Nature of Catalytically Active Sites over Solid Acids. II. Relationships between Acidic Properties of Silica-Alumina and Its Catalytic Activities for Olefin Polymerization

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The influences of the degree of hydration of a silica–alumina surface on its Brönsted or Lewis acid content and on its catalytic activity for *cis*-2-butene polymerization were investigated at 30 °C as a function of the evacuation temperature. The raise in the evacuation temperature, *i.e.*, the decrease in the degree of hydration, gave rise to an increase in both the Lewis acid content and the catalytic activity but to a decrease in the Brönsted acid concent. A good linear relationship, which could not be extrapolated through the origin, was found between the Lewis acid content and the catalytic activity. Thus, the conclusion is drawn that only strong Lewis acid sites are active in olefin polymerization on silica–alumina at low temperature.

Olefins such as propylene or butenes produce an irreversibly adsorbed species on silica–alumina[1–6] or some Y zeolites[7–9] at near room temperature. This species gives rise to IR absorption bands characteristic of saturated hydrocarbons.[4–8] Recently, the species has been proved to act as the proton-donating center in olefin isomerization[10,11] and to comprise branched oligomers having about four monomer units on the average.[1–3] However, the nature of the active site for this polymerization still remains unsettled, in spite of several intensive investigations.[3,5,6,8]

In the previous study,[12] we investigated this problem by using a series of silica–alumina samples whose Lewis acid sites were selectively poisoned *in situ* with pyridine to different extents, and concluded that strong Lewis acid sites were active in the polymerization on silica–alumina at 30 °C. The present study intends to provide additional evidence for this conclusion by correlating the catalytic activities of partially hydrated silica–aluminas with their acidic properties.

Experimental

Materials and Apparatus. Silica–alumina (SA-1, 13% Al_2O_3),[13] pyridine,[12] and *cis*-2-butene[12] were those used earlier. The IR cell and the preparation of the self-supporting 20-mm diameter wafers of SA-1 are described in detail elsewhere.[12]

Procedures. Partially hydrated samples were prepared as follows. After the wafer had been mounted in the sample holder and pretreated in a dry oxygen stream for 2 h at 450 °C, it was cooled to 150 °C for 1 h in an oxygen stream containing 20—25 Torr of water vapor, and then evacuated in the IR cell for 2 h at different temperatures of 150—450 °C.

The wafer was exposed to pyridine vapor at about 16 Torr for 1 h at room temperature, and evacuated for 1 h at 110 °C. The spectrum of chemisorbed pyridine was recorded. The peak absorbances of the 1460 and 1540 cm^{-1} bands due to Lewis- (LPY) and Brönsted-bound pyridine (BPY), respectively, were taken as a measure of the total acid content for the corresponding acid type.

The reaction was carried out in a closed circulation system including the IR cell as a reactor at an initial olefin pressure of 5 Torr and 30 °C. Its progress was followed in the same way as in the previous study.[12]

The IR spectrometer and the operating conditions have previously been described.[12] Peak absorbances were 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 the weight (g) of the wafer, respectively.

Results and Discussion

Hydroxyl Groups on Surfaces. Figure 1 shows the IR spectra in the O–H stretching region of partially hydrated SA-1 samples. A sharp band at 3750 cm^{-1} is due to isolated surface silanol groups, and a broad band around 3600 cm^{-1} is due to hydrogen-bonded surface hydroxyl groups and adsorbed water.[14] As the evacuation temperature was raised, the 3600 cm^{-1} band decreased in intensity and the 3750 cm^{-1} band became more and more definite without a significant change in intensity. This fact implies that the adsorbed water is only slightly hydrogen-bonded to the isolated silanol groups.[14] Since the original SA-1 had previously been calcined at 550 °C for 8 h, and every wafer was heated to 450 °C before use, the wet oxygen treatment and the

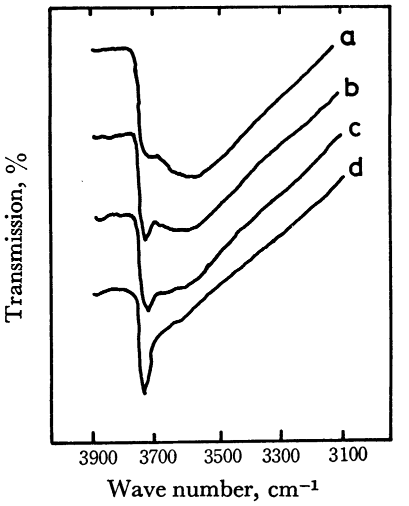

Fig. 1. IR spectra of surface hydroxyl groups on SA-1. A sample was evacuated for 2 h at 150 (a), 200 (b), 300 (c), or 450 °C (d).

subsequent evacuation probably bring about no drastic structural changes of the surface, except for hydration. The intensity of the band around 3600 cm^{-1} can therefore be taken as a qualitative measure of the degree of hydration of the surface. Thus, Fig. 1 indicates that a lowering in the evacuation temperature certainly results in an increase in the degree of hydration.

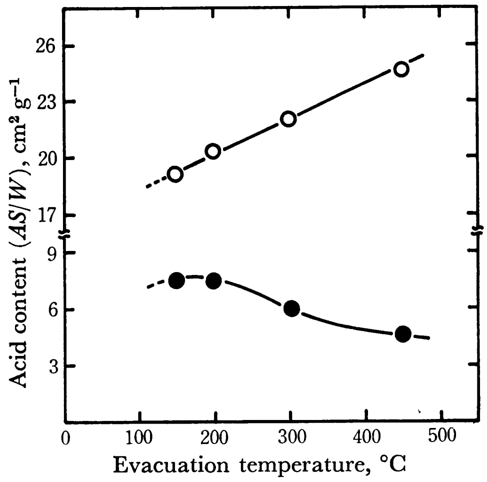

Fig. 2. Effect of evacuation temperature on surface acid content of Lewis (○) or Brönsted (●) type.

Acid Contents. Figure 2 illustrates the effects of the evacuation temperature, or, in other words, those of the added water, on the acid contents of SA-1. As the evacuation temperature was raised, the Lewis acid content increased while the Brönsted acid content decreased. Different values have been reported for the ratio of absorption coefficients of the LPY band to the BPY band: $\varepsilon_{1460}/\varepsilon_{1540} \approx 1$[15—17] or 2.6.[18] For our catalyst it was evaluated to be approximately unity from the differences in peak intensities resulting from the conversion of LPY to BPY upon dosing with quite small amounts of water. In view of this value, an increase in the Lewis acid content is compensated for with a decrease in the Brönsted acid content in the evacuation-temperature range of 200 to 450 °C. This implies that one Brönsted acid site is converted into one Lewis acid site when the surface is dehydrated. When the evacuation temperature was lowered from 200 to 150 °C, the Lewis acid content further decreased, while the Brönsted acid content remained approximately constant. It is quite reasonable to expect that comparatively large amounts of added water poison acid sites of both the Lewis and Brönsted types. Hence, a further lowering in the evacuation temperature may effect a decrease in the Brönsted acid content as well as in the Lewis acid content.

Polymerization Activity. *cis*-2-Butene produced, when it was introduced onto SA-1 at 30 °C, the polymeric species giving rise to IR absorption bands at 2960, 2930, and 2870 cm^{-1} in the saturated C–H stretching region and at 1470, 1385, and 1370 cm^{-1} in the saturated C–H bending region. The growth of each band occurred rapidly in the initial stage of the reaction, slowed down gradually, and finally ceased after 1—2 days. The peak intensity at 2960 cm^{-1} was well proportional to the amount of polymeric species formed.[12] The intensity of this peak after 1 min was therefore taken as the initial activity.

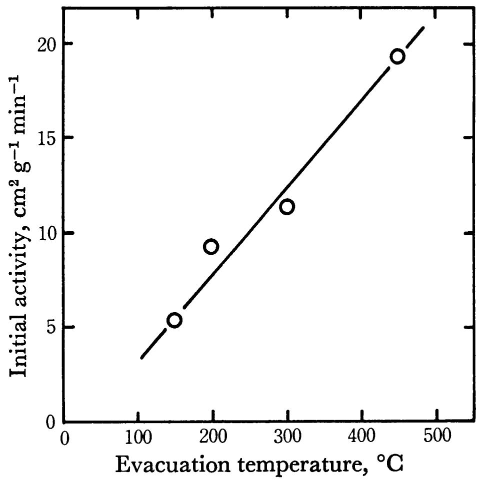

Fig. 3. Effect of evacuation temperature on catalytic activity for *cis*-2-butene polymerization at 30 °C.

Figure 3 is a plot of the initial activity against the evacuation temperature; it indicates that the initial activity decreases as the evacuation temperature is lowered, in other words, that added water certainly acts as an inhibitor for the formation of the polymeric species. This suggests that the Brönsted acid site is inactive in the present reaction. It can be seen from Figs. 2 and 3 that the influence of the evacuation temperature on the initial activity is similar to that on the Lewis acid content.

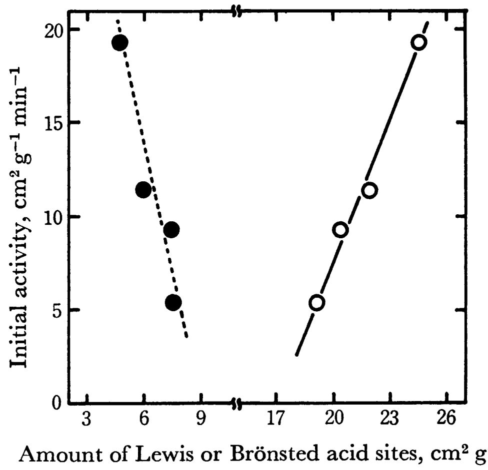

Fig. 4. Correlation of surface acidity with catalytic activity for *cis*-2-butene polymerization at 30 °C. ○: Lewis acidity, ●: Brönsted acidity.

Figure 4 shows correlations of the initial activity of SA-1 with its Lewis or Brönsted acid content. Since the initial activity decreases with an increase in the Brönsted acid content, this correlation is considered to be unreasonable. On the other hand, the initial activity decreases linearly with decreasing amounts of Lewis acid sites. This reasonable correlation probably indicates that the active acid site is of the Lewis type. Evidently, the straight line correlating the initial activity with the Lewis acid content does not extrapolate through the origin. This is easily explained on the assumption that only part of the Lewis acid sites are active. According to this interpretation, the majority of the active Lewis acid sites are those which can be liberated, as a result of desorption of water (or hydroxyl groups) from the sites, by raising the evacuation temperature from 150 to 450 °C. Since such water probably is strongly adsorbed, the active Lewis acid sites are reasonably concluded to be high in acid strength. This conclusion agrees well with the previous one.[12)]

In addition, the previous study[12)] showed that, in *cis*-2-butene polymerization at the same temperature as in the present study, an upper limit for the amount of the active Lewis acid sites on SA-1 evacuated at 450 °C amounted to about 30% of the total Lewis acid content. The correlation in Fig. 4 may permit a similar estimate. The point of intersection of the solid straight line and the abscissa can be regarded as the point representing a sample whose active Lewis acid sites have been just blocked with added water. Accordingly, with respect to SA-1 evacuated at 450 °C, an upper limit for the amount of the active Lewis acid sites is again evaluated to be about 30% of the total Lewis acid content. Thus, we are again led to the conclusion that strong Lewis acid sites are active in olefin polymerization over silica–alumina at the low temperature of 30 °C.

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