

# Sealing of Zeolite L Channels with Ethoxysilanes: Influence of Molecular Structure and Thermal Treatment

Simon Lustenberger<sup>[a]</sup> and Dominik Brühwiler\*<sup>[a]</sup>

The suitability of silanes  $\text{H}_2\text{N}(\text{C}_3\text{H}_6)\text{Si}(\text{OC}_2\text{H}_5)_{3-x}(\text{CH}_3)_x$  ( $x=0, 1, 2$ ) for the sealing of zeolite pores has been investigated. The sealing efficiency was evaluated by observing the exit kinetics of the fluorescent dye resorufin from the one-dimensional main channels of zeolite L (ZL). The best results in terms of sealing quality were obtained with  $x=0$ , indicating the importance of ensuring maximum probability for siloxane bond formation and cross-linking during the sealing process. The amino group

thereby plays a crucial role in the positioning of the silane prior to covalent bond formation. Samples sealed with 3-aminopropyltriethoxysilane (APTES) showed excellent stability against leaching in aqueous medium even under moderately alkaline conditions. Further evidence for the ability of APTES to efficiently seal the channels of ZL was obtained by nitrogen sorption measurements.

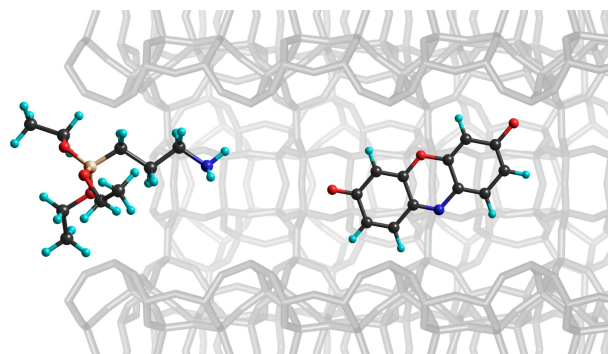
## Introduction

Zeolite L (ZL) is a crystalline aluminosilicate with main channels having a diameter of 0.71 nm at the narrowest and 1.26 nm at the widest section. These main channels (hereafter referred to as ZL channels) are connected by a two-dimensional channel system, which, due to its much smaller limiting aperture, does not represent potential diffusion paths.<sup>[1]</sup> Crystals of ZL can be synthesized in a large range of particle sizes and aspect ratios.<sup>[2–6]</sup> The inclusion of guests into the ZL channels has led to a variety of novel host-guest materials.<sup>[7]</sup> Examples of such ZL-based composites include colorants,<sup>[8]</sup> light-harvesting antenna systems,<sup>[9,10]</sup> white-light-emitting devices,<sup>[11]</sup> and fluorescent labels for optical imaging.<sup>[12,13]</sup> A key step in the synthesis of these materials is the intercalation of the guest species – often organic chromophores and fluorophores – into the ZL channels. Depending on the properties of the guest molecules, intercalation can be achieved by ion exchange from solution or in the absence of a solvent at elevated temperature.<sup>[7]</sup> An efficient displacement of neutral guests upon the uptake of water is typically observed due to the hydrophilic character of ZL.<sup>[14,15]</sup> To avoid leaching, it is therefore necessary to seal the channels. This can be achieved by selectively addressing the channel entrances<sup>[9]</sup> or by following a core-shell approach via the deposition of silica onto the ZL crystals.<sup>[16,17]</sup>

A two-step process based on 3-aminopropyltriethoxysilane (APTES) has been described as a method for channel sealing.<sup>[9]</sup> It has been assumed that the amino group of APTES first enters the channel, possibly in its protonated state and thus driven by

ion exchange, leading to an ideal positioning of the triethoxysilyl moiety for a reaction with ZL surface hydroxyl groups in its vicinity (Figure 1).<sup>[18,19]</sup> The concept of combining a high affinity towards the ZL channels and the ability of forming covalent bonds with surface hydroxyl groups has first been proposed by Ban et al.<sup>[20]</sup> using a triethoxysilylated coumarin to achieve a selective modification of the ZL channel entrances. In a similar approach based on a triethoxysilylated imidazolium salt, leaching of  $^{111}\text{In}^{3+}$  from the ZL channels has been successfully minimized.<sup>[21]</sup> While mostly employed in combination with ZL, channel sealing with APTES has also been shown to prevent the uptake of water by zeolite Y.<sup>[22]</sup> Apart from sealing the channel entrances, the modification of dye-ZL composites with APTES resulted in better dispersibility of the particles in polymer films.<sup>[9]</sup>

The covalent anchoring of APTES at the ZL channel entrances occurs upon thermal treatment in a solvent such as ethyl acetate or toluene after the initial physisorption.<sup>[7,19,23]</sup> In this two-step mechanism (physisorption and covalent attachment), the amino group and the triethoxysilyl moiety are considered essential for providing an efficient sealing of the channels. To evaluate the validity of this hypothesis and



**Figure 1.** Schematic representation of a ZL channel entrance (framework shown in light gray) with APTES in an ideal orientation for channel sealing and a resorufin anion ( $\text{Res}^-$ ) located in the channel.

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develop an optimized procedure for achieving efficient channel sealing, we have compared the sealing efficiency of various ethoxysilanes (Figure 2).

Covalent bond formation between an ethoxysilane and a zeolite involves surface hydroxyl groups. Studies on H-ZSM-5 with IR spectroscopic probes have shown that silanol (SiOH) groups are mainly located on the external zeolite surface, whereas Brønsted acid sites (bridged Si(OH)Al groups) are the prevalent hydroxyl species in the pores.<sup>[24]</sup> Internal silanol groups can exist and are typically caused by lattice defects.<sup>[25]</sup> These differences between the external and internal surface chemistry of zeolites are an important prerequisite for developing methods to efficiently block the pore entrances.

In principle, APTES (1) can form three covalent bonds to a zeolite surface, although the formation of more than two surface bonds is unlikely due to the geometric constraints involved.<sup>[19]</sup> A similar sealing efficiency would thus be expected when using 3-aminopropyldiethoxymethylsilane (APDEMS, 2), unless silane cross-linking contributes to the efficiency of the channel sealing process. In the case of 3-aminopropyldimethylethoxysilane (APDMES, 3), only one surface bond can be formed. Cross-linking would lead to dimerization and thus would not be contributing towards channel sealing. Finally, *n*-propyltriethoxysilane (PTES, 4) was used to evaluate the function of the amino group in the sealing process.

A quantitative assessment of the channel sealing efficiency can be achieved by measuring the exit kinetics of the organic dye resorufin (ResH).<sup>[15]</sup> The fluorescence of the deprotonated form of resorufin (Res<sup>-</sup>) is quenched when the dye is located in the ZL channels. Displacement of intercalated Res<sup>-</sup> by water and release into the surrounding solution restores the fluorescence.<sup>[15]</sup> The displacement of Res<sup>-</sup> from the channels is irreversible, as resorufin in aqueous solution cannot re-enter the channels due to the negatively charged aluminosilicate framework.

## Experimental Section

### Materials

3-aminopropytriethoxysilane (APTES, 99%, Sigma-Aldrich), 3-aminopropyldiethoxymethylsilane (APDEMS, 97%, Sigma-Aldrich), 3-aminopropyldimethylethoxysilane (APDMES, 95%, Sigma-Aldrich), *n*-propyltriethoxysilane (PTES, 95%, Fluorochem), *n*-butanol (99.9%, Sigma-Aldrich), ethanol (abs., VWR), ethyl acetate (99.95%, Chem-solute), KCl (99.5%, Fluka), KOH (85%, Acros), sodium dodecyl

sulfate (SDS, 99%, Roth), resorufin (ResH, 95%, Fluorochem), and zeolite L (ZL, Zeochem, 1.5 μm average particle size) were used as received.

### Intercalation of Resorufin

The synthesis of the Res<sup>-</sup>-ZL composite was adapted from a previously reported procedure.<sup>[15]</sup> A quantity of 8.0 g of ZL was dispersed in 320 mL of a 0.1 M aqueous KCl solution. After 20 min of sonication, the suspension was stirred for 1 h at room temperature. During this time, the pH was kept between 8 and 9 by adding 0.1 M aqueous KOH. The potassium-exchanged ZL crystals were isolated by centrifugation (10'000 rpm, 10 min), dried at 80 °C for 16 h, finely ground in a mortar, and activated at 160 °C under vacuum for 16 h.

600 mg of activated potassium-exchanged ZL and 6 mg of ResH were finely ground in a mortar and placed in a pre-dried round-bottom flask that was sealed with a septum. The powder mixture was heated to 150 °C with magnetic stirring and maintained at this temperature for 3 h, followed by stirring at 150 °C for 72 h under nitrogen atmosphere. The orange product particles were dispersed in 10 mL of 0.2 M ethanolic KOH, sonicated for 10 min, and isolated by centrifugation (10'000 rpm, 10 min). The particles were washed repeatedly with 0.2 M ethanolic KOH and *n*-butanol until the washing solution became colourless. The resulting purple particles were dispersed in *n*-butanol for storage, as it was previously observed that Res<sup>-</sup>-ZL shows negligible leaching in *n*-butanol.<sup>[15]</sup> The amount of non-intercalated ResH was determined by measuring the absorbance of the washing solutions.

### Channel Sealing

Channel sealing with ethoxysilanes was conducted following a previously reported procedure for APTES.<sup>[8]</sup> An amount of 1.015 mmol of the respective ethoxysilane (Figure 2) was used for sealing 80 mg of Res<sup>-</sup>-ZL. An aliquot of the Res<sup>-</sup>-ZL suspension, corresponding to 80 mg of Res<sup>-</sup>-ZL, was isolated by centrifugation (10'000 rpm, 10 min) and transferred to a GC headspace vial with 2 mL of ethyl acetate. After sonication for 10 min, 1.015 mmol of the respective ethoxysilane was added to the suspension and then stirred for 2 h at 500 rpm. After further stirring at 500 rpm for 16 h at 80 °C (thermal treatment step), the suspension was cooled to room temperature and washed three times with 10 mL of ethanol and once with 10 mL of *n*-butanol. The particles were stored in 8 mL of *n*-butanol. Potential loss of resorufin during the sealing process was determined by UV-Vis measurements. To evaluate the effect of the temperature on the channel sealing efficiency, the thermal treatment step was varied. Replacement of ethyl acetate with toluene led to similar results regarding the channel sealing efficiency.

### Measurement of Resorufin Release

Prior to the measurement, a suspension containing 80 mg of sealed or unsealed Res<sup>-</sup>-ZL in 8 mL of *n*-butanol was sonicated for 10 min. A volume of 300 μL of this suspension was removed, transferred to a Falcon tube, and centrifuged (10'000 rpm, 10 min). The supernatant was removed, and 3.0 mL of aqueous release medium (0.2% w/w SDS in water) was added to the particles. The addition of SDS was found to improve the quality of the dispersion and led to a better reproducibility of the resorufin release profiles. After briefly vortexing and sonicating, the suspension was transferred to a quartz cuvette (1 cm, equipped with a magnetic stir bar), which was then placed in the spectrofluorometer. The measurement was

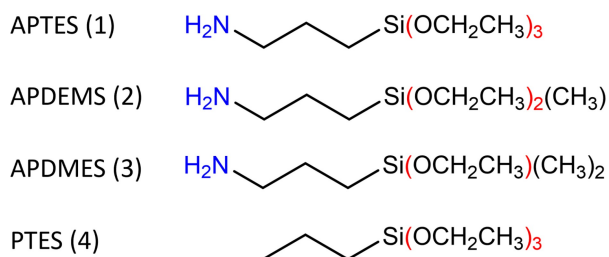


Figure 2. Ethoxysilanes used for evaluating the channel sealing efficiency.

started 1 min after the addition of the release medium. The suspension was stirred continuously during the measurement (90 min duration, excitation at 554 nm, emission detected at 585 nm, one measurement point every 5 s). At the end of the measurement, the solution was isolated from the particles using a syringe filter (PTFE, 0.45  $\mu\text{m}$ ) and the concentration of released resorufin was determined by UV-Vis absorption spectroscopy.

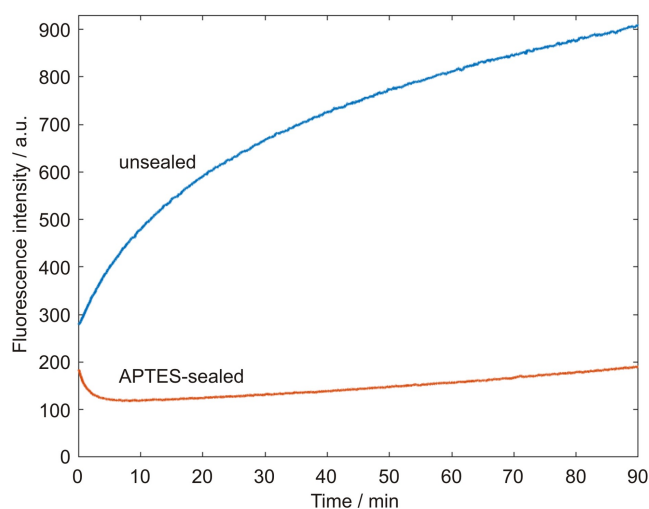
### Physical Measurements

A PerkinElmer LS55 spectrofluorometer was used for measuring fluorescence. UV-Vis absorption spectra were recorded with a PerkinElmer Lambda 650. To calculate the resorufin concentration in the 0.2% w/w aqueous SDS solution, an extinction coefficient of  $45\,426\text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$  was used (at 572 nm). Nitrogen sorption isotherms were measured at 77 K with a Quantachrome Autosorb iQ MP. The total pore volume  $V_{\text{tot}}$  was derived from the amount of adsorbed nitrogen at a relative pressure of  $p/p_0=0.95$ . Samples were dried under vacuum at 80 °C for 24 h prior to the measurement.

## Results and Discussion

### Comparison of Unsealed and APTES-Sealed Samples

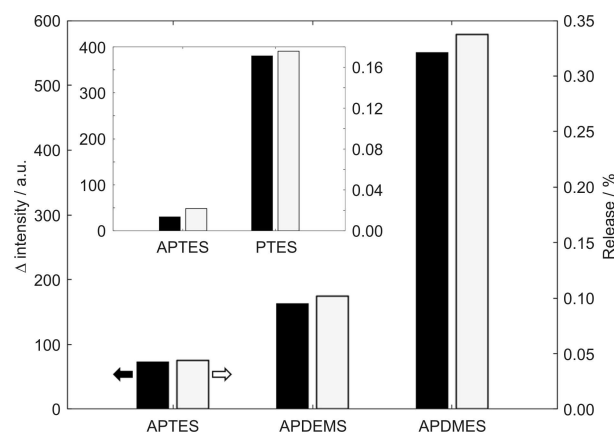
As shown in Figure 3, unsealed (pristine) Res<sup>-</sup>-ZL samples showed the expected and previously observed release profile upon dispersion in the aqueous medium.<sup>[15]</sup> After sealing with APTES, the release is significantly suppressed. The increase of the fluorescence intensity obtained after 90 min was taken as a characteristic figure for the ability of an ethoxysilane to seal the ZL channels. These values were further validated by measuring the concentration of the released resorufin by UV-Vis absorption spectroscopy.



**Figure 3.** Release profiles of unsealed Res<sup>-</sup>-ZL and APTES-sealed Res<sup>-</sup>-ZL in the aqueous release medium. The initial slight decrease of the fluorescence intensity visible in the case of the APTES-sealed sample can be attributed to a mixing effect.

### Influence of the Number of Ethoxy Groups

The loading of ZL with Res<sup>-</sup> refers to the number of occupied ZL unit cells divided by the total number of ZL unit cells.<sup>[8]</sup> In this case, Res<sup>-</sup>-ZL with a loading of 0.10 was utilized. APTES (three ethoxy), APDEMS (two ethoxy), or APDMES (one ethoxy) was used for sealing the channels. Figure 4 shows that the sealing efficiency correlates with the number of ethoxy groups. As anticipated, APTES yielded the best sealing quality owing to its pronounced tendency for the formation of siloxane bonds. The fact that APDEMS also provides adequate sealing is of interest for the selective functionalization of channel entrances using ethoxysilanes composed of two ethoxy groups, a group with a high affinity to the ZL channels (e.g. -NH<sub>2</sub>), and a further functional group, which then would reside in a more accessible position at the channel entrance.<sup>[26]</sup> APDMES is clearly inferior in terms of the sealing efficiency. While this might be attributed to the lower probability of siloxane bond formation with the ZL surface hydroxyl groups, it could also indicate that silane cross-linking contributes towards an efficient sealing of the channels. This is in agreement with a previous comparison between APTES and APDMES, which showed that the uptake and release of thionine by ZL was still possible after modification with APDMES, whereas treatment with APTES led to a complete blockage of the channels.<sup>[27]</sup> It should be mentioned in this context that the high sealing efficiency of APTES cannot be attributed to a tripodal attachment, as the formation of three covalent bonds to the zeolite surface can be ruled out. Bipodal binding was found to already feature a strained geometrical arrangement.<sup>[19]</sup>



**Figure 4.** Comparison of the sealing efficiency of APTES, APDEMS, and APDMES as well as of APTES and PTES (inset). The black bars indicate the sealing efficiency determined by measuring the increase of the fluorescence intensity after 90 min of exposure of the respective sealed Res<sup>-</sup>-ZL sample to the aqueous release medium (left y-axis). The percentage of released resorufin (white bars, right y-axis) was obtained by measuring the UV-Vis absorption spectrum of the respective resorufin solution after 90 min of release.

### Influence of the Amino Group

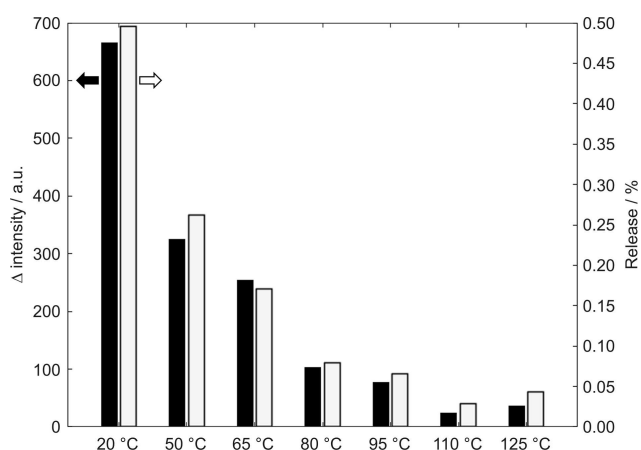
To clarify the role of the amino group, the sealing efficiency of APTES was compared to PTES. A Res<sup>-</sup>-ZL sample with a loading of 0.11 was used in this case. The results shown in Figure 4 clearly point to a central role of the amino group in the channel sealing process. The amino group in APTES is known to self-catalyze the siloxane bond formation and additionally promote the adsorption through hydrogen bonding to surface hydroxyl groups.<sup>[19,28]</sup> These effects are absent in PTES. Interestingly, it was observed that the addition of a base (the sterically hindered 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as well as triethylamine in separate experiments) did not improve the sealing efficiency of PTES. A mechanism based on the protonation of the amino group and an ion-exchange driven positioning of the protonated APTES at the ZL channel entrance is therefore a reasonable assumption.<sup>[9]</sup>

### Influence of the Temperature During Thermal Treatment

The temperature of the thermal treatment step has a significant influence on the sealing efficiency. This was investigated for sealing with APTES (Figure 5), indicating an excellent efficiency at temperatures above 80 °C. This is in agreement with studies on the attachment of APTES on silicon oxide surfaces, suggesting that higher temperatures promote the formation of siloxane bonds between APTES and the surface, while also enhancing APTES cross-linking.<sup>[29]</sup>

### Stability of APTES-Sealed Samples

Sealing with APTES was found to improve the stability of the samples against leaching of resorufin when exposed to



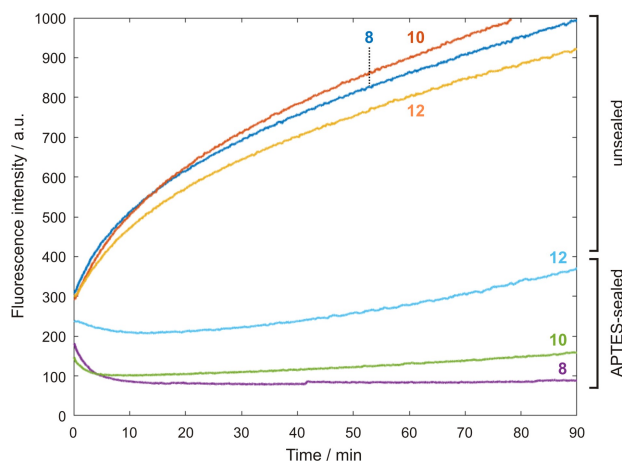
**Figure 5.** Comparison of the sealing efficiency of APTES after thermal treatment for 16 h at various temperatures. The black bars indicate the sealing efficiency determined by measuring the increase of the fluorescence intensity after 90 min of exposure of the respective sealed Res<sup>-</sup>-ZL sample to the aqueous release medium (left y-axis). The percentage of released resorufin (white bars, right y-axis) was obtained by measuring the absorption spectrum of the respective resorufin solution after 90 min of release.

laboratory air (average relative humidity of 45%). After 8 days, unsealed Res<sup>-</sup>-ZL lost 3.0% of the intercalated resorufin, whereas leaching of only 0.4% was observed for a corresponding APTES-sealed sample. Under these conditions, resorufin leaching is caused by the adsorption of water from the ambient air and subsequent displacement of the intercalated resorufin molecules. Storing the samples for 8 days in *n*-butanol caused leaching of 0.17% and 0.01% for the unsealed and the APTES-sealed sample, respectively.

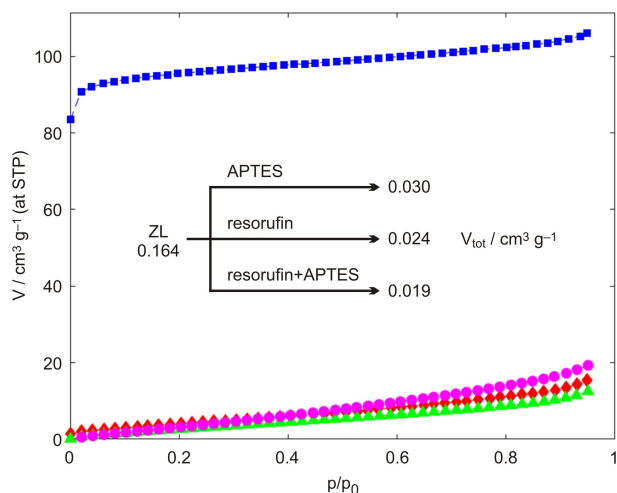
Sealing of zeolite channels with an ethoxysilane is based on the formation of siloxane bonds. As these bonds are prone to hydrolysis at high pH values,<sup>[30]</sup> it can be expected that increased leaching is observed under alkaline conditions. The release profiles shown in Figure 6 indicate good stability of APTES-sealed Res<sup>-</sup>-ZL at pH 8. Slightly increased leaching occurs at pH 10, and significant leaching at pH 12. Due to the limited stability of resorufin at pH > 12,<sup>[31]</sup> strongly alkaline conditions were not considered. It can be expected from these results that the stability of APTES-sealed samples is limited at high pH values. The release of Res<sup>-</sup> from unsealed channels was found to be essentially independent of the pH within the investigated range.

### Nitrogen Adsorption Isotherms

N<sub>2</sub> adsorption isotherms measured at 77 K provide further evidence for the ability of APTES to efficiently seal the channels of ZL. The adsorption isotherms shown in Figure 7 demonstrate that sealing of the ZL channels with APTES drastically reduces the pore volume (from 0.164 to 0.030 cm<sup>3</sup> g<sup>-1</sup>), thus indicating that the accessibility of the ZL channels for N<sub>2</sub> is restricted under these conditions. Loading with resorufin leads to a similarly decreased pore volume (0.024 cm<sup>3</sup> g<sup>-1</sup>). The smallest pore volume was obtained in the case of resorufin-loaded and APTES-sealed ZL (0.019 cm<sup>3</sup> g<sup>-1</sup>). Loading with resorufin and APTES-sealing has a comparable effect on the shape of the



**Figure 6.** Release profiles of unsealed Res<sup>-</sup>-ZL (top three curves) and APTES-sealed Res<sup>-</sup>-ZL (bottom three curves) in aqueous NaOH at pH values of 8, 10, and 12.



**Figure 7.**  $N_2$  adsorption isotherms (77 K) of ZL (blue squares), APTES-sealed ZL (magenta circles), Res<sup>-</sup>ZL (red diamonds), and APTES-sealed Res<sup>-</sup>ZL (green triangles). The numerical values show the change of the total pore volume of ZL upon APTES-sealing (without resorufin loading), resorufin loading (without APTES-sealing), and resorufin loading with subsequent APTES-sealing.

isotherm, transforming the type I isotherm of pristine ZL into a type II isotherm, representative of a non-porous material.<sup>[32]</sup>

## Conclusions

Res<sup>-</sup>ZL composites represent an excellent platform for evaluating the effectiveness of methods to seal the pores of zeolites. For ethoxysilanes, the sealing efficiency was found to increase with the number of ethoxy groups, indicating that ensuring a maximum ability of siloxane bond formation with the zeolite surface is essential. Furthermore, cross-linking between the ethoxysilanes is expected to contribute to pore blocking. The positioning of the 3-aminopropylethoxysilanes at the channel entrances of ZL is driven by the protonation and intercalation of the amino group, the presence of which is considered essential for efficient sealing. After adsorption of the ethoxysilane, siloxane bonds are formed during thermal treatment. In this step, temperatures above 80 °C are recommended to achieve sufficient stability against leaching of guest species in aqueous medium. The stability of APTES-sealed ZL channels against hydrolysis is limited under alkaline conditions. Increased leaching of the guest molecules was observed at a pH value of 10.

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## Conflict of Interests

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

**Keywords:** Zeolites · Silanes · Resorufin · Leaching · Channel Sealing

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