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# Polymerization of 1,3-Butadiene over Cobalt Exchanged Y-Zeolite

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## Summary

It was found that polymerization of 1,3-butadiene took place over cobalt(II) ion exchanged Y-zeolite without any additives.

## Introduction

A great number of investigations have been carried out so far on the polymerization of 1,3-butadiene mainly by using transition metal compounds combined with organometallic compounds (RICHARDS 1977, OHNISHI 1977, ASAI 1977). However, the precise mechanism of the polymerization is still open to discussion, which seems to be attributed to the complexity of the catalytic systems. The present authors have recently found that cobalt(II) ion exchanged Y-zeolite (Co-Y) catalyst initiates the polymerization of 1,3-butadiene without any additives. The catalyst is apparently simplest in compositions among the catalysts reported so far. This paper reports the brief results of the polymerization.

## Experimental

Materials Research grade $CoCl_2 \cdot 6H_2O$, $Co(NO_3)_2 \cdot 6H_2O$ (from Koso Chemical Co.), $Co(acac)_2$ and $Co(acac)_3$ (from Tokyo Kasei Kogyo Co. Ltd.) were commercially obtained and used without further purification. Research grade 1,3-butadiene (from Japan Synthetic Rubber Co., 99.5 % purity) and n-heptane (from Wako Pure Chemical Co.) were purified according to the usual procedures. Nitrogen of ultra high purity (from Nihon Sanso Co., 99.9989 % purity) was further purified by passing through the molecular sieve 3A column cooled at -196 °C. $SiO_2$ (surface area: 270 $m^2/g$, average pore diameter: 205 Å) from Fuji Devison Co. was dried at 150 °C for 2 h.

Preparation of the catalysts. Co-Y catalysts

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were prepared by the conventional ion exchange of Na form of Y-zeolite (Linde SK-40) with Co(II) ion according to the similar procedures reported earlier (SOGA et al. 1979). The Co-Y catalysts thus prepared were used for the polymerization after being evacuated at room temperature to 600 °C for 3 h.

Polymerization procedures. In a 50 ml stainless steel reactor equipped with a magnetic stirrer were placed the measured amounts of the catalyst and n-heptane under a nitrogen atmosphere. The reactor was cooled by liquid nitrogen, degassed i. vac. and then 0.2 mol of purified 1,3-butadiene was introduced. The polymerization was terminated by adding plenty of a dilute hydrochloric acid solution in methanol. The solid part was isolated by filtration, and was added plenty of an aqueous solution of hydrofluoric acid to remove the residual catalyst. The precipitate (polybutadiene) was dried i. vac. at room temperature.

Analytical procedures. The amount of cobalt contained in the catalysts were determined by atomic absorption spectrophotometry (Shimadzu AA-6105). The microstructure of the polymer was determined by the method of MORERO (MORERO et al. 1959) with IR using the potassium bromide pellet technique, from 740, 910 and 970 $cm^{-1}$ bands.

## Results and Discussion

The contents of Co supported on Y-zeolite measured by atomic absorption spectrophotometry were 1.28 matom/g-cat. for $CoCl_2$ and 1.05 matom/g-cat. for $Co(NO_3)_2$, respectively. These values indicate that most of Na ions were displaced by Co(II) ions. The typical results of the polymerization are summarized in Table 1. It should be noted that stereospecific polymerization of 1,3-butadiene took place over these Co-Y catalysts. These results strongly imply that neither Co-alkyl bonds nor halogen ligands are necessarily essential also for stereospecific polymerization of 1,3-butadiene (SOGA et al. 1979). With increasing the evacuation temperature of the Co-Y catalysts, the activity increased significantly, reached a maximum value at 500 °C, and then decreased slightly. The decrease in the activity over the catalysts evacuated at lower temperatures may be attributed to the water left in the zeolite cage. The polymer yield obtained over the catalyst prepared from $Co(NO_3)_2$ (Run No. 7) was in good agreement with that obtained over the catalyst from $CoCl_2$ (Run No. 5). On the other hand, the polymerization of 1,3-butadiene did not take place over the Na-Y and H-Y catalysts evacuated at 500 °C for 3 h. Most of the polymer produced was insoluble in boiling o-dichlorobenzen. This observation strongly suggests that the product might be a highly cross-linked polybutadiene. However, the microstructure of the soluble polybutadiene was identical with that of the insoluble one. It may be considered that such a cross-linkage is promoted by protons left in the zeolite. The massive $CoCl_2$ catalyst obtained from Tokyo Kasei Kogyo Co. Ltd. and evacuated at 150 °C for 3 h did not show any activity for the polymerization. It is considered that large Cl ligands surrounded with Co(II) prevent 1,3-butadiene from coordinating with the Co(II) species. From such a point of view, $SiO_2$-supported Co(II) catalysts were prepared (Table 1). Such dispersed catalysts showed considerably high activities as shown in Table 1. Then, similar catalysts were prepared by using Co(III) and Co(0), which did not show any activity for the polymerization (Table 1). These results suggest that Co(II) species is active for the polymerization. A more detailed study is now being tried out and the precise results will be reported in another paper.

## References

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TABLE 1

Results of Butadiene Polymerization over Co-Y and $SiO_2$-supported catalysts.a)

| Run No. | Catalyst | Evacuating Temp. (°C) | Yield (g/g-Co) | Microstructureb) cis 1,4- (%) | trans 1,4- (%) | 1,2- (%) |
|---|---|---|---|---|---|---|
| 1 | Y-$CoCl_2$ | r.t. | 0 | - | - | - |
| 2 | " | 200 | 3.6 | - | - | - |
| 3 | " | 300 | 6.2 | 61.6 | 30.6 | 7.8 |
| 4 | " | 400 | 5.3 | 87.4 | 7.9 | 4.7 |
| 5 | " | 500 | 12.8 | 85.1 | 10.3 | 4.6 |
| 6 | " | 600 | 9.4 | 83.1 | 7.8 | 9.1 |
| 7 | Y-$Co(NO_3)_2$ | 500 | 13.2 | 87.5 | 5.0 | 7.5 |
| 8 | $SiO_2$-$CoCl_2$c) | 300 | 87.8 | 91.4 | 6.0 | 2.6 |
| 9 | $SiO_2$-$Co(acac)_2$d) | " | 38.6 | - | - | - |
| 10 | $SiO_2$-$Co(acac)_3$d) | " | 0 | - | - | - |
| 11 | $SiO_2$-Coe) | - | 0 | - | - | - |

a) Polymerization was conducted at 40 °C for 48 h by using 0.2 mol of 1,3-butadiene, 1500 mg (Co-Y) or 500 mg ($SiO_2$-Co) of the catalyst and 5 ml of n-heptane in a 50 ml stainless steel reactor.

b) Determined by IR spectra (D.MORERO et al. 1959).

c) Prepared by supporting $CoCl_2 \cdot 6H_2O$ on $SiO_2$ in $H_2O$.

d) Prepared by supporting $Co(acac)_2$ or $Co(acac)_3$ on $SiO_2$ in acetone.

e) Prepared by supporting $Co(OH)_2$ on $SiO_2$ in $H_2O$, followed by reduction with hydrogen at 350 °C for 4 h (HÜTTIG 1930).

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