

Synthesis of Silsesquioxane Derivatives via Hydrosilylation of Alkenes and Alkynes Catalyzed by Pt/XAD-4 in Supercritical CO₂

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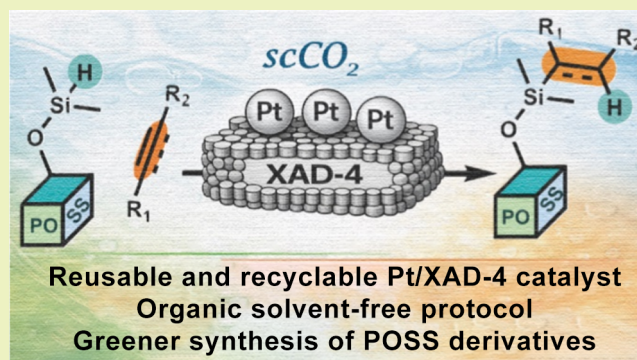
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ABSTRACT: A new heterogeneous platinum catalyst on the styrene–divinylbenzene resin (Pt/XAD-4) was developed for the hydrosilylation of various functional alkenes (**2b–f**) and alkynes (**2a–j**) using high-molecular-weight silsesquioxanes (**1a–d**) and applied in supercritical CO₂ (scCO₂) as a reaction medium. The obtained Pt/XAD-4 catalyst is competitive to previous Pt heterogeneous systems in these transformations and provides possibilities for effective catalyst reuse. Comparing the processes in scCO₂ to commonly used toluene showed that the catalyst was significantly more active and stable upon application of this green solvent. Extraction of the products with scCO₂ allowed for simple catalyst recycling over up to 40 cycles without visible loss of its activity, providing much higher accumulative total turnover numbers (TTONs) of 2375 vs 739 in toluene. The present work represents the first example of effective reaction and separation of high-molecular-weight silsesquioxyl derivatives in scCO₂, demonstrating the feasibility of synthesizing and isolating high-molecular-weight polyhedral oligomeric silsesquioxane (POSS) derivatives without the necessity of organic solvents.

KEYWORDS: hydrosilylation, silsesquioxanes, heterogeneous catalysis, supercritical CO₂, green synthesis



1. INTRODUCTION

Polyhedral oligomeric silsesquioxanes (POSSs) exhibit unique properties that merge features of both organic and inorganic compounds.^{1,2} Their structure consists of a cubic silicon–oxygen core, in which each silicon atom is bonded to three oxygen atoms (forming a T unit) and one functional group, either reactive or inert, enabling a wide range of property modulation. This well-defined nanostructure imparts high thermal, photochemical, and chemical stability along with excellent mechanical, optical, and biocompatible properties. Their robust Si–O framework combined with diverse functionalization options makes POSSs suitable for various applications, including as ligands or carriers in transition metal complexes, nanocomposites, biomaterials, OLEDs, and sensors.^{1–11} Among the typically used functionalization strategies, hydrosilylation is one of the most prevalent.^{12–15} This reaction involves the addition of silicon hydride units to unsaturated bonds (C=C, C≡C, C=O, or C–N) and is widely applied both in research and industry, typically catalyzed by molecular transition metal complexes but also earth-abundant and single-atom catalysts.^{16–19} The expanding use of silsesquioxanes is reflected in the increasing number of publications and patents (2495 publications and 15,913 patents in 2004–2014 vs 3604 publications and 26,697 patents in 2015–2025; Scopus,

22.06.2025), emphasizing the need for more sustainable and efficient synthetic strategies.

Based on our previous work on hydrosilylation of various silsesquioxanes—(HSiMe₂O)(i-Bu)₇Si₈O₁₂, (HSiMe₂O)(i-Oct)₇Si₈O₁₂, (HSiMe₂O)₃(i-Bu)₇Si₇O₉, (HSiMe₂O)₃(i-Oct)₇Si₇O₉, and (HSiMe₂O)₈Si₈O₁₂—we have identified synthetic challenges associated with these high-molecular-weight systems.^{20–29} While homogeneous catalysis can yield efficient and versatile processes, it often entails difficult catalyst recovery, metal contamination, and substantial solvent use to ensure the solubility of solid or viscous reagents. Even in heterogeneous systems such as Pt/SDB (styrene–divinylbenzene copolymer), where catalysts showed high TON and up to 20 reuses, organic solvents were still required for dissolving substrates like (HSiMe₂O)(i-Bu)₇Si₈O₁₂.²⁷ The applied solvents, while facilitating solubility, are often toxic, volatile,

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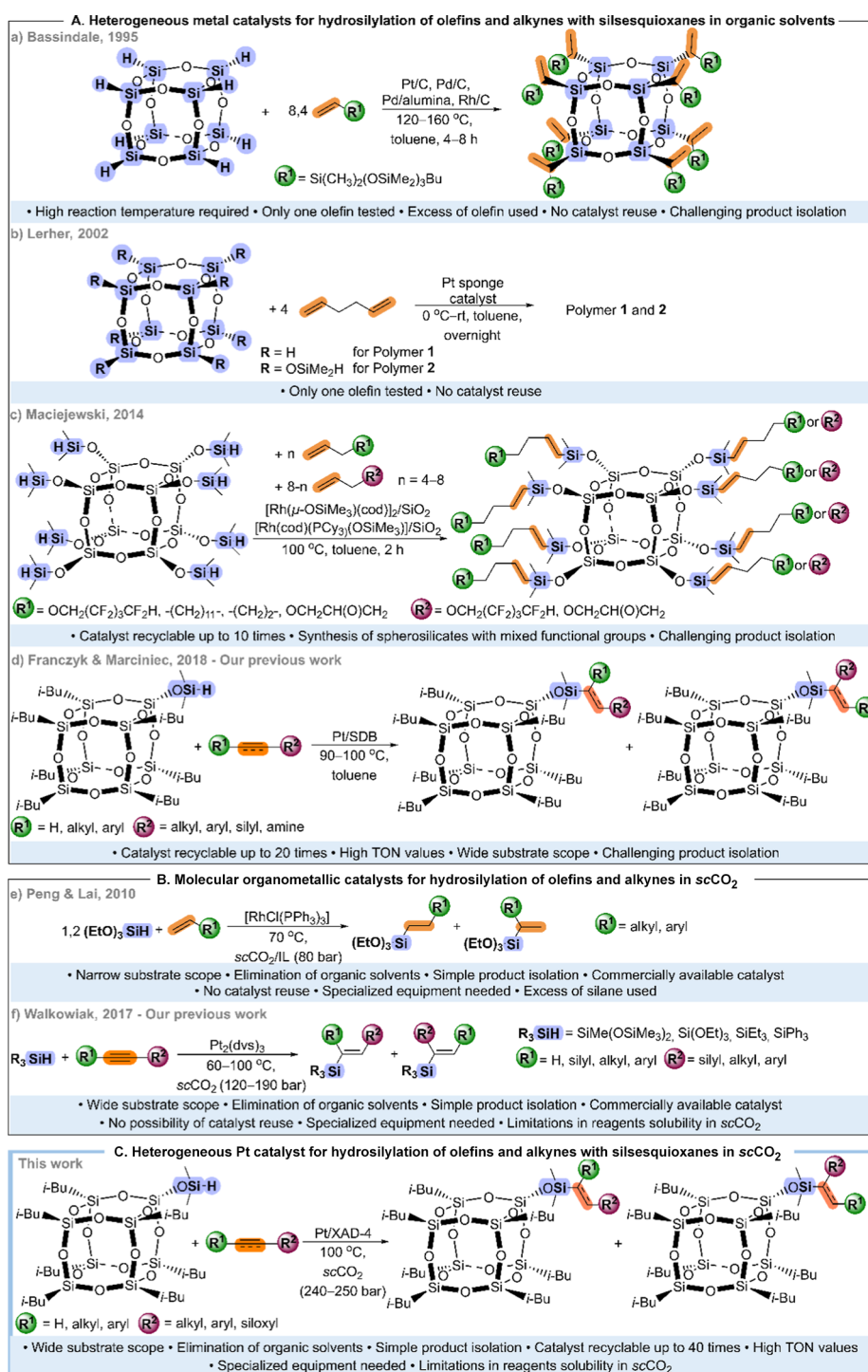
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Scheme 1. (A) Heterogeneous Metal Catalysts for Hydrosilylation of Olefins and Alkynes with Silsesquioxanes in Organic Solvents, (B) Molecular Organometallic Catalysts for Hydrosilylation of Olefins and Alkynes in $scCO_2$, and (C) Heterogeneous Pt Catalyst for Hydrosilylation of Olefins and Alkynes with Silsesquioxanes in $scCO_2$



flammable, and environmentally harmful and may contribute to catalyst deactivation *via* metal leaching.

Herein, we describe for the first time the synthesis of silsesquioxane derivatives performed in supercritical carbon dioxide ($scCO_2$) as a reaction medium. The reaction was enabled by a new heterogeneous catalyst Pt/XAD-4, achieving hydrosilylation of a wide range of alkenes and alkynes (2a–i) with different types of POSSs (1a–d). The application of the Pt/XAD-4/ $scCO_2$ catalytic system allows for multiple uses of a

catalyst, ensures easy product separation, eliminates the use of potentially harmful organic solvents, and improves process productivity.

To the best of our knowledge, beyond our previous study involving Pt/SDB-catalyzed hydrosilylation of alkenes and alkynes with $(HSiMe_2O)(i-Bu)_7Si_8O_{12}$,²⁷ only three other examples of alkene hydrosilylation using silsesquioxane $H_8Si_8O_{12}$ or octaspherosilicate $(HSiO_2)_8Si_8O_{12}$ with heterogeneous catalysts have been reported (Scheme 1).^{30–32} Gentle et

al. evaluated carbon-supported Pt, Pd, and Rh catalysts in the hydrosilylation of vinyl-terminated polysiloxanes with $\text{H}_8\text{Si}_8\text{O}_{12}$, forming octasubstituted silsesquioxanes. However, the reactions required elevated temperatures (120–160 °C) for complete conversion, and catalyst reusability was not investigated.³⁰ Lehrer's group employed a platinum sponge catalyst to prepare low-dielectric polymeric 3D network materials from $\text{H}_8\text{Si}_8\text{O}_{12}$ and $(\text{HSiO}_2)_8\text{Si}_8\text{O}_{12}$ via hydrosilylation of 1,5-hexadiene. Only two copolymers were synthesized, and no catalyst recycling was attempted.³¹ Szubert et al. synthesized functionalized spherosilicates by hydrosilylation of alkenes with $(\text{HSiMe}_2\text{O})_8\text{Si}_8\text{O}_{12}$ using a well-defined rhodium siloxide complex immobilized on silica. Two olefins were used to obtain products with mixed-functional groups. The catalyst remained active over 10 cycles.³² However, the synthesis of the rhodium complex is time-consuming and requires benzene as a solvent.

In all of the above-described procedures, the catalyst showed moderate or low activity, and only in two examples was the catalyst recycled. Additionally, organic solvents were required to isolate the products from the catalyst, as well as to separate various isomers. We envisaged scCO_2 as a potential green reaction medium due to its low critical parameters (73.8 bar, 31.2 °C, 0.456 g/mL), low cost, solvent-like properties, and tunable density (through temperature and pressure variations).^{33–36} A few publications describe hydrosilylation in scCO_2 , mainly using molecular organometallic catalysts. For instance, scCO_2 was employed as the solvent in one-pot hydrosilylation of functionalized polydimethylsiloxanes (PDMS) to produce superhydrophobic polysiloxane aerogels.³⁷ Additionally, hydrosilylation of alkenes (mainly substituted styrenes) with triethoxysilane has been conducted in a scCO_2 /ionic liquid (IL) biphasic system using Wilkinson's catalyst $[\text{RhCl}(\text{PPh}_3)_3]$.³⁸ Our studies on the hydrosilylation of internal and terminal alkynes using Karstedt's catalyst in scCO_2 demonstrated that a broad range of alkynes can be efficiently converted to alkenylsilanes with various organosilicon reagents. Selectivities achieved in scCO_2 were often superior to those obtained in conventional solvents such as toluene or THF. Reaction course and product extraction were influenced by the structure and functionality (aryl, alkyl, and alkoxy) of both substrates. Furthermore, disiloxane ligands attached to the Pt catalyst improved its solubility in scCO_2 , allowing homogeneous reaction conditions.²⁰

Beyond this general precedence, specific properties of POSSs suggested to us that CO_2 could potentially serve as an effective solvent for their functionalization. Due to their robust structure, POSSs have been applied to enhance the interaction of polar gases such as CO_2 with membrane matrices by reducing polymer crystallinity and increasing CO_2 solubility and permeability, thereby improving CO_2 separation efficiency.^{39–43} In order to exploit the benefits of scCO_2 in reaction and separation, the development of an active and selective heterogeneous catalyst was identified as a concomitant challenge to devise a fully integrated synthetic process.

Based on these insights and the challenges associated with hydrosilylation involving silsesquioxanes, our objectives were (i) to develop a new heterogeneous catalyst (Pt/XAD-4) with high activity and selectivity for C–C multiple bond hydrosilylation, (ii) to enhance process efficiency using scCO_2 for the integration of reaction and catalyst recycling *via* product extraction, and (iii) to compare the use of scCO_2 to that of

conventional organic solvents and assess the limitations of each catalytic system.

2. RESULTS AND DISCUSSION

2.1. Synthesis and Characterization of Pt/XAD-4

Since the platinum is still the most commonly used metal in hydrosilylation reactions and provides the best selectivities with the lowest concentration, searching for new heterogeneous catalysts, which will compete with typically used homogeneous systems, is highly demanded.⁴⁴ In line with this, we prepared a new heterogeneous catalyst Pt/XAD-4 by an incipient wetness technique using commercially available and relatively inexpensive components: hexachloroplatinic acid as a metal precursor and XAD-4 polymeric resin as a support. The platinum was reduced from oxidation state +4 to 0 by the application of a hydrogen stream. The detailed catalyst preparation procedure is available in ESI. The platinum content in the obtained catalyst was determined by ICP OES analysis and equals 1.43% Pt/g of catalyst.

Textural parameters, namely, the BET surface area (S_{BET}), total pore volume (V_{tot}), and average pore size, were evaluated according to the procedure described in the ESI for the support, freshly prepared catalyst, and catalyst after a series of consecutive catalytic reactions. As presented in Table 1, the

Table 1. Textural Parameters of the XAD-4 Polymeric Support and the Platinum Catalyst Prepared on Its Basis

sample	S_{BET} , m^2/g	V_{tot} , cm^3/g	average pore size, nm
XAD-4	754	0.85	4.5
Pt/XAD-4	775	0.92	4.7
Pt/XAD-4 after reaction ^a	18	0.07	16.7

^aPt/XAD-4 catalyst after 39 repetitive batch reactions of **2a** with **1a** in scCO_2 . Reaction conditions: $[\text{1a}]:[\text{2a}]:[\text{Pt}] = 1:1:1.43 \times 10^{-2}$, 100 °C, 4 or 18 h, scCO_2 (240–250 bar), $m_{\text{1a}}/V_{\text{CO}_2} = 25 \text{ mg mL}^{-1}$.

styrene–divinylbenzene resin (XAD-4) has a specific surface area of 754 m^2/g , while for the Pt/XAD-4 catalyst, a slight increase to 775 m^2/g can be observed. This is most likely due to the unblocking of some pores in the carrier with the solvent used during the procedure of support impregnation with a metal precursor. The unblocking of additional channels in the carrier texture by washing off the polymerization residues during catalyst synthesis can also be indicated by an increase in the total pore volume from 0.85 cm^3/g to 0.92 cm^3/g for the XAD-4 and Pt/XAD-4 samples, respectively.

All low-temperature nitrogen sorption isotherms depicted in Figure 1 are type IV(a) according to the IUPAC classification, which are characteristic of mesoporous sorbents.⁴⁵

The dominant nature of the mesopores is also noticeable in Figure 1b, which shows the corresponding PSD plots for the support, catalyst, and catalyst recovered after several reaction cycles. It can be seen that the XAD-4 and Pt/XAD-4 samples mainly have pores within the mesopore range up to 25 nm and also a small number of micropores less than 2 nm in diameter, as indicated by the sharp elevation of the curves at the limit of the instrument measurement range.

Low-temperature nitrogen sorption measurements also enabled the assessment of the effect of catalyst repetition use on its textural parameters. It turned out that during the sequential reaction cycles a film of reaction residues was deposited on the surface of the catalyst particles (see ESI,

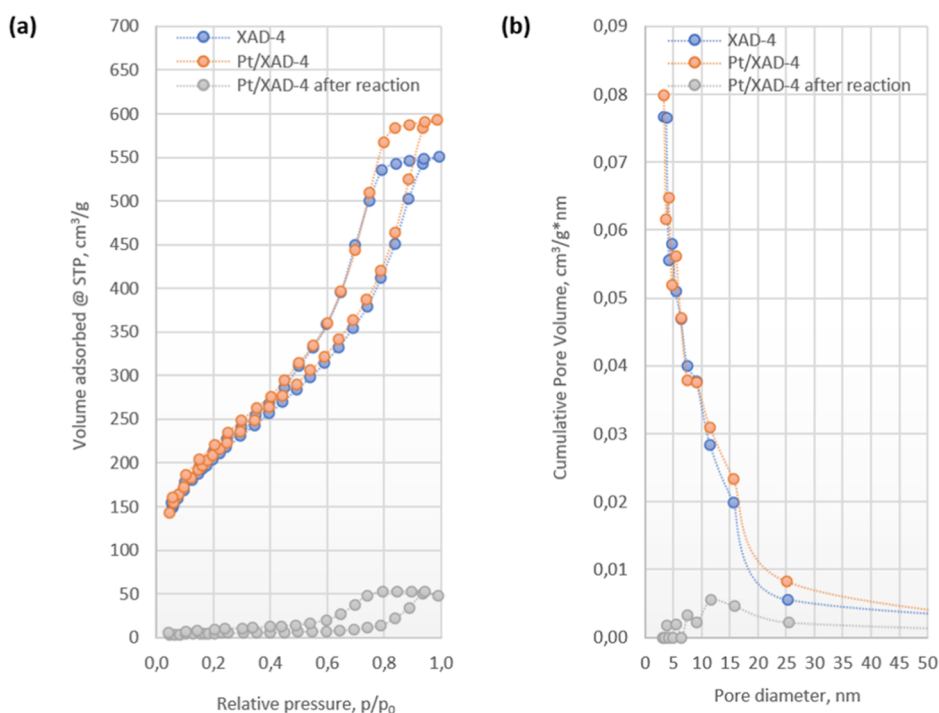


Figure 1. Low-temperature nitrogen adsorption/desorption isotherms (a) and pore size distributions (b) for XAD-4 resin and the catalyst prepared on the basis of this polymer.

Figure S3), leading to mechanical blocking of access to the catalyst pores. This is evidenced by a significant decrease in the specific surface area and total pore volume with an increase in the average pore size (Table 1), which is due to the inaccessibility of smaller pores for the adsorbate. This is also evident in the low-temperature isotherm of nitrogen adsorption/desorption and the pore size distribution (Figure 1), where for Pt/XAD-4 after reaction, in contrast to the XAD-4 carrier and the freshly prepared catalyst, the contribution of pores smaller than 10 nm in diameter to the cumulative pore volume is negligible.

The spherical particles of the catalyst with diameters ranging from 0.25 to 0.80 mm (see ESI) make it easy for handling, storage, and especially separation from the postreaction mixtures. When processes are conducted in organic solvents, simple decantation of the catalyst is sufficient to prevent particle removal from the reactor, eliminating the need for mechanical separators, such as filters.

According to the STEM measurements, the obtained Pt/XAD catalyst is characterized by the presence of predominantly small crystallites with a relatively high degree of dispersion (Figure S4a–c). In most cases, the active phase consists of crystallites not exceeding 16 nm in size, with a dominant contribution from particles ≤ 10 nm. After the use of the catalyst in a sequence of catalytic reactions, the particle size histogram changes markedly, indicating a significantly higher fraction of particles smaller than several tens of nanometers (Figure S4d–f). This observation may suggest preferential leaching of larger crystallites, which were initially deposited on the outer surface of the support during catalyst synthesis. In contrast, smaller crystallites formed in deeper regions of the polymer pores appear to be less susceptible to leaching by the reactants. Importantly, STEM analysis did not reveal any tendency toward crystallite agglomeration during the catalytic

reaction sequence, although the formation of a silicone-based deposit was confirmed (Figure S4e).

Based on the XRD and XPS analyses, it can be concluded that the active phase of the Pt/XAD-4 catalyst consists of Pt⁰ and partially of Pt²⁺ species, the latter most likely in the form of PtO. This is clearly indicated by the diffraction pattern shown in Figure S5, which displays reflections characteristic of both platinum species. Notably, these reflections are relatively broad, confirming the presence of very small crystallites. XPS analysis, in turn, indicates a dominant contribution of Pt²⁺ species in the surface layer of the catalyst (Figure S6b), with no detectable Pt⁰ phase. Such behavior is commonly reported for small, highly dispersed Pt crystallites and is attributed to their increased susceptibility to surface oxidation and other surface-related electronic effects.^{46–48} This predisposition of small crystallites on the surface of the Pt/XAD catalyst to oxidation is also indirectly supported by XPS measurements performed on the support impregnated with the metal precursor not subjected to hydrogen treatment (Figure S6c). The spectral shape and binding energy values of the Pt 4f_{5/2} peaks for this material and for the catalyst reduced during the synthesis procedure are very similar (~ 72 eV), indicating a comparable contribution of Pt²⁺ species. This observation suggests reoxidation of the small Pt⁰ crystallites at the catalyst surface that were previously reduced during hydrogen treatment. The initial reduction of the platinum precursor is confirmed by XRD analysis, which probes the deeper layers of the sample. Slightly more pronounced changes in the oxidation state of the catalyst active phase are observed in the XPS spectra for Pt/XAD after a series of catalytic reactions (Figure S6a), where the Pt 4f_{5/2} peak shifts toward higher binding energies, potentially indicating the formation of Pt species with oxidation states higher than that of Pt²⁺. However, this shift may also be influenced by postreaction surface deposits that partially cover the crystallites, rendering them inaccessible to

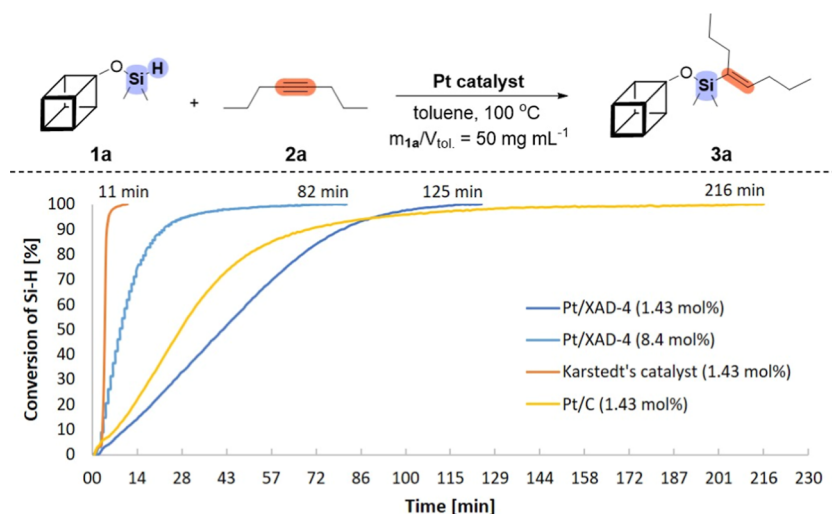
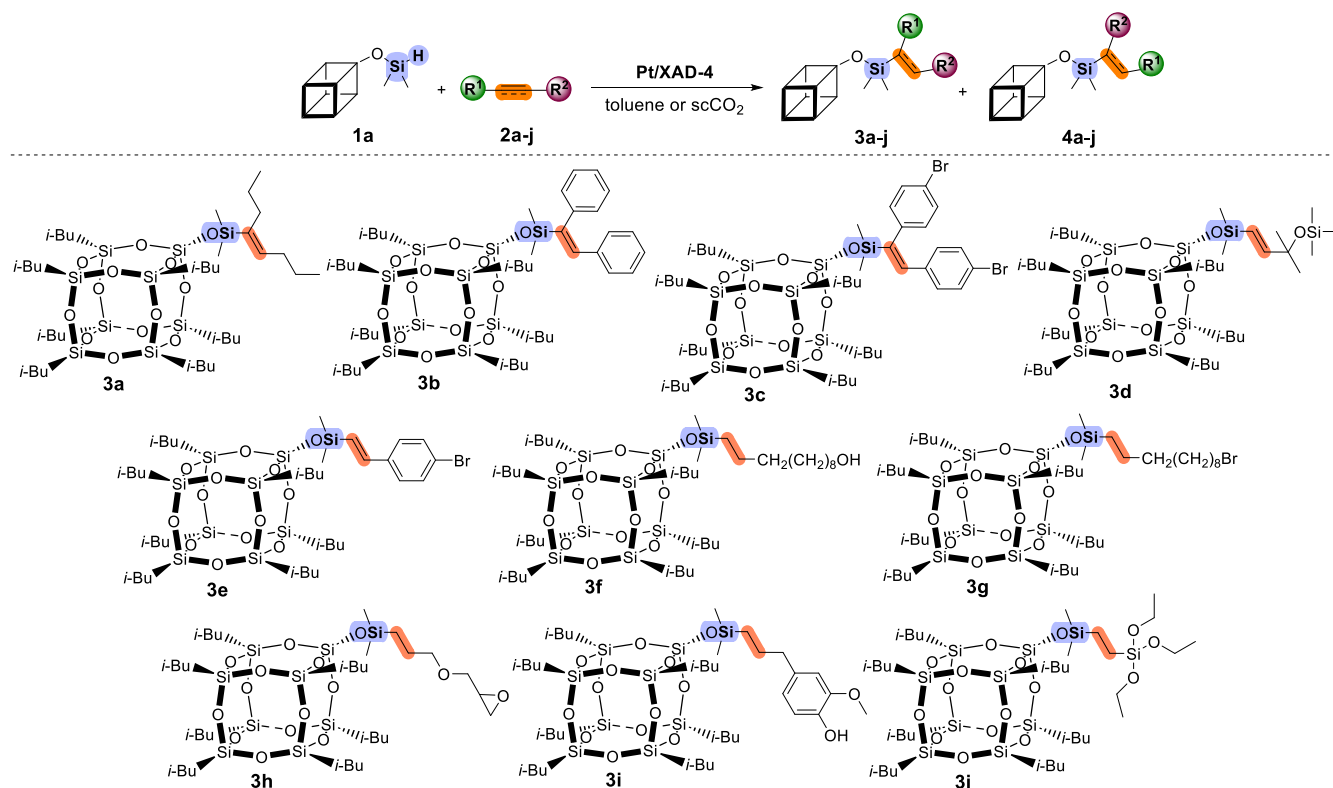


Figure 2. Plots presenting conversion vs time for the hydrosilylation of 4-octyne **2a** with silsesquioxane **1a** in the presence of Pt/XAD-4, Karstedt's catalyst, and Pt/C measured by *in situ* FT-IR.

Scheme 2. Scope of Alkynes **2a–e** and Alkenes **2f–j** Used in Catalytic Hydrosilylation



analysis. Consequently, this XPS measurement may be particularly susceptible to additional effects, such as sample charging, which could not be fully compensated by the application of low-kinetic-energy electrons. Therefore, EELS measurements were additionally performed for two samples, namely, the fresh (as prepared) and reused catalyst (after a series of consecutive catalytic reactions). The results show that no notable change in the oxidation state can be detected (Figure S4g), indicating that the oxidation state of the platinum crystallites remains essentially unchanged after repeated catalytic use.

2.2. Hydrosilylation of Alkynes and Alkenes with Silsesquioxanes **1a–d** in the Presence of Pt/XAD-4 in Toluene

The activity of the new catalyst was tested in the hydrosilylation of 4-octyne (**2a**) with silsesquioxane **1a**, which was chosen as a model reagent. The use of 1.43 mol% of Pt (22 mg of the catalyst was used per 100 mg of **1a**) at 100 °C in toluene allowed obtaining full conversion of the reagents after 125 min, while the process using the industrially applicable heterogeneous catalyst Pt/C required 216 min (Figure 2). The use of the Karstedt's catalyst reduced the reaction time by more than 11 times (11 min), but it is obvious that homogeneous

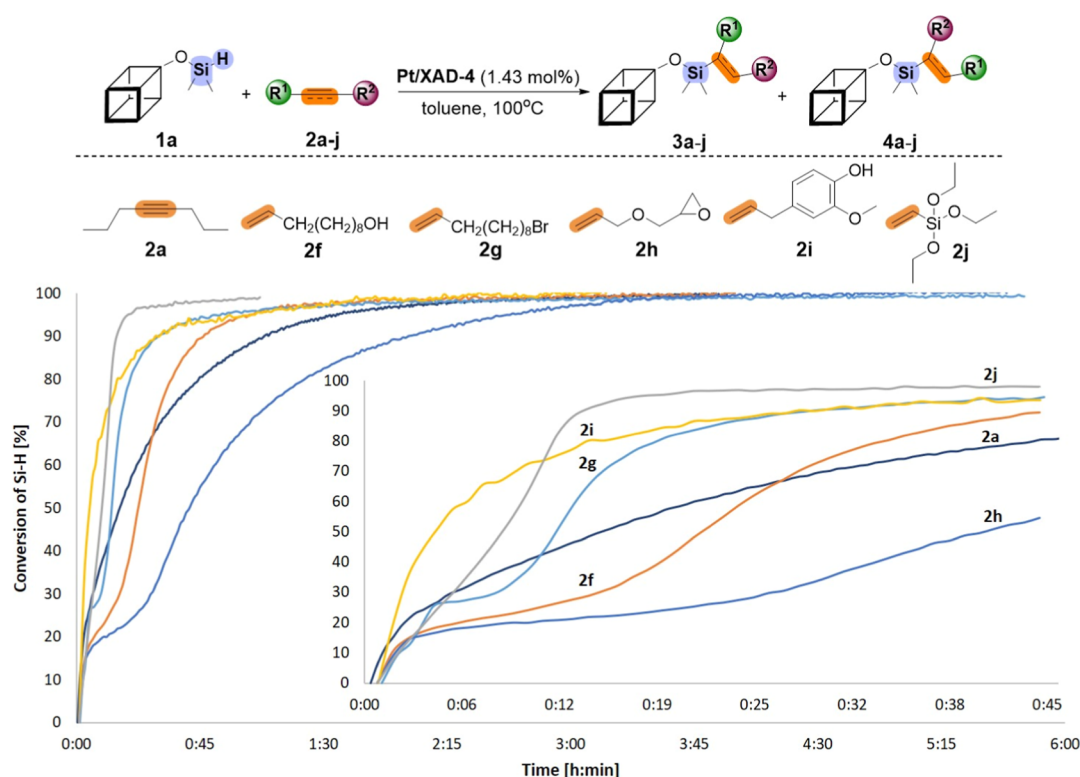


Figure 3. Kinetic plots for selected examples of hydrosilylation of alkyne **2a** and alkenes **2f–j** with **1a** determined by *in situ* FT-IR. Reaction conditions: $[1a]:[2]:[Pt] = 1:1:1.43 \times 10^{-2}$, 100 °C, toluene, $m_{1a}/V_{tol} = 25 \text{ mg mL}^{-1}$.

Table 2. Hydrosilylation of Alkynes **2a–e** and Alkenes **2f–j** with **1a** in the Presence of Pt/XAD-4 in Toluene Monitored by *in situ* FT-IR^a

entry	2	R ¹	R ²	reaction time ^b	selectivity of 3/4 ^c
1	a	C ₃ H ₇	C ₃ H ₇	3 h 56 min	100
2	b	Ph	Ph	13 h 19 min	100
3	c	PhBr-4	PhBr-4	18 h 54 min	100
4	d	H	C(CH ₃) ₂ OSi(CH ₃) ₃	8 h 5 min	85/15
5	e	H	PhBr-4	9 h 42 min	56/44
6	f	H	CH ₂ (CH ₂) ₈ OH	3 h 59 min	100/0
7	g	H	CH ₂ (CH ₂) ₈ Br	5 h 45 min	98/2
8	h	H	CH ₂ OCH ₂ CH(O)CH ₂	5 h 38 min	96/4
9	i	H	CH ₂ C ₆ H ₃ -2-(OCH ₃)OH	3 h 12 min	100/0
10	j	H	Si(OCH ₂ CH ₃) ₃	1 h 7 min	91/9

^aReaction conditions: $[1a]:[2]:[Pt] = 1:1:1.43 \times 10^{-2}$, $m_{1a}/V_{tol} = 25 \text{ mg mL}^{-1}$. ^bReaction time required to achieve complete conversion of reagents. ^cSelectivity was determined based on ¹H, ¹³C, and ²⁹Si NMR.

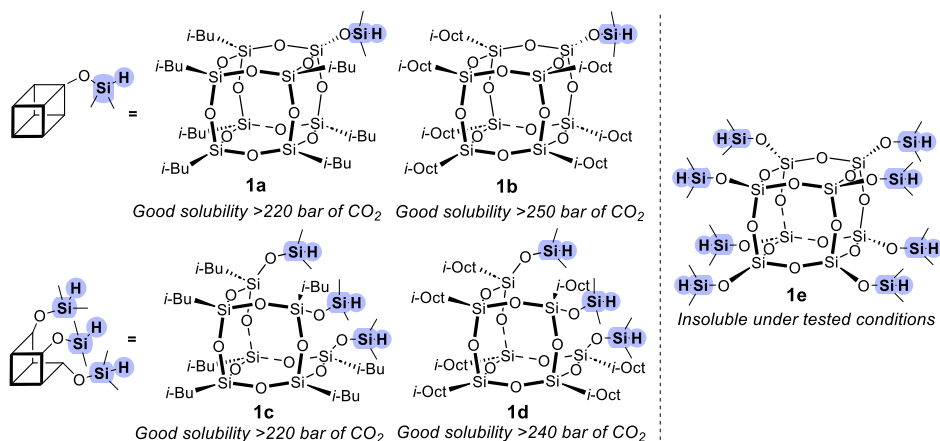
catalysts, due to their availability and lack of diffusion effects, will be the most active. Increasing the concentration of the Pt/XAD-4 catalyst from 1.43 to 8.4 mol% shortened the reaction time from 125 to 82 min.

Subsequent tests showed that the Pt/XAD-4 catalyst is active in the hydrosilylation processes of a wide range of reagents with various functional groups, including terminal and internal alkynes: diphenylacetylene (**2b**), bis(4-bromophenyl)-

acetylene (**2c**), [(1,1-dimethyl-2-propynyl)oxy]trimethylsilane (**2d**), and 1-bromo-4-ethynylbenzene (**2e**), and alkenes: 10-undecen-1-ol (**2f**), 11-bromo-1-undecene (**2g**), allyl glycidyl ether (**2h**), eugenol (**2i**), and triethoxyvinylsilane (**2j**) with silsesquioxane **1a** (Scheme 2).

In the first part of the study, the reactions were carried out with a stoichiometric ratio of reagents in the presence of Pt/XAD-4 (1.43 mol% of Pt) in toluene ($m_{1a}/V_{tol} = 25 \text{ mg mL}^{-1}$)

Scheme 3. Structures of Tested Silsesquioxanes 1a–e with the Corresponding CO₂ Pressures at Which Good Solubility Is Observed at 100 °C



at 100 °C, under an air atmosphere, without any purification of the acquired chemicals. The reaction progress was monitored in real-time using *in situ* FT-IR spectroscopy, which allowed tracking of changes in the area of the band at 880–930 cm^{−1}, assigned to stretching vibrations of the Si–H group at 15 s intervals. These measurements permitted the identification of changes in reagent conversion over time. The kinetic plots for selected experiments are presented in Figure 3 (for full information, see the ESI). Reaction times required to obtain full conversion of reagent **2** are summarized in Table 2.

¹H, ¹³C, and ²⁹Si NMR analyses of postreaction mixtures confirmed the complete conversion of both reagents in all experiments. Reactions with alkynes **2a–c** and alkenes **2f–i** yielded products **3** with a selectivity exceeding 96%. Slightly lower selectivities were observed for the reactions with [(1,1-dimethyl-2-propynyl)oxy]trimethylsilane (**2d**) and triethoxyvinylsilane (**2j**). However, products **3d** (85%) and **3j** (91%) predominated, while the ratio of **3e** to **4e** was almost 1:1, which is consistent with the results of reactions carried out in the presence of Karstedt's catalyst.⁴⁹

The results showed that the reaction time strongly depended on the alkene or alkyne structure. Therefore, the full conversions of the series of alkenes (**2f–j**) were reached in up to 5 h and 45 min. For comparison, the reaction of internal alkynes **2b** and **2c** needed 13 h and 19 min and 18 h and 54 min, respectively. The hydrosilylation of triethoxyvinylsilane (**2j**) was characterized by the shortest reaction time (1 h and 7 min). Lower reaction rates were observed for the processes using alkenes **2f** and **2i**, as the reaction completion took up to 3–4 h. Among the alkynes tested, only the hydrosilylation of 4-octyne (**2a**) was characterized by a relatively short reaction time and was completed in less than 4 h. This reaction proceeded even faster than the hydrosilylation reactions of terminal alkynes **2d** and **2e**. The longest reaction times were obtained for processes involving internal alkynes with Ph groups (**2f–g**).

The kinetic profiles derived from the *in situ* FT-IR measurements (Figure 3) illustrate that upon the addition of reagents to the mixture of catalyst in solvent and subsequent heating, an initial induction period of less than 20 min is observed in the reactions involving **1a** and alkenes **2d** and **2b–c**. Following this, a rapid consumption of reagents occurs, resulting in 80–95% conversion of the Si–H. Subsequently, the reaction rates decrease significantly due to the reduction in

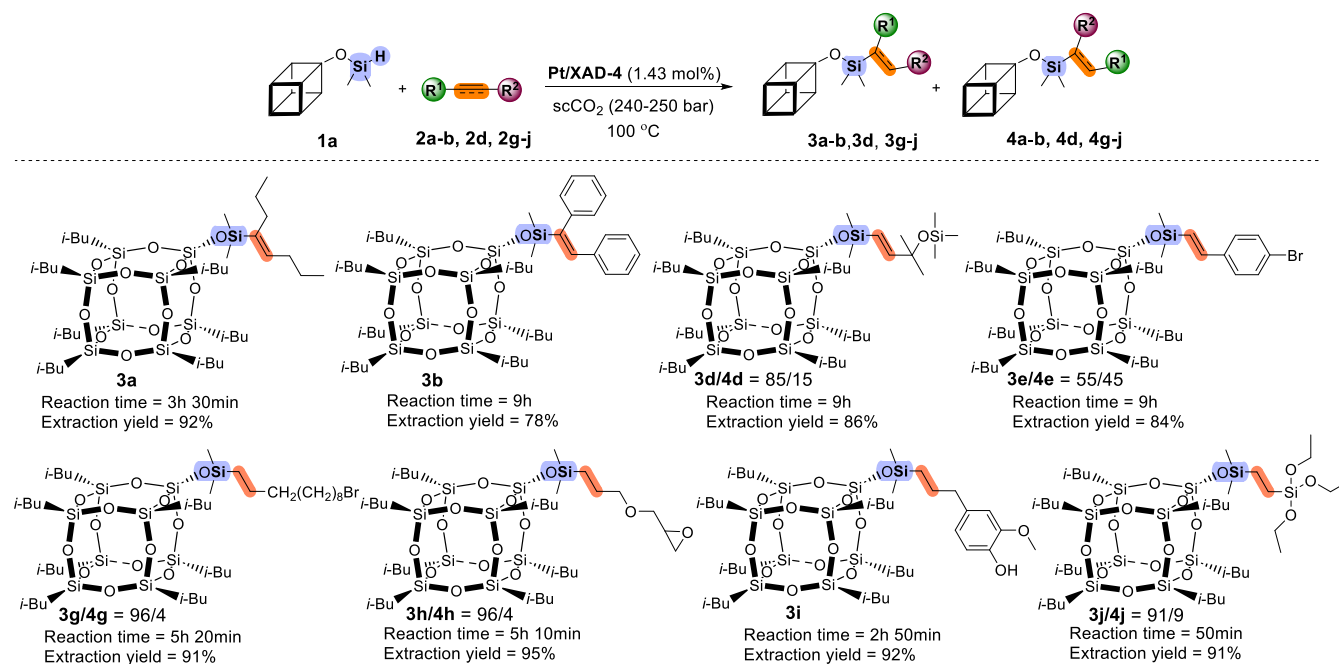
the concentration of reagents, with the remaining 20% of reagents being consumed over a period of approximately 3–5 h (for **2g** and **2i**). In contrast, the hydrosilylation of **2f** and **2h** exhibits a short induction period (10 min) and a moderate rate of reagent consumption throughout the process. The influence of the epoxide group on the activity of the Pt/XAD-4 catalyst is evident. A similar trend was observed in the hydrosilylation of 4-octyne (**2a**).

The postreaction mixtures were separated from the catalyst by simple decantation using a syringe. The effective separation of the products from the catalyst suggests that the catalyst can be reused in subsequent cycles, as discussed in subsection 2.4. However, the color of the postreaction mixtures indicated platinum leaching, which was confirmed by ICP-OES analysis. These findings led us to consider using a different reaction solvent.

Because silsesquioxanes, olefins, and alkynes are well-soluble in many organic solvents (e.g., hexane, toluene, and THF) and their affinity to the solvent depends on the molecular structure of the reagent, we thought that scCO₂ might also be used as a solvent for this type of reaction. Our previous studies on hydrosilylation of alkynes using silanes and siloxanes in scCO₂ showed that organosilicon compounds might be very well soluble in scCO₂ and that the products might also be extracted in this medium.²⁰ The phenomenon of the silyl groups attached to the molecules is comparable to perfluorinated substituents, which drastically improve the solubility of compounds in scCO₂.^{50,51} Moreover, a few papers and patents discuss the solubility of silsesquioxanes in scCO₂.^{52–55} Surprisingly, no hydrosilylation using silsesquioxanes as reagents was carried out in this green solvent. Therefore, we checked the opportunity to carry out reactions in scCO₂ and figured out the possibility of the extraction of the products in scCO₂ and simplified their separation procedures.

2.3. Phase Behavior Studies

Before hydrosilylation in supercritical CO₂ was investigated, phase behavior studies of the reagents in this medium were performed to determine under which conditions the reaction mixture occurred homogeneously and to identify any solubility limitations of the reagents. The solubility of alkynes **2a–e** in CO₂ has already been investigated in our previous research.²⁰ The results showed that except for **2c**, the reagents are well soluble in this solvent. The high solubility was achieved at 100 °C (120–190 bar pressure), the optimal temperature for

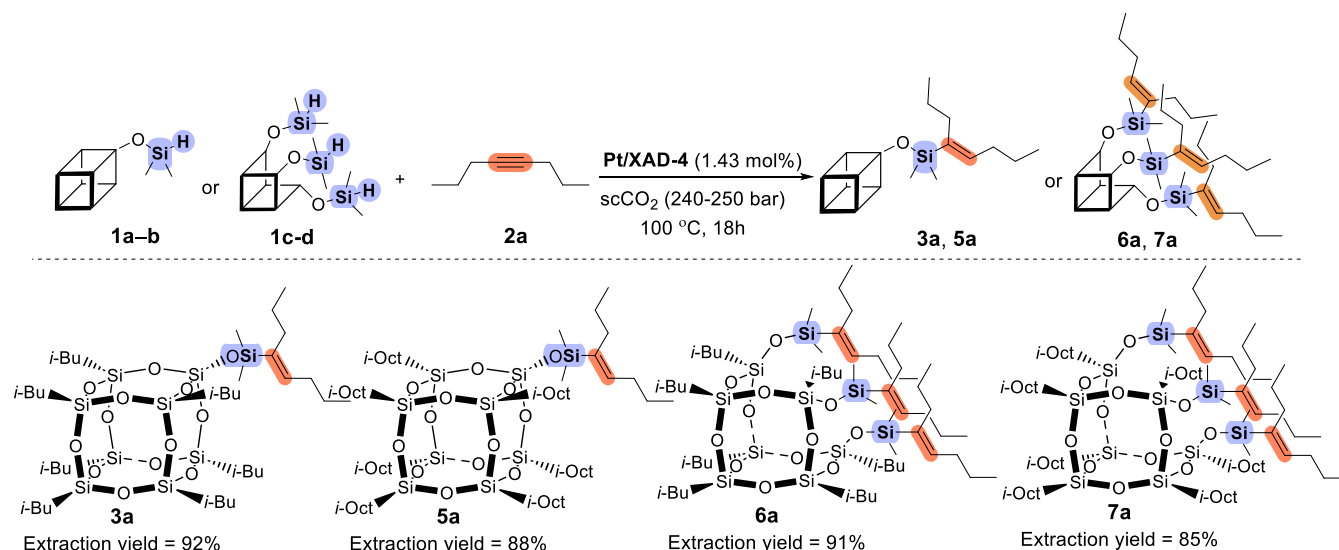
Scheme 4. Hydrosilylation of 2a–b, 2d–e, and 2g–j with Silsesquioxane 1a in scCO₂Table 3. Hydrosilylation of Alkynes 2a–e and Alkenes 2f–j with 1a in the Presence of Pt/XAD-4 in Toluene and scCO₂^a

entry	2	toluene		TON (±SD)	scCO ₂		TON (±SD)
		conv. of Si–H [%]	selectivity of 3/4 [%]		conv. of Si–H [%]	selectivity of 3/4 [%]	
1	a	25	100	1748 (±140)	28	100	1957 (±185)
2	b	40	100	2775 (±144)	85	100	5965 (±176)
3	c	44	100	3101 (±104)	–	–	–
4	d	53	85/15	3705 (±121)	<1	–	–
5	e	63	55/45	4380 (±246)	<1	–	–
6	f	51	100/0	3542 (±107)	–	–	–
7	g	77	100/0	5545 (±146)	91	100/0	6361 (±140)
8	h	15	100/0	1049 (±210)	63	99/1	4380 (±225)
9	i	35	100/0	2447 (±185)	61	100/0	4264 (±280)
10	j	75	90/10	5219 (±146)	<1	–	–

^aReaction conditions: [1a]:[2]:[Pt] = 1:1:1.43 × 10^{−4}, 100 °C, 18 h, toluene or scCO₂ (240–250 bar), m_{1a}/V_{tol./CO₂} = 25 mg mL^{−1}. Conversion of 1a was determined by ¹H NMR; the selectivity was confirmed by ¹H and ²⁹Si NMR. Conversion values are reported as the mean of three independent experiments and are rounded to the nearest integer. TON values are reported as the mean ± standard deviation (n = 3).

conducting hydrosilylation in toluene. Therefore, we assessed the solubility of only the alkenes 2f–j and silsesquioxane 1a at this temperature and under various CO₂ pressures (100–260 bar). Allyl glycidyl ether (2h) and triethoxyvinylsilane (2j) were soluble under pressures above 100 and 130 bar of CO₂, respectively, whereas alkenes 2g and 2i required CO₂ pressures

higher than 160 and 220 bar for their dissolution. The solubility problem occurred only for alkene 2f, which contains a hydroxyl group in its structure. Due to its polarity, this compound was not soluble in nonpolar CO₂ under the tested conditions.

Scheme 5. Hydrosilylation of 2a with Silsesquioxanes 1a–d in scCO₂

Dilek's group conducted detailed research on the solubility of various POSS derivatives in scCO₂.^{52–55} Most of the tested reagents possess eight of the same functional groups in the structures such as trifluoropropyl ((C₃H₄F₃)₈Si₈O₁₂), methyl ((CH₃)₈Si₈O₁₂), methacryl ((CH₃C(CH₂)C(O)O-(CH₂)₃)₈Si₈O₁₂), *isooctyl* ((*i*-Oct)₈Si₈O₁₂), *isobutyl* ((*i*-Bu)₈Si₈O₁₂), or octatrimethylsiloxyl ((Me₃SiO)₈Si₈O₁₂). The authors indicated that among all the POSS types that have been studied to date, including trifluoropropyl-modified POSS ((C₃H₄F₃)₈Si₈O₁₂), the methylsiloxy-functionalized POSS ((Me₃SiO)₈Si₈O₁₂) was found to have a remarkably higher solubility.⁵⁴ Moreover, changing only one of the eight functional groups to this methylsiloxy can significantly increase the solubility of POSS in scCO₂.⁵⁵

In light of the aforementioned information and the absence of data regarding the solubility of POSS-containing OSiMe₂H groups, we decided to explore the solubility not only of compound 1a but also of its analogous derivative with *i*-Oct groups (HSiMe₂O) (*i*-Oct)₇Si₈O₁₂ (1b) as well as trifunctional POSS with *i*-Bu (HSiMe₂O)₃(*i*-Bu)₇Si₇O₉ (1c) and *i*-Oct groups (HSiMe₂O)₃(*i*-Oct)₇Si₇O₉ (1d) and octaspherosilicate (HSiMe₂O)₈Si₈O₁₂ (1e) (Scheme 3).

The experiments revealed that the solubility of 1a–1e is affected by the presence of inert groups such as *i*-Bu and *i*-Oct in the POSS structures. Notably, octaspherosilicate (1e) lacking these groups proved to be insoluble in scCO₂, even under pressures as high as 260 bar. Furthermore, a slight difference was observed in the presence of *i*-Bu and *i*-Oct groups in the POSS structures. The dissolution of silsesquioxanes 1a and 1c required a lower CO₂ pressure (220 bar) compared to their *i*-Oct group analogues 1b and 1d (250 and 240 bar). Moreover, trifunctional silsesquioxanes featuring open-cage structures (1c–d) exhibited better solubility than 1a–b with completely condensed cages. This can be explained by the fact that incompletely condensed POSSs effectively restrict crystallinity by reducing rigidity, thereby improving solubility compared to completely condensed POSSs, which tend to aggregate.^{56–58}

2.4. Hydrosilylation of Alkynes and Alkenes with Silsesquioxanes 1a–d in the Presence of Pt/XAD-4 in scCO₂

In the next step, the hydrosilylation of alkynes and alkenes (2a–b, 2d–e, 2g–j), which were characterized by good solubility in scCO₂, was performed with 1a. The processes were carried out in the presence of Pt/XAD-4 (1.43 mol% of Pt) at 100 °C in scCO₂ (240–260 bar) (Scheme 4). Each reaction was completed in a shorter time compared to processes carried out in toluene (Table 2). The results demonstrated that these reactions proceeded with complete conversion of the reagents and selectivity comparable to those conducted in toluene. The products were efficiently extracted in a CO₂ stream, achieving yields of between 78% and 95%.

To determine the total TON values that might be achieved in a single batch, the processes in the presence of Pt/XAD-4 (0.0143 mol% of Pt) for 18 h in scCO₂ (240–260 bar) were performed (Table 3 and ESI, Table S5). Comparing the results of processes conducted in scCO₂ with analogous reactions performed in toluene, we observed that the hydrosilylation reactions involving 2a, 2b, and 2g–i with silsesquioxane 1a in scCO₂ exhibit higher efficiency. Furthermore, the TON value for the hydrosilylation with 2h in scCO₂ is over four times greater than that in toluene. Involving reagents 2b and 2i, by applying scCO₂ as a solvent, the catalyst was two times more effective. Surprisingly, despite the good solubility of alkenes 2d–e and 2j in scCO₂, only trace amounts of products were detected in processes involving these alkenes conducted in scCO₂. In contrast, processes carried out in toluene achieved conversions at levels of 77%, 54%, and 63%, respectively, using low Pt concentration. No changes in selectivities were observed between processes conducted in scCO₂ and toluene. In all cases, the *anti*-Markovnikov product of *syn* addition of silsesquioxane to the unsaturated C–C bond was formed.

Due to the good solubility of silsesquioxanes 1b–d in scCO₂, their reactivity was also tested in the hydrosilylation of 4-octyne (2a) (Scheme 5). The reactions were conducted using a Pt/XAD-4 catalyst (1.43 mol% of Pt) at 100 °C with CO₂ under a pressure of 240–250 bar for 18 h. The processes with silsesquioxanes 1a and 1b were carried out with a reagent ratio of 1a–b:2a equal to 1:1, while processes with

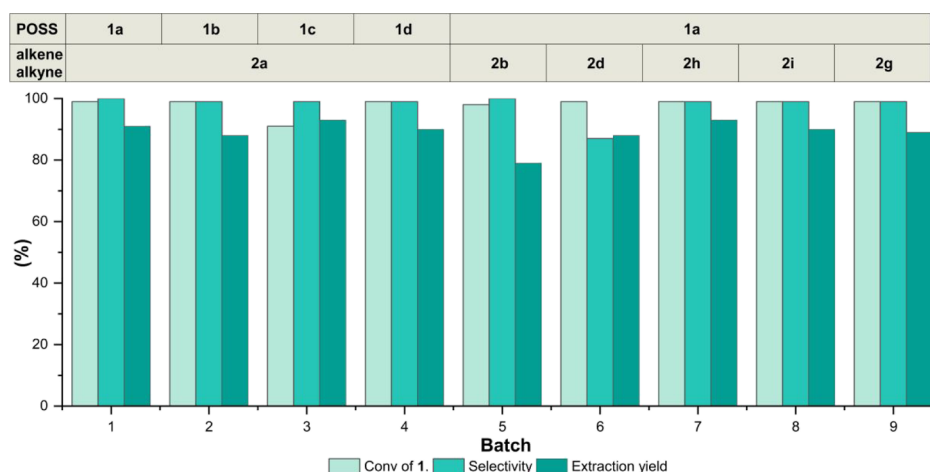


Figure 4. Consecutive hydrosilylation of various POSSs (1a–d) with alkynes (2b, d) and alkenes (2g–i) using a single catalyst load (1.43 mol% of Pt, 100 °C, 240–250 bar of CO₂, 18 h). Extraction conditions: 230–250 bar of CO₂, 100 °C, 80–120 min. Conversion and selectivity were determined by ¹H NMR.

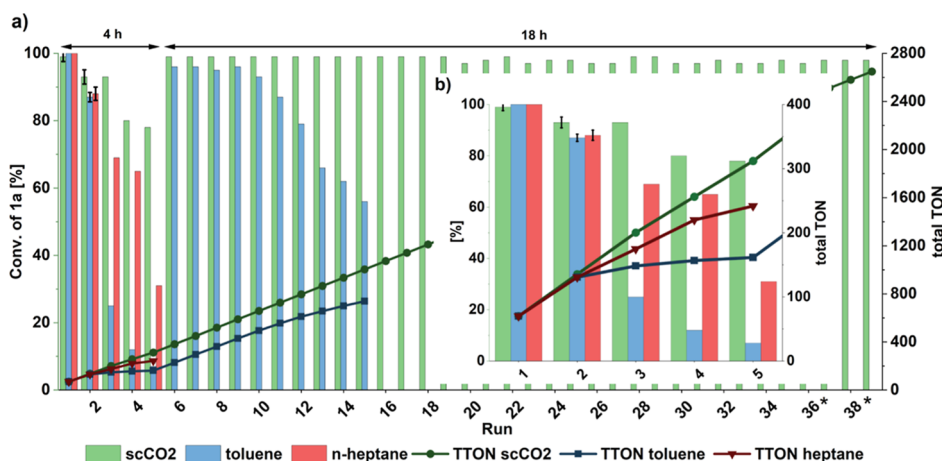


Figure 5. Repetitive batch reactions of 2a with 1a in the presence of 1.43 mol% of Pt/XAD-4 in scCO₂ and organic solvents. (a) Conversion of 1a and cumulative TON over consecutive runs. (b) Enlarged view of runs 1–5. Conversion of 1a was determined by ¹H NMR.

trifunctional silsesquioxanes 1c and 1d used reagents in a ratio of 1c–d:2a equal to 1:3. All reactions proceeded with complete conversions of reagents, leading exclusively to products 3a and 5–7a. Additionally, the obtained products were isolated by the extraction in a CO₂ stream with high yields (85–92%). The extraction process was conducted at 100 °C, under a pressure of 230–250 bar for 80–120 min. The extracted products were collected in the cold traps.

Encouraged by these positive results and our experience in catalysis in scCO₂ using heterogeneous catalysts,^{59–61} we decided to test the activity and versatility of the Pt/XAD-4 catalyst in consecutive hydrosilylation processes of 2a with four different silsesquioxanes 1a–d and olefins (2b, 2d, and 2g–i) using a single portion of the catalyst. The reactions were carried out with a Pt/XAD-4 catalyst concentration of 1.43 mol % of Pt (100 °C, 240–250 bar of CO₂, 18 h). Initially, the hydrosilylation of 2a with 1a was performed, and after the reaction time, the product was extracted using CO₂. Subsequently, silsesquioxanes 1b–d were successively utilized in the next cycles. The results of the hydrosilylation of 2a with 1a–d were comparable to those of the nonrepetitive batch reaction. The same strategy was used for the consecutive hydrosilylation of alkynes 2b and 2d and alkenes 2g–i with

silsesquioxane 1a. The reagents were changed in the following order: 2b, 2d, 2h, 2i, and 2g (Figure 4).

Overall, one catalyst loading was reused 9 times in the hydrosilylation reaction of various substrates using the same portion of the catalyst. The obtained results confirm the high activity and versatility of the Pt/XAD-4 catalyst, which tolerates many various functional groups. Very high conversion of the POSS (91–99%) was observed in each batch. Moreover, in subsequent hydrosilylation reactions using different types of alkenes and alkynes, no decrease in catalyst selectivity was observed. It is noteworthy that employing 1.43 mol % of Pt/XAD-4 catalyst allowed for the synthesis of product 3d with a selectivity of 83%, a result unattainable with the catalyst concentration at 0.0143 mol % of Pt.

All of the obtained products were extracted in CO₂ steam with a high efficiency of 79–93%. The lowest extraction yield was observed for product 3b, attributed to the presence of phenyl groups in its structure, as confirmed by our previous research.²² The extraction process was performed according to the same procedure described above. Extraction with supercritical CO₂ constitutes an attractive alternative for the isolation of POSS derivatives, as it enables efficient separation of high-molecular-weight products without the use of addi-

tional organic solvents. This advantage is particularly relevant for silsesquioxanes, whose isolation and purification from conventional solvents are often challenging and typically require large volumes of organic solvents.

At the same time, it should be emphasized that the use of supercritical CO₂ involves elevated pressure requirements, which are associated with increased energy input and technical complexity. Therefore, the sustainability of scCO₂-based processes must be evaluated in a balanced manner, taking into account both the operational costs related to high-pressure conditions and the benefits arising from simplified downstream processing.^{62–67} In the present case, when a single isomer is selectively formed and the product can be readily extracted with a CO₂ stream, no additional postreaction purification steps are required. This substantially reduces solvent consumption during workup and enhances overall atom and process efficiency. Moreover, under the applied conditions, reactions conducted in scCO₂ exhibited higher efficiency than analogous transformations performed in toluene, which can be attributed to improved mass transfer and more effective interaction of the substrates with the heterogeneous catalyst in the supercritical medium. These advantages partially compensate for the energetic costs associated with the use of scCO₂.

Proceeding to the next stage, the catalyst activity over an extended period of use was tested. For this purpose, the repetitive hydrosilylation of 4-octyne (**2a**) with silsesquioxane **1a** in scCO₂ and organic solvents was performed (Figure S5). Initially, the reaction was performed within 4 h at 100 °C with the catalyst concentration at 1.43 mol % of Pt. In the first five repetitive batches for all media, a decrease of catalyst activity was observed; however, the highest drop of catalyst activity was observed for organic solvents (7% for toluene and 31% for *n*-heptane vs 78% for scCO₂). Due to the lower catalyst activity after the fifth batch, the reaction time was extended to 18 h for reactions carried out in toluene and scCO₂. For both media, it resulted in higher conversion of the **1a**, but still for toluene, the lower yields were observed with gradual dropping up to the 15th batch. Conversely, the application of scCO₂ allowed the use of Pt/XAD-4 up to 35 batches with excellent reaction (96–99%) and extraction (75–91%) yields, which allowed us to achieve over three times higher total TON values than for the reaction in toluene (2375 vs 739). After that, the catalyst was sealed in a snapped vial and kept in ambient conditions for 15 months to determine the effect of aging on catalyst activity. Surprisingly, the Pt/XAD-4 was still highly active in the next four batches leading to **3a** with excellent yields (97–99%).

As part of the study on the Pt/XAD catalyst activity, it was also examined how an extended period of use affects its morphological and compositional characterization as well as its textural parameters. SEM-EDX images (Figure S3) taken for Pt/XAD-4 after a series of reactions in scCO₂ showed the deposition of silicon-containing postreaction deposits on the catalyst surface. Additionally, low-temperature nitrogen sorption measurements confirmed the mechanical blocking of the smaller pores of the catalyst by the film formed during the consecutive reactions (Table 1). Both the deposition of silicon-based material and the changes in textural parameters could be caused by a nonquantitative product extraction process and the gradual accumulation of postreaction deposits. However, note that the changes revealed by the SEM-EDX and BET analyses did not affect the catalyst activity, which remained very high even after 38 consecutive runs.

The ICP-MS analysis of postreaction mixtures for repetitive batch experiments reveals notably greater leaching of the Pt in toluene than in scCO₂ in the first and sixth batches (3.6 and 1.6 ppb vs 83.4 and 16.9 ppb, respectively). Interestingly, ICP-MS analysis also revealed a Pt leaching of 15.1 ppb in *n*-heptane, which is considerably lower than that observed for toluene and slightly higher than for CO₂. This suggests that Pt leaching in toluene likely originates from secondary aromatic interactions between the solvent and surface-exposed Pt species, which are absent in the aliphatic control solvent. These results align well with the repetitive batch experiments. The crucial influence of the solvent choice on catalyst leaching was also supported by a cross-check experiment in which the same amount of the catalysts (1.43 mol % of Pt) was heated (100 °C, 4 h) in toluene. After removal of the catalyst, **1a** and **2a** were added to toluene, and the reaction was performed in 18 h at 100 °C. A 96% conversion of **1a** was achieved, indicating significant leaching of the catalyst, which is still in active form in the toluene solution. Additionally, to distinguish homogeneous (molecular) catalysis from heterogeneous (cluster or nanoparticle metal) catalysis, mercury poisoning tests for the reaction of **1a** with **2a** in scCO₂ and toluene were performed. For both solvents, a significant drop of the **1a** conversion was observed; however, the conversion of **1a** in toluene was over three times higher than in scCO₂ (13 vs 4%). Interestingly, the presence of mercury reduced the conversion of **1a** to 26% when the reaction was carried out in a toluene solution, where the catalyst had previously been preheated and removed prior to the reaction. This may indicate that (i) some of the fine platinum crystallites were washed from the carrier surface into the reaction medium and (ii) the leaching of the active species of the catalyst is much faster in toluene than in scCO₂ due to the higher wettability of the catalyst surface with toluene, which can be considered a lower-polarity solvent compared to scCO₂. To support these findings, a hot-filtration test was carried out, and the filtrate exhibited only marginal further conversion compared to the unfiltered reaction. This behavior is consistent with catalysis being dominated by heterogeneous Pt species. However, a minor homogeneous contribution from leached Pt cannot be completely excluded (ESI, Table S6).

3. CONCLUSIONS

In summary, we successfully developed a novel synthetic approach for functionalized POSS derivatives following the principles of green chemistry. The procedure is based on hydrosilylation of a variety of functional alkenes and alkynes (**2a–j**) with different types of silsesquioxanes (**1a–d**) catalyzed by Pt/XAD-4 in scCO₂. It was found that Pt/XAD-4 is an effective catalyst for the hydrosilylation of a wide range of alkenes and alkynes. The results showed that the activity of Pt/XAD-4 is almost 2 times higher than that of the commercially available Pt supported on carbon.

It was proved that scCO₂ can replace traditionally used organic solvents, and in some cases, its positive influence on the catalytic activity of Pt/XAD-4 was observed. The Pt/XAD-4/scCO₂ system turned out to be a highly active and versatile catalytic setup, enabling consecutive hydrosilylation processes of **2a** with four different silsesquioxanes **1a–d** and olefins (**2b**, **2d**, and **2g–i**) using a single portion of the catalyst. Each batch resulted in a very high conversion of POSS (91–99%) without any decrease in the catalyst selectivity.

Moreover, the catalyst remained highly active over an extended period of use, allowing up to 35 repetitive batch cycles in scCO_2 with excellent reaction yields (96–99%) and total TON values three times higher than those achieved in toluene (2375 vs 739). The significant drop in catalyst activity in toluene was attributed to greater Pt leaching compared to scCO_2 , as confirmed by ICP-MS analysis of postreaction mixtures from the first and sixth batches (3.6 and 1.6 ppb vs 83.4 and 16.9 ppb, respectively). Remarkably, the catalyst remained active for at least 15 months following the last cycle.

In addition to the positive effect of using scCO_2 as a solvent on catalyst activity, the use of this reaction medium simplified the isolation of high-molecular-weight POSS derivatives to a single step—extraction with CO_2 —resulting in very high yields of the isolated products. Furthermore, when a single isomer is exclusively formed and the product is easily extracted with a CO_2 stream, no additional postreaction procedures are necessary.

Overall, the improvements of POSS functionalization reported in this paper exemplify the effectiveness of using green chemistry principles in the design of synthetic processes using an integrated approach of an atom-efficient reaction, catalyst development, and choice of the reaction medium.

4. EXPERIMENTAL SECTION

4.1. General Procedures

4.1.1. Phase Behavior Studies Performed in scCO_2 . To a clean and dry window-type 10 mL autoclave equipped with a stirring bar, 100–120 mg of substance was added. At the first step, the solubility of reagents in scCO_2 at 100 °C and in the pressure range of 100–260 bar was tested (the pressure was increased at a step of 20–30 bar). For the compounds for which solubility was low at 100 °C, phase behavior studies at 60 °C and in the pressure range 140–220 bar were performed. The solubility of the reagents was visually observed through the sapphire window of the reactor.

4.1.2. Procedure for Hydrosilylation of Alkynes (2a–e) and Alkenes (2f–j) with Silsesquioxane 1a in Toluene. The solution of silsesquioxane 1a (0.1 g, 0.11 mmol) and an appropriate alkyne or alkene (0.11 mmol) in toluene (4 mL) was stirred and heated up to 100 °C. Then, the Pt/XAD-4 catalyst in the amount of 1.43×10^{-4} – 1.43×10^{-2} mol of Pt/mol of 1a, depending on the experiment, was added. Reactions were carried out for 18 h or until full conversion of Si–H was detected by using *in situ* FT-IR spectroscopy. Then, the solution was decanted from the surface above the catalyst, and the solvent was evaporated under vacuum. The crude product was dissolved in petroleum ether and filtered through silica gel. After solvent evaporation, the product was washed with methanol and dried for 6 h under vacuum. Isolated products were characterized by ^1H , ^{13}C , and ^{29}Si NMR. Conversion of 1a, for the processes carried out for 18 h, was determined by ^1H NMR, and the selectivity was confirmed by ^1H and ^{29}Si NMR.

4.1.3. Procedure for Hydrosilylation of Alkynes (2a–b, 2d–e) and Alkenes (2g–j) with Silsesquioxanes 1a–d in scCO_2 . A silsesquioxane 1a (0.25 g, 0.275 mmol), 1b (0.35 g, 0.275 mmol), 1c (0.26 g, 0.275 mmol), 1d (0.37 g, 0.275 mmol), and an appropriate alkyne or alkene (0.275 mmol) were loaded into a 10 mL stainless steel autoclave reactor equipped with sapphire windows and a magnetic stirrer. The Pt/XAD-4 catalyst, in amounts ranging from 1.43×10^{-4} to 1.43×10^{-2} mol of Pt/mol of 1a depending on the experiment, was loaded into the basket and placed into the autoclave. The cell was sealed, and the autoclave was heated up to 100 °C. Then, the CO_2 was added to the cell until a clear homogeneous mixture was visually determined through the sapphire window (240–250 bar depending on the experiment). The reactions in scCO_2 were performed with stirring (350 rpm) for 18 h. Resulting products were extracted with CO_2 steam and collected in cold traps (30 mL of

n-heptane). The extraction process was carried out at 100 °C, under 230–250 bar pressure, for 80–120 min depending on the experiment. The conversion of the Si–H bond and selectivity of the product were determined by ^1H , ^{13}C , and ^{29}Si NMR. After the extraction process, the reactor was cleaned using ethyl acetate, and the efficiency of the process was estimated.

4.1.4. Procedure for Repetitive Batch Hydrosilylation in scCO_2 . The procedure of repetitive batch reactions is analogous to that described in subsection 4.1.3 with some modification. After the extraction, the basket with the catalyst was removed, and the autoclave was cleaned with ethyl acetate. Subsequently, to the dry autoclave, the new portion of the reagents was added, and the basket with the catalyst was reassembled. The reaction and extraction were performed according to subsection 4.1.3.

4.1.5. Procedure for Repetitive Hydrosilylation of 4-Octyne (2a) with Silsesquioxane 1a in Organic Solvents. To the single-neck round-bottom flask equipped with a stirring bar was added silsesquioxane 1a (0.25 g, 0.275 mmol). Subsequently, 10 mL of toluene or *n*-heptane and 4-octyne (0.275 mmol) were added. The cylinder-shaped glass frit (porosity G4) with the catalysts (1.43×10^{-2} mol of Pt/mol of 1a) sealed on the open side with a PTFE tape was inserted into the reaction mixture above the stirring bar by connecting it with a glass stopper. The reaction was carried out for 4 or 18 h at 100 °C. After the reaction, the basket with the catalysts was removed, and the reaction mixture was evaporated and analyzed. The next batch with the same catalyst loading was carried out using the above-described procedure.

4.1.6. Procedure for the Hydrosilylation of 4-Octyne (2a) with Silsesquioxane 1a in Preheated Catalysts in Toluene. A 10 mL portion of toluene was added to the 100 mL single-neck round-bottom flask equipped with a stirring bar. The cylinder-shaped glass frit (porosity G4) with the catalysts (1.43×10^{-2} mol of Pt/mol of 1a) sealed on the open side with a PTFE tape was inserted into the reaction mixture above the stirring bar by connecting with a glass stopper. The catalyst was heated for 4 h at 100 °C. Subsequently, the cylinder-shaped glass frit containing the catalyst was then removed, and silsesquioxane 1a (0.25 g, 0.275 mmol) and 4-octyne (0.275 mmol) were added to the toluene solution and heated for the next 18 h. The conversion of the Si–H bond and the selectivity of the product were determined by ^1H NMR.

4.1.7. Procedure for Mercury Poisoning Tests. Caution: Mercury and its compounds are toxic. All manipulations were carried out in a fume cupboard.

4.1.7.1. Hydrosilylation of 2a with 1a in the Presence of Pt/XAD-4@Hg. To the cylinder-shaped glass frit (porosity G4) containing the catalysts (1.43×10^{-2} mol of Pt/mol of 1a), 60 μL (800 mg, 1000 equiv., 4 mmol) of mercury was added and gently stirred to cover the surface of the catalyst. After 30 min, the cylinder-shaped glass frit with catalyst and mercury was placed in the stainless steel basket and mounted in the autoclave (for the reaction in scCO_2) or in the 100 mL single-neck round-bottom flask (for the reaction in toluene). The hydrosilylation of 4-octyne (2a) (0.275 mmol) with silsesquioxane 1a was carried out for 18 h at 100 °C for both solvents. The conversion of the Si–H bond and selectivity of the product were determined by ^1H NMR.

4.1.7.2. Hydrosilylation of 2a with 1a in the Presence of Hg and Preheated Catalysts in Toluene. To a 100 mL single-neck round-bottom flask equipped with a stirring bar was added 10 mL of toluene. The cylinder-shaped glass frit (porosity G4) with the catalysts (1.43×10^{-2}) sealed on the open side with a PTFE tape was inserted into the reaction mixture above the stirring bar by connecting with a glass stopper. The catalyst was heated for 4 h at 100 °C. Subsequently, the cylinder-shaped glass frit with the catalyst was removed, and to the toluene solution, 60 μL (800 mg, 1000 equiv., 4 mmol) of mercury was added and stirred for 30 min at 100 °C. Afterward, the silsesquioxane 1a (0.25 g, 0.275 mmol) and 4-octyne (0.275 mmol) were added and heated for the next 18 h. The conversion of the Si–H bond and selectivity of the product were determined by ^1H NMR.

4.1.8. Procedure for Hot-Filtration Tests. Silsesquioxane 1a (0.10 g, 0.11 mmol) was placed in a single-neck round-bottom flask

equipped with a magnetic stir bar. Toluene (10 mL) and 4-octyne (0.11 mmol) were added, followed by the insertion of a cylinder-shaped glass frit (porosity G4) containing the catalyst (1.43×10^{-2} mol of Pt per mol of **1a**), which was sealed on the open side with PTFE tape. The reaction mixture was heated at 100 °C for 30 min. After this time, a 1 mL aliquot was withdrawn for ^1H NMR analysis, and the remaining mixture was rapidly filtered through a 0.2 μm PTFE syringe filter. The filtrate was then returned to 100 °C and stirred for an additional 30 min. Conversion of the filtered mixture was determined by ^1H NMR spectroscopy.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acssuschemeng.5c09304>.

General information and product and catalyst characterization (PDF)

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Notes

The authors declare no competing financial interest.

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