Immobilization of Soluble Metal Complexes with a Hydrogen-Bonded Organic Network as a Supporter. A Simple Route to Microporous Solid Lewis Acid Catalysts

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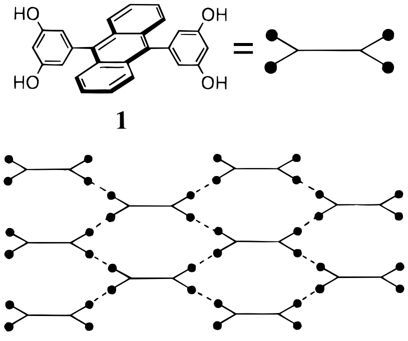
Received December 22, 1997

Despite much recent interest in microporous organic solids having zeolitic guest-binding properties,[1] their catalytic activities still remain a subject of challenge.[1j] We have recently shown that an anthracene bisresorcinol derivative **1** (apohost) as a hydrogen-bonded polycrystalline solid catalyzes the Diels−Alder[2] and related ene reactions.[3] This prompted us to move to metalated hosts, since metal ions play essential roles in organic syntheses. In the present work, we tried to convert the hydrogen-bonded network in apohost **1** (structure **2** in Scheme 1; ●- - -● = OH⋯OH) into a metal-coordination network (●- - -● = $O^-{-}M^{n+}{-}O^-$) by allowing the former to react with a soluble Lewis acid complex having labile ligands. We report here that this simple procedure affords microporous metal−organic amorphous powders, which exhibit remarkable activities and advantages as solid Lewis acid catalysts.

Treatment of host **1** with $(^i\mathrm{PrO})_2\mathrm{TiCl}_2$ affords a highly insoluble orange-colored amorphous solid (Ti-host hereafter) formulated as $\mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}]$ (eq 1).[4,5] Spectral (IR and ^{13}C CPMAS NMR) evidence for the exhaustive H/Ti exchange,[6] coupled with the stoichiometry of **1**:Ti = 1:2, i.e., O:Ti = 2:1,[5] indicates that deprotonated tetraanionic species of the host ($\mathbf{1}^{4-}$) are extensively networked via O−Ti−O bridges. This is illustrated by structure **2** (●- - -● = $O^-{-}(^i\mathrm{PrO})\mathrm{Ti(Cl)}{-}O^-$), although the actual network would likely be more random. Such a network may generate coordinatively unsaturated metal centers. Ti-host, in fact, binds 4 mol of polar guests (i.e., in a metal:guest ratio of 1:2)[5] such as ethyl acetate, ethyl acrylate, and acrolein. In the resulting adduct $\mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}]\cdot 4(\mathrm{CH_3CO_2CH_2CH_3})$,[5] ethyl acetate guests exhibit characteristic complexation-induced shifts in $\nu_{\mathrm{C=O}}$ by 56 cm^{-1} (from 1745 to 1689) and in δ_C (C═O) by 10 ppm (from 170 to 180). Desorption of the guests occurs readily even at room temperature and regenerates guest-free Ti-host $\mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}]$.[5]

Scheme 1



1

2

$$\mathbf{1} + 2[(^i\mathrm{PrO})_2\mathrm{TiCl}_2] \rightarrow \mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}] + 2\,^i\mathrm{PrOH} + 2\mathrm{HCl} \quad (1)$$

The use of $\mathrm{Al(CH_3)_3}$ in place of $(^i\mathrm{PrO})_2\mathrm{TiCl}_2$ affords an analogous Al-host $\mathbf{1}^{4-}\cdot 2(\mathrm{AlCH_3})$,[5,7] having again a 1:2 (**1** to metal) stoichiometry. It binds ∼6 mol of ethyl acetate. This results in spectral changes not only for the guest ($\Delta\nu_{\mathrm{C=O}} = 58$ cm^{-1} and $\Delta\delta_\mathrm{C} = 14$ ppm) but also for the metal. The ^{27}Al MAS NMR signals for Al-host are weak and broad (Figure 1a). Its adduct $\mathbf{1}^{4-}\cdot 2(\mathrm{AlCH_3})\cdot 6(\mathrm{CH_3CO_2CH_2CH_3})$ shows much sharper resonances of higher intensity preferentially at ∼0 ppm (1b) and regenerates the guest-off spectrum upon desorption of the guest (1c). Such a change in spectra suggests that the aluminum centers of low symmetry in guest-free Al-host become more symmetric in a hexacoordinated octahedral geometry upon guest binding.[8] Combined evidence from the metal:guest ratio, shifts in $\nu_{\mathrm{C=O}}$ and δ_C for the guest, guest-sensitive change in the metal (Al) coordination geometry, and interconvertible guest-on/guest-off spectra (^{13}C and ^{27}Al) leave almost no doubt that the polar guests are bound to each metal center via coordination (C═O⋯metal).

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

(2) Endo, K.; Koike, T.; Sawaki, T.; Hayashida, O.; Masuda, H.; Aoyama, Y. *J. Am. Chem. Soc.* **1997**, *119*, 4117−4122.

(3) Sawaki, T.; Endo, K.; Kobayashi, K.; Hayashida, O.; Aoyama, Y. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 3075−3079.

(4) A suspension of apohost **1** in a benzene or 1,3-cyclohexadiene solution of $(^i\mathrm{PrO})_2\mathrm{TiCl}_2$ (Ti/**1** = 2 or 4) was stirred under nitrogen at room temperature for 24 h. The solid, which had turned reddish-brown, was collected, washed, and dried in vacuo at 100 °C for 12 h. The orange powder thus obtained showed a broad reflectance extending into >600 nm, exhibited no XRPD, and was soluble in none of apolar organic solvents. All possible operations were carried out in a glovebox. Anal. Found: C, 56.48; H, 4.43; Cl, 9.79; Ti (X-ray fluorescence), 14.5. Calcd for $\mathrm{C_{32}H_{28}O_6Cl_2Ti_2}$ ($\mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}]$): C, 56.92; H, 4.18; Cl, 10.50; Ti, 14.2. Treatment of a THF solution of host **1** with $(^i\mathrm{PrO})_2\mathrm{TiCl}_2$ affords solid materials which have incomplete H/Ti exchange and are catalytically less active than Ti-host prepared under the present heterogeneous conditions.

(5) Ti-host, Al-host, and their adducts are readily hydrolyzed to liberate soluble organic components (host **1**, 2-propanol, and guest) and metal ion, which were analyzed by ^{1}H NMR (in DMSO-d_6) and atomic absorption (in 2 N $\mathrm{H_2SO_4}$), respectively, to confirm the stoichiometries indicated.

(6) The complete conversion of OH to OTi in host **1** was confirmed by the lack of $\nu_{\mathrm{O-H}}$ with concomitant appearance of new bands assignable (Bradley, D. C.; Mehrotra, R. C.; Gaur, D. P. *Metal Alkoxides*; Academic Press: London, 1978) to $\nu_{\mathrm{O-Ti}}$ at ∼640 cm^{-1} and $\nu_{\mathrm{C-OTi}}$ at 1026 cm^{-1} and a ∼10 ppm downfield shift (from 155 and 157 in apohost **1** to 166) in δ_C (^{13}C CPMAS) for *C*-OTi, characteristic of aryloxy titanium species (Mikami, K.; Terada, M.; Nakai, T. *J. Am. Chem. Soc.* **1989**, *111*, 1940−1941; **1990**, *112*, 3949−3954).

(7) Characterized in a manner similar to that for Ti-host ($\delta_\mathrm{C} = -9$ ppm for $\mathrm{CH_3{-}Al}$ by ^{13}C CPMAS) and also by volumetry for the methane evolved in the preparation ($\mathbf{1} + 2\mathrm{Al(CH_3)_3} \rightarrow \mathbf{1}^{4-}\cdot 2(\mathrm{AlCH_3}) + 4\mathrm{CH_4}$). Anal. Found: C, 70.63; H, 4.54; Al, 11.1. Calcd for $\mathrm{C_{28}H_{20}O_4Al_2}$: C, 70.89; H, 4.25; Al, 11.4.

(8) It is well-known that hexa- and tetracoordinated Al nuclei resonate at ∼0 and ∼70 ppm, respectively, (e.g., Müller, D.; Gessner, W.; Behrens, H.; Scheler, G. *Chem. Phys. Lett.* **1981**, *79*, 59−62) and less symmetrically coordinated nuclei give broader resonances due to enhanced quadrapole interactions (e.g., Hayashi, S.; Ueda, T.; Hayamizu, K.; Akiba, E. *J. Phys. Chem.* **1992**, *96*, 10922−10928).

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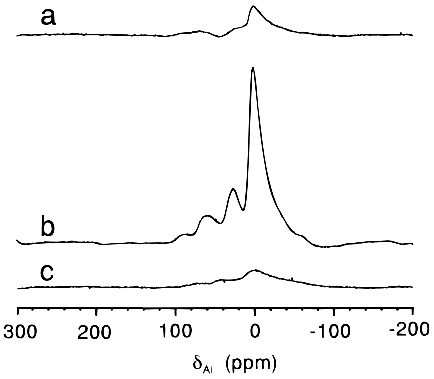

Figure 1. (a) ^{27}Al MAS NMR spectra at room temperature for Al-host, (b) ethyl acetate adduct thereof, (c) and Al-host regenerated upon guest removal. The chemical shifts are in reference to $Al(OH_2)_6^{3+}$ in water.

The specific surface areas are $A_{BET} = 80$ m^2/g for Ti-host and 240 m^2/g for Al-host.[9] Thus, they have a higher degree of microporosity as compared with apohost **1**, which is almost nonporous ($A_{BET} = 7$ m^2/g) and undergoes a phase change upon formation of hydrogen-bonded host−guest adducts. This may be why the present metalated hosts are also capable of reversible incorporation of hydrocarbon guests such as benzene and 1,3-cyclohexadiene (4−6 mol). Coadsorption of polar and nonpolar guests is also confirmed. When immersed in benzene, a 1:4 acrolein adduct of Ti-host picks up ∼2 mol of the former while keeping the metal-coordinated polar guests and gives rise to a ternary adduct $\mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}]\cdot 4(\mathrm{H_2C{=}CHCHO})\cdot 2(\mathrm{C_6H_6})$.[5] When 1,3-cyclohexadiene is used in place of benzene, a facile Diels−Alder reaction takes place. Most of the product remains inside of Ti-host but is released upon addition of acrolein.

As suggested by the above observations, Ti-host catalyzes the acrolein-1,3-cyclohexadiene Diels−Alder reaction. In Figure 2, are shown the time courses of the reactions at 25 °C in the absence (a, half-life is $\tau = 500$ h) and presence (3 mol % of the limiting substrate acrolein) of Ti-host[10] (b, $\tau = 5$ min) or apohost (c, $\tau = 50$ h)[2] as an insoluble catalyst or $(^i\mathrm{PrO})_2\mathrm{TiCl_2}$ (d, $\tau = 1$ h) as a soluble catalyst.[11] Those for Ti-host at 1 mol % (e, $\tau = 10$ min) and 6 mol % (f, $\tau = 2.5$ min) are also shown. The characteristic aspects are as follows: (1) The catalytic activity of Ti-host $\mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}]$ is much higher than those of its components, i.e., not only apohost **1** but also the soluble $\mathrm{Ti^{4+}}$ counterpart, $(^i\mathrm{PrO})_2\mathrm{TiCl_2}$. (2) The Ti-host-catalyzed reaction is not only the most efficient but also the most stereoselective; the endo/exo product ratios are 90/10 (run a), 95/5 (c), 97/3 (d), and >99/1 (b, e, and f). (3) Ti-host as a solid catalyst can be readily recovered by filtration or decantation followed by washing and, hence, repeatedly used without undergoing a significant deactivation (run b′ in Figure 2).[10] (4) Ti-host (3 mol %) also catalyzes ($\tau = 5.3$ h) the highly stereoselective (endo/exo ≅ 100/0) Diels−Alder reaction of ethyl acrylate with 1,3-cyclohexadiene at 60 °C, which apohost **1** fails to catalyze because of the lack of desorption of the product from the host cavities.[2] Al-host $\mathbf{1}^{4-}\cdot 2(\mathrm{AlCH_3})$ also catalyzes the Diels−Alder reactions in a similar manner (τ and endo/exo are <1 min and >99/1 for acrolein at 25 °C and 4.3 h and ∼100/0 for ethyl acrylate at 60 °C).

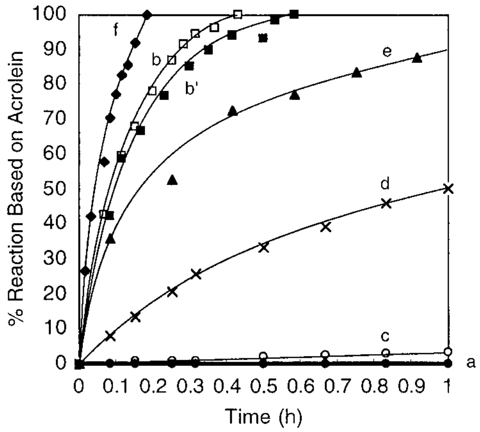

Figure 2. Time courses of the acrolein-1,3-cyclohexadiene Diels−Alder reaction under nitrogen at 25 °C in the absence (a) and presence of insoluble Ti-host $\mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}]$ (e, 1 mol %; b, 3 mol %; f, 6 mol %), insoluble apohost **1** (c, 3 mol %), or soluble $(^i\mathrm{PrO})_2\mathrm{TiCl_2}$ (d, 3 mol %) as a catalyst under conditions of acrolein/diene = 1/20; the amount of catalyst is in reference to the limiting substrate acrolein. Run b′ refers to the second run using Ti-host recovered from run b.

In summary, soluble Lewis acid complexes can be immobilized by using a known hydrogen-bonded organic supporting network as a microporous multiligand. The resulting metal−organic solid having potential internal cavities and vacant coordination sites[12] exhibits a mole-based turnover faster than its soluble counterpart and is readily separated from the product, recovered as such, and reusable. For the conventional homogeneous catalytic systems, product−catalyst separation is usually achieved only upon further workup involving acid treatment followed by extraction of the reaction mixture; this inevitably leaves organic as well as metal-containing aqueous wastes.

The present metal-insertion or admixture strategy may be applicable to various metal complexes and organic networks. The use of solid catalysts may thus open the door to the construction of waste-free, workup-free, and solvent-free molecular transformation processes which are friendly to the environment and resource-saving. In addition, the present particular work suggests a potential utility of such catalysts in fine organic synthesis, where soluble metal complexes and organometallic derivatives have been extensively used as either promotors or catalysts.

Acknowledgment. This work was supported by CREST (Core Research for Evolutional Science and Technology) of Japan Science and Technology Corporation (JST) and also by a Grant-in-Aid from the Ministry of Education, Science and Culture, Japan, for COE Research “Design and Control of Advanced Molecular Assembly Systems” (no. 08CE2005). We are grateful to Prof. K. Mikami (Tokyo Institute of Technology) for valuable discussion and also to Dr. K. Kobayashi (Tsukuba University) for his contribution in the early stage of this work.

JA9743351

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[9] Typical A values for zeolites are 500−700 m^2/g.

[10] Actually, Ti-host can be in situ prepared by adding a calculated amount (**1**/Ti = $^1/_2$) of apohost **1** to a solution of $(^i\mathrm{PrO})_2\mathrm{TiCl_2}$ in diene and quantitatively recovered as $\mathbf{1}^{4-}\cdot 2[(^i\mathrm{PrO})\mathrm{TiCl}]$[5] after the catalytic reaction.

[11] Soluble $\mathrm{Ti^{4+}}$ complexes derived from binaphthol and $(^i\mathrm{PrO})_2\mathrm{TiCl_2}$ have been used in asymmetric transformations: (a) Mikami, K.; Motoyama, Y.; Terada, M. *J. Am. Chem. Soc.* **1994**, *116*, 2812−2820. (b) Terada, M.; Matsumoto, Y.; Nakamura, Y.; Mikami, K. *J. Chem. Soc., Chem. Commun.* **1997**, 281−282. Also see references cited in ref 6.

[12] A potential strategy to generate coordinative unsaturation in metal−organic network materials is to remove volatile metal ligands: (a) ref 1c. (b) Yaghi, O. M.; Li, H.; Groy, T. L. *J. Am. Chem. Soc.* **1996**, *118*, 9096−9101. (c) Yaghi, O. M.; Li, G.; Li, H. *Nature* **1995**, *378*, 703−706.