

Epoxidation of olefins catalysed by polymer-supported metal β -ketoesterato complexes of iron(III), nickel(II) and cobalt(II)

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Abstract

The epoxidation of linear and cyclic olefins was catalysed by iron(III), nickel(II) and cobalt(II) centres immobilized on insoluble polymers. The latter were obtained by reaction of the polymerizable complexes of Fe(III), Ni(II) and Co(II) with 2-(acetoacetoxy)ethyl methacrylate with acrylamides.

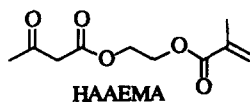
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1. Introduction

Since Mukaiyama discovered that olefins can be epoxidized using a catalytic system consisting of a metal diketonato complex, molecular oxygen and a sacrificial aldehyde [1] much effort has been devoted to the investigation of the potentialities of such a system. In this regard it has been shown by several research laboratories that organic substrates such as aldehydes [2], ketones [3], alkanes [4] α -alkoxy cyclic ketones [5] and lactams [6] can be smoothly oxidized under Mukaiyama's conditions, and that the sacrificial aldehyde can be successfully replaced by aldoacetals [7].

We have recently reported on the synthesis [8] and catalytic activity [9] of polymerizable β -ketoesterate complexes of formula $\text{Fe}(\text{AAEMA})_3$, $\text{Ni}(\text{AAEMA})_2$, $\text{Co}(\text{AAEMA})_2$

(AAEMA⁻ = deprotonated form of 2-(acetoacetoxy)ethyl methacrylate) towards the oxidation of alkenes, alkanes, alcohols, sulfides, aldehydes and ketones under Mukaiyama's conditions.



The peculiarity of our soluble catalysts was that, due to the methacrylic moiety borne by the AAEMA ligand, they might behave as precursor of supported metal complexes prone to be used in hybrid catalysis. In this paper we describe the synthesis of heterogeneous analogues of $\text{Fe}(\text{AAEMA})_3$, $\text{Ni}(\text{AAEMA})_2$ and $\text{Co}(\text{AAEMA})_2$ and their catalytic activity towards the epoxidation of various olefins [10].

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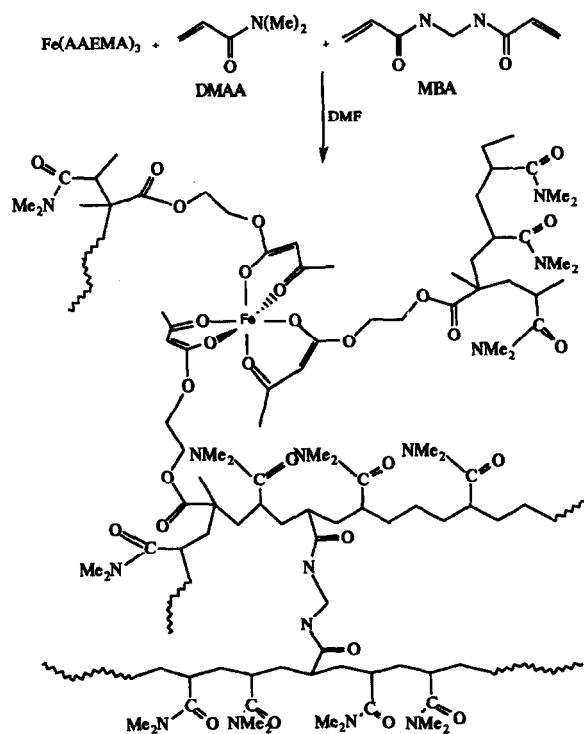
2. Results and discussion

We have already reported on the γ -ray induced synthesis of the homopolymer of $\text{Cu}(\text{AAEMA})_2$ [11]. But to obtain materials by means of radio-induced polymerization is an uneconomic method and the consequent access to the source of γ -radiation is difficult. The supported catalysts described in this paper were obtained by thermal (and therefore more convenient from the points of view of economy and the safety) copolymerization of the relevant AAEMA^- complexes with *N,N*-dimethylacrylamide (DMAA) and *N,N'*-methylenebisacrylamide (MBA) in *N,N*-dimethylformamide (DMF) (see Scheme 1).

The copolymers supporting the metals are non-hygroscopic coloured powders insoluble in all solvents. They swell well in acetone, halogenated solvents and dioxane and shrink when treated with diethyl ether or petroleum ethers. Their IR spectra in KBr show the features of coordinated β -ketoesterate at the same wavenumbers of the corresponding soluble AAEMA^- complexes, thus

substantiating that the metallo-organic units in the soluble and supported materials are similar. The presence of nitrogen in the elemental analyses of the polymers, together with the reduced percentage of metal compared to the starting complexes, attests to the reaction between the polymerizable complexes and the acrylic co-monomers.

We have already shown that cyclic and linear alkenes can be oxidized under Mukaiyama's conditions to the corresponding epoxides by using AAEMA^- complexes of Ni(II), Fe(III) and Co(II) [9]. In this regard, nickel(II) and iron(III) catalytic centres were found to be more active than the corresponding cobalt(II) based catalyst. Moreover it was found that cyclic olefins such as cholesteryl acetate, norbornene and cyclohexene are epoxidized in the presence of the sacrificial aldehyde and in the absence of the metal catalyst only if the reaction is carried out in daylight [12]. If the reaction is carried out without metal and in the dark no epoxidation takes place. In contrast, no light effect was observed in the epoxidation of linear olefins such as 1-octene and



Scheme 1. Synthesis of polymer-supported $\text{Fe}(\text{AAEMA})_3$.

1-dodecene, these olefins being epoxidized only in the presence of the metal catalyst. Taking into account these results we have tested polymer supported analogues of AAEMA⁻ complexes in the aerobic epoxidation of both cyclic and open chain substrates.

2.1. Catalytic tests

The catalytic activity of nickel(II), iron(III) and cobalt(II) supported systems was investigated in the epoxidation of norbornene, cholesteryl acetate, cyclohexene, 1-octene and 1-dodecene. The experiments on the cyclic substrates were carried out in the dark, whereas those on open chain olefins were carried out in daylight. In all cases, blank tests performed in identical conditions but without metal catalyst gave negligible conversions of the substrates. Table 1 summarizes the results obtained in two or three cycles of oxidation carried out for each substrate. Norbornene, cholesteryl acetate and cyclohexene were smoothly epoxidized both in the first run and in the recycles of the supported complex with yields ranging from 81 to 100% (entries 1–21). The stereoselectivity observed in the epoxidation of cholesteryl acetate is in all cases addressed towards the formation of the β -isomer. This tendency shows the difference between the behaviour of the supported metal complexes compared to that of their soluble analogues. In the latter case, nickel(II) and iron(III) catalysed reactions showed no significant degree of stereoselectivity [9] (b). The epoxidation of 1-octene (entries 22–27) proceeded with smaller conversions (maximum 43% with iron in the first run, entry 24). The small conversions observed in the first runs (entries 22, 24, 26) can be ascribed to the consumption of the sacrificial aldehyde, whereas the even smaller values of conversion in the recycles can be ascribed not only to the loss of catalyst during its recovery after the first cycle, but also to metal leaching. The resins recovered after the recycles, in fact, contained only 26% (Ni), 18% (Fe) and 72% (Co) of the metal initially present in the material. Similar results were observed in

the epoxidation of 1-dodecene which was carried out at 50°C and gave a maximum conversion as high as 53% with iron supporting resins. In this case the content of metal after two consecutive runs compared to the initial amount was 37% for nickel, 24% for iron and 53% for cobalt based polymers.

In conclusion, heterogenized AAEMA⁻ complexes are efficient and recyclable catalysts for the epoxidation of reactive substrates such as norbornene, cholesteryl acetate or cyclohexene, but suffer from severe metal leaching in the reaction of open chain substrates such as 1-octene and 1-dodecene.

3. Experimental

3.1. Materials and apparatus



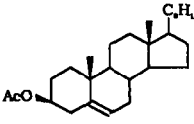
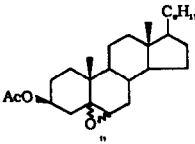






Chromatographic analyses were carried out on a Varian Vista 6000 instrument by using a capillary 30 m Carbowax 20M column or on a Hewlett Packard 5890 chromatograph using a 25 m SPB-1 capillary column. GCMS analyses were performed using a HP 5890 chromatograph (30 m SE30 column) coupled with a mass selective detector HP 5970B, 70 eV.

The aldehydes and the liquid olefins were distilled prior to use; cholesteryl acetate, norbornene and 1,2-dichloroethane were used as received.

All reactions were carried out in Schlenk tubes. A solution containing a mixture of the supported catalyst (corresponding to 0.020 mmol of metal), an olefin (2.5 mmol) and the aldehyde (7.5 mmol isobutyraldehyde or 15 mmol isovaleraldehyde) in 1,2-dichloroethane (10 ml) was stirred continuously under an atmosphere of oxygen at the desired temperature. After reaction the supported catalyst was recovered by addition to the suspension of petroleum ether and subsequent filtration. The recovered resin was washed with acetone and diethyl ether, dried under vacuum and recycled.

The epoxides were identified by comparison of their MS spectra and retention times in GC analysis with those of authentic samples.

Table 1
Epoxidation of various olefins with molecular oxygen

Entry	Substrate	Metal	Time(h)	Conv. (%)	Product
1 ^a		Ni	46	98	
2 ^{a,b}	"	"	"	98	"
3 ^a	"	Fe	"	100	"
4 ^{a,b}	"	"	"	98	"
5 ^a	"	Co	"	93	"
6 ^{a,b}	"	"	"	90	"
7 ^a		Ni	24	100 $\alpha=33\%$ $\beta=67\%$	
8 ^{a,b}	"	"	"	100 $\alpha=36\%$ $\beta=64\%$	"
9 ^{a,b}	"	"	"	85 $\alpha=37\%$ $\beta=63\%$	"
10 ^a	"	Fe	"	100 $\alpha=35\%$ $\beta=65\%$	"
11 ^{a,b}	"	"	"	98 $\alpha=31\%$ $\beta=69\%$	"
12 ^{a,b}	"	"	"	100 $\alpha=31\%$ $\beta=69\%$	"
13 ^a	"	Co	"	95 $\alpha=25\%$ $\beta=75\%$	"
14 ^{a,b}	"	"	"	93 $\alpha=24\%$ $\beta=76\%$	"
15 ^{a,b}	"	"	"	81 $\alpha=25\%$ $\beta=75\%$	"
16 ^a		Ni	40	86	
17 ^{a,b}	"	"	"	85	"
18 ^a	"	Fe	"	100	"
19 ^{a,b}	"	"	"	100	"
20 ^a	"	Co	"	100	"
21 ^{a,b}	"	"	"	90	"
22 ^c		Ni	45	28	
23 ^{c,b}	"	"	50	18	"
24 ^c	"	Fe	45	43	"
25 ^{c,b}	"	"	50	36	"
26 ^c	"	Co	45	26	"
27 ^{c,b}	"	"	50	23	"
28 ^{c,d}		Ni	50	48	
29 ^{b,c,d}	"	"	"	43	"
30 ^{c,d}	"	Fe	"	53	"
31 ^{b,c,d}	"	"	"	51	"
32 ^{c,d}	"	Co	"	29	"
33 ^{b,c,d}	"	"	"	27	"

Yields were calculated by GLC analyses as moles of epoxide per mole of starting olefin by using the internal standard method.

The diastereomer α/β ratio in 5,6-epoxycholesteryl acetate was determined by $^1\text{H NMR}$ [13].

The AAEMA⁻ complexes used in the synthesis of the supported catalysts were prepared as described in the literature [8] by adding to an ethanol solution of the relevant metal nitrate, the solution obtained by dissolving in ethanol HAAEMA and a base such as KOH or triethylamine.

3.2. Synthesis of the supported catalysts

Cobalt

The synthesis of supported Co(AAEMA)₂ was carried out in Schlenk tubes under nitrogen atmosphere. Co(AAEMA)₂ (2.0 g) was dissolved in *N,N*-dimethylformamide (DMF, 8 ml) and the resulting solution was added to the mixture of MBAA (0.32 g) and DMAA (3.0 g) in DMF (8 ml) and heated at 50°C under vigorous stirring. After 24 h reaction the pink solid which formed in the reaction vessel was filtered off, washed with acetone and diethyl ether, and dried under vacuum. Yield 5.0 g of polymer. Analysis: Co 2.98; C 56.89; H 9.39; N 12.00%. IR: 3450, 2941, 1725, 1627, 1512, 1257, 1164, 1074, 981, 780 cm⁻¹.

Iron

Fe(AAEMA)₃ (1.2 g) was dissolved in *N,N*-dimethylformamide (DMF, 7 ml) and the resulting solution was added to the mixture of MBAA (0.17 g) and DMAA (3.0 g) in DMF (7 ml) and heated at 50°C under vigorous stirring. After 24 h reaction the orange solid which formed in the reaction vessel was filtered off, washed with acetone and diethyl ether, and dried under vacuum. Obtained 4.3 g of polymer. Analysis: Fe 2.30; C

47.61; H 7.52; N 9.23%. IR: 3452, 2938, 1720, 1628, 1497, 1402, 1359, 1257, 1147, 1056 cm⁻¹.

Nickel

Ni(AAEMA)₂ (0.2 g) was dissolved in *N,N*-dimethylformamide (DMF, 8 ml) and the resulting solution was added to the mixture of MBAA (0.16 g) and DMAA (2.4 g) in DMF (8 ml) and heated at 120°C under vigorous stirring. After 24 h reaction the pale green solid which formed in the reaction vessel was filtered off, washed with acetone and diethyl ether, and dried under vacuum. Obtained 1.75 g of polymer. Analysis: Ni 1.62; C 50.73; H 7.78; N 9.11%. IR: 3453, 2937, 1721, 1629, 1511, 1400, 1354, 1260, 1143 cm⁻¹.

Acknowledgements

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Conditions: 0.02 mmol of supported metal (in the first run), 2.5 mmol substrate, 10 ml 1,2-dichloroethane, 1.0 atm O₂, room temperature.

^a Carried out in the dark in the presence of 7.5 mmol iso-butyraldehyde.

^b Recycle of the previous run.

^c In the presence of 15 mmol iso-valeraldehyde.

^d At 50°C.

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