

## Acid-Base Cooperativity in Functionalized Mesoporous Silica

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### Introduction

Many reactions catalyzed by enzymes employ acid-base pairs within their catalytic sites. Studies by Bass et al. [1,2] mimicked these acid-base cooperative catalytic sites by imprinting well-defined catalytic sites within silica. Using the Knoevenagel condensation reaction, they demonstrated acid-base cooperativity between silanol and aminopropyl groups within single sites. An important question is whether these isolated site results can be extended to catalysts with higher surface area while maintaining the catalytic cooperativity. The ability to achieve cooperative catalysis with functionalized mesoporous silica has recently been reported by Zeidan et al. [3,4] in aldol condensation reactions. In those studies cooperativity effects were seen between sulfonic acid and thiol groups and sulfonic acid and amine groups. The current work examined the extension of the single site work performed by Bass et al. to functionalized mesoporous silica where the catalytic sites exist on extended surfaces. Condensation of benzaldehyde and ethyl cyanoacetate to ethyl cyanocinnamate was used to test the catalytic domain and acid-base cooperativity of SBA-15 mesoporous silica co-condensed with aminopropyl groups. The study included capping of the surface silanols with silyl groups as well as comparison to the catalytic activity of propylamine free in solution.

### Materials and Methods

Tetraethyl orthosilicate from Fisher Scientific and benzaldehyde, ethyl cyanoacetate, propylamine, (3-aminopropyl)triethoxysilane, 1,1,1,6,6,6-hexamethyldisilazane (HMDS), and tetramethylammonium hydroxide (TMAH, 2.2 M in methanol) from Sigma-Aldrich were used as purchased. The aminopropyl-functionalized SBA-15 (APS) was synthesized using the co-condensation procedure of Wang et al. [5], including post-synthesis removal of excess protons with TMAH. For some materials the surface silanols of the aminopropyl-functionalized SBA-15 were capped via silylation using HMDS in refluxing toluene [6].

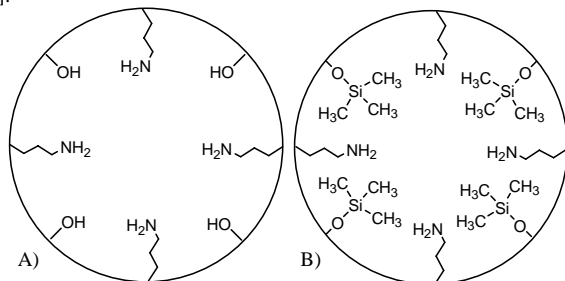


Figure 1. Uncapped (A) and capped (B) APS

All reactions were performed in a 50-mL round-bottom flask agitated with magnetic stirring. Nitrogen flowed into the flask through one neck and exited through a mineral oil bubbler connected to the outlet of the condenser. The catalyst was dried under vacuum at 100°C prior to use. A typical reaction consisted of 40 mL toluene, 0.07 mL benzene as an internal standard, 0.91 mL benzaldehyde, and 0.96 mL ethyl cyanoacetate at 25°C. Samples were taken by syringe through a septum. The samples were analyzed using a Varian gas chromatograph (CP-3800) with a Varian CP7417 column and a flame ionization detector.

### Results and Discussion

The APS catalyst was active for the condensation reaction whereas the free propylamine in solution gave negligible activity. Silylation of APS resulted in a significant loss of activity, as shown in Table 1. For comparison, the activity of free propylamine in the presence of either unfunctionalized SBA-15 or silylated SBA-15 was tested. Interestingly, combination of the unfunctionalized SBA-15 silica with free propylamine resulted in higher conversion than the free propylamine alone although the combination gave much lower conversion than the co-condensed aminopropyl-functionalized silica.

Table 1. Turnover Frequency: Conversion of Ethyl Cyanoacetate (mol/site/h)

APS	15.5
Silylated APS	1.52
Propylamine	0.66
Propylamine + SBA-15	3.78
Propylamine + silylated SBA-15	0.78

Nitrogen adsorption-desorption data of the silylated APS indicated a reduction in surface area and a slight reduction in pore size while maintaining structural order. This suggests that the reduction in reaction rate for the silylated APS is due to lack of surface silanols rather than blockage of amine sites.

### Significance

The study demonstrated that random placement of amines via co-condensation can yield cooperative catalysis with surface silanol groups. While the cooperativity results were even achieved with a solution containing a mixture of propylamine and SBA-15, the activity enhancement was more significant when the aminopropyl groups were attached near silanol groups. This study demonstrated that single-site results can in some cases be extended to a catalytic domain in functionalized mesoporous silica.

### References

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