



Spatial arrangement and acid strength effects on acid–base cooperatively catalyzed aldol condensation on aminosilica materials



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ABSTRACT

Weak acids are known to enhance the activity of amines in aldol condensation reactions on silica-based catalysts. The effects of acid strength and arrangement of the promoting site with respect to a secondary amine have been investigated in the aldol condensation of 4-nitrobenzaldehyde with acetone. Changing the substituent of this secondary amine from a methyl to an ethyl group decreases the activity. An intramolecular OH function provided by a primary alcohol incorporated on the β -carbon of the amine substituent exhibits a similar cooperativity as an intermolecular OH function provided by neighboring surface silanols. A maximum activity was achieved when the secondary amine with the same primary alcohol-containing substituent was surrounded by surface silanols, indicating the potential advantage of simultaneously activating both reactants by the formation of a hydrogen bond in contrast to the consecutive activation when there is only one promoting site in the vicinity of the amine. Changing the alcohol to stronger acids resulted in a reduced cooperativity with increasing acid strength. After removing the silanols from the surface, the activity of the catalysts which exhibit an intramolecular cooperativity retained about 68–83% of their activities while the activity of the conventional secondary amine was reduced by a factor of four compared to its intermolecularly cooperative counterpart.

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1. Introduction

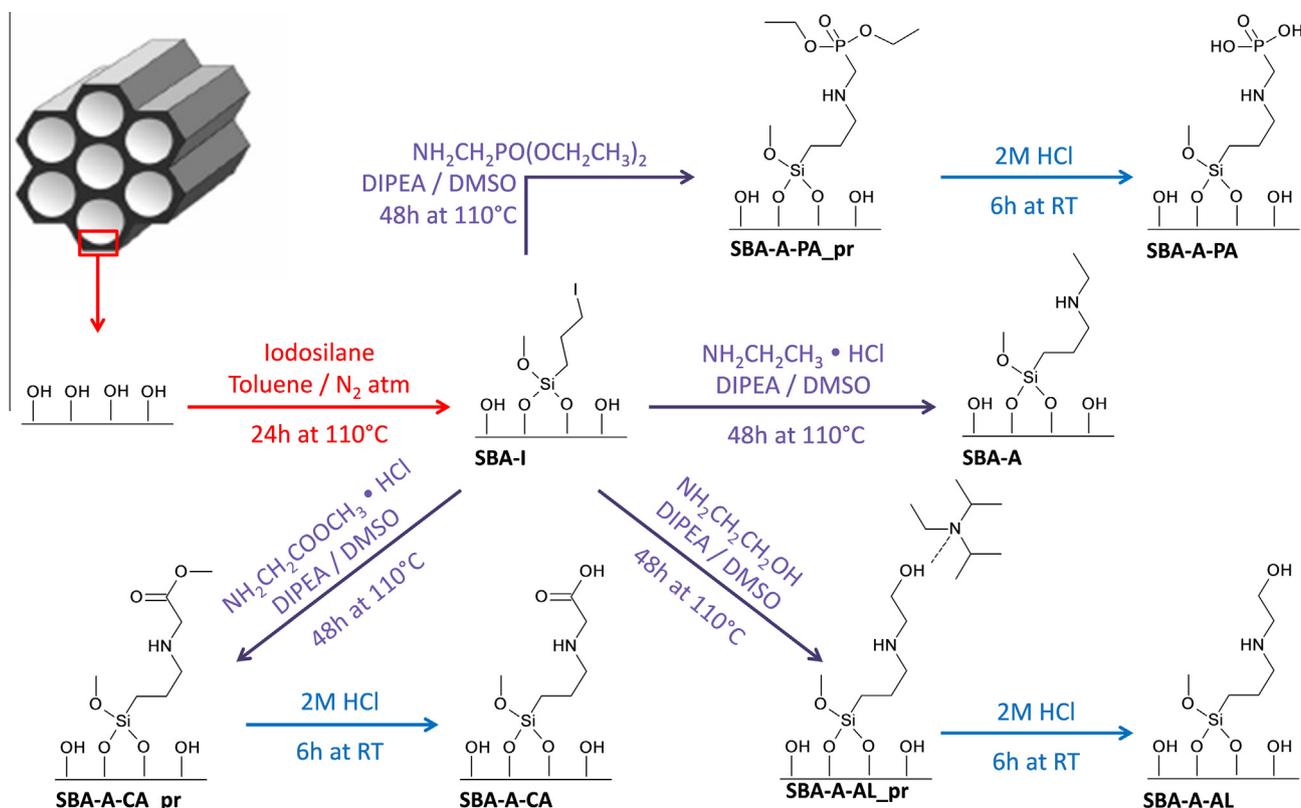
Aminated silica materials are known to efficiently catalyze carbon–carbon coupling reactions, especially when weak acid sites are neighboring the amine function [1–13]. An adequate understanding of the cooperativity between the two types of sites is crucial for the rational design of an optimal acid–base cooperative catalyst. One can think of several catalyst properties that have an important effect on the catalytic performance of the material, such as the proximity of the promoting sites to the amines [5–8], the structure and base strength of the amine site [3–5], and the acid strength of the promoting site [8–10].

Post-synthetic grafting by means of a stirring or reflux procedure is a popular technique to functionalize silica materials with amines. During the functionalization, a fraction of the weakly acidic silanols that are intrinsically present on the silica surface is replaced with an amine-containing silane [6,14]. It has been

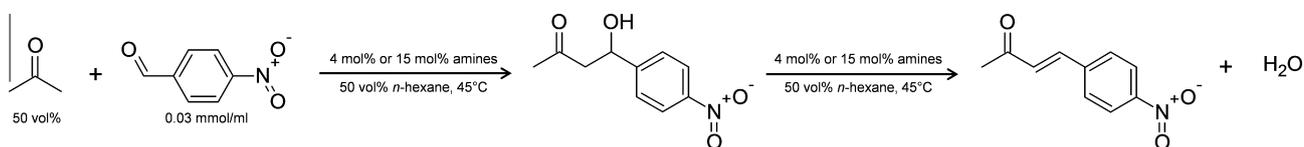
shown that the presence of the remaining silanols on the surface enhances the catalytic activity of the amines in the aldol condensation [1,2,5–9]. This cooperative effect does not only depend on the concentrations of both types of sites but also on their spatial arrangement with respect to each other [5,6]. Primary amine precursors have the tendency to form hydrogen bonds between each other during the grafting procedure [5,6,15–19]. Commonly used solvents such as toluene are typically unable to break these hydrogen bonds, and hence, primary amines remain associated with each other and are grafted in a clustered manner on the silica surface [5,6,15–17]. In contrast, secondary amines have a lower tendency to form such hydrogen bonds in the same solvents and are more randomly distributed over the silica surface [5]. Both the clustered and the random arrangement deviate from the ideal checkerboard pattern, meaning that at a silanol-to-amine ratio of 1, not every amine has a neighboring silanol and, hence, that the amines are not fully promoted. It has also been demonstrated that the cooperativity between amines and silanols can be tuned by controlling the alkyl chain length of the amine active site as well as the silica support pore size [7,8]. It was found that with short alkyl chains, the catalyst behaves as if the amine groups were

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Scheme 1. Schematic representation of the synthesis of SBA-X with X referring to the functional group, i.e., 'I' for the iodo-group, 'A' for the secondary amine, 'AL' for the alcohol group, 'CA' for the carboxylic acid, and 'PA' for the phosphoric acid. A similar scheme can be drawn for the synthesis of SBA-HMDS-X. In this case, an HMDS treatment is included between the grafting of the iodosilane (step 1) and the replacement of the iodo-group with the desired functional group (steps 2).



Scheme 2. Aldol condensation of acetone and 4-nitrobenzaldehyde toward 4-hydroxy-4-(4-nitrophenyl)butane-2-one and 4-(4-nitrophenyl)-3-buten-2-one.

isolated, irrespective of the presence of silanol groups. The catalytic cooperativity increases with the alkyl chain length up to a propyl chain, before leveling off for longer alkyl chains. For smaller silica pore sizes, however, the same maximum cooperativity is already established for an ethyl chain and significantly decreases for longer chains, suggesting that the long alkyl chain in the small pores perturbs the cooperativity.

To obtain an even better control of the spacing of the cooperating sites, one can draw inspiration from homogeneous catalysis. A series of homogeneous amino acids, in which the amine and the carboxylic acid are separated by 2 to 7 methylene groups, exhibits an increase in catalytic activity with decreasing distance between the two sites [8,20]. In addition, homogeneous amino acids such as proline and glycine are known to perform well as aldol condensation catalysts [21,22]. In both amino acids, the amine and the carboxylic acid groups are separated by a single carbon atom. Moreover, a recent study showed that L-proline could be immobilized on mesoporous silica that contained alternating hydrophilic and hydrophobic blocks to catalyze aldol condensations and Knoevenagel–Michael cascade reactions with higher yields and enantioselectivities when compared to their homogeneous precursors [23].

Although many primary, secondary, and tertiary amines have similar base strengths, these amines exhibit significant differences

in catalytic activities for the aldol condensation [2–5]. This observation can be attributed to differences in ability to form enamine intermediates, which is the key intermediate for the desired reaction to proceed [5], and imine species, which deactivate the amine site [3–5]. While the crucial enamine intermediate cannot be formed on a tertiary amine, the inhibiting imine species can only be formed on primary amine active sites. As a result, a secondary amine active site that can produce the reactive enamine intermediate without forming the inhibiting imine exhibits the highest catalytic activity, provided that it is not subject to steric hindrance [5]. A recent study examined the ability of several organocatalysts to form enamine and iminium intermediates in the cross-condensation of isobutyraldehyde and acetone and determined that organocatalysts that could form Seebach's oxazolindiones during the reaction favored the formation of aldol-type products instead of Mannich-type products, demonstrating that the intermediates can also affect the product selectivity and not only the activity [24]. The promoting effect of the weak acid sites is often ascribed to hydrogen bond interactions between the acid and the carbonyl moiety of the reactant, which results in a higher susceptibility of the electrophilic reactant for the nucleophilic attack of the amine [1,2,5–9]. Replacing the weakly acidic silanols with a stronger acid site seems to have a negative impact on the activity of primary amines [8–10], which could be explained by a more favorable

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