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Low temperature FTIR spectroscopic study of ozone interaction with phenol adsorbed on silica and ceria

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The reactivity towards O_3 of the different species formed from phenol adsorption on silica and ceria has been studied using IR spectroscopy by increasing the temperature from 77 K. It clearly appeared that on silica H-bonded phenol species were more reactive than phenoxy species, whereas on ceria monodentate phenoxy species were more active than bidentate species. Intermediate products of phenol oxidation were characterized by bands between 1800 and 1600 cm^{-1}, that at 1750 cm^{-1} being probably due to the formation of a carboxylic acid.

Keywords: FTIR; phenol; ozone; ceria; silica

1. Introduction

Studies of the mechanism of ozone interaction with complex organic and biological molecules are very important for the development of the efficient and ecologically clean industrial processes, for water and waste water purification, as well as for understanding the mechanism of ozone toxic action.

Phenol was chosen because it is a humic acids precursor [1], and can be considered as a typical representative of these compounds. The infrared spectrum of phenol has been described in various states: pure, in solutions or adsorbed on various oxides [2–4], and ozonolysis of phenol has been studied in aqueous solutions and in various solvents [5], but products were never characterized spectroscopically.

The purpose of this preliminary paper is to study the reactivity towards ozone of the different species resulting from phenol adsorption on metal oxides. This is an important point. For instance, it has been shown on Pd/ThO_2 that monodentate methoxy species, formed from methanol adsorption, decomposed into CO and H_2, whereas bidentate species, much less reactive, led to dimethyl ether [6]. In the present study, phenol has been adsorbed on silica on which hydrogen bonded species and phenoxy species are formed and on ceria, on which type I and type II phenoxy species are clearly differentiated. Ozone has been introduced at 77 K and the behaviour of the different species formed has been spectroscopically followed by increasing temperature.

2. Experimental

The stainless steel cell for studying the infrared spectra of adsorbed species at liquid nitrogen temperature has been previously described [7].

Silica (Degussa, 200 $m^2\ g^{-1}$) or ceria (Rhône Poulenc, 180 $m^2\ g^{-1}$) samples were pressed into pellets (10–15 mg for silica, 20–25 mg for ceria), and pretreated in vacuum at 770 K during 4 h. Ceria was then treated with oxygen at the same temperature to oxidize its surface.

Phenol (0.25 Torr pressure in the cell) was introduced under different conditions as indicated below.

Ozone was prepared from gaseous O_2 in an electric discharge at pressures of about 5–10 Torr, and manipulated as previously described [8].

All spectra have been recorded on a 710 Nicolet. Reported spectra have been subtracted from that of the corresponding activated metal oxide.

3. Results

3.1. Silica

Two different cases have been studied: phenol adsorption and evacuation at room temperature (RT) and phenol adsorption at 670 K followed by evacuation at the same temperature.

(i) The spectrum of phenol adsorbed at room temperature has been performed at 77 K (see fig. 1A spectrum 1). Main bands occur at 1600, 1502, 1478, and 1371 cm^{-1}. In agreement with ref. [3], we also observe the shift of the free ν(SiO–H) band from 3740 to 3400 cm^{-1}. This feature and the observation of the 1371 and 1478 cm^{-1} bands due to the OH in-plane bending vibration clearly indicate that phenol is molecularly adsorbed in the form of H-bonded species.

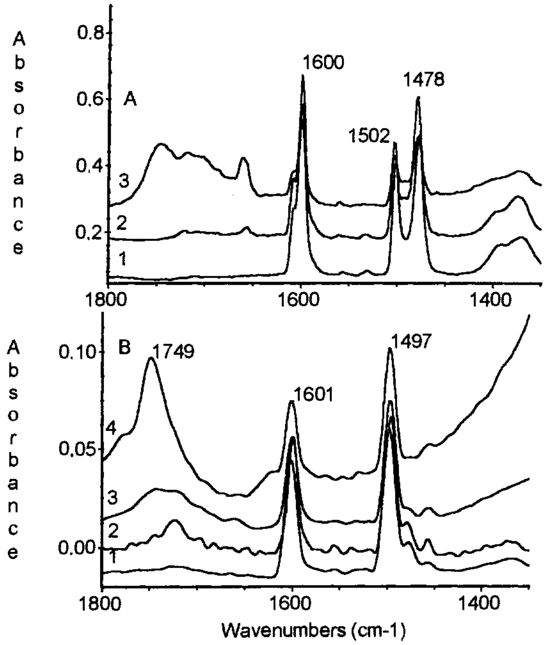

Fig. 1. Spectra of phenol adsorbed species formed on silica at RT (A) or 670 K (B) (1), followed by admission of ozone at 77 K (2), heating at 100 K (3) and at 220 K (4).

Ozone admission at nitrogen liquid temperature weakly decreases the intensity of the 1600 and 1502 cm^{-1} bands (fig. 1A spectrum 2), while a massif with two apparent bands at 1717 and 1660 cm^{-1} arises. Increasing the temperature provokes a neat intensity decrease of bands due to phenol species whereas a new band is observed at 1746 cm^{-1} with the growth of the massif already noted (fig. 1A spectrum 3). At 250 K, all the phenol bands vanish. Only a massif centred at 1750 cm^{-1} remains in the 1800–1300 cm^{-1} range.

(ii) The spectrum of phenol adsorbed at 670 K and evacuated at the same temperature, then cooled down to 77 K, is shown in fig. 1B spectrum 1. In the 1650–1450 cm^{-1} range, only the two bands at 1601 and 1497 cm^{-1} attributed to the aromatic cycle are observed, showing the exclusive formation of phenoxy species.

When ozone is introduced at 77 K, a new band appears at 1725 cm^{-1}, and at 100 K, another one at 1745 cm^{-1} the intensity of which increases slightly at 220 K (fig. 1B spectra 2–4). Concomitantly, the intensity of the phenoxy bands decreases but in a limited amount.

3.2. Ceria

On ceria activated at 670 K, phenol has been introduced and then evacuated at the same temperature. The spectrum of the species formed is shown in fig. 2 spectrum a (spectrum recorded at 77 K). The lack of any band around 1450 and 1350 cm^{-1} indicates that only phenoxy species are present. Two bands characteristic of the ν(CO) vibration of phenoxy species appear at 1266 and 1242 cm^{-1}. By analogy with results obtained from methanol adsorption on ceria [9], they are assigned to monodentate (type I) and bidentate (type II) phenoxy species, respectively.

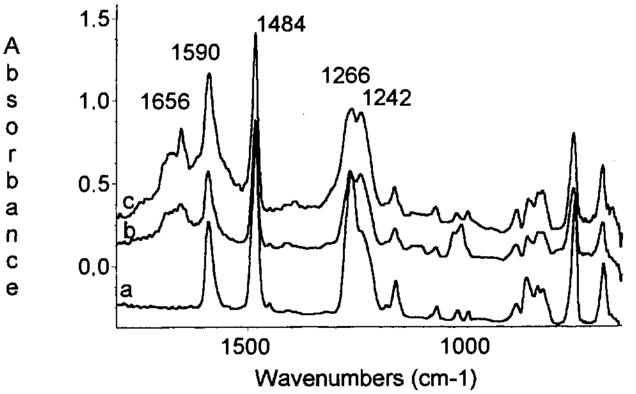

Fig. 2. Spectra of phenol adsorbed species formed on ceria at 670 K (a), followed by admission of ozone at 77 K (b), and heating at 170 K (c).

Ozone introduction at 77 K leads to the appearance of two weak bands at 1032 and 1014 cm^{-1} due to ozone adsorption. They vanish by increasing the temperature (fig. 2 spectra a–c). At 77 K, a massif appears between 1690 and 1645 cm^{-1} dominated by a band at 1656 cm^{-1}. Comparison of spectra a and b of fig. 2 shows that phenoxy I species characterised by the 1266 cm^{-1} band are specifically affected.

4. Conclusion

The results clearly show that the reactivity of ozone towards phenol on silica and ceria depends on its adsorption mode. On SiO_2, H-bonded species are more reactive than phenoxy species, whereas on CeO_2, monodentate (type I) phenoxy species are more reactive than bidentate (type II) species. On both samples, species resulting from phenol oxidation are characterized by bands between 1800 and 1600 cm^{-1} and can be considered as intermediates in the total oxidation of phenol into CO_2 and H_2O. In solution in different solvents [5], it has been reported that ozone reaction with phenol led to muconic acid. The 1750 cm^{-1} band observed on silica can be attributed to the ν(C=O) vibration of a carboxylic group, possibly of muconic acid. Bands between 1700 and 1600 cm^{-1} are due to less oxidized species like aldehydes. Further studies using $^{18}O_3$ have to be performed to specify their assignment. Nevertheless, the species formed seem to depend on the nature of phenol adsorbed species since the bands appearing between 1800 and 1600 cm^{-1} differ according to phenol adsorption.

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