



Synthesis of an oxo trialkyl tungsten fluoride complex and its dual reactivity with silica dehydroxylated at high temperature

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ARTICLE INFO

Article history:

Received 14 March 2018

Accepted 20 May 2018

Available online 22 May 2018

Keywords:

Olefin metathesis

Surface chemistry

Catalysis

Tungsten

Oxo ligand

Fluorine ligand

ABSTRACT

The novel complex $W(=O)Np_3F$ has been prepared by fluorination of the corresponding chloride counterpart with $AgBF_4$. The reactivity of this complex with silica dehydroxylated at 700 °C afforded a well-defined silica supported monopodal tungsten oxo trialkyl surface species $(\equiv SiO)W(=O)Np_3$. The reaction proceeds both through silanolysis of the W-F bond and opening of a siloxane bridge, with formation of a Si-F fragment, thanks to the affinity of silicon for fluoride. The resulting surface species was characterized by elemental analysis, DRIFT, solid state NMR and EXAFS spectroscopy. This material presenting fluorine on its surface shows an enhanced catalytic activity in propylene self-metathesis compared to its monopodal counterpart $(\equiv SiO)W(=O)Np_3$ (prepared from $W(=O)Np_3Cl$) suggesting that the Si-F in a close vicinity to the W decreases the electron density of the W and thus increases its reactivity towards the olefinic substrate.

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1. Introduction

The industrial olefin metathesis catalysts WO_3/SiO_2 discovered in the 1960's was put into operation less than a decade after in the multi-ton Phillips Triolefin Process, which converts propylene into ethylene and butene, and is still a source of intense research interest [1,2]. This is mainly driven by the high economic impact of the reverse reaction commercialized as ABB Lummus Olefins Conversion Technology[®], due to propylene shortage combined to the high abundance of ethylene from shale gas cracking. A noticeable number of recent publications are dedicated to the elucidation of

the nature of the active sites [3–6]. Evidences are pointing towards an isolated bipodal tungsten oxo carbene surface species arising from a bipodal tungsten bis oxo sites by a pseudo Wittig reaction, even if an alternative mechanism involving a reduction of the metal center cannot be ruled out [5]. The inherent difficulty for studying these systems is due not only to their heterogeneity, but also to the fact that among the different species present on the surface of the catalyst classically prepared by wetness impregnation, only a small fraction of the metal centers is active in olefin metathesis [3,4,7]. To overcome this difficulty, we rely on the surface organometallic chemistry strategy, which leads to well defined single atoms surface species by reacting organometallic precursors with silica surface silanol group and by entering directly into the catalytic cycle, or its immediate precursor [8]. The podality of the resulting surface species is usually dependent on the silanol concentration, which is controlled by the temperature used during the partial dehydroxylation of the silica used as support. Using this methodology, we have reported the preparation of well-defined monopodal tungsten oxo alkyl species amenable to carbene formation [9–12]. Then, the

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same approach has further led to the preparation of the first bipodal tungsten oxo bis alkyl species as well as the unprecedented selective synthesis of the bipodal bis oxo tungsten surface species $(\equiv\text{SiO})_2\text{W}(\text{=O})_2$, a postulated precursor to the active sites [13,14]. These systems, which are realistic models of the industrial catalyst, show sustained activity in olefin metathesis. A further increase of the activity was achieved by the preparation of molybdenum analogues or by the modification of the supported tungsten oxo tris alkyl species with one equivalent of phenol, in particular with electron withdrawing fluorinated phenol [15–17].

In light of these results, we were interested in replacing the pending neopentyl ligand with an even more electron withdrawing group as increased electrophilicity of the metal center is often correlated to improved catalytic activity [18]. As we targeted $(\equiv\text{Si-O})\text{W}(\text{=O})(\text{Np})_2(\text{X})(\text{Np} = -\text{CH}_2^t\text{Bu})$ surface species as precursor to tetrahedral $(\equiv\text{Si-O})\text{W}(\text{=O})(-\text{CH}^t\text{Bu})(\text{X})$, a selective and irreversible grafting reaction with the silica surface silanols was necessary. This ruled out the use of chloride and alkoxide derivatives, as we have already demonstrated that the chlorine and alkoxyde react with silanol groups [10,11,13,14,17]. We considered to reach our objective through grafting of the fluoride complex $\text{W}(\text{=O})\text{Np}_3\text{F}$ (**1**) as W-F are expected to be more stable toward protonolysis and hence would favor tungsten-alkyl silanolysis as the only reaction between the molecular precursor and the silica support (Scheme 1).

Along these lines, we disclose here the synthesis, characterization and grafting of the new complex $\text{W}(\text{=O})\text{Np}_3\text{F}$ (**1**), giving $1/\text{SiO}_2-700$ which has also been fully characterized. The generated surface species demonstrated outstanding catalytic performances in propene metathesis without addition of a Lewis acid activator. Remarkably, as expected from previous related SOMC examples, mere exposure to the olefinic substrate is shown to trigger the generation *in situ* of the active carbene species.

2. Results and discussion

Molecular precursor **1** has been synthesized in high yield (95%) from the known chloride analogue following a two-step, one-pot procedure developed for the synthesis of a related species $(\text{W}(\text{=N}(2,6\text{-}^i\text{PrC}_6\text{H}_3))(\text{Np})_3(\text{F}))$. AgBF_4 -mediated chloride abstraction afforded the BF_4 adduct from which BF_3 was extracted upon addition of an excess of triethylamine [19]. Raman spectrum displays a characteristic sharp $\text{W}=\text{O}$ stretching band at 975 cm^{-1} (Fig. 1 and Fig S1). ^1H NMR features of **1** are indicative of C_{3v} geometry, as the reported $\text{W}(\text{=O})(\text{Np})_3\text{X}$ derivatives ($\text{X} = \text{Cl}, \text{Br}, \text{ONp}$) [20,21]. This is evidenced by the doublet observed at 2.13 ppm for the methylenic protons coupled to the fluoride ligand ($^3J_{\text{H-F}} = 8.6\text{ Hz}$), with satellites due to coupling to the tungsten center ($^2J_{\text{H-W}} = 10.1\text{ Hz}$). Noteworthy, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum shows a multiplet centered at 94.9 ppm with the expected W satellites ($^1J_{\text{C-W}} = 46\text{ Hz}$, $^2J_{\text{C-F}} = 6.3\text{ Hz}$), accounting for the methylenic carbons. The $^{19}\text{F}\{^1\text{H}\}$ NMR spectrum consists in a singlet with the ^{183}W satellites centered at -0.6 ppm ($^1J_{\text{F-W}} = 82.2\text{ Hz}$) (Fig. S2). Elemental analysis,

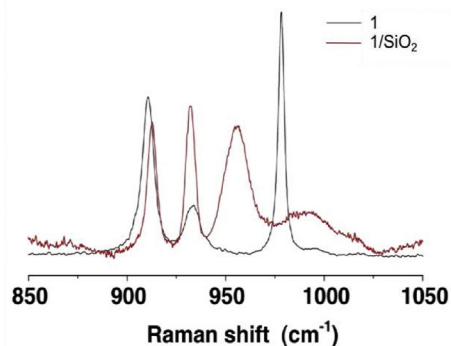
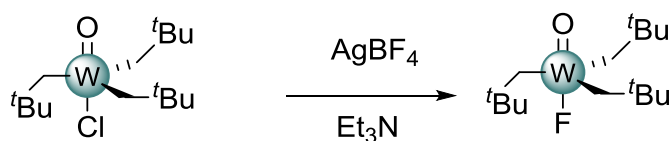


Fig. 1. Raman spectrum of **1** and $1/\text{SiO}_2-700$.

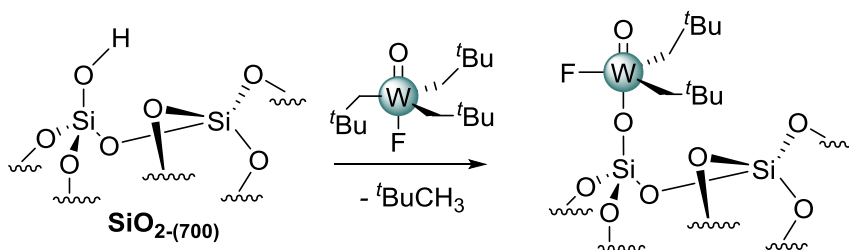
revealing 4.72 wt% of fluorine also corroborates the formation of the fluorinated complex (See Scheme 2).

1 was reacted with silica dehydroxylated at 700°C (SiO_2-700), which solely bears isolated silanol groups on its surface, a prerequisite for the targeted selective formation of monosiloxide surface species intermediate. Grafting proceeded efficiently, as demonstrated by consumption of the isolated silanol signal (at 3747 cm^{-1}). We noted that there is still a significant amount of interacting SiOH with alkyl groups (peak centered at 3700 cm^{-1}) on the infrared spectrum of the resulting material $1/\text{SiO}_2-700$. Simultaneously, the stretching and deformation signals of alkyl groups ($2990\text{--}2800\text{ cm}^{-1}$ and $1460\text{--}1480\text{ cm}^{-1}$, respectively) appeared (Fig. 2). ICP-AES analyses indicate a W loading of 4.43 wt%, and 4.27 wt% of carbon. The C/W ratio of 14.7 is close to the theoretical value of 15.0 for $(\equiv\text{Si-O})\text{W}(\text{=O})\text{Np}_3$. Quantitative gas phase analysis by GC indicates the formation of only traces of neopentane. This result is comparable to the grafting of the chlorine analogue $\text{W}(\text{=O})\text{Np}_3\text{Cl}$, **2**, where only traces of neopentane have been observed. The only difference relies in the tungsten loading which is higher in the case of the fluorinated analogue ($1/\text{SiO}_2-700$: 4.43 wt%, $2/\text{SiO}_2-700$: 4.02 wt%).

As shown in Fig. 1 and Fig. S2, the Raman spectrum of $1/\text{SiO}_2-700$ is quite similar to the one of the molecular precursor **1**. The modes related to neopentyl groups vibrations, detected at 905 and 935 cm^{-1} in **1**, encounter significant changes in intensity, while their frequency is only slightly affected upon grafting. On the other hand, after grafting on silica, the band at 975 cm^{-1} in **1** attributed to



Scheme 2. Synthesis of **1** by fluorination.



Scheme 1. Grafting strategy of **1** onto silica 700.

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