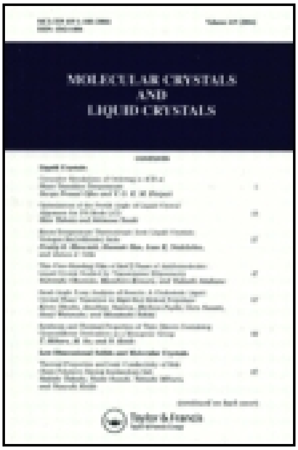

Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Confining Effects in Composites Containing Molecular Sieves

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Version of record first published: 18 Oct 2010

To cite this article: Ligia Frunza, Stefan Frunza, Irina Enache, Traian Beica, Andreas Schönhals, Hendrik Kosslick, Ursula Bentrup & Irene Pitsch (2004): Confining Effects in Composites Containing Molecular Sieves, Molecular Crystals and Liquid Crystals, 418:1, 69-85

To link to this article: http://dx.doi.org/10.1080/15421400490479145

Mol. Cryst. Liq. Cryst., Vol. 418, pp. 69/[797]–85/[813], 2004
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ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400490479145

CONFINING EFFECTS IN COMPOSITES CONTAINING MOLECULAR SIEVES

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Confinement of 4n-octyl-4′-cyanobiphenyl to nanoporous molecular sieves with hexagonal structure of cylindrical pores or with cellular structure is studied. It was found by differential scanning calorimetry and broadband dielectric spectroscopy that composites with the pores completely filled with liquid crystal show phase transitions characteristic for bulk, while the partially filled samples do not show these transitions. Thermogravimetric, differential thermal analysis and in situ infrared spectroscopic investigations have indicated first time that the dealkylation and oxidation of the confined liquid crystal is quite possible inside the nanopores of these molecular sieves, at temperatures much lower than for the bulk.

Keywords: confinement of liquid crystals; cyanobiphenyls; dielectric spectroscopy; infrared spectra; liquid crystals; nanoporous molecular sieves; thermal analysis

The financial support from Deutsche Forschungsgemeinschaft (Project Ko 1639/2-3) and Romanian Ministry of Education and Research (Project Ceres 59) is gratefully acknowledged.

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INTRODUCTION

Confinement studies have received in the last decade considerable attention from theoretical and experimental points of view. Confining condensed matter to restricted geometry significantly affects physical properties. Size restriction, surface effects, polydispersity, connectivity and confining topology are all simultaneously acting grounds of these changes. In certain cases the spatial constraints and sorption effects modify the chemical properties of the confined matter and these changes might have catalytic applications.

Liquid crystals (LC) were confined to restricted geometries in different porous media such as silica gel, Vycor, controlled porous glass, membranes, polymer networks (e.g., [1]). Different experimental techniques such as light scattering, high precision calorimetry, small angle X-ray scattering, X-ray diffraction, (deuterium) NMR, time-resolved optical Kerr effect, dielectric spectroscopy, optical spectroscopy and even ESR were applied in order to put in evidence characteristic properties: shift of the bulk transition temperatures, especially nematic-to-isotropic transition, gradual evolution of a nematic order instead of first order transition, appearance of surface induced para-nematic order in the isotropic state [2].

Recently, molecular sieves were also used for confinement of cyanobiphenyl LCs [3–8]. It was expected that confinement leads to higher stability of the LC molecules, to changes of their thermal behavior and to new properties as compared to the bulk. A bulk-like dynamical behavior was related to LC molecules located in the intergranular spaces or in the center of the pores, whereas the molecules located in the surface layer inside the pores have a much slower dynamics [4a,6]. IR spectra indicated several types of host-guest interactions as expected when the structure of the composite components is taken into consideration [3,4b,5,8]. It was found that hydrogen bonding by nitrile nitrogen is the main anchoring to the surface of molecular sieves, but also a bonding by π aromatic electrons might exist. Nitrogen coordination to Lewis sites is less possible inside pores/cavities due to sterical hindrance [8b].

In this contribution we focus on composites containing 4n-octyl-4′-cyanobiphenyl (8CB) confined to nanoporous molecular sieves with cylindrical pores or foam-like structure. The study was performed in order to identify the nature of the guest species and to monitor the changes observed during the composite heating up to 600 K. Information given by the thermal analysis and by infrared spectroscopy, especially *in situ* investigations, are correlated with molecular dynamics obtained by dielectric spectroscopy. It was found that dealkylation along with oxidation of confined 8CB take place at temperatures much lower than for bulk LC: the bond nature of

CB molecules interacting with the matrix surface is changed by increasing the temperature. A catalytic activity of the molecular sieves towards LC molecules was therefore supposed.

EXPERIMENTAL

8CB from Aldrich was used for confinement, without further purification. It undergoes three phase transitions C-S_A, S_A-N and N-I, in an experimentally convenient temperature interval at 294.1, 306.7 and 313.8 K respectively. C stands for the crystalline state, S_A for smectic A, N for nematic and I for the isotropic state. The characteristic length of this molecule is only 3–4 times smaller than the pore size (*vide infra*).

Nanoporous molecular sieves with large pores and different structures were chosen for confinement: A1SBA-15 with hexagonal (H) structure of cylindrical pores and cellular SiSBA-F with foam-like (F) structure of the pores. These molecular sieves were prepared [9] using known procedures [10,11] and have been fully characterized by X-ray diffraction, electron microscopy, nitrogen adsorption, thermal analysis measurements. Main characteristics of these materials are given in Table 1.

Finely grounded confining material was evacuated at 573 K to remove water and other volatile impurities. In order to be loaded with LC, it was then contacted either with LC in excess, at a temperature higher than N-I transition [4a] (method I) or with a LC solution in an easily removable solvent [12,13] (method S). LC excess was removed by vacuum pumping. Loaded samples were labeled 8CB/matrix. Until measuring, the samples were kept in a dessicator.

8CB content of the composites was determined by thermogravimetric (TG) measurements, since the mass of the molecular sieves changes insignificantly till 1100 K (by dehydrating), whereas 8CB is completely oxidized and removed from the system. TG measurements were carried out simul-

TABLE 1 Composition, Structure and Texture Characteristics of Confining Molecular Sieves

Sample	Oxide composition	Structure	S_{BET} (m^2/g)	Pore volume (cm^3/g)	Average pore diameter (nm)	Maximum LC loading %*
A1SBA-15	A1, Si	SBA-15	602	0.9	8.4	90
SiSBA-F	Si	cellular	546	1.9	17.2	190

*Maximum 8CB amount hosted in the dry molecular sieve, supposing a complete pore filling (density of confined 8CB is considered *ca.* 1 g/cm^3).

taneously with differential thermal analysis (DTA) ones using a Setaram TG-DTA 92 apparatus under dry air, flowing at a constant rate of 10 K/min [14]. In addition, these measurements allowed estimating the host-guest interactions between the LC molecules and the surface of confining matrix.

Phase transition behavior of the composites was studied with a conventional differential scanning calorimeter (DSC) from Perkin Elmer (DSC 7), at a scanning rate of 5 K/min [3]. Two-to-four runs of heating-cooling cycles were applied for each sample.

In order to quickly examine the interactions of the molecular sieve surface with 8CB molecules, FTIR spectra were recorded at room temperature, using a Mattson Galaxy 5020 spectrometer equipped with microscope (on undiluted samples). *In situ* FTIR spectra were collected (on pressed self-supported pellets) with a Bruker IFS 66 spectrometer, in a cell allowing heating and connected to a standard vacuum/adsorption rption installation [15]. The treatment/collecting conditions were as much as possibly close to those of TG-DTA measurements. All the IR spectra were analyzed using a fitting procedure based on the least square method. In order to facilitate the spectra comparison, the peaks of confined 8CB were normalized to the corresponding 8CB amount by using the peak at 1495 cm^{-1} of the stretching of aromatic ring CH bonds.

Measuring of the frequency dependent dielectric function (the complex dielectric permittivity) in the frequency range of 10^{-2}–10^{-9} Hz was previously described [4a]. To analyze the data in detail, especially to extract the relaxation rate f_p at maximal loss for the different relaxation regions as well as in the case if they overlap the model function of Havriliak and Negami (HN) were used to fit the isothermal data. The conductivity contribution to the dielectric loss was described as usually by an additional term σ/f^k.

RESULTS AND DISCUSSION

Molecular orientational dynamics of 8CB confined to nanoporous molecular sieves, in a large temperature interval (220–370 K) has been previously studied in detail by broadband dielectric spectroscopy; that is why here we present only the main results. Thus, in molecular sieves with pores larger than 2 nm, the dynamics of the LC molecules depends on the filling degree of the process [16]. Completely filled samples show two relaxation processes: A bulk-like relaxation process is related to liquid crystal molecules located in the center of the pores, which hardly feel the effect of the pore walls. The second relaxation process is assigned to molecules located in a surface layer. It has a much lower relaxation rate than the bulk-like process. Partially filled samples show only one relaxation process, due to the surface layer.

Relaxation of the molecules in the surface layer is a non-Debye process, much slower as the bulk LC one; it has a temperature dependence governed by Vogel-Fulcher-Tammeann law, which is characteristic for a glass forming liquid [4a]. This behavior is in agreement with that observed for related composites containing cyanobiphenyls in controlled porous glass, Vycor glass or different membrane systems [1,17–22] and also found for composites containing molecular sieves with pores of/less than 2 nm [4a].

Moreover, the behavior of the surface layer depends on the filling degree. At lower temperatures, the dynamics of surface layer is faster for samples partially filled than for those completely filled. The surface layer of completely filled silica cellular samples has the slowest relaxation [16]. Thus, at a given temperature, the relaxation rate of the relaxation process of partially filled samples has values situated between the characteristic frequencies of the relaxation processes observed for the completely filled pores. This behavior might give a measure of the extension of the wall influence on the neighboring LC molecules.

There are also differences observed for the dynamics of 8CB molecules confined to the two types of nanoporous materials that might be related to liquid crystal-surface interactions.

DSC Measurements

Figure 1 shows DSC thermograms of the highest loaded composite systems in comparison with the bulk LC. Several peaks can be seen at temperatures in the neighborhood of those characteristic for bulk 8CB. At variance, the composites containing 8CB confined to pores narrower that the present ones do not show any phase transition [4a]. The temperature of the phase transitions corresponding to the confined 8CB is shifted downward, meaning that the confinement introduces disorder in the LC structure. The shift depends on the transition type. The biggest shift is shown by the C-S_A phase transition, while the shift for the N-I transition is too small, to be unambiguously observed by this conventional technique. Crystallization C-S_A peak of the confined LC is broader and more asymmetric than that of the bulk.

The most important information comes by comparing the height of the peaks in the DSC thermograms, it appears that most of the confined 8CB does not show any phase transitions. This part of confined LC is spread in the surface layer, covering inner surface of the pores. The other part, much smaller than the former, giving phase transitions in Figure 1 is probably located in the center of the pores.

Depression of the phase temperature was predicted by the classical theories of solidification in a capillary and was also observed for different organic substances confined to pores [23,25], for which the temperature shift

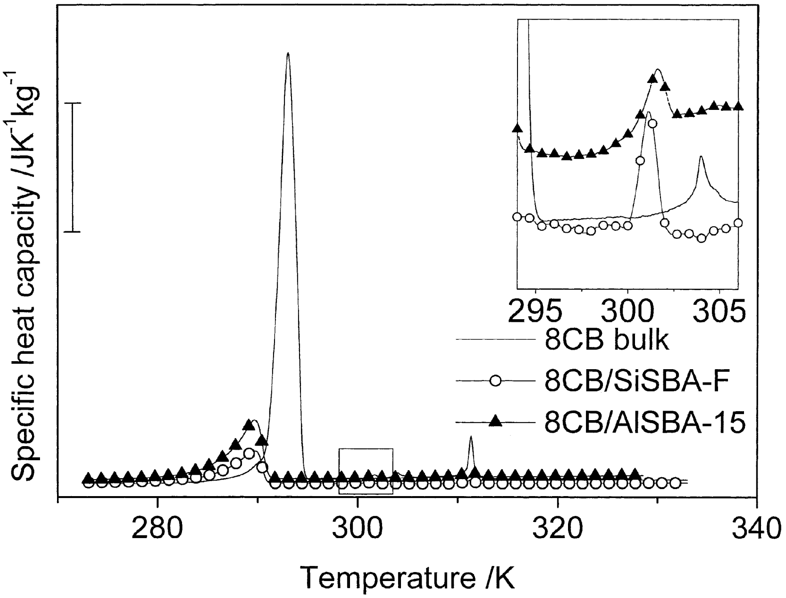


FIGURE 1 DSC thermograms of the composites and bulk 8CB. Specific heat capacity is given per mass of 8CB. The inset enlarges the temperature region corresponding to the S_A-N phase transformation.

depends on the inverse of the pore diameter. However, in our case, a direct correlation between the depression of the crystallization temperature and the reciprocal diameter of the pores cannot be established. One might only suppose that the structure of the confined phase for material with larger distribution of pores (SBA-F) is more disorganized [25] than for AlSBA-15.

We cannot make distinction between an axial and a radial configuration [26] of confined 8CB by these DSC measurements. However, due to highly restrictive geometry, one can suppose that the axial configuration is favored.

Using conventional DSC we failed to put in evidence phase transitions characteristic for bulk 8CB for partially filled samples and to make difference for pore size, shape and interconnectivity of the used nonporous materials. Further high precision calorimetric studies should be necessary in this respect.

Thermogravimetric Measurements

Thermogravimetric measurements allowed estimating the 8CB loading. Table 2 gives the obtained values for the samples prepared by both

TABLE 2 Loading of the Composites with 8CB

Sample	Confining method	Weight loss %	Filling degree
8CB/A1SBA-15	I	28	0.43
8CB/A1SBA-15	S	38.4	0.69
8CB/SiSBA-F	I	22	0.15
8CB/SiSBA-F	S	65	0.98

methods, I or S. It seems that the method I leads to lower filling degree than method S, unless a prolonged evacuation of the LC excess takes place even in this latter case. From the determined amount 8CB, the filing degree was estimated by reporting the found loading to the maximum possible loading.

DTA plots of the composites containing the highest 8CB amount are reproduced in Figure 2(A). DTA curves indicate several endothermal and exothermal processes taking place. The latter are due to oxidation/decomposition of the organic guest molecules (a more precise assignment of these processes was beyond the aim of this work). There are cleat

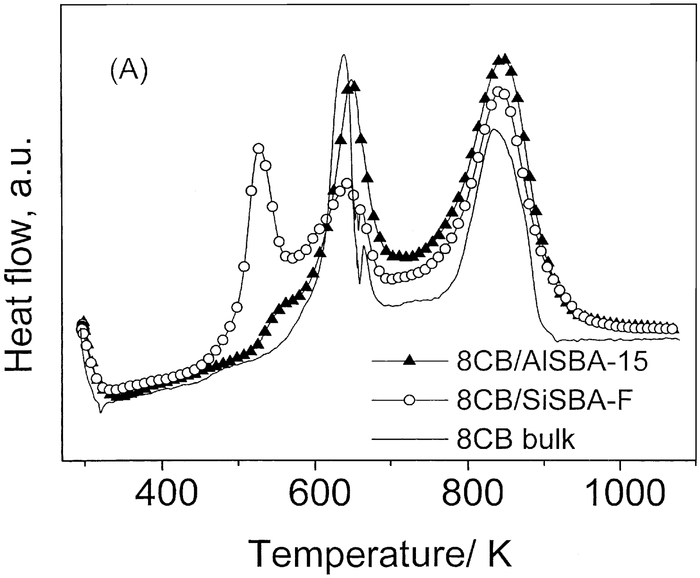


FIGURE 2 Thermal analysis curves of the composites resulting from: A) DTA and B) TG measurements (as derivative of TG curves). The symbols shown in A part are valid for B part too.

differences between the two types of composites and also when comparing with bulk 8CB.

Derivatives of the TG curves are represented in Figure 2(B). DTG peaks are asymmetric showing that there are several species contributing to the mass loss. One can notice that DTA curve do not have the same shape as the corresponding DTG curve, a new exothermal peak appears around 500 K on DTA plot of 8CB/SiSBA-f composites, most probably due to a thermal process involving species of the 8CB molecules bonded to the surface. At the same time, the DTG curve shows only a shoulder on the main peak at 640 K. The exothermal process around 500 K is only sketched for the other conposite sample. This behavior may indicate that different chemical transformations of confined 8CB take place inside the pores of the two molecular sieves. Consequently, a careful spectroscopic investigation was performed, under conditions as much as possible similar to those in TG-DTA apparatus.

FTIR Spectra of the Composite Systems

IR spectra of the composites are complex and contain peaks due to both components, which were assigned according to the rather rich literature. For the sake of brevity, since these spectra are similar with those of closely

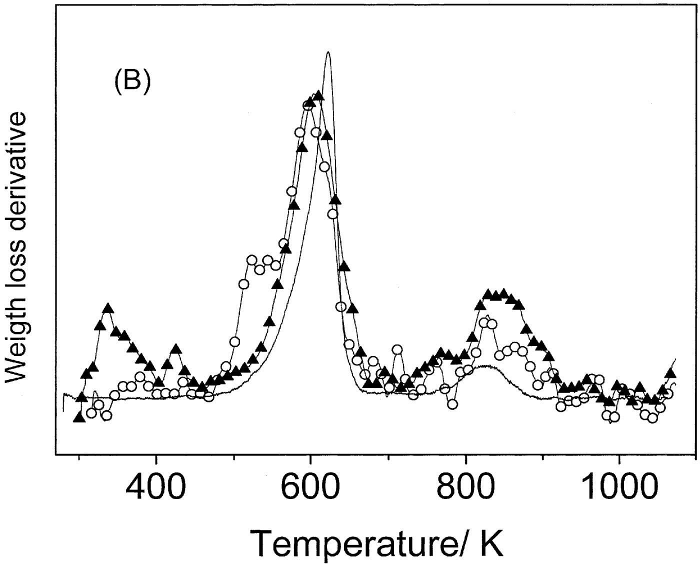


FIGURE 2 Continued.

related composites [8a], they are not illustrated here. Instead some general comments are given which are necessary to understand the spectra evolution with the temperature under *in situ* measurements.

In the region of matrix transparency, some bands were clearly identified as belonging to 8CB, such as: at frequencies 3026-3073 cm^{-1}, $C_{arom}H$ stretch; between 2956 and 2857 cm^{-1}, CH_3 and CH_2 asymmetrical and symmetrical stretch; at 2226 cm^{-1}, CN stretch; at 1606 and 1494 cm^{-1}, C_{arom}-C_{arom} stretch; at 1460, 1397 cm^{-1}, alkyl deformation and also at 1285 cm^{-1}, CC biphenyl bridge stretch. Assignment of the observed LC bands resulted from the extensive literature on bulk 8CB, related nitrile compounds and on nitrile interaction with different adsorption sites as well [3,4b,5,7b,8, 27–37]. However, none of these vibrations, except probably CN vibration can be truly described as a vibration of a localized group, since all the vibration modes are combined modes of motion. A number of intra- and inter-molecular coupling may be present, including Fermi resonance, combination bands, and phonons. Moreover, the spectral features of pure 8CB normally depends on the temperature (phase) and this might be also the case for bulk-like 8CB, still present in some samples.

Nitrile stretching region gives information on the LC species that are present in the composites. By studying a nitrile containing LC in contact wit silica surface, Zhou *et al.* [35] found three species: species in "LC" state, species in randomized state and hydrogen bonded species, leading to absorptions at 2226, *ca.* 2230 and 2241 cm^{-1} respectively. The spectra obtained for 8CB confined to nanoporous molecular sieves show large absorptions between 2220 and 2250 cm^{-1}, that can be decomposed in Gaussian bands centered at 2225, 2235 and 2241 cm^{-1}. For these bands, Zhou's assignment might be also suitable, taking into account the similitude of the adsorbed LC group and of the nature of adsorption surface in both cases. Moreover, since our composites still contain some bulk-like LC matter, and since the position is similar to the bulk 8CB, the peak at 2225 cm^{-1} might be assigned to this bulk-like 8CB. It has the half width larger than the bulk 8CB. The peaks appearing at higher frequencies show in interaction of nitrile group with surface OH groups, more or less hindered.

In order to monitor the changes observed during the heating up and to characterize the structure of surface 8CB layers, spectra of the composites were collected *in situ*. Typical IR spectra in three relevant spectral windows are shown in Figure 3, as three double sets (A, B, C and A′, B′, C′) of curves for the samples 8CB/SiSBA-F and 8CB/A1SBA-15 respectively, having the highest loading. There are spectral differences between the two samples, concerning the peak position, shape and intensity reflecting changes in the contributions of individual molecular species to the overall spectrum. These species arise from different microenvironments. Confinement restricts the motions leading to a slight increase of the force

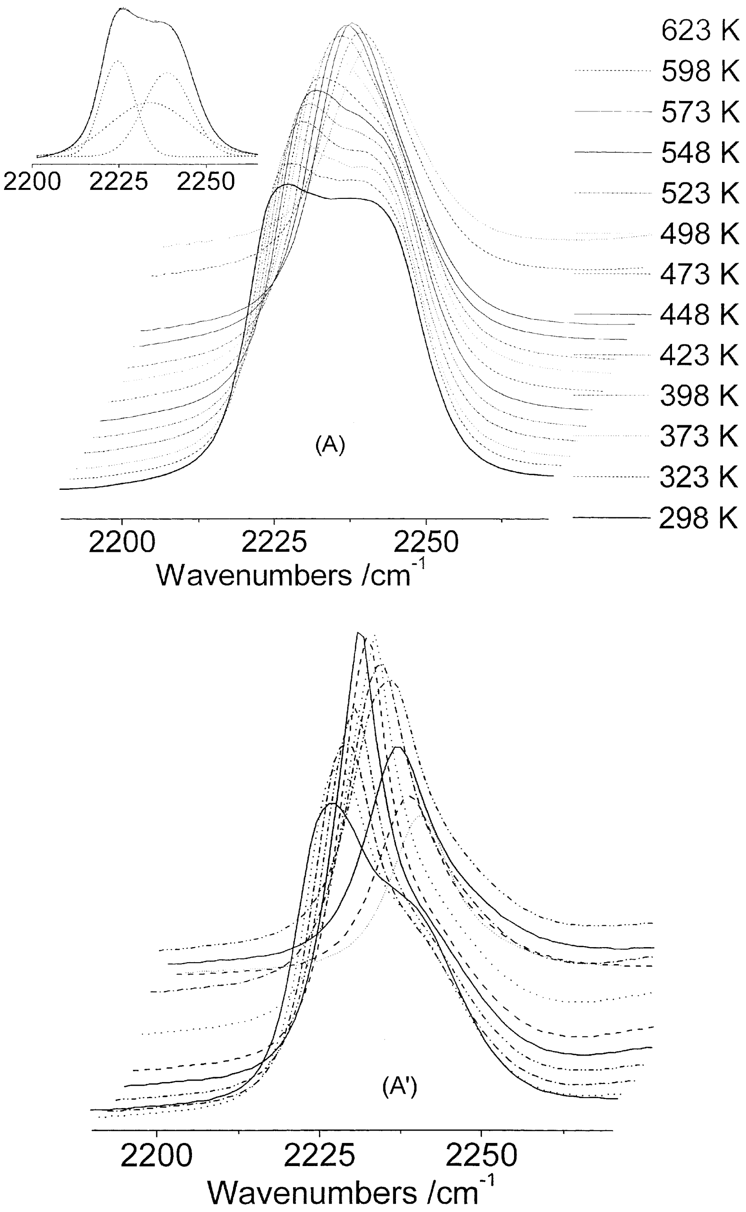


FIGURE 3 *In situ* IR spectra of molecular sieves loaded with 8CB at chosen temperatures in selected regions. The curve sets belong to A), B), and C) 8CB/SiSBA-F sample; A′), B′), and C′) 8CB/AlSBA-15 sample. The inset represents the Gaussian components of the absorption band in the nitrile stretching region.

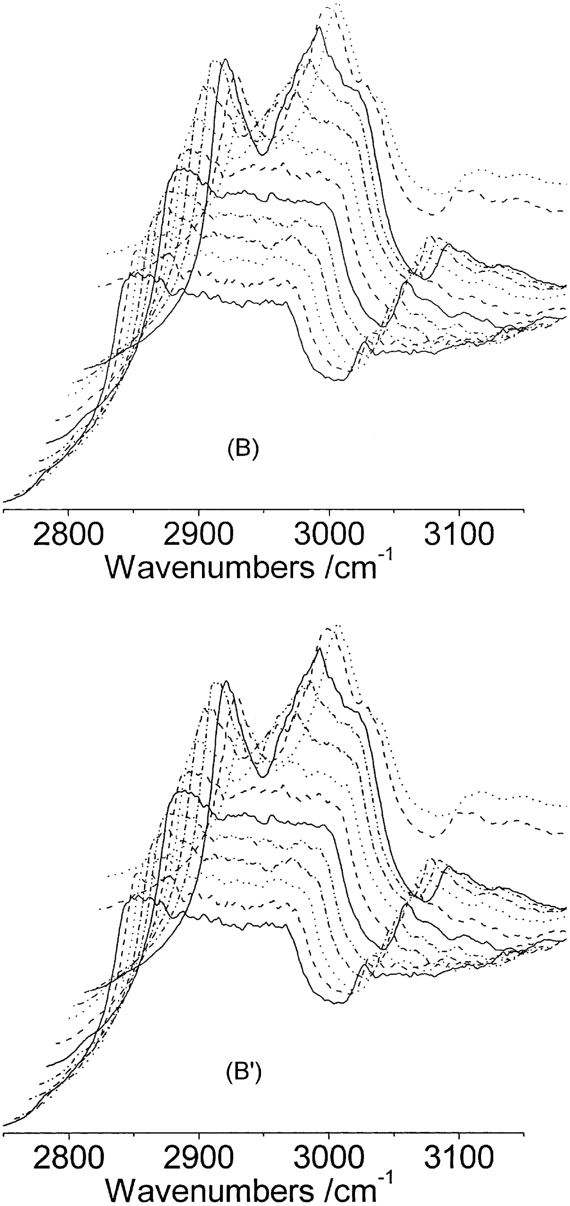


FIGURE 3 Continued.

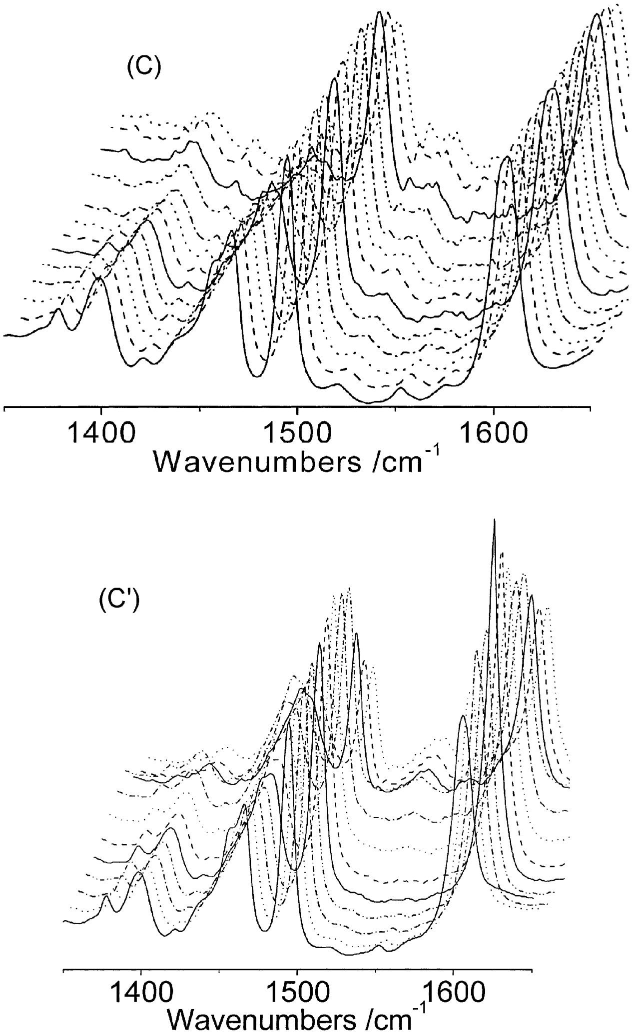


FIGURE 3 Continued.

constants and consequently, and upward shift of the frequencies in comparison with free state.

Peaks due to CH stretching vibrations of CH_2 and CH_3 groups and aromatic rings (region 2750-3200 cm^{-1}) are illustrated in Figure 3B and 3B′. Initially (at lower temperatures) they are not structured. This indicates a strong interaction of alkyl groups, especially of their ends, with pore walls. Structure starts to develop at temperatures higher than 523 K, in one case and at 573 K in the other case of confined 8CB, along with partial desorption and decomposition of the confined material. Peak shapes at temperatures higher than 523 K are similar to those in bulk 8CB. At variance from the sample 8CB/SiSBA-F, on 8CB/A1SBA-15 many species rich in methylene groups, absorbing at 2927 cm^{-1} are formed.

A certain structure of the peaks assigned to CH stretching of the aromatic rings is kept till high temperature, but then the peaks are splitted.

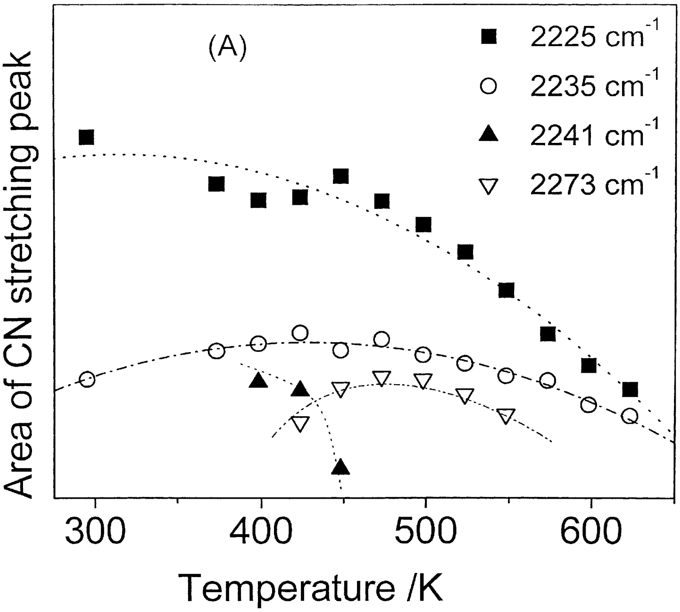
Peaks due to deformations vibrations of CH_2 and CH_3 groups decrease in intensity rather quickly with increasing temperature, faster than those due to the vibrations of aromatic part. This obviously indicates a dealkylation process of 8CB molecules (Figure 3, curve sets C and C′). Peaks assigned to stretching of CC_{arom} decrease in intensity due to disappearance of these rings from the system by gradual decomposition/desorption. Peak at 1495 cm^{-1} decreases faster than that at 1605 cm^{-1}, showing that a rather deep chemical transformation takes place. Since bulk 8CB is quite thermally stable, the behavior of these fragments also indicates a catalytic action of the molecular sieve on 8CB. A red shift of a few cm^{-1} in the peak positions can be also observed by increasing the temperature.

By their features, these IR spectra show clearly that a part of 8CB molecules are located inside the pores. As expected, aromatic rings are thermally more stable than alkyl part of 8CB molecules.

These *in situ* studies allow concluding that the exothermal peak at 500 K in the DTA curve must be related to desorption of released hydrogen bonded species.

The complex profile of the nitrile band was resolved into multiple Gaussian components via a curve-fitting procedure using no preset values for the frequency width and amplitude (inset of Figure 3A). Band shape analysis has shown that initially there are 3 or 4 peaks assigned as follows: 2224.7 cm^{-1} to bulk-like 8CB; 2235 cm^{-1} to "randomized" 8CB (sterically hindered to form H bonds); 2241 cm^{-1} to hydrogen bonded 8CB. Peak half-band widths are larger than for bulk 8CB. Peak position shifts downward by increasing temperature, while their intensity generally decreases.

The variation of the intensity components with the temperature is illustrated in Figure 4A and 4A′, for the samples 8CB/AISBA-15 and 8CB/SiSBA-F respectively. Hydrogen bonded species disappear around 500 K. At higher temperature, a peak at 2273 cm^{-1} due to coordination of CN groups to A1 sites might be supposed [3]. The number of bulk-like species decreases as expected with increasing temperature on AlSBA-15 but firstly increases and then further decreases on SiSBA-F. This behavior might indicate that initially other species are released and transformed into bulk-like ones. The same temperature-activated behavior seems to have the intermediate species absorbing at 2235 cm^{-1} like those assigned to species coordinated to Al ions, onto AlSBA-15. However, the changes of the nitrile



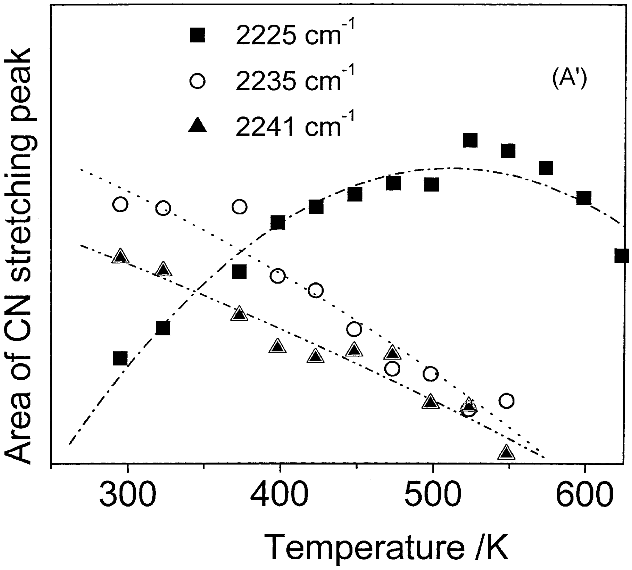


FIGURE 4 Temperature variation of the components of the main nitrile peaks for A) 8CB/AlSBA-15 sample; A′) 8CB/SiSBA-F sample.

part of confined species have to be considered along with the chemical transformations of the rest of the molecules, especially for the species with thermally activated behavior.

A catalytic action of molecular sieves on cyanobiphenyls must be also involved in the formation of some species reported at temperatures higher than 443 K on MCM-41 molecular sieves [5c].

CONCLUSIONS

Molecular dynamics of 8CB confined to nanoporous molecular sieves depends on the on the filling degree of the pores. A bulk-like relaxation process was related to liquid crystal molecules located in the center of the pores, which hardly feel the effect of the pore walls, while the molecules in the surface layer have a much lower relaxation rate.

Relaxation of the molecules in the surface layer is a non-Debye process; it has a temperature dependence governed by Vogel–Fulcher–Tamman law. Moreover, its behavior depends also on the filling degree, giving a measures of the extension of the wall influence on the neighboring LC molecules.

Most of the confined 8CB does not show any phase transitions, as resulted from DSC investigations. This part of confined LC is spread in the surface layer, covering inner surface of the pores. Another part, much smaller than the former, gives phase transitions at temperatures shifted downward as compared with the bulk ones, the biggest difference being for crystallization process. This part of 8CB is thought to be located in the center of the pores. Depression of the phase temperature might only express that the structure of the confined phase for material with larger distribution of pores (SBA-F) is more disorganized than for AlSBA-15.

Liquid crystal-surface interactions are shown by FTIR investigations. Characteristic features indicate that the LC molecules are in a tight contact with the surface of confining matrix, inside the pores. Thus, band shape analysis show that most of the 8CB molecules form hydrogen bonds between their CN groups and surface OH groups, may interact by π electrons of the aromatic rings, coordinate by nitrogen to Lewis sites (aluminium ions) in a lesser extend due to sterical hindrance. Moreover, it was possible to discriminate between 8CB species in the surface layer or in the middle of the pores/in the inter-grain space.

Dealkylation together with oxidation process takes place at temperatures much lower than for bulk 8CB: Therefore, a catalytic activity of the molecular sieves toward the LC molecules has to be supposed. The temperature and the degree of these chemical transformations of confined 8CB depend on the pore size and shape and on the filling level.

Host–guest interactions depend on the chemical composition of the pore walls too. These lead to different degradation degrees of the confined LC: in aluminium-containing matrices more than in the siliceous matrices.

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