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Preliminary communication

Preparation of poly(p-chlorostyrene)-supported phenyl(dipyridyl)nickel chloride

SAKUJI IKEDA and TAKASHI HARIMOTO

Research Laboratory of Resources Utilization, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo (Japan)

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In recent years several polymer-supported transition metal complexes have been prepared; these catalysts combine the advantages of both homogeneous and heterogeneous activity[1–3].

We report here the preparation and some characteristic properties of a poly(p-chlorostyrene)-supported phenyl(dipyridyl)nickel chloride. The related homogeneous complex (I) was previously isolated from a chlorobenzene solution of diethyl(dipyridyl)-nickel (II) in our laboratory[4].

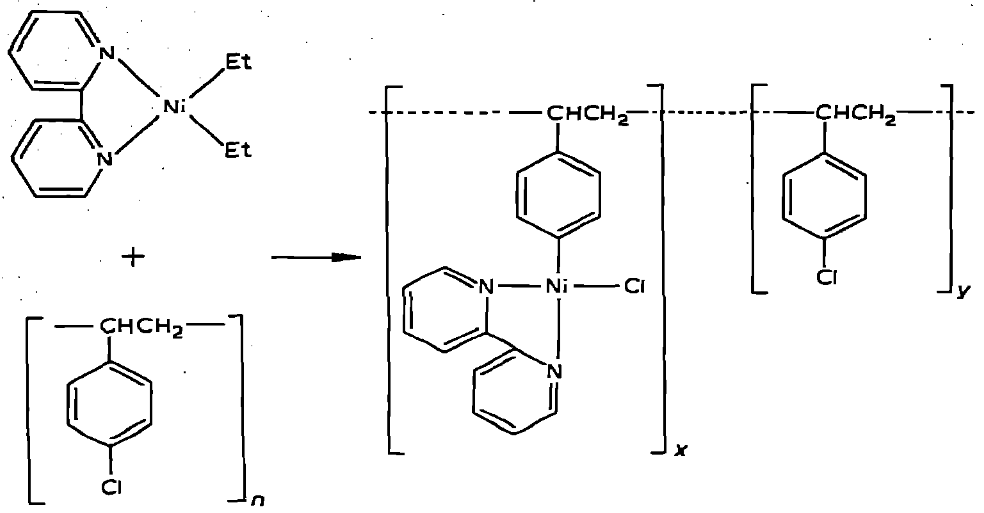
Diethyl(dipyridyl)nickel (II) and p-chlorostyrene (III) were prepared according to known procedures[5,6].

Poly(p-chlorostyrene) (IV) was obtained by polymerization of p-chlorostyrene (III) at 130°C for 4 h in an ampoule.

Poly(p-chlorostyrene)-supported phenyl(dipyridyl)nickel chloride was prepared as follows: Upon dissolving the compounds (II) and (IV) in purified benzene at 50°C in a nitrogen atmosphere, the greenish solution obtained gradually became red in color. The reaction mixture was kept at 50°C for 15 h. This reaction (Eq. 1) was accompanied by the evolution of n-butane together with small amounts of ethane and ethylene.

The product (V) was greatly affected by the molar ratios of (II) to the monomer units of (IV). At low molar ratios of (II) to the monomer units of (IV) (less than ca. 0.25) the product was soluble in benzene, toluene, chlorobenzene, dioxane, tetrahydrofuran, N,N-dimethyl formamide, etc., but at high molar ratios the product was insoluble in these solvents. If insoluble, the product was washed several times with purified benzene and dried under vacuum at room temperature. In the case of a soluble product, purified n-hexane was added to the benzene solution of (V) and the precipitate produced was freeze-dried by adding a small amount of purified benzene. Compound (V) in the solid state was stable at room temperature in a nitrogen atmosphere, but it decomposed gradually in solution.

The elemental analysis of (V) obtained by using 160 mg of (IV) and 140 mg of (II)



(1)

in 40 ml of toluene (molar ratio of (II) to the monomer units of (IV), 0.42; insoluble in solvents) was C, 62.14; H, 4.73 and N, 4.43. This result showed that about 25% of the monomer units of (IV) had reacted with (II).

The visible spectrum of (V), for example, obtained by using 130 mg of (IV) and 30 mg of (II) in 30 ml of toluene (molar ratio, 0.11; soluble in solvents) showed the λ_{max} value of 494 nm in toluene or chlorobenzene solution. This value is very close to that (494 nm) of a *p*-tolyl(dipyridyl)nickel chloride complex (VI) in chlorobenzene solution. On the other hand, the λ_{max} value of (VI) in toluene solution was 506 nm. These results suggested the existence of some interaction between the pendant nickel groups and the pendant chlorophenyl groups in the polymer complex (V).

Catalytic activities of (V). Several vinyl compounds were brought into contact in the dark with (V) at room temperature for 2 days in a sealed tube in the absence of any solvent. The results were shown in Table 1. The data in this table indicate that polymer

TABLE 1

POLYMERIZATION ACTIVITY OF (V)

Each reaction was carried out at room temperature for 2 days by using 80 mg of the soluble polymer complex (V) (molar ratio; 0.11).

Vinyl monomer	*Polymer yield (%)*	*Color change*
Acrylonitrile	0	from red to orange
Methyl methacrylate	8 [a]	to yellow
Vinyl acetate	3 [b]	to white
Methyl vinyl ether	0	to black

[a] Poly(methyl methacrylate) was extracted with hot isobutanol.
[b] Poly(vinyl acetate) was extracted with methanol.

complex (V) has the catalytic activity for the polymerization of some vinyl monomers. An attempt was made to polymerize methyl methacrylate at room temperature for 2 days with the use of (1) 10 ml of methyl methacrylate and 30 mg of (IV), and (2) 10 ml of methyl methacrylate, 30 mg of (VI) and 0.25 ml of *p*-chlorotoluene, but no polymer was obtained in either case. Complex (V), as well as the complexes (I) and (VI), also was a catalyst for the dimerization of ethylene and propylene in the presence of ethylaluminum dichloride.

A more precise study is now in progress.

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