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Catalytic Activity of Vanadium(III) and Oxovanadium(IV) Complexes in the Ziegler–Natta Synthesis of Ethylene–Propylene Elastomers

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Abstract

Vanadium and oxovanadium(IV) complexes with β-diketones, β,δ-triketones, ketophenols and their Schiff bases were prepared and their performance as components of Ziegler-Natta catalysts in ethylene–propylene copolymerization were investigated. Attempted correlations of catalytic activity with the coordination geometry, coordination number of the vanadium, steric and electronic effect of the ligands do not give regular trends. No significant improvement on the features of the copolymer produced nor on the catalyst activity was found over the commonly known vanadium catalysts.

Introduction

Ethylene–propylene copolymerization with Ziegler–Natta vanadium catalysts has been the subject of extensive academic and industrial research for many years. In this framework, investigations have been performed on the efficiency of many vanadium catalysts, since it is desirable to reduce catalyst residues in the final elastomers so as to improve their quality and performance levels, as well as to reduce cost. With this target in mind, we examined the activity of some new vanadium catalysts in ethylene–propylene copolymerization performed by both liquid monomer suspension and heptane solution processes. The new catalysts were prepared starting from some mono- and binuclear complexes of vanadium(III) and oxovanadium(IV).

Experimental

The β-diketones were commercial products. The ligands 1,5-bis(*p*-methoxyphenyl)-1,3,5-pentanetrione (H_2dmba), 1,5-diphenyl-1,3,5-pentanetrione (H_2dba), 2,4,6-heptanetrione (H_2daa), 2-acetoacetylphenol (H_2aap) and benzoylacetylphenol (H_2baap) were synthesized by literature methods [1–5].

VO(β-diketonates)$_2$ and V(β-diketonates)$_3$ were prepared as described in the literature [6], as were the Schiff base complexes [7] and complexes of triketones and their related Schiff bases [8–10].

Copolymerization Tests

Two methods were used for the polymerization tests:

(A) Polymerization in liquid monomers

The reactor was a 1.5 l autoclave, equipped with a comb stirrer, operating at controlled temperature.

Propylene, 1 l, was introduced into the reactor and then ethylene until the vessel pressure was 12.4 atm (under these conditions 5% of the ethylene was in the liquid phase). Diethylaluminium chloride (0.003 mol), diethylzinc (0.0002 mol) and the vanadium compound under test (0.05 mol), in toluene or CH_2Cl_2 medium were added, together with an activating agent (n-buthyl perchlorocrotonate [BPCC] or ethyltrichloroacetate [ETA]). During the reaction ethylene was continuously introduced into the reactor to keep constant pressure. The polymerization time was 1 h. Unreacted monomers were removed from the reactor; the obtained ethylene–

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propylene copolymer was dried at 100–110 °C and weighed.

(B) Polymerization in n-heptane solution

In each test the reactor was filled with 0.6 l of anhydrous n-heptane. Ethylene and propylene were bubbled into the solvent at rates of 1 and 2 l/min respectively. An air free solution containing ethylene and propylene in molar ratio 1:10 was obtained after 1 h. Diethylaluminium chloride (0.003 mol) n-buthylperchlorocrotonate (or ethyltrichloroacetate) (0.006 mol) and the vanadium complex under test (0.006 mol) were added; in some cases CH_2Cl_2 (10–20 ml) was also used to dissolve insoluble vanadium compounds.

The feeding of the monomers was continued for 1 h. The subsequent addition of acetone (0.5 l) to the solution caused the precipitation of the ethylene–propylene copolymer, which was separated by filtration, dried at 100–110 °C, and weighed.

Characterization of the Polymers

The polymers were dried at 100–110 °C in the presence of a stabilizer. The propylene content was determined by IR methods [11]; the intrinsic viscosity was determined in tetraline solution [12]. In addition the Mooney viscosity at 100 °C ($ML^{1+4}_{100\,°C}$), the product of the reactivity ratios $r_1 \times r_2$ [13] and the content of vanadium were determined.

Results and Discussion

Tables I and II record the results of ethylene–propylene polymerization tests (Table I by the heptane solution process; Table II by the liquid monomer

TABLE I. Yield and Properties of Ethylene–propylene Elastomers Obtained by Heptane Solution Process.

Oxovanadium(IV) complexes of the type VO(β-dike)$_2$

Ligands	Yield (g/gV)	Activator	%C$_3$ (wt)	V (ppm)	$r_1 \times r_2$	$[\eta]_{dl/g}$	$ML^{1+4}_{100°C}$
2,4-pentane dione	31800	ETA	45	29	0.73	1.5	23
2,4-pentane dione	45500	BFCC	53	12	0.43	2.0	70
3-oxobutanale	41200	BFCC	54	16	0.37	1.8	62
3,2,6,6-tetramethyl-3,5-heptane dione	29400	BFCC	52	46	0.49	1.7	43
2-acetylcyclopentanone	25500	BFCC	48	26	0.611	1.7	48
1,1,1,2,2,3,3-heptafluoro-4,6-heptane dione	43100	BFCC	55	18	0.45	2.0	76
4-(2′-anisil)-2,4-butane dione	49400	BFCC	45	33	0.69	2.1	100
3-(2′-anisil)-3-oxopropanale	26300	BFCC	45	44	0.60	2.0	64
Thenoyltrifluoroacetone	31400	BFCC	50	15	0.50	1.8	68
3-chloro-2,4-pentane dione	19600	BFCC	48	49	0.58	2.4	97

Vanadium(III) Schiff Base Complexes of the Type V(o-OC$_6$H$_4$–CH=NR)$_3$

R	R′	Yield (g/gV)	Activator	%C3 (wt)	V (ppm)	$r_1 \times r_2$	$[\eta]_{dl/g}$	$ML^{1+4}_{100°C}$
Methyl	H	35300	BPCC	54	21	0.42	2.0	73
Cyclohexyl	H	32500	BPCC	44	8	0.63	2.2	92
Phenyl	H	25500	BPCC	49	27	0.47	2.0	56
p-Tolyl	H	23900	ETA	45	29	0.60	1.3	20
p-Tolyl	H	24300	BPCC	52	–	0.39	1.9	68
o-chlorophenyl	H	19600	ETA	45	33	0.54	1.6	27
o-chlorophenyl	H	9800	ETA	41	95	0.63	1.5	–
m-chlorophenyl	H	22000	ETA	45	32	0.53	1.6	36
p-anisyl	H	11000	ETA	44	65	0.55	1.5	–
p-nitrophenyl	H	14100	ETA	43	65	0.85	1.1	10
p-Tolyl	H	15700	ETA	45	49	0.55	1.1	18

Oxovanadium(IV) Schiff Bases of the Type VO(o-OC$_6$H$_4$–CH=NR)$_2$

R	Yield (g/gV)	Activator	%C$_3$ (wt)	V (ppm)	$r_1 \times r_2$	$[\eta]_{dl/g}$	$ML^{1+4}_{100°C}$
Methyl	9800	BPCC	42	89	0.67	1.7	–
p-Tolyl	22800	BPCC	47	35	0.51	1.9	58

(continued on facing page)

TABLE I. *(continued)*

R	Yield (g/gV)	Activator	%C_3 (wt)	V (ppm)	$r_1 \times r_2$	$[\eta]_{\mathrm{dl/g}}$	$\mathrm{ML}_{100°\mathrm{C}}^{1+4}$
p-Chlorophenyl	39200	BPCC	52	19	0.41	2.0	71
m-Chlorophenyl	16400	BPCC	49	45	0.36	2.3	91
p-Anisyl	29400	BPCC	49	25	0.45	2.1	73
p-Nitrophenyl	4600	BPCC	41	–	n.d.	2.2	–

Homodinuclear Vanadyl(IV) Complexes with β,δ-Triketones

Compound	Yield	V (ppm)	$[\eta]$	%C_3 (wt)	$r_1 \times r_2$	CH_2Cl_2 (ml)	BPCC/V
$(VO)_2(dba)_2$	8800	30	2.3	45.7	0.57	20.	10
$(VO)_2(dba)_2$	7400	43	2.3	44.9	0.66	20	10
$(VO)_2(daa)_2$	5200	170	2.3	39	n.d.	23.5	10
$(VO)_2(baap)_2$	7700	49	2.6	37	n.d.	20	10
$(VO)_2(dmba)_2$	6400	81	2.7	38	0.66	23.5	10
$(VO)_2(aap)_2$	8500	30	2.4	40	n.d.	25	10

Commonly Known Vanadium Catalysts

Compounds	Yield	V (ppm)	$[\eta]_{\mathrm{dl/g}}$	%C_3 (wt)	$r_1 \times r_2$	CH_2Cl_2 (ml)	BPCC/V
$V(acac)_3$	13300	20	2.4	49	0.54	1.7	20
$V(acac)_3$	5100	30	2.3	41	–	20	20
$V(acac)_3$	3100	64	1.2	42	–	20	20
$VO(acac)_2$	14100	29	2.1	55	0.45	1.3	20
$VO(acac)_2$	6300	40	1.5	41	0.68	20	20
$VO(tme)_2$[a]	14100	32	2.3	49	0.56	2.1	20

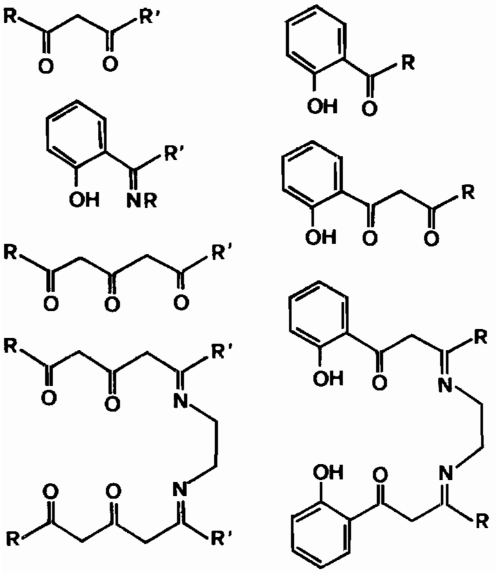
[a] Htme = 2,2,6,6-tetramethylheptanedione.

TABLE II. Yield and Properties of the Ethylene–Propylene Elastomers Obtained with Liquid Monomers Process by Mononuclear, Homo and Heterobinuclear Vanadium Complexes.

Compound	Yield	V (ppm)	$[\eta]_{\mathrm{dl/g}}$	$\mathrm{ML}_{100\,°\mathrm{C}}^{1+4}$	%C_3 (wt)	$r_1 \times r_2$
$VO(Hdba)_2$	16.800	41	1.68	40	–	–
$VO(Hdmba)_2$	7.800	–	1.31	39	42	0.6
$VO(Haap)_2$	13.700	47	1.96	55	–	–
$VO(Hbaap)_2$	6.900	82	1.80	–	40	0.8
$VO(Hbaap)_2$	6.800	–	1.44	–	37	0.7
VOH_2daaen	34.500	25	1.64	60	51	0.49
VOH_2daaen	28.200	–	1.53	49	49	0.51
VOH_2daaen Py	27.400	25	1.61	44	51	0.43
VOH_2daapd	26.600	31	1.81	53	45	0.59
VOH_2daapn	27.400	30	1.62	54	47	0.86
$(VO)_2(dba)_2$	11.800	34	1.65	52	49	0.5
$(VO)_2(dmba)_2$	9.800	50	1.70	52	45	0.6
$(VO)_2(dmba)_2$	5.900	72	1.33	46	43	0.7
$(VO)_2(dmba)_2$	5.000	80	1.98	–	40	0.6
$(VO)_2(daa)_2$	8.400	47	1.56	45	46	0.6
$(VO)_2(aap)_2$	14.700	43	1.85	63	50	0.4
$(VO)_2(aap)_2$	6.800	49	1.81	65	42	0.6
CuVOdaaen	11.800	38	2.04	–	39	0.58
NiVOdaaen	4.000	–	1.64	–	38	0.72
NiVOdaaen	8.200	61	2.20	–	37	0.70

process) for several complexes. Catalytic activity (calculated as the ratio of grams of polymer produced to grams of vanadium introduced) propylene content, intrinsic and Mooney viscosity, as well as $r_1 \times r_2$ values are given in each case.

The complexes synthesized and tested include oxovanadium(IV) and vanadium(III) complexes of β-diketones, β-ketophenol and Schiff bases; oxovanadium(IV) complexes of β,δ-triketones, β-diketophenols and compartmental ligands:



The complexes are mononuclear in the majority of cases, but binuclear complexes are derived in the case of the β,δ-triketones, β-diketophenols and compartmental ligands. The predominant geometry for the metal is square pyramidal and octahedral. The homobinuclear complexes are assayed in order to determine any enhancement of activity due to the presence of two metal atoms per ligand – an enhanced metal ratio. All of the complexes were prepared by literature routes and their purity was checked by microanalysis and physicochemical measurements.

The results show that in general there is no significant improvement, neither on the features of the copolymer produced nor on the catalyst activity, over the commercial catalyst. Attempts to correlate activity with parameters such as the coordination geometry and coordination number of the vanadium centre, steric effect of the ligand, and the electronic influence of the ligand (electronegativity, acidity of the ligand) showed no regular trend.

A plot of activity versus acidity for a series of V(β-diketonate)$_3$ complexes gave an apparently random result. The most likely influence appears to be the solubility features of the potential catalyst. This is manifest in the reduced activity figures given by the sparingly soluble homobinuclear complexes – an enhancement of activity can occur if a solubilising medium is added, and enhanced activities were seen when the very soluble, but expensive, heavily fluorinated V(β-diketonate)$_3$ complexes were used.

The heterobinuclear complexes derived from compartmental ligands were even less active than were the homobinuclear complexes, but the mononuclear oxovanadium(IV) precursors did give rates which were comparable with, or better than, the commercial species. This is again attributed to a good solubility and to the similarity of the complexes to the corresponding oxovanadium(IV) β-diketonates.

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