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SBA-15-Oxynitrides as a Solid-Base Catalyst: Effect of Nitridation Temperature on Catalytic Activity**

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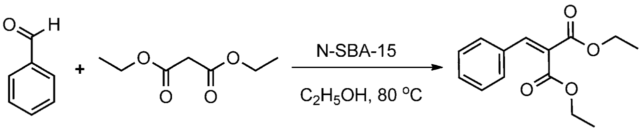
Abstract: *Solid bases, such as SBA-15-oxynitrides, have attracted considerable interest for potential applications as catalysts in important industrial processes. Reported herein is that by simply tuning the temperature of nitridation (ammonolysis), the catalytic activity of these solid bases can be enhanced. Solid-state NMR spectroscopy and XPS studies provided the reasoning behind this change in activity.*

Amine functionalization of high-surface-area silica,[1–7] such as SBA-15 and KCC-1, including their nitridation,[8–15] is key for the development of novel solid-base catalysts. However, nitridated SBA-15 was unable to catalyze reactions involving weakly acidic active methyl groups, such as Knoevenagel condensation reactions of diethyl malonate with benzaldehyde. Recently activation of SBA-15 oxynitrides was claimed by N-methylation.[16]

However, in continuation of the work on heterogeneous catalysis,[15,17–22] we herein report that by simply controlling the nitridation temperature, one can tune the types of amine sites to enhance their catalytic activity. We demonstrate our hypothesis by detailed synthesis studies and in-depth characterization of various surface amine sites by solid-state magic-angle-spinning-nuclear magnetic resonance (MAS-NMR) and X-ray photoelectron spectroscopy (XPS) studies.

The first step we performed to prove our hypothesis was to systematically study the nitridation of SBA-15 at various temperatures and evaluate their effectiveness as catalysts. SBA-15 was nitridated by thermal ammonolysis under the flow of ammonia gas (300 mL min^{-1}) at different temperatures (500, 700, 900, 1200 °C). Amine-functionalized SBA-15 (SBA-15-N) was obtained without destroying its ordered mesoporous structure, even after treatment at high temperature, although a decrease in the surface area and pore volume was observed. These oxynitrides were characterized by N_2-soprtion studies (see Figure S1), TEM (see Figure S2), SEM (see Figure S3), PXRD (see Figure S4 in the Supporting Information), elemental (CHN) analysis (Table 1), surface-area measurement using Brunauer–Emmett–Teller (BET) theory (Table 1), MAS-NMR (Figures 1 and 2), and XPS (Figure 3). SBA-15-oxynitride samples were then evaluated as a solid base for the Knoevenagel condensation reaction of diethyl malonate with benzaldehyde (Table 1).

Table 1: Catalytic activity SBA-15-N for the Knoevenagel condensation reaction between benzaldehyde and diethyl malonate.



Entry	Catalyst	BET surface area [m^2 gm^{-1}]	N content [mmol g^{-1}][a]	Yield [%][b]	TON
1	SBA-15	810	0.0	0	0
2	SBA-15-N500	653	1.1	6	2718
3	SBA-15-N700	600	2.5	16	3150
4	SBA-15-N900	426	8.6	14	817
5	SBA-15-N1200	354	20.4	12	295
6	Me-SBA-15-N700	23	0.0	0	0
7	Me-SBA-15-N900	12	0.0	0	0
8	Me-SBA-15-N1200	7	0.0	0	0

[a] Determined by CHN analysis. [b] Determined by GC analysis after 24 h.

The data in Table 1 (entries 1–5) indicate that although the nitrogen content in SBA-15 oxynitrides increases with an increase in nitridation temperature, it does not aid in increasing its catalytic activity as a solid base. In fact SBA-15-N700 showed the highest catalytic activity even though its N content is lower than that of SBA-15-N900 and SBA-15-N1200. This outcome proves our hypothesis that simple tuning of the nitridation temperature can improve the catalytic activity of silica oxynitrides.

Notably, unlike Ogura's results,[16] N-methylation of SBA-15-N700, SBA-15-N900, and SBA-15-N1200, using their reported procedure,[16] showed zero conversion. In fact, during N-methylation the SBA-15 mesostructures were destroyed, thus resulting in nearly no surface area and no catalytic activity [see Figures S5 (TEM), S6 (PXRD), and Table S1 (surface area, CHN, and catalytic results for N-methylated SBA-15-N700)]. This lack of activity is due to the

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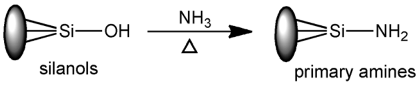
use of strong base during N-methylation of surface amines, base which is known to destroy the SBA-15 mesoporous structure.

Upon normalizing the gas chromatography (GC) yield per mole of amine per surface area (catalytic efficiency) of the respective SBA-15 oxynitrides, the values of catalytic efficiency were found to be 0.0, 0.008353, 0.010667, 0.003821, and 0.001662 for SBA-15, SBA-15-N500, SBA-15-N700, SBA-15-N900, and SBA-15-N1200, respectively (see Table S2). These results indicate that the total N content as well as surface area of the material plays an important role in its catalytic efficiency. However, the role of the structure of the amine sites was not clear from these results.

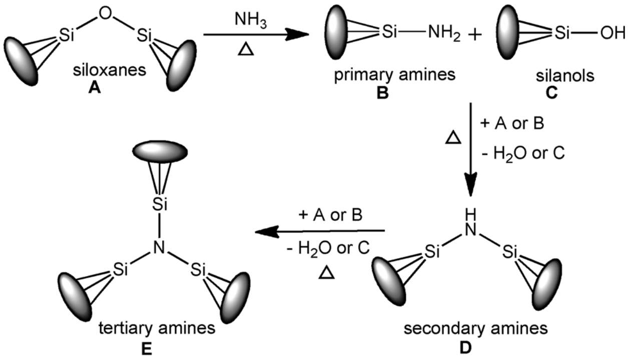
Our next attempt was to answer the question: Why does catalytic activity not increase with an increase in N content? Based on the reported literature by Asefa et al.,[8] the mechanism of nitridation during ammonolysis involves the replacement of silanols (Si-OH) by primary amines. The surface silanols, upon interaction with ammonia, causes the H_2O leaving group to be replaced by NH_2 (Scheme 1). If this reaction mechanism is correct, then the number of available silanol groups on the surface of SBA-15 should be the limiting factor for the degree of nitridation and hence the N content of the resultant oxynitrides. However, the SBA-15 used for all nitridations at various temperatures was derived from the same calcined material at 550 °C in air. Thus, the starting material (calcined SBA-15) has the same concentration of silanols and hence the degree of nitridation should be the same irrespective of nitridation temperature. However, the degree of nitridation (i.e., N content) increases with an increase in reaction temperature, thus indicating that nitridation is also taking place by some other mechanism, or there may also be generation of more silanols at higher temperature because of the elimination of water molecules (during ammonolysis), which can attack on siloxane bridges to produce silanols.



Scheme 1. Attack of ammonia on silanols.

Another possible mechanism is the attack of NH_3 on the siloxane (Si-O-Si) units of the silica framework (Scheme 2) to produce Si-NH_2 and additional silanols. Then, at higher temperatures, the generated Si-NH_2 attacks the neighboring silanols and/or siloxanes and formation of Si-NH-Si bridges (secondary amines) takes place. This process can continue and even produce tertiary amines at higher temperatures.

Thus two factors, a) concentration of silanol groups and b) reaction of siloxane with NH_3 molecules, jointly play a role in the degree of nitridation of SBA-15 at various temperatures. Therefore, even after having the same silanol concentration of the starting SBA-15 material, N content increases with the increase in nitridation temperature (Table 1). It is now clear that if nitridation takes place by the mechanism depicted in Scheme 1, only primary amines will be produced, whereas if it takes place by the mechanism in Scheme 2, secondary and even ternary amines could be produced. That is, although N-content increases with an increase in temperature, the concentration of various types of amine sites could be different in these materials. Ideally the primary amine concentration should decrease and the concentration of secondary amine sites should increase with an increase in reaction temperature, as the mechanism in Scheme 2 is dominant at higher temperatures. We observed this temperature-dependent phenomenon in the case of KCC-1-based silicon oxynitrides[15,22] and hence felt that it may be also true for SBA-15.



Scheme 2. Attack of ammonia on siloxanes.

We studied various silicon–amine sites of SBA-15 oxynitrides by solid-state CP-MAS ^{29}Si NMR spectroscopy, as well as ^{1}H-detected ^{15}N NMR spectroscopy. Figure 1 (A–E) shows the ^{29}Si NMR spectrum after cross-polarization for the untreated and nitridated SBA-15 samples. These spectra were deconvoluted into 3–5 Gaussian functions and the presence of different siloxane or silicon–amine moieties was inferred from the peak positions. Untreated pure SBA-15 exhibited signals at $\delta = -90$, -100 and -110 ppm, which can be attributed to Q^2 [$SiO_2(OH)_2$], Q^3 [SiO_3OH], and Q^4 [SiO_4] sites, respectively.[8] Upon treatment with ammonia at increasing temperatures, several peaks started appearing downfield at the expense of the peaks seen in untreated SBA-15. Interestingly, SBA-15-N500 and SBA-15-N700 showed only one additional peak at $\delta = -87.5$ ppm, which can be attributed to surface primary silicon–amine sites [$SiO_3(NH_x)$]. With a further increase in nitridation temperature, to 900 and 1200 °C, two additional signals appeared at $\delta = -69.5$ and -56 ppm, respectively, which can be attributed to the corresponding $SiO_2N(NH_x)$ and $SiON_2(NH_x)$ sites. In the case of SBA-15-N1200, one more signal at $\delta = -50$ ppm for SiN_4 also appeared. The cross-polarization experiment is sensitive to a number of factors (e.g., the rigidity of the silicon–amine sites and ^{1}H density in the sample and near the silicon–amine site), so a quantitative estimate of the ratio of different silicon-amine sites could not be obtained. For SBA-15-N900 and SBA-15-N1200, we directly confirmed the presence of secondary and tertiary amines using ^{1}H-detected ^{15}N–^{1}H correlation spectra at the natural ^{15}N abundance. Figure 2 shows that SBA-15-N900 predominantly has secondary amines present while SBA-15-N1200 has a high tertiary amine content. The corresponding ^{15}N–^{1}H correlation spectra

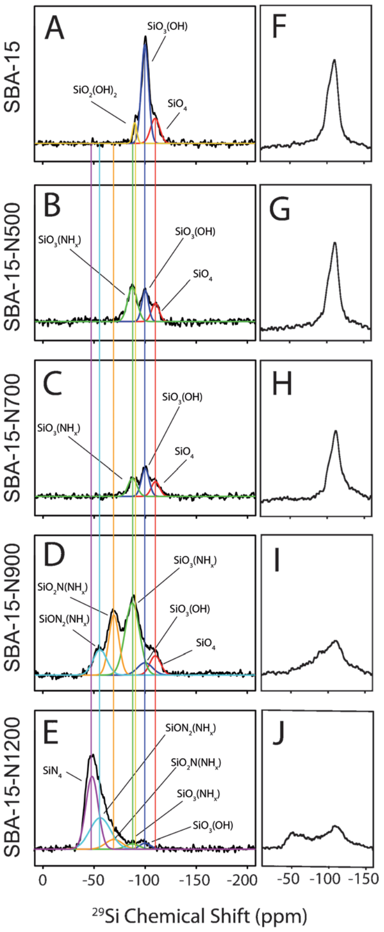


Figure 1. ^{29}Si CP-MAS (A–E) and ^{29}Si single-pulse (F–J) NMR spectra of the SBA-15-N series.

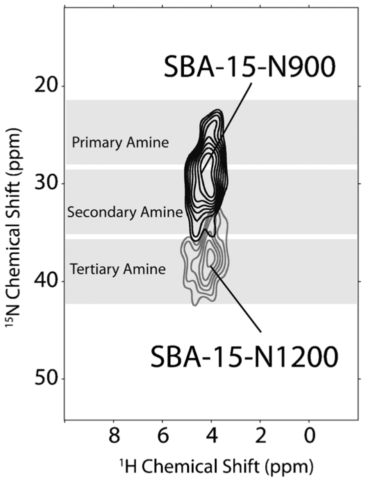


Figure 2. ^{1}H-detected ^{15}N–^{1}H correlation spectrum obtained for SBA-15-N1200 (gray) and SBA-15-N900 (black).

could not be obtained for SBA-15-N500 and SBA-15-N700 because of their low nitrogen content.

It is to be expected that the variation in peak position and intensity for the CP experiments (Figure 1 A–E) have contributions from differences in the ^{1}H-^{29}Si cross-relaxation rates as well as ^{1}H $T_{1\rho}$ [for different sites]. However, under the conditions of a saturating contact time, all peaks that can be effectively cross-polarized by ^{1}H should be seen. To ascertain that the variation was not an artefact of different CP-dynamics for different sites, we ran a CP-buildup experiment by varying the contact time between 1 and 10 ms. The different silanol–amine sites showed variation in their build-up dynamics, but attained near complete build-up between 8–10 ms of contact time. Among the five samples, all siloxane and silicon–amine species expected by the proposed mechanism could be identified, even for the smallest contact time used (1 ms). This finding indicates that all of the surface Si-containing species, when present, can be cross-polarized from ^{1}H. In-spite of the variation in build-up times for different sites, (see Figures S6 and S7), none of the samples showed additional or missing peaks for any of the contact times, thus indicating that the spectra reported in Figure 1 (A–E) are representative of the silicon–amine content in the samples. This data is also confirmed by single-pulse ^{29}Si NMR spectra for each of the samples (Figure 1 F–J), which show significant intensity in the build-up of downfield resonances upon increase in nitridation temperatures.

From Table 1, it can be seen that the nitrogen content increases as the nitridation temperature increases. For temperatures less than or equal to 700 °C, this nitrogen is primarily incorporated as the catalytically active primary amine. The high depletion of the Q^2 and Q^3 sites and moderate depletion of Q^4 sites offer evidence for the first step of the reaction proposed in Scheme 2. With an increase in nitridation temperature, for example, at 900 and 1200 °C, Q^4 sites are also converted into silicone–amine sites, thus indicating the cleavage of siloxanes at higher temperatures and confirming the second step in our proposed mechanism.

The amine content increases substantially upon an increase in nitridation temperatures, but only SBA-15-N500 and SBA-15-N700 have 100 % primary amine content. Given the higher content of total nitrogen in SBA-15-N700 (Table 1), it has a higher catalytic efficiency and turnover number than SBA-15-N500. The total amine content increases in SBA-15-N900, but this additional N content is in the form of secondary and tertiary amines. Hence, it shows a similar catalytic efficiency in terms of product yield, but a drastically reduced turnover number (TON). Also, for the SBA-15-N1200 sample, the primary amine content is similar to that of SBA-15-N500 and SBA-15-N700 samples despite the 10-fold higher nitrogen content. It shows a significantly elevated number of tertiary and quaternary silicon–amines, thus explaining why it shows similar catalytic efficiency but a much lower TON.

To further explore and confirm the changes observed in the NMR spectra, we studied SBA-15 oxynitrides by XPS[23] and the results are shown in Figure 3 for Si 2p, N 1s, and O 1s core levels. With an increase in nitridation temperature from 500 to 1200 °C, the binding energy (BE) and full-width at half maximum (FWHM) for the N 1s shifts from 399.4 (2.6) to 398 eV (2.2 eV). Similarly the Si 2p BE (and FWHM) changes from 103.4 (3.0) to 102.2 eV (2.3 eV) with increasing the nitridation temperature from 500 to 1200 °C. The maximum FWHM was observed for material nitridated at 900 °C and

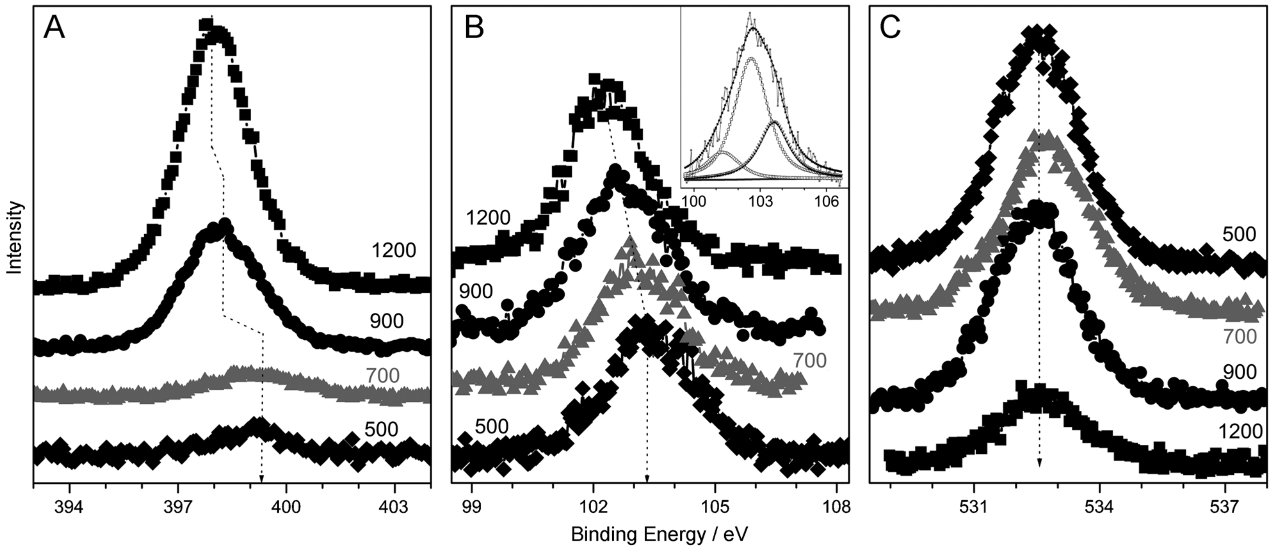


Figure 3. XPS spectra for A) N 1s, B) Si 2p, and C) O 1s core levels of various SBA-15-oxynitrides. Binding energy changes observed are indicated by a dotted line. Inset of panel (B) shows a deconvolution for Si 2p core level of SBA-15-N900.

having Si 2p and N 1s core levels. A decrease in the BE of the N 1s core level underscores an increase in electron density on N with the higher nitridation temperature.[24] As nitridation temperature increases, more and more silanol and siloxanes are converted into amines (Scheme 2). Predominantly primary amines were observed after nitridation at 500 and 700 °C, and this distribution changes to secondary and tertiary amines, and then predominantly tertiary amines after nitridation at 900 and 1200 °C, respectively. Change from the primary to tertiary amine, indeed, reduces the number of silicon atoms and its effective electron density increases. Protons of the primary amines, observed after nitridation at 500/700 °C, are increasingly replaced with more electropositive silicon atoms by nitridation at 900/1200 °C. Deconvolution of the XPS spectra was carried out and representative data is given in the inset of Figure 3B, and was recorded for material nitridated at 900 °C. Si 2p peaks at 103.6, 102.5, and 101.3 eV are attributed to Si bonded to primary, secondary, and tertiary amines, respectively. The above-mentioned changes in BE and FWHM demonstrate a change in electronic interaction between Si and N in the nitridated materials.

BE of the O 1s core level remains unchanged at 532.6 eV, even after nitridation at any temperature. High O 1s intensity observed after 500 °C nitridation indicates a predominant O-terminated surface. Nonetheless, the surface nature changes to the N-terminated surface after nitridation at 1200 °C. Further change in the N/O ratio from 0.05 to 1.14 after nitridation at 500 and 1200 °C, supports the above conclusion. High N/O ratios suggest a preferential surface N-doping resulting from nitridation. A comparison of the catalytic activity with XPS data suggests that the isolated primary amines are the catalytically active sites, which are observed after nitridation at 500/700 °C.

In summary, experimental results proved that by simply tuning the nitridation temperature one can achieve excellent catalytic activity of SBA-15-oxynitrides as solid bases. This activity depends upon a complex interplay between the total amine content, the fraction of primary amine content, and the available surface area. The presence of a high primary amine content is associated with high catalytic efficiency and the higher fraction of secondary/tertiary amines contributes to decreased TON. Solid-state NMR and XPS studies provided the reasoning behind this change in activity, and it is due to the differential formation of primary, secondary, and tertiary surface amines, whose concentrations are dependent on the nitridation temperature.

Keywords: heterogeneous catalysis · nanostructures · NMR spectroscopy · photoelectron spectroscopy · solid-state structures

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