phenylation of 1-decene (H_2, Pd/C), which gave a mixture of all five possible phenyldecane isomers. Cyclooctene gave a mixture of phenylcyclooctenes in addition to some diphenylcyclooctene.

Arylations with olefins carrying electron-donating substituents were less successful. Vinyl esters invariably reacted by cleavage of the carbon–oxygen bond leading to the formation of styrene and stilbene. Reaction of cyclohexyl vinyl ether gave some Heck product (25% yield) in which phenylation had exclusively taken place in the α position.[11] *N*-vinyl-2-pyrrolidinone was arylated to give a mixture of isomeric *N*-styrylpyrrolidinones (α:$\beta = 4$:1) in 25% yield of the isolated product. A major side product was *N*-benzoyl-2-pyrrolidinone (58%).

Other aromatic carboxylic anhydrides reacted similarly. *p*-Methoxybenzoic anhydride required a slightly higher temperature (190°C) for the reaction with *n*-butyl acrylate to go to completion. Furanoic anhydride was successfully used to furylate *n*-butyl acrylate.

In conclusion, we have discovered an environmentally benign method to arylate olefins. The products of these reactions can be hydrogenated to arylalkanes or oxidized as in the Wacker reaction to aryl alkyl ketones, thus providing a clean alternative to the Friedel–Crafts reaction.

Experimental Section[13]

A 300 mL Schlenk-tube, fitted with a rubber septum inlet and equipped with magnetic stirring, is charged with $(PhCO)_2O$ (23 g, 100 mmol), $PdCl_2$ (45 mg, 0.25 mmol), and NaBr (103 mg, 1 mmol). After repeated degassing under vacuum and purging with argon, nHex$_2$O (10 mmol) as internal standard, dibutyl maleate (28.0 mL, 120 mmol) and NMP (100 mL) are successively injected. The Schlenk tube is heated at 190°C for 3 h. The course of the reaction is monitored by gas chromatography (CP-Sil 8 CB column). A mixture of dibutyl phenylfumarate and dibutyl phenylmaleate (7:2) is obtained by fractional distillation (170°C/3 Torr) of the crude reaction mixture in 73% yield.

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[13] Use of only 0.1 mol% of $PdCl_2$ and 0.4 mol% halide is also possible without reducing the yield; reaction times increase to 3–5 h.

Synthesis of Microporous Transition Metal Oxide Molecular Sieves with Bifunctional Templating Molecules**

Tao Sun and Jackie Y. Ying*

Porous inorganic materials have been widely studied, and the mechanism by which their structures form remains an area of great interest. When synthesized with high surface area and narrow pore size distribution, these structures are highly useful as active and/or selective catalytic materials.[1] Inorganic and organic cations have been frequently used to construct microporous zeolitic frameworks, but our understanding of their function in the process remains rather limited and disparate.[2] In contrast, a more generalized approach for formation of mesoporous structures has been developed in the last five years with the discovery of M41S silicates by Mobil scientists.[3] Through charge matching between the hydrophilic head groups of surfactant molecules and inorganic precursors, silicates and surfactants can be self-assembled into supramolecular aggregates with long-range order of packing.[4] Upon removal of surfactants through

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calcination or organic washes, mesoporous silicates with ordered porous arrays can be achieved.

More recently, a ligand-assisted templating approach was developed to ensure proper precursor–template interaction and micellar self-assembly prior to precursor hydrolysis.[5] In this way a family of hexagonally packed mesoporous transition metal oxides termed TMS1 was derived by Antonelli and Ying.[5, 6] For example, Nb-TMS1, a niobium oxide analogue of the hexagonally packed mesoporous silicate-based MCM-41, was produced by first establishing a covalent bond between the niobium ethoxide precursor and an amine templating agent.[5] Narrow pore size distributions and high surface areas were obtained upon template removal from such systems by organic washes or calcination. By adjusting the molar ratio of metal precursor to templating molecule, new mesostructured transition metal oxides with a hexagonal *P*63/*mmc* phase (TMS2) and a lamellar phase (TMS4) could also be derived.[5b] Increasing the amine chain length also led to a new cubic *Pm*3*n* phase (TMS3).[5b] These approaches allowed mixed metal oxide molecular sieves to be easily achieved, and provided the fundamental chemical flexibility associated with compositional control and homogeneity. This, coupled with the possibility of tailoring pore sizes in the range of 20 to 100 Å, offers exciting new opportunities in catalytic and gas adsorption applications.

The hexagonally packed mesoporous structures of both MCM-41 and TMS1 were constructed around surfactant assemblies by a supramolecular templating mechanism.[3–7] The surfactant molecules have a hydrophilic head group and a hydrophobic hydrocarbon tail, and these species are organized into micellar rods under the proper conditions. The micellar cross section determines the pore diameter and can be varied by changing the length of the hydrocarbon chain of the surfactant; the chains usually range between 12 and 20 C atoms. Thus far, such a supramolecular templating approach has been utilized only in the derivation of mesoporous materials with pore openings larger than 20 Å. To generate microporous metal oxides, Maier et al. have developed a sol–gel technique to produce amorphous silicate-based mixed oxides with a narrow pore size distribution and a surface area as high as 523 $m^2 g^{-1}$.[8] In our study, the goal is to generate microporous structures systematically by controlling the micellar dimensions by a self-assembly approach. We report herein a novel approach that enables us to achieve microporous transition metal oxides by the introduction of a second hydrophilic functional group to the tails of amine-templating molecules.

In a typical synthesis, niobium ethoxide was added to an ethanolic solution of 1,12-diaminododecane to prepare a solution of the niobium diamine complex. This complex was then hydrolyzed in an aqueous solution at ambient conditions and then hydrothermally treated at temperatures ranging between 96 to 180 °C for four or five days. The light brown solids produced were collected, washed, and dried at 180 °C for 24 h to further condense the niobium oxide framework. The diamine molecules were effectively removed by an acidic alcohol wash at temperatures varying from 25 to 80 °C, depending on the pH of the solution and the duration of washing. The porous sample obtained was designated as Nb-TMS6. The microporosity of Nb-TMS6 was illustrated by the type I nitrogen adsorption–desorption isotherm in Figure 1. The Nb-TMS6 sample possesses a Brunauer-Emmet-Teller (BET) surface area of 150 $m^2 g^{-1}$ or higher, depending on the exact diamine removal conditions. The transmission electron micrograph (TEM) shown in Figure 2 further confirms the microporous nature of Nb-TMS6 synthesized with diaminododecane. Unlike Nb-TMS1 and Nb-TMS3, which displayed long-range packing of mesopores in a hexagonal and a cubic arrangement, respectively, the packing of micropores in Nb-TMS6 appeared to be rather disordered with no clearly defined crystal phases.

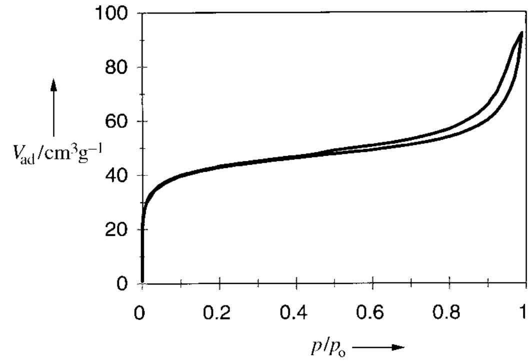

Figure 1. N_2 adsorption and desorption isotherms (V_{ad} = volume adsorbed, p/p_0 = relative pressure) of microporous Nb-TMS6 synthesized with a Nb:1,12-diaminododecane molar ratio of 1:0.5 at 180 °C. The isotherms were collected on a Micromeritics 2010 Gas Adsorption Analyzer.

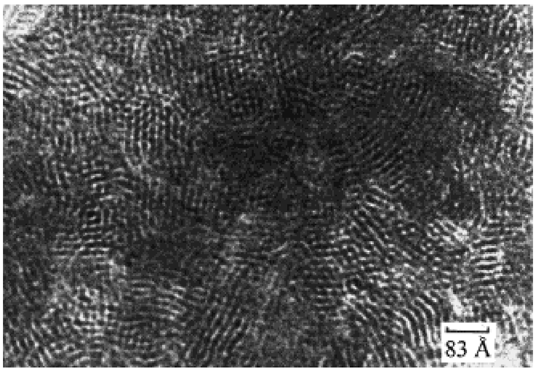

Figure 2. TEM image of as-prepared Nb-TMS6, synthesized with a Nb:1,12-diaminododecane molar ratio of 1:0.5 at 180 °C. This image was obtained with a 200 kV JEOL 002B transmission electron microscope.

The X-ray diffraction (XRD) pattern of Nb-TMS6 synthesized with diaminododecane (Figure 3) showed an intense (100) peak at 18.4 Å, and weaker peaks at 9.95 Å and 6.04 Å. The d_{100} spacing of 18.4 Å in Nb-TMS6 is much smaller than the d_{100} spacing of 28.0 Å in mesoporous Nb-TMS1 synthesized with dodecylamine.[5b] This confirms that the diamine molecules self-assemble by a mechanism very different from that of the monoamine molecules, leading to much finer porous structures upon their removal from the inorganic framework. Close examination of the high diffraction angles revealed the presence of a few weak peaks, which may be

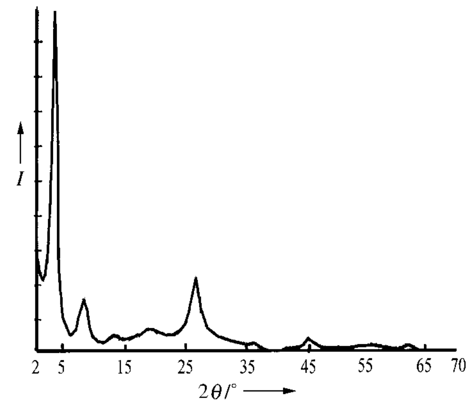

Figure 3. XRD patterns of as-prepared Nb-TMS6 synthesized with a Nb:1,12-diaminododecane ratio of 1:0.5, and aged at 180 °C for four days. The XRD patterns were obtained with a Siemens D5000 θ-θ diffractometer with $Cu_{K\alpha}$ radiation ($\lambda = 1.5418$ Å). I = intensity in arbitrary units.

attributed to minor impurities from a dense phase containing niobium oxide.

In addition to diaminododecane, we have investigated shorter chain diamine molecules as templating agents in an effort to derive even finer microporous structures. As shown in Figure 4, the (100) peak position shifted from 18.4 Å to 14.4 Å as the length of the diamine hydrocarbon chain was decreased from twelve C atoms to seven C atoms. The intensity of the (100) peak and the resolution of the higher order peaks were greater for the samples synthesized with longer diamine molecules. The lower order in pore packing of the samples associated with shorter diamine molecules may be due to the relatively lower hydrophobicity of the shorter hydrocarbon chains. Despite the lack of well-defined pore packing, this synthetic approach allows us to systematically tailor novel microporous structures with high surface areas for transition metal oxide molecular sieves.

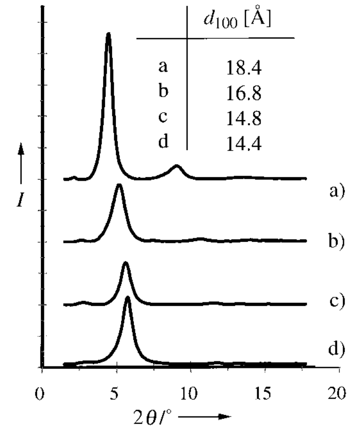

Figure 4. XRD patterns of as-prepared Nb-TMS6 synthesized with a) 1,12-diaminododecane, b) 1,10-diaminodecane, c) 1,8-diaminooctane, and d) 1,7-diaminoheptane as templating agents. The samples were prepared with a Nb:diamine ratio of 1:0.5 at 180 °C. I = intensity in arbitrary units.

The diamine template molecules could not be properly removed from the oxide framework without structure collapse by treating the materials at elevated temperatures or under high vacuum. The departure of diamines may be accounted for by a weight loss of 21 % in the as-prepared Nb-TMS6 at 325 °C in thermogravimetric analysis. This temperature for template removal is much higher than that in MCM-41 materials,[3] indicating a very strong interaction between niobium oxide and the diamine molecules. However, if the templates are removed by washing with acidic alcohol, the materials can retain their microporous structure and XRD pore packing order up to 400 °C. The covalent nature of the bonding between diamine and niobium is also unique at relatively high pH; synthesis at pH below 5 yields only amorphous materials since the head groups of the templating molecule will be protonated as ammonium cations and cannot donate electrons to empty d orbitals of niobium to form strong chemical interactions.

The present study illustrates for the first time that long-chain diamine molecules can be used to construct microporous oxides. This approach is in contrast to the conventional surfactant templating of mesoporous phases and is distinct from the typical molecular templating of zeolitic structures. Our synthesis was made possible because the hydrophilic affinity of the templating molecules was tailored by introducing more than one functional group to the hydrocarbon chain. As in the synthesis of Nb-TMS1,[5] we have chosen amine as the functional group for deriving Nb-TMS6 since the bonding between nitrogen and niobium is expected to be very strong. This should allow aging at high temperatures and leave the templating molecule in place for full condensation of the niobium oxide framework. In the case of Nb-TMS6, that the N–Nb bond formation was expected to be highly favorable was further exploited to facilitate self-assembly between the two functional groups of diamines with the niobium alkoxide precursors. A smaller micellar dimension is achieved with a diamine than with a monoamine of the same hydrocarbon chain length. The resulting smaller supramolecular template has led to the successful derivation of a novel microporous transition metal oxide molecular sieve, in contrast to the mesoporous structures obtained by using monoamine templates. Our approach enables the fine-tuning of the pore size below 20 Å by varying the chain length of a bifunctional molecule for not only niobium oxide, but also tantalum oxide, and titanium oxide. The resulting family of microporous transition metal oxides and mixed metal oxides offers exciting new flexibility in designing molecular sieves targeted for size selectivity and chemical functionality.

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Polymers for 193-nm Microlithography: Regioregular 2-Alkoxycarbonylnortricyclene Polymers by Controlled Cyclopolymerization of Bulky Ester Derivatives of Norbornadiene**

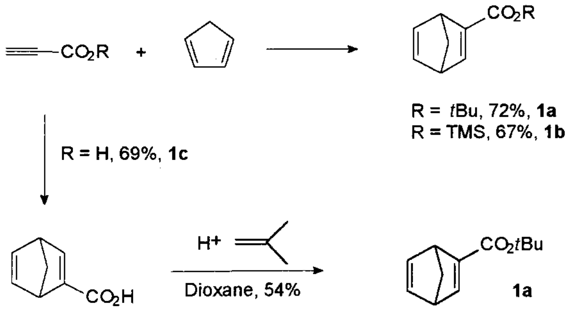
Q. Jason Niu and Jean M. J. Fréchet*

The rapid advances in miniaturization of microelectronic devices require that new imageable and etch-resistant polymeric materials be developed for use in 193-nm microlithography. Current research has focused on alicyclic polymers featuring adamantane or norbornane repeating units since such rigid units have been shown to be effective in terms of dry etch resistance.[1, 2] The absence of conjugated double bonds in these alicyclic building blocks is also a favorable feature since the polymers must be transparent at 193 nm. We now report the first synthesis of regioregular, uncross-linked poly(2-alkoxycarbonylnortricyclenes) that may be used for 193-nm microlithography.

In the early 1980s we described a novel family of chemically amplified resists for deep-UV (248 and 254 nm) microlithography.[3] These resists, which have been used commercially for more than a decade, operate on the basis of acid-catalyzed deprotection of a polymer in a process that renders the final product soluble in aqueous base. The chemistry of these resists is now well understood and has been reviewed recently.[4]

Early work by Graham et al. described the free radical polymerization of 2-ethoxycarbonylbicyclo[2.2.1]-2,5-heptadiene to afford an irregular product possessing a structure with more than one repeating nortricyclene-type unit as well as some unsaturated norbornene-type units.[5] As a result of a competing 5,6-directed polymerization, high conversion could not be achieved without gelation of the polymer. Our approach to overcome this problem, while both preserving the high reactivity of the C2–C3 double bond towards free-radical polymerization and introducing an imageable functional group in the side chain of the resulting polymer, is to increase the size of the ester group at the 2-position. This increased steric bulk of the monomer inhibits intermolecular addition at the crowded 2-position while favoring internal cyclopropanation through reaction with the neighboring C5–C6 double bond. As a result, monomers such as 2-*tert*-butoxycarbonylbicyclo[2.2.1]-2,5-heptadiene (**1a**) and 2-trimethylsiloxycarbonyl bicyclo[2.2.1]-2,5-heptadiene (**1b**), which have bulky ester groups, undergo ring-closing cyclopolymerization[6] instead of normal vinyl addition.

The bulky monomers **1a** and **1b** used in the preparation of the regioregular polynortricyclenes were obtained in good yield by Diels–Alder addition of propiolic acid esters to cyclopentadiene (Scheme 1).



Scheme 1. Synthesis of **1a** and **1b**.

Conversion of the adduct of propiolic acid and cyclopentadiene to the desired *tert*-butyl diene ester is also possible through acid-catalyzed esterification with 2-methylpropene. Monomer **1a** was easily purified by flash chromatography, while monomer **1b** was purified by vacuum distillation. These 2-substituted bicyclo[2.2.1]-2,5-heptadiene derivatives are colorless oils, which slowly polymerize upon extended storage at room temperature but can be stored for months as 10–25% solutions in dichloromethane at −20°C under nitrogen. In the presence of oxygen the monomers have a strong tendency to polymerize even at low temperature.

As shown in Scheme 2, the cyclopolymerizations of **1a** and **1b** were carried out using 0.5–2% of azoisobutyronitrile (AIBN) as the free-radical initiator in benzene at 65°C for 20 hours. A relatively large amount of AIBN (e.g. 2 mol%) is preferred for this polymerization since imaging applications generally require materials having a modest number average molecular weight.[4]

The resulting polymer **2a** was precipitated from methanol, while acetonitrile was used for the precipitation of **2b** to avoid complete loss of the trimethylsilyl protecting groups. All the

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