

Studies of New Zeolite Derivatives of Stilbite

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Natural zeolite stilbite and its Ag(I)-exchanged derivative have been studied by IR spectral, XRD and TG analyses and the results obtained have been reported. Both physical and chemical adsorptions have been indicated in the interactions of CO₂, NH₃ and H₂S adsorbates with adsorbents stilbite and its Ag(I)-exchanged form.

Naturally occurring mineral stilbite has been used to prepare cation-exchanged derivative with Ag(I) and both the zeolites have been used for adsorbing CO₂, NH₃ and H₂S. The aim of the present study is to test their suitability as cation exchangers and adsorbents for CO₂, H₂S and NH₃. Ag(I)-exchanged zeolites have found applications in radio-iodine monitoring¹ and isomerization of 1-butene². Similarly, adsorbates like H₂S and NH₃ pose hazards both in the atmosphere and water and need to be controlled³.

The stilbite specimen, from the region around Decan trap, was obtained from GSI, Pune. It was finely powdered in a mechanical grinder and sieved to obtain uniform particle size. Its Ag(I)-exchanged derivative was prepared by treating a portion repeatedly with aqueous silver sulphate solution followed by filtration, washing and air-drying. The adsorbed derivatives were prepared by the procedures described in an earlier communication⁴. Both stilbite and Ag(I)-exchanged form were analyzed for Na(I), Ca(II) and Al(III) using a Varian Techtron AA-6 Atomic Absorption Spectrometer. TG analysis of the samples was carried out upto 800°C at a heating rate of 10°C min⁻¹ on a thermobalance supplied by FCIL, Sindri IR spectra of the samples and their residues, after TG analysis, were recorded between 4000 and 200 cm⁻¹ in KBr on a Perkin-Elmer IR spectrophotometer. The X-ray diffractograms, obtained between 2θ angles of 5° and 70° using a Philips PW1140 XRD unit and copper target, are reproduced in Figs 1 and 2.

The analytical data of stilbite sample are given in Table 1. TG analysis gave a mass loss of 17.66% which can be attributed to its dehydration. The analytical data for Ag(I)-exchanged stilbite are also given in Table 1. It showed a mass loss of 20.99% on TG analysis. The change in the composition is the direct result

Table 1—Analytical Data

Sample	Na%	Ca%	Al%	Si% + O% (by difference)	H ₂ O%
1. Stilbite	0.62 (0.79)†	4.76 (5.50)	8.15 (9.28)	68.81 (64.63)	17.66 (19.80)
2. Ag(I)- stilbite	0.46	0.80	6.57	71.18	20.99

† Figures in parentheses are for the ideal composition of stilbite: NaCa₄Al₁₀Si₂₆O₇₂·32H₂O¹⁴

of cation exchange and can be interpreted as follows. Whereas stilbite showed Ca(II)/Na(I) ratio as 4.4:1, Ag(I)-exchange altered it to 1:1 thereby showing more than four times exchange of Ca(II) compared to that of Na(I). The reduction in the percentage of Al(III) is an indication of the extent of dealumination and increase in the Si/Al ratio. IR spectral data between 4000 and 200 cm⁻¹ and XRD data using CuK_α radiation of both stilbite and the Ag(I)-exchanged form have been used to characterize them⁵⁻⁷. The results of IR spectral studies (Table 2) of the adsorbed derivatives exhibit the presence of the adsorbate species. Additional bands for free CO₃²⁻(II) ions (1440 cm⁻¹), physically adsorbed H₂S (1390 cm⁻¹) and NH₄(I) ions (1450 cm⁻¹) are seen in the IR spectra of the CO₂, H₂S and NH₃ interacted derivatives of stilbite. On the other hand, IR band for physically adsorbed CO₂ (2300 cm⁻¹) appears in the case of CO₂-interacted Ag(I)-exchanged stilbite. There is also definite indication of complex formation with NH₃, giving rise to [Ag(NH₃)₂]⁺ species in the IR spectrum of ammonia interacted Ag(I)-exchanged stilbite which shows IR bands at 1500 and 250 cm⁻¹. The H₂S interaction results in the formation of a black sample, and the presence of Ag₂S species is indicated by the IR band at 2380 cm⁻¹. The IR spectra of the residues obtained after TG analysis show no bands for physically adsorbed water molecules and the adsorbed species indicating thereby dehydration, desorption and dehydroxylation as the major thermal events on heating the samples at a constant rate. Most of the TG plots exhibit loss of physically adsorbed water and the adsorbates at temperature upto 573K and dehydroxylation and decomposition above it. All the eight samples studied show distinct features in their TG plots and different values for total mass loss upto 1073K. Thus, H₂S interacted stilbite shows a fast rate of mass loss starting around 673 K over a 80 K stretch in its TG plot. Ammonia-interacted stilbite, on the other hand, shows an abrupt and very fast mass loss step around

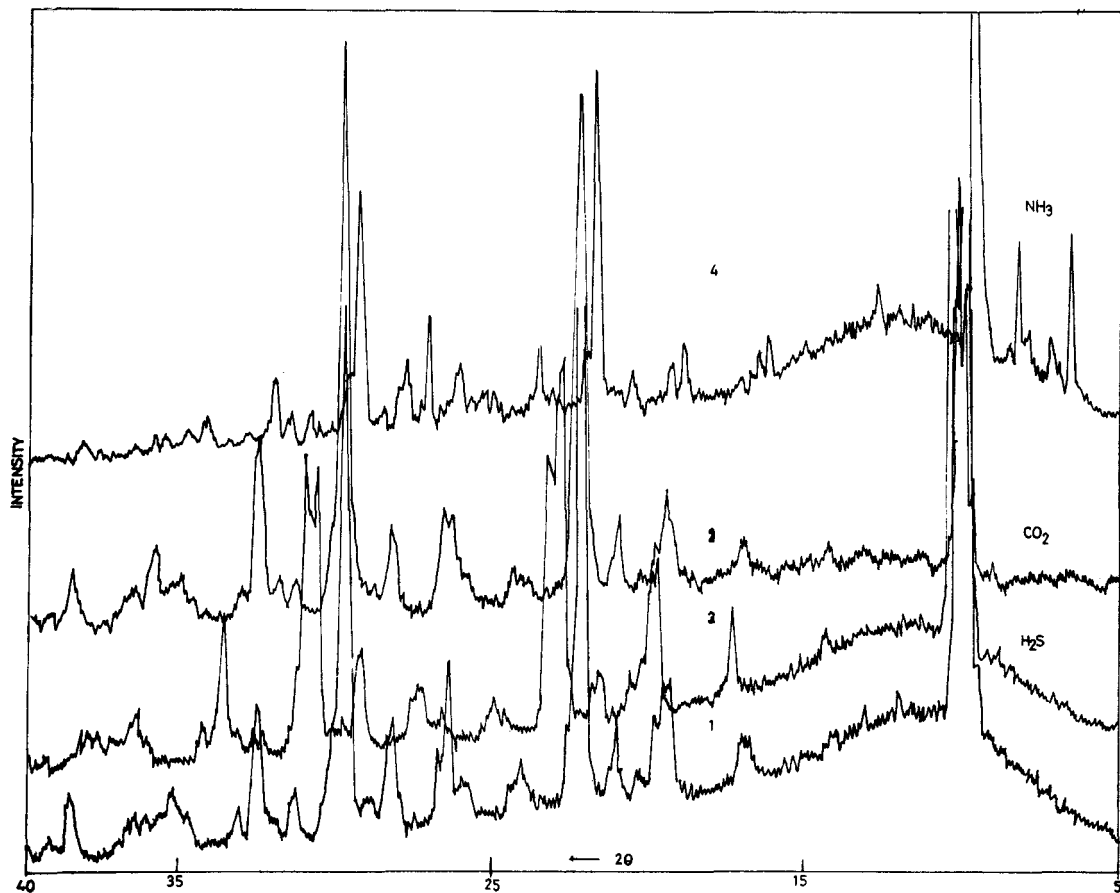


Fig. 1—X-ray diffractogram between 2θ -values of 5° & 40° of 1. stilbite, 2. stilbite + CO_2 , 3. stilbite + H_2S , 4. stilbite + NH_3

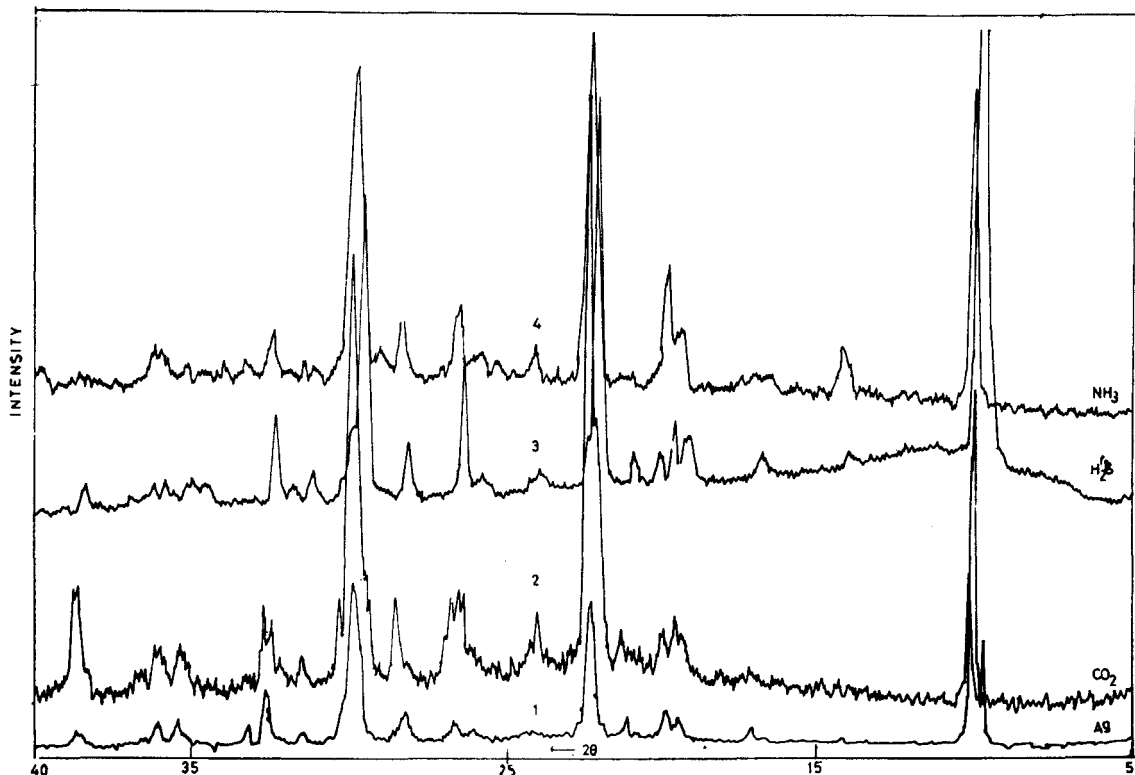


Fig. 2—X-ray diffractogram between 2θ -values of 5° & 40° of 1. Ag(I)-stilbite, 2. Ag(I)-stilbite + CO_2 , 3. Ag(I)-stilbite + H_2S , 4. Ag(I)-stilbite + NH_3

Table 2—Summary of Thermal & IR Spectral Data

Sample	Total mass loss(%)	IR peaks (cm ⁻¹) with assignments
1. Stilbite	17.66	3620 (O—H stretch), 1675 (O—H bend), 975-1095 (asymmetric T—O stretch), 710 (symmetric T—O stretch), 570 (double rings), 450 (T—O bend), 330 (pore opening).
2. Stilbite + CO ₂	16.45	3600 (O—H stretch), 1670 (O—H bend), 1440, 1430 (CO ₃ ²⁻), 1050 (asymmetric T—O stretch), 715 (symmetric T—O stretch), 580 (double rings), 460 (T—O bend), 310 (pore opening).
3. Stilbite + H ₂ S	20.18	3630 (O—H stretch), 1680 (O—H bend), 1390 (H ₂ S phys.), 1030 (asymmetric T—O stretch), 710 (symmetric T—O stretch), 560 (double rings), 445 (T—O bend), 280 (pore opening).
4. Stilbite + NH ₃	29.69	3590 (O—H stretch), 3470 (NH ₄ ⁺), 1695 (O—H bend), 1460 (NH ₄ ⁺), 960-1100 (asymmetric T—O stretch), 725 (symmetric T—O stretch), 580 (double rings), 450 (T—O bend), 360 (pore opening).
5. Ag(I)-Stilbite	20.99	3610 (O—H stretch), 1665 (O—H bend), 1030 (asymmetric T—O stretch), 710 (symmetric T—O stretch), 560 (double rings), 440 (T—O bend), 315 (pore opening).
6. Ag(I)-Stilbite + CO ₂	16.55	3420, (O—H stretch), 2320 (CO ₂ phys.), 1630 (O—H bend), 1020 (asymmetric T—O stretch), 690 (symmetric T—O stretch), 550 (double rings), 440 (T—O bend), 310 (pore opening).
7. Ag(I)-Stilbite + H ₂ S	25.10	3600 (O—H stretch), 2380 (H—S bend), 1665 (O—H bend), 1430 (H ₂ S phys.), 1080 (asymmetric T—O stretch), 565 (double rings), 430-460 (T—O bend, Ag—S bend), 345 (pore opening).
8. Ag(I)-Stilbite + NH ₃	13.53	3600 (O—H stretch), 3480 (N—H stretch), 1690 (O—H bend), 1530 (N—H bend), 1040 (asymmetric T—O stretch), 720 (symmetric T—O stretch), 570 (double rings), 440 (T—O bend), 250 (Ag—N linkage).

T=(Al, Si)O₄ tetrahedron

733K due to the loss of adsorbed H₂S and NH₃ respectively. Loss of water and CO₂ from stilbite and the CO₂-interacted sample occurs in more gradual steps and above 673K mass loss in both these cases becomes negligible. Among the four zeolite samples prepared by Ag(I)-exchange and subsequent interaction with the three adsorbates the high temperature mass loss is most prominent only in the case of the H₂S interacted derivatives. From around 873K the TG plot of this derivative indicates a fast mass loss step, comprising almost one-third of the total mass loss, due primarily to the decomposition of Ag₂S. Influence of dehydration and repetitive oxidation and reduction steps on the structures of Ag(I)-Y type zeolites⁸ and Ag(I)-stilbite⁹ has been investigated earlier. During the reduction Ag metal was found to precipitate as cluster within the void of the zeolite network and as crystallites on the surface. XRD plots are reproduced in Figs 1 and 2. Crystal structure of stilbite is known from earlier studies¹⁰. Evidence of site selectivity of Ag(I) in synthetic zeolites A and Y is also available¹¹⁻¹³ and the knowledge of these structural orientations forms the basis in the interpretation of the XRD data of stilbite derivatives obtained with Ag(I) and the various adsorbates. The intensities of the peaks of stilbite are decreased as a result of exchange with Ag(I) ions showing loss of crystal structure. The (230) reflection at 3.98Å becomes very strong from the adsorption of carbon dioxide on Ag(I)-stilbite, while the intensity of (001) reflection is increased to a considerable extent as a result of adsorption of hydrogen sulphide. Ammonia adsorption on Ag(I)-stilbite produces a new (030) reflection at 6.23Å while the (600) reflection becomes diffused. It has been suggested by earlier workers that interference by the high scattering power of silver may be misleading. Some differences exist in the X-ray diffractograms of stilbite and its adsorbed derivatives. Intensity of (001) reflection is reduced as a result of adsorption of CO₂. The H₂S adsorbed derivative exhibits doublets at 8.95Å, 3.90Å and at 2.97Å. Ammonia adsorption produces some new reflections.

References

1. SooHoo G Y, Lin Chien-Chang, Norris R M & Wilkinson C D, *IEEE Trans Nucl Sci*, **22** (1975) 657.
2. Sugihara H, Chen L Y & Yasumori I wao, *Bull Chem Soc Japan*, **47** (1974) 2089.
3. Manahan S E, *Environmental chemistry* (Willard Grant Press, Massachusetts) 1975.
4. Bhattacharya S & Banerjee S P, *Indian J Chem*, **25A** (1986) 104.
5. Pechar F & Rykl D, *Chem Zvesti*, **35** (1981) 189.
6. Joshi M S & Bhaskar B T, *Indian J pure appl Phys*, **19** (1981) 560.
7. Breck D W, *Zeolite molecular sieves, structure, chemistry & use* (John Wiley, New York) 1974.

NOTES

- 8 Gellens L R, Mortier W J & Uytterhoeven J B, *Zeolites*, **1** (1981) 85.
- 9 Herman K, Bica I & Jacob P A, *Magy Kim Foly*, **83** (1977) 34.
- 10 Slaughter M, *American Mineralogist*, **55** (1970) 387.
- 11 Nitta M, Matsumoto S & Aomura K, *JCS Chem Commun*, (1974) 552.
- 12 Nitta M, Ogawa K & Aomura K, *JCS Chem Commun*, (1974) 1015.
- 13 Matsumoto S, Nitta M, Ogawa K & Aomura K, *Bull chem Soc Japan*, **48** (1975) 1169.
- 14 Deer W A, Houri R A & Zussman J, *Rockforming minerals*, Vol. 4 (Longman, London) 1975.