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Surface Area Stability of Aluminas

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Measurements were made of the surface area of aluminas steamed for various times up to 1000 h, at constant temperature and water partial pressure. The data were fitted to the integrated form of the equation $-dS/dt = kS^n$, as a smoothing operation; this accounts for the strong effect of area on the rate of area loss. The derived constants, n and k, were used to calculate the rate of area loss at any given area level. This rate is proportional to water partial pressure, with an apparent activation energy of 40.4 kcal/mol. Under a given set of conditions, the rate of area loss increases as the content of amorphous alumina in the precursor increases. Several elements (Ba, Sr, La, Sn, SiO_2, PO_4) added to alumina markedly increase area stability. Pore distribution measurements show that small pores become enlarged as area decreases by the same factor as larger pores.

A model of the process of surface area loss is proposed which can explain the effects of surface area, water partial pressure, and stabilizing additives, involving condensation between hydroxyls on adjacent particles.

INTRODUCTION

Alumina, chiefly in the form of γ-alumina but often η-alumina, is widely used as a support for catalysts, such as those used in reforming processes for increasing octane number of gasoline components, or for hydrotreating processes to remove sulfur, nitrogen, and other undesirable impurities from petroleum fractions.

In the case of reforming catalysts, coking, deposition of contaminants, and loss of promoter dispersion are the chief causes of loss of catalyst activity (*1*). Surface area of the support does not directly affect reforming activity, other factors being equal (*2*), but high surface area is desirable to aid in maintenance of dispersion of the metallic promoter(s) and to facilitate retention of the chloride necessary for catalytic acidity. It follows that the alumina must not only start with high area, but must retain as much area as possible during the many months or years of service typical of a given catalyst charge.

It is common in many laboratories to compare surface area stabilities of various catalysts or supports by measuring one surface area for each sample after treatment under one set of time, temperature, and steam partial pressure conditions. Although a test procedure of this type is useful as a screening device, it suffers from the drawback that an unknown amount of area loss occurs during bring-up because of self-steaming, so that the time and temperature of treatment are not well defined. Also, such single-point measurements are not very useful in gaining knowledge about the area loss process.

In this work, runs were made at constant temperature and steam partial pressure for periods as long as 1000 h. As many as 10 samples were removed, at zero time and at other strategic times, for surface area measurements. By this procedure, rates of area loss could be calculated as functions of temperature, water partial pressure, alumina type, and the concentration of inorganic stabilizing additives.

Extensive data of this type, for runs of comparable length, were reported in 1957 for silica–alumina by Schlaffer, Morgan,

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and Wilson (*3*) (SMW), and in 1965 by Schlaffer, Adams, and Wilson (*4*) (SAW) for silica and for alumina. They showed that the area decline rate could be expressed by the empirical equation

$$\frac{-1}{S_0} \cdot \frac{dS}{dt} = k(S/S_0)^n \qquad (1)$$

where S is the area at time t, S_0 is the area at time 0, k is the proportionality constant, and n is an exponent.

The integrated form is

$$\ln(S/S_0) = -\frac{\ln(1 + k(n-1)t)}{(n-1)} \qquad (2)$$

SMW made their measurements over a wide range of temperatures (751 to 1223 K) and up to 7 atm of steam (1 atm = 1.013×10^5 N/m^2). For silica–alumina, their values of n ranged from 3.5 under the most severe conditions to 11.4 under the mildest condition. They could account for values of n as high as 4 by various transport processes, but postulated that the higher values must be due to the existence of a vapor-phase transport process involving the formation of a volatile species such as $Si(OH)_4$.

More recently, Hashimoto and Masuda (*5*) made similar measurements with silica–alumina, at 751 K to 1136 K and 0.1 to 7 atm steam, and observed values of n similar to those of SMW when the data were fitted to the form of Eq. (2).

In the present work, comparisons were made by calculating rates of area loss at a given area level, and under given conditions of temperature and steam partial pressure, using Eq. (1), and the values of n and of k determined by regression.

EXPERIMENTAL

Apparatus

The catalyst was contained on a 5-cm fritted disk in a Pyrex or Vycor reactor, fitted with a thermowell extending from the top of the reactor to the fritted disk. The moisturized air was brought upward to the fritted disk through 1 cm tubing coiled several times to provide preheat. The reactor ensemble was held in a furnace having three heater zones, each with its own temperature controller.

For the runs with Alumina I the air was humidified by sparging through a flask of water whose temperature was controlled by a heating mantle. The air was then cooled, to produce a saturated air stream, and passed through a plug of glass wool to remove spray. For the runs in which temperature and moisture level were varied, the cooling was accomplished by a glass vessel containing glass beads and a bare thermometer whose reading was taken as the dew point. For the other runs, the second vessel was a flask of water held at the desired dew point temperature, a few degrees below that of the first flask. Vapor-pressure tables were used to convert dew points to water partial pressures. Periodic checks made by collecting and measuring effluent water in a dry-ice trap showed that the water partial pressures calculated from dew points were accurate to within a few percent.

Runs at 0.004–0.005 atm water were made by immersing the sparger in ice water. Dew points were measured on the air leaving the catalyst bed by means of an Alnor dewpointer.

Procedures

Flow rates of about 7.9 cm^3/s of air and the temperatures were established overnight prior to the start of each run. To start a run, 30–35 g of catalyst or alumina was dropped in from the open top. After about one-half hour, when the desired temperature had been reattained, a gram or so of sample was removed by suction; this was taken to be the zero-time sample. Subsequent samples were taken in the same way. Frequent readings of catalyst and dew-point temperatures were used to determine weighted averages for each run. BET surface areas were corrected to ignited weight (1273 K) bases.

The relative area stabilities of different aluminas and the effects of stabilizing additives were determined at conditions chosen to be as severe as possible without exceeding temperatures and water partial pressures likely to be encountered in actual catalytic service: 866 K and 0.095 atm of water. The latter is equivalent to a dew point of 318 K.

Pore distributions by nitrogen desorption were obtained for selected samples at various stages of deactivation. The procedure was the same as that described in previous publications from this laboratory (*6, 7*), except that the calculations were continued until the increments became negative and were followed by normalizations to the total pore volumes at saturation.

Aluminas and Catalysts

Alumina I is a 0.6% Pt/Alumina-reforming catalyst extrudate, manufactured by Engelhard Corp.; it is no longer available. Its alumina precursor was largely a mixture of the three alumina trihydrates, with about 25% pseudo-boehmite plus amorphous alumina, as determined by quantitative XRD analyses. Its initial BET area was 446 m^2/g.

Alumina II was derived from an amorphous alumina prepared by ammonia precipitation of an aluminum nitrate solution, followed by washing and drying and impregnating with 0.6% Pt. XRD analysis of the calcined granules showed that 60% had been converted to γ-alumina.

Different portions of Alumina III were obtained from Engelhard Corp. as a dried powder and as a finished extruded catalyst. Typical XRD analyses of this type of alumina showed 52% boehmite, with a crystallite size of 5.9 nm. All samples were tested after forming into 0.16-cm extrudates and calcination in air, generally at 783 K.

Alumina IV was obtained from Conoco Co. as a dried powder, designated Catapal, containing 82% boehmite with a crystallite size of 4.5 nm. The preparations also were extruded and calcined.

Alumina V was prepared by slow precipitation from an aluminum chloride–urea solution to form a product having 84% of boehmite with a crystallite size of 10.5 nm (*7*). It was tested in granular form, after calcination at 755 K.

The stabilizers were added to the alumina–water slurries prior to extrusion. Barium and strontium were added as the nitrates, tin as the chloride, phosphorus as phosphoric acid. Silica was added either as tetraethyl orthosilicate (TEOS) or as Ludox, a colloidal Na-free product obtained from DuPont Corp.

RESULTS

Effects of Temperature and Moisture

Four of the runs with Alumina I are plotted in Fig. 1. The data for each run were fitted to Eq. (2), to obtain values of n and k, by means of a nonlinear regression program. The values of n and of k were used to draw the lines in the figure. Note that the log–log plots become linear after the first few hours, when $k(n - 1)t \gg 1$; this was true for all of the runs. The derived values of n and k for Alumina I are in Table 1.

All of the values of n derived from the measurements of area as a function of time at a given temperature and moisture level are too high to have physical significance; the fact of a fit to a log–log relationship after a few hours is not sufficient evidence to validate Eq. (1). Nevertheless, it is undoubtedly true that the rate of area loss has a strong dependence on area level.

A more useful method of treating the data is to calculate the rate of area loss at a given area ($R = -dS/dt$), using Eq. (1) and the constants, n and k. This has the effect of smoothing the data, to obtain more reliable values of rate. When the data at small values of t are not sufficient to permit determination of k, R can be calculated from the linear slope and Eq. (3), after interpolation to find the value of t corresponding to a given S.

$$-\text{slope} = \frac{d \log S}{d \log t} = \frac{t\,dS}{S\,dt} = \frac{t \cdot R}{S}. \qquad (3)$$

Rates of area loss at 250 m^2/g calculated from Eq. (1) are in Table 1.

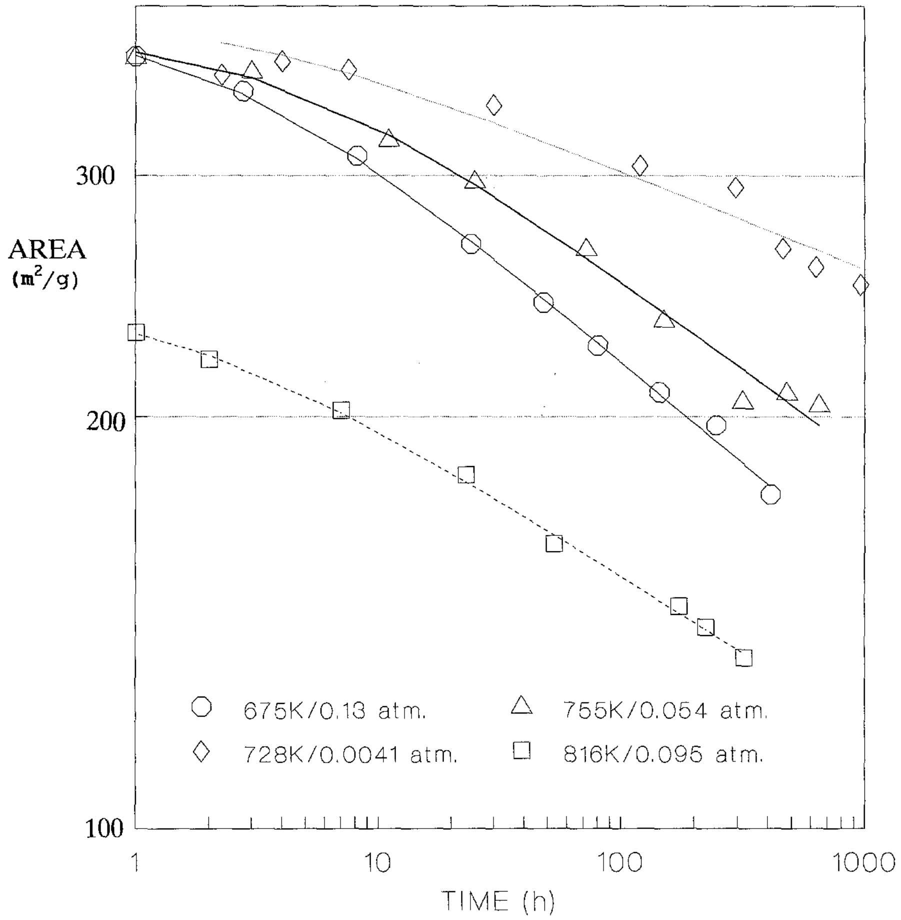

FIG. 1. Area loss by Alumina I. (Temperature (K) and water (atm) as shown.)

TABLE 1

Area Loss by Alumina I

Temp. (K)	Atm H_2O	Zero-time area (m^2/g)	Derived constants		Rate of area loss ($m^2/g/h$)[a]
			n	*k*	
675	0.127	408	9.96	0.0122	0.048
728	0.0041	392	14.75	0.0255	0.013
726	0.133	398	8.88	0.0389	0.25
755	0.054	380	8.68	0.0308	0.31
756	0.133	389	7.68	0.0678	0.88
784	0.0050	384	13.72	0.103	0.11
781	0.019	321	8.94	0.0107	0.37
785	0.037	371	10.46	0.119	0.71
811	0.078	352	9.31	0.199	2.10
866	0.095	242	9.87	0.067	22.4

[a] At 250 m^2/g.

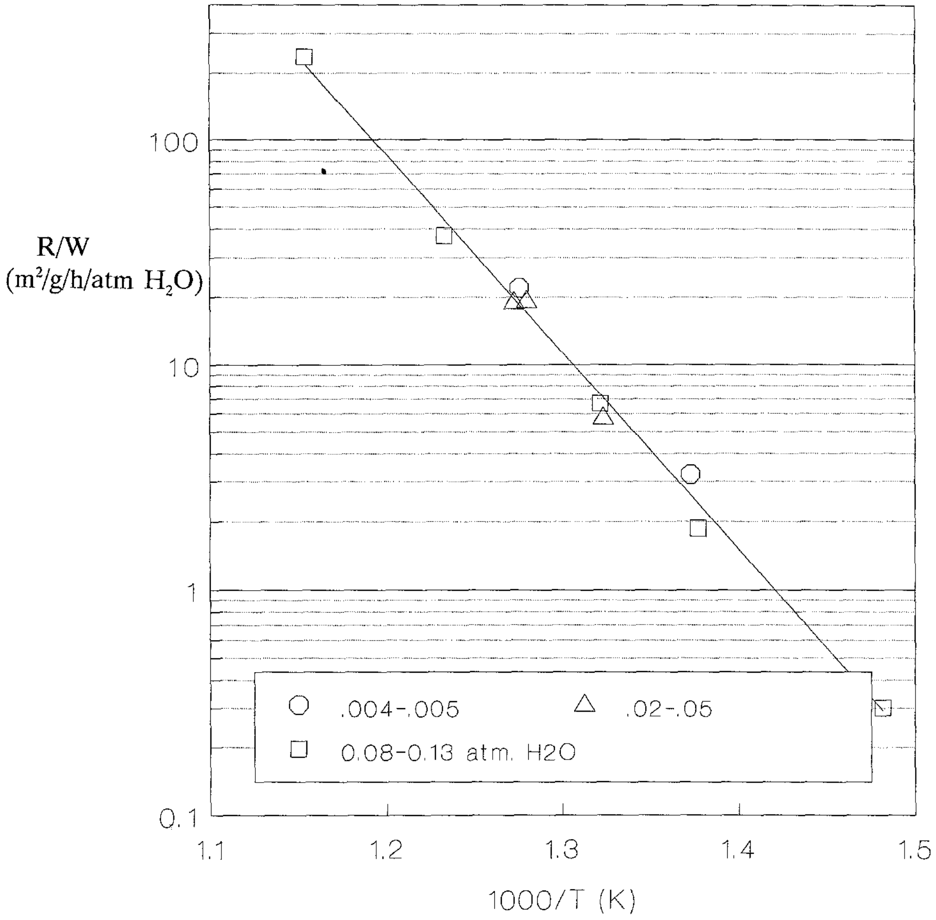

FIG. 2. Rate of area loss by Alumina I at 250 m^2/g.

SMW (3) found k for silica–alumina at constant temperature to be proportional to the second power of water partial pressure. In the present work with alumina, the rate of area loss at a given area, and at a given temperature, is found to be proportional to the first power of water partial pressure. No separate correlation could be found between n or k and temperature or water partial pressure.

As shown in Fig. 2, an Arrhenius-type plot of log (R/W) against reciprocal temperature fits the data of Table 1 very well, where $R = -dS/dt$ at 250 m^2/g/h and W = water partial pressure (atm). The slope is equivalent to an activation energy of 40.4 kcal/mol.

The rate of surface area loss therefore depends on temperature by an Arrhenius-type relationship, is proportional to water partial pressure, and is strongly dependent on the level of surface area itself. The observation of a different order in water for alumina sintering than for silica–alumina is probably related to the fact that silica can be transported in the vapor phase in the presence of steam at elevated temperatures (3), but alumina cannot.

Comparisons of Aluminas

Typical run data for three aluminas, under the test conditions of 866 K and 0.095 atm water, are shown in Fig. 3. The regressed constants, n and k, for these and other runs

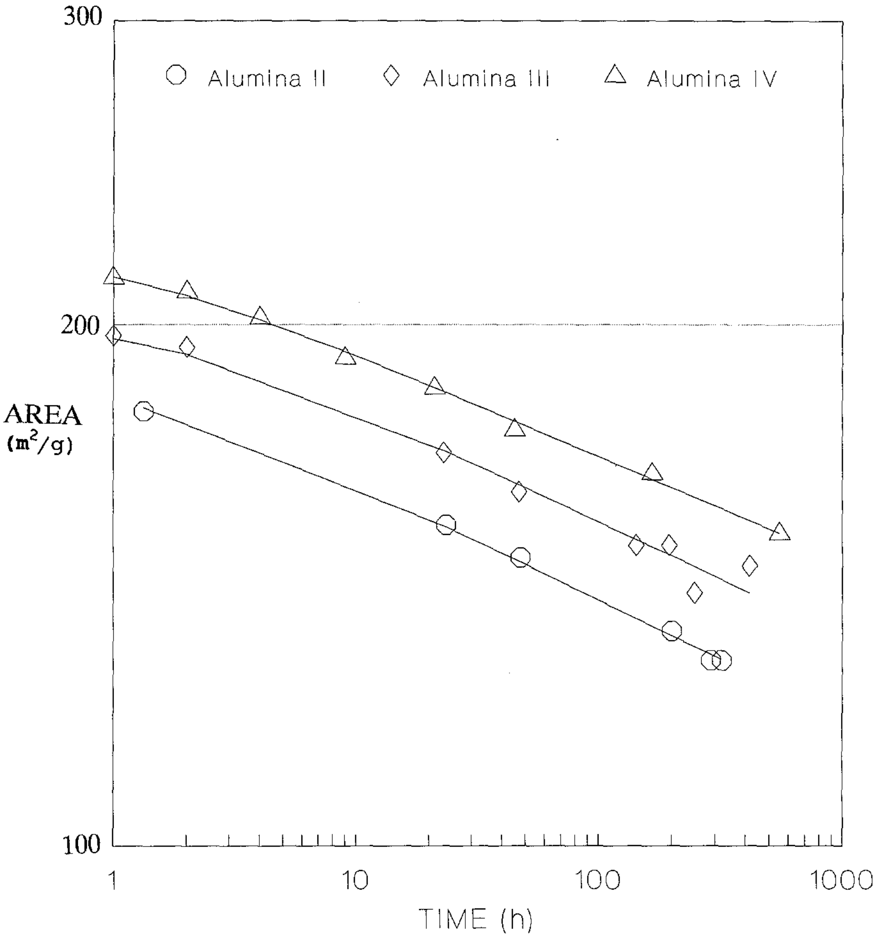

FIG. 3. Area loss by aluminas (866 K/0.095 atm water).

are in Table 2, with area-loss rates from Eq. (1) at 200 m^2/g. Note that for the four runs with Alumina III the values of R are more reproducible (estimated SD of 5.4% of the average) than the values of n or of k.

The nine-fold difference in area-loss rate for Alumina I at 250 m^2/g (Table 1) and at 200 m^2/g (Table 2) is the factor of $(250/200)^{9.87}$. The exponent 9.87 is near the average value of n for all of the runs with Alumina I.

Aluminas II–IV differ widely in area stability, an observation which appears related to the degree of crystallinity of the precursors (or, the amount of amorphous alumina present), as indicated by the following:

	% Amorphous	Ave. Area-Loss Rate (at 200 m^2/g/h)
II	100	29.1
III	48	6.8
IV	18	2.0

Alumina I is comparable to Alumina IV in terms of stability and also crystallinity, although the crystalline forms are not the same. This strongly suggests that area stability can be improved by reducing the percentage of poorly crystallized alumina in a given product.

On the other hand, although Alumina V was derived from a highly crystalline pre-

TABLE 2

Area Loss by Aluminas

Run conditions		Area (m^2/g)		Derived constants		Area-loss rate[a] (m^2/g/h)
Temp. (K)	atm H_2O	Initial[b]	Zero-time	n	k	
			Alumina I			
866	0.095	446	242	9.87	0.0665	2.48
			Alumina II			
866	0.095	235	189	15.7	0.0636	29.1
			Alumina III			
866	0.095	258[c]	203	16.0	0.0425	6.84
866	0.099	258[b]	217	18.1	0.151	7.16
866	0.095	275	203	16.1	0.0395	6.31
866	0.100	228[b]	214	18.7	0.114	6.58
			Alumina IV			
866	0.103	268[d]	223	17.6	0.0677	2.06
866	0.097	238	216	19.2	0.0565	2.73
866	0.095	314[c]	222	16.3	0.0333	1.35
			Alumina V			
866	0.097	261	240	10.4	0.798	28.0

[a] At 0.095 atm water and 200 m^2/g.
[b] As received.
[c] A commercial catalyst, with 0.35% Pt/0.35% Re.
[d] Contains 0.35% Pt/0.35% Re.

cursor, its area-loss rate is very close to that of the amorphous Alumina II, rather than to that of Alumina IV. This difference is probably related to its relatively large crystallite size, so that comparisons on the basis of degree of crystallinity alone are not valid. When crystallites exceed about 10 nm, slit-shaped pores resulting from the dehydration process become important (*8*).

Effects of Stabilizers

Several investigators have shown that addition of foreign ions to alumina will reduce the loss of surface area upon dry calcination at an elevated temperature. For example, when Levy and Bauer (*9*) impregnated various portions of an amorphous alumina with Li, K, or Mg, the surface areas after 873 K treatment increased with increasing stabilizer content, up to about 2–4 mol%, then decreased; the apparent XRD crystallinity also increased. Activation energies of 2–5 kcal/mol were obtained from similar data at higher temperatures. Parekh and Weller (*10*) found marked stabilization against area loss by impregnation of Co/Mo/alumina with 2% zirconia. On the other hand, 10 mol% of Li, Na, and K caused decreases in area of several supports, including alumina, when heated above 873 K, according to Perrichon and Durupty (*11*).

Lanthanum oxide at a concentration of about 1 mol% increased the area of an alumina after calcination at 873–1373 K; higher concentrations were not of much further value, according to Schaper *et al.* (*12*). Activation energies of 53–67 kcal/mol were independent of dopant. In another paper from the same laboratory (*13*), surface areas after treatments at 1113 K in 12 atm of steam increased steadily up to at least 5 mol% La_2O_3. In either case, $LaAlO_3$ was observed by X-ray diffraction in all La-containing sintered samples.

Several patents have claimed various metallic additives to stabilize aluminas used in catalysts for removal of noxious gases from engine exhausts (*14–16*); no surface area data were reported.

Group 2A oxides impregnated with Ir on alumina were found to inhibit sintering of the dispersed Ir when present in excess of the concentration of acid sites of the alumina (*17*).

Murrell and Dispenziere (*18*) observed that the addition of 5% silica to boehmite alumina by reaction with TEOS led to marked stabilization against loss of surface area by calcination at 1223 K. In another paper from the same group (*19*), it was shown that 2–5% silica (derived from Ludox colloidal silica) if dispersed upon the surface of an alumina caused less area loss when steamed at 1143 K.

In the present work various concentrations of various inorganic additives on Aluminas III and IV were tested under the standard hydrothermal sintering conditions. Some typical plots are in Figs. 4 and 5; as above, the lines were drawn using Eq. (2) and the values of n and k obtained by regression. The full set of rate of area losses at 200 m^2/g are in Tables 3 and 4 and are plotted in Figs. 6 and 7 against additive concentration.

It is clear from Fig. 6 that increasing the concentration of phosphorus, silica, barium, strontium or tin on Alumina III increases area stability, at least up to about 700 μmol/g. The stabilization is similar at similar molar concentrations. Silica appears to be somewhat superior to the others at low concentrations.

Similar plots in Fig. 7 show similar effects for tin, phosphorus, and silica (added as TEOS) on Alumina IV. However, silica added as colloidal silica is much less effective in improving area stability. This difference appears to be due to the lack of complete interaction between the Ludox colloidal silica and the alumina surface. The mean particle size of the original Ludox was close to 10 nm, whereas TEOS interacts molecularly with surface hydroxyls of alumina.

Differential infrared spectra have in fact verified this hypothesis. The spectra of the silica were obtained with a Perkin–Elmer 580B spectrometer, using the KBr disk technique, by subtracting the spectrum of the silica-free catalyst from those of the silica-containing catalysts. In all of the Ludox-containing catalysts there were strong peaks at 1120–1125 cm^{-1}, corresponding to Si–O–Si bending, much like the spectrum of the Ludox itself after drying in the absence of alumina, or of a silica gel. On the other hand, the spectra of those catalysts prepared using TEOS had either no clearly defined peak or a broad 1000 cm^{-1} peak due to a Si–O–Al configuration, the result of an interaction of silica with the alumina.

Pore Distribution Changes

All of the pore distribution data for Alumina IV were well represented by log-normal distributions: straight lines on log-probability paper were observed at least up to 95% of total pore volumes, and usually up to 98%. On the other hand, similar plots for Alumina III produced two straight lines on log-probability paper, indicative of two populations. These probably represent pores from boehmite and pores from amorphous alumina. The dual populations were not apparent in the usual cumulative or differential pore distribution plots.

The differential pore distribution plots for Alumina IV + 1% Ludox (fresh, after 1 h and after 296 h at 866 K and 0.095 atm water) are shown in Fig. 8. Clearly, the shapes of each plot are the same, but shifted to larger pore radii as surface area is lost. This observation can best be expressed by use of the geometric standard deviations derived from the slopes of the log-probability plots (*20*). The data for Alumina IV, with and without additives, fresh and deactivated, are listed in Table 5.

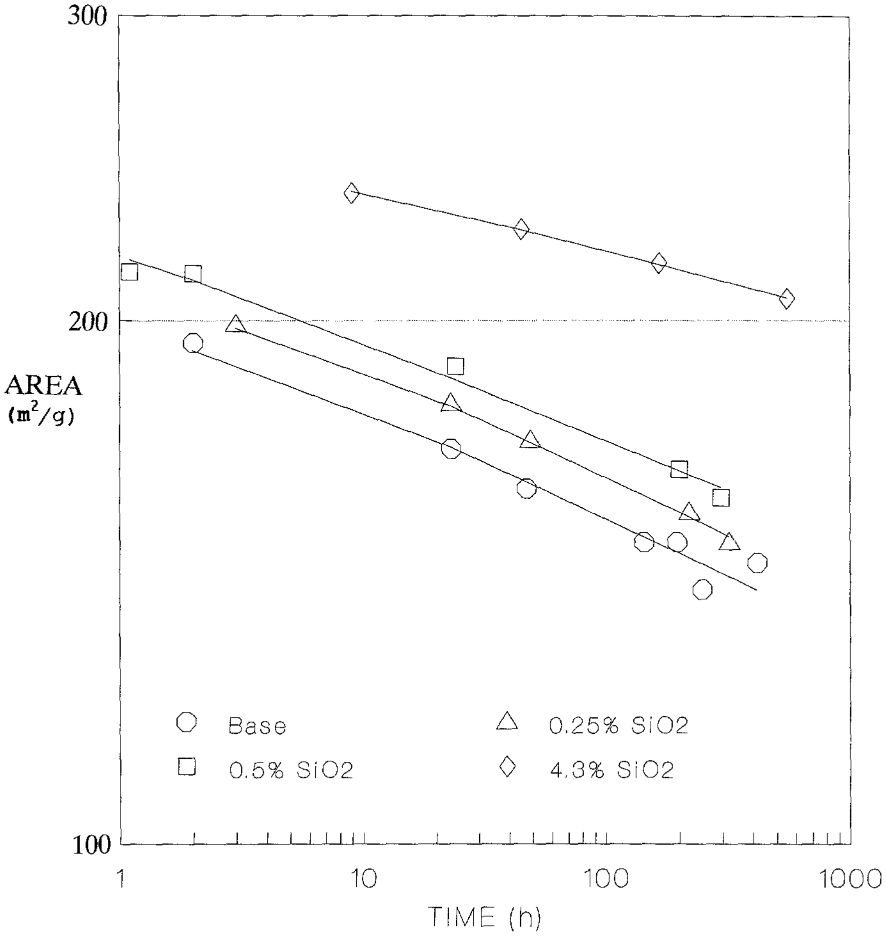

FIG. 4. Area loss by Alumina III + silica (TEOS) (866 K/0.095 atm water).

The pore volumes and the geometric standard deviations are not identical for each fresh sample, since each was the product of a separate extrusion. However, as surface area of a given preparation decreases, and its median pore radius increases, the geometric standard deviations remain about the same for each sample. As area is lost and pores are enlarged, therefore, pores of all sizes increase by about the same factor. This is a clear indication that pore size differences have no effect on hydrothermal area stability.

The pore volumes also remain unchanged as alumina area is lost, in agreement with the SAW findings (*4*). In contrast, loss of pore volume was observed by SMW for silica–alumina (*3*).

A MODEL OF HYDROTHERMAL SINTERING

Previous Models

In models of sintering of highly dispersed metals supported on oxides (*21*), particle growth can occur by movement of single atoms or of small particles across the oxide surface. Sintering of the support itself cannot involve that mechanism.

SMW (*3*) envisaged silica–alumina to consist of small impervious particles bonded together in aggregates by fillets of the same material. The surface of these particles is

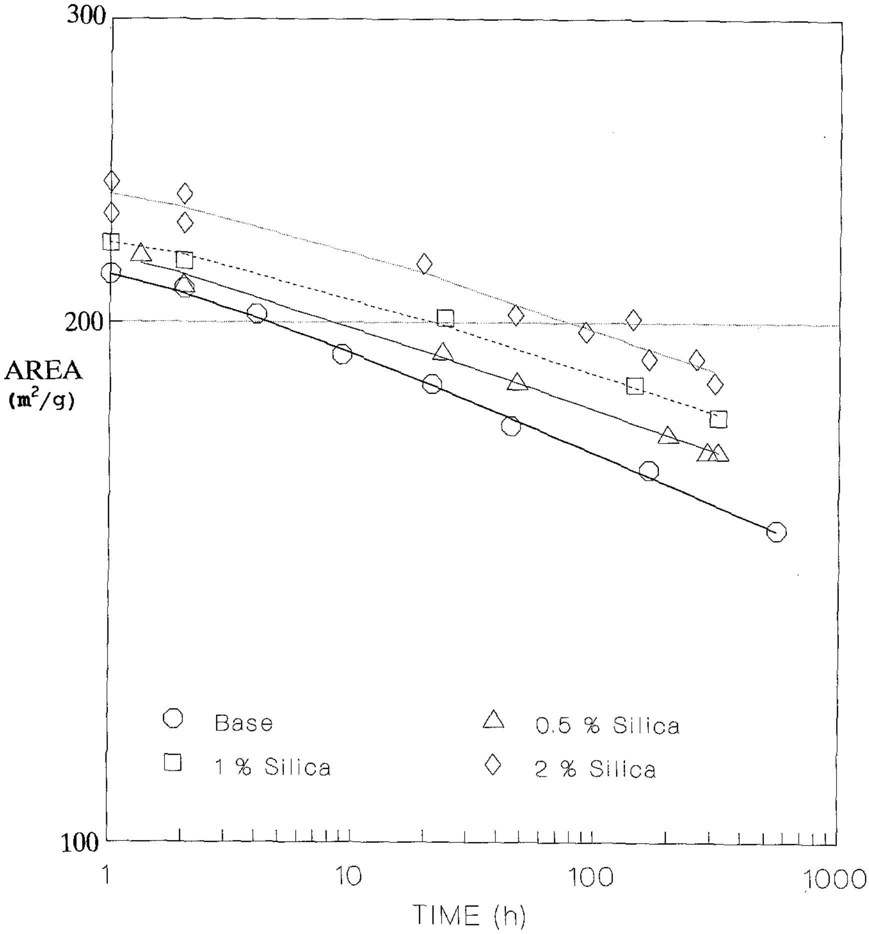

FIG. 5. Area loss by Alumina IV + silica (TEOS) (866 K/0.095 atm water).

the surface area, and the pore volume is the space between particles. In their model, surface area is lost by migration of material from smaller to larger particles. Transport occurs by surface or volume diffusion, as well as by vapor-phase for the silica.

Alumina particles are not likely to have the pseudospherical shapes of silica–alumina, but will nevertheless be bonded together as aggregates; their shapes may be regular shapes if, for example, the precursors contained alumina trihydrates (*4*). Again, particle growth occurs by gross transport of alumina, but no explanation of the role of water was proposed by SAW.

Levy and Bauer (*9*) ascribed a diffusion mechanism to the hydrothermal sintering of alumina. Their activation energy, 4.1 kcal/mol for pure alumina, is consistent with a solid-state transport mechanism. Diffusion alone, however, will not account for the water pressure dependence. Schaper *et al.* (*12*) also concluded that sintering of alumina in air at 1073–1373 K proceeds by surface diffusion, with an activation energy of 58 kcal/mol; again, the role of water was not explained.

The model of Hashimoto and Masuda (*5*) for steam-sintering of silica–alumina considers transfers of solid material at the points of contact between 5-nm spheres to

TABLE 3

Area Loss by Alumina III + Stabilizers

Stabilizer	Area (m^2/g)		Derived constants		Area-loss rate[a] ($m^2/g/h$)
	Initial[b]	Zero-time	n	k	
None (four run ave.)					
(cf. Table 2)	255	209	17.2	0.087	6.83
0.5% Strontium	274	228	20.0	0.075	1.22
2.0% Strontium	271	237	28.8	0.079	0.138
3.0% Barium	250[c]	228	26.7	—	0.235
0.25% Silica[d]	270[b]	209	15.8	0.0275	2.87
0.5% Silica[d]	280[b]	235	18.4	0.155	1.93
4.3% Silica[d]	267[b]	249	28.0	0.0107	0.0053
0.05% Phosphorus	279[b]	223	16.3	0.082	3.05
0.5% Phosphorus	297[b]	252	18.0	0.136	0.513
2.0% Phosphorus	251[b]	226	41.5	0.018	0.0247
1.28% Lanthanum	291	247	18.3	—	0.98

[a] At 866 K, 0.095 atm water, 200 m^2/g.

[b] As received.

[c] Contains 0.6% Pt and 0.85% Re.

[d] Added as tetraethyl orthosilicate (TEOS).

TABLE 4

Area Loss by Alumina IV + Stabilizers[a]

Stabilizer	Area (m^2/g)		Derived constants		Area-loss rate[b] ($m^2/g/h$)
	Initial[c]	Zero-time	n	k	
None (three run ave.)					
(cf. Table 2)	—	220	17.7	0.0525	2.05
0.5% Phosphorus	309	240	17.9	0.0207	0.189
1.5% Tin[d]	281	225	26.9	0.0837	0.834
0.5% Silica[e]	292	229	21.3	0.0824	1.055
1% Silica[e]	298	228	22.5	0.0339	0.355
1% Silica[e]	286	234	18.3	0.0230	0.298
2% Silica[e]	307	241	22.0	0.0569	0.222
1% Silica[f]	291	231	21.9	0.126	1.238
1% Silica[f]	287	236	20.4	0.141	1.148
1% Silica[f]	287	233	19.9	0.109	1.201
2% Silica[f]	291	217	29.4	0.0183	0.386

[a] Silica-containing samples have 0.6% Pt/0.85% Re.

[b] At 866 K, 0.095 atm water, 200 m^2/g.

[c] As received.

[d] Contains 0.6% Pt.

[e] Added as tetraethyl orthosilicate (TEOS).

[f] Added as Ludox.

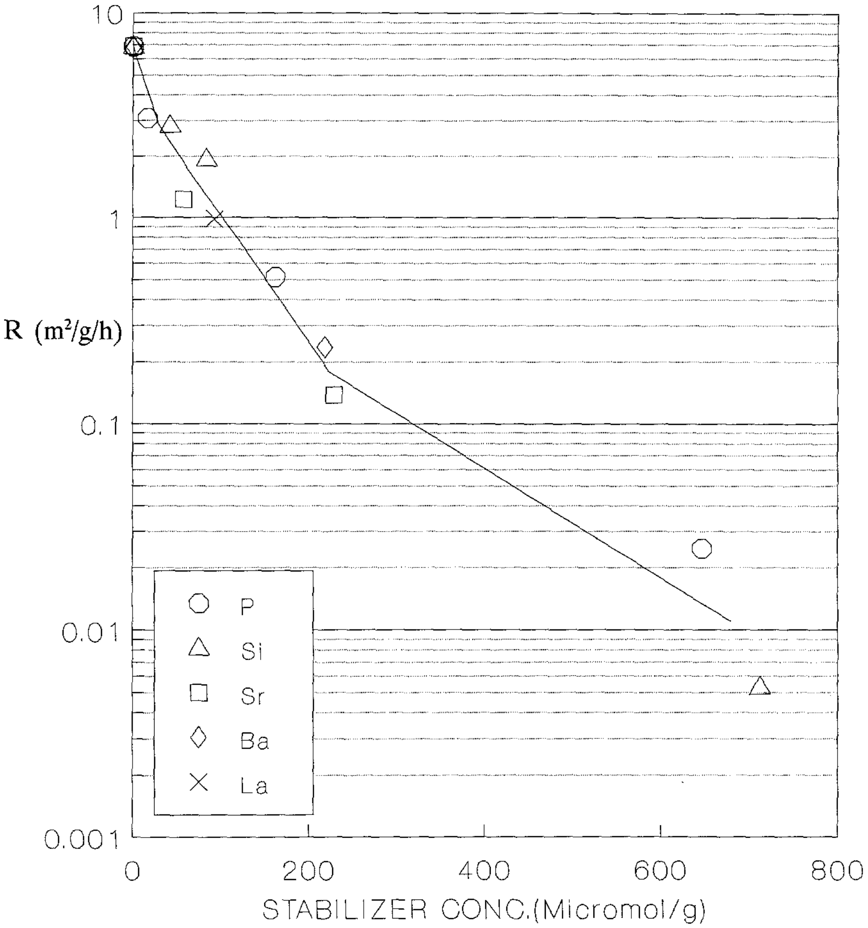

FIG. 6. Rate of area loss by Alumina III (866 K/0.095 atm water/200 m^2/g).

form "necks," a process which occurs by vapor transfer or surface diffusion. The rate data could be expressed as the sum of a sixth-power and an eighth-power dependence on area.

Proposed Model

Any model devised for the process of hydrothermal sintering of alumina must take into account the effects of surface area and of water partial pressure on the rate of loss of area.

The alumina consists of aggregates of ultimate particles of undetermined shape. For surface areas between 120 and 283 m^2/g in this work, equivalent spheres would have diameters of 6 to 14 nm. In order for the aggregates to have physical strength, each particle must be not only in contact with several others, but must be chemically bound to them by Al–O–Al bonds, in a three-dimensional network. If the number of contacts per particle is roughly constant, then the number per gram will increase as surface area increases, since there are more particles per gram.

It is proposed that particles growth (= loss of surface area) occurs by successive elimination of water from two hydroxyl groups residing on adjacent particles, close to an area of contact. This will result in new Al–O–Al bonds. Each such step can bring more hydroxyls into adjacency, with the possibility of more such condensations. A

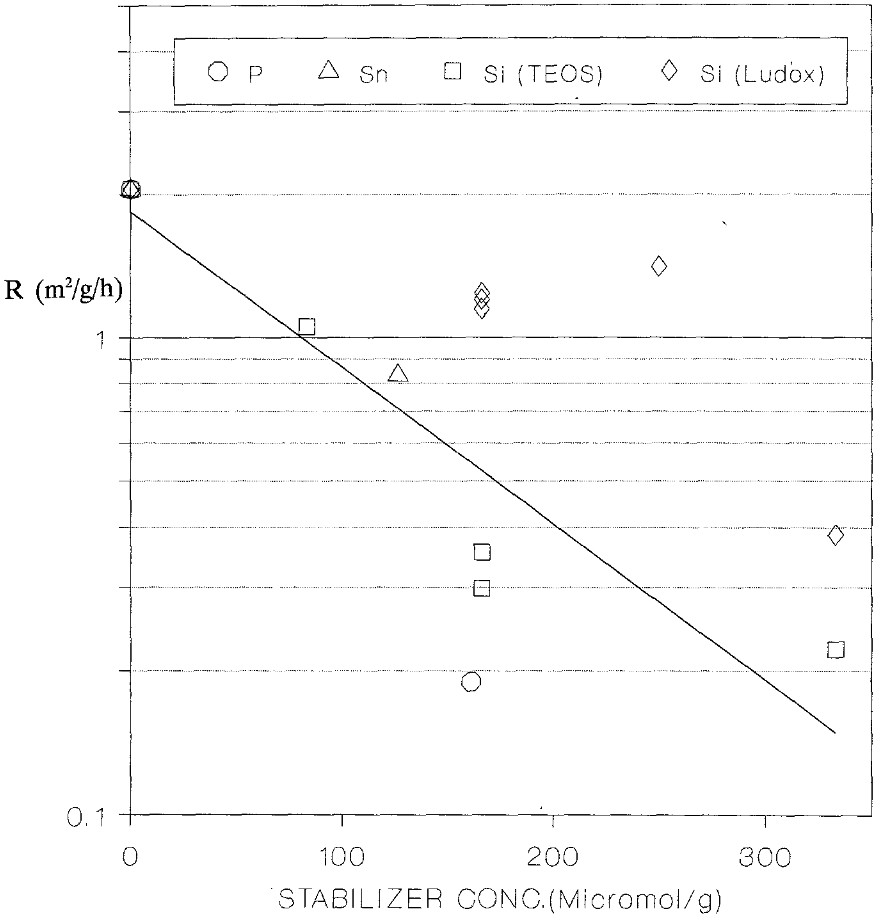

FIG. 7. Rate of area loss by Alumina IV (866 K/0.095 atm water/200 m^2/g).

diffusive process must follow condensations, to form "necks," and subsequent pore enlargement. In time, smaller particles become larger ones, with the overall structure intact; i.e., pore volume remains the same and pore radius increases in inverse proportion to surface area decreases.

This model accounts for the effect of surface area on rate of area loss by virtue of the fact that when area is high there are more points of contact for the processes of particle growth to occur.

The effect of the presence of amorphous alumina in the precursor is probably due to a different concentration of surface hydroxyls. There is no direct evidence of this, but catalytic differences between amorphous and quasi-crystalline aluminas have been observed (*22*).

The role of water is to maintain the surface concentration of hydroxyls. In the absence of vapor-phase water, the concentration of surface hydroxyls decreases with increasing temperature, to about 20% of a monolayer at 866 K, for example (*23*). As water partial pressure increases, partial rehydration of the surface will occur, to an undetermined extent, leading to increased rate of sintering.

The model can account for the effect of stabilizing elements if we can assume that they replace surface hydroxyls. Using Peri's (*23*) value for full coverage to be 6.25 molecules of water per square nanometer, 20% of a monolayer corresponds to 415 μmol

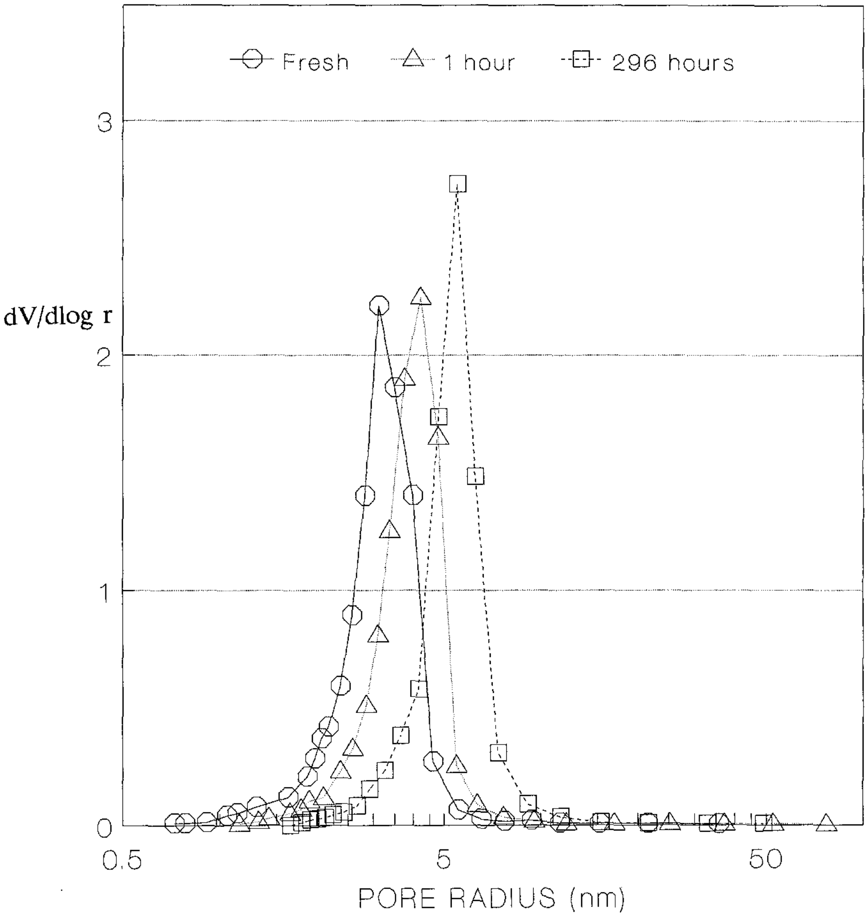

FIG. 8. Pore distributions (Alumina IV/1% Ludox + 866 K/0.095 atm water).

TABLE 5

Alumina IV Pore Distribution Data

Additive	Time (h)[b]	Area (m^2/g)	Total pore volume (cm^3/g)	Median pore radius (nm)	Sigma[a]
None	(Fresh)	214	0.586	4.4	0.079
None	24	180	0.567	5.7	0.063
None	319	154	0.569	6.9	0.084
0.6% Pt/0.85% Re	2	212	0.478	4.0	0.071
0.6% Pt/0.85% Re	220	163	0.493	5.3	0.058
1% S_iO_2 from Ludox	(Fresh)	283	0.486	3.2	0.078
1% S_iO_2 from Ludox	1	219	0.471	4.1	0.082
1% S_iO_2 from Ludox	296	169	0.463	5.4	0.086
1% S_iO_2 from TEOS	(Fresh)	298	0.470	3.4	0.108
1% S_iO_2 from TEOS	319	176	0.482	5.4	0.104

[a] Geometric standard deviation of log-normal pore distribution.

[b] At 866 K, 0.095 atm water.

water/g at 200 m^2/g, or 830 μmol/g of hydroxyls. A somewhat higher value of 1470 μmol/g of hydroxyl is derived from the monolayer value reported by deBoer *et al.* (*24*).

In any case, since the hydroxyl content at 200 m^2/g is stoichiometrically greater than the highest levels of stabilizer reported here, further increases in stabilizer content should further decrease the rate of area loss. For comparison, note that about 700 μmol/g of silica reduced R by a factor of about 1000 (Fig. 6).

It is probable that metallic elements will interact with hydroxyls by an exchange mechanism, decreasing the number of hydroxyls necessary to the sintering process. The infrared spectra provide clear evidence that TEOS interacts with alumina, probably at the hydroxyls, to produce a Si–O–Al structure, with an IR band near 1000 cm^{-1}, compared to the Si–O–Si for pure silica, having a band near 1100 cm^{-1} (*2*).

CONCLUSIONS

(1) Surface area data for alumina measured at constant temperature and water partial pressure as a function of time can be fitted to an equation from which the rate of area loss at a given area can be calculated.

(2) This rate is proportional to water partial pressure, is a strong function of area, and has an Arrhenius-like temperature relationship.

(3) The rate is also a function of alumina type, being greater for one derived from an amorphous precursor than from one with a high boehmite content.

(4) The rate of area loss is lowered by the addition of inorganic additives, such as Sr, Ba, La, Sn, Si, and P. The degree of stabilization is a function of concentration and is similar for each additive on an equimolar basis.

(5) A model of the hydrothermal sintering process is proposed which can account for the experimental data.

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