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Complete Filling of Zeolite Frameworks with Polyalkynes Formed in Situ by Transition-Metal Ion Catalysts

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We report the use of transition-metal-exchanged zeolites as media for the catalytic formation and encapsulation of both polyethyne and polypropyne, and computer modeling studies on the composites so formed. Alkyne gas was absorbed into the pores of zeolite Y (Faujasite) exchanged with transition-metal cations [Fe(II), Co(II), Cu(II), Ni(II), and Zn(II)]. Ni(II) and Zn(II) were found to be the most efficient for the production of poly-ynes. These cations were also found to be effective in polymer generation when exchanged in zeolites mordenite and β. The resulting powdered samples were characterized by FTIR, Raman, diffuse reflectance electronic spectroscopy, TEM, and elemental analysis, revealing nearly complete loading of the zeolite channels for the majority of the samples. Based on the experimental carbon content, we have derived the percentage of channel filling and the proportion of the channels containing a single polymer chain for mordenite. Experimentally, the channels for Y are close to complete filling for polyethyne (PE) and polypropyne (PP), and this is also true for polyethyne in mordenite. Computer modeling studies using *Cerius2* show that the channels of mordenite can only accept a single polymer chain of PP, in which case these channels are also completely filled.

Introduction

Polyalkynes such as polyethyne or -propyne have been of interest in recent years due to their high conductivity in the doped state, yielding the potential for use as active electrode materials within lightweight rechargeable batteries.[1−6] Unfortunately, their lack of air stability makes them costly and difficult to handle.[7]

Encapsulation of conducting polymers is a subject of recent interest.[8] For alkynes, encapsulation within zeolite frameworks provides a means of stabilizing these highly desirable polymers and allowing their study.[9] Previously, we reported the loading of mesoporous MCM-41, with almost complete channel filling, with polyethyne and polypropyne formed through the catalytic action of Zn(II) and Ni(II) cations.[10] Here, we report the effects on the formation of polyalkynes observed for exchanged Fe(II), Co(II), Ni(II), Cu(II), and Zn(II) in zeolite Y. We also report similar results for Ni(II) and Zn(II) in zeolites mordenite and β.

Previous studies have reported very low loadings (or unspecified amounts) of oligomers or polymers. Loadings were minimal or low owing to the use of hydrogen-zeolite without active catalyst,[11−13] inactive alkali metal-zeolites,[14−16] or transition-metal-zeolite[17,18] catalysts at low temperatures, without agitation or recycling. The estimated maximum pore filling in these reports is below 50 vol %.[16] The only report of substantial channel filling relates to mesoporous materials.[10] Here, we observe complete filling of the zeolite channels, in most cases, for nickel- and zinc-exchanged species.

Experimental Section

The sodium forms of the zeolites were refluxed for 2 h with saturated nickel(II) acetate (for Ni) or 1 M aqueous solutions of the transition-metal chlorides (for other metals) to give the

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Table 1. Measured Chemical Compositions of the Exchanged Zeolites Prior to Reaction

zeolite	exchanged ion	chemical composition
Y	Ni(II)	$Ni_{24.78}Na_{8.26}Al_{53}Si_{139}O_{384}$
Y	Zn(II)	$Zn_{24.1}Na_{9.56}Al_{53}Si_{139}O_{384}$
β	Ni(II)	$Ni_{2.9}Na_{0.15}Al_6Si_6O_{24}$
β	Zn(II)	$Zn_{2.9}Na_{0.15}Al_6Si_6O_{24}$
mordenite	Ni(II)	$Ni_{3.1}Na_{1.73}Al_8Si_{40}O_{96}$
mordenite	Zn(II)	$Zn_{3.16}Na_{1.7}Al_3Si_{40}O_{96}$

Table 2. Carbon Loading and Polymerization Conditions Using Ethyne

sample	zeolite	ion	temperature/°C	time/h	carbon loading/wt %
1	Y	Zn	20	24	7.33
2	Y	Zn	100	2	9.31
3	Y	Zn	130	2	14.5
4	Y	Zn	200	2	18.1
5	Y	Ni	20	24	4.15
6	Y	Ni	130	24	18.47
7	Y	Co	20	24	3.03
8	Y	Co	100	24	9.55
9	Y	Co	150	24	18.29
10	Y	Cu	20	24	2.47
11	Y	Cu	100	24	2.84
12	Y	Cu	150	24	4.89
13	Y	Fe	20	24	1.14
14	Y	Fe	100	24	3.42
15	Y	Fe	130	24	4.68
16	Mor	Zn	20	24	6.34
17	Mor	Zn	130	24	8.86
18	Mor	Zn	130	24	9.04
19	Mor	Ni	20	24	1.60
20	Mor	Ni	100	24	8.79
21	Mor	Ni	130	24	7.85
22	*β*	Zn	20	24	6.68
23	*β*	Zn	100	24	10.95
24	*β*	Zn	130	24	9.60
25	*β*	Ni	20	24	5.77
26	*β*	Ni	100	24	5.01
27	*β*	Ni	130	24	7.35

exchanged zeolite samples. Thus prepared, the samples were exhaustively washed with distilled water to remove adsorbed metal cations and then dried in an oven at ca. 130 °C. Samples were analyzed for their nickel:sodium and zinc:sodium ratios using atomic absorption spectrometry (Perkin-Elmer model 1100B AA Spectrophotometer) and the chemical compositions derived are listed in Table 1. The samples were activated immediately prior to use by heating in a Schlenk vessel under a dynamic vacuum (8×10^{-2} mm Hg) in a furnace at 280 °C for up to 12 h to remove occluded water and gases from the surface and pores. This is a similar procedure to that used by Cheetham and co-workers prior to neutron scattering studies.[19] Following the dehydration, the HOH deformation IR band for water was absent from the sample. After the sample cooled to room temperature, the Schlenk was back-filled with dry oxygen-free argon (BOC "Pureshield" grade) and transferred to a nitrogen glovebox (oxygen content < 1 ppm; water < 2 ppm). Required amounts of activated zeolite material were weighed into a Schlenk tube provided with two high-vacuum taps in the glovebox. For the polymerization stage, one tap of the Schlenk tube was connected to a vacuum pump and the other to the ethyne source. Ethyne (BOC technical grade) was purified by passage successively through concentrated sulfuric acid, KOH pellets, and a cold trap to remove residual traces of acetone and propyne. Propyne was used as received (Lancaster Synthesis, 99%). Samples were stirred during the reaction either magnetically or mechanically depending on the sample size. The Schlenk vessel was immersed in an oil bath maintained at the required temperature for the reaction. The vessel was initially evacuated, the vacuum tap closed, and alkyne carefully admitted to atmospheric pressure. After varying amounts of time (see Table 2) the alkyne inlet tap was closed and the Schlenk was evacuated and removed from the oil bath to cool. At room temperature the vessel was opened to the atmosphere and the product removed. Samples with filled pores retain their appearance and spectroscopic properties for several months, whereas samples having a low percentage of pore filling degrade over minutes in air. Their initial color is generally lighter than that of filled samples (orange/red as opposed to black) and fades on exposure to air. Furthermore, the characteristic polyethyne spectra (vibrational and electronic) are lost on the same time scale. We also found that polymerizations of ethyne conducted in a Kugelrohr (rotating) apparatus eliminated the development of hot spots in the zeolite powder.

Zeolite Y has a three-dimensional channel system with supercages (11.8 Å) connected tetrahedrally through 12-ring openings (7.4Å). *β* is also a three-dimensional pore system having 12-ring channels in the *c*-direction (7.6 × 6.4 Å) and two channels perpendicular having pores of 7.6 × 6.4 Å and 5.5 × 5.5 Å. Mordenite has a 2-dimensional pore arrangement with channels of 7.0 × 6.5 Å connected perpendicularly by small 8-ring channels (∼3 Å).

Results and Discussion

Samples obtained as described in the Experimental Section were characterized using a range of techniques. The elemental compositions were obtained using crystallographic data for the zeolites and atomic absorption measurements made on the samples for Ni, Zn, and Na.

On admission of gas to the activated zeolite, the sample turned to brown, gray, or black depending on the sample, indicative of alkyne polymerization, as subsequently confirmed spectroscopically. Those samples which had high carbon loadings [see below] were stable indefinitely in air. The reaction was observed to be exothermic, in particular, with Ni-containing materials. Constant agitation is thus required to avoid intense local heating and the formation of graphitic fibers.[20]

Evidence for the formation of polyethyne derives from Raman spectroscopy. The Raman spectrum of ethyne encapsulated in a clathrate shows a strong band at 1967 cm^{-1}.[22] This band is clearly observed at 1957 cm^{-1}in the Raman spectrum of Cs-mordenite in which the pores have been filled with ethyne. The Raman spectra of the composites resulting from admission of ethyne to Ni-exchanged mordenite or *β* do not show this band, but the spectra correspond closely to those reported for pure polymer,[13,15,22,23] Figure 1. Furthermore, the sharp, strong band seen in polycrystalline graphite at 1 580 cm^{-1} is not present in our sample and excludes the possibility of surface graphite formation.[24] For the more heavily loaded samples, inadequate Raman spectra were obtained, resulting from a combination of fluorescence, absorption, and laser damage from the incident beam of the

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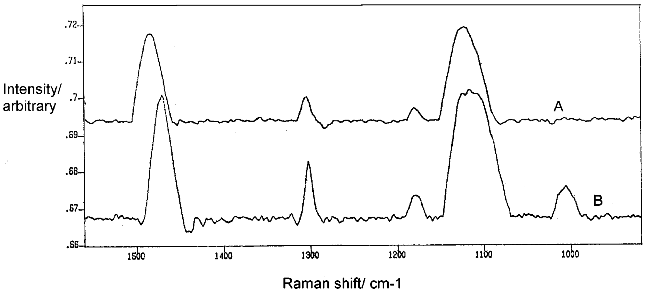

Figure 1. Raman spectra of polyethyne in Ni-mordenite (A) and Ni-β (B).

He−Ne laser. Samples 1, 2, 5, 7, 8, 10, 13, and 14 had Raman bands all lying in the ranges 1475−1485, 1298−1302, and 1116−1125 compared with literature values for free polyacetylene of 1480, 1295, and 1111 cm^{-1}.[22,23] For all the other samples, IR data were recorded as KBr disks. The IR spectra of polyalkynes show bands at 1350−1400 cm^{-1}, with additional bands 1450−1500 cm^{-1} for substituted polyalkynes. Bands in the first range are observed for all our composites, and composites having polypropyne also show weak bands in the second range. Although the spectra of the host zeolites show strong absorptions in the range 900−1200 cm^{-1}, and have bands associated with water [ca. 1600 and 3300−3500 cm^{-1}], the range 1300−1500 cm^{-1} is transparent.

Having characterized the material in the pores, elemental analysis for carbon provided a means of assessing the degree of channel filling. In the case of zeolite Y, ethyne polymerization was explored with nickel, zinc, cobalt, and iron exchanged as divalent cations, and using a range of temperatures (see Table 2). Zinc(II), nickel(II), and cobalt(II) gave high carbon loadings, (C, 18−18.5% at or above 100 °C) whereas from copper(II) or iron(II) exchanged samples the maximum loadings did not exceed 5% carbon under similar conditions, and these are clearly less effective catalysts. In all cases the C:H ratio is less than 12:1, although within 1% of this value, suggestive of the presence of polymer rather than bulk carbon. That this ratio is not precisely 12:1 is due to the presence of residual hydroxyl groups bound to the host. With certain materials and under different conditions, bulk graphite formation was observed,[20] and the C:H ratio was substantially greater than 12:1. In such cases, external graphite can be clearly seen in transmission electron microscopy, but is absent from the samples described here. Careful searching of the TEM images failed to reveal any external carbon, which is immediately obvious when formed under other conditions.[20] Figure 2 shows a representative image from our TEM observations. However, this by no means establishes the absence of graphitic carbon on the surface of the particles. Under conditions which do form carbon (as graphite fibers) on the outside of the particles, the samples have appreciable conductivity. The polymer-filled samples have immeasurably low conductivity (below 10^{-6} S cm^{-1}), and hence cannot have surface carbon. These samples are indefinitely stable in air, as shown by spectroscopic studies. Since polyethyne is a highly air-sensitive material, this also establishes that there is no appreciable quantity of surface polymer which would be rapidly oxidized. Although it is realized that BET surface area measurements are not quantitatively applicable to microporous materials, the measured areas are in agreement with complete channel filling, being essentially equal to the outside surface areas of the zeolite particles only.

Figure 2. TEM image of a sample of Zn−Y treated with ethyne gas at 200 °C and having complete pore filling by polyethyne.

Table 3. Carbon Loading and Polymerization Conditions Using Propyne[a]

sample	zeolite	ion	temperature/°C	carbon loading/wt %
28	Y	Ni	20	13.82
29	Y	Ni	100	15.98
30	Y	Ni	130	16.73
31	Y	Zn	20	16.42
32	Y	Zn	100	16.74
33	Y	Zn	130	16.96
34	β	Ni	20	7.81
35	β	Ni	100	11.34
36	β	Ni	130	13.64
37	β	Zn	20	12.09
38	β	Zn	100	14.65
39	β	Zn	130	15.59
40	Mor	Ni	20	5.31
41	Mor	Ni	100	5.58
42	Mor	Ni	130	5.85
43	Mor	Zn	20	4.96
44	Mor	Zn	100	5.93
45	Mor	Zn	130	5.99

[a] All experiments for 24 h.

For ethyne in zeolites β and mordenite, experiments were concentrated on nickel(II) and zinc(II) exchanged hosts. As the temperatures were increased, the loadings, as reflected in the elemental carbon analysis, also increased, but the maximum levels observed here were respectively ca. C, 9% for mordenite and ca. C, 9.6% for β. For the slightly higher value quoted for sample 23, we cannot be absolutely certain that traces of graphite are completely absent. Interestingly, the carbon loadings of polypropyne samples (see Table 3) show little effect from variation of reaction temperature. Using Y as host, the maximum loadings were C, 16.7% with Ni and C, 17% for Zn; and for mordenite the figures are C, 5.9% for Ni and C, 6% for Zn. These values are slightly lower than with polyethyne, implying less efficient filling. In contrast, the values for β, C, 13.6% for Ni, and C, 15.6% for Zn, are higher than those observed for polyethyne.

Diffuse reflectance electronic spectroscopy (see below) has been used to further study the composites. In general, we observe an increase in the relative absorbance toward longer

Table 4. Maximum Percentage Filling of Channels

sample	no.	polymer[a]	void volume/cm^3 g^{-1}	percentage filling/%
Y, Ni	6	PE	0.28[27]	99.89
Y, Zn	33	PP	0.28[27]	91.87
β, Zn	23	PE	0.24[28]	65.45
β, Zn	39	PP	0.24[28]	95.64
Mor, Zn	18	PE	0.15[27]	80.64[b]
Mor, Zn	45	PP	0.15[27]	54.80[b]

[a] PE is polyethyne; PP is polypropyne. [b] See text for percentage filling assuming one polymer chain per channel.

wavelengths with increased loading, as has been reported for increasing length polyethyne species.[25−27]

Pore Filling. We have calculated the percentage pore filling using the void volume of the zeolites from cyclohexane absorption data[28,29] and the carbon analysis. Cyclohexane data were chosen because values are available for all three zeolites, and because this substrate will exclude the volume of small diameter pores and cross-channels inaccessible similarly to the polymer/monomer. The assumptions are that the carbon is all present as polyethyne, completely contained within the pores, as established by our TEM images; see Figure 2. A further assumption must be made for the appropriate density to use for the polymer. Given that the polymer is noncrystalline, it is reasonable to use a density similar to that of amorphous polyethene (0.92). This is an intermediate value between that of crystalline polyacetylene, [ca. 1.1, reported in 1976[30]] and the value of 0.8 assumed by Cox et al.[12] This value is thus more pessimistic when calculating the degree of pore filling [than 0.8], but realistic in relation to pure, crystalline material. The density of polyethyne is known to vary with the degree of crystallinity, the sample history, and the relative proportions of cis- and trans-isomers.[30] Data for the percentage channel filling based on the highest loaded sample of each type are presented in Table 4.

The data demonstrate that, for zeolite Y, complete channel filling is achieved, and also for β, with polypropyne, even under these mild conditions. These highly loaded materials show no physical degradation on exposure to air or moisture over long periods. Lightly loaded samples, e.g., samples 10 and 11, showed degradation over several minutes on exposure to the atmosphere. We attribute this difference to the fact that highly loaded samples have the zeolite channels essentially blocked, and air is unable to attack the encapsulated polymer, which when free, is known to be readily oxidized. The lightly loaded samples allow ingress of air into the channels, and consequent degradation of the encapsulated material.

In the case of mordenite, which is essentially a unidirectional zeolite [the transverse channels being too small and short to accommodate polymer], polypropyne has a comparatively low carbon loading. We postulate that, in this case, size restriction in the channels limits the content to a single polymer chain per channel. Our calculations are based on a monomer length of 2.5 Å, and a total channel length for both channels in the unit cell of the zeolite of 15 Å, taken from the crystal structure,[31] and the unit-cell contents [based on the crystal data, but taking into account the degree of nickel incorporation, using the analytical data above]. These show

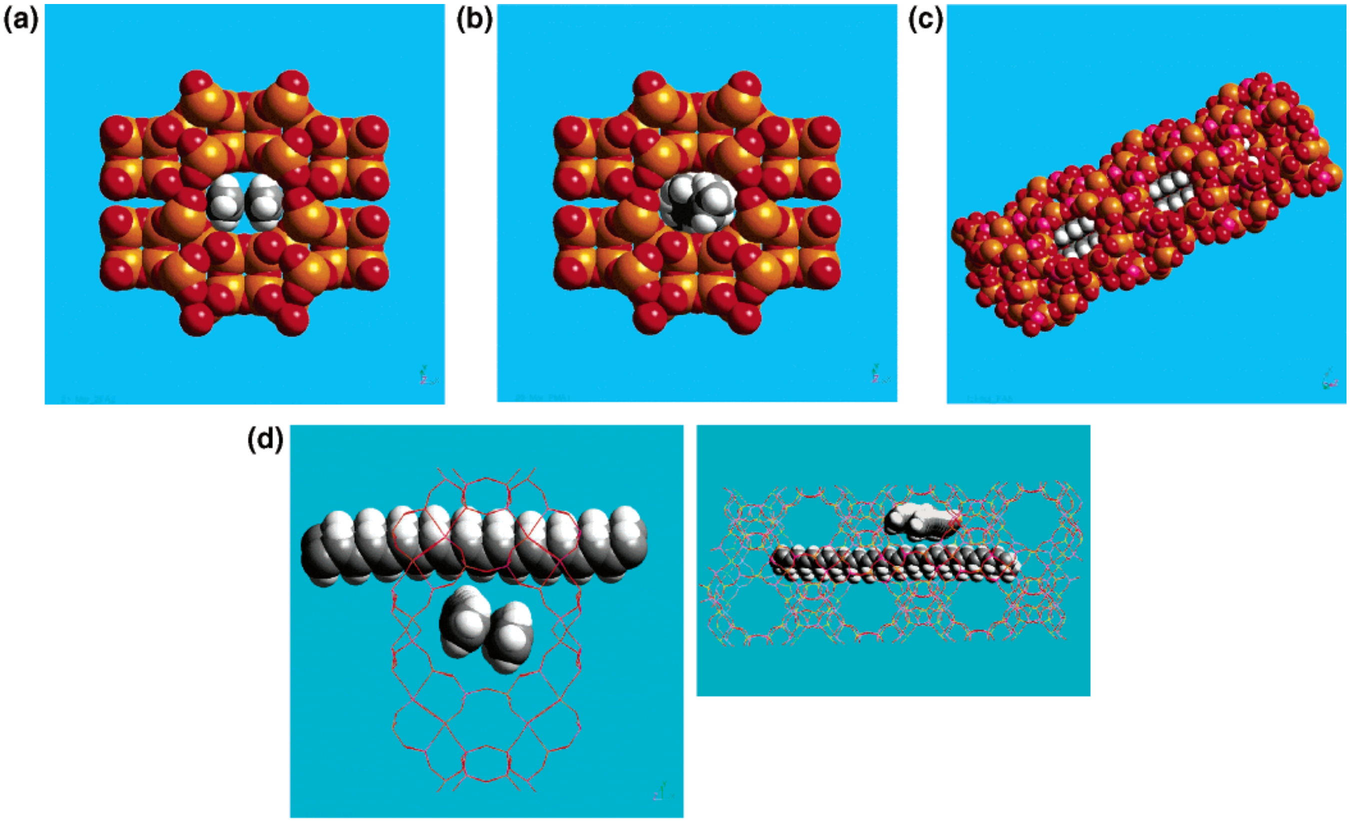

Figure 3. (a) Image of two polyethyne chains in a channel of mordenite generated by *Cerius2* as described in the text. (b) Image of a single chain of polypropyne in a major channel of mordenite generated by *Cerius2* as described in the text. (c) Image of two chains of polyethyne in a channel in zeolite Y, calculated using *Cerius2* as described in the text. (d) Two views showing accommodation of two chains of polyethyne in zeolite Y and how two orthogonal pores can be filled.

that, for polypropyne, the degree of channel filling if each channel can only accommodate a single polymer chain is 89.6%. However, for polyethyne, the analogous value [obtained by the same method] is 215%, suggesting that two polymer chains can be incorporated into each channel. We therefore decided to examine the situation using computer modeling.

Simulations were carried out using the *Cerius2* suite of programs (v.3.5, Accelrys Inc., San Diego) running on an SGI O2 workstation. Crystal structures used for mordenite and zeolite Y (faujasite) were those embedded within *Cerius2*. Molecular mechanics calculations were based on the *Drieding II* force field (v.2.2.1), with full charge equilibration.

A section of the mordenite structure large enough to accommodate a fully extended, 30-carbon polyethyne chain within a single pore was first constructed, and the atomic positions of the zeolite atoms were fixed in all subsequent calculations. An oligomeric model for *trans*-polyethyne, $CH_2{=}CH{-}(CH{=}CH)_{13}{-}CH{=}CH_2$, was modeled, energy-minimized, and inserted fully into the zeolite pore. To determine whether more than one polyethyne chain could be accommodated, a second molecule of the oligomer was then inserted only halfway into the same pore and the system was allowed to minimize in energy, with all nonzeolite atoms free to move. Rather than being expelled, the second chain was in fact drawn into the pore, and convergence of the calculation was achieved only when the ends of the two chains were almost (though not quite) fully aligned within the zeolite (Figure 3a). The π-systems of the two chains were parallel and stacked at essentially their van der Waals contact distance (average C−C separation 3.46 Å). The polyethyne chains showed no significant distortion from their free-space conformation, and the final model showed clearly that no more than two such chains could be accommodated within the pore channel.

Incorporation of a single polypropyne chain into mordenite was modeled by removing one of the two 30-carbon *trans*-polyethyne oligomers from the pore, substituting the appropriate number of methyl groups for hydrogen on the remaining chain and then allowing the system to minimize in energy. At convergence, the methyl groups were randomly distributed to either side of the polymer backbone, and it was clear that in *any* conformation the effective volume of polypropyne would be such that only a single chain could be accommodated within the pore (Figure 3b).

Results for incorporation of polyethyne within the largest pore channel of zeolite Y essentially parallel those for mordenite, although the channel structure of the former seems to induce a very slight sinuosity of the polymer chains. Again two (but no more than two) polyethyne molecules, π-stacked at approximately their van der Waals contact distance, are readily accommodated; alternatively, a single molecule of polypropyne is sufficient to fill the pore almost completely. The energy-minimized model for zeolite Y containing a pair of 30-carbon polyethyne chains within the largest pore is shown in Figure 3c, viewed perpendicular to the chain direction. Figure 3d shows two views illustrating how two polymer chains can be accommodated in the framework of zeolite Y, and how the 3-dimensional pore structure can be filled without steric hindrance.

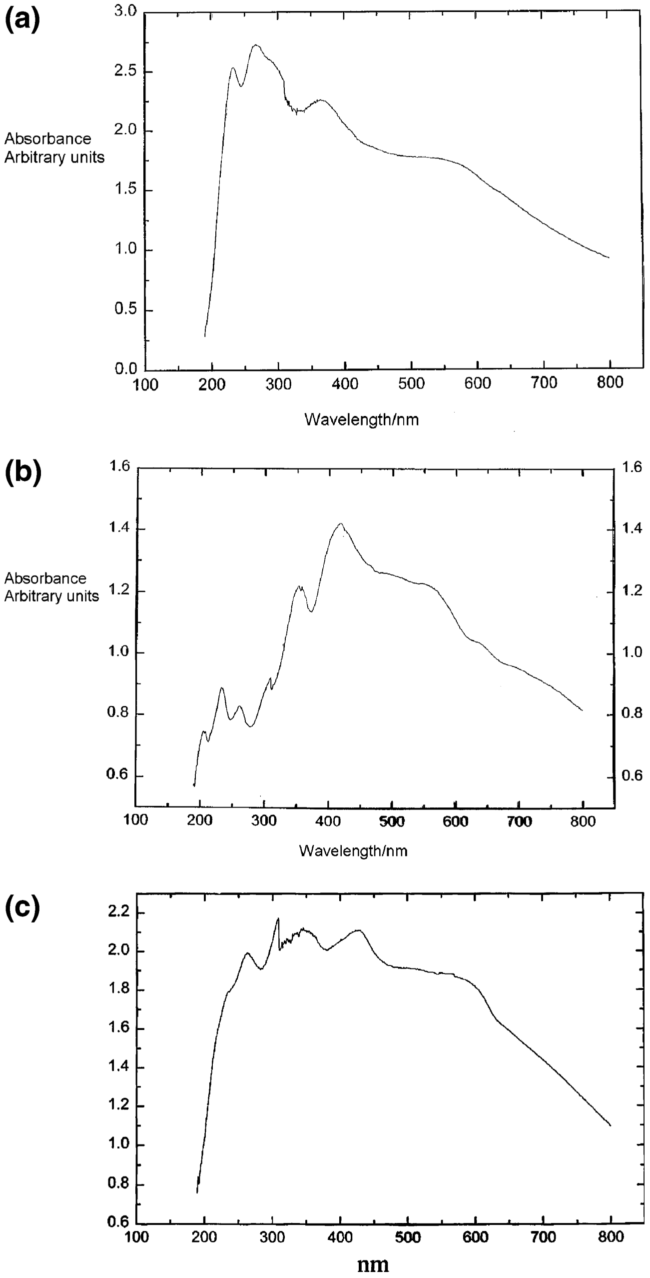

Figure 4. (a) Electronic spectrum of polyethyne in mordenite. (b) Electronic spectrum of polyethyne in zeolite β. (c) Electronic spectrum of polypropyne in zeolite β.

The results of computational modeling, showing a clear preference for two-chain pore occupancy of mordenite by polyethyne but only single-chain occupancy by polypropyne,

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are thus entirely consistent with the experimental data reported here.

The molecular weights of the polyethyne formed are not easy to assess reliably. Attempts to remove polymer by extraction into hot aniline (one of the few solvents known to dissolve polyethyne) failed to remove any material, additionally demonstrating the lack of polymer on the particle surfaces. The zeolite may be dissolved from the composite using aqueous sodium hydroxide solution, but this procedure also gives rise to polymer degradation. After dissolution of samples containing polyethyne using 0.2 M NaOH at room temperature, samples were examined by MALDI-TOF mass spectrometry. Peaks were observed up to a mass of ca. 1066, corresponding to a polymer of 41 monomer units, with lower m/z values observed at regular intervals of m/z 26 with decreasing intensity, down to an oligomer of 10−12 monomer units. These molecular weights are almost certainly limited by polymer degradation caused by the extraction process, as it is known that even in the absence of caustic alkali oxidative chain scission occurs.[32] Higher molar mass polymers are likely to be present, but could not be confirmed by this method, as insoluble high molecular-weight polymers are not applied to the sample plate. Similar results are reported by Grubbs.[33] Another method which has been used is electronic spectroscopy, which shows long absorption tails extending into long wavelength regions, as seen in Figures 4a−c. These long wavelength absorptions have been interpreted by Koll and Schrock in terms of extended, conjugated polymer chains,[27] but these authors draw attention to the care needed in interpreting such data. For example, calculations show that the maximum wavelength can be extrapolated to a value characteristic of an infinite chain [e.g., 1.78 eV for the $0 \rightarrow 0$ transition of an all-trans polyene in pentane (ca. 680 nm)], so the method is not suitable for high molecular weight samples. Furthermore, the λ_{max} can be red-shifted by up to 100 nm in the solid state. Although this is in good agreement with the long-wavelength absorptions of some of our samples, such agreement is probably fortuitous, as the values also depend on the degree of doping, which we have no method of assessing in the composites. The data can be said, therefore, to be in agreement with high-molecular weight polyenes, but not to provide strong evidence for such material.

Conclusions

We have shown that the sodium forms of zeolites Y, β, and mordenite after exchange with Ni(II), Zn(II), Fe(II), or Cu(II), when treated with ethyne or propyne gas at temperatures up to 150 °C, form composites containing encapsulated polyynes. The presence of polyynes has been demonstrated using IR, Raman, electronic spectra, and mass spectrometry, and the lack of conductivity and extensive TEM comparison with samples containing carbon show the absence of extraneous carbonaceous material. Experimental pore fillings, based on carbon loadings, show almost complete filling of the voids as described in the text. Computer modeling confirms these experimental findings, in that mordenite can encapsulate two polyethyne chains per channel but only one polypropyne chain per channel in the fully loaded samples.

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