

Methyltrioxorhenium heterogenized on commercially available supporting materials as cyclooctene metathesis catalyst

Alexandra M.J. Rost, Horst Schneider, Jochen P. Zoller,
Wolfgang A. Herrmann *, Fritz E. Kühn *

Lehrstuhl für Anorganische Chemie der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching bei München, Germany

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Abstract

Methyltrioxorhenium (MTO) is immobilized on various commercially available supporting materials by sublimation under vacuum. Up to 15 wt% MTO (10 wt% Re) can be immobilized on the different supporting materials. Metathesis experiments with *cis*-cyclooctene as substrate are performed aiming at a high yield of low molecular weight metathesis products (dimers, trimers, tetramers), which are interesting for aroma and flavour industries. Up to ca. 60% of these desired products can be obtained. A high rhenium loading leads usually to good catalytic activities of the materials in the cyclooctene metathesis. Prolonged reaction times lead to higher yields of the high molecular weight metathesis products. When the same catalyst material is used repeatedly in several catalytic runs, leaching of the grafted Re compounds plays an increasing role, resulting in a reduction of the catalyst performance. None of the examined commercially available carrier materials, however, presents an ideal means for the heterogenization of MTO to obtain particularly high amounts of the desired low molecular weight metathesis products of cyclooctene.
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1. Introduction

Since the 1980s several research groups [1–17] developed homogeneous systems usable as highly active W-, Mo- and Ru-based catalysts for metathesis. Some of these catalysts were successfully immobilized on polystyrene [18]. The most active heterogeneous metathesis catalysts known to date are based on the elements rhenium, molybdenum and tungsten [19].

The system $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ is an effective heterogeneous catalyst for carrying out olefin metathesis under mild conditions and its activity can be further increased by the addition of tetraalkyl tin compounds [20–23]. This observation led to the methyl tin based synthesis

of methyltrioxorhenium (MTO) [24]. Since tin containing co-catalysts are essential for the metathesis of functionalized olefins [25,26], it was soon discovered that MTO supported on acidic metal oxides forms metathesis catalysts that are active without additives, even for functionalized olefins [27]. Standard supports are $\text{Al}_2\text{O}_3\text{-SiO}_2$, or Nb_2O_5 and the activity was reported to be related to the surface acidity [19,28–30]. A high metathesis activity was observed when MTO is chemisorbed on the surface. Evidence for a surface carbene species was found to be somewhat controversial, but there appeared to be a correlation between the catalytic activity and the presence of alkyl fragments on the surface [27–29,31]. It has been shown later, however, that matrix-isolated MTO tautomerizes to $\text{H}_2\text{C=Re(OH)O}_2$ under the influence of UV light; the carbene has been characterized in its normal, D- and ^{13}C -enriched isotopic forms by IR spectroscopy with results

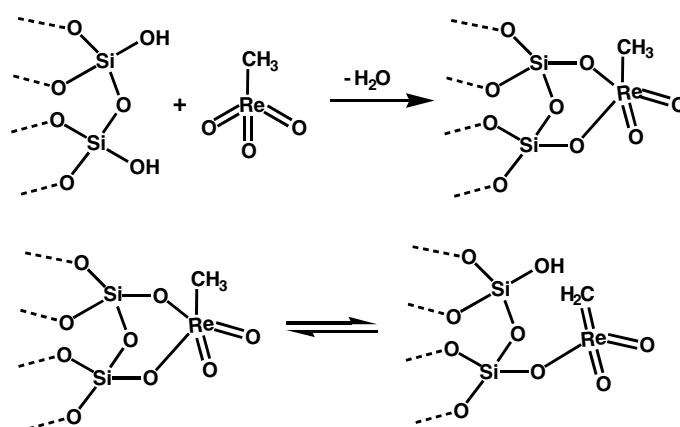
* Corresponding authors. Fax: +49 89 289 13473.

E-mail addresses: wolfgang.herrmann@ch.tum.de (W.A. Herrmann), fritz.kuehn@ch.tum.de (F.E. Kühn).

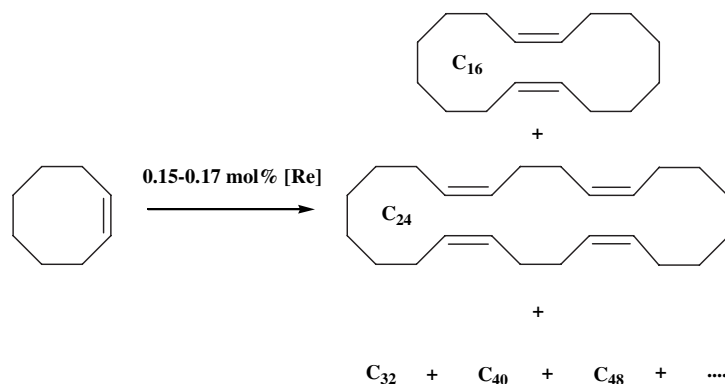
in good agreement with quantum chemical calculations [32]. DFT calculations indicate that $\text{H}_2\text{C}=\text{Re}(\text{OH})\text{O}_2$ lies nearly 90 kJ/mol higher in energy than MTO, and hence is inaccessible under normal thermal conditions. Using the complex $\text{CH}_3\text{ReO}_2\{(\eta^2\text{-OSiH}_2)_2\text{O}\}$ as a model, i.e., the condensation product of MTO with disilanol, $\{\text{H}_2\text{Si}(\text{OH})\}_2\text{O}$, shows that the tautomeric H-atom transfer occurs preferentially to an Re–O–Si bridging oxygen rather than to an Re=O unit. The resulting carbene species, $\text{H}_2\text{C}=\text{Re}\{(\eta^2\text{-OSiH}_2)(\text{O})(\text{SiH}_2\text{OH})\}$, is effectively stabilized by nearly 50 kJ/mol relative to $\text{CH}_3\text{ReO}_2\{(\eta^2\text{-OSiH}_2)_2\text{O}\}$. This alternative H-atom transfer to the Re–O–Si bridge appears to be a more plausible mechanism for carbene formation on the supporting materials [32,33]. A surface compound of similar composition is considered to be a plausible candidate for the catalytic active species in heterogeneous MTO catalyzed metathesis reactions by some researchers (see Scheme 1) [32–36]. Isolated and fully characterized Rhenium carbene complexes featuring Re in high oxidation states and displaying also oxo ligands attached to the rhenium carbene moiety are, however, still quite rare

[37–40]. Nevertheless, the application of MTO as heterogeneous metathesis catalyst is of significant interest, due to the very easy synthetic accessibility and the usually high stability of this organometallic compound [41,42].

C_{15-20} -bodies of cyclic and unsaturated hydrocarbons are used in high quantities in aroma and flavour industry. Such substances can be synthesized by metathetic dimerization of *cis*-cyclooctene with $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalysts pre-activated with tin compounds. However, besides the lower weight metathesis products considerable amounts of products, consisting of five and more cyclooctene units are often obtained as by-products (see Scheme 2) [43,44]. In this work, we examine the application of supported MTO as catalyst without pre-activation to compare the product yields with the $\text{Re}_2\text{O}_7/\text{Al}_2\text{O}_3$ catalyst system. We apply different commercially available carriers in order to find out whether some of these systems could be utilized as carrier materials for heterogeneous MTO without further modifications and may be applied in the cyclooctene metathesis.



Scheme 1. Reaction of methyltrioxorhenium (MTO) with a SiO_2 -surface containing free $-\text{OH}$ groups may lead to a Re-carbene species as suggested by Morris et al. [33]. The presence of excess water (e.g., in a not sufficiently dried solvent) inverts the reaction, leading to the removal of MTO from the surface.



Scheme 2. Metathesis of *cis*-cyclooctene.

2. Results and discussion

2.1. Supporting materials and catalyst loading

For our examinations, we tested primarily commercially available supporting materials with well-defined surface areas (BET) and pore volumes (see Table 1).

MTO, being a highly volatile, easily sublimable solid can be brought on the supporting material by sublimation under vacuum. Excess MTO, which does not undergo a reaction with the surface –OH groups is removed from the surface under vacuum. The supporting material has to be thermally pre-treated in order to reduce the decomposition of the immobilized and easy hydrolysable rhenium species [35].

In the immobilization experiments an excess of MTO (15 wt% with respect to the supporting material) has been used to reach a maximum Re loading of the respective supporting materials. The rhenium content of the product materials was determined by elementary analysis (EA). A high quantity of molybdenum in the supporting material **9** prevents the rhenium content determination by elementary analysis. The rhenium content is in this case calculated from the amount of resublimated MTO after immobilization. This method has proven to be a reliable method to determine the Re content also in cases where no molybdenum is present and the Re content of the layer can be independently determined by EA. The extremely low Re loading in the cases of **9**, **10** and **13** originates from the low specific surface area (BET) < 5 m²/g and the few surface hydroxyl groups available for reaction (²⁹Si CP-MAS-NMR evidence).

The resulting Re/C ratio being approximately 1:1 in most examined cases shows that MTO decomposition during the immobilization process is not pronounced

in most cases. This was already demonstrated previously in quantitative experiments [27]. Only for samples **1** and **3** significant decomposition is observed. During the immobilization of MTO on SiO₂/Al₂O₃ the formation of methane, ethane and ethene resulting from the decomposition of MTO was monitored by GC–MS. The decomposition of MTO observed during the immobilization process was <5% in all examined cases [27], with the exception of **1** and **3**, where it was significantly higher. MTO without any co-catalyst in homogeneous phase, however, is also not an active metathesis catalyst with cyclooctene being the substrate.

2.2. Results of the metathesis experiments

2.2.1. Batch experiments

In order to test the activity of the prepared heterogeneous catalyst systems, metathesis experiments with 0.15–0.17 mol% Re, with respect to the substrate cyclooctene, at 50 °C were performed with *n*-hexane being the solvent (Scheme 1). The results of the catalysis experiments are summarized in Table 2. None of the supporting materials catalyzed the cyclooctene metathesis under the applied conditions when no MTO was grafted on it prior to application.

Aiming at a high yield of lower homologues, which are used in aroma and flavour industry no highly active metathesis catalyst is needed. Such catalysts produce rapidly a quite large amount of higher homologues due to their fast conversion of the starting material. A catalyst with lower activity and conversion gains a higher yield of lower homologues.

Material **2** having a higher MTO loading, a higher specific surface area and a higher pore volume than material **1** is a good metathesis catalyst, particularly

Table 1
Prepared catalysts

No.	Supporting material	Ratio (wt%)	Re (wt%) ^a	Re:C ^b	BET (m ² /g)	Pore volume (cm ³ /g)
1	SiO ₂ /Al ₂ O ₃	84/16	2.0	1.0:2.6	170	0.4
2	SiO ₂ /Al ₂ O ₃	87/13	8.0	1.0:1.0	264	0.7
3	Al ₂ O ₃ /CoO/MoO ₃	82.5/3.5/14	8.1	1.0:1.8	<200	0.3
4	Al ₂ O ₃ ^c	100	8.1	1.0:1.0	<200	0.3
5	Al ₂ O ₃ ^d	100	9.0	1.0:1.1	<200	0.3
6	Al ₂ O ₃ ^e	100	10.0	1.0:1.0	<200	0.3
7	Al ₂ O ₃ /MoO ₃	86/14	8.7	1.0:1.4	<200	0.3
8	Al ₂ O ₃ /CoO	96.5/3.5	9.8	1.0:0.9	<200	0.3
9	MoO ₃	100	0.6	–	<5	–
10	CoO	100	1.4	–	–	–
11	Al ₂ O ₃ ^c /CoO/MoO ₃	82.5/3.5/14	7.5	1.0:1.1	<200	0.3
12	Al ₂ O ₃ ^c /CoO/MoO ₃	82.5/3.5/14	8.7	1.0:1.1	<200	0.3
13	Nb ₂ O ₅	100	<0.1	–	<5	–

^a Relative error: ±2%.

^b For Re relative error: ±2%, for C absolute error: ±0.3%.

^c Neutral.

^d Alkaline.

^e Acid.

Table 2

Results of the metathesis experiments with *cis*-cyclooctene as substrate at 50 °C (reaction time: 24 h; 0.15–0.17 mol% Re:cyclooctene)

No.	Cyclooctene (%) ^c	Lower ^a homologues (%) ^c	Higher ^b homologues (%) ^c
1	100	–	–
2	–	57	43
3	–	46	54
4	1	60	39
5	1	59	40
6	4	58	38
7	–	53	47
8	–	61	39
9	100	–	–
10	100	–	–
11	4	58	38
12	–	61	39
13	100	–	–

^a Sum of dimer, trimer and tetramer.

^b Sum of pentamer and higher homologues.

^c Relative error: ±5%.

with respect to forming the lower molecular weight products. Materials **1**, **9**, **10** and **13** display no metathesis activity.

The comparatively low Re loading of these materials seems not to be sufficient to obtain metathesis activity.

A larger content of heavier metathesis products is observed with material **3**. Materials **2**, **4–8**, **11**, and **12**, having all a Re loading between 7.5% and 10% display a comparable metathesis activity. In all these cases the amount of the desired lower weight metathesis products is somewhat higher than the amount of the heavier metathesis products.

Some of the catalysts leading to the favoured reaction products were tested at a lower reaction temperature (20 °C), in order to see whether this would additionally contribute to a higher amount of lower molecular weight metathesis products (see Table 3). The observed

Table 3

Results of the metathesis experiments with *cis*-cyclooctene as substrate at room temperature (reaction time: 24 h; 0.15–0.17 mol% Re:cyclooctene; 20 °C)

No.	Cyclooctene (%) ^c	Lower ^a homologues (%) ^c	Higher ^b homologues (%) ^c
2 ^d	–	56	44
3	2	49	49
4	4	45	51
5	–	58	42
6	7	48	45
7	–	59	41
8	–	49	51
11	–	55	45

^a Sum of dimer, trimer and tetramer.

^b Sum of pentamer and higher homologues.

^c Relative error: ±5%.

^d In chloroform soluble components.

amounts, however, were in most cases quite similar to those listed in Table 2 (50 °C reaction temperature).

2.2.2. Time-dependent experiments

Time-dependent metathesis experiments were performed in a tubular reactor in order to evaluate the long time effect on selectivity and catalytic activity. In the tubular reactor unit, the reaction medium was circulated (flow rate 5 mL/min. The results are shown in Table 4).

The product distribution is similar to the batch experiments. The conversion is completed after 7 h. If the reaction is continued, the dimer concentration decreases and the concentration of the higher homologs increases slowly. The higher viscous components of the reaction mixture, however, cause technical problems. After 2 days the reaction medium is so viscous that the flow rate has to be increased. In consequence the contact time changes and the steady state model can not be applied any more.

2.3. Leaching-experiments

An important parameter in heterogeneous reactions is the stability of the heterogeneous catalyst. It can be determined by leaching tests. Catalyst **3** was refluxed with the reaction mixture at 50 °C for 24 h. Then the solution was filtered off, the catalyst was washed and new substrate was added. Two further cycles were performed. After three cycles 4 wt% Re were detected by EA to remain on the supporting material. This amount is approximated half of original Re content. The product yield decreases from nearly quantitative (first cycle) to 63% (second cycle) to 10% (third cycle). No free MTO was detectable by NMR in the concentrated washing solution. A deactivation process, removing the Re compound from the surface leads to perrhenates (EA evidence) and the formation of methane, ethane, etc.

Another deactivation process of the heterogeneous catalyst occurs if wet solvent is present. Water promotes the catalyst deactivation by leading to the formation of free MTO (inactive in olefin metathesis), which can be detected by NMR and IR spectroscopy and perrhenic

Table 4

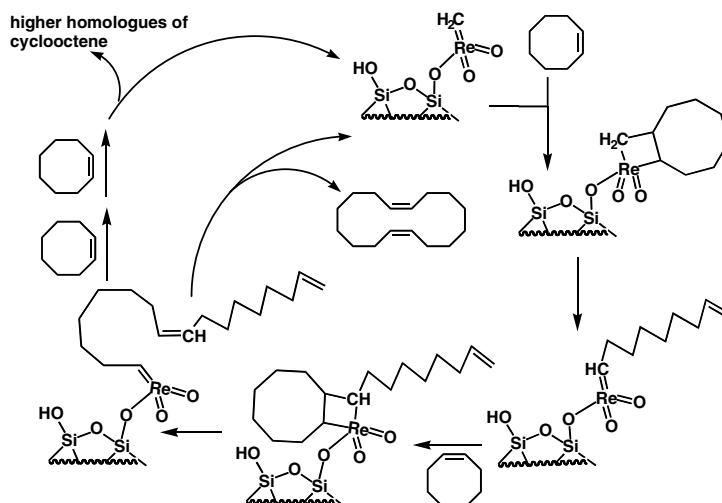
Results of the continuous metathesis experiments with *cis*-cyclooctene with catalyst **2** (Re:substrate: 1.3 mol%; 20 °C)

Time (h)	Cyclooctene (%) ^c	Lower ^a homologues (%) ^c	Higher ^b homologues (%) ^c
7	–	55	45
24	–	50	50
48	–	47	53

^a Sum of dimer, trimer and tetramer.

^b Sum of pentamer and higher homologues.

^c Relative error: ±5%.



Scheme 3. Hypothetical mechanism of the metathesis of *cis*-cyclooctene with a heterogeneous MTO catalyst, based on a “Scherer-type” catalytic active species.

acid as decomposition product. If ^{17}O -labelled water is added, the labelled oxygen is included both into the formed MTO and into the perrenic acid. This reaction may be explained by an inversion of the catalyst formation reaction (see Scheme 1).

3. Conclusions

Methyltrioxorhenium (MTO) can be heterogenized by simple sublimation on several commercially available supporting materials. A quite high Re loading of ca. 10 wt% can be reached with some of these materials. All materials containing a reasonable Re loading maintain cyclooctene metathesis without any additives. The amount of lower weight metathesis products (consisting of less than four cyclooctene units), which are interesting for the aroma and flavour industry are obtained at room temperature and 50 °C in ca. 50–60% yield after 24 h reaction time. Longer reaction times lead to a slow increase of the content of higher homologues. During several runs the catalyst materials loose Re due to catalyst decomposition. This leads to a considerable reduction of the metathesis activity. A hypothetical reaction mechanism, based on previously published examinations is shown in Scheme 3. This mechanism might help to explain the observed water sensitivity of the heterogeneous systems, however, further work will be necessary to elucidate the real mechanism of such reactions. Further work in this direction is currently under way in our laboratory.

The obtained results show that despite of some differences in the obtained yields of the desired lower molecular weight products, none of the yet commercially available carrier materials presents an ideal supporting system for MTO to be applied in the catalytic cyclooctene metathesis.

4. Experimental

4.1. General procedures

All experiments were carried out under argon atmosphere using glove box and Schlenk technique. All solvents were dried and distilled under argon with the standard methods. Nitrogen gas was deoxygenated by a BTS-catalyst and dehydrated by molecular sieves (4 Å) prior to use.

NMR spectra were measured on a Bruker Avance DPX-400. ^1H NMR spectra were obtained at 400.13 MHz, ^{13}C NMR spectra at 100.85 MHz. ^{29}Si -CP-MAS-NMR spectra are recorded at 79.49 MHz, with a (9.4 T) Bruker MSL 400P spectrometer, with 5.5 μs ^1H 90° pulses, 8 ms contact time, a spinning rate of 4.5 kHz and 4 s recycle delays. The molar mass distribution of the metathesis products was obtained by GPC. The solvent in the samples of the reaction mixture were distilled off and replaced by CHCl_3 for the measurements. The determination was performed at a Hewlett-Packard HP series 110 gel permeation chromatograph with two polystyrene cross-linked columns (10³ and 10⁵ Å), refraction index detectors and UV-detectors. The support morphology was obtained by the BET-method on an AS AP 2010 nitrogen sorption porosimeter (Micromeritics).

4.2. Synthesis procedures

4.2.1. Preparation of the supporting material

The following commercial available products were used as supporting materials. Materials **7**, **8**, **11** and **12** are mixed substances consisting of the corresponding pure metal oxides (see Table 5).

For dehydration of the supporting materials under vacuum and nitrogen flow a tube furnace (Heraeus,

Table 5
Supporting material

No.	Supporting material	Ratio (wt%)	Distributor
1	SiO ₂ /Al ₂ O ₃	84/16	Degussa-Hüls AG
2	SiO ₂ /Al ₂ O ₃	87/13	STREM
3	Al ₂ O ₃ /CoO/MoO ₃	82.5/3.5/14	STREM
4	Al ₂ O ₃ ^a	100	Merck
5	Al ₂ O ₃ ^b	100	Merck
6	Al ₂ O ₃ ^c	100	Merck
7	Al ₂ O ₃ ^c /MoO ₃	86/14	Merck/STREM
8	Al ₂ O ₃ ^c /CoO	96.5/3.5	Merck/STREM
9	MoO ₃	100	STREM
10	CoO	100	Aldrich
11	Al ₂ O ₃ ^a /CoO/MoO ₃	82.5/3.5/14	Merck/Aldrich/STREM
12	Al ₂ O ₃ ^c /CoO/MoO ₃	82.5/3.5/14	Merck/Aldrich/STREM
13	Nb ₂ O ₅	100	STREM

^a Neutral.

^b Alkaline.

^c Acid.

Typ ROK/A 4/30) was used. Support **1** was first heated at 400 °C for 12 h in a nitrogen flow in order to obtain dehydrated silica. All other supporting materials were heated at 200 °C for 3 h in a nitrogen flow.

4.2.2. Immobilization of MTO on the supporting material

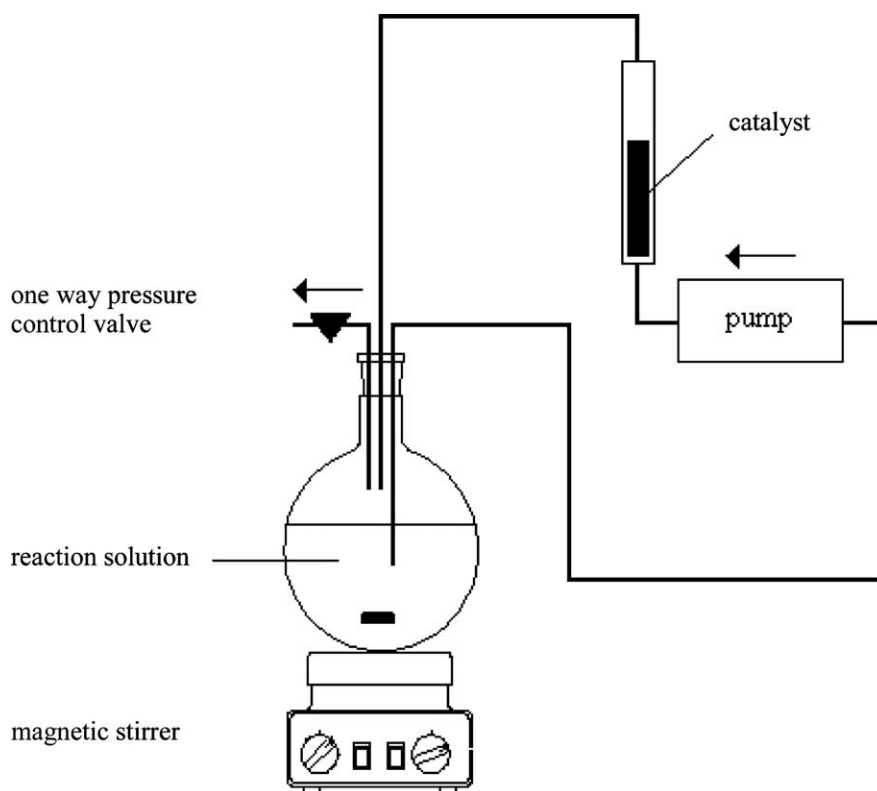
After dehydration MTO was added to the supporting material under argon atmosphere. The flask was closed

and cooled with liquid nitrogen to avoid the loss of MTO during the evacuation. MTO was sublimated on the support under vacuum. To get evenly distributed sublimation the flask was regularly shaken. After 24 h reaction time a pre-weighed and liquid nitrogen cooled cold trap was installed between the flask and the vacuum line and the excess of MTO was removed within 5 h. The immobilized amount of MTO was calculated from the amount of removed MTO and determined by Re elemental analysis. The resulting solid with immobilized rhenium was used as metathesis catalyst.

4.3. Metathesis experiments

Twelve millilitre of a 0.1 M *cis*-cyclooctene/*n*-hexane solution were added to 300 mg catalyst under argon atmosphere. The mixture was stirred, as indicated, for 24 h at 50 °C or room temperature. After this samples for analysis were taken. Depending on the Re content of the catalyst the reactions were performed with a 0.15–0.17 mol% ratio of immobilized rhenium:cyclooctene.

Time-dependent metathesis experiments were done in a tubular reactor (Scheme 4) 500 mL 0.1 M *cis*-cyclooctene/*n*-hexane solution were filled in a storage vessel and catalyst **2** (9.6 g, 1.3 mol% [Re]) in the tubular reactor (chromatographic column, Aldrich, *L* = 30 cm,



Scheme 4.

$d = 1.5$ cm) under argon atmosphere. The displacement of the pump was 5 mL/min. Samples were taken after 7, 24 and 48 h.

4.4. Leaching-experiments with the immobilized MTO systems

Three hundred milligram of catalyst **3** were added to 12 mL 0.1 M *cis*-cyclooctene/*n*-hexane solution under argon atmosphere. The mixture was refluxed at 50 °C for 3 days. After each 24 h a sample was taken, the catalyst was filtered, washed three times with 10 mL hexane and new substrate was added. Two further cycles were performed. Then the catalyst was filtered, washed, dried under vacuum and the Re content of the material was determined by elementary analysis.

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