III coordinates very strongly to molybdenyl and vanadyl cations giving thermally stable complexes. These complexes manifest as high an activity as the homogeneous catalysts like molybdenyl or

Table II Characteristics of the Polymer Supports and Their Molybdenyl and Vanadyl Complexes

No.	Support, Complexes (No. from Table I)	[N] [COOH] [OH] [CH ₂ —CH ₂ —O]* (meq/g)	Metal Content (meq/g)	Weight Loss up to 150°C (%)	$\nu_{\text{Me}} = 0$ (cm ⁻¹)
I.	EPR-PVP	0.99		0	
1	EPR-PVP-Mo	0.88	0.89	3	920, 960
13	EPR-PVP-V	0.88	0.69	1	460, 965
II.	EPR-PMA	1.15		0	
2	EPR-PMA-Mo	1.10	0.21	0	922
III.	PEO-PVP	3.4		3	
7	PEO-PVP-Mo-1	2.8	1.02	5	
8	PEO-PVP-Mo-2	2.7	1.43	5	922, 955
14	PEO-PVP-V	2.9	1.61	4	463, 961
IV.	PEO-PBuA-PAA	3.5			
9	PEO-PBuA-PAA-Mo-1	3.0	1.44	5	922
10	PEO-PBuA-PAA-Mo-2	3.2	0.87	2	920, 930
15	PEO-PBuA-PAA-V	3.3	0.83	6.5	480, 1005
V.	PEO-PVA	3.61		6	
11	PEO-PVA-Mo-1	3.0	1.32	8	922
12	PEO-PVA-Mo-2	2.93	1.46	7	919
16	PEO-PVA-V	2.57	1.71	16	480, 1005
	cr-PEO	21.1			
3	PEO-Mo-1	21.0	0.75		
4	PEO-Mo-2	21.0	0.83		
	cr-PVP	8.6			
5	PVP-Mo-1	7.4	0.94	0	
6	PVP-Mo-2	7.8	1.38	0	

* Refers only to nos. 3 and 4.

Table III Activity of Some Immobilized Molybdenum and Vanadium Catalysts in Epoxidation of Styrene With Ethylbenzene Hydroperoxide

No. (from Table I)	Catalyst	Conversion (%)	Selectivity (%)	Yield (%)
1	EPR-PVP-Mo	71.0	73.6	52.6
13	EPR-PVP-V	68.8	58.1	39.7
3	PEO-Mo-1	61.7	90.9	56.0
4	PEO-Mo-2	72.2	97.6	70.4
5	PVP-Mo-1	12.4	58.8	7.3
6	PVP-Mo-2	9.3	96.9	9.0
7	PEO-PVP-Mo-1	32.8	34.1	11.2
8	PEO-PVP-Mo-2	76.0	79.6	60.5
14	PEO-PVP-V	76.1	49.3	37.5
	MoO ₂ (acac) ₂	78.6	69.6	55.0
	Mo(CO) ₆	66.0	89.0	59.0
	VO(acac) ₂	86.7	53.7	46.6

T = 70°C; ROOH : Styrene = 1 : 10; [Me] = 1.25 × 10⁻³ mol/L; [Styrene] = 2.0 mol/L; solvent: ethylbenzene.

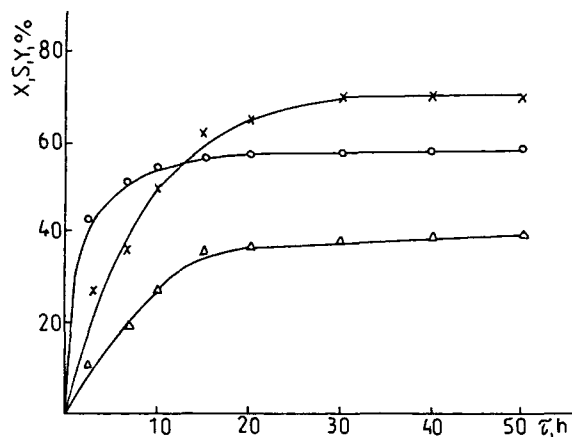


Figure 2 Epoxydation of styrene with ethylbenzene hydroperoxide in the presence of catalyst PEO-PVP-Mo-2 (no. 8 in Table I). $T = 70\text{ }^{\circ}\text{C}$; ROOH, styrene = 1; $[\text{Me}] = 1.25 \times 10^{-3}\text{ mol/L}$; $[\text{styrene}] = 2.0\text{ mol/L}$; solvent, ethylbenzene. (Δ) Y, yield; (X) X, conversion; (O) S, selectivity.

vanadyl acetylacetonate. In a continuous process of the epoxidation, no loss of activity was observed over 50 h (Fig. 2). Molybdenyl complex of macroporous cr-PVP is found to be much less active than the complexes of gel supports with "mosaic" structure. Evidently, to achieve higher conversion in the case of polymer-bound catalysts, it is necessary that all active sites on the surface and in the bulk of the particles to be accessible for the reactant molecules.

It should be noted that molybdenum catalysts immobilized on PEO-based supports in aqueous medium (nos. 4 and 8 in Table III) show higher activity and, especially, much higher selectivity than those obtained in organic media. Moreover, the selectivity is very high irrespective of the ligand type (nos. 3 and 6 in Table III). Possibly, in the case of complexes prepared in aqueous solutions, a loosely bound water molecule plays a significant role in the subsequent formation of the molybdenum-hydroperoxide reversible complex. It is known that the easy formation of this complex determines the high catalytic activity and selectivity of the molybdenyl catalysts.^{3,23}

CONCLUSION

Potent catalysts for epoxidation of alkenes are obtained by immobilization of molybdenyl cations on polymer supports composed of inert ethylene-propylene rubber or crosslinked poly(ethylene oxide) and poly(4-vinylpyridine) ligands. Because of their

microheterogeneous mosaic-like structure better accessibility of the active sites is achieved.

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