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ISOMERIZATION OF 1-HEXENE CATALYZED OVER POLYMER-SUPPORTED $RuCl_2(PPh_3)_3$

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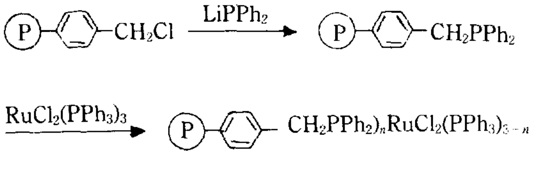
Abstract—Polymer-supported ruthenium catalyst was prepared by anchoring dichlorotris(triphenylphosphine)ruthenium, $RuCl_2(PPh_3)_3$, onto the phosphinated polystyrene bead. The polymer-supported $RuCl_2(PPh_3)_3$ could be reused several times with only small loss of catalytic activity in the isomerization of 1-hexene. The activity rather increased during the few initial runs. In both homogeneous and heterogenized catalysts, an induction period was required to initiate the isomerization. The catalyst efficiency was promoted in the mixture of good swelling solvent and potent hydrogen donor. Upon heterogenizing, the activity was reduced by a factor of 2.0-8.2.

INTRODUCTION

There have been many recent attempts to prepare heterogenized catalysts by supporting homogeneous transition metal complexes onto polymer materials [1-3]. Such heterogenized catalysts offer advantages over homogeneous analogs in ease of recovery and recycling as well as enhanced activity and selectivity.

While almost the homogeneous catalysts have already been anchored, heterogenized forms of $RuCl_2(PPh_3)_3$ have been scarcely reported. Supported complex of $RuCl_2(PPh_3)_3$ was utilized for H-D exchange in ethanol and for hydrogenation of olefins [4]. Also, Zoran and Sasson [5] reported the anchoring of $RuCl_2(PPh_3)_3$ to a polystyrene matrix and demonstrated its application in double bond migration of allylarene and in the transformation of alkylvinylcarbinols into ketones. In this work, $RuCl_2(PPh_3)_3$ was heterogenized through the following procedures:



The isomerization of 1-hexene was carried out using both homogeneous and polymer-supported $RuCl_2(PPh_3)_3$. The nature of active site, solvent effect, and recycling effect were investigated.

EXPERIMENTAL

All the manipulations described in this section were carried out using standard methods for air-sensitive reagents.

1. Materials

Chloromethylstyrene (Tokyo Kasei Kogyo Co., Ltd) and divinylbenzene (Tokyo Kasei Kogyo Co., Ltd) were washed with 5% sodium hydroxide aqueous solution to remove stabilizer. Toluene (J. T. Baker Chem. Co.), benzene (J. T. Baker Chem. Co.), tetrahydrofuran (J. T. Baker Chem. Co.), and 1-hexene (Aldrich Chem. Co.) were dried and deoxygenated by distillation over sodium metal under a nitrogen atmosphere. Chlorodiphenylphosphine (Strem Chem. Co.) and $RuCl_2(PPh_3)_3$ (Strem Chem. Co.) were used as supplied.

2. Phosphination

Chloromethylated polystyrene beads were prepared directly by polymerization of chloromethylstyrene. The resulting beads were functionalized by the phosphination procedure. The phosphination involved the reaction of lithium diphenylphosphide prepared by a literature [6] with the $-CH_2Cl$ groups of chloromethylated polystyrene.

Excess lithium metal, cleaned of residual packing

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*Present Address: Department of Chemical Engineering, Gyeongsang National University, 900, Kajwa-dong, Chinju 660-701, Korea oil with dry tetrahydrofuran(THF) and subsequently sliced to expose surface, was charged in a 500 ml two-neck round-bottom flask stopped with rubber septa. Oxygen was purged from the system by alternate vacuum/nitrogen flushes. 250 ml of dry and deoxygenated THF was transferred into the flask under a nitrogen atmosphere. 30 ml of chlorodiphenylphosphine was then added carefully under a nitrogen atmosphere to the mixture to produce lithium diphenylphosphide. The mixture gradually turned deep red. The reaction was performed for 12 hours at 50℃. The mixture was allowed to cool to room temperature and maintained under a nitrogen atmosphere. The chloromethylated beads were placed in a second flask. Enough lithium diphenylphosphide prepared previously was transferred into this second flask using standard handling techniques for air-sensitive reagents. Additional THF was introduced as required to completely cover the swollen beads. The phosphination reaction was allowed to proceed for 3 days at reflux under a nitrogen atmosphere. During this period the color of the reaction mixture changed from red to orange. The mixture was cooled to room temperature, and then the phosphinated polymer beads were separated from the solution and washed consecutively with THF, 10% NH_4Cl aqueous solution, toluene, hexane, THF, and petroleum ether. The resulting polymer beads were dried under vacuum for 20 hours and stored under nitrogen.

3. Attachment of $RuCl_2(PPh_3)_3$ to Phosphinated Polystyrene Bead

Polymer-supported $RuCl_2(PPh_3)_3$ was prepared by the following procedure. A mixture of 2.0 g of 2% crosslinked polymer-bound triphenylphosphine (3.4 meq. of P), 3.5 g of $RuCl_2(PPh_3)_3$ (3.65 meq. of Ru), and 20 ml of dry benzene was refluxed under nitrogen for 7 days. The solvent was decanted, and the residue was extracted several times with hot benzene. The purple beads were dried at 80℃ under vacuum and stored under a nitrogen atmosphere. By elemental analysis, the content of ruthenium of the polymer-supported catalyst was known to be 0.12 meq./g.

4. Isomerization of 1-Hexene

The reactor consisted of a 30 ml round-bottom flask equipped with a stopcock sidearm and a rubber septum injection/sampling port. A water cooled condenser was connected immediately above the reactor. The reactor temperature was maintained by a water bath, and the reaction mixture was stirred by a magnetic stirrer. The isomerization experiments were performed by placing a weighed quantity of catalyst into the reaction flask and then injecting a solution of solvent and 1-hexene into it. The flask was immersed at once into a water bath. Samples were withdrawn periodically from the mixture and analyzed using a gas chromatograph with a 9-m long, 1/8-in. diameter stainless steel column packed with 7% Squalane on Chromosorb P. After reaction the liquid was decanted off under nitrogen, and the polymer catalysts were washed several times with purified benzene, dried under nitrogen at 75℃ for 20 hr, and then an identical reaction procedure was carried out again.

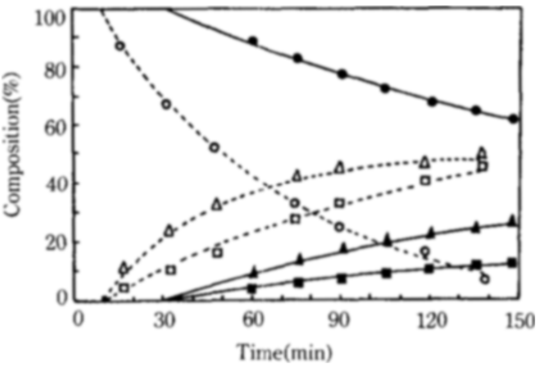

Fig. 1. Composition changes in the isomerization of 1-hexene by $RuCl_2(PPh_3)_3$ with 6.4×10^{-3} mol of substrate, 4.36×10^{-3} meq. of catalyst and 1.7 ml of solvent at 95°C: solvent; toluene(—), toluene-1-propyl alcohol(3 : 1) (---): 1-hexene(●, ○), trans-2-hexene(■, □), cis-2-hexene(▲, △).

RESULTS AND DISCUSSION

Fig. 1 showed the change of composition in the isomerization of 1-hexene catalyzed by homogeneous ruthenium catalysts. The experiment with $RuCl_2(PPh_3)_3$ dissolved in toluene showed that an induction period is required before the isomerization occurs. This initiation was accompanied by a color change of the solution from brown to red-violet. Double bond migration essentially involves movement of a hydrogen, from the alkyl group adjacent to the double bond, to the α-carbon of the double bond. It is generally known that the active species in this sequence is a metal-hydride. Sherman and Olson [8] reported that homogeneous ruthenium catalysts formed isolable ruthenium hydride species (Ru-H) during allylbenzene isomerization. Such a metal-hydride is formed in the presence of a external hydrogen donor, by ortho metalation [9], and by slow hydrogen abstraction from the solvent or substrate [10]. As $RuCl_2(PPh_3)_3$ did not contain any hydrogen ligand at first, this organo complex should be converted into Ru-H to catalyze the isomerization

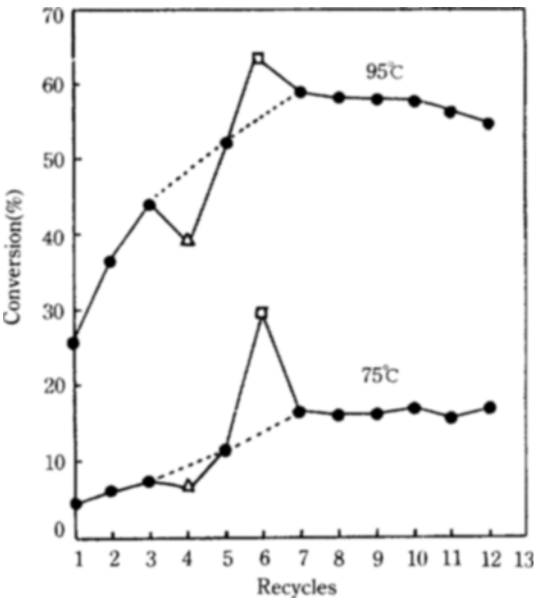

Fig. 2. Recycling effect in the isomerization of 1-hexene by polymer-supported $RuCl_2(PPh_3)_3$ in toluene(●), n-decane(△) and toluene-1-propyl alcohol(3 : 1) (□). Each run was performed for 60 min with 6.4×10^{-3} mol of substrate, 3.96×10^{-2} meq. of catalyst and 1.7 m*l* of solvent.

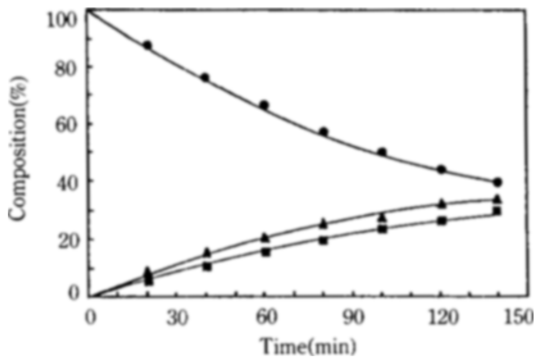

Fig. 3. Composition changes at maximum activity in the isomerization of 1-hexene by polymer-supported $RuCl_2(PPh_3)_3$ with 6.4×10^{-3} mol of substrate, 3.96×10^{-2} meq. of catalyst and 1.7 m*l* of toluene at 95°C: 1-hexene(●), trans-2-hexene(■), cis-2-hexene(▲).

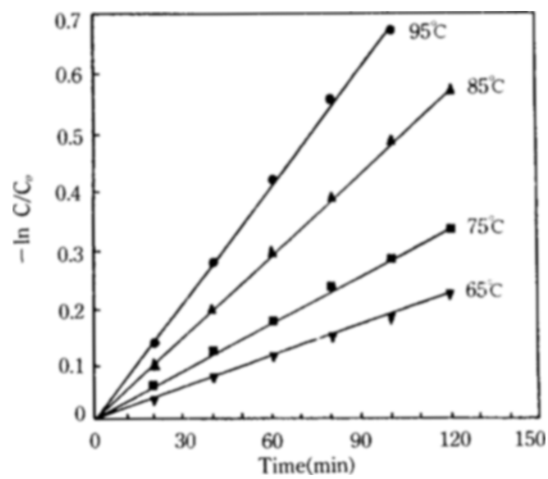

Fig. 4. First-order plots in the isomerization of 1-hexene by polymer-supported $RuCl_2(PPh_3)_3$ with 6.4×10^{-3} mol of substrate, 3.96×10^{-2} meq. of catalyst and 1.7 m*l* of toluene: 65°C(▼), 75°C(■), 85°C(▲), 95°C(●).

reaction. From this point of view it was considered that the slow formation of Ru-H may be responsible for the induction period and the color change of the homogeneous catalyst. This consideration was proved by the experiment in which the external hydrogen donor, 1-propyl alcohol, was added to promote the formation of Ru-H. In this experiment, the induction period was shorten, and the activity also increased.

Dichlorotris (triphenylphosphine) ruthenium, $RuCl_2(PPh_3)_3$, was anchored onto a phosphinated polystyrene bead. The resulting polymer-supported ruthenium catalyst was employed as a catalyst for the isomerization of 1-hexene, which provided trans- and cis-2-hexenes without any side products. Also the catalyst could be reused several times with only exceedingly small loss of catalytic activity as shown in Fig. 2. In fact, the activity proved to increase during the few initial runs until maximum activity has been reached. As described above, it was considered that the rate acceleration during the first few cycles resulted from slow formation of polymer-supported ruthenium hydride. A similar trend has already been noted in olefin hydrogenation by some polymer-supported $RuCl_2(PPh_3)_3$ [5]. When the catalyst was filtered and recycled, the conversion of 1-hexene increased to 25.5, 37.4, and 44.4% in the first, second, and third cycle at 95℃, respectively. As shown in Fig. 2, the catalytic activity gradually decreased at 95℃ after the maximum activity reached.

As shown for some other polymer-supported catalysts [11], the activity of polymer-supported ruthenium catalyst was solvent dependent. Aromatic hydrocarbons of good swelling capacity leads to higher rate than aliphatic hydrocarbons. Mixture of good swelling solvent and potent hydrogen donor may promote catalyst efficiency. The activity decreased in poor swelling

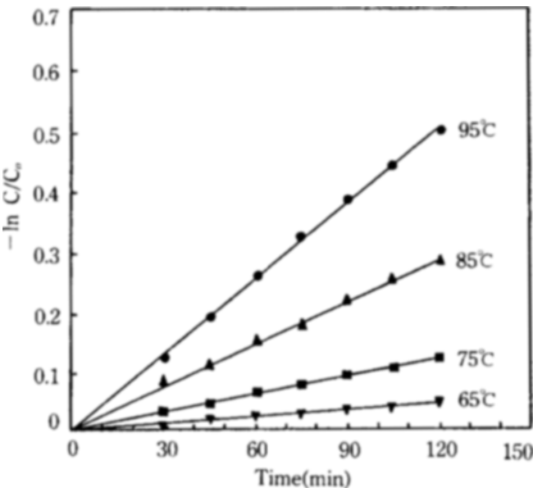

Fig. 5. First-order plots in the isomerization of 1-hexene by $RuCl_2(PPh_3)_3$ with 6.4×10^{-3} mol of substrate, 4.36×10^{-3} meq. of catalyst and 1.7 ml of toluene: 65°C(▼), 75°C(■), 85°C(▲), 95°C(●).

solvent(decane) and increased in a mixture of good swelling agent(toluene) and hydrogen donor(1-propyl alcohol) as shown in Fig. 2. The effect of the solvent on the activity of the catalyst proved to be reversible. When the medium was changed after several turnovers to a better or a worse solvent, the conversion changed accordingly as shown in Fig. 2. Typical composition curves for the isomerization of 1-hexene catalyzed by polymer-supported ruthenium complex at maximum catalytic activity were shown at 95℃ in Fig. 3.

The isomerization of 1-hexene was studied at various temperatures between 65 and 95℃ using polymer-supported and homogeneous ruthenium catalysts. From plots of $-\ln C/C_o$ versus time shown in Fig. 4 and Fig. 5, the isomerization followed first-order kinetics, and the rate constants could be calculated and were listed in Table 1. The values of rate constants were 0.08-1.40 min^{-1} per meq. of Ru for homogeneous catalyst and 0.04-0.17 min^{-1} per meq. for Ru heterogenized catalyst. The rate constants are of limited values, however, because of uncertainty concerning the concentration of active species (Ru-H). Comparison of the isomerization rates of 1-hexene by the polymer-supported catalyst with those obtained by soluble counterpart indicated that the catalytic activity was reduced by a factor of 2.0-8.2 upon heterogenizing. However, as the activity of the homogeneous catalyst is often lost upon recycling but the polymer-supported ruthenium complex can be reused in further runs, the polymer-supported catalyst can be regarded as the more efficient one. The ruthenium catalyst became particularly efficient after 4-5 turnovers. This increase in activity of the catalyst was accompanied with color change of the beads from purple to orange, resulting from the formation of a ruthenium hydride. The activation energies of polymer-supported and homogeneous systems were found to be 10.9 and 24.9 kcal/mol from Arrehenius plots shown in Fig. 6, respectively. The difference in the observed E_a values for homogeneous and heterogenized catalysts suggests that the latter reaction is diffusion controlled. The ratio of $E_{a,\,homo}/E_{a,\,hetero}=2.5$ is in good agreement with the prediction [12] that observed activation energies of reactions that are influenced by strong pore resistance are equal to half of the true activation energies. Here the detailed study on diffusion phenomena was not investigated. While the 1-hexene was transformed by polymer-supported ruthenium complex into the cis- and trans-2-hexenes in a ratio of 1.4 at 20% conversion, the catalysis by homogeneous ruthenium complex showed a cis-trans ratio of 2.3. It was considered that the selectivity changes were associated with the structural differences between the homogeneous and polymeric catalysts. The isomerization mechanisms divide

Table 1. Rate constants of the isomerization of 1-hexene by homogeneous and polymer-supported $RuCl_2(PPh_3)_3$

T(℃)	k (min^{-1}·meq.$^{-1}$)	
	homogeneous	polymer-supported
65	0.08	0.04
75	0.23	0.07
85	0.59	0.12
95	1.40	0.17

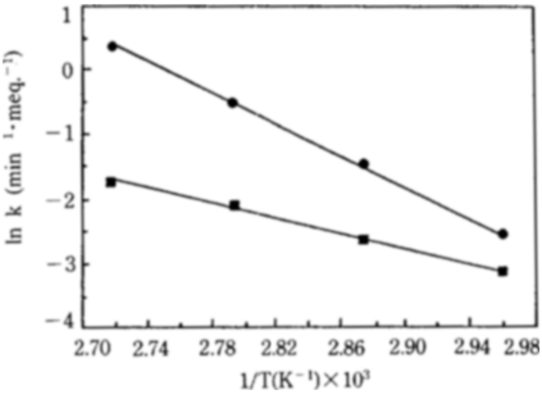

Fig. 6. Arrhenius plots in the isomerization of 1-hexene by homogeneous and polymer-supported $RuCl_2(PPh_3)_3$: homogeneous(●), polymer-supported(■).

into two main types [13] : those involving metal-alkyl and those involving metal-allyl intermediates. The active species in the isomerization via metal-alkyl intermediates is a metal-hydride complex in which cis-isomer is a favored product. On the other hand trans-isomer is a favored one in the isomerization associated with the formation of a metal-allyl complex. In the present work, cis-isomer was a preferential product, indicating that the isomerization catalysis by homogeneous and polymer-supported $RuCl_2(PPh_3)_3$ occurred via the reaction mechanism containing Ru-H intermediate, as previously described.

CONCLUSIONS

Polystyrene beads containing chloromethyl groups were prepared and phosphinated with lithiodiphenylphosphide prepared directly from lithium metal and chlorodiphenylphosphine. $RuCl_2(PPh_3)_3$ was then anchored onto the phosphinated polystyrene bead. The polymer-supported ruthenium catalyst promoted the isomerization of 1-hexene and could be reused several times with only small loss of catalytic activity. The activity rather increased during the few initial runs. In both homogeneous and heterogeneized catalysts, an induction period was required, resulting from slow formation of the active species, ruthenium hydride. The catalytic activity of polymer-supported $RuCl_2(PPh_3)_3$ was dependent on solvent. Mixture of good swelling solvent(toluene) and potent hydrogen donor(1-propyl alcohol) promoted catalyst efficiency. Upon heterogenizing, the activity was reduced by a factor of 2.0-8.2.

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