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# Encapsulated $AlCl_3$: a convenient catalyst for the alkylation of benzene with dodecene

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**Abstract**—A novel method for the encapsulation of $AlCl_3$ was successfully carried out using an insoluble polymer wall. The polymer wall was formed by the reaction of poly(styrene-*co*-dimethylaminoethyl methacrylate) and hydrogenated telechelic polybutadiene containing -COOH groups. The encapsulated $AlCl_3$ was used to catalyze the Friedel–Crafts alkylation of benzene with dodecene. The alkylbenzenes were obtained in excellent yields and the encapsulated $AlCl_3$ catalyst was separated by simple filtration. © 2002 Elsevier Science Ltd. All rights reserved.

Friedel–Crafts reactions are amongst the most important reactions in organic synthesis. In the course of more than 100 years of Friedel–Crafts chemistry, only two catalysts, $AlCl_3$ and $BF_3$ have gained wide recognition.[1] Especially, anhydrous $AlCl_3$ has maintained its use ever since it was introduced by Friedel and Crafts,[2] despite some unfavorable properties such as decomposition or deactivation in water, safety and lack of recoverability. Lewis acid-catalyzed reactions are still of great interest because of unique reactivities and selectivities that can be achieved as well as the mild conditions used.[3]

The utilization of polymer–supported catalysts offers several advantages in preparative procedures. The simplification of the workup and separation of products and catalysts are useful for industrial processes. There are a few examples of polymer-supported Lewis acids.[4–6] They comprise a polymer carrier attached by weak chemical or physical interactions to a Lewis acid. The Lewis acid can be partially washed out of the polymer support during reaction.[7] For the polymer-supported scandium based Lewis acid using Nafion[8] and a polyacryronitrile derivative,[9] reactivities were lower than that of the monomeric Lewis acid. For polymer-supported aluminum chloride,[4] $AlCl_3$ was immobilized onto polymer or inorganic support materials, but successful applications have been limited.[3]

The emphasis in this study was on the establishment of an encapsulation procedure to preserve highly reactive $AlCl_3$ which easily loses activity in the air or a highly moist atmosphere.

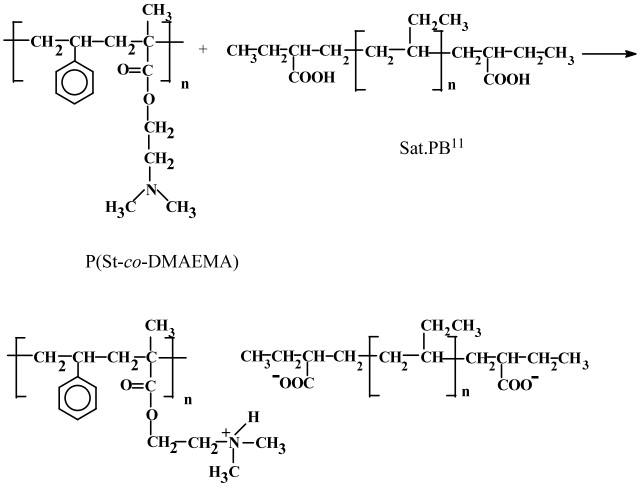

**Figure 1.** Formation of the insoluble salt of the polymer wall from the P(St-*co*-DMAEMA) and Sat. PB.

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*Keywords*: encapsulated $AlCl_3$; Friedel–Crafts alkylation; alkylbenzene; hydrogenated telechelic polybutadiene.

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The capsules were prepared by a solvent evaporation technique.[10] The polymer wall was formed by the reaction of the dimethylamino groups from poly(styrene-*co*-dimethylaminoethyl methacrylate),[11] P(St-*co*-DMAEMA) and -COOH groups of hydrogenated telechelic polybutadiene (Sat. PB)[12] to form the insoluble salt of the polymer[13] (Fig. 1) by using liquid polybutadiene (PBD) as a stabilizer. In this study, the size distribution of all the capsules was not wide because the $AlCl_3$ capsules have a tendency to agglomerate as shown by optical microscopy (Fig. 2) and scanning electron microscopy (Fig. 3). At 10 wt% of Sat. PB, 10 wt% of P(St-*co*-DMAEMA) and 2 wt% of PBD, the capsules had a smoother surface and achieved more complete encapsulation than at other ratios.

Alkylation of benzene with 1-dodecene was chosen as a model reaction to study the catalytic activity of the encapsulated $AlCl_3$.[14] The product was analyzed by GC and GC–MS. The capsules at various polymer wall and stabilizer concentrations were effective in alkylation of benzene with 1-dodecene to give the phenyldodecanes (2-p, 3-p, 4-p, 5-p and 6-phenyldodecane) except for the 1-phenyl isomer. This is consistent with a carbonium ion mechanism. The absence of 1-phenyldodecane is due to the instability of the primary carbonium ion. It has been shown that the capsules can be an effective catalyst for the Friedel–Crafts alkylation of benzene with 1-dodecene, and the capsules can be easily recovered by a simple filtration. The reaction in the presence of unencapsulated $AlCl_3$ (free $AlCl_3$) under the same conditions gave a similar yield to those of encapsulated $AlCl_3$ (Table 1). The catalytic activity of the encapsulated $AlCl_3$ was affected by the amounts of stabilizer (runs 2–4). This indicated that 2 wt% of PBD was enough to stabilize the capsules. The effectiveness of the capsules at different amounts of Sat. PB (runs 3, 5 and 6) was not so different when compared with the capsules with different amounts of P(St-*co*-DMAEMA) (runs 3, 7 and 8). It shows that at 10 wt% of Sat. PB and 10 wt% of P(St-*co*-DMAEMA), the capsules had high conversion and complete encapsulation.[15]

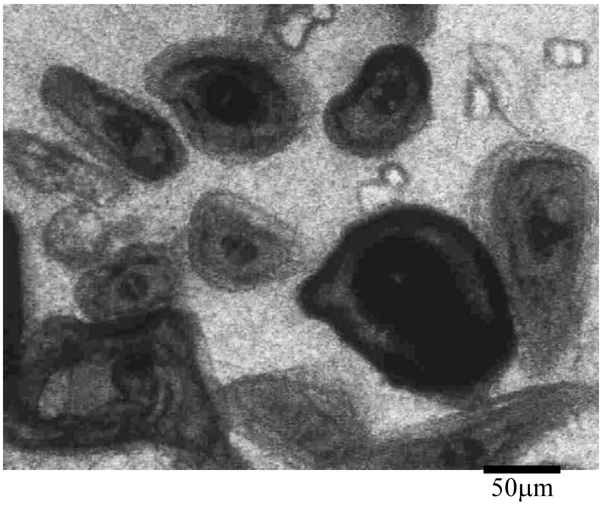

**Figure 2.** Photograph of capsules taken by an optical microscope at 10 wt% Sat. PB, 10 wt% P(St-*co*-DMAEMA) and 2 wt% of PBD.

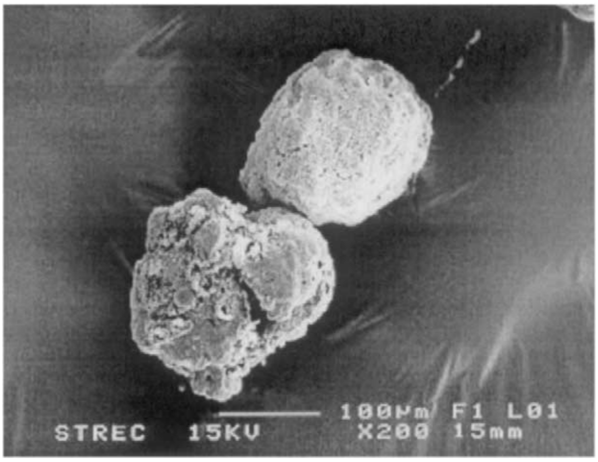

**Figure 3.** Scanning electron micrograph of capsules at 10 wt% Sat. PB, 10 wt% P(St-*co*-DMAEMA) and 2 wt% of PBD.

Most of the conventional Friedel–Crafts catalysts generally give complex reaction mixtures which can be worked up and separated only with difficulty[16] and with the loss of catalysts producing environmentally unfriendly, toxic waste.[17] In the case of this encapsulated $AlCl_3$, the capsules could be dispersed well in benzene and remained in the solid state, and thus could be conveniently separated quantitatively at the end of the reaction by simple filtration. The capsules showed

**Table 1.** The encapsulation recipe for $AlCl_3$ and its catalytic activity in the reaction of benzene and 1-dodecene[a]

| Run No. | Sat. PB (Wt.%) | PS-DMAEMA (Wt.%) | PBD (Wt.%) | Conversion[c] (%) |
|---|---|---|---|---|
| 1[b] | – | – | – | 97 |
| 2 | 10 | 10 | 1 | 74 |
| 3 | 10 | 10 | 2 | 97 |
| 4 | 10 | 10 | 5 | 97 |
| 5 | 5 | 10 | 2 | 97 |
| 6 | 2.5 | 10 | 2 | 94 |
| 7 | 10 | 15 | 2 | 76 |
| 8 | 10 | 5 | 2 | 13 |

[a] All experiment were carried out at 36°C for 1 h.

[b] Unencapsulated $AlCl_3$ (free $AlCl_3$).

[c] Total conversion (2-p, 3-p, 4-p, 5-p and 6-p) by GC analysis using a capillary column (DB-PSWAX).

very good stability to organic solvents and to high temperature. They also exhibited good catalytic activity.[18] Therefore, the encapsulated $AlCl_3$ made $AlCl_3$ safer and more convenient to handle.

In conclusion, we have successfully developed a new method for the encapsulation of $AlCl_3$ using an insoluble polymer wall. The capsules have effectiveness and stability in Friedel–Crafts alkylation reactions. Moreover, they are strong enough for long-term use. We are currently studying the activity of these capsules for other applications. The present technique should be useful for the encapsulation of other sensitive catalysts or substances.

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10. A typical experimental procedure, run no. 2, was as follows: hydrogenated telechelic polybutadiene (Sat. PB) 1.5 g was dissolved in 15 g of cyclohexane, $AlCl_3$ 0.8 g was added into the polymer solution and stirred in the reactor at 40°C. Then the solution of P(St-co-DMAEMA) in cyclohexane (1.5 g/15 g) was added dropwise at 40°C with constant stirring for 30 min; a crosslinking polymer was formed around the $AlCl_3$, and to this solution, a solution of stabilizer (PBD 0.9 g in 90 g of dodecane) was added and stirred. After evaporation of the solvent at 35–40°C under vacuum, the supernatant was separated by centrifugation. The capsules were washed with hexane, and dried under $N_2$ atmosphere.
11. Styrene (St, Kishida Chemical Co., Japan) and dimethylaminoethyl methacrylate (DMAEMA, Wako Pure Chemical Industries, Ltd, Japan) were commercial grade. They were distilled under reduced pressure. 2,2′-Azobis(2,4-dimethylvaleronitrile) (V-65, ADVN) was reagent grade (Wako Pure Chemical Industries, Ltd, Japan), and was used as an initiator. A typical procedure was as follows: A mixture containing 90 g of St, 13 g of DMAEMA, 1 g of ADVN and 20 ml of distilled toluene was added to the reactor with a stirrer. After the mixture was bubbled with nitrogen gas for 1 h, the nozzle was lifted up above the surface of the mixture and the temperature was elevated to 50°C gradually for the polymerization. The polymerization was carried out for 24 h under a nitrogen atmosphere. The polymer was precipitated by methyl alcohol, separated by centrifugation and dried in a vacuum.
12. Sat. PB is a hydrogenated telechelic polybutadiene obtained from Nippon Soda Co., Japan. Trade name: PG CI-1000 hydrogenated.
13. IR (KBr, $cm^{-1}$): 3300 (OH stretching), 1600 (C=O stretching) and 1500 (combination of NH bending and C–N stretching), along with characteristic absorption bands of aromatic compounds at 3050 and 1600 $cm^{-1}$.
14. The reaction was carried out as follows: 1-Dodecene (0.015 g. 0.089 mmol) was added gradually to a mixture of encapsulated $AlCl_3$ (30 mg) and benzene (0.885 g. 11.3 mmol) at 36°C for 1 h. The capsules were separated by simple filtration. The benzene was evaporated and the product was analyzed by gas chromatography and gas chromatography/mass spectrometry.
15. Observed from photograph of capsule taken by optical microscope (Olimpus DP-10, Tokyo).
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18. Encapsulated $AlCl_3$ can be stored at room temperature for more than a few months without losing its activity.