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A Convenient Method for the Preparation of a Highly Active SiO2-supported CoCl2 Catalyst for the Polymerization of Isoprene

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Summary

A highly dispersed SiO_2-supported $CoCl_2$ catalyst was prepared by supporting the complex of $CoCl_2$ $2C_5H_5N$ on SiO_2 in n-heptane, followed by evacuating at room temperature. The catalyst combined with $AlEt_2Cl$ showed a very high activity for the polymerization of isoprene.

Introduction

A great number of investigations have been carried out so far on the polymerization of isoprene by using alkyllithium or transition metal compounds combined with organometallic compounds (SALTMAN et al. 1973, KOMATSU et al. 1977, ALEV et al. 1980). However, because of considerably low activities of the catalysts the reduction of catalyst residues in the polymer to a reasonably low level is necessary to ensure stability toward oxidative degradation and uniformity in vulcanization characteristics.

We have recently succeeded in preparing a highly active SiO_2-supported $CoCl_2$ catalyst. This paper reports the preparative method of the catalyst together with the results of the polymerization of isoprene.

Experimental

Materials Commercial extra pure grade n-heptane, pyridine and research grade isoprene (from Japan Synthetic Rubber Co.) were purified with the usual procedures. $CoCl_2$ (from Yoneyama Chemical Reagent Ltd.) was dried at 150 °C for 3 h immediately before use. SiO_2 (#244, average pore diameter; 20 - 21 nm, 300 m^2/g, from Fuji Devison Chemical Ltd.) was dried at 300 °C for 4 h. Diethylaluminum chloride (DEAC) and triethylaluminum (TEA) were used without further purification. Nitrogen of ultra high purity (from Nihon Sanso Co. Ltd., 99,9995 % purity) was further purified by passing through the molecular sieve 3A colomn cooled at -196 °C.

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Preparation of the SiO_2-supported $CoCl_2$ catalyst. The complex of $CoCl_2 \cdot 2C_5H_5N$ was prepared from the reaction of $CoCl_2$ with pyridine at room pemperature. [$CoCl_2 \cdot 2C_5H_5N$ (288.03) Calc. C, 41.67 H, 3.42 N, 9.72; Found C, 41.38 H, 3.43 N, 9.57.

The mixture of the measured amounts of SiO_2 and $CoCl_2 \cdot 2C_5H_5N$ in n-heptane was kept standing with vigorous stirring for 1 h at room temperature. The precipitate was separated by filtration and washed adequately with n-heptane, followed by evacuating at room temperature to give the supported catalyst.

Polymerization procedures. In a 100 ml stainless steel reactor equipped with a magnetic stirrer were placed the measured amounts of the supported catalyst, DEAC and n-heptane under nitrogen. The reactor was cooled by liquid nitrogen, degassed i. vac. and then 0.25 mol of isoprene was introduced. The polymerization was terminated by adding plenty of a dilute hydrochloric acid solution in methanol containing a small quantity of 2,6-di-tert-butyl-p-cresol. The precipitate (polyisoprene) was dried i. vac. at room temperature.

Analytical procedures. The amount of cobalt contained in the catalyst was determined by atomic absorption spectrophotometry (Shimadzu AA-6105). The DSC measurement of the complex was made on a Shimadzu Thermal Analyzer DT-30 at a heating rate of 10 °C/min. under nitrogen atmosphere. The microstructure of the polymer was mainly determined by ^1H NMR spectrum (CHEN 1963). The intrinsic viscosity of the polymer was measured at 25 °C in toluene. The molecular weight was calculated by using the equation reported by BEATTIE et al. (1963).

Results and Discussion

BRENDEL et al. (1978) have recently investigated the thermal decomposition of the compounds $CoX_2 \cdot 2C_5H_5N$ (X: Cl, Br, I) in detail, and the present DSC curve of the complex completely agreed with that obtained for $CoCl_2 \cdot 2C_5H_5N$. From the result together with the elemental analysis, the complex can be formulated as $CoCl_2 \cdot 2C_5H_5N$. One of the supported catalysts was treated with a DEAC solution in n-heptane (Al/Co: 500) at 65 °C for 30 min., followed by washing with n-heptane, and the product was subjected to the elemental analysis. The result obtained strongly suggested that most of pyridine was removed from the complex of $CoCl_2 \cdot 2C_5H_5N$ by the reaction with DEAC as found in the $TiCl_3 \cdot 3C_5H_5N$ on $MgCl_2$-DEAC system (SOGA et al. 1979).

Several SiO_2-supported $CoCl_2$ catalysts with different molar ratio of $SiO_2/CoCl_2$ were prepared and isoprene polymerization was conducted at 65 °C for 30 min. using ca. 40 mg of each catalyst combined with DEAC. The polymerization was also conducted under similar conditions by using carrier-free $CoCl_2$ or $CoCl_2 \cdot 2C_5H_5N$ as catalyst for reference (Runs no. 1 and 2). The results obtained are summarized in Tab. 1 together with some analytical data. It should be noted that the SiO_2-supported $CoCl_2$ catalysts showed extremely high activities. The results obtained by changing the molar ratio of DEAC/$CoCl_2$ (Runs no. 3-9) indicate that the activity increases significantly and reaches a constant value with an increase in the molar ratio. The decrease in the activity with decreasing the molar ratio may be attributed to the pyridine left in the catalyst. The use of TEA in place of DEAC gave only oligomers (Run no. 12), the reason of which is not clear at present.

Similar catalysts were prepared by using γ-Al_2O_3, (140 m^2/g), MgO (26.4 m^2/g) or $MgCl_2$(43.3 m^2/g) in place of SiO_2 (Runs no 13-15). It is well known that the polymerization activity of α-olefins is extremely accelerated by using $MgCl_2$ as a carrier (SOGA et al. 1981). However, the present results suggest that $MgCl_2$ doesn't show such an excellent property for isoprene polymerization.

On the other hand, whole the polymers produced were soluble in usual organic solvents such as o-dichlorobenzene, benzene, toluene, chloroform, THF, cyclohexane, n-heptane, etc. The microstructure of the polymers obtained over these supported catalysts was about 65 % cis-1,4 with 35 % 3,4- groups, which is not so different from that of the polymer produced over the carrier-free $CoCl_2$. Therefore, the remarkable increase in the polymerization activity over the present supported catalysts may reflect the highly dispersion of $CoCl_2$ on the surfaces of the carriers.

A more detailed study is now being tried out and the precise results will be reported in another paper.

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Table 1. Polymerization Results over the $CoCl_2$-DEAC Catalysts[a)]

Run No	Carrier	Co supported (matom/g-carrier)	Molar Ratio of Al/Co	Activity (kg-polym./g-Co•h)	Mn ($x10^4$)	Microstructure of the Polymer (%)		
						cis-1,4	trans-1,4	3,4-
1	($CoCl_2$)	-	7,200	0.04	-	63.2	6.1	30.7
2	($CoCl_2$•2Py)	-	220	3.0	2.1	66.0	0	34.0
3	SiO_2	$2.16x10^{-3}$	0	0	-	-	-	-
4	"	"	50	37	8.0	64.8	5.6	29.6
5	"	"	80	64	-	60.9	3.6	35.5
6	"	"	150	66	-	64.8	0.2	35.0
7	"	"	260	109	-	-	-	-
8	"	"	750	156	-	70.8	0.2	29.2
9	"	"	2,900	132	6.1	-	-	-
10	"	$1.86x10^{-2}$	350	52	1.7	70.0	0	30.0
11	"	$3.72x10^{-4}$	500	220	5.3	65.9	2.3	31.8
12	"	"	230	-	-		oligomer[b)]	
13	γ-Al_2O_3	$7.90x10^{-4}$	520	76	-	66.1	0.9	33.0
14	MgO	$1.52x10^{-3}$	150	29	-	59.8	6.4	33.8
15	$MgCl_2$	$3.48x10^{-3}$	460	48	-	65.8	0	34.2

a) Polymerization was conducted at 65 °C for 30 min. by using 10 ml of n-heptane and 0.25 mol of isoprene.

b) TEA was used in place of DEAC.

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