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Active Centers for the Isomerization of Linear Butenes on Silica Gel: Specific Poisoning of Brønsted Acid Sites by Silylation

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The catalytic activity of commercial silica gels in the isomerization of linear butenes at 600–700 K showed an inverse proportionality to the calcination temperature and a direct proportionality to the concentration of aluminum, the latter being present as a trace impurity. From a comparison with literature data it is concluded that the reaction mechanism for butene isomerization on silica gel is the same as that on silica–alumina, and that the reaction takes place on identical active centers. Combination of the kinetic measurements with the results of a recent infrared study showed that the isomerization activity is related to the presence of hydrogen-bonded silanol pairs on the catalyst surface. The catalytic activity is thought to be achieved through cooperation of these weakly Brønsted-acidic silanols with monomeric or oligomeric butene chemisorbed on Lewis-acidic surface aluminum ions. The silanol pairs, then, serve as adsorption–desorption sites, and the chemisorbed butene units as proton donor–acceptor sites. *In situ* treatment of silica gel with gaseous hexamethyldisilazane strongly suppressed the isomerization activity. It is concluded that the inhibition is caused by a highly specific poisoning of the weakly Brønsted-acidic sites; no effects assignable to Lewis acid site poisoning were observed. Ammonia proved to be a far less effective catalyst poison under the applied conditions. Aluminum-induced, strongly Brønsted-acidic hydroxyls did not appear to be present on catalysts activated at 750 K.

INTRODUCTION

Silica gel is an inert material with a large surface area and a high mechanical strength. To these properties silica gel owes its widespread use as a catalyst support. Nevertheless, commercial silica gel shows some catalytic activity of its own, especially in the isomerization of alkenes (*1*). This activity can vary considerably between products from different manufacturers. It has been supposed that the catalytic activity is caused by impurities, such as aluminum. Several authors have found that deposition of small amounts of alumina on very pure silica gel obtained from the hydrolysis of tetraethoxysilane or tetrachlorosilane greatly enhances the activity in alkene double-bond isomerization (*1–3*). Other important sites on silica gel are the surface hydroxyls: adsorption of gases usually takes place on these groups (*4*). Moreover, the degree of surface hydroxylation has a marked influence on the activity of many catalysts (*5*).

Here, we present a study on the kinetics of butene double-bond isomerization on commercial and laboratory-prepared silica gels. The purpose of the investigations was to elucidate the nature of the active centers. We used samples with a Al/Si atomic ratio between 10^{-2} and 10^{-6}. The surface hydroxyl concentration was controlled by calcination at various temperatures; the results of a recent infrared study (*6, 7*) enabled us to predict the relative abundances of the different hydroxyl groups on the silica surface.

The apparent influence of surface aluminum and hydroxyl groups on the catalytic activity indicates that both Lewis- and Brønsted-acidic active sites can be present on silica gel. Applying a reagent which specifically poisons either type of active site should facilitate the interpretation of activity measurements. Usual poisoning

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agents for acidic catalysts, such as ammonia and pyridine (*8*), produce surface complexes that are rather ill-defined and usually unstable above 550 K. Moreover, they do not discriminate significantly between Lewis and Brønsted acid sites.

The silylating agent hexamethyldisilazane (HMDS) reacts easily with weakly Brønsted-acidic hydroxyl groups, with the formation of stable silyl ethers (*6, 9*):

$$2\ \text{-OH} + \text{HN(Si(CH}_3)_3)_2 \rightarrow 2\ \text{-O-Si(CH}_3)_3 + \text{NH}_3. \quad (1)$$

Lewis acids may react with HMDS as well: because HMDS is a nitrogen base, it can form coordination complexes. It is to be expected, however, that these complexes are less stable than the silyl ethers from Eq. (1), since a Lewis acid–nitrogen base complex such as triethylamine–trimethylboron was found to be unstable at room temperature (*10*), whereas Fripiat *et al.* (*11*) observed that the decomposition temperature of silylated silica gel is 930 K.

These considerations prompted us to treat some silica gels *in situ* with various quantities of gaseous HMDS and measure the effect of this treatment on the isomerization activity. Because ammonia is produced during the reaction of HMDS with silica (Eq. (1)), we briefly investigated the influence of treatment with gaseous ammonia.

EXPERIMENTAL

Materials

Commercial silica gels were obtained from Davison (Grace 62), Rhône-Progil (Spherosil XOA-400), Ketjen, and Mallinckrodt. FR-3 silica gel was prepared in the laboratory by acid hydrolysis of tetraethoxysilane (*12*). The Ketjen and FR-3 silicas were milled before use. Mallinckrodt silicic acid was converted to a usable material by granulating the sieve fraction under 80 μm with doubly distilled water. Strict care was taken to avoid contamination. The silicas were calcined as described in the Results section.

The specific surface area of the silicas, s, was calculated from the nitrogen adsorption isotherm at 77 K, recorded on a Carlo Erba Sorptomatic (BET method). Values for s were: Davison, 364 $m^2\ g^{-1}$; Rhône-Progil, 361 $m^2\ g^{-1}$; Ketjen, 449 $m^2\ g^{-1}$; Mallinckrodt, 520 $m^2\ g^{-1}$; FR-3, 631 $m^2\ g^{-1}$. The molar fraction of aluminum, x(Al), was determined by atomic absorption spectroscopy. The sieve fraction used was 150–250 μm.

The butenes (Matheson, CP), hexamethyldisilazane (HMDS) (Aldrich-Europe, 98%), and anhydrous ammonia (Baker, 99.99%) were used without purification.

Equipment and Procedures

The kinetic experiments were carried out in a closed-circulation system with a total volume of 25 × 10^{-5} m^3. By means of a four-way cross valve the system could either be filled with butene, helium, or oxygen, or evacuated with a rotary oil pump and a liquid-nitrogen trap (10 Pa). The circulation speed was 1–2 × 10^{-5} $m^3\ s^{-1}$. The reactor was a quartz-glass tube, equipped with a sieve plate and mounted in a thermostated oven. Samples could be taken through a silicon-rubber septum. By varying the circulation speed it was found that the reaction was not influenced by mass-transfer limitations under the applied conditions.

Typically, 0.5–1.0 g of calcined silica was activated by 18-h evacuation at 750 K. Next, the reactor was cooled to the reaction temperature, butene was introduced up to the desired pressure within 10 s, the circulation pump was started, and samples were withdrawn for gc analysis after 1, 5, 10, and 20 min. After the last sample had been taken, the pump was stopped and the system was evacuated for 10 min, or for the time needed to reach another temperature. Then, another batch of butene was introduced.

Ketjen silica was too active to use as such. Therefore, it was diluted with 95% Davison silica. In the calculation of the rate constant, corrections were made for the activity of the diluent.

The rate constant k' was derived from a first-order rate equation:

$$-x_e \ln (1 - x_t/x_e) = k't, \qquad (2)$$

where x_t and x_e are the molar fractions of product butene at time t and at equilibrium, respectively. Values for x_e were calculated from the formulas given by Meyer and Stroz (*13*). k' was converted to a rate constant k expressed in moles per square meter per second.

The gc analyses were performed on a 2-m × 4-mm stainless-steel column packed with 30% 2,5,8,11,14-pentaoxapentadecane on Chromosorb P-AW (212–250 μm) at 303 K, using flame-ionization detection and nitrogen carrier gas. Response factors were assumed to be equal for all butenes. The conversions were corrected for impurities in the feed.

The silylation experiments were carried out with the Davison and Rhône-Progil silicas. After measuring the isomerization activity of these silicas at 700 K (in triplicate) the system was filled with 1.0 × 10⁵ Pa of helium, the circulation pump started, and the reactor cooled to 525 K. At this temperature the appropriate amount of HMDS (or ammonia) was injected with a hypodermic syringe and allowed to react for 20 min. Next, the system was evacuated briefly at the same temperature, and for 10 min at 700 K. Then, the activity of the silica was measured again. The activity after poisoning was calculated as a percentage of the original rate constant, so that the results for both silicas could be shown in one graph. The amount of HMDS was expressed as moles per 2 moles of hydroxyl groups, in accordance with the stoichiometry of the reaction in Eq. (1).

To determine the hydroxyl concentration on our silica gels, about 50 mg of freshly calcined silica was placed in a Cahn RG thermobalance (*7*) and degassed fro 1 h at 750 K (final weight W). Then, the temperature was lowered to 525 K, and 4×10^2 Pa of HMDS was introduced. After a 1-h reaction the sample was degassed for 0.5 h at 525 K, and for 1 h at 750 K (final weight W_s). The surface hydroxyl concentration, n(OH), expressed in moles per square meter, was calculated from:

$$n(\mathrm{OH}) = \frac{W_s - W}{72Ws}, \qquad (3)$$

where s represents the specific surface area.

RESULTS

Aluminum Content

Samples of the five silicas were calcined in the reactor for 3 h in a stream of dry oxygen at 825 K, and activated as described in the Experimental section. The molar fraction of aluminum in these silicas, x(Al), and the respective activities for the isomerization of 1-butene at 600 K and 1.1×10^5 Pa are summarized in Table 1. In this table, k_1 is the overall reaction rate constant for 1-butene isomerization, k_{1c} is the rate constant for *cis*-2-butene formation from 1-butene, etc. All conversion data obeyed a first-order rate equation (Eq. (2)). No reac-

TABLE 1

Aluminum Content and 1-Butene Isomerization Activity of Some Silica Gels[a]

Silica	$x(\mathrm{Al}) \times 10^4$	$k_1 \times 10^9$ (mol m^{-2} s^{-1})	k_{1c}/k_{1t}[b]
Ketjen	20–100	260(±10)	1.10
Rhône-Progil	1–10	31(±4)	1.14
Mallinckrodt	0.01–0.1	1.9(±0.4)	1.02
Davison	0.01–0.1	1.9(±0.4)	1.08
FR-3	<0.03	<0.08	—[c]

[a] Reaction rate constants determined at 600 K and 1.1×10^5 Pa.

[b] Accuracy ±0.02; thermodynamic equilibrium ratio 0.64 (*13*).

[c] The selectivity ratio could not be determined because of the very low conversion.

tion products other than linear butenes were observed.

Table 1 shows that the catalytic activity of the silicas is proportional to their aluminum content. The k_{1c}/k_{1t} ratio is close to one for all silicas. Aluminum-free silica appears to be inactive.

Calcination Temperature

The effect of calcination on the catalytic activity and the hydroxyl concentration was studied on Rhône-Progil silica gel. We chose this product because its specific surface area was found to remain unchanged at temperatures up to 1150 K. An amount of this silica was heated for 3 h in a stream of dry nitrogen at 750 K. Samples of this precalcined silica were heated for 1 h in a pot oven at 775, 875, 975, and 1075 K, respectively, quickly cooled over phosphorus pentoxide, and transferred either to the reactor or to the thermobalance. The calcined samples were activated as described in the Experimental section.

The results of the 1-butene isomerization measurements at 675 K and 2.0×10^5 Pa and the gravimetrically determined surface hydroxyl concentrations are summarized in Table 2. The apparent activation energy, E_a, was calculated from a plot of ln k vs T^{-1}, where T is the reaction temperature. In these experiments T was varied in 25 K steps from 675 to 600 K, and then from 750 to 675 K. The activities thus obtained did not differ significantly from the results of experiments where a fresh silica sample was studied at each temperature. The selectivity ratio k_{1c}/k_{1t} was independent of the reaction temperature.

TABLE 2

Surface Hydroxylation and 1-Butene Isomerization on Rhône-Progil Silica Gel as a Function of the Calcination Temperature[a]

Calcination temp. (K)	$n(OH) \times 10^6$ (mol m^{-2})	$k_1 \times 10^9$ (mol m^{-2} s^{-1})	k_{1c}/k_{1t}	E_a[b] (kJ mol^{-1})
775	3.22	390(±40)	1.10	33
875	3.14	250(±20)	1.11	39
975	2.78	105(±4)	1.12	49
1075	2.32	50(±5)	1.16	66

[a] Kinetic constants determined at 675 K and 2.0×10^5 Pa.
[b] Accuracy ±2 kJ mol^{-1}.

Table 2 shows that the activation energy increases with increasing calcination temperature, whereas both the overall rate constant and the hydroxyl concentration decrease. The selectivity ratio is hardly affected by the heat treatment.

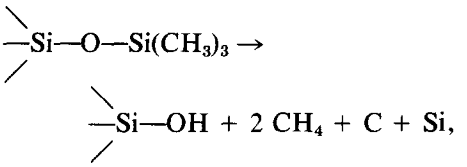
Similar results were obtained in the isomerization of *cis*- and *trans*-2-butene. The observed selectivity ratios k_{c1}/k_{ct} and k_{t1}/k_{tc} at 675 K were in the range 1.3–1.6, and about equal at the same calcination temperature.

Silylation

Samples of the Rhône-Progil and Davison silicas were calcined for 3 h at 825 K in air, and activated as described in the Experimental section. The respective rate constants for *trans*-2-butene isomerization at 700 K and 2.0×10^5 Pa were about 0.11×10^{-6} and 0.007×10^{-6} mol m^{-2} s^{-1}. Figure 1 shows the influence of HMDS on the catalytic activity. It can be seen that the results are roughly the same for both silica gels.

To check for mass-transfer limitations in the reaction of HMDS with the catalyst surface, the time of reaction was lengthened to 3 h in some experiments. Possible loss in HMDS owing to condensation on the walls of the reaction system was checked by spreading the introduction of HMDS over several successive treatments. Neither of these two modifications in the poisoning procedure resulted in significant deviations from the curves in Fig. 1.

From repeated isomerization experiments it appeared that the activity of the poisoned silicas increased slowly with time. This indicates decomposition of the surface complexes, which can also account for the observed evolution of methane. Assuming a reaction according to



$$-\text{Si}-\text{O}-\text{Si}(\text{CH}_3)_3 \rightarrow -\text{Si}-\text{OH} + 2\,\text{CH}_4 + \text{C} + \text{Si}, \qquad (4)$$

the amount of methane produced corresponds to a silyl-ether decomposition rate of about 0.03×10^{-6} mol m^{-2} h^{-1}. For comparison, the hydroxyl concentration on our silicas is about 3×10^{-6} mol m^{-2}; see Table 2.

Treatment of Rhône-Progil silica with 4.7 $\times$ 10^{-6} mol m^{-2} of anhydrous ammonia reduced the catalytic activity to 63% of the initial value. The activity of Davison silica decreased to 68% after a similar treatment.

DISCUSSION

Active Centers

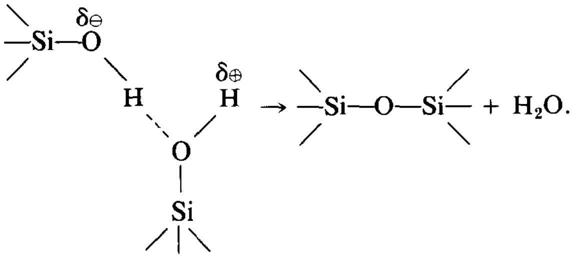
We observed that the rate of butene isomerization on silica gel is directly proportional to the aluminum content of the catalysts (Table 1). Holm *et al.* (*14*) observed a similar proportionality between aluminum content and catalytic activity in the polymerization of ethene on silica–alumina with less than 25% alumina. Ballivet *et al.* (*15*) reported a decrease in the isomerization activity of silica–alumina when surface aluminum was removed by acid leaching. Increasing the calcination temperature of silica gel was found to decrease the isomerization activity (Table 2). Again, the same behavior has been reported for silica–alumina (*16, 17*). X-Ray scattering has shown that silica–alumina with less than 15% alumina has a silica-like structure with part of the silicon atoms isomorphously replaced by aluminum (*18, 19*).

It appears that silica gel and silica–alumina cracking catalyst are closely related materials, differing only in aluminum content. Hence, we conclude that on silica gel the same active sites are present as on silica–alumina with less than 15% alumina, and that the butene isomerization proceeds via the same mechanism. In agreement with this conclusion, extrapolation of the data given by Hightower and Hall (*20*) for butene isomerization on silica–alumina yields product distributions and activation energies very close to those observed by us on silica gel. Moreover, in the isomerization of *cis*-2-butene at 400 K, the Ketjen silica and a commercial cracking catalyst (Ketjen LA-C-25; 13 wt% Al_2O_3) showed the same product selectivity and about the same activity per aluminum atom (*21*).

Our calcination experiments show that surface hydroxyls are involved in the isomerization of butene. Between 775 and 1075 K, however, only 28% of the hydroxyl groups on the silica gel surface are removed, whereas the catalytic activity decreases by about 90%. All hydroxyl groups are readily accessible, because even a large molecule such as hexamethyldisilazane has been found to react easily (*6*). During the heat treatment no change on the surface other than silanol removal occurs, so that we must assume the existence of certain easily condensable, very active hydroxyl groups.

The hydroxyl concentrations in Table 2 differ considerably from the values that can be calculated from the water content of silica–alumina reported by Gerberich and Hall (*16*) and by Finch and Clark (*17*). Probably, the water content given by these authors is not a quantitative measure for the surface hydroxyl concentration, because their experimental methods introduce a number of systematic errors: (a) deuterium exchange with deuterium gas (*16*) has been reported to be complete only after several hours at 975 K (*12*); (b) soaking annealed silica in water (*17*) introduces internal hydroxyls not accessible for surface reactions (*7*); (c) firing silica gel at 1475 K (*17*) does not eliminate all hydroxyl groups (*22*).

In a recent infrared study (*6, 7*) we showed that heating silica gel results in the exclusive removal of surface silanol pairs with a mutual hydrogen bridge:



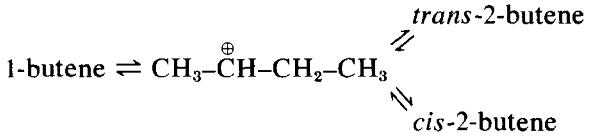
(5)

I

This condensation was nearly complete after calcination in air at 1075 K. The isolated, i.e., not hydrogen-bonded, silanols and silanediols remained intact under the applied conditions (*6*). Physisorption of water vapor was found to occur mainly on the silanol pairs from Eq. (5), whereas the isolated silanols hardly participated in water adsorption. We attributed the high affinity of the silanol pairs toward polar species, e.g., water vapor, to an enhanced dipole strength in species **I** relative to the non-hydrogen-bridged hydroxyls (*7*).

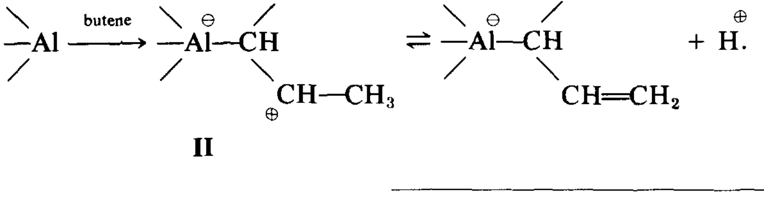
Combination of the results of the infrared study with the present work indicates a direct relationship between the catalytic activity and the presence of hydrogen-bridged silanol pairs (**I**).

For the isomerization of linear butenes on silica–alumina an *s*-butyl carbenium-ion mechanism is widely accepted (*20*):



$$\text{1-butene} \rightleftharpoons CH_3\text{-}\overset{\oplus}{C}H\text{-}CH_2\text{-}CH_3 \begin{matrix} \rightleftharpoons \textit{trans}\text{-2-butene} \\ \rightleftharpoons \textit{cis}\text{-2-butene} \end{matrix} \qquad (6)$$

It has been found, however, that the hydroxyl groups on the catalyst surface are not the source of the protons necessary for the formation of the carbenium-ion intermediate in Eq. (6). Actually, the proton donor was identified as an organic residue, probably monomeric or oligomeric butene chemisorbed on exposed aluminum ions (*5, 17, 23, 24*). This can be depicted as



(7)

II

Still, the degree of surface hydroxylation strongly affects the activity of silica gel and silica–alumina.

This apparent contradiction can be reconciled by assuming that the butene molecules to be isomerized are not readily physisorbed on the organic residue, and that the surface silanols are needed to make the gas-phase butene attainable for proton exchange. The first step in the isomerization, then, will be adsorption of reactant on a silanol pair (**I**), and the second step acceptance of a proton from a neighboring butene unit chemisorbed on tricoordinated aluminum (**II**). The carbenium ion thus formed might be stabilized by coordination to the negative side of the silanol-pair dipole **I**. In the third step, a proton is donated back to the organic residue and finally, in the fourth step, the reaction product desorbs from the silanol pair.

Heightening the calcination temperature of silica gel affects not only the catalytic activity, but also the activation energy. For example, in the case of 1-butene isomerization, we found E_a to increase from 33 to 66 kJ mol^{-1} when the calcination temperature was raised from 775 to 1075 K (Table 2). An explanation for this phenomenon can be derived from the following considerations. On heating, the silanol pairs with the lowest O–O distance and the highest interaction will condense first (*7*). This means that the remaining hydroxyls have a lower average dipole strength and, therefore, less affinity toward polar and polarizable species. The apparent activation energy, E_a, will depend on the strength of the butene–silanol pair interaction. When the silica is calcined at higher temperatures, the average adsorptive strength of the surface hydroxyl groups decreases and, hence, E_a will increase. The decrease in adsorptive strength should be accompanied by a decrease in the entropy of activation, because the mobility of the adsorbed molecules increases. This means that in the Arrhenius equation:

$$k = A \exp(-E_a/RT), \tag{8}$$

the preexponential factor A will become larger with rising calcination temperature. It can be calculated from the data in Table 2 that this does indeed occur. The estimated maximum change in the entropy of activation is about 30 J mol^{-1} K^{-1} on going from a calcination temperature of 775 to 1075 K.

Silylation

Silylating silica gel strongly suppresses the activity for the isomerization of *trans*-2-butene (Fig. 1). Because HMDS can react in more than one way with the catalyst surface, we will now discuss some conceivable models for this poisoning action.

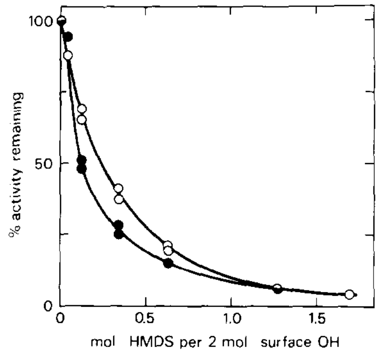


FIG. 1. Isomerization of *trans*-2-butene on silylated silica gel at 700 K and 2.0 × 10^5 Pa: (○) Davison; (●) Rhône-Progil.

(a) In the simplest model, HMDS reacts exclusively with surface hydroxyl groups. All hydroxyls are assumed to have the same affinity toward HMDS. Because certain surface silanols appear to be involved in the isomerization, the catalyst activity is expected to be inversely proportional to the amount of HMDS added. The surface silanols are silylated almost quantitatively (*6*), so that the activity of the silicas after treatment with excess HMDS will amount to only a few percent of the initial value.

(b) A much higher activity after exhaustive silylation is expected when the hydroxyls involved in the isomerization are not attacked by HMDS. From the surface hydroxyl concentration (Table 2) and the dimensions of the trimethylsilyl group (*11*) we calculate that 30–40% of the catalyst surface remains uncovered after silylation. Because in this case the only effect of HMDS treatment is surface screening, the activity of the silicas will decrease by 60–70% after treatment with excess HMDS.

(c) The above two models apply to situations where reaction of HMDS with Lewis acid sites, i.e., surface aluminum ions, can be neglected. However, if HMDS is rapidly and irreversibly adsorbed on Lewis acid sites, the catalyst activity will fall to zero on addition of very small amounts of

HMDS because of the low aluminum concentration in our samples, i.e., less than 0.01 times n(OH). A similar effect will be observed if aluminum-induced, strongly Brønsted-acidic hydroxyls are present on the catalyst surface, as has been frequently suggested (*8*).

(d) If the reaction of HMDS with the Lewis acid sites is slow, e.g., because of a low rate constant or mass-transfer limitations, an activity drop less steep than in model c is predicted. Moreover, the catalyst activity will show a further decline on prolonged exposure to HMDS.

From the shape of the curves in Fig. 1 it follows that models b and c cannot be correct. We found the poisoning effect to be independent of the time of reaction with HMDS, so that model d can be rejected as well. From the models under consideration, model a obviously offers the best description of the poisoning process. The experiments demonstrate that aluminum-induced, strongly Brønsted-acidic hydroxyls are not involved in the isomerization, and probably not even present on catalysts activated at 750 K. The latter would be in accordance with the explanation given by Basila *et al.* (*25*) for their pyridine adsorption experiments on silica–alumina.

Model a predicts a linear relationship between the isomerization rate and the amount of HMDS added. The observed nonlinearity (Fig. 1) can be explained from the heterogeneity of the catalyst surface: because the activity of the silanol pairs (**I**) is thought to be proportional to their affinity toward polar and polarizable species, HMDS will react more readily with the more active silanol pairs, resulting in a concave poisoning curve. The residual activity after exhaustive silylation may be ascribed to hydroxyls in narrow pores that cannot be reached by the large HMDS molecules.

Treating the silicas with excess ammonia lowered the catalytic activity to 63–68% of the initial value. This is in agreement with the findings of Finch and Clark (*17*), who observed that saturating silica–alumina, calcined at 773 K, with gaseous ammonia at 673 K lowered the activity for butene isomerization by about one-third. The 673 K ammonia treatment in their experiments did not appreciably lower the amount of chemisorbed butene on the catalyst surface. It appears, therefore, that ammonia blocks surface hydroxyl groups, probably through amine formation (*26*). The effectiveness of ammonia, however, is much less than that of HMDS: the ammonia treatment lowered the activity of the silicas to only 63–68%, whereas half as much HMDS caused a decrease to about 5% (Fig. 1).

From the foregoing, we conclude that hexamethyldisilazane is an irreversible, specific poison for Brønsted-acidic hydroxyls under the applied conditions. We observed no effects that could be ascribed to poisoning of Lewis acid sites.

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