Communication

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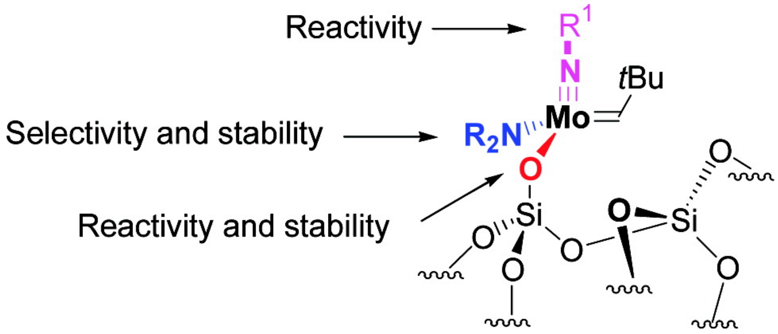

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Dramatic Improvements of Well-Defined Silica Supported Mo-Based Olefin Metathesis Catalysts by Tuning the N-Containing Ligands

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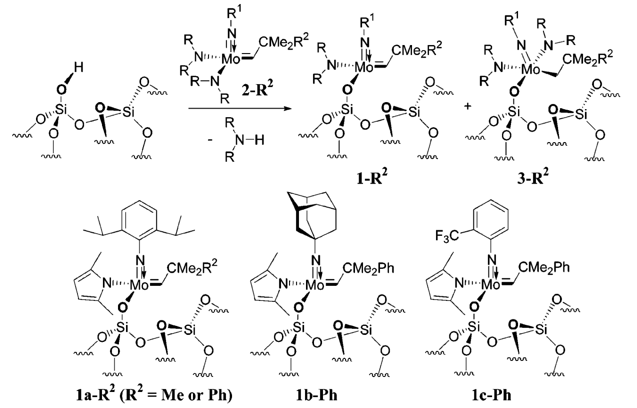
Despite the recent advances in the design of olefin metathesis catalysts, optimal systems combining high activity, selectivity, stability, and functional group tolerance still need to be discovered, whether based on d^0 transition metals (Mo, W, Re) or Ru, homogeneous[1,2] or heterogeneous catalysts.[3−8] In the specific case of d^0 systems, we have recently shown that asymmetry at the metal center and site isolation through grafting on rigid oxide supports can allow an increase in the performances of these systems:[9−12] today well-defined silica supported heterogeneous catalysts out-perform their homogeneous equivalents (rates and TON). The current best catalysts are based on the amido complexes **1** $[(\equiv SiO)Mo(\equiv NR^1)(=CHCMe_2R^2)(NR_2)]$:[12,13] the pyrrolyl derivatives (NR_2=pyrrole) are very attractive, because they can be readily accessible in two steps from the triflate derivative $[Mo(\equiv NR^1)(=CHCMe_2R^2)(OTf)_2(dme)]$ (synthesis of $[Mo(\equiv NR^1)(=CHCMe_2R^2)(NR_2)_2]$ followed by grafting),[14] but they undergo a fast deactivation. On the contrary, the diphenylamido systems are more stable catalysts, but these systems require a longer synthetic route.[15] We have therefore investigated the use of 2,5-dimethylpyrrolyl derivatives $[Mo(\equiv NR^1)(=CHCMe_2R^2)(NR_2)_2]$ (**2a**−**c**, R_2N = 2,5-dimethylpyrrolyl), also readily available from the triflate derivatives,[16] as an access to the well-defined silica supported system **1a**−**c**, $[(\equiv SiO)Mo(\equiv NR^1)(=CHCMe_2R^2)(NR_2)]$. Here, we show (1) the dramatic effect of this 2,5-dimethylpyrrolyl ligand on the structures, the stability and the activity of the resulting surface species compared to the parent pyrrolyl system, and (2) the improvement (activity and stability) of this new generation of catalysts by tuning the imido ligand.

First, grafting of **2a**-Ph (NR_2 = 2,5-dimethylpyrrolyl, R^1 = 2,6-i-$Pr_2C_6H_3$, R^2 = Ph) on $SiO_{2-(700)}$ gives the corresponding monosiloxy complex **1a**-Ph as the major species (ca. 80%) along with **3a**-Ph (ca. 20%) according to mass balance analysis, IR, and NMR studies (Scheme 1, **3a**-Ph = **3**-R^2 with R^1 = 2,6-i-$Pr_2C_6H_3$ and R^2 = Ph) in contrast to the diphenylamido and the parent pyrrolyl systems, which give a single surface species **1**. Upon grafting, the surface silanols, observed at 3747 cm^{-1} in the IR spectrum of $SiO_{2-(700)}$, are consumed while ν(C−H) and δ(C−H) vibrations of aromatic and alkyl ligands appeared in the 3100−2700 and 1600−1350 cm^{-1} regions, respectively (Figure S1). The appearance of a broad band centered at 3620 cm^{-1} is consistent with the presence of remaining silanols in interactions, probably with the ligands of the grafted Mo complex. Conversely, 0.8 equiv of 2,5-dimethylpyrrole are formed during grafting, and the elemental analyses on the resulting solid for Mo (1.30 ± 0.05 wt %), C (5.1 ± 0.1 wt %) and N (0.4 ± 0.1 wt %) are consistent with the consumption of 55% of the surface silanols (0.14 mmol $Mo \cdot g^{-1}$ for 0.26 mmol $SiOH \cdot g^{-1}$ of $SiO_{2-(700)}$) and the presence of an average of 31 ± 2 carbons and 2.2 ± 0.5 nitrogens per grafted Mo by comparison with 28 C/Mo and 2 N/Mo expected for **1a**-Ph. Furthermore, the ^1H MAS solid-state NMR spectrum and especially the constant time (CT) ^1H MAS NMR spectrum (Figure S2) display the following resonances: 12.2 (=C*H*CMe$_2$Ph), 7.1 (Csp^2-H), 5.5 (pyrrolyl-Csp^2-H), 3.3 (C*H*Me$_2$), 1.8 (unreacted SiOH), 1.3 (=CHC*Me*$_2$Ph, pyrrolyl-Csp^3-H) and 1.0 (CH*Me*$_2$) ppm in full agreement with the presence of **1a**-Ph as a major surface species. The ^{13}C CP MAS spectrum displays the expected signals for **1a**-Ph at the exception of the carbenic carbon (Figure S3; Table S1). However, an extra signal is observed at 69 ppm in agreement with the presence of another surface species. In fact, when the ^{13}C labeled neopentylidene complex, **2a**-Me $[Mo(\equiv NR^1)(={}^*CHCMe_3)(NR_2)_2]$ (R^2 = Me), 99% ^{13}C labeled on the α-carbon to Mo (Figures S4−S6; Table S1), is grafted on $SiO_{2-(700)}$ in place of **2a**-Ph, two isotropic signals at 69 and 285 ppm, corresponding to the ^{13}C labeled carbons, appear in the ^{13}C NMR spectrum. These signals have distinct correlation peaks ($^1H/^{13}C$) at (12.2/285) and (2.3/69) ppm in the 2D ^1H-^{13}C HETCOR NMR spectrum, consistent with the presence of two surface species: one having one neopentyl ligand and the other one having kept the neopentylidene ligand. All the data are consistent with the major species being **1a**-Me, and the minor species **3a**-Me (Scheme 1). Heating this mixture of surface species (**1a**/**3a**) in toluene at 80 °C for 4 h does not show the formation of 2,5-dimethylpyrrole, and the ^{13}C NMR spectrum remains unchanged, which is consistent with the high stability of **3a**. This also probably shows that **1a** is probably formed by the direct electrophilic cleavage of the Mo−N bond by the surface silanols, while **3a** results from the competing addition of the surface silanol to the Mo−C double bond of **2a**.

Scheme 1



Second, contacting [**2a**-Ph/$SiO_{2-(700)}$] with propene in a flow reactor (ca. 400 $mL \cdot mn^{-1}$; 4800 mol of propene.mol of $Mo^{-1}.min^{-1}$) gives selectively ethene and 2-butenes with a very fast initial rate (5.2 s^{-1}), and over 1500 min, 101 000 TON have been achieved

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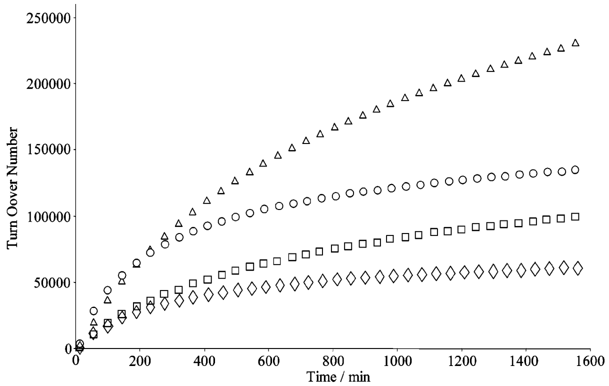

Figure 1. Activity in propene metathesis: TON as a function of time (min). Comparison of [**2a**-Ph/$SiO_{2-(700)}$] (□), [**2b**-Ph/$SiO_{2-(700)}$] (△), [**2c**-Ph/$SiO_{2-(700)}$] (○), and **1d**-Ph (◇).

Table 1. Comparative Activity in Olefin Metathesis of Various Pyrrolyl Catalysts

	propene[a]		ethyl oleate[b]	
catalyst	TOF[c]	TON[d]	TOF[c]	time/h[e]
[**2a**-Ph/$SiO_{2-(700)}$]	5.2	101 000	0.05	3
[**2b**-Ph/$SiO_{2-(700)}$]	8.3	231 000	0.5	1
[**2c**-Ph/$SiO_{2-(700)}$]	13.2	135 000	1.2	0.5
1d-Ph	6.2	62 000	0.04	(10%)[f]
4			0.04	(30%)[f]

[a] Experimental conditions: flow reactor of propene, 30 °C. [b] Experimental conditions: 1.16 M solution of EO in toluene, 0.05 mol % of Mo. [c] TOF is the initial turn over frequency measured after 5 min of reaction expressed in mol of substrate converted per mol of Mo per second. [d] Maximum turn over number obtained in a flow reactor. [e] Time necessary to reach the equilibrium conversion in h (ca. 50%). [f] The number in parentheses corresponds to the maximum conversion reached after 8 h.

{Figure 1, TON = *f*(*t*)}. While the initial rate is similar to this obtained for the parent pyrrolyl system [$(\equiv SiO)Mo(\equiv NR^1)(=CHCMe_2Ph)(NR_2)$] ($NR_2$ = pyrrolyl, R^1 = 2,6-di-*i*-PrC_6H_3) **1d**-Ph (TOF = 6.2 s^{-1}, TON = 62 000), the stability of the catalyst has been improved (slower deactivation).[12] This is especially true if one corrects the rates and the TON for the actual number of active sites in [**2a**-Ph/$SiO_{2-(700)}$] (ca. 80%, $TOF_{corr.}$ and $TON_{corr.}$ of 6.5 s^{-1} and 126 000, respectively). The difference between these two systems is even more pronounced in the self-metathesis of ethyl oleate (EO)—*used as received without any purification*: the equilibrated mixture (1:1:2 ratio of 9-octadecene, the diester, and EO) is obtained within 3 h in the presence of 0.05 mol % of [**2a**-Ph/$SiO_{2-(700)}$] with an initial rate of 0.05 s^{-1}, while only 10% conversion could be achieved with **1d**-Ph after 8 h of reaction (initial rate, 0.04 s^{-1}; Figure S7).[12] Third, while changing the substituents on the imido ligand, from a 2,6-*i*-$Pr_2C_6H_3$ in **2a**-Ph to an 1-adamantyl in **2b**-Ph or a 2-CF_3-C_6H_4 in **2c**-Ph, provides a homologous mixture of surface complexes **1b**-Ph/**3b**-Ph and **1c**-Ph/**3c**-Ph (see Supporting Information, Figures S8−14), this significantly increases the catalytic performances of the catalysts (higher initial rates and TON). The adamantyl imido system is the most stable system for propene metathesis and only slowly deactivates, allowing 231 000 TON to be achieved in 1500 min {Figure 1, TON = *f*(*t*)}. Noteworthy, the order of efficiency is different in the self-metathesis of EO: with 0.05 mol % of catalyst, the reaction mixture is equilibrated in 1 h and 30 min for [**2b**-Ph/$SiO_{2-(700)}$] and [**2c**-Ph/$SiO_{2-(700)}$], respectively, which is much faster than this obtained for [**2a**-Ph/$SiO_{2-(700)}$] (3 h). Conversely, the initial turnover frequencies increase to 0.5 [**2b**-Ph/$SiO_{2-(700)}$] and 1.2 [**2c**-Ph/$SiO_{2-(700)}$] from 0.05 s^{-1} for [**2a**-Ph/$SiO_{2-(700)}$]. Note that these performances are far better than those obtained for [$(R_{F6}O)_2Mo(\equiv NAr)(=CHCMe_2Ph)$] (**4**) and **1d**-Ph (Figure S7). In fact, EO is still equilibrated with only 0.02% of [**2c**-Ph/$SiO_{2-(700)}$] in 8 h.

In conclusion, the silica supported 2,5-dimethylpyrrolyl family of silica supported Mo imido alkylidene complexes constitutes the most efficient d^0 olefin metathesis developed so far, which can be prepared in two steps from the readily available triflate derivatives. We have shown in this preliminary account (1) that having methyl substituents on the pyrrolyl ligand in position 2 and 5 improves the stability of the system and (2) that the activity of the catalyst can be increased by tuning the imido substituents: 2-CF_3-C_6H_4 (**1c**-Ph) is best for EO (cat. loading as low as 0.02%) and Ad (**1b**-Ph) for propene metathesis (TON = 231 000 in 1500 min), respectively. While we are currently looking for optimal imido ligands, we believe that these supported systems have already reached catalytic performances compatible with their use in fine chemical synthesis, and we are currently further exploring the scope of these systems.

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Supporting Information Available: Full experimental details, Table S1 and Figure S1−S14. This material is available free of charge via the Internet at http://pubs.acs.org.

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