

## Polymerization of Alkynes in the Channels of Mesoporous Materials Containing Ni and Zn Cations: Almost Complete Filling of the Voids

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Encapsulated conducting polymers are attractive materials since they may exhibit increased mechanical, thermal, and chemical performance compared with the pure polymer. We report (i) the first polymerization of alkynes within MCM-41, (ii) the first polymerization of alkynes, catalyzed by zinc(II), (iii) the filling of the voids by polyalkynes in these mesopores, and (iv) the characterization of the encapsulated composites.

Earlier reports in this field include the formation of polyalkynes, polypyrrole, polyaniline, and polythiophene, and focused on characterization.<sup>1,2</sup> For any application, a crucial issue is the polymer content of the resulting composite. For example, to achieve equivalent charge-storage capacity with current battery materials, at least 25% polymer content is required.<sup>3</sup> A major limitation to date in the use of hosts has been the low loadings which have been achieved.<sup>4,5</sup>

Polyethylene is structurally the simplest conducting polymer, but it is difficult to process.<sup>6</sup> When suitably doped, it has both the highest conductivity and the highest charge/weight storage capability,<sup>7</sup> but its air-instability makes it unsuitable for most commercial applications. MCM-41, prepared first in 1992,<sup>8,9</sup> has been extensively used as a catalyst support, because of its large, uniform pore-size and ordered structure. Its high pore volume ( $> 1 \text{ cm}^3 \text{ g}^{-1}$ ) contrasts with that of a typical zeolite (0.4 and 0.2  $\text{cm}^3 \text{ g}^{-1}$  for Y and Mordenite, respectively), so MCM-41 should allow much higher polymer loading than conventional zeolites.

It has been shown already that small amounts of polyethylene or polypropyne may be synthesized within the micropores of H- or metal cation-exchanged zeolites. However, the polymer loading achieved in previous work was too low (below 10%) or not specified.<sup>10–13</sup> We now report substantial filling of the much larger pores of MCM-41 materials.

Our studies of polymerization in zeolites [Y,  $\beta$ , mordenite, ZSM-5] show complete channel filling when the materials have

been exchanged with nickel(II), zinc(II), and other transition metal ions.<sup>14</sup> We have now prepared an aluminum MCM-41 (Si/Al 13, pore size 3.2 nm) and introduced Ni(II) or Zn(II) by ion exchange with aqueous salt solutions.<sup>15</sup> When these mesoporous aluminosilicates are evacuated to remove water and oxygen at 300 °C (0.1 Torr, 24 h), followed by exposure to alkyne vapor at 1 atm at various temperatures and time periods, an exothermic uptake of reagent produced dark brown or gray products.<sup>16</sup> Combustion elemental analysis of the resulting solids shows the presence of carbon in varying amounts (see Table 1), hydrogen values being as expected for the polymer and traces of residual water. In many cases, the carbon content after polymerization is about 60% of that of the original Al/MCM-41 containing the hexadecylammonium template agent (carbon content ca. 40%), with the best case being 75%. This filling by the template represents the maximum possible packing of any embedded organic guest. Therefore approximately three-quarters of the pore volume can be filled with polymer.<sup>17</sup>

Although some polymer is formed at low temperatures with ethyne, heavy pore loading is achieved above 150 °C. For comparison, ethyne polymerization was also attempted with Al/MCM-41 (no Ni(II) or Zn(II) ions) and Ni(II) or Zn(II) exchanged SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> (25 wt %, 200  $\text{m}^2 \text{ g}^{-1}$ , no mesopores), but neither gave polymerization. This shows the requirement for Ni(II) or Zn(II), and the positive influence of porosity and confinement on ethyne polymerization. Zn(II)/MCM-41 treated with ethyne at 250 °C for 24 h generated the greatest polymer occupancy. Zn(II) ions have been reported not to catalyze such polymerization,<sup>13</sup> furthermore their Lewis acidity (as has been suggested<sup>10</sup>) cannot be the sole factor, as many other M(II) or M(III) ions when incorporated failed to produce polymer. These data do not permit firm conclusions on a mechanism, but the failure to correlate with Lewis acidity, the fact that metal ions in porous media are substantially softer than might be expected,<sup>18</sup> and the observation of ESR signals from the polymer lead us to suggest a homopolar or free-radical mechanism, rather than an ionic process.

These composites show electronic spectra and FT Raman spectra characteristic of polyalkyne, although for a few solids good quality Raman spectra could not be obtained owing to the strong fluorescence. Figure 1 shows the influence of the reaction temperature on the electronic spectra of the composites. Above 150 °C the optical spectrum shows a continuous increase in absorbance toward longer wavelengths as reported for increasing length polyethylene oligomers.<sup>19–21</sup> The absorbance at ca. 800 nm is characteristic of well-polymerized neutral polyethylene.<sup>19</sup>

The Raman spectra of polyethylene/MCM-41 composites totally coincide with those previously reported for the pure polymer<sup>4,11,22,23</sup> (see Figure 2a). For polyethylene the peaks appearing

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(1) Ruiz-Hitzky, E.; Aranda, P. *An. Quim. Int. Ed.* **1997**, *93*, 197–212.

(2) (a) Bein, T. Recent Advances And New Horizons in Zeolite Science and Technology. In *Stud. Surf. Sci. Catal.* **1996**, *102*, 295–322; Elsevier Science. (b) For polymers and organic porous media, see: Ago, H.; Petritsch, K.; Shaffer, M. S. P.; Windle, A. H.; Friend, R. H. *Adv. Mater.* **1999**, *11*, 1281–1285. (c) Smith, R. C.; Fischer, W. M.; Gin, D. L. *J. Am. Chem. Soc.* **1997**, *117*, 4092.

(3) Personal communication, F. Trinidad, Sociedad Española del Accumulador Tudor, S.A., Laboratorio de Investigacion, Carretera Nacional II, Azuqueca de Henares, Guadalajara, ES-19200, Spain.

(4) Pereira, C.; Kokotailo, G. T.; Gorte, R. J. *J. Phys. Chem.* **1991**, *95*, 705–709.

(5) Cox, S. D.; Stucky, G. D. *J. Phys. Chem.* **1991**, *95*, 710–720.

(6) Chien, J. C. W. *Polyacetylene: Chemistry Physics and Materials Science*; Academic Press: New York, 1984.

(7) Novak, P.; Muller, K.; Samthanan, K. S. V.; Hans, O. *Chem. Rev.* **1997**, *97*, 207–281.

(8) Kresge, C. T.; Leonowicz, M. E.; Roch, W. J.; Vartuli, J. C.; Beck, J. S. *Nature* **1992**, *359*, 710–712.

(9) Beck, J. S.; Vartuli, J. C.; Roth, W. J.; Leonowicz, M. E.; Kresge, C. T.; Schmitt, K. D.; Chu, C. T. W.; Olson, D. H.; Sheppard, E. W.; McCullen, S. B.; Higgins, J. B.; Schlenker, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 10834–10843.

(10) Millar, G. J.; Lewis, A. R.; Bowmaker, G. A.; Cooney, R. P. *J. Mater. Chem.* **1993**, *3*, 867–872.

(11) Lewis, A. R.; Millar, G. J.; Cooney, R. P.; Bowmaker, G. A. *Chem. Mater.* **1993**, *5*, 1509–1517.

(12) Bordiga, S.; Ricchiardi, G.; Spoto, G.; Scarano, D.; Carnelli, L.; Zecchina, A.; Arean, C. O. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 1843–1855.

(13) Dutta, P. K.; Puri, M. *J. Catal.* **1988**, *111*, 453–456.

(14) Cardin, D. J.; Constantine, S. P.; Gilbert, A.; Lay, A.; Alvaro, M.; Garcia, H.; Gassetero, M. S.; Marquez, F.; Thorpe, J. H. To be submitted for publication. For data see Supporting Information.

(15) A typical analysis was the following: Ni content 7.8 wt %, relative crystallinity with respect to the as-synthesised Al/MCM-41 80%, BET area 720  $\text{m}^2 \text{ g}^{-1}$ .

(16) For details of catalyst activity, see Supporting Information.

(17) BET measurements show initially 767  $\text{m}^2 \text{ g}^{-1}$ , and following polymerization values below 60  $\text{m}^2 \text{ g}^{-1}$ , in agreement with the analytical data.

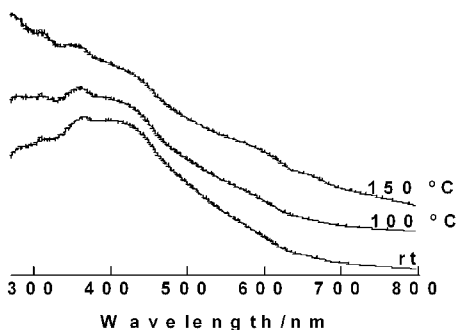
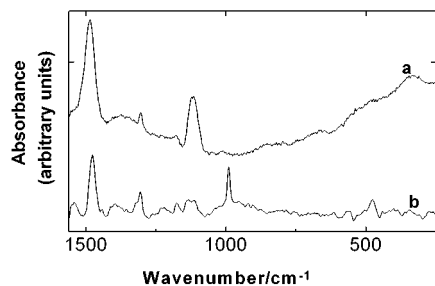
(18) Baldovi, M. V.; Corma, A.; Fornés, V.; Garcia, H.; Martinez, A.; Primo, J. *J. Chem. Soc., Chem. Commun.* **1992**, 949–951.

(19) Arbuckle, G. A.; MacDiarmid, A. G.; Lefrant, S.; Verdon, T.; Mulazzi, E.; Brivio, G. P.; Yang, X. Q.; Woo, H. S.; Tanner, D. B. *Phys Rev. B* **1991**, *43*, 4739–4747.

**Table 1.** Reactants, Conditions, and Analytical Data for Polymer/M(II)-MCM-41 Composites [M = Ni or Zn]

metal ion <sup>a</sup>	monomer	temp, °C	exposure period	C(H) (wt %) <sup>b</sup>	
Ni(II)	ethyne	room temp	3 min	5.9	
		room temp	24 h	7.4 (2.24)	
		75–100	3 min	6.5	
		100	2 h	4.4	
		130	2 h	13.8 (2.40)	
		150–165	3 min	25.4 (1.96)	
	propyne	290–300	3 min	24.1 (1.94)	
		room temp	3 min	8.4	
		90	3 min	9.8 (2.91)	
		150	3 min	11.7	
		220	3 min	25.0 (2.33)	
		phenyl-ethyne	100	3 min	12.28
	Zn(II)	ethyne	200	3 min	11.8
			300	3 min	15.3
200			3 min	9.8	
300			3 min	10.1	
room temp			24 h	1.78	
100			24 h	4.59	
	150	60 h	10.28		
	200	24 h	15.30 (1.89)		
	250	24 h	29.00 (2.96)		

<sup>a</sup> For Ni polymerizations, the exotherm is significantly larger than that for Zn, and more difficult to control, leading to a wider variation in apparent productivity. <sup>b</sup> H analyses may be high owing to residual water or absorbed water at low loadings.

**Figure 1.** Diffuse reflective electronic spectrum of Ni(II) exchanged Al/MCM-41 after reacting with ethyne at the indicated temperatures.**Figure 2.** FT-Raman spectra of polyethyne (a) and polypropyne (b) embedded in Ni(II)/Al/MCM-41 obtained from reaction at 150 °C.

at 1480 (vs) [ $\nu(\text{C}=\text{C})$ ] symmetry, mixed with C–H in-plane deformation], 1295 (m) [ $\nu(\text{C}-\text{C})$ ], and 1111  $\text{cm}^{-1}$  (s) [C–H in-plane deformation, mixed with  $\nu(\text{C}-\text{C})$ ] are readily assigned based on the literature data.<sup>21,22</sup> Our polyalkyne/MCM-41 materials do not undergo detectable spectroscopic variations in air after several months.

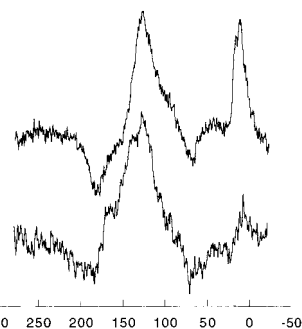
At temperatures in excess of 300 °C (or when the initial exotherm of the reaction is not controlled) combustion elemental analysis indicated a C:H weight ratio above 12:1 and a total carbon content up to 50 wt %, well above the maximum possible loading in the mesopores. Transmission electron microscopy (TEM) of

(20) Bally, T.; Roth, K.; Tang, W.; Schrock, R. R.; Knoll, K.; Park, L. Y. *J. Am. Chem. Soc.* **1992**, *114*, 2440–2446.

(21) Knoll, K.; Schrock, R. R. *J. Am. Chem. Soc.* **1989**, *111*, 7989–8004.

(22) Takeuchi, H.; Furukawa, Y.; Harada, L.; Shirakawa, H. *J. Chem. Phys.* **1986**, *84*, 2882–2890.

(23) Takeuchi, H.; Arakawa, T.; Furukawa, Y.; Harada, I.; Shirakawa, H. *J. Mol. Struct.* **1987**, *158*, 179–193.

**Figure 3.** MAS/CP <sup>13</sup>C NMR spectrum of (a) polyethyne/MCM-41 (lower) and (b) polypropyne/MCM-41 (upper).

such samples reveals the formation of fibrous graphitic carbon on the surface of the MCM-41 particles. The formation of such fibers has not been previously observed at such low temperatures and is responsible for the remarkably high bulk conductivity of these materials ( $0.6\text{S cm}^{-1}$ ). However, TEM shows that for polymerizations at or below 300 °C with careful temperature control and loadings  $\leq 29$  wt %, no observable external carbon formed. XPS surface analysis of graphite-free polyethyne/MCM-41 shows a polyethyne carbon peak at 284.7 eV [ $\approx 20\%$  total external atoms], accompanied by minor peaks (288.8 and 291 eV) attributable to highly oxidized C produced by oxidation of the surface polymer undetectable by Raman spectroscopy.

Representative polyethyne/polypropyne Ni(II)/MCM-41 samples have been analyzed by IR and <sup>13</sup>C CP/MAS NMR, both showing the presence of polyalkyne in agreement with FT Raman and electronic spectra (Figures 1 and 2). The CP <sup>13</sup>C NMR spectra (Figure 3a and b) show a strong, broad signal at  $\delta$  130.0 [ $\text{sp}^2$  carbons] and a barely detectable feature around  $\delta$  40 (area ratio ca. 30:1), and a peak at ca.  $\delta$  15 for Me in polypropyne (Figure 3b). The  $\delta$  40 band is associated with defects in the polymer, and has been observed in zeolite encapsulated polymer.<sup>8</sup> It was stated that polyethyne can contain “up to 40%  $\text{sp}^3$  hybridized carbon”, which was responsible for the  $\delta$  40-peak. Thus, our polymerization procedure with Ni(II)-exchanged Al/MCM-41 produces a polyethyne containing substantially fewer defects than previously reported polymerizations in acid or basic zeolites.

Ni(II)-Al/MCM-41 also polymerizes phenylethyne and methyl propiolate (see Table 1). However, the steric requirements of substituents attached to the polyne backbone produced looser packing of the polymer chains, resulting in substantially lower polymer loading. High loadings could only be achieved for ethyne and propyne at higher temperatures. For substituted polyalkynes, the most significant Raman feature is the absence of the C $\equiv$ C stretch and the presence of a band at ca. 1480  $\text{cm}^{-1}$  characteristic of a conjugated polyne backbone. Only samples with phenylethyne polymerized at low temperatures show some residual monomer [IR band at 2100  $\text{cm}^{-1}$ ].

In summary, we have shown for the first time that simple alkynes can be polymerized within modified MCM-41. For polyethyne and polypropyne, complete filling of the mesopores has been attained, producing a material with a high content of low-defect polymer.

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**Supporting Information Available:** Details of evidence that Ni and Zn are active sites, incorporation of metal ions into the mesopores, structural integrity of the composite, Al content of the mesopore following cation exchange, catalyst activity, ESR spectra, and filling of the pores in mesoporous and microporous media (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.