

## Luminescent Probes of Acidity in Heterogeneous Catalysts

Peter Szedlacsek,<sup>a</sup> Steven L. Suib,<sup>\* a,b</sup> Michel Deeba<sup>c</sup> and Gerald S. Koermer<sup>c</sup>

<sup>a</sup> Department of Chemistry, U-60, University of Connecticut, Storrs, CT 06269-3060, USA

<sup>b</sup> Department of Chemical Engineering, University of Connecticut, Storrs, CT 06269-3139, USA

<sup>c</sup> Engelhard Corporation, Menlo Park, CN 28 Edison, NJ 08818, USA

Luminescence experiments have been used to distinguish Brønsted and Lewis sites in alumina and zeolite catalysts.

We report here that luminescence methods can be used to study acid-base adduct formation in alumina and zeolite catalysts. All solid supports were evacuated at elevated temperatures between 400 and 600 °C to pressures of less than  $1 \times 10^{-4}$  Torr (1 Torr = 133.322 Pa) prior to sorption of pyridine at room temperature. Samples were then evacuated at 50 °C intervals from 50 °C up to the calcination temperature and luminescence spectra were recorded.<sup>1,2</sup> The same sample was analysed throughout these studies in an *in situ* cell that was weighed before each experiment and after each thermal treatment.

Alumina, zeolite NH<sub>4</sub>Y and zeolite NH<sub>4</sub>mordenite were studied. The luminescence emission spectra are shown in Fig. 1 for alumina, zeolite NH<sub>4</sub>Y and zeolite NH<sub>4</sub>mordenite dehydrated at 400 °C, exposed to pyridine vapour and subsequently evacuated at 300 °C. Alumina has a broad luminescence spectrum particularly in the 380–550 nm region which is due to phosphorescence of bound pyridine. The luminescence band 300–360 nm is due to fluorescence of bound pyridine. In the case of NH<sub>4</sub>Y zeolite both of these bands are present with the lower wavelength being more intense than the higher (phosphorescence) band. For NH<sub>4</sub>mordenite both bands are present with approximately the same intensities.

The mordenite and Y zeolite samples have relatively broad fluorescence bands and a maximum intensity near 340 nm whereas the alumina sample has a maximum that is closer to 330 nm.

Fig. 2 shows luminescence spectra for the same three samples that have been dehydrated to 600 °C prior to room temperature adsorption of pyridine followed by evacuation at 400 °C. Here the Y zeolite and alumina samples only show a fluorescence band, whereas the mordenite sample shows some fluorescence and phosphorescence. A second fluorescence

maximum for zeolite Y and mordenite occurs at 334 and 340 nm, respectively.

These data are qualitatively in line with observations made from IR and catalytic methods used to study acidity in solid supports.<sup>1–11</sup> The fluorescence band centred on 325 nm is assigned to Lewis sites whereas the fluorescence band near 340 nm is assigned to Brønsted sites. In addition, the phosphorescence band appears to predominantly reflect Brønsted sites.

The phosphorescence region has at least two peaks one centred around 430 nm and another near 480 nm. It is possible that the lower wavelength band again reflects Lewis acidity whereas the higher wavelength reflects Brønsted acidity similar to the fluorescence region. The qualitative trends for Y

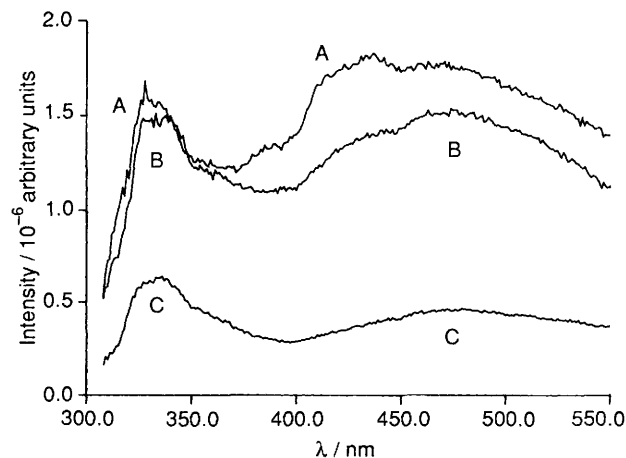


Fig. 1

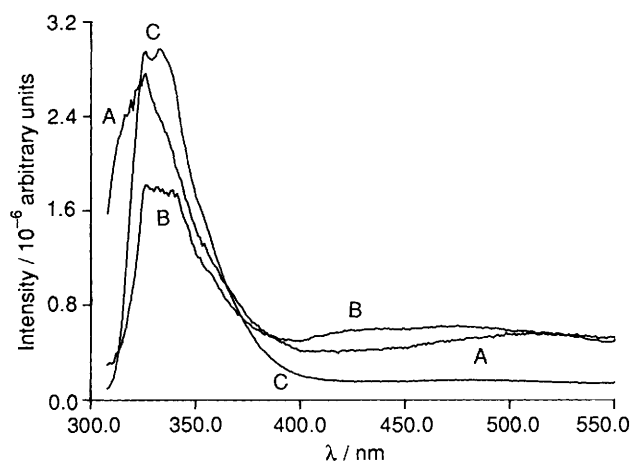


Fig. 2

zeolite show that dehydration at 400 °C leads to both Lewis and Brønsted sites, whereas 600 °C dehydration gives predominantly Lewis sites. In the case of alumina, Lewis sites are predominant at both dehydration temperatures. For mordenite, the luminescence bands are quite broad and intense in all regions, suggesting that both Lewis and Brønsted sites having a range of strengths are present.

Another intriguing possibility is that alumina shows five bands in the phosphorescence region at 375, 410, 440, 470 and 520 nm. These bands may be the five different hydroxy groups on alumina proposed by Peri.<sup>9</sup> If so, then the phosphorescence region could show the different types of hydroxy groups, some of which are not acidic for such supports. In fact, this alternative more satisfactorily explains the reduction in intensity in the phosphorescence region of the Y zeolite after

600 °C dehydration, as well as the structure and intensity of the phosphorescence of the mordenite sample.

These data are consistent with known trends in acidity for alumina, and zeolites Y and mordenite<sup>10</sup> as well as homogeneous solutions.<sup>12,13</sup> In fact, catalytic data for mordenite<sup>11,14</sup> suggest that Lewis acid sites are important in cracking reactions for samples dehydrated to 400 °C.

Received, 14th May 1990; Com. 0/02127J

## References

- 1 J. F. Tanguay and S. L. Suib, *Catal. Rev. Sci. Eng.*, 1987, **29**, 1.
- 2 M. L. Occelli, D. Psaras and S. L. Suib, *J. Catal.*, 1985, **96**, 363; M. W. Anderson, S. L. Suib and M. L. Occelli, *J. Catal.*, 1989, **118**, 31.
- 3 L. L. Murrell and N. C. Dispenziere, *J. Catal.*, 1989, **117**, 275.
- 4 H. Pfeifer, *J. Chem. Soc., Faraday Trans. 1*, 1988, **84**, 3777.
- 5 D. Barthomeuf, *Stud. Surf. Sci. Catal.*, 1987, **38**, 177.
- 6 J. C. Vedrine, G. Coudurier and B. F. Mentzen, *ACS Sympos. Ser.*, 1988, **368**, 66.
- 7 J. Dwyer, J. Dewing, N. E. Thompson, P. J. O'Malley and K. Karim, *J. Chem. Soc., Chem. Commun.*, 1989, **13**, 843.
- 8 E. P. Parry, *J. Catal.*, 1963, **2**, 371; M. Deeba and W. K. Hall, *J. Catal.*, 1979, **60**, 417; M. Deeba and W. K. Hall, *Z. Phys. Chem.*, 1985, **144**, 85.
- 9 J. Peri, *J. Catal.*, 1976, **41**, 227; J. Peri, *J. Phys. Chem.*, 1965, **69**, 211; 220; 231.
- 10 W. J. Mortier and R. A. Schoonheydt, *Prog. Sol. State Chem.*, 1985, **16**, 1.
- 11 E. A. Lombardo, G. A. Sill and W. K. Hall, *J. Catal.*, 1989, **119**, 426; H. A. Benesi and B. H. C. Winquist, *Adv. Catal.*, 1978, **27**, 97.
- 12 K. Hensen and W. Sarholz, *Theoret. Chim. Acta*, 1968, **12**, 206.
- 13 J. Juffernbruch and H. H. Perkampus, *Spectrochim. Acta Part A*, 1983, **39**, 905.
- 14 F. R. Cannings, *J. Phys. Chem.*, 1968, **72**, 4691; A. K. Aboul-Gheit, *Thermochim. Acta*, 1988, **132**, 257.