The Synthesis of Polymeric Catalyst Using Ion Exchange Resin and Its Application for Esterification

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Synopsis. The copolymer complexes have been synthesized from cation and/or anion resin with metal catalyst such as aluminum chloride or iron(III) chloride. Electron microprobe X-ray analysis demonstrated that aluminum and iron were distributed uniformly in the copolymer complex. The catalytic activity for esterification of dibasic organic acids was discussed and showed that copolymer complex from porous type cation exchange resin was much better catalyst than that from gel type.

Polymers have been used broadly as a supporter[1] or as a catalyst[2,3] in various organic syntheses. Some of the advantages cited include substrate stabilization, reaction selectivity, increased yield and effective separation of the products. When used as a catalyst, they are usually polymer-metal complexes formed by linking polymers to metal catalyst such as $AlCl_3$ or $FeCl_3$. Such metal complexes are no longer volatile and far less hygroscopic.[4] Furthermore, the catalyst can be reused repeatedly, because the polymer-metal complexes are stable in the air,[5] and the products are more readily separable from the bulk.

Although these metal complexes have been used extensively in pharmaceutical industry for their improved catalytic effect, there have been some difficulties in material handling and even loss of polymer complexes when they were used in styrene–divinylbenzene matrix.[6] We have used ordinary ion exchange resins to form copolymers of $AlCl_3$ or $FeCl_3$ and found that they are much better catalysts in esterification of organic acids than either cation exchange resin itself or metal catalyst. The microstructures of both $AlCl_3$ and $FeCl_3$ copolymers have been analyzed using scanning electron microscope and electron microprobe X-ray analyzer.

Aluminum chloride copolymer complex (Ⓟ-$AlCl_3$) and iron(III) chloride copolymer complex (Ⓟ-$FeCl_3$) have been prepared from anhydrous $AlCl_3$ powder and anhydrous $FeCl_3$ powder with cation and/or anion exchange resin respectively following the method of Neckers.[7] The resins used in this experiment were gel and porous types with 30—50 mesh beads. The beads were the commercial cation and/or anion exchange resin beads (gel type : DIAION SK 1B and SA 10A, porous type : DIAION PK 212 and PA 312, Mitsubishi Chemical Ltd.); These beads were treated with $AlCl_3$ and/or $FeCl_3$ for periods of 30, 60, 90, 120, 150, and 180 min.

The aluminum and iron contents of the above complexes were analyzed with atomic absorption spectrophotometer. In general, the aluminum contents of Ⓟ-$AlCl_3$ synthesized from cation exchange resin of 30—50 mesh size (gel type : SK, porous type : PK) were greater than Ⓟ-$AlCl_3$ synthesized from anion exchange resin. As shown in Table 1, the aluminum content of the porous type resin complex was the highest when it was treated with $AlCl_3$ for 30—60 min.

Table 1. Aluminum and iron content in copolymer complex according to the various reaction times and type of cation exchange resins

Reaction time / min	Content/mg g^{-1}			
	Al/Ⓟ-$AlCl_3$		Fe/Ⓟ-$FeCl_3$	
	PK	SK	PK	SK
30	0.19	0.04	0.65	0.32
60	0.19	0.07	0.80	0.53
90	0.15	0.10	0.63	0.65
120	0.12	0.07	0.53	0.52
150	0.08	0.05	—	—
180	0.06	0.04	0.55	0.48

PK; DIAION PK 212, porous type. SK; DIAION SK 1B, gel type.

But the aluminum content of the gel type resin complex was highest when the resin was treated with $AlCl_3$ for 90 min. The iron content of the complex synthesized from gel type resin was also the highest when the resin was treated with $FeCl_3$ for 90 min, while that of the complex synthesized from porous type was the highest when the resin was treated with $FeCl_3$ for 60 min. In addition, it was observed that the content of iron of the complex was four to six times as much as that of the aluminum of the complex at their maximum activities.

To investigate the microstructure of copolymer complexes, these several beads were examined in detail using energy dispersive X-ray spectrometer, scanning electron micorscope and electron microprobe X-ray analyzer.

For the microscopic analysis, samples of copolymer complex were embeded in epoxy resin and then sectioned by microtome. In the micrographs of sectioned beads, the pores of SK Ⓟ-$AlCl_3$ and SK Ⓟ-$FeCl_3$ beads appeared smaller than those of SK Ⓟ bead. The difference between these beads were also observed with the porous types. Therefore, it is suggested that Al^{3+} and Fe^{3+} of the copolymer complexes may have replaced hydrogen ion in cation exchange resin. As shown in Fig. 1 we observed the singnal intensity of aluminum and iron respectively in the electron micropobe profiles of the copolymer complex of gel type bead. These singnal intensity were also observed with porous type bead. The present results demonstrated that aluminum and iron were distributed uniformly in the copolymer complex.

The esterifications of various dibasic acids with alcohols were carried out in order to examine the catalytic effect of copolymer complexes by the method described in our previous work.[6] The reactions of various aliphatic acids with alcohols using Ⓟ-$AlCl_3$ and Ⓟ-$FeCl_3$ as catalysts in mole ratio of 1 : 1 at 120 °C for 5 h are compared with the reaction using

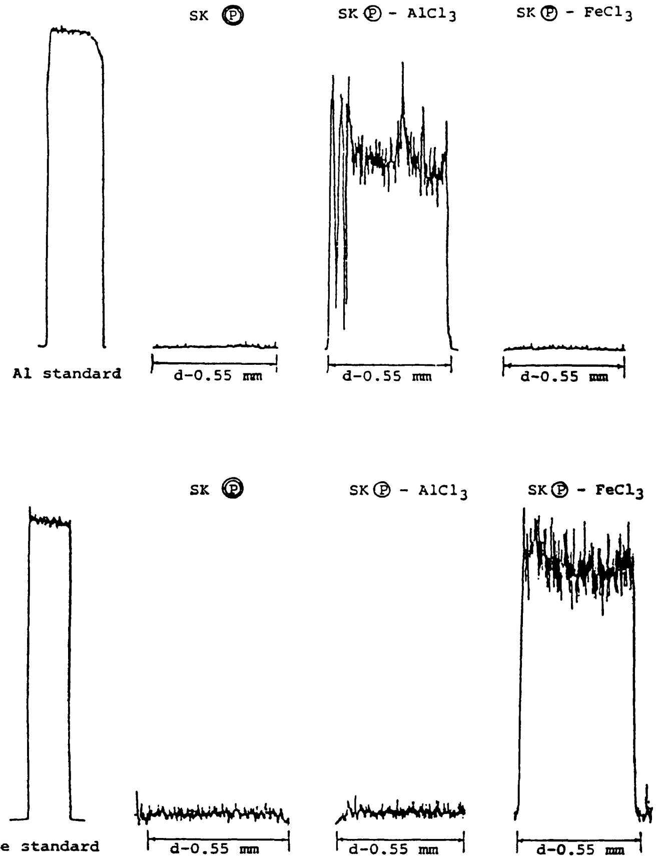

Fig. 1. Electron microprobe X-ray (Al-*K*α and Fe-*K*α) profiles of a sectioned spherical bead of copolymer complex.
Treated with CS_2 only: SK Ⓟ.
Prepared from $AlCl_3$ for 90 min: SK Ⓟ-$AlCl_3$.
Prepared from $FeCl_3$ for 90 min: SK Ⓟ-$FeCl_3$.

TABLE 2. YIELD OF ESTERIFICATION OF THE VARIOUS ACIDS WITH ALCOHOLS

Acid	Alcohol	Mole ratio (acid : alcohol)	Yield/%					
			PSVB-SO_3H		Ⓟ-$AlCl_3$		Ⓟ-$FeCl_3$	
			PK	SK	PK	SK	PK	SK
Oxalic	Ethyl	1 : 1	31.66	25.43	83.10	67.26	70.44	56.25
Malonic	Ethyl	1 : 1	23.78	5.76	56.50	46.62	46.83	30.84
Succinic	Ethyl	1 : 1	20.49	3.49	49.14	32.45	34.37	24.75
Adipic	Ethyl	1 : 1	8.68	0.23	22.77	14.91	16.26	11.56
	Isopropyl	1 : 1	2.82	0	20.46	14.17	11.33	9.83
Maleic	Ethyl	1 : 1	6.95	4.11	25.51	19.45	19.68	15.29
Fumaric	Ethyl	1 : 1	1.19	0	20.34	14.37	12.86	8.22
Phthalic[a)]	Ethyl	1 : 2	0	0	22.09	8.89	3.18	2.00
1,2-Cyclohexane dicarboxyric[a)]	Ethyl	1 : 2	4.43	3.21	27.18	16.82	6.36	4.42

All reactions were carried out at 120 °C for 5 h using 0.5 g polymer catalyst respectively. a) Reaction time: 10 h. Ⓟ is cation exchange resin matrix.

cation exchange resin (PSVB–SO_3H) as shown in Table 2. The reactions of aromatic and alicyclic dibasic acids with alcohols in the mole ratio of 1 : 2 were also carried out for 10 h, and the result is included in Table 2. The yields of esterifications shown in Table 2 were determined by gas chromatography. Matsumoto[8)] has demonstrated previously the catalytic activity of cation exchange resin. We now have observed that the Ⓟ-$AlCl_3$ and Ⓟ-$FeCl_3$ are better catalysts in esterification. Furthermore, the Ⓟ-$AlCl_3$ is a more effective catalyst than Ⓟ-$FeCl_3$. This agrees with the fact that $AlCl_3$ is a better catalyst than $FeCl_3$.[9)] In the case of esterification of saturated aliphatic dibasic acid with ethyl alcohol, the more methylene groups in the acid, the less yield is observed. This result shows that the electron-withdrawing group at the α-position of carboxylic acid enhances esterification. In the case of maleic acid, the reaction occured more quickly than its trans isomer fumaric acid. This has also been observed in the formation of maleic anhydride.[10)] As shown in Table 2, the copolymer complexes are less effective catalysts in esterification of aromatic acid and alicyclic acids than aliphatic acid. Furthermore, the copolymer complex is very stable and not fragile, so can be reused. In Table 3, the catalytic effect of the resynthesized copolymer complex is the almost same as the original one whereas, in genaral, the recycled catalyst has less activity than the original one. Generally, copolymer complexes synthesized from porous type of cation exchange resin are better catalysts in the esterification than those synthesized from gel type resin. The catalytic activity is observed proportional to the aluminum and iron contents of copolymer complexes respectively.

TABLE 3. YIELD OF ESTERIFICATION OF MALONIC ACID WITH ETHYL ALCOHOL ACCORDING TO MOLE RATIO OF ACID AND ALCOHOL

Mole ratio (acid : alcohol)		Yield/%	
		PSVB-SO_3H	Ⓟ-$AlCl_3$
1 : 1	Original	23.78	56.50
	Resynthesized	23.57	53.39
	Recycled	8.50	17.39
1 : 2	Original	16.98	48.72
	Resynthesized	16.26	45.00
	Recycled	4.29	13.34
1 : 4	Original	11.40	41.00
	Resynthesized	9.97	39.10
	Recycled	2.17	10.61

All reactions were carried out at 120 °C for 5 h using 0.5 g polymer catalyst respectively. Ⓟ is cation exchange resin matrix with porous type (PK).

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