Polymerization of Ethylene Induced by Fractured Metallic Oxides. III. Factors Affecting the Polymerization

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Synopsis

Mechanochemical polymerization of ethylene was found to be induced by fracture of γ-alumina under quite low pressure and room temperature. The factors to control the polymerization yield, for example, calcination temperature of the alumina, spin concentration after ball milling, milling time, and changes of acidity before and after the fracture, were investigated in order to know the polymerization mechanism. It was found that the polymerization yield did correlate not with the spin concentration responsible to paramagnetic species produced by the fracture, but the calcination temperature of the γ-alumina and the milling time. The resultant polymeric material on the fractured alumina was extracted with solvents, and the fraction extracted with petroleum ether was characterized using GC and a GC mass spectrometer. The results indicated that odd-numbered linear hydrocarbons were produced, although the major products of this polymerization were even-numbered. It is concluded from the accumulated experimental results that a carbonium ion mechanism rather than radical mechanism is probable for the mechanochemical polymerization induced by fracture of γ-alumina.

INTRODUCTION

In previous papers,[1,2] the mechanochemical polymerizations of ethylene and propylene were reported for the cases of metallic oxides, B_2O_3, Al_2O_3, SiO_2, and TiO_2. Among these metallic oxides alumina was very interesting for two reasons: first, it is the highest yield of mechanochemical polymerization and, second, it is known to be a catalyst for polymerization of ethylene with a low yield under conditions of high pressure and temperature. Thus, from the viewpoint of mechanochemistry, it is very important to establish whether the polymerization of ethylene initiated by milled γ-alumina is caused by the ordinary catalytic action of γ-alumina. For this purpose the effect of pretreatment of γ-alumina, which controlled catalytic activities of γ-alumina, were carefully studied and surface acidity of γ-alumina was compared before and after milling of alumina in connection with the polymerization efficiency. The products of mechanochemical polymerization were extracted from the alumina surfaces with organic solvents and studied in order to explain polymerization mechanism. Although the polymeric products were found to distribute very widely from 10^2 and 10^6 in molecular weight, the low molecular weight fraction extracted with petroleum ether was carefully investigated by a GC mass spectrometer. It was concluded that the polymerization was primarily caused by the mechanical effect which causes a decrease in acidity of the alumina at each acid strength. The polymerization of ethylene under quite mild conditions

will be discussed in terms of active sites, which have been produced on the alumina by the fracture and which initiate the polymerization.

EXPERIMENTAL

Materials. γ-Alumina was obtained from Merck Co., Ltd. and prior to all experiments was degassed by calcination at either 200°C, 350°C, 500°C, 700°C, or 850°C at ca. 10^{-4} Torr. Ethylene used in this study was supplied from Nippon Sanso Co., Ltd. After calcination, γ-alumina was fractured in the presence of dry ethylene using specially designed ball-milling instrument.[1,3] The products were extracted by purified solvents, petroleum ether, n-heptane, and xylene for fractionation.

Characterization of Surface Natures. Specific surface areas of γ-alumina calcined at each temperature were determined from conventional a BET absorption isotherm of nitrogen at 77 K. Total acids, both Lewis and Brønsted, were determined by titration with n-butylamine method using Hammett indicators.[4] Surface acidity at various acid strengths was determined by Benesi's method using the following indicators: methyl red (pKa = +4.8), methyl yellow (+3.3), benzeneazodiphenylamine (+1.5), dicinnamalacetone (−3.0), and benzalacetophenone (−5.6).

Spectroscopic Analyses. ^{13}C-NMR spectra were recorded in 1,2,4-trichlorobenzene solution at 120°C using a JEOL FX-200 spectrometer. Infrared spectra were recorded as KBr disk using a JASCO A-102 Spectrometer. Low molecular weight hydrocarbon extracted from the polyethylene was analyzed by a Hitachi M-52 GC Mass Spectrometer (bombardment voltage = 20 eV). ESR spectrometer used was JEOL PE X-band type with 100-kHz modulation. Absolute spin concentrations were estimated by comparing intensity of an observed spectrum with a standard spectrum obtained from the benzene solution of α,α'-diphenyl-β-picryl hydrazyl (DPPH).

RESULTS

Yields. γ-Alumina, 3.0 g, calcined at either 200°C, 350°C, 500°C, 600°C, 700°C, or 900°C under vacuum around 10^{-4} Torr for 2 h, was fractured in the presence of ethylene gas, 12 mmol, for 3 days at room temperature using specially designed glass ampoules.[1,3] The detailed experimental method has been described in our previous papers.[1,2] The total yields of polymer products after milling of 72 h were plotted against the calcination temperatures in Figure 1. The effect of calcination to the mechanochemical polymerization may be divided into three stages. First the yield gradually increased with increasing calcination temperatures up to ca. 500°C, followed by an abrupt increase at ca. 600°C and then a slow increase above 600°C. In order to establish an effect of ball milling to the calcined γ-alumina ethylene gas were exposed with the unfractured γ-alumina and allowed to stand for 3 days. After that, consumption of the monomer gas was measured. The result is shown in the same figure. It was found that the unfractured alumina produced little polymeric materials, only 2% and 7%, after calcinations at 200°C and 700°C, respectively. It appears that yield of polymers produced by the nonfractured γ-alumina are much less than those by the
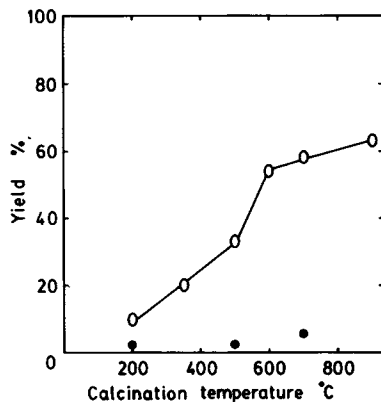
Fig. 1. The yield is plotted against the calcination temperature: (○) ethylene gas consumption yield, when γ-alumina was fractured after the calcination; (●) yield for the nonfractured but calcined alumina.

fractured one at each temperature. Thus, polymerization of ethylene was primarily caused by mechanical effect, although the calcination may have some effect on the polymerization yield.

Specific Surface Area. The specific surface areas of γ-alumina were measured by the BET method and the results are shown in Table I. The calcination of unfractured alumina resulted in no change of the surface area up to 700°C but decreases at 850°C. This trend accords well with the results of Shirazaki et al.[5] In contrast it appears that the specific surface areas were reduced by the milling apparently.

Spin Concentration. An ESR signal, singlet, $\Delta H_{msl} \simeq 25$ G with $g = 2.0073$ was observed after calcination under vacuum. The spin concentration was measured as 1.2×10^{15} spin/g alumina calcined at 500°C for 2 h. However, no significant drop of gas pressure was observed even when this alumina was in contact with the ethylene gas during several days. In contrast, fracture of the calcined alumina under vacuum using the ball-mill instrument, increased the spin concentration with milling time, as shown in Figure 2. In Figure 3 spin concentrations are plotted against the calcination temperature for the alumina fractured for 72 h, and shows a maximum at 500°C.

Product Analyses. γ-Alumina calcined at 700°C, was fractured in an atmosphere of ethylene for 3 days at room temperature, followed by frac-

TABLE I
Specific Surface Areas of γ-Alumina, the Fractured and Nonfractured

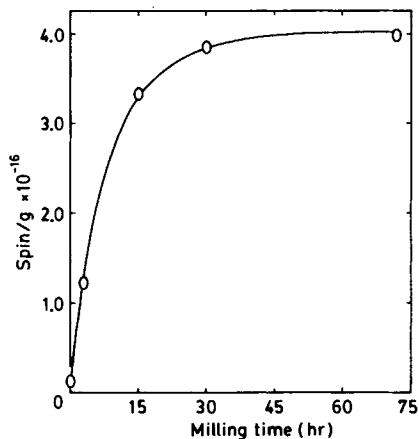| Temp (°C)	Fracture time (h)/surface area (m²·g⁻¹)		
	0	30	72
200	142	110	—
350	149	—	73
500	142	110	70
700	141	116	59
850	104	98	56

Fig. 2.   Spin concentration is plotted as function of the milling time (h) of alumina after calcination at 500°C.

tional extraction using petroleum ether, n-heptane, and xylene. The product yields obtained are shown in Table II.

The petroleum ether extracted product was found to be viscous liquid, and this component was subjected to gas chromatographic analysis, as shown in Figure 4. The peaks corresponding to different hydrocarbons were identified using standard hydrocarbon samples having an even number of carbon atoms. The result of each peak assignment is shown in Figure 4. However, peaks corresponding to odd-numbered linear hydrocarbons were also found, and these were assigned by GC with the aid of standard hydrocarbons having an odd number of carbon atoms. All assignments were confirmed unequivocally using GC mass spectrometer (bombardment voltage = 20 eV).

Infrared Spectra. IR spectra of the three components extracted with the petroleum ether, n-heptane, and xylene were recorded to detect any unsaturated double bonds in the polymeric materials. The three IR spectra
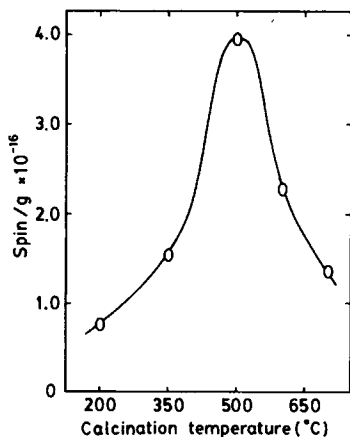
Fig. 3.   Spin concentration observed after 3 days fracture of the alumina is plotted against calcination temperature of the alumina.

TABLE II
Correlation of Polymer Yield with Extraction Solvent

Solvent	Yield (%)[a]
Petroleum ether	7.4
n-Heptane	2.5
Xylene	36.0
Total	45.9

[a] Total weight of polyethylene was estimated from the consumption of ethylene gas. The fraction extracted by the solvents was estimated for the total weight of polyethylene. 54.1% of the produced polyethylene was not extracted but stuck to the alumina surface.

are shown in Figure 5. The unsaturated double bonds were readily detected in the sample extracted from petroleum ether, i.e., trans double bond: $RCH=CHR$, 965 cm^{-1}, vinyliden double bond: $R_1R_2C = CH_2$, 890 cm^{-1}, and terminal vinylic bond, $RCH=CH_2$, 910 cm^{-1}.[6] The absorption bands at both 730 and 720 cm^{-1} are known to be due to crystalline and amorphous forms, respectively, in these polymers.[7] The multiplet absorptions at around 1350 cm^{-1} and 2850 cm^{-1} indicate that the polyethylene produced is highly branched, and this structure is in good agreement with the NMR data reported previously.[2]

Surface Acidity. A correlation between calcination temperature and acidic properties of the commercial γ-alumina was investigated using the Hammett indicators recommended by Tamele.[8] The results are shown in Figure 6. The acidity at the acid strength, $H_0 \geq -5.6$, was found to differ markedly after fracture. For example, the fracture of γ-alumina calcined at 500°C for 2 h caused a decrease in acidity from 0.45 $\mu mol \cdot m^{-2}$ to 0 $\mu mol \cdot m^{-2}$. Similar decrease was also observed for γ-alumina calcined at 700°C and 850°C. Based on these results, it is concluded that the fracture of the calcined alumina under vacuum induces a decreases in acidity at each acid strength. In particular, milling markedly decreased the acidity of the strong acid strength region, between -5.6 and 0 in the H_0 scale. It
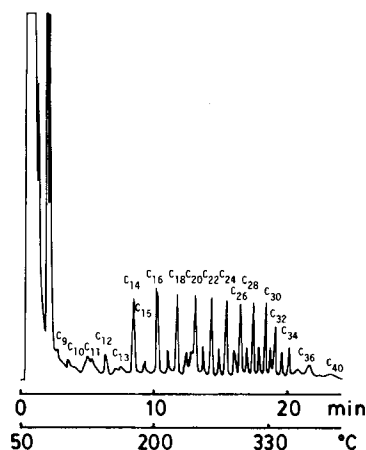

Fig. 4. Gas chromatogram from the product extracted with petroleum ether from alumina fractured in the presence of ethylene monomer.
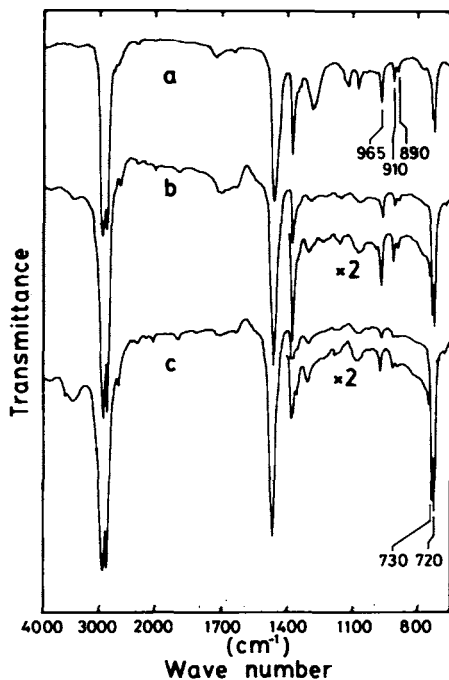
Fig. 5. IR spectra from the products extracted with petroleum ether (a), hot n-heptane (b), and xylene (c).

may be concluded that the active sites on the alumina surface which had been produced by the calcination were considerably affected by the mechanical action.

DISCUSSION

The clear difference in polymer yield between the fractured and non-fractured γ-alumina, shown in Figure 1, demonstrates that the polymerization of ethylene was initiated by the fracture and proceeded mechanochemically. Little ethylene gas was consumed during contact with the nonfractured γ-alumina, which had been pretreated and which exhib-
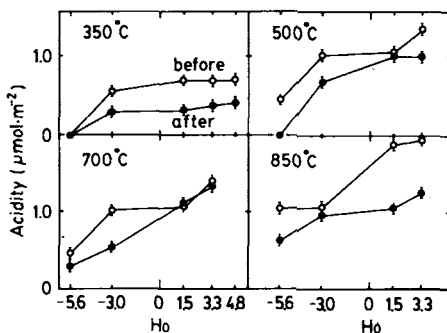

Fig. 6. Changes of acidities for alumina surface before and after fracture with ball milling under vacuum. The acidities are plotted as function of various acid strength together with the temperatures.

ited an ESR spectrum. This indicates that neither the active centers nor the spin centers which were formed by the pretreatment have activity to initiate polymerization of ethylene at such a low pressure and room temperature. This demonstrates that mechanochemical agitation is essential for polymerization of ethylene initiated by γ-alumina under the conditions. It is therefore concluded that the polymerization is caused not by the catalytic activity of unfractured γ-alumina but by the fracture of the γ-alumina.

Although the polymerization is mechanochemically induced, the calcination of the γ-alumina also has an apparent effect on the polymerization, as shown in Figure 1. The yield increased with increase in the calcination temperature up to ca. 900°C, and no maximum was reached. In contrast the spin density was found to be maximum at a calcination temperature of ca. 500°C. No correlation was found between polymer yield and the spin density produced by the calcination before milling. This suggests that the neutral radicals showing ESR signal not directly induce mechanochemical polymerization in the γ-alumina–ethylene system, as suggested previously.[1] Similarly, correlation between spin density and the mechanochemical polymerization was found for milled silicon. Fractured silicon gave rise a broad and extremely strong ESR signal, while no ESR was observed before milling. This ESR signal is due to neutral radicals, which are generated by the homolitic scission of Si—Si bonds in solid silicon with a diamondlike structure. This high concentration of broken bonds does not initiate polymerization of ethylene even after milling the silicon in the atmosphere of ethylene. Moreover, it is also worth mentioning that no pressure drop was detected when commercial high density polyethylene (Sholex 6050), 1.0 g, was fractured in an atmosphere of ethylene, 10 mmol, for 72 h at room temperature. The experiment indicates that the chain-scission radicals of polymer produced by ball milling never produce the polyethylene of detectable weight by consuming the ethylene monomer.

Since a radical polymerization mechanism for the mechanochemical polymerization induced by the fractured γ-alumina is not compatible with the above facts, an ionic polymerization mechanism seems more likely. It is well known that the acidic sites, both Brønsted and Lewis acid, are produced by the calcination of γ-alumina.[5] Monomers being in contact with acidic points on the alumina surface convert themselves into ionic species, and then an ionic polymerization may start from an acidic site on the alumina surface. Thus effect of pretreating γ-alumina on the mechanochemical polymerization may be readily explained by an ionic polymerization mechanism. In order to support this hypothesis, ammonia gas, which poisons the acidic sites of γ-alumina, was introduced into the milling ampoule, and the γ-alumina was fractured in the atmosphere of ethylene. This experiment resulted in decreasing markedly the yield of polyethylene and indicates that the majority of active sites produced by the fracture of γ-alumina was poisoned by the ammonia. Little polymerization proceeded mechanochemically after this poisoning. This result supports an ionic polymerization mechanism in this case, and, while the mechanochemical effect on alumina may be not simple, it appears to involve creations of specific active sites suitable for ethylene polymerization.

Formation of Odd-Numbered Linear Hydrocarbons

In order to establish the origin of the low boiling point fraction extracted with petroleum ether, calcined alumina, 10 g, and polyethylene flake, 1.0 g, were cofractured for 3 days at room temperature, followed by extraction with petroleum ether. After evaporation of petroleum ether, the yield of product was only 0.4% for the polyethylene flake, which is extremely low when compared with the alumina–ethylene system. These experiments also suggest that the lower boiling point products obtained in the alumina–ethylene system are created by a carbonium ion reaction and not by the main chain scission of polymer fraction. One of the most interesting features of this mechanochemical polymerization is the formation of odd numbered chain hydrocarbons, as shown in Figure 4. Ethylene monomer, which is the unit of polyethylene, consists of two carbon atoms, and therefore even-numbered carbon chains are the expected products for polyethylene (see Fig. 4). However, it is worth noting that a number of oligomers having odd-numbered linear hydrocarbons were also produced, as shown in Figure 4. This production of odd-numbered carbon chains, called "heteropolymerization," is explained in terms of a carbonium ion process, as suggested by Langlois for propylene polymerization.[9] Heteropolymerization also characterizes mechanochemical polymerization induced by the fracture of metallic oxides, like Al_2O_3.

The accumulated experimental results mentioned above favors ionic mechanism, not radical mechanism, of mechanochemical polymerization in the case of γ-alumina and ethylene. This mechanism is compatible with the report of Schwab[10] that the ordinary calcination of γ-alumina in air creates Lewis acid sites as the major sites of catalysis together with Brønsted site as the minor species. However, at the present state, it is difficult to determine which site acts as the major active species for the ethylene polymerization.

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