

# CHEMISORPTION OF PYRROLE-SILOXANE ON ZEOLITE L AND X: A THIN LAYER INFRARED STUDY

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**Abstract**--Surface modification of Zeolite L and X by pyrrole-siloxane occurs under mild conditions. The chemisorption is investigated by infrared spectroscopy on self-supporting wafers of 15-20  $\mu\text{m}$  thickness and on 1  $\mu\text{m}$  zeolite layers coated on ZnSe crystals. The desorption of water from the modified zeolites coated as thin layers on ZnSe surfaces is astonishingly fast, under evacuation at room temperature. Indeed, for zeolite X the water bending vibration at  $1645\text{ cm}^{-1}$  is much less intense relatively to the wafer spectra after evacuation, and it is absent in the spectra of zeolite L taken on ZnSe. This allows the observation of small bands in the spectra of the 1  $\mu\text{m}$  layers, otherwise obscured by the broad intense absorption of water bending in the spectra of wafers.

## INTRODUCTION

Chemical modification of zeolites has attracted considerable attention owing to the molecular sieving properties of these materials. Ion exchange was performed ever since, with the aim to improve the catalytic and acidic properties of zeolites [1]. The complex framework structures of zeolites are, however, by far not limited to modifications of this type. Recently, some effort has been devoted to anchor specific molecules in the channels or on the surface of zeolites. Characterization of acid and basic sites has been undertaken through adsorption of organic species like benzene [2,3], pyridine [4] and pyrrole [2,5-8]. Silanes [9-13] and siloxanes [14,15] are a well known class of reagents for the modification of oxide surfaces.

A promising way to develop selective and stable coatings for sensors such as optical wave guides, chemiresistors and electrodes is to anchor zeolite crystals to a surface through a bifunctional coupling agent [16,17]. As part of our effort to extend the study of zeolite modified electrodes [18], we made use of transmission FTIR spectroscopy to characterize the chemisorption of N-(3-trimethoxysilylpropyl)pyrrole on the surface of zeolite L and X on both self-supporting wafers of 15-20  $\mu\text{m}$  thickness and 1  $\mu\text{m}$  layers coated on ZnSe crystals. Water desorption from a thin layer coating of modified zeolite on a ZnSe surface is remarkably fast on evacuation without heating.

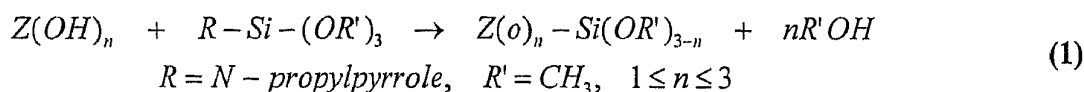
## EXPERIMENTAL

Commercially available zeolite L (Union Carbide, ELZ-L),  $\text{Na}_9[(\text{AlO}_2)_9(\text{SiO}_2)_{27}] \cdot 22\text{H}_2\text{O}$ , and zeolite X (Bender & Hobein, 13 X),  $\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}] \cdot 264\text{H}_2\text{O}$ , were used as starting materials. N-(3-trimethoxysilylpropyl)pyrrole supplied by Huels was applied without further purification. The modified zeolites were prepared by adding 1 ml of N-(3-trimethoxysilylpropyl)pyrrole to a suspension of 2 g zeolite in 50 ml of ethanol presonicated during 5 minutes. The suspension was stirred for four days at room temperature, afterwards centrifuged, the residue washed several times with ethanol and finally dried in an oven at 100 °C for 48 hours.

The IR spectra of the modified zeolites were obtained by using the following procedure. The samples were pressed into thin self-supporting wafers of 6 mm diameter and 15-20  $\mu\text{m}$  thickness, containing approximately 800  $\mu\text{m}$  of zeolite powder. ZnSe window disks (8 mm x 1 mm) were covered, on both sides, with a spot of 5  $\mu\text{l}$  of a suspension of 30  $\mu\text{m}$  of modified zeolite in 4 ml of water. The thickness of the thus obtained thin layers is about 1  $\mu\text{m}$  which corresponds to 75  $\mu\text{g}$  of zeolite on both sides. Both types of samples were mounted on a stainless steel sample holder, designed to accommodate four samples at the same time, and placed into an external high vacuum cell as described in detail elsewhere [19]. Spectra were recorded after 30 minutes of dynamic evacuation at a pressure of about  $10^{-3}$  Pa. For the measurements at normal pressure, the IR cell was purged with nitrogen for 20 minutes to remove water and carbon dioxide. Uncoated ZnSe substrates, cleaned before the measurements with ethanol, and the empty hole for the wafer spectra were used for the acquisition of background spectra. As an instrument we used a Bomem DA3 FTIR spectrophotometer equipped with a globar source, a calcium fluoride beamsplitter and a narrow range MCT detector. Measurements were done between 4000-1200  $\text{cm}^{-1}$  with a resolution of 2  $\text{cm}^{-1}$ . Good quality spectra were obtained after 200 scans for self-supporting wafers and after 1000 scans for thin layers on ZnSe.

## RESULTS AND DISCUSSION

The chemisorption of pyrrole-siloxane by both sodium L and X zeolites occurs according to Eq. (1) in which Z represents the zeolite framework.



Structural integrity of the surface modified zeolites was proved by X-ray powder diffraction [18c]. Our interest in the modification of zeolites is motivated by the aim to develop zeolite modified electrodes and photoelectrodes. Applications involving electrodes demand in some cases long term stability of the surface layer, especially under reactive conditions. A thin layer

coating of a modified zeolite sticks better to the surface of an electrode than a coating of an unmodified zeolite. Hence, the modification improves the adhesion of these zeolites to a substrate. We have found that IR experiments with ZnSe disks coated with a thin layer of pyrrole-siloxane modified zeolites L and X are helpful to characterize the coatings of electrodes.

Table 1 summarizes the observed IR frequencies of modified zeolites L and X on both self-supporting wafers and thin layers on ZnSe disks. For comparison, peak positions of the spectrum of pyrrole-siloxane in  $\text{CCl}_4$  are also given. The bands in the aliphatic stretching region ( $3200\text{-}2800\text{ cm}^{-1}$ ) and in the ring stretching region ( $1500\text{-}1200\text{ cm}^{-1}$ ) in the IR spectra of zeolites L and X undoubtedly proves the chemisorption of pyrrole-siloxane by both zeolites. No absorptions between  $3200$  and  $2800\text{ cm}^{-1}$  have been observed for  $1\text{ }\mu\text{m}$  layers of zeolite X on ZnSe. The bands characteristic of the aliphatic vibrations are, however, observed in measurements carried out with a more concentrated suspension (70 mg of zeolite in 4 ml of water). They are present in the spectrum of zeolite L (30 mg/4 ml) on ZnSe, probably because zeolite L gives rise to more homogeneous coatings than zeolite X. This fact is correlated with the particle size and hydrophobicity. Zeolite L has smaller particle size,  $0.2\text{ }\mu\text{m}$  compared to  $1\text{ }\mu\text{m}$ , and is more hydrophilic than zeolite X. An overview of the IR spectra of zeolite L and X is shown in Figures 1 and 2. Spectra of zeolite X show a steeper slope due to scattering losses than spectra of zeolite L because Rayleigh scattering is a function of the particle size and frequency, namely it is proportional to the third power of the particle diameter and to the fourth power of the frequency [20]. Thus, scattering is most severe for large particles and high wavenumbers. In case of zeolite L on ZnSe the water bending vibration at  $1645\text{ cm}^{-1}$  is absent and a significant decrease in the intensity of this band is observed for Zeolite X on ZnSe, in the spectra taken under dynamic evacuation at room temperature. Under the same conditions this band is, however, present for both zeolites in the wafer spectra. The IR spectra taken under nitrogen clearly display a broad absorption around  $3400\text{ cm}^{-1}$  and the water bending at  $1645\text{ cm}^{-1}$  is intense. Thus, water is present in the thin layers of both zeolites on ZnSe before evacuation. The desorption of water from these layers is extremely fast. It is much slower in the wafers which are roughly 10-15 times thicker. The thickness alone is perhaps not sufficient to account for the retention of water inside the zeolite channels in case of the wafers. The water molecules seem to have more difficulties in desorbing because several layers are pressed together, while in a thin film the water molecules easily find a way out of the zeolite channels. To our knowledge, desorption of water from zeolites was up to now always accomplished under evacuation and heating at temperatures higher than at least  $100\text{ }^\circ\text{C}$  [17,21,22].

The bands observed within the range of  $3800\text{-}3600\text{ cm}^{-1}$  are due to hydroxyl stretching modes [21,22]. Zeolite L contains two different types of hydroxyl groups responsible for the peaks at  $3741\text{ cm}^{-1}$  and  $3692\text{ cm}^{-1}$ , while for zeolite X only one absorption band at  $3692\text{ cm}^{-1}$  is observed. The band at  $3741\text{ cm}^{-1}$  is not observed in the spectrum of zeolite L on ZnSe. It is, however, clearly visible in the spectra of more concentrated samples (70 mg/4 ml) on which water desorption is still very fast. The attribution of the hydroxyl stretching vibration frequencies to the different kinds of hydroxyl groups in zeolites is still a matter of controversy

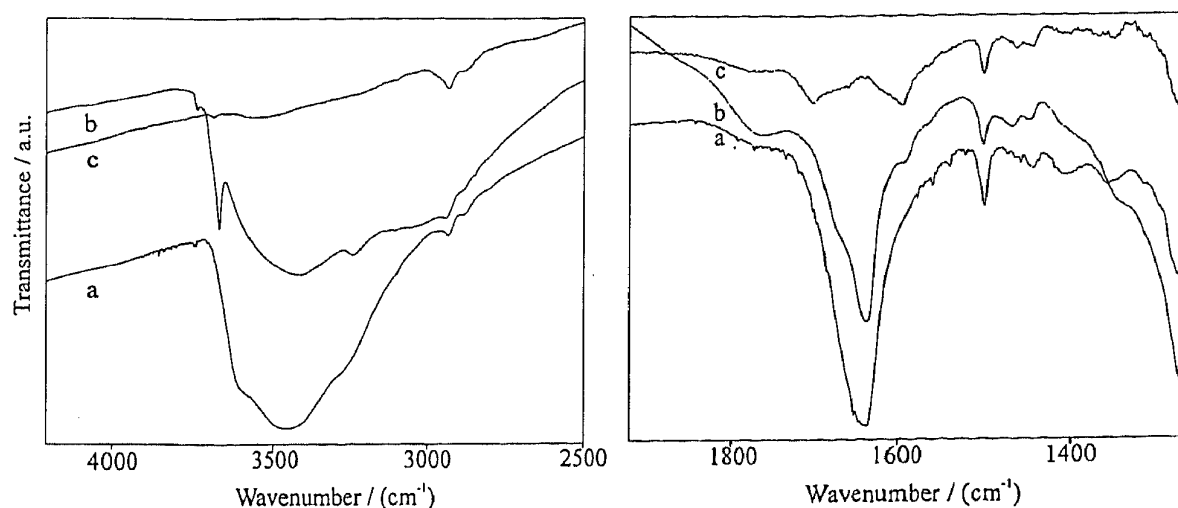
[14,22-27]. In spite of this, our experiments are consistent with the following assignment: terminal Si-OH groups at the outer surface of zeolite L at  $3741\text{ cm}^{-1}$  and the bridging hydroxyls at  $3692\text{ cm}^{-1}$  for zeolite L and X.

Table 1

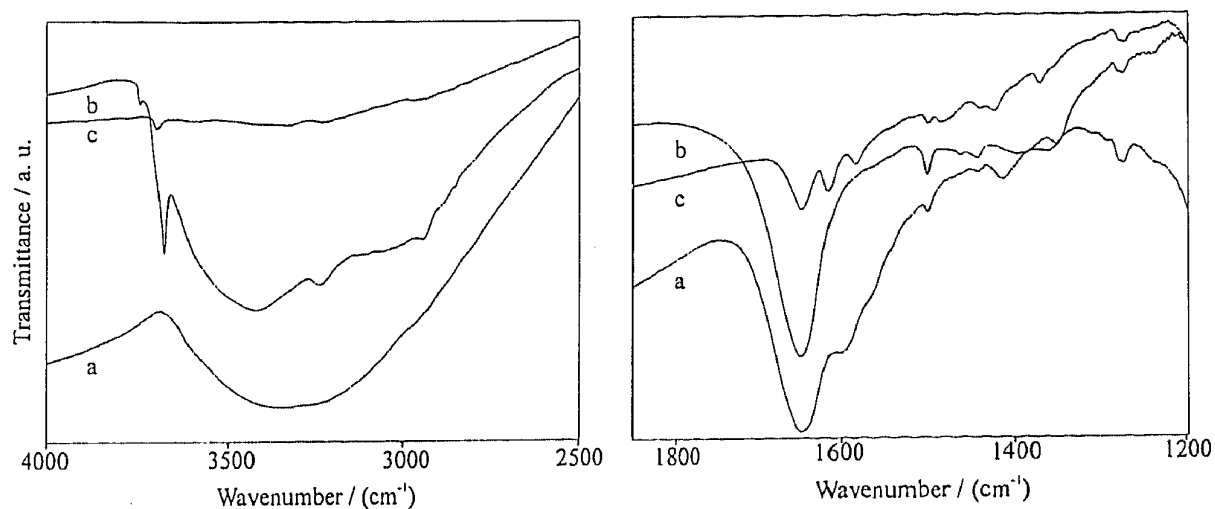
IR frequencies of pyrrole-siloxane, modified zeolite L and X.

Wavenumber range/ $(\text{cm}^{-1})$	Pyrrole-siloxane ( $\text{CCl}_4$ )	Zeolite L		Zeolite X		Assignment
		wafer	ZnSe	wafer	ZnSe	
3800-3600		3741				ZO-H str.
		3962	3692	3692	3962	<i>idem.</i>
3200-2800	3123	3130	3130	3125		pyrrole, C-H str.
	3105	3103	3103	3099		<i>idem.</i>
	2970					N-CH <sub>2</sub> , CH <sub>2</sub> str. asym.
	2943	2941	2932	2931		Si-CH <sub>2</sub> , CH <sub>2</sub> str. asym.
	2875	2877	2877	2877		Si-OCH <sub>3</sub> , CH <sub>3</sub> str.
	2841	2847	2847			asym. and/or Si-, N-CH <sub>2</sub> , CH <sub>2</sub> str. asym.
1700-1500		1695				H <sub>2</sub> O, bending range
		1645		1645	1645	(The bands are due to different types of water molecules)
					1615	
		1591	1591		1581	
1500-1200	1498	1500	1500	1500	1500	pyrrole, ring str.
	1463	1468	1461	1462	1482	<i>idem.</i>
	1445	1446	1446	1444	1441	N-CH <sub>2</sub> , CH <sub>2</sub> def.
					1425	pyrrole, ring str.
	1412		1406	1394		pyrrole, ring str. and/or Si-CH <sub>2</sub> , CH <sub>2</sub> def.
						assym.
					1371	not assigned
			1369	1362		<i>idem.</i>
	1358		1346			<i>idem.</i>
	1310			1312	1312	<i>idem.</i>
	1296			1295	1297	<i>idem.</i>
1283	1276		1274	1275	pyrrole, ring str.	
1238			1238	1236	Si-CH <sub>2</sub> , CH <sub>2</sub> def. sym.	

Zeolite X contains less terminal Si-OH groups because it has a smaller external surface area than zeolite L [22]. The bands around  $3123$  and  $3105\text{ cm}^{-1}$  of pyrrole-siloxane in liquid phase are due to the four CH stretching modes [28]. Absorptions due to CH<sub>2</sub> stretching vibrations are observed at  $2943$ ,  $2877$  and  $2847\text{ cm}^{-1}$  (weak shoulder). The band at  $2970\text{ cm}^{-1}$ , present in



**Figure 1.** Overview of the infrared transmission spectra of pyrrole-siloxane modified zeolite L: a) on ZnSe under nitrogen, b) self-supporting wafer under dynamic evacuation, c) on ZnSe under dynamic evacuation.



**Figure 2.** Overview of the infrared transmission spectra of pyrrole-siloxane modified zeolite X: a) on ZnSe under nitrogen, b) self-supporting wafer under dynamic evacuation, c) on ZnSe under dynamic evacuation.

the spectrum of liquid pyrrole and assigned to the N-CH<sub>2</sub> stretching vibration, is not observed in the spectra of zeolites. It is probably obscured by the peak at 2932 cm<sup>-1</sup>. The bands in this region are quite weak, near the detection limit, due to the low concentration of the sample and the few CH and CH<sub>2</sub> groups on it. All absorptions belonging to the aliphatic stretching region do not shift significantly upon chemisorption which means that there is no specific interaction between these groups and the framework atoms of both zeolites. The vibrations observed in the window 1700-1500 cm<sup>-1</sup> are ascribed to the presence of water, namely to its bending mode [21,22,25]. The wafer spectrum of zeolite L presents the characteristic feature at 1645 cm<sup>-1</sup> and a weak shoulder at 1591 cm<sup>-1</sup>, while for the thin layer on ZnSe the strong absorption at

1645  $\text{cm}^{-1}$  disappears, giving rise to a weak one at 1695  $\text{cm}^{-1}$ , Figures 1b and 1c. In case of zeolite X, only the band at 1645  $\text{cm}^{-1}$  is observed in the wafer spectrum, while three bands (1645, 1615 and 1581  $\text{cm}^{-1}$ ) are present in the spectrum taken on ZnSe, Figures 2b and 2c. The appearance of several vibrations in this region indicates that water molecules are adsorbed at different sites in the zeolites. It turns out that zeolite L has much less water adsorbed than zeolite X since the band at 1645  $\text{cm}^{-1}$  is not observed in the spectrum of zeolite L on ZnSe. It is well known that water is strongly adsorbed on zeolites with high concentration of aluminium and cations [21,22]. In fact, zeolite L has lower aluminium content ( $\text{Si/Al} = 2.6\text{--}3.5$ ) compared to zeolite X with  $\text{Si/Al} = 1.0\text{--}1.5$ . The bands at 1695 and 1591  $\text{cm}^{-1}$  observed on zeolite L correspond to trace amounts of water coordinatively adsorbed *via* its oxygen to metal cations at different locations, probably in one of the side-channels. Whereas for zeolite X the three bands at 1645, 1615 and 1581  $\text{cm}^{-1}$  are very likely due to "free" water and to water molecules involved in hydrogen bonding and/or bound to cations at different sites. These observations are similar to the results reported for synthetic faujasites with low and maximum content of aluminium under evacuation at 400 °C [21]. All spectra show several vibrations within the pyrrole ring stretching region between 1500 and 1200  $\text{cm}^{-1}$ . Among them five modes belong to the ring stretching according to the assignment of pyrrole bands observed in organic solvents [5,7,29]. The bands around 1498, 1463, 1412 and 1283  $\text{cm}^{-1}$  of pyrrole-siloxane in  $\text{CCl}_4$  are thus attributed to the ring stretching vibrations. The spectrum of zeolite X on ZnSe shows an additional band at 1425  $\text{cm}^{-1}$  which is also due to pyrrole stretching. The shifts of the pyrrole stretching vibrations are more pronounced in the spectra of zeolite X on ZnSe than in those of zeolite L. This may be due to electrostatic interactions between the alkali metal cations of zeolite X and the pyrrole  $\pi$ -electron cloud. Such interactions are known to occur by adsorption of "electron rich aromatics" (e.g. benzene and pyrrole) on zeolites [2,3,5]. The assignment of the bands between 1371 and 1297  $\text{cm}^{-1}$  is not straightforward considering the IR data reported in the literature for pyrrole and derivatives.

We have shown that IR transmission spectroscopy is helpful to characterize chemisorption of pyrrole-siloxane by sodium zeolites L and X and we expect that our observation can be extended to other zeolites. The very fast desorption rate of water for the thin zeolite layers on ZnSe is remarkable and may turn out to be very useful in different areas of zeolite chemistry.

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