

Electronic Supplementary Information

Well Defined Silica Supported bipodal Molybdenum Oxo Alkyl Complexes: Model of the Active Sites of Industrial Olefin Metathesis Catalyst

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General Procedure. All experiments were carried out using standard air-free methodology in an argon-filled glovebox, on a Schlenk line or in a Schlenk-type apparatus interfaced to a high-vacuum line (10^{-5} Torr). Grafting is performed in double Schlenk flask that allows filtration through sintered frits. In this apparatus solvent can be redistilled on the grafted oxide side, and thus further washing can be carried out avoiding use of fresh solvent. Solvents were purified and dried according to standard procedures.

Elemental analyses were performed at Mikroanalytisches Labor Pascher. Gas-phase analyses were performed on a Hewlett-Packard 5890 series II gas chromatograph equipped with a flame ionization detector and HP5 column (30 m \times 0.32 mm).

Diffuse reflectance infrared spectra were collected in a Nicolet 6700 FT-IR spectrophotometer in 4 cm^{-1} resolution. An air-tight IR cell with CaF_2 window was applied and the final spectra comprise 64 scans.

Solution NMR spectra were recorded on an Avance-300 Bruker spectrometer. All chemical shifts were measured relative to residual ^1H or ^{13}C resonances in the deuterated solvent: C_6D_6 , δ 7.16 ppm for ^1H , 128.06 ppm for ^{13}C . ^1H and ^{13}C solid-state NMR spectra were recorded on Brüker Avance-500 spectrometers with a conventional double-resonance 4 mm CP-MAS probe. The samples were introduced under argon in a zirconia rotor (4 mm), which was then tightly closed. In all experiments, the rotation frequency was set to 10 kHz. Chemical shifts were given with respect to TMS as external reference for ^1H and ^{13}C NMR. MoONp_3Cl was prepared according to the literature.

For these ESR Characterizations and measurements, a sample was loaded in a 4 mm quartz tube in a glovebox. ESR spectra were recorded at room temperature and at 77 K on a Varian E9 spectrometer at ENS-Lyon (Ecole Normale Supérieure, Lyon) and compared to a vanadyl sulfate standard recorded under the same conditions. After a double integration of both signals, the amount of Mo(V) species could be estimated.

Preparation of SiO₂-200. Aerosil silica from Evonik with a specific area of 200 m².g⁻¹, was partly dehydroxylated at 200 °C under high vacuum (10⁻⁵ Torr) for 15 h to give a white solid having a specific surface area of 190 m².g⁻¹ and containing 2.6 OH.nm⁻².

Preparation of Mo(=O)(CH₂^tBu)₃Cl/SiO₂-200

A mixture of finely ground Mo(=O)(CH₂^tBu)₃Cl^[S1] (120 mg, 0.33 mmol) and SiO₂-200 (1 g) were stirred at 25 °C under dynamic vacuum for 4 h, whereas all volatile compounds were condensed into a cold trap. Pentane was then added and the solid was washed 5 times. The resulting white powder was heated under vacuum (10⁻⁵ Torr) at 80 °C for 16 h. Analysis by infrared spectroscopy of the condensed volatiles indicated the formation of 0.22 mmol of HCl during the grafting. Elemental anal.: %Mo = 2.38 wt%, %C = 1.56 wt%, C/Mo = 5.2; ¹H MAS NMR (500 MHz) δ 2.6, 1.1 ppm. ¹³C CP MAS NMR (125 MHz) δ 86.7, 35.4, and 30.6 ppm.

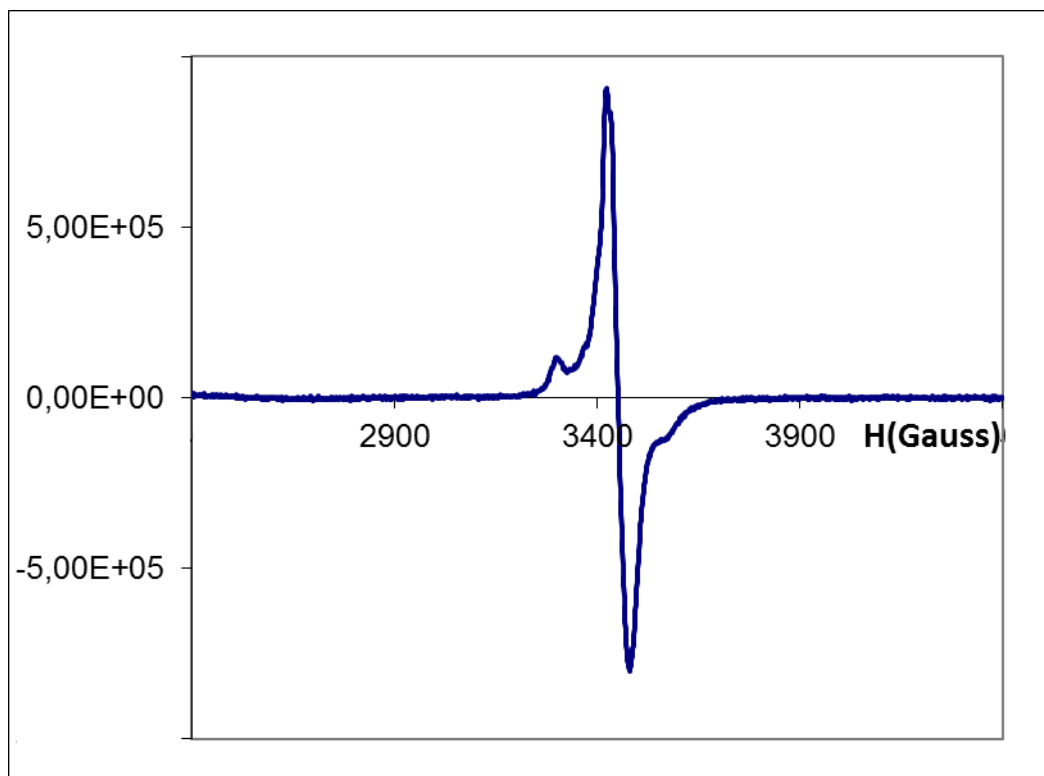


Fig. S1: ESR spectrum of the sample obtained after the grafting of $\text{Mo(O)Np}_3\text{Cl}$ on $\text{SiO}_2\text{-200}$ followed by a thermal treatment at $80\text{ }^\circ\text{C}$.

Catalytic tests

General procedure. In the glove box, 2000 equivalents of the substrate were added to a vial containing 10 mg of the supported catalyst suspended in 10 ml of toluene and tetradecane as internal standard preheated at the desired temperature using a sand bath and stirred at 600 rpm. After 4h the reaction was quenched using wet toluene outside the glovebox. The product solution was filtrated to remove the catalyst and the remaining liquid product was analyzed by GC-FID and GC-MS. The conversion was determinate from product formation without taking into consideration substrate cis/trans isomerization.

Ethyl oleate self-metathesis. In the glove box, ethyl oleate (2000 equivalents) was added to a vial containing a teflon coated stirrer bar, 20 mg of the supported catalyst suspended in 10ml of toluene and tetradecane as internal standard preheated at $60\text{ }^\circ\text{C}$ using a sand bath. $20\text{ }\mu\text{l}$ aliquots were sampled and diluted in $100\text{ }\mu\text{l}$ of wet toluene. The resulting solution were analyzed by GC.

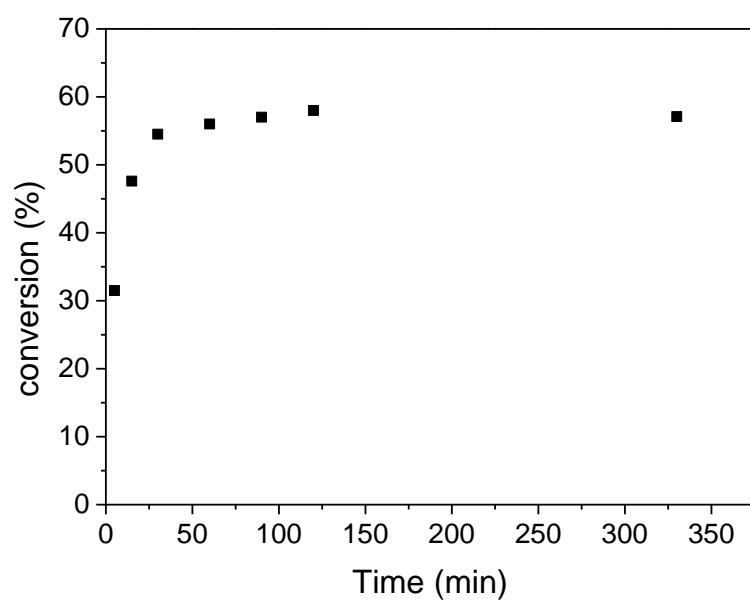


Fig. S2: Conversion of Ethyl oleate self metathesis (2000 equivalents/Mo) over $2/\text{SiO}_2\text{-200}$ (■)

[S1] J. R. M. Kress, M. J. M. Russell, M. G. Wesolek, J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1980,**0**, 431-432.