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Layered Materials with Coexisting Acidic and Basic Sites for Catalytic One-Pot Reaction Sequences

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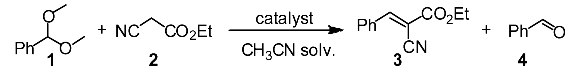
Bifunctionalized nanomaterials have received much attention because of their potential usefulness for novel light-emitting diodes,[1] hosts of semiconductors,[2] drug targetings,[3] and high-performance catalysts.[4] Particularly nanomaterials with coexisting two antagonist functions, such as acid and base, are of great interest owing to their potential novel functions and a wide range of applications to various catalyses.

In 2006, Alauzun and co-workers reported the first mesoporous materials with sulfonic acids in frameworks and amine bases in pores.[5] In addition, we and other groups also demonstrated both acid and base sites on the same oxide surfaces, which showed enhancement of single-reaction steps by their cooperative catalysis.[6] However, catalytic acid−base one-pot reaction sequences by bifunctional materials have never succeeded because acidic and basic functions with sufficient strength are necessary for the promotion of both acid- and base-catalyzed reactions but they easily deactivate each other in single materials and homogeneous systems. Acid−base reaction sequences by acidic and basic materials separated in a single reactor have been already reported,[7] but the reaction sequence catalyzed by a single acid−base bifunctional material is still a challenging theme from both academic and industrial standpoints.[6a]

We have found that immobilization of organic bases on solid acid surfaces such as silica and silica−alumina by a silane-coupling reaction enables efficient bifunctional catalysis without neutralization between the surface acid sites and the immobilized organic bases.[6e,f] Here, we present immobilization of organic primary amines in acidic montmorillonite interlayers (H-mont-NH_2), which is the first material to make one-pot acid−base reaction sequences possible. The acidity and basicity of the H-mont-NH_2 were influenced by the preparation solvent,[8] and the base-catalyzed reaction was enhanced by interlayer acid sites.

Montmorillonites, denoted as monts, are hydrophilic clays with a layered structure.[9] An acidic proton-exchanged mont (H-mont) was prepared from Na^+-mont (Kunipia F, Kunimine Industry) by using a HCl solution.[10] The H-mont-immobilized 3-aminopropyl functional group was prepared by treatment of H-mont with a solution of 3-aminopropyltriethoxysilane (APS) at 298 K for 2 h. Then the solid was filtered and washed with the same solvent, followed by drying under vacuum. The samples are denoted as H-mont-NH_2[solvent] hereafter. The typical amine loadings were determined as 0.83 and 0.75 mmol/g, respectively, for H-mont-NH_2[heptane] and [acetonitrile] by elemental analysis. On the basis of XRD analysis the layered structure of the H-mont-NH_2[heptane] was identified and the basal spacing was expanded from 2.6 Å (H-mont) to 7.7 Å. The interlayer space for the H-mont-NH_2[acetonitrile] (5.4 Å) was smaller than that for the H-mont-NH_2[heptane]. FT-IR and solid-state ^{13}C NMR spectra for precursor APS (7.5, 27.2, and 45.1 ppm) were also confirmed in the H-mont-NH_2 samples. Solid-state ^{29}Si MAS NMR analysis revealed new signals around −60 ppm after immobilization of APS, indicating the formation of T^n sites [$RSi(OEt)_n(OSi)_{3-n}$]. It is suggested from these results that the amine groups were immobilized in the interlayer of the H-mont by a silane-coupling reaction with retention of its primary amine structure. We examined various organic and inorganic solvents for the preparation of the H-mont-NH_2[solvent] (SI).

Table 1. Acid−Base Reaction Sequences by Amine Catalysts[a]



entry	catalyst [prep. solvent]	amine (mmol/g)[b]	conv. of **1** (%)[c]	yield of **4** (%)[c]	yield of **3** (%)[c]
1	H-mont-NH_2 [heptane]	0.83	>99	trace	>95
2	[THF]	0.56	22	7	14
3	[toluene]	0.86	9	trace	9
4	[DMSO]	0.42	13	9	trace
5	[acetonitrile]	0.75	<1	trace	trace
6	[water]	1.06	<1	trace	trace
7	SiO_2-NH_2 [heptane]	0.90	<1	trace	trace
8	$Al_2O_3-NH_2$ [heptane]	0.59	<1	trace	trace
9	H-USY-NH_2 [heptane]	0.75	<1	trace	trace
10[d]	H-mont + n-$C_6H_{13}NH_2$	−	30	30	trace
11	H-mont	−	26	26	trace
12[d]	n-$C_6H_{13}NH_2$	−	<1	trace	trace

[a] Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol), catalyst (3.0×10^{-2} g), acetonitrile (1 mL), 60 °C, 1 h. [b] Determined by elemental analysis. [c] Determined by GC and ^{1}H NMR. [d] n-Hexylamine (2.5×10^{-2} mmol).

The acid−base bifunctionality of the immobilized amine catalysts was investigated in tandem deacetalization-Knoevenagel condensation,[7c,f] as shown in Table 1. Remarkably, the H-mont-NH_2 prepared in n-heptane solvent showed an excellent catalytic performance, affording the condensation product (**3**) at 95% yield (entry 1). The formation of bezaldehyde (**4**) as an intermediate was detected from the time course of the reaction, which suggests that both the deacetalization and Knoevenagel condensation were catalyzed by the H-mont-NH_2[heptane]. The H-mont-NH_2 samples prepared in other less polar solvents, such as THF and toluene, were much less active (entries 2 and 3), and the final product (**3**) was not obtained in the case of highly polar solvents (entries 4−6). The deacetalization reaction step was not promoted by the primary amine catalysts on other oxide supports (entries 7−9). A mixture of H-mont and n-hexylamine showed a similar activity to the H-mont itself for an acetalization reaction without addition of water[11] (entries 10 and 11). It is notable that the homogeneous

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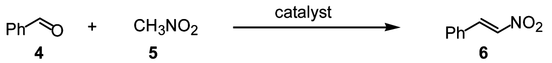
primary amine showed no catalytic activity for the Knoevenagel condensation in the presence of the H-mont.

The H-mont-NH_2[heptane] was also found to be active for a tandem deacetalization-nitro-aldol reaction of acetal **1** with nitromethane (**5**), affording β-nitrostyrene (**6**) quantitatively. To compare the basicity of immobilized amines, initial reaction rates for a nitro-aldol reaction of **5** with **4** catalyzed by immobilized and free amines are summarized in Table 2. The H-mont-NH_2[heptane] showed a much higher activity (entry 1) than the homogeneous amine (entry 4), and the activity of *n*-hexylamine is decreased by addition of the H-mont (entry 3). It can be said that the immobilized amine-catalyzed nitro-aldol reaction is enhanced by the interlayer acid sites,[12] whereas the homogeneous amine is deactivated by the acid sites. Interaction between the acid site and NH_2 group is decreased by the immobilization of amines through the silane-coupling reaction between the ethoxysilane moieties and Si−OH groups in the interlayer of the H-mont.[6a,c,e,f]

Table 2. Nitro-Aldol Reaction by Amine Catalysts[a]



entry	catalyst	initial rate (mmol/h)[b]
1	H-mont-NH_2 [heptane]	0.83
2	H-mont-NH_2 [acetonitrile]	0.34
3[c]	H-mont + *n*-$C_6H_{13}NH_2$	0.06
4[c]	*n*-$C_6H_{13}NH_2$	0.25
5	H-mont	<0.01

[a] Reaction conditions: **4** (0.5 mmol), **5** (1.0 mL), catalyst (1.0×10^{-2} g), 100 °C. [b] Determined by ^1H NMR. [c] *n*-Hexylamine (8.3×10^{-3} mmol).

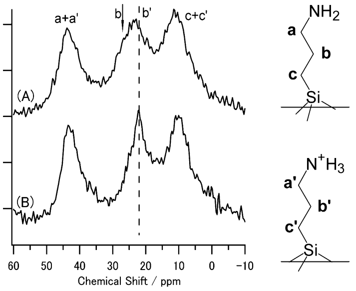
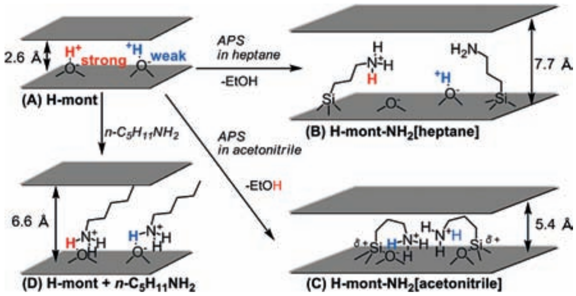


Figure 1. ^{13}C CP/MAS NMR spectra for (A) H-mont-NH_2[heptane] and (B) H-mont-NH_2[acetonitrile].

Scheme 1



The solid state ^{29}Si MAS NMR spectra in the T-sites region are shown in Figure 2S (Supporting Information). The signals for the H-mont-NH_2 samples prepared in acetonitrile and water slightly shifted downfield (B and C, ∼5 ppm) compared with that prepared in heptane (A). These small shifts are not derived from the difference between T^n and T^{n+1} sites, which shows an ∼10 ppm shift generally.[13] Thus, the downfield shift may be due to the decreasing electron density at the Si atom, indicating the reaction between the interlayer Brønsted acid site, which is catalytic site for the deacetalization, and the ethoxysilane moiety in APS to form the T sites in the polar solvents. Solid-state ^{13}C CP/MAS NMR spectra for the H-mont-NH_2[heptane] (Figure 1A) showed the presence of both protonated (b′: 22 ppm for the center carbon atom of propylamine, dotted line) and unprotonated (b: 27 ppm, arrow) amines, whereas almost all amines were protonated in the H-mont-NH_2[acetonitrile] (B). Proposed structures for the amine-immobilized H-mont are shown in Scheme 1.[14] NH_3-TPD analysis for the H-mont indicated the presence of both a very strong acid site and weak acid site.[10a] The NH_3^+ species from the strong acid site might act as an acidic site for the deacetalization (Scheme 1B), but this acid site disappeared in H-mont-NH_2[acetonitrile] as illustrated in Scheme 1C.[14] The presence of a free NH_2 group induced the high catalytic performance of the H-mont-NH_2[heptane] in the base-catalyzed reaction (Table 2).[14]

In conclusion, the one-pot acid−base reaction sequences were successfully promoted by the layered materials with coexisting acid and base sites. These montmorillonite-immobilized primary amines are the first bifunctional materials with chemically antagonistic sites for tandem C−C bond forming reactions. A further detailed understanding of the behavior of the coexisting acidic and basic sites in a single material will open new possibilities of the application to a variety of catalytic one-pot reaction sequences.

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Supporting Information Available: Details of experimental procedures and characterizations. This material is available free of charge via the Internet at http://pubs.acs.org.

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