Nickel Cyanide as a Polymerization Catalyst

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The ability of nickel cyanide to initiate polymerizations is critically dependent on its hydration state. Under the appropriate conditions, polymerizations of N-vinyl-carbazole and of certain vinyl ethers are initiated by the cyanide, whereas 4-methoxystyrene and other monomers less susceptible to cationic attack, fail to polymerize. Evidence is presented that the reaction involves weak Bronsted activity of residual water molecules coordinated with nickel cations exposed at the crystal edges.

INTRODUCTION

Although no detailed analysis has been published, it is known that the crystal structure of anhydrous nickel cyanide consists of layers, each 3.2 Å thick, superimposed one on another. Individual layers consist of a network of bivalent nickel cations and tetracyanonickelate anions (Fig. 1). The nitrogen-coordinated nickel cations can form two additional ligand bonds, one projecting above and the other below the layer plane, with suitable donor molecules such as amines, alcohols and water (1). It has been shown (2) that hydrated nickel cations as well as cyano groups are exposed at the layer edges, and that the relative proportions of these can be varied by treatment with solutions containing either nickel or cyanide ions.

The unit cell dimensions of a hydrated nickel cyanide (basal spacing 4.4 Å)[1] in which water molecules exist between the cyanide layers have been determined by Ludi and Huegi (3), and they have concluded that adjacent layers are displaced from each other by half a unit cell. This allows the interlayer water molecules to key deeply into the opposing cyanide surfaces, and explains why the basal spacing increases to only 4.4 Å when interlayer water is present.

[1] Other hydrated species exist (1, 2). Only the 4.4 Å hydrate is referred to herein.

Under appropriate conditions, the cyanide layers separate to allow the intercalation of organic molecules with the formation of "sandwich" complexes (1). While studying the intercalation of organic monomers, we observed incidentally that polymerization of certain of these occurred in the presence of the dry cyanide. The present communication reports on these observations and considers a possible mechanism for the reaction.
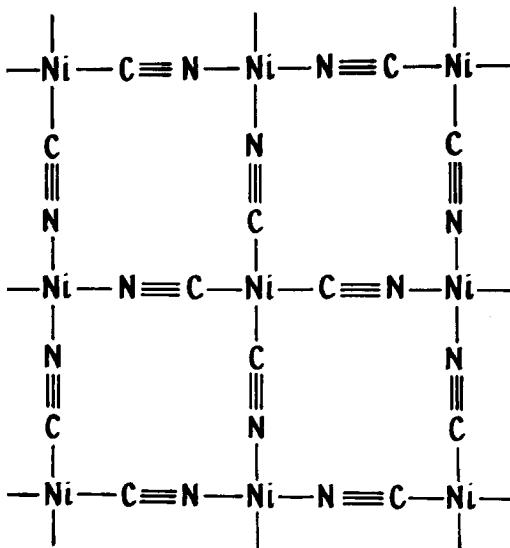

FIG. 1. Structural arrangement of nickel cations and tetracyanonickelate anions in a single layer of nickel cyanide.

Experimental

Hydrated nickel cyanide, giving an X-ray diffraction pattern with a unique 4.4 Å basal spacing, was obtained from Hopkin and Williams. Samples with a 4.4 Å basal spacing were also crystallized over a period of 48 hr from a mixture of equivalent amounts of 2.5 mM aqueous potassium cyanide and nickel chloride maintained at 40° and washed by repeated decantation with distilled water. The hydrated material was dehydrated at various temperatures and 10^{-3} mm pressure for 4 hr, and the hygroscopic anhydrous cyanide subsequently handled under a dry nitrogen atmosphere in a glove box.

Samples of cyanide with cation-saturated crystal edges were prepared by treatment of the hydrate with nickel chloride solution at room temperature for 24 hr followed by washing and dehydration. n-Butylamine treated samples were prepared by reacting material dehydrated at 160°C with a solution of the amine in hexane, followed by heating at 160°C/10^{-3} mm for 4 hr to desorb volatile material.

The purified alkyl vinyl ethers, other monomers and solvents were dried over calcium hydride and redistilled in an inert atmosphere immediately before use. N-Vinylcarbazole (Fluka, pure grade), free from hexane-insoluble material, was dried in $vacuo$ over phosphorus pentoxide.

Adsorption isotherms of monomer vapors on nickel cyanide were obtained using a quartz-spiral adsorption balance connected by mercury float valves to a vacuum line and to a sample reservoir containing monomer at 0°C. The cyanide (0.5 g) was outgassed at 160°C/10^{-5} mm for 4 hr in the adsorption balance, and exposed to the vapor of styrene (1.1 mm presure) and 4-methoxystyrene (0.02 mm pressure) for 24 hr.

Sealed evacuated ampoules containing mixtures of the volatile monomers (8–10 ml) with freshly dehydrated nickel cyanide (2 g) were prepared on a vacuum line with rigorous exclusion of air and moisture. All other reaction mixtures were prepared in a dry oxygen-free nitrogen atmosphere, with solid monomers added

as 30% solutions in benzene. The mixtures were allowed to react in darkness at room temperature with periodic shaking for 24 hr in the case of the vinyl ether and N-vinylcarbazole systems, and for 7 days with the other monomers.

The reaction products were diluted with benzene, the cyanide removed by filtration or dissolution in aqueous potassium cyanide, and the benzene extracts freed from unconverted monomer and solvent by fractional distillation in $vacuo$. Polyvinylcarbazole was purified by precipitation in hexane, and all polymer samples were dried in $vacuo$ at 80–100°C. The limiting viscosity numbers were determined in benzene solution at 30°C.

The copolymerization of styrene with ethyl vinyl ether or N-vinylcarbazole was tested by reacting mixtures containing equimolar amounts of the monomers in benzene with nickel cyanide in p-toluene sulphonic acid. The IR and NMR spectra of the N-vinylcarbazole polymer were compared with those of authentic homopolymer, and the vinyl ether polymer was tested for the presence of styrene copolymer by its solubility in cold methanol or hexane.

Nickel cyanide was deuterated on a vacuum line by repeated additions of deuterium oxide to samples partially hydrated at 100°C/0.1 mm. The deuterated samples (0.4 g) were heated at specified temperatures and pressures less than 1 μ for 4 hr, and allowed to equilibrate at 20°C with measured amounts of pure anhydrous methanol (10–20 μl) for 2–7 days. The methanol–deuteromethanol was recovered by evaporation in $vacuo$ from the cyanide at 100°C, and the proportion of deuteromethanol estimated by comparison of the gas-phase IR spectrum with those of standard samples prepared from equilibrated mixtures of methanol and deuterium oxide, and recorded under identical conditions. The equilibrium absorption intensities of the P and R branches of O–D vibrations at 2695 and 2740, 840, and 883 cm^{-1} were used in the calculation, and it was assumed that the exchange constant for the methanol–deuterium oxide reaction

(4) were, to a first approximation, applicable to the present system.

For electron microscopy, thin films of pure nickel cyanide were deposited on glass slides by evaporation from a dilute aqueous suspension. The coated slides were dehydrated at 160°C/10⁻⁵ mm in a grease-free vacuum line, and exposed at 20°C to a n-butyl vinyl ether at 13 mm vapor pressure for 2 hr, after which the apparatus was re-evacuated to remove unreacted monomer. Platinum-shadowed carbon replicas of the treated catalyst were prepared, and washed with aqueous potassium cyanide to remove the nickel cyanide substrate.

X-Ray diffraction measurements were made on a Philips PW1050 diffractometer using Cu–Kα radiation. Gas-phase IR spectra were recorded on a Perkin-Elmer 521 spectrophotometer, and other IR spectra on a Unicam SP200 instrument; polymers were examined as thin films, and the nickel cyanide as dispersions in KCl prepared and recorded under anhydrous conditions. The EPR spectra of catalyst samples at 20°C were recorded with a Varian V-4501, and the NMR spectra of polymer samples dissolved as 5% solutions in deuterochloroform at 38°C or nitromethane at 80°C with a Varian A60 spectrometer.

RESULTS

Shadowed electron micrographs of the 4.4 Å nickel cyanide hydrate (commercial) show it to be composed of square platelets with lateral dimensions in the range 1000–5000 Å and an average thickness approximating 500 Å. Heating the hydrate at 110°C in vacuo removed the bulk of the water, and the X-ray basal spacing shifted to 3.2 Å indicating that the interlayer water had been removed.

X-Ray diffraction patterns of the cyanide dehydrated at various temperatures in the range 110–200°C were almost identical with that of the irreversibly dehydrated material formed by prolonged heating at 200°C (1). No differences at all were observed in the basal spacings of the two species. However, the absence or diffuse

nature of some of the nonbasal reflections in the former are indicative of lattice disorder in the stacking of the cyanide layers.

No obvious differences were observed between the EPR spectra of catalytically active and inactive samples. However, broad-band NMR spectra indicated the presence of residual protonic species in the dehydrated samples. Thermogravimetric analysis indicated a gradual loss in weight up to 120°C and no detectable loss thereafter. The IR C≡N stretching frequencies (Table 1) of samples dehydrated at 110°C and above are 30–45 cm⁻¹ greater than the hydrated material. The differences between the various dehydrated samples are of doubtful significance. Two rather broad OH stretching bands are observed at unusually high frequencies, viz. 3850 and 3650 cm⁻¹, in all samples. These bands are of comparable intensity for the active material, whereas for the other samples the 3850-cm⁻¹ band appears only as a weak shoulder on the other. This seems to indicate that there are two separate environments for OH groups adsorbed at the crystal surfaces, and that the 3850-cm⁻¹ band originates from a group responsible for or directly connected with catalytic activity. The water contents of three sam-

TABLE 1

INFRARED ABSORPTION FREQUENCIES, WATER CONTENT ESTIMATED FROM DEUTERATION DATA AND CATALYTIC ACTIVITY OF NICKEL CYANIDE DEHYDRATED AT VARIOUS TEMPERATURES FOR 4 HR

Dehydration temperature (°C)	Water content H₂O:Ni(CN)	Catalytic activity	C≡N (cm⁻¹)
(Hydrated material)	1.5:1[a]	Nil	2250
110	1:80	Nil	2285
130	—	Low	2295
160	1:700	Maximum	2290
180	—	Low	—
200	1:900	Very low	2280
200[b]	—	Nil	—

[a] From thermogravimetric analysis.
[b] Irreversibly dehydrated material, heat-treated for 168 hr.

ples estimated from deuterium exchange reactions are also listed in Table 1.

Samples of cyanide dehydrated at 160°C were observed to initiate the polymerization at room temperature of N-vinylcarbazole (NVC) and various alkyl vinyl ethers, viz., methyl, ethyl, n-butyl, isobutyl, and 2-ethylhexyl. No reaction was

TABLE 2
X-Ray Basal Spacings in Angstrom Units of Anhydrous Nickel Cyanide (Basal Spacing 3.2 Å) Immersed in Various Monomers and its Catalytic Activity with Respect to These Monomers

Monomer	Basal spacing (Å)	Catalytic activity
N-Vinylcarbazole	3.2	+
Methylvinylether	3.2	+
Ethylvinylether	3.2	+
n-Butylvinylether	3.2	+
i-Butylvinylether	3.2	+
2-Ethylhexylvinylether	3.2	+
2,3-Dihydropyran	3.2	−
Methylvinylketone	7.1	−
Allylamine	7.8	−
Methyl methacrylate	3.2	−
Hydroxyethyl methacrylate	10^a	−
Dimethylaminoethyl methacrylate	12.8	−
Ethyl acrylate	3.2	−
Acrylamide	7.4	−
Acrylonitrile	7.4	−
Methacrylonitrile	7.9	−
Styrene	3.2	−
α-Methylstyrene	3.2	−
p-Methoxystyrene	3.2	−
Anethole	3.2	−
2-Vinylpyridine	Indefinite	−
4-Vinylpyridine	Indefinite	−
N-Vinylpyrrolidone	3.2	−

^{a} Very diffuse.

observed with styrene, p-methoxystyrene, α-methylstyrene, anethole, 2- or 4-vinylpyridines, N-vinylpyrrolidone, methylvinylketone, methyl methacrylate, or various acrylic esters, amides, and nitriles (Table 2). A temperature close to 160°C appears to be the optimum for activation of the cyanide: Above and below this

value a gradual but significant falling-off in activity is observed.

The data of Table 2 indicate that none of the monomers which polymerize are intercalated by the cyanide and, of those which fail to polymerize, some form intercalation complexes while others do not. It follows therefore that catalytic activity cannot be directly related to intercalation of the monomer. In order to test whether the monomers which failed to polymerize were simply not being adsorbed by the cyanide even on external surfaces, outgassed cyanide was exposed to the vapors of styrene and 4-methoxystyrene separately over a period of 24 hr. Both were adsorbed in significant amounts; styrene to the extent of 6.2% by weight of cyanide and 4-methoxystyrene 1.7%.

The NVC was the most reactive of the monomers tested, yielding high polymer (m.p. > 230°C) in 55% conversion with cyanide dehydrated at 130°C, and 95% conversion with material dehydrated at 160°C. The vinyl ethers failed to react with cyanide dehydrated at 130°C, but yielded polymers in 70–90% conversion with material dehydrated at 160°C. Cyanide samples pretreated to saturate the crystal edges with nickel cations proved to be appreciably more active than the standard material, while samples pretreated with cyanide anions were somewhat less active. Normally the reaction commenced immediately and proceeded to completion within 24 hr with noticeable evolution of heat. The reactions could be reversibly inhibited by cooling the mixtures below 0°C. Addition of small amounts (1% of catalyst weight) of acetaldehyde, dioxan, ethanol, butylamine, or triphenylphosphine completely inhibited the polymerization of NVC and the vinyl ethers.

Attempts to copolymerize styrene with NVC or the vinyl ethers in the presence of the active cyanide failed, no phenyl groups being detected in the IR spectra of the products. The active catalyst did not give a positive benzidine blue reaction (5), nor did it decolorize solutions of 1,1-diphenyl-2-picryl-hydrazyl (DPPH). Moreover, the latter reagent had no effect on the polym-
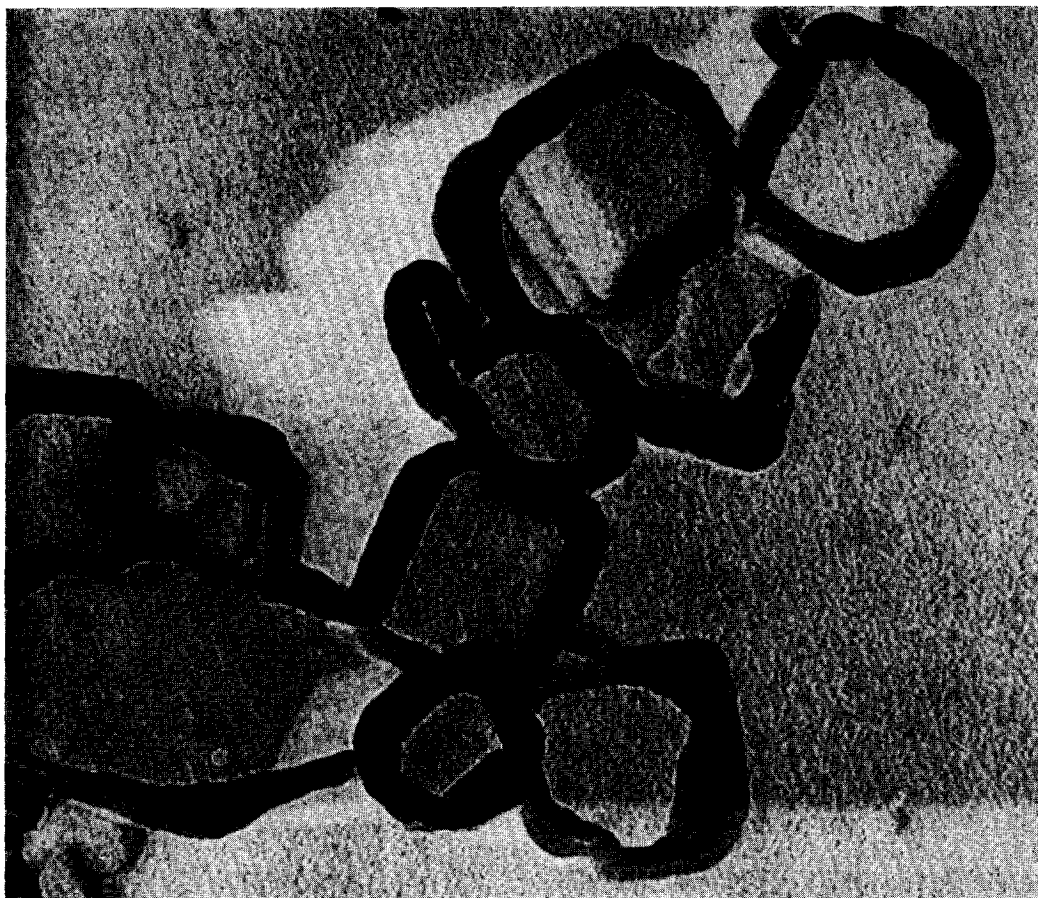
NICKEL CYANIDE AS CATALYST

FIG. 2. Electron micrograph of nickel cyanide crystals after exposure to n-butyl vinyl ether vapor (platinum-shadowed carbon replica).

erization of NVC nor did it decolorize during the reaction.

The polyvinyl ethers obtained were tacky, viscous gums, readily soluble in cold acetone, hexane, or methylethylketone. Their limiting viscosity numbers ranged from 0.47 to 0.59 corresponding to average molecular weights in the range 4.6–6.7×10^4 (6). The solubility data and the NMR and IR spectra indicated that all the polymers produced, including the poly NVC, were essentially atactic.

Electron micrographs of the active cyanide which had been exposed to n-butylvinyl ether vapor showed a uniform band of polymer, about 100 Å thick, around the edges of the crystals (Fig. 2). The basal surfaces were almost completely free of polymer.

DISCUSSION

The polymerization of acid-sensitive monomers, NVC (7) and the alkyl vinyl ethers $(8, 9)$ by nickel cyanide together with the inhibiting effect of basic contaminants on the reactions suggests that propagation proceeds via carbonium-ion intermediates, i.e. by a cationic mechanism. This view is reinforced by the absence of inhibition by DPPH and by the failure of the attempts at copolymerization. In the latter, alkyl vinyl ether or NVC homopolymers are formed in the presence of styrene, whereas a radical process would be expected to yield styrene-rich copolymers $(10, 11)$.

A cationic polymerization process could be initiated by the transfer of protons from

Bronsted acid sites to adsorbed monomer molecules, forming carbonium-ion intermediates. Alternatively, a one-electron transfer process could occur between adsorbed monomer molecules and Lewis acid sites on the catalyst surface, followed by rapid dimerization of the intermediate radical-cations. The latter process seems less likely since active nickel cyanide does not oxidize benzidine, a substance readily converted to a radical-cationic species (5).

The failure of 4-methoxystyrene and the less cation-sensitive monomers (9) to polymerize suggests that the cyanide is unable to generate a sufficient concentration of carbonium ions for appreciable reaction to occur in these instances. The possibility that the critical factor might lie in whether adsorption of the monomer takes place or not is discounted by the fact that styrene and p-methoxystyrene are both adsorbed without undergoing significant polymerization.

Hydrated nickel cyanide is catalytically inactive, and activity only develops when dehydration is substantially advanced. The X-ray evidence indicates that the material formed by dehydration at 110°C, which is inactive, contains no interlayer water. Deuterium-exchange studies, however, show that it still retains approximately one water molecule per 80 $Ni(CN)_2$ molecules, sufficient to occupy all the accessible ligand sites on the external surfaces of the crystals. As the cyanide is heated above 110°C, the water molecules on the external basal surfaces are gradually lost, only the water strongly coordinated with nickel cations at the layer edges being retained. Catalytic activity appears at this stage and, in the material with maximum activity, there is still about one water molecule per 700 $Ni(CN)_2$ molecules, which is equivalent to about half a water molecule for each nickel cation exposed at the layer edges. Since the electron micrograph evidence clearly locates the initiating sites at crystal edges, it is reasonable to assume that Bronsted activity is generated by these residual edge waters. This view is consistent with the increased activity of

samples pretreated to saturate the layer edges with nickel cations, and with the complete absence of activity when the catalyst is pretreated with butylamine, so as to displace the adsorbed water.

One can imagine the development of activity on dehydration to be related to increased electrophilicity induced in the cyanide layers as water molecules are desorbed from the surfaces, leading in turn to increased Bronsted acidity in the water molecules remaining. Destruction of active centers by thermal hydrolysis may explain the subsequent decline in activity on heating to higher temperatures, but this has not been established unequivocally. Both Bronsted and Lewis acidity have been invoked previously to explain the catalytic properties of nickel sulphate (12). In this instance, the acidity was ascribed basically to an intermediate metastable structure formed during the conversion of the monohydrate to the anhydrous form. The possibility that a similar mechanism applies in the present case cannot be excluded in view of the X-ray diffraction evidence which indicates a degree of lattice disorder in the catalytically-active material.

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