

Characteristics of phosphinated styrene-divinylbenzene copolymer containing $\text{RuCl}_2(\text{PPh}_3)_3$ for 1-hexene isomerization

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Summary

Chloromethylated styrene-divinylbenzene(S-DVB) copolymer beads were prepared in macroporous type via direct copolymerization of chloromethylstyrene and divinylbenzene and then phosphinated. Dichlorotris(triphenylphosphine)ruthenium, $\text{RuCl}_2(\text{PPh}_3)_3$, was anchored on the phosphinated S-DVB copolymer, and then applied to the isomerization of 1-hexene. The physical properties of the catalysts varied with degree of crosslinking and type of pore-forming agents. Anchoring the ruthenium complex onto the phosphinated S-DVB resin favored *trans*-isomer and stabilized the catalyst in the isomerization of 1-hexene comparing with the homogeneous reaction. Solvent effects on catalytic activities of polymer-anchored catalysts were also discussed.

Introduction

In recent years, considerable attentions have been paid to the commercial application of polymer-anchored catalysts which combine advantages of both homogeneous and heterogeneous catalysts. These hybrid catalysts can be readily separated through coarse filtration and they can be very selective and highly effective(1). Several hundreds of papers have been published annually on supported metal complex catalysts including a number of good reviews(2-5). Air-sensitive transition metal complexes can be stabilized(6,7), or site-isolated(8) when they are anchored on functionalized polymer.

The S-DVB copolymer is one of the most attractive supports with a wide range of physical properties and chloromethylated derivatives are main intermediates in many resin preparations. In preparation of chloromethylated beads, the studies have been mainly focused on the chloromethylation of S-DVB copolymers(9,10) which may be responsible for a strong change in copolymer structure(11).

In this work, the polymer beads containing chloromethyl groups were prepared by direct copolymerization of chloromethylstyrene and divinylbenzene, which may avoid the use of the carcinogenic agent chloromethylmethylether. A ruthenium complex was anchored onto phosphinated S-DVB resins obtained via phosphination with LiPPh_2 , and then the isomerization of 1-hexene was carried out using the catalysts. The characteristics of the catalysts were analyzed in terms of the properties of the polymer support.

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Experimental

Materials

Styrene, chloromethylstyrene, and divinylbenzene(Tokyo Kasei) were washed by aqueous NaOH solution and water several times prior to use in order to remove inhibitors. Azobisisobutyronitrile(Tokyo Kasei, AIBN), gelatin(Junsei Chemical), poly(diallyldimethylammoniumchloride)(Calgon, Catfloc T), and *n*-heptane(Kanto Chemical) were used as received. Lithium wire and chlorodiphenylphosphine(Aldrich) were treated under nitrogen without further purification. Tetrahydrofuran, *n*-hexane, toluene(J.T. Baker) and 1-hexene(Aldrich, 99+ %) were purified under nitrogen prior to use.

Preparation of catalysts

Polymer beads were prepared by suspension copolymerization following the procedures described elsewhere(12). The phosphinated polystyrene beads were prepared via phosphination with LiPPh₂. About 1.933g of lithium wire (ca. 2.785×10^{-1} mole of Li) was sliced into pieces and then suspended in 250 ml of tetrahydrofuran(THF), to which 50ml of chlorodiphenyl phosphine (ca. 2.785×10^{-1} mole of ClPPh₂) was added. Stirring the mixture at 50°C provides a colorful red LiPPh₂ solution. The beads containing chloromethyl groups were placed in the degassed side-armed flask, into which the LiPPh₂ solution was transferred. The reaction was carried out for 3 days under reflux. The resulting beads were washed sequentially by THF, toluene, *n*-hexane, and THF, and then dried under vacuum. The phosphinated resin and RuCl₂(PPh₃)₃ were placed in a side-armed flask under nitrogen. Ligand exchange reaction was accomplished under reflux in benzene for 6 days(13). Five different catalysts, 20H, 40H, 40HT, 40T, and 40T1, were prepared as shown in the Table 1. NMR study with Bruker 300 AC was done to characterize the phosphinated and ruthenium-anchored beads.

Isomerization of 1-hexene

In liquid phase reaction, ruthenium complex or the polymer catalyst was introduced into a side-armed reactor in a glove box. The reactor was sealed and taken out from the glove box, and then 1-hexene and solvent were added to the reactor. 1-Hexene was isomerized in gas phase over the ruthenium complex supported on the macroporous resin. The reaction system consisted of nitrogen inlet, 1-hexene inlet (Sage 341 syringe pump) and heating line. The products were analyzed by a gas chromatograph (Gow-Mac 750, FID) interfaced by an integrator(HP 3390A). In order to separate olefin isomers a 6m x 1/8 in ss-316 tube packed with 7% squalane on Chromosorb P was used.

Results and Discussion

Characterization of the catalysts

The ruthenium complex anchored onto phosphinated macroporous S-DVB resin was applied to the isomerization of 1-hexene in liquid and in gas phase. In Fig. 1, the ³¹P-NMR spectra of ruthenium complex(A), phosphinated polymer(B), and ruthenium-containing polymer(C) are illustrated. The phosphine groups of ruthenium

complex has a sharp peak around 30ppm(A), and diphenylphosphine anchored onto polymer shows a sharp peak around -3ppm(B). The ruthenium-containing polymer has 3 peaks around -3ppm, 30ppm, and 70ppm, respectively, representing a successful anchoring of the ruthenium complex onto the phosphinated polymer(14).

In Table 1 are shown the properties of macroporous catalysts in each step of preparation. Five different polymer beads were prepared. The degree of crosslinking was 20% or 40%, and the pore-forming agents used were n-heptane and/or toluene. The degree of crosslinking was defined as the mole percent of divinylbenzene per total moles of all monomers. The swelling ratios of the catalysts were dependent on the degree of crosslinking and the swelling medium. It can be seen that 20H in toluene had the highest swelling ratio while 40H, 40HT, 40T, and 40T1 in n-decane were swollen only slightly. The chlorine contents of polymer support 20H, 40H, 40HT, and 40T were controlled to have the same values(ca. 2.1 meq/g), while that of 40T1 was adjusted to contain about one fifth of 40T.

The anchoring stoichiometry of ruthenium complex onto the phosphinated S-DVB copolymer was estimated by comparing experimental values with the calculated ones. It was confirmed that a ruthenium complex might be anchored onto about 2 phosphine groups on the polymer for 20H and 40H catalysts and about 1.5 phosphine groups for 40HT, 40T, and 40T1 catalysts, respectively. The unit for the content of ruthenium in the catalyst beads was converted into the one based on S-DVB copolymer weight by using the estimated stoichiometry.

The extent of phosphination and anchoring were defined as the mole% of chlorine substituted by diphenylphosphine in phosphination and the mole% of phosphine groups taking part in anchoring reaction, respectively. The extent of phosphination was not affected by the degree of crosslinking with the same pore-forming agent, while it was affected by the type of pore-forming agent with the same degree of crosslinking. Depending on the amount and the type of pore-forming agent, the final product can be either macroporous or gelular(15,16). The pore volume as well as the surface area can be controlled in a wide range by changing the volume and type of pore-forming agents and the degree of crosslinking. The higher degree of crosslinking resulted in the larger surface area with the same pore-forming agent. At the same degree of crosslinking, the polymers with good solvent such as toluene provided higher surface area than those with poor solvent such as n-heptane. Even though the surface area of 40H was much larger by about

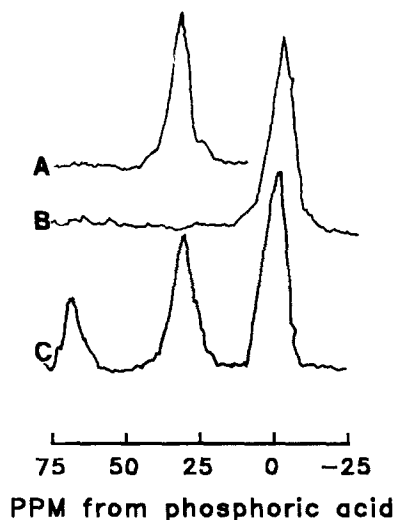


Figure 1 Spectra of solid state MAS ^{31}P -NMR for ruthenium complex(A), phosphinated polymer(B), and ruthenium-anchored polymer(C)

five times than that of 20H, its extent of phosphination was almost the same and the ruthenium content in 40H was only slightly larger than that in 20H. In the case of same crosslinking density, the higher extent of phosphination and ruthenium anchoring could be obtained with the larger surface area. That is, 40HT and 40T catalysts had higher content of phosphine and ruthenium than 40H catalyst. In the case of the same surface area, the polymer beads prepared with toluene were phosphinated to more extent comparing with that prepared with the mixture of toluene and n-heptane. Macroporous resins consisted of small microparticles as illustrated in Fig.2. Considering that the polymer supports had the similar surface area and chlorine content, toluene might have more favorable effects on phosphination and anchoring reaction than n-heptane. Though 40T1 contained chlorine group of one fifth of 40T, it is believed that phosphination and anchoring reaction progressed to similar extent in 40T and 40T1. It is also noted that the surface area based on S-DVB copolymer weight remains unchanged through phosphination and anchoring reaction. This could be evidenced by the SEM images of 40HT in Fig.2. The morphologies did not change noticeably on phosphination and anchoring reaction and similar results were obtained for the other ones.

Table 1. Properties of macroporous resins

		20H	40H	40HT	40T	40T1
degree of crosslinking		20	40	40	40	40
pore-forming agent		n-heptane	n-heptane	n-heptane/ toluene(1/4)	toluene	toluene
swelling ratio	toluene	1.40	1.21	1.19	1.22	1.20
	n-decane	1.17	1.05	1.07	1.04	1.05
Cl in support bead [meq/g]		2.10	2.09	2.10	2.07	0.39
Cl/P in phosphinated bead [(meq/g)/(meq/g)] (phosphination %)		1.39/0.71 (33.8%)	1.37/0.70 (33.5%)	0.71/1.38 (65.7%)	0.36/1.72 (83.1%)	0.08/0.31 (79.5%)
Ru in catalyst [meq/g] (anchoring %)		0.13 (38.5%)	0.17 (40.8)	0.42 (50.0%)	0.97 (78.9%)	0.17 (68.2%)
surface area [m ² /g]	before phosphination	28.4	148	307	331	325
	after anchoring	27.8	142	303	319	311

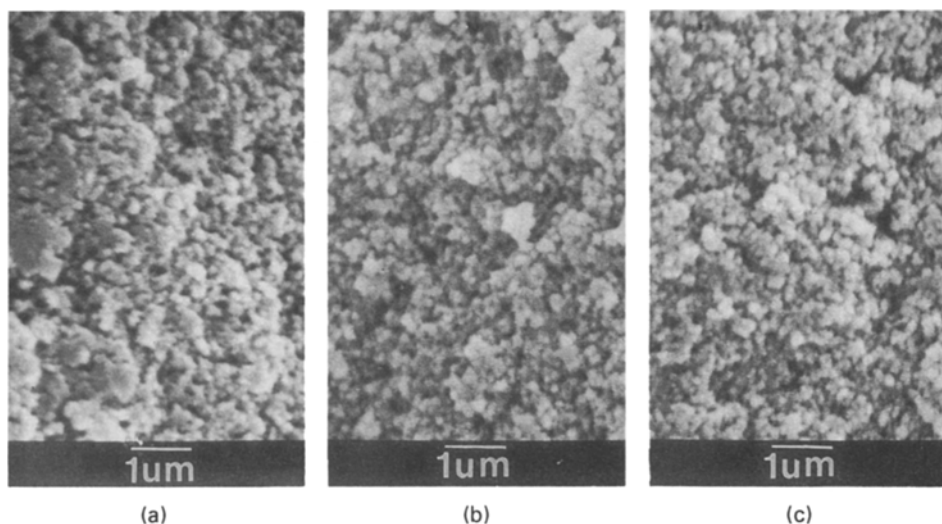


Figure 2 The SEM images of 40HT for chloromethylated beads(a), phosphinated beads(b), and ruthenium anchored beads(c)

Catalytic performance

Isomerization in liquid phase was carried out with the polymer-anchored ruthenium complex catalysts by using toluene and n-decane as solvents and only *cis*- and *trans*-2-hexenes were obtained without any other side products. The solvents affected the activities of macroporous catalysts as shown in Fig.3. Good swelling solvent(toluene) provided higher activities than poor swelling solvent(n-decane). Higher degree of crosslinking resulted in lower activities, which might be attributed to poor swelling of the catalyst.

In Fig.4 are illustrated the activities in gas phase reaction with time at various temperatures for the 40HT catalyst. The activities were observed to increase for the initial stage at 80°C and 100°C. The reactivity at 80°C increased rather slowly, which might be due to a slow formation of the active site, presumably metal-hydride(13). The catalyst maintained constant activity and overnight exposure to air did not reduce its activity much. The activity at 100°C increased at the initial stage and then decreased. The activity decreased more drastically at temperatures of 120°C and 140°C. Similar tendencies were obtained in other catalysts. Even though the $\text{RuCl}_2(\text{PPh}_3)_3$ complex was highly air-sensitive in homogeneous solution, it became air-insensitive on being anchored. It was confirmed that the prepared catalysts could be recycled in air and they are fairly stable in the air even up to several months. After the run at 140°C in gas phase, the catalyst became decolorated and a slight loss in weight was observed through soxhlet extraction by benzene. In the absence of 1-hexene, such feature was not observed at all temperatures. Therefore, it is believed that 1-hexene was responsible for deactivation through the promotion of P-C bond cleavage.

It was also found that irrespective of the surface area, the specific activities of 40H, 40HT, 40T, and 40T1 were almost the same while the activity of 20H was much lower than the others. This might be due to the different distribution of ruthenium complexes in microparticles. For 20H catalyst, the ruthenium complex might be located at inner part as well as on the surface of the microparticles while those of the others are located mainly on the surface of microparticles. In a good solvent, the ruthenium located at the inner part could also take part in reaction. Since the catalysts can not be swollen in gas phase reaction, the ruthenium complexes located only on the surface of microparticles are available for the reaction. Therefore, the specific activity of 20H catalyst was lower than those of the others. The efficiencies of active sites located at both parts of microparticles were discussed for the sulfonated macroporous resin catalysts elsewhere(17).

It was confirmed in the homogeneous reaction that an induction period existed, which might be attributed to a slow formation of ruthenium-hydride. The earlier works showed that the active site of some transition metal complexes(13,18,19) is metal-hydride in the isomerization reaction. Transition metal complexes without hydrogen ligand should be converted into metal-hydride by the protonating reagents. Provided such reagents were absent, metal-hydride was formed via intramolecular reaction, or orthometallation of triphenylphosphine ligand with metal(20). Since $\text{RuCl}_2(\text{PPh}_3)_3$ does not contain any hydrogen ligand, this complex should be converted into ruthenium-hydride to catalyze isomerization reaction. The color of reaction medium changed from brown to red violet as the reaction proceeded, while it did not change without the addition of 1-hexene. In order to promote formation

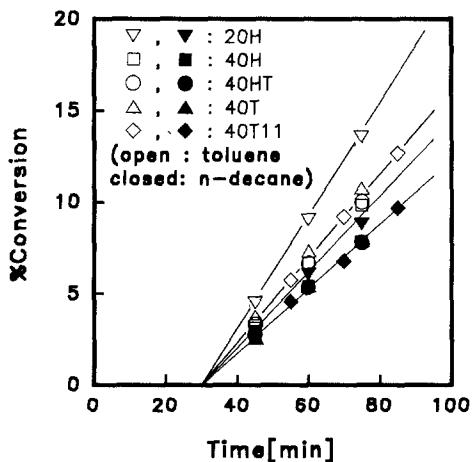


Figure 3 Catalytic activities of macroporous catalysts at 80°C in liquid phase; ruthenium complex of 3.96 meq, 1-hexene of 32 mmol, and solvent of 8.5 ml

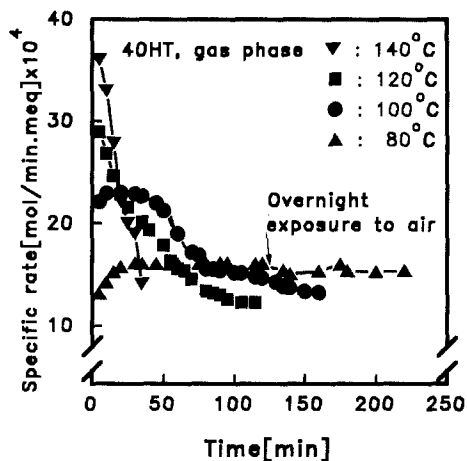


Figure 4 Change of specific rate in gas phase; 1-hexene partial pressure of 0.04 atm and total volumetric flow rate of 50 ml/min

of ruthenium-hydride, in this work, hydrogen was bubbled through the ruthenium complex solution about an hour at room temperature until the color of the solution has changed into red violet. Reaction proceeded immediately on adding 1-hexene to the ruthenium solution. At the same concentration of the ruthenium complex, the activities in homogeneous reaction were much higher than those in heterogeneous catalysis, which might be attributed to pore diffusion limitation in the resin catalyst.

The *cis/trans* ratio in product is an important feature and varies widely depending upon the reaction mechanism and environments. When isomerization proceeds via π -allylic intermediate, *trans*-isomer forms rather easily(19). On the other hand *cis*-isomer is favored when isomerization is catalyzed by metal-hydride and when interactions between reaction intermediate and bulky phosphine ligand are important(18). This might be attributed to the bulky phosphine ligand which restricted rotation of carbon-metal bond in metal-alkyl species.

Fig.5 illustrates the selectivity to *cis*-products at the conversion of about 8.5% with varying concentration of ruthenium complex dissolved in toluene. *Cis*-2-hexene was favored with higher concentration of the complex. As the concentration of the ruthenium complex decreases, dissociation of the bulky phosphine is promoted and this might reduce restriction to the rotation of alkyl group as reported for other transition metal complexes(18). It can be confirmed that the initial selectivity increased with the addition of triphenylphosphine as expected by suppressing the dissociation of the phosphine group from the ruthenium complex.

As illustrated in Fig.6, the macroporous catalyst favored *trans*-isomer irrespective of the capacity and degree of crosslinking. Comparison of Fig.5 and Fig.6 indicates that anchoring the ruthenium complex onto the phosphinated polymer might isolate the active sites allowing the metal-alkyl bond to rotate rather freely.

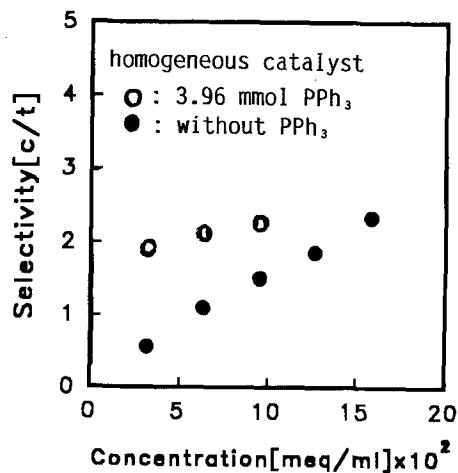


Figure 5 Initial selectivity at 80°C of homogeneous ruthenium complex catalyst; 1-hexene of 32 mmol and toluene of 8.5 ml

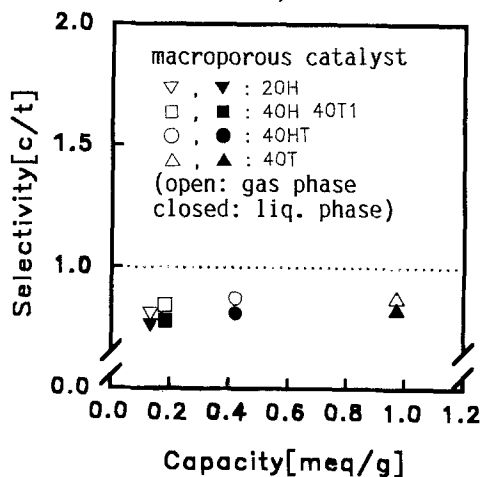


Figure 6 Initial selectivity at 80°C of macroporous catalyst with capacities under reaction condition of Figure 3 and Figure 4, respectively

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