

## Raman Spectra of Molecules Adsorbed on Heavy Metal Oxides. Propylene on ZnO: the Anionic Nature of the Adsorbed Allyl Species

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**Summary** Raman results, in combination with recent more detailed i.r. data, provide spectroscopic evidence that the chemisorbed allyl species from propylene on zinc oxide is of an anionic nature.

A SUBSTANTIAL number of successful studies of molecules adsorbed on surfaces have been made by means of Raman spectroscopy. The majority of these studies have been concerned with adsorption on very high area oxides of the silica, alumina, and zeolite types.<sup>1,2</sup> Heavy metal oxides such as zinc oxide, and mixed oxides of the tin-antimony or bismuth molybdate types are of importance in industry but are usually only available with much lower specific areas. It would be of great interest if it were possible to obtain good Raman spectra of molecules adsorbed on such catalysts.

In catalytic terms the allyl species obtained from the adsorption of propylene on such catalysts is of particular interest. Dent and Kokes<sup>3</sup> have previously studied the chemisorption of propylene on zinc oxide by i.r. spectroscopy. They showed that the chemisorption is dissociative and that one of the methyl C-H bonds is broken to give an OH<sup>-</sup> species by combination with an adjacent oxide ion. The remaining adsorbed hydrocarbon species was shown to be a symmetrical allyl species of the formula CH<sub>2</sub>CHCH<sub>2</sub> by elegant isotopic studies. Dent and Kokes described the hydrocarbon species as  $\pi$ -allyl in nature, but there remains more than one possible structure for such a species. We noted that the mean frequency of the strongest bands from the chemisorbed species in the  $\nu$ (CH) bond-stretching region was considerably lower than the corresponding mean frequency for neutral  $\pi$ -allyl species with transition metals such as Pd (see Table). This latter species has most of its  $\nu$ (CH) absorptions above 3000 cm<sup>-1</sup> whereas the  $\pi$ -allyl-ZnO spectrum has the strongest bands below 3000 cm<sup>-1</sup>. We considered that this suggested the structure to be that of an allylic anion [C<sub>3</sub>H<sub>5</sub>]<sup>-</sup> as the additional electron in the  $\pi$ -system could lead to hybridisation of the carbon atoms between *sp*<sup>2</sup> and *sp*<sup>3</sup>. Kokes later expressed some preference for an anionic structure on chemical grounds<sup>4</sup> but did not relate this view to the spectroscopic results.

More recently some comparative studies have been reported by Sourisseau and his colleagues<sup>5</sup> of the i.r. and Raman spectra from allyl groups that are  $\sigma$ -bonded, or  $\pi$ -bonded to neutral metal atoms, or are anionic, [C<sub>3</sub>H<sub>5</sub>]<sup>-</sup>, with respect to metal cations. In the light of these results we considered that it would be worthwhile to re-investigate the propylene-ZnO system by Raman spectroscopy and by Fourier-transform i.r. spectroscopy.

The ZnO powder used was Kadox 15 from the New Jersey Zinc Co.; its surface area was reported<sup>6</sup> to be 8.40 m<sup>2</sup> g<sup>-1</sup>. The white powder was pressed into the form of a disc and was pretreated in a greaseless silica cell according to a method slightly modified from that reported recently.<sup>7</sup> After a final heating in pure oxygen at 450 °C for 5 h, the ZnO disc was slowly cooled in oxygen to 250 °C and then

degassed at that temperature for 1 h. This revised procedure was found to be more effective in removing bands in the 2850–2950 cm<sup>-1</sup> region in the background Raman spectrum resulting from hydrocarbon contamination. The oxygen used was from B.D.H. (99.6% pure) and the propylene gas was from the National Physical Laboratory, Teddington (99.9% pure). Raman spectra were recorded on a Spex 1401 double monochromator coupled to a Coherent Radiation 52 mixed gas argon-krypton ion laser. The exciting line at 488 nm was used and right-angle viewing optics were employed. Spectra were normally recorded at 12 cm<sup>-1</sup> resolution. The laser power incident on the sample was ca. 35 mW. I.r. spectra were obtained at a resolution of 4 cm<sup>-1</sup> using a Digilab FTS 14 i.r. interferometer.

In general, at moderate propylene coverage, our i.r. results agreed very closely with those obtained by Dent and Kokes.<sup>3</sup> However the ratioing facilities of our Fourier-transform i.r. instrument did allow the observation of absorption bands over a rather wider wavenumber range. At lower coverages than were reported previously somewhat different absorption bands were obtained but with a very similar distribution of frequencies. We conclude that there are two sets of very slightly different (Zn<sup>2+</sup>O<sup>2-</sup>) sites which give closely similar adsorbed species.

The Raman background spectrum of ZnO was fairly complex below 800 cm<sup>-1</sup>, the most intense band being a fundamental lattice mode at 437 cm<sup>-1</sup>.<sup>8</sup> Above 800 cm<sup>-1</sup> a multi-phonon feature obscured the region of ca. 980–1240 cm<sup>-1</sup>, and two very weak hydroxy features occurred near 3620 and 3672 cm<sup>-1</sup>. Adsorption of propylene followed by evacuation of the gas phase gave only very weak features at low wavenumbers, but a well-defined spectrum in the  $\nu$ (CH) region as illustrated in the Figure.

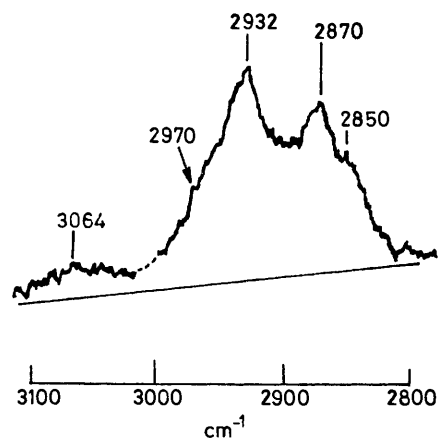


FIGURE. Raman spectrum from propylene chemisorbed on ZnO (the very weak, very broad band near 3065 cm<sup>-1</sup> is always readily discernible in spectra recorded with a compressed wavenumber scale).

A very weak additional band appears near  $3600\text{ cm}^{-1}$  corresponding to the i.r. absorption at  $3593\text{ cm}^{-1}$  resulting from  $\text{OH}^-$  species formed by dissociative adsorption of the propylene.<sup>3</sup>

The Raman and i.r. band wavenumbers from the chemisorbed propylene in the  $\nu(\text{CH})$  region, and the wavenumbers of the stronger i.r. bands in the accessible lower frequency region, are summarized in the Table. These data are

TABLE. Vibrational band wavenumbers ( $\text{cm}^{-1}$ ) for different allyl species and the allyl species from propylene chemisorbed on  $\text{ZnO}$ .<sup>a</sup>

Allyl species from propylene/ $\text{ZnO}$		Anion $[\text{C}_3\text{H}_5]^-$ <sup>b</sup>		$\pi\text{-C}_3\text{H}_5^c$ I.r.
Raman	I.r.	Raman	I.r.	
3065(vw)		3067(vw)	3068(vw)	3084(vw)
	3053(w)			3069(w)
	3040(w)			3056(vw)
	3000(w)	3015(w)	3004(m)	3037(vw)
2970(m)	2970(st)	2972(m)	2962(m)	2999(vw)
	2947(w)			
2932(st)		2933(st)		
	2915(st)		2916(m)	
2870(m)	2865(w)	2871(m)	2854(vw)	
2850(w)	2840(w)			
	2820(vw)			
	1547(st)		1512(vst)	
			1420(st)	1458(st)
	1390(m)		1373(st)	1383(st)
			1248(st)	
	1200(m)	1227(vst)	1223(m)	1228(m)
d	1035(m)		1033(m)	1192(m)
		1011(vst)		1023(st)

<sup>a</sup> st = strong; m = medium; w = weak; vst = very strong; vw = very weak. <sup>b</sup> In the compound  $\text{C}_3\text{H}_5\text{MgCl}$ , see ref. 5a. <sup>c</sup> In the compound  $(\pi\text{-C}_3\text{H}_5\text{PdCl})_2$ , see ref. 5b. <sup>d</sup> Considerably intense and very broad multi-phonon features from  $\text{ZnO}$  with a maximum at  $1155\text{ cm}^{-1}$  make detection of bands arising from the adsorbed species in the region  $980\text{--}1240\text{ cm}^{-1}$  very difficult.

compared with the results from the  $[\text{C}_3\text{H}_5]^-$  anion and the neutral  $\pi$ -allyl species in the  $\text{C}_3\text{H}_5\text{MgCl}$ <sup>5a</sup> and  $(\pi\text{-C}_3\text{H}_5\text{-PdCl})_2$  compounds,<sup>5b</sup> respectively. It is seen that the correspondence is very good between the spectra of the

chemisorbed species and that from the anion. This is particularly evident in the  $\nu(\text{CH})$  region where the bands from the neutral  $\pi$ -allyl species all fall virtually above  $3000\text{ cm}^{-1}$ , with a mean value of  $3049\text{ cm}^{-1}$ . By contrast, the strongest bands from both the anion and the adsorbed species are all found below  $3010\text{ cm}^{-1}$ . Also the  $1547\text{ cm}^{-1}$  i.r. absorption from the adsorbed species, which was assigned by Dent and Kokes<sup>3</sup> to the asymmetrical  $\nu(\text{CCC})$  stretching mode, agrees much better with the  $1512\text{ cm}^{-1}$  absorption of the anion than with that at  $1383\text{ cm}^{-1}$  assigned to the same mode for the neutral  $\pi$ -allyl species. We conclude, with confidence, that the main features in both the i.r. and Raman spectra from the adsorbed species are best accounted for in terms of an anionic symmetrical  $[\text{CH}_2\text{-CHCH}_2]^-$  structure for the adsorbed hydrocarbon group. A few additional absorptions observed by spectrum ratioing in the poorly-transmitting i.r. region below  $1000\text{ cm}^{-1}$  may denote the presence of a proportion of a species of a different structure.

Kokes<sup>4</sup> has pointed out that *cis:trans* ratios from the isomerisation of but-1-ene, and the relative ease of desorption of butenes in comparison with propylene, on  $\text{ZnO}$  are consistent with the formation of anionic hydrocarbon species by chemisorption. We have provided direct spectroscopic confirmation by this.

Kokes and his colleagues<sup>4,9</sup> supposed that the basic properties of the oxygen anions led to dissociation of C-H bonds with  $\text{p}K$  values  $< 36$ . On adjacent acid-base, *i.e.* ( $\text{Zn}^{2+}\text{O}^{2-}$ ) sites, the interaction with propylene leads to  $[\text{C}_3\text{H}_5]^- \text{Zn}^{2+}\text{OH}^-$ . We presume that the allyl species is anionic because the very small zinc ions are insufficiently accessible on the surface to form covalent  $\pi$ -type bonds. The fact that both  $\text{H}_2$  and propylene are adsorbed on only a small fraction of the total ( $\text{Zn}^{2+}\text{O}^{2-}$ ) site-pairs available<sup>10</sup> even suggests that only a small proportion of specially located zinc ions are sterically accessible for the formation of stable carbanions. These zinc ions may be associated with edges or edge-type defects on crystallite faces.

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