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Oxidative Polymerization of 1,4-Diethynylbenzene into Highly Conjugated Poly(phenylene butadiynylene) within the Channels of Surface-Functionalized Mesoporous Silica and Alumina Materials

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Properly functionalized and structurally ordered mesoporous materials, such as MCM-type silicas and aluminas, with tunable pore size and narrow pore-size distributions have attracted much attention for their potential applications as new catalytic scaffolds to direct and orient the conformation of desired products. For example, recent interest in encapsulation or synthesis or both of conducting polymers within the channels of MCM-41 has highlighted the future application of these materials as directional electron/energy transfer nanodevices.[1] However, several fundamental obstacles, such as low content and lack of the structural alignment of these polymer materials within the porous hosts, have yet to be overcome. Herein, we report the synthesis of Cu^{2+}-functionalized MCM-41 silica and alumina, with different pore diameters, which can oxidatively catalyze the formation of a highly conjugated poly(phenylene butadiynylene) polymer (PPB)[2] as depicted in Figure 1. The alignment and extent of the conjugation of the conducting polymer within the mesoporous materials were characterized.

Previous studies on the electronic properties of polyalkynylene-based conducting polymers, such as poly(phenylene ethynylene) (PPE) and PPB, demonstrated that these supermolecules have very high conductivity and charge/weight storage capability, when suitably doped.[3] Utilizing the mesoporous channels as catalytic nano-reactors for the fabrication of highly conjugated polyalkynylenes will stabilize their architecture in the desired, aligned form.

Clearly, the rate and extent of polymerization within the mesoporous channels of MCM-41 directly depend on (1) the amount and spatial distribution of catalytic sites and (2) the diffusion rate of monomeric precursors and their local concentration near the catalytic sites. Both factors can be adjusted by varying the pore size and by tailoring the catalytic activity of the surface through proper functionalization. To examine how these factors influence the oxidative polymerization of 1,4-diethynylbenzene, we synthesized two mesoporous silica and alumina materials (**Cu−MCM** and **Cu-MAL**, respectively) with different pore sizes and tested two different methods of Cu^{2+} surface functionalization.

Several approaches to surface functionalization of mesoporous materials have been reported, including direct grafting, impregnation, and co-condensation. Direct grafting and impregnation to the as-synthesized MCM-41 silicas usually give rise to an inhomogeneous surface coverage of the functional groups.[4] Most of the incorporated functional groups are located on the exterior surface or at the opening portion of the porous channels. In contrast, the co-condensation method yields a more homogeneous distribution of the functional groups within the mesopores.[4]

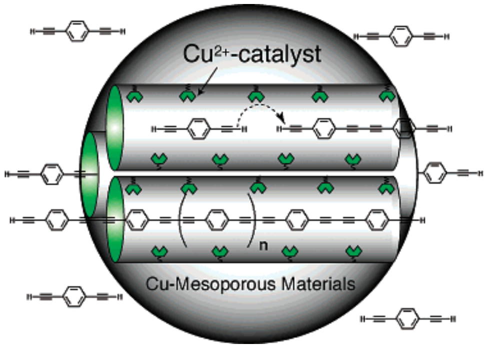

Figure 1. Schematic representation of Cu^{2+}-functionalized mesoporous silica (**Cu−MCM**) and alumina (**Cu-MAL**) catalysts for oxidative polymerization of 1,4-diethynylbenzene into conjugated oligo(phenylene butadiynylene).

Thus, we prepared the Cu^{2+}-incorporated MCM-41 silica material (**Cu−MCM**) by co-condensation using a Cu^{2+}-chelating molecule, *N*-[3-(trimethoxysilyl)propyl]ethylenediamine, as the precursor.[5] The powder XRD,[6] BET N_2 sorption isotherm, and BJH pore-size distribution measurements indicated that the **Cu−MCM** contains a typical MCM-41-type of ordered cylindrical porous structure with a high surface area of ca. 655.0 m^2/g and a BJH average pore diameter of ca. 25.6 Å (Figure 2a,b). A mesoporous alumina catalyst was also synthesized using a method reported earlier[7] followed by Cu impregnation (**Cu-MAL**). The mesoporous structure of Cu^{2+}−alumina catalyst was also characterized with aforementioned spectroscopic methods and exhibits a surface of ca. 448.0 m^2/g and a BJH average pore diameter of ca. 68.0 Å (Figure 2c,d). The amounts of Cu^{2+} catalytic sites of both **Cu−MCM** and **Cu-MAL** were quantified to be ca. 5.2×10^{-4} and 1.3×10^{-5} mol/g, respectively.[6]

Our studies of 1,4-diethynylbenzene polymerization with the two Cu^{2+}-functionalized mesoporous catalysts gave very different results. In the case of **Cu−MCM**, a 245-nm bathochromic shift (emission $\lambda_{max} = 643.5$ nm) of the fluorescence emission spectra of the PPB polymer was observed after 56 h of refluxing in pyridine (Figure 3). The result indicates the effective π-conjugation length of the PPB polymer synthesized within the mesoporous channels of **Cu−MCM** is perhaps comparable to that of PPBs synthesized in homogeneous solutions.[8] Interestingly, the oxidative polymerization using **Cu-MAL** showed two bathochromic-shifted fluorescence peaks ($\lambda_{max} = 472.5$ and 551.5 nm) under the same reaction conditions. However, both shifts are significantly smaller than in the case of **Cu−MCM**. This spectral difference is consistent with

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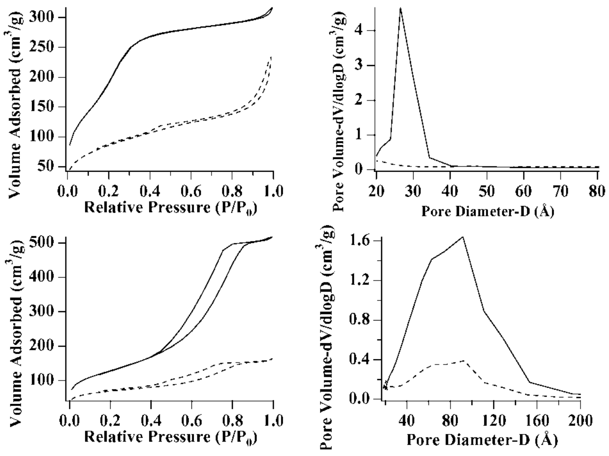

Figure 2. Nitrogen adsorption/desorption isotherms and the pore size distributions of the **Cu−MCM**, **(**a**)**, **(**b**)**, and **Cu-MAL**, **(**c**)**, **(**d**)**, materials before (solid line) and after (dashed line) PPB polymerization within the mesoporous channels.

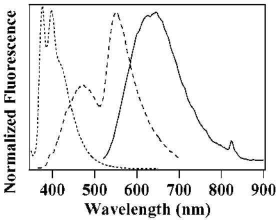

Figure 3. Normalized fluorescence emission spectra of 1,4-diethynylbenzene (dotted line) and the PPB-containing composite materials of **Cu-MAL** and **Cu−MCM** catalysts (dashed and solid lines, respectively) after 56 h of polymerization.

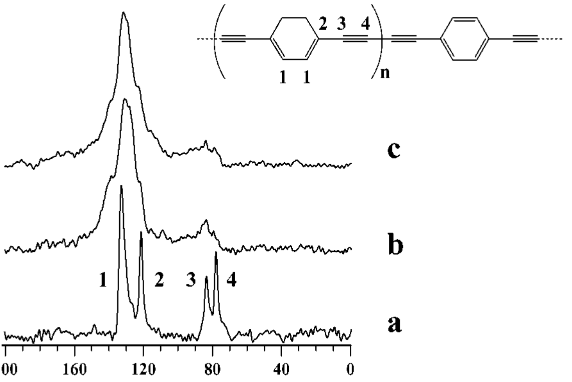

Figure 4. ^{13}C CPMAS spectra of **(**a**)** structurally aligned PPB polymer catalyzed by **Cu−MCM**, **(**b**)** PPB polymer synthesized with **Cu-MAL**, and **(**c**)** bulk PPB. The spectra were measured at room temperature, using 4680 scans, 10-s intervals, sample rotation rate of 5 kHz, contact time of 2 ms, CW ^{1}H decoupling at 70 kHz and sideband suppression (TOSS).

smaller π-conjugation of the PPB polymer in the case of **Cu-MAL**. Other photophysical and MALDI mass spectroscopy measurements of the PPB polymers syntheiszed by both catalysts also confirmed the significant difference in the degree of polymerization.[9]

While the aforementioned results clearly established that the polymerization indeed occurred, direct evidence of the spatial arrangement of the synthesized structures has been obtained using ^{13}C solid-state NMR. The measurements were carried out using ^{1}H→^{13}C cross polarization (CP) at 100.6 MHz on a Chemagnetics Infinity spectrometer equipped with a 5-mm magic angle spinning (MAS) probe. Three representative ^{13}C spectra of the studied samples are shown in Figure 4. The spectrum of a sample catalyzed by **Cu−MCM** (a) is notably different from those of a randomly oriented polymer (c) and a polymer that was synthesized with the **Cu-MAL** material (b). The former is well resolved and consists of four resonance lines, which are assigned as shown in the figure. The spectrum of bulk polymer exhibits considerable line broadening, with only two resolved bands at around 80 and 130 ppm, corresponding to sp and sp^2 carbons, respectively. The observed broadening reflects the conformational heterogeneity in the three-dimensional arrangements of polymeric chains. The same morphology is observed in the case of **Cu-MAL**. Additional significant differences are observed in spectra (b) and (c) with respect to (a): (i) both resonances are not only broader, but comprise more than two lines, and (ii) the intensities of sp^2 and sp bands do not match the 3:2 ratio expected for PPB. These spectral features are consistent with considerable polydiacetylene-type cross-linking[10] that occurred in the bulk polymer and **Cu-MAL**. In the case of **Cu−MCM**, the sharpness of the observed resonances and lack of cross-linking demonstrate that isolated molecular wires are formed within the parallel channels of MCM-41.

We have demonstrated that a linearly aligned conducting polymer can be catalytically synthesized within the porous channels of MCM-41 silica. Fluorescence and solid-state NMR provided spectroscopic evidence that the synthesis of extended polymeric chains with a high degree of alignment requires homogeneously distributed catalytic sites throughout the entire matrix. This type of homogeneity has been achieved via co-condensation of the catalytic groups in narrow pores.

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Supporting Information Available: Experimental details, XRD measurements, UV/vis absorption spectra, and MALDI mass spectroscopy measurements (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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