Insights into the Catalytic Activity of Nitridated Fibrous Silica (KCC-1) Nanocatalysts from $^{15}$N and $^{29}$Si NMR Spectroscopy Enhanced by Dynamic Nuclear Polarization**

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**Abstract:** Fibrous nanosilica (KCC-1) oxynitrides are promising solid-base catalysts. Paradoxically, when their nitrogen content increases, their catalytic activity decreases. This counterintuitive observation is explained here for the first time using $^{15}$N-solid-state NMR spectroscopy enhanced by dynamic nuclear polarization.

High surface area silica materials have applications in many fields, including catalysis, medical imaging, and drug delivery.[1] Nevertheless, poor accessibility to active sites can limit applications where mass transport is vital. Hence, higher surface silica nanospheres with better accessibility are needed. Recently, we discovered KCC-1 silica nanospheres,[2] and observed that their unique fibrous morphology dramatically increases accessibility of active sites.[3–7] However, KCC-1 is made of neutral silica frameworks, without active sites, thus limiting its application to fields like adsorption and catalysis. To overcome this limitation, we explored the functionalization and metal coating of KCC-1 for supported catalytic systems.[1–5]

Recently, KCC-1 silicon oxynitride was prepared by ammonolysis and showed excellent activity for CO$_2$ capture,[6] and as a solid base.[7] Higher nitridation temperatures ($T_N$) increase the nitrogen content of these silicon oxynitrides, but, paradoxically, decrease their catalytic activity. This property has not been explained so far, despite exhaustive characterization by N$_2$ sorption, TEM, SEM, XPS, FT-IR, etc. Similarly, previous studies by conventional NMR techniques did not allow the identification of the silylamine sites in nitridated mesoporous silica.[7–11]

Herein, we explain for the first time the decrease of the catalytic activity of nitridated KCC-1 when increasing the nitrogen content. This phenomenon is due to the conversion of primary silylamine sites into secondary ones at $T_N$ values greater than or equal to 800°C. This structural information is obtained by solid-state $^{15}$N NMR spectroscopy, where the sensitivity is boosted by dynamic nuclear polarization (DNP). DNP-enhanced $^{29}$Si NMR spectra also prove the formation of geminal amine surface sites (separated by two Si–N bonds) at $T_N$ values greater than or equal to 800°C. This work is the first application of DNP-enhanced NMR spectroscopy to moisture-sensitive fibrous nanoparticles. So far, DNP NMR spectroscopy has been demonstrated for nonporous or mesoporous nanoparticles.[12–16]

Nitridation of KCC-1 was performed by treating KCC-1 with pure ammonia (300 mL min$^{-1}$) at various nitridation temperatures, $T_N$, for 12 hours (see the Supporting Information). The samples are labeled by KCC-1-$T_N$ to indicate the nitridation temperature. Samples named KCC-1-$^{15}$N$_{100}$ are enriched in $^{15}$N. As shown in Table 1, the nitrogen content increases with $T_N$. For KCC-1-$^{15}$N$_{100}$, the N content was lower than that for KCC-1-N900, because of a shorter reaction time (3 h) and reduced ammonia flow (50 mL min$^{-1}$). We did not observe any significant changes in shape, size, and morphology after nitridation at various $T_N$ values (see Figure 1).

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For DNP NMR experiments, KCC-1-N samples were impregnated with a solution of bis(TEMPO)-bis(ketal) (bTbK) biradical (TEMPO = 2,2,6,6-tetramethylpiperidin-1-oxyl) in 1,1,2,2-tetrachloroethane (TCE). TCE was used since nitridated KCC-1 is moisture sensitive. Here, bTbK was synthesized in two steps with a 51% overall yield, according to a procedure adapted from the literature with slight modifications. The bTbK was obtained by oxidation of diamine precursor using sodium tungstate dihydrate in 30% aqueous hydrogen peroxide and methanol (see the Supporting Information).

The EPR spectrum of KCC-1-N900 right after impregnation with 16 mM bTbK solution was dominated by a narrow triplet corresponding to bTbK molecules in solution. A broader and less intense triplet with a larger splitting was also visible. This broadening can be ascribed to the anisotropic hyperfine coupling with 14N in bTbK molecules adsorbed onto the KCC-1-N900 surface. The deconvolution of the EPR spectrum shows that the fraction of adsorbed bTbK molecules was larger than that of free bTbK. During impregnation, the fraction of adsorbed bTbK increases (see Figure 2b).

Figure 3a shows how the sensitivity enhancement afforded by DNP permits the detection of 1H–15N CPMAS spectra of KCC-1-N900 with 15N in natural abundance (0.37%), whereas these signals can hardly be detected without microwave irradiation. The enhancement factor per scan resulting from microwave irradiation was $e_{\text{on/off}}^{\text{scan}} > 17$. For 15N-enriched samples, the enhancement factor was $e_{\text{on/off}}^{\text{scan}} = 30$ (see Figure S7 in the Supporting Information). As expected, a similar enhancement was observed for the 1H polarization (see Figure S8).

Furthermore, as for other biradicals, the build-up time, $T_{\text{DNP}(1H)}$, of the 1H magnetization enhanced by DNP was found to be equal to the longitudinal relaxation time, $T_{1}(1H) = 8.5$ s. Hence, for KCC-1-N900, it would take more than 900 days to obtain a 1H–15N CPMAS spectrum without microwave irradiation, with a similar S/N ratio as that in Figure 3a. The 1H–15N CPMAS preferentially enhances the polarization of 15N nuclei near the surface, since there are few protons in the bulk of silicon oxynitrides. The comparison of DNP-enhanced 1H–15N CPMAS spectra in Figures 3b–f show that the local environments of the 15N nuclei are affected by $T_{\text{N}}$. The 15N spectra of KCC-1-N600 and KCC-1-15N700 are dominated by two resolved peaks near $\delta = 10$ and 25 ppm and can be assigned to NH$_2$Si and NHSi$_2$ sites, respectively. The deconvolution of the KCC-1-15N700 spectrum indicates the presence of an additional site near $\delta = 0$ ppm, which can be assigned to ammonium ions. In none of the samples could we detect any signals for 15NH$_3$ near $\delta = -32$ ppm. For $T_{\text{N}}$ values greater than or equal to 800°C, the NHSi$_2$ peak becomes dominant. Its chemical shift increases with increasing $T_{\text{N}}$. This increase must stem from the formation of geminal amine sites, as evidenced by 29Si NMR spectroscopy. Furthermore, the spectra of KCC-N900 and

| Table 1: Textural properties and nitrogen content of nitridated KCC-1. |
|------------------|-----------------|-----------------|-----------------|
| Sample           | BET surface area | Langmuir surface area | BJH pore volume | Nitrogen content[^a] |
|                  | [m$^2$ g$^{-1}$] | [m$^2$ g$^{-1}$] | [cm$^3$ g$^{-1}$] | [wt%]               |
| KCC-1            | 669             | 964             | 1.27            | 0                   |
| KCC-1-N600       | 603             | 871             | 1.22            | 2.02                |
| KCC-1-15N700     | 610             | 885             | 1.29            | 3.18                |
| KCC-1-N800       | 565             | 815             | 1.17            | 6.37                |
| KCC-1-N900       | 492             | 711             | 1.06            | 11.94               |
| KCC-1-15N1100    | 285             | 399             | 0.72            | 6.52                |

[^a]: Determined by C, H, N analysis.
Table S1. NHSi$_2$ and KCC-1-N prepared at 500–700°C show that the surface Si sites are bound to a larger number of N atoms at higher $T_N$ values. The lower fraction of Q$^3$ sites with respect to Q$^4$ sites with increasing $T_N$ values (see Table S2) proves that silanol groups are more reactive toward NH$_3$ than siloxane bridges in KCC-1.

Based on the $^{15}$N and $^{29}$Si DNP NMR spectra and the previously reported mechanisms for the nitridation of MCM-41,[39] we propose a mechanism for the KCC-1 nitridation. This mechanism involves the attack of NH$_3$ on 1) silanol groups to form primary silylamines (see Scheme S3) or on 2) the siloxane bridge to form primary amines and subsequently secondary and tertiary amines (see Scheme S4).

In conclusion, we have shown for the first time that the decrease in the catalytic activity of KCC-1-N prepared at higher $T_N$ values stems from the disappearance of primary amine sites and the formation of secondary ones. This novel structural information has been derived from solid-state $^{15}$N DNP NMR spectroscopy. Furthermore, the EPR spectra provided direct evidence for the adsorption of bTbK onto the KCC-1-N surface.

Keywords: EPR spectroscopy · nanostructures · NMR spectroscopy · fibrous silica (KCC-1) · nanocatalysis


