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Nature of Catalytically Active Sites over Solid Acids. I. Selective Poisoning of Lewis Acid Sites on Silica-Alumina with Pyridine and Its Application to Olefin Polymerization

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When pyridine chemisorbed on silica–alumina was evacuated at 350 °C, the 1460 cm^{-1} band due to Lewis-bound pyridine (LPY) remained while the 1540 cm^{-1} band due to Brønsted-bound pyridine (BPY) completely disappeared. This disappearance of the BPY band was revealed to accompany a loss of the Brønsted acid sites themselves besides their liberation. However, the lost Brønsted acid sites were regenerated by allowing the sample to stand overnight at 110 °C. Thus, strong Lewis acid sites of silica–alumina were able to be selectively poisoned by pyridine without any damage to the Brønsted acid sites. By poisoning catalysts *in situ* by controlled amounts in this way, the nature of the active site was investigated for polymerization of propylene or *cis*-2-butene at a low temperature of 30 °C. The initial activity declined sharply as the extent of pyridine poisoning of the Lewis acid sites increased. Therefore, it was concluded that strong Lewis acid sites (25—30% of the total Lewis acid content) were active in polymerization over silica–alumina.

The catalytic activities and selectivities in solid acid catalysts may be governed by the type of acid site, the acid strength, and the acid content. One of the characteristics of solid catalysts is that, in general, they have many kinds of chemisorption sites of different nature. Therefore, the determination of the role of these sites in reactions, especially the nature of catalytically active sites may be essential to the elucidation of reactions over solid acid catalysts. Infrared spectroscopy of chemisorbed pyridine has been recently proposed as a method for distinguishing between Brønsted and Lewis type surface acid sites.1) Of a variety of methods so far proposed for the determination of the acidic properties of solid surfaces, this method is probably the most reliable. Only in a few studies2,3) has this technique been applied to determine the nature of catalytically active sites. Even these determinations, however, require correlations between IR data on the acidic properties and reaction data, both obtained in separate experiments, and therefore, are rather indirect. If only a certain type of acid sites can be selectively poisoned with a base, the use of such a poisoned catalyst should permit a more direct determination of the nature of catalytically active sites. It has been found that upon evacuation at above 300 °C some Lewis-bound pyridine (LPY) over silica–alumina remains, whereas Brønsted-bound pyridine (BPY) disappears completely.4,5) In the present study, it was attempted first, on the basis of this experimental fact, to prepare silica–alumina whose Lewis acid sites were selectively poisoned by pyridine without any poisoning of the Brønsted acid sites, and second, by using *in situ* such catalysts, to elucidate the nature of active sites for polymeric olefin formation reactions.

It is well known that an olefin such as propylene or butene forms an adsorbed residue giving rise to IR bands characteristic of a saturated hydrocarbon over silica–alumina6) and deamminated ammonium Y (or HY) zeolite7) at room temperature. Deuterium-tracer studies of butene isomerization over silica–alumina revealed that the residue is the active site for the isomerization.8,9) Recently, the residue proved to consist of oligomers (about four monomer units, on the average).10–12) However, the nature of active sites in the polymeric olefin formation has been controversial because of the lack of conclusive evidence. Ozaki and Kimura8) have speculated that olefin was chemisorbed on Lewis acid sites as a monomer. Hirschler10) concluded that Brønsted acid sites were active over silica–alumina on the basis of the similarity in composition of polymeric species formed over silica–alumina and those formed over deamminated Y zeolite. On the contrary, Weeks *et al.*7) concluded that the active sites were dehydroxylated (surface Al^{3+} ions, *i.e.*, Lewis acid sites) over Y zeolite because no significant difference was found between products over deamminated and dehydroxylated zeolites. Peri6) regarded an α-site, a pair consisting of an Al^{3+} ion (Lewis acid) and an oxide ion, to be active. Holm, Bailey, and Clark13) and Sato, Aonuma, and Shiba14) have reported that the catalytic activity of silica–alumina for propylene polymerization at an elevated temperature varied in proportion to the Brønsted acid content. However, reasonable objections have been presented to their determinations of the Brønsted acid content.15) The present study employing silica–alumina, whose Lewis acid sites were selectively poisoned, revealed that the catalytic activity for the polymeric olefin formation declined sharply as the extent of pyridine poisoning of the Lewis acid sites increased. Therefore, it is concluded that strong Lewis acid sites are active in polymerization over silica–alumina.

Experimental

Materials. The silica–alumina (SA-1, 13% Al_2O_3, 540 m^2/g) was used in a previous study.16) Pyridine distilled from a GR reagent was dried over KOH under vacuum, and finally vacuum-distilled into a vessel containing molecular sieve 5A evacuated at 350 °C before use. Propylene and *cis*-2-butene (Matheson Co.) were dried by circulation for 1.5 h over anhydrous magnesium perchlorate prepared freshly by evacuation up to 240 °C, and then were thoroughly degassed by the freeze-pump-thaw technique.

Sample Preparation. Self-supporting 20 mm diameter wafers of SA-1 were formed by pressing the oxide powder at 6200 kg/cm^2 in a conventional KBr die. For each wafer, 20—80 mg of sample was used.

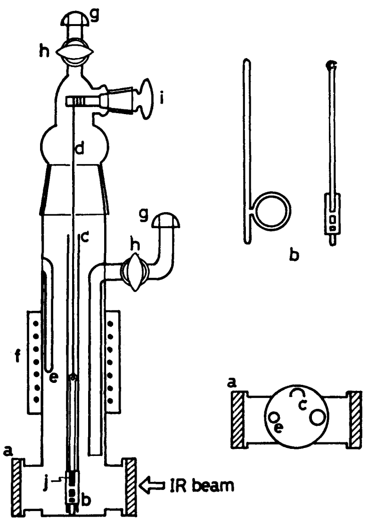


Fig. 1. Sketch of infrared cell. (a) CaF_2 window; (b) sample holder; (c) guideway; (d) Pt wire (0.2 mmϕ); (e) thermowell; (f) furnace; (g) ball joint; (h) stopcock; (i) reel; (j) sample wafer.

Infrared Cell. The cell used for IR-spectral measurements and as the reactor in reaction runs is shown in Fig. 1. The body was made of Pyrex or quartz, and equipped with CaF_2 windows (a) 40 mm in diameter and 5 mm thick. The middle of the cell was surrounded by a thermostatically controlled furnace (f).

A Pyrex or quartz sample holder (b), in which the wafer was mounted, was suspended with a Pt wire (d) from a reel (i), and could be moved through a guideway (c) up and down by winding up and off the Pt wire. This permitted reproducible positioning of the wafer in the analytical beam of the infrared spectrometer.

The cell could readily be connected through two ball joints (g) to a conventional vacuum manifold or to a closed circulation system (about 570 ml including the cell) for reaction runs.

Procedures. The wafer was inserted between two rings of the sample holder, pretreated in an oxygen stream as described earlier,[17] and finally activated in the cell by evacuation at 450 °C and about 10^{-4} mmHg usually for 15 h.

The amounts of Brønsted and Lewis acid sites were determined on the basis of IR absorption spectra of chemisorbed pyridine. The wafer was dosed with about 0.2 mmol/g of pyridine for 0.5 h at room temperature, and then evacuated for 1 h at 110 °C (referred to as the standard pyridine treatment) in order to eliminate hydrogen-bonded pyridine (HPY) which gives rise to the 1438 cm^{-1} band. The peak absorbances of the bands at 1540 and 1460 cm^{-1} (ascribable to BPY and LPY, respectively) were taken as the amount of acid sites of the corresponding type. The amount of acid sites thus obtained proved to agree excellently with that determined by means of the usual method in which a wafer was exposed to a large excess of pyridine vapor. By the use of such a small amount of pyridine, we were able to protect the wafer from surface contaminations with pyridine dissolved in the grease, as was evidenced, for example, by the absence of the slow reappearance of the HPY band after the 110 °C evacuation.

The polymeric olefin formation reaction was carried out in the closed circulation system provided with the cell at an initial olefin pressure of 10 mmHg and 30 °C. Its progress was followed by observing the IR spectrum of the polymeric species formed over the wafer after gaseous and physically-adsorbed olefin had been removed with a liquid nitrogen trap. During the course of this removal, the spectra of the polymeric species showed no significant change. The pressure decrease of the olefin was negligibly small for the period of the reaction.

Infrared spectra over the range of 4000 to 1300 cm^{-1} were recorded on a model DS-401G grating spectrometer (Japan Spectroscopic Co.) at room temperature. Attenuation of the reference beam with specially-designed screens was necessary to compensate for the energy loss due to light scattering by the wafer. Spectral slit widths were $\sim 3\ cm^{-1}$ at 1500 cm^{-1} and $\sim 10\ cm^{-1}$ at 3000 cm^{-1}.

Peak absorbances are all normalized so as to indicate the absorbance per unit optical thickness of the wafer. This normalized absorbance, AS/W (cm^2/g), corresponds to the quantity $\varepsilon M/W$, where A and ε are respectively the absorbance and the absorption coefficient of a band, M is the amount (mmol) of the responsible species, and S and W are the cross section (cm^2) and weight (g) of the wafer, respectively.

Results

Selective Poisoning of Lewis Acid Sites over Silica–Alumina. Figure 2 shows the IR spectra of pyridine chemisorbed on SA-1. The standard pyridine treatment of SA-1 produced spectrum (a), in which three bands appear at 1540, 1490, and 1460 cm^{-1} in accordance with spectra in the literature.[1,18] The bands at 1540, 1460, and 1490 cm^{-1} are ascribed to BPY, LPY, and to both species, respectively. Every band decreased in intensity when the wafer was evacuated at higher temperatures. On evacuation at 350 °C for 1 h (spectrum (b)), the LPY band remained while the BPY band completely disappeared. Seemingly this disappearance of the BPY band may indicate the desorption of BPY and hence mere liberation of the Brønsted acid sites. If this were true, the BPY band should reappear with the same intensity as the original when the standard pyridine treatment is repeated after the 350 °C evacuation.

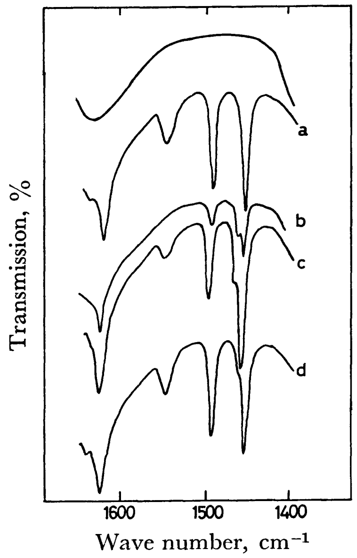


Fig. 2. IR-spectral changes of adsorbed pyridine induced by 350 °C-evacuation: (a) original; (b) after 350 °C evacuation for 1 h; (c) immediate standard pyridine treatment of (b); (d) standard pyridine treatment of (b) after 110 °C standing overnight.

TABLE 1. CHANGES OF ACIDIC PROPERTIES INDUCED BY EVACUATION AT 350 °C

Catalyst No.	1		2		3		4	
(Activation time, h)	(2)		(2)		(5)		(15)	
	Acid content$^{a)}$							
	B-	L-	B-	L-	B-	L-	B-	L-
Original	5.0	19.0	3.9	20.7	4.1	17.5	2.2	20.6
After 350 °C evacuation followed by standing								
110$^{b)}$	5.1	17.6	4.3	19.2	↓	↓	↓	↓
RT$^{c)}$	4.1	16.7	↓	↓				
none	↓	↓	2.9	21.8	1.9	19.1	1.7	20.7
110	4.6$^{d)}$	17.7$^{d)}$	4.2	20.4	4.4	16.5	2.5	20.7
RT	4.5$^{d)}$	17.4$^{d)}$	3.1	19.9	↓	↓	↓	↓

a) cm^2g^{-1}. b) Overnight at 110 °C. c) Overnight at room temperature. d) After standing for 2 days.

Table 1 summarizes the results of an examination of this problem. The acid content of a fresh wafer, which is labelled "original," was determined first for both acid types. After the wafer had been successively evacuated at 350 °C for 1 h and allowed to stand under the conditions given in Table 1, its acid contents were determined again. Acidity data obtained from several cycles of this procedure, in which the conditions for standing were altered in the sequence cited, are given in the lines indicating the corresponding treatment. The arrows indicate the particular treatments that were not followed. The immediate standard pyridine treatment after the 350 °C evacuation ("none" in Table 1 and spectrum (c)) revealed that the intensity of the BPY band decreased definitely while the intensity of the LPY band did not significantly change. This indicates that evacuation at 350 °C gives rise to the loss of some Brønsted acid sites themselves over SA-1, in addition to the liberation of these sites resulting from the desorption of BPY. On the other hand, when the wafer was allowed to stand overnight at 110 °C after the 350 °C evacuation, spectrum (d) was observed to be identical to spectrum (a). This fact demonstrates that the Brønsted acid sites lost are regenerated by allowing the wafer to stand overnight at 110 °C. These observations are reproducible as is seen in Table 1. In conclusion, the selective poisoning of Lewis acid sites over silica–alumina is attainable without any damage to the Brønsted acid sites when the following treatment is employed: the wafer is dosed with pyridine, evacuated at 350 °C, and allowed to stand overnight at 110 °C.

The mechanism of the loss and regeneration of Brønsted acid sites is not completely clear at present. In view of the same absorption coefficients for the BPY and LPY bands,[19–21] inspection of Table 1 indicates that the total number of acid sites (Brønsted plus Lewis) remains sensibly constant at all stages. The loss of Brønsted acid sites is compensated with the generation of Lewis acid sites, and the regeneration of the former with the loss of the latter. This observation may be associated with the well-known interconversion of Brønsted and Lewis acid sites on silica–alumina:[5,18] the conversion of Brønsted to Lewis acid sites occurs on dehydration and the reverse occurs on hydration. Some empirical evidence was reported to suggest that the presence of bases such as pyridine facilitates dehydration or dehydroxylation of the surface.[22,23] However, the regeneration, especially of an exact amount, of the lost Brønsted acid sites after standing overnight at 110 °C is surprising in view of the experimental procedure employed in which no water was added. The hydroxylation may result from the action of water from the bulk of the catalyst. Table 1 also suggests that this regeneration includes a slow chemical process.

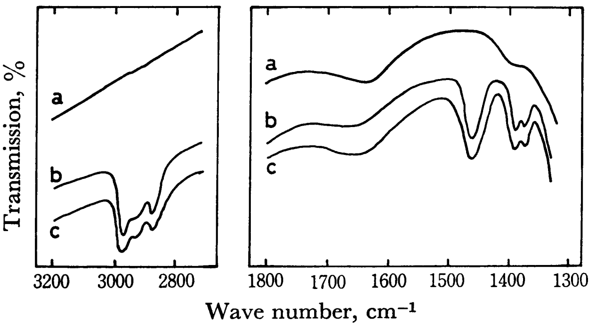


Fig. 3. IR spectra of polymeric *cis*-2-butene over SA-1. Background spectra (a); spectra of polymeric *cis*-2-butene 2 (b) and 20 h (c) after the reaction at 30 °C and 10 mmHg.

Polymeric Olefin Formation. Introduction of propylene or *cis*-2-butene onto SA-1 immediately produced the irreversibly adsorbed species giving rise to IR absorption bands at 2970—2960, 2930, and 2870 cm^{-1} in the C–H stretching region and at 1470, 1385, and 1370 cm^{-1} in the C–H deformation region. Figure 3 shows some spectra recorded, which are characteristic of saturated hydrocarbons. Each band grew steadily and reached a constant intensity 1—2 days after the introduction of the olefin (see Fig. 4). At any stage of the reaction, no olefinic species was detected, as evidenced by the absence of absorption in the unsaturated C–H stretching (3300—3000 cm^{-1}) and C=C stretching regions (1700—1600 cm^{-1}). The adsorbed species was not desorbed on evacuation at room temperature, and was desorbed by about 50, 80, and 95% on evacuation at 100, 200, and 450 °C, respectively, indicating that it is strongly held to the surface. Recently, the adsorbed species have been proven to be oligomers.[10–12]

The amount of polymeric propylene formed and its

TABLE 2. DISTRIBUTION OF DESORPTION PRODUCTS OF POLYMERIC PROPYLENE (100 °C)

Reaction time, min	Amount of polymeric propylene,$^{a)}$ μmol/g	H/C Ratio	Desorption products, mol %						
			C_3	C_4	C_5	C_6	C_7	C_8	C_9
1	70	1.9	26	44	18	7	1	1	2
5	142	—	19	46	21	11	1	1	1
30	223	1.9	6	52	22	14	2	1	3

a) On propylene basis.

H/C ratio were determined by means of the combustion method. The results are given in Table 2. The experiments were carried out in a separate closed circulation system (ordinarily, 1300 ml) with SA-1 powder (*ca.* 1 g) which had been pretreated and activated in the same manner as in the IR study. After exposure to olefin for the times described and removal of gaseous and physically-adsorbed hydrocarbons with a liquid nitrogen trap, dry oxygen at about 500 mmHg was circulated over the wafer at 450 °C overnight. The carbon dioxide and water produced were separated with a liquid nitrogen trap and a dry ice/ethanol trap, and the corresponding amounts were determined volumetrically. The amount of the polymeric species obtained by means of the present method, which is given on the olefin monomer basis, agreed well with that from the pressure decrease of the gaseous olefin. With either propylene or *cis*-2-butene, the peak intensity at 2970—2960 cm^{-1} was found to be proportional to the amount of the polymeric species. The intensity of this peak was therefore taken to be the amount of the polymeric species formed.

The distribution of desorption products of the polymeric propylene are also given in Table 2. After removal of gaseous and physically-adsorbed hydrocarbons with a liquid nitrogen trap, the sample was inserted into a furnace previously regulated thermostatically at 100 °C and maintained at the same temperature for 1 h. The desorbed products were collected into a trap maintained at −196 °C with or without evacuation, and analyzed with two FID gas chromatographs equipped with a VZ-7 column operating at room temperature and with a silicon DC-11 column temperature-programmed from room temperature to 150 °C at 6 °C/min, respectively. No hydrocarbons other than reactant propylene were detected in the gas phase. Neither C_1- nor C_2-hydrocarbons were detected in the desorption products. The C_3-hydrocarbons consisted only of propylene and the C_4-hydrocarbons contained mainly 1-butene and/or isobutylene. Although the VZ-7 column used could not separate 1-butene from isobutylene, this GLC peak may be due to isobutylene because of the absence of 2-butene. The C_4-, C_5-, C_7-, and C_8-hydrocarbons are probably cracking products of polymeric propylene. As the reaction proceeded, the amount of propylene (a C_3-hydrocarbon) decreased, whereas the amount of higher (C_4—C_9) hydrocarbons increased, suggesting that monomeric olefin changes successively into dimer, trimer, and higher oligomers over the surface.

Selective Poisoning Study of Polymeric Olefin Formation. Preliminary experiments revealed that the catalytic activity of SA-1 decreased in a drastic way when its Lewis acid sites were selectively poisoned with an amount of pyridine (*ca.* 0.2 mmol/g) similar to that in the acid content measurements, strongly suggesting that Lewis acid sites are active in the polymerization. Confirmation of this suggestion required that a series of more active, selectively poisoned wafers were prepared by using smaller amounts of pyridine. For this reason, it was necessary to determine the acid contents of a wafer after activity tests, assuming that the acid content was conserved for each acid type before and after the reaction.

Table 3. Conservation of acid contents before and after reaction

	Peak intensity, cm^2 g^{-1}		
	BPY (1540)	LPY (1460)	BPY+LPY (1490)
Before reaction:			
a. acid content	2.2	20.7	7.4
b. selectively poisoned	0	5.6	1.6
After reaction:			
c. removal of gaseous propylene with a liq. N_2 trap	0	—	1.7
d. acid content	2.3	18.3	8.0

As is shown in Table 3, the validity of the assumption was confirmed by an examination with one wafer poisoned selectively with about 0.2 mmol/g of pyridine. The acid contents after reaction (d), which were determined by a method described below, agree with those before reaction (a) to within the experimental error. Table 3 also shows that no pyridine held on the Lewis acid sites migrates onto Brønsted acid sites during the course of the reaction (b and c). This is evidenced by the absence of the BPY band after the reaction and the invariability of the intensity of the 1490 cm^{-1} band. After the reaction, the LPY band overlapped with the strong 1470 cm^{-1} band assigned to the CH_2 and asymmetrical CH_3 deformations of the polymeric olefin.

On the basis of these results, the following procedure was employed for reaction experiments. An activated wafer was dosed with a small amount of pyridine for 0.5 h at room temperature, evacuated for 1 h at 350 °C, and allowed to stand overnight at 110°C. The poisoned state of the wafer surface was ascertained on the basis of its IR spectra. The reaction was conducted as described above. After the polymeric olefin had been removed by evacuation for 1 h at 350 °C, the wafer was dosed with about 0.2 mmol/g of pyridine, allowed to stand overnight at 110 °C, and finally evacuated

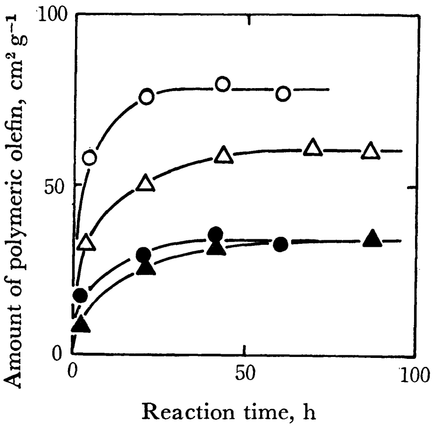


Fig. 4. Time-course of the formation of polymeric olefin: propylene over clean (△) and selectively poisoned (▲) SA-1; *cis*-2-butene over clean (○) and selectively poisoned (●) SA-1.

for 1 h at the same temperature, in order to determine its acid contents.

Figure 4 shows the time evolution of the formation of the polymeric olefin over a clean and a selectively poisoned wafer. On both wafers, the formation of the polymeric olefin took place rapidly in the early stage of the reaction, slowed down gradually, and finally ceased after 1—2 days. At any stage of the reaction, the amount of polymeric olefin formed was smaller on a selectively poisoned wafer than on a clean wafer. The amount of the polymeric olefin formed after 1 min was taken as the initial activity.

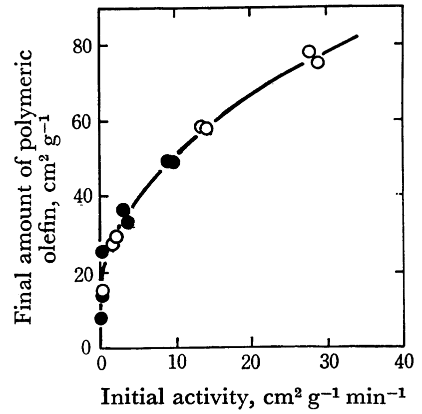


Fig. 5. Correlation between the initial activity and the final amount of formation of polymeric olefin: propylene (●) and *cis*-2-butene (○).

Figure 5 shows a correlation of the initial activity with the amount of polymeric olefin formed after 20 h (the final amount of formation). The final amount of formation of the polymeric olefin increased with an increase in the initial activity.

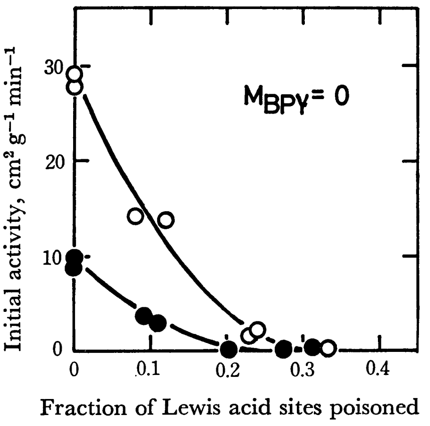


Fig. 6. Effect of pyridine poisoning on the initial activity for the formation of polymeric olefin: propylene (●) and *cis*-2-butene (○).

Figure 6 illustrates a relationship between the initial activity and the fraction of Lewis acid sites poisoned. The fraction of Lewis acid sites poisoned was calculated for each wafer from the amount of Lewis acid sites poisoned (the intensity of the LPY band) before the reaction and the Lewis acid content determined after the reaction. It should be noted here that for all the wafers used no Brønsted acid sites are poisoned, *i.e.*, $M_{\mathrm{BPY}}=0$.

Discussion

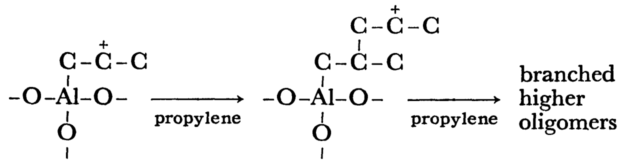
Nature of the Polymeric Species. The polymeric species have characteristics of saturated hydrocarbons, as characterized in their IR spectra by the absence of unsaturated =C–H and C=C stretching bands and by the presence of saturated C–H stretching and bending bands. Unlike an adsorbed paraffin, however, the species is strongly held to the surface. Such characteristics are also evidenced by the finding that the H/C ratio is close to 2 for the polymeric species (Table 2) and that no materials other than reactant olefins were detected in the gas phase. This, as well as the absence of a band around 1600 cm⁻¹ arising from a conjugated polyene structure, indicates that no dehydrogenation of the polymeric species occurs under the experimental conditions employed. It has been reported that dehydrogenation occurs at higher temperatures.[24–26)]

IR bands in the C–H deformation region provide, in general, valuable structural information about hydrocarbons. Hirschler[10)] characterized the extracted polymeric species as a mixture of highly-branched polymeric monoolefin on the basis of its IR spectrum. In the symmetrical CH_3 deformation region, the doublet at 1385 and 1370 cm^{-1} is an indication of the presence of a $(CH_3)_2CH$–, $(CH_3)_2CR$–, or $(CH_3)_3C$– group in the species.[27)] Therefore, the polymeric species probably is branched and consists of saturated oligomers with a cationic property. Recent Raman and IR spectra[28)] of butyl cations show that in the relevant frequency regions no significant difference is found between butyl cations and the corresponding neutral butyl groups. A cationic property of the polymeric species is also suggested by difference in the reactivity of various olefins (isobutylene$\gg$*cis*-2-butene$>$propylene $\gg$ethylene).

Nature of Active Sites. Figure 6 indicates that the initial activity of SA-1 declines sharply for polymeric olefin formation as the fraction of Lewis acid sites poisoned increases, in spite of the fact that the Brønsted acid sites remain unpoisoned for all the samples. Since the initial activity should depend directly upon the number of active sites, these results unequivocally demonstrate that some of the Lewis acid sites (25—30% of the total Lewis acid content) play a vital role in initiating the reaction over silica–alumina. The pyridine molecules held to Lewis acid sites of all samples are those which remain unremoved on the Lewis acid sites even by evacuation at a temperature as high as 350 °C. It can be stated, therefore, that such Lewis acid sites are strongly acidic. Consequently, the conclusion is drawn that strong Lewis acid sites are active in the formation of the polymeric olefin over silica–alumina. This conclusion is consistent with our recent results that added-back water sharply decreases the initial activity of SA-1 and to a slight extent the Lewis acid content, in spite of an increase in the Brønsted acid content.[21)] Although the catalysts of Friedel-Crafts type have been thought to require a co-catalyst such as water and alcohol,[29] recent studies of isobutylene polymerization in the liquid phase revealed that $AlBr_3$[30] and $AlCl_3$[31] both catalyzed the reaction even in the absence of a co-catalyst.

As expected from Fig. 5, a correlation similar to that in Fig. 6 was found between the final amount of formation of the polymeric olefin and the extent of pyridine poisoning of the Lewis acid sites. This correlation indicates that the final amount of formation decreases with a decrease in the number of the active sites. If polymeric olefin migrated onto sites other than the active sites, where it was formed, and liberated them, the final amount of formation of the polymeric olefin should ultimately become essentially the same for all the samples, independent of the number of unpoisoned active sites. Therefore, the above correlation is easily explained on the assumption that the polymeric olefin grows on the active sites that initiated the reaction and remains on them.

In view of this interpretation as well as the nature of the polymeric olefin described above, the formation of the polymeric olefin may be visualized as follows:



Polymerization may accompany isomerization resulting in further branching of the oligomers. Since the distribution of products shown in Table 3 is substantially the same as that found in the gas phase in the olefin polymerization over silica–alumina at higher temperatures,[25,26] the high-temperature polymerization may proceed *via* a polymeric olefin intermediate.

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