puted for the element by Pauling (7) i.e., 1.5, it may be concluded that the increase due to the formation of a Lewis site ranges from 0.3 to 0.9 electronegativity units.

As can be seen in Fig. 1, ammonia adsorbed on Lewis sites produces a band between 1350 and 1200 cm^{-1}, the frequency of which depends on the strength of the sites. When the outgassing temperature is increased, the ammonia molecules adsorbed on weak acid centers are released, resulting in a frequency shift to higher values. For example, the frequency for the 5% SiO_2 sample shifts from 1250 cm^{-1} at 25°C to 1311 cm^{-1} at 300°C. For pure alumina the corresponding values range between 1210 and 1300 cm^{-1}, according to the pretreatment conditions.

The evaluation of the number of Lewis and Bronsted sites has usually been based on the integrated intensity of the asymmetrical deformation bands. For a relative comparison of both types of acidity, the ratio of the absorption coefficients $R = \epsilon_{NH_4^+}/\epsilon_{NH_3}$ has to be estimated. From our determination, it appears to be of the order of magnitude of 7. This implies that the asymmetrical band of NH_3 between 1630 and 1620 cm^{-1} is often very small and that the determination of the relative number of Lewis sites is not accurate. On the contrary, the symmetrical deformation band between 1350 and 1200 cm^{-1} (curve 5, Fig. 1) is several times greater than the asymmetrical deformation band for ammonium after conversion of NH_3 into NH_4^+ (curve 6) and, *a fortiori* than that of NH_3. Therefore, the symmetrical deformation mode due to ammonia on Lewis sites is an easier tool for studying the surface acidity of aluminas and silica-aluminas rich in Al_2O_3.

Curve 6 also clearly shows that the transformation of ammonia into ammonium is quite complete when the sample is exposed to the atmospheric moisture. This could not be demonstrated earlier because of the superposition of the deformation bands of ammonia and water in the 1650–1600 cm^{-1} range.

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The Isomerization of *n*-Butenes over a Deuterated Ion Exchange Resin

Extensive studies have been carried out on the active sites of solid acid catalysts, such as silica-alumina. On such catalyst surfaces a variety of acid sites has been observed and a catalyst with a homogeneous acid surface would be helpful in

elucidating the nature of the acid sites. Various ion exchange resins have been employed as acid catalysts (*1*), and their surfaces are generally accepted to be homogeneous. The isomerization of *n*-butenes over acid catalysts was suggested by Ozaki and Kimura (*2*) to proceed through a proton donor–acceptor mechanism. To obtain further information on the mechanism as well as the nature of the active sites, the reaction over deuterated Amberlyst 15 was investigated.

The catalyst employed was evacuated at 100°C for 1 hr before each run. A deuterated surface was prepared by soaking the catalyst in deuterium oxide at room temperature for about 15 hr before evacuation. Other experimental procedures were the same as described previously (*2*).

The isomerization of *n*-butenes over Amberlyst 15 has been investigated in the range of 0–25°C. In the present case, all the active sites on the catalyst are probably Brönsted acid sites, therefore the proton-donating and -accepting process should be observed when the reaction proceeds over a deuterated catalyst.

Table 1 gives the results of isomerization of *n*-butenes over deuterated catalyst. Whenever both 1-butene and *cis*-2-butene were the reactants, deuterated products were observed, while the reactants were scarcely deuterated. The results are consistent with the view that hydrogen exchange is involved in the slow step of isomerization itself as concluded previously (*2*). It is accordingly concluded that the isomerization of *n*-butenes is catalyzed by Brönsted acid sites as expected, being accompanied with a hydrogen exchange process. When 1-butene was the reactant, the deuterium concentration of *cis*-2-butene approximately agreed with that of *trans*-2-butene in all deuterated species. The result suggests that *cis*- and *trans*-2-butene were formed via the same deuterated intermediate from 1-butene. At a low conversion stage, monodeuterobutene was mainly observed, which agreed with the previous (*2*) result over silica-alumina and others.

It is concluded that the catalytic action of Amberlyst 15 is essentially the same as that of Brönsted acid sites on typical solid acids.

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TABLE 1

The Results of Isomerization of *n*-Butenes over Deuterated Amberlyst 15

Reactant	Temperature (°C)	Reaction time (sec)	Butene composition			D distribution			
			cis-2	*trans*-2	1-	d_0	d_1	d_2	d_3
1-Butene	25	180	28			24	31	29	14
				45		24	31	30	14
					27	98	1	1	—
1-Butene	0	30	15			51	46	3	—
				27		54	43	3	—
					58	97	3	—	—
cis-2-Butene	25	180	51			51	33	15	—
				46		32	45	23	—
					3	70	20	10	—
cis-2-Butene	0	60	60			41	49	10	—
				38		41	45	14	—
					2	46	52	2	—
cis-2-Butene	0	45	78			79	16	5	—
				20		43	46	11	—
					1	—	—	—	—
cis-2-Butene	0	15	98			97	3	—	—
				2		45	55	—	—
					—	—	—	—	—

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The Formation of Palladium Hydride by Reaction of Formic Acid at Palladium Electrodes

The hydrogen in palladium hydride electrodes can be used for the catalytic hydrogenation of ethylene (*1*) or acetylene (*2*). We have now examined the reverse type of catalytic process at a palladium electrode where hydrogen is a product of the reaction and not one of the reactants. Formic acid was chosen for study since the usual mode of decomposition on metal catalysts (*3*) is

$$HCOOH \rightarrow CO_2 + H_2 \qquad (1)$$

Treatment with aqueous formic acid (*4*) has been used to convert a palladium electrode into palladium hydride but rate data are lacking. The behavior of formic acid at metal electrodes is of interest in connection with some research on fuel cells as it may appear either as a by-product or an intermediate in the oxidation of methanol or of formaldehyde (*5*).

The experimental technique was similar to that previously described (*1, 6*). The amount of hydrogen in a fine palladium wire (0.0122-cm diam.) was determined by measurement of the ratio R/R_0, R being the electrical resistance and R_0 the resistance of the wire free from hydrogen. In some cases, electrode potentials of the wire were also determined and expressed with respect to a Pt/H_2 electrode in the same solution as the palladium wire. Experiments were carried out at 25° or 50°C and the specimens were immersed in aqueous solutions of formic acid which were stirred by a stream of argon. Some experiments were carried out with formic acid supplied by Hopkin and Williams, Ltd., others with AnalaR grade material from British Drug Houses, Ltd., but both gave similar results.

RESULTS AND DISCUSSION

Some characteristic results for R/R_0 are shown in Fig. 1(a) and the derived values of H/Pd are given in Fig. 1(b). No evolution of gas at the electrode was observed.

The initial rates of absorption of hydrogen were determined from the slopes of the curves for H/Pd at zero time. Nine results in separate experiments with 5 M formic acid at 50° gave rates within the limits of 7.3×10^{16} to 13.9×10^{16} molecules/sec cm^2 of apparent surface; the average value was 10.0×10^{16}. Initial rates with 1 M solutions were smaller by a factor of 2.0 to 2.5 and the apparent activation energy for both strengths of solution was about 5 to 6 kcal/mole. An initial rate at 50°C close to that for 5 M formic acid was found using 2.5 M sodium formate and so formate ions may react as readily as undissociated formic acid molecules.

Now rates of absorption of hydrogen of 10^{17} molecules/sec cm^2 are comparable with those obtained for wires immersed in aqueous solutions saturated with hydrogen gas under a pressure of about 10 atm and with similar conditions of stirring (*6*) and