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Immobilization of Ru(II)(salen)(PPh_3)$_2$ on Mesoporous MCM-41/SBA-15: Characterization and Catalytic Applications

**Syukri Syukri · Ayyamperumal Sakthivel ·
Wei Sun · Fritz E. Kühn**

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Abstract Ru(II)(salen)(PPh_3)$_2$ immobilized on MCM-41 and SBA-15 modified with aminopropyl groups as linkers has been synthesized and characterized by elemental analysis, TEM, FTIR, BET, and TGA. Elemental analysis shows that the grafted samples contain 0.7–0.8 wt.% Ru. The retaining of long range ordering of the mesoporous MCM-41 and SBA-15 supporting materials after grafting is evident from TEM and N_2 adsorption/desorption measurements. FTIR and TGA spectra show the formation of metal salen complexes with the amino groups acting as connectors to the SiO_2 surface. Both grafted materials were successfully applied as catalysts for the olefination of various aldehydes with very good yields and high *E*-selectivity. The catalyst materials are recyclable for several catalytic runs.

Keywords Olefination · Catalysis · Ruthenium · Immobilization · Mesoporous materials

1 Introduction

Many of the so called salen ligands can be easily substituted, ligated to a broad variety of transition metals and applied in several catalytic reactions [1–3]. It has been reported, for example, that several Ruthenium(II) salen complexes (Scheme 1) are efficiently applied as catalysts for the olefination of a broad variety of aldehydes in homogeneous phase with very good product yields [4]. Their high catalytic activity is probably due to the flexibility of the ethylenediamine backbone of the salen ligands as described for a number of transition metal complexes with bidentate oxygen ligands [5]. However, there are drawbacks of using metal salen compexes in homogeneous solutions, e.g., the formation of μ-oxo dimers and other polymeric species leading to irreversible catalyst deactivation. In principle, this problem can be solved by isolating the metal salen complexes from each other by immobilization in the pores of molecular sieves. Treated in this way, the isolated catalytic active centres will not undergo fast degradation as their homogeneous counterparts do [6, 7]. Furthermore, the porosity of mesoporous molecular sieves plays an important role in the environment of catalysts and catalyst heterogenization usually eases its recovery after each catalytic run significantly [8–10].

In this work, a Ruthenium(II) salen complex of formula **4** is grafted on mesoporous MCM-41 and SBA-15 using aminopropyl triethoxysilane (APTES) as linker to the surface. The resulting new material is applied as heterogeneous catalysts for the olefination of various aldehydes (Scheme 2) [11–13].

2 Experimental Part

2.1 Synthetic Procedures

MCM-41 was synthesized following published procedures with molar gel compositions of 1.0 SiO_2:0.2 NaOH:0.27 TMAOH:0.27 CTABr:60 H_2O [14]. A typical synthetic procedure is as follows: first TMAOH is dissolved in water

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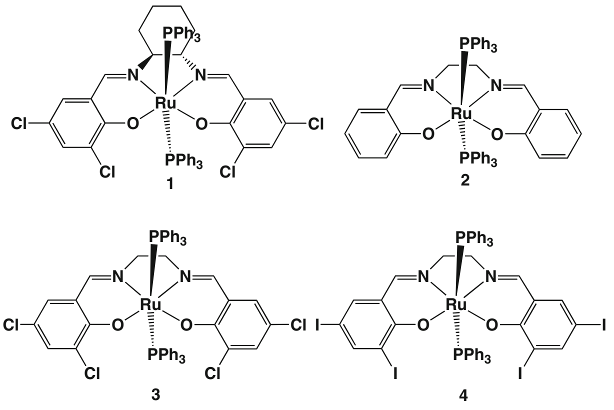
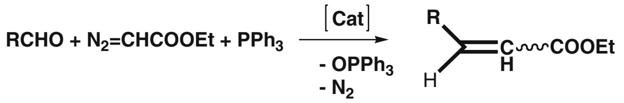
S. Syukri · A. Sakthivel · W. Sun · F. E. Kühn (✉)
Department für Chemie der Technischen Universität München,
Molekulare Katalyse, Lichtenbergstrasse 4, 85747 Garching,
Germany
e-mail: fritz.kuehn@ch.tum.de

S. Syukri · A. Sakthivel · W. Sun · F. E. Kühn
Department of Chemistry, Instituto Tecnológico e Nuclear
(ITN), Estrada Nacional No. 10, 2686-953 Sacavém, Portugal



Scheme 1

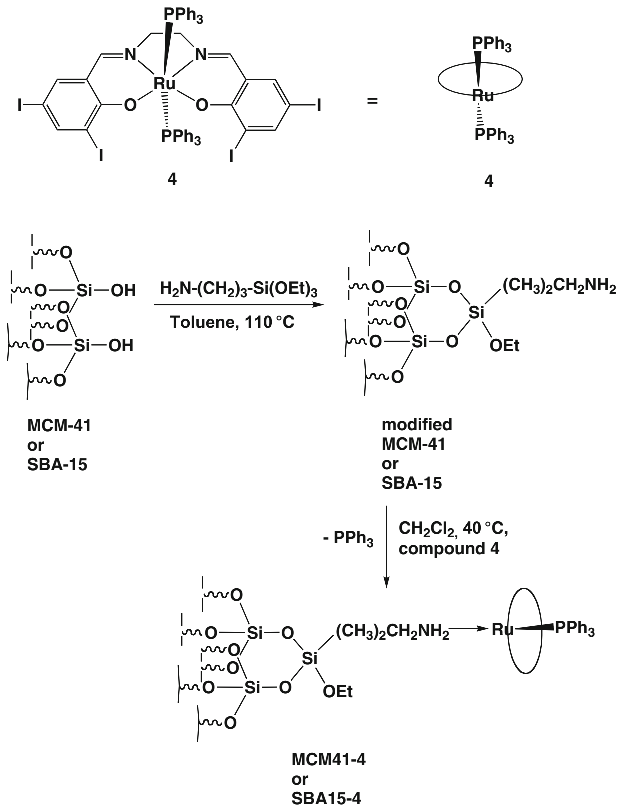


Scheme 2

and stirred for 5 min. Fumed silica is slowly added to this solution (the resulting solution is designated as A). Another solution, B, is prepared by mixing CTABr and NaOH in distilled water and stirred for about 30 min. Both solutions, A and B, are mixed together and kept stirring for 1 h. The pH of the resulting gel is adjusted to 11.0 with diluted sulphuric acid, and kept for 16 h. The gel is transferred into a polyethylene bottle and kept in an oven under air for crystallization at 373 K for 3 days. The obtained solid product is washed repeatedly, filtered and dried at 353 K for 12 h.

SBA-15 silicas were synthesized in a similar way as originally reported by Zhao et al. [15, 16] using Pluronic123 triblock copolymers (poly(ethylene oxide)–poly(propyleneoxide)–poly(ethylene oxide); Aldrich) EO_n-$PO_{70}EO_n$ as templates. In a typical synthesis, 4.0 g of $EO_{20}PO_{70}EO_{20}$ copolymer was dissolved in 150 g of 1.6 M HCl. To this solution a 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 $6.89 \cdot 10^{-4}$ P123 triblock copolymers: 0.24 HCl:0.041 TEOS:7.88 H_2O. The mixture was placed in an oven for 24 h at 308 K and then additional 24 h at 373 K under static condition.

Silica products were filtered, dried, and calcined at 823 K. 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.



Scheme 3

The Ruthenium(II) salen complex **4** was synthesized as described earlier [17, 18]. Grafting experiments (Scheme 3) were carried out using standard Schlenk techniques under an argon atmosphere with the following procedure: Prior to the grafting the SBA-15 and MCM-41 molecular sieves are heated to 523 K under vacuum (10^{-3} mbar) and kept at this temperature for 6 h to remove physisorbed water. For the indirect grafting the pre-heated SBA-15 and MCM-41 (1.5 g, respectively) are treated, respectively, with 3 mmol (0.5379 g) of APTES in 30 mL dry toluene under argon atmosphere and stirred for 24 h at 383 K. The resulting solids were then separated from the solvent by filtration and washed repeatedly with CH_2Cl_2. Afterwards, both modified mesoporous materials were treated, respectively, with 0.16 mmol (223.9 mg) of complex **4** in 30 mL of dry CH_2Cl_2 and stirred for three days at 313 K. The resulting solutions were filtered off and the brown solids were washed several times with CH_2Cl_2 until all physisorbed complexes were removed from the surfaces. The washed

Table 1 BET N_2 adsorption/desorption measurement of parent MCM-41, SBA-15 and MCM41-**4** and SBA15-**4**

Sample	S_{BET} (m^2/g)	Pore volume (mL/g)
MCM-41	434.12	0.66
MCM41-**4**	123.56	0.35
SBA-15	805.56	1.12
SBA15-**4**	350.83	0.61

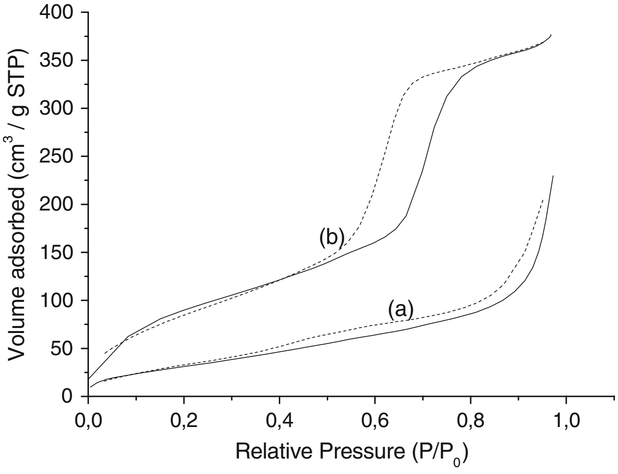


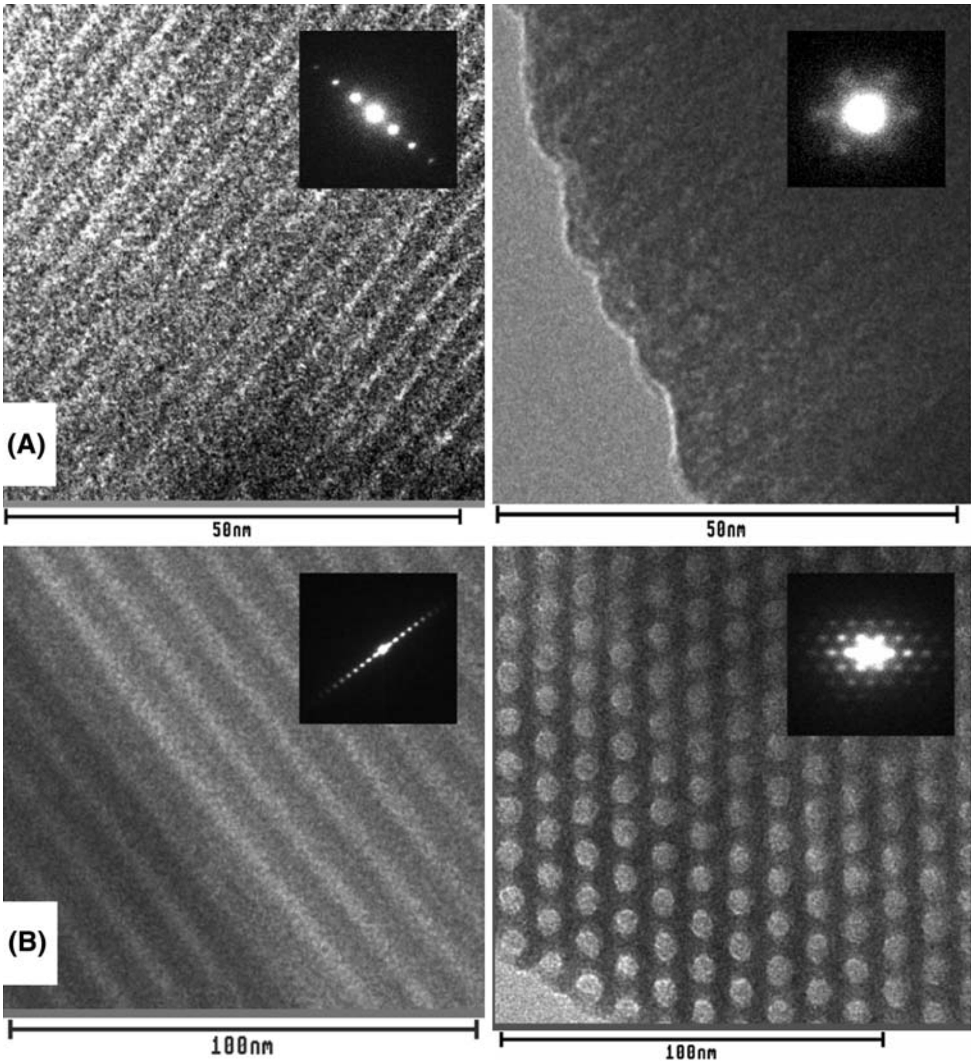
Fig. 1 N_2 adsorption/desorption analysis of (**a**) MCM41-4 and (**b**)SBA15-4

samples were dried under vacuum at RT. The samples synthesized by this method are designated as MCM41-**4** and SBA15-**4**.

2.2 Characterization Methods

IR spectra are measured with a Unican Mattson Mod 7000 FTIR spectrometer using KBr pellets. Microanalyses were performed at the Mikroanalytisches Labor of the Technische Universität München (M. Barth and co-workers). Nitrogen adsorption/desorption measurements are 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, calcined MCM-41 and SBA-15 are degassed at 723 K overnight to a residual pressure of ca. 10–24 mbar. A lower degassing temperature of 413 K is used for the modified materials (to minimize destruction of the grafted complex). The specific surface areas (SBET) are determined by the BET method. Transmission electron microscopy (TEM) is recorded on a JEOL JEM2010 operated at 120 kV. Thermogravimetry (TGA) is conducted with a Netzsch TG209 system; typically about 10 mg of a sample were heated from 300 to 1473 K at a heating rate of 10 K min^{-1} under an argon atmosphere.

Fig. 2 TEM images of (**a**) MCM41-**4** and (**b**) SBA15-**4** viewed along the direction of (left) and perpendicular to the hexagonal pore arrangement (right)



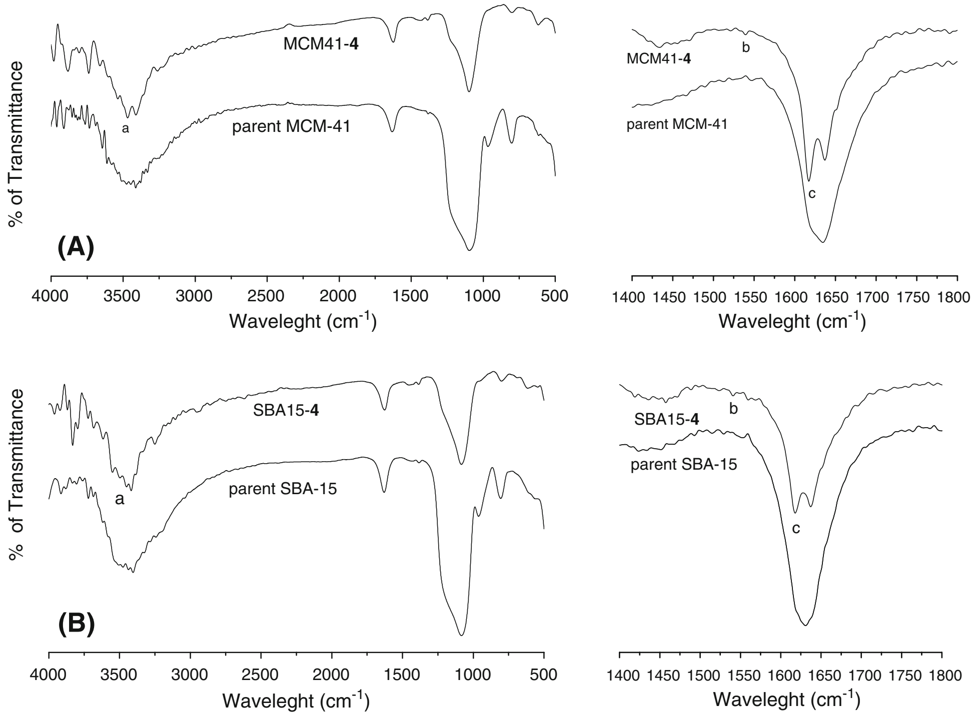


Fig. 3 FT-IR spectra of (A) parent MCM-41 and MCM41-4 and (B) parent SBA-15 and SBA15-4 with the appearance of N–H stretching vibrations (**a**), the typical band of a metallosalen complexes at ca. 1,540 cm^{-1} (**b**) the imine stretching vibration at ca. 1,615 cm^{-1} (**c**) for both grafted materials

2.3 General Procedure for Aldehyde Olefination in Toluene

In an oven dried Schlenk tube 1 mol % (based on the Ru-loading of the heterogeneous catalyst), aldehyde (0.25 mmol), PPh$_3$ (78.69 mg; 0.30 mmol) and 3.5 mL of THF were placed and heated to 60 °C in an oil bath. EDA (34.23 mg; 0.30 mmol), dissolved in 1.5 mL THF, was added and then the mixture was kept for the times given in Table 1. The suspension was then cooled to room temperature and the solution was separated from the catalyst by filtration. Afterwards, the residue was concentrated and chromatographed over a silica gel column with *n*-hexane/ethyl acetate (20:1–8:1) affording the olefins.

3 Results and Discussion

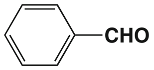
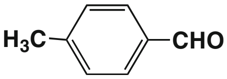
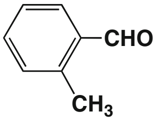
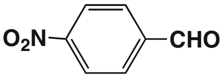
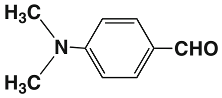
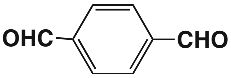
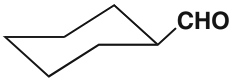
The obtained Ruthenium loading of the complex grafted on MCM-41 and SBA-15 determined by elemental analyses (EA) show that a slightly higher amount of Ruthenium is grafted on MCM-41 (0.8 wt.% Ru) than of SBA-15 (0.7 wt.% Ru). The immobilization of Ruthenium(II) complex **4** on MCM-41 and SBA-15 was evidenced by the decrease of the specific surface area and the pore volume of both materials (Table 1).

The low temperature N$_2$ adsorption/desorption isotherms of parent MCM-41 and SBA-15 are of type IV according to the IUPAC nomenclature and characteristic for mesoporous solids (surface area 434.12 m^2 g^{-1} and pore volume 0.66 mL/g for parent MCM-41, surface area 805.56 m^2 g^{-1} and pore volume 1.12 mL/g for parent SBA-15). Reversible type IV isotherms similar to the parent MCM-41/SBA-15 [19–21] are obtained for the grafted Ruthenium salen samples (Fig. 1). Compared to parent mesoporous samples, the samples bearing grafted complex **4** exhibit a significant decrease in N$_2$ uptake, probably due to the steric bulk of the organometallic compounds on the surface of the mesoporous channels. The grafted materials exhibit a decrease in both surface area and pore volume (see Table 1) supporting the view that the Ruthenium complexes in the mesoporous samples are mainly located on internal surfaces materials.

The mesoporous structures of the supports retain long range ordering [22, 23] for both grafted materials as seen in Fig. 2. The fact that SBA15-**4** is more accessible than MCM41-**4** throughout the grafting process as indicated by their TEM images is probably due to the pore openings being only one dimensional in the case of MCM-41.

As can be seen in Fig. 3, FT-IR spectra of parent calcined mesoporous MCM-41 and SBA-15 and grafted samples show bands at 1,206, 1,060, and 794 cm^{-1}, which are due to stretching vibrations of the mesoporous framework (Si–O–Si) [24]. The interactions between the linkers (APTES) and surface silanol groups of mesoporous MCM-41 and SBA-15 obviously affected the framework Si–O–Si vibrations, decreasing their intensities. Furthermore, the appearance of N–H stretching vibrations with medium intensity around 3,500 cm^{-1} can also be considered as additional evidence for the presence of APTES on the

Table 2 Olefination of various aldehydes using EDA with MCM41-**4** and SBA15-**4** as the catalysts[a]

No.	Substrate (olefin)	Time (h)	MCM41-**4** *E/Z*-Ratio[b]	MCM41-**4** Yield[c] (%)	SBA15-**4** *E/Z*-Ratio[b]	SBA15-**4** Yield[c] (%)
1		24	19.0	92	24.0	93
2		24	19.0	91	19.0	92
3		24	15.7	85	13.3	83
4		24	32.3	95	13.3	94
5		72	Only *E*	31	Only *E*	30
6		24	15.7	88	19.0	87
7		24	32.3	85	32.3	90

[a] Reaction were carried out in 5 mL of THF with 1 mol % (based on the Ru-loading) of MCM41-**4** or SBA15-**4**, 0.25 mmol of aldehyde, 0.3 mmol (34.23 mg) of EDA and 0.3 mmol (78.69 mg) of PPh_3 at 333 K under argon

[b] GC–MS measurement

[c] Isolated yield

surface of the grafted materials. The most important finding in this respect is that for both grafted materials the imine stretching vibration around 1,615 cm^{-1} can be observed as can be the typical band of a metallo salen complexes at 1,540 cm^{-1}, evidencing the presence of the complexes in the channels of both mesoporous materials. Only insignificant shifts of the bands associated with the ligand stretching modes could be measured, but these slight deviations (<15 cm^{-1}) are more likely to be caused by ligand distortion due to inclusion in the pores of the solid carrier materials [25].

The TGA spectra of MCM41-**4** and SBA15-**4** show their thermal stability up to ca. 200 °C. MCM41-**4** and SBA15-**4** display successive weight losses without clearly distinct steps of in total ca. 8.5 and 7.5 wt.%, respectively, in the region of 200–550 °C. According to the loading of the carrier material with organometallic complexes (see above) this mass loss represents the removal of most of the organic ligands. The total mass of the organic ligands can be estimated, based on the Ru content of the material, to be ca. 10–11% of the total mass of MCM41-**4** and SBA15-**4** (The molecular mass of Ru is ca. 9% of the mass of the surface fixed complex, without the linking unit).

The materials with complex **4** grafted on both MCM-41 and SBA-15 were applied as catalysts for olefination of various aldehydes (Table 2). With the exception of dimethylamino benzaldehyde, all applied aldehydes either are electron neutral (Table 2, entries 1–3) or electron poor (Table 2, entry 4). The isolated yields of benzaldehyde, are >80%, and can be reached at 60 °C within 24 h. The steric hindrance of the substrates plays a significant role in the olefin product yield decrease under the same conditions (Table 2, entry 3).

The presence of electron rich groups in dimethylamino benzaldehyde might lead to the remaining of not reacted substrate molecules in the channels of the carrier materials close to the active Ruthenium(II) sites of the catalyst and thus blocking the access to these sites (Table 2, entry 5). Such behaviour might contribute to the observed low yield, since the reaction did not go to completion, even when it was carried out for 3 days. In the case of a dialdehyde (Table 2, entry 6) both yield and selectivity are comparable to a mono-aldehyde (Table 2, entry 1). Non-aromatic aldehydes, e. g., a cyclic aldehyde (Table 2, entry 7), are also good substrates to be reacted by both MCM41-**4** and SBA15-**4**.

When compared to their homogeneous counterparts, MCM41-**4** and SBA15-**4** are less active (see Table 3). Both heterogenous catalysts need 24 h to reach 92% conversion of *p*-methylbenzaldehyde while their homogeneous counterparts yield 97% of the olefin in just 1 h. The lower catalytic reactivity of the immobilized catalysts is likely due to the immobilization of the active sites inside (comparatively narrow) channels. However, the selectivities of MCM41-**4** and SBA15-**4** are generally higher than those obtained with their homogeneous counterparts.

MCM41-**4** and SBA15-**4** were recycled for several catalytic runs of benzaldehyde olefination, as shown in Table 4. Leaching experiments with MCM41-**4** and SBA15-**4** were also carried out under the same conditions. The filtered solution shows product yields of 8–10% formed after the separation from the catalyst carrier materials at reaction temperature. Leaching of active catalyst is therefore occurring to a certain degree and responsible for the decrease in activity during the recycling experiments, very likely due to the weak N→Ru interaction. Adsorption of reactant/product molecules on the surface together with a steric hindrance as a consequence of the presence of large size complexes on the modified mesoporous materials may also play a role in decreasing the catalytic activity during repeated runs. Regardless of these problems, the easier product/catalyst separation, higher selectivity and (at least) partial recyclability is promising for the utilization of such catalysts for aldehyde olefination [26, 27]. A stronger metal-linker interaction, however, is desirable to completely avoid leaching. Experiments in this direction are currently under way in our laboratories.

Table 3 Olefination of *p*-methylbenzaldehyde using heterogeneous and homogeneous Ruthenium(II) salen complexes

Catalyst	Reaction temperature (°C)	Reaction time (h)	Solvent	*E/Z*-Ratio[c]	Yield[d] (%)
MCM41-**4**	60	24	THF	19.0	95
SBA15-**4**	60	24	THF	19.0	92
2[b]	60	3	toluene	18.9	96
3[b]	60	1	toluene	11.3	97
4[b]	60	1	toluene	9.5	97

[a] Reactions were carried out in 5 mL THF with 1 mol % (based on the Ru-loading) of MCM41-**4** and SBA15-**4**, respectively, 0.25 mmol of *p*-methylbenzaldehyde (30.04 mg), 0.3 mmol of EDA (34.23 mg) and 0.3 mmol of PPh_3 (78.69 mg) under argon

[b] Reactions were carried out in 2.5 mL toluene with 1 mol % of complex **2, 3** and **4**, respectively, with 0.5 mmol of *p*-methylbenzaldehyde (60.08 mg), 0.6 equiv of EDA (68.46 mg) and 0.6 equiv of PPh_3 (157.38 mg) under N_2

[c] GC–MS measurement

[d] Isolated yield

Table 4 The catalytic stability test of MCM41-**4** and SBA15-**4** for several runs of benzaldehyde olefination[a]

Run	MCM41-**4** *E/Z*-Ratio[b]	MCM41-**4** Yield[c] (%)	SBA15-**4** *E/Z*-Ratio[b]	SBA15-**5** *E/Z*-Ratio[b]
1	19.0	92	24.0	93
2	19.0	83	15.7	81
3	15.7	75	19.0	50
4	19.0	60	19.0	29

[a] Reaction were carried out in 5 mL of THF with 1 mol % (based on the Ru-loading) of MCM41-**4** or SBA15-**4**, 0.25 mmol (26.63 mg) of benzaldehyde, 0.3 mmol (34.23 mg) of EDA and 0.3 mmol (78.69 mg) of PPh_3 at 333 K under argon

[b] GC–MS measurement

[c] Isolated yield

4 Conclusion

Ru(II)(salen)$(PPh_3)_2$ can be attached to the walls of mesoporous MCM-41 and SBA-15 channels using aminopropylsilane as a bridging ligand (linker). The modified grafted materials retain long range ordering and are found to be active and highly selective for the olefination of various aldehydes. However, their catalytic activities are lower than the activities observed for the non immobilized Ru(II)(salen)$(PPh_3)_2$ in homogeneous phase, due to the more difficult accessibility of the active sites inside the pores and some leaching occurs during successive catalytic runs.

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