Supported Catalysts

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Cationic Silica-Supported N-Heterocyclic Carbene Tungsten Oxo Alkylidene Sites: Highly Active and Stable Catalysts for Olefin Metathesis

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Abstract: *Designing supported alkene metathesis catalysts with high activity and stability is still a challenge, despite significant advances in the last years. Described herein is the combination of strong σ-donating N-heterocyclic carbene ligands with weak σ-donating surface silanolates and cationic tungsten sites leading to highly active and stable alkene metathesis catalysts. These well-defined silica-supported catalysts, [(≡SiO)W(=O)(=CHCMe$_2$Ph)(IMes)(OTf)] and [(≡SiO)W(=O)(=CHCMe$_2$Ph)(IMes)$^+$][B(Ar^F)$_4^-$] [IMes = 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene, B(Ar^F)$_4$ = B(3,5-(CF$_3$)$_2$C$_6$H$_3$)$_4$] catalyze alkene metathesis, and the cationic species display unprecedented activity for a broad range of substrates, especially for terminal olefins with turnover numbers above 1.2 million for propene.*

In recent years, tremendous advances in the design of alkene and alkyne metathesis catalysts have been made for both homogeneous and heterogeneous systems.[1–3] In particular, the development of highly active tungsten oxo alkylidene molecular catalysts[4] and the adaption of N-heterocyclic carbene (NHC) ligands, widely used in ruthenium-based alkene metathesis catalysts,[5] to molybdenum and tungsten systems[6] have significantly widened the range of applications of d^0-metal-based olefin metathesis catalysts.

For heterogeneous catalysts, major advances have been possible through surface organometallic chemistry,[3,7] which enables the generation of well-defined active sites at the surface of oxide supports.[8] This approach identified the electronic dissymmetry at the metal center as a key factor for greatly improved activity of silica-supported Schrock alkylidene complexes.[9] DFT calculations[10] have revealed that this increase in activity is due to the easier coordination of the olefin substrate to the metal-alkylidene sites and the destabilization of metallacyclobutane intermediates because of the presence of both weak and strong σ-donor ligands, that is, one surface siloxy and either one alkyl or amide ligand, respectively. This conclusion has inspired the synthesis of catalysts with enhanced dissymmetry at the metal site.[1c,11] One of the most recent and compelling examples is the use of poor σ-donor surface silanolates[12] with strong σ-donating thiolate ligands in silica-supported tungsten oxo alkylidene catalysts,[4e,15] which display substantially enhanced activity towards terminal olefins.

The recent report of highly active and stable tungsten oxo alkylidenes supported by an NHC[6c] as a strong σ-donor ligand thus opens new avenues to significantly improve the activity of silica-supported metathesis catalysts by combining cationic intermediates and a strong σ-donating NHC ligand with a weak σ-donating surface silanolate. Herein we report the synthesis and characterization of silica-supported neutral and cationic tungsten oxo alkylidene complexes bearing an NHC ligand and show the unprecedented activity and stability of the supported cationic olefin metathesis catalyst.

Grafting W(=O)(=CHCMe$_2$Ph)(IMes)(OTf)(O*t*Bu$_{F6}$)[13] (**1**) and the related cationic species [W(=O)(=CHCMe$_2$Ph)-(IMes)(O*t*Bu$_{F6}$)$^+$] [B(Ar^F)$_4^-$] (**2**) onto SiO$_{2-700}$ afforded the corresponding materials **1**@SiO$_2$ and **2**@SiO$_2$, respectively (Scheme 1). Quantification by solution NMR spectroscopy of *t*Bu$_{F6}$OH released upon grafting indicates that about 47 and 51 % of the surface silanols (0.26 mmol g^{-1}) reacted with **1** and **2**, respectively. This data is in agreement with the tungsten loading of 2.51 % (**1**@SiO$_2$, 0.13 mmol g^{-1}) and 2.67 % (**2**@SiO$_2$, 0.14 mmol g^{-1}) as determined by elemental analysis and the presence of residual silanols interacting with nearby aromatic residues according to infrared (IR) spectroscopy (a broad band at 3647 cm^{-1}; Figure S25 in the Supporting Information).[9c]

The ^{1}H magic angle spinning (MAS) NMR spectrum of **1**@SiO$_2$ showed resonances at $\delta = 11.2$, 7.1, and 2.1 ppm, which were assigned to the alkylidene, the aromatic, and methyl proton signals, respectively (Figure S19). A similar ^{1}H MAS spectrum was observed for **2**@SiO$_2$ (Figure S21), with peaks at $\delta = 10.4$, 7.4 and 1.9 ppm, accounting for the alkylidene, aromatic, and methyl moieties, respectively. As generally observed for supported tungsten alkylidene complexes, the carbene signals were not detected at natural abundance in the ^{13}C cross-polarization (CP) MAS spectra, but all the other signals corresponding to the ligands were observed (Figures S20–S22). The ^{11}B NMR spectrum of **2**@SiO$_2$ shows only one signal at $\delta = -6.3$ ppm and it is consistent with the presence of isolated B(Ar^F)$_4^-$ anions as observed for the molecular precursor **2** (Figure S23).

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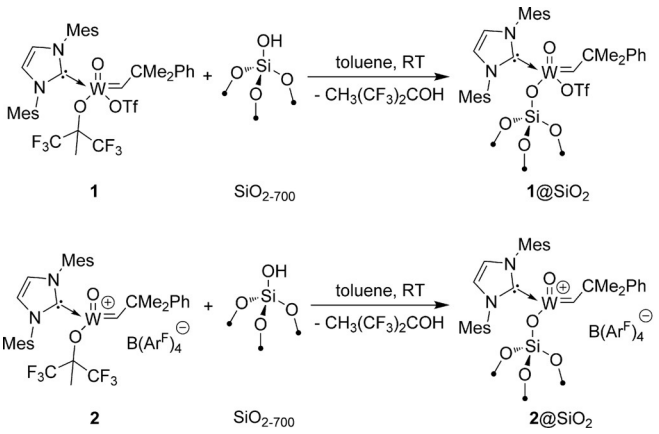

Scheme 1. Grafting **1** and **2** onto SiO_{2-700}. $B(Ar^F)_4 = B(3,5\text{-}(CF_3)_2C_6H_3)_4$, Mes = mesityl, Tf = trifluoromethanesulfonyl.

As the alkylidene signals of supported species are difficult to detect, because of their large chemical shift anisotropy and low site density,[14] we prepared ^{13}C-enriched compounds both at the alkylidene and NHC carbene positions, **1*** and **2***, respectively. The ^{13}C-enriched silica-supported complexes **1***@SiO_2 and **2***@SiO_2 were synthesized and characterized by ^{13}C CPMAS and two-dimensional (2D) ^1H-^{13}C HETCOR NMR spectroscopy (see the Supporting Information). Alkylidene signals were observed at $\delta = 300$ and 296 ppm for **1***@SiO_2 and **2***@SiO_2, respectively, and the NHC carbene was observed at $\delta = 186$ ppm for **1***@SiO_2 and $\delta = 181$ ppm for **2***@SiO_2. The spectroscopic characterization of **1**@SiO_2 and **2**@SiO_2, combined with elemental (C, H, B and F; see the Supporting Information) analyses, are in agreement with the proposed structures [(≡SiO)W(=O)(=CHCMe$_2$Ph)(IMes)(OTf)] and [(≡SiO)W(=O)(=CHCMe$_2$Ph)(IMes)$^+$][B(Ar^F)$_4^-$] as the main species in **1**@SiO_2 and **2**@SiO_2, respectively.

To harness the potential of **1**@SiO_2 and **2**@SiO_2 in alkene metathesis, we first tested them with the benchmark substrates *cis*-4-nonene and 1-nonene (Table 1).[4c,d,5a,b,12,15] Both materials are active in self-metathesis of *cis*-4-nonene and 1-nonene at 30 °C, but they significantly differ in activity. **1**@SiO_2 showed moderate activity with *cis*-4-nonene, while **2**@SiO_2 displays high activity, similar to some of the best silica-supported tungsten alkylidene catalysts.[4c,d,5a,b,12] For comparison, **1** was inactive under similar reaction conditions, and **2** showed high activity [TOF = 170 min^{-1} (TOF = turnover frequency), with fast equilibrium conversion, ca. 3 min]. The catalyst **2**@SiO_2 can however be recycled more than three times without loss of catalytic activity. In addition, quantification of the number of active sites indicated that more than 95% of the tungsten centers in **2**@SiO_2 are active (see the Supporting Information). More importantly, **2**@SiO_2 displayed an unprecedented activity for the metathesis of 1-nonene, a terminal olefin. TOFs as high as 2460 min^{-1} could be measured at a 50 ppm loading, about two orders of magnitude higher than the best well-defined silica-supported catalyst known to date under the same reaction conditions. In contrast, the molecular catalyst **2** showed faster deactivation in the metathesis of 1-nonene at a 0.02% catalyst loading, with the conversion reaching only 80%. This difference presumably arises from the low stability of the methylidene species generated from **2** and illustrates the advantage of site isolation of the corresponding supported catalysts, which prevents deactivation through dimerization.[9b] This exceptionally high stability allowed a decrease in the catalyst loading to 10 ppm in the 1-nonene metathesis with **2**@SiO_2, thus reaching a TON of about 61100, at the expense of the TOF, which fell to 830 min^{-1}. This loss of activity (TOF) is attributed to poisoning of active species with adventitious impurities not removed by the purification protocol.

Table 1: Catalytic activity of **1**@SiO_2 and **2**@SiO_2 in self-metathesis of *cis*-4-nonene and 1-nonene in toluene at 30 °C.

Substrate	Catalyst	mol%	TOF_{3min}[a]	Time to equilibrium[b]
cis-4-nonene	**1**@SiO_2	0.1	10 (3%)	5 h (490)
cis-4-nonene	**2**@SiO_2	0.1	90 (27%)	5 min (510)
cis-4-nonene	**2**@SiO_2	0.02	120 (7%)	1 h (2510)
1-nonene	**1**@SiO_2	0.02	4 (<1%)	26% in 24 h (1300)
1-nonene	**2**@SiO_2	0.02	420 (25%)	5 h (4530)
1-nonene	**2**@SiO_2	0.002	2460 (15%)	74% in 24 h (37090)
1-nonene	**2**@SiO_2	0.001	830 (2%)	60% in 24 h (61070)

[a] TOF at 3 min, given in min^{-1} and the corresponding conversion is given within parentheses. [b] TON given within parentheses. Also given is the percent conversion for cases in which equilibrium was not achieved.

The activity of **2**@SiO_2 in self-metathesis, ring-closing metathesis, and cross-metathesis with functionalized substrates was also investigated (Table 2). **2**@SiO_2 displayed high activity for functionalized substrates, which is generally challenging for supported catalysts. With ethyl oleate, fast equilibrium conversion is observed at a 0.1 mol% loading. Decreasing the catalyst content to 10 ppm allows a maximum TON of about 12000 with a TOF_{3min} of 400 min^{-1}. **2**@SiO_2 is also active for the ethenolysis of ethyl oleate where TONs of up to 930 were achieved. Ring-closing metathesis of diallyl ether proceeded with a TON of 780, while the molecular precursor **2** was inactive,[6c] and likely results from the increased stability provided by grafting.

The heterogeneous nature of **2**@SiO_2 allowed us to investigate its activity in gas-phase reactions under flow conditions. Remarkably, the catalyst **2**@SiO_2 achieved more than 1200000 turnovers in the self-metathesis of propene within 6 days, with a metathesis selectivity greater than 99%, and with only about 40% deactivation over that period.

In summary, grafting neutral and cationic tungsten oxo alkylidene NHC complexes onto SiO_{2-700} afforded the well-defined surface species [(≡SiO)W(=O)(=CHCMe$_2$Ph)(IMes)(OTf)] and [(≡SiO)W(=O)(=CHCMe$_2$Ph)(IMes)$^+$]-

Table 2: Catalytic activity of **2**@SiO_2 with functionalized substrates in toluene.

Substrate	*T* [°C]	mol%	TON[a]
ethyl oleate	70	0.001	11874 (1 h)
diallyl ether	30	0.1	780 (24 h)
diallyl diphenylsilane	30	0.1	880 (24 h)
ethyl oleate ethenolysis	60	0.1	930[b] (1 h)

[a] Time is given within parentheses. [b] 82% selectivity for ethenolysis, 18% of homodimerization products.

$[B(Ar^F)_4^-]$. Both complexes are active in alkene metathesis, but the cationic species displayed unprecedented activity and stability in the metathesis of olefins, coupled with improved functional-group tolerance by comparison with other silica-supported complexes. Most remarkable are the high activity and stability with terminal olefins, thus allowing over a 1 million TON in propene self-metathesis with **2**@SiO_2 to be achieved. These results may open a new prospective for the use of well-defined catalysts in chemical processes. The results provide further evidence that enhancing the dissymmetry at the metal center by using a strong σ-donating ligand such as an NHC in silica-supported d^0-metal alkylidene complexes leads to an increased activity in olefin metathesis and that site isolation provided by the support leads to exceptionally high stability.

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[13] During the course of this study we could determine the crystal structure of **1**. Details are given in the Supporting Information (see Figure S54).

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