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Hexacyanometallate Salts Used as Alkene-Oxide Polymerization Catalysts and Molecular Sieves

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New hexacyanocobaltate-based catalyst systems for the polymerization of propylene oxide have been found, together with a new type of cyanometallate, $Zn[Co(CN)_6]OH$. A detailed investigation of the cyanometallate structures has revealed that several are capable of separating small molecules, e.g., CO_2 and CH_4, with high selectivity.

INTRODUCTION

Our general interest in catalysts for alkene-oxide polymerization and in compounds with molecular sieving properties led us to investigate the hexacyanometallate salts.

Over 20 years ago the common coordination catalysts for propylene-oxide polymerizations were metal-alkoxide compounds in which only one type of transition metal was present, e.g., resulting from the reaction of $ZnEt_2$ with ROH (R = alkyl) (*1*) or of $FeCl_3$ with propylene oxide (PO) (*2*). Because of their low activity and the absence of chain transfer with uncoordinated alcohol groups these catalysts were not of interest for the propoxylation of polyfunctional alcohols to polyether polyols.

However, Milgrom *et al.* (*3*) found that certain $Zn_3[Fe(CN)_6]_2$-based systems, which contained both transition metals, were highly active catalysts for PO polymerizations. Also, these catalysts were involved in chain-transfer reactions between coordinated and free alcohol groups. Their subsequent work (*4*) showed that a particular system, which had the approximate composition $Zn_3[Co(CN)_6]_2 \cdot 0.91ZnCl_2 \cdot 2.21DME \cdot 4.29H_2O$ (DME = 1,2-dimethoxyethane) was particularly active for the propoxylation of alcohols to polyols of medium molecular weight, which are of great interest for soft polyurethane foam manufacture. However, the straightforward (and commercially most attractive) preparation of these catalysts by the reaction of the relatively cheap $Na_3[Co(CN)_6]$ or $K_3[Co(CN)_6]$ with $ZnCl_2$ did not result (*4*) in catalysts with high enough activity.

In view of the attractive properties of the catalyst of Milgrom *et al.* we further investigated this system with the intention of finding new systems, giving even higher polyether–polyol yields and allowing simpler (low-cost) preparation methods. This investigation resulted not only in the discovery of new hexacyanocobaltate-based catalyst systems, but also in the discovery of cocatalysts and a new type of inorganic compounds, the "basic" hexacyanometallate salts $Zn_2[Co(CN)_6](OH)$. These turned out to be the preferred intermediates in the preparation of the catalyst.

Investigation of the structural properties of these compounds made us aware of the adsorption properties of several hexacyanometallate salts, which have been reported in a large number of articles. As early as 1912 the uptake of H_2O and NH_3 by ferrocyanides was reported (*5*). Seifer found evidence for the adsorption of relatively large molecules (up to a kinetic diameter of 0.59 nm), such as ethanol, acetone, benzene, and toluene, by a large variety of hexacyanometallate salts (*6*). Recently ad-

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sorption data of CO, N_2, CH_4, and C_2H_6 on $K_2Zn_3[Fe(CN)_6]_2$ (rhombohedral crystal lattice) were reported (7).

However, so far no data have been published on the use of cyanometallates in physical separations. In view of our interest in such separations (e.g., CO_2 from CH_4 in natural gas) we investigated physical separations with various hexacyanometallate salts. It was found that several cyanometallates are indeed molecular sieves, capable of separating in high selectivity CO_2 from CH_4.

Since both the new polymerization systems and the molecular sieves resulted from our research on the properties of the hexacyanometallate salts, and in both cases the novel basic $Zn_2[Co(CN)_6](OH)$ was of particular importance, the results are presented here in one paper.

EXPERIMENTAL

Materials

Solid $K_3[Co(CN)_6]$ was from Alfa Inorganics (≈95% pure) or BDH (≈99% pure). Industrial solutions (purity ≈95%) of $Na_3[Co(CN)_6]$ and $K_3[Co(CN)_6]$ containing also the sodium or potassium chloride salts were from Marquart (subsidiary of Degussa in Bonn). C555-1 is a triol obtained by propoxylation of glycerol with KOH to M_n = ≈290 and is a commercial product (Shell). Propylene oxide and ethylene oxide (>99.8% pure) were from Shell.

Preparation of $Zn_3[Co(CN)_6]_2 \cdot 12\text{–}14H_2O$ *(cubic modification).* $ZnCl_2$ (40 g) was dissolved in 350 g H_2O, and 360 g of an industrial $K_3[Co(CN)_6]$ solution (12.4%) in water was added at a rate of 5 ml/min with rapid stirring. Additional water can be added to lower the viscosity of the reaction mixture. After the addition, the mixture was filtered on a G3 frit. The sticky filter cake was reslurried in 1200 g H_2O and again filtered on the same frit. This was repeated three times. Finally 176 g of a wet cake containing 55.3 g $Zn_3[Co(CN)_6]_2 \cdot 13H_2O$ (dried sample) was collected (96% yield based on $K_3[Co(CN)_6]$). The analytical data of the dried sample follow (calculated values in parentheses): Zn = 23.1% (22.8); Co = 13.2% (13.7); K = 0.09%; C = 16.5% (16.7); N = 19.0% (19.5); H = 3.03% (3.05). Excess $ZnCl_2$ was used and the order of addition of the starting materials is essential for a low potassium content.

Preparation of $Zn_3[Co(CN)_6]_2 \cdot 3H_2O$ *(rhombohedral modification).* A solution of 11.10 g $K_3[Co(CN)_6]$ (Alfa) in 225 ml H_2O was added slowly to a well-stirred solution of 7.17 g $ZnCl_2$ in 90 ml H_2O. Subsequently the reaction mixture was heated to 100°C for 15 min. The precipitate was collected on a filter and washed five times with 100 ml warm water. The yield was 9.4 g (84%), and analytical data are as follows: Zn = 29.0% (28.8); Co = 17.4% (17.3); K < 25 ppm. The order of addition of the starting materials had no significant effect on the potassium content. An excess of $ZnCl_2$ is not required. The amount of absorbed water largely depends upon the drying conditions.

Preparation of $Mg_3[Co(CN)_6]_2$. A suspension of $Zn_3[Co(CN)_6]_2 \cdot 12\text{–}14H_2O$ in water was treated with the stoichiometric amount of $3Mg(OH)_2$ with stirring for 2 days. The resulting mixture was filtered and the filtrate was evaporated to dryness (80–100°C, 20–40 mbar). $Mg_3[Co(CN)_6]_2 \cdot 12\text{–}14H_2O$ was obtained almost quantitatively: Mg = 8.1% (10.1); C = 19.7% (20.0); N = 23.7% (23.4); H = 3.3% (3.4); Zn = 307 ppm; K = 2.5%. The high potassium content is caused by the fact that $Zn_3[Co(CN)_6]_2 \cdot 12\text{–}14H_2O$ was prepared by the simultaneous addition of $K_3[Co(CN)_6]$ and $ZnCl_2$ to the reaction flask (see first preparation).

Preparation of $Zn_3[Co(CN)_6] \cdot 12\text{–}14H_2O/Zn(OH)_2$. $ZnCl_2$ (40 g) was dissolved in 350 g water and a solution of 44.4 g $K_3[Co(CN)_6]$ (Alfa) in 900 g water was added at a rate of 10 ml/min, with rapid stirring. Subsequently a solution of 5.50 g NaOH in 400 ml H_2O was added at the same rate. The reaction mixture was filtered and the filter cake was treated as in the previous example. The nonsticky final cake weighed 270 g and contained 62.7 g (98% yield) of $Zn_3[Co(CN)_6]_2 \cdot 13H_2O/Zn(OH)_2$ according to elemental analysis of a dried sample: Zn = 27.1% (27.2); Co = 11.9% (12.3); K = 0.1%; C = 14.9% (15.0); N = 17.0% (17.5); H = 2.9% (2.9). It was observed that the filtration rate was two to three times faster than in the previous preparation of $Zn_3[Co(CN)_6]_2 \cdot 13H_2O$. The cake was easier to handle since it was not sticky.

Preparation of "hexagonal" $Zn_2[Co(CN)_6](OH) \cdot 4H_2O$. A cake of $Zn_3[Co(CN)_6]_2 \cdot 12H_2O/Zn(OH)_2$ free of KCl and NaCl, prepared according to the previous experiment, was reslurried in 1 liter H_2O. The mixture was heated slowly to 54°C with stirring until the viscosity drastically reduced (about 1 h). The solid was collected on a filter; filtration was extremely rapid (a few minutes, G3 frit, 5 cm diameter). After drying, 49 g $Zn_2[Co(CN)_6](OH) \cdot 1.5H_2O$ was obtained as a free-flowing powder: Zn = 33.8% (33.5); Co = 14.5% (15.1), K = 200 ppm. In moist air the compound absorbed more water up to the composition $Zn_2[Co(CN)_6](OH) \cdot 4H_2O$, as is evidenced by a reversible 19% weight loss of the product under vacuum (according to infrared spectroscopy all water was lost under vacuum). A hexagonal crystal lattice structure with cell parameters a = 1291 pm and c = 1668 pm agrees completely with the observed X-ray diffraction powder pattern.

Preparation of other modifications of $Zn_2[Co(CN)_6]OH$. $ZnCl_2$, $K_3[Co(CN)_6]$, and NaOH were reacted in water as described in the previous experiment. The resulting reacting mixture (with all KCl and NaCl dissolved in it) was heated for 10 min at 66°C, the sudden reduction in viscosity indicating the occurrence of the reaction. The solid was collected on a filter and washed four times with 60 ml warm H_2O. Again, filtration was extremely rapid in comparison with the unheated reaction mixture. The solid product was air-dried and 50 g $Zn_2[Co(CN)_6](OH) \cdot 1.1H_2O$ was obtained (≈100% yield). Elemental analysis: Zn = 34.2% (33.9); Co = 14.7% (15.3); C = 18.8% (18.7); H = 0.82% (0.84); N = 21.8% (21.8); K = 50 ppm; Cl < 0.3%. The order of addition of starting materials had no significant effect on the amount of potassium or sodium impurities.

When $K_3[Co(CN)_6]$ or $Na_3[Co(CN)_6]$ (Marquart) was used, the reaction mixture had to be heated to 85°C. X-ray diffraction powder data showed that other (nonhexagonal) modifications had formed, different reaction conditions or starting materials favoring one over the other occasionally. Unfortunately, no assignment to a particular lattice could be made (neither by observation nor by computer). The number of water molecules varied between 0.5 and 2, depending upon the preparative conditions. In dry air or under vacuum the water is lost reversibly (IR evidence).

Preparation of $Zn_2[Fe(CN)_6](OH)$. A solution of 22 g $K_3[Fe(CN)_6]$ in 450 ml H_2O was added at a rate of 5 ml/min to a well-stirred suspension of 20 g $ZnCl_2$ in 175 ml H_2O. Subsequently a solution of 2.75 g NaOH in 200 ml H_2O was added similarly. Stirring was continued for one additional hour, after which the temperature was raised to 75°C for 15 min. The product was isolated by filtration and subsequent washings. The yield was quantitative. X-ray diffraction powder data were identical to those of hexagonal $Zn_2[Co(CN)_6](OH)$.

When the suspension was heated for 10 min at 100°C, a nonhexagonal modification formed, according to X-ray data again similar to one of the nonhexagonal modifications of the cobalt analog. For both modifications the infrared absorptions assigned to the OH group were identical with those of $Zn_2[Co(CN)_6](OH)$.

Zinc Chloride Hexacyanocobaltate (ZCCH)-Based Catalyst Preparations

Catalyst 1. 44 g cake of $Zn_3[Co(CN)_6]_2 \cdot 12\text{–}14H_2O$, thoroughly freed from K^+ (see above), prepared from 13.6 g $K_3[Co(CN)_6]$ (Marquart), was mixed with 150 ml 1,2-dimethoxyethane. To 44.1 g of this suspension a mixture of 0.60 g $ZnCl_2$ in 4 ml H_2O

+ 8 ml DME was added. After 5 days of stirring the ZCCH concentration in the mixture was determined by drying a small sample in air (8.47% ZCCH). Then 39.0 g of the mixture was mixed with 98.1 g C555-1 (triol) in a rotating evaporator. After mixing, about 36 g volatiles was removed under vacuum (20–40 mbar) at 55°C in 2 h. This left a stable ZCCH suspension in C555-1 with a catalyst concentration of 3.27%.

Catalyst 2. 233 g final cake of $Zn_3[Co(CN)_6]_2 \cdot 12\text{–}14H_2O/Zn(OH)_2$, prepared as above from 44.2 g $K_3[Co(CN)_6]$, 40.8 g $ZnCl_2$, and 5.4 g NaOH, was mixed with 646 g DME. Subsequently, 163 g of this mixture was taken and a mixture of 4.4 ml concentrated (37%) aqueous HCl + 4 ml H_2O + 25 ml DME was added with rapid stirring. After 3 days of gentle stirring, the ZCCH concentration in the mixture was determined (11.6 g mixture contained 0.736 g ZCCH, corresponding with a concentration of 6.34%). After a "solvent" switch as above, a 3.67% ZCCH suspension in C555-1 was obtained. The solid ZCCH catalyst left after evaporation of the original DME/H_2O suspension in air (relative humidity lower than 50%) was analyzed. The analytical data corresponded well with the formula $Zn_2[Co(CN)_6]Cl \cdot 0.5HCl \cdot DME.2.75H_2O$: Zn = 23.9% (24.3); Co = 11.2% (10.9); Cl = 9.5% (9.8); N = 15.2% (15.6); C = 21.9% (22.3); H = 2.9% (2.9). A suspension of the solid catalyst or of the C555-1 catalyst in water reacted strongly acidic ($pH < 1$).

Catalyst 3. This preparation was completely analogous to catalyst 1, except for the addition of 0.7 ml concentrated (37%) aqueous HCl together with the 0.60 g $ZnCl_2$ in DME/H_2O. The final C555-1 suspension contained 3.61% catalyst and was strongly acidic.

Catalyst 4. 4.0 g $Zn_2[Co(CN)_6](OH) \cdot 2H_2O$ was suspended in a mixture of 29 g DME and 6.5 g H_2O at 40°C. Subsequently 2.1 g (37%) aqueous HCl was added with rapid stirring. Within 2 min the suspension became very viscous, but within 2.5 h the viscosity was again much lower. Then 113.2 g C555-1 was added and volatiles were removed under vacuum in a rotating evaporator (20–30 mbar, 50–60°C, 2 h), leaving 118.7 g of a C555-1 suspension containing 4.6% ZCCH.

Catalyst 5 + cocatalyst. 5.0 g $Zn_2[Co(CN)_6](OH) \cdot 1.13H_2O$ was suspended in 21.4 g DME and subsequently 7.5 ml (15%) aqueous HCl was added in 30 s with rapid stirring. Stirring was continued overnight, after which a solution of 1.8 g $ZnSO_4 \cdot 7H_2O$ in 3.2 g H_2O was added to the viscous suspension. After 20 s a very thixotropic suspension was obtained, which was set aside for a few days. Subsequently 90.2 g C555-1 was added and the mixture homogenized. After stripping in a rotating evaporator (55–60°C, 20–30 mbar) 98.4 g of a thixotropic C555-1 suspension containing 6.5% ZCCH was obtained. Instead of $ZnSO_4 \cdot 7H_2O$ other cocatalysts may be added. In most cases the final ZCCH concentration in C555-1 was kept at about 4%.

Catalyst 6. A mixture of 3.8 g $Zn_2[Co(CN)_6](OH) \cdot 2H_2O$, 9.3 g H_2O, and 31 g DME was stirred and 3.2 g aqueous (46%) HBr was added dropwise. Subsequently the stirred mixture was set aside for 6 days. 33.7 g of the mixture was evaporated to dryness under vacuum, leaving 4.10 g of a solid residue. The analytical data corresponded well with the formula $Zn_2[Co(CN)_6]Br \cdot 0.8HBr \cdot 1.5DME \cdot 2H_2O$: C = 21.0% (21.7); H = 2.84% (3.02); N = 11.7% (12.6); Br = 21.0% (21.7).

Catalyst 7. The preparation was similar to catalyst 6, except that 8.0 g (18%) aqueous HCl was added instead of HBr. The resulting reaction mixture was evaporated to dryness under vacuum, in two portions. Elemental analysis showed that the resulting two products differed slightly: $Zn_2[Co(CN)_6]Cl \cdot 0.8HCl \cdot 1.25DME \cdot 2.4H_2O$, Zn = 22.4% (23.0); Co = 10.3% (10.4); Cl = 11.1% (11.3); C = 23.2% (23.3); H = 3.1% (3.2); N = 14.7% (14.8) vs $Zn_2[Co(CN)_6]Cl \cdot 0.6HCl \cdot 1.2DME \cdot 1.85H_2O$, Zn = 23.7% (24.0); Cl = 10.3% (10.4); N = 15.1% (15.4); C = 23.0% (23.8); H = 2.8% (3.0).

Various other catalysts were prepared by variation of the relative amounts of HCl, DME, $ZnSO_4$, or by using $K_3[Co(CN)_6]$ or $Na_3[Co(CN)_6]$ from different suppliers.

Polymerization Experiments

Polymerizations took place in a 2.5-liter reactor. C555-1 was used as the initiator. The addition of propylene oxide (containing 11 wt% ethylene oxide) was pressure controlled. Usually 0.1–0.2 g ZCCH per mole of hydroxyl group was used. Operating conditions: 115°C, 3 bar (abs.), and rapid stirring of the reaction mixture. Surprisingly, it was found that the lower catalyst concentrations ($0.1 \text{ g} \cdot \text{mol OH}^{-1}$) gave somewhat lower polyether–polyol yields than the higher concentrations ($0.2 \text{ g} \cdot \text{mol OH}^{-1}$). The polymerization reactions were stopped when the catalyst no longer showed any activity (6–8 h). The results are given in Table 1.

TABLE 1

Polyether-Polyol Yields Obtained with Various Catalysts

Catalyst	Source $K_3Co(CN)_6$	Nature	Cocatalyst	ZCCH, $g \cdot (\text{mol OH})^{-1}$	Polyether–polyol yield[a,b] $kg (g \cdot cat)^{-1}$
1	Marquart	Suspension	—	0.20	3.1
1	Alfa	Suspension	—	0.20	4.5
2	Marquart	Suspension	—	0.20	5.8
2	Marquart	Suspension	—	0.10	3.3
2	Alfa	Suspension	—	0.20	7.5
2	Alfa	Solid	—	0.20	7.7
3	Marquart	Suspension	—	0.20	5.8
4	Alfa	Suspension	—	0.15	7.1
5	Alfa	Suspension	$ZnSO_4$	0.20	15.3
5	Marquart	Suspension	$ZnSO_4$	0.20	14.6
5	Marquart	Suspension	$ZnSO_4$	0.10	12.7
5	Marquart	Suspension	H_2SO_4	0.10	10.2
5	Marquart	Suspension	$MgSO_4$	0.10	12.0
6	Alfa	Solid	—	0.22	5.6[c]
7	Alfa	Solid	—	0.20	7.5

[a] M_w/M_n ratios are between 1.15 and 1.30.

[b] Reproducibility ±4% or better.

[c] When a correction is made for the molecular weight increase of the catalyst due to the substitution of bromine for chlorine, the yield would be $7.5 \text{ kg} \cdot (\text{g cat})^{-1}$.

Adsorption Experiments

Two experimental methods were used to obtain information about adsorption capacities and diffusion rates.

Method a. After dehydration of the cyanide, the weight increase during gas adsorption was followed with time, with the aid of a microbalance. Two balances were used, a magnetic suspension balance, Model 4201, and a microbalance, Type 4410, both from Sartorius. The former is accurate to 10 μg and the latter to 1 μg.

Typically, sample weights were between 0.5 and 1 g and 30–80 mesh fractions were selected.

Method b. This method was developed in order to follow the actual separation of gas mixtures. After dehydration of the cyanometallate a volume was filled with the CO_2/CH_4 gas mixture. The composition of the gas mixture above the cyanometallate was recorded every 10 s by a mass spectrometer and followed over a 1-h period. We used a Balzers quadrupole mass spectrometer QMG 111 (minimum pressure $< 10^{-7}$ Torr; maximum pressure 5×10^{-5} Torr), with a sensitivity of $> 10^{-4}$ A/Torr.

RESULTS AND DISCUSSION

I. Catalysts for Alkene-Oxide Polymerization

As reported by Herold *et al.* (*4*), incorporation of Na^+ or K^+ ions into the zinc chloride hexacyanocobaltate-based catalyst, further designated as the ZCCH catalyst, results in a substantially reduced activity. This finding, which was confirmed by us, necessitates careful removal of these ions when the catalyst is prepared according to Eqs. (1) and (2):

$$2K_3[Co(CN)_6] + 3ZnCl_2 \longrightarrow Zn_3[Co(CN)_6]_2 + 6KCl \quad (1)$$

$$Zn_3[Co(CN)_6]_2 + ZnCl_2 \xrightarrow{DME/H_2O} Zn_3[Co(CN)_6]_2 \cdot xZnCl_2 \cdot yDME \cdot zH_2O \quad (2)$$

(normally x varies between 0.7 and 1.2, y

between 1.5 and 2.5, and z between 3 and 10).

However, a great disadvantage of this seemingly simple preparative route is the tendency of $Zn_3[Co(CN)_6]_2$ (cubic modification) to form "water-rich" cakes from which KCl is hard to remove. Boiling of the KCl-containing $Zn_3[Co(CN)_6]_2$ suspension gave the rhombohedral modification (*8*) of $Zn_3[Co(CN)_6]_2$, which could easily be collected on a filter and freed from KCl. However, catalysts prepared with this rhombohedral compound according to Eq. (2) had a low activity (normally the polyether–polyol yield was <2.5 kg · g cat^{-1}).

Preparation of a mixed precipitate of $Zn_3[Co(CN)_6]_2/Zn(OH)_2$ facilitated the isolation of a product with a low potassium content ($<\approx 0.1\%$). The ZCCH preparation was adapted correspondingly, according to Eqs. (3) and (4):

$$4ZnCl_2 + 2K_3[Co(CN)_6] + 2KOH \longrightarrow Zn_3[Co(CN)_6]_2/Zn(OH)_2 + 8KCl \quad (3)$$

$$Zn_3[Co(CN)_6]_2/Zn(OH)_2 + 2HCl \xrightarrow{H_2O/DME} Zn_3[Co(CN)_6]_2 \cdot ZnCl_2 \cdot y\text{DME} \cdot zH_2O. \quad (4)$$

Surprisingly, using more than the stoichiometric amount of HCl gave catalysts that were more active (polyether–polyol yields of 5.5–7.5 kg · g cat^{-1} when 50% or more excess HCl is used) than the ones obtained via the stoichiometric reaction (4).

Further investigation of this HCl effect showed that (1) addition of HCl to the reaction mixture obtained according to Eq. (2) gave a similar effect, and (2) the resulting ZCCH catalysts had a new composition. According to elemental analysis the new composition is approximately

$$Zn_2[Co(CN)_6]Cl \cdot 0.5HCl \cdot DME \cdot 2H_2O.$$

(The amounts of HCl, DME, and H_2O may vary, e.g., for HCl between 0.05 and 0.6, in general.) After the incorporation of HCl the catalyst formula has been changed since X-ray powder data showed that the ZCCH crystal lattice structure is definitely different from that of either $Zn_3[Co(CN)_6]_2$ or $ZnCl_2$. In addition the new formula is more in line with the formula of the hydroxo complexes, discussed below.

A final improvement in the ZCCH preparation involved the discovery of new type of inorganic compounds, the basic hexacyanometallate salts.

Hydroxyhexacyanometallate zinc salts. These new compounds were prepared by heating a mixture of the hexacyanometallate salts with the corresponding hydroxide according to

$$Zn_3[Co(CN)_6]_2 + Zn(OH)_2 \xrightarrow[H_2O]{50-100°C} 2Zn_2[Co(CN)_6](OH)(H_2O)_n \quad (5)$$

(n depends on the crystal-structure modification and drying conditions).

The reaction according to Eq. (5) is typical of hexacyanometallate salts, as is shown by the corresponding reaction with $Zn_3[Fe(CN)_6]_2$. These zinc hexacyanocobaltate hydroxides have low contents of alkali metal impurities (50–500 ppm) and are rapidly isolatable by simple techniques (filtration, sedimentation, centrifugation). This makes these compounds excellent starting materials for the preparation of the ZCCH catalyst according to

$$Zn_2[Co(CN)_6](OH) + HCl\ (\text{excess}) \xrightarrow{DME/H_2O} Zn_2[Co(CN)_6]Cl \cdot 0.5HCl \cdot DME \cdot 2H_2O. \quad (6)$$

Again, depending upon the drying conditions, the actual amounts of HCl, DME, and/or H_2O may vary without appreciably affecting the catalytic activity. Polyether–polyol yields up to 8 kg · g cat^{-1} were obtained.

A bromide analog of the ZCCH catalyst, which has a similar activity and crystal structure (powder diffraction data), was prepared with HBr instead of HCl. $Zn_2[Fe(CN)_6](OH)$ gave the corresponding hexacyanoferrate analog, which is, however, less suitable for polyol manufacture as has been reported previously (*4*).

Cocatalysts. So far, the maximum obtainable polyol yield with the triol initiator was limited to about 8 kg · g cat^{-1} because of catalyst deactivation during the polymerization reaction. Attempts to increase the yield by partial or complete replacement of zinc by other metals were not successful. However, attempts to decrease the deactivation rate by addition of certain inorganic salts resulted in increased yields.

We assumed deactivation to be a consequence of an irreversible dissociation of Zn^{2+} from the active sites. Since addition of zinc compounds to the polymerization mixture may reverse such a dissociation, several zinc salts were screened for this purpose. This led to the finding that zinc sulfate increased the polyether–polyol yield, particularly when added to the ZCCH suspension in DME/H_2O. Via a solvent switch (see Experimental) the zinc sulfate and the catalyst were suspended in the triol initiator. Polyether–polyol yields up to 17 kg · g cat^{-1} were obtained with a ZCCH : $ZnSO_4$ ratio of 1 : 1 to 1 : 2. A fortunate feature of the cocatalyst is that differences in yield caused by the use of batches of $K_3[Co(CN)_6]$ or $Na_3[Co(CN)_6]$ of different origin are absent.

Further studies surprisingly showed the sulfate ion, and not the zinc, to be responsible for the cocatalyst effect: $Ce(SO_4)_2$, $MgSO_4$, $Al_2(SO_4)_3$, $TiOSO_4$, and even H_2SO_4 gave yield increases similar to or somewhat less than $ZnSO_4$ (in all cases the hydrated salts were used). In contrast, addition of $ZnCl_2$, $Zn(NO_3)_2$, or $Zn(O_2CCH_3)_2$ did not affect the polyol yield significantly. Kinetic studies indicated the increased yield to be mainly due to an increased lifetime of the catalyst. Apparently, the sulfate ion stabilizes the catalyst surface.

Structural properties. X-ray powder diffraction data gave fairly simple line patterns. Depending upon the preparative conditions (particularly during the isolation of the solid catalyst), at least three different, though similar, diffraction patterns were obtained. Unfortunately, no assignment of cell parameters was found. The only useful structural information came from the electron microscope. Small (largest dimension 0.1–1.0 μm), thin, hexagonally shaped plates were observed, suggesting a structure (*9*) similar to that of $[Cu(CO)]_2[Pt(CN)_6]$ or $Zn_2[Fe(CN)_6](H_2O)_2$. The occurrence of the various similar modifications of ZCCH is assumed to arise from differences in the number of molecules between the hexacyanometallate layers.

In view of our interest in new molecular sieves, we investigated the structure of cyanometallates in more detail.

The crystal structure of $Zn_3[Co(CN)_6]_2$ (=ZHC) has been reported (*10a*). It possesses a cubic space group (*Fm3m*) with a density of 1.72 g/cm^3 and bond lengths Co—C = 0.190; Zn—N = 0.210; Zn—O = 0.213, and C≡N = 0.114 nm. The lattice structure is shown in Fig. 1. As can be deduced from the structure and its stoichiometry, ZHC has vacancies created by the omission of 33% of the $[Co(CN)_6]^{3-}$ ions (0.88 nm) in a NaCl-type lattice, charge neutrality thus being maintained.

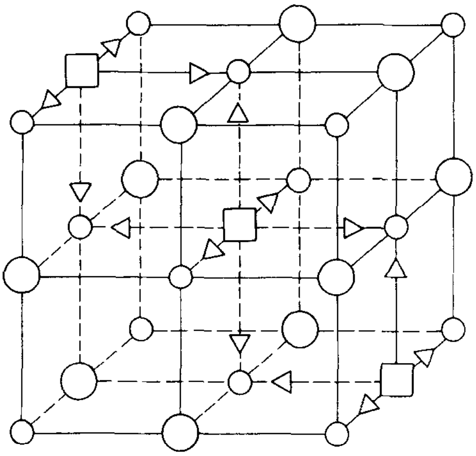

FIG. 1. Lattice structure of $M_3[Co(CN)_6]_2 \cdot xH_2O$ small circles, M^{2+} ions; large circles, $Co(CN)_6^{3-}$ ions with the ligands bonded as Co^{3+}–CN–M^{2+}; triangles, H_2O coordinated to M^{2+}; squares, empty positions (in principle a more random distribution over the lattice can exist in such a way that $\frac{1}{3}$ of the four "$Co(CN)_6^{3-}$ positions" in the lattice are unoccupied).

By connecting the structural vacancies present, channels can be formed, with pore openings after dehydration of ca. 0.56 × 0.86 nm for the cubic symmetry. It is possible to vary *x* and *y* in $M^{I}_{x}[M^{II}(CN)_6]_y$ and thus the number of vacancies in the cyanide complexes, from 50% in, e.g., $Cu_2[Fe(CN)_6]$ to none in $Zn[Fe(CN)_5NO]$. From the unit cell we can calculate the number of vacancies required to have all vacancies interconnected, thereby forming a channel system. A channel is formed in the unit cell when three $M(CN)_6$ positions are vacant: one for entering, one for the center position, and one for leaving. Therefore the number of vacancies must be $1 + 2 \times \frac{1}{4} = 1\frac{1}{2}$ (the in and out positions share only $\frac{1}{4}$ with the unit cell). In total, there are four $M(CN)_6$ positions in the unit cell and thus the requirement of an interconnecting pore structure is 37.5% of vacant $M(CN)_6$ positions. Furthermore, when the cyanide complex possesses no vacancies, e.g., $Zn[Fe(CN)_5NO]$, a small opening of ca. 0.3 nm is still present, which is probably large enough to adsorb small molecules.

We selected various cyanometallates with increasing numbers of vacancies for adsorption studies; most of them were of the cubic structure type (see Table 2). $Zn_3[Co(CN)_6]_2$ with the rhombohedral symmetry is isostructural with $K_2Zn_3[Fe(CN)_6]_2$ (*7b*). The latter complex has a pore opening of 0.39 × 0.52 nm, which is significantly smaller than that of $Zn_3[Co(CN)_6]_2$ with the cubic symmetry.

For the $Zn_2[Co(CN)_6](OH)$ compounds in one case the lattice parameters were determined: a hexagonal unit cell with $a = 1291$ pm and $c = 1668$ pm. This modification resulted when the compound was prepared in the absence of KCl and NaCl, at mild temperatures (50–60°C). In the presence of KCl two other modifications (not resolved) were formed. With $Zn_2[Fe(CN)_6](OH)$ similar results were obtained.

The infrared spectra of all modifications of $Zn_2[Co(CN)_6](OH)$ (dehydrated) showed three sharp absorptions (3671, 969, and 590 cm^{-1}) related with the OH group. The peak at 3671 cm^{-1} shows that HO · · · H interactions are absent. Hydration of the com-

TABLE 2

Sorption Measurements of CO_2 and CH_4 on Cyanometallates[a] (1 bar, 22°C)

Cyanometallate	Structure on basis of XRD[a]		Temperature (°C)		Adsorption capacity		Diffusion rate	
	After synthesis	After dehydration	Dehydration	Decomposition	CO_2 (mmol/g)	CH_4 (mmol/g)	CO_2 (s^{-1})	CH_4 (s^{-1})
$Cu_2[Fe(CN)_6]$	Cubic	Amorph	rt	170	marg[b]	marg	—	—
$Ni_2[Fe(CN)_6]$	Cubic	Cubic + extra lines	200	320	0.4	marg	1×10^{-3}	—
$Mg_3[Co(CN)_6]_2$	Cubic	Cubic	150	615	3.6	0.7	0.5×10^{-3}	Too fast
$Ca_3[Co(CN)_6]_2$	Cubic	Low symmetry	195	340	0.6	nm	2.7×10^{-5}	nm
$Zn_3[Co(CN)_6]_2$	Cubic	Cubic + extra lines	310	640	1.5	0.4	1.5×10^{-3}	Too fast
$Zn_3[Co(CN)_6]_2$	Rhomb	nm	175	640	1.7	0.4	2.1×10^{-3}	Too fast
$Zn_3[Co(CN)_6]_2$	Rhomb	nm	175	640	1.8	0.4	1.3×10^{-3}	Too fast
$Co_3[Co(CN)_6]_2$	Cubic	Cubic	111	>480	2.9	0.5	1.0×10^{-3}	7.5×10^{-3}
$Fe_4[Fe(CN)_6]_3$	Cubic	Cubic	150	130	1.1	0.2	1×10^{-4}	Too fast
$Zn[Fe(CN)_5NO]$	Cubic	Cubic	rt	≈430	1.9	0.4	3.5×10^{-4}	3.5×10^{-6}
$Zn_2[Co(CN)_6]OH$	Hexag	nm	rt	≈470	2.7	0.4	2.7×10^{-4}	2.7×10^{-3}
$Zn_2[Co(CN)_6]OH$	Hexag	nm	110	≈470	2.5	0.9	1.0×10^{-3}	Too fast
$CoK_2[Co(CN)_6]$	?[c]	?[c]	160	560	0.8[d]	marg	3.1×10^{-4}	Too fast

[a] Abbreviations: XRD, X-ray diffraction; amorph, amorphous; rt, room temperature; marg, marginal; nm, not measured; rhomb, rhombohedral; hexag, hexagonal.

[b] Similar results were obtained for $Ca_2[Fe(CN)_6]$; $K_3[Fe(CN_6]$; $K_4[Fe(CN)_6]$ and $Na_2[Fe(CN)_5NO]$.

[c] See Ref. (*13*).

[d] Not reproducible.

pound did not affect the absorptions related with the cyanide group (2197 and 474 cm^{-1}). Since this hydration is also reversible, it is concluded that the absorbed water molecules do not coordinate (*10*) to the zinc ion and are present as zeolite-type water. In view of the energies of the three OH-related frequencies and the fact that a coordination number of at least four is expected for zinc, the OH group is expected to be bridging between two zinc ions.

The presence of zeolite-type water is known (*7, 10*) for transition metal salts of the hexacyanometallates. For instance, in the case of $Zn_3[Co(CN)_6]_2 \cdot 12H_2O$ six of the water molecules are coordinated to zinc ions, while the other six are present as zeolite-type water.

II. Molecular Sieving Properties

Here we will illustrate the CO_2/CH_4 sieving properties of the present series of cyanometallates. Sorption equilibria and sorption rates were determined under various conditions of pressure and temperature. Diffusion rates and, derived from them, diffusion coefficients can be calculated using the equations of Ref. (*11*).

Table 2 gives a survey of the CO_2/CH_4 adsorption data (at 1 bar, room temperature) on various cyanometallates measured with the microbalance.

Prior to use, the complexes were completely dehydrated. The dehydration temperature (measured under a nitrogen atmosphere with a thermoanalyzer) are indicated in the table, together with the temperatures of decomposition. This dehydration was found to be reversible for all complexes, with the exception of $Cu_2[Fe(CN)_6]$.

In going from cubic $M^{I}_{2}[(M^{II}(CN)_6]$ (50% of vacancies) to $M^{I}_{4}[M^{II}(CN)_6]_3$ (25% of vacancies), porosity is expected to decrease. As is shown in the table, no or little adsorption of CO_2 and CH_4 was found for the $M_2[Fe(CN)_6]$-type complexes in which M = Ca^{2+}, Cu^{2+}, and Ni^{2+}. The marginal adsorption of these complexes is caused by the reduced pore opening as a result of symmetry change after dehydration (reversible for M = Ni^{2+}). Furthermore it was found that these complexes have a low stability, in agreement with Ref. (*12*).

In the series of the cubic $M_3[Co(CN)_6]_2$ complexes (M = Mg^{2+}, Ca^{2+}, Zn^{2+} and Co^{2+} with ionic radii of 0.066, 0.099, 0.074, and 0.072 nm, respectively) an increase of adsorption capacity is expected with an increase of the size of the charge-balancing cation. However, the highest CO_2 adsorption capacity (in mmol/g) is found for the magnesium hexacyanocobaltate. If we calculate from the adsorption capacity the number of CO_2 molecules per mole M^{2+}, a value of 0.6 mol/mol for $M^{2+} = Mg^{2+}$ and Co^{2+} is obtained, which might be the highest possible interaction between CO_2 and the cation side for this type of complex under these conditions of temperature and pressure. Again, the low CO_2 adsorption found for $M_3[Co(CN)_6]_2$ (in which M = Ca^{2+} or Zn^{2+}) might be explained by the reduced pore opening as a result of the lowering of symmetry after dehydration of the complex. This is also reflected in the low CO_2 adsorption capacity found for rhombohedral $Zn_3[Co(CN)_6]_2$ in comparison with the cubic $Zn_3[Co(CN)_6]_2$ modification.

The high adsorption found for CO_2 and the low adsorption obtained for CH_4 indicate that these types of cyanometallate complexes are molecular sieves for the separation of CO_2 and CH_4. Diffusion rates of CH_4 could not always be calculated as a result of too fast (surface) adsorption.

In going from $M_3[M(CN)_6]_2$ to $Fe_4[Fe(CN)_6]_3$ the number of vacancies is further reduced from 33 to 25%. The requirement for an open structure is 37.5% of vacant $M(CN)_6$ positions. This means that in an ordered $Fe_4[Fe(CN)_6]_3$ lattice the pores are partly blocked, leading to a low sorption capacity and a low diffusion rate. We wish to remark that dehydration of $Fe_4[Fe(CN)_6]_3$ is difficult due to the low decomposition temperature of the complex (see Table 2).

Furthermore, when no vacancies are present in a cubic cyanide lattice, e.g., Zn $[Fe(CN)_5NO]$, separation of CO_2 and CO_4 is still possible via the small openings of ca. 0.3 nm, but with a lower diffusion rate. This indicates that in $M^{I}_{x}[M^{II}(CN)_6]_y$ complexes two types of channel are present with different pore diameters.

Due to a different structure or pore blocking by small cations little or no CO_2 adsorption was measured for $K_3[Fe(CN)_6]$, $K_4[Fe(CN)_6]$, $Na_2[Fe(CN)_5NO]$, and $CoK_2[Co(CN)_6]$.

The new complex $Zn_2[Co(CN)_6]OH$ with a hexagonal unit cell has a CO_2 adsorption comparable to the other zinc hexacyanocobaltates, since for all these complexes 0.3–0.5 mol of CO_2 per mole of zinc was measured, as was also found for the ZCCH catalyst: ZCCH is based on a $Zn_3[Co(CN)_6]_2$ lattice in which $ZnCl_2$, DME, and H_2O are incorporated. After removal of DME and H_2O the lattice only contains $ZnCl_2$. When x in the catalyst formula used in Eq. (2) is equal to 1, the structural formula can be rewritten as $Zn_2[Co(CN)_6]Cl$. Using this formula, again a maximum capacity of 0.35 mol CO_2 per mole of zinc was measured at this temperature and pressure.

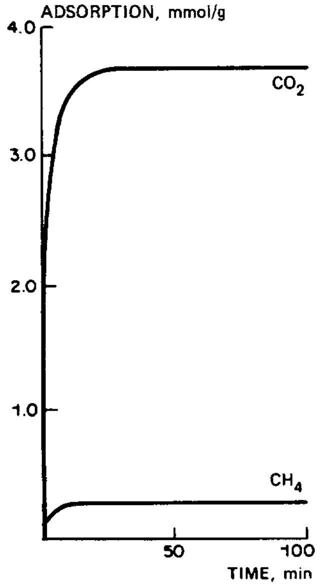

FIG. 2. The adsorption of CO_2 and CH_4 on $Mg_3[Co(CN)_6]_2$, 20°C, 1 bar.

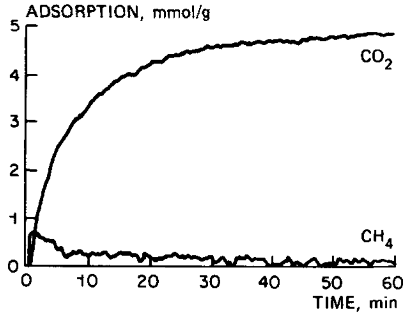

FIG. 3. Mass spectrometer measurements of the adsorption of CO_2 and CH_4 on $Mg_3[Co(CN)_6]_2$ at −42°C, P_{CO_2} = 1 bar.

From Table 2 we can conclude that $Mg_3[Co(CN)_6]_2$ (= MHC) is most suitable for the separation of CO_2 and CH_4 (see Fig. 2). We therefore investigated the properties of this complex in more detail and found that both the adsorption capacities and the diffusion rates are hardly affected when a 1 : 1 $CO_2 : CH_4$ gas mixture is used instead of pure CO_2 and CH_4 separately.

The data presented in Table 2 were obtained from the total uptake of the adsorbates, which are measured separately as pure gases or in mixtures. These data yield an indication of the possible sieving behavior. In order to gain more information about the actual separating properties of these complexes, we made an experimental setup using a mass spectrometer as described in the Experimental section. After dehydration of the cyanometallate and evacuation, the volume was filled with a 1 : 1 mixture of CO_2 and CH_4. The data obtained were corrected for the CO_2/CH_4 consumption by the mass spectrometer, by measuring the $CO_2 : CH_4$ ratios without the molecular sieve. From the change in relative concentrations the adsorption capacities of CO_2 and CH_4 were calculated and from these the diffusion rates as in the microbalance experiments. An illustration of the CO_2/CH_4 adsorption properties of $Mg_3[Co(CN)_6]_2$ (at −42°C, 1 bar) as measured by the mass spectrometer is shown in Fig. 3. The diffusion rates were found to be comparable with those obtained in the microbalance experiments, indicating that this technique is a valuable alternative method (see Table 3). Unfortunately, the absolute adsorption capacities cannot be derived with this system, since during the filling operation a considerable amount of gas is already adsorbed (30%). The above-mentioned results and the fact that CO_2 can be desorbed completed (see Fig. 4) confirms that the cyanometallates are molecular sieves capable of separating CO_2 from CH_4 with a high selectivity.

CONCLUSIONS

The new catalysts, which were highly active in propylene oxide polymerizations, contained HCl in their lattice structure. The approximate formula is $Zn_2[Co(CN)_6]Cl \cdot 0.5HCl \cdot DME \cdot 2H_2O$, although the amounts of HCl, DME, and H_2O may vary.

TABLE 3

Microbalance Experiments on MHC[a]

Gas	p (bar)	T, (°C)	$Mg_3[Co(CN)_6]_2$	
			D/r_0^2 (s^{-1})	a_∞ (mmol/g)
CO_2	1	−42	0.3×10^{-3}	6.12
		20	0.5×10^{-3}	3.58
		50	1.5×10^{-3}	2.03
CO_2	0.5	−42	0.3×10^{-3}	5.47
		20	0.6×10^{-3}	2.62
		50	ne	1.41
CO_2	0.25	−42	0.2×10^{-3}	6.08
		20	0.6×10^{-3}	1.96
		50	ne	1.09
CO_2	0.125	−42	0.2×10^{-3}	5.28
		20	ne	1.33
		50	ne	0.74
CH_4	1	20	*	0.70
		50	*	0.19
$CO_2 : CH_4$, (1 : 1)	0.5[b]	−42	0.2×10^{-3}[c]	6.68[d]
		20	0.6×10^{-3}	2.52
		50	0.9×10^{-3}	1.54
	0.25	−42	0.1×10^{-3}	6.08
		20	0.4×10^{-3}	1.90
		50	0.8×10^{-3}	1.09
	0.125	20	0.5×10^{-3}	1.31

[a] ne, not estimated; a_∞, adsorption capacity; *, too fast.
[b] Partial pressure of CO_2, total pressure 1 bar.
[c] Diffusion rate of CO_2 and CH_4.
[d] Adsorption capacity of CO_2 and CH_4.

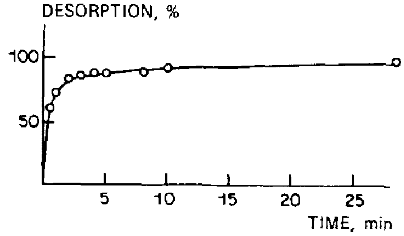

FIG. 4. Desorption of CO_2 from $Mg_3[Co(CN)_6]_2$ (after adsorption at 20°C, 1 bar).

Various water-soluble metal sulfates and sulfuric acid were found to be cocatalysts for this polymerization, increasing the yield of polyether–polyol by a factor of 2 to 3.

Novel hydroxycyanometallate salts were formed by the reaction of hexacyanometallate salts with the corresponding hydroxides, e.g., $Zn_2[Co(CN)_6](OH)$.

Hexacyanometallate salts were found to be excellent molecular sieves. Models showed that, e.g., in the case of cubic $M_3^I[M^{III}(CN)_6]_2$ two types of channel structure were present, one with a relatively large pore opening of ca. 0.56 × 0.86 nm, and one with a pore opening of ca. 0.3 nm, making separation of small molecules possible. Adsorption measurements of CO_2 and CH_4 on $Mg_3[Co(CN)_6]_2$ indicated that with this type of complex CO_2 and CH_4 can be separated effectively.

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