

# Immobilization of a Soluble Metal Complex in an Organic Network. Remarkable Catalytic Performance of a Porous Dialkoxyzirconium Polyphenoxide as a Functional Organic Zeolite Analogue

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Received January 4, 1999

**Abstract:** Treatment of anthracenebisresorcinol **1** (a tetraphenol) with Zr(O<sup>t</sup>Bu)<sub>4</sub> in THF results in polycondensation to give an O–Zr–O network and affords a poly(dialkoxyzirconium phenoxide), **1**<sup>4-</sup>·2[Zr(O<sup>t</sup>Bu)<sub>2</sub>] (Zr host), in quantitative yield as an insoluble, amorphous, microporous powder with a particle size of ~0.7 μm, a pore size of ~0.7 nm, and a specific surface area of ~200 m<sup>2</sup>/g. The powder exhibits reversible Langmuir-type adsorption/desorption of N<sub>2</sub> at 77 K and hexane at 298 K. Adsorption and coadsorption of ethyl acetate, benzene, and other polar and apolar guests also occurs readily at 298 K. The Zr host catalyzes the Diels–Alder reaction of acrolein with 1,3-cyclohexadiene in a remarkable manner. As a solid metal–organic catalyst, it has a formula-based turnover rate constant of 40 h<sup>-1</sup>, which far exceeds those of its components, i.e., the soluble Lewis acid Zr(O<sup>t</sup>Bu)<sub>4</sub> (0.1 h<sup>-1</sup>) and the hydrogen-bonded insoluble organic network **1** (0.3 h<sup>-1</sup>). The solid catalyst can be easily separated from the organic product, which is not contaminated with Zr or the reactants. The recovered catalyst can be used repeatedly without deactivation. The reaction can also be conducted in a flow system with the insoluble Zr host catalyst and a reactant mixture as a mobile phase. The remarkable catalytic performance of the Zr host and its easy preparation suggest that insoluble microporous metal–organic solid catalysts are workup-free and waste-free as well as resource- and energy-saving.

## Introduction

Metal ions play key roles in organic transformations. Many investigators work with soluble species in a homogeneous solution. They assume that encounters of reactant molecules are most efficient when the molecules are dissolved. Mechanistic and selectivity problems are simpler for homogeneous reactions than for reactions at a heterogeneous interface. From a process-engineering viewpoint, however, homogeneous catalytic systems have disadvantages. They require separation of organic product(s) from metallic species, usually by extraction. This inevitably creates organic and aqueous wastes, the latter containing deactivated metal species.

An advantage of heterogeneous catalysts is their ready recoverability, and they are important in industry. However, solid catalysts have so far been almost exclusively inorganic materials. Especially useful are microporous inorganic zeolites.<sup>1</sup> Despite much recent interest in organic solids with zeolitic guest-binding properties,<sup>2</sup> their catalytic activities are largely unexplored. The target of this work is catalytically active porous metal–organic solids, which can be characterized on the basis of the criteria applied to conventional zeolites. From a practical viewpoint, there are a number of other criteria for such materials to be useful. One is generality and ease of preparation. Another is catalytic activity, especially compared to their soluble counterparts. A third is complete catalyst recoverability.

Our strategy is simple. We try to immobilize soluble metal complexes in a known cavity-forming hydrogen-bonded network

via polycondensation in the scheme O–H···O–H + MX<sub>n</sub> → O···[MX<sub>n-2</sub>]<sup>2+</sup>···O<sup>-</sup> + 2HX (X = RO<sup>-</sup>, etc).<sup>3</sup> Anthracenebisresorcinol **1** forms a network shown in structure **2** (··· = O–H···O–H, Chart 1). In the large cavities left are incorporated two guest molecules via host–guest hydrogen-bonding. The crystal structures of the resulting adducts have been determined.<sup>2i,4</sup> The present work is concerned with a Zr(IV) material<sup>3</sup> obtained from Zr(O<sup>t</sup>Bu)<sub>4</sub> and **1**. We report here the well-behaved porosity and the remarkable catalytic performance of the material, which encourage the construction of other self-workup and environ-

(2) For examples of recent work, see: (a) Ermer, O.; Lindenbergh, L. *Helv. Chim. Acta* **1991**, *74*, 825–877. (b) Kaszynski, P.; Friedli, A. C.; Michl, J. *J. Am. Chem. Soc.* **1992**, *114*, 601–620. (c) Reddy, D. S.; Goud, B. S.; Panneerselvam, K.; Desiraju, G. J. *Chem. Soc., Chem. Commun.* **1993**, 663–664. (d) Abrahams, B. F.; Hoskins, B. F.; Michail, D. M.; Robson, R. *Nature* **1994**, *369*, 727–729. (e) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152. (f) Goldberg, I.; Krupitski, H.; Stein, Z.; Hsiou, Y.; Strouse, C. E. *Supramol. Chem.* **1995**, *4*, 203–221. (g) Subramanian, S.; Zaworotko, M. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2127–2129. (h) Kolotuchin, S. V.; Fenlon, E. E.; Wilson, S. R.; Loweth, C. J.; Zimmerman, S. C. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2654–2657. (i) Endo, K.; Sawaki, T.; Koyanagi, M.; Kobayashi, K.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1995**, *117*, 8341–8352. (j) Ung, A. T.; Gizachew, D.; Bishop, R.; Scudder, M. L.; Dance, I. G.; Craig, D. C. *J. Am. Chem. Soc.* **1995**, *117*, 8745–8756. (k) Gardner, G. B.; Kiang, Y.-H.; Lee, S.; Asgaonkar, A.; Venkataraman, D. *J. Am. Chem. Soc.* **1996**, *118*, 6946–6953. (l) Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2861–2868. (m) Brunet, P.; Simard, M.; Wuest, J. D. *J. Am. Chem. Soc.* **1997**, *119*, 2737–2738. (n) Russell, V. A.; Evans, C. C.; Li, W.; Ward, M. D. *Science* **1997**, *276*, 575–579.

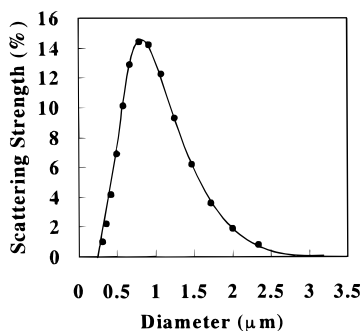
(3) A preliminary study on the catalytic properties of related Ti<sup>4+</sup> and Al<sup>3+</sup> species appeared in the following: Sawaki, T.; Dewa, T.; Aoyama, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8539–8540.

(4) (a) Aoyama, Y.; Endo, K.; Kobayashi, K.; Masuda, H. *Supramol. Chem.* **1995**, *4*, 229–241. (b) Endo, K.; Koike, T.; Sawaki, T.; Hayashida, O.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4117–4122.

<sup>†</sup> CREST.

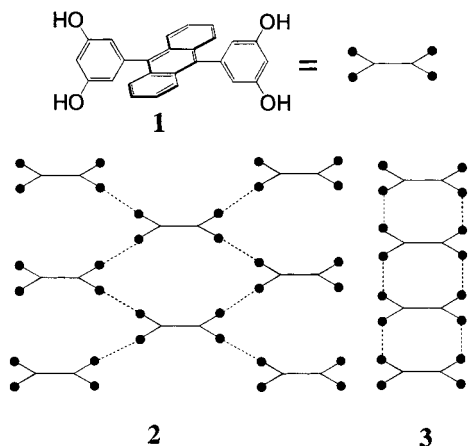
<sup>‡</sup> Kyushu University.

(1) Breck, D. W. *Zeolite Molecular Sieves, Structure, Chemistry, and Use*; John Wiley and Sons: New York, 1974.



**Figure 1.** Distribution of particle sizes in the Zr host as determined by dynamic light scattering for a dispersion of Zr host, 1 mM (in THF), at 25 °C.

### Chart 1

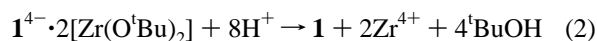
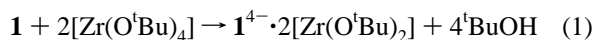


mentally friendly metal–organic catalysts for organic transformations.

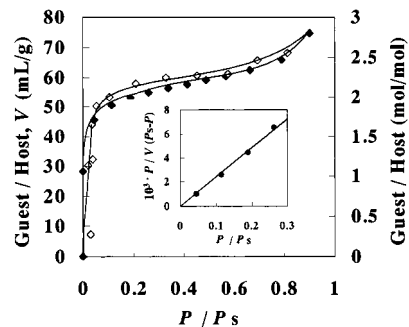
## Results and Discussion

### Preparation and Relevance to the Sol–Gel Method.

Reaction of apohost **1** and  $\text{Zr}(\text{O}^t\text{Bu})_4$  (1:Zr = 1:2) in THF solution with sonication results in precipitation of grayish brown fine particles with concomitant liberation of  ${}^t\text{BuOH}$  (eq 1); the solution thereby becomes a slurry. The precipitation is very rapid, even when a relatively dilute solution (0.01 M in **1**) is used. The yield of the particles (called the Zr host hereafter) is quantitative (>98%) and leaves nothing other than 4 mol of *tert*-butyl alcohol in the bulk solution. The Zr host is readily recovered by centrifugation followed by washing with THF and drying at 80 °C in vacuo. It is formulated as  $\text{1}^{4-} \cdot 2[\text{Zr}(\text{O}^t\text{Bu})_2]$  ( $\text{1}^{4-}$  is the fully deprotonated, tetraanionic form of host **1**) on the basis of elemental (C, H, Zr) analysis, spectral evidence, and the reaction stoichiometry (vide infra). The 1:2 (1 to metal) stoichiometry is strict. When, for example, a 1:4 mixture is used, the 1:2 adduct results as above, and 2 equiv of excess  $\text{Zr}(\text{O}^t\text{Bu})_4$  remains as such in the solution.



The Zr host thus obtained is amorphous and shows no X-ray powder diffraction pattern. Dynamic light scattering indicates a particle size distribution in the range 0.25–3 μm with an average diameter of ~0.7 μm (Figure 1). The IR spectrum (Nujol) shows no absorption in the  $\nu_{\text{OH}}$  region and new bands



**Figure 2.** Isotherm for  $\text{N}_2$  adsorption by the Zr host at 77 K and BET plot (inset): adsorption ( $\blacklozenge$ ) and desorption ( $\blacklozenge$ ).  $V$  (mL) refers to the standard state and  $P_s = 760$  Torr.

at 491 and 541  $\text{cm}^{-1}$  assignable to  $\nu_{\text{Zr}-\text{O}}$ .<sup>5</sup> The solid-state  ${}^{13}\text{C}$  CPMAS spectrum exhibits an ~8 ppm downfield shift (from 155 and 157 ppm in apohost **1** to 164 ppm in the Zr host) in  $\delta_{\text{C}}$  for C–OZr, characteristic of aryloxy zirconium species.<sup>6</sup> This observation, coupled with the IR result, leaves little doubt that host **1** in the Zr host is completely deprotonated ( $\text{1}^{4-}$ ) to give O–Zr bonds.

The Zr host is insoluble in all common aprotic and protic organic solvents and cannot be recrystallized as a consequence. Compared with an analogous Ti–host<sup>2</sup>  $\text{1}^{4-} \cdot 2[\text{TiCl}(\text{O}^i\text{Pr})_3]$  that readily decomposes upon treatment with water, the present Zr host is much more resistant to hydrolysis. However, when treated with 1 N HCl or  $\text{HNO}_3$ , it decomposes into its components (eq 2), where the 1:2:4 stoichiometry is confirmed by  ${}^1\text{H}$  NMR and ICP (inductively coupled plasma) analyses of the solubilized organic (**1** and  ${}^t\text{BuOH}$  in  $\text{DMSO}-d_6$ ) and inorganic ( $\text{Zr}^{4+}$  in 1 N  $\text{HNO}_3$ ) components, respectively. The 1:2 host-to-metal ratio indicates a 2:1 oxygen-to-metal stoichiometry. From the evidence, the Zr host is best described as an amorphous 1:2 coordination polymer composed of tetraanionic polyphenoxide  $\text{1}^{4-}$  and dialkoxyzirconium dications with  $\text{O} \cdots [\text{Zr}^{4+}(\text{O}^t\text{Bu})_2]^{2+} \cdots \text{O}^-$  bridges.<sup>7</sup> Assembly of a divergent tetradentate ligand ( $\text{1}^{4-}$ ) using a 2-connector ( $[\text{Zr}^{4+}(\text{O}^t\text{Bu})_2]^{2+}$ ) may occur in various ways, possibly leading to a 2D (as shown in structure **2**, where  $\cdots = \text{O} \cdots [\text{Zr}^{4+}(\text{O}^t\text{Bu})_2]^{2+} \cdots \text{O}^-$ ) or 1D (structure **3**) network. The actual network may be random, as suggested by the amorphous nature of the material.

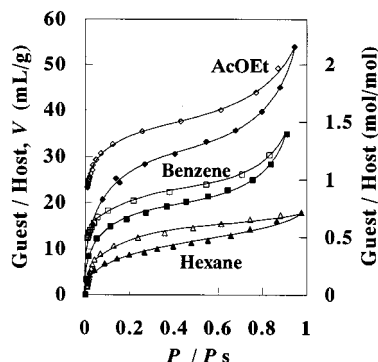
Upon treatment with aqueous alcohol, metal alkoxides (schematically represented as  $-\text{O}-\text{M}-\text{OR}$ ; M = Si, Ti, Zr, etc.) undergo hydrolysis (eq 3), followed by condensation (eq 4; 2(eq 3) + eq 4 = eq 5), to give first a sol containing soluble oligomers and then a polymeric metal oxide gel (wet gel) with entrapped solvent molecules. Removal of the solvent from the wet gel leaves a solvent-free dry gel, which is further calcined at an elevated temperature. This is the so-called sol–gel method.<sup>8</sup> Controlled preparation of porous silica gel from  $\text{Si}(\text{OR})_4$  provides a typical example. In the present procedure, a polyphenol (schematically represented as  $\text{HO}-\text{A}-\text{OH}$ , where A is an organic spacer) is used in place of water to give an  $\text{M}-\text{O}-\text{A}-\text{O}-\text{M}$  bridge (eq 6) rather than  $\text{M}-\text{O}-\text{M}$  (eq 5). Thus, the present procedure may be called an organic modifica-

(5) Chamberlain, L.; Huffman, J. C.; Keddington, J.; Rothwell, I. P. *J. Chem. Soc., Chem. Commun.* **1982**, 805–806.

(6) Kobayashi, S.; Komiyama, S.; Ishitani, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 979–981.

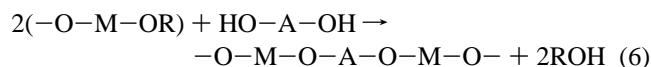
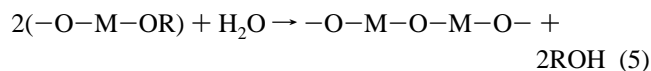
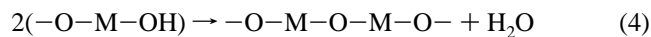
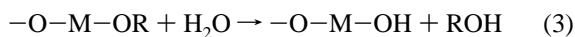
(7) For the reaction of  $\text{Zr}(\text{O}^t\text{Bu})_4$  and binaphthol to form a 1:2 complex with concomitant liberation of 4 mol of  ${}^t\text{BuOH}$ , see: Ishitani, H.; Ueno, M.; Kobayashi, S. *J. Am. Chem. Soc.* **1997**, *119*, 7153–7154.

(8) Hüsing, N.; Schubert, U. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 22–45.



**Figure 3.** Isotherms for hexane, benzene, and ethyl acetate adsorption by the Zr host at 298 K: adsorption ( $\blacktriangle$ ,  $\blacksquare$ ,  $\blacklozenge$ ) and desorption ( $\triangle$ ,  $\square$ ,  $\lozenge$ ). BET plots are shown in the Supporting Information.  $V$  (mL) refers to the standard state and  $P_s = 151, 95,$  and  $97$  Torr for hexane, benzene, and ethyl acetate, respectively.

tion of the sol–gel method,<sup>9</sup> although apparent gelation is observed neither in the preparation of the Zr host nor in its subsequent treatment with a solvent. Pronounced swelling does not occur either. In view of its rapid precipitation, it is not surprising that the Zr host lacks crystalline order. In fact, many dry gels obtained by the sol–gel method are initially amorphous and only crystallize on subsequent calcination.

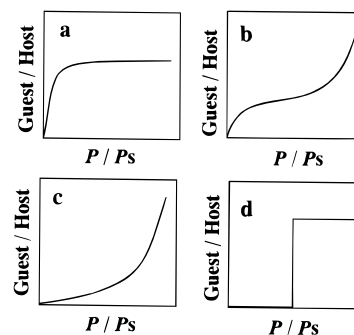


**Guest Binding and Porosity.** The Zr host binds various guest molecules in the gas phase. Typical binding isotherms for  $\text{N}_2$  at 77 K and for hexane, benzene, and ethyl acetate at 298 K are shown in Figures 2 and 3, respectively, where the ratios (mL/g or mol/mol) of guest adsorbed by the Zr host are plotted against guest pressures ( $P$ ) up to 90% of the saturation value ( $P_s$ ) for the adsorption ( $\blacklozenge$ ) and down to 1% for the desorption ( $\lozenge$ ) processes upon computer-controlled stepwise addition or removal of the guest vapor. Each point represents a state where the change in pressure ( $\Delta P$ ) in 3000 s has become smaller than 1% of the pressure ( $P$ ) at that point, i.e.,  $\Delta P \leq 0.01P$ . As a consequence, the isotherms (especially the desorption curves) do not necessarily represent equilibria.

Various types of guest-binding isotherms have been extensively studied for porous and nonporous inorganic materials (Figure 4).<sup>10</sup> Microporous materials generally exhibit a Langmuir curve (type a), since the guest molecules form only a monolayer at micropores with a guest-compatible pore size (diameter 0.5–2 nm). When significant areas of mesopores (2–50 nm) or nonrestricted flat surfaces are available, guest molecules may form multilayers, as characterized by an *exponential* buildup of bound guest. The adsorption curve becomes either type b or c, depending on which of the host–guest or guest–guest interactions is stronger. A nonporous rough material could still

(9) For the preparation of porous organic–inorganic hybrid gel materials by the sol–gel method, see, for example: (a) Choi, K. M.; Shea, K. J. *J. Phys. Chem.* **1994**, *98*, 3207–3214. (b) Choi, K. M.; Shea, K. J. *J. Am. Chem. Soc.* **1994**, *116*, 9052–9060. (c) Choi, K. M.; Hemminger, J. C.; Shea, K. J. *J. Phys. Chem.* **1995**, *99*, 4720–4732.

(10) Gregg, S. J.; Sing, K. S. W. *Adsorption, Surface Area and Porosity*, 2nd ed.; Academic Press: London, 1982.



**Figure 4.** Schematic representation of typical guest adsorption curves. See text for explanation.

form stoichiometric host–guest adducts by a mechanism involving a phase change. This is a phenomenon governed by the phase rule, and guest adsorption occurs suddenly at the equilibrium pressure (type d).<sup>11</sup>

The isotherm for  $\text{N}_2$  adsorption on the Zr host at 77 K (Figure 2) is typical of type a (or type I according to the BDDT classification<sup>12</sup>) but also exhibits characteristics of multilayer formation at higher guest pressures. The rise in guest–host ratio at high  $P/P_s$  may also be due to filling of interparticle spaces. Analysis of the isotherm according to the standard BET equation,<sup>13</sup>  $P/V(P_s - P) = 1/V_m C + [(C - 1)/V_m C](P/P_s)$ , gives  $V_m = 45$  mL/g and  $C = 967$ , where  $V$  (mL/g) is the amount (in terms of volume in the standard state) of guest adsorbed per gram of Zr host,  $V_m$  is the saturation monolayer coverage, and  $C$  is a constant related to the binding strength. The BET plot is shown in the inset of Figure 2. From the known cross-sectional area (0.162 nm<sup>2</sup>) of  $\text{N}_2$ ,  $V_m = 45$  mL/g can be converted into the specific surface area of the Zr host:  $A_{\text{BET}} = 196$  m<sup>2</sup>/g. If the surface area of 200 m<sup>2</sup>/g is to be provided by nonporous spherical particles, they must be ultrafine, with a diameter of  $\sim 30$  nm (0.03  $\mu\text{m}$ ). The particle size of the Zr host is  $\sim 0.7$   $\mu\text{m}$  as noted above, and it must, therefore, be porous.

More detailed information is available from the so-called *t*-plot analysis,<sup>14</sup> which compares the measured isotherm with the standard isotherm for a nonporous material. The *t*-plot for the present  $\text{N}_2$  adsorption isotherm (Figure 5) is of the type characteristic of microporous materials. The slope of the linear AB portion is correlated with the total specific surface area; the derived value of 202 m<sup>2</sup>/g agrees with that obtained from the BET plot (196 m<sup>2</sup>/g). That of the linear CD portion leads to an external (nonmicroporous) surface area of 44 m<sup>2</sup>/g, thus leaving  $202 - 44 = 158$  m<sup>2</sup>/g assignable to the surface of micropores. The external surface may be provided by mesopores.<sup>15</sup> Cross point E shows the average micropore diameter of  $2t \cong 0.8$  nm, while intercept F (45 mL of  $\text{N}_2$  at the standard state) shows the total micropore volume of 63 mm<sup>3</sup>/g. The observed micropore volume is fairly small as compared with

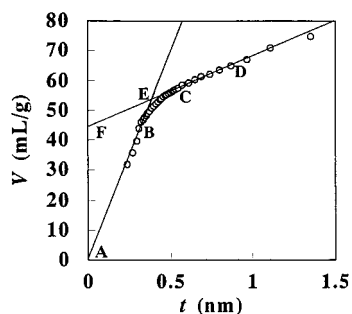
(11) Dewa, T.; Endo, K.; Aoyama, Y. *J. Am. Chem. Soc.* **1998**, *120*, 8933–8940.

(12) Brunauer, S.; Deming, L. S.; Deming, W. E.; Teller, E. *J. Am. Chem. Soc.* **1940**, *62*, 1723–1732.

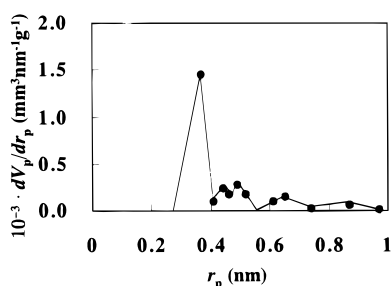
(13) Brunauer, S.; Emmett, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309–319.

(14) (a) Lippens, B. C.; de Boer, J. H. *J. Catal.* **1965**, *4*, 319–323. (b) de Boer, J. H.; Linsen, B. G.; Osinga, Th. J. *J. Catal.* **1965**, *4*, 643–648. (c) de Boer, J. H.; Lippens, B. C.; Linsen, B. G.; Brökhoff, J. C. P.; van den Heuvel, A.; Osinga, Th. J. *J. Colloid Interface Sci.* **1966**, *21*, 405–414.

(15) The so-called DH method (Dollimore, D.; Heal, G. R. *J. Colloid Interface Sci.* **1970**, *33*, 508–519), applied to the present  $\text{N}_2$  adsorption, shows the presence of a small amount of large pores with a diameter of  $\sim 5$  nm.



**Figure 5.**  $t$ -Plot for the adsorption of  $N_2$  by the Zr host at 77 K.  $V$  has the same meaning as in Figure 2, and  $t$  is the thickness of adsorbate ( $N_2$ ) on a standard nonporous adsorbent: each point of  $P/P_s$  in Figure 2 was converted to  $t$  by using the standard isotherm for nonporous silica.



**Figure 6.** Distribution of micropore sizes in the Zr host:  $r_p$  is the pore radius, and  $V_p$  is the total volume of pores having a radius of  $\leq r_p$ .

those (200–300  $\text{nm}^3$ ) for zeolites,<sup>16</sup> but it still compares to that of, e.g., ZSM-5 with 30% crystallinity. As suggested by the relatively sharp break point in the nonlinear BC portion, the present micropores have a rather uniform distribution in size (Figure 6, obtained by the so-called MP method<sup>17</sup>); a maximal population occurs at a pore radius of  $r_p \approx 0.35$  nm and hence a pore diameter of  $\sim 0.7$  nm, which falls in a typical range of pore sizes in zeolite molecular sieves.<sup>1</sup>

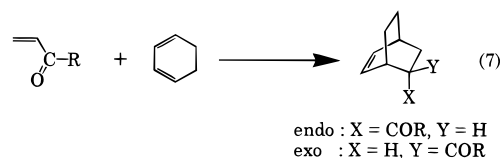
<sup>129</sup>Xe NMR spectroscopy is a popular technique for the study of microporous materials.<sup>18</sup> When incorporated in zeolite pores, <sup>129</sup>Xe resonances usually undergo significant (50–300 ppm) downfield shifts. A study on H-Rho shows two types of resonances: one at  $\delta_{Xe} \approx 110$  ppm downfield of gaseous Ze ( $\delta_{Xe} = 0$ ) is insensitive to temperature, and the other is highly temperature-dependent, changing from  $\delta_{Xe} = 140$  ppm at 343 K to 230 ppm at 218 K.<sup>19</sup> Preliminary studies indicate that, in the presence of the Zr host, <sup>129</sup>Xe resonates in a temperature-dependent manner at  $\delta_{Xe} = 120$  (273 K), 140 (223 K), or 175 ppm (173 K); another signal at 90 ppm also appears at 173 K. These data might indicate two types of pores.<sup>19</sup>

The adsorption isotherms for organic guests (Figure 3) are similar to that for  $N_2$ . The BET plots (Supporting Information) give  $V_m = 6.9$ , 14, and 15 mL/g for hexane, benzene, and ethyl acetate, respectively, at 298 K. The desorption curves for different guests are, again, more or less similar to each other. The excess amount adsorbed in multilayers at higher guest

pressures can be desorbed readily but with hysteresis. This is characteristic of guest desorption from the mesopores<sup>15</sup> having an ink bottle shape, where the hysteresis is often explained in terms of capillary condensation. The ease of desorption of a guest adsorbed in a monolayer at low guest pressures is guest-dependent. The least polar guests ( $N_2$  and hexane) can be desorbed most readily (Figures 2 and 3) and exhibit a high degree of adsorption/desorption reversibility. There are examples of robust crystalline coordination networks capable of sustaining guest-free cavities.<sup>20</sup> Some of them show well-behaved reversible Langmuir-type binding isotherms for small guests.<sup>21</sup> As an amorphous coordination polymer, the Zr host can do the same thing. The more polar guests (benzene and ethyl acetate) resist desorption at 298 K (Figure 3), although they are removed readily at higher temperatures. The IR spectrum for the ethyl acetate adduct at an approximate host:guest ratio of 1:1.3 exhibits a significant complexation-induced shift in  $\nu_{C=O}$  of 41  $\text{cm}^{-1}$  (from 1745 to 1704  $\text{cm}^{-1}$ ), indicative of metal coordination (Zr(IV)···O=C).

Guest binding occurs rapidly when the Zr host is treated with benzene (6), 1,3-cyclohexadiene (4), ethyl acetate (4), acrolein (4), methyl vinyl ketone (4), or alkyl acrylate (4, alkyl = methyl, ethyl, hexyl, or *tert*-butyl) as a liquid; the numbers in parentheses are the approximate guest:host ratios in the resultant adducts. Since the guest:host ratios at monolayer coverage are  $\leq 1$  for benzene and ethyl acetate (Figure 3), the excess amount of guest adsorbed may be trapped in mesopores.<sup>15</sup> As suggested by the above data, the present solid-state complexation is rather indiscriminate between polar and apolar guests. When immersed in an equimolar mixture of ethyl acetate and benzene, the Zr host affords an apparent ternary adduct with a molar ratio of host:ester:benzene  $\approx 1:5:2$ . On the other hand, the present complexation is highly size-selective. Competition between methyl acrylate and *tert*-butyl acrylate is in favor of the former by a factor of 98:2. Guest exchange also occurs readily. When immersed in methyl acetate, the ethyl acetate adduct (Zr host)·4(CH<sub>3</sub>CO<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>) undergoes complete guest exchange to give the methyl acetate adduct (Zr host)·4(CH<sub>3</sub>CO<sub>2</sub>CH<sub>3</sub>) within 1 min.

**Catalysis.** The Zr host catalyzes the Diels–Alder reaction between acrolein and 1,3-cyclohexadiene (eq 7, R = H).<sup>22</sup> The



reaction is complete in  $\sim 3$  h when a mixture of dienophile and diene (1:20)<sup>23</sup> is stirred at 25 °C with the Zr host (3 mol % (as  $1^4 \cdot 2[\text{Zr}(\text{O}^i\text{Bu})_2]$ ) of the limiting reactant acrolein). Centrifugation, followed by washing with the diene, readily separates the liquid organic layer and the solid catalyst. The organic layer is (by ICP) free of Zr ( $< 0.001\%$  of that used) and, after removal

(16) Breck, D. W.; Grose, R. W. *Prepr. 3rd Conf. MS Zeolites* **1973**, 319.

(17) Mikhail, R. S.; Brunauer, S.; Boder, E. E. *J. Colloid Interface Sci.* **1968**, 26, 45–53.

(18) (a) Ito, T.; Fraissard, J. *J. Chem. Phys.* **1982**, 76, 5225–5228. (b) Ripmeester, J. A. *J. Am. Chem. Soc.* **1982**, 104, 289–290. (c) Dybowski, C.; Bansal, N.; Duncan, T. M. *Annu. Rev. Phys. Chem.* **1991**, 42, 433–464. (d) Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. *Appl. Magn. Reson.* **1995**, 8, 385–399. (e) Moudrakovski, I. L.; Ratcliffe, C. I.; Ripmeester, J. A. *J. Am. Chem. Soc.* **1998**, 120, 3123–3132.

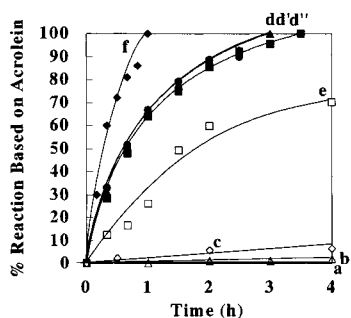
(19) Ito, T.; Fraissard, J. *Zeolites* **1987**, 7, 555–562.

(20) (a) Venkataraman, D.; Gardner, G. B.; Lee, S.; Moore, J. S. *J. Am. Chem. Soc.* **1995**, 117, 11600–11601. (b) Yaghi, O. M.; Li, H. *J. Am. Chem. Soc.* **1996**, 118, 295–296. (c) References 2k and 2l. (d) Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, 118, 9096–9101. (e) Yaghi, H.; Davis, C. E.; Groy, T. L.; Kelly, D. G.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, 120, 2186–2187.

(21) (a) Li, H.; Eddaoudi, M.; Groy, T. L.; Yaghi, O. M. *J. Am. Chem. Soc.* **1998**, 120, 8571–8572. (b) Kondo, M.; Yoshitomi, T.; Seki, K.; Matsuzaka, H.; Kitagawa, S. *Angew. Chem., Int. Ed. Engl.* **1997**, 36, 1725–1726.

(22) See refs 6 and 7 for catalytic asymmetric transformations using soluble Zr(IV) complexes derived from binaphthol.

(23) A large excess amount of diene is used to keep the mixture fluid.



**Figure 7.** Time courses of acrolein-1,3-cyclohexadiene Diels–Alder reactions under nitrogen at 25 °C in the absence (a) and presence of soluble  $\text{Zr}(\text{O}^t\text{Bu})_4$  (b, 3 mol % based on acrolein), insoluble apohost **1** (c, 3 mol %), or insoluble Zr host  $\mathbf{1}^{4-} \cdot 2[\text{Zr}(\text{O}^t\text{BuO})_2]$  (e, 1 mol %; d, 3 mol %, f, 6 mol %) as a catalyst with molar acrolein:diene = 1:20; the amount of catalyst is in reference to the limiting reactant acrolein. Runs d' and d'' refer to the second and third runs using the Zr host recovered from runs d and d', respectively.

of excess diene, affords the Diels–Alder product (endo:exo = 95:5) in a practically pure form in  $\geq 98\%$  yield (based on dienophile) with no contamination by host **1** or  $^t\text{BuOH}$ . The solid catalyst recovered weighs  $>98\%$  of the original catalyst  $\mathbf{1}^{4-} \cdot 2[\text{Zr}(\text{O}^t\text{Bu})_2]$  and is analyzed as such; the butoxy moieties remain intact during the catalytic process. Thus, there is no leak of metallic or organic components of the catalyst into the organic product.

Figure 7 shows the time courses of the above reaction in the absence (a, half-life is  $\tau = 500$  h) and presence (3 mol % of acrolein) of  $\text{Zr}(\text{O}^t\text{Bu})_4$  (b,  $\tau = 140$  h) as a soluble catalyst or apohost **1** (c,  $\tau = 50$  h)<sup>4b</sup> or the Zr host (d,  $\tau = 40$  min) as an insoluble catalyst. Those for Zr host at 1 mol % (e,  $\tau = 100$  min) and 6 mol % (f,  $\tau = 20$  min) are also shown. There is good linearity between catalytic rates and amounts of Zr host. As in the case of apohost **1**,<sup>4b</sup> the catalytic efficiency of the Zr host is little affected by pulverization, and there is no notable dependence on the sample batch (see Experimental Section). When the Zr host is removed in the course of reaction, the time course for the supernatant liquid left has the same slope as for the uncatalyzed reaction a. Thus, the solid state of the Zr host is convincingly responsible for its catalysis, and the catalytic activity far exceeds those of its precursors, i.e., the soluble Lewis acid and the insoluble hydrogen-bonded network. The turnover rate constants, (mol of product formed)/[(mol of catalyst used) · h], at an early stage of the reactions are 40, 0.3, and 0.1  $\text{h}^{-1}$  for the Zr host, apohost **1**, and  $\text{Zr}(\text{O}^t\text{Bu})_4$ , respectively. Time courses d' and d'' represent repeated runs using the catalyst recovered from runs d and d', respectively. There is almost no deactivation of the catalyst upon recovery and it can be used repeatedly.

The reaction can also be carried out as a flow system by using the Zr host as an immobile catalyst phase. Application of a 1:20 (dienophile to diene)<sup>23</sup> reactant mixture to the Zr host (3 mol % of acrolein) packed in a glass column affords a continuous elution of Diels–Alder product without contamination by the catalyst or unreacted acrolein. This procedure can be repeated many times without causing a notable deactivation of the catalyst (see Experimental Section).

The reaction of methyl vinyl ketone (eq 7,  $\text{R} = \text{CH}_3$ ), methyl acrylate ( $\text{R} = \text{OCH}_3$ ), ethyl acrylate ( $\text{R} = \text{OCH}_2\text{CH}_3$ ), or *tert*-butyl acrylate ( $\text{R} = \text{OC}(\text{CH}_3)_3$ ) with cyclohexadiene is also catalyzed by the Zr host (3 mol %) with a half-life ( $\tau_{\text{hetero}}$ ) of 2.6 h at 25 °C, 2.8 h at 40 °C, 3.7 h at 60 °C, or 250 h at 60 °C, respectively. The half-lives ( $\tau_{\text{homo}}$ ) of the corresponding reactions catalyzed by homogeneous  $\text{Zr}(\text{O}^t\text{Bu})_4$  (3 mol %) under otherwise

identical conditions are 200, 60, 16, and 230 h, respectively. The preference factors ( $r = \tau_{\text{homo}}/\tau_{\text{hetero}}$ ) for the heterogeneous catalysis over the homogeneous one decrease sharply with increasing steric bulkiness of the dienophiles,  $r = 210, 80, 20, 4$ , and 0.9 for acrolein, methyl ethyl ketone, methyl acrylate, ethyl acrylate, and *tert*-butyl acrylate, respectively. Competitive reactions indicate that the methyl and *tert*-butyl esters have similar intrinsic reactivities when the reactions are uncatalyzed. In the presence of the Zr host, an exclusive ( $>200:1$ ) reaction of the less bulky methyl ester takes place, in accord with the high methyl/*tert*-butyl selectivity (98/2) in competitive guest-binding to the Zr host (vide supra).

The Zr host has microporous and nonmicroporous regions as the sites of guest binding. A question is how they contribute to the catalytic processes. A criterion to distinguish reactions in the pores and those on the surface is the size dependence. The surface reactions may be dependent on the particle size of the catalyst and hence pulverization thereof, while those in the pores should exhibit some kind of size selectivity with respect to the reactants. In the present system, as noted above, the catalytic efficiency depends little on the particle size of the catalyst (Zr host) but dramatically on the molecular size of the dienophiles. This is taken as evidence that internal micropores of pore size of 0.7 nm play essential roles in the catalysis by the Zr host.

Control runs reveal the following elementary processes. (1) When immersed in a reactant mixture of acrolein and cyclohexadiene (1:20), the Zr host rapidly forms a ternary adduct. (2) When the resulting adduct with a Zr host:dienophile:diene ratio of 1:1.9:2.4 is isolated and kept in contact with guest vapors in a sealed vessel, the guest molecules trapped react completely with each other to give the Diels–Alder product as an adduct in  $\sim 10$  min. (3) When the product adduct (with a Zr host:product:dienophile:diene ratio of 1:1.9:0:0.2) is immersed again in the reactant mixture, a facile product/reactant exchange occurs in  $<1$  min to regenerate the reactant adduct. These results suggest a catalytic cycle composed of coadsorption of dienophile and diene, rate-determining intrapore Diels–Alder reaction, and turnover of the catalyst upon product/reactant exchange. This assignment of the rate-determining reaction is supported by the observation that the catalyst exists as the reactant adduct during the catalytic process. The enhancement of intrapore reactions may result from proximity of coadsorbed reactants in the pores and polarization of the dienophile via metal coordination, although the amorphous nature of the catalyst allows no deeper insight into the catalytic mechanism.

## Concluding Remarks

This work is a step toward functional zeolite analogues, especially from the practical point of view. The Zr host is prepared in a remarkably simple manner. It possesses permanent pores capable of reversible guest binding. It is far more catalytically active than its precursors. It is completely insoluble and can be used repeatedly or continuously in a batch or flow system. This opens the door to the construction of reactant-in/product-out type automatic molecular transformations that are workup- and waste-free and hence energy-saving, resource-saving, and friendly to the environment.

It is a pity that the amorphous nature of the Zr host prevents its further structural elucidation. However, various analytical methods used for porous inorganic materials can also be applied to the present system, allowing useful insight into the pores. The micropores with pore size of 0.7 nm may essentially result from cavities intrinsic to the network.

As an organic modification of the sol–gel procedure,<sup>9</sup> the present method may be applicable to various combinations of network-forming polyphenols and soluble metal complexes with labile ligands. Sol–gel processes generally proceed slowly. In marked contrast, the precipitation of the Zr host is rapid and apparently irreversible. In addition, the geometrical requirements of hydrogen-bonding and metal coordination differ greatly. The amorphous nature of the present type of material might be a necessity of the strategy used. An important future concern is how we can *control*, in both kinetic and thermodynamic senses, the polycondensation between polyphenols and metal alkoxides. This may allow crystalline modification of the materials and provide a means of manipulating pore and particle sizes.

## Experimental Section

**Materials and Instruments.** The IR and <sup>1</sup>H, <sup>13</sup>C CPMA, and <sup>129</sup>Xe NMR spectra were obtained with a JEOL JIR-WINSPEC-50 FT-IR spectrophotometer and a Bruker DPX 400, a Bruker DRX 300, and a JEOL  $\alpha$ -400 spectrometer, respectively. Combustion (C and H) analyses were performed at the Microanalysis Center of Kyushu University. To determine Zr contents, samples were treated with 1 N HNO<sub>3</sub>, and the resultant Zr<sup>4+</sup>-containing solutions were analyzed by inductively coupled plasma (ICP) spectroscopy using a Shimadzu ICPS-7500 sequential plasma spectrometer with calibration against standard Zr<sup>4+</sup> solutions (0–50 ppm) in 1 N HNO<sub>3</sub>. The binding isotherms were obtained as reported<sup>11</sup> with a BELSORP 18 automated gas adsorption apparatus with a waiting time of 3000 s. The dynamic light-scattering experiments were performed on an Otsuka Electronics DLS 7000 DL apparatus for a dispersion of the Zr host (1 mmol) in THF. Capillary GLPC was carried out with a Shimadzu GC-14B gas chromatograph on a column (0.32 mm  $\times$  30 m) of Neutra Bond-1 (GL Science Inc.) at 100–200 °C with helium as a carrier gas. The endo and exo stereoisomers of the acrolein–cyclohexadiene Diels–Alder product had retention times of 6.37 and 5.69 min, respectively. THF, benzene, 1,3-cyclohexadiene, and polar guests (ethyl acetate, acrolein, methyl ethyl ketone, and alkyl acrylate (alkyl = methyl, ethyl, hexyl, and *tert*-butyl) were dried on Na, CaH, and 4-Å molecular sieves, respectively. The diene for catalytic runs was degassed by freeze–thaw cycles. Zr(O<sup>*t*</sup>-Bu)<sub>4</sub> (Aldrich) was used as received. Host **1** was prepared as described.<sup>4a</sup>

**Zr Host.** Into a THF solution (5 mL) of host **1** (25 mg, 0.063 mmol) was added at once under nitrogen at room temperature Zr(O<sup>*t*</sup>-Bu)<sub>4</sub> (50  $\mu$ L, 49 mg, 0.128 mmol) from a microsyringe under magnetic stirring and sonication (bath type). Precipitation of grayish brown powders immediately occurred, and the slurry mixture was stirred for 1 h under sonication and for 24 h without sonication. Sonication was essential to obtain the material as powders. Otherwise, it was obtained as a block, which often prevented smooth stirring. The powders were recovered by centrifugation and washed with THF. At this stage, the material contained a significant amount of THF, which was removed upon heating at 80 °C in vacuo to leave the solvent-free Zr host (54 mg, 0.062 mmol as  $\text{I}^{4+} \cdot 2[\text{Zr}(\text{O}^t\text{Bu})_2]$ ) in a yield of 98%: mp  $\sim$ 185 °C dec; IR (Nujol) 1573, 1459, 1162, 1014, 862, 541, 491 cm<sup>-1</sup>; <sup>13</sup>C CPMA  $\delta$  164 (C–OZr), 138, 129, 114, 76, 32. On standing, even when kept in a sealed vessel, the Zr host gradually absorbed 4 mol of water. Anal. Calcd for C<sub>42</sub>H<sub>50</sub>O<sub>8</sub>Zr<sub>2</sub>·4H<sub>2</sub>O ( $\text{I}^{4+} \cdot 2[\text{Zr}(\text{O}^t\text{Bu})_2] \cdot 4\text{H}_2\text{O}$ ): C, 53.82; H, 6.24; Zr, 19.46. Found: C, 53.90; H, 6.16; Zr (ICP), 19.3. For measurements of isotherms, the Zr host obtained was ground into powders in a mortar. The Zr host, separated from a THF solution and recovered by centrifugation as above, was washed with two 3-mL portions of THF and two 3-mL portions of 1,3-cyclohexadiene and was used, without isolation, for catalytic reactions.

Upon treatment with two drops of 1 N HCl, the Zr host suspended in DMSO-*d*<sub>6</sub> gradually turned to pale yellow and gave a homogeneous solution whose <sup>1</sup>H NMR spectrum showed the presence of host **1** and *tert*-butyl alcohol (1:4) with no unidentified signals. A mixture of Zr host (20 mg) and 1 N HNO<sub>3</sub> (100 mL) was shaken for 5 min, left for 24 h, and then filtered. The aqueous solution was analyzed for the Zr

content as above, and the organic solid dissolved in DMSO-*d*<sub>6</sub> was analyzed for host **1** by <sup>1</sup>H NMR with an appropriate internal standard. A ratio of **1**:Zr = 1:2 in the Zr host was thereby confirmed.

**Catalytic Reactions.** A mixture of acrolein (0.116 g, 2.07 mmol), 1,3-cyclohexadiene (3.4 g, 43 mmol), and Zr host (54 mg, 0.062 mmol) was stirred at 25 °C for 24 h under nitrogen. The catalyst, recovered by centrifugation followed by washing with benzene and drying at 80 °C in vacuo, weighed 53 mg (98%) and was assigned as unchanged Zr host on the basis of all the above analytical methods. The organic layer and the benzene washings were combined. Removal of the solvent and excess diene left  $\sim$ 0.280 g ( $\sim$ 100%) of the Diels–Alder product (endo:exo = 95:5 by <sup>1</sup>H NMR and GLPC), which was free of organic (**1** or <sup>*t*</sup>BuOH, by <sup>1</sup>H NMR) as well as metallic ( $<$ 0.001% of Zr<sup>4+</sup> used, by ICP) components of the catalyst.

A 750 mg (0.87 mmol) portion of the Zr host was packed in a glass column (inner diameter 1 cm) to a height of 3 cm. To the resulting immobile catalyst phase was added continuously under nitrogen at room temperature a mixture of acrolein (1.34 g, 24 mmol) and cyclohexadiene (50 mL, 42 g, 525 mmol) at a rate that maintained a 3-cm height of the mobile reactant phase above the catalyst phase. Elution took 2.5 h to be completed. The eluate, with an additional small amount of diene, used to flush the column was analyzed as above; the yield of Diels–Alder product was 3.19 g (98%) and the absence of host **1**, <sup>*t*</sup>BuOH, or Zr<sup>4+</sup> ( $<$ 0.001% of Zr<sup>4+</sup> used) was confirmed as in the batch system. This procedure was repeated 3 more times using the same column to give a nearly quantitative yield of the product each time: 3.18 (97%), 3.19 (98%), and 3.17 g (97%). Even in the fourth run, the reaction was complete with no leak of the catalyst into the organic product.

Kinetic runs were initiated by adding 0.116 g (2.07 mmol) of acrolein to cyclohexadiene (3.4 g, 43 mmol) with or without a catalyst under stirring. The reaction was monitored by <sup>1</sup>H NMR for aliquots taken at appropriate time intervals ( $\delta$  = 9.41 and 9.55 for the formyl proton in the product (endo) and reactant acrolein, respectively). The Zr host used in standard kinetic runs was obtained by centrifugation followed by washing (sample a, *vide supra*). Isolated samples were also used with (sample b) or without (sample c) pulverization in a mortar. Even nonpulverized samples readily gave a slurry when treated with a reactant mixture. The catalytic efficiencies, in terms of half-lives of the reactions, of the three samples a, b, and c of the Zr host were remarkably similar (within 15%) to each other. Another set of control runs were carried out by using the Zr host from five different batches, where the half-lives were reproducible within 10%.

The reactions using a dienophile other than acrolein were carried out with the same reactant molar ratios at 25 °C for methyl vinyl ketone, 40 °C for methyl acrylate, or 60 °C for ethyl and *tert*-butyl acrylate. They were followed by monitoring the characteristic <sup>1</sup>H NMR signals in the products, *CHCOX* at  $\delta \approx$  2.9 (X = CH<sub>3</sub>, OCH<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub>, or OC(CH<sub>3</sub>)<sub>3</sub>) and/or the methyl or methylene (OCH<sub>2</sub>) protons which resonated 0.1–0.15 ppm upfield of those in the reactant dienophiles.

**Acknowledgment.** This work was supported by CREST (Core Research for Evolutional Science and Technology) of the Japan Science and Technology Corp. (JST) and also by a grant-in-Aid for COE Research (No. 08CE2005) from the Ministry of Education, Science, and Culture, Japan. We are grateful to Ms. Miyuki Kazunori (Asahi Chemical Industry Co., Ltd.) for measuring <sup>129</sup>Xe NMR spectra, Dr. N. Tamura (JST) and Prof. S. Kobayashi (University of Tokyo) for helpful suggestions and discussions, and Prof. J. A. Ripmeester (National Research Council of Canada) for calling our attention to Xe-NMR spectroscopy.

**Supporting Information Available:** One figure, showing BET plots for the adsorption of hexane, benzene, and ethyl acetate by the Zr host (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.