Use of Polypropyleneimine Tetrahexacontaamine (DAB-Am-64) Dendrimer as a Single-Molecule Template To Produce Mesoporous Silicas

Gustavo Larsen,*,† Edgar Lotero,‡ and
Manuel Marquez§,||

Department of Chemical Engineering, University of Nebraska—Lincoln, Nebraska 68588-0126, Department of Chemistry, University of Nebraska—Lincoln, Nebraska 68588-0304, Chemical Science & Technology Division, CST-DO, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, and The Nanotechnology Laboratory (NanoteK), Research & Development, Kraft Foods Inc., 801 Waukegan Rd. Glenview, Illinois 60025

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Tailored organic polymers[1] and micro-[2] and mesoporous[3] structures are easily produced via template chemistry. Alkylamine micelles are versatile for the design of mesoporous materials,[3] but the use of single polyamine macromolecules as meso-porogens still awaits demonstration. After the pioneering dendrimer research of Tomalia et al.[5] and of Newkome and collaborators,[6] it appears that such unimolecular templates are already available. Thus, the goal of this communication is to report on the synthesis of mesoporous solids using $[CH_2CH_2N[(CH_2)_3N[(CH_2)_3N[(CH_2\}_3N[(CH_2)_3N[(CH_2)_3\text{-}NH_2]_2]_2]_2]_2]_2]$ i.e., DAB-Am-64. With the exception of one recent paper[7] (a study of the porosity of carbosilane dendrimer/sol−gels *without template removal*), we believe this communication to be the first to report on the synthesis of dendrimer-mediated mesoporous silicas.

A typical sample preparation was as follows. Tetraethyl orthosilicate (TEOS, 1.024 g) was mixed with 1.61 g of a 1-propanol/DAB-Am-64 mixture consisting of 0.25 g of dendrimer per gram of solution. Anhydrous methanol (0.57 g) was also added to the TEOS/dendrimer/1-propanol mixture. Prior to adding 0.25 g of HCl (0.12 N), the mixture was heated for 5 min in a closed 10 mL vial at 373 K. Partial gelation occurred during this initial synthesis step. The gel was then acidified by addition of the HCl solution, and subsequently aged for 12 h at 343 K in a closed container. The resulting solid was oven-dried at 373 K for 20 h. To ultimately produce the mesoporous material, 0.3 g of solid were heated in a quartz U-tube under flowing nitrogen for 3 h at 803 K. A deep brown powder was produced during this high-temperature drying step, which was finally heated under flowing air from room temperature to 833 K. This temperature was maintained for another 2 h. The choice of drying and calcination protocols was not in any way arbitrary. Mass spectrometric analysis (not shown) of gases evolved during the high-temperature drying/curing step shows that a complex decomposition pattern takes place. It involves primarily the evolution of olefinic fragments, carbon monoxide, alkanes, alcohols, and N-containing species. Alcohol and carbon monoxide result from the reactive desorption of alkoxy groups still present in the oven-dried sample. During calcination, carbon dioxide and water evolved, and the choice of a plateau temperature of 833 K was based on the observation that no carbon-containing gases evolve beyond that temperature (other tests were run with upper temperature limits of 1073 K). The resulting carbon-free white powder was labeled as NU-1. The chosen pretreatment protocol is relatively mild for these types of materials but at the same time, it guarantees proper removal of the template.

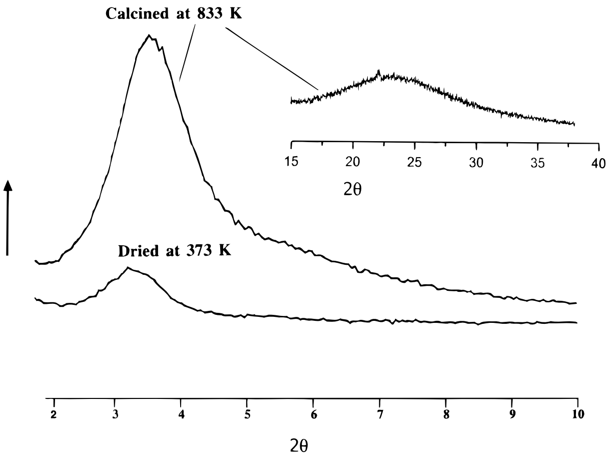

Figure 1. XRD patterns of NU-1 dried at 373 K and calcined at 833 K. Inset is for the calcined material in the Si−O region.

X-ray diffraction (XRD) experiments were performed on a computer-interfaced Rigaku instrument using Cu Kα radiation. A custom-built adsorption line equipped with a Baratron pressure transducer, mechanical and diffusion pumps and bakeable three-O-ring Teflon (greaseless) stopcocks was used for the adsorption measurements.

The XRD patterns of NU-1 are shown in Figure 1. Upon drying of the aged gel at 373 K, a single broad $2\theta \approx 3.25°$ diffraction peak became apparent. This signal increases in intensity and shifts to a higher angle by ∼0.35° after calcination. A 2θ value of 3.6° corresponds to a coherent distance of roughly 25.0 Å. The increase in intensity after calcination is most likely due to the removal of low-Z, poor backscatterer-type elements such as C, N, and H, leading to the creation of cavities. Prior to template removal, the constructive interference among

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* To whom all correspondence should be addressed.
† Department of Chemical Engineering, University of Nebraska—Lincoln.
‡ Department of Chemistry, University of Nebraska—Lincoln.
§ Los Alamos National Laboratory.
|| Kraft Foods Inc.
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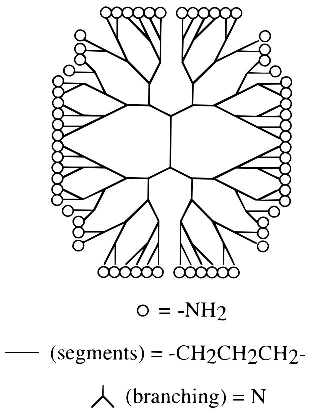

Figure 2. Planar representation of DAB-Am-64.

sol−gel walls is somewhat diminished by the low-Z element filling of voids. The upward shift, on the other hand, is due to shrinkage of the gel after heating, as a natural result of improved cross-linking and densification relative to the oven-dried (373 K) state.

The hydrodynamic diameter of the soft-core DAB-Am-64 (see Figure 2) in D$_2$O is 39.6 Å.[8] When the structure of DAB-Am-64 approaches the dense-core limit (extensive degree of back-folding), a molecular diameter of $\sim$25.0 Å is predicted.[8] However, since broad size density distribution functions are predicted by theory,[8] there is a priori reason to believe that the peak broadening observed in Figure 1 is likely due to the freezing of a distribution of dendrimer conformations upon gelation. In a typical sol−gel synthesis medium like the one adopted here, the ionic strength is expected to be low. Approximately one HCl molecule per dendrimer was added. The final HCl concentration in the synthesis medium is roughly 0.009 M. This translates into a very modest ionic strength, and we do not expect a polyamine such as DAB-Am-64 to be unstable under such conditions. Amine bonds are expected to become protonated, but they do not undergo hydrolysis. There is thus, no chemical basis for assuming that equally charged, stable DAB polyamines (roughly one proton per dendrimer molecule) might undergo aggregation or degradation. Even dendritic species with much more reactive bonds such as PAMAM (polyamidoamine) dendrimers, are stable indefinitely at pH values around 2−3.[9] Thus, the template is expected to maintain its integrity during the sol−gel process. However, other issues such as shrinkage during drying can impact the ultimate cavity size since the rather soft dendrimer structure will likely yield to capillary forces resulting from solvent evaporation. Furthermore, disklike structures have been observed in PAMAM dendrimers adsorbed on Si surfaces.[10]

The amorphous character of the pore walls in our material is apparent from the breath of the $2\theta \approx 22°$ line (inset, Figure 1). The latter is $\sim$6° at half-maximum, which indicates the presence of a rather broad distribution of Si−O bonds and Si−O−Si angles.

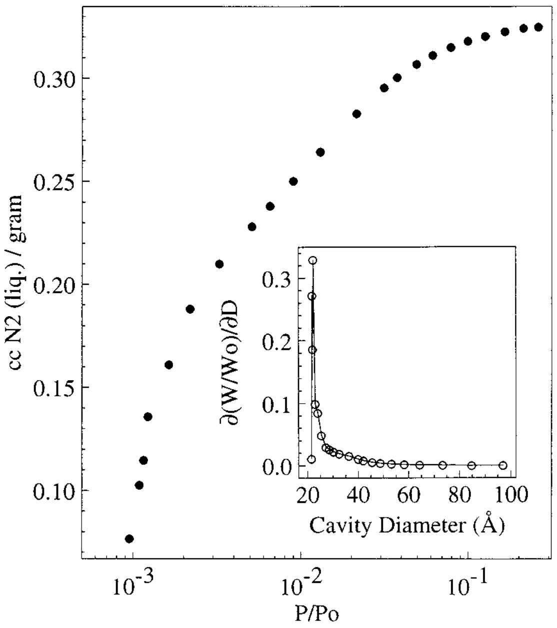

Figure 3. Nitrogen adsorption isotherm at 77 K. The inset is the Horvath−Kawazoe pore size distribution function.

Figure 3 shows the N$_2$ adsorption isotherm at 77 K, the inset being the Horvath−Kawazoe (HK) pore size distribution function. The calcined sample has a BET specific surface area of 637 m^2/g. To model the data, we have adopted the equations developed by Cheng and Yang[11] (CY) for spherical cavities, but have maintained the assumption of isotherm linearity as originally conceived by Horvath and Kawazoe.[12] All physical parameters (e.g., oxide ion and nitrogen polarizabilities and magnetic susceptibilities) were strictly taken from literature.[11,12] No free parameters were necessary, a fact that we have confirmed in our laboratory by using standard samples of known pore sizes. This combined CY-HK formalism, in the form of a Fortran 77 code, was found to perform very well for both nitrogen (77 K) and Kr (195 K) adsorption on zeolites and mesoporous carriers. A maximum in the pore size distribution at $\sim$23 Å is consistent with the idea that most dendritic centers adopt a dense-core conformation upon heat-induced cross-liking of the gel. We hypothesize that the dendrimer is forced to adopt a dense structure during gel densification. The pore size distribution appears to tail off toward larger pore diameters, presumably due the many (yet of little relative weight) allowed conformations of the dendritic structure. A blank, dendrimer-free preparation gave a broad pore size distribution centered at $\sim$16 Å, characteristic of conventional microporous silicas.[7] In the context of mesoporous silica materials synthesis, the specific surface area of NU-1 is about 50−70% that of mesoporous MCM-41.[3] The ultimate surface area, however, is strongly influenced by the silica/template ratio. Our material has been prepared at a ratio of $\sim$1.5 Si per dendrimer terminal amine group, which should lead to a thin-walled porous structure. Under such conditions, one would expect somewhat higher surface areas than the one obtained in our study, but our synthetic scheme is yet to be optimized.

To gain further insight into the structure of NU-1, we proceeded to conduct transmission electron micros-

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copy (TEM) studies. Unlike Mobil's MCMs,[3] we did not expect our material to enjoy sharp contrast "top views" along channels, since the template in our case is spheroidal. This in fact negated the direct observation of the cavities in the as-synthesized and calcined samples. However, by "staining" the as-prepared sol–gel with small amounts of Cu^{2+} (8 Cu^{2+} ions per dendrimer molecule), the microstructure of these solids was revealed. Amine dendrimers are macrochelating agents for copper and other transition metals,[13–15] and the "staining" technique used here has the added bonus that it becomes a method for preparation of metal oxide clusters of well-defined size embedded in a glassy matrix. The Cu-loaded solid gave an XRD pattern nearly identical to that of the Cu-free sample, but the low 2θ reflection shifted toward higher angles by ~0.25° presumably due to a small contraction of the dendritic structure upon charging via Cu^{2+} complexation. Transmission electron microscopy analysis (Supporting Information) shows the two most common structures found in stained NU-1. We chose to called them "globular" and "disordered filaments", but the key observation is that a disordered distribution of stained dendritic molecules throughout the glass becomes apparent. Upon close inspection of the TEM pictures, one might be tempted to propose the sporadic presence of very small ordered domains. We prefer to claim that under the current synthetic conditions the material is disordered, and very uniform pores (or supported metal clusters) can be prepared by the proposed technique without necessarily implying long-range ordering of the mesoscopic building units.

While our results are encouraging, a number of issues still remain to be addressed. First, it is conceivable that a high degree of structural ordering can be effected by proper manipulation of all preparation variables. If so, XRD patterns should reveal the type of mesostructure present (e.g., cubic, hexagonal, etc.). Second and foremost, there is the issue of pore connectivity. This is a critical aspect if these materials are intended as sorbents or catalysts, since rather unhindered molecular traffic is a most desirable feature in such cases. Clearly, the dendrimer/TEOS ratio is expected to play a role in the pore connectivity (and also in the resistance toward collapse) of these materials, because this variable will be key in tailoring the wall-thickness between voids. Finally, dendrimers of higher and lower generations, as well as dendritic molecules with different chemical functionalities, and different Si precursors must be studied, in an effort to determine whether this approach enjoys some level of generality. While this paper was under review, we successfully prepared a similar material with the smaller member of the DAB family i.e., DAB-Am-32. The physical properties of this material are consistent with the idea that tunable pore sizes can be achieved with the aid of a family of dendritic templates. Likewise, polyamidoamine (PAMAM) dendrimers can also be used as templates.[16] Results from these studies will be discussed in separate contributions.

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Supporting Information Available: Transmission electron microscopy images of "Cu-stained" NU-1. This material is available free of charge via the Internet at http://pubs.acs.org.

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