of nickel which was determined precisely by Auger spectroscopy. However, the present evidence is not yet conclusive as to whether only the surface content of nickel is connected with the catalytic activity or the electronic factor is connected with it.

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REFERENCES

1. SACHTLER, W. M. H., AND DORGELO, G. J. H., *J. Catal.* **4**, 654 (1965).
2. SACHTLER, W. M. H., AND JONGPIER, R., *J. Catal.* **4**, 665 (1965).
3. CAMPBELL, J. S., AND EMMETT, P. H., *J. Catal.* **7**, 252 (1967).
4. TAKASU, Y., YAMASHINA, T., SHIMIZU, H., ONO, M., AND NAKAYAMA, K., *Shokubai* **13**, 170P (1971).
5. NAKAYAMA, K., ONO, M., AND SHIMIZU, H., *J. Vac. Sci. Technol.* **9**, 749 (1972).
6. ONO, M., *J. Vac. Soc. Jap.* **14**, 94 (1971).
7. SHOOTER, D., AND FARNSWORTH, H. E., *J. Phys. Chem. Solids* **21**, 219 (1961).
8. ELEY, D. D., AND SHOOTER, D., *J. Catal.* **2**, 259 (1963).
9. ELEY, D. D., AND NORTON, P. R., *Discuss. Faraday Soc.* **41**, 135 (1966).
10. ONO, M., TAKASU, Y., NAKAYAMA, K., AND YAMASHINA, T., *Surface Sci.* **26**, 313 (1971).
11. TARNG, M. L., AND WEHNER, G. K., *J. Appl. Phys.* **42**, 2449 (1971).
12. QUINTO, D. T., SUNDARUM, V. S., AND ROBERTSON, W. D., *Surface Sci.* **28**, 504 (1971).

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Determination of Proton Acidity of Solid Catalysts by Chromatographic Adsorption of Sterically Hindered Amines

To be useful, an acidity measurement of a solid catalyst should fulfill two requirements: (1) it should be simple to carry out; and (2) it should determine the seat of catalytic activity. Adsorption measurements of basic reagents such as ammonia (*1*, *2*), *n*-butylamine (*3*), or quinoline (*4*) appear to fulfill the first requirement but do not fulfill the second. For example, on a unit surface basis pure alumina chemisorbs more ammonia than silica–alumina (*1*), yet alumina is inactive for cumene cracking* under conditions that silica–alumina is highly active (*5*). On the other hand, though infrared measurements of chemisorbed pyridine provide proton acidity values that correlate with catalytic activity (*7*), this type of measurement is not simple. It would be much easier to determine surface acidity by measuring chemisorption of a basic reagent that is specific for proton acidity—if such a reagent exists.

Thirty years ago, Brown, Schlesinger, and Cardon (*8*) began a series of studies of the acid–base reactions of substituted boranes with a variety of substituted amines. These studies revealed that the stability of the resulting "salts" was strongly dependent on the size and number of alkyl groups attached to the acid and

* Presumably, the inactivity of alumina results from its lack of proton acidity—infrared measurements show that pyridine chemisorbed on alumina is entirely in a coordinated state (*6*).

to the base. For example, the nitrogen atom in a substituted amine such as 2,6-dimethylpyridine or, better yet, 2,6-di-*tert*-butylpyridine was so sterically hindered that the amine would not undergo reaction with a Lewis acid such as trimethylboron (*9*, *10*). Such amines did form stable salts with hydrogen chloride. Thus, Brown *et al.* demonstrated that a sterically hindered amine can be a specific basic reagent for proton acids in the presence of a strong Lewis acid. In view of the above findings we chose the hindered amine, 2,6-dimethylpyridine, as the adsorbate for the determination of proton acid sites in the presence of Lewis acid sites on solid surfaces. To form a frame of reference the adsorption of an unhindered amine, pyridine, was also measured.

Because of its relative simplicity and speed, a chromatographic technique was used to carry out adsorption measurements (*11*, *12*). The present variant of this method consists of passing a dilute mixture of amine vapor in helium at a constant flow rate through a bed of the catalyst at 400°C and noting the time required for the amine vapor to emerge from the catalyst bed. This "breakthrough" time is determined by continuously monitoring the exit stream by means of the thermal conductivity detector and recorder in an Aerograph GLC unit. A correction for dead space is applied by repeating the above procedure with quartz powder in place of the catalyst sample and subtracting the resulting time from that obtained in the case of the catalyst sample. The amount of amine adsorbed on the catalyst sample is calculated from the corrected breakthrough time, the helium flow rate, and the partial pressure of amine vapor. The partial pressure of amine is given by its vapor pressure of 0°C, since it is introduced by bubbling the helium through liquid amine that is kept in an ice bath. After breakthrough occurs, the catalyst sample is swept with pure helium (that now bypasses the amine saturator) for 30 min at the same temperature to remove physically adsorbed amine. Helium is then diverted through the saturator and a second breakthrough time determined. Two sets of data are obtained. "Physical plus chemical" adsorption (calculated from the first breakthrough time) is the total amount of amine taken up at 400°C per gram of solid at the vapor pressure of the amine at 0°C. "Chemical" adsorption (calculated from the difference between the first and second breakthrough times) is the amount of amine that remains adsorbed per gram of solid after the sample is swept with helium at 400°C.

Three solids were chosen as adsorbents: silica–alumina, alumina, and silica gel. The silica–alumina sample (MS-A-3 cracking catalyst obtained from American Cyanamid Company) had an aluminum content of 11.7 wt %, a surface area of 520 m^2/g and a pore volume of 1.1. cm^3/g. The alumina sample was Alcoa's Grade F-20 alumina which had been rendered sodium free by means of repeated treatments with 1 *M* ammonium acetate. The purified product had a surface area of 210 m^2/g and a pore volume of 0.23 cm^3/g. The silica gel sample was Davison's Grade 950 silica gel, and had a surface area of 750 m^2/g and a pore volume of 0.37 cm^3/g. In each case, the adsorbate was dried in flowing helium at 550°C directly before adsorption was measured.

TABLE 1
ADSORPTION OF AMINES ON SILICA–ALUMINA, ALUMINA AND SILICA GEL AT 400°C[a]

	Amine adsorption (micromoles/gram)			
	2,6 Dimethylpyridine[b]		Pyridine[c]	
Solid	Physical plus chemical	Chemical	Physical plus chemical	Chemical
Silica–Alumina	63	31	86	36
A'umina	30	13	109	60
Silica gel	2	0	5	2

[a] Helium flow rate: 50 cm^3/min.
[b] Vapor pressure of 2,6-dimethylpyridine: 1.1 mm Hg at 0°C.
[c] Vapor pressure of pyridine: 4.5 mm Hg at 0°C

Adsorption measurements at 400°C are reported in Table 1. The data show that more pyridine is chemisorbed on alumina than on silica–alumina. Chemisorption on silica gel is negligible under the same conditions. In the case of 2,6-dimethylpyridine, however, the relative order of adsorption on silica–alumina and alumina is reversed, i.e., silica–alumina chemisorbs 2.5 times as much amine as does alumina. As has been indicated in the previous discussion, we assume that this reversal occurs because steric hindrance of the nitrogen atom in 2,6-dimethylpyridine tends to prevent its coordination to aluminum atoms in the alumina surface but does not prevent its reaction with proton acids in the silica–alumina surface. This reagent therefore appears to show a reasonable degree of specificity for proton acidity at 400°C.

Separate tests by means of a pulse reactor (*13*) showed that the alumina and silica gel samples were inactive for cumene cracking at a temperature (300°C) at which the silica–alumina sample cracked 30% of the cumene. We therefore conclude that chemisorption measurements of a sterically hindered amine such as 2,6-dimethylpyridine have potential utility as an index of catalytic activity of acidic solids.

References

1. Barth, R. T., and Ballou, E. V., *Anal. Chem.* **33**, 1080 (1961).
2. Clark, A., Holm, V. C. F., and Blackburn, D. M., *J. Catal.* **1**, 244 (1962).
3. Benesi, H. A., *J. Phys. Chem.* **61**, 970 (1957).
4. Mills, G. A., Boedeker, E. R., and Oblad, A. G., *J. Amer. Chem. Soc.* **72**, 1554 (1950).
5. Tamele, M. W., Ryland L. B., Rampino, L., and Schlaffer, W. G., *World Petrol. Congr. Proc. 3rd 1951* **IV**, 98 (1951).
6. Parry, E. P., *J. Catal.* **2**, 371 (1963).
7. Ward, J. W., and Hansford, R. C., *J. Catal.* **13**, 154 (1969).
8. Brown, H. C., Schlesinger, H. I., and Cardon, S. Z., *J. Amer. Chem. Soc.* **64**, 325 (1942).
9. Brown, H. C., and Johanneson, R. B., *J. Amer. Chem. Soc.* **75**, 16 (1953).
10. Brown, H. C., and Kanner, B., *J. Amer. Chem. Soc.* **75**, 3865 (1953).
11. Eberley, P. E., *J. Phys. Chem.* **65**, 1261 (1961).
12. Mosely, R. B., and Archibald, R. C., *J. Catal.* **2**, 131 (1963).
13. Benesi, H. A., *J. Catal.* **8**, 368 (1967).

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