Fluoro Tetrasilicic Mica as a Unique Support for Metal Ion Catalysts

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Fluoro tetrasilicic mica which is a synthesized inorganic ion exchanger has no acid sites, as revealed by temperature programmed desorption of ammonia, hence its potential as a catalyst support.

In studies on catalysis with metal ion-exchanged forms of zeolitic and layered silicate minerals, the characteristic activities of the exchanged metal ions are not observed distinctly because the strong acidity of the minerals promotes acid-catalysed reactions.[1] We now report that fluoro tetrasilicic mica (TSM) [$Na{\cdot}Mg_{2.5}Si_4O_{10}F_2$] is likely to be suitable as a support for metal ion catalysts.

We investigated the acidity of four kinds of layered silicate minerals by temperature programmed desorption (T.P.D.) of ammonia. TSM, taeniolite (Taen) [$Li{\cdot}Mg_2LiSi_4O_{10}F_2$], and hectorite (Hect) [$Li_{1/3}{\cdot}Mg_{8/3}Li_{1/3}Si_4O_{10}F_2$] are synthesized minerals.[2] Bentonite (Bent) [$Na_{1/3}{\cdot}Al_{5/3}Mg_{1/3}Si_4O_{10}(OH)_2$] is a natural clay mineral. The interlayer cations of these minerals are easily exchangeable with any desired metal ions. In addition to the layered minerals, we also examined the acidity of molecular sieve 13X (Zeol) and silica gel (SiO_2) for comparison.

The T.P.D. of ammonia was started at 200 °C to eliminate the participation of weakly adsorbed ammonia. Each sample (400 mg) was pretreated at 400 °C for 2 h in helium carrier gas (20 ml/min). Ammonia was adsorbed at 200 °C until the acid sites of the minerals were saturated. The T.P.D. was conducted up to 400 °C at a heating rate of 10 °C/min.

The T.P.D. curves obtained are illustrated in Figure 1. Mass spectroscopic analysis showed that no gases besides ammonia were desorbed in the T.P.D. measurements of any of the samples. The amount of ammonia desorbed was calculated from the peak area and the values per unit weight of the samples are summarized in Table 1, where the peak temperature of the T.P.D. curve and the surface area of each sample are also tabulated. The amounts of ammonia desorbed

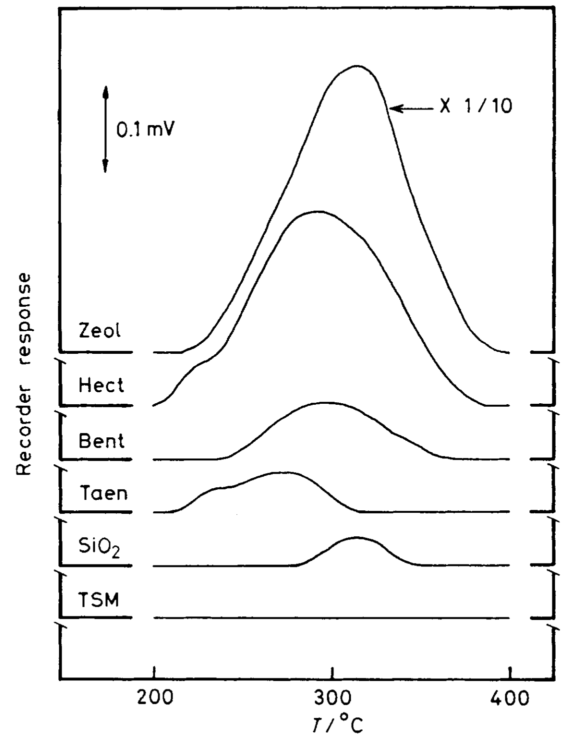

Figure 1. T.P.D. of ammonia from various silicate minerals. The curves are displaced vertically for clarity.

Table 1. Amount of ammonia desorbed and peak temperature observed in T.P.D.

Mineral	Surface area[a] /(m^2/g)	Peak temperature /°C	Amount of ammonia desorbed (μmol/g)	(nmol/m^2)
TSM	9.1	—	0	0
Taen	25.2	272	1.7	67
Bent	38.1	296	2.3	60
Hect	14.2	292	11	770
SiO_2	347	314	0.54	1.6
Zeol	575	316	140	240

[a] Brunaner–Emmett–Teller measurements with nitrogen after the sample had been evacuated at 400 °C.

from the layered minerals were from 1/10 to 1/80 smaller than that from Zeol, and the peak temperatures with the layered minerals were lower than that with Zeol. The results show that there were fewer acid sites on the layered minerals than on Zeol and the acid strength of the minerals was weaker than that of Zeol. The observations are consistent with the acidic properties of these minerals described in some reviews.[3] The amount of ammonia desorbed from unit surface area is listed in the last column of Table 1. The values suggest that the population of acid sites on the layered minerals Taen, Bent, and Hect is comparable to that on zeolites. SiO_2 is often used as an inert carrier to prepare a supported catalyst, even though the result shows that SiO_2 certainly has acid sites.

It is unusual that no chemisorbed ammonia was detected in the T.P.D. from TSM because inorganic cation exchangers have acidic properties in general. We also prepared the proton exchanged form of TSM by passing its dilute aqueous sol through a column packed with an ion exchange resin (Amberlite IR-120B) and again found no chemisorbed ammonia in the T.P.D. These facts suggest that the silicate sheets of TSM have no acid sites and are probably inactive as a catalyst. The results of our studies on the conversion of methanol show that the catalytic activities of the metal ion-exchanged forms of TSM (M–TSM's) differ widely depending on the metal ion.[4] Cu–TSM catalyses the dehydrogenation of methanol to form methyl formate selectively whereas Cu-exchanged forms of the other silicate minerals catalyse the dehydration simultaneously, because of the acidity of the minerals.[5] It is likely that TSM is a particularly appropriate carrier for use in the study of the intrinsic activities of metal ions in heterogeneous catalysis.

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References

1 P. B. Venuto and P. S. Landis, *Adv. Catal.*, 1968, **18**, 259; J. M. Adams, D. E. Clement, and S. H. Graham, *Clays Clay Miner.*, 1982, **30**, 129.

2 K. Kitajima and N. Daimon, *Nippon Kagaku Kaishi*, 1974, 685; *ibid.*, 1975, 991; *ibid.*, 1976, 597; H. Toraya, S. Iwai, F. Marumo, M. Daimon, and R. Kondo, *Z. Kristallogr. Kristallgeom. Kristallphys., Kristallchem.*, 1976, **44**, 42.

3 C. N. Satterfield, in 'Heterogeneous Catalysis in Practice,' McGraw-Hill, New York, 1980, p. 151; H. E. Swift, in 'Advanced Materials in Catalysis,' eds. J. J. Burton and R. L. Garten, Academic Press, New York, 1977, p. 209.

4 Y. Morikawa, T. Goto, Y. Moro-oka, and T. Ikawa, *Chem. Lett.*, 1982, 1667.

5 Y. Morikawa, K. Takagi, Y. Moro-oka, and T. Ikawa, *Chem. Lett.*, 1982, 1805.