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Raman Studies of Aldol Condensation Reactions on Sodium Hydroxide-Treated Silica Gel

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Adsorbed species from the reaction of acetaldehyde on NaOH-treated silica gel were studied using Raman spectroscopy. Catalytic activity for acetaldehyde condensation reactions increased with coverage of Na^+ ions. At room temperature and an acetaldehyde vapor pressure of 300 Torr, the Raman spectrum of acetaldehyde adsorbed on NaOH-treated silica gel is characteristic of adsorbed acetaldehyde and 6-hydroxy-2,4-dimethyl-1,3-dioxane. The latter compound is a trimer of acetaldehyde from the base-catalyzed condensation of the monomer. At lower pressures the above dioxane decomposes and chemisorbed acetaldol is the dominant surface species. At elevated temperatures, Raman bands of crotonaldehyde, which is produced by the dehydration of adsorbed species, appear in spectra of the acetaldehyde reaction system. The reactions of crotonaldehyde on the catalyst surface are similar to those of acetaldehyde. Two condensation products result from the reactions of crotonaldehyde with adsorbed acetaldol and with adsorbed acetaldehyde. When acetaldehyde is adsorbed in the presence of pyridine, the rate of the condensation reaction is not significantly affected. In the presence of formic acid the catalytic activity for aldol condensation reactions is destroyed.

INTRODUCTION

Infrared spectroscopy has been used by investigators to study the adsorption of acetaldehyde on silica (*1*, *2*), on nickel supported on silica gel (*2*), on magnesium oxide (*3*, *4*), on tin oxide (*5*), and on γ-alumina and γ-alumina treated with HCl (*6*). Robinson and Ross (*2*) attributed a shift of the carbonyl stretching vibrational band of acetaldehyde adsorbed on silica gel to an interaction between the adsorbate and surface hydroxyl groups. A similar assignment of infrared bands of acetaldehyde adsorbed on MgO was made by Low *et al.* (*4*). Evidence for an adsorbed alkoxide species on silica gel was discussed by Young and Sheppard (*1*), and bands in the infrared spectrum of acetaldehyde adsorbed on γ-alumina have been assigned to a carboxylate group and an unstable alkoxide form of chemisorbed acetaldehyde (*6*).

The infrared spectra of several products of acetaldehyde reactions have also been discussed. Thornton and Harrison (*5*) reported bands attributed to acetate ions at 1530–1520, 1430, and 1347 cm^{-1} in infrared spectra of acetaldehyde adsorbed on tin oxide. Several other authors have assigned bands in the infrared spectra to products of aldol condensation reactions. The carbonyl stretching vibration of saturated aldehydes gives a strong band at approximately 1720 cm^{-1} in both infrared and Raman spectra. When the carbonyl is conjugated with a double bond, as in 2-buten-1-al (crotonaldehyde), the carbonyl stretching vibrational band is lowered to 1680 cm^{-1}, and a second strong band due to the C=C vibration appears near 1640 cm^{-1}. Thus, bands near 1682 and 1641 cm^{-1} in spectra of acetaldehyde adsorbed on silica (*1*) and on MgO (*4*) were attributed to adsorbed crotonaldehyde resulting from the self-condensation of acetaldehyde. Multiple condensation reactions leading to the formation of conjugated double bonds have been inferred from the presence of infrared bands between 1640 and 1560 cm^{-1} in infrared spectra of acetaldehyde adsorbed on MgO (*3*). One report of Raman spectra of adsorbed acetaldehyde is pertinent to this report.

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Hendra and Loader (*7*) assigned bands in the Raman spectrum of acetaldehyde adsorbed on silica to physically adsorbed paraldehyde, a trimer of acetaldehyde. No evidence for additional condensation products was reported.

It has been shown that silica gel can be made more active for aldol condensation reactions by treating it with sodium hydroxide (*8*). Since the catalytic activity is a linear function of the sodium ion coverage (*9*), the catalyst can be tailored for a particular application. Furthermore, the background noise that is particularly troublesome in Raman spectra of heterogeneous catalytic systems is relatively weak if silica gel is used. The intensity of this background is reduced further by the NaOH treatment (*10*). This paper describes the results of a series of Raman studies of aldol condensation reactions catalyzed by NaOH-treated silica gel.

MATERIALS AND METHODS

BDH chromatographic grade silica gel was used in this study. Silica gel samples were impregnated with a known quantity of 4.0 *M* NaOH solution, dried at 100–120°C for 30–45 min, and stored in air. Prior to impregnation, the surface area of the silica gel was 561 m^2/g. After impregnation and calcination, areas of 422, 52, and 42 m^2/g were measured for Na^+ loadings of 0.3, 0.7, and 0.9 mmole/g, respectively.

Acetaldehyde (Aldrich Chemical Company) and crotonaldehyde (Eastman Organic Chemicals) were freed of noncondensable gases by repeated freeze–pump–thaw cycles and introduced into the catalyst cell in the vapor phase. 6-Hydroxy-2,4-dimethyl-1,3-dioxane was prepared following the procedure of Saunders *et al.* (*11*). It was very difficult to prepare a pure sample of the material; repeated vacuum distillations tended only to increase the amount of decomposition products. Thus, it was not practical to contact the catalyst with vapor-phase dioxane. Rather, the freshly prepared dioxane was dissolved in methanol and the catalyst was slurried with the mixture. The methanol was removed by careful distillation.

A typical catalyst preparation involved heating the catalyst overnight at 300°C in 300–500 Torr oxygen, evacuating the sample at the same temperature for 30 min and cooling to room temperature at approximately 5×10^{-5} Torr. Adsorbates were introduced to the catalyst in the vapor phase and allowed to react for the specified time. Because of the surface reactions it was not possible to equilibrate the vapor-phase and adsorbed species. At room temperature over the less active catalyst preparations, the reaction system appeared to reach a pseudoequilibrium with respect to vibrational band intensities after 60 h.

Raman spectra were recorded with a Spex Industries Ramalog-5 spectrometer using the 488.0-nm line of the Spectra-Physics Model 164 argon ion laser. Power intensity at the catalyst surface was maintained at less than 100 mW. At the low power levels employed, the laser had no noticeable effect on the reaction.

RESULTS

Acetaldehyde reacts slowly on NaOH-treated silica gel at room temperature, and several intermediate and final products can be identified in Raman spectra of the surface. Figure 1 illustrates a sequence of six spectra recorded during a single reaction of acetaldehyde on silica gel containing 0.7 mmole Na^+/g. For each spectrum in this series the catalyst was cooled to room temperature before the spectrum was recorded, and was then reheated to the reaction temperature at the conclusion of the scan. The reaction mixture was held at room temperature for the first 84 h, during which time Spectra A and B were recorded. The temperature was then increased to 50°C; the effect of continued reaction is illustrated in Spectra C, D, and E. The final scan (Spectrum F) was recorded after the catalyst had been held at 133°C for an additional 5 h.

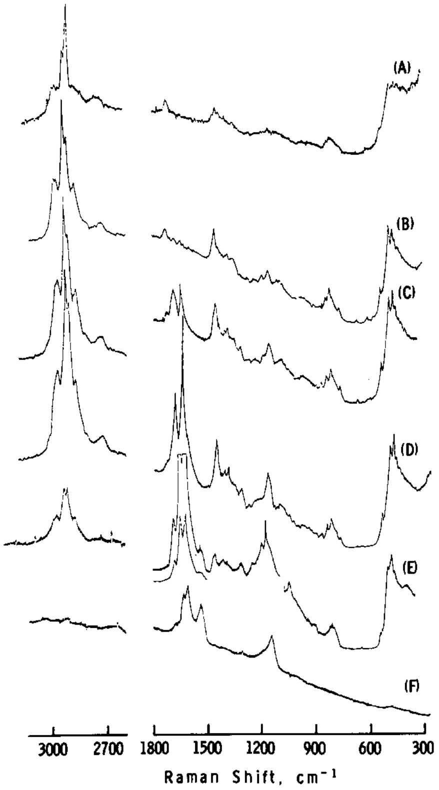


FIG. 1. Sequence of Raman spectra of acetaldehyde on NaOH-treated silica gel. Acetaldehyde adsorbed for: (A) 4 h at 20°C, (B) an additional 45 h at 20°C, (C) an additional 27 h at 20°C and 1 h at 50°C, (D) an additional 26 h at 50°C, (E) an additional 65 h at 50°C, (F) an additional 5 h at 133°C.

Before these spectra can be described in detail, it is necessary to show that a heterogeneous catalytic reaction is involved. According to Dudzik and George (*12*) some of the sodium ions on NaOH-treated silica gel can be leached from the surface with a water wash. In the present case, the weakly held sodium ions might be expected to exchange with water, forming an aqueous alkaline surface layer in which aldehyde condensation reactions could take place. The reaction conditions in this investigation were not severe enough to remove the water, and reactions taking place in this aqueous layer could be mistaken for reactions occurring on the catalyst surface. However, the experimental evidence weighs heavily against this possibility. The catalyst pretreatment effectively removed physically adsorbed water from the surface; any water present on the surface had to come from condensation reactions catalyzed by an initially "dry" surface. In fact, the catalytic activity of the treated catalyst was inhibited when water was absorbed prior to adsorption of acetaldehyde. The results which follow clearly support the conclusion that the reactions discussed here occurred via heterogeneous catalysis on specific sites associated with surface sodium ions.

Most of the bands in Fig. 1A can be assigned to acetaldehyde. Bands at 2921 (CH_3 stretch), 1719 (C=O stretch), and 1452 cm^{-1} (CH_3 deformation) (*13*) are most representative of the adsorbed aldehyde. An additional strong band at 513 cm^{-1} assigned to a C—C=O bending motion was not observed. It is not likely that this band was completely obscured by the strong band envelope centered at 459 cm^{-1}, which is due to SiO vibrations. Rather, it is proposed that a decrease in the intensity of the C=O vibrational band was due to activated chemisorption of acetaldehyde. This is supported by the effect of adsorption on the carbonyl stretching vibrational band at 1719 cm^{-1}. Figure 2 shows that the intensity of the CH_3 stretching vibrational band in-

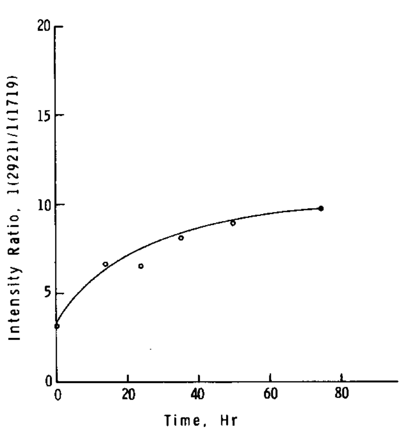
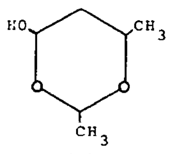


FIG. 2. Effect of time on the relative intensities of the CH_3 vibrational band (2921 cm^{-1}) and the C=O vibrational band (1719 cm^{-1}) of acetaldehyde adsorbed on NaOH-treated silica gel.

creased relative to the carbonyl vibrational band during the first 84 h of adsorption and reaction, when the spectral features of few reaction products were observed. Since the 2921-cm^{-1} band can be assigned solely to adsorbed acetaldehyde under these conditions, it is suggested that adsorption of acetaldehyde through the carbonyl group reduced the intensity of the 1719-cm^{-1} band. This gives a clue to the configuration of the adsorbed species.

Some reaction products can be identified from Fig. 1B. In addition to the bands due to acetaldehyde, new bands appear in the region of CH stretching vibrations above 2800 cm^{-1} and a band suggestive of a CH_3 deformation vibration is observed at 1452 cm^{-1}. The bands observed at 816, 535, and 489 cm^{-1} can be assigned to a dioxane or a trioxane species. Indeed, Hendra and Loader (*7*) assigned Raman bands in spectra of acetaldehyde adsorbed on silica gel to paraldehyde, from the surface-catalyzed trimerization of acetaldehyde. There is qualitative agreement between the Raman spectrum of paraldehyde (*14*) and the bands shown in Fig. 1B, but several inconsistencies cannot be explained by this assignment. A more satisfactory match is achieved between the given spectrum and that of 6-hydroxy-2,4-dimethyl-1,3-dioxane (hereafter called dioxane(I)) (see Table 1).



(I)

This compound is often a predominant product in the base-catalyzed condensation of acetaldehyde (*15*) and is not unexpected at the reaction conditions employed in this study.

However, the activity of adsorbed dioxane(I) cannot be anticipated fully from a knowledge of its behavior as a liquid or in aqueous alkaline solution. Many of the Raman bands assigned to dioxane(I) were quickly removed at elevated temperatures, but were restored when the reaction vessel was cooled to room temperature. Evacuation of the adsorbed species at room temperature also had the effect of removing

TABLE 1

Raman Bands of Adsorbed Acetaldehyde and of 6-Hydroxy-2,4-Dimethyl-1,3-Dioxane

Adsorbed acetaldehyde[a] (cm^{-1})	Liquid dioxane[b] (cm^{-1})
	265
	423
435	
451	453
466	
489	493
535	538
570	
606	
665	665
769	762
780	
804	
816	818
837	842
870	871
970	970
1074	
1091	1096
1155	1150
1185	1184
1236	1232
	1258
1271	
1354	1340
1380	1377
1405	
1436	
1452	1452
1641	
1680	
1698	
1723	
2670	
2738	2731
2772	
2882	2876
2922	
2945	2937
2983	2987
2996	

[a] Bands from Fig. 1B.
[b] Saunders *et al.* (*11*).

these bands. In fact, only dioxane (I) bands due to C–H vibrations (at 2985, 2945, 2885, and 1452 cm^{-1}) were observed in spectra recorded at 50°C. Those bands were also the only ones to remain after evacuation at room temperature.

In contrast, dioxane(I) adsorbed onto the catalyst surface from methanol solution gave a spectrum significantly different from that of Fig. 1B. In particular, bands at 2882 and 816 cm^{-1} were much reduced in intensity, the 489-cm^{-1} band was shifted to 474 cm^{-1}, and the strong 535-cm^{-1} band was not observed. These changes are to be expected if the dioxane(I) which had been adsorbed from solution decomposed to acetaldol ($CH_3CH(OH)CH_2CHO$) on the surface. Table 2 supports this assignment. An interesting aspect of the observed phenomena is the stability of acetaldol on the surface relative to its instability in solution or as a pure compound.

TABLE 2

Raman Bands of Adsorbed 6-Hydroxy-2,4-Dimethyl-1,3-Dioxane and Raman Bands of Liquid Acetaldol

Adsorbed dioxane (I)[a] (cm^{-1})	Liquid acetaldol[b] (cm^{-1})
474	474
555	
819	817
849	854
945	
951	950
1025	1027
1091	1096
1154	1149
1228	
	1276
1344	
1380	1332–1380
1403	
1443	
1455	1458
1566	
1636	
1686	
	1719
2740	
2884	
2936	2933
2975	2975

[a] This work.

[b] Wiemann and Maitte (*16*).

TABLE 3

Raman Bands of Acetaldehyde and of Crotonaldehyde Adsorbed on NaOH-Treated Silica Gel

Adsorbed acetaldehyde[a] (cm^{-1})	Adsorbed crotonaldehyde[b] (cm^{-1})
452	
466	471
488	
534	
761	
803	
815	
837	
864	
1091	
1158	1161
1176	
1232	
1312	1311
1380	1382
1395	1400
1449	1451
	1566
1644	1644
1683	1680
1722	
2883	
2926	2927
2945	
2981	

[a] Bands from Fig. 1C.

[b] Crotonaldehyde adsorbed on silica gel treated with NaOH (0.7 mmole Na/g).

The decrease in the intensity of the ring vibrational bands of dioxane(I) was usually accompanied by the appearance of a new set of bands. The most conspicuous bands in the new set were those of equal intensity near 1680 and 1640 cm^{-1}. (See Fig. 1C.) These bands imply the formation of an adsorbed material with a carbonyl group conjugated with a double bond, consistent with the formation of crotonaldehyde by dehydration of the surface species. Tables 3

TABLE 4

Raman Bands of Liquid Crotonaldehyde

This work (cm^{-1})	Durig *et al.* (*17*) (cm^{-1})
299	300
461	464
544	545
778	780
930	931
1042	1046
1078	1080
1147	1149
1304	1306
1375	1380
1392	1393
1443	1445
1640	1641
1682	1682
2734	2732
2845	2851
2877	2879
2919	2918
2949	2949
2979	2976
3005	3006
3032	3032

and 4, which compare Raman bands from Fig. 1C with the spectrum of adsorbed crotonaldehyde and the spectrum of liquid crotonaldehyde, verify this assignment. In all these spectra the 1682- and 1640-cm^{-1} bands, assigned to vibrations of the carbonyl group and the double bond, respectively, are of approximately equal intensity.

Two changes in the Raman spectra of the NaOH-treated silica gel surface characteristically occurred when adsorbed acetaldehyde was heated above 50°C. The 1682-cm^{-1} band began to decrease in intensity relative to the one at 1640 cm^{-1}. It eventually disappeared from the spectrum. Accompanying this decrease, though not necessarily associated with it, was the appearance of a band at 1607 cm^{-1}. This band eventually dominated the spectra under most reaction conditions. One might expect that the decrease in the intensity of the carbonyl stretching vibrational band indicates the chemisorption of crotonaldehyde. However, the Raman spectra will not support this hypothesis, since the spectrum of crotonaldehyde during a liquid-phase homogeneous condensation showed very similar trends in the relative intensities of the bands at 1682, 1640, and 1607 cm^{-1}. Apparently the observed spectrum was due to additional condensation reactions of crotonaldehyde.

Two new bands at 1536 and 1146 cm^{-1} are observed in Fig. 1E. These bands rapidly increased in intensity at 130°C and dominate the spectrum in Fig. 1F. During the increase in intensity of these bands the catalyst samples became colored, changing from white through yellow to deep red, depending on the severity of the heat treatment.

The effect of the NaOH loading on the activity of the catalyst is illustrated in Fig. 3. Untreated silica gel and silica gel treated with 0.3, 0.7, and 0.9 mmole Na^+/g were investigated. For each spectrum the catalyst was pretreated, evacuated, and contacted with 300-Torr acetaldehyde and allowed to react for approximately 28 h at

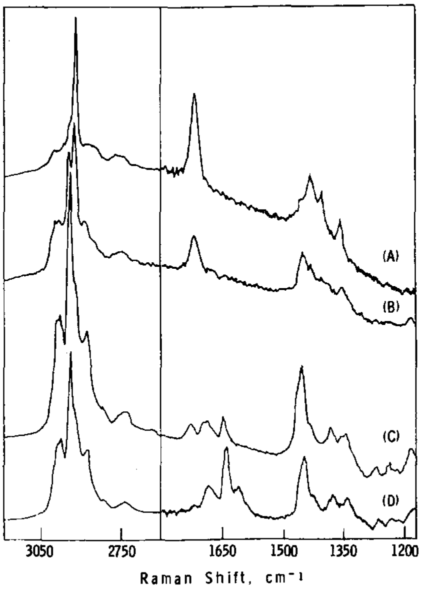


FIG. 3. Effect of sodium loading on spectra of adsorbed acetaldehyde. Loading: (A) no sodium, (B) 0.3 mmole/g, (C) 0.7 mmole/g, (D) 0.9 mmole/g.

room temperature before a spectrum was recorded. Raman bands in the spectrum of acetaldehyde on untreated silica gel were nearly all representative of liquid-phase acetaldehyde (see Table 5). Several bands which could be assigned to dioxane(I) appeared as shoulders on the stronger bands. A shoulder at 522 cm^{-1} was a significant exception, for this band is coincident with the strong ring vibration of liquid paraldehyde (*14*). Since the dioxane(I) band at 535 cm^{-1} and the paraldehyde band at 522 cm^{-1} are not sensitive to the presence of the surface, the bands at 2999, 2945, and 522 cm^{-1} are assigned to paraldehyde, in agreement with Hendra and Loader (*7*). As there is a clear distinction in these results between untreated and NaOH-treated silica gel, the catalytic sites responsible for paraldehyde formation are assumed to be acidic. The relative significance of these sites is reduced by the NaOH treatment.

TABLE 5

Effect of Sodium Ion Loading on Raman Bands of Adsorbed Acetaldehyde

	Loadings (mmole Na^+/g)		
None	0.31	0.70	0.92
(cm^{-1})	(cm^{-1})	(cm^{-1})	(cm^{-1})
393		406	
		421	
433		437	431
	450	456	450
		468	465
	486	493	488
514	512		
522			
	530	537	533
609			600
		667	662
	765	764	759
	810	818	814
	837	840	834
		870	868
		896	894
		965	
		1093	1088
1117			
	1152	1156	1156
	1183	1182	
		1236	1230
		1266	1263
1356	1353	1345	1340
		1383	1378
1404			
1433	1429	1432	
	1449	1452	1449
			1607
		1647	1640
		1686	1680
1716	1715	1725	
		2738	2736
2769			
2875	2888	2883	2881
2924	2920		
2945	2941	2944	2941
	2980	2984	2981
2999	2994	2996	2993

The spectra of acetaldehyde adsorbed on NaOH-treated silica gel samples are a record of increased condensation activity as sodium loading on the catalyst was increased. The spectrum of the catalyst with 0.3 mmole Na^+/g has bands at 2980, 2941, 2920, and 2888 cm^{-1}, all of which have been previously assigned to adsorbed acetaldehyde and dioxane(I). The only band in the region between 1800 and 1600 cm^{-1} is the strong band at 1715 cm^{-1} assigned to physically adsorbed acetaldehyde.

The spectrum of the catalyst with 0.7 mmole Na^+/g has two bands of equal intensity at 1686 and 1647 cm^{-1}, indicative of physically adsorbed crotonaldehyde, and the band at 1725 cm^{-1} assigned to acetaldehyde. This carbonyl stretching vibrational band was consistently shifted to higher frequencies (10 cm^{-1} in this case) in spectra of acetaldehyde adsorbed on NaOH-treated silica gel with loadings above 0.6 mmole Na^+/g. Neither of the crotonaldehyde bands is observed in Fig. 3B. The bands due to CH stretching vibrations in Spectrum C also suggest a more advanced state of reaction. The band around 2923 cm^{-1} due to acetaldehyde can scarcely be resolved, while the bands at 2984, 2944, and 2883 cm^{-1} have increased considerably in intensity.

Spectrum D in Fig. 3 gives indications of condensation reactions which are more ad-

TABLE 6

Raman Bands of Adsorbed Acetaldehyde During Evacuation at 25°C

Alumina (cm^{-1})	NaOH-treated alumina (cm^{-1})
497	496
1170	1152
	1536
	1596
	1605
1617	
1644	1635
2880	
2945	2943
2981	

vanced than are those of any of the other three catalyst samples discussed. The additional reactions of crotonaldehyde leading to a decrease in the relative intensity of the 1680-cm^{-1} band and the appearance of a 1607-cm^{-1} band are again observed in this spectrum.

The reactions of acetaldehyde on alumina and on NaOH-treated alumina were similar to those which occurred on silica gel, but were much faster. The catalyst samples immediately turned yellow when contacted with acetaldehyde, and the spectrum did not change gradually with time, as was the case with silica gel. The Raman bands of the surface, listed in Table 6, are comparable to those of NaOH-treated silica gel recorded after many hours of reaction. The bands at 2981, 2945, and 2880 cm^{-1} were similar to the CH vibrations of dioxane(I), though none of the other bands from this heterocycle were present. In addition, bands not present in spectra of silica gel catalysts were observed at 1596 and 1152 cm^{-1}.

DISCUSSION

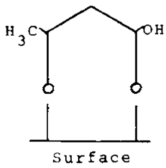
The spectra of acetaldehyde adsorbed on NaOH-treated silica gel illustrate the sequence of reactions forming crotonaldehyde by the aldol condensation mechanism. From the spectra in Fig. 1, it appears that the reaction goes through four distinct stages. Adsorbed acetaldehyde is observed first as a physically adsorbed species. Reactions at room temperature give a product identified as 6-hydroxy-2,4-dimethyl-1,3-dioxane (dioxane(I)). Both this product and its precursor react and desorb from the surface to give crotonaldehyde, which undergoes further condensation reactions at elevated temperatures or in the presence of a more active catalyst.

Two characteristic vibrations of physically adsorbed acetaldehyde indicate the type of bonding involved. Acetaldehyde molecules represented by the band at 1719 cm^{-1} are physically adsorbed, probably to surface hydroxyls. However, it is shown in Fig. 2 that physical adsorption does not completely explain the intensity of the 2921-cm^{-1} band, since the CH_3 vibrational band increases in intensity more rapidly than does the 1719-cm^{-1} band assigned to a carbonyl stretching vibration. Some of the acetaldehyde molecules contributing to this $-CH_3$ vibrational band appear to be chemisorbed to the catalyst surface through the carbonyl group.

In addition, when adsorbed acetaldehyde was evacuated, the 2921-cm^{-1} band due to the $-CH_3$ stretching vibration was shifted to 2926 cm^{-1}. This upward shift is not characteristic of a hydrogen-bonding interaction with the surface. Such an interaction would lower the vibrational frequency. An increase in vibrational frequency is more consistent with an increase in the double-bond character of the adsorbed species. It is possible that this shift is the first indication of the formation of a stabilized surface enolate species as an intermediate in the condensation reaction. Enolate intermediates have previously been postulated for crotonaldehyde condensation reactions by Blanc (*18*).

6-Hydroxy-2,4-dimethyl-1,3-dioxane is the first product of the condensation reaction which can be identified from Raman spectra. At acetaldehyde pressures above 100 Torr the spectrum of adsorbed dioxane(I) is very similar to that of the liquid phase. However, there are distinct differences between liquid and adsorbed dioxane(I) which give indications of the mechanism of the acetaldehyde condensation reaction. Dioxane(I) in methanol solution was quite stable, and the spectrum of the mixture held at room temperature did not change over several weeks. When a NaOH-treated silica gel catalyst sample was slurried with the dioxane(I)/methanol mixture, evacuated to remove the solvent, and left overnight, the spectrum of the adsorbed materials had little resemblance to that of the original dioxane(I) sample. It is known that dioxane(I) decomposes under certain conditions to acetaldol and acetaldehyde (*19*). Thus, it is not coincidental that the observed bands of dioxane(I) adsorbed from a methanol solution and the Raman bands of acetaldol (*16*) are very similar. The only major difference is in the absence of the C=O stretching vibrational band at 1719 cm^{-1} in the spectrum of the adsorbed material. Either the acetaldol was bonded to the surface through the carbonyl group or it was bonded to another molecule in such a way that the overall Raman spectrum was not affected by the association, while the carbonyl stretching band was completely suppressed. This absence of the C=O vibrational band was also observed in spectra of adsorbed propionaldehyde and benzaldehyde on NaOH-treated silica gel. It appears to be characteristic of adsorbed carbonyls.

In contrast to the results obtained with untreated silica gel there were no indications of weakly bound acetaldol in the spectrum of acetaldehyde adsorbed on silica gel after treatment with NaOH. At high adsorbate vapor pressures and at room temperature, bands of dioxane(I) dominated the Raman spectrum. At elevated temperatures and/or at low adsorbate pressures, the only bands assigned to this heterocycle that remained were those near 2985, 2945, 2885, and 1452 cm^{-1}. On the basis of vibrational assignments for similar molecules, these bands are all associated with methyl and C–H vibrations of dioxane(I). The evidence supports a chemisorbed form of dioxane with a badly distorted or ruptured ring structure in which only the CH vibrations closely resemble those of the original molecule. One such structure is that of adsorbed acetaldol, bonded through two oxygen atoms to the catalyst surface.



It is assumed that the methyl and methylene groups of adsorbed acetaldol were relatively unaffected by adsorption giving CH vibrational bands similar to those of the dioxane. However, all vibrations due to the ring were suppressed. Bands from C–O–surface vibrations, which would confirm the identification of the adsorbed species, were not observed. The absence of vibrations due to these bonds has been documented by others in systems similar to ours (*20*).

Assignments of bands in the Raman spectra of the catalyst surface under *in situ* reaction conditions is complicated by the number of reactions which acetaldehyde undergoes on NaOH-treated silica gel. Diethyl ether and ethanol from a Cannizzaro reaction, methyl ethyl ketone, acetone, and propionaldehyde from a free-radical reaction, and crotonaldehyde from the aldol condensation reaction were separated from the product mixture by gas chromatography. However, none of the identified products, with the exception of those from the aldol condensation reaction, account for the Raman spectra of the reacting system. In addition, only crotonaldehyde and acetaldehyde were collected when the catalyst was evacuated, first at room temperature to remove weakly bound compounds, and then at 200°C. The presence of significant amounts of crotonaldehyde and the absence of all other products suggest that only the ionic pathway was operative when gas-phase and weakly bound species were removed from the reaction system. Therefore, the CH stretching vibrational bands observed in the spectrum of the evacuated catalyst are assigned to a chemisorbed species that participated only in the ionic reaction. This is additional evidence that this species was chemisorbed acetaldol. The two reactions of adsorbed acetaldol that can be observed via Raman spectra are condensation and dehydration. Crotonaldehyde is the product of the dehydration of the adsorbed acetaldol; acetaldehyde results from the decomposition of the adsorbed molecule. When sufficient gas-phase acetaldehyde was present, a third acetaldehyde molecule reacted with adsorbed acetaldol to give dioxane(I). Possible mechanistic routes are indicated in Fig. 4.

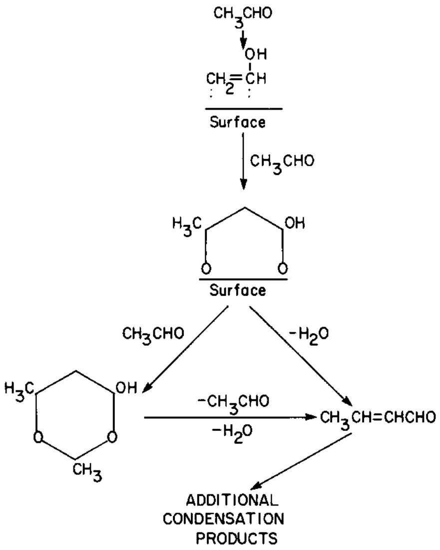
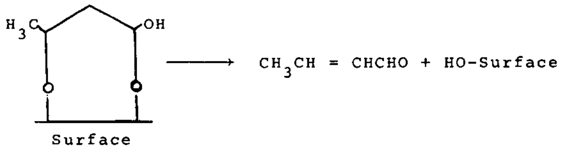


FIG. 4. Proposed reaction sequence of acetaldehyde on NaOH-treated silica gel.

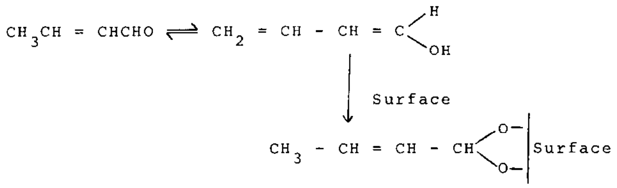
If a NaOH-treated silica gel sample which has been equilibrated with acetaldehyde at room temperature is then heated to 50°C, a third series of reactions of adsorbed compounds is observed. Dioxane bands quickly diminish in intensity and bands of approximately equal intensity appear near 1682 and 1640 cm^{-1}. The latter bands, assigned to physically adsorbed crotonaldehyde, are equivalent to bands observed in spectra of crotonaldehyde freshly adsorbed on similar catalysts. When acetaldehyde was allowed to react on NaOH-treated silica gel at low pressures or at 50°C, dioxane(I) bands were not observed, though crotonaldehyde bands appeared as before. Under these conditions the source of crotonaldehyde was the chemisorbed acetaldol species. The formation of physically adsorbed crotonaldehyde from chemisorbed acetaldol requires that the acetaldol be simultaneously dehydrated and desorbed from the catalyst by rupture of the two bonds to the surface.



From the Raman spectra, it appears that this transition from chemisorbed species to physically adsorbed crotonaldehyde was rapid, as no evidence for intermediate structures was observed.

The common features of all spectra of freshly adsorbed crotonaldehyde were bands of equal intensity at approximately 1682 and 1640 cm^{-1}. Reaction and adsorption were indicated by the relative decrease in the intensity of the carbonyl stretching vibrational band at 1682 cm^{-1}. Under certain conditions, other bands appeared as the 1682-cm^{-1} band diminished in intensity, but there is no consistent evidence that the two events were related. In particular, a band at 1607 cm^{-1} which cannot be identified with any of the liquid-phase spectra was a prominent feature in spectra of adsorbed crotonaldehyde.

These changes in the spectrum during reaction cannot be interpreted on the basis of the Raman information alone. It is certain that the observed reactions involved the carbonyl group of crotonaldehyde, and three possibilities can be suggested. If chemisorption occurred, a realistic configuration for the adsorbed species is one suggested by Young and Sheppard (*21*). Crotonaldehyde, postulated to be particularly active in the enol form (*18*), would attack a basic site and form an adsorbed alkoxide species.



This structure is consistent with many details of the Raman spectra, in which most of the crotonaldehyde vibrational bands, other than that from the carbonyl vibration, are observed. A much stronger possibility is the condensation of crotonaldehyde and acetaldol or the condensation of two molecules of crotonaldehyde to give methylbenzaldehyde (*22*).

NaOH-treated silica gel in the presence of acetaldehyde gradually changed color from white to bright red. The Raman spectrum of this colored material was dominated by bands at 1536 and 1146 cm^{-1}, a result which is consistent with the formation of linear polyenes from the repeated condensation of acetaldehyde. In polyenes with conjugated double bonds, the vibrations of adjacent functional groups mix, and spectral activity is significantly enhanced (*23*). Thus, the two bands due to these polyenes were easily observed above the background. This assignment has received support from Heaviside *et al.* (*24*). In their work, strong bands of acetylene on alumina and on type KX zeolite near 1510, 1120, and 1020 cm^{-1}, which appeared to be intensified by resonance enhancement, were also assigned to a linear polyene product.

The classical mechanism for homogeneous aldol condensation requires the base-initiated abstraction of a proton from the reacting molecule. On NaOH-treated silica gel, the catalytically active basic sites are associated with the surface sodium ions. In the absence of sodium, surface hydroxyl groups are acidic enough to catalyze the formation of paraldehyde. With sodium ions present, base-catalyzed reactions are observed. The rates of these reactions increase with sodium ion coverage, but the overall mechanism is not affected by the amount of sodium present. In addition, the active sites are poisoned by acidic adsorbates, but are relatively unaffected by bases. This is illustrated in Figs. 5 and 6. When acetaldehyde was adsorbed on NaOH-treated silica gel poisoned with formic acid, Raman bands of condensation products could not be observed, even after the catalysts were heated to 59°C. Bands of physically adsorbed acetaldehyde remained through heating and evacuation of the sample. In contrast, pyridine preadsorbed on NaOH-treated silica gel did not poison the condensation of acetaldehyde, although it appeared to inhibit its physical adsorption. All of the crotonaldehyde and dioxane(I) bands in Fig. 6B (without pyridine) can also

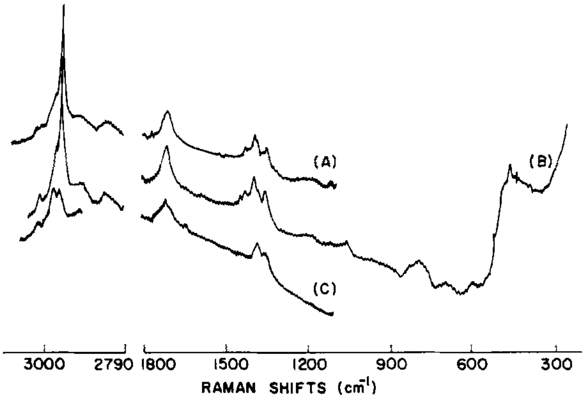


FIG. 5. Effect of formic acid poisoning on acetaldehyde condensation. Conditions: Formic acid first adsorbed and evacuated. Acetaldehyde adsorbed for: (A) 2.5 h at 20°C, (B) an additional 1 h at 59°C, (C) an additional 30 min at 59°C, followed by evacuation of the sample.

be identified in Fig. 6A (with pyridine). However, the 2921, 1719, and 1445 cm^{-1} bands of physically adsorbed acetaldehyde are not observed. Since it is generally accepted that pyridine adsorbs on surface hydroxyls with acidic character, it is proposed that the physically adsorbed acetaldehyde adsorbs on the same hydroxyl sites. These sites are different from those responsible for the condensation of chemisorbed acetaldehyde.

On alumina, the NaOH-treatment resulted in the formation of a new band on adsorption of acetaldehyde. In addition to the bands at 1635 and 1605 cm^{-1} assigned to a chemisorption or condensation product, and the 1536 and 1152 cm^{-1} oligomer bands, a band was observed at 1596 cm^{-1}. This coincides with the C–O asymmetric stretching vibrational band of aluminum acetate (*25*), giving an indication of additional surface reactions. Clearly the potential of alumina as an oxidation catalyst was enhanced by sodium ions in the same way that its activity as a basic catalyst was improved. Unlike the case of NaOH-treated silica gel, the acetate ions which were formed on the alumina surface were

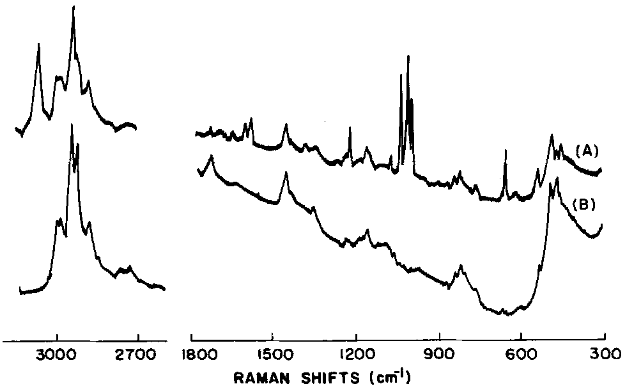


FIG. 6. Effect of pyridine poisoning on acetaldehyde condensation. Pyridine first adsorbed and evacuated. (A) Acetaldehyde adsorbed for 9.5 h at 20°C; (B) acetaldehyde adsorbed for 23 h at 20°C.

present in sufficient concentration to be observed in the Raman spectrum as chemisorbed species.

CONCLUSION

The sequence of reactions involved in the condensation of acetaldehyde on NaOH-treated silica gel has been described in detail. Reaction of acetaldehyde proceeds via an adsorbed enolate intermediate which is stabilized by surface sites associated with surface sodium ions. The chemisorbed intermediate is a type of acetaldol, bonded through two R–O–Si bonds with the surface. Reaction of the adsorbed acetaldol with excess acetaldehyde at room temperature gives 6-hydroxy-2,4-dimethyl-1,3-dioxane, a trimer of acetaldehyde. At slightly elevated temperatures adsorbed acetaldol desorbs with dehydration, giving crotonaldehyde. In the presence of the active surface, crotonaldehyde undergoes additional polymerization reactions which eventually lead to catalyst deactivation.

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