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A Simple Modification Creates a Great Difference: New Solid-Base Catalyst Using Methylated N-Substituted SBA-15

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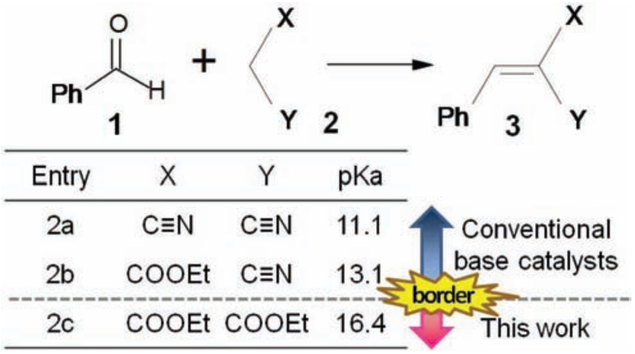
Ⓢ *Supporting Information*

ABSTRACT: A simple modification, methylation of the nitrogen-substituted mesoporous silica SBA-15, enhances the basicity of a solid-base catalyst. The methyl group donates an electron to the nitrogen atom in the silica framework. This catalyst accelerates Knoevenagel condensation using benzaldehyde and diethyl malonate, which conventional solid-base catalysts reported to date cannot do. This report demonstrates a possible new type of base catalyst using nitrogen-substituted mesoporous silica materials.



Entry	X	Y	pKa
2a	C≡N	C≡N	11.1
2b	COOEt	C≡N	13.1
2c	COOEt	COOEt	16.4

Figure 1. Knoevenagel condensation using benzaldehyde with active methylene compounds.

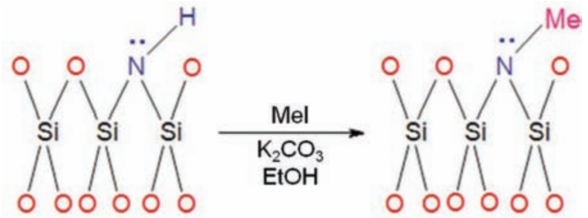
Mesoporous silica materials, first reported almost two decades ago, have become the focus of a great deal of current research in the field of nanostructured materials because of their regular structures, uniform and large pore sizes, and high surface areas.[1] Furthermore, many researchers envision using these materials as catalysts because they can be easily separated from a reaction mixture.[2] Therefore, they are very desirable for industrial processes in terms of cost and environmental loads.

A new class of nitrogen-substituted solid-base materials using MCM-41 and SBA-15 (SBA) with high specific surface area was recently developed.[3] The basic sites in such materials arise from the presence of nitrogen atoms in their frameworks. These nitrogen species are considered to be as strongly basic as conventional solid-base catalysts such as alkali- or alkaline-earth-metal oxides, alkaline-ion-exchanged zeolites, or mesoporous silica materials impregnated with basic salts.[4] Before these conventional base catalysts are used, pretreatment at high temperatures (>873 K) is essential because their catalytic sites tightly adsorb ambient water or carbon dioxide.[4a,c] On the other hand, our group previously reported that nitrogen-substituted mesoporous silica (NS-MSM) materials do not require such pretreatment, which is a compelling reason to pursue research on NS-MSM and also suggests that these materials would be useful and practical for industrial processes.[5]

The performance of solid-base catalysts is generally evaluated by a Knoevenagel condensation in which benzaldehyde (**1**) is reacted with active methylene compounds such as malononitrile (**2a**) or ethyl cyanoacetate (**2b**).[2b,4,5] However, because the nitrogen species is a secondary amine, its basicity and catalytic activity are limited, so Knoevenagel condensation using **1** and diethyl malonate (**2c**) cannot be catalyzed by conventional base catalysts (Figure 1). To the best of our knowledge, no one has reported successful a Knoevenagel condensation catalyzed by conventional base catalysts or NS-MSM. Here we report the methylation of nitrogen-substituted SBA-15 (Me-NSBA) to improve its basicity by a simple modification, and we demonstrate its catalytic performance as a new, stronger base catalyst.

Me-NSBA was synthesized as shown in Scheme 1. The methyl group is expected to increase the basicity of the amine part by donating an electron to the nitrogen atom. Nitrogen-substituted SBA-15 (NSBA) was prepared essentially as described in a previous work, but the flow rate of ammonia was changed to 1 L/min to enhance nitridation.[5] NSBA was then methylated by using methyl iodide with potassium carbonate (NSBA:MeI:K_2CO_3 molar ratio = 1:15:3). The reaction was conducted in anhydrous ethanol at 350 K for 48 h with a reflux condenser, after which the product was filtered, washed, and dried at 373 K. After the catalyst was synthesized, its basicity was evaluated by means of Knoevenagel condensation of **1** and **2c**. The substrate (2 mmol) and catalyst

Scheme 1. Methylation of NSBA



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(20 mg) were mixed in ethanol (2.13 mL), and the mixture was heated at 353 K with a reflux condenser. An aliquot of the reactant solution was analyzed by gas chromatography afterward.

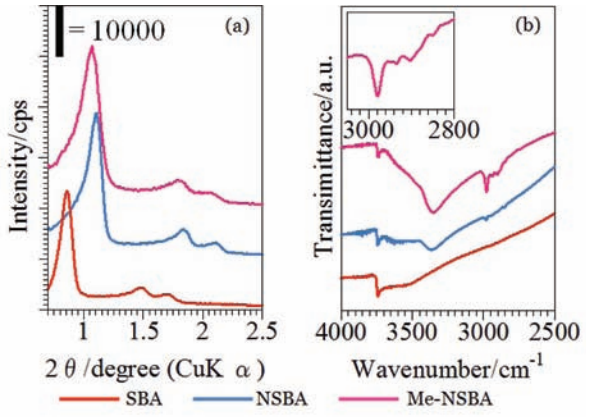

Figure 2. (a) PXRD results and (b) FT-IR spectra.

Powder X-ray diffraction (PXRD) revealed three typical peaks from SBA-15 (Figure 2a). After methylation, Me-NSBA maintained its two-dimensional hexagonal periodic structure. Fourier transform IR spectra of the samples were also measured (Figure 2b). The peak at 3736 cm^{-1} observed for all the samples is attributed to the OH bond of silanol.[6a,b] After nitrogen substitution, a wide band at 3356 cm^{-1} corresponding to the NH stretching vibration appeared.[6a,b] The sharp peak at 2978 cm^{-1} and the small peak at 2900 cm^{-1} appearing after the methylation reaction are assigned to CH stretching of methyl groups connected to nitrogen atoms,[6c] providing powerful evidence that NSBA was methylated. However, two bands at 2850 and 2935 cm^{-1}, which could be assigned to the stretching vibration of CH bonds connected to O atoms, were also detected. This indicates that a portion of the silanol might also have been methylated.

Table 1. Elemental Analyses of NSBA and Me-NSBA

	N		C	
sample	wt %	mmol/g	wt %	mmol/g
NSBA	24.2	17.3	–	–
Me-NSBA	18.4	13.1	3.81	3.17

To clarify the number of carbon and nitrogen atoms in the structures of the samples, elemental analysis was performed (Table 1). Carbon derived from the methyl group was detected, although the amount of nitrogen decreased after methylation. Because the amine bridge is weak against water, it was hydrolyzed even though an anhydrous solvent was used. The ratio of methyl groups to nitrogen was limited to C/N = 0.3, even though methylation was carried out under several conditions.

Knoevenagel condensation using **1** and **2c** was performed to investigate the catalytic performance of Me-NSBA. Ethanol was used as the solvent for this reaction because a protic solvent is known to assist proton transfer in the reaction.[7] To clarify the effect of the methylated nitrogens, a catalyst that was methylated but contained no amine bridges was also used.

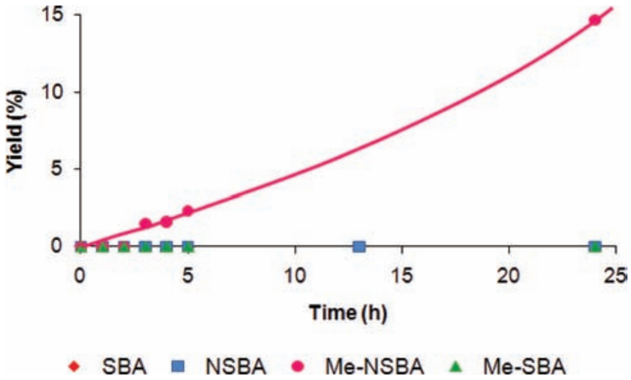

Figure 3. Effect of methylation of nitrogen on the Knoevenagel condensation.

The results for each sample are summarized in Figure 3. It is noteworthy that only Me-NSBA catalyzed the reaction, whereas the other samples showed almost no catalytic ability. These results clearly show that the addition of methyl groups to nitrogen atoms in the framework greatly increased the basicity of the catalyst and that the catalytic activity was significantly increased by methylation. On the basis of the nitrogen adsorption isotherm on MeNSBA, methylation did not result in mesopore blockage. This means that the methylation was not limited to sites near the mesopore mouth. The catalytic performance might suggest that the catalytically active N species attached to methyl group is inside the mesopore, which leads to slow product formation by diffusion.

Another mesoporous silica, MCM-41, was used as the support of methylated nitrogen in the silica framework. First of all, it was *quite* difficult to conduct nitridation and methylation on MCM-41 because the periodic mesoporous structure was easily destroyed by those treatments. This occurred because MCM-41 has a much thinner mesopore wall than SBA-15. Thus, SBA-15 is superior as the substrate for the methylated nitrogen group on silica inside a confined mesospace. Finally, Me-NMCM-41 was obtained successfully by nitridation at 973 K for 12 h followed by methylation at 350 K for 4 h (Figure S1 in the Supporting Information). The contents of nitrogen and carbon in Me-NMCM-41 are shown in Table S1. The amount of doped nitrogen in MCM-41 was much less than that in SBA-15; this is due not only to the low temperature for nitridation but also to the smaller amount of silanol on the surface of MCM-41. Knoevenagel condensation using **1** and **2c** was also carried out (Figure S2). The catalytic activity of Me-NMCM-41 was comparable to that in Me-NSBA, and the smaller reaction rate is due to the smaller number of catalytic active sites. There was no induction period, as the reaction product was seen in the reactant mixture of Me-NMCM-41, while there existed an induction in that of Me-NSBA-15. It is also interesting to note that the C/N ratio in Me-NMCM-41 was close to 1, as shown in Table S1; almost all of the N atoms could be methylated, which was never done in Me-NSBA. This is due to the location of the methylated N atom along within a shorter mesopore of Me-NMCM-41, while N atoms also exist in the micropores of SBA-15, resulting in less methylation of N atoms because of slow diffusion of methyl iodide in the micropore.

As previously reported,[5] the microporous space was too small to react benzaldehyde with ethyl cyanoacetate. It is also worth mentioning that methyl iodide for the methylation of the N atom in the silicate cannot penetrate into micropores of Nsilicalite. From these results, we can stress that a mesospace that is at least larger than the microporous space obtained in zeolites is needed to promote such a reaction on a basic surface. More bulky substrates are normally used in most of the reactions required for organosynthesis using basic catalysts; thus, we can conclude the potential application seen in our newly developed samples.

In summary, we have successfully synthesized a new solid-base catalyst, methylated nitrogen-substituted SBA-15, by a very simple method and demonstrated Knoevenagel condensation using benzaldehyde and diethyl malonate with this catalyst. The results indicate that the methyl group enhances the basicity of the amine part and enables this Knoevenagel condensation, which is impossible using known conventional solid-base catalysts.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

XRD patterns, N and C contents, and catalytic performance of MCM-41, NMCM-41, and Me-NMCM-41. This material is available free of charge via the Internet at http://pubs.acs.org.

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