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Active Sites of Alumina and Silica–Alumina as Observed by Temperature Programmed Desorption*

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The active sites for chemisorption of ethylene on alumina and on a series of mixed gel silica–alumina catalysts have been investigated by the temperature programmed desorption technique as a function of the temperature of activation of alumina and of the composition of silica–alumina. The activity of these catalysts for ethylene hydrogenation and dimerization at low temperatures has also been measured to obtain additional qualitative and quantitative characterization of the active sites. The total number of sites on alumina is increased when the temperature of evacuation (i.e., the activation temperature) is raised but a treatment with moisture is necessary to create the stronger sites, the sites which are responsible for ethylene dimerization. The specific activity (the activity per site) of the weaker sites of alumina, the sites responsible for ethylene hydrogenation at low temperatures, increases with the evacuation temperature while the specific activity of the stronger sites does not change at evacuation temperatures higher than 550°.

The total number of active sites on silica–alumina increases monotonously with the alumina content, but the specific activity per site for ethylene dimerization goes through a maximum (and the activation energy through a minimum) at about 35 mole % alumina. The results show that the composition of silica–alumina determines both the number of sites and their specific activity. The activity for ethylene hydrogenation is highest with pure alumina and drops sharply when small amounts of silica are added. The transition from alumina to silica–alumina is clearly shown by the activity curves for these two reactions, hydrogenation and dimerization of ethylene.

INTRODUCTION

The nature of active sites of solid acid catalysts is of great fundamental and practical interest. Alumina acquires catalytic activity when it is heated and numerous studies of the development of the catalytic activity for various chemical reactions as a function of the temperature of activation have been carried out (*1–10*). A great deal of information has also been obtained on the relation between the catalytic activity and the composition of silica–alumina catalysts (*11–16*). In most of this work, attempts were made to correlate changes in activity with the surface acidity as measured by the chemisorption of basic vapors, ion exchange, chemical titration, or infrared spectroscopy. Although the techniques for measuring the acidity of solid catalysts are well established, other approaches have also been used in attempts to characterize the active sites. These are based, for example, on the ESR determinations of the electron-donor–acceptor properties of alumina (*17, 18*), the differential surface entropy of ammonia on silica–aluminas (*19, 20*), and the oxidation mode of ammonia retained on silica–alumina catalysts (*21*).

Although there seems to be little doubt that the catalytic activity of alumina and silica–alumina is due to surface acidity, a question still remaining is whether all, or

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even a substantial fraction, of the acid centers detected by the standard techniques for measuring surface acidity are actually involved in catalytic reactions. Since chemisorption of a reactant must occur in the course of the catalytic reaction, it was thought worthwhile to use the temperature programmed desorption technique (TPD), recently developed in this laboratory, to obtain further information on the relation between the active centers for chemisorption and the catalytic activity of alumina and silica alumina. In previous work, this technique has revealed the existence of two different types of active sites (sites I and II) on alumina for ethylene chemisorption and their surface concentration has been determined (*22*). It has also been used to investigate the catalytic reactions of ethylene on these active sites and has shown that ethylene polymerizes at relatively low temperatures on sites II (the stronger sites) but not on sites I (the weaker sites) (*23*). Ethylene hydrogenation at low temperatures, on the other hand, takes place readily on sites I but is negligible on sites II of alumina (*24*). On silica–alumina there is only one group of active sites for ethylene chemisorption and ethylene polymerizes on these sites much faster than on alumina (*25*).

In the present work the number of active sites and the activity of alumina were determined at successfully increasing activation temperatures (the evacuation temperatures) while those of silica–alumina were measured as a function of catalyst composition. In view of the selective nature of ethylene hydrogenation and dimerization mentioned above, these two reactions were used as test reactions to characterize the active sites. The adsorbed amount of ethylene during these reactions was measured to determine the specific activities per site and this provided not only the total number of active sites but also made it possible to follow changes in their quality.

EXPERIMENTAL METHODS

Materials. Wet gels of alumina and silica were obtained by the hydrolysis of purified aluminum isopropoxide (J. T. Baker Chem. Co.) and ethylorthosilicate (Fisher Sci. Co.) dissolved in isopropyl alcohol. The alumina and silica catalysts were prepared by grinding their wet gels for a few hours in a motorized mortar grinder and drying them overnight in an oven at 120°. A series of silica–alumina catalysts was prepared by mixing and grinding various proportions of the two wet gels and drying them overnight at 120°. The composition of the catalysts, estimated from the weights of the gels used and the weight loss on calcination, agreed well with the chemical analyses.

The catalysts dried overnight at 120° were crushed and screened on a perforated aluminum sheet to obtain particles averaging about 1 mm in diameter. For the study of the effect of the activation temperature, i.e., the temperature at which the catalyst was subjected to prolonged evacuation, a sample of about 1 g of alumina was placed in the reactor without further drying. For the series of experiments with silica–alumina, on the other hand, all the catalysts, including pure alumina and pure silica, were first heated in air for 3 hr at 600° and samples of about 0.2 g were then placed in the reactor. These catalysts were evacuated in the reactor for 6 hr at 650° before the experimental measurements.

Phillips research grade ethylene was used after thorough degassing. Matheson ultra-high purity hydrogen (99.999%) was passed through a liquid nitrogen trap to remove traces of moisture and was used without further purification.

Apparatus and procedure. A detailed description of the apparatus has been given previously (*25*). For the study of the effect of the activation temperature of alumina, ethylene was adsorbed at room temperature at 2–3 Torr for about 5 min and the catalyst was then evacuated for 30 min at the same temperature prior to the temperature programmed desorption. It has been observed before (*22*) that even at much lower pressures ethylene chemisorption at room temperature on the active sites of alumina is completed within a few minutes. In the temperature programmed desorption (TPD), described in greater detail elsewhere (*25*), the chemisorbed ethylene was desorbed by programmed heating of the catalyst into a stream of helium carrier gas and was detected by a thermistor thermal conductivity detector. The peak or peaks of the desorbed gas were recorded in the form of a "chromatogram." The heating was programmed so that the temperature of the catalyst increased at a constant speed of about 17.5°/min. The size and the position (i.e., the desorption temperature) of the peaks depends on the number of chemisorbed molecules and the "strength" of the sites, respectively.

Hydrogenation of ethylene was carried out by admitting hydrogen into the reactor after ethylene had been preadsorbed on alumina. Ethylene was preadsorbed and evacuated for 30 min at room temperature as described above, so that it was not present in the gas phase when hydrogen was admitted. Two sets of reaction conditions were employed: (i) 20-min contact with several Torr of hydrogen at room temperature, to determine the reaction rate, and (ii) 60-min contact with 150 Torr of hydrogen at room temperature, to convert all ethylene on the weaker sites (sites I) into ethane. After the reaction the catalyst was evacuated at room temperature through a liquid nitrogen trap to collect the ethane produced, which was then analyzed gas chromatographically. The total amount of ethylene preadsorbed was obtained as the sum of ethane produced and the unreacted ethylene, desorbed later by TPD. A more detailed description of the experimental procedure for ethylene hydrogenation has been given previously (*24*).

Dimerization of ethylene was carried out by admitting a sufficient amount to have it both on the catalyst surface and in the gas phase. It has been found before (*23*) that dimerization takes place by reaction of ethylene in the gas phase with ethylene chemisorbed on the stronger sites (sites II) of alumina. The reaction was carried out at room temperature for 20 min at ethylene pressures of 10–15 Torr. The product butenes were desorbed by TPD together with the unreacted ethylene and analyzed by gas chromatography. In some instances the reaction was carried out at a higher ethylene pressure of 35 Torr and for a longer contact time of 60 min to convert all ethylene on sites II into polymer and leave ethylene only on sites I.

In the investigation of the effect of the composition of silica–alumina catalysts, the temperature programmed desorption, hydrogenation, and dimerization of ethylene were carried out in the same manner as with alumina except that ethylene was adsorbed for 5 min and evacuated for 30 min, both at —75°, prior to TPD, which also was started from —75°. This low temperature was used to prevent loss of ethylene from the active sites by desorption during the evacuation and by chemical reaction during the adsorption because of its weaker chemisorption and higher reactivity on silica–alumina than on alumina (*25*).

The hydrogenation of ethylene on the silica–alumina catalysts was carried out at 0°. The activity for ethylene dimerization was compared at two different temperatures, —10° and room temperature, and a constant pressure of about 2 Torr. Reaction time was 15 min. Some products more highly polymerized than C_4 were found beside the butenes but the yield of the butenes was always proportional to the total amount of ethylene reacted and was therefore taken as a measure of the catalyst activity for polymerization.

In all TPD experiments the gas desorbed was condensed in a liquid nitrogen trap located downstream from the detector and its amount was accurately determined by gas chromatography.

RESULTS AND DISCUSSION

Effect of the Activation Temperature of Alumina

Ethylene chemisorbs strongly on alumina treated with atmospheric air at 600° and evacuated at the same temperature for many hours. Temperature programmed desorption gives then two ethylene peaks, at about 80 and 200°, respectively (*22, 25*). In the present study, alumina dried in an oven at 120° was evacuated in the reactor without further treatment with air. The

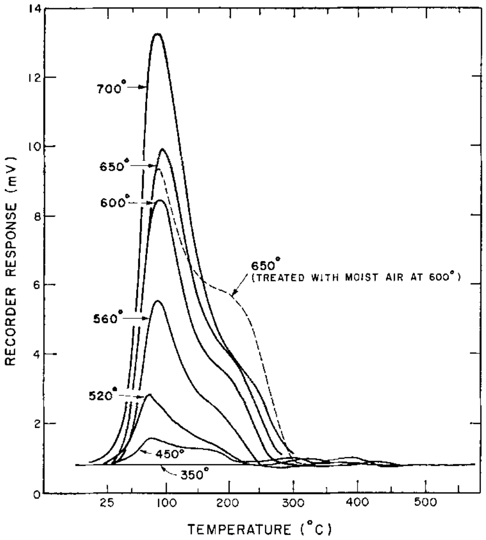

FIG. 1. TPD chromatograms of ethylene on alumina evacuated at various temperatures: evacuation temperatures are indicated.

first evacuation was at 350° for 6 hr and was followed by the measurement of the surface area (BET with N_2), TPD, ethylene hydrogenation, and ethylene dimerization experiments, as described in the Experimental section. After each of these measurements or experiments the catalyst was evacuated for 1 hr at a temperature about 20° lower than the evacuation temperature previously applied, to avoid further dehydration. This procedure was repeated at different evacuation temperatures increased stepwise up to 700°.

The TPD chromatograms obtained in this manner are shown in Fig. 1. As shown, no active sites were created by evacuation at 350° but they began to develop at 450°. The first peak (sites I) appears at about 80° and the second peak (sites II) at about 200° when the alumina is evacuated at temperatures higher than 560°, in good agreement with the peak temperatures reported earlier (*22*, *25*). The peaks are larger for higher evacuation temperatures and the total number of sites per gram of catalyst for evacuation at 700° (5.5×10^{18}) is 17 times larger than for evacuation at 450° (3.3×10^{17}). The surface area decreases almost linearly from 244 m^2/g for alumina evacuated at 350° to 202 m^2/g for alumina evacuated at 650°.

For alumina evacuated without previous treatment in air at high temperature, the second peak (sites II) is much smaller and appears only as a shoulder of the first peak (sites I), as shown by the solid curves in Fig. 1. This is in sharp contrast to the ratio (II/I) of about 0.7 obtained previously (*22*, *25*) with alumina heated at 600° in atmospheric air before evacuation. Moreover, when alumina evacuated at 600° without previous air treatment at high temperature was subsequently treated with *dry* air for 2 hr at 600° and evacuated again, the number of sites and the catalytic activity for the two reactions studied remained unaltered. On the other hand, when the alumina which gave the 700° solid curve in Fig. 1 was subsequently treated with *moist* air (atmospheric air, 1.5 hr at 25° followed by 3 hr at 600°) and was then evacuated at 650°, the second peak was markedly increased and the first peak decreased, as shown by the broken line in Fig. 1. Similar increase of sites II was also observed when the evacuated alumina was contacted with about 4 Torr of water vapor for a few hours at 600° without air and was subsequently evacuated at 650°.

In order to see in greater detail the development of the two types of sites at different evacuation temperatures, their number was estimated by TPD after: (i) severe hydrogenation (60 min at 150 Torr of hydrogen), to convert all ethylene on sites I to ethane, and (ii) severe polymerization (60 min at 35 Torr of ethylene), to convert all ethylene on sites II to polymer. The results are shown in Fig. 2(a), which includes also the results obtained with the alumina treated with moist air (filled points). The number of both types of sites increases sharply after 520°, but it levels off for sites II at about 650° unless the alumina had been treated with moist air. Water removed by evacuation was measured roughly by trapping in a liquid nitrogen trap during evacuation, and it was found that most water (98% of water removed up to 700°) was removed before 520°. After this temperature the curve of the water lost against the evacuation temperature became nearly flat, i.e., it became more

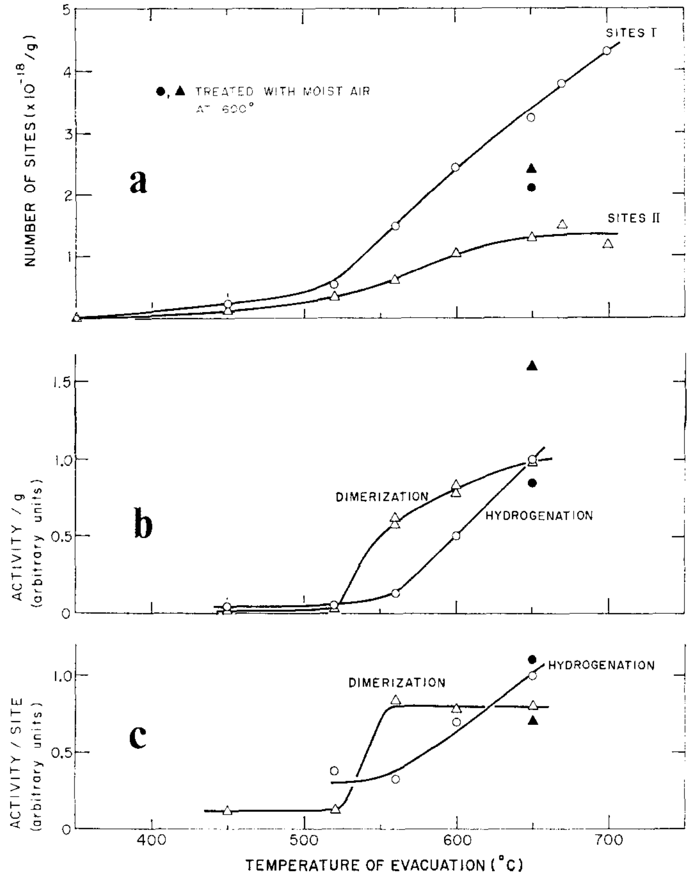

FIG. 2. The number and activity of sites on alumina as a function of the evacuation temperature: (a) the number of active sites/g of catalyst; (b) the activity/g of catalyst; (c) the activity per site. Filled points were obtained with the alumina treated with moist air, corresponding to the broken line in Fig. 1.

difficult to remove water. Thus, on the average, the ratio of the number of water molecules removed to the number of sites created was 2 to 3 × 10^4 for both sites at 450° and it dropped sharply to 8 × 10^1 for sites I and 2 × 10^2 for sites II at 560°. After this temperature, the ratio did not change too much; at 650°, for example, it was 4 × 10^1 and 1 × 10^2 for sites I and II, respectively. It is apparent, therefore, that a critical temperature for the activation of alumina exists at around 550°. Other authors have also reported that the activity of alumina greatly increases at an activation temperature of 550° (*2–4*).

At low temperatures, the hydrogenation of preadsorbed ethylene preferentially occurs on sites I while the polymerization takes place only on sites II, as already mentioned. These two reactions were therefore used to measure the activity of the two types of sites. The activities per gram of catalyst (in arbitrary units) for these reactions are shown in Fig. 2(b). As expected, their increase with the evacuation temperature paralleled the increase in the number of each type of sites. The activity for hydrogenation was measured at an approximately constant pressure of hydrogen and with the saturated amount of preadsorbed ethylene at room temperature, and for dimerization at an approximately constant pressure of ethylene.

The trend in the specific activity per site is different for the two reactions, as shown in Fig. 2(c). The activity per site was calculated by dividing the number of molecules produced at constant pressure and reaction time by the number of ethylene molecules initially adsorbed on sites I or

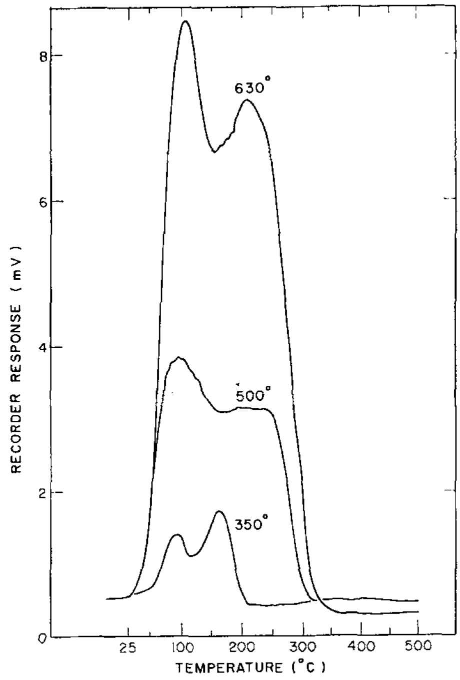

FIG. 3. TPD chromatograms of ethylene on alumina evacuated at various temperatures: The alumina was heated in atmospheric air at 600° prior to evacuation. Evacuation temperatures are indicated.

II. Figure 2(c) shows that the activity of sites I (hydrogenation) increases with the evacuation temperature but that of sites II (dimerization) remains unchanged at evacuation temperatures higher than 550°. It is of interest to note that the activity per site of alumina treated with moist air at 600° (filled points) does not deviate significantly from the curves in Fig. 2(c), while the total number of active sites of either type was considerably changed by this treatment, as shown in Fig. 2(a). This indicates that the treatment with moisture changes the number of sites but creates the sites of about the same activity as long as the evacuation temperature is the same.

Figure 3 shows the TPD chromatograms of ethylene on alumina which was taken from the same batch of alumina gel as in the experiments of Figs. 1 and 2 but was heated in atmospheric air for 3 hr at 600° prior to evacuation. As shown, sites II develop at higher evacuation temperature together with sites I, as already pointed out. The appearance of some sites at 350° apparently indicates the removal of considerable amount of water during air pretreatment at 600°; subsequent exposure to atmosphere in the course of the handling and transfer to the reactor has no doubt poisoned a substantial fraction although evidently not all of the sites thus generated. The number of sites I of this alumina was of the same order of magnitude as of the alumina evacuated at the same temperature but without pretreatment with air, although the former was a little larger than the latter (3×10^{12} vs 1.6×10^{12} sites/cm^2 for evacuation at 650°). When the latter alumina was treated with moist air (broken line in Fig. 1), the number of sites II became comparable to that of the pretreated alumina. X-Ray analyses showed that both aluminas after evacuation at 650° were principally γ-alumina, although the alumina evacuated without air pretreatment had finer particles.

It is obvious that the active sites of alumina are created by dehydration of the surface, as has been accepted by many authors. However, the growth of the sites is different for the two types of sites. Sites I develop by evacuation independent of whether or not alumina has been pretreated with air, but the strength of the sites varies with the evacuation temperature (i.e., with the degree of dehydration). Sites II do not develop unless alumina is treated with moisture and their strength does not change with the evacuation temperature. In present experiments, treatment with moisture was necessary for the development of sites II after alumina was dehydrated by high temperature evacuation. *Before evacuation,* however, even dry air treatment should contribute to the development of sites II, because the moisture from the catalyst itself would have the same effect as moist air, as was suggested by Peri (*26*).

Peri derived an interesting model of the surface of γ-alumina from a computer study (*27*). He suggested the existence of various types of hydroxyl groups, depending on their neighbors, and of various types of defects. Besides the difficulty of justifying all the assumptions employed in Peri's idealized model, it is also difficult to correlate the degree of dehydration in his treatment with the dehydration achieved experimentally in the present study at different evacuation temperatures. Nevertheless, the sites discussed in the present paper are probably either the sites associated with hydroxyl groups or the defects (aluminum or oxide ions) proposed by Peri. The fact that sites II are capable of donating protons to adsorbed olefins (*23*) and that their formation requires participation of water indicates that they are those associated with hydroxyl groups. Although the exact structure of sites II is not yet known, it is likely that they are a combination of hydroxyl group and a defect since their number increases (and becomes almost constant between 650 and 700°) with the evacuation temperature while the number of hydroxyl groups should be monotonously decreasing. At the same time, the results of Fig. 2(c) suggest that the degree of dehydration does not significantly change the energy state of sites II.

As already pointed out, the treatment with moisture markedly accelerates the development of sites II of alumina. Figure 2(a) shows that the total number of active sites (I and II) thus developed (filled points) is 4.6×10^{18}/g and this is the same as that created by evacuation at the same temperature (650°) but without moisture treatment (4.5×10^{18}/g). This fact suggests that sites II are produced by the interaction between water and sites I, which are the defects of the surface. These defects, either oxide or aluminum ions, appear to be energetically affected by the degree of dehydration, as shown in Fig. 2(c).

Effect of Composition of Silica–Alumina

Some typical results of the temperature programmed desorption of ethylene on silica–alumina are shown in Fig. 4, in which ethylene was adsorbed at —75° and the TPD was also started from —75°, as described in the Experimental section. Because of the start of TPD at this low temperature, a large peak due to physical adsorption appears at about —30°, in addition to the peaks due to chemisorption. It is therefore believed that there is no loss of *chemisorbed* ethylene during evacuation prior to TPD. As shown in Fig. 4, TPD gives two chemisorption peaks for catalysts with high alumina content, but only one chemisorption peak when the content of silica exceeds 50 mole %. It appears therefore that some alumina character is retained until 50% or more silica is added.

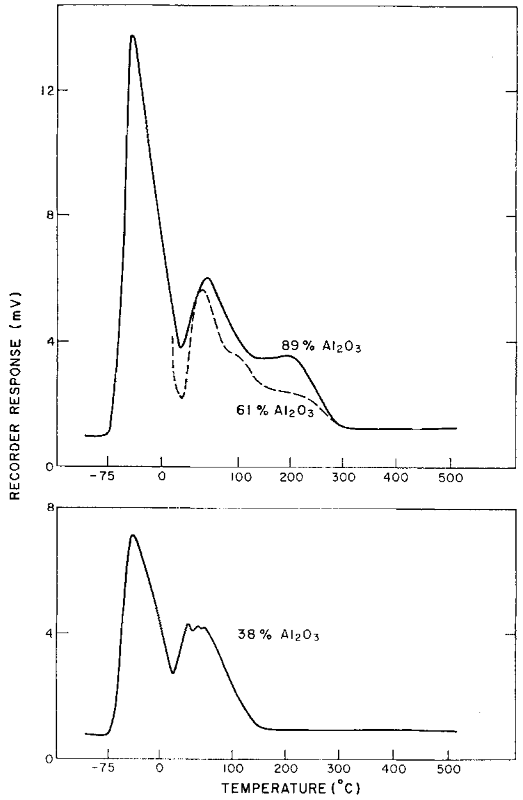

FIG. 4. TPD chromatograms of ethylene on silica–alumina catalysts: The composition of the catalysts is indicated as Al_2O_3 mole %.

The number of active sites was determined from the total amount of ethylene desorbed by TPD, measured gas chromatographically, and the fraction of the peak area in the TPD chromatogram corresponding to chemisorption. The latter was obtained by drawing a vertical line through the minimum between the physisorption and the chemisorption peaks. The results thus obtained are listed in Table 1 together with the composition of the catalysts and their surface area. For catalysts with high

TABLE 1
NUMBER OF ACTIVE SITES OF SILICA–ALUMINA CATALYSTS

Catalyst[a]	Al_2O_3 content[b] (mole %)	Surface area (m^2/g)	Total no. of sites ($sites/cm^2$)	Activation energy of dimerization (kcal/mole)
A	100	206	8.7×10^{12}	
SA-1	96	200	8.1×10^{12}	
SA-2	89	222	6.7×10^{12}	
SA-3	61	270	3.9×10^{12}	4.8
SA-4	38	414	1.7×10^{12}	1.0
SA-5	12	539	1.5×10^{12}	1.2
SA-6	6	549	6.5×10^{11}	2.9
S	0	633	$<1.5 \times 10^{11}$	

[a] All catalysts were heated in air for 3 hr at 600° and evacuated for 6 hr at 650°.
[b] Chemical analysis.

percentage of alumina, where more than one chemisorption peak appears, the total number of active sites is given. Table 1 shows that the surface area monotonously increases with silica content, as was observed by previous workers (*13*), while the number of active sites per unit surface area (and also per unit weight) monotonously decreases.

However, the activity per site changes with the composition in a different way, as shown in Fig. 5. The activity per site for both hydrogenation and dimerization of ethylene was calculated in the same manner as described for alumina and is plotted (in arbitrary units) against the Al_2O_3 content in the catalyst. The activity per site for the hydrogenation of preadsorbed ethylene sharply drops as soon as a small amount of silica is added, while with these same catalyst compositions the activity for dimerization at low temperature is negligibly small. The dimerization activity starts to increase at about 70 mole % of alumina, but decreases again to almost zero after passing through a maximum at about 35% of alumina. This composition corresponds to an atomic ratio of Al to Si of unity. The results shown in Fig. 5 apparently indicate that the composition of silica–alumina controls not only the number of active sites but also their strength. This appears to be also supported by the existence of a minimum in the

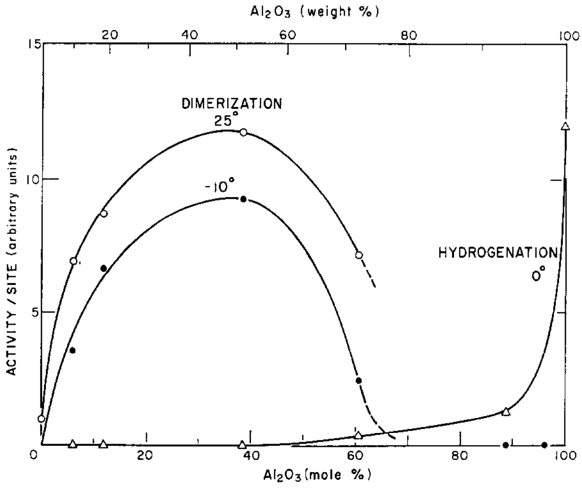

FIG. 5. The activity per site as a function of the composition of silica–alumina.

activation energy of dimerization, listed in the last column of Table 1, calculated roughly from the results obtained at 25 and −10°.

As already mentioned in the Experimental section, higher polymers are also found in the dimerization reaction, and their amount is proportional to that of butenes (C_4). The activity per site was calculated by dividing the amount of C_4 produced by the initial amount of ethylene adsorbed, and the latter was calculated from the pressure decrease in the gas phase minus the amount of the C_4 produced. Therefore there is a possibility that the adsorbed amount of ethylene might have been overestimated, particularly at higher activity where larger amount of higher polymers is formed. The shape of the curves in Fig. 5 could therefore be more accentuated.

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