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Acetylene polymerization on sulfated zirconia: detection of intermediates by infrared spectroscopy

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Polymerization of acetylene was found to take place on sulfated zirconia at room temperature, and the process has been followed by FTIR spectroscopy with the purpose of identifying both final products and intermediate species. The polymerization process is initiated on the surface OH groups with formation of H-bonded species which are then protonated to form a cationic monomer, $C_2H_3^+$. This monomer adds acetylene molecules from the gas phase giving rise to several oligomers which have a number of conjugated double bonds varying from 3 to 12, the oligomer with five double bonds being the most common.

Keywords: sulfated zirconia, acetylene polymerization, infrared spectroscopy

1. Introduction

Catalytic polymerization of acetylene has been investigated by several research groups [1,2] mainly owing to the relevant properties of the polymer. Polyacetylene, an insulator in its pure state, can be considered as the archetype of all conducting polymers since it develops high electrical conductivity when doped with either oxidizing or reducing agents [3] and represents the simplest conjugated structure. Polymerization of acetylene can be accomplished in homogeneous systems, normally using titanium derivative complexes as catalysts [4–6]. Alternatively, the polymerization can also be achieved in heterogeneous systems and the process can be initiated on either Lewis [7,8] or Brønsted acid sites [9].

Zecchina et al. [9] have recently reported a spectroscopic study on the polymerization of acetylene in an acid zeolite (H-ZSM5). Acetylene interacts with the Brønsted acid sites of this zeolite with formation of hydrogen-bonded (precursor) species. These precursors are then protonated, and polymerization proceeds to yield intensely coloured carbocationic species.

Sulfated zirconia is a highly acid solid [10–20]; the presence of the sulfate groups on the zirconia surface enhances, with respect to the pure zirconia, the strength of both Brønsted and Lewis acid sites. Therefore, sulfated zirconia is a good candidate for acetylene polymerization and the process could take place on either Brønsted or Lewis acid sites. This paper describes an FTIR investigation of the interaction and polymerization of acetylene on a partially hydroxylated sulfated zirconia. The results obtained are compared with those corresponding to pure zirconia.

2. Experimental

Sulfated zirconia (subsequently called SZ) was obtained by thermolysis at 1000 K of zirconium sulfate (BDH, analytical grade). Structural, textural and infrared characterization of this material was reported elsewhere [18,19,21]. Briefly, the SZ sample was found to be mainly in the monoclinic form with about 15% of the tetragonal phase and it showed a BET surface area of 90 $m^2\ g^{-1}$ and a most frequent pore radius of 8 nm. Chemical analysis showed a sulfur content of 1.1%, which comes from the sulfate precursor. IR spectroscopy [18,19] proved that this residual sulfur was present in the form of both isolated and polynuclear sulfate groups at the zirconium oxide surface. These sulfate groups are responsible for the enhanced Lewis and Brønsted acidity showed by the SZ sample [19].

Pure zirconia (subsequently called PZ) was obtained by hydrolysis of zirconium propoxide followed by calcination at 650 K for 3 h. This PZ sample was found to be in the tetragonal form and showed an IR spectrum characteristic of pure zirconia [16].

For IR studies, thin self-supporting wafers of each sample (about 0.03 $g\ cm^{-2}$) were prepared and activated inside an IR cell [22] which allowed in situ high-temperature treatments, gas dosage and room-temperature measurements to be performed. For activation, the sample wafers were heated in a dynamic vacuum (residual pressure $< 10^{-3}$ Pa) for 45 min at the desired temperature. After the activation period, each sample was allowed to cool to room temperature and IR spectra were taken. Spectra were collected, at 3 cm^{-1} resolution, on an FTIR Bruker IFS66 spectrometer. For each sample the spectrum taken before the dosage of the acetylene has been used as a background, and some of the spectra shown in this work are background subtracted. High-

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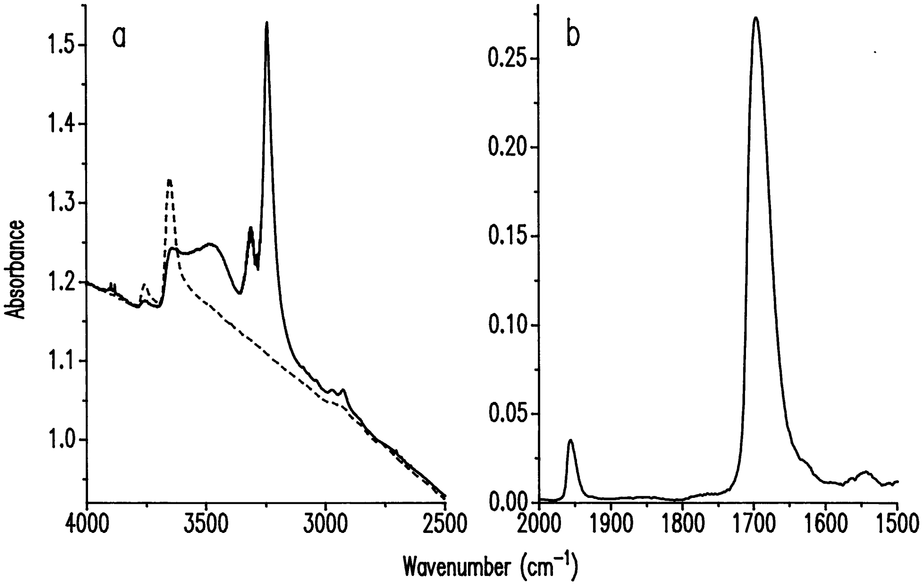


Figure 1. IR spectra of sample SZ outgassed at 673 K. (- - -) background, (——) immediately after dosing with 20 Torr of C_2H_2. The spectrum shown in (b) has been blank subtracted.

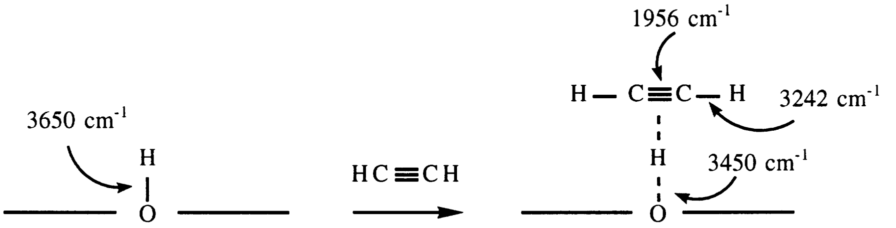
purity acetylene (C-26) was used without further purification.

3. Results and discussion

3.1. Interaction of acetylene with sulfated zirconia and ensuing polymerization

Figures 1a and 1b, show the IR spectrum of acetylene adsorbed on the SZ sample, immediately after dosage at room temperature. Figure 1a also shows the IR spectrum of SZ, outgassed at 673 K, before acetylene dosage. The OH stretching bands of SZ (at 3758 and 3650 cm^{-1}) are eroded when acetylene is adsorbed and new bands developed at 3450 (broad with a tail on the high-wavenumber side), 3242 (m), 2973 (vw), 2921 (vw), 1956 (w) and 1696 cm^{-1} (m). The bands at 3450, 3242 and 1956 cm^{-1} will be discussed first.

The low intensity band at 1956 cm^{-1} is assigned to the C≡C stretching of hydrogen-bonded C_2H_2 molecules. Hydrogen bonding renders the Raman mode of free acetylene at 1974 cm^{-1} [23] IR-active, and causes a bathochromic shift of 18 cm^{-1} (because electronic charge is subtracted from the π orbitals). The corresponding C–H stretching expected at 3287 cm^{-1} [23] appears as a narrow component at 3242 cm^{-1}, superimposed on the bands due to the ≡C–H stretching mode of C_2H_2 gas. Formation of the hydrogen-bonded complexes is further proved by the changes observed in the spectrum of the hydroxy groups. The O–H stretching band at 3758 cm^{-1}, also present in pure zirconia [16], is eroded upon adsorption of acetylene, and the hydrogen-bonded adduct is responsible for the tail observed on the high-frequency side of the 3450 cm^{-1} band. Similarly, the stronger 3650 cm^{-1} band (characteristic of sulfated zirconia) shifts to 3450 cm^{-1} upon adsorption of acetylene by the solid. In conclusion, we can state that the main species formed during the initial stages of the interaction between acetylene and sulfated zirconia is the hydrogen-bonded complex (**1**) depicted in scheme 1. This species is an intermediate in the process of acetylene polymerization on sample SZ, since upon standing at the IR-beam equilibrium temperature (spectra reported in



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Scheme 1.

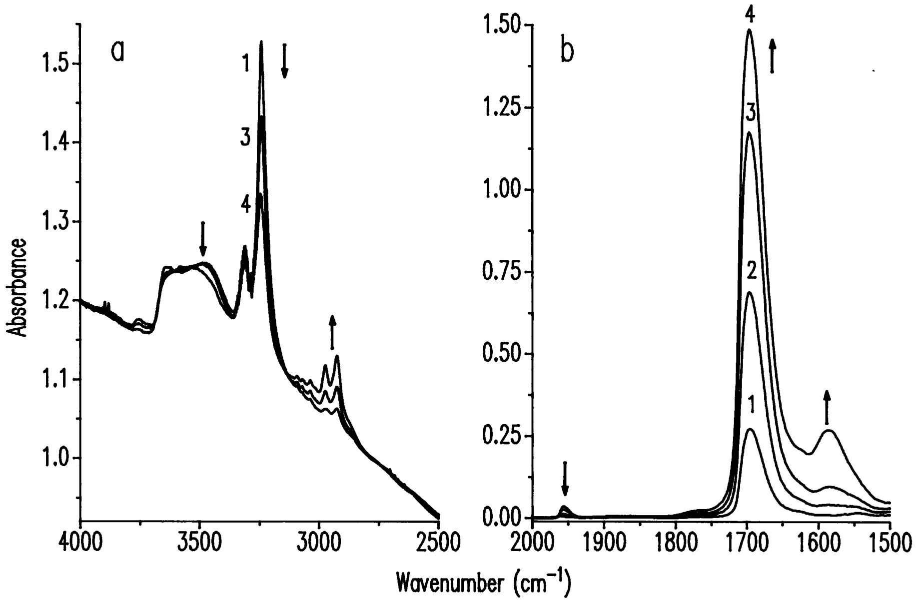


Figure 2. Evolution with time of the IR spectra of the SZ–acetylene system: immediately after C_2H_2 dosage (1), and after 5 (2), 10 (3) and 30 min (4) of contact. In (b), the zirconia blank has been subtracted from each spectrum.

figures 2a and 2b), the bands at 3450, 3242 and 1956 cm^{-1} gradually decrease while two complex groups of bands develop in the 3100–2850 and 1700–1500 cm^{-1} ranges.

1700–1500 cm^{-1} is the typical range of the C=C stretching modes of neutral and charged polyenes of variable lengths [4,24–28]; while the corresponding C–H stretching modes appear in the 3100–2850 cm^{-1} range. The most significant IR absorptions (figure 2) are observed in the 3100–3000 cm^{-1} range (several very weak bands), at 2973 (vw), 2921 (vw), 1696 (s) and 1585 cm^{-1} (m-broad). These last two bands do not correspond to the same chemical species because they do not appear simultaneously in the IR spectra. The band at 1696 cm^{-1} is formed immediately after acetylene adsorption; it was already present (with low intensity) in the IR spectrum of figure 1. However, the band at 1585 cm^{-1} develops later.

The band at 1696 cm^{-1} is assigned to another intermediate in the process of acetylene polymerization. In fact, this band initially grows (figure 2b) and after 30 min it is observed to decrease (figure 3). Contrary to this behaviour, the band at 1585 cm^{-1} continuously grows and becomes more complex showing a broad shoulder on the high-wavenumber side and a tail on the opposite side. This band corresponds to the final product of the polymerization process because it is not observed to decrease in the period of time considered in this experiment (15 h). The presence of the isosbestic point at 1660 cm^{-1} suggests that the species related to the 1696 cm^{-1} band is transformed into the species related to the 1585 cm^{-1} band. At the end of the experiment, the colour of the sample was deep blue. This colour did not disappear upon exposure to the atmosphere.

In general terms these data indicate that the hydrogen-bonded complexes (species **1**) are consumed because they are protonated by the acidic OH groups at the surface of the SZ sample. The monomer thus formed: $C_2H_3^+$, species **2** in scheme 2, gives rise to the absorption bands at 1696 cm^{-1} ($\nu_{(C=C)}$), and at 2973 and 2921 cm^{-1}

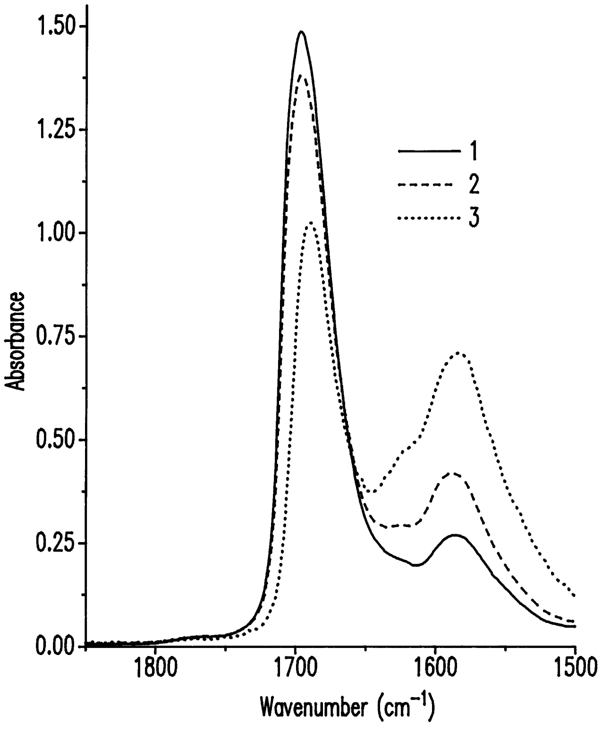
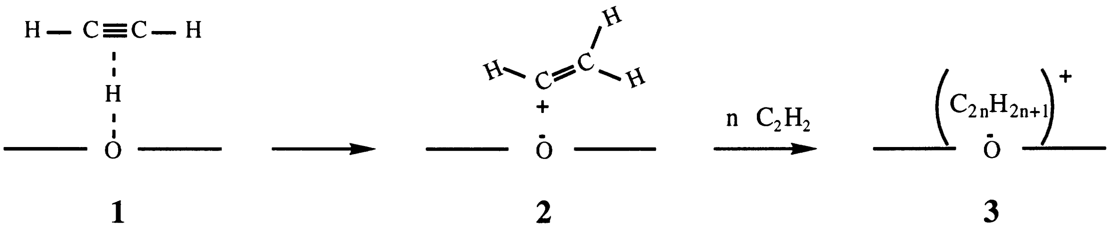


Figure 3. Evolution with time of the IR spectra of the SZ–acetylene system after (1) 30 min, (2) 1 h and (3) 15 h of contact.



Scheme 2.

($\nu_{(=C-H)}$). This monomer adds acetylene molecules from the gas phase forming conjugated polyenic carbocations (species **3** in scheme 2) responsible for the broad band with a maximum at 1585 cm^{-1} and for the several bands in the 3100–3000 cm^{-1} range. When monomers $C_2H_3^+$ are considered, the positive charge is obviously confined to the single π-bond present in the moiety. For longer oligomers, the extent of delocalization will be larger.

Several authors [8,26] have shown that the characteristic IR absorption corresponding to the C=C stretching of a conjugated polyenic chain shifts to lower wavenumbers as the chain length increases, and the corresponding relationship between the number of conjugated double bonds and frequency of the C=C stretching mode can be used to estimate the chain length. Presence of a broad IR absorption band in the 1615–1520 cm^{-1} range (figure 3) strongly suggests the formation on sulfated zirconia of several oligomers with a number of conjugated double bonds varying from 3 to 12, the oligomer with 5 double bonds (corresponding C=C stretching at 1585 cm^{-1}) being the most common.

An experiment carried out on a more dehydroxylated SZ sample (activated at 973 K) has shown that the polymerization process takes place to much less extent: the bands due to the oligomers were much less intense and the final colour of the sample was faint (pale-violet). These results confirm the proposed mechanism with participation of the OH groups of sulfated zirconia. It is worth mentioning in this respect that the mechanism proposed for the polymerization of acetylene on sulfated zirconia is the same as proposed by Zecchina et al. [9] for polymerization on a highly acidic H-ZSM-5 zeolite.

3.2. Interaction of acetylene with pure zirconia

For comparison, the interaction of acetylene with partially hydroxylated pure zirconia (PZ sample activated at 673 K) has also been studied by IR spectroscopy. The corresponding IR spectra are reported in figure 4. Spectrum 2, obtained immediately after dosing with acetylene at room temperature, shows that a portion of the acetylene molecules interacts with OH groups at the solid surface giving rise to hydrogen-bonded complexes similar to those described for the SZ sample (species **1** in scheme 1). The remaining acetylene molecules stay in the gas phase. The hydrogen-bonded complexes are respon-

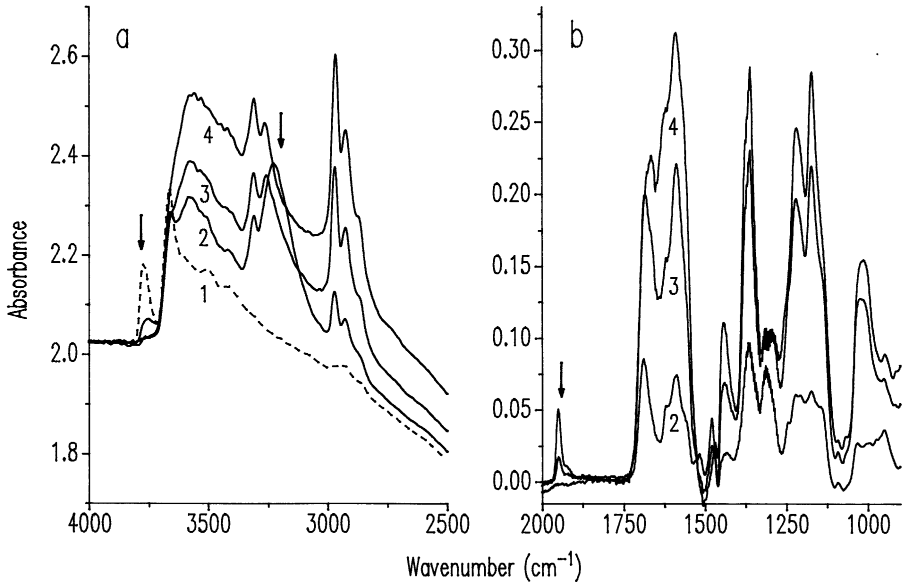


Figure 4. (1) Blank spectrum of the PZ sample; (2) immediately after dosing with 20 Torr of C_2H_2; (3) and (4), after 1 and 15 h of contact, respectively. In (b), the zirconia blank has been subtracted from each spectrum.

sible for the bands at 3225 (≡C–H stretching) and at 1950 cm^{-1} (C≡C stretching). Upon standing at the IR-beam equilibrium temperature, these bands gradually decrease and finally disappear (spectra 3 and 4), indicating the total transformation of the hydrogen-bonded complexes into protonated species. Simultaneously, a complex profile of bands is developed in the range 1750–800 cm^{-1}. Some of these bands, those observed at 1690 and 1590 cm^{-1}, may be assigned to the formation of mono- and oligomeric carbocationic species. However, their low intensity (in comparison with those observed in figure 2), and the pale pink colour reached by the PZ sample after 15 h of contact with acetylene indicate that the polymerization process hardly takes place on pure zirconia. Some of the remaining bands in figure 4 can be assigned to several hydrogenated products [24], which will not be discussed here.

Comparing the results obtained with sulfated and with pure zirconia, it can be concluded that polymerization of acetylene, via Brønsted acid sites, is greatly enhanced by the presence of OH groups with Brønsted acidity higher than that shown by pure zirconia, the acidity shown by the OH groups on sulfated zirconia being enough. In this respect, it is worthwhile mentioning that the O–H stretching frequencies of the acidic hydroxy groups in H-ZSM-5, sulfated zirconia and pure zirconia are, respectively, 3610, 3650, and 3665 cm^{-1}, thus showing the corresponding gradation of Brønsted acidity.

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