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Surface and Some Catalytic Properties of a Germanic Near-Faujasite Molecular Sieve

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The germanic homologue of the silicic near-faujasite (Linde X) molecular sieve has been synthesized. The (cubic) unit cell parameter is 25.59 Å and the Ge/Al ratio is exactly unity. With respect to the unit cell molecular weight, the N_2, NH_3, and water adsorption isotherms are nearly identical with those obtained for the silicic Linde X zeolite, suggesting a very similar surface area and pore volume.

Introduction

A germanic near-faujasite zeolite has been synthesized. This contribution aims to describe some surface properties derived from ir spectroscopy study of the adsorption of NH_3, H_2O, CO_2, and of some organic molecules. From the spectroscopic viewpoint, one advantage of the germanic sieve arises from its optical transparency in the 1050–1300 cm^{-1} spectral region.

This is especially interesting when studying the mechanisms of reactions involving molecules in which skeleton C–C or C=O deformation vibrations exist, such as isopropanol and acetone for instance.

Experimental

Material

A pure sodium-germanic near faujasite of chemical formula $Na_2O \cdot Al_2O_3 \cdot GeO_2 \cdot x\ H_2O$ has been synthesized as described elsewhere (*1*). The X-ray powder diagram of this germanic zeolite is similar to the one of the Linde Na–X, with, however, slight shifts in the interplanar distances.

The unit cell parameter established according to the extrapolation method of Parrish et al. (*2*), is 25.59 Å, significantly higher than the values reported for the silicic X and Y Linde sieves which range between 24.63 and 24.97 Å for Si/Al ratios between 3.0 and 1.2 (*3*).

The ir spectrum of this germanic zeolite shows that the Ge–O stretching vibration is centered near 870 cm^{-1}, which is about 115 cm^{-1} lower then the Si–O vibration in the Linde Na–X.

The porous volume, derived from the N_2 and H_2O adsorption isotherms measured at −195 and 20.5°C, are almost identical to the values obtained for the Linde Na–X.

Adsorbed NH_3 on Na-Germanic Faujasite

Four bands are observed in the ir spectra of adsorbed NH_3 (Fig. 1) at 1178 and 1135 cm^{-1}, and at 3370 and 3260 cm^{-1}.

By comparison with the ir spectrum of gaseous ammonia (*4*) and taking into account the results of Wilmhurst on metal amine complexes (*5*), the two former absorptions are attributed to the symmetrical deformation of NH_3 coordinated to the Na cations, whereas the 3260 cm^{-1} would be the corresponding N–H stretching. The 3370 cm^{-1} band may represent the N–H stretching of weakly sorbed NH_3 molecules, with the correspond-

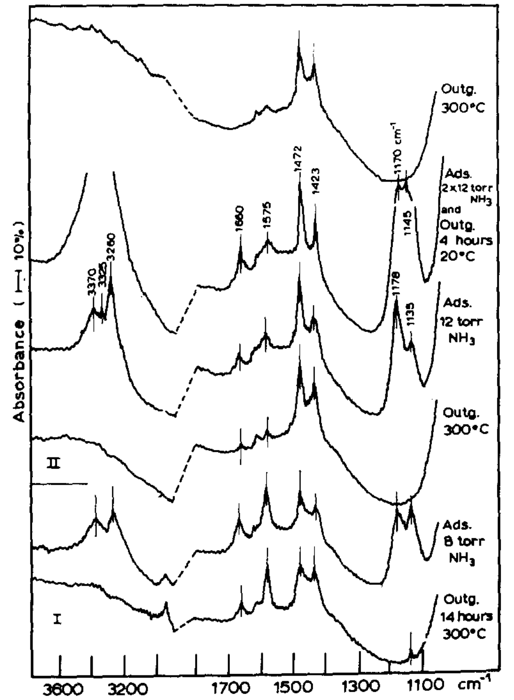

FIG. 1. Infrared spectra of NH_3 adsorbed at room temperature on two different samples, (I, 8 Torr, II, 12 Torr) of a germanic zeolite. The sequence of the experiments is from below to the top.

ing symmetrical and asymmetrical deformation bands absorbing near 950 and 1600 cm^{-1} (*4*), the former overlapping with the Ge–O stretching and the latter with some carbonate band.

Adsorbed H_2O and CO_2 on Na, NH_4 and Ca-Germanic Faujasite

The ir spectra recorded in the 3000–3500 and 1300–1700 cm^{-1} spectral regions of Na^+ and of partially NH_4^+ (3%) and Ca^{++} (62%) are shown elsewhere (*6*). The main frequencies and the proposed assignments have been compiled in Table I.

In agreement with the literature (*7, 8*), the 3690 cm^{-1} band is assigned to OH groups of water molecules coordinated to Na^+. The absorption band at 3658 cm^{-1}, developing after repeated washings in the Na-germanic faujasite, and observed in the NH_4^+ and Ca^{+2} partially exchanged samples, as shown in Table I, is assigned to GeOH groups, produced by partial lattice hydrolysis (Na^+), or by decationation (NH_4^+), or due to water dissociation (Ca^{2+}). This is in agreement with the findings by Uytterhoeven et al. (*9, 10*) and by Ward (*11*). The absorption at 3590 cm^{-1} by analogy with the results of Jacobs

TABLE I

OBSERVED ABSORPTION FREQUENCIES FOR Na, NH_4 AND Ca-GERMANIC WAFERS AFTER HEATING UNDER VACUUM AT THE INDICATED TEMPERATURES, AND PROPOSED ASSIGNMENTS

Na		NH_4		Ca		
100°C	250°C	100°C	250°C	100°C	250°C	Assignment
3690	—	3690	—	—	—	OH stretching of H_2O coordinate to Na^+
—	—	3658	3658	3655	3655	OH stretching of Ge–OH groups
3590	—	3605	3605	3593	3583	OH stretching of hydrolysis products
—	—	—	—	3520	—	OH stretching of $Ca(OH)^+$ ions
3340	—	3357	—	—	—	OH stretching of adsorbed H_2O
3250	—	3240	—	—	—	OH stretching of adsorbed H_2O
1664	1664	—	—	1660	—	H_2O deformation + chemisorbed CO_2 II
—	1615	—	—	—	—	Chemisorbed CO_2 I
—	1572	—	—	—	—	Chemisorbed CO_2 II
1480	1480	—	—	1460	1495	Carbonated species
1432	1432	—	—	—	1430	Carbonated species
—	1375	—	—	—	—	Chemisorbed CO_2 II

et al. (*8*) on ultrastable silicic zeolites, is probably due to amorphous material produced by lattice hydrolysis. Finally, the two bands near 3340 and 3250 cm^{-1} represent the OH stretching of hydration water.

In the 1700–1300 cm^{-1} spectral region, the 1664 is assigned to the deformation vibration of hydration water, with a small contribution of a chemisorbed CO_2 species. All the other bands in this region are due to chemisorbed CO_2 or to carbonate species (*6*).

Infrared Study of the Reaction of Methylacetylene on Na-Germanic Faujasite

The ir spectra shown in Fig. 2 were scanned after heating a Na-germanic wafer in the presence of 6 Torr of methylacetylene (MA) and 20 Torr of H_2 for 2 hr at increasing temperatures. Upon adsorption of MA, the formation of OH structural groups (band at 3638 cm^{-1}) strongly suggests the opening of Al–O–Ge linkages, with, in agreement with the observations of Chang and Kokes (*12*) on zinc oxide, the formation of surface propargyl anions as follows:

$$\mathrm{Al{-}O{-}Ge} + \mathrm{CH_3{-}C{\equiv}CH} \rightarrow |\mathrm{Al{-}CH_2{-}C{\equiv}CH} \rightleftarrows \mathrm{Al{-}CH_2{=}C{=}CH_2}| + \mathrm{GeOH}.$$

The GLC analysis of the gas phase of a duplicate experiment carried out at 300°C showed that the main products were allene acetylene, propylene and unreacted methylacetylene.

The attribution of the different bands observed are summarized in Table II.

The formation of acetone at high temperature would involve the presence of water, either of residual origin, of from the reaction of H_2 with lattice oxygens.

Detailed discussion on the assignments and a schema accounting for the different reaction products are given in Ref. (*6*).

Infrared Study of the Reaction of Isopropanol on Na-Germanic Faujasite

Infrared spectra of the reaction of isopropanol (1 Torr) adsorbed on a Na-germanic wafer (pretreated for 2 hr at 250°C under vacuum) heated at increasing temperatures are shown in Fig. 3.

Gas phase analyses performed with GLC on separate experiments carried out at 300°C in a batch reactor, show that the main reaction products are propylene, acetone, diisopropylether, and saturated C_4.

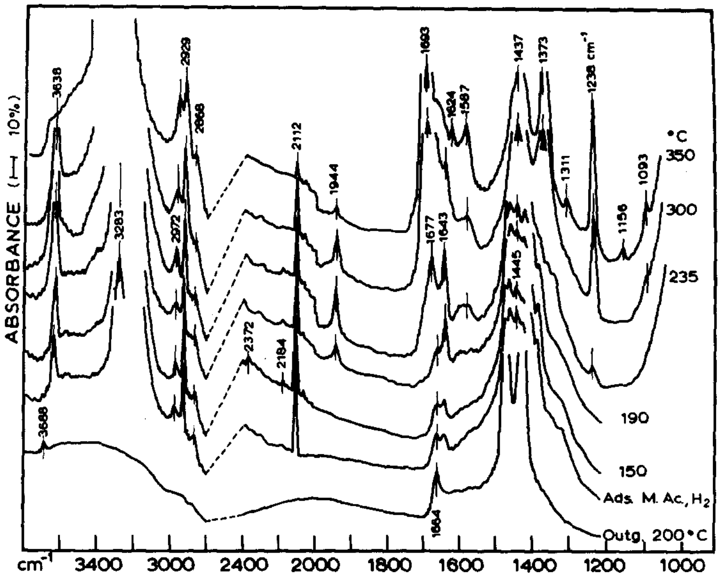

FIG. 2. Infrared spectra showing the reaction of methylacetylene (6 Torr) and hydrogen (20 Torr) on Na-germanic faujasite heated for 2 hr at increasing temperatures.

TABLE II

INFRARED ABSORPTION BANDS OBSERVED IN THE REACTION OF METHYLACETYLENE WITH H_2 IN Na-GERMANIC SIEVE

Adsorbed species					
$CH{=}C{=}CH_2$	$CH_2{=}C{=}CH_2$	$CH_3{-}CH{=}CH_3$	$HC{\equiv}CH$	CH_3COCH_3	Assignment
			3300–3200		$\nu C{\equiv}C$
3300–3200	2972	2972			$\nu (C{=}C){-}H$
				2929	$\nu (C{-}C){-}H$
				2868	
				1707	$\nu C{=}O$
2112	1944		1944		ν C=C in allene or C≡C in acetylene
		1643			$\delta{\equiv}C{=}C$ in propylene
			1330		$\delta C{-}H$
	1373	1377–1470		1350–1450	$\delta{=}C{-}H$ and $\delta{-}C{-}H$
				1238	$\delta C{=}O$

Beside the bands due to chemisorbed CO_2 (1432, 1488, 1578 cm^{-1}) and to hydration water (1663 cm^{-1}), spectral modifications upon heating at various temperatures are clearly visible, especially those corresponding to the skeleton vibrations of the isopropyl group at 1160, 1131, and 1113 cm^{-1} (all three hidden by the broad Si–O band near 1000 cm^{-1} in silicic zeolite). As isopropanol transforms, propylene is produced (bands at

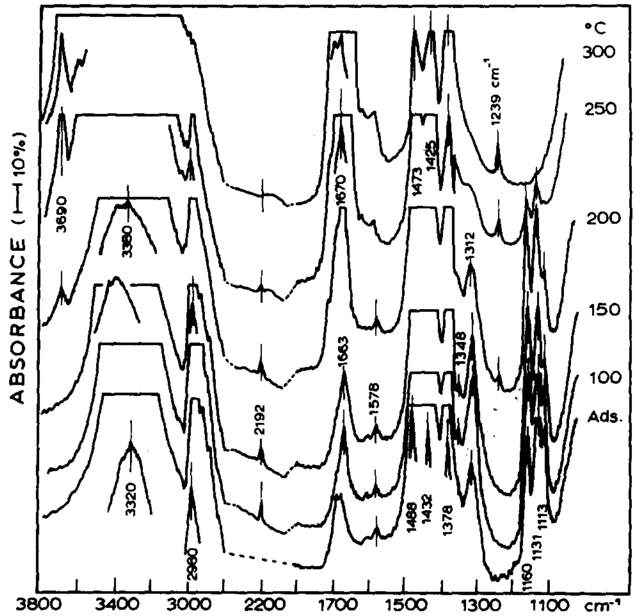

FIG. 3. Infrared spectra showing the reaction of isopropanol (1 Torr) on Na-germanic faujasite heated for 2 hr at increasing temperatures.

1670 and 1378 cm^{-1}), acetone appears (evidenced by the bands at 1239 and shoulder at 1700 cm^{-1}) and water molecules give rise to the 3690 cm^{-1} band and a contribution to the 3380 and 1663 cm^{-1} absorptions.

Discussion

These preliminary results aimed to characterize some surface and catalytic properties of a germanic near faujasite.

Structural similarities with the Linde-X sieve and nearly identical porous volumes have been found.

Infrared investigation on adsorbed NH_3 and on the transformation of isopropanol have illustrated an interesting aspect of the germanic zeolite, which is the transparency in a spectral region where silicic sieves are blind. Furthermore, reacting methylacetylene on germanic sieve resulted in a small production of acetone which was readily identified by ir, whereas GLC analyses did not reveal its presence in the gas phase.

The main difference observed between silicic and germanic sieves is the greater structural fragility of the latter. This has been clearly shown by their relative thermal stability (*1*). The Ni^{2+} and Cu^{2+} saturation also provoked deeper lattice damage in the germanic sieve. The reaction of methylacetylene, with the simultaneous formation of surface propargyl group and structural GeOH group further support the instability of the Al–O–Ge linkage.

The explanation for this is that Ge can exist in two coordination states with respect to oxygen, the fourfold and the sixfold coordination, the latter being slightly more stable. In the case of silicic sieves, the silica tetrahedra would have a stabilizing effect onto the alumina tetrahedra. In germanic sieves this effect would be rather small and would explain the relatively lower structural stability, the tendency of germanic to realize its octahedral configuration, whenever possible, being stronger.

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