Adjacent acid-base pair sites on silica surface constructed by hydrolysis of pre-anchored amide

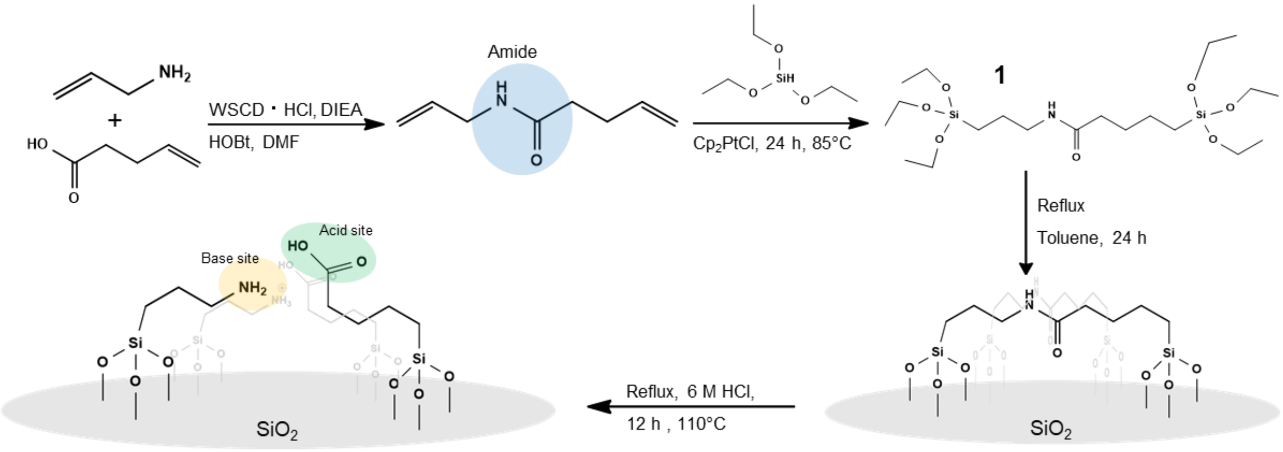
Wontae KIM,[a] **Loida O. Casalme,**[b] **Taiki UMEZAWA,**[b] **Fuyuhiko MATSUDA,**[b]
Ryoichi OTOMO,[b] **Yuichi KAMIYA,**[b,*]
[a] *Graduate School of Environmental Science, Hokkaido University, Sapporo, 060-0810, Japan*
[b] *Faculty of Environmental Earth Science, Hokkaido University, Sapporo, 060-0810, Japan*
**kamiya@ees.hokudai.ac.jp*

Abstract: In the present study, we demonstrated a method to construct adjacent acid (carboxylic acid)-base (amine) pair sites on silica by hydrolysis of pre-anchored amide. The catalyst had both acid and base sites, while amount of the base sites was less than that of acid ones due to partial neutralization. The catalyst showed higher activity for aldol condensation than the catalyst with either acid or base sites. The proposed method can expand to precise control of the distance between each active sites by using rationally designed amides.

Keywords: acid-base pair sites, bifunctional catalyst, aldol condensation

1. Introduction

Rationally designed molecular catalysts with both acid and base sites at appropriate conformation and distance show high catalytic activity and selectivity compared to the catalysts with either of the two.[1] For heterogeneous catalysts, immobilization of both acid and base sites on solid surface has been attempted so far and the resulting catalysts are superior in activity and selectivity to homogeneous analogues.[2] It is expected that catalytic performances of such bifunctional catalysts are highly dependent on the distance between the acid and base sites on the surface and the catalyst having the appropriate distance is advantageous especially for complex multi-step (cascade) reactions. However, it is usually difficult to precisely control the distance between the two active sites if both are separately immobilized with two different reagents. In this study, we attempted to construct adjacent acid-base pair sites on silica surface by hydrolysis of pre-anchored amide (Scheme 1) and applied the catalysts for aldol condensation.



Scheme 1 Synthetic route for the acid-base bifunctional catalyst with adjacent acid-base pair sites on silica.

2. Experimental

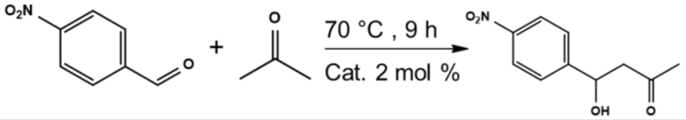
Bis-triethoxysilyl amide **1** was synthesized by condensation of amine with carboxylic acid, followed by hydrosilylation with triethoxysilane (Scheme 1). Immobilization of **1** on SiO_2 was carried out in toluene at reflux temperature for 24 h. The obtained solid is referred to as **1**/SiO_2. Here, **1**/SiO_2 having different surface density of **1** on SiO_2 (0.1, 0.5, and 1.0 nm^{-2}) were prepared. Finally, amide on **1**/SiO_2 was hydrolyzed in 6 M hydrochloric acid at 110°C for 12 h (refers to as **A**cid-**B**ase/SiO_2). As a reference, the catalyst anchoring either carboxylic or amino group was prepared (refers to as **A**cid/SiO_2 and **B**ase/SiO_2, respectively). Aldol condensation of 4-nitrobenzaldehyde with acetone was carried out using a batch-type reactor at 70°C for 9 h with 4-nitrobenzaldehyde/acetone = 0.5 mmol/1.5 mmol. Products were analyzed by gas chromatography.

3. Results and discussion

The IR spectrum of **A**cid-**B**ase/SiO_2 indicated that both carboxyl (1592 cm^{-1}) and amino (1730 cm^{-1}) groups were formed by hydrolysis of **1**/SiO_2. The amounts of acid and base sites on the samples were estimated by acid-base titration with NaOH and HCl solution, respectively. The results indicated that no acid and base sites was present on **1**/SiO_2 (Table 1). In contrast, **A**cid-**B**ase/SiO_2 with the density of 1.0 nm^{-2} had 0.58 and 0.11 mmol g^{-1} of acid and base sites, respectively, which corresponds to 122 % and 23 % of carboxyl and amino groups calculated from the density of **1**. Overestimation of the acid sites was probably because acidic silanol group on SiO_2 was measured. The less amount of the base sites than the acid ones was due to partial neutralization of amine during the hydrolysis in hydrochloric acid.

Table 1 also shows the catalytic results of aldol condensation. **1**/SiO_2 did not show any activity for the reaction (entry 1). Since **B**ase/SiO_2 gave high conversion (entry 2), while **A**cid/SiO_2 was inactive for the reaction (entry 3), the reaction was basically promoted on amino groups. In other words, there was no direct contribution of the carboxyl groups to promote the reaction. **A**cid-**B**ase/SiO_2 showed activity and the conversion was increased with increase in the density of the active sites (entries 4, 5, and 6). Since the physical mixture of **A**cid/SiO_2 and **B**ase/SiO_2 was less active than **A**cid-**B**ase/SiO_2 (entry 7), adjacency of acid and base sites is important to give high catalytic activity. It should be noted that **A**cid-**B**ase/SiO_2 with the density of 1.0 nm^{-2} was much more active than **B**ase/SiO_2, though **A**cid-**B**ase/SiO_2 has only about one-fifth amount of base site of **B**ase/SiO_2. In a separate experiment, we prepared **B**ase/SiO_2 partially neutralized with HCl and carried out the aldol condensation. The results indicated that such neutralization of the base sites lowered the catalytic activity of **B**ase/SiO_2. Therefore, we concluded that adjacent acid-base pair sites constructed by hydrolysis of pre-anchored amide **1** cooperatively promoted the reaction, leading to the high catalytic activity of **A**cid-**B**ase/SiO_2.

Table 1 Acid-base properties and catalytic results



Entry	1	2	3	4	5	6	7
Catalyst	**1**/SiO_2	**B**ase/SiO_2	**A**cid/SiO_2	**A**cid-**B**ase/SiO_2	**A**cid-**B**ase/SiO_2	**A**cid-**B**ase/SiO_2	**B**ase/SiO_2 + **A**cid/SiO_2
The amount of **A**cid / **b**ase (mmol g^{-1})	0 / 0	0 / 0.53	0.49 / 0	0.60 / 0.17	0.52 / 0.32	0.58 / 0.11	0.49 + 0.53
Density of organic group (nm^{-2})	0.5	0.5	0.5	0.1	0.5	1.0	0.5 + 0.5
Aldehyde conversion (%)	0	51	0	29	40	79	8

4. Conclusions

Acid-base bifunctional catalysts with adjacent acid-base pair sites on silica surface were successfully synthesized by hydrolysis of pre-anchored amide. The adjacent acid-base pair sites on the catalysts cooperatively promoted the aldol condensation and the catalyst activity was higher than that with either acid or base sites. As an extension of the present method, it is possible to control the distance between the acid-base pair sites using different rationally designed amide. This method can finely control the distance between the acid-base pair sites and thus help to understand the cooperative activation of reactant on the acid-base pair sites, as well as the preparing of the catalyst showing high performance in a specific reaction.

References

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