

# A Formulation Protocol with Pyridine to Enable DNP-SENS on Reactive Surface Sites: Case Study with Olefin Polymerization and Metathesis Catalysts

*Alexander V. Yakimov<sup>a</sup>, Deni Mance<sup>a</sup>, Keith Searles<sup>a</sup>, Christophe Copéret<sup>a\*</sup>*

<sup>a</sup>ETH Zurich, Vladimir-Prelog Weg 1-5/10, Zurich, Switzerland

## AUTHOR INFORMATION

### Corresponding Author

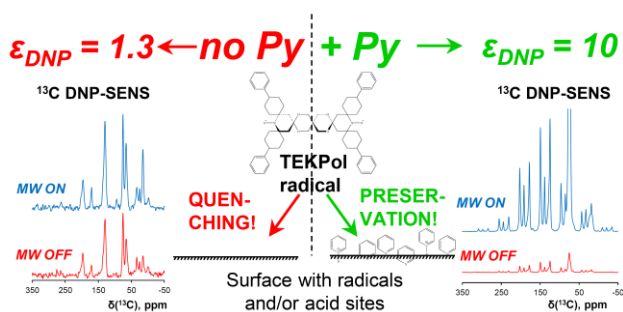
\* Christophe Copéret

[ccoperet@ethz.ch](mailto:ccoperet@ethz.ch)

**Abstract.** Dynamic nuclear polarization surface-enhanced NMR spectroscopy (DNP-SENS) has emerged as a powerful characterization tool in material chemistry and heterogeneous catalysis by dramatically increasing, by up to two orders of magnitude, the NMR signals associated with surface sites. DNP-SENS mostly relies on using exogenous polarizing agents (PAs) – typically dinitroxyl radicals, to boost the NMR signals, that may interact with the surface or even react with highly reactive surface sites, thus leading to loss/quenching of DNP enhancements. Herein, we describe the development of a DNP-SENS formulation that allows us to broaden the application

of DNP-SENS to samples containing highly reactive surface sites, namely a Ziegler-Natta propylene polymerization catalyst, a sulfated zirconia-supported metallocene and a silica-supported cationic Mo alkylidene. The protocol consists of adsorbing pyridine prior to the impregnation of the DNP formulation (TEKPol/TCE). The addition of pyridine does not only preserve the PAs and thereby restore the DNP enhancement, but it also allows probing the presence of Lewis acid and Brønsted acid surface sites that are often present on these catalysts.

## TOC GRAPHICS



**KEYWORDS.** Heterogeneous catalysts, surface modification, solid-state NMR spectroscopy, DNP-SENS, olefin metathesis catalysts, olefin polymerization catalysts.

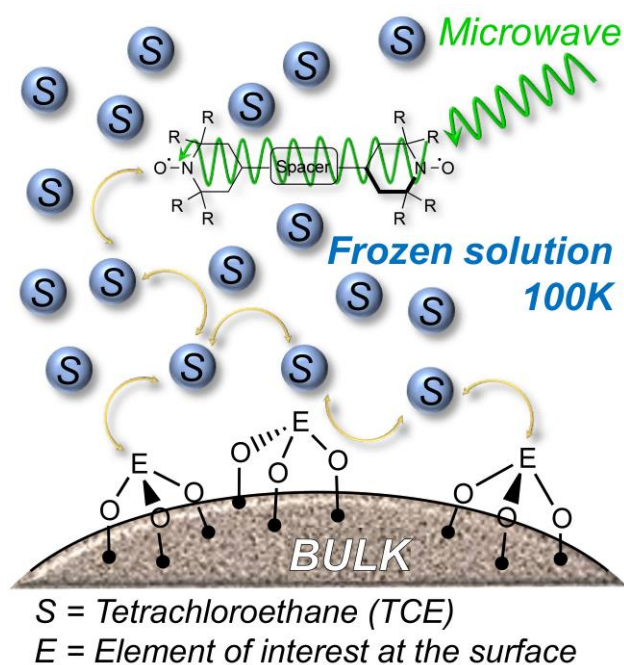
Characterization of active sites and reaction intermediates is one of the key challenges in catalysis research. These issues are particularly acute for heterogeneous catalysts because of the low content of surface sites, combined with their intrinsic complexity and heterogeneity. In addition, most spectroscopic methods provide average information and/or are not surface sensitive, yielding spectra dominated by features from the bulk of the materials, making it very difficult interrogating the nature of surface sites and thereby establishing structure-activity relationships, a first step towards rational development of catalyst.[1]

In that context, solid-state NMR spectroscopy has emerged as a very powerful tool to characterize surface sites with atomic resolution. While NMR is particularly sensitive to the local environment, allowing to probe each site individually,[2, 3] conventional solid-state NMR suffers from intrinsic lack of sensitivity, that is typically worsened by the low natural abundance of NMR active nuclei of high importance, e.g.  $^{13}\text{C}$  (1.1 %),  $^{15}\text{N}$  (0.4 %),  $^{29}\text{Si}$  (4.7 %) among others.

To solve this problem, cross-polarization, in particular when combined with hyperpolarization techniques, can boost the NMR signal and also make NMR surface sensitive. Of various approaches, dynamic nuclear polarization surface-enhanced NMR spectroscopy (DNP-SENS) is particularly noteworthy because it can increase NMR sensitivity by up to two orders of magnitude (i.e. 660 for protons), decreasing NMR times from years to minutes,[4-7] while being surface sensitive. It is thus not surprising that this approach has gained importance to characterize the surfaces of materials and has been used to detect reaction intermediates in heterogeneous catalysts.[5, 8-11]

The main principle of DNP-SENS lies in exploiting the large polarization of electrons and to transfer this polarization to targeted nuclei (with a nuclear spin) at the surface of a material [9].

The unpaired electrons are introduced to the solid sample, in most cases by incipient wetness impregnation of a solution containing a tailored diradical molecule, typically dinitroxyl radicals. The sample is then cooled in the magnet to ca. 100 K, and the spectra are recording under magic angle spinning (MAS) and microwave (MW) irradiation (Fig. 1), that allow the efficient polarization transfer from the electron to the proton bath of the frozen glassy solvent matrix and through spin diffusion combined with CP to the targeted nuclei at the surface of the material. An efficient DNP formulation requires that upon freezing at 100 K, a homogenous distribution of the polarizing source (the radical) into a glassy matrix is obtained.[5, 9] It also requires that the polarizing agents (the radicals) do not react or even interact with the substrate as the latter would lead to (paramagnetic) signal quenching. Such experiments can be done in aqueous or non-aqueous environment depending on the material(s) of interest.[9, 12]



**Fig. 1.** The general scheme of DNP-SENS: microwave-assisted polarization transfer from unpaired electrons through solvent protons to the surface.

Enhancements up to 250 have been obtained with TEKPol radical in TCE (1,1,2,2-tetrachloroethane) solution.[9, 12, 13] While a broad range of polarizing agents are now available, these exogeneous radicals and the polarization solution may not be innocent (interaction with the surface) and can even be reactive towards the surface sites, such as organometallic fragments,[14, 15] radicals and/or acid sites present on the surfaces, eventually quenching the NMR signals as evidenced by the lack of DNP enhancement of the frozen solution [10]. Thus, although DNP-SENS has already helped to characterize a broad range of catalytic materials, the choice of the DNP formulation is critical, and the exploration of DNP formulation compatible with reactive surfaces remains an important goal [9, 16-20]. Several strategies have already been explored, comprising the use of mesoporous supports in combination with bulky radicals to protect the active sites present within the mesopores [21, 22] or the use of dendritic radicals that cannot interact with the reactive sites.[9] However, these are not general solutions, and alternative DNP formulations still need to be developed.

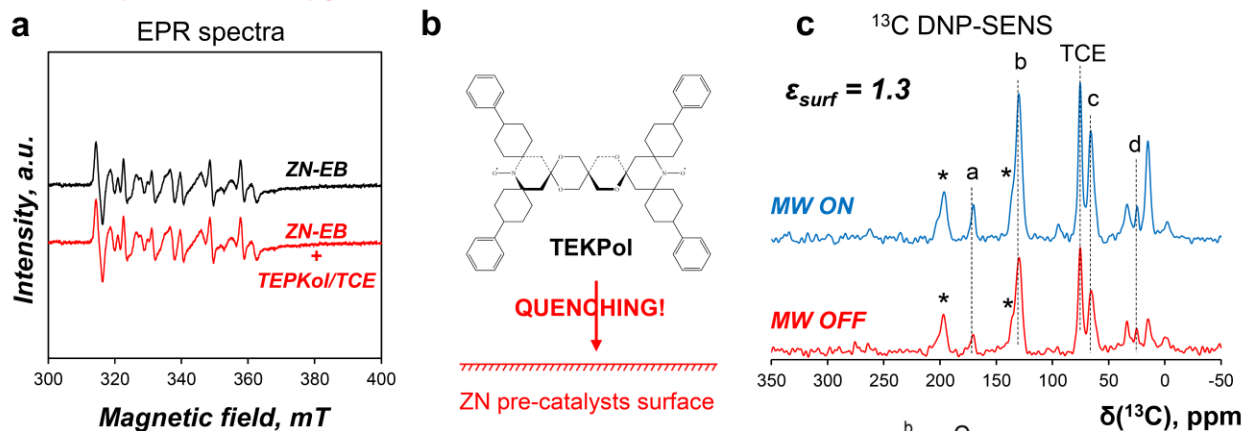
Pyridine (Py) is a classical surface probe that allows interrogating the presence of Lewis and Brønsted acid sites by using IR or solid-state NMR spectroscopy. Recent studies have shown that  $^{15}\text{N}$  MAS NMR,[23-25] in particular when combined with DNP-enhanced NMR techniques,[26] is particularly powerful by enabling to readily distinguish between Py bound to Lewis and Brønsted sites with different strength,[25] as well as H-bonded Py [26]. Pyridine is also a typical ligand in coordination chemistry and has been used to tame (passivate) the reactivity of metal sites. [27-29] We thus reasoned that it would be worthwhile investigating the addition of Py in DNP formulation with the goal to both protect highly reactive sites enabling their characterization and to probe the Lewis acid or Brønsted acid property of the surface sites. To accurately evaluate DNP performance, Py enriched with  $^{15}\text{N}$  isotope was used in the  $^{15}\text{N}$  NMR studies.

For the first step, we selected, a Ziegler-Natta propylene polymerization pre-catalyst (ZN-EB) [30], based on  $\text{TiCl}_4/\text{MgCl}_2/\text{EB}$  with ethyl benzoate (EB) as the internal donor, because earlier unreported studies from our group showed the absence of DNP enhancements in these sample using classical formulation, namely 16 mM solution of TEKPol in TCE (TEKPol/TCE).[9] EPR studies of ZN-EB indicated the presence of surface radicals with g-factors 1.76-2.17 (Fig. 2a), that could be assigned to Ti(III), Mn(II) and some organic species.[30] While these spectral features remain unchanged after impregnation of the sample with a TEKPol/TCE solution, no EPR signal corresponding to TEKPol could be detected, pointing to the disappearance of the DNP polarizing agent upon impregnation of this material (Fig. 2b). The loss of polarizing agent consequently caused the low DNP enhancements for solvent signals, both in  $^1\text{H}$  ( $\delta = 6.1$  ppm:  $\epsilon_{\text{solv}} = 1.5$ ) and  $^{13}\text{C}$  ( $\delta = 75$  ppm:  $\epsilon_{\text{solv}} = 1.5$ ). Hence, very low overall surface DNP enhancements ( $\epsilon_{\text{surf}} = 1.6$ -1.7) were observed for carbon moieties related to EB, detected at their expected resonances (Fig. 2c).[31]

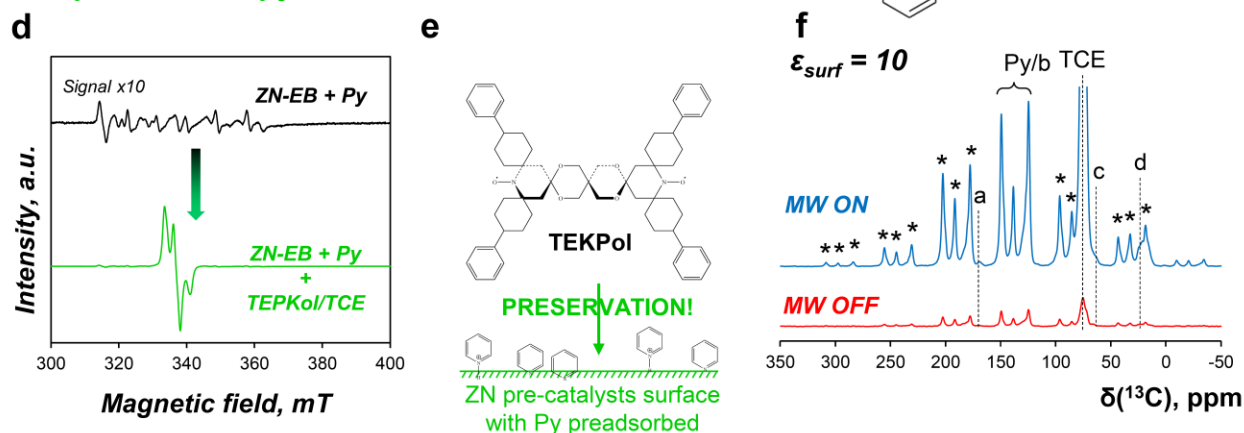
In contrast, when Py was added as a passivating agent by adsorption on the material (ZN-EB) prior to impregnation of a TEKPol/TCE solution, the characteristic EPR signals of the nitroxyl radicals were observed (Fig. 2d-e).[32] Consequently,  $^1\text{H}$  and  $^{13}\text{C}$  solvent DNP enhancements of 18 and 22, respectively were obtained (Fig. 2f), leading to  $^{13}\text{C}$  surface DNP enhancements of ca. 10 and the observation of the highly intense signals associated with these of EB ( $\delta(^{13}\text{C}) = 24$  ( $\text{PhCOO}-\text{CH}_2-\text{CH}_3$ ), 66 ( $\text{PhCOO}-\text{CH}_2-\text{CH}_3$ ), 130 ( $\text{PhCOO}-\text{CH}_2-\text{CH}_3$ ) and 171 ( $\text{PhCOO}-\text{CH}_2-\text{CH}_3$ ) ppm) and pyridine (149 (Py,  $\alpha$ -C), 138 (Py,  $\gamma$ -C) and 125 (Py,  $\beta$ -C) ppm). Important to note that only negligible changes in EB chemical shifts or line broadening were observed upon introduction of polarizing matrix (Fig. S1) as well as upon Py adsorption (Fig. 2c, f). These results show that Py adsorption can be used to prevent the quenching of the TEKPol radical without compromising the

structural information obtained by NMR and thus lead to expanding the possibility of DNP SENS to larger class of materials.

**Without preadsorbed pyridine**



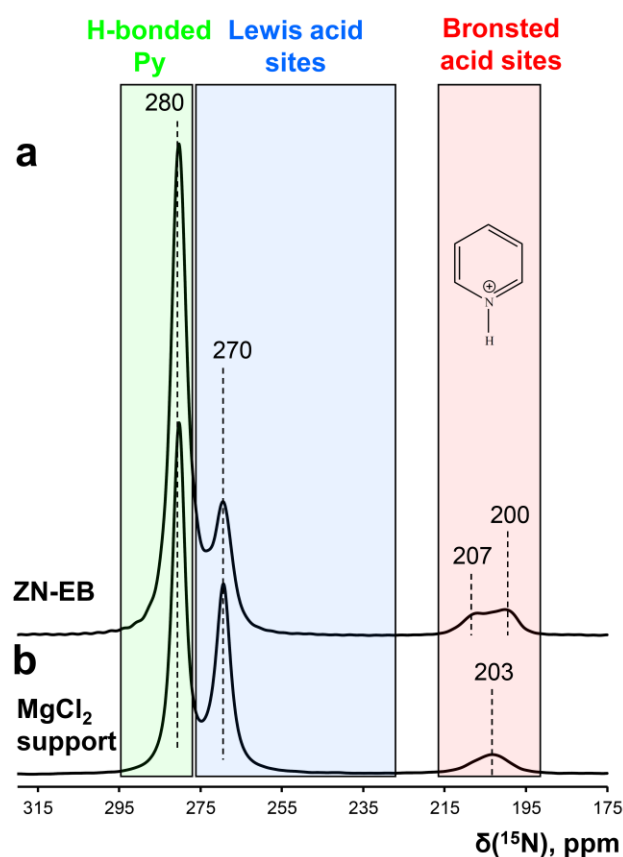
**With preadsorbed pyridine**



**Fig. 2.** Studies of the influence of TEKPol at the ZN-EB surface without (a-c) and with (d-f) preadsorbed Py: EPR spectra of catalysts before and after impregnation of TEKPol/TCE (a, d), schematic illustration of surface modification upon adsorption of Py (b, e),  $^{13}\text{C}$  DNP-SENS studies with microwave on and off (c, f).

In addition, the DNP  $^{15}\text{N}$  NMR spectrum of adsorbed Py was recorded and showed four signals with different enhancement factors: two at ca. 280 ( $\epsilon = 7$ ) and 270 ( $\epsilon = 14$ ) ppm attributed to H-

bonded Py and Py bound to Lewis acid sites at the surface of ZN-EB (Fig. 3a) and two others at ca. 200 ( $\epsilon = 7$ ) and 207 ( $\epsilon = 7$ ) ppm, indicating the presence of two types of  $\text{PyH}^+$  likely associated to the reaction of pyridine with different types of Brønsted acid surface sites.[25] The presence of  $\text{PyH}^+$  indicate the presence of Brønsted acid sites in Ziegler-Natta pre-catalysts,  $\text{TiCl}_4/\text{MgCl}_2/\text{EB}$ , an unexpected species that has thus far not been reported and is certainly noteworthy. While these findings may have some importance implication for the formation of the active sites in Ziegler-Natta catalysts, the presence of these type of acid sites as well as surface radicals may explain the source of TEKPol quenching (Fig. 2b), as it is known that nitroxyl radicals are inclined to disproportionation in acidic media.[33]



**Fig. 3.**  $^{15}\text{N}$  DNP-SENS spectra of ZN-EB pre-catalyst (a) and  $\text{MgCl}_2$  support (b) measured with MW ON.



Thus, the next step was to understand the nature and origin of sites responsible of quenching of TEKPol. For that purpose, the ball-milled  $\text{MgCl}_2$  support of ZN-EB catalyst prepared under “air and moisture” free conditions, was also studied by DNP-SENS. For this material,  $^1\text{H}$  solvent enhancement was 32; however, formulation with pre-adsorbed Py allowed for more than 3-fold increase leading to  $\epsilon_{\text{solv}} = 102$ . This implies partial quenching of TEKPol at the surface of  $\text{MgCl}_2$  itself. The EPR spectrum prior to Py adsorption showed a low-intensity feature at g-factor of ca. 2 (Fig. S2), likely corresponding to surface vacancies in  $\text{MgCl}_2$ . Furthermore,  $^{15}\text{N}$  DNP-SENS spectra of adsorbed Py showed the same signals of H-bonded Py and Py bound to Lewis acid sites as for ZN-EB, as well as a low-intensity signal centered at 203 ppm, pointing to the presence of Brønsted acid sites in  $\text{MgCl}_2$  (Fig. 3b). Origin of these Brønsted sites was probed by means of  $^1\text{H}$  SQ-DQ correlation NMR spectroscopy (Fig. S3), where strong auto-correlation of features centered at 4.67 and 3.53 as well as 1.07 and 0.86 ppm were observed. This result points to the presence of adsorbed  $\text{H}_2\text{O}$  and interacting OH groups respectively [34], even if these Ziegler-Natta catalysts and the support were manipulated under strictly anaerobic conditions (glove-box, Schlenk line techniques, etc.) pointing to the high sensitivity and reactivity of these materials towards trace amounts of moisture (below ppm level). The combination of these acid sites with surface radicals in  $\text{MgCl}_2$  as well as in ZN-EB are most likely responsible for the quenching of TEKPol, while formulation protocol with pre-adsorbed Py allows to overcome this issue since the latter removes acidic protons, while not impacting radical species.

Thus, we show that pre-adsorption of Py at the surface of catalysts is an effective method to restore DNP enhancements that would otherwise be hindered by loss of the polarizing agents (the radicals) at the surface by reaction with acid sites and surface-radicals. This approach also increases the proton density at the surface that might lead to further diffusion of the electron polarization and

hence influence the overall DNP performance [35]. To evaluate this effect of increased proton density, deuterated Py ( $C_5D_5N$ ) was used instead of protonated Py for adsorption studies of ZN-EB. The  $^1H$  and  $^{13}C$  solvent DNP enhancement were 10 and 17 correspondingly, while  $^{13}C$  surface enhancements were 1.6 (Fig. S4). Measurements of relaxation times in the case of deuterated and protonated Py adsorption showed ca. 10 times longer relaxation times for deuterated Py, likely due to formation of a Py layer at the surface that prevents polarization to reach the surface, which is consistent with elevated solvent DNP enhancement while surface enhancements are lower. This effect also likely contributes to the absence of additional NMR line broadening caused by the adsorption of Py.

These encouraging results led us to evaluate the use of Py in DNP formulation for other reactive systems. To further evaluate the applicability of utilizing pre-adsorbed pyridine (Py) as catalyst surface passivation method to prevent radicals from being quenched, we evaluated this approach on two other types of highly air, moisture and DNP formulation sensitive supported catalysts: 1) alkyl zircononene supported on sulfated zirconia ( $ZrMe^+@SZO_{300}$ ), that are well-known highly active olefin polymerization and hydrogenation catalysts,[36, 37] and 2) a recently developed supported olefin metathesis catalyst based on well-defined silica-supported cationic Mo-alkylidenes ( $Mo=CHR^+@SiO_{2-700}$ ) that show outstanding activity towards terminal olefins.[38]

These materials were prepared as previously reported (see experimental details):  $ZrMe^+@SZO_{300}$  was prepared by grafting of  $(C_5H_5)_2Zr(^{13}CH_3)_2$  onto sulfated zirconia pretreated at 300°C in air followed by evacuation at  $10^{-5}$  mbar, and  $Mo=CHR^+@SiO_{2-700}$  by grafting of  $Mo^+(=N-Ar)(=^{13}CH-C(CH_3)_2Ph)(^{13}C-1,3-(2,4,6)-(Me)_3C_6H_2-imidazol-2-ylidene)(OCH(CF_3)_2)B(Ar^F)_4)^-$  onto  $SiO_{2-700}$  – silica pretreated at 700°C under  $10^{-5}$  mbar for 48 hours. In order to adequately evaluate the DNP performance and obtain reliable data, we resorted to utilizing  $^{13}C$ -labeled materials (100%

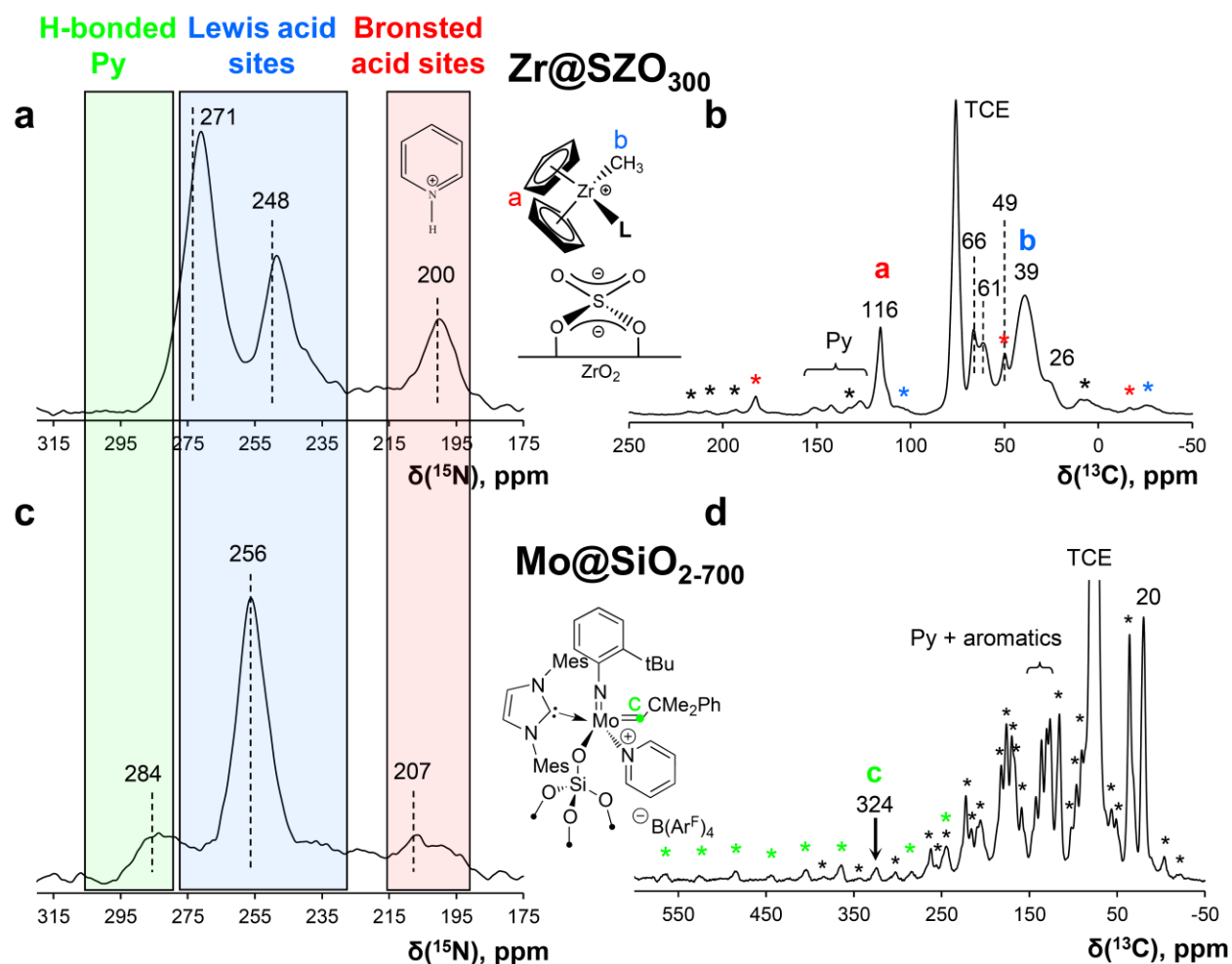
enrichment of methyl groups for  $\text{ZrMe}^+@\text{SZO}_{300}$  and 30% enrichment of the alkylidene carbon in  $\text{Mo=CHR}^+@\text{SiO}_{2-700}$ ) for this study. Both samples were formulated for the DNP studies by saturation with adsorbed  $^{15}\text{N}$ -Py with consecutive incipient wetness impregnation by 16 mM solution of TEKPol in TCE (TEKPol/TCE) under Ar atmosphere. The EPR spectra of the catalysts with pre-adsorbed Py, impregnated by TEKPol/TCE solution showed preservation of the polarizing agent similarly to what was observed for the ZN-EB case (Fig. 2d). For comparison, sample without pre-adsorbed Py were also studied by DNP-SENS using incipient wetness impregnation by TEKPol/TCE as well; in those cases, only  $^1\text{H}$  DNP-SENS spectra were recorded because of the low observed enhancement. Solvent and surface DNP enhancements obtained for  $\text{ZrMe}^+@\text{SZO}_{300}$  and  $\text{Mo=CHR}^+@\text{SiO}_{2-700}$  in the  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  NMR spectra are summarized in Table 1. The highest surface DNP enhancement of 24 achieved by this method were obtained for  $\text{ZrMe}^+@\text{SZO}_{300}$  catalyst, indicating up to 600-fold experiment time savings. In the case of  $\text{Mo=CHR}^+@\text{SiO}_{2-700}$ , surface DNP enhancements of 6-7 were observed, corresponding to up to 50 experiment time reduction.

**Table 1.** DNP enhancements in  $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{15}\text{N}$  DNP-SENS spectra for all the samples studied with adsorbed Py. Values for  $^1\text{H}_{\text{solv}}$  in parentheses are given for samples without Py.

| Catalyst                             | DNP enhancement (nuclei)   |                               |                               |                               |
|--------------------------------------|----------------------------|-------------------------------|-------------------------------|-------------------------------|
|                                      | $^1\text{H}_{\text{solv}}$ | $^{13}\text{C}_{\text{surf}}$ | $^{13}\text{C}_{\text{solv}}$ | $^{15}\text{N}_{\text{surf}}$ |
| $\text{ZrMe}^+@\text{SZO}_{300}$     | 25(5.7)                    | 24                            | 25                            | 11                            |
| $\text{Mo=CHR}^+@\text{SiO}_{2-700}$ | 11(1.2)                    | 6                             | 7                             | 7                             |

### ZrMe<sup>+</sup>@SZO<sub>300</sub>

The use of formulation with pre-adsorbed Py allows for more than 4-fold increase of solvent DNP enhancement (25), indicating the preservation of TEKPol as further evidenced by EPR spectroscopy (Figure S5). The <sup>15</sup>N DNP SENS NMR spectra of adsorbed Py shows broad intense signals at ca. 271, 248 ppm and 200 ppm, that can be attributed to H-bonded pyridine, pyridine coordinated to Lewis acid sites, likely to the cationic Zr moiety and pyridinium, respectively, as expected for this type of material.[36] In the <sup>13</sup>C DNP SENS spectra for ZrMe<sup>+</sup>@SZO<sub>300</sub> (Fig. 4b), besides the signals of pyridine (151, 142, 127 ppm) and TCE (75 ppm), signals appear at 116, 66, 61, 49, 39 and 26 ppm associated with different carbon-moieties resulting from grafting Cp<sub>2</sub>ZrMe<sub>2</sub> at the surface of ZSO<sub>300</sub>. The signal at ca. 116 ppm corresponds to C<sub>5</sub>H<sub>5</sub>(Cp)-rings bound to Zr-sites, the large and broad signals at ca. 39 is associated with CH<sub>3</sub>-group in cationic Zr-sites [Cp<sub>2</sub>Zr<sup>+</sup>CH<sub>3</sub>((L))] weakly coordinated to either pyridine or oxygen at the surface; the shoulder at 26 ppm being attributed to the neutral μ-oxo species (Surface-O-Zr(CH<sub>3</sub>)Cp<sub>2</sub>).[36] The additional peaks of lower intensity and narrower linewidth at 49, 61 and 66 ppm are associated to surface methoxy species in different environments, namely bound to sulfur and Zr, presumably related to the reduction of sulfated sites upon grafting Cp<sub>2</sub>ZrMe<sub>2</sub> on the SZO<sub>300</sub> support. Overall, adsorption of Py provided high DNP enhancements and as a consequence allowed to observe the reactive cationic zirconium alkyl species in ZrMe<sup>+</sup>@SZO<sub>300</sub> polymerization catalyst.



**Fig. 4.**  $^{15}\text{N}$  (a, c) and  $^{13}\text{C}$  (b, d) NMR spectra of  $\text{ZrMe}^+\text{@SZO}_{300}$  (a, b) and  $\text{Mo=CHR}^+\text{@SiO}_{2-700}$  (c, d) with pre-adsorbed Py measured with MW ON.

### $\text{Mo=CHR}^+\text{@SiO}_{2-700}$

We then turned our attention to the supported cationic Mo alkylidene, where addition of pyridine also helped to restore the DNP enhancements. The  $^{15}\text{N}$  DNP-SENS spectra show the presence of two major signals at 284 and 256 ppm, corresponding to H-bonded Py as well as Py bound to Lewis acid sites, along with a minor signal at 207 ppm corresponding to  $\text{PyH}^+$ , evidencing the presence of small amount of Brønsted acid sites (Fig. 4c). These Brønsted acid sites are most likely

attributed to OH-group in close proximity to cationic Mo-sites as recently discussed for the related silica-supported W-oxo system.[39] Regarding the  $^{13}\text{C}$  DNP-SENS spectrum of  $\text{Mo}=\text{CHR}^+@\text{SiO}_2$ -700 with pre-adsorbed Py (Fig. 4d), besides the signals of Py (147, 136 and 126 ppm) and TCE (75 ppm), these at 20, 130, 142 and 324 ppm are consistent with the presence of the cationic Mo alkylidenes, in view of their similar chemical shift with the molecular compound.[38] One should note the alkylidene signal is slightly more deshielded than in the molecular complex ( $\delta = 313$  ppm [38]), which is consistent with coordination of Py, a  $\pi$ -acceptor ligand, to the Mo-sites [40]. In fact, addition of pyridine to the molecular complex leads to similar observation (Fig. S6). Overall these results demonstrate that pre-adsorption of Py is an effective approach to observe highly sensitive alkylidene species with a decrease of NMR time reaching 100.

In summary, we have shown that adsorption of Py prior to formulation with the polarizing agents (TEKPol/TCE) is a powerful protocol to record DNP-SENS on heterogeneous catalysts and materials that contain acidic or radical containing surfaces, which normally lead to decomposition of exogeneous radicals like TEKPol and the loss of DNP enhancement. Overall, application of the formulation protocol with pre-adsorbed Py, here on three prototypical highly sensitive catalysts, enables the simultaneous characterization of Lewis/Brønsted surface acid sites and observation of “passivated” active sites, coordinated by the adsorbed pyridine, of catalysts by DNP-SENS. This protocol is likely applicable to a variety of materials containing reactive surface sites.

## ASSOCIATED CONTENT

**Supporting Information.** Procedures of synthesis, modification and characterization of catalysts,  $^{13}\text{C}$  solution NMR, MAS NMR and DNP-SENS spectra, EPR spectra,  $^1\text{H}$  SQ-DQ NMR spectrum.

## AUTHOR INFORMATION

E-mail: ccoperet@ethz.ch

## Notes

The authors declare no competing financial interests.

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