Polymerization of 1,3-Butadiene over Metal Oxides-Supported Nickel Chloride Catalysts

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Summary
        Polymerization of 1,3-butadiene was
conducted by two series of catalysts: nickel
ion exchanged Y-zeolite and metal oxides-
supported nickel chloride. For these
polymerizations, a plausible active species
was proposed.

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). Nevertheless, the precise mechanism of the
polymerization is still open to discussion, which seems
to be attributed to the complexity of the catalytic
systems. We have recently reported that cobalt ion
exchanged Y-zeolite catalyst causes the polymerization
of 1,3-butadiene without cocatalyst (SOGA et al. 1980).
The catalyst is apparently simplest in composition among
the catalytic systems reported so far. However, the
catalytic activity was very small, and most of polymer
produced was insoluble in usual organic solvents. More
recently, we have found that nickel ion exchanged Y-
zeolite (Ni-Y) as well as nickel chloride supported
by metal oxides catalyze 1,3-butadiene polymerization
to give soluble cis-1,4-polybutadiene without any
additives.
        In this paper are described the results on the
polymerization and proposed a plausible active species
for the polymerization.

Experimental

        Materials Research grade $NiCl_2 \cdot 6H_2O$, MgO (from
Koso Chemical Co.), $NiCl_2$ (from Yoneyama Chemical
Industry Co.) and $MgCl_2$ (from Toho Titanium Co.) were
used without further purification. Research grade 1,3-
butadiene (from Japan Synthetic Rubber Co., 99.5 %
purity) and heptane (from Wako Pure Chemical Co.) were

purified according to the usual procedures. Nitrogen of 99.9995 % purity (from Nihon Sanso Co.) was further purified by passing through the molecular sieve 3A column, cooled at -196 °C. SiO_2 (270 m^2/g) and γ-Al_2O_3 (143 m^2/g) were commercially obtained from Fuji Devison Co. and Nishio Industry Co. respectively, and dried at 350 °C for 3 h immediately before use.

Preparation of the catalysts. A Ni-Y catalyst was prepared by the conventional ion exchange of Na form of Y-zeolite (Linde SK-40) with Ni(II) ion according to the similar procedures reported earlier (SOGA et al. 1979). The Ni-Y catalyst thus prepared was evacuated at 200 - 500 °C for 3 h immediately before use. The SiO_2- and γ-Al_2O_3- supported nickel chloride catalysts were prepared as follows : In an aqueous solution of $NiCl_2 \cdot 6H_2O$ at room temperature was immersed SiO_2 or γ-Al_2O_3. The solid product was separated by filtration, dried i. vac. at room temperature over night, and then evacuated at 200 - 500 °C for 3 h. A MgO supported catalyst was prepared according to the same method. SiO_2-supported nickel chloride catalyst was also prepared by grinding the mixture of $NiCl_2$ (evacuated at 150 °C for 3 h) and SiO_2 in a ball mill at room temperature for 24 h under nitrogen.

Polymerization procedures. In a 50 ml stainless steel reactor equipped with a magnetic stirrer were placed the measured amounts of each catalyst and heptane under nitrogen. The reactor was cooled by liquid nitrogen, degassed i. vac. and then 0.20 mol of purified 1,3-butadiene was introduced. The polymerization was terminated by adding a dilute hydrochloric acid solution in methanol. The polymer produced was extracted by hot o-dichlorobenzene followed by dring at room temperature.

Analytical procedures. The amounts of Ni and Cl contained in the catalysts were determined by atomic absorption spectrophotometry (Shimadzu AA-6105) and elemental analysis, respectively. The microstructure of the polymer was determined by the method of Morero with IR using the KBr pellet tequnique, from 740, 910 and 970 cm^{-1} bands (MORELO et al. 1959). The ESR spectrum was taken in a pyrex glass tube of 3 mm diameter at -196 °C on a JEOL JES-PE-IX ESR Spectrometer with $100 \cdot 10^3$ cycles per s field modulation, DPPH and Mn^{2+} doped on MgO were used to determine the g-value, respectively.
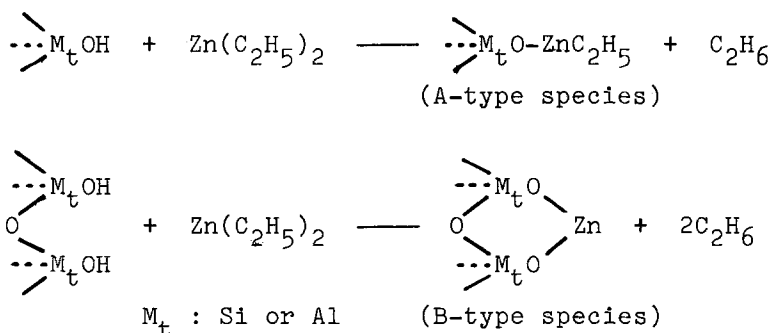
Results and Discussion
The amount of Ni supported on Y-zeolite measured by atomic absorption spectrophotometry was 1.56 matom/g-cat., which implies that Na ions were completely displaced by

Ni(II) ions. As shown in Table 1, stereospecific polymerization of 1,3-butadiene proceeded over the Ni-Y catalyst alone. The catalytic activity, which was greater by several times compared with that over the Co-Y catalyst, depended significantly upon the evacuation temperature of the catalyst. The decrease in the activity over the catalysts evacuated at lower temperatures may be attributed to the water left in the zeolite cage. The results obtained suggest that neither Ni-alkyl bonds nor halogen ligands are necessarily essential for stereospecific polymerization of 1,3-butadiene.

Then nickel chloride supported by metal oxides catalysts were prepared to improve the catalytic efficiency. The results of the polymerization over these catalysts are also shown in Table 1. These catalysts except for the one prepared by grinding (Run no. 9 in Table 1) showed much higher activities in comparison to the Ni-Y catalyst. The polymers produced were wholly soluble in usual hydrocarbon solvents. The low activities of the catalysts evacuated at lower temperatures may also be attributed to the water left in the catalysts.

In order to make clear the active species in these catalysts, both the ESR measurement and the elemental analysis were attempted for typical catalysts (Runs no. 3, 7, 9, and 12 in Table 1). None of these catalysts displayed any signal attributable to Ni(I) and Ni(0) in the ESR spectra (YASHIMA et al. 1975).
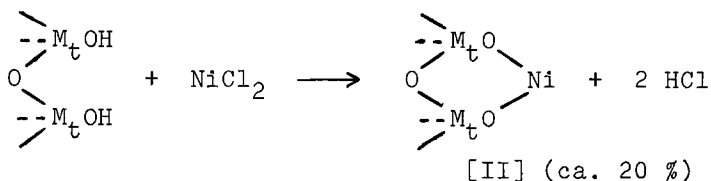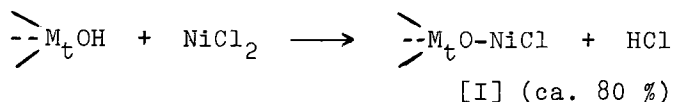
We have previously examined the reactions between diethylzinc and these metal oxides and found that diethylzinc reacts with the surface hydroxyl groups of SiO_2 or γ-Al_2O_3 to give the following two types of species evolving ethane,

$$\cdots M_t OH \ + \ Zn(C_2H_5)_2 \ \longrightarrow \ \cdots M_t O\text{-}ZnC_2H_5 \ + \ C_2H_6$$

(A-type species)

$$O\begin{matrix} \cdots M_t OH \\ \\ \cdots M_t OH \end{matrix} + \ Zn(C_2H_5)_2 \ \longrightarrow \ O\begin{matrix} \cdots M_t O \\ \\ \cdots M_t O \end{matrix}Zn \ + \ 2C_2H_6$$

M_t : Si or Al   (B-type species)

and that the fractions of A-type (f_A) and B-type (f_B) species are $f_A \fallingdotseq 80$ % and $f_B \fallingdotseq 20$ % for the same γ-Al_2O_3 and SiO_2 (SOGA et al. 1980).

Therefore, it may be considered that about 80 % of the supported nickel species should exist in the

form [I] in the catalysts prepared by immersing SiO_2
or $\gamma-Al_2O_3$ in an aqueous solution of $NiCl_2 \cdot 6H_2O$
followed by evacuation.

$$\text{--} M_t OH \; + \; NiCl_2 \; \longrightarrow \; \text{--} M_t O-NiCl \; + \; HCl$$

$$[I] \; (ca. \; 80 \; \%)$$

$$
\begin{array}{c}
\text{--}M_tOH \\
O \\
\text{--}M_tOH
\end{array}
\; + \; NiCl_2 \; \longrightarrow \;
\begin{array}{c}
\text{--}M_tO \\
O \quad\quad Ni \\
\text{--}M_tO
\end{array}
\; + \; 2 \; HCl
$$

$$[II] \; (ca. \; 20 \; \%)$$

The data shown in Table 1 (Runs no. 7 and 12) are
fairly close to these values.

Whereas in the catalysts prepared by grinding, most
of the nickel species may exist as a massive $NiCl_2$ not
in the forms [I] and [II] (c.f. elemental analysis of
Ni and Cl, Run no. 9 in Table 1). The present finding
that this type of catalysts showed very low activities
agrees with the well-known fact that $NiCl_2$ alone doesn't
initiate the polymerization of 1,3-butadiene. It is
considered that large Cl ligands densely surrounded with
the surface of $NiCl_2$ prevent 1,3-butadiene from
coordinating with the potentially active Ni(II) species.

To obtain a better insight into the active species,
$NiCl_2$ was supported on MgO and $MgCl_2$ which possess very
small amounts of surface hydroxyl groups (SOGA et al.
1980). These catalysts, in which most of the nickel
species should exist as a massive $NiCl_2$, showed very
small activities (Runs no. 14 and 15 in Table 1) as
expected.

NiO, and $\gamma-Al_2O_3$-supported NiO catalysts were also
used as catalyst. However, these catalysts didn't
initiate the polymerization of 1,3-butadiene (Runs no.
16 and 17 in Table 1).

The conclusion reached from the results shown
above is that the Ni(II) species in the form of [I]
formed by the reaction between nickel chloride and the
surface hydroxyl groups of the metal oxides, with which
1,3-butadiene can easily be coordinated, is the active
species for the stereospecific polymerization of 1,3-
butadiene in the present catalysts. As reported earlier,
(SOGA et al. 1979, SOGA et al. 1980), the active species
existing in small pores of the supporting materials is
actually of no virtue for the polymerization.

Table 1

Results of Butadiene Polymerization over Ni-Y and Metal Oxides Supported Catalysts.a)

Run No.	Catalyst	Evac. Temp. (°C)	Yield (g/g-Ni)	Microstructure b)			Content		
				cis 1,4- (%)	trans 1,4- (%)	1,2- (%)	Cl c) (matom/g-cat)	Ni d) (matom/g-cat)	Cl/Ni
1	Y-NiCl₂	200	11.8	91.5	6.3	2.2	—	—	—
2	"	300	30.7	92.2	6.5	1.3	—	—	—
3	"	400	43.5	93.9	4.9	1.2	0.05	1.56	0.03
4	"	500	36.3	92.2	5.7	2.1	—	—	—
5	SiO₂-NiCl₂ e)	200	9.7	—	—	—	—	—	—
6	"	300	47.3 f)	92.8	5.2	2.0	0.72	0.92	0.79
7	"	400	330 f)	94.0	4.5	1.5	—	—	—
8	"	500	316	94.3	4.9	0.8	—	—	—
9	g)	400	trace	—	—	—	1.70	0.82	2.07
10	Al₂O₃-NiCl₂ e)	200	trace	—	—	—	—	—	—
11	"	300	174 h)	93.8	4.9	1.3	—	—	—
12	"	400	396 h)	90.3	7.0	2.7	0.43	0.50	0.86
13	"	500	596	93.3	4.7	2.0	—	—	—
14	MgO-NiCl₂ e)	400	trace	—	—	—	—	—	—
15	MgCl₂-NiCl₂ g)	"	trace	—	—	—	—	—	—
16	NiO	150	—	—	—	—	—	—	—
17	Al₂O₃-NiO g)	—	—	—	—	—	—	—	—

a) Polymerization was conducted at 40 °C for 48 h by using 0.2 mol of 1,3-butadiene, 800 mg (Ni-Y), 250 mg (SiO₂-Ni) or 700 mg (Al₂O₃-Ni) of the catalyst and 5 ml of n-heptane in a 50 ml stainless steel reactor. b) Determined by IR spectra. c) Determined by elemental analysis. d) Determined by atomic absorption spectrophotometry. e) Prepared in H_2O by using $NiCl_2 \cdot 6H_2O$. f) $\overline{M}w$ (in o-dichlorobenzene at r.t.); 1.4×10^4. g) Prepared by grinding the mixtures. h) $\overline{M}w$ (in o-dichlorobenzene at r.t.); 4.0×10^4.

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