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

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Abstract: In the present study, we demonstrated a method to construct adjacent acid (carboxylic acid)-base (amine) pair sites on silica surface 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. 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. 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.

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 SiO₂ was carried out in toluene at reflux temperature for 24 h. The obtained solid is referred to as 1/SiO₂. Here, 1/SiO₂ having different surface density of 1 on SiO₂ (0.1, 0.5, and 1.0 nm²) were prepared. Finally, amide on 1/SiO₂ was hydrolyzed in 6 M hydrochloric acid at 110°C for 12 h (refers to as Acid-Base/SiO₂). As a reference, the catalyst anchoring either carboxylic or amino group was prepared (refers to as Acid/SiO₂ and Base/SiO₂,
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 Acid-Base/SiO₂ indicated that both carboxyl (1592 cm⁻¹) and amino (1730 cm⁻¹) groups were formed by hydrolysis of 1/SiO₂. 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/SiO₂ (Table 1). In contrast, Acid-Base/SiO₂ with the density of 1.0 nm² 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 SiO₂ 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/SiO₂ did not show any activity for the reaction (entry 1). Since Base/SiO₂ gave high conversion (entry 2), while Acid/SiO₂ 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. Acid-Base/SiO₂ 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 Acid/SiO₂ and Base/SiO₂ was less active than Acid-Base/SiO₂ (entry 7), adjacency of acid and base sites is important to give high catalytic activity. It should be noted that Acid-Base/SiO₂ with the density of 1.0 nm² was much more active than Base/SiO₂, though Acid-Base/SiO₂ has only about one-fifth amount of base site of Base/SiO₂. In a separate experiment, we prepared Base/SiO₂ 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 Base/SiO₂. 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 Acid-Base/SiO₂.

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