SUB-MONOLAYER, MONOLAYER, AND BI-LAYER TRANSITION METAL SOLID ACIDS PREPARED ON FUMED ALUMINA

L.L. MURRELL * and N.C. DISPENZIERE Jr.

Exxon Research and Engineering Company, Route 22 East, Annadale, New Jersey 08801, U.S.A.
** Engelhard Corporation, Menlo Park, CN 40, Edison, New Jersey 08818, U.S.A.*

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Fumed alumina made by flame pyrolysis has very different acidity compared to conventional aluminas. Supported transition metal oxides on fumed alumina have higher stability and a greater proportion of Bronsted acid centers than the corresponding systems on conventional aluminas. Binary, supported mixed oxide monolayer and "bi-layer" structure on fumed alumina have a wide and a controllable range of acidic properties.

1. Introduction

Very little work has been published on the significance of one alumina *compared to another* in altering the acidity of a supported oxide phase. In addition, the intrinsic acidity of fumed alumina has not been discussed in the literature to the best of our knowledge. We have found that it is possible to prepare tungsten oxide on fumed alumina over a wide range of concentrations where Bronsted acid centers dominate the acid centers on the catalyst. Mixed surface oxide structures where one oxide is tungsten and another is a Group IV or V oxide have been found to be stable at 1100 °C in steam; after this steaming treatment significant surface acidity is retained for these binary oxide systems. In the case of the W-Ta system after 1100 °C steam treatment the surface area stability is consistent with a "monolayer" structure.

We have investigated the acidity of single and binary oxides on fumed alumina compared to conventional aluminas employing a gas oil cracking test reaction [1] and these results will be described in a subsequent publication. This cracking test has been shown in other work [2,3] to correlate with the acid strength of solid acids as measured by model compound tests. This paper establishes that the *surface concentration* of the supported phase(s) is related to the acid sites present on the oxide surface. The charge of the transition metal oxides (TMO) in the mixed oxide surface phase structure also alters the acid strength. Related recent publications [2,4], have come to the conclusion that a combination of *surface* *concentration and metal cation charge* of the supported TMO on alumina alters the acidity over a very wide range. A functional definition of the "monolayer" capacity of WO_3 on the surface of gamma-alumina based on detailed work in ref. [2] corresponds to ca. 4 micromoles/m^2 on 9.3 wt% WO_3 per 100 m^2 of surface area.

2. Results and discussion

A reforming grade gamma-alumina powder prepared by Cyanamid employing conventional aqueous procedures [6], of 220 m^2/g surface area has a surface acidity dominated by Lewis acid centers [7]. This result is consistent with other typical aluminas [8]. All acid center values were obtained by a new quantitative procedure based on the Benesi titration procedure [7]. Preparation details for these TMO on fumed alumina catalysts have been described previously [1,5]. The Cyanamid alumina, after calcination at 500 ° C has 430 micromoles/g of $Ho \leq -8.2$ strength acid centers. This is about 2 micromoles/m^2 or 1.2 acid centers per 1 nm^2 of surface area. A fumed alumina of 100 m^2/g surface area prepared by flame pyrolysis, Cabot Corporation-Alon Grade, also has an acidity dominated by Lewis acid centers. However, the density of acid centers of this fumed alumina is very different compared to conventional aluminas. The fumed alumina after calcination had 50 micromoles/g of Lewis acid centers, which is 0.5 micromoles/m^2 or 0.3 acid centers per 1 nm^2 of surface area. This density of acid centers per unit surface area on fumed alumina is only one-fourth that of a conventional reforming alumina.

For the case where tungsten oxide is dispersed onto the Cyanamid alumina and onto the fumed alumina at a concentration of 430 micromoles/g loading level (10 wt% WO_3), by impregnation of ammonium *meta*-tungstate as described elsewhere [5], the surface acidity of the 500 ° C calcined materials are completely different. In the case of 10% WO_3 on fumed Al_2O_3 (WO_3 on F-Al_2O_3) there were 275 micromoles/g of strong, $Ho \leq -8.2$, strength Bronsted sites and *50 micromoles/g of Lewis sites*. For 10% WO_3 on the aqueous-prepared alumina (WO_3 on A-Al_2O_3) there were 325 micro moles/g of Lewis sites and 100 micromoles/g of strong Bronsted acid centers. The density of acid centers for the WO_3 on F-Al_2O_3 has increased substantially compared to fumed Al_2O_3 itself from; 0.5 micromoles/m^2 to 2.75 micromoles/m^2, respectively. The density of strong acid centers for WO_3 on A-Al_2O_3 has not changed compared to the alumina without WO_3. There were 100 micromoles/g of Bronsted acid centers introduced for WO_3 on A-Al_2O_3 as described in recent publications [2,5]. These results suggest that the relatively high density of Lewis sites on aqueous-prepared alumina react with the dispersed WO_3 groups forming new Lewis sites which are associated with the W^{+6} center. About one-third of the W^{+6} centers on this alumina form Bronsted sites also associated with the W^{+6} center as proposed in a recent model [2]. The low density of Lewis

Table 1
Lewis and Bronsted acid sites of WO_3 on fumed Al_2O_3

Sample	Number Bronsted sites Ho ≤ -8.2 (micromoles/g)	Number Lewis sites Ho ≤ -8.2 (micromoles/g)
5 wt% WO_3 on F-Al_2O_3	200	0
10 wt% WO_3 on F-Al_2O_3	275	50
20 wt% WO_3 on F-Al_2O_3	250	25
10 wt% WO_3 on A-Al_2O_3	100	325

sites on the fumed alumina apparently allow the surface WO_3 groups to react with the fumed alumina surface forming local structures with Bronsted acid centers associated with the tungsten centers. The concept of "monolayer" coverage of an alumina surface by surface bound WO_3 groups has been published recently [2], and shows that the acidity is maximum at the surface coverage limit near to a close-packed "monolayer" structure. Further examples of characterization of surface phase oxides bound to support surfaces can be found in a recent publication [9], and references therein.

Studies of WO_3 on fumed alumina from 5–20 wt% were investigated by sequential impregnation of 5 wt% WO_3. This corresponds to a loading from about one-half to two-fold "monolayer" or "bi-layer" coverage of the fumed alumina [2]. Between each impregnation using AMT the samples were dried at 120 ° C and calcined at 500 ° C. These results are shown in table 1, and it is clear that the acidity is dominated by strong Bronsted centers. In the case of the 5 wt% WO_3 sample, it is significant that the total number of Bronsted sites is almost equivalent to the amount of WO_3 added. This would make a case that the WO_3 centers introduce one Bronsted sites per WO_3 group, and that the WO_3 centers react with the fumed Al_2O_3 surface to generate isolated centers with one Bronsted site associated with the isolated WO_3 group. Subsequent addition of WO_3 even for a "bi-layer" structure does not perturb the density of Bronsted centers, and only a relatively small number of Lewis acid centers are introduced.

The high temperature stability of about equal densities of WO_3 per unit surface area on fumed alumina versus aqueous-prepared alumina are shown in table 2. The 900 ° C and the 1100 ° C steam treatments distinguish between WO_3 on F-Al_2O_3 and WO_3 on A-Al_2O_3. WO_3 on fumed alumina compared to a conventional alumina support at both 900 ° C and 1100 ° C is more stable. The surface area of the fumed alumina sample after 1100 ° C steam treatment is about monolayer coverage of a compact, probably non-polymeric layer [2,5]. For comparison purposes, the relative surface area stabilities of other Group IV, V, and VI oxides are shown in table 3. Titania, Hf, Nb, and Ta all show stabilization *at one-half monolayer coverage*. These results correspond to 70–80% retention of the original fumed alumina surface area, and are the most high temperature

Table 2
Steam stability of WO_3 on fumed Al_2O_3 compared to WO_3 on aqueous-prepared Al_2O_3

	Steam temperature (°C, 90% H_2O-10% N_2 16 hrs.)	Surface area (m^2/g)
5% WO_3 on fumed-Al_2O_3	500	97
5% WO_3 on fumed-Al_2O_3	900	95
5% WO_3 on fumed-Al_2O_3	1100	34
10% WO_3 on aqueous-prepared Al_2O_3*	500	163
10% WO_3 on aqueous-prepared Al_2O_3*	900	71
10% WO_3 on aqueous-prepared Al_2O_3*	1100	8

* Engelhard gamma-alumina of 180 m^2/g, see ref. [5].

Table 3
Relative stability of group IV, V and VI-B transition metal oxide on fumed-alumina

Sample supported on fumed Al_2O_3	Surface area (m^2/g) after steam treatment at 1100 °C for 16 hours
1.7 wt% TiO_2	67
4.5 wt% HfO_2	77
2.9 wt% Nb_2O_5	71
4.8 wt% Ta_2O_5	80
3.1 wt% MoO_3	21
5 wt% WO_3	34
Fumed Al_2O_3	7

stable supports to steam environments reported in the literature. Only supported MoO_3 after steaming goes to a low surface area theta-alumina phase.

The surface area stability and the number of Bronsted acid centers of binary oxides are shown in table 4. These samples were prepared by first impregnating

Table 4
Acidity and surface area stability for mixed oxide systems on fumed-Al_2O_3

Sample supported on fumed Al_2O_3	Number Bronsted sites ($Ho \leq -8.2$) for a 500 °C calcined sample (micromoles/g)	Surface area after 1100 °C steam treatment, 16 hrs	Number Bronsted sites ($Ho \leq -8.2$) for 1100 °C steam samples (micromoles/g)
5 wt% WO_3	225	34	25
5 wt% WO_3 + 1.7 wt% TiO_2	75	20	0
5 wt% WO_3 + 2.6 wt% ZrO_2	125	36	25
5 wt% WO_3 + 4.5 wt% HfO_2	75	39	38
5 wt% WO_3 + 2.9 wt% Nb_2O_5	125	25	25
5 wt% WO_3 + 4.8 wt% Ta_2O_5	25	56	75

Table 5
Lewis and Bronsted acid sites of Ta_2O_5 and WO_3 "bi-layer" solid acid systems

	Number (Ho ≤ -8.2) Bronsted sites for a 500 ° C calcined sample	Number (Ho ≤ -8.2) Lewis sites for a 500 ° C calcined sample	Bronsted-to Lewis Ratio
Ta_2O_5 * (1st) + WO_3 * (2nd) (A)	50	325	0.15
WO_3 * (1st) + Ta_2O_5 * (B)	225	100	2.30
WO_3 * + Ta_2O_5 * (Co-impregnation (C)	200	175	1.10
A Steamed at 900 ° C	200	125	1.10
B Steamed at 900 ° C	275	0	∞
C Steamed at 900 ° C	287	38	7.60

* Ta_2O_5, 9.6 wt%; WO_3, 10 wt%; both equivalent to H30 micromoles/g.

Ti, Zr, Hf, Nb, and Ta oxide precursors [1,5] followed by depositing AMT. All of the samples show a significant reduction in the number of Bronsted acid centers compared to the WO_3 catalyst for the 500 ° C calcined samples. This would suggest that by reacting the fumed alumina surface with a strongly acidic oxide the surface is altered so that the subsequent addition of WO_3 cannot form the Bronsted center characteristic of WO_3 on the fumed alumina surface. In the case of the W-Ta sample the number of Bronsted sites was lowered by a factor of 9 compared to W alone. The Bronsted acidity of the 1100 ° C steamed samples are generally lower than the 500 ° C calcined samples with a density of Bronsted sites being about 0.5 to 1 micromole/m^2. In the case of the W-Ta sample there was an increase in the number of Bronsted centers for this steamed sample compared to the 500 ° C calcined sample. This W-Ta sample also shows the greatest surface area stability of all the samples investigated.

Three "multi-layer" binary oxide samples were prepared with W and Ta, and the Bronsted and Lewis sites were determined after a 500 ° C calcination and after a 900 ° C steam treatment (see table 5). These three samples were prepared at about "bi-layer" loading levels of the combined W plus Ta concentration. For one sample a near "monolayer" amount of Ta was deposited followed by a "monolayer" amount of W. For another sample the inverse order of W and Ta was prepared. In the third sample Ta and W were co-impregnated to give a "bi-layer" structure. Dramatic shifts in the ratio of Lewis-to-Bronsted sites was observed in this series of samples. In addition, steam treatment at 900 ° C showed a shift in all three samples to a greater fraction of Bronsted acid centers. Restructuring of the surface structures apparently occurs despite the fact that the surface area is not changing dramatically in this series of 900 ° C steamed samples. All of the samples show a shift towards a greater surface density of Bronsted acid sites for the steamed versus the unsteamed catalysts with very little change in the total number of strong acid sites. The catalysts with a tungsten outer layer and the mixed W-Ta "bi-layer" were active catalysts for cracking normal hexane. In contrast, the catalyst with a Ta outer layer was completely inactive . Following steam treatment all of the catalysts showed high cracking activity. Apparently, steam treatment creates active sites for the inactive catalyst by causing restructuring of the inactive Ta outer layer generating an active mixed oxide structure.

3. Conclusions

The density of Lewis acid centers on fumed alumina is only one-fourth that of aqueous-prepared alumina. Tungsten oxide supported on fumed alumina has a very high density of Bronsted acid sites for half-monolayer, monolayer, and bi-layer loading levels. By pre-deposition of Group IV and V oxides onto fumed alumina the number of Bronsted acid centers introduced by a secondary WO_3 deposition step is greatly decreased. Ti, Zr, Nb, Ta, W and other oxide supported on fumed alumina have 1100 °C steam stability as do binary oxide couples containing WO_3. "Bi-layer" structures containing Ta-W show significant shifts in the Bronsted-Lewis site density depending on which oxide is first reacted with the fumed alumina surface. A mixed Ta-W oxide "bi-layer" for comparison had four-fold the number of Bronsted sites compared to a sample with Ta reacted with the alumina surface followed by W deposition. The hexane cracking activity of the Ta-W "bi-layer" oxide structure showed that the configuration with Ta oxide "coating" W oxide was inactive whereas the mixed "bi-layer" oxide and the configuration with W oxide "coating" Ta oxide were highly active.

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