Confinement of the Grubbs Catalyst in Alkene-Functionalized Mesoporous Silica

Hélène Staub, [a,b,c] Freddy Kleitz [a,b]* and Frédéric-Georges Fontaine [a,c]*

[a] Department of Chemistry, Université Laval, 1045 Avenue de la Médecine, Québec (Qc), G1V 0A6, Canada

[b] Centre de recherche sur les matériaux avancés (CERMA), Université Laval, Québec, Canada

[c] Centre de recherche sur la propriété des interfaces et de la catalyse (CERPIC), Université Laval, Québec, Canada

E-mails: frederic.fontaine@chm.ulaval.ca and freddy.kleitz@chm.ulaval.ca

Abstract:

Herein, we report on the impact of alkyl chain length of olefin moieties anchored into silica mesopores on the confinement behavior and stability of the first-generation Grubbs catalyst, *i.e.* [$RuCl_2$(=CH)(Ph)(PCy_3)$_2$]. In this contribution, ordered mesoporous SBA-15 silica materials were functionalized with alkenyl-trichlorosilanes exhibiting different carbon chain lengths, e.g., vinyl- (C2), allyl- (C3), hexenyl- (C6) and octenyl- (C8) trichlorosilanes. Subsequently, the Grubbs I catalyst was incorporated into these different host materials in the presence of organic solvent. The thus-obtained materials, before and after interaction with Grubbs I, were characterized by a variety of methods, including N_2 physisorption, thermogravimetric analyses, solid state NMR (^{13}C, ^{31}P and ^{29}Si) and attenuated total reflectance (ATR) spectroscopy. Our investigations reveal a pronounced dependence of the Grubbs surface stability as a function of the grafted alkyl chain length of the alkene moieties. The nature of the immobilized Ru-based species is function of the surface modification and the presence of residual silanol groups.

Keywords: Grubbs catalyst; Mesoporous silica; SBA-15; Surface functionalization; Olefin metathesis; Organosilanes; Phosphine; Solid state NMR

1. Introduction

The first-generation Grubbs' catalyst, $(PCy_3)_2Ru(Cl)_2=C(H)(Ph)$, remains one of the most commonly used homogeneous reagent for metathesis reactions, although more durable and more active generations of catalysts have been introduced since [1-4]. Nevertheless, the stringent requirements for removal of trace transition metals from products still limit the use of such metathesis catalysts in industry, especially in the pharmaceutical industry. To overcome these issues, two main strategies have been developed: the immobilization of the catalysts on solid supports and scavenging of residual catalysts [5-7]. In both cases, several materials have been selected as supports or scavengers [8-14], and nanoporous silica has proved to be one of the most suitable [15-17]. In most cases, the different generations of Grubbs' catalyst were supported on silica by a tethering of ancillary ligands onto the surface, e.g. grafting of triethoxysilyl-functionalized diphenyl and dicyclohexylphosphine ruthenium carbene complex on mesoporous silica [18-34]. Most of the resulting heterogenized catalysts show good catalytic activity in ring-closing metathesis (RCM) and ring-opening metathesis polymerization (ROMP); however, they have lower activity compared to their homogeneous analogues and substantial leaching of the ruthenium is observed. Mechanistic studies have shown that one key step in the activation of the first- and second-generation Grubbs' catalyst is the loss of one phosphine ligand [35]. However, on a mesoporous solid support, the catalyst will have to overcome interactions with the surface (functionalized or not) as well as with other grafted substituents in order to obtain the desired catalytic activity. In order for the catalyst to keep its optimal activity, proper understanding of the grafting properties must be acquired.

A series of recent reports [36,37] allowed gaining practical insights into the

3

interactions between Grubbs' catalyst and mesoporous SBA-15-type materials. In particular, Polarz and coworkers characterized ruthenium side-products in the liquid-phase, thus obtaining some evidence of interactions between the catalyst and silica [36]. We then supplemented these findings by focusing on solid-state characterization of a series of SBA-15 silica materials modified with different surface functional groups and their interactions with the Grubbs I catalyst and the liberated phosphine species [37]. In particular, it was revealed that in the presence of a long olefin chain, C8, some part of the introduced catalysts could transit into the mesopores and undergo ring-closing metathesis, corresponding to the expected activity of the ruthenium compound diffusing into the silica mesopores. Grubbs I was also shown to react with residual silanol accessible on the surface thus trapping the catalyst and terminating catalytic activity. A total silylation of surface SiOH could prevent trapping and thus deactivation of the catalyst. However, a better understanding of the role of the alkene chain in the confinement and nanopore surface behavior of the Grubbs catalyst is still needed in order to optimize immobilization or scavenging processes.

Herein, to supplement our previous study, [37] we now focus specifically on the impact of alkyl chain length of olefin moieties anchored into silica mesopores on the confinement behavior and surface stability of the first-generation Grubbs catalyst, i.e. $[RuCl_2(=CHPh)(PCy_3)_2]$. To this aim, ordered mesoporous SBA-15 silica materials were functionalized with alkene-trichlorosilanes exhibiting different carbon chain lengths, e.g., vinyl- (C2), allyl- (C3), hexenyl- (C6) and octenyl- (C8) trichlorosilanes. Subsequently, the Grubbs I catalyst was incorporated into these

different host materials in the presence of organic solvent. The resulting materials, before and after interaction with Grubbs I, were characterized by a variety of methods, including N_2 physisorption, thermogravimetric analyses, solid state NMR (^{13}C, ^{31}P and ^{29}Si) and attenuated total reflectance (ATR) spectroscopy. This contribution confirms that the nature of the immobilized Ru-based species is strongly depending on the surface modification, i.e., the chain length of the alkenyl-silane moeities grafted on the mesopores.

2. Experimental Section

2.1 Materials

All grafting manipulations were carried out under an atmosphere of nitrogen, using standard Schlenk and glove box techniques. All support materials were outgassed under vacuum overnight, at 200 $^{\circ}$C in the case of pure silica and at 80 $^{\circ}$C for the hybrid organosilicas. Dry toluene was distilled from sodium/benzophenone. Deuterated solvents were dried over NaK, degassed using freeze-pump thaw cycles, and purified by vacuum transfer.

SBA-15 silica. Mesostructured SBA-15 silica material was prepared under aqueous acidic conditions using poly(alkylene oxide)-based triblock copolymer Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800, Aldrich) dissolved in a HCl solution (0.3 M) [38]. The silica source was TEOS (ACROS 98%). The molar composition of the starting reaction mixture was 0.0012 P123 / 0.069 TEOS / 0.102 HCl / 6.771 H_2O. The reaction temperature with TEOS was fixed at 35 $^{\circ}$C and the hydrothermal temperature was 100 $^{\circ}$C. A typical preparation of the mesoporous 2-D silica is as follows: 6.71 g of P123 is

dissolved in 121.87 g of distilled water and 3.72 g of 37 % wt HCl solution with stirring at 35 °C. After complete dissolution, 14.45 g of TEOS is added at once to the homogeneous clear solution. This mixture is left under vigorous stirring at 35 °C for 24 h. Subsequently, the mixture is aged at 100 °C for 24 h under static conditions. The white precipitated product is filtered hot without washing and dried at 100 °C for 24 h in air. Surfactant-free mesoporous material is obtained after a brief ethanol/HCl washing and subsequent calcination at 550 °C in air.

Functionalization with the trichlorosilanes (C_x). The trichlorosilane (Gelest 95%) (8.4 mmol, 3.25 eq.) was added to a suspension of calcined SBA-15 (2.0 g, 1.19 mmol -SiOH/g [39,40]) in dry toluene (60 mL) and then heated at 110 °C for 24 h. After cooling, the powder was filtered and washed with equivalent volumes of toluene and hexane. The resulting organic/inorganic hybrid material was dried at 85 °C overnight.

Incorporation of the Grubbs I catalyst (C_x-Ru). To a suspension of a given silica support (0.5 g) in toluene (50 mL), Grubbs I catalyst (Sigma-Aldrich) (0.2 g, 0.24 mmol) was added and the mixture stirred for 2 h at room temperature. After filtration, the resulting material was washed in CH_2Cl_2 using Soxhlet extraction to obtain a grey/brown powder.

2.2 Characterization

Solid state NMR spectra were recorded with a Bruker Avance 300 MHz spectrometer (^{13}C: 75.4 MHz; ^{31}P: 121.4 MHz; ^{29}Si: 59.6 MHz) equipped with a MAS probe head using 4mm ZrO_2 rotors and a sample spinning rate of 8000 Hz. The NMR spectra were recorded using cross-polarization/magic angle spinning (^{13}C) or magic angle spinning (^{29}Si and ^{31}P). Nitrogen adsorption-desorption isotherms were

measured at liquid nitrogen temperature (-196 °C) over the full micropore-mesopore range using a Quantachrome Autosorb-1MP volumetric adsorption analyser. Before the measurements, the samples were outgassed under turbomolecular pump vacuum for 24h at 200 °C for purely siliceous SBA-15 and 80 °C for the functionalized organosilica materials, as implemented previously [37,41]. Note that for the sake of accuracy of the N_2 measurements, the equilibrium time was set in the micropore range, to 3 min and the tolerance factor to the value of 0, whereas in the relative pressure range between 0.5 and 1(P/P_o), the values were set to 2 min and a tolerance factor of 3. The Brunauer-Emmett-Teller (BET) equation was used to calculate the apparent surface area from adsorption data obtained at *P/P$_0$* between 0.05 and 0.2. Total pore volume of micro-mesopores was calculated from the amount of nitrogen adsorbed at $P/P_0=0.95$, assuming that adsorption on the external surface was negligible compared to adsorption in pores. Cumulative pore volumes and pore size distributions were determined by using *non-local density functional* (NLDFT) methods considering sorption of nitrogen at -196 °C in cylindrical silica pores [42,43]. Both the kernel of equilibrium NLDFT isotherms (desorption branch) and the kernel of (metastable) NLDFT adsorption isotherms (adsorption branch) were applied for pore width determination [44]. For comparison, the pore size distributions were also calculated by analyzing the adsorption branch of the isotherm using the Barret-Joyner-Halenda (BJH) method. Note that in contrast to the DFT analysis, pore sizes obtained using the classical BJH model on the desorption branch (equilibrium conditions) are known to be underestimated (by ~ 25%). It has clearly been demonstrated that the macroscopic, thermodynamic methods fail to correctly describe

the thermodynamic and thermophysical properties of the confined pore fluid. Thus, microscopic methods based on statistical mechanics, such as NLDFT, which allow describing the configuration of the adsorbed phase on a molecular level, are considered much more accurate [44,45,46].

Thermogravimetry-differential thermal analysis (TG-DTA) measurements were performed using a Netzsch STA 449C thermogravimetric analyzer. The analyses were carried out under air flow at a heating rate of 10 °C/min. Infrared spectra spectra were recorded using a Thermo-Nicolet Magna 850 FTIR spectrometer with a narrow band MCT detector and a diamond ATR Golden-Gate accessory (Specac Ltd., London). The spectra were obtained from 128 scans with a 4 cm^{-1} resolution. The elemental analyzes were performed at the Guelph Chemical Laboratories Ltd, Guelph, Ontario, Canada. Carbon, Hydrogen and Nitrogen analysis was performed by the combustion method using a Carlo Erba Model 1108 CHNS Analyzer. In this method, a known amount of sample (~2 to 3 mg) was combusted at 1000° C in the presence of an oxidant catalyst in an oxidation quartz reactor tube. The resulting product gases were passed through the catalytic reduction chamber. The final product gases (CO_2, H_2O and N_2) were analyzed by gas chromatography using a thermal conductivity detector. Certified NIST traceable standards (acetanilide, cyclohexanone) with known % C, % H, % N were also analyzed under the same experimental conditions from which the % of CHN were calculated in the sample. The method error limit on Carbon is +/- 0.5% of absolute value, Hydrogen is +/- 0.4% absolute value and Nitrogen is +/- 0.3% absolute value.

3. Results and Discussion

3.1 Synthesis and characterization of the alkene-functionalized SBA-15 supports

First, native SBA-15 material was synthesized according to the standard procedure developed by Choi et al.[38] and exhibited a concentration of surface silanols of 1.29 mmol/g, as evaluated by titration following a published procedure [39,40]. The different alkene-modified silica SBA-15-C_X (X = 2, 3, 6, and 8) were then obtained through post-synthesis grafting of pristine SBA-15 silica using 3.25 equivalents of $H_2C=CH(CH_2)_nSiCl_3$ (X = 2, n = 0; X = 3, n = 1; X = 6, n =4, and X = 8, n = 6) in dry toluene under reflux conditions. All these support materials exhibit similar nitrogen sorption properties, showing typical type IV isotherms characteristic of highly ordered materials with large mesopores, as shown on Figure 1 [47-49]. The physicochemical parameters derived from nitrogen physisorption for the parent SBA-15 and the differently functionalized support materials are grouped in Table 1. In all cases, the contribution of external surface area to the total porosity of the materials is obviously very small and will thus be neglected. Note that, the porosity values obtained for the parent SBA-15 are quite typical of this material when it is aged 24 hours at 100°C. The pure silica material exhibits rather large cylindrical mesopores (> 8 nm) accompanied with a contribution of small intrawall mesopores ranging between 2 and 5 nm, as evidenced by the NLDFT cumulative pore volume analysis (see Figure 1b). No micropores (pores < 2nm) could be detected through our nitrogen physisorption measurements, which is fully consistent with the reports of Galarneau, *et al.* [50] and Kleitz, *et al*. [44] describing in detail the evolution of the intrawall porosity of such materials aged at elevated temperatures.

As expected, the introduction of organic moieties within the pores of SBA-15 results in decreased adsorption capacity, which is reflected by lower BET specific surface areas and reduced pore volumes as compared to the parent SBA-15. It is observed that the decrease in mesopore volume and specific surface is more important for materials having been functionalized with longer organic chains, the latter values ranging from 1.12 $cm^3.g^{-1}$ and 791 $m^2.g^{-1}$ to 0.81 $cm^3.g^{-1}$ and 534 $m^2.g^{-1}$, for SBA15-C_2 and SBA15-C_8, respectively, but does not differ significantly between SBA15-C_6 and SBA15-C_8. Similarly, the evolution of the mean mesopore size follows the same pattern with the smaller pore size measured for samples grafted with C6 and C8-alkene chains ($\sim$ 7.6 nm, $NLDFT_{des}$, Table 1). From the NLDFT cumulative pore volume plots (Figure 1b), it can also be seen that the intrawall pore volume typically observed for SBA-15-type silica is significantly reduced upon grafting of longer chain alkenes (C6 and C8), which is similar to what we observed previously for silane-grafted SBA-15[37]. Some secondary intrawall (meso)porosity remains present in the case of C2 and C3 alkene chains. However, in all of the organosilane-modified samples, no evidence of intrawall microporosity could be deduced from the nitrogen sorption isotherms. These data are thus consistent with an efficient covalent grafting of the carbon chains on the mesopore surface inducing a progressive decrease in the pore volume and mesopore size (see Table 1).

 In the next step, the first-generation Grubbs' catalyst ($(PCy_3)_2RuCl_2(=CHPh)$) was added to all support materials SBA15-C_X by an immobilization procedure performed by dispersing the different powders in a 4.8 mM solution of the catalyst in toluene under stirring over a period of 2 hours at room temperature. The resulting solids were then filtered, washed with methylene chloride using a Soxhlet extractor, yielding the materials

designated as SBA15-C_2-Ru, SBA15-C_3-Ru, SBA15-C_6-Ru, and SBA15-C_8-Ru. The materials SBA15-C_8 and SBA15-C_8-Ru were already discussed in our previous report [37], but will be described herein for comparison purposes.

The thermogravimetric analysis (TGA) curves for the different mesoporous materials SBA15-C_X and SBA15-C_X-Ru are depicted in Figure 2. The corresponding weight losses (%) and elemental analysis (EA) results are compiled in Table 2. Materials SBA15-C_{8-2} exhibit weight loss of 15.8, 10.7, 7.4, and 1.7 %, respectively, and contents of carbon of 10.5, 8.8, 2.9, and 0.8%, and hydrogen 2.8, 1.7, 1.7, and 1.5%, respectively. The values are in line with the expected trend of a grafting reaction with similar yield in every case.

All of the SBA15-C_X-Ru materials show an increased weight loss and larger C and H content than the respective support materials before Grubbs I insertion. This suggests that the organic moieties of the Grubbs' catalyst, that is mainly the tricyclohexylphosphine, remain adsorbed on the surface. Although a difference in hydrogen content in SBA15-C_3 and SBA15-C_3-Ru is not detected, the difference in carbon content (2.7%) and TGA weight loss (5.6%) is significant. Material SBA15-C_2-Ru exhibit a much higher organic content than the related support material SBA15-C_2, demonstrated by large difference values for weight loss (10.1%) and carbon content (7.9%), suggesting stronger interactions between the organic portion of the Grubbs' catalyst and the surface. Compared to the latter two materials, the difference in weight loss and C and H content before and after grafting of the Ru-species remains rather small for the C6 and C8 materials, which is indicative of limited chemisorbed species originating from the ruthenium complex in the latter two samples.

The DTA profiles of all materials under investigations are shown in Figure 3. These data confirm that the organic moieties are chemically absorbed on the surface since the weight loss of materials SBA15-C_X occur at temperatures over 200 °C, which is typical for the degradation of grafted organic materials [51-54]. It can be observed that the longest organic chains decompose earlier than short moieties, as can be observed by the main DTA effect occurring at the maxima of 230, 265, and 350°C for SBA15-C_8, SBA15-C_6 and SBA15-C_3, respectively. No significant transition was observed for the SBA15-C_2 material which can be ascribed to the fairly low organic content in that material. In case of SBA15-C_8, a broad additional peak was observed in the DTA profile expending up to higher temperatures (300-450 °C) which is reminiscent of the transition observed for materials with shorter chain length, (e.g., C3). This suggests that smaller fragments are formed throughout the degradation of the occluded organics [55-60]. The following behavior is in accordance with an aerobic oxidation of the organic materials that occurs by radical propagation starting from the extremities of organic materials [61]. Upon addition of the Grubbs' catalyst, the DTA profile was drastically altered and several processes can be identified during combustion. For all SBA15-C_x-Ru materials, a thermal event appears at temperatures above 365°C that can be closely related to the degradation of Grubbs' catalyst [37], in agreement with the fact that some part of the content of the Grubbs' catalyst remain on the surface. A process can also be observed at 280 °C for both SBA15-C_6-Ru and SBA15-C_8-Ru. This step can be associated to the loss of the grafted chains. The occurrence of these events at higher temperature than in the SBA15-C_6 and SBA15-C_8 supports (+20 °C and +50 °C for the C6 and C8, respectively) suggest that a

12

pronounced modification has occurred to the anchored organic chains, such as a ring closing metathesis, as will be confirmed in the following section (*vide infra*).

3.2 Spectroscopic characterization of the materials

The organo-functionalized host materials were characterized using solid state NMR spectroscopy. As can be seen in Figure 4, with the exception of material SBA15-C_2, aliphatic resonances were clearly observed in the ^{13}C CP/NMR spectra in the 10-40 ppm region. In material SBA15-C_3, the presence of resonances at 55 and 66 ppm suggests that functionalization of the allylic moiety (by chlorination) is taking place in significant proportion under our synthetic conditions, notably by a Markovnikov addition of HCl on the alkenyl group to generate the corresponding chloroalkyl species [62,63].

For SBA15-C_6 and SBA15-C_8, four major resonances were observed for the vinylic carbons at 137, 129, 124, 112 ppm for C6 and at 140, 132, 125, 114 ppm for the C8, rather than two, which suggest that either isomerization has occurred on the surface or that the alkene functionalities somewhat interact with the silica surface resulting in chemically different environments, which has been previously observed [64].

The ^{29}Si MAS NMR experiments were also carried out for all materials (Figure 5) and the expected Q and T resonances were visible, with the exception of SBA15-C_2 where the T peaks could not clearly observed. Upon addition of the Grubbs I catalyst to the alkene-functionalized SBA-15, the ^{13}C CP/ NMR spectra for all resulting materials revealed an important resonance at 30 ppm corresponding to the chemical shift of the cyclohexyl

13

groups of PCy$_3$ (Figure 6). For the cases of SBA15-C$_6$-Ru and SBA15-C$_8$-Ru, a single new vinylic resonance is also observed at 133 ppm that is characteristic of a di-substituted alkene, demonstrating that the ring-closing metathesis has indeed occurred on these substrates. In contrast, no new signal was observed in the vinylic region in the case of SBA15-C$_2$-Ru and SBA15-C$_3$-Ru materials, suggesting that the carbon chains could be too short to undergo metathesis with the neighboring olefinic moieties.

As it was previously reported, ^{31}P MAS NMR spectroscopy provides a reliable route to observe the nature of the interaction between the phosphorous moieties and silica [65-68]. It was demonstrated that a resonance at 56 ppm was corresponding to the oxidized OPCy$_3$ interacting with silica, whereas resonances around 31 ppm were present for HPCy$_3$$^+$ interacting with silica or when PCy$_3$-Ru moieties in interaction with the surface of the materials. As seen in Figure 7, it can clearly be observed that the high-field resonances are the main phosphorous-containing components in the presence materials possessing longer carbon chains, i.e., SBA15-C$_6$-Ru and SBA15-C$_8$-Ru, suggesting either that a large portion of phosphonium or organometallic moieties are present on the surface of the materials. With SBA15-C$_3$-Ru, the latter signal is also predominant, although the concentration of the bound OPCy$_3$ seems to be slightly more important than that observed with the longer chain analogues.

Finally, the ^{31}P MAS NMR spectrum of species SBA15-C$_2$-Ru, that possesses a lower organic content, is principally constituted of the oxide species. These data agree well with our results previously reported in regard of the interaction of the Grubbs' catalyst with SBA-15-type supports [37] Indeed, with a more hydrophobic environment originating

from the longer alkyl chain moieties, oxidation of the PCy_3 is less likely to occur. Thus, the phosphonium species and the organometallic fragments are more prone to be stabilized by the organic-rich surface. On the contrary, with highly mineral surfaces, such as in pristine SBA-15, oxidation of the phosphine occurs much more readily and will interact more strongly with the surface silanols.

Attenuated total reflection infrared spectroscopy (ATR-IR) was further used to obtain additional insights into the integrity of the surface species in the different synthesized materials. SBA-15-C_6, and SBA-15-C_8 both possess vibrations at 2930 and 2860 cm^{-1} that can be attributed respectively to the asymmetric and symmetric CH_2 elongations (Figure 8a). With all of the alkene-modified materials, a band is observed at 3100 cm^{-1} corresponding to the C-H elongations of alkenes (Figure 8b). The samples SBA15-C_3, SBA15-C_6, and SBA15-C_8 also possess a sharp signal at 1650 cm^{-1} corresponding to the C=C stretching of alkenes, with the resonance of SBA15-C_3 being shifted to slightly lower wavenumbers (Figure 8c). However, the materials also reveal a broader band around 1630 cm^{-1}, which is somewhat less pronounced for the SBA-15-C_8. It is here rather difficult to disentangle that signal from the possible bending mode of adsorbed water (usually observed with silanol are present) or a shift of the alkenyl moiety vibration caused by interactions with the surface. Indeed, for all of the materials, a very broad signal was observed between 3650 and 3400 cm^{-1}, representative of surface hydroxyl groups or physisorbed water. In addition to the resonance for the organic moieties, a sharp signal at 3750 cm^{-1} has been observed for SBA15-C_2 that corresponds to the SiO-H vibration of free silanols, pointing to an incomplete coverage of silanols upon grafting and that some free silanols remain (Figure 8). Note that the presence of residual silanol

groups was proven to induce a decrease in the lifetime of the catalyst during metathesis reaction [36,37].

After the addition of the Grubbs' catalyst to materials SBA15-C_x, IR bands at 2930 cm^{-1} and 2860 cm^{-1} are now clearly visible for all materials, while they were not observed for SBA15-C_2, and SBA15-C_3. These results are in accordance with the NMR data that indicate that phosphine-containing compounds (PCy_3) are now present inside the pores of the material. The sharp signals observed at 3100 cm^{-1} and at 1650 cm^{-1}, which are attributed to the C-H vibrational mode for the alkenes, are no longer present for all the SBA15-C_x-Ru materials, suggesting that metathesis could have occurred (for C3, C6 and C8). The broad signals between 3400 cm^{-1} and 3650 cm^{-1} are however more intense, which reflects important amounts of physisorbed water, suggesting that the pore surface is becoming more hydrophilic by the addition of metallic moieties on the surface. In the SBA-15-C2 case, the pronounced peak at 3750 cm^{-1} corresponding to the Si-OH elongation is still present after the addition of the catalyst, but its intensity decreased noticeably.

4. Conclusions

In this contribution, Grubbs I catalyst was incorporated into host materials functionalized with alkenyl-trichlorosilanes exhibiting different carbon chain lengths, e.g., vinyl- (C2), allyl- (C3), hexenyl- (C6) and octenyl- (C8) trichlorosilanes. The thus-obtained materials, before and after interaction with Grubbs I, were characterized and the investigations revealed a pronounced dependence of the Grubbs stability as a function of the alkyl chain

length of the grafted alkene moieties. The nature of the immobilized Ru-based species is clearly function of the surface modification, i.e. chain length of the alkenyl-silane.. Upon addition of the Grubbs I catalyst to the alkene-functionalized silica, the ^{13}C CP/NMR spectroscopy provided in all cases evidence of the cyclohexyl groups of PCy$_3$. For SBA15-C$_6$-Ru and SBA15-C$_8$-Ru, a single new vinylic resonance characteristic of a di-substituted alkene is also observed, demonstrating that the ring-closing metathesis has unambiguously occurred on these substrates. In contrast, no new signal was observed in the vinylic region in the case of SBA15-C$_2$-Ru and SBA15-C$_3$-Ru materials, suggesting that the carbon chains could in these cases be too short to undergo metathesis with the neighboring olefinic moieties. We believe that these findings contribute to a better understanding of the interactions between mesoporous silica supports (e.g. SBA-15 and related materials) and Grubbs' type catalysts, and that new insights into the reactivity of phosphine-containing catalytic systems will be useful for further expanding the use of metal-phosphorous coordination chemistry on solid surfaces.

References

[1] A. M. Lozani-Vila, S. Monsaert, A. Bajek, F. Verpoort, Chem. Rev. 110 (2010) 4865.

[2] T. J. Donohoe, T. J. C. O'Riordan, C. P. Rosa, Angew. Chem. Int. Ed. 48 (2009) 1014.

[3] G. C. Vougioulakakis, R. H. Grubbs, Chem. Rev. 110 (2010) 1749.

[4] C. Samojlowicz, M. Bieniek, K. Grela, Chem. Rev. 109 (2009) 3743.

[5] J. A. Gladysz, Chem. Rev. 102 (2002) 3215.

[6] A. Kirschning, H. Monenschein, R. Wittenberg, Angew. Chem. Int. Ed. 40 (2001) 650.

[7] G. Jas, A. Kirschning, Chem. Eur. J. 9 (2003) 9, 5708.

[8] a) A. Mendonca, in *Power of Functional Resins in Organic Synthesis*; J. Tulila-Puche and F. Albericio, Eds.; VCH-Wiley, Weinheim, Germany, 2008, pp 227-243.

[9] R. Anwander, "Immobilization of Molecular Catalysts", In *Handbook of Heterogeneous Catalysis*, *2nd edition*, G. Ertl, H. Knötzinger, F. Schüth and J. Weitkamp, Eds., VCH-Wiley, Weinheim, 2008, Vol. 1, pp 583-614;

[10] C. A. McNamara, M. J. Dixon, M. Bradley, Chem. Rev. 102 (2002) 3275.

[11] M. R. Buchmeister, Chem. Rev. 109 (2009) 303.

[12] K. McEleney, D. P. Allen, A. E. Holliday, C. M. Crudden, Org. Lett. 8 (2006) 2663.

[13] C. M. Crudden, K. McEleney, S. L. MacQuarrie, A. Blanc, M. Sateesh, J. D. Webb, Pure Appl. Chem. 79 (2007) 247.

[14] X. Feng, G. E. Fryxell, L. Q. Wang, A. Y. Kim, J. Liu, K. M. Kemner, Science 276 (1997) 923.

[15] A. Taguchi, F. Schüth, Microporous Mesoporous Mater. 77 (2005) 1.

[16] S. Minakata, M. Komatsu, Chem. Rev. 109 (2009) 711.

[17] Z. Wu, D. Zhao, Chem. Commun. 47 (2011) 3332.

[18] M. Mayr, M. R. Buchmeiser, K. Wurst, Adv. Synth. Catal. 344 (2002) 712.

[19] J. O. Krause, S. Lubbad, O. Nuyken, M. R. Buchmeiser, Adv. Synth. Catal. 345 (2003) 996.

[20] X. Elias, R. Pleixats, M. W. C. Man, J. J. E. Moreau, Adv. Synth. Catal. 348 (2006) 751.

[21] F. Michalek, W. Bannwarth, Helv. Chim. Acta 89 (2006) 1030.

[22] K. Vehlow, S. Maechling, K. Köhler, S. Blechert, J. Organomet. Chem. 691 (2006) 5267..

[23] J. Lim, S. S. Lee, S. N. Riduan, J. Y. Ying, Adv. Synth. Catal. 349 (2007) 1066.

[24] X. Elias, R. Pleixats, M. W. C. Man, J. J. E. Moreau, Adv. Synth. Catal. 349 (2007) 1701..

[25] X. Elias, R. Pleixats, M. W. C. Man, Tetrahedron 64 (2008) 6770,

[26] J. Lim, S. S. Lee, J. Y. Ying, Chem. Commun. 46 (2010) 806.

[27] D. Bek, N. Zilkova, J. Dedecek, J. Sedlacek, H. Balcar, Top. Catal. 53 *(*2010) 200.

[28] F. Michalek, D. Mädge, J. Rühe, W. Bannwarth, J. Organomet. Chem. 691 (2006) 5172.

[29] L. Li, J.-L. Shi, Adv. Synth. Catal. 347 (2005) 1745.

[30] D. Fischer, S. Blechert, Adv. Synth. Catal. 347 (2005) 1329.

[31] D. P. Allen, M. M. Van Wingerden, R. H. Grubbs, Org. Lett. 11 (2009) 1261.

[32] B. Van Berlo, K. Houthoffd, B. F. Sels, P. A. Jacobs, Adv. Synth. Catal. 350 (2008) 1949.

[33] H. Balcar, T. Shinde, N. Zilkova, Z. Bastl, Beilstein J. Org. Chem. 7 (2011) 22

[34] D. Bek, H. Balcar, N. Zilkova, A. Zukal, M. Horacek, J. Cejka, ACS Catal. 1 (2011) 709.

[35] M. S. Sanford, M. Ulman, R. H. Grubbs, J. Am. Chem. Soc. 83 (2001) 3306.

[36] S. Polarz, B. Völker, F. Jeremias, Dalton Trans. 39 (2010) 577.

[37] H. Staub, R. Guillet-Nicolas, N. Even, L. Kayser, F. Kleitz, F.-G. Fontaine, Chem. Eur. J. 17 (2011) 4254.

[38] M. Choi, W. Heo, F. Kleitz, R. Ryoo, Chem. Commun. (2003) 1340.

[39] S. A. Kozlova, S. D. Kirik, Microporous Mesoporous Mater. 133 (2010) 124.

[40] X. S. Zhao, G. Q. Lu, A. K. Whittaker, G. J. Millar, H. Y. Zhu, J. Phys. Chem. B 101 (1997) 6525.

[41] N. V. Reichhardt, R. Guillet-Nicolas, M. Thommes, B. Klosgen, T. Nylander, F. Kleitz, V. Alfredsson, Phys. Chem. Chem. Phys. 14 (2012) 5651.

[42] P. I. Ravikovitch, A. V. Neimark, J. Phys. Chem. B 105 (2001) 6817.

[43] A. V. Neimark, P. I. Ravikovitch, Microporous Mesoporous Mater. 44 (2001) 697.

[44] F. Kleitz, F. Bérubé, R. Guillet-Nicolas, C.-M. Yang, M. Thommes, J. Phys. Chem. C 114 (2010) 9344.

[45] F. Kleitz, T. Czuryszkiewicz, L. A. Solovyov, M. Lindén, Chem. Mater. 18 (2006) 5070.

[46]A. V. Neimark, P. I. Ravikovitch, A. Vishnyakov, J. Phys. Condensed Matter. 15 (2003) 347-365.

[47] A. V. Neimark, K. S. W. Sing, M. Thommes, in *Handbook of Heterogeneous Catalysis, 2nd edition,* G. Ertl, H. Knözinger, F. Schüth, J. Weitkamp, Eds., VCH-Wiley, Weinheim, 2008, pp 721-738.

[48] M. Thommes, in *Nanoporous Materials; Science and Engineering*; G. Q. Lu,X. S. Zhao, Eds., Imperial College Press, London, U.K., 2004, pp 317-364.

[49] M. Thommes, Chem. Ing. Tech. 82 (2010) 1059.

[50] A. Galarneau, H. Cambon, F. D. Renzo, R. Ryoo, M. Choi and F. Fajula, New J. Chem. 27 (2003) 73.

[51] K. Dimos, P. Stathi, M. A. Karakassides, Y. Deligiannakis, Microporous Mesoporous Mater. 126 (2009) 65.

[52] J. M. Notestein, C. Canlas, J. Siegfried, J. S. Moore, Chem. Mater. 22 (2010) 5319.

[53] S. A. Mirji, S. B. Halligudi, D. P. Sawant, N. E. Jacob, K. R. Patil, A. B. Gaikwad, S. D. Pradhan, Appl. Surface Science 252 (2006) 4097.

[54] V. Autochshuk, M. Jaroniec, J. Phys Chem. B 103 (1999) 6252.

[55] F. Kleitz, W. Schmidt, F. Schüth, Microporous Mesoporous Mater. 44-45 (2001) 92.

[56] F. Kleitz, W. Schmidt, F. Schüth, Microporous Mesoporous Mater. 65 (2003) 1.

[57] C. P. Jaroniec, M. Kruk, M. Jaroniec, A. Sayari, J. Phys. Chem. B 102 (1998) 5503.

[58] Y. Q. Wang, C. M. Yang, B. Zibrowius, B. Spliethoff, M. Lindén, F. Schüth, Chem. Mater. 15 (2003) 5029.

[59] J. Huang, G. Tian, H. Wang, L. Xu, Q. Kan, J. Mol. Cat. A 271 (2007) 200.

[60] R. Palkovits, D. Artl, H. Stepwoska, F. Schüth, Chem. Eur. J. 15 (2009) 9183.

[61] C. Decker, J. Marchal, Die Makromolekulare Chemie,166 (1973) 117.

[62] F. Amar, D. R. Dalton, G. Eisman, M. J. Haugh, Tetrahedron Lett. 35 (1974) 3033.

[63] K. B. Wiberg, W. E. Pratt, W. F. Bailey, J. Org. Chem. 45 (1980) 4936.

[64] B. Onida, M. Allian, E. Borello, P. Ugliengo, E. Garrone, Langmuir 13 (1997) 5107.

[65] B. A. Morrow, S. J. Lang, J. Phys. Chem. 98 (1994) 13319.

[66] P. Smet, F. Verpoort, G. De Doncker, A. R. Bossuyt, L. Fiermans, L. Verdonck, Appl. Spectro. 50 (1997) 1807.

[67] Y. Yang, B. Beele, J. Bluemel, J. Am. Chem. Soc. 130 (2008) 3771.

[68] H. Staub, I. Del Rosal, L. Maron, F. Kleitz, F.-G. Fontaine, J. Phys. Chem. C 116 (2012) 25919.