Our catalytic data suggest that the unusual product patterns observed could be attributed to this cage effect superimposed on the conventional cracking mechanism.

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Infrared Studies of Hydroxyapatite Catalysts

Adsorbed CO_2 2-Butanol and Methyl Ethyl Ketone

Previous infrared investigations of primary alcohols adsorbed on alumina (*1–4*) have been interpreted as follows: in addition to physically adsorbed alcohol, a chemisorbed species with an alkoxide structure is formed at low temperatures, and it has been suggested that the molecules are cleaved by the dual acid–base sites in a manner analogous to rehydration of the surface (*5*); ammonia has been shown to react in this way (*6*); at higher temperatures the alkoxide species is converted into a surface carboxylate (*1*), and H_2 appears in the gas phase (*2*). Although alumina is not a catalyst for dehydrogenation, the carboxylate species could be interpreted as a dehydrogenation intermediate too stable to desorb as product aldehyde. It is the purpose of the present communication to show that these same infrared bands appear with slight modification when 2-butanol is adsorbed on hydroxyapatite catalysts.

In the course of our experiments, infrared bands attributable to bound carbonate were found, and studies were made to ascertain whether CO_2 might have been incorporated into the surface in a manner similar to the formation of the carboxylate species.

Three catalyst preparations were studied. The first of these was a stoichiometric hydroxyapatite ($Ca/P = 1.67$), which was active for both dehydrogenation and dehydration of alcohols; the others were nonstoichiometric preparations ($Ca/P = 1.58$ and 1.63), which were active for dehydration only (*7*). The properties of these materials and the procedures used in their preparation are detailed elsewhere (*8*). Infrared spectra were obtained with a Beckman IR-12 spectrometer from pressed wafers mounted in a cell which could be heated to elevated temperatures (*9*).

The infrared spectra of the parent catalysts (Fig. 1) contained bands in the 1400- to 1500-cm^{-1} region which have been attributed to bound carbonate (*11*). While these bands were weak relative to the P–O vibrational bands, they increased monotonically with the Ca/P ratio, and small shifts in wavelength and relative intensity were recorded. Although the double peak could be attributed to the presence of a basic, rather than a simple, carbonate (*11, 12*), it has been observed in natural apatites where it has been interpreted (*10*) as either a splitting of the ν_3 vibration of CO_3^{2-} in an environment of low symmetry or as CO_3^{2-} in

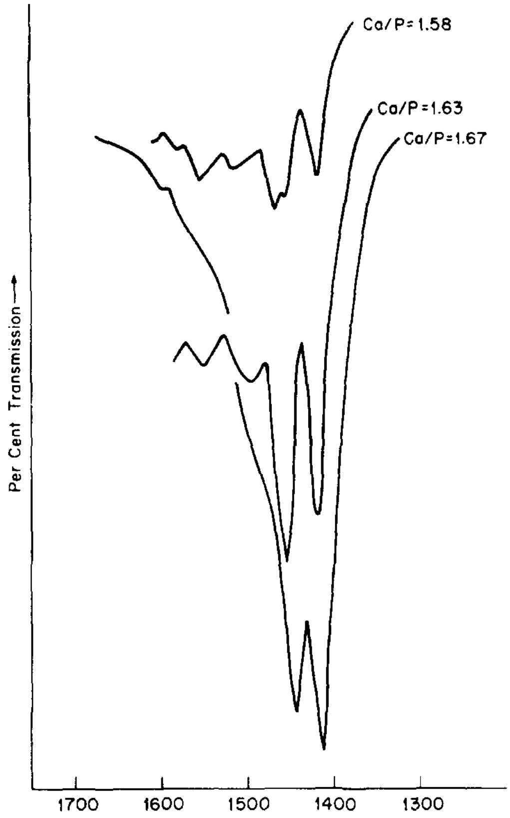


FIG. 1. Infrared spectra of hydroxyapatites of varying Ca/P ratios showing carbonate.

more than one high-symmetry site. The presence of more than two bands in some cases points to the latter explanation. Although the X-ray diffraction patterns and TGA determinations showed no evidence of a separate carbonate phase (*8*), the presence of CO_2 was confirmed by chemical analyses and by heating to temperatures to above 900°C where the hydroxyapatite structure was decomposed.

The preparations shown in Fig. 1 were made under a nitrogen atmosphere from solutions varying only slightly in volume and concentration (*8*). Since the carbonate bands varied systematically in intensity with composition, the carbonate evidently did not stem from an impurity in the reagents. This was confirmed by making additional preparations from different sources of $Ca(OH)_2$ and H_2O. Catalysts having Ca/P = 1.67 gave bands of similar intensity regardless of the purity of the reagents, even when extraordinary precautions were taken to exclude CO_2 until after the precipitation and growth of the crystals. It was concluded, therefore, that the carbonate was probably formed by inclusion of CO_2 from the atmosphere into the surface. Analyses of catalysts having the most intense carbonate bands indicated a CO_2 content of 0.2% or 5×10^{13} CO_2/cm^2 of surface.

The data shown in Fig. 2 were obtained when 2-butanol was admitted to the stoichiometric catalyst. At room temperature (Curve 2) a weak band at 1382 cm^{-1} and a shoulder at about 1470 cm^{-1} appeared on the sides of the much stronger carbonate bands at 1415 and 1445 cm^{-1}, respectively. Kagel (*2*) reported bands at 1380 and 1470 cm^{-1} for *n*-butanol adsorbed on alumina and attributed them to a surface alkoxide species. A band also appeared at about 1650 cm^{-1}, suggesting that H_2O was formed during the chemisorption. The weak band at 1565 cm^{-1} may be attributed to a small amount of surface carboxylate (see below).

The alkoxide bands shown in Fig. 2 were accompanied by the corresponding C–H stretching frequency bands in the 2800- to 3000-cm^{-1} region which have been reported previously (*1*, *2*). Both sets of bands were stable on evacuation at room temperature, but disappeared at 145° even in the presence of 2-butanol. No new bands were detected until the sample was heated in 2-butanol vapor to 240°, where a pair of strong bands at 1545 and 1575 cm^{-1} appeared (Curve 3) together with the weak pair of bands at 1740 and 1755 cm^{-1}. The latter were associated with methyl ethyl ketone vapor (produced at this temperature by dehydrogenation), characterized, together with butenes, by GLC analysis. The 1545- and 1575-cm^{-1} bands were stable to prolonged evacuation at 240°. Kagel (*2*) and Corso (*3*) reported bands at 1465 and 1565 cm^{-1} for *n*-butanol adsorbed on alumina at elevated temperatures and attributed them to the symmetric and antisymmetric vibrations, respectively, of a surface carboxylate species. The weak band of the symmetric vibration could not be detected in the present work because of the strong carbonate bands in the 1450-cm^{-1}

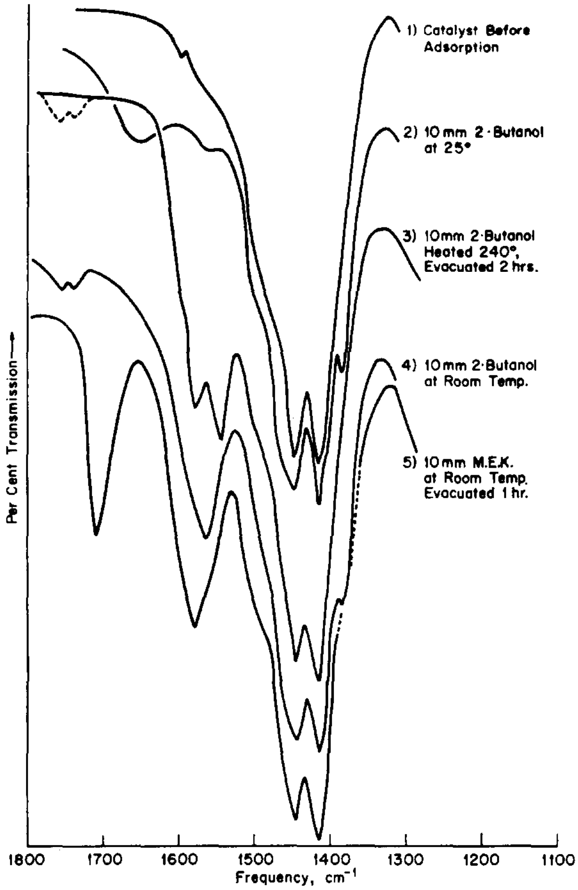


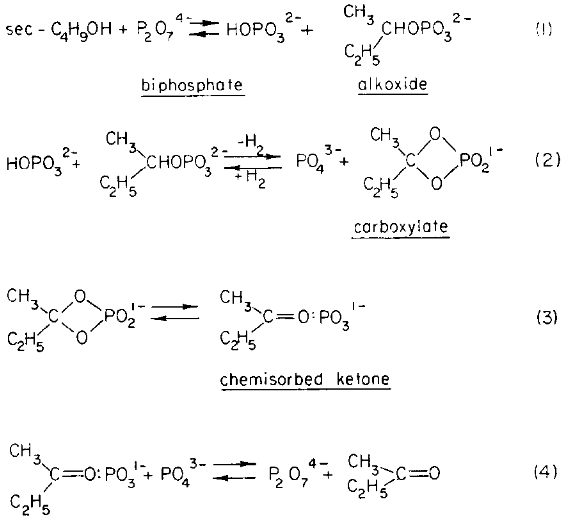
FIG. 2. Infrared spectra of 2-butanol adsorbed on stoichiometric hydroxyapatite ($Ca/P = 1.67$).

region. The origin of the 1545-cm^{-1} band (or the doublet) is unknown, but the presence of more than one carboxylate species is suspected. The two bands coalesced into one, however, when the catalyst was cooled in 2-butanol vapor to room temperature, where the alkoxide bands reappeared. This band (at 1565 cm^{-1}) remained after evacuation at room temperature, but the original pair reappeared on raising the temperature to 140°.

When methyl ethyl ketone was adsorbed on the sample, the very strong doublet in the 1750-cm^{-1} region due to gas-phase carbonyl decreased rapidly in intensity leaving bands at 1710 and 1565 cm^{-1}. These adsorbed ketone bands were stable to evacuation at room temperature (Curve 5), but were removed at 135° leaving the carboxylate doublet. The two ketone bands were probably not associated with a single surface species because the 1710-cm^{-1} band was obtained on calcium-deficient hydroxyapatites without the appearance of the 1565-cm^{-1} band. The shift in carbonyl frequency from 1740 to 1710 cm^{-1} was similar to that found when 2,5-hexanedione was adsorbed on a calcium montmorillonite (*13*) and may be indicative of a charge-transfer interaction between the carbonyl group and the catalyst surface.

A similar set of experiments was performed using calcium-deficient hydroxyaptite ($Ca/P = 1.58$) over which only dehydration occurred (*7*), and indeed only butenes were found in the gas phase by GLC in these experiments. At room temperature the alkoxide species was formed, as evidenced by the appearance of bands at 1380 and 1460 cm^{-1}. These bands persisted on heating to 150° but disappeared below 250°. Bands attributable to surface carboxylate or chemisorbed ketone were never observed. On adsorbing methyl ethyl ketone, the 1710-cm^{-1} carbonyl band appeared at about equal intensity to that with the stoichiometric catalyst; however, bands in the 1565-cm^{-1} region were not observed. Although olefins appeared in the gas phase, bands attributable to adsorbed olefin were not found. Olefins are known to adsorb only weakly on these catalysts (*7*, *8*). Thus, CO_2 and alcohol adsorption had two things in common: they gave more than one band in the carbonate or carboxylate region and these bands were very much weaker or not observed with nonstoichiometric preparations.

The two main differences between the present and earlier work (*1–3*) are (a) hydroxyapatite catalysts were used instead of alumina, and (b) a secondary alcohol was investigated rather than a primary alcohol. With the secondary alcohol, it is supposed that the surface carboxylate species with one alkyl group, the carbonyl workers have pictured the carboxylate species with one alkyl group, the carboxyl carbon stripped of its hydrogen and bound to two oxygens with more than single bonds. Greenler (*1*) in discussing the surface formate stated, "What is determined from the spectra is this: Resulting from the interaction of the methanol with the surface alumina, a structure is formed which has two oxygen atoms and *one* hydrogen atom attached to the carbon atom." Clearly, this point deserves further attention. The salient feature, however, is that the same bands appeared in the spectra obtained with the secondary alcohol on hydroxyapatite as with primary alcohols on alumina. Since the surface chemistry of the latter involves its reactions as an anhydride, a similar chemistry is suggested for the hydroxyapatite system. The anhydride present in hydroxyapatite is $P_2O_7^{4-}$, and the present results can be tentatively rationalized by Eq. (1)–(4).



The presence of $P_2O_7^{4-}$ may be essential for dehydrogenation, but it is not a sufficient condition because the nonstoichiometric preparations actually contain more, not less, of this ion (*8*).

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