

에틸렌 중합을 위한 양이온이 교환된 규산염 촉매

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Cation Exchanged Silicate Catalyst for Ethylene Polymerization

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요약. Montmorillonite가 주성분인 산성백토로부터 여러 양이온을 교환시켜 촉매를 제조하여 ethylene의 중합활성에 대하여 연구하였다. Ni²⁺-Mont 촉매상에서는 ethylene이 선택적으로 n-butene으로 이량화 되었으며, 그 활성은 150°C의 진공온도에서 최고로 나타났다. 그리고 촉매활성의 변화는 촉매의 산도와 밀접한 관계가 있었다. Cr³⁺-Mont 촉매는 ethylene의 중합에 높은 활성을 나타내었으며, 그 활성은 450°C의 진공온도에서 최고로 나타났다. 그리고 Cr³⁺-Mont의 활성점은 Cr³⁺이온으로 생각되었다.

ABSTRACT. Several cation exchanged-layer silicate catalysts were prepared from acid clay mainly consisted of montmorillonite, and their catalytic activities for the ethylene polymerization were studied at room temperature. It was found that over Ni²⁺-Mont, dimerization of ethylene to n-butene proceeded selectively. Ni²⁺-Mont was activated by evacuation at elevated temperature, giving a maximum temperature, 150°C. The variations in catalytic activities were closely correlated to the acidity of the catalysts. Cr³⁺-Mont exhibited a high activity for the polymerization, showing a maximum at the evacuation temperature of 450°C. The active site in Cr³⁺-Mont was considered to be Cr³⁺ion.

INTRODUCTION

There are several heterogeneous catalyst systems of interest for low pressure polymerization of olefins to high polymers: chromium oxides supported mainly on silica or silica-alumina¹⁻³, molybdenum oxide-alumina catalysts⁴⁻⁶ and Ziegler-Natta systems⁷⁻⁹. It is also known that nickel oxide-silica exhibits a high activity for the dimerization of lower olefins, even at room temperature¹⁰⁻¹¹. It was also previously reported that the dimerization activity is related to acidic property of the catalyst and a low valent nickel ion¹³. In fact nickel oxide which is active for C₂H₄-C₂D₄ equilibration acquires an

activity for ethylene dimerization upon addition of nickel sulfate, which is known to be an acid¹⁴.

Polymerization of ethylene over several transition-metal exchanged Y zeolites at near room temperature was studied by T. Yashima *et al.*¹⁵ who found that over NiY, RhY, and RuY catalysts, dimerization of ethylene to n-butenes proceeded selectively. Over CrY catalyst, high polymerization of ethylene occurred, and the produced polyethylene showed a high melting point and high density. Montmorillonite is also used extensively for making hydrocracking catalysts¹⁶⁻¹⁷. Acid treatment results in increase in the acidity as well as the cracking activity.

Galway studied the reaction mechanism of alcohol dehydration over montmorillonite and proposed a reaction mechanism involving initial adsorption at Lewis acid site¹⁸. Hassan *et al.*¹⁹ showed that, upon activating with H₂SO₄, bentonite acquires a new Brønsted acid site which are active for the catalytic polymerization of styrene. However, the polymerization of ethylene over cation-exchanged montmorillonite was not reported so far. In this paper, new catalysts were prepared from natural montmorillonite and its activity for ethylene polymerization was examined.

EXPERIMENTAL

Catalysts and Material. Acid clay mainly consisted of montmorillonite was obtained from Youngil, Kyungpook. The fraction of less than 2 μ size clay whose cation exchange capacity was known to be 120 meq/100g were exchanged by the cations, Ni²⁺, Co²⁺, Fe²⁺, Cr³⁺, Fe³⁺, and Al³⁺ as described in the preceding publication²⁰⁻²¹. The cation-exchanged clay was washed successively with distilled water until sulfate ion was not detected and was molded into 2mm diameter pellet. Some were used as catalyst after drying at room temperature and others were used after heating at 500°C for 2 hrs in the air. Catalysts thus prepared were denoted by symbol like Mⁿ⁺-Mont followed by the exchanged cation, where Mⁿ⁺ means the exchanged cation.

Ethylene was obtained from a commercial source and was purified by low temperature distillation before use.

Procedure. The catalytic activity for ethylene polymerization was determined at 20°C by a conventional static system following pressure change from an initial pressure of 300 torr. Fresh catalyst sample of 0.1g was used for every run after evacuation to 10⁻⁴ torr at diffe-

rent temperature for 1hr. Reaction products were analyzed by gas chromatography with a VZ-7 column at room temperature. The specific surface area was determined by adsorption of oxygen at -183°C.

Acidity of noncolored catalyst was determined by *n*-butylamine titration in benzene using dicinnamalacetone and dimehtyl yellow as the indicator according to the Johnson method²².

X-ray diffractograms of catalyst were taken by Jeol Model JDX-88 X-ray diffractometer using copper target and nickel filter at 30KV and 800 cps.

RESULTS AND DISCUSSION

Composition of Catalyst. In the X-ray diffraction pattern of catalyst as shown in *Fig. 1*, montmorillonite is evidenced by *d* values of 15.3, 4.5, and 2.56Å and quartz is also evidenced by *d* values of 4.26, 3.34, and 2.46Å. These results say that the primary component of catalyst is montmorillonite mixed with quartz. The chemical composition of catalyst obtained by the wet analytical method is listed in *Table 1*.

In the differential thermal analysis of catalyst, it was found that two endothermic peaks appear at 150° and 715°C. This agreed closely with the DTA data of bentonite by other authors^{23,24}. The specific surface area of catalyst was 123m²/g by BET method at -183°C.

Polymerization of Ethylene. Six catalysts were tested for their effectiveness of the ethylene polymerization. It was found that on Ni²⁺-Mont and Cr³⁺-Mont, ethylene was continuously consumed as shown in *Fig. 2*. On Fe²⁺-Mont,

Table 1. Chemical composition of catalyst.

Chemical composition	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Ignition loss	The others
Percent	67.6	17.7	2.0	4.1	6.0	2.6

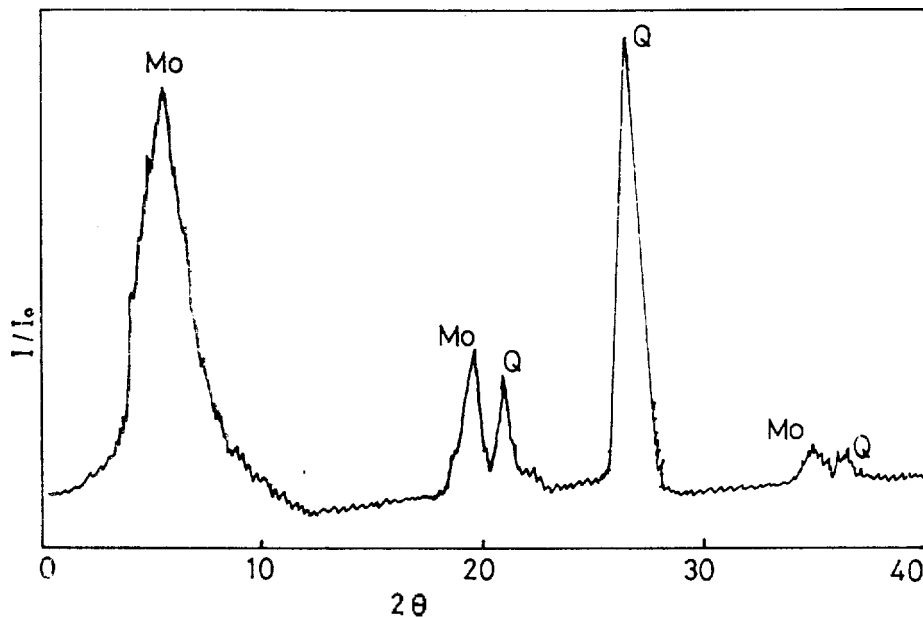


Fig. 1. X-ray diffraction pattern of catalyst. Mo : Montmorillonite. Q : Quartz.

Fe^{3+} -Mont, and Al^{3+} -Mont, on the other hand, only an adsorption of ethylene was observed in the initial stage and no gaseous reaction products could be detected under these conditions. However, Co^{2+} -Mont showed weak activity for the dimerization of ethylene. Therefore, in this paper emphasis has been placed to the only Ni^{2+} -Mont and Cr^{3+} -Mont catalysts. The catalytic activity was calculated as the amount of ethylene consumed in the initial 5 minutes.

Dimerization over Ni^{2+} -Mont. On Ni^{2+} -Mont, ethylene was selectively dimerized to *n*-butenes. In the composition of *n*-butenes analyzed by gas chromatography, 1-butene was found to predominate exclusively at the initial reaction time as compared with *cis*-butene and *trans*-butene. However, it was shown that the amount of 1-butene decreases with the elapse of reaction time, while the amount 2-butene increases with that of reaction time. Therefore, it seems that the initial product of ethylene dimerization is 1-butene and the produced 1-butene is also isomerized to 2-butene during the reaction time

as the case of NiO-SiO_2 catalyst^{12,13}.

In Fig. 3, the ethylene dimerization activities per surface area are plotted against the evacuation temperature at which the catalyst was pretreated for 1 hr. It can be seen that the catalytic activity appears above 50°C reaching a maximum at 150°C. As for nickel oxide-silica catalyst in the previous paper, it was reported that there were two maxima of dimerization activity at 100°C and 550~650°C and a minimum at 200~350°C.^{11,12} It is considered that these different activities of two catalysts according to the evacuation temperature are responsible for the different chemical composition and structure of catalysts to each other.

Fig. 3 shows that the catalytic activities decrease gradually after the evacuation temperature of above 150°C. In general, it is known that water from the surface of catalyst is desorbed at higher evacuation temperature²⁵. Consequently, to clarify the cause of deactivation after the evacuation temperature of 150°C, the catalyst was treated with water as described

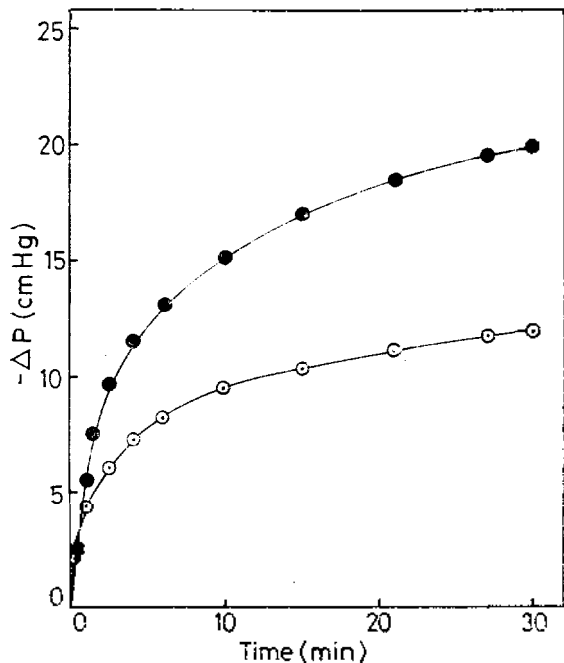


Fig. 2. Time course of ethylene dimerization and polymerization. Amount of catalyst: 0.2g; ●: Cr³⁺-Mont evacuated at 450°C. ○: Ni²⁺-Mont evacuated at 150°C

below. The catalyst deactivated at 300°C or more higher evacuation temperature was cooled to room temperature and was treated with water vapor. After that, the catalyst was reevacuated at 150°C for 1 hr which was optimum temperature for dimerization activity, and its activity was measured again at room temperature. In Fig. 4, black points indicate the catalytic activity of catalyst reactivated with water treatment. As shown in Fig. 4, with water treatment the catalytic activity of catalyst deactivated at higher evacuation temperature was nearly recovered. However, the lower was the recovery of catalytic activity, the higher was the pretreatment temperature. This result is attributed to the fact that the active site of catalyst was degenerated due to the higher evacuation temperature.

Namely, this is due to the change of oxida-

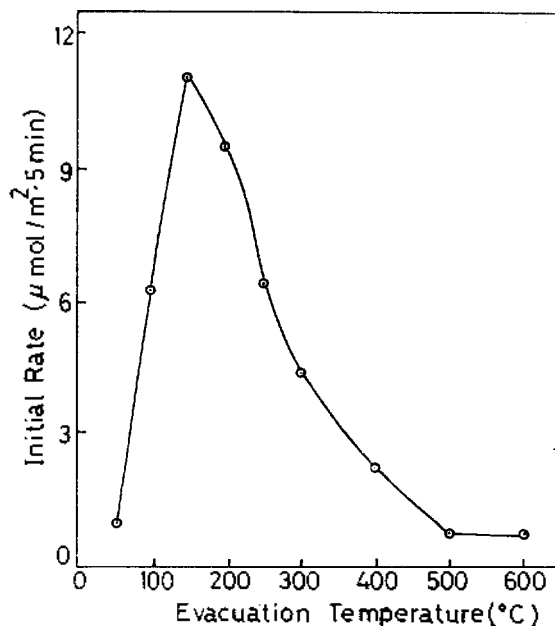


Fig. 3. Dimerization activities of the Ni²⁺-Mont at various evacuation temperatures.

tion state in nickel ion which is cooperated with acid sites as mentioned in the following section. We could not attribute the low recovery of catalytic activity through water treatment to the structural change of catalyst because the structure of montmorillonite was not changed at the heating temperature of 500°C. Therefore, it is now concluded from these experiments that the deactivation of catalyst is resulted from the dehydration of catalyst. Reactivation of catalytic activity by water treatment explains that the active site is related to the Brønsted acid. However, when the catalyst deactivated at 300°C was reevacuated at 50°C for 1 hr after water treatment, its catalytic activity was lower than that at 300°C of evacuation temperature. This fact indicates that water adsorbed at the surface of catalyst poisons the Ni²⁺-Mont at lower evacuation temperature as 50°C.

The water adsorbed on the catalyst surface and Brønsted acid formation can be visualized

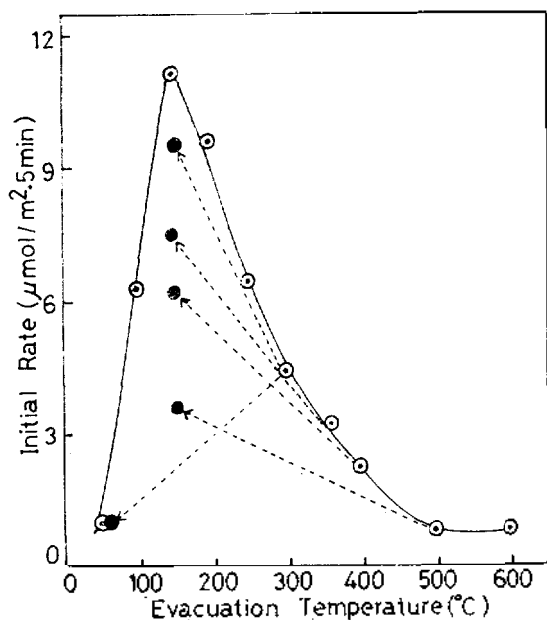
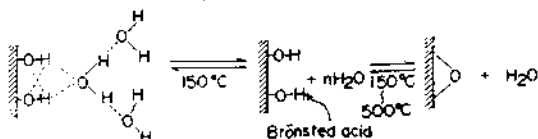


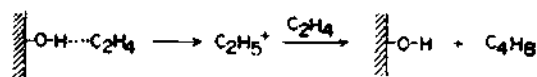
Fig. 4. Poison effect and reactivation of deactivated Ni²⁺-Mont by water treatment.

as the following model. When exposed to the



atmosphere, the surface hydroxyl groups on Ni²⁺-Mont adsorb water. As shown above, when heated under vacuum, the catalyst surface first loses physical water and is mostly covered with hydroxyl groups which are considered to be active sites for the dimerization. When evacuated at higher temperature, however, the surface loses additional water via condensation of adjacent hydroxyls. The gradual decrease of catalytic activity after the evacuation above 150°C in Fig. 3 can be explained in terms of disappearance of surface hydroxyls, Brønsted acid sites. Therefore, it may be now suggested from the above experiments that ethylene molecule have to combine with the surface proton in the course of dimerization reaction to

form carbonium ion, C₂H₅⁺ as following model.



The pressure change with time on Ni²⁺-Mont is exemplified in Fig. 5, where the catalyst is evacuated at 150°C for 1 hr. The reaction rate decreases with the rise of reaction temperature. It is suggested that at higher reaction temperature, the active site on Ni²⁺-Mont is degenerated by a contact with ethylene and produced *n*-butene.

Correlation Between Acidity and Catalytic Activity. Another series of experiments were carried out to study the correlation between acidity and dimerization activity of Ni²⁺-Mont. The acidity was measured by *n*-butylamine titration in benzene using dimethyl yellow and dicinnamalacetone indicator to know the acid strength of acid responsible for the dimerization. The acidity of catalyst thus determined was given as a function of evacuation temperature in Fig. 6, where dimerization activity was also given. As shown in Fig. 6, the dimerization activity and acidity increase with the evacuation temperature in the regions of 25~150°C. It seems that the increase in the acidity causes the increase in the activity. However, using dimethyl-yellow indicator, the experimental results in the regions of 150~600°C can't explain the relationship between acidity and activity. Using dicinnamalacetone indicator, on the other hand, it is clear that the catalytic activity decreases with the decrease acidity even in the regions of 150~600°C. Therefore, it was found that from these experimental results that the real acid site responsible for the dimerization are getting higher acid strength given by the indicator, dicinnamalacetone (pK_a=-3.0) than that given by dimethyl yellow (pK_a=3.30).

In the preceding paragraph, it was mentioned

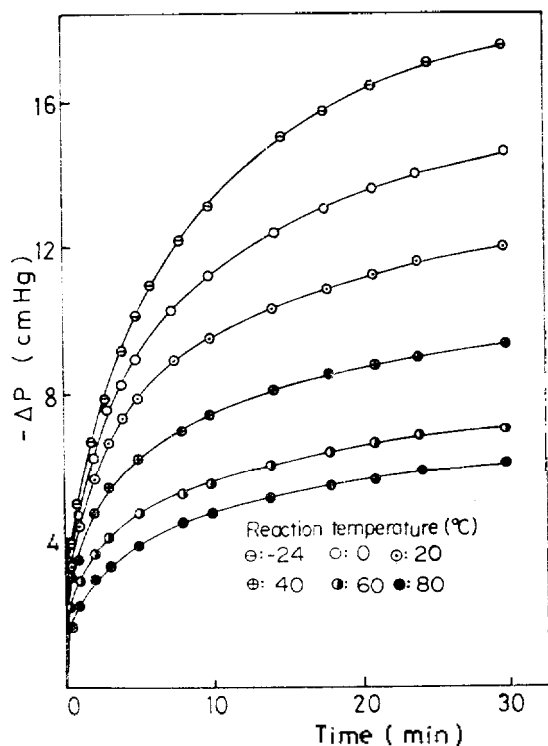


Fig. 5. Effect of reaction temperature on the dimerization activities of the Ni^{2+} -Mont. Amount of catalyst: 0.2g.

that the deactivation of catalyst at the evacuation temperature of above 150°C was resulted from the dehydration of catalyst, and that the dimerization activity ran parallel to the acidity. If the above mention is true, the acidity of catalyst deactivated at higher evacuation temperature might be recovered by water treatment. In fact, when the catalyst evacuated at 300°C was cooled to room temperature and was reevacuated at 150°C for 1 hr after treatment, the acidity measured was identical with that measured after direct evacuation at 150°C as shown in Fig. 6. However, the acidity of catalyst deactivated at 400°C was not completely recovered by water treatment as it was in the case of reactivation by water treatment. It seems

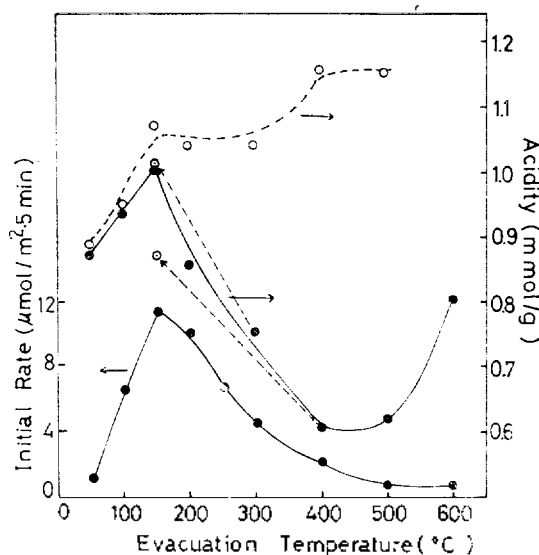


Fig. 6. Catalyst acidities and initial rate of the Ni^{2+} -Mont with evacuation temperature. Hammett indicators: \circ ; dimethyl yellow (IK_a : +3.3), \bullet ; dicinnamalacetone (pK_a : -3.0), \odot ; dicinnamalacetone after water treatment.

likely that the active sites on Ni^{2+} -Mont are degenerated due to a higher evacuation temperature. Accordingly, it is concluded that the decrease of activity at the evacuation temperature of above 150°C is mainly responsible for the decrease of Brönsted acidity.

If the proton on the catalyst, that is, Brönsted acid, is the real active site for the dimerization, the other catalysts exchanged with Fe^{2+} , Co^{2+} , Fe^{3+} , and Al^{3+} must be effective for the dimerization, where these catalysts exhibit Brönsted acidity. Nevertheless, as mentioned in the foregoing, these catalysts were not effective for the dimerization. Therefore, the dimerization of ethylene seems to be effected by cooperation of the exchanged nickel ion with the acid site.

It has been suggested that the active site for dimerization is formed by an interaction of a low valent nickel ion with an acid site¹³. The characteristic reaction on the low valent nickel

is the chemisorption of CO and the isotopic mixing in ethylene. The acid site is characterized by butene isomerization²⁵. It has been known that nickel oxide alone is activated for the isotopic mixing in ethylene by evacuation above 300°C, but it is not effective for the dimerization²⁶. This is possibly due to the fact that no acid site can be developed on pure nickel oxide. An acid nature of nickel oxide-silica has been shown^{12,13,25}. Since Ni²⁺-Mont in this work consists of nickel ion and acid, it is clearly considered that this catalyst exhibits the effectiveness for the dimerization.

Polymerization over Cr³⁺-Mont. Cr³⁺-Mont catalyst was tested for the ethylene polymerization, where Cr³⁺-Mont was calcined at 500°C in the air for 2 hr. On Cr³⁺-Mont evacuated at 450°C for 1 hr, ethylene was consumed at relatively high speed. After the reaction had occurred, the IR spectrum of the product on the catalyst exhibited three doublets at 2920 and 2850 cm⁻¹, 1475 and 1465 cm⁻¹, and 735 and 723 cm⁻¹, which are attributed to polyethylene. The solid state polyethylene was recovered from the catalysts used in activity experiments with *p*-xylene solvent at 70°C. The melting point and density of this polyethylene were measured to be 142°C and 0.968 g/cm³ respectively. This result suggests that the Cr³⁺-Mont promoted the high polymerization of ethylene.

In Fig. 7, ethylene polymerization activities per surface area are plotted against the evacuation temperature. Unlike the Ni²⁺-Mont, Cr³⁺-Mont did not exhibit the catalytic activity at low evacuation temperature of below 300°C, but exhibited at the above 300°C attaining a maximum at 450°C as shown in Fig. 7. From the fact that the catalytic activity does not appear at low evacuation temperature, it is considered that the active site for the ethylene

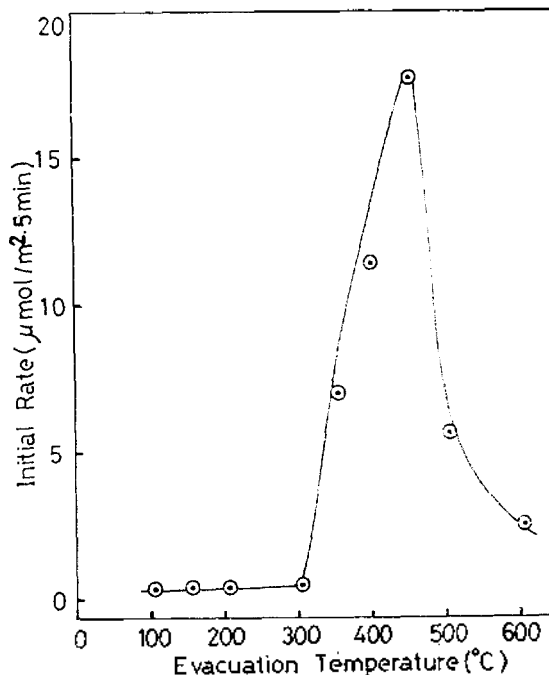
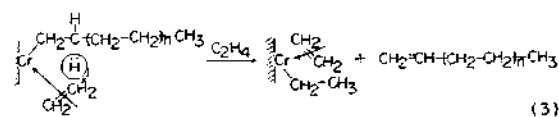
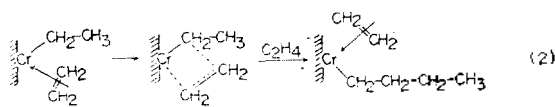
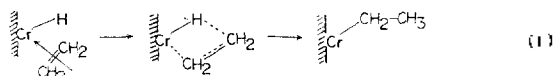


Fig. 7. Polymerization activities of the Cr³⁺-Mont at various evacuation temperatures.

polymerization is not related to the Brønsted acid, but is related to the Lewis acid, Cr³⁺ ion. It is probably considered that the decrease of activity after the evacuation temperature of above 45°C is due to the change of oxidation state in chromium ion.

We now support the polymerization mechanism suggested by Hogan² as follows. Initiation of polymerization begins with the gain of a hydride ion, polymer growth can be pictured in eq. 2, and termination of the growing chain may occur by hydride ion transfer as in eq. 3.



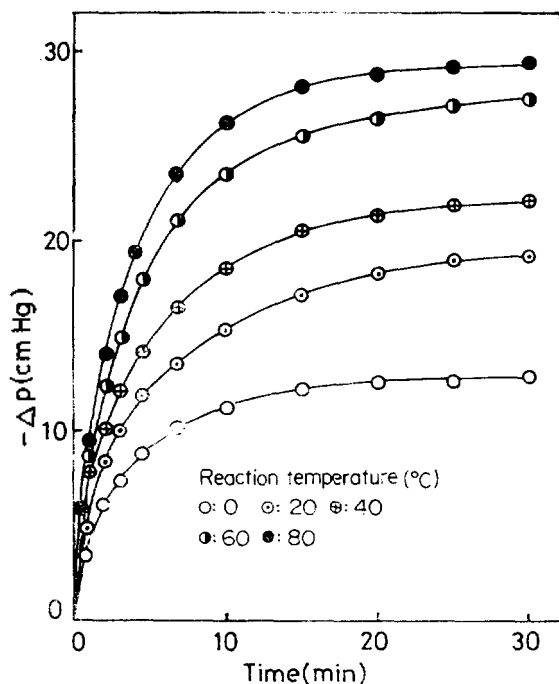


Fig. 8. Effect of reaction temperature on the polymerization activities of the Cr^{3+} -Mont. Amount of catalyst: 0.2g.

The pressure change with time on Cr^{3+} -Mont is exemplified in Fig. 8, where catalyst was evacuated at the optimum evacuation temperature of 450°C for 1 hr. The rate of pressure drop increased with reaction temperature. In each instance the rate of change in pressure gradually decreased to zero with time. It is because the active site is covered with the produced polyethylene.

CONCLUSION

It was found in the present work that Ni^{2+} -Mont is effective for the ethylene dimerization, while Cr^{3+} -Mont is effective for the polymerization. The catalytic activity of Ni^{2+} -Mont for the ethylene dimerization is closely correlated with the surface acidity of the catalyst, and the active site consists of nickel ion and Brønsted

acid. The active site of Cr^{3+} -Mont for the polymerization is related to the Cr^{3+} ion. Water is a poison for the Ni^{2+} -Mont evacuated at low temperature, while an appropriate amount of water is required for the Ni^{2+} -Mont to give the catalytic activity.

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