JOURNAL OF CATALYSIS **61**, 515–518 (1980)

NOTES

Raman and Infrared Spectra of Ethynylbenzene Adsorbed on Zinc Oxide

In a preceding paper Raman and infrared spectra from 3-phenyl-1-propyne and 1-phenyl-1-propyne adsorbed on zinc oxide have been reported (*1*). These isomeric compounds yield both adsorbed acetylide species and propargyllic species on zinc oxide. The ethynylbenzene molecule ($C_6H_5C\equiv CH$) is also a strong Raman scatterer but differs from the former two adsorbate compounds in that it cannot isomerize via an intermediate propargyllic species. Recently, infrared results have been reported (*2*) which showed the existence of acetylide species following adsorption of this alkyne on zinc oxide. We now present a brief but informative report on Raman spectra obtained from adsorbed ethynylbenzene.

As a check to ensure agreement with the previous work, infrared spectra were recorded again, and a few features from them deserve mention. As has been found previously (*2*), dissociation of the acetylenic hydrogen occurs to yield phenylacetylide species which are characterized by two weak infrared absorptions at 2075 and 2105 cm^{-1} assignable to the $\nu(C\equiv C)$ mode. It has been shown (*3*) that two different types of adsorption sites are involved in the formation of these species leading to the two slightly different $\nu(C\equiv C)$ wavenumbers. The use of spectral ratioing facilities associated with the Digilab FTS 14 interferometer in the present study proved to be more advantageous. The background OH band at 3670 cm^{-1} was found to be substantially removed (thus leaving a transmission peak at 3670 cm^{-1} in Fig. 1) and displaced to a broad absorption with a maximum near 3510 cm^{-1}. It is therefore assigned to OH groups of the surface involved in hydrogen bonding interaction probably with the aromatic ring of the adsorbate molecule. The intensity of the background OH band at 3620 cm^{-1} also decreased slightly, suggesting that these OH groups were also involved, to a lesser extent, in hydrogen bonding interaction. The other very broad absorption with a maximum near 3350 cm^{-1} has previously been attributed (*2*) to new OH species formed from the dissociation of the acetylenic hydrogen. These observations are in good agreement with results from other adsorbed aromatic compounds (*1*).

An infrared absorption band of rather strong intensity was observed at 1205 cm^{-1} (see Fig. 1). This band was not reported in the earlier infrared study (*2*). It cannot be assigned to an overtone of $\delta(C\equiv CH)$, which appears at 1242 cm^{-1} in the liquid infrared spectrum (*4*), because of its too low wavenumber. We prefer to assign it as the counterpart of the intense band in the Raman spectrum of the liquid at 1190 cm^{-1} which has been attributed (*4*) to an acetylene-substitution sensitive mode of vibration considerably localized in the bond between the phenyl ring and the acetylene group. Its characteristic strong intensity has been related (*5*) to the conjugation effect arising from the direct

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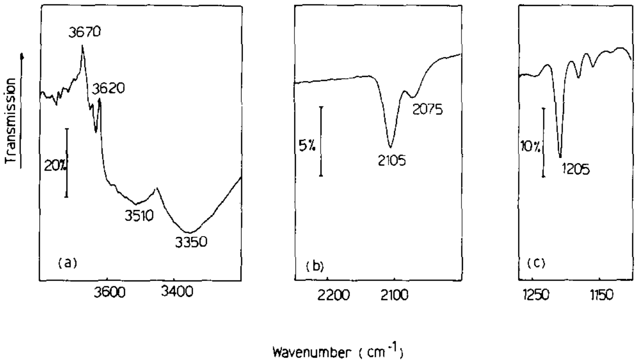

FIG. 1. Infrared spectra of adsorbed species from ethynylbenzene on zinc oxide. The spectra were ratioed against ZnO background. (a) The region 3200 to 3800 cm^{-1} with two absorption maxima at 3510 and 3350 cm^{-1} and two minima at 3670 and 3620 cm^{-1}; (b) The region 2000 to 2250 cm^{-1}; (c) the region 1100 to 1250 cm^{-1}.

linkage of the aromatic ring to the acetylenic triple bond. This mode is however very weak in the infrared absorption (*4*).

The Raman spectrum (laser excitation wavelength $\lambda = 568.2$ nm) obtained after a very rapid exposure (a few seconds) of a pretreated ZnO sample to ethynylbenzene shows most of its stronger bands to be very similar in position to those in the liquid spectrum. The acetylene-substitution sensitive mode was, however, shifted more strongly, by 15 cm^{-1}, to 1205 cm^{-1} in agreement with the infrared spectrum described above. In the ν(C≡C) region, an

TABLE 1

Raman Spectra ($\Delta\tilde{\nu}$/cm^{-1}) from Ethynylbenzene Adsorbed on ZnO[a]

Liquid[b]	After first evacuation		After second evacuation	
			First scan	Repeated scan
996 (71)		1002 (45)[c]	1000 (26)[c]	1000 (33)[c]
1024 (8)				
1157 (6.5)		See note[c]	See note[c]	
1174 (18)				
1190 (35)		1205 (16)[c]	1205 (13)[c]	1208 (13)[c]
1330 (1)		1338 (2)	1338 (2)	1338 (2)
1444 (2)				
1488 (2)		1490 (8)	1488 (9)	1490 (6)
		1533 (8)	1530 (10)	1530 (9)
1597 (40)		1598 (42)	1595 (29)	1600 (36)
2110 (99)	2106 (22)[d]	2106 (36)	2103 (22)	2103 (21)
	2190 (2)[d]	2190 (10)	2191 (0)	2193 (10)
	n.o.[e]	2218 (4)	n.o.	2218 (4)
3066 (18)		3070 (11)[c]	3065 (6)[c]	3063 (7)[c]
3292 (0.5)				

[a] Arbitrary relative peak intensity in parentheses. Laser excitation wavelength $\lambda = 568.2$ nm.

[b] For assignments see Ref. (*4*).

[c] Intensity figures are not very certain because of interfering features from ZnO (the region 940 to 1240 cm^{-1}) or from localized fluorescence features from adsorbed species (the region 3040 to 3100 cm^{-1}).

[d] Recorded immediately after the first evacuation.

[e] n.o., not observable.

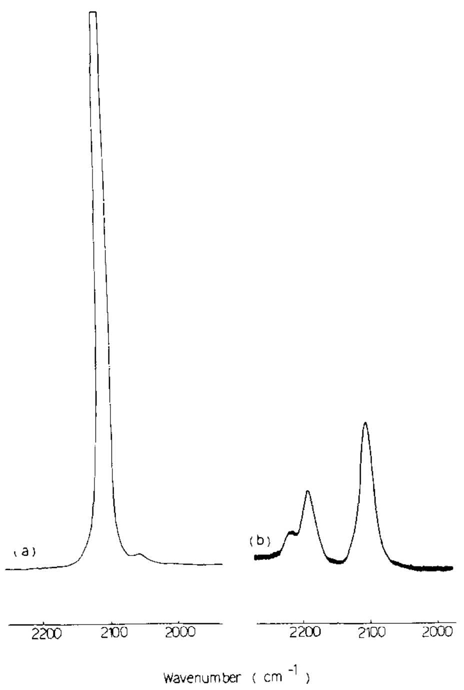

FIG. 2. Raman spectra in the region 2000 to 2300 cm^{-1} (a) of liquid ethynylbenzene; (b) of the adsorbed species from ethynylbenzene on zinc oxide.

intense band was observed at 2106 cm^{-1} together with two weaker bands near 2190 and 2218 cm^{-1} (see Fig. 2). The former band is attributed to the acetylide species $C_6H_5C{\equiv}C\ldots Zn$ (surface) resulting from the dissociative chemisorption. This is consistent with Raman spectra (*1*) from adsorbed 3-phenyl-1-propyne and 1-phenyl-1-propyne. The extra Raman bands at higher wavenumbers (2190 and 2218 cm^{-1}) seemed to develop in intensity shortly after exposure of the adsorbed phase to the laser beam (see Table 1 and Fig. 2). These two bands were invariably observed at the same positions, though with somewhat nonreproducible relative peak intensities, in several repeated experiments and also in spectra excited with the laser blue line at 488 nm. The use of this excitation wavelength, however, led to serious fluorescence problems arising from the adsorbed species. The Raman spectra from adsorbed ethynylbenzene together with its liquid spectrum are summarized in more detail in Table 1.

The Raman and infrared results clearly indicate the principal chemisorbed species to be an acetylide type. The observation that the acetylene-substitution sensitive mode at 1205 cm^{-1} is shifted from its liquid position and particularly intensified in the infrared absorption can be related to the inductive effects through the conjugated system resulting from the replacement of the acetylenic hydrogen by effectively a zinc ion. The position of the additional Raman bands near 2190 and 2218 cm^{-1} suggests that they are likely to arise from some other acetylenic species. These Raman bands were, however, not observable in the infrared spectrum in both the present and earlier studies (*2*). The possibility that this lack of infrared activity arises for symmetry reasons could not be excluded. However, the observation that the bands seem to form immediately after exposure of the sample plus adsorbed phase to the laser beam suggests that the formation of these acetylenic species is related to the irradiation effect of the laser beam. Zinc oxide is well-known as an *n*-type semiconducting oxide having a band-gap energy of 3.2 eV (*6*). The sensitization of photoconductive effects in zinc oxide has been a complex subject (*7*), and spectral sensitization by adsorbed polyethynylbenzene has been reported (*8*). The Raman bands observed here are in fact similar to the $\nu(C{\equiv}C)$ frequencies reported in the Raman spectra of pure diphenylacetylene ($C_6H_5{-}C{\equiv}C{-}C_6H_5$; 2200 cm^{-1}) (*9*) and diphenylbutadiyne ($C_6H_5{-}C{\equiv}C{-}C{\equiv}C{-}C_6H_5$; 2235 cm^{-1}) (*10*). In connection with the latter case, it has been shown (*10*) that copper phenylacetylide dissociates under uv light irradiation to yield phenylacetylide radicals which then dimerize to form diphenylbutadiyne. In the absence of other information, the vibrational spectroscopic results in the present study thus tend to suggest that polymerization of chemisorbed phenylacetylide species occurs under the irradiation effect of the laser beam. It is also informative to note here that excitation of the Raman spectrum with another laser wavelength ($\lambda = 488$ nm) also results in chemical transformation of the adsorbed species. Further investigations should prove to be worthwhile in determining the structures of the photoinduced species.

ACKNOWLEDGMENTS

Support of the Science Research Council is gratefully acknowledged. Professor N. Sheppard (Norwich), Professor R. M. Hammaker (Kansas) and Dr. J. C. Lavalley (Caen) are thanked for helpful discussion, and the latter also for drawing my attention to Ref. (*9*).

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Received February 9, 1979