

Letter

Ligand control of the catalytic activities of Al^{3+} -immobilized solid Lewis acids

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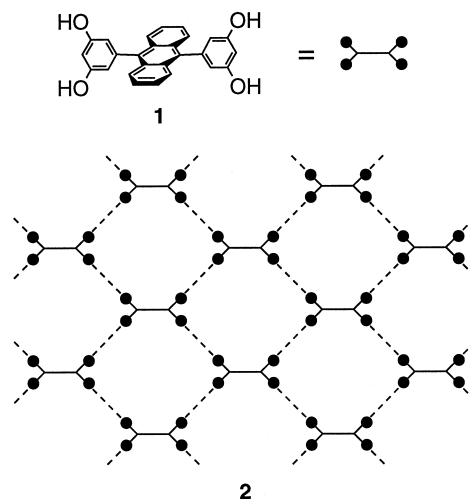
Abstract

Treatment of anthracenebisresorcinol **1** (a tetraol) with $\text{Al}(\text{CH}_3)_2\text{Cl}$ or $\text{Al}(\text{O}^i\text{Pr})_3$ affords an amorphous solid formulated as $\mathbf{1}^{4-} \cdot 2[\text{AlCl}]^{2+}$ or $\mathbf{1}^{4-} \cdot 2[\text{AlO}^i\text{Pr}]^{2+}$ ($\mathbf{1}^{4-}$ is the deprotonated tetraanionic species of host **1**). These solids (AlCl and AlOⁱPr hosts) as recoverable and reusable Lewis acids catalyze the Diels–Alder reaction of acrolein with 1,3-cyclohexadiene, where the former (AlCl) at 3 mol% exhibits a much higher catalytic activity with a halflife of the reaction of $\tau = 1$ min than the latter (AlOⁱPr) with $\tau = 80$ min. The efficient solid-state catalysis by the AlCl host with a turnover rate of 30/min is based on the combination of space vacancy (microporosity) and coordination vacancy (coordinative unsaturation) as revealed by ^{27}Al MAS NMR spectroscopy. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Aluminum; Solid Lewis acid catalyst; Microporous solid; Diels–Alder reaction; ^{27}Al MAS NMR

Application of modified inorganic solid catalysts to organic transformations is an area of much recent interest [1–3]. We [4–6] and others [7] have recently uncovered a simple route to solid Lewis acid catalysts. Our method is based on immobilization of soluble metal complexes in the hydrogen-bonded network in the scheme $\text{O}-\text{H} \cdots \text{O}-\text{H} + \text{MX}_n \rightarrow \text{O}^- \cdots [\text{MX}_{n-2}]^{2+} \cdots \text{O}^- + 2\text{HX}$ ($\text{X} = \text{RO}^-$, etc.). Anthracenebisresorcinol **1**, an X-shaped tetraol, forms a network shown in structure **2** ($\cdots = \text{O}-\text{H} \cdots \text{O}-\text{H}$) [8–10], in which the Lewis acid (Ti^{4+} , Al^{3+} , or Zr^{4+}) [4,5] or rare-

earth (La^{3+}) [6] metal centers have been immobilized along the line.



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The resulting amorphous solids catalyze the Diels–Alder [4,5] or Michael and (nitro)aldol reactions [6], respectively, in a remarkable manner. In general, catalytic activities of metal–organic solids may arise from two types of “vacancy”. One is space vacancy or microporosity, which is well-demonstrated for the above catalysts. The other is coordination vacancy at the metal centers. Little is known, however, as to whether coordinative unsaturation can be readily maintained in the infinitely concentrated solid states. This work concerns with ligand modification in the aluminum series. We report here that coordinative saturation/unsaturation can be controlled by the choice of metal ligands.

Treatment of host **1** and $\text{Al}(\text{CH}_3)_2\text{Cl}$ (1:Al = 1:2) in a homogeneous THF solution under argon resulted in rapid evolution of methane with concomitant precipitation of amorphous powders assignable as $\mathbf{1}^{4-} \cdot 2[\text{AlCl}]^{2+}$ (hereafter called the AlCl host); $\mathbf{1} + 2\text{Al}(\text{CH}_3)_2\text{Cl} \rightarrow \mathbf{1}^{4-} \cdot 2[\text{AlCl}]^{2+} + 4\text{CH}_4$ ($\mathbf{1}^{4-}$ is the deprotonated tetraanionic species of host **1**). The isopropoxy analog $\mathbf{1}^{4-} \cdot 2[\text{AlO}^i\text{Pr}]^{2+}$ (AlO^iPr host)² was obtained under heterogeneous conditions [4], i.e., by stirring a suspension of host **1** in a benzene solution of $\text{Al}(\text{O}^i\text{Pr})_3$ for 18 h; $\mathbf{1} + 2\text{Al}(\text{O}^i\text{Pr})_3 \rightarrow \mathbf{1}^{4-} \cdot 2[\text{AlO}^i\text{Pr}]^{2+} + 4^i\text{PrOH}$. In a similar manner as the AlCH_3 host ($\mathbf{1}^{4-} \cdot 2[\text{AlCH}_3]^{2+}$) derived from $\text{Al}(\text{CH}_3)_3$ and the $\mathbf{1}^{4-} \cdot 2[\text{TiCl}(\text{O}^i\text{Pr})]^{2+}$ and $\mathbf{1}^{4-} \cdot 2[\text{Zr}(\text{O}^t\text{Bu})_2]^{2+}$ analogs [4,5], the AlCl and AlO^iPr hosts are

¹ Careful washing with THF followed by drying in vacuo for 2 days gave reddish-yellow powders of the AlCl host. When treated with 1 N HCl, it decomposed into its components, where the ratios of **1**:THF \cong 1:2 and Al:Cl \cong 1:1 were confirmed by ¹H NMR (for **1** and THF), ICP (inductively coupled plasma) (for Al^{3+}), and titration (for Cl^- with AgNO_3) analyses. The IR spectrum (Nujol) showed a broad adsorption in the range of 1150–1200 cm^{-1} assignable to $\nu_{\text{C-O-Al}}$. Found: C, 59.65; H, 4.79; Al (ICP), 8.1%. Calculated for $\text{C}_{34}\text{H}_{32}\text{O}_7\text{Al}_2\text{Cl}_2$ ($\mathbf{1}^{4-} \cdot 2[\text{AlCl}] \cdot 2\text{THF} \cdot \text{H}_2\text{O}$): C, 60.28; H, 4.76; Al, 7.97%.

² Found: C, 68.12; H, 5.09; Al (atomic absorption), 9.9%. Calcd for $\text{C}_{32}\text{H}_{28}\text{O}_8\text{Al}_2$ ($\mathbf{1}^{4-} \cdot 2[\text{AlO}^i\text{Pr}]$): C, 68.33; H, 5.02; Al, 9.59%.

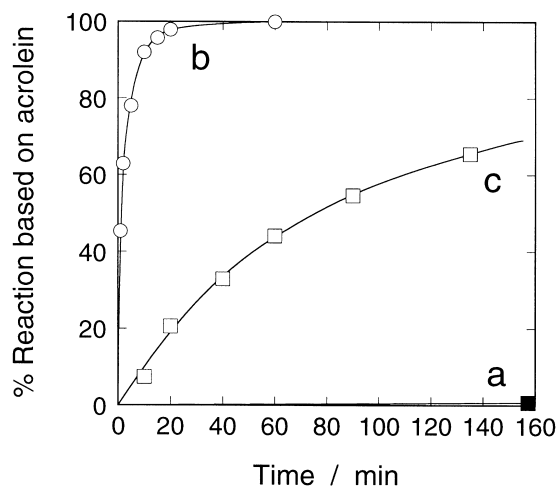
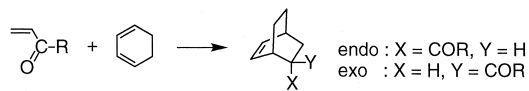


Fig. 1. Time courses of the acrolein-1,3-cyclohexadiene Diels–Alder reactions under argon at 25°C in the absence (a) and presence (3 mol%) of AlCl host (b) or AlO^iPr host (c) as a solid catalyst under conditions of acrolein/diene = 1/20; the amount of catalyst is in reference to the limiting substrate acrolein.

insoluble in all common organic solvents, exhibit characteristic guest-binding properties,³ and catalyze the Diels–Alder reactions between acrolein and 1,3-cyclohexadiene (Eq. 1).



(1)

Fig. 1 shows the time courses of the reactions in the absence (a, half-life of the reaction is $\tau = 500$ h) and presence (3 mol% with respect to dienophile) of the AlCl (b, $\tau = 1$ min) or AlO^iPr host (c, $\tau = 80$ min) at 25°C. Catalysis by any soluble Al^{3+} species can be rigorously ruled out since the supernatant separated from the solid catalyst in the course of the reaction shows no catalysis at all. In accord with this observation, the Diels–Alder product ($\sim 100\%$,

³ Specific surface areas, obtained by the BET analysis of the N_2 adsorption at 77 K, are $A_{\text{BET}} = 48$ and $90 \text{ m}^2/\text{g}$ for the AlCl and AlO^iPr hosts, respectively. Adsorption of polar (e.g., ethyl acetate) and apolar (e.g., benzene) guests and coadsorption thereof also occur.

endo/exo = 97/3 with AlCl and 98/2 with AlOⁱPr) can be recovered free of metallic contamination by a simple workup procedure involving centrifugation, washing, and evaporation of the diene in excess.

The higher activity of the AlCl host as compared with the AlOⁱPr may be readily understood on the basis of different electron-donating abilities of the Cl⁻ and ⁱPrO⁻ ligands; Lewis acidities of the Al³⁺ centers are often reflected on their coordinative saturation/unsaturation, evaluable by ²⁷Al NMR spectroscopy [11,12].⁴ By their very nature, Lewis acids tend to self-aggregate via metal bridge by the ligands to achieve higher coordination [13]. Fig. 2 shows the solid-state ²⁷Al MAS NMR spectra for the present solid catalysts. The Al³⁺ centers in the AlOⁱPr host are mostly hexa-coordinated ($\delta_{\text{Al}} = -2$ ppm), while broad resonances at lower fields ($\delta_{\text{Al}} = 25$ and 51 ppm) might be ascribed to the reactive Al³⁺ centers having lower coordination numbers (Fig. 2a).⁴ On this criterion, most of the Al³⁺ centers in the AlCl host would be coordinatively unsaturated and hence reactive (Fig. 2b). In view of efficient packing in the solid state, it may not be surprising that the immobilized aralkyloxy-aluminum centers in the AlOⁱPr host tend to form saturated AlO₆ octahedra in a similar manner as Al(OⁱPr)₃ which is exclusively hexa-coordinated in the solid state (Fig. 2c). It is remarkable that coordinative unsaturation can be maintained to a significant extent by a slight change in the metal ligand from OⁱPr to Cl even in the solid state.

This work may be summarized as follows. (1) The AlCl and AlOⁱPr hosts give the same 1:2:2 (host:metal:ligand) stoichiometry, suggesting that the basic metal–organic framework is preserved. (2) As a consequence, the different

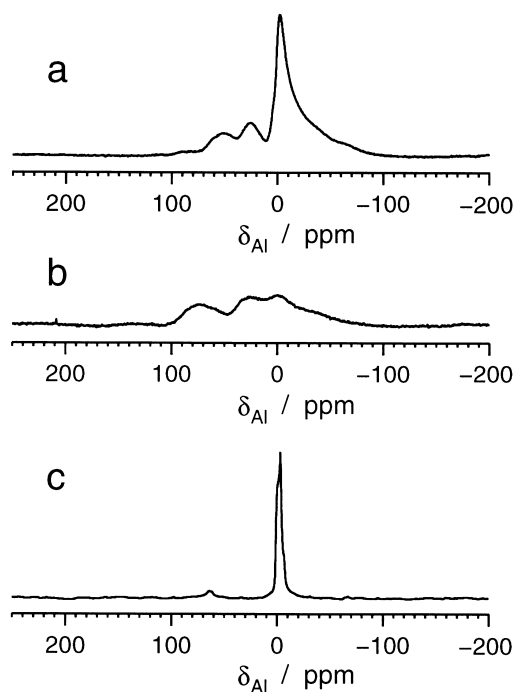


Fig. 2. ²⁷Al MAS NMR spectra at room temperature for the AlOⁱPr host (a), the AlCl host (b), and Al(OⁱPr)₃ (c). The chemical shifts are in reference to Al(OH₂)₆³⁺ in water.

catalytic activities of the AlCl and AlOⁱPr hosts can be ascribed to different Lewis acidities of the less-coordinated AlCl centers and the more coordinated AlOⁱPr centers. (3) Thus, the AlCl host is not only microporous, owing to the metal–organic network, but also coordinatively unsaturated. It catalyzes the Diels–Alder reaction in concern with a turnover rate of 30/min.⁵ (4) Nevertheless, the AlCl host retains all the advantages as a solid catalyst; it is readily recovered and reused, without being leaked into the organic product.

⁴ It is well known that hexa- and tetra-coordinated Al nuclei resonate at ~0 and ~70 ppm, respectively, and less-symmetrically coordinated nuclei give broader resonances due to enhanced quadrupole interactions.

⁵ Catalytic Diels–Alder reactions of other dienophiles also take place with other dienophiles such as methyl vinyl ketone ($\tau = 1$ min at 25°C; endo/exo = 99/1), methyl acrylate ($\tau = 22$ min at 60°C; endo/exo = 98/2), ethyl acrylate ($\tau = 50$ min at 60°C; endo/exo = 98/2), butyl acrylate ($\tau = 50$ min at 60°C; endo/exo \cong 100/0), isobutyl acrylate ($\tau = 46$ min at 60°C; endo/exo \cong 100/0), and hexyl acrylate ($\tau = 25$ min at 60°C; endo/exo \cong 100/0).

Acknowledgements

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