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Supported Catalysts for the Polymerization of 1,3-Butadiene

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Summary

Highly dispersed supported catalysts were prepared by supporting various complexes of $CoCl_2$, $CoBr_2$ and $NiCl_2$ on SiO_2, MgO, Al_2O_3 and $MgCl_2$ in n-heptane, followed by evacuating at room temperature. The catalysts combined with $AlEt_2Cl$ or $Al_2Et_3Cl_3$ showed very high activities for cis-1,4-polymerization of 1,3-butadiene.

Introduction

Many catalysts have been reported for the preparation of polybutadiene high in 1,4-content, eg, the alfin catalysts (MORTON 1980), alkyllithium compounds (KUNTZ et al. 1960) and coordinate catalysts. The catalysts which promote cis addition fall into the following three classes: those containing iodine in some form combined with a trialkylaluminum, those containing cobalt in some form with an alkylaluminum halide, and those containing nickel in some form combined with a trialkylaluminum and a Lewis acid.

Among the iodine systems, the combinations of (a) a trialkylaluminum and TiI_4 (ZELINSKI et al. 1957), and (b) a trialkylaluminum, $TiCl_4$ and I_2 (FIRESTONE TIRE & RUBBER Co. 1961) are most effective catalysts. In the cobalt family of catalysts, on the other hand, the cobaltous halides (COOPER 1963), oxides, hydroxide, stearate, naphthenate (COOPER 1963), octanoate, sulfate and complexes with pyridine (GIPPIN 1962) and other amines are useful. The preferred salts are those such as cobaltous octanoate, which are soluble in the solvent used. On the other hand, among the nickel systems, the combination of nickel naphtenate, $AlEt_3$ and $BF_3 \cdot OEt_2$ is most effective (MATSUMOTO et al. 1968).

However, because of considerably low activities of these catalytic systems , the polymer formed contains an appreciable amount of catalyst residues. Therefore, the reduction of catalyst residues in the polymer to a reasonably low level is necessary to ensure stability toward oxidative degradation and uniformity in vulcani-

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zation characteristics.

We have recently succeeded in preparing a highly active SiO_2-supported $CoCl_2$ catalyst for isoprene polymerization (SOGA et al. 1981). In the present study was prepared similar catalysts by supporting various complexes of $CoCl_2$, $CoBr_2$ and $NiCl_2$ on SiO_2, MgO, Al_2O_3 and $MgCl_2$, and the polymerization of 1,3-butadiene was carried out by using them as catalysts.

Experimental

Materials Commercial extra pure grade n-heptane and research grade 1,3-butadiene (from Japan Synthetic Rubber Co.) were purified with the usual procedures. $CoCl_2$, $CoBr_2$ and $NiCl_2$ were obtained from Yoneyama Chemical Reagent Ltd., and were dried at 150 °C for 3 h immediately before use. Research grade SiO_2 (300 m^2/g), Al_2O_3 (143 m^2/g), MgO (26.4 m^2/g) and $MgCl_2$ (43.3 m^2/g) were dried at 300 °C for 3 h. $AlEt_3$, $AlEt_2Cl$ and $Al_2Et_3Cl_3$ were commercially obtained and 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.

Preparation of the supported catalysts. The complex of $CoCl_2 \cdot 2C_5H_5N$, for example, was prepared from the reaction of $CoCl_2$ with pyridine at room temperature [$CoCl_2 \cdot 2C_5H_5N$ (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 each complex and carrier (More details see Tables I and II) 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 each supported catalyst, alkylaluminum compound, and n-heptane under nitrogen. The reactor was cooled by liquid nitrogen, degassed i. vac. and then 0.25 mol of 1,3-butadiene 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 was dried i. vac. at room temperature.

Analytical procedures. The amounts of Co and Ni contained in the catalysts were determined by atomic absorption spectrophotometry (Shimadzu AA-610S). The microstructure of polybutadiene was determined by the method of Morero with IR using the KBr pellet tequnique, from 740, 910 and 970 cm^{-1} bands (MORERO et al. 1959).

The number average molecular weight of polybutadiene was measured at 150 °C by gel permiation chromatography (Showa Denko Shodex LC-HT3) using o-dichlorobenzene as solvent.

Results and Discussion

In the previous paper, we prepared the SiO_2-, Al_2O_3-, MgO- and $MgCl_2$-supported $CoCl_2$ catalysts from the complex of $CoCl_2 \cdot 2C_5H_5N$, and conducted isoprene polymerization using them as catalysts combined with $AlEt_2Cl$. Among these catalysts the SiO_2-supported $CoCl_2$ catalyst showed an extremely high activity for the polymerization (SOGA et al. 1981).

Therefore, similar catalysts were prepared by supporting several complexes of $CoCl_2$ and $CoBr_2$ on SiO_2. Polymerizations of 1,3-butadiene were conducted at 65 °C for 15 min using them as catalysts combined with $AlEt_2Cl$. The polymerization was also conducted under similar conditions with the use of carrier-free $CoCl_2$ or $CoCl_2 \cdot 2C_5H_5N$ for reference. The results obtained are summarized in Table I together with some analytical data.

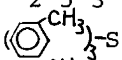
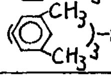
These SiO_2-supported $CoCl_2$ catalysts showed much higher activities as compared with the carrier-free catalysts (Runs no. 1 and 2). As reported earlier, the activity of the SiO_2-supported $CoCl_2$ catalysts for isoprene polymerization significantly decreased with an increase in the molar ratio of $CoCl_2$ to SiO_2. This phenomenon was attributed to the lack of efficient dispersion of $CoCl_2$ on the surface of SiO_2. In the polymerization of 1,3-butadiene in this study, a similar phenomenon was observed. Thus, the catalyst used in Run no. 6 showed a lower activity in comparison with the one used in Run no. 7. The use of $Al_2Et_3Cl_3$ in place of $AlEt_2Cl$ also gave a very high activity (Run no. 5), while $AlEt_3$ didn't (Run no. 4).

Then, one of the supported catalysts (used in Runs no. 3-5) was treated with an $AlEt_2Cl$ solution in n-heptane (0.3 mmol $AlEt_2Cl$ in 10 ml n-heptane) at 65 °C for 15 min, followed by washing with n-heptane and the solid part was subjected to the elemental analysis. From the result obtained it was confirmed that most of pyridine was removed from the complex of $CoCl_2 \cdot 2C_5H_5N$ by the reaction with $AlEt_2Cl$ as found in the $TiCl_3 \cdot 3C_5H_5N$ on $MgCl_2$-$AlEt_2Cl$ system (SOGA et al. 1979).

However, the microstructure of polybutadiene varied to some extent with each run, the precise reason of which is not clear at present.

Similar catalysts were then prepared by supporting $NiCl_2 \cdot 2C_5H_5N$ on SiO_2, Al_2O_3, MgO and $MgCl_2$ and the polymerization of 1,3-butadiene was conducted using them as catalysts combined with $AlEt_2Cl$. The results obtained are summarized in Table II. The activity, which was generally much poorer than that of the CoX_2

Table I. Results of 1,3-butadiene polymerization over the CoX_2-$AlEt_2Cl$ catalysts[a)]

Run No.	Catalytic System	Co Supported [mg-Co/g-carrier]	Activity [kg/g-Co•h]	Microstructure of the polymer [%]		
				cis 1,4-	trans 1,4-	1,2-
1	$CoCl_2\cdot$ —— - ——	-	0.1	87.9	7.1	5.0
2	$CoCl_2\cdot 2C_5H_5N$- ——	-	38	92.9	3.9	3.2
3	$CoCl_2\cdot 2C_5H_5N$-SiO_2[b)]	2.32	470	98.0	1.7	0.3
4	$CoCl_2\cdot 2C_5H_5N$-SiO_2[c)]	2.32	1	-	-	-
5	$CoCl_2\cdot 2C_5H_5N$-SiO_2[d)]	2.32	460	93.9	3.7	2.4
6	$CoCl_2\cdot 2P(C_6H_5)_3$-SiO_2	6.28	190	92.7	2.1	5.2
7	$CoCl_2\cdot 2P(C_6H_5)_3$-SiO_2	0.56	800	95.7	3.4	0.9
8	$CoBr_2\cdot 2P(C_6H_5)_3$-SiO_2	1.01	650	94.3	2.2	3.5
9	$CoBr_2\cdot 2P(C_2H_5)_3$-SiO_2	1.21	400	95.7	1.4	2.9
10	$CoBr_2\cdot 2P$  -SiO_2	0.85	510	92.7	3.1	4.2
11	$CoBr_2\cdot 2P$  -SiO_2	0.83	540	94.7	2.1	3.2

[a)] Polymerization was conducted at 65 °C for 15 min by using ca. 20 mg of catalyst, 10 ml of n-heptane, ca. 0.3 mmol of $AlEt_2Cl$ and 0.25 mol of 1,3-butadiene.

[b)] Mn : 42,000, Tg : -115 °C, Tm : -14.5 °C

[c)] $AlEt_3$ was used in place of $AlEt_2Cl$.

[d)] $Al_2Et_3Cl_3$ was used in place of $AlEt_2Cl$.

Table II. Results of 1,3-butadiene polymerization over the $NiCl_2$-$AlEt_2Cl$ catalysts[a)]

Run No.	Catalytic System	Ni Supported [mg-Ni/g-carrier]	Activity [kg/g-Ni·h]	Microstructure of the polymer [%] cis 1,4-	trans 1,4-	1,2-
1	$NiCl_2$· —— - ——	-	0.4	94.0	4.6	1.4
2	$NiCl_2 \cdot 2C_5H_5N$- ——	-	3.5	92.3	5.3	2.4
3	$NiCl_2 \cdot 2C_5H_5N$-SiO_2	1.66	90	93.4	4.5	2.1
4	$NiCl_2 \cdot 2C_5H_5N$-Al_2O_3	0.66	44	89.9	7.1	3.0
5	$NiCl_2 \cdot 2C_5H_5N$-MgO	1.37	41	92.0	5.2	2.8
6	$NiCl_2 \cdot 2C_5H_5N$-$MgCl_2$	1.79	21	93.0	4.8	2.2
7	$NiCl_2 \cdot 2C_5H_5N$-SiO_2[b)]	1.66	trace	-	-	-
8	$NiCl_2 \cdot 2C_5H_5N$-SiO_2[c)]	1.66	trace	-	-	-
9	$NiCl_2 \cdot 2C_5H_5N$-SiO_2[d)]	1.66	190	84.2	11.9	3.9
10	$NiCl_2 \cdot n(C_2H_5OH)$-SiO_2	4.10	49	93.3	4.7	2.0

a) Polymerization was conducted at 65 °C for 15 min by using ca. 20 mg of each catalyst, 10 ml of n-heptane, ca. 0.3 mmol of $AlEt_2Cl$ and 0.25 mol of 1,3-butadiene.

b) $AlEt_3$ was used in place of $AlEt_2Cl$.

c) $Al(i\text{-}Bu)_3$ was used in place of $AlEt_2Cl$.

d) $Al_2Et_3Cl_3$ was used in place of $AlEt_2Cl$.

catalysts, increased in the following order: $MgCl_2 <$ $MgO < Al_2O_3 < SiO_2$. $MgCl_2$, which extremely accelerates the activity of α-olefins (SOGA et al. 1981), didn't show such an excellent property for the polymerization of 1,3-butadiene.

The SiO_2-supported $NiCl_2$ catalyst was treated with $AlEt_2Cl$ according to the same procedure as described before, and it was found that a small amount of pyridine was left in the catalyst. This seems to be attributed to the fact that $NiCl_2$ is a little stronger than $CoCl_2$ in acidity (DOWDEN, 1968). However, it is obscure whether such a poor activity of these catalysts might owe to the pyridine left in the catalysts or not.

From this point of view, another type of a SiO_2-supported $NiCl_2$ catalyst was prepared by adding SiO_2 into a $NiCl_2$ solution in ethanol, followed by evacuating at room temperature. This catalyst was found to be free from ethanol by the elemental analysis.

It may be considered that ethanol, which seems very weak in basicity, could be removed only by evacuating at room temperature. However, the catalyst gave rather lower activity as compared with the one prepared from $NiCl_2 \cdot 2C_5H_5N$ (c.f. Runs no. 3 and 10). We have already reported in the $TiCl_3 \cdot 3C_5H_5N$ on $MgCl_2$ catalytic system that catalyst evacuating results in the diffusion of $TiCl_3$ into the grain bulk as well as the agglomeration of $TiCl_3$ (SOGA et al. 1979). Such a phenomenon might also occur in the present system. Therefore, it is still obscure whether the Co-species are much more reactive than the Ni-species or not.

Anyhow, we succeeded in preparing extremely highly active SiO_2-supported CoX_2 catalysts for cis-1,4-polymerization of 1,3-butadiene.

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

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