Olefin Metathesis Catalyzed by a Novel Surface Vanadium-Alkylidene

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Catalysts that break and form carbon-carbon double bonds are essential for producing fuels, plastics, and other chemical products. Olefin metathesis is a powerful reaction that enables this chemistry. While highly effective catalysts based on molybdenum and tungsten are known, developing systems based on more earth-abundant metals remains an important challenge. In this work, researchers developed a new catalyst based on vanadium, an earth-abundant transition metal, that promotes olefin metathesis when immobilized on a silica surface.

The team prepared the catalyst by attaching a molecular vanadium complex to silica using surface organometallic chemistry (SOMC), which anchors molecular catalysts onto solid supports while preserving their structure. Because these surface species cannot be studied using conventional solution techniques, the researchers used high-field magic-angle spinning solid-state nuclear magnetic resonance spectrscopy (MAS ssNMR) at the Advanced Magnetic Resonance Imaging and Spectroscopy Facility, a branch of the National High Magnetic Field Laboratory. These measurements confirmed the key vanadium-alkylidene active site, marking the first ssNMR characterization of this catalyst, and showed that immobilization greatly improved catalytic activity for olefin metathesis.

This work advances efforts to develop catalysts based on earth-abundant metals for reactions traditionally dominated by heavier transition metals and highlights how MAS ssNMR can reveal the structures of complex catalytic materials.

Facilities and instrumentation used: AMRIS Facility: 600 MHz Bruker Avance Neo spectrometer with a 4.0 mm MAS, variable temperature probe.

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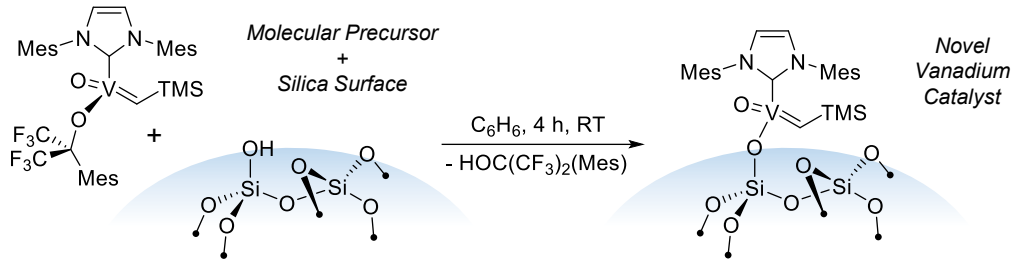
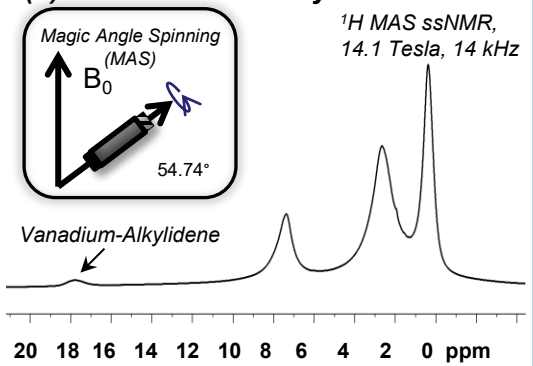
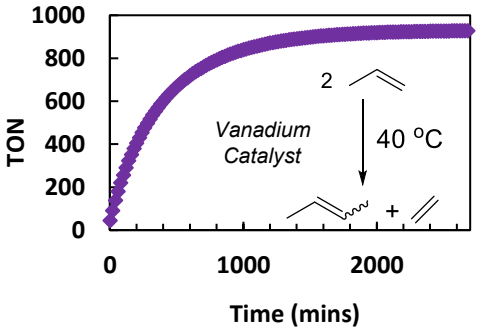
(a) Immobilization of Vanadium-Alkylidene Catalyst on Silica Surface



(b) Characterization by MAS ssNMR



(C) Catalytic Activity in Olefin Metathesis



(a) Reaction schematic of the precursor molecule with the silica to produce a vanadium alkylidene catalyst bonded to the surface via an oxygen bridge.
(b) ^{1}H MAS NMR spectroscopy is used to confirm the formation of vanadium-alkylidene, observable at 18 ppm.
(c) The novel V-Si catalyst produced a TON (Turnover Number, the ratio of product to catalyst) of 950