Role of Grafted Alkoxybenzylidene Ligand in Silica-Supported Hoveyda-Grubbs-Type Catalysts

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General
All reactions were carried out in oven-dried glassware under an inert atmosphere of dry argon. All chemicals used were obtained from Aldrich or Alfa Aesar and used as received. All MCF-supported catalysts were prepared according to the previous report. An isocratic pump from Agilent (1100 series G13104 with a control module) and a degasser from Waters (In-Line Degasser AF, 4 Channels) were used for the circulating flow-type reactions. $^{13}$C CP-MAS and $^{29}$Si CP-MAS NMR spectra were recorded on a 400 MHz Bruker spectrometer for the supported catalysts. GC analyses were conducted with an Agilent 7890A instrument equipped with an HP-5 column. ICP-MS was performed on a Perkin Elmer DRC II ELAN ICP-MS.

Preparation of packed beds
A stainless steel column (4.6 mm × 50 mm, Alltech) was filled with MCF-supported metathesis catalysts (Catalyst loading: 0.2 mmol/g, 210 mg, 42 μmol) eluting with DCM at high pressure (8000 psi) by using a slurry packer. By using the above procedure, MCF-supported Hoveyda-type ligands (ligand loading: 0.25 mmol/g, 110 mg, 27.5 μmol) were packed into a stainless steel column (4.6 mm × 30 mm, Alltech) eluting with DCM. The prepared packed beds were dried under high vacuum before use.

Catalytic reactions under circulating flow conditions
The column was fitted into a solvent delivery system as shown in figure 1 and set to a desired temperature by a column heater. Diethyl diallylmalonate (504.6 mg, 0.15 M) and dodecane (178.8 mg, 0.075M) in DCM (14 ml) was circulated at a flow rate of 0.5 ml/min. An aliquot was taken from the outlet of the column, and the conversion at each time point was measured by GC. After completion of the catalytic reaction, the reaction solution was collected from the outlet of the column, and the whole line with the reservoir flask was completely washed with DCM. The washings were combined with the product solution. The combined solution was evaporated and dried for ICP-MS analysis.

Ring-closing metathesis reaction in a batch reactor
Diethyl diallylmalonate (144.2 mg, 0.05 M) and dodecane (51.1 mg, 0.025M) were added to MCF-supported catalysts (catalyst d, 60 mg, 0.012 mmol, 2 mol%) in DCM (12 ml) at room
temperature. During the catalytic reaction, an aliquot (200 μl) was taken from the reaction solution, filtered and then quenched with methanol. The conversion at each time point was measured by GC. The same procedure was applied to cataly e and f.

Scheme S1. Synthesis of MCF-supported DMT. a. Hexamethylsilazane (HMDS), toluene; b. APTES, toluene; c. HMDS, vapor-phase reaction; d. Cyanuric chloride, triethylamine, anhydrous THF; e. NaSH, anhydrous ethanol.

Synthesis of MCF-supported dimercaptotriazine (DMT) as metal scavenger
MCF-supported DMT was synthesized according to scheme S1. MCF (3.0 g) was degassed at 120 °C overnight under vacuum before reaction. HMDS (253 mL, 1.2 mmol) was added to a suspension of MCF in toluene (20 mL). The mixture was stirred at room temperature under argon for 5 h, and then heated at 60 °C overnight. The resulting suspension was filtered, washed with methanol, and then dried under vacuum. The resulting TMS-capped MCF (5.0 g) was degassed at 120 °C overnight under vacuum before reaction and then dispersed in anhydrous toluene (30 ml). 3-aminopropyltriethoxysilane (APTES) (464 mg, 2.10 mmol) was added to the mixture. The mixture was stirred at room temperature under argon for 3 h, and then heated at 90 °C overnight. The mixture was cooled down, filtered and washed with toluene, CH₂Cl₂, and methanol. The collected particles were dried under vacuum. The NMR spectrum of the filtrate after solvent evaporation confirmed the immobilization of all APTES.
The particles were post-capped with TMS by the vapor-phase reaction with HMDS. Elemental analysis, C:7.41, H:1.75, N:0.55. The calculated loading amount of NH$_2$ on MCF is 0.40 mmol/g.

A little bit excess of cyanuric acid (221 mg, 1.2 mmol, 1.5 eq) in 2 ml of THF was slowly added to the resulting amine-functionalized MCF (2 g, 0.8 mmol of -NH$_2$) in THF (8 ml), and then triethylamine (223 µl, 1.6 mmol) in 2 ml of THF was added to the mixture solution. After overnight reaction at room temperature, the MCF particles were recovered through filtering, completely washed with anhydrous THF and dried in vacuum. The dried MCF particles were reacted with NaSH (134 mg, 2.4 mmol) in anhydrous ethanol (10 ml) for 6 hr and then recovered by filtration. The recovered MCF particles were completely washed with ethanol and water, and then dried under vacuum to yield MCF-supported DMT scavenger. The calculated loading amount of DMT on MCF is 0.38 mmol/g.

MCF-supported dichlorotriazine, Elemental analysis, C:8.70, H:1.72, N:2.12.
MCF-supported DMT, Elemental analysis, C:8.80, H:1.73, N:2.15, S:2.42.

References
**Fig. S1** CPMAS $^{13}$C NMR spectra of (a) MCF-supported alkoxybenzylidene ligands recovered from the ligand bed B of the system b after one round of the flow reaction at 25 °C, (b) MCF-supported Hoveyda-Grubbs-type catalyst (3), and (c) MCF-supported alkoxybenzylidene ligand (4). Red arrows indicate the presence of the ruthenium complexes.
Fig. S2 Conversion of diethyl diallylmalonate in the reservoir flask at 25 °C, isolated from the main circulating flow reaction system at 3 min from the initiation. The conversion was 10.7% at the point of isolation.
Fig. S3 Conversion of diethyl diallylmalonate by MCF-supported catalysts with different catalyst loading amount. Conditions: catalyst (2 mol%), diethyl diallylmalonate (144.2 mg, 0.05 M), dodecane (51.1 mg, 0.025 M), DCM (12 ml), 25 °C.
Fig. S4 Conversion of diethyl diallylmalonate in the presence of MCF-supported DMT. Conditions: catalyst $\text{d}$ (60 mg, 2 mol%), MCF-DMT (150 mg), diethyl diallylmalonate (144.2 mg, 0.05 M), dodecane (51.1 mg, 0.025M), DCM (12 ml), 25 °C.
Fig. S5 CP-MAS NMR spectra.
Spinning rate = 10k Hz

Spinning rate = 12k Hz
System a
MCF-supported metathesis catalyst (A) recovered after one cycle
System b
MCF-supported metathesis catalyst (A) recovered after one cycle
System b
MCF-supported bidentate benzylidene ether ligand (B) recovered after one cycle
**System c**

MCF-supported metathesis catalyst (A) recovered after one cycle
System c
MCF-supported bidentate benzyldene ether ligand (B) recovered after one cycle
Catalyst 5
$\text{Ru}

\begin{align*}
\text{Cl}_2
\end{align*}

\begin{align*}
\text{Cl} \equiv \text{Ru} \equiv \text{Cl}
\end{align*}

\begin{align*}
\text{O} \equiv \text{O} \equiv \text{EtO}
\end{align*}

\begin{align*}
\text{Si} \equiv \text{Si} \equiv \text{SiO}_2
\end{align*}

\begin{align*}
\text{N} \equiv \text{N} \equiv \text{N} \equiv \text{N}
\end{align*}

\begin{align*}
\text{a} \equiv \text{b}
\end{align*}

\begin{align*}
3
\end{align*}

\begin{align*}
14.65
\end{align*}

\begin{align*}
-55.97
\end{align*}

\begin{align*}
64.35
\end{align*}

\begin{align*}
-99.69
\end{align*}

\begin{align*}
-108.10
\end{align*}

\begin{align*}
\text{ppm}
\end{align*}

S20
System a
MCF-supported metathesis catalyst (A) recovered after one cycle