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A RING STRUCTURE MODEL OF THE ACID CENTERS OF AMORPHOUS SILICA-ALUMINA CATALYSTS

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Calcination of a 500 m^2/g SiO_2–Al_2O_3 co-gel from 350 to 875 °C leads to a constant ratio of Lewis-to-Bronsted sites over this temperature range. A model is proposed to account for this surprising result: a 3–4 member ring structure of SiO_2 reacts with aluminum ions and inserts between Si groups in the ring. This expanded ring structure is proposed to be the local structure responsible for the acidity. The density of WO_3 clusters formed on SiO_2 of 1.2 nm size is analogous to the density of Si-Al ring structures proposed to be present on the surface of SiO_2–Al_2O_3 solid acid catalysts.

In a classic paper [1], J.A. Schwarz used infrared of chemisorbed pyridine at different coverages of silica-alumina catalysts to simultaneously determine the number of Lewis and Bronsted sites. In this work, it was established that for high-silica-content silica-alumina, following a 500 °C calcination, that the ratio of Lewis-to-Bronsted (LTB) sites was about 2. This constancy in the LTB ratio was observed for 75 wt% SiO_2–25 wt% Al_2O_3 and 90 wt% SiO_2–10 wt% Al_2O_3. This remarkable constancy of LTB ratio *and* total number of acid sites (both samples having similar surface areas, ca 425 m^2/g) over such a wide range of alumina contents presents substantial challenge to J.B. Peri's model [2] of the acid centers on silica-alumina catalysts. Schwarz' paper [1] also showed that addition of water vapor to each of these silica-alumina compositions converted one-half of the Lewis sites to Bronsted sites. We have investigated in some detail, a silica-alumina catalyst (Davison Lo-Al, 550 m^2/g) analogous to those investigated by Schwarz [1], using a modified Benesi titration procedure [3,4] which determine quantitatively the number of Lewis and Bronsted acid centers. Because of the discovery of transition metal oxide solid acid systems on alumina stable to > 900 °C [5], we investigated the number of Lewis and Bronsted acid centers on Davison silica-alumina at calcination temperatures from 350 to 900 °C. To our surprise, there was a constant LTB ratio over this entire range of temperatures with a decrease in number of sites at high temperature which was independent of surface area. To

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the best of our knowledge, this is the first report of the surface acidity of silica-alumina treated at high temperature conditions.

From these high temperature studies, we propose a new model of the acid centers on silica-alumina. We propose that ring structures are formed on silica-alumina by reaction of alumina centers with the three- and four-member ring structure which have been recently reported by Tallant et al. [6] to dominate the terminating surface of all types of silicas. Specific silica ring structures react to expand the ring size to five and six member rings with all Al groups with Si next nearest neighbors.

The acid centers on Davison silica-alumina were determined by a two step titration procedure [3,4].

The procedure relies on a standard Benesi titration [7] with butylamine to determine the total number of Lewis and Bronsted acid centers, coupled with a second Benesi titration where either 2, 6-dimethylpyridine or 2, 6-di*tert*butylpyridine is equilibrated with the solid acid suspended in a non-aqueous solution. This allows the sterically-hindered amine to coordinate to the Bronsted sites so that a second n-butylamine titration determines quantitatively the number of Lewis centers. By the difference from the two titrations, one determines quantitatively the number of strong Bronsted sites. In later work, Benesi [8] and others [9] propose use of sterically-hindered amines as a method to quantify the Bronsted site density on solid acids. Table 1 shows the comparison between this procedure and the detailed method of Schwarz [1]. The results in table 1 show that Davison silica-alumina has a nearly identical Lewis-Bronsted site distribution to that obtained earlier by Schwarz [1] on co-gel prepared materials.

Table 1
Comparison of Lewis and Bronsted site densities for comparable surface area, high-silica-content silica-aluminas calcined 500 ° C

Sample	Surface area (m^2/g)	Number $Ho \leqslant 8.2$ strength Lewis sites (micro moles/g)	Number $Ho \leqslant 8.2$ strength Bronsted sites (micro moles/g)
Davison $SiO_2-Al_2O_3$ (14 wt% Al_2O_3) [a]	500	263	125
Davison $SiO_2-Al_2O_3$ (14 wt% Al_2O_3) [a]	500	255	125
Davison $SiO_2-Al_2O_3$ (14 wt% Al_2O_3) [a]	500	260	145
Schwarz $SiO_2-Al_2O_3$ (10 wt% Al_2O_3) [b]	450	224	127
Schwarz $SiO_2-Al_2O_3$ (25 wt% Al_2O_3) [b]	400	227	119

[a] Repeat titrations of separate samples taken from the top, middle, and bottom of 1 gal. container of freshly-opened Davison SiO_2-Al_2O_3.

[b] Ref. [1].

In the case of the silica-alumina samples calcined between 350–900 ° C, the acidity was determined using this two step titration procedure. In one series of experiments samples of, Davison SiO_2–Al_2O_3 were calcined at 350, 500, 800, 850, 875, and 900 ° C for four hours and then allowed to equilibrate with ambient air in a capped bottle overnight before re-calcination at 500 ° C prior to acid center titration. In a separate series of experiments, samples were calcined at 300, 500, 600, 700, and 750 ° C for 16 hrs, and the acid centers determined after cooling the

Table 2
Lewis and Bronsted acid site densities for high temperature calcined Davison silica-alumina

Sample treatment procedure	High temperature calcination temperature	Number $Ho \leqslant -8.2$ strength Lewis sites (micro moles/g)	Number $Ho \leqslant -8.2$ strength Bronsted sites (micro moles/g)	Ratio of sites: Lewis to Bronsted
Calcined (4 hrs) Rehydrated (16 hrs) Calcined 500 ° C (2 hrs)	350	325	150	2.2
Calcined (4 hrs) Rehydrated (16 hrs) Calcined 500 ° C (2 hrs)	500	260	125	2.1
Calcined (4 hrs) Rehydrated (16 hrs) Calcined 500 ° C (2 hrs)	800	188	112	1.7
Calcined (4 hrs) Rehydrated (16 hrs) Calcined 500 ° C (2 hrs)	850	138	62	2.2
Calcined (4 hrs) Rehydrated (16 hrs) Calcined 500 ° C (2 hrs)	875	110	50	2.2
Calcined (4 hrs) Rehydrated (16 hrs) Calcined 500 ° C (2 hrs)	900	0	0	–
Calcined 16 hrs. at high temperature only	300	225	100	2.3
Calcined 16 hrs. at high temperature only	500	175	150	1.2
Calcined 16 hrs. at high temperature only	600	175	100	1.8
Calcined 16 hrs. at high temperature only	700	125	100	1.3
Calcined 16 hrs. at high temperature only	750	125	50	2.5

samples to ambient temperature in a dry box. Table 2 shows the results for these two separate methods of determining the surface acidity.

This work convincingly demonstrates that Bronsted acid centers are present on silica-alumina samples even after a high temperature calcination treatment. Similar results have been obtained for tungsten oxide supported on alumina even after a 900 °C calcination treatment [10]. In addition, these studies show for many of the samples in table 2, that two Lewis sites are present for every Bronsted site, despite the fact that the total acidity varies over a wide range. The number of acid sites present has no relationship to the surface area as the 900 °C sample with no Lewis or Bronsted sites still has a surface area of 200 m^2/g. We believe that the results in table 1 and 2 present a strong case that the surface acidity of silica-alumina is due to a small ring or oxide-cluster structure; i.e., a local structure involving isolated rings of silica with alumina substituted into the ring structure of silica. After high temperature calcination, the *surface density* of these cluster structures change but the immediate local ring structure maintains two Lewis sites for every Bronsted site.

In an elegant paper, Tallent et al. [6], using laser spectroscopy, makes a convincing case that the terminating surface of silica is dominated by a three- or four-member ring structure present every 0.5 nm^2 on the surface. We propose that these ring structures are also present on silica-alumina surfaces, and are the local structure responsible for the LTB ratio being constant over a very wide range of calcination conditions. Only one in fourteen silica ring structures need to react with two aluminum oxide centers per ring to account for the observed density of acid centers if every alumina in a ring introduces a Lewis acid center. Apparently, only a minor number of all the silica ring structures react with aluminum cations, or only a minor number are capable of generating a local structure which is highly acidic. If the aluminum cations in the ring structure are the structure of the Lewis centers then one silica center per ring, probably located between aluminum centers or a strained-bridge between silica and alumina cations, is the structure of the Bronsted acid centers. Such a ring model could also account for the suggestions in a wide number of catalytic studies that a couple exists between Lewis and Bronsted centers. This stable ring or cluster structure would also explain how Bronsted centers are stable on silica-alumina at the high temperatures observed in this work, and would also explain why there is a constant LTB ratio at widely different calcination temperatures.

As we have discussed, if one calculates for a 500 m^2/g silica-alumina surface area how many Lewis sites are present if two aluminum centers per silica ring (one ring per 0.5 nm^2) are coordinatively-unsaturated then one obtains a number much higher than experimentally observed. The experimental values of the Lewis site concentration, however, are quite close to the value calculated from another measure of "reactive" silica rings on a silica support. The density of WO_3 clusters formed [11] on a high surface area silica support may be such a measure of the "reactive" ring density. If WO_3 clusters measure the silica rings which can react with aluminum cations and if two alumina centers per ring are Lewis acid centers, then one calculates a value of 250 micro moles/g as the Lewis site concentration. This is a model where the small WO_3 clusters *bond specifically* with the ring structures which also react with alumina cations to form acidic ring structures isolated from each other by 2.6 nm. A highly regular array of WO_3 clusters with one Lewis center per W^{+6} cation was, in fact, observed by high resolution transmission electron microscopy to be present on the silica surface in earlier work. The 1.2 nm diameter WO_3 cluster were isolated from each other by 2.6 nm on the silica surface. It may be that only 4 member silica rings are reactive toward Al ion insertion, and their density on the surface corresponds to that observed for WO_3 on SiO_2 [11]. The Lewis centers present on the silica-alumina surface present in these "reactive" ring structures, can convert partially to strong Bronsted centers by re-hydration with H_2O as shown in Schwarz's work [1]. We feel that this model of a stable ring or cluster with a local ordered structure on amorphous silica-alumina catalysts explains three observations: 1) why there are an identical number of Lewis and Bronsted centers [1] for either a 10 or a 25 wt% alumina content silica-alumina, and 2) why there is a constant ratio of Lewis and Bronsted centers for either low or high temperature calcined silica-alumina samples, and 3) why Bronsted sites are stable even for 750–875 °C calcination conditions on amorphous silica-alumina catalysts.

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