

## Methyltrioxorhenium Encapsulated in Zeolite Y: Tunable Olefin Metathesis Catalyst

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We report the encapsulation and structure of methyltrioxorhenium (MTO) in different zeolite hosts, and the activity of the resulting hybrid catalysts for olefin metathesis. The remarkable chemistry and catalytic behavior of rhenium oxo complexes such as MTO have been thoroughly studied by the group of Herrmann and others.<sup>1,2</sup> This exciting family of organometallics exhibits versatile catalytic behavior: olefin metathesis (without Lewis acid cocatalyst and alkylating agent when supported on Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>),<sup>3</sup> polymerization, and oxidation reactions<sup>4</sup> of olefins and other substrates have been reported. The structural features of MTO in zeolite Y determined in this study essentially confirm those reported recently.<sup>5</sup>

Metathesis is attractive because it is a clean equilibrium reaction from which undesired products may be recycled, it is almost thermoneutral, allowing the use of high reactant concentrations, and no metal salts are produced.<sup>6</sup> Rhenium heptoxide/alumina/SnR<sub>4</sub> catalyst combinations are commonly applied in metathesis reactions, but the active species is unknown.<sup>7</sup> The new catalyst MTO is a very compact molecule and is therefore a promising candidate for encapsulation in both small- and large-pore zeolites. These hosts have the advantage of (i) adjustable, well-defined acidity and (ii) the potential for size- and shape-selective reactions. This study continues our exploration of the intrazeolite reactivity of organometallics.<sup>8</sup>

Methyltrioxorhenium, synthesized according to reported procedures,<sup>9</sup> and freshly sublimed at 60 °C/10<sup>-3</sup>

Torr before each use, was immobilized into several types of zeolite Y containing different proton concentrations. NaY (commercial Linde LZ-Y52 ([Na<sub>57</sub>Al<sub>57</sub>Si<sub>135</sub>O<sub>384</sub>]·235H<sub>2</sub>O), ammonium-exchanged/degassed HnY (*n*H<sup>+</sup>/supercage, sodalite cage), and highly acidic H6Y (6 H<sup>+</sup>/supercage, sodalite cage) from Linde LZ-Y62 ((NH<sub>4</sub>)<sub>45</sub>-Na<sub>10</sub>Al<sub>55</sub>Si<sub>137</sub>O<sub>384</sub>]·235H<sub>2</sub>O) were used. The hosts were calcined and degassed in high vacuum.<sup>10</sup> In a typical loading procedure for the EXAFS samples, 1.5 g of the host was stirred for 18 h with 50 mL of hexane containing 1 molecule of MTO/supercage of the host. The slurry was filtered and the product washed several times with pentane and then vacuum-dried. Selected samples were heated to 200 and 300 °C.

The rhenium concentrations in selected zeolite samples were determined with X-ray fluorescence spectroscopy, using mixtures of Re<sub>2</sub>O<sub>7</sub> with NaY zeolite as standards. These data show that about 60% of the MTO offered in solution is retained in the host after filtration, suggesting rather weak adsorption energies, in agreement with the observations discussed below.

Powder x-ray diffraction data show that the zeolite hosts maintain their crystallinity both after loading with MTO and after metathesis reactions.

Nitrogen sorption isotherms of a representative MTO–H2Y sample (2.6 wt % Re or about 0.2 MTO/zeolite supercage; degassed at 120 °C/10<sup>-5</sup> Torr for 12 h) show that the typical micropore isotherm shape is maintained after loading with complex, although the pore volume is slightly reduced.<sup>11</sup>

Raman spectra of MTO/H2Y, taken with HeNe excitation (ca. 2 mW at sample), show the two bands due to the Re=O stretch vibrations at about 1000 cm<sup>-1</sup>, as well as the Re–C stretch at 575 cm<sup>-1</sup>.<sup>12</sup> These data confirm that the intact complex is encapsulated in the zeolite.

The structural features of MTO and of MTO encapsulated in different hosts were determined with EXAFS spectroscopy at the Re edge.<sup>13</sup> The Fourier-transformed EXAFS spectrum of solid MTO confirms the expected structure. Fit results based on ReO<sub>4</sub><sup>-</sup> reference data show 3 oxygen atoms/Re at 1.70 Å, in addition to 1 carbon at 2.05 Å. No outer shell scattering is observed. When the complex is introduced into the neutral host NaY and into the partially exchanged host H2Y, no

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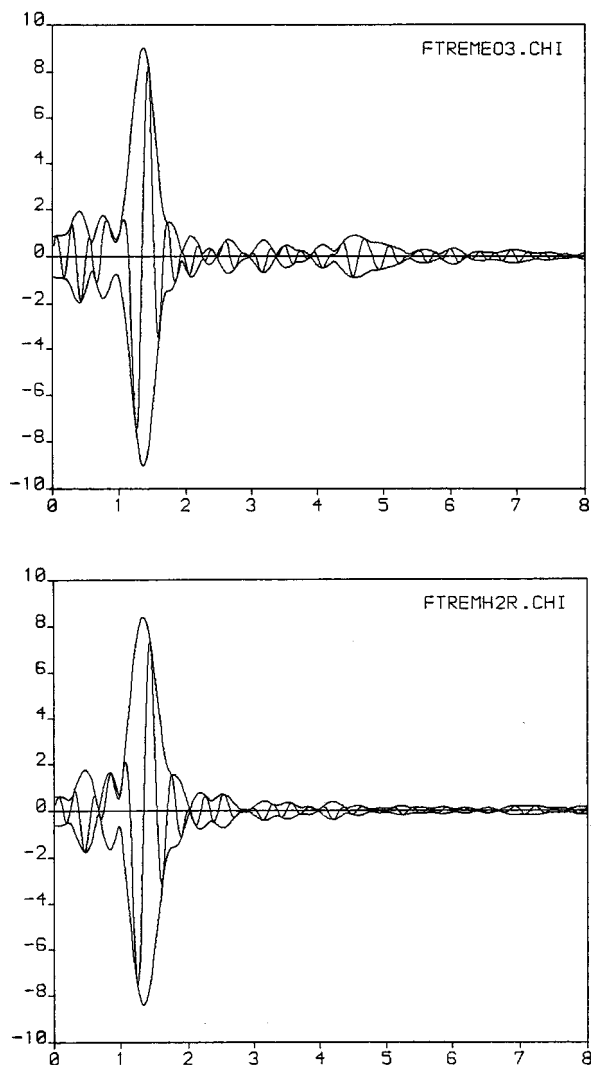
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(10) NaY was degassed by calcination in oxygen for 12 h at 400 °C, followed by evacuation at the same temperature for 6 h (10<sup>-5</sup> Torr; heating rate 1 °C/min). Heating the ammonium-exchanged zeolite under oxygen flow at 100 °C for 4 h and at 400 °C for 10 h and then under vacuum at the same temperature for 5 h (at a rate of 1 °C/min) resulted in the desired acid form.

(11) The micropore volume for calcined H2Y (0.26 cm<sup>3</sup>/g) decreases to 0.14 cm<sup>3</sup>/g on loading with MTO, and increases again to 0.20 cm<sup>3</sup>/g when the sample is calcined at 300 °C. The micropore volumes are slightly less than expected (both for the empty zeolite and based on the volume of the complex); residual solvent may still be trapped in the zeolite after degassing.

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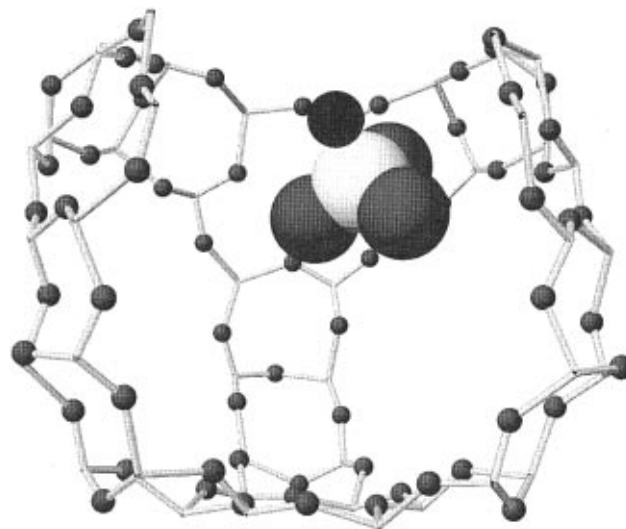


**Figure 1.** Fourier transformed EXAFS data of methyltrioxorhenium (MTO) samples. (A, top) MTO in solid form. (B, bottom) MTO in H<sub>2</sub>Y zeolite, room temperature adsorption.

significant changes in the coordination are observed, thus the MTO molecule including the methyl ligand is rather stable even in the moderately acidic forms (Figure 1). This was also observed by Ozin and Malek in their recent EXAFS study.<sup>5</sup> In the highly acidic form H<sub>6</sub>Y (6 protons total/supercage), there is some minor reactivity toward forming Re–Re bonded species already at room temperature. We note that these products become dominant when the samples are heated to 200–300 °C, and contain approximately one Re–Re bond at a distance of 2.6 Å (and new Re–O single bonds, Re–O at 2.0 Å), suggesting the formation of ReO<sub>2</sub>-type structures with Re-bridging oxygen ligands in a redox reaction.

The stability of the zeolite-encapsulated MTO complex (in the form of a thin layer of sample on a heatable Si wafer) was determined with temperature-programmed

(13) EXAFS measurements (in transmission, at ca. –170 °C) at the Re L<sub>III</sub> edge (10 531 eV) were carried out at NSLS (Brookhaven National Laboratories) at beamline X-11A with a stored energy of 2.5 GeV and ring currents between 100 and 200 mA. The powdered samples (ca. 10 mg) were mixed under nitrogen with degassed molten 1:1 octadecane/eicosane, sealed with Kapton tape in a thin aluminum holder, and kept under nitrogen until measurement. Re metal, KReO<sub>4</sub>, and MTO were used as references to extract phase shifts and backscattering amplitudes. The EXAFS data were analyzed using standard procedures, as described previously: Borvornwattananont, A.; Bein, T. *J. Phys. Chem.* **1992**, *96*, 9447.



**Figure 2.** Proposed surface attachment of intrazeolite MTO.

desorption mass spectrometry (TPD-MS), at a heating rate of 2 °C/min. We find a peak in methane evolution into high vacuum at 90 °C for MTO in H<sub>6</sub>Y and a peak at 150 °C for MTO in the NaY host. These observations show (i) that the methyl ligand on MTO is not lost during impregnation and (ii) that the acidic zeolite is significantly more reactive toward the MTO complex than the NaY host.

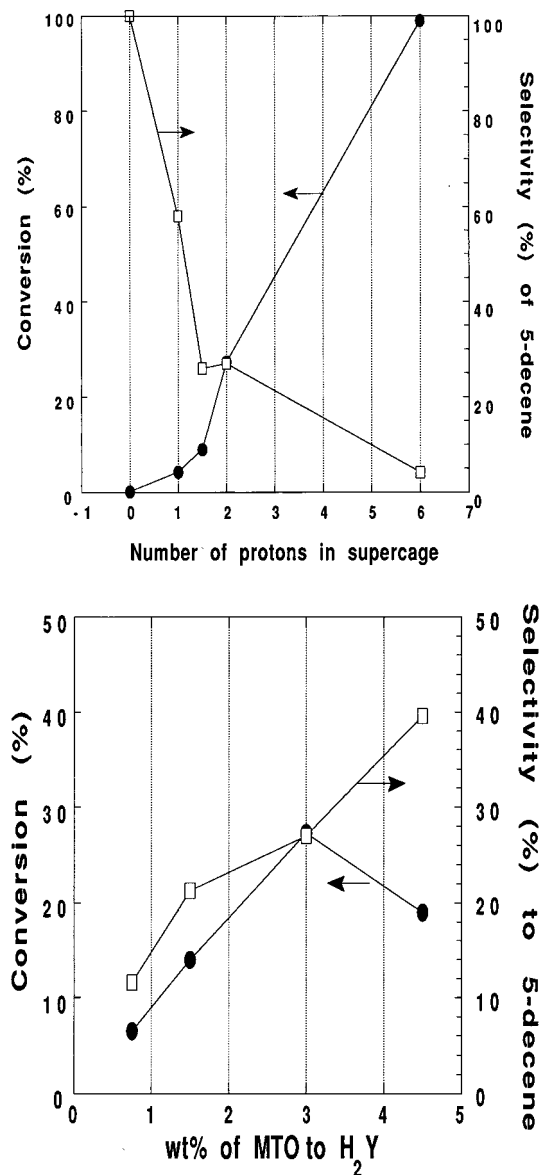
For the metathesis catalyst derived from MTO on Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>, it was suggested that MTO could be attached to two surface oxygens analogous to glycol complexes MeRe(O)<sub>2</sub>(OCR<sub>2</sub>CR<sub>2</sub>O),<sup>14</sup> but no structural evidence has been reported yet. A recent study shows that MTO can also catalyze olefin metathesis when adsorbed in Nb<sub>2</sub>O<sub>5</sub>.<sup>15</sup> The involvement of surface methylene species in the metathesis reaction was excluded. ESCA indicated the presence (of a minor fraction) of reduced Re as required in a  $\pi$ -allyl mechanism; however, the nature of the MTO–Nb<sub>2</sub>O<sub>5</sub> surface species is still unknown. The structural EXAFS data presented above exclude a significant degree of surface oxygen chelation, because it would require Re–O single bonds that are not detected at room temperature. We propose that surface hydrogen bonding to the terminal Re=O oxygen is the major activation mechanism of intact MTO in zeolites (Figure 2).

Metathesis studies<sup>16</sup> of 1-hexene on a series of Y zeolite hosts with different acidities establish (i) a profound effect of the zeolite acidity on metathesis vs double bond isomerization and (ii) an increase of metathesis yield with increasing loading of MTO in the moderately acidic H<sub>2</sub>Y host. Figure 3A shows the correlation of overall conversion of 1-hexene with the

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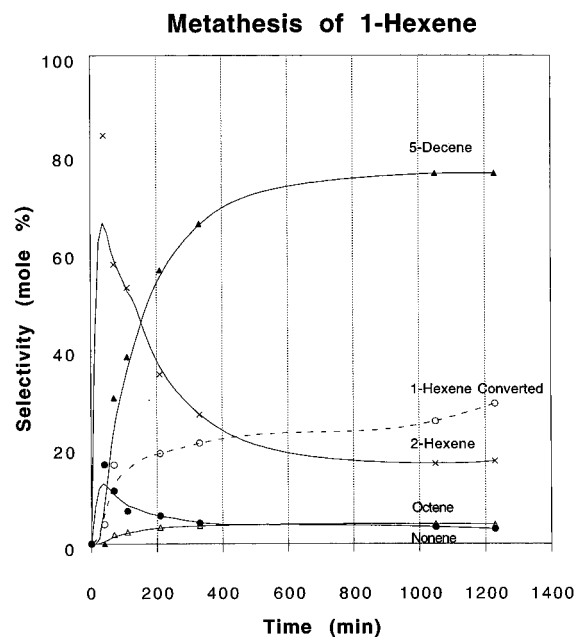
(16) In a typical experiment, 3.0 mL of 1-hexene (24 mmol) was added to a prestirred (for 10 min) solution of 0.45 g of synthesized MTO–H<sub>2</sub>Y catalyst (3 wt % of MTO, freshly sublimed, 0.054 mmol of MTO) and 0.5 mL of cyclohexane (internal standard) in 15 mL of dichloromethane. The reaction was kept stirring under nitrogen at room temperature (25 °C) for up to 20 h. The product distribution in the reaction mixture at different times was monitored with GC, by injecting 2  $\mu$ L each of syringe-filtered solution taken from the reaction vessel.



**Figure 3.** Metathesis reaction of 1-hexene on supported MTO zeolite Y catalysts (at 25 °C). In (A) a ratio of 0.020 g MTO/0.67 g of host (3 wt % MTO; 0.18 MTO per sc) was dissolved in 15 mL of methylene chloride, stirred for 1 h, and 2.5 mL of 1-hexene (20 mmol) were added, resulting in a molar ratio of olefin: MTO of 250:1. (A) Effect of acidity on conversion and metathesis selectivity after 2 h. (B) Influence of MTO loading on conversion and selectivity after 2 h.

Bronsted acidity of the MTO–zeolite catalyst (at the same loading level, see figure caption). Almost no reactivity is observed with MTO alone or with MTO–NaY. The selectivity toward the primary metathesis product 5-decene is highest at low acidity (60% with H1Y after 2 h) and drops to a few percent with MTO–H6Y, while isomerization activity increases with higher acidity (metathesis activity is higher than suggested by the 5-decene production because isomerization products also undergo metathesis).

The selectivity toward 5-decene, with the same host H2Y, strongly increases with the MTO loading, almost linearly from 10 to 40% when raising the loading to about 4 wt % (Figure 3B). This effect demonstrates that MTO can block the isomerization activity. One example of the evolution of conversion and 5-decene selectivity with time, of MTO in the H2Y host in Figure 4, shows the initial (acid catalyzed) activity toward isomerization to 2-hexene, followed by increasing production of the



**Figure 4.** Metathesis activity of MTO (2.56 wt %, 0.15 MTO/sc) in the H2Y host as a function of time, showing overall conversion and evolution of the product distribution. Conditions are similar to those in Figure 3A.

metathesis product 5-decene. The formation of 4-octene and 4-nonene is associated with metathesis of 2-hexene/1-hexene in the reaction mixture. The final selectivity toward 5-decene after 20 h reaches almost 80% of all products.

Additional experiments establish that no 1-hexene metathesis but rapid isomerization is observed with dry H6Y and H2Y zeolites alone (at 25 °C, after 4 h). Almost no reaction at all is observed with either the NaY zeolite, or with the MTO–NaY system. Several initial passivating experiments were performed.<sup>17</sup> Moderately sized PhSi(OMe)<sub>3</sub> (which can enter the zeolite pores and block acid sites) almost completely blocked hexene conversion, while the large silane Ph<sub>2</sub>Si(OEt)<sub>2</sub> reduced the activity of the catalyst to about one-half of its original value. These trends suggest that while the latter silane probably blocks the surface activity, a significant fraction of the catalytic activity is located inside the zeolite cage system.

In summary, the MTO molecule is activated by the intrazeolite protons, and simultaneously blocks their isomerization activity. The ability to tune intrazeolite acidity and the doping levels of the intact MTO pre-catalyst permit control over selectivity in metathesis reactions. In addition, the superb structural definition and molecular sieving capabilities of zeolite hosts offer great promise in future shape-selective catalyst designs. Work along these lines is in progress in this laboratory.

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(17) 2.0 mol of the passivating silane agent of C<sub>6</sub>H<sub>5</sub>Si(OCH<sub>3</sub>)<sub>3</sub> or (C<sub>6</sub>H<sub>5</sub>)<sub>2</sub>Si(OC<sub>2</sub>H<sub>5</sub>)<sub>2</sub> per supercage of zeolite was used in two separate reactions. The silane agent was first stirred with an MTO–H<sub>2</sub>Y (2.6 wt % MTO) catalyst in CH<sub>2</sub>Cl<sub>2</sub> for 30 min before starting the 1-hexene metathesis reaction as described above.