Grafting of cyclopentadienyl ruthenium complexes on aminosilane linker modified mesoporous SBA-15 silicates[†]

Ayyamperumal Sakthivel,^a Filipe M. Pedro,^a Anthony S. T. Chiang^b and Fritz E. Kühn^{*a,c}

Received 10th August 2006, Accepted 24th October 2006 First published as an Advance Article on the web 15th November 2006 DOI: 10.1039/b611550k

Cyclopentadienyl ruthenium phosphane and carbene complexes are grafted on the surface of mesoporous SBA-15 molecular sieves through an aminosilane linker. The nature of the support after the grafting is examined by powder XRD, TEM and N_2 adsorption/desorption analysis. Elemental analysis, FT-IR, DRIFTS, TG-MS and MAS-NMR studies confirm the successful grafting of the complexes on the surface. The grafted materials are applied for catalytic aldehyde olefination and cyclopropanation.

Introduction

Organic synthesis has made remarkable progress due to transition metal catalysts in recent decades.1 In particular, the implementation of organometallic complexes as catalysts for organic syntheses is a continuously developing field. Ruthenium compounds of the general formula $Cp^*RuX(PR_3)_2$, $Cp^*RuX(PR_3)(C_3N_2R_5)$, etc., have found widespread applications in catalysis.²⁻⁵ Recently, various research groups have started to apply this compound family for aldehyde olefination²⁻⁶ and more recently for cyclopropanation reactions.^{7,8} Aldehyde olefination is an important transformation for the production of carbon-carbon double bonds.8 Ruthenium complexes, such as $CpRuCl(PPh_3)_2$, $Cp*RuX(PR_3)_2$, Cp*RuX(PR₃)(C₃N₂R₅), (1-3) besides displaying a high activity, are among the most selective catalysts for this reaction reported to date.⁶ On the other hand cyclopropanation of olefinic bonds utilizing diazo compounds as a carbene source is one of the best developed and most useful transformations available to the synthetic organic chemist.910 The ruthenium-catalysed cyclopropanation reaction experienced a fast development in recent years. The main reasons for this lay in the lower price of the ruthenium based catalysts, when compared to rhodium derivatives, and their richer reaction chemistry.10

Catalyst heterogenization, *i.e.* the immobilization of the catalyst on a supporting material allowing an easy product isolation and catalyst recycling, attracts also considerable industrial attention.¹¹ Among the various supporting materials studied, the mesoporous silicate known as SBA-15¹² with a regular pore size, a large surface area, a large number of surface silanol groups, and a high chemical and thermal stability, is a potential and promising candidate as both catalyst and catalyst support.^{13,14} To the best of our knowledge the only extensive studies published on ruthenium catalysts heterogenization deal with Ru(II) porphyrin

^bNational Central University, Chung-Li, Taiwan, 320, Republic of China ^cDepartment of Chemistry, Instituto Tecnológico e Nuclear (ITN), Estrada Nacional No 10, 2686-953, Sacavém, Portugal. E-mail: fekuhn@itn.pt; Fax: +351-219946185

Published on 15 November 2006. Downloaded by York University on 23/10/2014 14:41:50

and amine derivatives, which were also exclusively heterogenized on hydrothermally less stable mesoporous MCM-41 materials.¹⁵ These particularly effective immobilized catalysts were mainly applied in alkene epoxidation^{15b,8g} and in a few cases also in intermolecular cyclopropanation.^{15f}

In the present work, cyclopentadienyl ruthenium phosphane complexes 1–3 are grafted on the surface of aminosilane linker modified mesoporous SBA-15 silicate material (designated as SBA-15SNH₂) (Scheme 1). Complexes 1–3 grafted in samples of SBA-15SNH₂ are designated as SBA-15SNH₂CpRu, SBA-15SNH₂Cp*Ru and SBA-15SNH₂Cp*RuNHC, respectively. The grafted materials were systematically characterized and applied as catalysts for benzaldehyde olefination, as well as for styrene cyclopropanation using ethyl diazoacetate (EDA).

Experimental

Synthetic procedure

SBA-15 silicas were synthesized in a similar way as originally reported by Zhao *et al.*^{12,13d} using Pluronic 123 triblock copolymers (poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide); (Aldrich)) $EO_nPO_{70}EO_n$ as templates. In a typical synthesis, 4.0 g of the $EO_{20}PO_{70}EO_{20}$ copolymer was dissolved in 150 g of 1.6 M HCl. To this solution 8.50 g of TEOS (tetraethyl orthosilicate), was added and the resulting mixture was stirred until TEOS was dissolved. The final molar gel composition of the synthesis mixture was 6.89 × 10⁻⁴ P123 triblock copolymers: 0.24 HCl: 0.041 TEOS : 7.88 H₂O. The mixture was placed in an oven for 24 h at 308 K and then additional 24 h at 373 K under static conditions. Silica products were filtered, dried, and calcined at 823 K under air.

Solvents were dried by standard procedures (THF, toluene with Na/benzophenone ketyl; CH_2Cl_2 with CaH_2), distilled under argon and kept over 4 Å molecular sieves. Grafting experiments (Scheme 1) were carried out using standard Schlenk techniques under argon atmosphere with the following procedure: prior to the grafting the SBA-15 molecular sieve was heated at 523 K under vacuum (10^{-3} mbar) for 6 h to remove physisorbed water. The activated mesoporous molecular sieve (SBA-15; 1 g) was treated with aminopropyl trimethoxy silane (2 mmol) using dry toluene (30 mL) as solvent under argon atmosphere at 383 K

^aDepartment für Chemie der Technischen Universität München, Lichtenbergstraße 4, D-85747, Garching bei München, Germany

[†] Electronic supplementary information (ESI) available: Spectroscopic details (Fig. S1–S3). See DOI: 10.1039/b611550k



 $(CpR_5)RuR'_{2-n}R''_nX$ where R = H (or) CH_3 ; $R' = PPh_3$; R'' = carbene; X = Cl; Cy = cyclohexyl





for 24 h. Then excess silane was removed by filtration followed by repeated washing with dichloromethane. The resulting solid was dried under vacuum at room temperature. The aminosilane modified sample is designated as SBA-15SNH₂.

Grafting experiments are carried out using standard Schlenk techniques under argon atmosphere with the following procedure: the cyclopentadienyl ruthenium complexes **1–3** are synthesized as described earlier.^{6,7} SBA-15SNH₂ is again pre-activated at 473 K under vacuum (10^{-3} mbar) for 4 h to remove any physisorbed water. Then, the sample (1 g) is treated with 0.6 mmol of complexes **1–3** in 30 mL of dry THF under an argon atmosphere. The mixtures are stirred at 313 K for 3 d. The resulting solutions are filtered off and the white solids are repeatedly washed with THF until all physisorbed complexes are removed from the surfaces. The washed samples are dried under vacuum at RT.

Characterization techniques

FT-IR spectra were recorded on a Perkin Elmer FT-IR spectrometer using KBr pellets as matrix. DRIFT spectra were recorded at room temperature in the spectral range of 400–4000 cm⁻¹ with a Nicolet Impact 410 spectrophotometer equipped with a DRIFT chamber. The fine powders were loaded into a sample cell equipped with a CaF₂ window. The spectra thus obtained were converted into Kubelka-Munk units. Thermogravimetric analyses were performed using a Netzsch TG209 system at a heating rate of 10 K min⁻¹ under argon. Elemental analyses were measured at the Mikroanalytisches Labor of the TU München (M. Barth). Powder XRD data were collected with a Philips X'pert diffractometer using Cu Ka radiation filtered by Ni. Nitrogen adsorptiondesorption measurements were carried out at 77 K, using a gravimetric adsorption apparatus equipped with a CI electronic MK2-M5 microbalance and an Edwards Barocel pressure sensor. Before analysis, the calcined SBA-15 samples were degassed at 723 K overnight to a residual pressure of ca. 10-24 mbar. A degassing temperature of 413 K was used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) were determined by the BET method. The total pore volume was estimated from the N₂ uptake at $p/p_0 = 0.95$, using the liquid nitrogen density of 0.8081 g cm⁻³.

The pore size distribution curves (PSD, the differential volume adsorbed with respect to the differential pore size per unit mass as a function of pore width) were computed from the desorption branch of the experimental isotherms, using a method based on the area of the pore walls. Transmission electron microscopy (TEM) was recorded on a JEOL JEM2010 operated at 120 kV. ²⁹Si CP MAS NMR spectra were recorded at 59.627 MHz, with a (7.05 T) Bruker Avance 300 spectrometer, with 5.5 μ s ¹H 90° pulses, 8 ms contact time, a spinning rate of 5 kHz and 4 s recycle delays. ¹H MAS NMR spectra were recorded at 300 MHz using a Bruker Avance 300 spectrometer with 3.0 μ s ¹H 90° pulses and a spinning rate of 8 kHz.

Typical procedure for styrene cyclopropanation

EDA (0.114 g, 1.0 mmol) in 2.0 mL of dichloromethane is slowly added (addition time 1 h) to a 4.0 mL dichloromethane solution of styrene (0.520 g, 5.0 mmol) and catalyst (0.02 mmol; based on Ru content). The reaction is followed by GC-MS. After the reaction is finished the Z: E products distribution was identified by GC-MS. The products were isolated by flash chromatography, using ethyl acetate : hexane (1:10) as eluent. Isolated yields were calculated based on the amount of EDA used.

Typical procedure for benzaldehyde olefination

Benzaldehyde (0.318 g, 3 mmol), PPh₃ (0.865 g, 3.3 mmol), catalyst (0.01 mmol, based on Ru content, *i.e.* 337, 49 and 36 mg of SBA-15SNH₂CpRu, SBA-15SNH₂Cp*Ru and SBA-15SNH₂Cp*RuNHC, respectively), and fluorene (0.2 g, used as internal standard) were dissolved in 15 mL of toluene. The mixture was heated to 353 K and EDA (0.410 g, 3.6 mmol) was—all at once—added to the solution. The reaction was monitored by GC-MS. Yields were determined by GC using a previously recorded calibration curve (R^2 >0.999).

Results and discussion

The low angle powder XRD pattern of the grafted Ru complex samples is depicted in Fig. 1. The XRD pattern of SBA-15 (Fig. 1a), where the main reflection corresponds to a hexagonal unit cell^{12,13d} is observed at a 2θ range of 0.84° , and two other weak reflections are found in the 2θ range of $1-2^{\circ}$, with an indexing referring to the (110) and (200) planes. The grafted ruthenium complex samples exhibit a main reflection corresponding to the (100) plane. However, compared to parent SBA-15 (Fig. 1a),^{13d} the grafted samples show a decrease in the relative intensities and line broadenings of the XRD reflections and there is a clear shift to higher 2θ values (2θ range 0.94, 0.97 and 0.98° for SBA-15SNH₂CpRu, SBA-15SNH₂Cp*Ru and SBA-

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Fig. 1 Low angle powder XRD pattern of (a) SBA-15, (b) SBA-15SNH₂-CpRu, (c) SBA-15SNH₂Cp*Ru and (d) SBA-15SNH₂Cp*RuNHC.

15SNH₂Cp*RuNHC, respectively) and also a decrease in the interplanar distance (see Table 1). These changes originate from the immobilization of the bulky organometallic Ru complexes inside the channels of SBA-15.^{13,14}

Fig. 2 depicts the FT-IR spectra of parent calcined mesoporous SBA-15, aminosilane grafted SBA-15 and of the grafted samples. The bands at 1216, 1076, and 802 cm⁻¹ are attributed to stretching vibrations of the mesoporous framework (Si–O–Si). The presence of weak bands around 1564 cm⁻¹ is due to amino group of the linker, which is largely masked by the hydroxyl vibrations. New, comparatively weak bands around 3000, 2957, and 2927 cm⁻¹ can be assigned to the cyclopentadienyl (Cp, Cp*) moiety, and triphenylphosphane group vibrations of the grafted compounds. Furthermore, the presence of another band in the range of 2853 cm⁻¹ is due to C–H stretching vibrations, originating from



Fig. 2 FT-IR spectra of (a) SBA-15, (b) SBA-15SNH₂, (c) SBA-15SNH₂-CpRu, (d) SBA-15SNH₂Cp*Ru and (e) SBA-15SNH₂Cp*RuNHC.

Table 1	Textural	properties	of SBA-15	and the	grafted	Ru samples
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	Ru/wt	%				
Sample	Fresh	Recycled	Interplane distance/nm	BET surface area/m ² g^{-1}	Pore volume/cm ³ g^{-1}	Pore diameter/nm
SBA-15			10.5	750	1.1	7.4
SBA-15SNH ₂ CpRu	0.3	0.3	9.39	380	0.5	6.5
SBA-15SNH ₂ Cp*Ru	1.9	1.7	9.04	340	0.4	6.0
SBA-15SNH ₂ Cp*RuNHC	2.8	2.0	8.99	260	0.3	5.5



Fig. 3 DRFT-IR spectra of (a) SBA-15, (b) SBA-15SNH₂, (c) SBA-15SNH₂CpRu, (d) SBA-15SNH₂Cp*Ru and (e) SBA-15SNH₂Cp*RuNHC.

the CH_2 groups present in the silane ligand. Additional bands appear at 697 and 721 cm⁻¹, due to C–C bending vibration from the phenyl ring.¹⁶

The DRIFT spectra of SBA-15, aminosilane grafted SBA-15 and of the grafted samples are shown in Fig. 3. After the aminosilane grafting new bands appear at 2863, 2939, 2970, 1438, 1456, 1540 and 1560 cm⁻¹, characteristic of C–H vibrations, further evidencing the CH₂ group vibration of the aminosilane



Fig. 4 N₂ adsorption–desorption analysis of (a) SBA-15, (b) SBA-15S-NH₂CpRu, (c) SBA-15SNH₂Cp*Ru and (d) SBA-15SNH₂Cp*RuNHC.

ligand. The appearance of broad bands at 3062 and 1603 cm⁻¹ are typical of NH vibrations. The broadening of peak areas near 3245 cm^{-1} and also the appearance of a weak band at 699 and 721 cm⁻¹ are observed from phenyl groups of the phosphane ligand. Elemental analyses (EA) indicate (Table 1) that the RuCp complex 1 shows relatively low loading in comparison to the RuCp* complex, which may probably be due to the enhancement of the leaving ability of the chloride ions by the Cp* moiety, thus favouring very high loadings in the case of compounds 2 and 3.

The low temperature N_2 adsorption/desorption isotherms are of type (IV) according to IUPAC¹⁷ and characteristic for mesoporous solids. However, compared to the parent mesoporous sample (Fig. 4a),^{13d} the samples bearing grafted Ru complexes (Fig. 4b–4d) exhibit a drastic decrease in N_2 uptake due to the presence of aminosilane linkers and the relatively bulky organometallic compounds on the surface of the mesoporous channels. Furthermore, the parent SBA-15 sample exhibits a narrow pore size distribution with average pore diameters of 7.4 nm. The grafted materials exhibit an overall decrease of pore size and a broadening of the pore size (6.5–5.5 nm) distribution.

Additionally they display a decrease in surface area and pore volume (see Table 1). The decrease of the pore volume and the pore size evidences that the aminosilane linker and the organometallic complexes in the grafted mesoporous samples are mainly located on the internal surfaces of the mesoporous materials. However, the micropore volume is not affected much after grafting, which might be due to the difficulty of bulky organometallic complexes to access small micropores.

The TEM images (see Fig. 5) of the parent and grafted samples (SBA-15SNH₂CpRu, SBA-15SNH₂Cp*Ru and SBA-15SNH₂Cp*RuNHC) provide strong evidence that the meso-porous structures have an uniform pore size distribution and



Fig. 5 TEM images of (a) SBA-15, (b) SBA-15SNH₂CpRu, (c) SBA-15SNH₂Cp*Ru and (d) SBA-15SNH₂Cp*RuNHC.

a well ordered pore structure. The long range ordering^{12,13} is kept throughout the grafting process and the channels remain accessible. The well resolved ED pattern spots of the grafted samples, typical of (110) and (100) planes, further support the presence of long range ordering in the samples, even after blocking of some pores by linker molecules and Ru complexes.

The parent SBA-15 and the grafted samples were examined by solid-state ²⁹Si CP MAS NMR spectroscopy. The parent SBA-15 material exhibits two broad elaborate resonances in the ²⁹Si CP MAS NMR spectrum at $\delta = -110.3$ and -100.5 ppm, assigned to the Q_4 and Q_3 species of the silica framework, respectively, $[Q_n =$ $Si(OSi)_n(OH)_{4-n}$].¹¹⁻¹⁴ A weak shoulder is also observed at $\delta =$ -96.2 ppm for the Q₂ species. The grafting of (MeO)₃Si(CH₂)₃NH₂ also results in the reduction of the Q_2 and Q_3 resonances, and a concurrent increase of the Q_4 resonance. The changes of the Q_4 resonances are more pronounced due to the comparatively high loading. This is consistent with an esterification of the isolated silanol groups (single and geminal) by nucleophilic substitution at the silicon atom of the organic ligand.13 The 29Si CP MAS NMR spectra also exhibit two additional signals at $\delta = -59.2$ and -64.3 ppm assigned to T₂ and T₃ organosilica species, respectively, $[T_m = RSi(OSi)_m(OR)_{3-m}]$. However, as expected, the silvlated samples show (nearly) identical²⁹Si CP MAS NMR spectra before and after the grafting with the organo-ruthenium samples, thus indicating that during the grafting process no significant changes in the silicon environment take place. The observed changes in the ²⁹Si CP MAS NMR spectra arise only during the silylating procedure using aminosilane. The ¹H MAS NMR spectra (see ESI[†]) of all the samples show broad signals between $\delta = 8.1$ –4.5 (centre at 5.2, 7.3 ppm) and 1.9 ppm characteristic for the Cp, phenyl and methyl groups of the complexes 1-3. The additional peak at 3.30 ppm for the grafted samples is due to the residual OMe groups attached to silane.

TG-MS spectra of SBA-15SNH₂Cp*Ru and SBA-15SNH₂Cp*RuNHC show (Fig. 6) 12 and 18% of weight loss up to 1000 °C, due to decomposition of the Cp*Ru(PPh₃)₂

and the Cp*Ru(PPh₃)(C₃N₂H₂(Cy)₂) moieties. The expected mass loss for SBA-15SNH₂Cp*Ru and SBA-15SNH₂Cp*RuNHC is 14 and 19%, respectively, based on the TG-MS spectra of the organometallic complexes, the TG-MS of the SBA support with aminosilane linker and the complex loadings. The observed mass values $m/z^+ = 77$, 31 and 15 correspond to the phenyl, phosphorous and methyl groups of complexes **2** and **3**. The observed mass values $m/z^+ = 83$, 69, 14 in case of SBA-15SNH₂Cp*RuNHC originates from the carbene ligand, the peak $m/z^+ = 83$ being characteristic of the cyclohexyl group. In addition, the presence of mass values $m/z^+ = 14$ and 31 in the grafted sample are characteristic of methylene (CH₂) and residual methoxy groups of the silane linker. All the above-described observations support the successful grafting of complex **1–3** in the mesoporous channels of the SBA-15 molecular sieves.

The homogeneous catalysts (1–3) and the grafted materials containing complexes 1–3 are applied in styrene cyclopropanation with EDA at room temperature for 24 h (Scheme 2) and the results are displayed in Table 2. The catalytic activities increase in the order 1 < 2 < 3. The grafted materials show comparable activity to their homogeneous counterparts (see Table 2),⁷⁶ with prevailing *E*-selectivity, as expected. However, in the case of SBA-15SNH₂CpRu the catalyst reaches only relatively low yields as well as an equivalent amount of *E*- and *Z*-isomers, possibly due to the relatively low ruthenium content and therefore a significant diffusion limitation slowing down the reaction.



Scheme 2



Fig. 6 TG-MS spectra of (a) SBA-15SNH₂Cp*Ru and (b) SBA-15SNH₂Cp*RuNHC.

Table 2 Cyclopropanation of styrene over the grafted ruthenium complexes⁴

			Product d	listribution
Samples	Ru content/atom nm ⁻²	Isolated yield ^b (%)	cis- (Z)	trans-(E)
Compound 1		47	47.8	52.2
Compound 2		56	31.3	68.7
Compound 3	—	77	24.9	75.1
SBA-15SNH ₂ CpRu	0.047	21	46.7	53.3
SBA-15SNH ₂ Cp*Ru	0.33	50	30.1	69.9
1 st recycle		42	29.1	70.9
2 nd recycle		46	23.7	76.3
SBA-15SNH ₂ Cp*RuNHC	0.637	73	20.1	79.9
1 st recycle		63	22.3	77.1
2 nd recycle		66	19.9	80.1

considerably higher, after the same pehe case of SBA-15SNH₂Cp*Ru and SBA-C. The presence of more ruthenium atoms per promotes the higher activities. Importantly, re-usable for several catalytic runs. There is activity on the second run, but the fact that equally active for a third run shows that the are stable on the surface. The small decrease during the first catalytic run (5-8%) may be g of the ruthenium complexes on the surface rials, which is supported by elemental analysis henium content in the filtrate. However, the ltrate solution of subsequent runs, as well as the absence of catalytic conversion in the filtrate, indicate that the catalysts are then stable and the leaching is insignificant after the first run. There are no C-H insertion side products, which are observed in homogeneous catalysis.7b This is a clear advantage over the homogeneous catalyst system. The similarity between the homogeneous and heterogeneous results, regarding both selectivity and overall yield is noteworthy, showing that the silica mesopores are not imposing significant structural or electronic perturbations on the immobilized metal centre.

Complexes 1-3 and the corresponding grafted materials are applied for the benzaldehyde olefination (Table 3) (using the same catalyst: benzaldehyde ratio based on the Ru content on the samples), with ethyldiazoacetate (EDA) in the presence of triphenylphosphane (PPh₃) (Scheme 3). Again the homogeneous catalysts show the same general trend as observed for cyclopropanation, *i.e.* the olefin yields are higher in the case of the Cp* compounds when compared to the Cp derivatives due to the better leaving ability of phosphane from the more electron rich ruthenium complexes.6b

The heterogeneous catalysts show comparable yields with considerable azine formation. Both SBA-15SNH₂Cp*Ru and SBA-15SNH₂Cp*RuNHC show similar olefin yields, in the range 30-33%, with an E: Z ratio of 96: 4 in the olefinic products. In case of

Table 3 Benzaldehyde olefination over the heterogenized ruthenium complexes

		Ratio of olefin	
Catalysts	Yield ^{b} (%)	cis	trans
Compound 1	25	8	92
Compound 2	73	10	90
Compound 3	35	9	91
SBA-15SNH ₂ CpRu	43	5	95
SBA-15SNH ₂ CpRu–PPO	10	14	86
SBA-15SNH ₂ Cp*Ru	30	4	96
SBA-15SNH ₂ Cp*RuNHC	33	4	96

^{*a*} Catalyst : benzaldehyde = 1:325; temperature = 353 K; time = 24 h. ^b The error range in the GC results is $\pm 2\%$.

SBA-15SNH₂CpRu the initial activity is lower, however, slightly higher olefin yields of ca. 43% are reached after 24 h with an E: Zratio of 95:5. Although the ruthenium content is quite low, the overall yield is better than in the case of the other two catalysts. As can be seen from Fig. 7, the initial catalytic activity is high in the case of SBA-15SNH₂Cp*Ru and SBA-15SNH₂Cp*RuNHC, probably due to the high ruthenium loading per unit volume.

However, the reaction velocity slows down during the course of the reaction. The observed slowing down of the catalytic process during the course of time seems to be due to adsorption of the bulky triphenyl phosphine or triphenyl phosphine oxide (PPh₃ or PPh₃O) molecules on the surface of the supporting material. This is evident from the phosphorus elemental analysis of fresh and used catalysts, where the phosphorus content is increased from 0.4-0.6 to 0.8-3.4 wt%. The adsorption of phosphine on the surface of SBA-15 is further confirmed by treatment of SBA-15 with PPh₃ or PPh₃O under identical reaction conditions, which results in adsorptions of 6-8 wt% of PPh3 or PPh3O (TGA and EA). Thus, the PPh₃ or PPh₃O molecules block the SBA-15 channels and reduce the reaction rate, resulting in an overall low yield. However, in case of SBA-15SNH₂CpRu although the initial activity is lower





Fig. 7 Kinetic profiles for benzaldehyde olefination reaction over (a) SBA-15SNH₂CpRu, (b) SBA-15SNH₂CpRu-PPO, (c) SBA-15SNH₂-Cp*Ru and (d) SBA-15SNH₂Cp*RuNHC.

the kinetic curve shows a steady increase in yield during the course of the reaction. Due to the higher amounts of supporting material necessary (337 mg in case of 1 compared to 49 and 36 mg in the case of 2 and 3) to reach the same catalyst amount, higher amounts of phosphine or phosphine oxide can be adsorbed before the pores get blocked and the catalytic reaction comes to a halt. This result is supported by the catalytic reaction carried out on PPh₃O pre-treated SBA-15SNH₂CpRu catalyst (designated as SBA-15SNH₂CpRuPPO). Such pre-treated samples give only very low yield (10%) and the kinetic curve also shows no significant improvement in yield with time (see Fig. 7b).

Conclusions

Ruthenium phosphane and carbene complexes are successfully grafted on the aminosilane modified surface of SBA-15 materials. The grafted samples are stable and the structures of the supporting materials remain intact. The heterogenized catalysts are active in the aldehyde (benzaldehyde) olefination and cyclopropanation of styrene with EDA. The catalytic activities remain in the same order of magnitude even after three catalyst leaching can be considered as being minimal. In the case of benzaldehyde olefination, however, the catalytic reaction is hampered by adsorption of PPh₃ or PPh₃O on the carrier material.

Acknowledgements

A.S. is grateful to the Bayerische Forschungsstiftung for financial support. F.M.P. thanks the Fundação para a Ciência e a Tecnologia for a Ph.D. scholarship. The authors also thank Dr Marianne Hanzlik, and Dr G. Raudaschl-Sieber for experimental support. The Fonds der Chemischen Industrie and the Leonhard-Lorenz-Stiftung are acknowledged for financial support.

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