

## Note

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### SOLID-STATE INTERACTION OF KALIGNOST AND Tl(I)-EXCHANGED 3A ZEOLITE

SATI PRASAD BANERJEE

*Department of Chemistry, Dr H. S. Gour Vishwavidyalaya, Sagar 470 003 (India)*

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TG behaviour of a sodium tetraphenyl boron (kalignost)-adsorbed 3A zeolite and its preheated form have been reported earlier [1]. The adsorption of the organic reagent was in aqueous phase. In the present study a partially thallium(I)-exchanged 3A zeolite was heated with an excess of solid kalignost on a Bunsen burner and the products of this interaction investigated by thermal, IR spectroscopic and X-ray diffraction methods. The aim of this work was to determine the nature of the solid-state interaction between Tl(I)-3A zeolite and kalignost with the available heat of decomposition of the latter. This study indicates that with the breaking up of the zeolite framework as a result of such an exothermic reaction at high temperature a new material consisting of oxides of Tl(I), B(III), Al(III) and Si(IV) together with any other alkali metal can be produced. Such a product would possess glass-like characteristics with high refractive index.

#### EXPERIMENTAL

Commercial 3A zeolite ( $K_{12}Al_{12}Si_{12}O_{48} \cdot 21H_2O$ ), obtained from Union Carbide Corporation (U.S.A.) in powder form, was repeatedly treated with a saturated aqueous AnalaR grade (B.D.H.) thallium(I) nitrate solution. The resulting partially-exchanged Tl(I)-zeolite [2] was filtered, washed free of excess ions and dried in air. A portion of this sample was mixed with solid kalignost (99% Merck) and heated in a silica crucible on a Bunsen burner. A vigorous reaction occurred with the decomposition of the organic reagent and burning of the carbonaceous matter. After continuous heating for several hours a heterogeneous mixture of yellowish granules, greyish powder and hard glassy material remained as residue. The glassy material tended to adhere to the walls of the crucible and could be removed only after scrapping. This mixed residue was studied by thermal methods like TG, DTA and DTG beyond 1000°C on an automatic derivatograph (MOM, Budapest, Type OD-102) at 10°C min<sup>-1</sup> heating rate. IR spectroscopy was

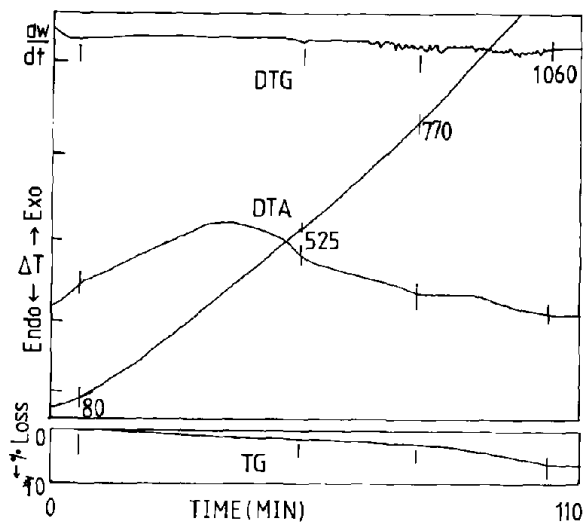


Fig. 1. Thermograms of the mixed product of interaction between kalignost and Tl(I)-3A zeolite showing DTG, DTA and TG plots up to 1100°C.

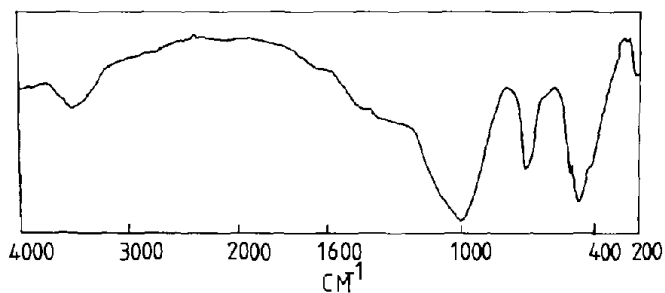


Fig. 2. IR spectra between 4000 and 200  $\text{cm}^{-1}$  of the mixed product in KBr phase.

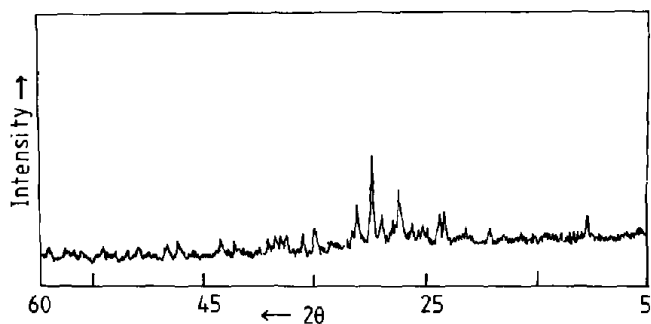
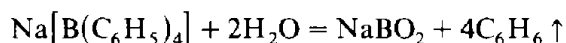


Fig. 3. X-ray diffractogram of the mixed product.

carried out between  $4000^{-1}$  and  $200\text{ cm}^{-1}$  in KBr phase on a Perkin-Elmer IR spectrophotometer and XRD analysis on a Philips PW1140 unit using a copper target. Figures 1–3 show the thermal analysis curves, IR spectra and the X-ray diffractogram of the mixed residue. The  $d$  spacings and intensities derived from the XRD studies are given in Table 1.

## RESULTS AND DISCUSSION

The solid-state interaction under study can be considered in the light of what is known about the thermal behaviour of the reactants. The Tl(I)-3A zeolite would lose water and the organic reagent would decompose at around  $200^{\circ}\text{C}$ . Direct heating brings about these events quickly with the result that burning of organic matter starts almost immediately after heating commences. The thermal reactions in the present case bring about the following changes. The steam evolved from the zeolite lattice would partly react with kalignost to produce sodium metaborate and benzene



Part of the benzene in the liquid phase is absorbed by the zeolite while most of it burns off leaving a carbonaceous residue. The mixed product thus contains both the glassy metaborate and the adsorbed derivative having a greyish appearance. The third major product, distinguished by its yellowish granular appearance, is obtained as a result of the partial interaction within the zeolite between Tl(I) ions and steam at elevated temperature, since the heat of decomposition of kalignost raises the temperature. The thermochemical reaction takes place as follows

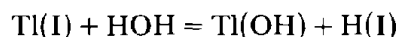


TABLE 1

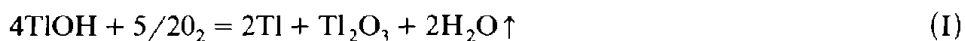
X-ray data for the product of interaction of Tl(I)-exchanged 3A zeolite and kalignost

$d$ (Å)	Intensity <sup>a</sup>	$d$ (Å)	Intensity <sup>a</sup>
8.51	m	2.50	m
3.83	m	2.39	w
3.74	m	2.37	w
3.51	w	2.33	w
3.40	w	2.30	w
3.26	s	2.14	w
3.08	m	2.09	w
3.00	s	1.92	w
2.87	m	1.88	w
2.56	m	1.79	w

<sup>a</sup> s, strong; m, medium; w, weak.

Tl(I) ions in the partially-exchanged 3A zeolite are thus partly replaced by the H(I) ions with the formation of thallium(I) hydroxide.

The thermal behaviour, as well as the IR spectral data of the mixed product, amply supports the sequence of events in the solid-state interaction. The desorption of adsorbed benzene and burning of the carbonaceous matter is indicated by a slow yet regular weight loss step of about 2.0% between 80 and 770°C. The DTA exotherm over the same temperature range also confirms this. The benzene molecules with their  $\pi$  electrons are capable of a strong interaction with the zeolite surface [3] and the extent of adsorption, only about 2.0%, is not large because of the high temperature. The thermograms also reveal the presence of Tl(OH) as it decomposes beyond 800°C with a corresponding weight loss of about 4.0% in a fast step up to about 1060°C. A weak but distinct exothermic DTA peak also appears around 850°C. The decomposition may proceed by either of the following two ways



The theoretical weight loss for the two reactions, about 3.9 and 3.8% for I and II, respectively, agrees well with the fast weight loss step of about 4.0% beyond 800°C. Heating the reactants together causes a total loss of water molecules from the zeolite framework. The thermal analysis plots, therefore, show no evidence of a dehydration process. As expected, the plots also do not conform to the known behaviour of either potassium(I) or thallium(I) tetraphenyl boron [4].

Earlier studies with synthetic zeolites revealed that the zeolite framework possessed two basic types of vibrations due to internal  $\text{TO}_4$  tetrahedra and external linkages between tetrahedra [5]. The IR spectra of the mixed product exhibits bands around 220, 470, 510, 710, 1000 and 3500  $\text{cm}^{-1}$  and shoulders in the region 1750–1300  $\text{cm}^{-1}$ . Of these bands only those at 470, 710 and 1000  $\text{cm}^{-1}$  are due to the internal T–O vibrations. These remain unchanged during thermal decompositions of zeolites [6]. Amorphous materials and zeolites calcined at temperatures greater than 1000°C do not show bands around 550–650  $\text{cm}^{-1}$  [7]. However, a small peak appears at 510  $\text{cm}^{-1}$  in the present case. Basically, the IR spectral data of the mixed product represent a dehydrated, adsorbed derivative of synthetic zeolite which has undergone hydrolysis and which retains its crystalline character. The band around 3500  $\text{cm}^{-1}$  is a clear indication of the presence of OH groups as a result of the cationic hydrolysis reaction mentioned earlier. Shoulders in the region 1750–1300  $\text{cm}^{-1}$  are due to the adsorbed benzene molecules.

X-ray data show that the zeolite, in general, retains its crystalline character even after undergoing the thermochemical changes such as dehydra-

tion, cationic hydrolysis and adsorption as a result of the solid-state interaction. These changes bring about the disappearance or diminishing of intensities of some peaks in the diffractogram (Fig. 3) when the X-ray data are compared with the known crystal structures of both hydrated and dehydrated Tl(I)-exchanged A zeolite [8].

This work thus helps to establish the fact that given the right conditions of temperature to break up the zeolite framework, this solid-state interaction can produce a material having Tl(I) and B(III) in the proper stoichiometric ratio alongside Al(III) and Si(IV). Such a material would possess a high refractive index and density.

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