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A NOVEL NICKEL CATALYST SUPPORTED ON POLYSTYRENE WITH NICKEL-CARBON σ-BOND

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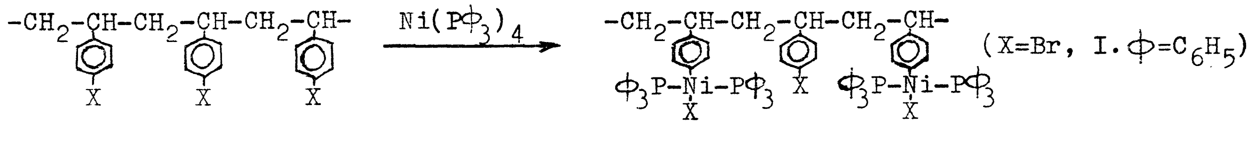
Nickel complexes bound to polystyrene with nickel-carbon σ-bond were prepared by oxidative addition of halogenated polystyrene to tetrakis(triphenylphosphine)nickel(0). The nickel complex, suspended in toluene solution, exhibits nearly the same activity for ethylene dimerization as that of bis(triphenylphosphine)σ-phenyl(bromo)nickel(II).

Recent development in organometallic chemistry has given many well-defined organonickel complexes, and much interest has been paid in their ability as a highly active and selective catalyst for the homogeneous oligomerization or polymerization of olefin, dienes, acetylene etc. From a practical point of view, however, such a homogeneous process has an inevitable draw-back in separation of reaction products from the catalyst. Thus some attempts have been made to immobilize the complex by fixing it on a solid surface. This paper presents a new method of preparation of the insoluble organonickel complexes without lowering their catalytic activities.

In the preceding papers,[1,2] it was shown that the homogeneous catalyst system composed of bis(triphenylphosphine)σ-aryl(halo)nickel(II) and trifluoro boron etherate, is highly active for ethylene dimerization and selective for the codimerization of ethylene with styrene. The σ-aryl nickel(II) complexes are known to be easily prepared by the oxidative addition of aryl halide to tetrakis (triphenylphosphine)nickel(0)[3]. This method of preparation was extended to the reaction with halogenated polystyrene as follows:



(X=Br, I. $\phi=C_6H_5$)

To a well dry toluene solution (150 ml) of brominated polystyrene4)(4.5 g. Average degree of polymerization, 1100. Bromination, 80% based on total para-position of phenyl rings in polystyrene) was added another toluene solution (100 ml) of tetrakis(triphenylphosphine)nickel(0) prepared from bis(acetylacetonate)nickel(II) (5 g), triphenylphosphine (20 g) and diethyl(ethoxy)aluminium(III) (8 ml). The mixture was left standing at room temperature under nitrogen atmosphere for about 12 hr. A brown precipitate (5.1 g) was formed. The toluene solution was decanted before the precipitate was well washed with toluene or n-hexane and it was dried under vacuum. The dried precipitate was stable in the ambient atmosphere at room temperature. By the treatment with a mixture of concentrated nitric acid and sulfuric acid,the dried precipitate liberated aqueous nickel(II) ion, the amount of which was determined to be 0.495 mmol/g by an ordinary EDTA titration method. This nickel content in the dried precipitate corresponds to about 130 atoms of nickel in one molecule of the brominated polystyrene. When about twice amount of tetrakis(triphenylphosphine)nickel(0) was used in the above preparation, the nickel content in the dried precipitate (6.5 g) was increased up to 0.704 mmol/g. The same treatment of iodonated polystyrene5) with tetrakis(triphenylphosphine)nickel(0) or tetrakis (triphenylphosphine)palladium(0) gave the corresponding complexes supported on polystyrene.

The nickel complex supported on brominated polystyrene has nearly the same catalytic activity for ethylene dimerization as that of bis(triphenylphosphine) σ-phenyl(bromo)nickel(II) as shown in Fig. 1. Ethylene was introduced at 0 °C under atmospheric pressure with vigorous stirring into a 2-necked flask (50 ml) containing the nickel complex supported on brominated polystyrene(0.1 g, with Ni 0.0495 mmol) as a suspension in toluene (10 ml) and trifluoro boron etherate (0.8 mmol) was added. The pressure was kept constant at 1 atm. The reaction of ethylene as observed by the volume decrease took place with acceleration(-⊙-) giving butene selectively. The catalyst was separated by decantation from the toluene solution, followed by adding another fresh toluene (10 ml) without adding trifluoro boron etherate and the successive runs of ethylene dimerization were repeatedly carried out 6 times exchanging toluene run by run. Since trifluoro boron etherate was not resupplied in the run No. 2 and after, the trifluoro boron added in the first run must be absorbed and remained on the polymer surface. The

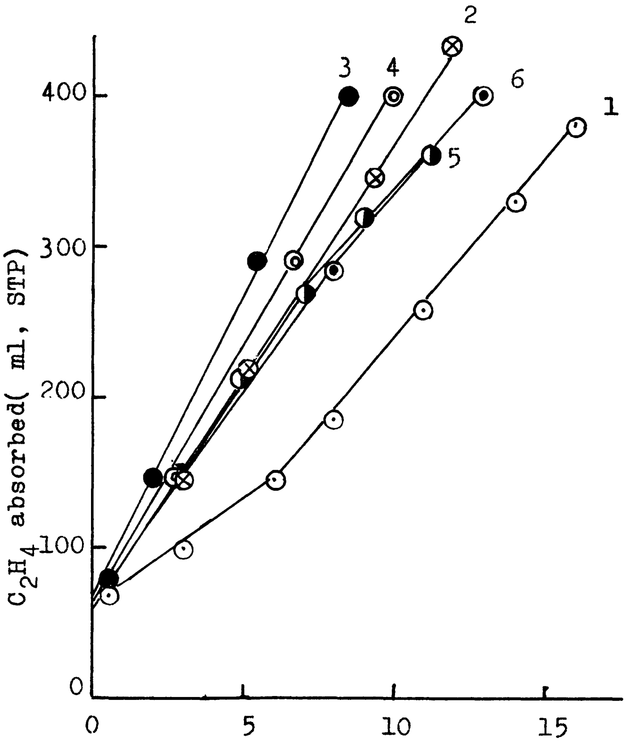


Fig.1 Dimerization rate of ethylene catalyzed by the nickel complex supported on brominated polystyrene

amounts of absorbed ethylene are plotted against time in Fig. 1. No acceleration was observed since the second run. The toluene solution separated from the catalyst was proved to have no catalytic activity at all for the ethylene dimerization. This means that the ethylene dimerization is catalyzed by the suspended nickel complex supported on brominated polystyrene and that it is not soluble in toluene. As shown in Fig. 1, the activity of the complex increases with run No. up to No. 3, and then decreases to a steady value attained at No. 5. The reason of such changes is not yet identified. After the run No. 6, the catalyst was separated by decantation followed by evacuation, and was tested for the catalytic activity in the gas-solid system at 0 °C. It also absorbed ethylene with a fairly rapid rate. In this case, however, the selectivity to butene was lower than that in the presence of solvent, giving considerable amounts of hexenes and octenes in addition to butenes. This suggests that the solvent has a beneficial effect on the selective dimerization of ethylene.

Rhodium(I) complexes supported on phosphorous-containing polystyrene has been reported to catalyze the hydrogenation and hydroformylation[6,7] of olefin. They seem to be also insoluble in organic solvent, while the rhodium(I) complexes would get out of polystyrene during these catalytic reaction, because rhodium(I) complexes are bound to the polymer only through the coordination of tertiary phosphines. In the present catalyst, however, it was proved that no nickel complex is liberated from the polystyrene.

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