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DISPERSION OF BULK SILICA ONTO ALUMINA TO FORM A DISPERSED, SURFACE PHASE OXIDE STRUCTURE

L.L. MURRELL *, N.C. DISPENZIERE, Jr. and K.S. KIM **

Exxon Research and Engineering Company, Route 22 East, Annandale, NJ 08801, U.S.A.

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Addition of colloidal silica to a porous alumina results in gelation onto the exterior surface of the alumina. Subsequent steam treatment with a high steam content allows silica to migrate into the pores of the alumina to form a surface phase oxide structure. The dispersed silica phase on alumina has low acidity in comparison to silica-alumina co-gels as measured by a standard gas oil cracking test. ESCA was useful to follow the migration of silica from the external surface to the internal surface of the particles. The dispersed silica phase stabilized the alumina surface area at severe high temperature conditions. Bulk silicic acid was also found to disperse onto alumina under analogous steaming conditions.

A new synthesis procedure has been discovered to prepare alumina supports stable to high temperature conditions where the alumina surface has been partially, or completely, covered by a silica surface phase oxide (SPO) structure. This work suggests that silica migrates in high temperature steam by surface diffusion of a mobile species and not by gas phase transport. Dispersion of a spectrum of materials, some under surprisingly mild conditions, has been reported recently [1–3].

In this new synthesis method of silica-modified aluminas, a conventional, reforming grade gamma-alumina (Engelhard Industries, 325 mesh, i.e. 50 micron size, 190 m^2/g surface area) is first contacted with a solution of colloidal silica (Dupont "Ludox" AS-40) with just sufficient liquid to fill the pore volume of the dehydrated support (120 °C dried). Silica contents up to 25 wt% of the final composite were investigated by this impregnation procedure. After drying of the samples at 120 °C for 16 hrs., the dispersion of silica was accomplished by control of the steam content in the gas phase at a temperature of 870 °C.

After drying of the colloidal silica impregnated alumina powder at 120 °C the gelled silica was found to be largely restricted to the exterior surface of the alumina powder forming a "rim" or "shell" configuration on the alumina

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* Present Address: Engelhard Corporation, Specialty Chemical Div., Menlo Park CN 40, Edison, New Jersey 08818, U.S.A.

** Present Address: Polaroid Corporation, 750 Main St. Cambridge, Mass. 02139, U.S.A.

particles. We established this rim configuration by ESCA studies to be described subsequently. In the impregnation of the silica sol or colloidal silica particles onto the alumina support, a rim configuration of silica is probably occurring due to two factors. One factor is that the porous alumina particles act like a microscopic filter upon impregnation causing rapid concentration of the sol phase which leads to gellation. Another factor is the strong adsorption of the silica sol particles onto the positively-charged alumina surface which is present at the pH of the silica sol suspension (pH, 9.2). The key to dispersing the silica phase onto the alumina surface and *into the pores of the alumina particles* was the temperature and the steam content of the atmosphere. In fact, our studies showed convincingly that silica would *not disperse* at 870 ° C with 5 wt% steam content. This result suggests that silica probably does not form a volatile oxide in our systems at significant steam content in the gas phase. The primary mechanism of silica migration is likely a molecular migrating species, probably a silica hydroxide or oxyhydroxide species, perhaps polymeric in nature.

The diffusion of silica onto the alumina surface was followed experimentally in two ways. One method used ESCA to determine at what conditions the silica "rim" migrated from the exterior surface of the alumina particles into the interior of the alumina to form a surface phase oxide structure. The second method tracked the formation of a silica SPO structure by using a modified gas oil test reaction to detect the relatively-weak acid centers associated with the highly-dispersed SPO structure. An even more direct expression of the formation of a SPO structure upon high temperature steam treatment of a colloidal silica impregnated sample was the surface area stability impacted by the silica SPO structure bound to the alumina surface. For example, a 200 m^2/g alumina when steamed under conditions when a silica SPO was formed would have a surface area of 160 m^2/g following an 870 ° C steam treatment if the silica content was 5 wt% or higher. With no silica present, the alumina surface area would have decreased to 120 m^2/g for this steam treatment.

In table 1, we show the ESCA results and the surface area for the case of 2 and 5 wt% silica on the gamma-alumina support. These ESCA results are quite graphic in demonstrating that specific steaming conditions are essential to dispersed silica onto the alumina surface within the porous article. In the case of the 2 wt% silica sample, prepared by impregnation of "Ludox" AS-40 colloidal silica, following drying at 120 ° C for 16 hrs. and calcination at 500 ° C, the silica atomic % determined by ESCA was 9.6. This shows that silica is essentially present on the exterior of the alumina particles. In comparison, the estimated silica atomic % based on analysis of gamma-alumina dehydrated at 500 ° C and reacted with tetraethoxysilane at 2 wt% silica content is 1.1. Physical grinding of the "rim" configuration 2 wt% SiO_2 sample resulted in the silica, which was isolated on the extreme outer surface of the alumina particles, to be completely undetectable by ESCA for the ground sample. This result is also consistent with the silica being isolated on the extreme exterior surface of the alumina particles.

Table 1
ESCA analysis of silica-modified gamma-alumina

Sample	Treatment condition for 16 hrs.	Surface area (m^2/g)	At % Si	At % Al	At % O
2 wt% SiO_2 on Al_2O_3	Calcined 500 °C, air	196	9.6	19.5	70.8
2 wt% SiO_2 on Al_2O_3	Steamed 870 °C (20% O_2/5% H_2O/He balance)	120	9.0	21.0	70.1
2 wt% SiO_2 on Al_2O_3	Steamed 870 °C 20% O_2/5% H_2O/He-balance (sparged through 1 NH_4OH)	120	9.2	22.0	68.9
2 wt% SiO_2 on Al_2O_3	Steamed 870 °C (90% H_2O-10% N_2)	117	1.0	31.8	67.2
5 wt% SiO_2 on Al_2O_3	Steamed 870 °C (90% H_2O-10% N_2)	160	1.6	31.8	66.6
2 wt% SiO_2 on Al_2O_3 [From $Si(OC_2H_5)_4$ preparation]	Decomposed in 5% H_2O/He, calcined 500 °C air	220	1.1	32.2	66.4
5 wt% SiO_2 on Al_2O_3 [From $Si(OC_2H_5)_4$ preparation]	Decomposed in 5% H_2O/He, calcined 500 °C air	220	2.0	31.9	66.9

The aggregated silica in a "rim" on the outer alumina surface is also "shadowing" the underlying alumina from analysis by ESCA [4]. The measured alumina atomic % for the 500 °C calcined 2 wt% SiO_2 on alumina sample was only 19.5%, whereas that for an alumina not shadowed by silica was 32. Therefore, both the silica atomic % and the "shadowed" alumina atomic percent measured by ESCA were found to be a very sensitive measure of migration of silica from the outer "rim" of the alumina particles into the pores of the alumina particle. Note that air sparged through water or air sparged through a 1N NH_4OH solution failed to change either the silica atomic % or the suppressed alumina atomic % due to "shadowing" by the silica on the exterior surface of the particles, table 1. Note that these steaming conditions were sufficient to reduce the alumina surface area from 200 m^2/g to 120 m^2/g forming theta-alumina, without any apparent change in the atomic %'s of silica or alumina. Only in the case of steaming the 2 wt% silica on alumina sample at 870 °C in 90% steam-10% N_2 did both the silica and the alumina atomic %'s obtained from ESCA analysis indicate formation of a dispersed silica SPO phase on the alumina surface. Calculation of the silica atomic percent expected for a dispersed 2 wt% silica on an alumina of 120 m^2/g,

Table 2
ESCA analysis of silica-alumina CO-gel prepared samples

Sample	Treatment condition for 16 hrs.	Surface			
		area (m^2/g)	At % Si	At % Al	At % O
2 wt% SiO_2-Al_2O_3 Co-gel	Calcined 500 °C, air	550	0.1	30.3	69.6
2 wt% SiO_2-Al_2O_3 Co-gel	Steamed 870 °C (90% H_2O-10% N_2)	130	0.6	31.5	66.9
5 wt% SiO_2-Al_2O_3 Co-gel	Calcined 500 °C, air	449	1.2	–	–
15 wt% SiO_2-Al_2O_3 Co-gel	Calcined 500 °C, air	523	3.8	–	–

based on preparation of a 2 wt% silica SPO structure on a 190 m^2/g alumina prepared using tetralkoxysilane, gave a value of 1.1 wt%. This value is in excellent agreement with the observed value of 1.0. Note also that the alumina atomic % has increased to that expected for no "shadowing" of the alumina support by a dispersed silica SPO [4,5].

In order to compare the ESCA results in table 1 to a 2 wt% silica content alumina made as a solid solution, a silica-alumina co-gel was made and characterized. A 2 wt% silica content alumina was made by gelling a mixture of alumina *sec*-butoxide and tetraethoxysilane by addition of water. The ESCA results for this sample calcined at 500 °C and steamed in 90% steam-10% N_2 for 16 hrs. are shown in table 2. Note that the silica atomic % measured by ESCA is much less than in the case of the 2 wt% silica on alumina materials described in table 1. The increase in the silica atomic % for the co-gel prepared silica-alumina sample steamed at high temperature probably reflects partial silica migration towards the outer alumina surface upon high temperature steam treatment in concert with formation of a transitional alumina phase. In any case, one can see that ESCA is very sensitive to silica being present within the alumina structure for the case of the 500 °C calcined sample in table 2. The measured atomic percent silica for 5 and 15 wt% co-gels are also shown in table 2 for comparison.

Table 3 shows the ESCA results for 10 wt% SiO_2 on gamma-alumina prepared as described previously employing "Ludox" AS colloidal silica. The ESCA results in table 3 when compared to those in table 1 show that only for a steaming condition containing a high steam content does the alumina atomic % approach that for a monolayer SPO silica sample. Considerable retention of silica on the exterior alumina particle surface is indicated by the measured atomic % silica of 6.95 being considerably higher than the actual atomic % silica present in the sample, i.e., 3.38. Incomplete diffusion of silica onto the alumina surface is also

Table 3
ESCA analysis of silica-modified gamma-alumina prepared on 50 micron alumina particles

Sample	Treatment condition	Surface area (m^2/g)	At % Si	At % Al
10 wt% SiO_2 on Al_2O_3 (From colloidal silica)	Dried 120 ° C, air	201	14.8	6.60
10 wt% SiO_2 on Al_2O_3 (From colloidal silica)	Calcined 500 ° C, air	190	14.8	16.3
10 wt% SiO_2 on Al_2O_3 (From colloidal silica)	Steamed 870 ° C (20% O_2/5% H_2O/He balance)	–	10.6	11.3
10 wt% SiO_2 on Al_2O_3 (From colloidal silica)	Steamed 870 ° C (90% H_2O–10% N_2)	157	6.95	24.9

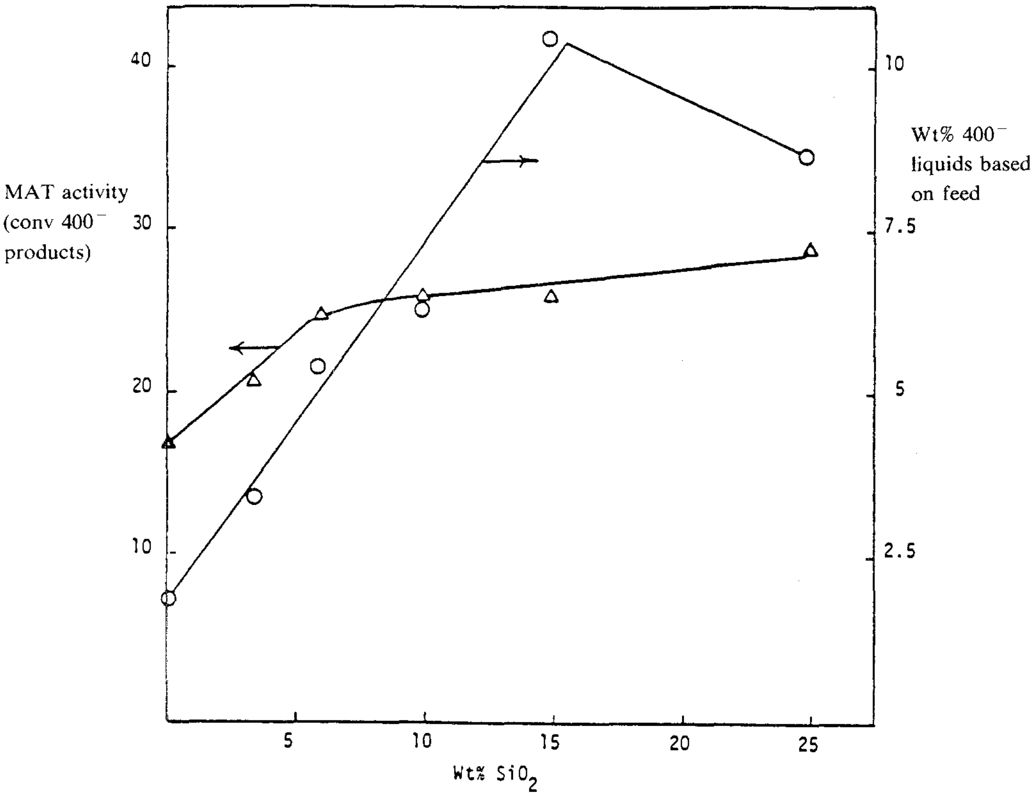

Fig. 1. Micro activity test catalytic results for SiO_2 on gamma-Al_2O_3 samples prepared using "LUDOX" SiO_2 on gamma-Al_2O_3 steamed at 870 ° C for 16 hrs.

supported by the fact that the alumina atomic % is much lower than for a submonolayer or monolayer silica on alumina sample made from a tetraalkoxysilane preparation procedure. However, the catalytic activity of this sample, see fig. 1, suggests that the gamma-alumina surface is covered to near monolayer capacity. This then suggesting that the silica mal-distribution is largely restricted to the extreme outer surface of the alumina particles which is the main contributor to the measured ESCA values.

Figure 1 shows the gas oil cracking activity as a function of silica content for samples prepared by impregnation of silica sol, dried, and then steamed at 870 ° C in 90% steam-10% N_2 for 16 hrs. At these low MAT activities, the wt% 400^- liquids produced based on feed is a more sensitive indicator of selectivity to formation of useful liquid products in the cracking reaction. One can clearly see that activity and selectivity are increasing with silica content and that a plateau is reached for about 10–15% silica content.

Figure 2 summarizes the ESCA analysis of three distinct classes of high-alumina-content silica-alumina materials: 1) co-gel prepared silica-aluminas, 2) surface phase silica on alumina prepared by reaction with tetraethoxysilane with dehydrated alumina, and 3) silica surface phases prepared by steam treatment of a silica sol impregnated alumina powder. One can see that there are three distinct lines for the ESCA intensity versus silica wt%. Because of the large discrepancy of the ESCA determined Si atomic percents for the alkoxysilane-prepared samples to those for the steam-treated silica sol prepared samples, the 15 wt% sample which was steamed for 16 hrs. was steamed for a second 16 hr. period in 90% steam-10% N_2. Note the marked drop in the silica atomic percent upon the second steaming treatment. Also, both the 16 and 32 hr. steam-treated samples were thoroughly ground and then re-analyzed to determine the change of the silica atomic % determined by ESCA. Note the marked change in the ESCA determined atomic % for the 16 hr. treated sample upon grinding compared to the change for the 32 hr. treated sample.

The silica is apparently rather sluggish to disperse completely from the extreme outer surface into the pores of the alumina substrate especially for high silica content samples. The grinding experiments prove that greater silica enrichment occurs towards the outer surface of the alumina particle. Since the silica surface coverage for the 15 wt% silica content sample is approximately twice monolayer surface coverage of the available alumina surface (ca. 160 m^2/g), then diffusion probably becomes sluggish for surface migration of silica *on top of a monolayer of silica on alumina*. To test this observation further, silica diffusion for colloidal silica deposited on to a 60 mesh or 250 micron size gamma-alumina particles was investigated, see table 4. Silica diffusion into these larger alumina particles to form a dispersed silica phase certainly occurs for either a 16 or a 32 hr. steaming period as judged by the silica atomic % for the thoroughly ground samples. However, the suppressed alumina atomic % for the 16 and 32 hr. steamed samples suggests that the outer surface is still significantly enriched in a bulk silica phase.

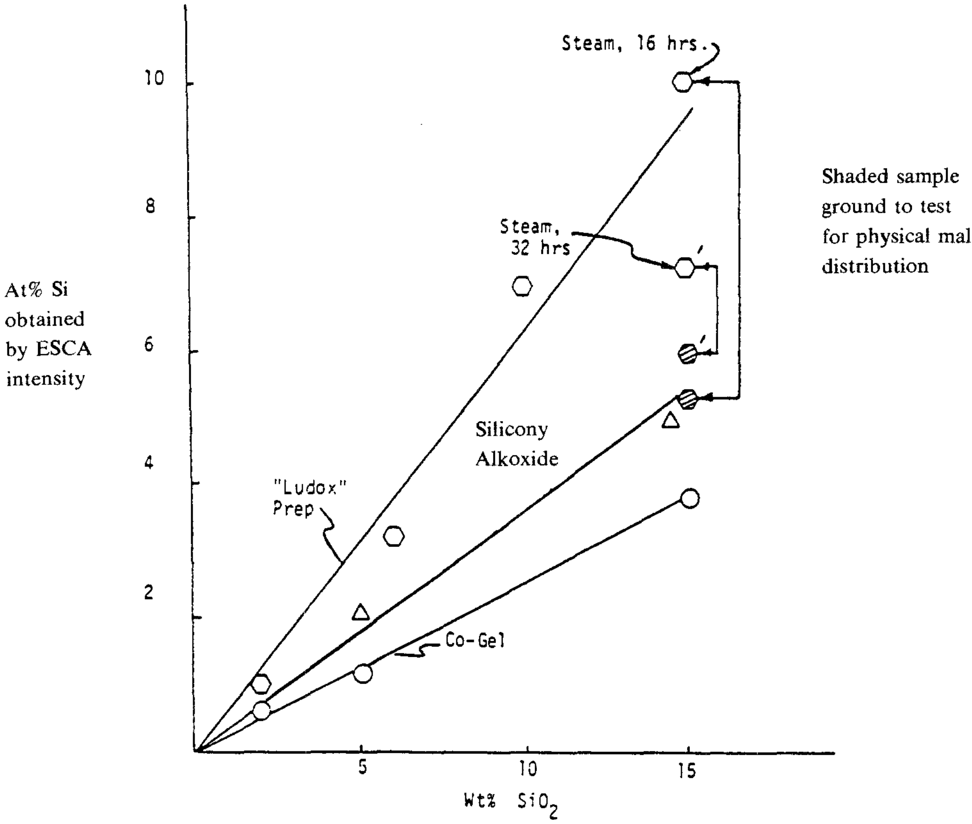

Fig. 2. Summary of ESCA analysis of silica atomic percent versus silica weight percent for three classes of SiO_2-Al_2O_3 systems: 1) Co-Gel, 2) Silicon alkoxy reacted gamma-Al_2O_3, 3) Steamed silica on gamma-Al_2O_3 made from colloidal "LUDOX" SiO_2 deposited on alumina.

Apparently, silica diffusion becomes quite sluggish in the presence of silica-covered alumina surface compared to a partially covered alumina surface.

A sample was also prepared at 10 wt% SiO_2 content using silicic acid added to 325 mesh alumina instead of colloidal silica and treated as described previously at 870 °C with 90% steam – 10% N_2. The surface area of this sample was 142 m^2/g compared to 160 m^2/g in the case employing colloidal silica. ESCA analysis showed almost complete dispersion onto the alumina as found in the case employing colloidal silica. This result demonstrates that bulk silica does migrate onto the alumina surface and that colloidal silica need not be employed to form silica SPO structures employing this novel preparation method.

In conclusion, a nearly complete two monolayer silica surface phase is produced for a 32 hr. treatment period of 15 wt% SiO_2 on a 325 mesh alumina particle as shown by the ESCA results in fig. 2. In contrast, much more sluggish diffusion is observed in the case of a 60 mesh alumina particle. This is an interesting case where migration to form a uniform dispersed phase can be

Table 4
ESCA analysis of silica-modified gamma-alumina prepared on 250 micron alumina particles

Sample	Dispersion treatment	Atomic % Si	Atomic % Al
15% SiO_2/Al_2O_3	Stm. 870 °C ($90\% \ H_2O$-$10\% \ N_2$, 16 hrs.)	23.0	4.9
Above sample, mild grinding	–	4.9	27.1
Above sample, thorough grinding	–	3.7	29.2
15% SiO_2/Al_2O_3	Stm. 870 °C ($90\% \ H_2O$-$10\% \ N_2$, 32 hrs.)	17.6	10.9
Above sample, mild grinding	–	4.6	28.2
Above sample, thorough grinding	–	3.4	29.6

inhibited by the support surface structure, and also by the support particle size over which the migrating species must diffuse to form the dispersed phase. Another way of looking at this phenomenon is that a multi-layer silica phase on alumina probably acts as a barrier to the molecular, or polymeric, migrating species.

Trivial blocking of the pores of the exterior surface by silica was eliminated as an explanation of the observed differences between 60 and 325 mesh alumina particles as the BET surface area and the pore distribution of colloidal silica impregnated and dried onto the 60 mesh alumina particles were the same as an identically-treated 325 mesh alumina particles. To the best of our knowledge no other examples of this phenomenon of diffusion to form a dispersed phase being dependent on the support particle size are known.

In summary, colloidal silica deposited onto the exterior surface of alumina particles, or bulk silica acid added to alumina particles can be dispersed in a high-steam-content atmosphere to form a highly-stable, silica surface phase oxide structure at temperatures greater than 760 °C [6]. The migration of silica from the exterior surface of alumina particles onto the alumina surface within the alumina particles occurs sufficiently rapidly that the alumina support does not re-crystallize to a low surface transitional alumina before the silica migration occurs, and simultaneously stabilizes the alumina support by formation of a surface phase oxide structure. Therefore, this new procedure is a viable way to readily form silica-modified aluminas of high temperature stability. The extent of silica diffusion onto the alumina surface under different experimental conditions can be readily followed by ESCA, and also by the onset of catalytic cracking activity of the sub- and multi-monolayer silica structures on the alumina surface.

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