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Silica-Stabilized Aluminas Resistant to Vanadium Attack under Severe High-Temperature Conditions

Silica stabilization of alumina by direct reaction of alkoxysilanes with the dehydrated surface of a 500°C calcined silica–alumina cogel (5 wt% SiO_2 content) leads to a vanadium-tolerant support when exposed to severe high-temperature conditions. To the best of our knowledge no other supports are known which are stable to loss of surface area by a dispersed vanadium oxide phase in high-temperature steam and/or air atmosphere. Vanadium present in heavy petroleum feedstocks is known to attack many conventional heterogeneous catalyst supports under regeneration conditions when coke deposits are removed under oxidizing conditions. We have found that it is the dispersed, vanadium oxide surface structure (*1–3*) which causes the facile loss in surface area of conventional γ-alumina supports with, or without, steam present under high-temperature conditions. The only supports which are stable to loss of surface area by a dispersed, vanadium oxide surface structure are (i) a silica-stabilized, transitional alumina which has been produced by reaction of the dehydrated, terminating hydroxyl structure of a boehmite-like, high-alumina content silica–alumina with tetraalkoxysilane, and (ii) a silica-stabilized alumina produced by reaction of boehmite itself with tetraalkoxysilane.

A high-purity reforming-grade γ-alumina of 200 m^2/g (Cyanamid PHF-4) when steamed at 870°C (1600°F) for 1 h in 90% H_2O–10% N_2 has a surface area of about 70 m^2/g. If the alumina has first been impregnated with vanadyl triethoxide in methanol by the incipient wetness impregnation method (1 wt% V as the metal) and then steamed or calcined in dry air at 870°C the alumina transforms to α-Al_2O_3 of <5 m^2/g surface area. This same alumina can be ball-milled with V_2O_5 (1 or 3 wt% as the metal) and then steamed at 870°C without formation of low-surface-area α-alumina. In fact, the surface area is identical to that of the alumina with no vanadium present. This result suggests that bulk V_2O_5 does not disperse readily in steam at high temperatures onto the alumina support to give the dispersed vanadium phase which is responsible for the facile conversion of γ-alumina to α-alumina. Therefore, most of our investigations focused on stabilization of alumina to vanadium attack where the vanadium was deposited from vanadyl triethoxide in methanol by the incipient wetness method to form a highly dispersed surface phase structure. Most of these studies focused on stability to loss of surface area for 3 wt% V levels when calcined at 950°C for 16 h, as high-temperature air calcination and/or steaming conditions produced identical loss of surface area for the systems of interest in this work.

A two-step preparation procedure was employed to prepare a *bulk and surface, silica-stabilized alumina.* A 5 wt% silica-content silica–alumina was prepared by addition of 16 ml H_2O to a mixture of 96.63 g of 95% $Al(OC_4H_9)_3$ (containing 19 g Al_2O_3) and 2.53 g $Si(OCH_3)_4$ (containing 1 g SiO_2). The precipitate was dried at 120°C for 16 h in a N_2 atmosphere and the alkoxy groups were decomposed by increasing the temperature to 500°C in a N_2 atmosphere. The sample was then calcined in air at 500°C. To the dehydrated silica–alumina cogel sample, $Si(OC_2H_5)_4$ in methanol was added by the incipient wetness impregnation tech-

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TABLE 1

Surface Areas of Various Silica-Stabilized Aluminas after 950°C Calcination with 3% Vanadium Present as a Dispersed, Surface Phase Oxide

Support and description	Surface area (m^2/g)
γ-Al_2O_3	<5
Boehmite alumina	<5
5% SiO_2 reacted with γ-Al_2O_3	<5
5% SiO_2 reacted with boehmite alumina	86
5% SiO_2-content SiO_2–Al_2O_3 cogel	<5
6% SiO_2 reacted with dehydrated 5% SiO_2-content SiO_2–Al_2O_3 cogel	136

nique to give 6 wt% SiO_2 content silica present as a highly dispersed surface phase oxide structure on the 5 wt% silica-content cogel. This 11 wt% silica-content sample was then steamed in air sparged through water (at 35°C) for 2-h periods at 120 and 250°C and then for 1 h at 500°C. The sample was then calcined in flowing air for 4 h at 500°C.

Table 1 shows the relative stability of several aluminas and silica-modified aluminas at 950°C for 16 h with 3 wt% V (as the metal) present as a highly dispersed surface phase oxide. Supports which were unstable include γ- and boehmite alumina, 5 wt% silica-content alumina (where tetraethoxysilane was reacted as previously described with the γ-alumina support surface), and 5 wt% silica-content silica–alumina cogel prepared as described previously. Supports which were remarkably stable include 1. 5 wt% silica-content silica–alumina prepared by reaction of tetraethoxysilane with the surface of a 120°C dehydrated boehmite as described previously, and 2. 11% silica-content silica–alumina (prepared from a 500°C calcined 5% silica-content silica–alumina cogel, followed by reaction of tetraethoxysilane with the surface of the cogel to give 6 wt% silica present as a surface phase oxide structure).

The conclusion from this work is that the terminating hydroxyl structure with which an alkoxysilane reacts is critical to achieve stability to V attack at high temperatures. Reaction of alkoxysilane with a boehmite surface hydroxyl structure apparently forms a different *and* much more stable surface structure than reaction with a γ-alumina formed from the same boehmite. The best high-temperature stability to vanadium attack was realized where a relatively low level of silica is present within the alumina structure and where the terminating hydroxyl structure is reacted with an alkoxysilane. This could be referred to as a silica-in and silica-on stabilization strategy. The silicon-in material probably has a boehmite-like surface hydroxyl structure which reacts with the alkoxysilane to form the surface silica phase which is highly resistant to vanadium attack. To the best of our knowledge this is the first reported case (*4*) for significant stability to V attack under severe conditions where the V is present in high concentrations as a dispersed phase.

In addition to the stability to V attack the 11% silica–alumina (with silica-in and silica-on the alumina) maintained a surface area of 189 m^2/g when calcined at 1050°C in air for 16 h. In comparison, the 5% silica–alumina (silica-in) support had a surface area of 125 m^2/g when calcined at 1050°C. In the case of the 5% silica-content sample prepared by reacting the boehmite surface with alkoxysilane the surface area after 1050°C calcination was 162 m^2/g. The boehmite without surface silica stabilization in contrast had a surface area <5 m^2/g after calcination at 1050°C.

In summary, in these studies vanadium *must be present as a dispersed phase* to cause the decrease in surface area of alumina supports under high-temperature calcination and/or steaming conditions. Silica apparently must be present in a unique structure on specific alumina or silica–alumina surfaces in order to preclude vanadium attack. Loss of surface area may occur by formation of a mobile VO_x–AlO_y species, which cannot form in the case of specific silica surface phase oxide structures. Reacting alkoxysilane with a high-alumina-content silica–alumina results in the most stable material to vanadium attack in these studies.

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