Polymerization of Ethylene over Transition-Metal Exchanged Y Zeolites

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Polymerization of ethylene over several transition-metal exchanged Y zeolites was studied at near room temperatures. It was 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 (143°C) and high density (0.964 g/cm³). The dimerization of ethylene over NiY and RhY was studied in detail and the nature of the active sites on these catalysts was discussed. It was found that the activity of the catalyst appeared after the calcination *in vacuo* or hydrogen at higher than 200°C, and was remarkably poisoned by the addition of carbon monoxide. It was concluded by ir and ESR studies that the active sites on NiY and RhY for the ethylene dimerization were zero-valent Ni and Rh which were dispersed highly in zeolite framework, respectively.

INTRODUCTION

It is well known that the multivalent cation exchanged and decationated zeolites have solid acid properties, and they have often been applied as useful catalysts to the reactions through a carbonium ion mechanism. A transition metal can also be supported on zeolite in the state of a cation or a finely dispersed metal. The zeolite catalysts loaded with finely dispersed noble metals have been used in hydrogenation (*1*), hydrocracking (*2*) and hydroisomerization (*3*). Recently, the transition-metal cation exchanged zeolite catalysts were applied in the oxidation of hydrocarbons at a relatively low temperature, and it was found that the active sites for this oxidation were transition-metal cations in the zeolite (*4–6*). It has been found that the amination of chlorobenzene proceeded in an ammonia carrier over the transition-metal Y zeolites, and the activity of these catalysts related to the ammine complex formation constant of metal cations (*7*). It was suggested that the tran-

sition-metal cation exchanged zeolite could be used in a heterogeneous reaction just like a transition-metal complex catalyst in a homogeneous reaction.

It has been known that a rhodium complex (*8,9*) and a nickel complex (*10*) easily accelerate the dimerization of ethylene at lower than 50°C. It is expected that the dimerization of ethylene may proceed over Rh or Ni exchanged zeolites. Over NiY zeolite, the polymerization of ethylene has been reported by Riekert (*11*); however, he observed that the rate of polymerization was very slow at lower than 70°C. We found that the dimerization, or the polymerization in general, of ethylene was effectively accelerated even at room temperature by Y zeolites containing transition-metal cations. In this paper, the polymerization of ethylene over transition-metal exchanged Y zeolites is reported, especially on the conditions of reaction and catalyst activation; and the characteristics of the active sites on the catalyst are discussed.

320

EXPERIMENTAL METHODS

Material. Ethylene, having a purity of over 99.8%, was obtained from a commercial source.

Catalyst. CdY, CoY, CrY, CuY, NiY, MnY and ZnY were prepared by a conventional cation exchange procedure using Linde SK-40 and 0.5 N aqueous solution of the corresponding transition-metal chlorides at 70°C. FeY and RuY were prepared by the ion exchange of SK-40 in the aqueous solutions of 0.15 N Fe(III) and Ru(III) chlorides for 10 min at room temperature. In the preparation of PdY, [Pd(NH$_3$)$_4$]Cl$_2$ prepared from Pd(II) chloride and excess NH$_4$OH was used as a cation exchange reagent. RhY was prepared from SK-40 and 0.03 N Rh(III) chloride aqueous solution which was regulated at pH 3.6 by the addition of sodium acetate at 70°C. The degree of ion exchange was measured by flame photometry. The exchanged zeolites were washed by pure water, dried at 100°C, pelleted without any binder, crushed and sized in 14–20 mesh. X-Ray diffraction measurements showed that all zeolites held their crystallinities through cation exchange procedure. However, the crystallinities of CrY and RhY were partially decomposed by the calcination at a higher temperature.

Apparatus and procedure. The experiments were carried out in a fixed bed type apparatus. The catalyst (0.8 g, except the case for Fig. 1) was placed in an electrically heated quartz reactor, calcined at various temperatures under evacuation, in hydrogen, in oxygen or in carbon monoxide, and set at a given reaction temperature with a water bath *in situ.* Ethylene was fed at 200 Torr to the reaction system and circulated through the catalyst bed. The rate of pressure drop was measured with a mercury manometer. The products for analysis were periodically collected and fed into a gas chromatograph through a sampling stopcock.

Analysis. The reaction mixture was analyzed with a gas chromatograph; using a 4 mm × 4 m column with the stationary phase of β,β'-oxydipropionitrile on active alumina and a hydrogen flame ionization detector.

Infrared measurement. All infrared measurements were made with the catalysts in the form of self-supporting wafers prepared by pressing 20 mg of fine powder in a 20 mm diameter die at 200 kg/cm^2. The wafers were electrically heated at various temperatures and various atmospheres in an infrared cell. After the calcination and the evacuation, the wafers were exposed to CO at 200 Torr for 30 min followed by evacuation at room temperature. The spectra of the wafers were recorded at room temperature.

ESR measurement. All the ESR measurements were carried out at room temperature and liquid nitrogen temperature (− 196°C) with an X-band spectrometer.

Poisoning treatment by CO, water, ammonia and pyridine. After the activation at 300°C for 1 hr under evacuation, CO and water were separately adsorbed on the catalyst in certain amounts from the
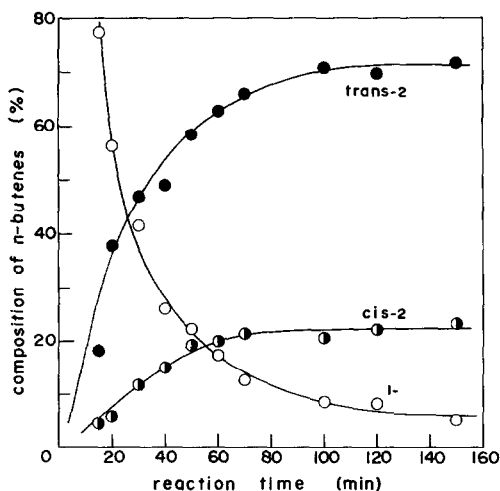

FIG. 1. Composition change of produced n-butenes with reaction time. Reaction conditions: catalyst, RhY (0.30 g) activated by evacuation at 300°C for 1 hr; temperature = 0°C; ethylene initial pressure = 200 Torr.

gas phase at room temperature. In the case of pyridine and ammonia, the adsorption on the catalyst was also carried out at 150°C to make a stronger interaction between these basic reagents and the acid sites of the catalyst.

RESULTS AND DISCUSSION

Polymerization of ethylene. The relative activity of the various transition-metal exchanged Y zeolites is shown in Table 1. All the catalysts were activated by evacuation at 400°C for 2 hr. In the initial stage of reaction, ethylene rapidly absorbed on the zeolite, so that the pressure in the reaction system suddenly dropped and after this period gradually decreased by polymerization. The relative activity of the catalyst was shown by the rate of pressure drop at the reaction time of 10 min.

It was found that on CrY, NiY, RhY and RuY, ethylene was continuously consumed, while on CuY, CoY, FeY, MnY, CdY, PdY and ZnY, only an adsorption of ethylene was observed in the initial stage and no gaseous reaction products could be detected under these conditions. Therefore, these results were omitted from Table 1. However, CoY showed weak activity for the dimerization of ethylene when it was activated by evacuation at 450°C for 2 hr, followed by calcination in hydrogen at 450°C for 5 hr.

TABLE 1
RELATIVE ACTIVITY OF TRANSITION-METAL EXCHANGED Y ZEOLITE CATALYSTS[a]

Catalyst[b]	Ion exchanged (%)	Rate of pressure drop at reaction time of 10 min (Torr/min)
CrY	82	2.00
NiY	70	0.85
RhY	65	2.30
RuY	70	0.07

[a] Reaction temperature = 20°C, ethylene initial pressure = 200 Torr.

[b] Catalysts were activated by the evacuation at 400°C for 2 hr.

TABLE 2
SOME PROPERTIES OF POLYETHYLENE

Yield of polyethylene[a] (g)	Density (g/cm³)	MW[b]	mp (°C)
1.734	0.964	2.07×10^6	143

[a] Reaction conditions: Catalyst, CrY (0.60 g) activated by the evacuation at 400°C for 2 hr; temperature = 50°C; time = 6 hr; ethylene initial pressure = 50 kg/cm²; solvent, benzene (25 ml).

[b] The value was measured by the viscosity method using decaline as solvent at 135°C (14).

On CrY, ethylene was consumed at a relatively high speed, but only a trace of gaseous products, mainly butenes and hexenes, were detected. The infrared spectrum of CrY was taken after 2 hr of contact with ethylene at 25°C, followed by an evacuation at room temperature for 1 hr. Four absorption bands were observed at 2920, 2850, 1470 and 720 cm⁻¹ which are attributed to polyethylene. This result suggests that the CrY catalyst promoted the high polymerization of ethylene. In the batch system using benzene as a solvent, a solid state polyethylene was formed. Table 2 shows the physical properties of this polyethylene. Such very high melting point, density and molecular weight show that this polyethylene has a very high crystallinity.

On NiY, RhY and RuY, ethylene was selectively dimerized to *n*-butenes. Figure 1 confirms that initially 1-butene was formed predominantly, but it isomerized to attain the equilibrium composition of *n*-butenes after some reaction time. A small amount of *n*-butane and ethane was formed by hydrogenation in the initial stage. Neither higher polymers nor cracking products were detected in this process.

Figure 2 shows that on RhY, the rate of pressure drop attained the maximum value at 20°C. In the initial stage of the reaction the rate at 40°C was more rapid than that at 0°C, but it slowed down and became
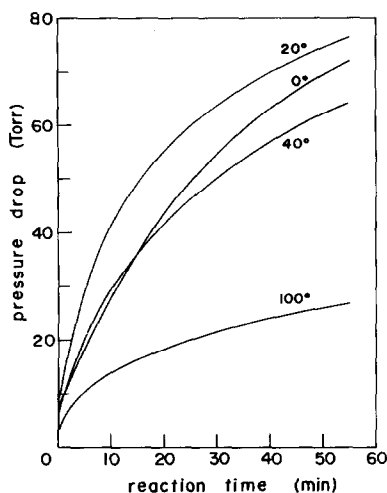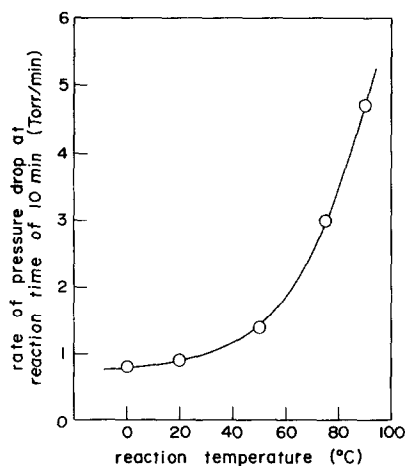
FIG. 2. Effect of reaction temperature on RhY. Reaction conditions: catalyst, RhY activated by evacuation at 300°C for 1 hr; ethylene initial pressure = 200 Torr.

lower than 0°C rate. It was suggested that at a higher temperature, the active sites on RhY catalyst degenerated by a contact with ethylene. On NiY, the rate of pressure drop increased with reaction temperature as shown in Fig. 3. It was found that the dimerization of ethylene proceeded selectively up to 50°C, and at a higher tem-

perature, ethylene oligomers and cracking products were simultaneously formed.

The effect of the evacuation temperature was shown in Fig. 4. The rate of pressure drop increased with evacuation temperature up to 400°C. On RhY, the reaction rate decreased at higher than 400°C, and on NiY, only a little change of catalytic activity was observed at higher than 500°C. It was observed by X-ray measurement that the crystal strucure of RhY was partially decomposed by the evacuation at higher than 500°C, while NiY held the crystal structure up to 700°C. The zeolitic structure of NiY was more stable than that of RhY, because Ni cation was more difficult to reduce to a metallic state than Rh cation, and pH value of an ion exchange solution of Rh chloride was lower than that of Ni chloride.

When propylene and 1-butene were in contact with RhY and NiY catalysts, it was observed that in the initial stage, the pressure drop was greater than in the case of ethylene, but after a few minutes, the rate of pressure drop of these olefins was much slower than that of ethylene. This order of olefin reactivity did not agree with that on a solid acid catalyst. On HY, which is a typical solid acid catalyst, ethylene was not converted up to 200°C, and at

FIG. 3. Effect of reaction temperature on NiY. Reaction conditions: catalyst, NiY activated by evacuation at 400°C for 2 hr; ethylene initial pressure = 200 Torr.
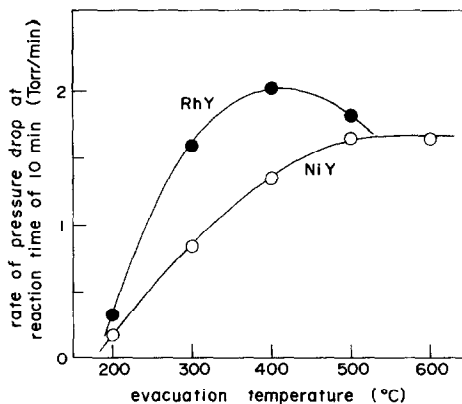

FIG. 4. Effect of evacuation temperature. Reaction conditions: temperature, 0°C on RhY and 50°C on NiY; ethylene initial pressure = 200 Torr.

a higher temperature, many kinds of lower hydrocarbons were formed by polymerization followed by cracking. These results suggest that the polymerization over RhY and NiY does not proceed through a carbonium ion mechanism.

Figures 5 and 6 show the effect of a calcination atmosphere on the dimerization activity of RhY and NiY, respectively. After calcination in oxygen, the reaction rate was very slow but gradually increased with reaction time. Such phenomena were also observed on the catalyst which was activated by evacuation at 200°C. These results suggest that on the incompletely activated catalysts, the active sites were formed by the contact with olefins under reaction conditions.

After calcination in hydrogen, the catalyst was more active than that activated by evacuation. However, when the catalyst was calcined under severe conditions such as a higher temperature and a longer treatment time in hydrogen, the reaction rate was decreased. It is postulated that metallic rhodium and nickel clusters were formed on the zeolites by over-reduction
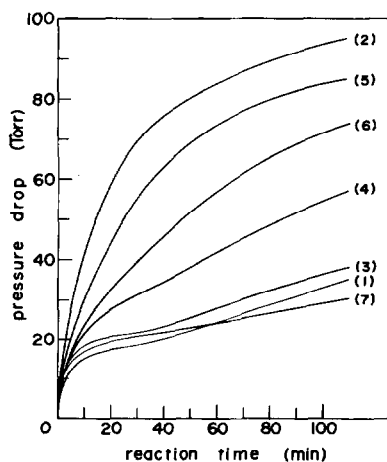

FIG. 6. Calcination atmosphere on NiY. (1) Evacuation at 600°C for 2 hr; calcination in H_2 for 3 hr at (2) 300°C, and (3) 500°C; calcination (4) in CO at 500°C for 3 hr, and (5) in O_2 at 500°C for 3 hr. Reaction conditions: temperature = 50°C; ethylene initial pressure = 200 Torr.

and so the activity of such catalysts decreased.

Moreover, it was observed that on NiY calcined in CO, the activity increased. These results suggest that the active sites of RhY and NiY consist of low valent Rh and Ni, respectively.

Active site. Figure 7 shows that the addition of basic reagents (ammonia and pyridine) decreased catalytic activity of RhY. But these poisoning effects were relatively small and similar to the case of water addition, though CO remarkably poisoned the active sites of RhY. The catalytic activity of NiY was also decreased by the addition of a basic reagent, and the poisoning effect of CO on NiY is shown in Fig. 8. It was observed that the catalytic activity was remarkably poisoned by CO addition, but after some period, the activity recovered, and the length of this period (recovery time) related to the amount of CO. This result was different from the case of a RhY catalyst. The activity of RhY and NiY poisoned completely by CO was recovered by evacuation at higher than 300 and 100°C, respectively. Thus,

FIG. 5. Calcination atmosphere on RhY. Evacuation for 1 hr at: (1) 200°C, and (2) 400°C; (3) calcination in O_2 at 300°C for 1 hr; calcination in H_2 at: (4) 200°C for 1 hr, (5) 300°C for 1 hr, (6) 300°C for 5 hr, and (7) 500°C for 2 hr. Reaction conditions: temperature = 0°C; ethylene initial pressure = 200 Torr.
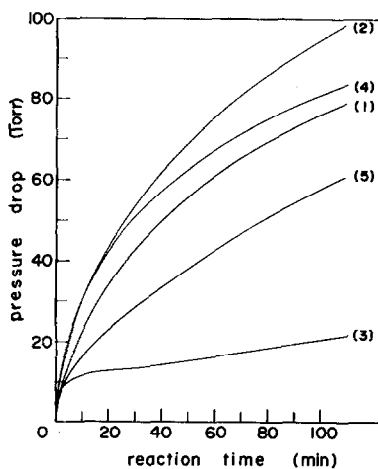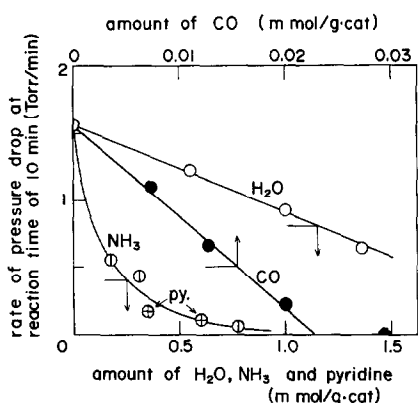
FIG. 7. Effect of additives on RhY. Reaction conditions: catalyst, RhY activated by evacuation at 300°C for 1 hr; temperature = 0°C; ethylene initial pressure = 200 Torr.

FIG. 9. Infrared spectra of CO adsorbed on RhY. (1) Background of RhY evacuated at 300°C for 1 hr; RhY activated by evacuation for 1 hr at (2) 200°C, and (3) 300°C; calcination at 300°C for 1 hr (4) in H_2, and (5) in O_2; CO desorption by evacuation for 30 min at (6) 200°C, and (7) 300°C.

the active sites did not interact so strongly with basic reagents but were firmly bonded to CO. These results suggest that the active sites of these catalysts were composed by low valent Rh and Ni, respectively.

Figures 9 and 10 show the infrared spectra of CO adsorbed on RhY and NiY, respectively. The absorption bands were observed at 2045 and 2110 cm⁻¹ and were attributed to the interaction between CO and RhY. These absorption bands agreed

with the bands on the interaction between CO and Rh metal on alumina (12). It was found that such absorption bands disappeared under evacuation at 300°C. When RhY was activated by evacuation up to 200°C or the calcination in oxygen at 300°C, the absorption bands due to the in-
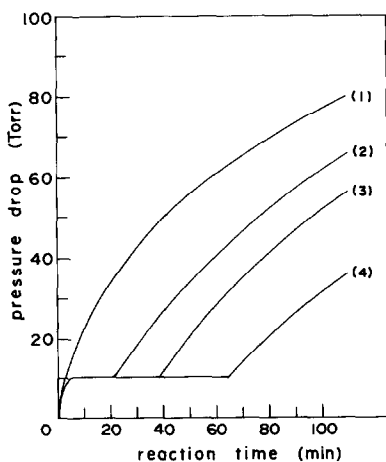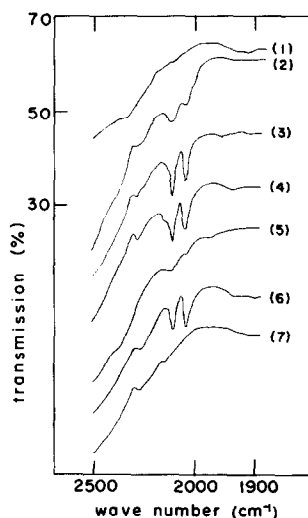

FIG. 8. Effect of CO addition on NiY. Amount of CO (μmol/g·cat): (1) 0, (2) 2.34, (3) 2.69, (4) 5.96. Reaction conditions: catalyst, NiY activated by evacuation at 600°C for 2 hr; temperature = 50°C; ethylene initial pressure = 200 Torr.
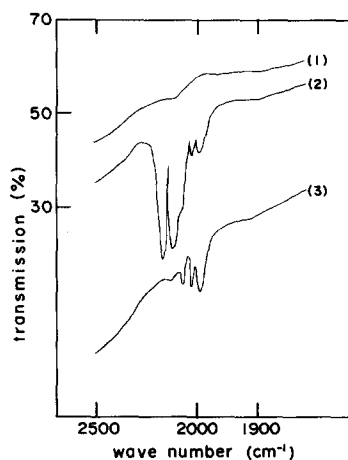

FIG. 10. Infrared spectra of CO adsorbed on NiY. (1) Background of NiY evacuated at 500°C for 2 hr; (2) exposed to CO at room temperature for 24 hr; (3) evacuated at room temperature for 30 sec.

teraction between CO and RhY were scarcely observed. These data suggest that the active sites on the RhY seemed to be the same sites where CO adsorbed to give the absorption bands of 2045 and 2110 cm^{-1} in the infrared spectrum. They further suggest that the active sites in the zeolite were metallic rhodium rather than cationic rhodium, whose catalytic activity was decreased by excessive reduction.

On NiY, no absorption bands attributed to the interaction between CO and NiY was observed when NiY was treated in CO for a short time (30 min). However, after exposing NiY to CO for a long time (24 hr) followed by the evacuation for a very short time (30 sec), the absorption bands due to the interaction of CO with NiY were observed at 1995, 2030 and 2070 cm^{-1}. These bands were lower in wave number than those at 2217 cm^{-1} attributed to the interaction between CO and Ni^{2+} and those at 2188 cm^{-1} attributed to the interaction between CO and Ni^+ (13). Therefore, these absorption bands could be attributed to the CO adsorbed on metallic nickel. However, they were easily made to disappear by evacuation at room temperature, though the activity of NiY could not be recovered under this condition.
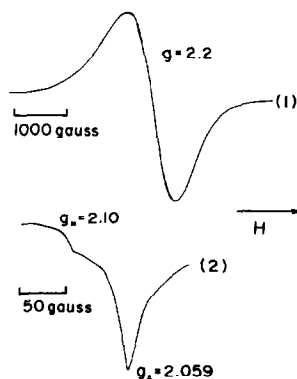
An ESR signal was observed on NiY at

room temperature after evacuation at higher than 400°C (Fig. 11). This signal (g value = 2.2, width = 920 G) could be attributed to Ni^0, and the signal strength increased by the calcination in hydrogen or carbon monoxide. When the ESR measurements were operated at −196°C, another signal was observed at g = 2.059 on NiY evacuated at 400°C. This signal could be attributed to Ni^+, because this g value was near g = 2.065 of which the signal was attributed to Ni^+ (at S_{II} sites in Y zeolite) (13). This signal could not be observed when NiY was calcined in hydrogen or CO at 400°C.

These results suggest that the active sites of NiY were not composed by Ni^+, but by zero-valent nickel dispersed highly in zeolite, similarly in the case of RhY.

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FIG. 11. ESR spectra of NiY evacuated at 500°C for 2 hr. Measurement at: (1) room temperature; (2) −196°C.