Journal of Catalysis 367 (2018) 1–6

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Hydrosilylation of alkenes and alkynes with silsesquioxane $(HSiMe_2O)(i\text{-}Bu)_7Si_8O_{12}$ catalyzed by Pt supported on a styrene-divinylbenzene copolymer

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ARTICLE INFO

Article history:
Received 6 June 2018
Revised 9 August 2018
Accepted 13 August 2018

Keywords:
Hydrosilylation
Silsesquioxane
Alkene
Alkyne
Pt/SDB
Heterogeneous catalysis

ABSTRACT

This paper reports on detailed studies on the hydrosilylation of alkenes and alkynes with silsesquioxane $(HSiMe_2O)(i\text{-}Bu)_7Si_8O_{12}$, catalyzed by Pt, supported on a styrene-divinylbenzene copolymer (**Pt/SDB**). The obtained results clearly indicate that **Pt/SDB** was a very efficient catalyst, characterized by high TON in the hydrosilylation of a wide spectrum of reagents. The heterogeneous character of the catalyst permitted reuse up to 20 times. The selectivity of all the hydrosilylation reactions was very high, regardless of the catalyst concentration. **Pt/SDB** is the first example of a heterogeneous catalyst being used for the functionalization of silsesquioxane $(HSiMe_2O)(i\text{-}Bu)_7Si_8O_{12}$. Under the tested conditions it was found to be more effective than commercially available and industrially applied Pt catalysts supported on activated carbon, making it one of the most versatile and potentially interesting heterogeneous systems in hydrosilylation reactions.

1. Introduction

Polyhedral oligomeric silsesquioxanes (POSS) with the formula $R_8Si_8O_{12}$ are unique molecules with hybrid characteristics, typical for both inorganics and organics [1].

Their structure is based on a cubic core consisting of silicon atoms bonded to three oxygen atoms and one function, situated on the periphery of the cube. This well-defined, almost ceramic core, nanometric in scale, provides POSS with features such as high thermal-, photo- and chemical stability, remarkable mechanical and optical properties, and biocompatibility, which are similar for all compounds of this family [2].

Eight organic groups attached to the silicon atom define POSS molecules appearance, solubility, and chemical reactivity. Unlike the inorganic part, these factors can be easily modified by the introduction of various substituents *via* a wide spectrum of catalytic and non-catalytic chemical modifications (e.g. nucleophilic substitution, condensation, metathesis and silylative coupling, Heck coupling, thiol-one reaction, hydrosilylation, and others) [1].

Among all of the tested methods, hydrosilylation [3] of the unsaturated carbon-carbon bonds is one of the most commonly used for the synthesis of POSS derivatives, and is characterized by its diverse functionality and architecture. However, most of the studies published so far have not focused on the optimization of the hydrosilylation process, but rather on the characterization of the obtained compounds and their applications. Due to this fact, investigating improvements in methods of synthesis based on the hydrosilylation process are highly desirable.

On the basis of our extensive experience in the study of the hydrosilylation process [4], we have recently examined in detail the reactivity of a wide spectrum of functional alkenes and alkynes with silsesquioxane $(HSiMe_2O)(i\text{-}Bu)_7Si_8O_{12}$ (**1**), in the presence of highly effective, easily available, homogeneous catalytic systems [5,6]. Due to its simplicity and versatility, the developed procedure can be easily repeated, rapidly scaled up, and widely applied.

Herein, we attempt to go one step further and study the heterogeneous catalyst, which is especially important for the industrial production of POSS. A heterogeneous system will simplify the separation procedures, especially the purification of the obtained products from transition metal residues, and allow for catalyst reuse, making the process more economical.

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https://doi.org/10.1016/j.jcat.2018.08.012
0021-9517/

To the best of our knowledge, only three examples of hydrosilylation of alkenes with silsesquioxane $H_8Si_8O_{12}$ or octaspherosilicate $(HSiO_2)_8Si_8O_{12}$, in the presence of heterogeneous catalysts have been published so far [7].

Gentle et al. distinguished the activity of a series of carbon supported platinum, palladium and rhodium catalysts in the synthesis of octasubstituted silsesquioxanes *via* hydrosilylation of vinyl-terminated polysiloxanes with silsesquioxane $H_8Si_8O_{12}$ [7a]. The reusability of the applied catalyst was not studied.

A platinum sponge was used by Lehrer's group as a catalyst for the synthesis of low dielectric materials, based on silsesquioxane $H_8Si_8O_{12}$ and spherosilicate $(HSiO_2)_8Si_8O_{12}$. Three-dimensional polymer networks were obtained by the hydrosilylation of 1,5-hexadiene [7b]. Also, in this case, the catalyst was not recycled.

We have also previously reported the synthesis of functionalized spherosilicate $(HSiMe_2O)_8Si_8O_{12}$ *via* alkene hydrosilylation, catalyzed by a well-defined rhodium siloxide complex immobilized on silica. Spherosilicate was functionalized with two different olefins to produce products with mixed functional groups. The selected reactions were conducted repeatedly. One catalyst portion was used 10 times without a noticeable reduction in the activity [7c].

Despite the above-mentioned examples, there are no reports on the hydrosilylation of alkenes or alkynes with silsesquioxanes catalyzed by heterogeneous catalytic systems.

On the other hand, the uses of these systems in the hydrosilylation of alkenes and alkynes with silanes has been widely reported, which indicates the importance of this issue.

Alkene hydrosilylation was examined in the presence of platinum, supported on silica [8], carbon [9], epoxy-based monolithic columns [10], polyethylene glycol (PEG) [11], polyamide [12], glass fiber, poly(methylene) sulfide [13], or other polymeric resins [14]. The activity of the above-mentioned catalysts was tested in hydrosilylation of *n*-alkenes [8–9d], allyl chloride [8c], or allyl glycidyl ether [8g], with simple silanes. Depending on reaction conditions, platinum loading, and substrates used in the reactions, between 3 and 20 repetitive cycles were conducted, using a single catalyst portion.

In contrast to the large number of reports describing the uses of the heterogeneous catalyst in alkene reduction with agents containing Si-H, the field of alkyne hydrosilylation with silanes is limited to only eight works [15–19], in which the following catalysts were used: platinum dioxide (PtO_2) [15], platinum supported on carbon [16], SiO_2 [17], and TiO_2 [18]; PtO/PtO_2-Fe_3O_4 [19], platinum, iridium, rhodium, and ruthenium nanocrystals stabilized by quaternary ammonium salts [17c].

Bearing the above-mentioned information in mind, we decided to examine the hydrosilylation of a wide range of functional alkenes and alkynes (terminal and internal) with silsesquioxane $(HSiMe_2O)(i\text{-}Bu)_7Si_8O_{12}$ (**1**), in the presence of Pt supported on a styrene-divinylbenzene copolymer (**Pt/SDB**). In doing so, we describe the scope of catalyst uses, and compare the obtained results with the commercially available and industrially applied Pt supported on activated carbon, in order to indicate the potential of the studied system.

2. Results and discussion

2.1. Hydrosilylation of alkenes with silsesquioxane 1

Pt/SDB was prepared according to the previously reported method [20]. The catalyst is in the form of spherical particles, 0.3–0.8 mm in diameter (see ESI, Fig. 1) which simplifies storage, measurements, and especially separation from the post-reaction mixtures. Simple decantation of the catalyst is entirely sufficient to avoid removal of the particles from the reactor. There is no requirement to use any mechanical separators, e.g. filters. Moreover, the support recovered after multiple uses can be utilized again for the preparation of a new portion of the catalyst. Additionally, **Pt/SDB** can be easily prepared from commercially available, relatively inexpensive components. This makes **Pt/SDB** a perfect candidate for application in hydrosilylation process performed in heterogeneous mode.

Supplementary data associated with this article can be found, in the online version, at https://doi.org/10.1016/j.jcat.2018.08.012.

Therefore, in our studies, the activity of **Pt/SDB** in the hydrosilylation of alkenes (**2a-j**) with reactive functionalities was performed (Scheme 1).

It was determined that the reaction between 10-undecen-1-ol (**2a**) and silsesquioxane **1** in the presence of low concentration of **Pt/SDB** (0.0134 mol%, 90 °C, toluene) was completed in around 18 h (turnover number – TON = 7387). The selectivity of the formation of product **3a** reached 95%. The remaining 5% was identified as a product **4a** (Table 1).

Subsequent testing showed that the same reaction conditions are suitable for effective hydrosilylation of eugenol (**2c**), 11-bromo-1-undecene (**2d**), and methyl 10-undecenoate (**2f**). In all cases, high TONs were obtained.

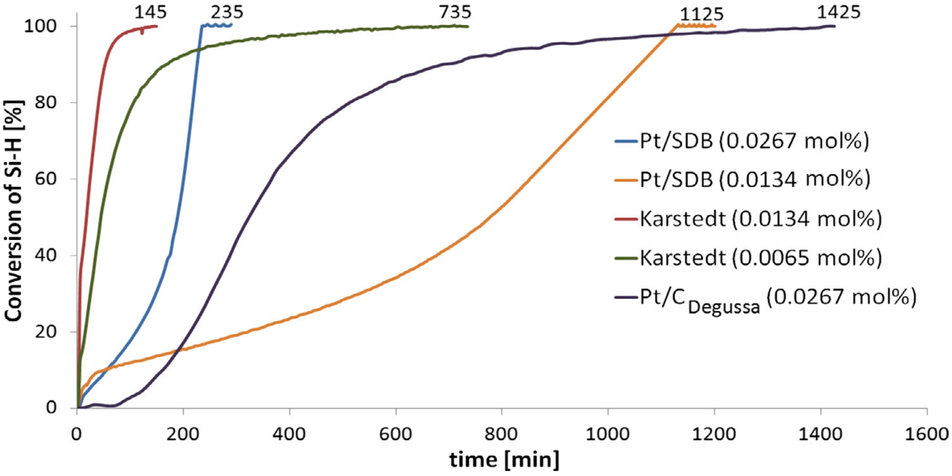

Fig. 1. The plots of conversion *vs.* time for the hydrosilylations of alkene 2a with silsesquioxane 1, in the presence of Pt/SDB, Karstedt's catalyst and $Pt/C_{Degussa}$ measured by *in situ* FT-IR. Reaction conditions: toluene, 90 °C, m_1: V_{tol} = 50 mg mL^{-1}.