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NOTES

A Modified Benesi Titration Procedure Useful to Quantify the Lewis and Brønsted Sites of Solid Acids

The Benesi method of acid center titration has been modified using dry box techniques so that only 1 g of sample is required to determine the strength distribution of a given sample. Addition of an excess of sterically hindered pyridine to a second 1-g sample, and subsequent titration with *n*-butylamine using dry box procedures, also allows the strong Lewis acid sites to be quantitatively assessed. By combination of this titration procedure with the modified Benesi procedure the number of Brønsted sites could be determined accurately. Four classes of solid acids were investigated: γ-alumina, high-silica silica–alumina, fluorided alumina, and WO_3 on Al_2O_3. © 1989 Academic Press, Inc.

Reitsma and Boelhouwer (*1*) adapted dry box techniques to the acid center titration of solid acids using the Benesi method (*2*). In this paper they also reported an improved method to establish the titration endpoint by using small samples to which the indicator was added, where equilibrium of the *n*-butylamine was established to the strongest acid sites using ultrasonic mixing of the samples. We have combined the use of dry box procedures with ultrasonic treatment where a 1-g sample is used to establish the manifold of acid sites of a solid acid sample. We employed a procedure different from that of Reitsma and Boelhouwer where small aliquots of the sample were removed after each addition of aliquots of butylamine, equilibrated by ultrasonic treatment, to which a series of Hammett indicators were added. One can establish accurately the endpoint for each indicator by this aliquot procedure. In this fashion, the complete manifold of acid centers can be determined using just 1 g of sample. It is the use of dry box procedures which makes this procedure practical.

We have adapted the above procedure so that the strong Lewis and Brønsted acid centers of a solid acid can be established (*3*). In this procedure two 1-g samples of a solid acid are employed. One sample establishes the total strong Lewis and Brønsted centers by the above procedure using the modified Benesi method described. The second 1-g sample is titrated as described previously *after equilibration of excess 2,6-disubstituted pyridine* (DSP, dimethyl or di-*tert*-butyl) *with the strong Brønsted centers of the sample*. This procedure is based on the fact that 2,6-disubstituted pyridine can bond strongly to Brønsted acid centers but are sterically hindered to the extent that they only weakly bond to Lewis acid centers, as found in the classic work of Brown and Johanneson (*4*). By addition and equilibration of excess 2,6-disubstituted pyridine the subsequent butylamine titration will give accurately the number of Lewis acid centers of the sample. By the difference between the two titrations of a given solid acid the strong Brønsted sites can be established. Benesi employed (*5*) 2,6-dimethylpyridine (DMP) to determine the Brønsted acid centers of solid acids using a chromatographic method. In work relevent to the use of the method described in this paper to determine the Lewis–Brønsted site ratio Knozinger *et al.* (*6*) reported that 2,4,6-trimethylpyridines form coordination bonds to the strong Lewis acid centers of alumina but are displaced by the much weaker, but sterically unhindered base, pyridine. Our dual-sample titration method (DSTM) relies on the ability of a sterically

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unhindered base to displace the weakly coordinated, sterically hindered base from strong Lewis acid centers but not from strong Brønsted acid centers.

Four acidic solid acids were characterized by the DSTM: (i) reforming grade γ-Al_2O_3, (ii) Davison high-silica silica–alumina (Lo-Al, 14% Al_2O_3 content), (iii) fluorided alumina prepared out under mild conditions using HCF_3 (*7*), and (iv) 10% WO_3 on Al_2O_3 of different acidity (*8–10*). In the case of tungsten-based solid acids, comparisons of Lewis–Brønsted acid centers obtained by temperature-programmed desorption of 2,6- and 3,5-dimethylpyridine (*10*) and those determined by the DSTM of this paper will be compared.

EXPERIMENTAL

In the method development phase of our dual-sample titration procedure, three supports were investigated:

1. A reforming grade γ-alumina support of 180 m^2/g (Engelhard Industries, Inc.) with a high density of strong Lewis acid centers.
2. A Davison silica–alumina (14 wt% Al_2O_3 content) of 550 m^2/g surface area with a distribution of Lewis and Brønsted sites.
3. Fluorided aluminas of different surface area which were prepared under mild conditions using HCF_3 (*7*) with a high density of strong Brønsted sites.

All of these supports were calcined in an air-purged muffle furnace at 500°C for 16 h prior to transfer to the dry box.

It was important at the start of this work to learn how to combine dry box procedures with ultrasonic treatment to best utilize the time required for analysis. Ultrasonic treatment was first established to be essential to allow equilibration, as indicated in previous work (*1, 11*), to the strongest sites of a given sample.

We found that 1400 μmol/g of *n*-butylamine could be added to the above dehydrated γ-alumina without titration of the -8.2 strength Lewis sites (see Ref. (*2*)). With a 10-min ultrasonic treatment between butylamine aliquot additions, the number of strong -8.2 strength Lewis acid centers was found to be 300–325 μmol/g. This sample of alumina provided a base case for our DSTM without deviation from the above number of Lewis sites for over an 8-year period. Clearly, ultrasonic treatment is required to achieve equilibration of adsorbed butylamine to the Lewis sites of alumina.

Our standard procedure was to dehydrate the support at 500°C for 16 h before transfer to a nitrogen-purged dry box. We found that samples treated in a horizontal tube furnace equipped with stopcocks gave titration results identical to those of samples transferred directly at 200°C to the nitrogen-purged transfer port of the dry box. The samples were quickly evacuated after transfer. Four or five samples were analyzed by the dual-sample method at a given time, i.e., 8 to 10 samples were transferred. The still hot samples were weighed in the dry box, and 10 ml of benzene (subsequently toluene) was added upon cooling of the samples.

In most titrations we had a fair idea what the number of total Lewis and Brønsted sites would be so the first additions of butylamine were 50 or 100 μmol/g in order to quickly approach the endpoint. Subsequent additions were then 25 or 10 μmol/g depending on the accuracy of the titration desired. To the sample used to titrate the Lewis sites only a 400 μmol/g addition of 2,6-disubstituted pyridine was added and equilibrated by ultrasonic treatment before addition of 25 μmol/g aliquots of butylamine to titrate the Lewis sites. In actual practice, the two portions of a given sample, with and without the 400 μmol/g of DSP addition, were analyzed side-by-side even though different aliquot additions of butylamine were usually added to each sample. This was done for practical reasons as the tightly capped and taped sample bottles were all removed from the dry box for simultaneous ultrasonic treatment in a bath at 65°C for 10 min. Upon completion of the ultrasonic treatment all of the samples were returned to the transfer port of the dry box. It was found upon experimentation that a good method to establish the titration endpoint was to remove three drops of each sample containing suspended powder and to put the drops into a small, disposable, aluminum weighing dish. To each separate drop the −8.2, −5.6, and −3.0 strength Hammett indicator solutions were added (*2*), and the endpoints for each indicator were readily established. The benzene, and subsequently toluene, solution used in this work was dried using activated 4A molecular sieves. The butylamine and 2,6-dimethyl- and 2,6-di-*tert*-butylpyridine (DTBP) were dried by distillation from KOH. The crystalline indicators were dried in a desiccator using molecular sieves before preparation of 0.1 *M* solutions in benzene or toluene.

RESULTS AND DISCUSSION

First we established using 1 g of catalyst in 10 ml of benzene that all three of these classes of materials, alumina, silica–alumina, and fluorided alumina, required an ultrasonic treatment to equilibrate both *n*-butylamine and the sterically hindered amine to the strong acid centers. One could add 1400 μmol/g of *n*-butylamine to alumina without titration of the strong −8.2 strength Lewis sites. With ultrasonic equilibration the number of sites was established to be 300–325 μmol/g using butylamine titration. Without employment of the ultrasonic equilibration step the evaluation of the total acidity by butylamine titration for silica–alumina and the 162 m^2/g fluorided-alumina sample also failed to reach a titration endpoint at a butylamine level of 1000 μmol/g. This amount of butylamine was at least twice the number of strong sites for both of these acidic oxides established in other work (*1, 11*). Obviously, addition of amine to a dehydrated hydroxylated support will not equilibrate the base to the strong acid centers (*1, 11*). Some discussion of the potential overestimation of support acidity by the Benesi method has recently surfaced in recent work; see Deeba and Hall (*12*) and Mishima and Nakajima (*13*). In our view the Benesi method using ultrasonic equilibration shows good agreement with other detailed methods (*10, 14*) and will be discussed subsequently.

The next step was to add the sterically hindered pyridine to the three classes of solid acids, equilibrate the base to the strong acid centers, and then titrate the samples with butylamine. For all of the samples 400 μmol/g of dimethylpyridine or di-*tert*-butylpyridine was added. This amount of sterically hindered base was in excess of the number of Brønsted sites for all of the samples. In the case of the alumina support the number of acid sites titrated was not influenced by the DMP or DTBP addition. The number of Lewis sites with and without DMP or DTBP addition was found to be 300–325 μmol/g.

For the fluorided aluminas the acidity has been described in detail elsewhere (*7*). Fluoride contents from the submonolayer to where bulk alumina fluoride was formed were characterized by the DSTM, and the results are shown in Table 1. One can see from these results that the surface acid centers are primarily Brønsted acid centers over a wide range of fluoride contents. Therefore, we have established the use of

TABLE 1

Lewis–Brønsted Site Distribution of Fluorided Aluminas[a]

Sample wt% AlF_3	Surface area (m^2/g)	Number of Lewis sites (μmol/g)	Number of Brønsted sites (μmol/g)
3.5	175	<50	275 ± 25
6.9	171	<50	250 ± 25
13.3	162	<50	225 ± 25
25.4	143	<50	225 ± 25
46.1	96	<50	125 ± 25
63.5	79	<25	100 ± 12
78.2	47	<25	75 ± 12
100	9	None	None

[a] McVicker *et al.* (*7*).

TABLE 2

Lewis–Brønsted Site Distribution of Amorphous Silica–Alumina Catalysts

Sample	Surface area (m^2/g)	Number of Lewis sites (μmol/g)	Number of Brønsted sites (μmol/g)
10% Al_2O_3–90% SiO_2[a]	448	224	127
10% Al_2O_3–90% SiO_2[a] (water exposed)	448	128	220
25% Al_2O_3–75% SiO_2[a]	412	227	119
25% Al_2O_3–75% SiO_2[a] (water exposed)	412	104	245
14% Al_2O_3–86% SiO_2[b]	550	263 ± 10	125 ± 10
14% Al_2O_3–86% SiO_2[b]	550	255 ± 10	125 ± 10
14% Al_2O_3–86% SiO_2[b]	550	260 ± 10	145 ± 10
14% Al_2O_3–86% SiO_2[c]	550	163 ± 12	250 ± 25

[a] Schwarz (*14*).

[b] Davison silica–alumina (Lo-Al), separate portions from top, middle, and bottom of freshly opened 1-gal. can evaluated by the dual-sample titration procedure.

[c] Two samples were equilibrated with ultrasonic treatment with 7 μl H_2O/1 g of sample before the dual-sample titration was employed.

this two-step titration procedure for solid acids dominated by either Lewis or Brønsted acidity.

For amorphous silica–alumina the dual-sample titration method shows excellent agreement with detailed characterization of analogous silica–aluminas by Schwarz using infrared spectroscopy (*14*); see Table 2. The characterization of Davison silica–alumina calcined up to 900°C using the DSTM is the subject of a separate report (*15*). Addition of 7 μl of water (just sufficient to titrate the strong acid centers of amorphous silica–alumina) to the dehydrated silica–alumina sample in benzene and the equilibration of the sample with an ultrasonic treatment for 10 min resulted in a shift of a significant number of Lewis sites to Brønsted sites using the DSTM; see Table 2. This shift from Lewis to Brønsted acid centers upon contact with water is quite similar to that observed in the work of Schwarz (*14*); also, see Table 2.

In conclusion, it is clear from the excellent agreement between these two separate methods of determining Lewis–Brønsted site density of silica–alumina that our new titration procedure can be employed to define the acidity of supports with either Lewis or Brønsted acid sites, or to a support with both centers present simultaneously.

In previous work we have shown (*8–10*) that WO_3 on Al_2O_3 is a strong acid with both Lewis and Brønsted acid centers of strength analogous to high-silica silica–aluminas. In Table 3 we compare the DSTM and temperature-programmed desorption using 3,5- and 2,6-dimethylpyridine to define the number of Lewis and Brønsted acids of two WO_3 on Al_2O_3 solid acids. These two solid acids differ in surface area by over a factor of 2. For the steamed 10% WO_3 on Al_2O_3 sample the DSTM measured the Lewis and Brønsted acid centers to be 80 and 95 μmol/g, respectively. In the TPD method, the estimate of the acid centers was 57 and 98 μmol/g. Clearly, this is acceptable agreement between the two methods. In the case of the unsteamed 10% WO_3

TABLE 3

Effect of Steaming on Acid Site Distribution for 10% WO_3/Al_2O_3

Steam treatment (90% H_2O/10% N_2)	BET surface area (m^2/g)	Total acid sites[a] of strength $H_0 < -8.2$	Total Brønsted acid sites of strength $H_0 < -8.2$	Total Lewis sites of strength $H_0 < -8.2$	Acid site density[b]		
					Total	B	L
None (calcined, 500°C)	211	425 (367)[c]	150 (185)[c]	275 (182)[c]	2.01	0.71	1.30
16 hr at 760°C	111	225	150	75	2.03	1.35	0.68
16 hr at 870°C	79	175 (155)[d]	95 (98)[d]	80 (57)[d]	2.22	1.20	1.01

[a] Titration technique (in parentheses, acid sites within ± 25 μmol/g cat.)

[b] Acid site density is defined as number of acid sites per square meter catalyst = micromoles per square meter.

[c] TPD analysis, Ref (*10*).

[d] TPD analysis, WO_3 in Al_2O_3 calcined at 950°C of 70 m^2/g surface area.

on Al_2O_3 catalyst the DSTM measured the acid centers to be 275 and 150 μmol/g. In the TGA method the estimate of the acid centers was 182 and 185 μmol/g. The total numbers of strong acid centers measured by these two methods are in fair agreement, 425 versus 367 μmol/g. However, the TPD method gives higher values for the Brønsted sites and lower values for the Lewis sites than the DSTM for the unsteamed sample. Certainly, the distributions of acid centers made up by both Lewis and Brønsted sites on the 10% WO_3 on Al_2O_3 samples by both methods are in agreement. In the case of the unsteamed sample where WO_3 groups are responsible for only about 30% of monolayer coverage of the alumina surface, the two acid center titration methods are perhaps in disagreement because of specific local restructuring of the hydroxyl surface upon interaction with these strong bases at the different temperatures employed for equilibration of the bases.

Note that there is a significant shift in the density of Brønsted centers upon steam treatment of 10% WO_3 on Al_2O_3 as measured by the DSTM. This shift from Lewis to Brønsted centers was also observed by infrared studies using pyridine (*10*). For all three samples, in Table 3, the density of total strong sites stays essentially constant as measured by the DSTM over a wide range of surface areas.

CONCLUSIONS

Employing dry box procedures coupled with ultrasonic treatment provides a modified Benesi titration procedure where the acid center strength distribution from ≤ -3.0 to ≤ -8.2 H_0 strength can be determined using a single 1-g sample. By the technique of equilibration of the Brønsted acid centers with a sterically hindered amine the Lewis centers can be titrated in an analogous fashion. By combination of these two titration techniques of two portions of a single sample the Lewis–Brønsted acid center distribution can be determined. Good agreement of results using such a dual-sample titration method with other techniques has been demonstrated for high-silica silica–aluminas, and for WO_3 on Al_2O_3 solid acids. In principle, this DSTM could also be applied to determine the distribution of acid centers for solid acids with acid centers of H_0 strength > -3.0. It would be necessary to establish that the indicators employed could displace the weakly bound, sterically hindered amine from the weak Lewis acids of such solid acid systems. Using the DSTM the Lewis–Brønsted acid centers of six solid acids could be obtained per day. This is a much faster method for a reasonably accurate estimate of the acid center strengths, and the number of strong Lewis and Brønsted centers of solid acids, than TPD or detailed infrared spectroscopy studies.

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L. L. MURRELL[1]
N. C. DISPENZIERE, JR.

Exxon Research and Engineering Company
Route 22 East
Annandale, New Jersey 08801

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[1] Present address: Engelhard Corp., Menlo Park, CN40, Edison, NJ 08818.