Quantitative Tin Loading Determination of Supported Catalysts by ^{119}Sn HRMAS NMR using a Calibrated Internal Signal (ERETIC)

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Summary: As an alternative to tedious elemental analysis, tin loading of a grafted organotin catalyst is quantified using an electronic reference (ERETIC) in ^{119}Sn HRMAS NMR. The results are in excellent agreement with elemental analysis data and display a significantly higher precision.

NMR spectroscopy is a very powerful tool for quantitative analytical purposes, since the area under a given resonance is proportional to the number of nuclei generating that resonance. Quantitative measurements by NMR are generally performed in the liquid state using a chemical internal reference which has to meet many standards in terms of solubility, stability, relaxation time, chemical shift, and chemical inertness toward the sample. The ERETIC (*e*lectronic *re*ference *t*o access *i*n vivo *c*oncentration) method efficiently circumvents these issues by using a calibrated electronic signal as an internal reference. Up to now, the method has been successfully applied for quantitative measurements in 1D[1–5] and 2D[6] liquid-phase NMR, MRI,[7] and solid-state NMR[8] and for diffusion measurements.[9]

In this paper, the use of the ERETIC method is introduced in HRMAS (*h*igh-*r*esolution *m*agic *a*ngle *s*pinning) NMR, a technique by which high-resolution NMR spectra of grafted mobile molecular moieties immersed in a liquid can be recorded in situ at the solid−liquid interface.[10–12] In particular, HRMAS NMR has proven to be very powerful for monitoring synthetic and catalytic processes of grafted organometals and in transition-metal chemistry on silica gel support,[13] as well as in grafted organotin catalysis using cross-linked polystyrene as a solid carrier.[14–16] With regard to applications in catalysis under well-controlled conditions, accurate quantitative data on the tin loading of these type of insoluble catalysts are indispensable. So far, they rely exclusively on elemental analysis. However, the time-consuming and tedious nature of tin elemental analysis, which does not always lead to entirely satisfactory data,[16] prompted us to explore the use of an ERETIC calibration signal as an internal reference in ^{119}Sn HRMAS NMR as an alternative to tin elemental analysis to quantify the catalyst's tin content.

In practice, the ERETIC signal is calibrated against a reference solution of known concentration, followed by quantification of the sample of interest using the ERETIC signal as an internal reference (Figure 1). The chemical shift of the ERETIC signal can be set at will in the spectrum, whereas its intensity is easily scalable using the power control settings. In the present study, a solution of tetramethyltin (Me_4Sn) in $CDCl_3$ (120 mM) is used for the calibration. Quantification experiments are performed on three separate batches of polystyrene-grafted undecyltin trichloride catalyst, $\mathbf{P}-(CH_2)_{11}-SnCl_3$, differing from each other only in their tin loading.

For quantitative purposes, full relaxation in the ^{119}Sn resonances of both the reference solution and the catalyst needs to be ensured. As a rather long relaxation delay of 6 s is required to fulfill this prerequisite for the organotin trichloride catalyst, it was first investigated whether a shorter delay would be acceptable in the calibration step. The Student *t* test for paired series on two sets of calibration measurements with a delay of 3 and 6 s indicated no significant difference (probability $p < 0.01$) between the two experiments (Table 1). As a result, the relaxation delay for all calibration measurements was reduced to 3 s, leading to a gainful reduction in total experiment time, while it was 6 s for all actual measurements involving grafted catalyst. For 5000 scans, the total recording time was 5 h for the calibration and 9 h for the catalyst quantification.

To ensure correct integration of all ^{119}Sn resonances, the integration limits are systematically enlarged on both sides of the resonances and an average value with corresponding standard deviation is calculated. In Table 1, the mean integral value for the catalyst resonance is expressed as the molar amount of Sn ($n_{\mathrm{Sn,ERETIC}}$) present in the HRMAS sample. From this value, the corresponding mass fraction $\gamma_{\mathrm{Sn,ERETIC}}$ is calculated. Accordingly, $n_{\mathrm{Sn,EA}}$ represents the molar amount of Sn calculated from γ_{Sn} as determined by elemental analysis data using the sample weight taken for the ERETIC measurements. When both

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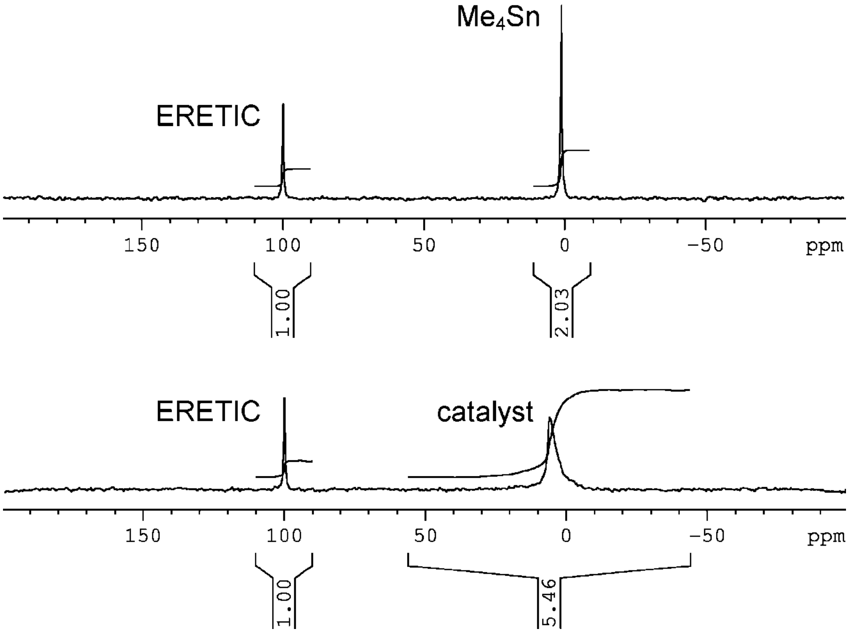

Figure 1. Use of an ERETIC signal as electronic reference in ^{119}Sn HRMAS NMR for tin loading quantification of a grafted catalyst of the type **P**−(CH$_2$)$_{11}$−SnCl$_3$. The method consists of a calibration step (top) and a quantification step (bottom).

Table 1. Quantitative Tin Loading Data for Three Different Batches of Grafted Organotin Trichloride Catalyst Obtained by Elemental Analysis (EA) and by the ERETIC Method in ^{119}Sn HRMAS NMR

cat. (sample wt (mg))	EA		ERETIC	
	γ_{Sn} (wt %)	n_{Sn} (μmol)	n_{Sn} (μmol)	γ_{Sn} (wt %)
1 (15.3)	12.16 ± 1.00	15.68 ± 1.29	15.56 ± 0.25 15.58 ± 0.25[a]	12.07 ± 0.19 12.09 ± 0.19[a]
1 (15.1)[b]	12.16 ± 1.00	15.47 ± 1.27	15.43 ± 0.13	12.13 ± 0.10
2 (15.0)	13.02 ± 1.00	16.45 ± 1.26	16.17 ± 0.17	12.79 ± 0.13
3 (10.0)	8.34 ± 1.00	7.03 ± 0.84	7.02 ± 0.07	8.33 ± 0.08

[a] The calibration was performed using a relaxation delay of 6 s; all other calibration measurements were performed with a relaxation delay of 3 s. The spectrum recording involving the grafted catalyst was performed with a relaxation delay of 6 s. [b] Verification of the reproducibility for catalyst **1**.

methods are compared, it is clear that, in all three cases, the ERETIC data are highly consistent with elemental analysis data, while the ERETIC method provides an increase in the precision of the measurement. The reproducibility of the ERETIC method is demonstrated for catalyst **1**.

The results demonstrate that the totality of the grafted organotin moieties present in the freshly synthesized catalyst is fully observable by ^{119}Sn HRMAS NMR. Because of the presence of a single characteristic chemical shift, they consist only of organotin trichloride. Experiment **3** shows that 10 mg of material, i.e. 2 times less than for elemental analysis, is sufficient to obtain a reliable measurement. Since the method also prevents contamination of the sample, the catalyst can be easily recovered for any further purposes.

Once the grafted alkyltin trichloride is used as a catalyst in the transesterification reaction of ethyl acetate and *n*-octanol, an additional cross-linking of the catalyst at the interface occurs upon an increasing number of catalytic runs.[16] Since cross-linking reduces the conformational mobility of the catalyst and since rotationally immobilized chemical moieties are not visible in HRMAS NMR, this resulted, after 10 subsequent catalytic cycles, in a ^{119}Sn signal-to-noise ratio decrease to about one-fifth of the original value for freshly synthesized catalyst, which could not be accounted for by tin leaching alone.[16] As the implementation of the ERETIC method in ^{119}Sn HRMAS NMR proves to be a highly reliable technique for quantification purposes, it now also enables one to measure the amount of remaining rotationally mobile catalyst moieties after 10 transesterification cycles. The ERETIC experiment reveals that, after 10 runs, only 24% of the original SnCl$_3$ catalyst remains unaltered and preserves its initial conformational mobility at the interface, meaning that 76% of the organotin moieties underwent a chemical modification through which they became rotationally immobilized and therefore invisible by HRMAS NMR.[12]

The presented ERETIC approach provides direct quantitative data on the grafted organotin loading with a precision which is significantly higher than by elemental analysis. Moreover, with a total recording time of 14 h for calibration and quantification, which can be performed mostly overnight, a considerable gain in time is achieved as compared to the outsourced elemental analysis.

The ERETIC-based method presented here is of general scope, as it can be easily extended to other NMR nuclei. ^{1}H HRMAS NMR offers interesting possibilities, especially in view of its shorter recording time, provided that a well-isolated, characteristic ^{1}H resonance can be properly exploited in the spectrum. Application of the method to heteronuclei such as ^{31}P, ^{13}C, and ^{29}Si, as well as to other types of solid catalyst supports, such as silica, can also be envisaged, provided the appropriate probe is available and the moiety observed is fully HRMAS visible. Finally, the method should find application in the field of synthesis monitoring, where it can, for instance, be readily applied to the quantification of grafted impurities.

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Supporting Information Available: Text giving experimental details. This material is available free of charge via the Internet at http://pubs.acs.org.

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