

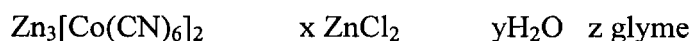


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Double metal cyanide catalysts for the preparation of polyether polyols

5 The invention relates to novel double metal cyanide (DMC) catalysts for the preparation of polyether polyols by the polyaddition of alkylene oxides to starter compounds having active hydrogen atoms.

10 Double metal cyanide (DMC) catalysts for the polyaddition of alkylene oxides to starter compounds having active hydrogen atoms are known (q.v., for example, US-A 3 404 109, US-A 3 829 505, US-A 3 941 849 and US-A 5 158 922). In comparison with the conventional preparation of polyether polyols by means of alkali catalysts such as alkali metal hydroxides, the utilisation of these DMC catalysts for the preparation of polyether polyols brings about in particular a reduction in the content of monofunctional polyethers having terminal double bonds, so-called monools. The polyether polyols thus obtained may be processed to afford high-grade polyurethanes (for example elastomers, foams, coatings). DMC catalysts are normally obtained by reacting an aqueous solution of a metal salt with the aqueous solution of a metal cyanide salt in the presence of an organic complexing ligand, for example an ether. In a typical catalyst preparation, for example, aqueous solutions of zinc chloride (in excess) and potassium hexacyanocobaltate are mixed, followed by the admixture of dimethoxyethane (glyme) to the suspension which has been formed. After filtration and washing of the catalyst with aqueous glyme solution, an active catalyst corresponding to the general formula



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is obtained (q.v., for example, EP-A 700 949).

30 JP-A 4 145 123, US-A 5 470 813, EP-A 700 949, EP-A 743 093, EP-A 761 708 and WO 97/40086 disclose DMC catalysts which, as a result of the utilisation of tert.-butanol as an organic complexing ligand (alone or in combination with a polyether (EP-A 700 949, EP-A 761 708, WO 97/40086)), in the preparation of polyether



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polyols bring about a further reduction in the content of monofunctional polyethers having terminal double bonds. Furthermore, the induction time in the polyaddition reaction of the alkylene oxides with corresponding starter compounds is reduced, and the catalyst activity increased, by the utilisation of these DMC catalysts.

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It has now been found that in the preparation of polyether polyols DMC catalysts which comprise a cyclic polyol as a complexing ligand have greatly increased activity.

10 The present invention therefore provides a double metal cyanide (DMC) catalyst comprising

a) at least one double metal cyanide compound,

15 b) at least one organic complexing ligand which is not a cyclic polyol, and

c) at least one cyclic polyol.

The catalyst according to the invention may optionally comprise d) water, preferably
20 from 1 to 10 wt.%, and/or e) one or more water-soluble metal salts, preferably from 5 to 25 wt.%, corresponding to the formula (I) $M(X)_n$ from the preparation of the double metal cyanide compounds a). In the formula (I) M is selected from among the metals Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(IV), Sr(II), W(IV), W(VI), Cu(II) and Cr(III). Zn(II), Fe(II), Co(II)
25 and Ni(II) are particularly preferred. The anions X are the same or different, preferably the same, and are preferably selected from the group comprising the halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates or nitrates. The value of n is 1, 2 or 3.

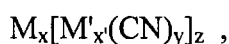
The double metal cyanide compounds a) comprised in the catalysts according to the invention are the reaction products of water-soluble metal salts and water-soluble metal cyanide salts.

- 5 Water-soluble metal salts suitable for the preparation of double metal cyanide compounds a) preferably have the general formula (I) $M(X)_n$, with M being selected from among the metals Zn(II), Fe(II), Ni(II), Mn(II), Co(II), Sn(II), Pb(II), Fe(III), Mo(IV), Mo(VI), Al(III), V(V), V(IV), Sr(II), W(IV), W(VI), Cu(II) and Cr(III). Zn(II), Fe(II), Co(II) and Ni(II) are particularly preferred. The anions X are the same
10 or different, preferably the same, and are preferably selected from the group comprising the halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates or nitrates. The value of n is 1, 2 or 3.
- 15 Examples of suitable water-soluble metal salts are zinc chloride, zinc bromide, zinc acetate, zinc acetylacetonate, zinc benzoate, zinc nitrate, iron(II) sulfate, iron(II) bromide, iron(II) chloride, cobalt(II) chloride, cobalt(II) thiocyanate, nickel(II) chloride and nickel(II) nitrate. Mixtures of various water-soluble metal salts may also be utilised.
- 20 Water-soluble metal cyanide salts suitable for the preparation of double metal cyanide compounds a) preferably have the general formula (II) $(Y)_a M'(CN)_b (A)_c$, with M' being selected from among the metals Fe(II), Fe(III), Co(II), Co(III), Cr(II), Cr(III), Mn(II), Mn(III), Ir(III), Ni(II), Rh(III), Ru(II), V(IV) and V(V). M' is
25 particularly preferably selected from among the metals Co(II), Co(III), Fe(II), Fe(III), Cr(III), Ir(III) and Ni(II). The water-soluble metal cyanide salt may comprise one or more of these metals. The cations Y are the same or different, preferably the same, and are selected from the group including the alkali metal ions and alkaline earth metal ions. The anions A are the same or different, preferably the same, and are
30 selected from the group comprising the halides, hydroxides, sulfates, carbonates, cyanates, thiocyanates, isocyanates, isothiocyanates, carboxylates, oxalates or

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5 nitrates. Both a and also b and c are integers, with the values of a, b and c being selected such that the metal cyanide salt is electrically neutral; a is preferably 1, 2, 3 or 4; b is preferably 4, 5 or 6; c preferably has the value 0. Examples of suitable water-soluble metal cyanide salts are potassium hexacyanocobaltate(III), potassium hexacyanoferrate(II), potassium hexacyanoferrate(III), calcium hexacyanocobaltate(III) and lithium hexacyanocobaltate(III).

10 Preferred double metal cyanide compounds a) which are comprised in the catalysts according to the invention are compounds corresponding to the general formula (III)



in which M is defined as in the formula (I), and
M' is defined as in the formula (II), and
15 x, x', y and z are integers and are selected such that the double metal cyanide compound is electrically neutral.

Preferably,

20 $x = 3$, $x' = 1$, $y = 6$ and $z = 2$,
 $M = \text{Zn(II)}$, Fe(II) , Co(II) or Ni(II) , and
 $M' = \text{Co(III)}$, Fe(III) , Cr(III) or Ir(III) .

25 Examples of suitable double metal cyanide compounds a) are zinc hexacyanocobaltate(III), zinc hexacyanoiridate(III), zinc hexacyanoferrate(III) and cobalt(II)hexacyanocobaltate(III). Further examples of suitable double metal cyanide compounds are to be found in, for example, US-A 5 158 922. Zinc hexacyanocobaltate(III) is particularly preferably used.

30 The organic complexing ligands b) comprised in the DMC catalysts according to the invention are known in principle and are described in detail in the prior art (for

example in US-A 5 158 922, US-A 3 404 109, US-A 3 829 505, US-A 3 941 849, EP-A 700 949, EP-A 761 708, JP-A 4 145 123, US-A 5 470 813, EP-A 743 093 and WO 97/40086). Preferred organic complexing ligands are water-soluble organic compounds having heteroatoms such as oxygen, nitrogen, phosphorus or sulfur, which are able to form complexes with the double metal cyanide compound a). Suitable organic complexing ligands are, for example, alcohols, aldehydes, ketones, ethers, esters, amides, ureas, nitriles, sulfides and mixtures thereof. Preferred organic complexing ligands are water-soluble aliphatic alcohols such as ethanol, isopropanol, n-butanol, iso-butanol, sec.-butanol and tert.-butanol. Tert.-butanol is particularly preferred.

Suitable cyclic polyols c) have at least two hydroxyl groups per molecule. They preferably possess 2 to 4 OH groups per molecule, with the numerical ratio of carbon atoms and OH groups in the molecule preferably not exceeding 4. The polyols may have aromatic or aliphatic ring structures; cycloaliphatic polyols are preferably utilised. The polyols preferably have 6 to 20 carbon atoms, the number of carbon atoms in the ring is preferably at least 8. Examples of cyclic polyol compounds which are preferably utilised are 1,2-cyclooctanediol and 1,5-cyclooctanediol.

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The DMC catalysts according to the invention comprise the double metal cyanide compounds a) in quantities of from 20 to 90 wt.%, preferably 25 to 80 wt.%, in relation to the quantity of finished catalyst, and the organic complexing ligands b) in quantities of from 0.5 to 30, preferably 1 to 25 wt.%, in relation to the quantity of finished catalyst. The DMC catalysts according to the invention normally comprise from 1 to 80 wt.%, preferably 1 to 40 wt.%, of at least one cyclic polyol c), in relation to the quantity of finished catalyst.

The catalyst composition is normally analysed by means of elemental analysis, thermogravimetric analysis or extractive removal of the ionic surface-active, or interface-active, compound content, followed by gravimetric determination.

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The catalysts according to the invention may be crystalline, partially crystalline or amorphous. The crystallinity is normally analysed by powder X-ray diffractometry.

5 Catalysts according to the invention which comprise

- a) zinc hexacyanocobaltate(III),
- b) tert.-butanol and
- c) a cyclic polyol

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are preferred.

The DMC catalysts according to the invention are normally prepared in aqueous solution by the reaction of α) metal salts, in particular corresponding to the formula (I), with metal cyanide salts, in particular corresponding to the formula (II), β) organic complexing ligands b), which are not cyclic polyols, and γ) at least one cyclic polyol c).

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In this case, the aqueous solutions of the metal salt (for example zinc chloride which is utilised in stoichiometric excess (at least 50 mol% in relation to the metal cyanide salt)) and of the metal cyanide salt (for example potassium hexacyanocobaltate) are preferably reacted first in the presence of the organic complexing ligand b) (for example tert.-butanol), with a suspension forming which comprises the double metal cyanide compound a) (for example zinc hexacyanocobaltate), water d), excess metal salt e), and the organic complexing ligand b).

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The organic complexing ligand b) may here be present in the aqueous solution of the metal salt and/or of the metal cyanide salt, or it is added in direct manner to the suspension obtained following the precipitation of the double metal cyanide compound a). The organic complexing ligand is usually utilised in excess. It has proved advantageous to mix the aqueous solutions and the organic complexing

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ligand b) with vigorous stirring. The suspension formed is normally then treated with the component c). The component c) is in this case preferably utilised in a mixture with water and organic complexing ligand b).

5 The catalyst is then isolated from the suspension by known techniques such as centrifuging or filtration. In a preferred embodiment variant the isolated catalyst is then washed with an aqueous solution of the organic complexing ligand b) (for example by re-suspension followed by re-isolation by filtration or centrifuging). Water-soluble by-products such as potassium chloride may, for example, be
10 removed in this way from the catalyst according to the invention.

The organic complexing ligand b) content of the aqueous washing solution is preferably from 20 to 80 wt.%, in relation to the total solution. It is furthermore advantageous to add to the aqueous washing solution a small quantity of the cyclic
15 polyols c) which are utilised as the component γ), preferably from 0.5 to 5 wt.%, in relation to the total solution.

It is moreover advantageous to wash the catalyst more than once. The first washing operation may, for example, be repeated for this purpose. It is, however, preferable
20 to use non-aqueous solutions for further washing operations, for example a mixture of organic complexing ligand and the cyclic polyols c) which are utilised as the component γ).

The washed catalyst is then, optionally after pulverisation, dried at temperatures of
25 generally from 20 to 100°C and pressures of generally from 0.1 mbar to normal pressure (1013 mbar).

The present invention also provides the use of the DMC catalysts according to the invention in a process for the preparation of polyether polyols by the polyaddition of
30 alkylene oxides to starter compounds having active hydrogen atoms.

Ethylene oxide, propylene oxide, butylene oxide as well as mixtures thereof are utilised as the alkylene oxides. The construction of the polyether chains by alkoxylation may, for example, be effected with only one epoxide monomer or also in random or block manner with 2 or 3 different epoxide monomers. More detailed information may be found in "Ullmanns Encyclopädie der industriellen Chemie", Vol. A21, 1992, pages 670 et seq..

Compounds having (number average) molecular weights of 18 to 2,000 and 1 to 8 hydroxyl groups are preferably utilised as the starter compounds having active hydrogen atoms. The following are named by way of example: ethylene glycol, diethylene glycol, triethylene glycol, 1,2-propylene glycol, 1,4-butanediol, hexamethylene glycol, bisphenol A, trimethylol propane, glycerol, pentaerythritol, sorbitol, cane sugar, degraded starch or water.

Starter compounds having active hydrogen atoms, such as have been prepared, for example, by conventional alkali catalysis from the aforementioned low molecular weight starters, and which constitute oligomeric alkoxylation products having (number average) molecular weights of 200 to 2,000, are advantageously utilised.

The polyaddition of alkylene oxides to starter compounds having active hydrogen atoms, which is catalysed by the catalysts according to the invention, generally takes place at temperatures of from 20 to 200°C, preferably within the range 40 to 180°C, particularly preferably at temperatures of from 50 to 150°C. The reaction may be carried out at total pressures of from 0.0001 to 20 bar. The polyaddition may be carried out without solvent or in an inert organic solvent such as toluene and/or THF. The quantity of solvent is normally from 10 to 30 wt.%, in relation to the quantity of polyether polyol to be prepared.

The catalyst concentration is selected such that good control of the polyaddition reaction can be achieved under the given reaction conditions. The catalyst concentration is generally within the range 0.0005 wt.% to 1 wt.%, preferably within

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the range 0.001 wt.% to 0.1 wt.%, particularly preferably within the range 0.001 to 0.0025 wt.%, in relation to the quantity of polyether polyol to be prepared.

5 The (number average) molecular weights of the polyether polyols prepared by the process according to the invention are within the range 500 to 100,000 g/mol, preferably within the range 1,000 to 50,000 g/mol, particularly preferably within the range 2,000 to 20,000 g/mol.

10 The polyaddition may be carried out in continuous or discontinuous manner, for example in a batch or semi-batch process.

15 Owing to their markedly increased activity the catalysts according to the invention may be utilised at very low concentrations (25 ppm and less, in relation to the quantity of polyether polyol to be prepared). If the polyether polyols prepared in the presence of the catalysts according to the invention are used for the preparation of polyurethanes (Kunststoffhandbuch, Vol. 7, Polyurethane, 3rd Edition, 1993, pp. 25-32 and 57-67), the removal of the catalyst from the polyether polyol may be omitted without disadvantage to the product qualities of the polyurethane which is obtained.

Examples**Example 1** Preparation of a DMC catalyst with 1,5-cyclooctanediol

5 9 ml of an aqueous 7.4 wt.% potassium hexacyanocobaltate solution were added, with vigorous stirring, to a mixture of 15 ml of an aqueous 11.8 wt.% zinc chloride solution, 13 ml tert.-butanol and 0.4 g 1,5-cyclooctanediol. The precipitate which formed was washed with a mixture of 10 ml tert.-butanol and 30 ml water, and was filtered off. 20 ml tert.-butanol were then added to the filter residue, which was
10 filtered again. Following the filtration the catalyst was dried at 50°C at reduced pressure (10 mbar) to constant weight.

Elemental analysis, thermogravimetric analysis and extraction:

cobalt = 10.7 wt.%, zinc = 26.1 wt.%, tert.-butanol = 6.0 wt.%, 1,5-cyclooctanediol
15 = 20.3 wt.%.

Example 2 Preparation of a DMC catalyst with 1,5-cyclooctanediol

9 ml of an aqueous 7.4 wt.% potassium hexacyanocobaltate solution were added, with vigorous stirring, to a mixture of 15 ml of an aqueous 11.8 wt.% zinc chloride
20 solution, 13 ml tert.-butanol, 6.5 ml of an aqueous 4 wt.% nicotinic acid solution and 0.4 g 1,5-cyclooctanediol. The precipitate which formed was washed with a mixture of 10 ml tert.-butanol and 30 ml water, and was filtered off. 20 ml tert.-butanol were then added to the filter residue, which was filtered again. Following the filtration the
25 catalyst was dried at 50°C at reduced pressure (10 mbar) to constant weight.

Elemental analysis, thermogravimetric analysis and extraction:

cobalt = 12.4 wt.%, zinc = 31.6 wt.%, tert.-butanol = 5.9 wt.%, 1,5-cyclooctanediol
30 = 6.0 wt.%.

Example 3 Preparation of a DMC catalyst with 1,2-cyclooctanediol

9 ml of an aqueous 7.4 wt.% potassium hexacyanocobaltate solution were added, with vigorous stirring, to a mixture of 15 ml of an aqueous 11.8 wt.% zinc chloride solution, 13 ml tert.-butanol, 6.5 ml of an aqueous 7 wt.% lactic acid solution and 0.4 g 1,2-cyclooctanediol. The precipitate which formed was washed with a mixture of 10 ml tert.-butanol and 30 ml water, and was filtered off. 20 ml tert.-butanol were then added to the filter residue, which was filtered again. Following the filtration the catalyst was dried at 50°C at reduced pressure (10 mbar) to constant weight.

Elemental analysis, thermogravimetric analysis and extraction:

cobalt = 13.2 wt.%, zinc = 30.6 wt.%, tert.-butanol = 6.2 wt.%, 1,2-cyclooctanediol = 4.82 wt.%.

Example 4 Preparation of a DMC catalyst with 1,5-cyclooctanediol

26.1 ml of an aqueous 1.84 wt.% hexacyanocobalt acid solution were added, with vigorous stirring, to a mixture of 10 ml of an aqueous 6.6 wt.% zinc acetate solution, 13 ml tert.-butanol, and 0.4 g 1,5-cyclooctanediol. 15 ml of an aqueous 11.8 wt.% zinc chloride solution were then also added. The precipitate which formed was washed with a mixture of 10 ml tert.-butanol and 30 ml water, and was filtered off. 20 ml tert.-butanol were then added to the filter residue, which was filtered again. Following the filtration the catalyst was dried at 50°C at reduced pressure (10 mbar) to constant weight.

Elemental analysis, thermogravimetric analysis and extraction:

cobalt = 14.9 wt.%, zinc = 26.4 wt.%, tert.-butanol = 7.0 wt.%, 1,5-cyclooctanediol = 4.6 wt.%.

Example 5 Preparation of a DMC catalyst with 1,2-cyclooctanediol

26.1 ml of an aqueous 1.84 wt.% hexacyanocobalt acid solution were added, with vigorous stirring, to a mixture of 10 ml of an aqueous 6.6 wt.% zinc acetate solution, 13 ml tert.-butanol, 3 ml of an aqueous 7 wt.% lactic acid solution and 0.4 g 1,5-cyclooctanediol. 15 ml of an aqueous 11.8 wt.% zinc chloride solution were then also added. The precipitate which formed was washed with a mixture of 10 ml tert.-butanol and 30 ml water, and was filtered off. 20 ml tert.-butanol were then added to the filter residue, which was filtered again. Following the filtration the catalyst was dried at 50°C at reduced pressure (10 mbar) to constant weight.

Elemental analysis, thermogravimetric analysis and extraction:

cobalt = 14.9 wt.%, zinc = 28.0 wt.%, tert.-butanol = 7.0 wt.%, 1,2-cyclooctanediol = 3.2 wt.%.

Comparison Example 6 Preparation of a DMC catalyst without cyclic polyol

9 ml of an aqueous 7.4 wt.% potassium hexacyanocobaltate solution were added, with vigorous stirring, to a mixture of 15 ml of an aqueous 11.8 wt.% zinc chloride solution, 13 ml tert.-butanol. The precipitate which formed was washed with a mixture of 10 ml tert.-butanol and 30 ml water, and was filtered off. 20 ml tert.-butanol were then added to the filter residue, which was filtered again. Following the filtration the catalyst was dried at 50°C at reduced pressure (10 mbar) to constant weight.

Elemental analysis, thermogravimetric analysis and extraction:

cobalt = 15.7 wt.%, zinc = 27.8 wt.%, tert.-butanol = 7.9 wt.%.

Preparation of polyether polyols**General method**

5 In order to determine the activity of the catalysts, 50 g polypropylene glycol starter (molecular weight = 1000 g/mol) and 20 mg catalyst were introduced under protective gas (argon) into a 500 ml pressure reactor and heated to 130°C, with stirring.

10 A maximum of 50 g propylene oxide was dispensed-in at a pressure of 2.5 bar within 30 minutes. After 30 minutes the reaction mixture was cooled to room temperature, and propylene oxide was removed by purging with argon.

The product was characterised by a molecular weight distribution (weight average) determined by GPC.

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The results obtained are recorded in the Table below:

Catalyst of Example No.	M _w [g/mol]
1	2140
2	2200
3	2200
4	2190
5	2180
6 (Comparison)	1310

Claims

1. Double metal cyanide (DMC) catalyst comprising
 - 5 a) at least one double metal cyanide compound,
 - b) at least one organic complexing ligand which is not a cyclic polyol, and
 - 10 c) at least one cyclic polyol.
2. DMC catalyst according to claim 1, comprising additionally d) water and/or e) water-soluble metal salt.
- 15 3. DMC catalyst according to claim 1 or 2, wherein the double metal cyanide compound a) is zinc hexacyanocobaltate(III).
4. DMC catalyst according to any one of claims 1 to 3, wherein the organic complexing ligand b) is tert.-butanol.
- 20 5. DMC catalyst according to any one of claims 1 to 4, wherein the catalyst comprises 1 to 80 wt.% of at least one cyclic polyol.
6. Process for the preparation of a DMC catalyst, comprising the steps
 - 25 i) reaction in aqueous solution of
 - α) metal salts with metal cyanide salts
 - β) organic complexing ligands which are not cyclic polyols, and
 - γ) cyclic polyols,
 - 30 ii) isolation, washing and drying of the catalyst obtained in step i).

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7. Process for the preparation of polyether polyols by the polyaddition of alkylene oxides to starter compounds having active hydrogen atoms in the presence of one or more DMC catalysts according to any one of claims 1 to 5.