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Infrared and Raman Spectra of Benzaldehyde Adsorbed on Alumina

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Infrared and laser Raman spectra indicate that the adsorption of benzaldehyde on alumina results in the formation of two adsorbed species, having a benzoate and a benzylalcoholate structure, respectively. By comparison with the benzoate the alcoholate is formed in only small quantities. The production of the benzoate is explained by the oxidative properties of the alumina surface. A possible explanation of the alcoholate formation is the occurrence of a Cannizzaro reaction, catalyzed by basic sites.

INTRODUCTION

By means of spectroscopic investigations it has been established that the alumina surface has acidic as well as oxidative properties. Chapman and Hair (*1*) reported that aldehydic compounds were readily oxidized to the corresponding carboxylate salts. Previously Greenler (*2*) had shown that alcohols first adsorb as surface alkoxides; on heating the alkoxide in vacuum a surface species spectroscopically identical to the carboxylate ion is formed. Acidic properties of the alumina surface have been studied spectroscopically by means of adsorption of nitrogenous bases (*3*). In order to discriminate between Lewis and Brønsted acid sites on alumina surfaces it is sometimes preferred to use ketones and aldehydes as bases. The advantage of using these carbonyl compounds is that the shift of the carbonyl stretching is a measure of the acidity of the coordinating Lewis acid (*4*).

Peri (*5*) showed that the alumina surface also possesses an acid–base type of site, called an α site. According to Hair (*6*) these sites could be due to a surface aluminum–oxygen bond which is covalent. With the aid of this covalently bonded oxygen Hair was able to explain the reactions of alumina with NH_3, H_2O, HCl and CO_2.

Despite the criterion mentioned by Hair (*7*) that a suitable ligand for the study of Lewis acidity on alumina surfaces should not be easily oxidized we used benzaldehyde for infrared and Raman spectroscopic investigation of the surface acidity, mainly because the aromatic aldehyde is a very suitable compound for study by Raman scattering. All aromatics show a strong Raman band at 1600 cm^{-1} and monosubstituted compounds, as well as benzene, have a very strong symmetric stretching vibration at about 1000 cm^{-1}.

The application of laser Raman spectroscopy to the study of adsorbed molecules was described by Gilson and Hendra (*8*). The technique is simple and versatile. However, in the case of alumina serious difficulties may arise because of its strong fluorescence (*8*).

In this paper the infrared and laser Raman spectra of benzaldehyde adsorbed on alumina are discussed. It is shown that the two spectroscopic techniques give complementary results.

EXPERIMENTAL METHODS

Two types of alumina were used for this study; an alumina known as type C from Degussa (Frankfurt, Germany) and a pure γ-alumina with a surface area of 280 m^2/g obtained from Ketjen N. V. (Amsterdam, The Netherlands). For infrared investigations the Degussa product was pressed into self-supporting disks with a thickness of 7 mg/cm^2. The properties of this alumina have been described before (*9*). All other reagents used were reagent grade chemicals.

Infrared spectra were recorded on a Cary 90 double beam spectrophotometer. Two identical cells, one placed in the sample beam and the other in the reference beam were used; in this way the spectra were corrected for absorption by alumina. Both cells could be evacuated and heated, thus permitting spectra of molecules adsorbed on alumina to be recorded *in situ*. The infrared spectra of the Ketjen alumina samples were recorded utilizing the KBr disk technique, as it is very hard to press self-supporting disks from this material. The spectra showed no evidence for ion exchange.

Laser Raman spectra of the adsorbed species were recorded on a Cary 82 and a Cary 83 spectrometer. Both instruments were equipped with an argon ion laser. Samples were placed in the powder holders of the instruments, in glass capillaries or in a glass cell with an optical flat. All Raman spectra were recorded using the Ketjen alumina. The spectra of aluminum benzoate and benzyl alcohol were recorded on a Cary 81, supplied with a helium neon laser.

Before adsorption the samples were partly dehydrated by heating at 360°C for 1 hr *in vacuo* (10^{-4} Torr) or by evacuating for 20 hr at room temperature. Adsorbates were introduced via the vapor phase at a pressure of a few Torr. Spectra were recorded after 30 min evacuation.

The alumina used for *in situ* experiments only showed very weak infrared absorptions in the 1200–1600 cm^{-1} region, which were not reflected in the spectra because of the use of a reference disk. Under certain circumstances the introduction of adsorbates enabled a volatile compound of the vacuum grease to adsorb on the alumina samples, causing absorptions between 1400 and 1600 cm^{-1}. This was avoided by prolonged heat and vacuum treatment of the valves and joints.

RESULTS AND DISCUSSION

Figure 1 shows the infrared spectrum of benzaldehyde adsorbed at room temperature on an alumina disk evacuated at 360°C. The dotted lines indicate the spectral changes caused by heating the sample to 230°C. Comparison of this spectrum with the spectrum of pure benzaldehyde (Fig. 2) reveals that after evacuation hardly any physically adsorbed benzaldehyde is present. The intense C=O vibration at 1700 cm^{-1} is reduced to a small shoulder at 1685 cm^{-1}. This small shift suggests that some physisorption occurs by hydrogen bonding through the oxygen atom of the carbonyl group.

The strong bands which are observed at 1550 cm^{-1} and 1420 cm^{-1} in the spectrum of the adsorbed species must be ascribed

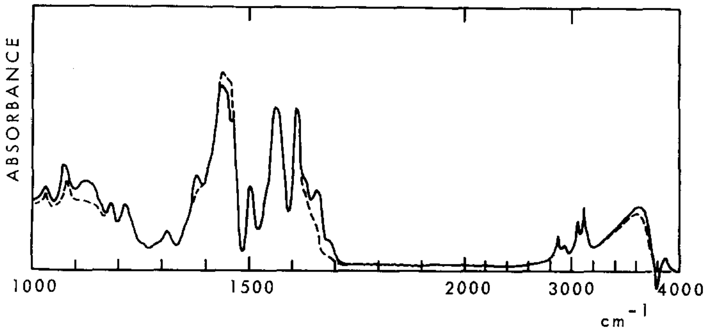


FIG. 1. Infrared spectra of benzaldehyde adsorbed on partly dehydrated alumina: (—) after evacuation at room temperature, (- - -) after evacuation at 230°C.

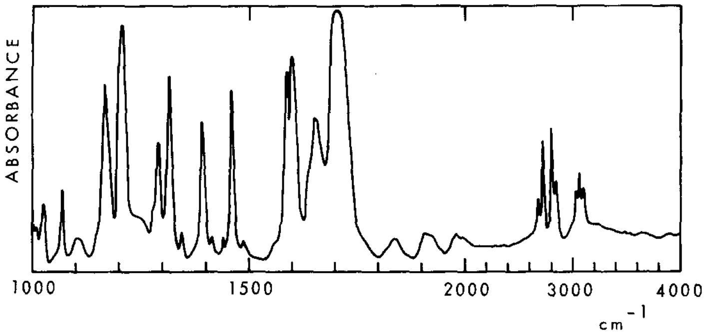
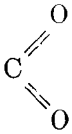
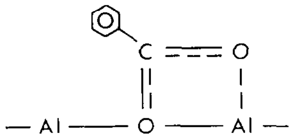


FIG. 2. Infrared spectrum of benzaldehyde (liquid).

to the asymmetric and symmetric stretching vibrations of the  grouping which is present in salts of carboxy acids (*1*, *2*). Moreover, the characteristic aldehyde C–H absorptions (2735 and 2815 cm^{-1}) are missing. Therefore the structure of adsorbed benzaldehyde is probably:



Comparison of the spectra of adsorbed benzaldehyde with the spectrum of aluminum benzoate (Fig. 3) shows that the majority of peaks in the adsorbed benzaldehyde spectrum can be attributed to aluminum benzoate. The formation of this structure is understandable because of the oxidative properties of the alumina surface. Adsorption of benzaldehyde on alumina which has not been heated before use results in the same spectrum.

Our results are, so far, identical with those of Chapman and Hair (*1*). However, a closer investigation of the infrared spectrum of adsorbed benzaldehyde reveals some absorptions (2850, 1370, 1205 and 1100 cm^{-1}) which definitely do not correspond to benzoate vibrations. (As the infrared spectrum of aluminum benzoate is obtained from a KBr disk, it could be that these absorptions are not observed in Fig. 3 because of ion exchange. However, from comparison with the spectrum of potassium benzoate reported by Green, Kynaston and Lindsey (*10*), the occurrence of ion exchange can be precluded.) It is also impossible to assign these absorptions to physically adsorbed benzaldehyde because at higher temperatures the C=O vibration completely disappears, whereas the unidentified peaks remain.

The spectra of benzaldehyde adsorbed on Ketjen alumina recorded by means of the KBr disk technique show the same absorptions. (This indicates that ion ex-

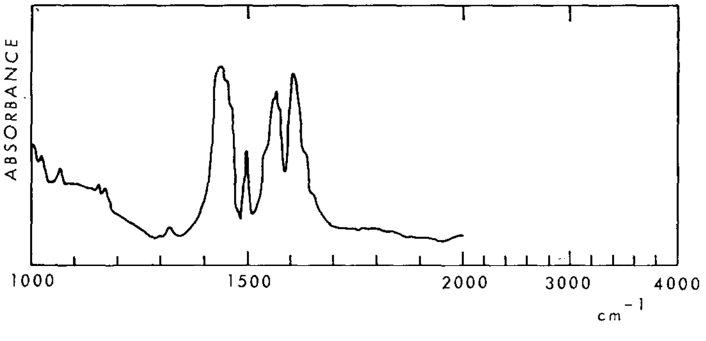


FIG. 3. Infrared spectrum of aluminum benzoate (KBr disk).

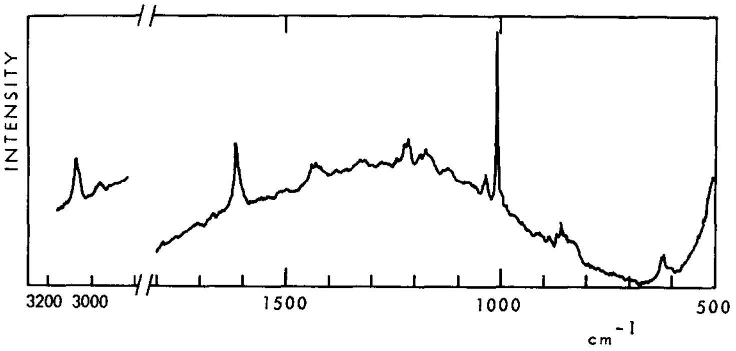


FIG. 4. Raman spectrum of benzaldehyde adsorbed on evacuated alumina.

change with the KBr has not occurred.)

The Raman spectrum of benzaldehyde adsorbed on alumina is given in Fig. 4. Figures 5 and 6 show the spectra of aluminum benzoate and benzaldehyde, respectively. Comparison of the spectra reveals that in this case also the carbonyl stretching at 1700 cm^{-1} has disappeared in the spectrum of the adsorbed molecule. Instead, some minor peaks, which can be attributed to the benzoate ion, appear. However, the peak at about 1200 cm^{-1} is absent in the aluminum benzoate spectrum, but clearly visible in the spectrum of benzaldehyde and adsorbed benzaldehyde. A Raman spectrum recorded on a Joel JRS-S1 spectrometer also reveals the presence of CH_2 vibrations (2960 cm^{-1}).

The aromatic vibrations at about 820 and 620 cm^{-1} in the Raman spectrum are not visible in the infrared spectrum because the alumina is not transparent in the region below 1000 cm^{-1}. In this fashion Raman spectroscopy provides complementary information to that obtained from infrared.

The peaks in the infrared and Raman spectra of adsorbed benzaldehyde which cannot be attributed to aluminum benzoate probably belong to an adsorbed species closely resembling benzaldehyde but without the carbon–oxygen double bond. To help identify this adsorbed species the spectra of the three compounds were assigned as far as possible. In Table 1 the absorptions and assignments are given.

Comparison of the Raman shifts of the tabulated values clearly shows that the unidentified compound gives rise to an out-of-plane aromatic CH vibration at 820 cm^{-1}, an in-plane aromatic CH bending at 1210 cm^{-1} and a very weak CH_2 stretching at about 2960 cm^{-1}. The vibrations at 820 and 1210 cm^{-1} are both very sensitive to the type of group present in monosubstituted benzenes (*11*). This ex-

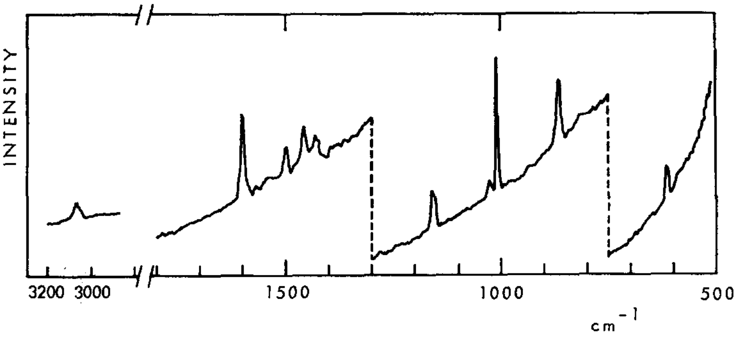


FIG. 5. Raman spectrum of aluminum benzoate (solid).

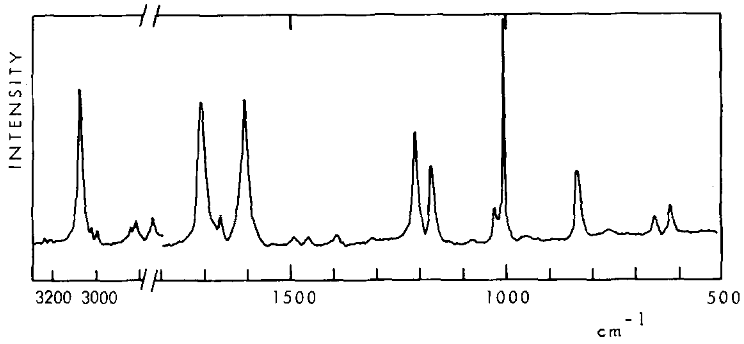


FIG. 6. Raman spectrum of benzaldehyde (liquid).

plains why it is possible that the 1210 cm^{-1} vibration is present in benzaldehyde but missing in aluminum benzoate, benzoic acid and benzyl methyl ester. The fact that these vibrations are present in adsorbed benzaldehyde gives rise to the conclusion that the unknown compound contains an aromatic ring (820 and 1210 cm^{-1}) and probably a CH_2 or CH_3 group (2960 cm^{-1}). Moreover, the aromatic ring is substituted in such a way that the 1210 cm^{-1} vibration is relatively strong.

It is much more difficult to draw equally straightforward conclusions from the comparison of the infrared spectra. In this case absorptions not belonging to aluminum benzoate are observed at 2850 cm^{-1} (weak), 1370 cm^{-1} (medium), 1205 cm^{-1} and 1100 cm^{-1} (broad). The absorption at 2850 cm^{-1}, which is much more evident than the 2960 cm^{-1} in the Raman spectrum, indicates the presence of a CH_2 group. The absorption at 1370 cm^{-1} falls in the region of CH_3 deformation vibrations and for alcohols it is sometimes assigned to an in-plane OH bending (*12*). The vibration at 1205 cm^{-1} in the infrared spectrum is particularly difficult to interpret. Some authors (*13*, *14*) assign this peak to a C–C vibration in aldehydes activated by the carbonyl stretching. In the case of benzene ring compounds this vibration appears with strongly fluctuating intensity and is mostly ascribed to an in-plane CH deformation. The aromatic CH vibration that occurs at a Raman shift of 1210 cm^{-1} strongly suggests that the infrared absorption at 1205 cm^{-1} must be assigned to an in-plane carbon–hydrogen deformation mode. The broad absorption centered an 1100 cm^{-1} is probably caused by a C–O stretching (*12*). Because of all this spectroscopic evidence the IR spectrum of adsorbed benzyl alcohol was also considered. This spectrum (Fig. 7) shows all unidentified absorptions in the infrared spectrum of adsorbed benzaldehyde.

A remarkable feature in the spectrum of adsorbed benzyl alcohol is that during removal of the physically adsorbed species the ν (C–O) absorption at 1020 cm^{-1} is much diminished. Also the absorption at 1450 cm^{-1} assigned to β(OH) is diminished more than the other peaks. Greenler (*2*) argued that the disappearance of the ν (C–O) absorption indicates the formation of an alcoholate. However, in that case all vibrations assigned to β(OH) (1450–1370 cm^{-1}) should have strongly decreased in intensity, too. This does not occur in the spectrum of chemisorbed benzyl alcohol; the 1450 cm^{-1} vibration is only partly decreased in intensity whereas the 1370 cm^{-1} absorption is practically undiminished. An explanation for these anomalies may be found in the assumption of another adsorbed species besides the alcoholate. However, this is in contradiction with the well-founded arguments of Greenler for the formation of an alcoholate. Therefore, it seems much more reasonable to assign at least part of the 1450 cm^{-1} vibration of benzyl alcohol to the ν (C=C) absorption which is rather intense in aromatic compounds. The 1370 cm^{-1} band is probably due to an alcoholate vibration such as that observed at 1385

TABLE 1

Absorptions in the Infrared and Raman Spectra of Benzaldehyde, Benzaldehyde Adsorbed on Alumina and Aluminum Benzoate[a]

Benzaldehyde		Benzaldehyde/Al_2O_3		Aluminum benzoate		
ir	LR	ir	LR	ir	LR	Assignment
3085 (w)	3070 (s)	3070 (m)	3070 (m)	3070 (w)	3080 (m)	$\nu(=CH)$
3030 (m)		3035 (w)		3030 (w)		$\nu(=CH)$
2845 (w)	2845 (w)	2850 (w)	2960 (w)			$\nu(-CH_2)$
2815 (m)						$\nu(\overset{\displaystyle O}{\overset{\|}{—C}}H$ aldehyde$)$
2735 (m)	2740 (w)					$\nu(\overset{\displaystyle O}{\overset{\|}{—C}}H$ aldehyde$)$
1700 (vs)	1700 (s)					$\nu(C=O)$
		1620 (sh)		1620 (sh)		?
1595 1583	1604 (s)	1600 (s)	1608 (s)	1600 (s)	1602 (s)	$\nu(C=C)$
		1555 (s)		1560 (s)		asym $\nu\left(C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}\right)$
		1495 (m)		1495 (m)	1498 (m)	$\nu(C=C)$
1455 (s)	1460 (w)	1450 (s)	1440 (m)	1450 (sh)	1460 (m)	$\nu(C=C)$
		1425 (s)		1435 (s)	1430 (mw)	sym $\nu\left(C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}\right)$
		1370 (m)				?
1310 (s)			1310 (w)			$\nu(C=O)$
1205 (s)	1208 (s)	1205 (m)	1210 (m)			$\beta(=CH)X$
1165 (m)	1170 (m)	1174 (w)	1170 (m)	1170 (vw)	1160 (m)	$\beta(=CH)X$
		1100 (br)				$\nu(C—O)$
1070 (w)		1064 (m)		1070 (w)		$\beta(=CH)X$
1020 (w)	1027 (m)	1020 (w)	1033 (w)	1020 (w)	1026 (w)	$\beta(=CH)$
	1005 (vs)		1005 (vs)		1005 (vs)	$\nu(C=C)$
	832 (m)		860 (m) 820 (sh)		858 (m)	$\gamma(=CH)$
	620 (m)		620 (m)		617 (m)	$\beta(CCC)$

[a] Symbols used: ν, stretch; β, in-plane bend; γ, out-of-plane bend; ( ), intensity; vs, very strong; s, strong; m, medium; mw, medium weak; w, weak; vw, very weak; sh, shoulder; br, broad; =CH, aromatic CH vibration; $-CH_2$, alkane CH vibration; $\overset{\displaystyle O}{\overset{\|}{—C}}—H$, aldehydic CH vibration; CCC, ring vibration; C=C, aromatic stretch or bend; C=O, carboxyl stretch or bend; $C\begin{smallmatrix}\diagup O\\ \diagdown O\end{smallmatrix}$, carboxylate ion stretch or bend; X, vibration is very sensitive for substituent in aromatic ring.

cm^{-1} by Greenler (*2*) during the adsorption of ethanol on alumina and which is also present in the infrared spectrum of aluminum ethoxide. Greenler did not find a similar peak in aluminum methoxide, so it seems obvious that this absorption is connected with the $-CH_2-O-$ group. However, this assumption is speculative because the infrared assignments are not completely certain.

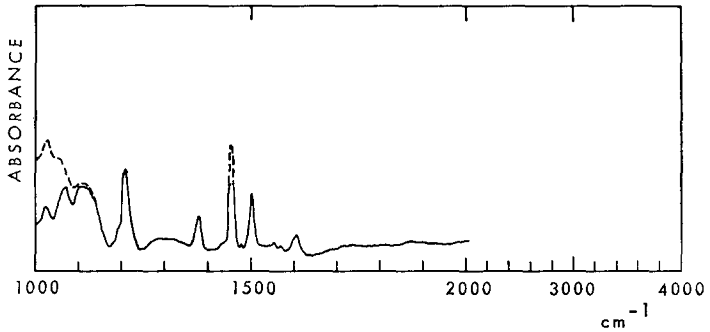


FIG. 7. Infrared spectrum of benzyl alcohol adsorbed on alumina: (- - -) after 15 min evacuation, (—) after 1 hr evacuation.

The Raman spectrum of benzyl alcohol (Fig. 8) shows a peak at 1210 cm^{-1}. This fits the observed Raman band at 1210 cm^{-1} in the spectrum of adsorbed benzaldehyde. Therefore, it can be concluded that aluminum benzyl alcoholate is formed together with aluminum benzoate upon adsorption of benzaldehyde on alumina.

As indicated by the infrared spectrum at a higher temperature (Fig. 1) the benzyl alcoholate is, on heating, converted into aluminum benzoate, in complete accordance with the results of Greenler (*2*). The quantity of benzyl alcohol that adsorbs on alumina is smaller than the amount of benzaldehyde. Therefore, the Raman spectrum of adsorbed benzyl alcohol did not yield further information.

The formation of benzyl alcohol from adsorbed benzaldehyde was also checked with the aid of a gas chromatographic analysis. For this experiment 5 g benzaldehyde was allowed to react with 5 g alumina for 24 hr. The reaction mixture was then extracted with 500 ml 100% ethanol; 0.1 μl of this solution was injected in both a polar and an apolar column. The chromatograms showed two peaks. From comparison with the retention times of the pure liquids they were identified as benzaldehyde and benzyl alcohol. Benzoic acid was not eluted in the columns used.

This now raises the question of how benzyl alcohol could be formed from benzaldehyde on an alumina surface. Normally, with the exclusion of oxygen, aldehydes are stable in an acid environment. Therefore, the acid function of the alumina cannot be responsible for this reaction. The assumption that alumina contains strongly reducing sites is not very acceptable. Another possible route to benzyl alcohol is a Canizzaro reaction in which one benzaldehyde molecule is oxidized to benzoate and another reduced to benzyl alcohol. This reaction only occurs in the presence of bases, so basic sites have to be assumed on the alumina surface. Man-

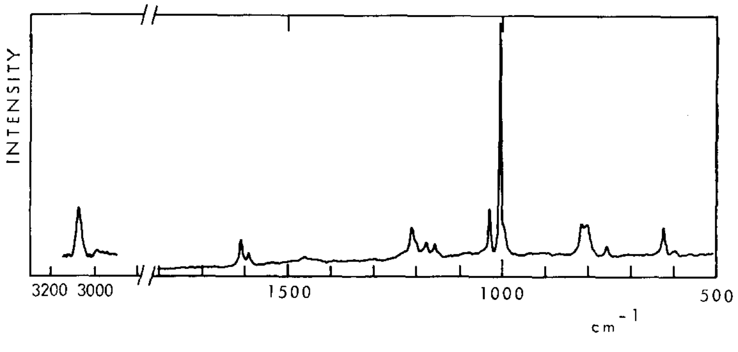
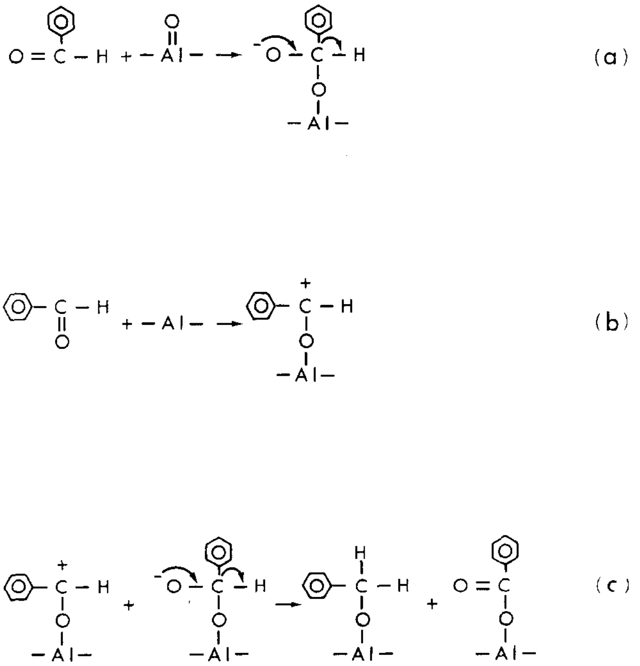


FIG. 8. Raman spectrum of benzyl alcohol (liquid).

assen and Pines (*15*) proposed the existence of such sites on aluminas to explain the mechanism of alcohol dehydration. Similar conclusions were drawn by Schwab (*16*). It is possible that the basic sites are identical with the α sites of Peri (*5*) which are responsible for strong CO_2 adsorption and to the covalently bonded oxygen as suggested by Hair (*6*). If this is true the reaction mechanism for the benzaldehyde disproportionation is probably:



Reaction (a) represents the initial adsorption of benzaldehyde on a covalently bonded oxygen. Reaction (b) gives the adsorption of benzaldehyde on a Lewis acid site. The two adsorption products react, according to Eq. (c), to give aluminum benzoate and aluminum benzyl alcoholate. With the present results it is not possible to verify this mechanism. However, as in every Cannizzaro reaction, it seems very likely that a hydride ion shift from one molecule to another is involved.

CONCLUSIONS

a. Benzaldehyde is both physically and chemically adsorbed on alumina. The physically adsorbed fraction can be removed by evacuation. Most of the chemically adsorbed benzaldehyde is transformed into aluminum benzoate but benzyl alcohol is also formed.

b. Alumina is able to initiate the formation of benzyl alcohol from the corresponding aldehyde. This reaction is probably of the Cannizzaro type catalyzed by basic sites of the alumina.

c. Laser Raman spectra of adsorbed species can give essential information about the structure of adsorbed molecules in addition to that obtained from infrared spectra.

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