A new heterogeneous metathesis catalyst: preparation and activity of a highly active catalyst for the metathesis of pent-2-ene

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Very promising heterogeneous metathesis catalysts are developed based on aryloxy tungsten complexes anchored on a NbO_x/SiO_2 support; upon activation with Bu^iAlCl_2, highly active and long-lived systems are formed; the nature of the aryloxy ligands affects the activity of the system.

Aryloxycarbene tungsten complexes are highly active and well characterized homogeneous catalysts. In the past few years, it has been shown that some neopentylidene–tungsten(VI) complexes with alkoxide,[1,2] imido,[2] or aryloxide ligands[3] are efficient homogeneous metathesis catalysts. Aryloxides prove to be particularly useful ligands since their steric and electronic properties can be varied substantially by changing the number, the nature and the position of the substituent(s) on the aryloxide ligands.

On the other hand Weiss and Lössel[4] synthesized heterogeneous catalysts *via* protonation of the corresponding tungsten alkylidyne complexes by Brønsted acids [eqn. (1), HX represents ≡Si–OH].

$$W(CCMe_3)(OCMe_3)_3 + 2\ HX \rightarrow W(CHCMe_3)X_2(OCMe_3)_2 + Me_3COH \quad (1)$$

Electron-withdrawing ligands, crucial for good catalytic activity,[1,5,6] are provided here by the surface siloxy groups. Buffon *et al.*[7] extended this concept using Nb_2O_5 as a support. Nb_2O_5 is characterized by a stronger surface Brønsted acidity[8] but its specific surface area is much lower than that of silica.

In this study we report the synthesis of a high surface area NbO_x/SiO_2 support with a high Brønsted acidity. On this support we have anchored the aryloxytungsten complexes $WCl_4(OC_6H_3Bu^t{}_2\text{-}2,6)_2$ and $WCl_4(OC_6H_3Br_2\text{-}2,6)_2$.

For the preparation of this novel support, silica (Polypor, specific surface area = 345 $m^2\ g^{-1}$) was preheated at 473 K for 2 h under vacuum to control the OH concentration to 5 OH nm^{-2} (nearly complete monolayer). A hexane solution of $Nb(OEt)_5$ was added and the suspension refluxed for 1 h under a dry argon atmosphere.[9,10] After separation of the residual solution, the modified SiO_2 was washed with hexane three times, under an inert atmosphere, to remove unreacted $Nb(OEt)_5$. Heating at 473 K for 1 h under vacuum completes the reaction. Thereafter a treatment with aqueous ammonia (1 mol dm^{-3}) converts the Nb–OEt moieties to $Nb–O^-NH_4^+$ species. The ammonium cations are decomposed at 473 K under vacuum and the sample was then treated with 5 cm^3 double distilled water. In this way an SiO_2 support covered by a niobic acid monolayer was obtained.

The attachment of the aryloxy tungsten complexes, to obtain the heterogeneous tungsten precursors, was performed by heating the modified NbO_x/SiO_2 support at 200 °C for 2 h to remove the physically adsorbed water and liberate the acquired Lewis and Brønsted acid sites. The aryloxy tungsten complexes[11] were dissolved in *n*-hexane and added to the NbO_x/SiO_2 support. During the reflux for 2 h under a continuous argon flow, a drastic colour change was observed for both the support and the solution, and HCl was detected.

The catalytic activity towards alkene metathesis of the $WCl_4(OC_6H_3X_2\text{-}2,6)_2/NbO_x/SiO_2$ (X = Br or Bu^t) precursor activated by Bu^iAlCl_2 has been studied with pent-2-ene (*cis* + *trans*) as a model substrate.

In a typical experiment, the $WCl_4(OC_6H_3X_2\text{-}2,6)_2/NbO_x/SiO_2$ (X = Br or Bu^t) precursor (50 mg) was introduced into the reactor under argon and activated with 0.1 cm^3 Bu^iAlCl_2 (2.72 mol dm^{-3}) in dry, oxygen-free PhCl (4.5 ml). The substrate, pent-2-ene, is added after activation for 5 min.

$$\underset{\text{pent-2-ene}}{2MeCH{=}CHCH_2Me} \rightleftharpoons \underset{\text{but-2-ene}}{MeCH{=}CHMe} + \underset{\text{hex-3-ene}}{MeCH_2CH{=}CHCH_2Me} \quad (2)$$

At room temp. 500 equiv. of pent-2-ene was equilibrated within 5 min [eqn. (2)]. Isolation by filtration of the active species and addition of another 500 equiv. of pent-2-ene, led to reproduction of the initial reaction rate. In this way up to 2500 equiv. of pent-2-ene can be metathesised (Fig. 1).

On separation and drying under reduced pressure, the heterogeneous catalyst can be stored for weeks at room temperature under an inert atmosphere without any substantial

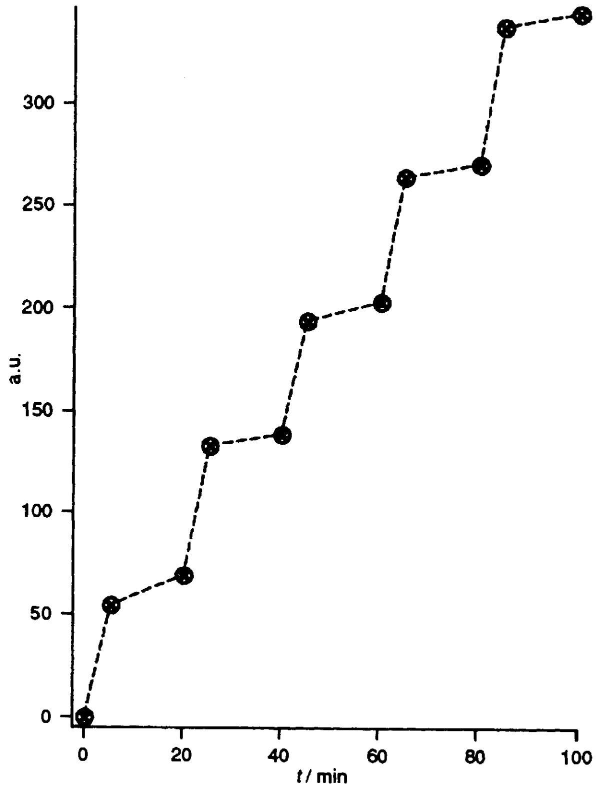

Fig. 1 Metathesis (a.u. = arbitrary unit) of pent-2-ene with the $WCl_4(OC_6H_3Bu^t{}_2\text{-}2,6)_2/NbO_x/SiO_2/Bu^iAlCl_2$ heterogeneous system

Table 1 Comparison of the heterogeneous tungsten phenoxide catalysts to the homogeneous tungsten phenoxide analogues

Catalyst	Mol alkene/ atom W	Al/W	Butene yield (mol%)[e]	Equilibrium time	Ref.
A $WCl_4(OC_6H_3Br_2\text{-}2,6)_2/NbO_x/SiO_2$[a]	500	28	25	<5	this work
B $WCl_4(OC_6H_3Bu_2^t\text{-}2,6)_2/NbO_x/SiO_2$[a]	500	28	23	<5	this work
C $WCl_4(OC_6H_3Cl_2\text{-}2,6)_2$[b]	360	42.8	21.7	20	14
D $WCl_4(OC_6H_4Cl\text{-}4)_2$[b]	50	6	2.2	300	14
E $WCl_4(OC_6H_3Br_2\text{-}2,6)_2$[b]	360	21.4	24.3	30	14
F1 $W(=CR^1R^2)R^3X(OC_6H_3F_2\text{-}2,6)$[c]	100	—	20	20	15
F2 $W(=CR^1R^2)R^3X(OC_6H_3Ph_2\text{-}2,6)$[c]	100	—	≈1.6	55	15
F3 $W(=CR^1R^2)R^3X(OC_6H_3Cl_2\text{-}2,6)$[c]	100	—	17.5	55	15
G $WCl_6 + SnMe_4$[d]	100	—	6.6	55	15

[a] At room temp., cocatalyst Bu^iAlCL_2. [b] At room temp., cocatalyst $EtAlCl_2$. [c] At 85 °C, no cocatalyst; R^1 = alkyl, $R^2 = R^3$ = H or alkyl, X = halogen. [d] At 85 °C. [e] Butene yield (mol%) after 5 min.

loss of activity. These are clear indications for a highly active and long-lived catalytic system.

The nature of the phenoxy ligands $–OC_6H_3Br_2$-2,6 and $–OC_6H_3Bu^t$-2,6, with different electronic and steric properties, has a moderate influence on the catalytic activity towards pent-2-ene. The initial rates for both are quite similar while the bromophenoxy species reaches a virtual higher conversion.

These results indicate that the aryloxide ligands are useful not only in homogeneous catalytic systems but also for heterogeneous catalysis. In general, aryloxide ligands with electron-withdrawing substituents in the 2,6 positions, increase the electrophilic character of the tungsten centre. This electrophilic increment will promote the initial step in metathesis processes, *i.e.* the coordination of olefins to the W=C bond.

The electrophilic character of the tungsten centre decreases for aryloxide ligands with electron releasing substituents in the 2,6 positions. This is in agreement with the results of Schrock[12] and Osborn *et al.*[13] where metathesis-inactive carbene tungsten(VI) complexes have been activated by the addition of Lewis acids or by substitution of electron-donating ligands by strongly electron-withdrawing perfluoroalkoxy or imido ligands. Furthermore, the 2,6 di-*tert*-butylaryloxide ligand also affects the tungsten centre sterically. This results in a further decrease of the ease of alkene addition to the active site.

If we compare these heterogeneous tungsten phenoxide catalysts with the homogeneous tungsten phenoxide analogues (Table 1) it can be seen that catalysts A and B show reaction rates which are considerably increased in comparison to the homogeneous systems. Equilibrium is attained within 5 min for catalysts A and B, after 10 and 30 min for catalysts C and E, and after 55 min for catalysts F and G while 300 min are required for catalyst D.

Catalysts A and B are particularly interesting due to the rapid speed of the metathesis. The fact that these new heterogeneous systems can convert up to 2500 equiv. without any reduction in rate makes them ideally acceptable industrially.[16]

The exceptional catalytic properties are due to the unique combination of immobilized tungsten phenoxy moieties on a niobic acid monolayer supported on silica. The chemical link between Nb and W, probably *via* a Nb–O–W bond, modulates the coordination sphere of tungsten in such a way that the metathetic process is optimized.

Fine tuning of the catalytic activity for specificity towards special substrates can be performed by directed choices of substituents on the phenoxy ligands.

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