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Infrared Spectroscopic Study of Ethylene Adsorbed on Silicalite: Experiments and Molecular Dynamics Simulation

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Abstract. The present paper deals with a fundamental infrared (IR) study of the interaction of a gas on a microporous adsorbent at room temperature. Both in situ FTIR spectroscopy and molecular dynamics simulation were carried out to investigate the adsorption process of ethylene on a siliceous ZSM-5 zeolite at 300 K. Orthorhombic aggregates of 18 unit cells of silicalite and molecules of ethylene were simulated using a full atomic model. At a first step, FTIR spectra of the zeolite and the adsorptive were computed separately and compared with experimental spectra. At the second step, spectra of zeolite and ethylene adsorbed were calculated at different loadings and analyzed in shape, location and area, with regard to experimental results. Simulated and experimental data were in good agreement and characterized a continuous adsorption process.

Keywords: adsorption, ethylene, infrared spectroscopy, silicalite, molecular dynamics simulation

Introduction

Adsorption isotherms for microporous adsorbents are usually of type-I. However, stepped isotherms are sometimes obtained, as for the interaction of large enough admolecules on MFI zeolites at high temperature (Guo et al., 1989; Lee and Chiang, 1996; Long et al., 1997). Many experimental and theoretical investigations have been dedicated to the understanding of adsorption process of aromatic compounds on MFI zeolites. It was reported that stepped isotherms might be the signature of adsorption site heterogeneity and/or adsorbate adsorbent phase transitions. To further examine the effects of size, symmetry and polarity of the admolecule on the existence of a step in the isotherms, we have also largely studied the adsorption of ethylenic compounds on a series of MFI zeolites (Bouvier and Weber, 1998; François et al., 2001; Floquet et al., 2003). Tetrachloroethylene and trichloroethylene have been first chosen as adsorptives because these molecules show a diameter very close to the pore opening of the zeolite but differ in symmetry and polarity. Stepped isotherms were observed only for the adsorption of tetrachloroethylene, the nonpolar and symmetric compound. Moreover, along the step in the isotherms, the adsorption of tetrachloroethylene induces a pronounced exothermic effect of around 10 $kJ.mol^{-1}$ and the adsorbed phase is close to a solid state. In return, trichloroethylene adsorption isotherms and the corresponding heat and entropy curves do not indicate any particularities during the accumulation of the polar molecules within microporosity. On the other hand, successive structural changes of the zeolite were characterized during the adsorption of both adsorptives without any adsorbate phase transitions, indicating that the presence of the step in the isotherms cannot be the signature of adsorbent and/or adsorbate phase transitions. Structural data suggested that micropore filling proceeds by sites, the course of the adsorption process depending for a significant part on the symmetry and the size of admolecules. To test the validity of this assumption, additional adsorption experiments were

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further performed using ethylene as a new adsorptive. This molecule as tetrachloroethylene is highly symmetric but displays a much lower molecular size. As anticipated, adsorption isotherms did not show any step in a wide range of temperature.

The present paper is dedicated to a microscopic study of the adsorption process of ethylene on a siliceous ZSM-5 zeolite at 298 K, by means of in situ FTIR spectroscopy and molecular dynamics simulation. FTIR absorption spectra of the zeolite in contact with gaseous ethylene were recorded as a function of micropore filling, at increasing constant pressures. The dependence of vibration bands of the adsorbed phase and the adsorbent on loading is analyzed with regard to simulated data.

Materials and Methods

Adsorbent and Adsorptive

The adsorbent used in this study was a powdered templated-ZSM-5 zeolite (Si/Al = 500) synthesized by Degussa. Before each adsorption experiment, the sample was first calcined under air up to a temperature of 873 K for 24 hours to remove the organic template then outgassed under high vacuum at 673 K for 12 hours. Air Liquide Company supplied ethylene of 99% purity.

FTIR Spectroscopy

Characterization of the Unloaded Adsorbent Before Adsorption Experiments. Both self-supported and KBr diluted sample preparations were used to characterize the vibrational spectra of the starting material. Self-supported sample allowed analyzing weak vibration bands with a high accuracy. Strong lattice vibration bands were better defined if the adsorbent was diluted in KBr because the amount of zeolite analyzed was very small. In both cases, FTIR spectra were collected at room temperature and pressure on a BRUKER Equinox 55 spectrometer over the wavenumber range 4000–400 cm^{-1}. The resolution was 2 cm^{-1} and 50 scans were averaged to improve the signal-to-noise ratio. In the same conditions, the background spectrum was collected without sample.

In Situ Characterization of the Pure Gaseous Adsorptive and Ethylene Adsorbed in Zeolite. Experiments were performed in a home-built glass system, which permits heat treatments and infrared measurements under pure controlled gas pressure. For the spectroscopic characterization of the pure adsorptive, 900 hPa of ethylene were introduced in the cell previously evacuated under high vacuum at room temperature. The spectrum of gaseous ethylene was recorded as for the unloaded zeolite, over the wavenumber range 4000–400 cm^{-1} by coadding 50 scans and ratioed to a background spectrum of the cell under vacuum. Self-supported calcined zeolite pieces were used for studying the interaction of ethylene on the ZSM-5 zeolite. Before adsorption measurements, the sample was first outgassed under high vacuum at 673 K overnight. After cooling at room temperature, the sample was moved down in the optical cell to collect FTIR spectra and then exposed to increasing pressures of ethylene, from 10^{-2} to 10^{3} hPa. The equilibrium amounts of ethylene adsorbed were determined from the corresponding sorption isotherms obtained by gravimetry. Spectra of the zeolite in equilibrium with gaseous ethylene were recorded as a function of loading, in the same conditions as for the starting materials, and ratioed to background spectra of the cell without sample at constant ethylene pressures.

Computational Procedure

Molecular dynamics simulations were performed to improve the interpretation of the experimental results. We simulated at 300 K an aggregate of silicalite loaded with molecules of ethylene in equilibrium with the gas. Then we calculated the infrared spectra of both the zeolite and the adsorbed phase. A flexible atomic model was used to simulate silicalite and ethylene molecules. The number of molecules of ethylene (N^{add}) defined as the sum of both gaseous and adsorbed molecules, was fixed at each simulation. We modeled seven different states corresponding to N^{add} equal to 10, 35, 50, 75, 100, 150 and 200 molecules, respectively. The aggregate of silicalite was composed of 18 unit cells with an orthorhombic Pnma crystallographic structure (van Köningsveld et al., 1987). The crystallographic parameters a, b and c were 2.0022, 1.9899 and 1.3383 nm, respectively, the straight channels were aligned along the [010] direction and the dimensions of the aggregate were 3a, 2b and 3c. The dynamics of all the atoms (silicalite and ethylene) was governed by inter and intramolecular interaction potentials with no electrostatic potential. The potentials and the simulation procedures that we used were detailed elsewhere (Bernardet et al., 2004).

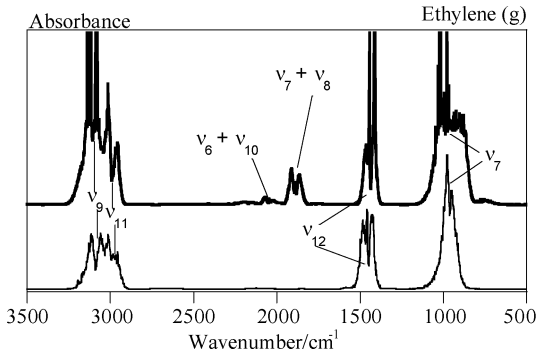

Figure 1. Experimental (top) and simulated (bottom) infrared spectra of ethylene obtained at room temperature at 900 and 1000 hPa, respectively.

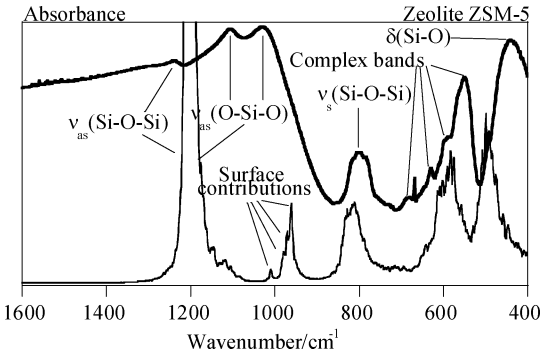

Figure 2. Experimental (top) and simulated (bottom) infrared spectra of the ZSM-5 zeolite, obtained at room temperature and pressure.

Results and Discussion

FTIR Spectra of Pure Gaseous Ethylene

Experimental and simulated spectra of pure ethylene were performed at 298 K under a pressure of 900 and 1000 hPa, respectively. The experimental spectrum shows the four ν_7, ν_9, ν_{11} and ν_{12} fundamental bands located at 948, 3105, 2988 and 1443 cm^{-1}, respectively, and the two $(\nu_6 + \nu_{10})$ and $(\nu_7 + \nu_8)$ combination bands located at 2046 and 1888 cm^{-1}, respectively (Fig. 1). The simulated IR spectra were modeled using the trajectories of atoms therefore, combination bands cannot be calculated. In return, the four fundamental bands were well simulated and were very similar in shape in contrast to those obtained experimentally, but blue shifted by around 30 cm^{-1}. Refining model parameters may reduce this absolute blue shift. However, in this study, we focussed on the relative displacement of vibration bands and we assumed that the blue shift does not change our interpretation.

FTIR Spectra of the Unloaded MFI Zeolite

The vibrational spectrum of ZSM-5 was characterized using both self-supported and KBr diluted techniques. The spectrum of self-supported zeolite exhibited fundamental bands assigned to the ν_sSi—O—Si and δSi—O vibrations located at 800 and 455 cm^{-1}, respectively, harmonic bands located at 2008, 1883, 1696 cm^{-1}, and complex bands located at 689, 626, 588 and 549 cm^{-1} (Fig. 2). The region of detector saturation from 1300 to 1000 cm^{-1} was observed by using KBr-diluted sample instead of self-supported zeolite. The corresponding spectrum shows an additional broad band within this wavenumber range. This band consists of a single peak located at 1239 cm^{-1} and a doublet located at 1107 and 1029 cm^{-1}. The singlet was assigned to the ν_{as}Si—O—Si vibration and the doublet to ν_{as}O—Si—O vibrations (Fig. 2). The change from a doublet to a single band may be correlated to a size effect of crystallites. Indeed, previous spectroscopic studies performed on a series of MFI zeolites of different crystallite sizes indicated that the doublet becomes always a singlet if the mean diameter of the crystallites is below around 1 μm (Bouvier, 1998). Such a result is corroborated too, by another published study by Zecchina et al. (1992).

The simulated spectrum in comparison with experimental data shows a blue shift of simulated vibration bands, except for the ν_{as}Si—O—Si vibration. This blue shift is ranging from 15 cm^{-1} for the ν_sSi—O—Si vibration to 96 cm^{-1} for the ν_{as}Si—O—Si vibration. Moreover, a single peak located at around 1203 $cm^{-1}$was simulated for the ν_{as}Si—O—Si and ν_{as}O—Si—O vibrations.

On the other hand, simulation allowed characterizing surface contributions by the presence of four additional bands located at 1009, 978, 972 and 960 cm^{-1} attributed to Si—O vibrations. The first one was assigned to surface vibration and the three others to aggregate edge vibrations. These four weak vibration bands cannot be observed experimentally because the ν_{as}O—Si—O vibration band is broad and strong. An improvement of the zeolite force field and a smaller time step would minimize discrepancy between simulated and experimental data. However, in this study, we focussed on the qualitative spectrum differences between the unloaded zeolite and the zeolite loaded with an amount of ethylene adsorbed. We assumed that the evolution was qualitatively not disturbed by the shifts.

FTIR Spectra of Ethylene Adsorbed on the Zeolite

Experimental study was performed using self-supported zeolite. Detector (DTGS) saturation was observed in the range 1300–1000 cm^{-1} and for the bands located at 800, 549 and 450 cm^{-1}. All experimental and simulated vibration bands were analyzed in shape, location and area. For sake of clearness, we successively investigated absorption bands of ethylene adsorbed, framework zeolite and additional bands, which appear during the adsorption process. Here, we compared the most significant experimental results with simulation.

Evolution of Ethylene Vibration Bands. Except for the weak ($\nu_6 + \nu_{10}$) combination band, which is superimposed to a zeolite contribution, all other experimental vibration bands of ethylene adsorbed were analyzed as a function of loading. The ν_7, ν_9, ν_{11} and ($\nu_7 + \nu_8$) vibration bands qualitatively underwent the same modifications during the adsorption process. These bands appeared as soon as the first amount of ethylene of 0.25 molec.uc^{-1} is adsorbed within statistical uncertainty at the same position as for the gaseous phase. They continuously increased in area on increasing loading without significant change of location. The evolution of the same simulated vibration bands showed the same trend, indicating that these vibration modes are not significantly affected during the adsorption process. In contrast, the experimental dependence on loading of the CH_2 scissoring vibration mode of ethylene (ν_{12}) was different from that of the CH_2 stretching (ν_{11}) and wagging vibration (ν_7) modes (Fig. 3). At the lowest loading (0.25 molec.uc^{-1}) the position of this band was that of the pure gaseous phase, i.e. at 1443 cm^{-1}. Up to a loading of around 3 molec.uc^{-1}, the band was continuously shifted down to 1438 cm^{-1}. The accumulation of additional molecules did not induce any further location change. However, it should be pointed out that an additional band located at 1441 cm^{-1} was observed for loadings higher than around 6 molec.uc^{-1}. We assumed this new band to be the result of a splitting of the ν_{12} vibration band. Simulations evidenced such behavior too (Fig. 3(b)). Moreover, the simulated molecules were uniformly distributed inside the pores whatever the loading was. Hence, the ν_{12} splitting cannot be attributed to a structural effect of the zeolite but to a cooperative effect of ethylene adsorbed molecules. On the other hand, the experimental and simulated area of the band linearly increased with loading

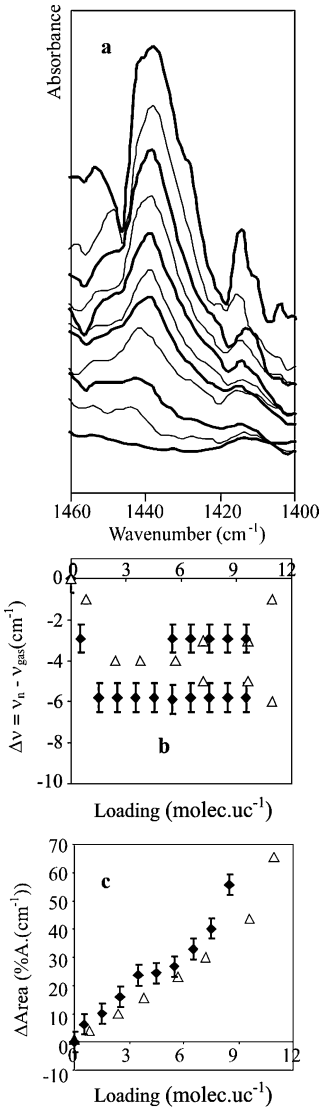

Figure 3. Dependence of shape (a), location (b) and area (c) of the ν_{12} vibration band of ethylene adsorbed on ZSM-5 zeolite on loading: (from bottom to top) (a) 0, 0.25, 1, 2, 3, 4, 5, 6, 7, 8 and 9 molec.uc^{-1} (•: experiments, △: simulation).

(Fig. 3(c)). The absorption intensity per molecule adsorbed was then identical whatever was the micropore loading.

Evolution of Zeolite Framework Vibration Bands. All well-defined experimental zeolite vibration bands were analyzed in shape, intensity and location, as a function of loading. The zeolite vibration bands located at 2008, 1883 and 588 cm^{-1} for the unloaded zeolite does not significantly change in location

during the adsorption process. The adsorption of ethylene molecules only induces a constant decrease of the area of these vibration bands over the entire domain of micropore filling. On the other hand, the weak complex vibration bands located at 689 and 626 cm^{-1} change in both intensity and location. The band at 689 cm^{-1} is continuously shifted to lower wavenumbers as the amount of ethylene adsorbed is increased. The presence of molecules slightly exacerbates the intensity of the vibration and the variation is constant whatever the loading is. This behavior is surprising because the presence of molecules should rather hinder than exacerbate the vibration. In counter part, the band located at 626 cm^{-1} undergoes a red shift of around 2 cm^{-1} (Figs. 4(a) and (b)) and a small and constant decrease in intensity with loading (Fig. 4(c)). The IR simulated spectrum of the zeolite did not change in location and area during micropore filling. These results indicate that the molecules adsorbed in micropores hardly changed vibration modes of the zeolite framework. The most significant effects concerned the variation of the location of the complex bands located at 626 and 689 cm^{-1}. In addition, the intensity of vibration bands except that located at 689 cm^{-1}, was either unchanged or slightly decreased on loading. Therefore, it can be suggested that the ethylene molecules, which are of smaller size than the pore opening of the zeolite does not strongly interact with the zeolite and that the adsorption process is homogeneous.

Appearance of New Bands. The absorption spectrum of ethylene adsorbed on the ZSM-5 zeolite shows at least an additional band, which cannot be assigned to vibration modes of either ethylene or zeolite. This band that is located at around 1715 cm^{-1} (Fig. 5), was recently observed by Ikegami et al. (2002) for the adsorption of succinic acid on silicalite and assigned to a carbonyl stretching vibration of the adsorbate. With regard to the present work, this assignment is questionable even more because we evidenced too the existence of this band at around 1715 cm^{-1} for the adsorption of tetrachloroethylene, trichloroethylene, *p*-xylene or dichloromethane on the same zeolite. Therefore, the appearance of this band, which seems to be independent of the nature of the adsorptive, may be the consequence of adsorbent/adsorbate interactions. Owing to the fact that the microporous surface of the sample is far higher than the external surface, this band can be regarded as representative of the interaction of the microporous surface of the zeolite with the adsorbed phase. For ethylene adsorption, this band appears at 1715 cm^{-1} as soon as the first amount of ethylene is adsorbed, then continuously increases in area without any significant change of location during the progressive accumulation of molecules up to micropore saturation. This band which does not account for fundamental vibration modes cannot be simulated by molecular dynamics.

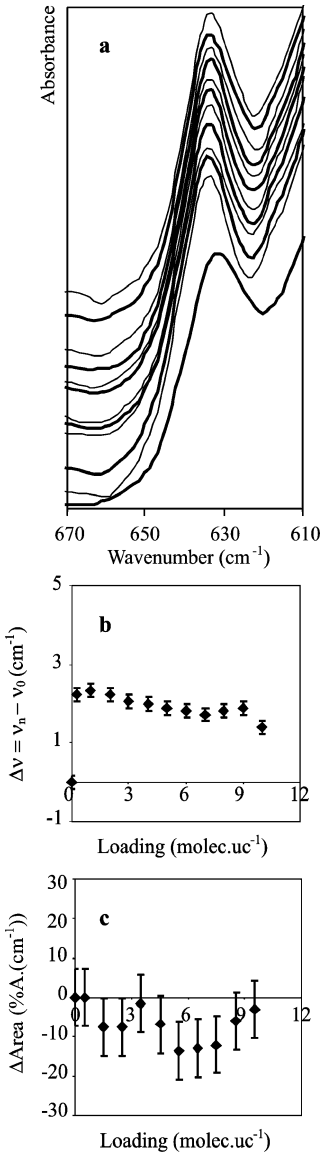

Figure 4. Dependence of shape (a), location (b) and area (c) of the complex band of the zeolite initially located at 628 cm^{-1} on loading: (from bottom to top) (a) 0, 0.25, 1, 2, 3, 4, 5, 6, 7, 8, 9, 10 molec.uc^{-1} (•: experiments).

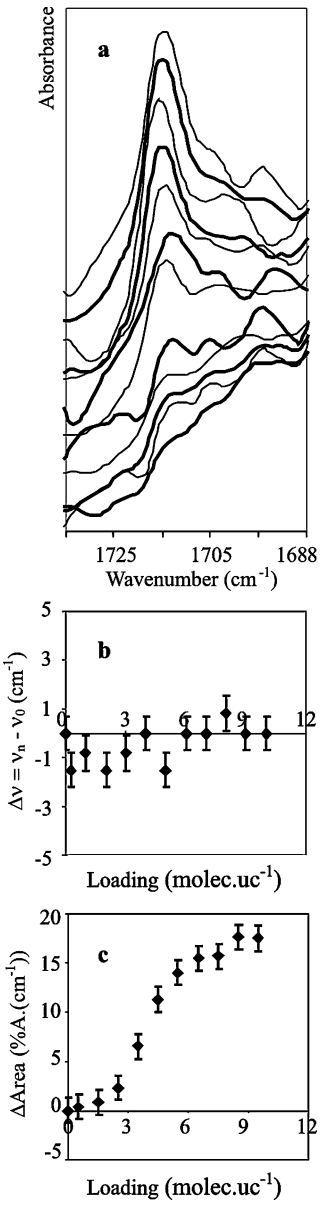

Figure 5. Dependence of shape (a), location (b) and area (c) of the new band located at around 1715 cm^{-1} on loading: (from bottom to top) (a) 0, 0.25, 1, 2, 3, 4, 5, 6, 7, 8, 9 molec.uc^{-1} (•: experiments).

Conclusion

This spectroscopic study contributes to the knowledge of the evolution of the systems zeolite/gas under equilibrium conditions, more specifically for the interaction of ethylene on a ZSM-5 zeolite. The originality of the paper resides in considering an experimental approach combined with molecular dynamics simulation. Another singular part of the present study is the analysis of the evolution of the framework vibration bands of the adsorbent and that of ethylene adsorbed, during the physisorption process. The starting materials, i.e. the pure gaseous adsorptive and the unloaded ZSM-5 zeolite, were first spectroscopically characterized. For ethylene, the experimental and simulated spectra were in good agreement, except for a constant wavenumber shift of all fundamental vibration bands. For the unloaded zeolite, the experimental and simulated vibration bands were of the same shape with shifts depending on the specific bands over the wavenumber range 900–400 cm^{-1}. The two ν_{as}Si─O─Si, ν_{as}O─Si─O asymmetric stretching vibration bands located in the range 1600–900 cm^{-1}, emerged at distinct positions in the experimental spectrum and as a strong vibration band in the simulated spectrum. Molecular dynamics simulation exhibited additional vibration bands assigned to external surface contributions. Thereafter, the evolution of well-defined vibration bands of both ethylene adsorbed and zeolite were investigated as a function of loading. Concerning ethylene, simulated data agreed well with experimental results, in particular they showed a split of the ν_{12} vibration band above 6 molec.uc^{-1}. The analysis of the simulations clearly indicated that ethylene molecules are uniformly distributed within micropores and we attributed the splitting behavior to a cooperative effect of adsorbed molecules. For the zeolite, the vibration bands are weakly modified by the presence of admolecules in micropores. All these results suggested a continuous adsorption process. Moreover, an additional vibration band located at around 1715 cm^{-1} appeared on loading in the experimental spectra that we attributed to surface vibration modes of the zeolite. This last issue will be analyzed in a forthcoming article.

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