

DECOMPOSITION OF ALCOHOLS OVER DIFFERENT FORMS OF GERMANIUM SUBSTITUTED FAUJASITE AND PHILLIPSITE

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(Received 11th February, 1978)

Several cation forms of germanium substituted X zeolite and phillipsite are tested for their dehydration/dehydrogenation properties of alcohols. Both types of sites are present and act independently, excluding E_1cB type mechanism. No secondary reactions occur in striking contrast to their silicium homologues. Isotope effects measured on different samples indicate the mechanism is in between E_1 and E_2 , depending on the zeolite and the cation.

Upon ion exchange with polyvalent cations, the same behavior is observed as for other zeolites and other proton catalysed reactions. Dehydrogenation seems to occur at exposed surface germanium atoms.

Very weak acid sites related to the presence of residual surface carbonate are shown to dehydrate only tertiary alcohols.

Introduction

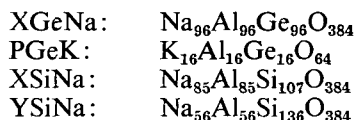
The catalytic decomposition of alcohols is strongly dependent upon the alcohol structure but also on the nature of the catalyst and, therefore, may provide information on the general way a catalyst functions in elimination and even other reactions. Practically, the use of alcohols as source of fuels and basic chemicals nowadays is being considered very seriously.

The dehydration/dehydrogenation capability of silicic zeolites was investigated intensively and the knowledge was reviewed several times [1—3]. The dehydration reaction was found to be catalysed by very weak acid sites [1, 2, 4] and is therefore a measure of the overall Brønsted acidity, although for polyvalent ion exchanged zeolites the direct influence of cations cannot be excluded experimentally [3, 5]. The dehydrogenation reaction of alcohols was related to the presence of cations, even at the impurity level [6].

It is the aim of the present work to test these ideas about reaction mechanism and active sites on the germanium homologues of faujasite and phillipsite zeolites.

Experimental

The synthesis and physico-chemical characterization of germanium substituted faujasite and phillipsite were described in detail [7—10]. The samples are denoted as follows. The first capital indicates the type zeolite (X, Y or P, phillipsite). This is followed by the indication whether the zeolite is silicic (Si) or germanic (Ge). Then is given the parent cation (Na or K) followed by the exchanged cation and its degree of exchange in %. The parent zeolites have the following anhydrous unit cell composition:



Other cations were exchanged into these zeolites, using diluted solutions and low solid to liquid ratios [4, 10]. The reactants were of analytical grade and deuterated alcohols were prepared according to a procedure found in literature [11].

Decomposition of alcohols was studied either in a conventional recirculation reactor or in a continuous flow reactor operating in the differential mode. Analysis of the products was done *in situ* using gas chromatography. *In situ* infrared spectra were recorded on a BECKMAN IR—12 double beam grating spectrometer.

Results

Reaction selectivity for isopropanol decomposition

Under the experimental conditions, the main reaction products from isopropanol were acetone and propylene. At the relatively high reaction temperatures ($>200^{\circ}\text{C}$), only traces of di-isopropylether were found. They will be neglected further on. In Table I, it is shown that neither the reaction time in the recirculation reactor, the alcohol pressure, nor the reaction temperature have a pronounced influence on the reaction selectivity. This is confirmed in the flow reactor for a wide range of contact times (0.5—3.5 s). The data therefore indicate that the sites responsible for dehydration and dehydrogenation act independently.

Fig. 1 shows the evolution of the amount of secondary products formed at increasing degree of isopropanol conversion in comparable conditions and for several catalysts. In the silicic faujasites (X and Y) they are of major importance, while on the germanic X and P zeolites, they are found in negligible amounts. This allows to state that in a wide range of reaction conditions, the germanium zeolites are highly selective towards primary products. Dehydrogenation is favored on PGe zeolite while the XGe zeolite has more pronounced dehydration power (see Table I).

Influence of the degree of cation exchange

Fig. 2 shows the relative rates of isopropanol dehydration and dehydrogenation for XGe in which Ca^{2+} was exchanged for Na^{+} , Ni^{2+} for Na^{+} , and Ni^{2+} for Ca^{2+} . In each case, there is a more than proportional increase of the dehydration activity.

Table I
Influence of reactant pressure and reaction temperature on selectivity of isopropanol decomposition

Catalyst	Reaction temp. °C	P kNm ⁻²	Selectivity ⁽¹⁾ in % for		S ⁽²⁾
			propylene	acetone	
XGeNaNi (60)	250	3.733	76.5	23.5	2.3
	280	3.733	76.9	23.1	2.5
	300	3.733	77.0	23.0	1.8
XGeCaNi (60)	300	1.333	78.9	21.1	1.2
	230	3.733	88.4	11.6	1.1
	270	3.733	88.3	11.7	0.5
	300	3.733	89.3	10.7	1.2
PGeKNi (60)	300	1.333	91.3	8.7	2.2
	350	3.733	85.1	14.9	2.4
	230	3.733	4.9	95.1	0.8
PGeKNi (60)	300	1.333	11.4	88.6	1.1
	300	3.600	10.6	89.4	1.3

⁽¹⁾ Calculated on the basis of primary products.
⁽²⁾ Standard deviation of selectivity during reaction.

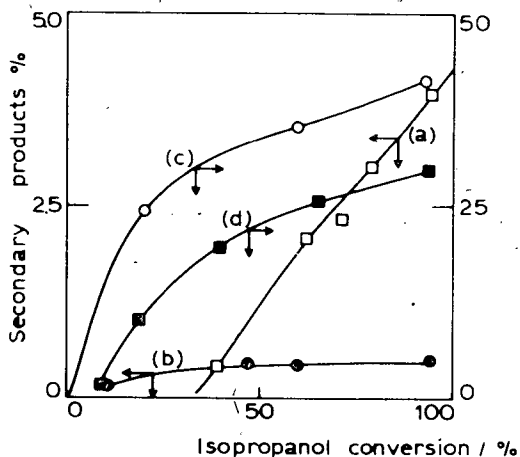


Fig. 1. Amount of secondary products formed against the degree of isopropanol conversion over: a) PGeNaNi (46) at 300° C; b) XGeCaNi (56) at 350° C; c) YSiNaCa (67) at 300° C; d) XSiNaCa (50) at 300° C

at exchange levels exceeding 50%. A very similar relation has been observed for the silicic analogues X and Y, and also for many other reactions (for a review, see ref. [2]). In the case of nickel exchanged zeolites, the behavior during dehydrogenation is similar, indicating the participation of nickel. For the XGeNaCa catalysts, dehydrogenating sites with different nature are present.

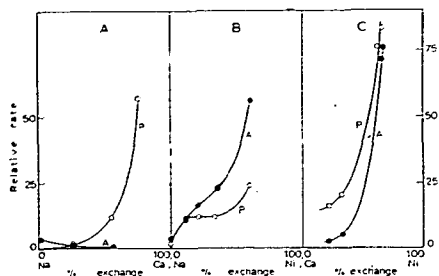


Fig. 2. Influence of the degree of cation exchange of XGeNa (A, B) or XGeCa (C) zeolites on the relative rate of propylene (P) and acetone (A) formation from isopropanol

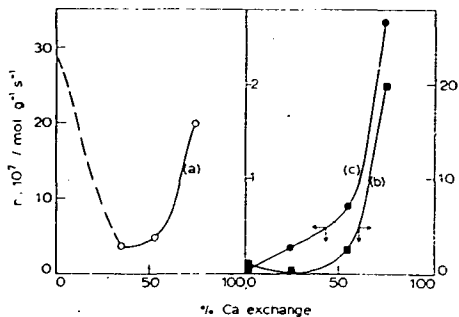


Fig. 3. Initial rate of alcohol dehydration (r) on Ca-exchanged XGeNa; a) $(\text{CH}_3)_3\text{COH}$ at 200°C ; b) $(\text{CH}_3)_2\text{CHOH}$ at 300°C ; c) $\text{CH}_3\text{CH}_2\text{OH}$ at 300°C

Influence of the nature of the alcohol

The initial rate of alcohol dehydration over XGeNaCa catalysts is given in Fig. 3. The activity decreases in the following sequence: tert. butanol \gg isopropanol \gg ethanol. This general order of reactivity parallels the generally observed order of stability of the corresponding carbonium ions [13]: tertiary \gg secondary \gg primary.

Surprisingly, the parent sodium form of XGe is more active than the Ca exchanged forms in the case of dehydration of the tertiary alcohol. In the case of isopropanol dehydration, the Na form is only slightly more active than the samples with low Ca content. This effect does no longer exist for the primary alcohol. This indicates that weak acid sites exist on XGeNa, which still catalyze the dehydration of tertiary and to a minor extent of secondary alcohols. Fig. 4 shows that these sites exist on the

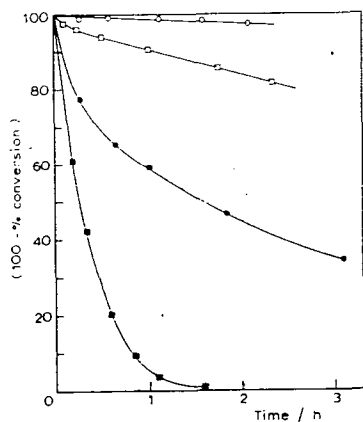


Fig. 4. Dehydration of tertiary-butanol on sodium X zeolites: XSiNa at 200°C (○) and 230°C (□); XGeNa at 200°C (●), and 230°C (■)

Table II

Initial rate of isopropanol decomposition on Ge substituted faujasite and phillipsite at 300°C

Catalyst	$r_p \times 10^8$ $\text{mol g}^{-1} \text{s}^{-1}$	$r_A \times 10^8$
PGeNa	3.4	4.8
XGeNa	3.7	5.6
PGeNi	2.5	23.7
PGeZn	2.2	196.0

germanium form, but not on the silicium homologue. Indeed, the dehydration activity of $(\text{CH}_3)_3\text{COH}$ is highest on the germanium form compared to the silicium X zeolite. The latter effect has to be related to the existence of residual carbonate species on the germanium sieve.

Influence of nature of cation and of zeolite

It was already pointed out that the parent germanium forms of phillipsite have stronger dehydrogenating properties than the faujasite. This is confirmed in Table II. From this table it is further clear that upon exchange with Ni and Zn, the dehydrogenating properties increase drastically. This is indicative of two kinds of dehydrogenating sites, one set being present on the parent zeolite, another appearing upon exchange with Ni^{2+} or Zn^{2+} .

The dehydrogenation properties of the germanium zeolites could be poisoned gradually with carbon monoxide (Fig. 5). At the same time an IR band at 2190 cm^{-1} with increasing intensity was observed. This band is due to chemisorbed CO.

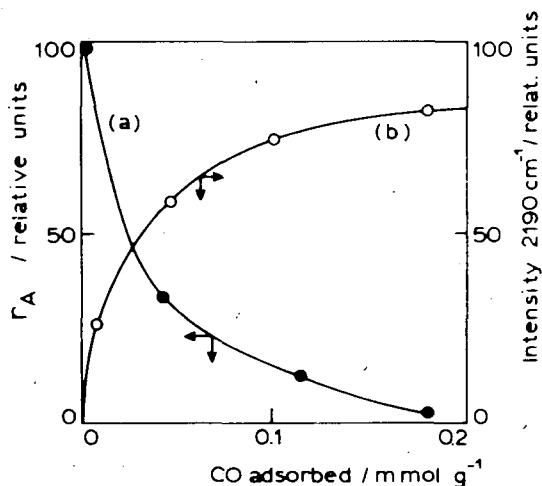


Fig. 5. Carbon monoxide poisoning on rate of acetone formation (a) on XGeNa at 275°C and intensity changes of the IR band (b) of adsorbed carbon monoxide at 200°C

Isotope effects

In Table III are given the isotope effects in the dehydration of 2-butanol. A significant effect is observed in the case of deuteration of the alcohol H atom over XSiNa, XGeCa and PGeNaCa. On the other zeolites this primary isotope effect is much less important, while a significant effect is observed when deuteration of the H atoms on a carbon atom in β position has occurred.

Table III
Dehydration of 2-butanol over zeolite

Zeolite	Temperature °C	$\alpha^{(1)}$	$\beta^{(2)}$
XSiNa ⁽³⁾	200	2.9	1.10
XGeNa	275	1.8	1.90
XGeCa	250	2.4	1.25
PGeNa	300	1.4	2.10
PGeNaCa (60)	300	2.0	1.75

(1) Isotope effect for $\text{CH}_3\text{—CH}_2\text{—CHOD—CH}_3$.

(2) Isotope effect for $\text{CD}_3\text{—CD}_2\text{—CHOH—CH}_3$.

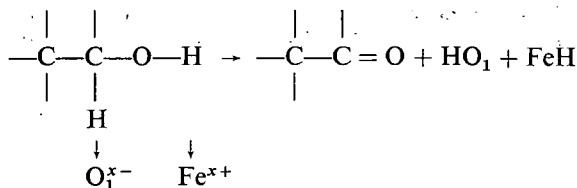
(3) From ref. [4].

Discussion

Reaction mechanism

Dehydration of alcohols may occur *via* a continuous sequence of possibilities, E_1 , E_2 and E_1cB eliminations being limiting cases [5]. In case of elimination near the E_1cB side, reaction starts with rupture of the most acidic C—H bond and dehydrogenation is occurring as well as dehydration [3, 5]. In the present case, there is strong evidence that distinct sites exist for dehydration and dehydrogenation (see Table I). This means necessarily that the alcohol dehydration mechanism is between E_1 and E_2 on the germanium zeolites. For the silicic X and Y zeolites, it has been proved that the reaction is on the E_1 side for most alcohols, methanol not taken into account [4]. When a primary isotope effect exists, the reaction has to shift to the E_1 side. When the mechanism is concerted (E_2 side) an isotope effect in H at C_β should exist. In this respect, Table III allows to conclude that: (i) upon germanium incorporation in the structure, the mechanism tends to shift more to the E_2 side, this being more pronounced for the germanium phillipsite; (ii) exchange with polyvalent cations (Ca^{2+}) shifts the mechanism again to the E_1 side, due to an increase of the electron pair acceptor properties of the structure [5], regardless whether the cations or protons act as active sites.

The dehydrogenation over Y and XSi was found to occur over an acid-base pair of sites, the impurity iron species playing a dominant role:



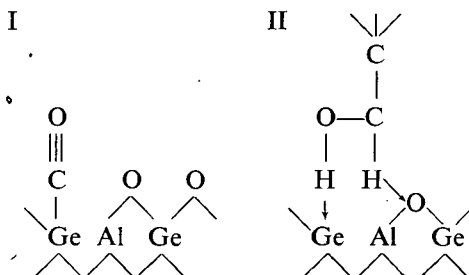
O_1 represents lattice oxygen. In the case of Ni^{2+} and Zn^{2+} exchanged samples, a similar mechanism may exist. The same mechanism can be invoked to explain the dehydrogenating activity of the parent unexchanged germanium sieves. The nature of the active site will be discussed later.

Active sites for dehydration

The activity sequence: tertiary > secondary > primary alcohols indicates a proton catalyzed E_1 type reaction, since it parallels the stability of the corresponding carboonium ions. The behaviour upon Ca^{2+} exchange (more than linear increase above 50% exchange) tends to favor this interpretation. Indeed, this is a common behavior observed for most zeolites and for most proton catalyzed reactions in zeolites. However, since at this degree of exchange, Ca^{2+} ions become available in the supercage, it cannot be excluded that they act as active sites, since they have electron pair acceptor properties [3, 5]. At the moment, no direct experimental evidence is present, that could reject the generally accepted views in zeolite catalysis and favor the second hypothesis. The remarkable selectivities for primary reaction products observed on the present zeolites, are also observed for olefin isomerization on $XGeNaNH_4$ zeolites [13]. This suggests that in both cases protons may be the active sites. The parent $XGeNa$ contains weak sites, not present on $XSiNa$ and strong enough to catalyze the dehydration of tertiary alcohols (Figs 3 and 4). This has to do with the presence of residual surface carbonate species in the germanic sieve [7, 10]. Upon addition of water under reaction conditions bidentate carbonate species (bands at $1580-1250\text{ cm}^{-1}$) are replaced by monodentate species ($1660-1375-1175\text{ cm}^{-1}$) [14]. A similar observation was reported on MgO [15] and carbon dioxide was also found to enhance the dehydration properties of silicic zeolites by similar surface reactions [2].

Active sites for dehydrogenation

Besides the dehydrogenation sites on Ni and Zn exchanged germanium zeolites associated with a cation—lattice oxygen pair of sites, the parent germanium zeolites have dehydrogenating sites of distinct nature (Table II) which can be poisoned with CO (Fig. 5). This form of chemisorbed CO (2190 cm^{-1}) never observed on the silicium zeolites, is most probably bonded to germanium at oxygen deficient sites, and can be schematized as follows (I)



The reaction can occur over an acid-base pair of sites as illustrated in II.

Acknowledgment

P. A. JACOBS acknowledges a permanent research position as "Bevoegdverklaard Navorser" from N. F. W. O. (Belgium).

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