Available online at www.sciencedirect.com
SCIENCE DIRECT
Journal of Molecular Catalysis A: Chemical 243 (2006) 158–169
JOURNAL OF MOLECULAR CATALYSIS A: CHEMICAL
www.elsevier.com/locate/molcata

Catalytic oxidation of a thioether and dibenzothiophenes using an oxorhenium(V) dithiolate complex tethered on silica

Keith J. Stanger, Jerzy W. Wiench, Marek Pruski, James H. Espenson, George A. Kraus, Robert J. Angelici *

Ames Laboratory and Department of Chemistry, Iowa State University, Ames, IA 50011-3111, USA

Received 14 June 2005; received in revised form 13 July 2005; accepted 14 July 2005
Available online 23 September 2005

Abstract

A silica-tethered version of the oxorhenium(V) dithiolate oxidation catalyst [–S(CH_2)$_3$S–]Re(O)(Me)(PPh_3) was prepared and characterized by solid state ^{13}C and ^{31}P NMR spectroscopy. This tethered complex (SiO_2-RTA)Re(O)(Me)(PPh_3) (Fig. 2) catalyzes the selective oxidation of methyl(*p*-tolyl)sulfide (MTS), dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-Me_2DBT)) to their corresponding sulfoxides and sulfones by *tert*-butylhydroperoxide (TBHP) and can be recycled at least four times without loss in activity. Although the rate of oxidation catalyzed by the immobilized catalyst is about a factor of three times lower than the homogeneous analog [–S(CH_2)$_3$S–]Re(O)(Me)(PPh_3), the supported catalyst is much more long-lived achieving approximately 3000 turnovers in the oxidation of DBT at 100 °C. The immobilized catalyst effectively catalyzes the oxidation of DBT and the hindered 4,6-Me_2DBT to their sulfoxides or sulfones in simulated petroleum feedstocks.
© 2005 Elsevier B.V. All rights reserved.

Keywords: Immobilized metal catalysts; Tethered complexes; Oxidation; Rhenium; Dithiolates; Silica; Dibenzothiophene; Thioether

1. Introduction

The EPA has mandated by 2006 substantial reductions in the total sulfur content of gasoline and diesel fuels [1]. It is the refractory dibenzothiophenes not currently removed by the hydrodesulfurization (HDS) of petroleum feedstocks that will need to be eliminated in order to achieve this goal [2]. One approach to their removal is to oxidize the dibenzothiophenes to their sulfones, which have a low solubility in petroleum feedstocks [3–23]. For example, the sulfone of dibenzothiophene ($DBTO_2$) is an order of magnitude less soluble in octane than in octanol [6], and $DBTO_2$ precipitation from hydrophobic solvents during oxidation of DBT has been reported [7,8]. Therefore, oxidized organosulfur compounds can be removed from fuel feedstocks using various separation methods such as distillation, extraction or adsorption [3–23].

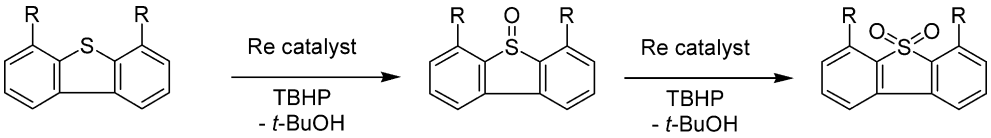
The oxidation of sulfides to sulfoxides and sulfones can be achieved by a variety of biological and chemical methods [24–27], and several groups have explored the possibility of using these methods to remove organosulfur compounds from fuel feedstocks [3–23]. A number of different catalysts (cytochrome *c* [6], metal-sulfophthalocyanine [9], phosphotungstic acid [7,10,11], formic acid [5,12], acetic acid [13], polyoxometalates [14], titanium silicate [15–17], vanadosilicates [18], magnesium lanthanide oxides [19], Mo/Al_2O_3 [20] and cobalt salts [21]) and oxidants (hydrogen peroxide [5,7,10–19], monopersulfate [9], cumene hydroperoxide [6], photooxidation [16], *tert*-butylhypochlorite [23], *tert*-butylhydroperoxide [20] and aldehydes [21]) have been examined, with the majority of work utilizing hydrogen peroxide as the oxidant. Since H_2O_2 is not soluble in hydrophobic petroleum feedstocks, reactions involving two or more phases are required. Such oxidations usually require an additional extraction step [3–7,9–20] (with polar solvents such as MeCN or H_2O) or adsorption step (silica [7,21], alumina [5], celite [6]) in order to remove the last vestiges of the oxidant,

* Corresponding author. Tel.: +1 515 294 2603; fax: +515 294 0105.
E-mail address: angelici@iastate.edu (R.J. Angelici).

1381-1169/$ – see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.molcata.2005.07.019

catalyst, spent oxidant or oxidation products from the fuel. One major disadvantage of all of these methods is the low solubility of the polar oxidizing agents in the hydrocarbon phase, which reduces their rates of reaction.

In order to avoid this problem, we have focused on catalysts that utilize the oxidant *tert*-butylhydroperoxide (TBHP), which is soluble in non-polar hydrocarbon solvents. Oxorhenium(V) dithiolate compounds, such as [–S(R)$_n$S–]Re(O)(Me)(PPh$_3$), are catalysts that use TBHP for the rapid and selective oxidation of organosulfur compounds to their sulfoxides or sulfones [8,29–38]. Of particular importance for the present studies is the oxorhenium(V) dithiolate-catalyzed oxidation of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-Me$_2$DBT) by TBHP at temperatures above 50 °C, Eq. (1) [8]. In order to improve the



R=H DBT
R=Me 4,6-Me$_2$DBT

(1)

usefulness of these catalysts, we sought to devise a synthetic strategy that would lead to catalysts composed of tethered rhenium catalysts on a silica support. Such catalysts are expected to have the advantages of both homogeneous (selectivity, tuneability and homogeneous sites) and heterogeneous (recovery and separation) catalysts [26–28]. In the present investigation, we compare the catalytic activity and reusability of the tethered rhenium catalyst, (SiO$_2$–RTA)Re(O)(Me)(PPh$_3$), with those of the analogous homogeneous catalyst for the oxidation of DBT, 4,6-Me$_2$DBT and methyl(*p*-tolyl)sulfide.

2. Experimental

2.1. General considerations

The chemicals *tert*-butylhydroperoxide (TBHP, 5–6 M solution in nonane), 3-chloropropyltriethoxysilane (RCl), 1,3-propanedithiol (pdt), 1,2-ethanedithiol (edt), DBT, 4,6-Me$_2$DBT, methyl(*p*-tolyl)sulfide (MTS), thioctic acid (TA), chloroform (CHCl$_3$), deuterated chloroform (CDCl$_3$) and silica gel (40–140 mesh) for column chromatography were purchased from commercial sources and used as received. Merck grade 10184 silica gel (B.E.T. surface area, 300 m^2 g^{-1}; pore size, 100 Å) (Aldrich) was dried under vacuum at 150 °C for 12 h and kept under argon before use. Toluene, hexanes and methylene chloride were dried prior to use by passage through an alumina column under argon [39]. Benzene was distilled from CaH$_2$ under nitrogen. The compounds 3-iodopropyltriethoxysilane (RI) [40] and (PhS)$_4$Re$_2$(O)$_2$(Me)$_2$ [41] were prepared according to literature methods. Gas chromatographic (GC) analyses were performed on a Hewlett Packard HP 6890 GC using a 25 m HP-5 capillary column at 190 °C and a flame ionization detector (FID).

Rhenium analysis of (SiO$_2$-RTA)Re(O)(Me)(PPh$_3$) was performed using inductively coupled plasma-mass spectrometry (ICP-MS). Rhenium was hydrolyzed from the silica support by heating 1.0 mg of the catalyst in 5.0 mL of hydrogen peroxide (39%) with 2.5 mL of 2% nitric acid (2% by volume of concentrated nitric acid in purified water) at 50 °C for 10 min [42]. The resulting solution was filtered and diluted to 25 mL in a volumetric flask. A 10-fold dilution of this solution with 2% nitric acid in a second 25 mL volumetric flask provided samples with rhenium analyses in the range of 100 ppb. These samples were analyzed on a HP 4500 ICP-MS with instrumental parameters adjusted to provide the optimal signal at 1200 W RF power. Working standards were diluted from a 1000 ppm Re stock standard solution. Relative standard deviations on individual samples were within ±5%.

^{1}H, ^{13}C and ^{31}P NMR spectra of liquid samples were run on a Bruker DRX spectrometer at 400.1, 100.6 and 161.9 MHz, respectively. Samples were dissolved in CDCl$_3$, CD$_3$OD, or C$_6$D$_6$ and placed in 5-mm glass tubes. Typically, 30° pulse and 1 s repetition rate were used for direct polarization experiments. ^{13}C and ^{31}P solid-state NMR experiments were carried out at the same frequencies using a Chemagnetics CMX 400 Infinity spectrometer. Samples were placed in 5-mm zirconia rotors and spun under the magic angle (MAS) at 9 kHz in a doubly tuned Chemagnetics probe. The cross polarization (CP) method was used to enhance magnetization of the observed nuclei and shorten the pulse delay [43]. To that end, a 90° pulse was applied at the ^{1}H resonance frequency to create the transverse magnetization, which was spin locked by continuous wave rf irradiation corresponding to the magnetic field of 35 kHz. At the same time, the rf magnetic field was applied at the ^{31}P (or ^{13}C) frequency, whose magnitude was ramped between 14 and 44 kHz using 2 kHz increments in order to increase the efficiency of polarization transfer [44]. The acquisition of ^{31}P (or ^{13}C) free induction decay was carried out under continuous wave ^{1}H decoupling at 65 kHz. All chemical shifts are reported using the δ scale, with positive values being downfield, and are referenced to an 85% solution of H$_3$PO$_4$ in water (^{31}P) or TMS (^{1}H and ^{13}C).

2.1.1. Preparation of ligands

(EtO)$_3$SiCH$_2$CH$_2$CH$_2$OC(O)CH$_2$CH$_2$CH$_2$CH$_2$CH(S–)CH$_2$CH$_2$(S–), RTA (Fig. 1): To a solution of 0.10 g

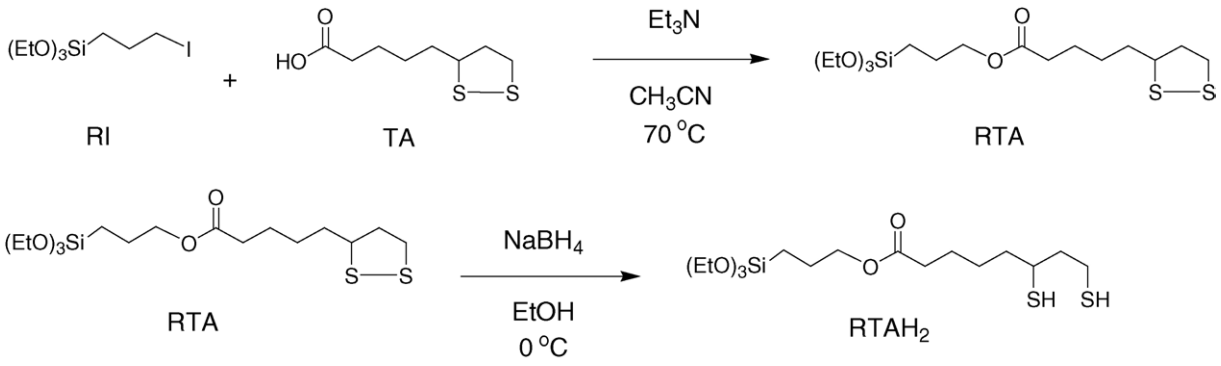


Fig. 1. Synthesis of RTA and $RTAH_2$.

(0.48 mmol) of TA dissolved in 5.0 mL of dry acetonitrile, 0.07 mL (0.5 mmol) of Et_3N and then 0.15 mL (0.45 mmol) of RI were added via syringe [45]. The reaction was refluxed under argon at 70 °C for 3 days. Upon cooling to room temperature, the reaction mixture was flash-column chromatographed (2.5 cm × 63 cm) on silica (40–140 mesh, untreated) with EtOAc:hexane (1:4). Fractions were monitored by silica TLC, and the RTA fraction was collected, $R_f = 0.25$. Yield 92 mg (50%) as a light yellow oil. ^{1}H NMR ($CDCl_3$): δ 4.00 (t, $J = 8.0$ Hz, 2H, $SiCH_2$–CH_2–$\underline{CH_2}O_2C$), 3.78 (q, $J = 8.0$ Hz, 6H, $SiO\underline{CH_2}CH_3$), 3.53 (m, 1H, CH), 3.12 (m, 2H, CH(S–)$\underline{CH_2}$$CH_2$(S–)), 2.42 (m, 1H, CH(S–)$CH_2\underline{CH_2}$(S–)), 2.3 (t, $J = 7.4$ Hz, 2H, O_2CCH_2), 1.88 (m, 1H, CH(S–)$CH_2\underline{CH_2}$(S–)), 1.7 (m, 6H, $O_2CCH_2\underline{CH_2}CH_2CH_2$, $O_2CCH_2CH_2CH_2\underline{CH_2}$ and $SiCH_2$–$\underline{CH_2}$–CH_2O_2C–), 1.4 (m, 2H, $O_2CCH_2CH_2\underline{CH_2}CH_2$), 1.19 (t, $J = 8.0$ Hz, 9H, $SiOCH_2\underline{CH_3}$), 0.60 (m, 2H, $SiCH_2$). ^{13}C NMR ($CDCl_3$): δ 173.7 ($\underline{C}O_2$), 66.5 ($SiCH_2$–CH_2–$\underline{C}H_2O_2C$), 58.5 ($SiO\underline{C}H_2CH_3$), 56.4 (CH), 40.2 (CH(S–)$CH_2\underline{C}H_2$(S–)), 38.5 (CH(S–)$\underline{C}H_2CH_2$(S–)), 34.6 ($O_2CCH_2CH_2CH_2\underline{C}H_2$), 34.1 ($O_2C\underline{C}H_2CH_2CH_2CH_2$), 28.8 ($O_2CCH_2CH_2\underline{C}H_2CH_2$), 24.7 ($O_2CCH_2\underline{C}H_2CH_2CH_2$), 22.3 ($SiCH_2$–$\underline{C}H_2$–$CH_2O_2C$), 18.3 ($SiOCH_2\underline{C}H_3$), 6.6 ($SiCH_2$). ^{13}C NMR assignments were made using COSY spectra and simulated spectra.

High resolution mass spectrometry. Anal. calcd. for $C_{17}H_{34}O_5S_2Si$: 410.16170. Found: 410.16265, deviation 2.3 ppm.

$(EtO)_3SiCH_2CH_2CH_2OC(O)CH_2CH_2CH_2CH_2CH(SH)CH_2CH_2SH$, $RTAH_2$ (Fig. 1): Solid $NaBH_4$ (8.8 mg, 0.23 mmol) was added to a solution of 80 mg (0.20 mmol) of RTA dissolved in 2.0 mL of dry ethanol at 0 °C and stirred at that temperature for 2 h under argon. The majority of ethanol was removed under vacuum. After the addition of 20 mL of 0.01 M HCl (aq.), the solution was extracted with 30 mL of CH_2Cl_2. After this solution was dried over $MgSO_4$, 62 mg (75% yield) of $RTAH_2$ was isolated by removal of CH_2Cl_2 under vacuum. The product was pure as indicated by its ^{1}H and ^{13}C NMR spectra. ^{1}H NMR (MeOH-d_4): δ 4.05 (t, $J = 6.9$ Hz, 2H, CO_2CH_2), 3.82 (q, $J = 7.2$ Hz, 6H, $SiO\underline{CH_2}CH_3$), 2.91 (m, 1H, CH), 2.67 (m, 2H, (CH(SH)$\underline{CH_2}CH_2$(SH)), 2.34 (m, 1H, (CH(SH)$CH_2\underline{CH_2}$(SH)), 2.0–1.4 (m, 13H, unspecified CH_2 groups and SH protons), 1.20 (t, $J = 7.2$ Hz, 9H, $OCH_2\underline{CH_3}$), 0.64 (m, 2H, $SiCH_2$). ^{13}C NMR (MeOH-d_4): δ 175.6 (–$\underline{C}O_2$), 67.6 ($CO_2\underline{C}H_2$), 59.6 ($SiO\underline{C}H_2CH_3$), 18.8 ($SiOCH_2\underline{C}H_3$), 7.5 ($SiCH_2$) and 44.4, 40.2, 39.9, 35.1, 27.7, 25.9, 23.5, 22.9 unassigned.

SiO_2-$RTAH_2$: A mixture of 0.50 g of SiO_2 and 0.12 g (0.29 mmol) of RTA were slurried together in 10.0 mL of dry toluene. The mixture was refluxed for 4 h and then stirred overnight at room temperature. The resulting solid was washed with 4 × 10 mL of toluene and dried under vacuum to give SiO_2-RTA. This solid was then treated with 0.30 g (7.9 mmol) of $NaBH_4$ in 5.0 mL of EtOH at 0 °C for 4 h. Addition of 40 mL of 0.01 M HCl (aq.), followed by filtration and washing the solid with 4 × 10 mL of H_2O and then 2 × 10 mL of EtOH gave after vacuum drying a white solid which was stored under argon prior to use.

2.1.2. Preparation of rhenium complexes

(pdt)Re(O)(Me)(PPh_3) ***(1)***: A mixture of 25.0 mg (57.4 μmol Re) of $(PhS)_4Re_2(O)_2(Me)_2$ and 15.0 mg (57.4 μmol) of PPh_3 were dissolved in 1.0 mL of chloroform, benzene or toluene. After stirring for 10 min at room temperature, 6.0 μL (60 μmol) of pdt was added to the green solution. After 8 h, the solvent was removed under vacuum; the resulting green solid was washed with hexanes and recrystallized by layering hexanes over a toluene solution of the solid. ^{1}H NMR (C_6D_6): δ 7.78 (m, 6H, PPh_3), 6.95 (m, 9H, PPh_3), 3.16 (m, 2H, CH_2), 3.13 (m, 1H, CH_2–S), 2.90 (d, $J_{P\text{-}H} = 8.7$ Hz, 3H, Re-CH_3), 2.75 (m, 1H, CH_2–S), 2.40 (m, 1H, CH_2–S), 2.30 (m, 1H, CH_2–S). ^{13}C NMR (C_6D_6): δ 134.73 (d, $J_{P\text{-}C} = 10.4$ Hz, PPh_3), 131.10 (d, $J_{P\text{-}C} = 19.7$ Hz, PPh_3), 129.26 (d, $J_{P\text{-}C} = 22.5$ Hz, PPh_3), 128.77 (d, $J_{P\text{-}C} = 10.5$ Hz, PPh_3), 36.41 (d, $J_{P\text{-}C} = 2.0$ Hz, CH_2–S), 36.10 (CH_2), 34.30 (d, $J_{P\text{-}C} = 11.8$ Hz, CH_2–S), 19.27 (d, $J_{P\text{-}C} = 3.9$ Hz, Re-CH_3). ^{31}P NMR (C_6D_6): δ 28.05; (CDCl): δ 27.7. ^{1}H-^{31}P CPMAS NMR: δ 31.3 and 27.7 ppm. Anal. calcd. for $C_{22}H_{24}OPReS_2$: C, 45.11; H, 4.13; S, 10.95. Found: C, 44.81; H, 4.33; S, 11.11.

(edt)Re(O)(Me)(PPh3): A mixture of 35 mg (80 μmol Re) of $(PhS)_4Re_2(O)_2(Me)_2$ and 27 mg (80 μmol) of PPh_3 were dissolved in 1.5 mL of benzene. After stirring for 10 min at room temperature, 8.0 μL (90 μmol) of edt were added to the green solution. After stirring for 8 h, solvent was removed under vacuum; the red solid was washed with hexanes and recrystallized by layering hexanes over a toluene solution of the solid. ^1H and ^{13}C NMR (C_6D_6) chemical shifts are the same as those already reported for this compound [34]; ^{13}C NMR $J_{P\text{-}C}$ (Hz) values are a factor of 4 smaller than reported earlier due to a miscalculation of Hz in the original paper. ^{31}P NMR (C_6D_6): δ 31.69.

(RTA)Re(O)(Me)(PPh3): A mixture of 85 mg (0.20 mmol Re) of $(PhS)_4Re_2(O)_2(Me)_2$ and 51 mg (0.20 mmol) of PPh_3 were dissolved in 4.0 mL of benzene. After stirring for 10 min at room temperature, 82 mg (0.20 mmol) of $RTAH_2$ was added to the green solution. After stirring for 8 h, the solvent was removed under vacuum, and the green oil was dissolved in hexanes. After the solution was filtered, the hexanes were removed under vacuum, which yielded 110 mg of a green oil (60% yield). Four isomers in approximately equimolar amounts were observed by ^{31}P NMR and ^1H NMR spectroscopy. The isomers were identified in the ^1H NMR spectrum by four ReMe doublets near 2.87 and in the ^{31}P NMR spectrum by four distinct signals near 27 ppm. The ^1H-^{31}P CPMAS spectrum of the oil (10 mg) physically mixed with SiO_2 (100 mg) exhibits signals at 23 and 33 ppm. ^1H NMR (C_6D_6): δ 4.04 (t, J = 6.8 Hz, 2H, CO_2CH_2), 3.73 (q, J = 7.0 Hz, 6H, $SiO\underline{CH_2}CH_3$), 3.25 (m, 2H, CH_2), 2.89 (d, J = 8.4 Hz, 3H, ReMe), 2.87 (d, J = 8.8 Hz, 3H, ReMe) 2.85 (d, J = 8.0 Hz, 3H, ReMe) 2.85 (d, J = 8.4 Hz, 3H, ReMe), 2.42 (m, 1H, $(CH(S\text{–})\underline{CH_2}CH_2(S\text{–}))$, 2.07 (m, 2H, CH_2), 1.81 (m, 2H, $SiCH_2\text{–}\underline{CH_2}\text{–}CH_2O_2C\text{–}$), 1.3–1.7 (m, 8H, CH_2), 1.19 (t, J = 7.0 Hz, 9H, $SiOCH_2\underline{CH_3}$), 0.63 (m, 2H, $SiCH_2$). ^{31}P NMR (C_6D_6): δ 27.74, 27.69, 27.49, 27.19.

2.1.3. Preparation of silica-tethered complexes

(SiO_2-RTA)Re(O)(Me)(PPh3), method (A) (Fig. 2, path a): A solution of 143 mg (0.161 mmol Re) of (RTA)Re(O)(Me)(PPh_3) dissolved in 5.0 mL of toluene was added to 0.20 g of SiO_2. The resulting slurry was refluxed for 12 h and then stirred overnight at room temperature. Filtration of the mixture followed by washing of the solid with 3 × 5.0 mL of CH_2Cl_2, and then drying under vacuum gave a catalytically inactive red solid (see Sections 3.1 and 3.4). The same reaction run for 1 week at room temperature instead of 110 °C yielded a light green solid that had a very low rhenium content and low activity which is consistent with the reduced rhenium content, ∼2% of that obtained by method (B).

Method (B) (Fig. 2, path b): A mixture of 70 mg (0.16 mmol Re) of $(PhS)_4Re_2(O)_2(Me)_2$ and 45 mg (0.17 mmol) of PPh_3 were dissolved in 8.0 mL of benzene. After stirring for 10 min at room temperature, the green solution was added to 0.60 g (estimated 0.35 mmol ligand) of SiO_2-$RTAH_2$ and stirred together at room temperature for

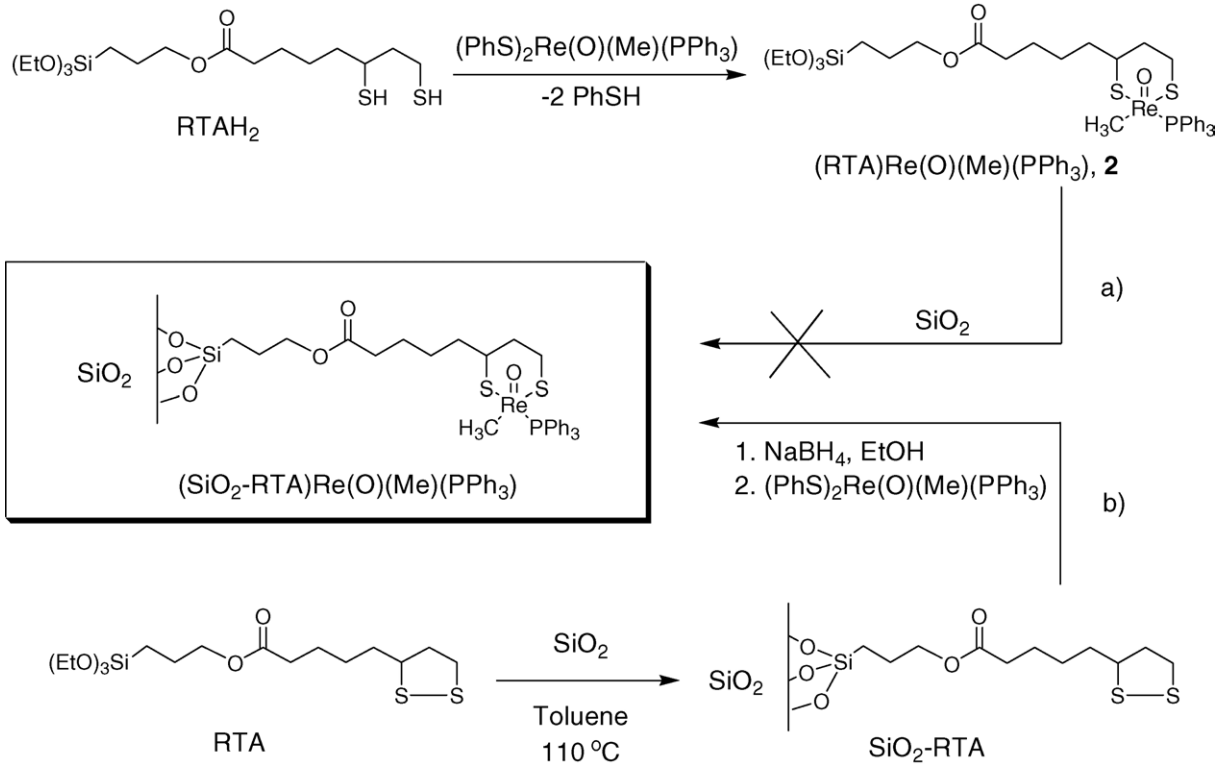


Fig. 2. Synthesis of the (SiO_2-RTA)Re(O)(Me)(PPh_3) catalyst.

18 h. The resulting green solid was filtered and washed with 3 × 10 mL of toluene and 3 × 10 mL of CH_2Cl_2. The resulting solid catalyst was dried under vacuum. ICP-MS rhenium content (Section 2.1.): 0.18 (±0.02) μmol Re/1.0 mg SiO_2. ^{1}H-^{31}P CPMAS NMR: δ 34 and 24 ppm. For an idealized, uniformly dispersed tethered metal complex on the surface, this loading corresponds to one rhenium atom per 280 Å^2 of surface area.

$(PhS)_2Re_2(O)(Me)(PPh_3)/(SiO_2)$: A mixture of 70 mg (0.16 mmol Re) of $(PhS)_4Re_2(O)_2(Me)_2$ and 45 mg (0.17 mmol) of PPh_3 was dissolved in 8.0 mL of benzene. After stirring for 10 min at room temperature, the green solution was added to 0.60 g of SiO_2 and the mixture was stirred at room temperature for 18 h. The resulting green solid, containing $(PhS)_2Re_2(O)(Me)(PPh_3)$ physisorbed on SiO_2, was filtered, washed with 3 × 10 mL of toluene and 3 × 10 mL of CH_2Cl_2, and dried under vacuum.

2.2. Catalytic oxidation reactions

The rhenium catalyst was placed in a round bottom flask open to the atmosphere; solvent (typically 1 mL) and substrate (0.60 or 9.45 mM) were added and allowed to stand at room temperature for 1 min; then, TBHP in nonane was added via syringe. The reaction flask was immediately immersed in a constant temperature bath of desired temperature. The reaction was followed by GC analysis of samples removed with a syringe from the reaction solution during and after the reaction. For MTS oxidation, the disappearance of MTS and appearance of methyl(*p*-tolyl)sulfoxide (MTS(O)) and methyl(*p*-tolyl)sulfone (MTS$(O)_2$) were followed. For DBT and 4,6-Me_2DBT, disappearance of the substrate was monitored with the aid of the internal standard diphenylmethane added to the initial reaction solution and present throughout the reaction. Product identities and extents of reaction were confirmed by ^{1}H NMR spectra of reaction mixtures from the first reaction with each of the substrates. Data from each run were fit to a first-order rate law, $\ln[A]_t = -kt + \ln[A]_0$, which gave rate constants and errors. These rate constants were used to calculate the $t_{1/2}$ and TO data in Tables 3–9. The data are averages of one to three runs. For reactions with half-lives <5 h, data was taken to at least 90% reaction completion. For reactions with half-lives >5 h, data were obtained over ∼24 h. The lack of data points near the end of the slower oxidations accounts for their larger relative errors.

For studies in which the tethered catalyst (SiO_2-RTA)Re(O)(Me)(PPh_3) was reused in subsequent oxidation reactions, the catalyst was filtered after each reaction, washed with pure reaction solvent and vacuum-dried before being re-weighed and re-used.

2.3. Attempted epoxidation reactions

Both (SiO_2-RTA)Re(O)(Me)(PPh_3) and (pdt)Re(O)(Me)(PPh_3) were tested for their activities towards the epoxidation of 1-hexene and cyclooctene. Both TBHP and 4-picoline-N-oxide were examined as oxidants at 25, 50 or 100 °C in $CDCl_3$ and toluene. Under none of these conditions was 1-hexene or cyclooctene oxidized to an epoxide or other products even after several days.

3. Results and discussion

3.1. Synthesis of (SiO_2-RTA)Re(O)(Me)(PPh_3)

When (RTA)Re(O)(Me)(PPh_3) is formed in solution by the reaction of equimolar amounts of $RTAH_2$ with $(PhS)_4Re_2(O)_2(Me)_2$ (Fig. 2), four isomeric species with distinct ^{31}P NMR signals (C_6D_6: δ 27.74, 27.69, 27.49, 27.19) and ReMe doublets in the ^{1}H NMR spectrum are observed. These isomers probably differ by the orientation of the inequivalent sulfur donors relative to the PPh_3 and –CH_3 ligands and the Re=O oxygen relative to the side chain on the chiral carbon. Silica column chromatography of this mixture of isomers results in a redistribution of their relative amounts and a decrease in the amount of rhenium-containing material recovered. The presence of free PPh_3 in several fractions suggests that PPh_3 dissociates from the complex, which allows the isomers to interconvert on the silica of the column. When this mixture of (RTA)Re(O)(Me)(PPh_3) isomers was immobilized on silica (Fig. 2, path a) by refluxing in toluene, the resulting red solid was not active as an oxidation catalyst, presumably due to decomposition at the high temperature (110 °C) of the immobilization. Only when the synthesis of the catalyst was changed to a sequential method (Fig. 2, path b), where $(PhS)_4Re_2(O)_2(Me)_2$ and PPh_3 were added to SiO_2-$RTAH_2$, was an active catalyst of (SiO_2-RTA)Re(O)(Me)(PPh_3) obtained.

3.2. Characterization of the homogeneous and immobilized rhenium complex catalysts by liquid and solid state NMR spectroscopy

*(pdt)Re(O)(Me)(PPh_3) **(1)***: ^{13}C and ^{31}P NMR spectra of complex **1** in $CDCl_3$ acquired at room temperature are shown in Fig. 3a and c. Three CH_2 signals were observed at 36.4 (doublet, 2 Hz), 36.0 (singlet), and 34.5 ppm (doublet, 12 Hz). Since the $^3J_{P\text{-}C3}$ coupling constant is expected to be larger than $^3J_{P\text{-}C1}$ because of its position *trans* to the PPh_3 ligand, these signals are assigned to C1, C2 and C3 carbons, respectively (Scheme 1). The doublet resonance at 19.2 ppm is assigned to the methyl carbon. Triphenylphosphine carbons are observed at 134.7, 131.5, 129.8 and 129.0 ppm (not shown). The ^{31}P spectrum (Fig. 3c) is dominated by complex **1** at 27.7 ppm, although a weak resonance representing O=PPh_3 is also observed at 29.8 ppm. [46]

The resolution of the ^{1}H-^{13}C CPMAS spectrum (not shown) of the solid complex **1** was insufficient to distinguish all carbon sites. However, three groups of overlapping resonances are observed at 18, 35 and 132 ppm, as expected for structure **1**. The ^{13}C chemical shift data for pdt and its

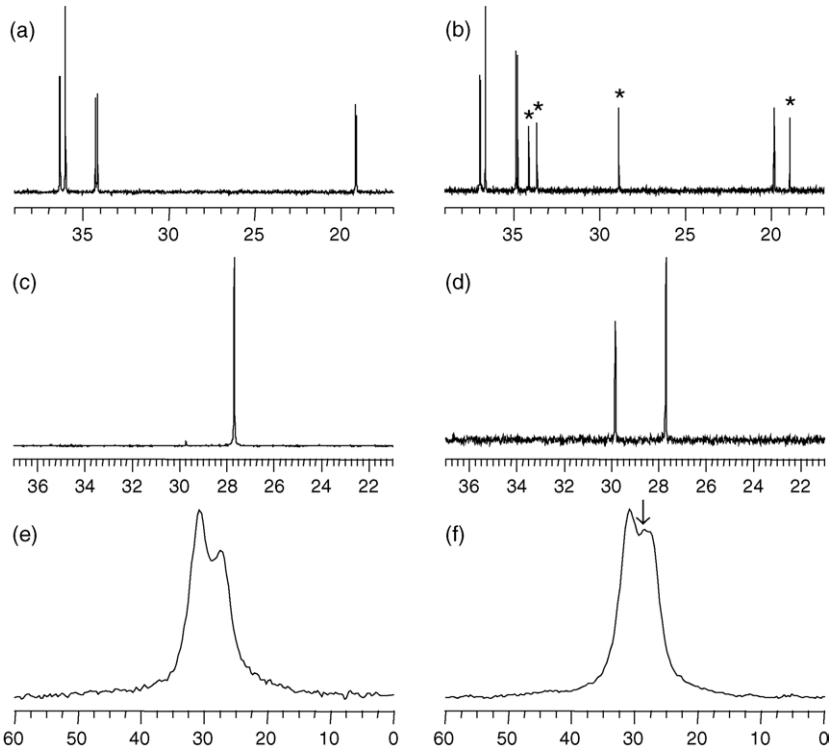


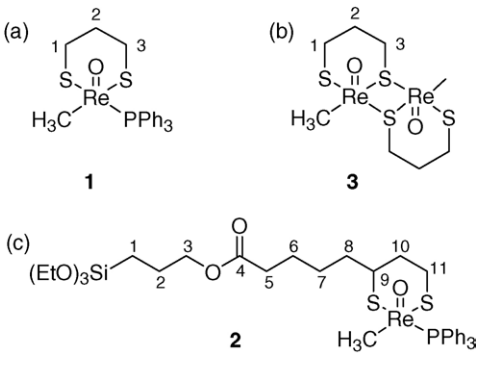
Fig. 3. ^{13}C (a and b) and ^{31}P (c–f) NMR spectra of (pdt)Re(O)(Me)(PPh_3) complex. Spectra (a–d) were measured in $CDCl_3$ solution at room temperature, using as-synthesized complex (a and c) and the complex that was exposed to 40 °C prior to dissolution in $CDCl_3$ (b and d). Spectra (e and f) of the solid complex were taken under 9 kHz MAS at ∼0 and ∼40 °C, respectively. Note that only the aliphatic region of the ^{13}C spectra is shown. Asterisks in spectrum (b) mark the dimer [(pdt)Re(O)(Me)]$_2$ resonances; arrow in spectrum (f) denotes the resonance representing O=PPh$_3$.

oxorhenium complexes in the liquid and solid states are summarized in Table 1. The ^{1}H-^{31}P CPMAS spectrum of solid **1** (Fig. 3e) is dominated by two resonances at 31 and 27 ppm, with approximately 4:3 intensity ratio. This is possibly due to the presence of two conformers of the pdt oxorhenium complex. Indeed, two conformations of (pdt)Re rings, referred to as pseudo-chair and pseudo-boat, were found in an earlier XRD study of the crystalline [(pdt)Re(O)(Me)]$_2$ dimer [see supporting information in ref. [37]]. The existence of a single ^{31}P resonance for the dimer in solution is likely due to rapid chair ⇄ boat interconversion. We note that the ^{1}H-^{31}P CPMAS spectrum in Fig. 3e was acquired using cooled air to spin the rotor, in order to maintain the sample temperature at around 0 °C. When ambient air was used for sample spinning at 9 kHz, the frictional heating elevated its temperature to approximately 40 °C [47], which accelerated dimerization according to Eq. (2). The CPMAS spectrum acquired under

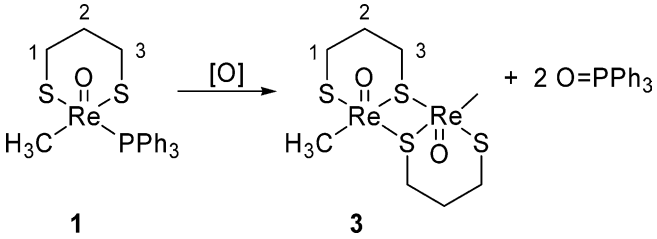
Table 1
^{13}C NMR chemical shifts (in ppm) of aliphatic carbons and $^nJ_{C\text{-}P}$ coupling constants (Hz, in parenthesis) measured for pdt and its rhenium complexes

	pdt	(pdt)Re(O)(Me)(PPh_3), **1**		[(pdt)Re(O)(Me)]$_2$, **3**	
	Liquid[a]	Liquid	Solid	Liquid[b]	Solid
C1	22.2	36.4 (2.0)	36	34.0[c]	32[c]
C2	36.5	36.0	36	33.1[c]	31[c]
C3	22.2	34.5 (11.8)	34	29.5[c]	29[c]
Me		19.2	17.5	19.6	18.6

[a] Data taken from ref. [48].
[b] Data taken from ref. [37].
[c] Assignment of these resonances may be reversed.



Scheme 1.



(2)

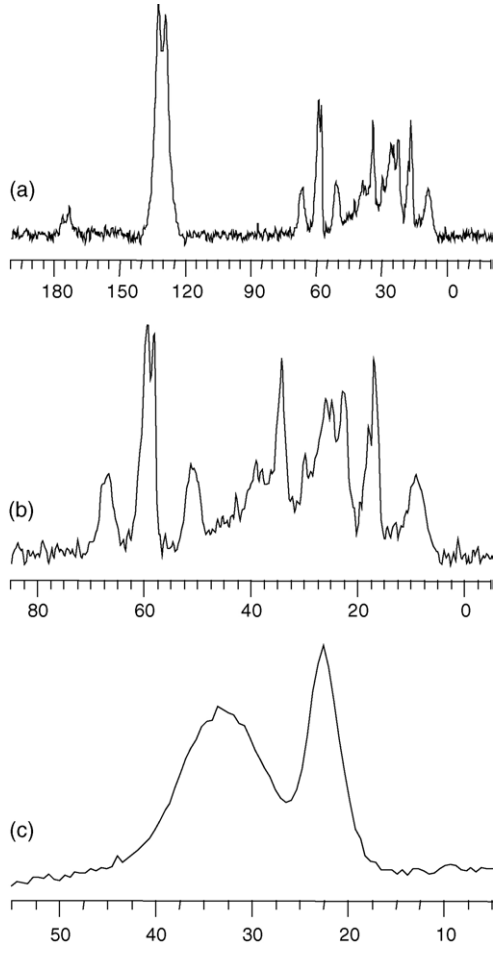


Fig. 4. ^{13}C (a and b) and ^{31}P (c) CPMAS NMR spectra of (RTA)Re(O)(Me)(PPh_3) physisorbed on SiO_2, measured under 9 kHz MAS at ~40 °C. Spectrum (b) shows the expanded aliphatic ^{13}C region of spectrum (a).

such conditions (Fig. 3f) also shows a resonance at 28.5 ppm for O=PPh_3. The corresponding liquid state ^{13}C and ^{31}P spectra, shown in Fig. 3b and d, also demonstrate the dimerization process. The ^{13}C resonances marked with asterisks in Fig. 3b agree with those reported earlier for the [(pdt)Re(O)(Me)]$_2$ dimer in solution [37] and with those measured in the present study (spectrum not shown) by ^1H-^{13}C CPMAS NMR at 40 °C (see Table 1). A further increase of dimer concentration was observed upon heating the sample to 70 °C (spectra not shown).

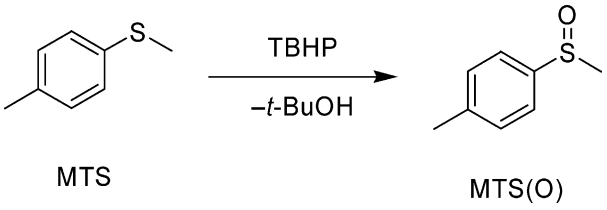
*(RTA)Re(O)(Me)(PPh_3) (**2**)*: Solid-state ^{31}P and ^{13}C NMR spectroscopy has been used to characterize **2** in the tethered and physisorbed forms on the silica surface. Since the spectra of both samples were similar, the following discussion is limited to the physisorbed complexes, which could be studied at a higher concentration. These physisorbed samples, (RTA)ReO(Me)(PPh_3)/SiO_2, were prepared by stirring SiO_2 with a CH_2Cl_2 solution of (RTA)Re(O)(Me)(PPh_3); then, the solvent was evaporated under vacuum. The ^1H-^{13}C CPMAS spectrum taken without precooling of the air used for MAS (i.e., at ~40 °C) is shown in Fig. 4a. The number of resonance lines in the aliphatic region, which is enlarged in Fig. 4b, exceeds the number of carbon nuclei in (RTA)Re(O)(Me)(PPh_3). For example, resonances representing C4, C7 and C9 (Scheme 1) were clearly doubled. The ^{13}C resonances were separated using spectral editing techniques (dipolar dephasing and variable contact time experiments) and assigned based on the chemical shifts of similar compounds reported in the literature [37,48]. The results, summarized in Table 2, are consistent with the presence of both the (RTA)Re(O)(Me)(PPh_3) monomer and [(RTA)Re(O)(Me)]$_2$ dimer species, the analog of **3** (Eq. (2)). A quantitative analysis of these spectra was not practical because the dimerization proceeded while the NMR experiments were in progress. The ^1H-^{31}P CPMAS spectrum of the same sample (Fig. 4c) includes a line at 23 ppm assigned to complex **2**. The presence of two conformers of **2**, as found for **1**, could not be established. Instead, a broad ^{31}P resonance at 33 ppm was observed, which is possibly due to O=PPh_3 adsorbed on silica. The ^{31}P chemical shift of O=PPh_3 can change considerably upon interaction with acid surface sites as a result of lengthening of the phosphorus–oxygen bond, in a range that can be comparable to the observed linewidth [49]. Further evidence of dimerization was provided by liquid state ^{31}P NMR spectra of solutions obtained by extracting (RTA)Re(O)(Me)(PPh_3)/SiO_2 samples (after running their CPMAS spectra) with CH_2Cl_2; these spectra showed the presence of [(RTA)Re(O)(Me)]$_2$, (RTA)Re(O)(Me)(PPh_3), O=PPh_3 and unidentified minor species. The presence of the dimer in the physisorbed sample of **2** is similar to the presence of the [(pdt)Re(O)(Me)]$_2$ dimer in solid (pdt)Re(O)(Me)(PPh_3). The immobilized dimeric species on the surface is not expected to reduce the catalytic activity of (SiO_2-RTA)Re(O)(Me)(PPh_3) as both rhenium monomer and dimer complexes in solution are known to be catalytically active [50]. In fact, dimeric oxorhenium(V) dithiolate compounds are known to be more active than their corresponding phosphine- and amine-coordinated monomers.

Table 2
^{13}C chemical shifts (aliphatic region) measured using ^1H-^{13}C CPMAS NMR of freshly prepared (RTA)Re(O)(Me)(PPh_3) physisorbed on SiO_2

	(RTA)Re(O)(Me)(PPh_3), **2**	[(RTA)Re(O)(Me)]$_2$
C1	9.2	10.6
C2	23.0	21.5
C3	66.0	66.0
C4	176.6	173.8
C5	34.4	34.4
C6	25.0	26.2
C7	29.0	30.0
C8	35.4	35.4
C9	67.8	66.6
C10	40.5, 39.2	36.4
C11	51.4, 52.7	50.8, 50.0
CH_3	18.2	19.6
Phenyl group	133–127	
$\underline{C}H_3CH_2O$–	17.1	17.1
$CH_3\underline{C}H_2O$–	58.3	58.3

3.3. Homogeneous catalytic oxidation of MTS

The selective oxidation of methyl(*p*-tolyl)sulfide (MTS) to methyl(*p*-tolyl)sulfoxide (MTS(O)) utilizing *tert*-butylhydroperoxide (TBHP) as the oxidant (Eq. (3)) at room temperature in



(3)

$CDCl_3$ solvent was used to evaluate the activities of the tethered rhenium catalysts, as well as the analogous homogeneous catalysts. The homogeneous (RTA)Re(O)(Me)(PPh_3) catalyst (Table 3, entry 3, $t_{1/2}$ = 1.5 h) has an activity comparable to that of the parent (pdt)Re(O)(Me)(PPh_3) catalyst (Table 3, entry 2, $t_{1/2}$ = 1.1 h). Thus, the tetherable chain only slightly decreases the catalytic activity. This result also suggests that the four ^{31}P NMR signals arising from (RTA)Re(O)(Me)(PPh_3) do indeed correspond to four geometrical isomers which are all catalytically active as the overall activity is so similar to the pdt analog. The catalytic activity of (pdt)Re(O)(Me)(PPh_3) (Table 3, entry 2, $t_{1/2}$ = 1.1 h) is higher than that of (edt)Re(O)(Me)(PPh_3) (Table 3, entry 1, $t_{1/2}$ = 2.7 h) which has been investigated in much greater detail [8]. There is little reaction in the absence of catalyst (entry 9) or in the presence of only SiO_2 (entry 7). Entry 8 shows that active catalyst does not leach from the tethered catalyst.

Table 3
Catalyst activities for MTS oxidation by TBHP at 20 °C[a]

Entry	Catalyst	Catalyst[b] (mol%)	$t_{1/2}$ (h)[c]	TO at 1 h[d]
1	(edt)Re(O)(Me)(PPh_3)	1.0	2.7 (2)	23
2	(pdt)Re(O)(Me)(PPh_3)	1.0	1.1 (1)	48
3	(RTA)Re(O)(Me)(PPh_3)	1.0	1.5 (1)	37
4	(SiO_2-RTA)Re(O)(Me)(PPh_3)[e]	3.0	1.4 (1)	13
5	(SiO_2-RTA)Re(O)(Me)(PPh_3)[e,f]	0.060	18 (2)	NA[g]
6	$(PhS)_2Re_2$(O)(Me)(PPh_3)/(SiO_2)[e]	0.060	11 (2)	NA[g]
7	SiO_2[e]	0.0	25 (5)	NA[h]
8	Mother liquor[i]	0.0	32 (4)	NA[h]
9	Blank[j]	0.0	39 (9)	NA[h]

[a] Reaction conditions: 0.10 mL of $CDCl_3$ solvent, 0.60 M MTS, 0.66 M TBHP, 20 °C.
[b] Ratio of rhenium to substrate (MTS) expressed as a percentage. Amount of rhenium: 3 mol% = 1.8 μmol Re, 1 mol% = 0.6 μmol Re and 0.06 mol% = 0.036 μmol Re.
[c] Errors, given in parenthesis after each $t_{1/2}$, were obtained from fitting of reaction data from 1 to 3 runs to a first-order rate equation of the form $\ln[A]_t = -kt + \ln[A]_0$ and reflect the uncertainty in the last digit of the half-life.
[d] Catalytic turnover (mol MTS reacting/mol Re) after 1 h of reaction based on rhenium content.
[e] 10.0 mg of solid catalyst.
[f] (SiO_2-RTA)Re(O)(Me)(PPh_3) prepared by method (A).
[g] Catalyst turnover not applicable (NA) as the majority of the activity is due to the background oxidation from the silica support.
[h] Catalyst turnover not applicable (NA) as no rhenium is present.
[i] Filtered reaction solution from entry 4.
[j] No catalyst. Only MTS and TBHP.

Table 4
Solvent effects on MTS oxidation by TBHP[a]

Entry	Solvent	$t_{1/2}$ (h)[b]	TO at 1 h[c]
1	C_6H_6	0.94 (7)	52
2	$CDCl_3$	1.1 (1)	47
3	$CHCl_3$[d]	1.5 (2)	37
4	CH_2Cl_2	2.13 (6)	28
5	$CDCl_3$ with 10% EtOH	6.52 (2)	10

[a] Reaction conditions: 0.10 mL of solvent, 0.60 M MTS, 0.66 M TBHP, 20 °C, 1.0 mol% (pdt)Re(O)(Me)(PPh_3) catalyst (0.6 μmol Re).
[b] Table 3, footnote c.
[c] Table 3, footnote d.
[d] Commercial $CHCl_3$ contains 1% EtOH as stabilizer.

A study (Table 4) of the effect of solvent on the oxidation of MTS as catalyzed by (pdt)Re(O)(Me)(PPh_3) shows that the reaction is fastest in benzene solvent (Table 4, entry 1, $t_{1/2}$ = 0.94 h). The reaction rate in $CDCl_3$ (entry 2, $t_{1/2}$ = 1.1 h) is only slightly less than that in benzene. Reactions in both chloroform (entry 3, $t_{1/2}$ = 1.5 h) and methylene chloride (entry 4, $t_{1/2}$ = 2.13 h) were slower than those in $CDCl_3$. The slower rate in $CHCl_3$ as compared to $CDCl_3$ was due to the ethanol (1%) stabilizer in commercial $CHCl_3$, because the addition of 10% ethanol to $CDCl_3$ greatly reduces the rate (entry 5, $t_{1/2}$ = 6.5 h) of MTS oxidation (by a factor of 5.9).

3.4. Heterogeneous catalytic oxidation of MTS using (SiO_2-RTA)Re(O)(Me)(PPh_3)

Two strategies were used for the immobilization of (RTA)Re(O)(Me)(PPh_3) on the silica surface (Fig. 2). The catalyst (SiO_2-RTA)Re(O)(Me)(PPh_3) prepared by method (B) (Fig. 2, path b; Table 3, entry 4, $t_{1/2}$ = 1.4 h) required three times as much rhenium to achieve activity comparable to that of the homogeneous (RTA)Re(O)(Me)(PPh_3) catalyst (Table 3, entry 3, $t_{1/2}$ = 1.5 h). However, (SiO_2-RTA)Re(O)(Me)(PPh_3) prepared by method (A) (Fig. 2, path a; Table 3, entry 5, $t_{1/2}$ = 18 h) was over an order of magnitude slower than the homogeneous catalyst and only slightly more active than silica without rhenium (Table 3, entry 7, $t_{1/2}$ = 25 h). The low activity of the catalyst prepared by method (A) is most likely due to the low loading of Re achieved by this tethering process. As the (SiO_2-RTA)Re(O)(Me)(PPh_3) prepared by method (B) provided substantially better activity, it was used in subsequent experiments, and future references to (SiO_2-RTA)Re(O)(Me)(PPh_3) refer to the version prepared by method (B).

While the homogeneous catalyst (RTA)Re(O)(Me)(PPh_3) (Table 3, entry 3, $t_{1/2}$ = 1.5 h with 1 mol% catalyst) was faster than (SiO_2-RTA)Re(O)(Me)(PPh_3) (entry 4, $t_{1/2}$ = 1.4 h with 3 mol% catalyst) for methyl(*p*-tolyl)sulfide oxidation under

Table 5
Re-use of (SiO_2-RTA)Re(O)(Me)(PPh_3) for MTS oxidation by TBHP[a]

Use no.	$t_{1/2}$ (h)[b]	TO at 1 h[c]
1	1.4 (1)	13
2	1.3 (2)	14
3	1.4 (1)	13
4	1.3 (4)	14
5	1.4 (2)	13

[a] Reaction conditions: 0.10 mL of $CDCl_3$, 0.60 M MTS, 0.66 M TBHP, 20 °C, 3.0 mol% (SiO_2-RTA)Re(O)(Me)(PPh_3) catalyst (10.0 mg of solid catalyst, 1.8 μmol Re).
[b] Table 3, footnote c.
[c] Table 3, footnote d.

our standard conditions, the immobilized catalyst was completely recyclable. Five consecutive oxidation reactions, in which the catalyst was filtered and washed between reactions (Section 2.3), were performed with no loss of catalyst activity (Table 5). No activity was detected in the mother liquors after each of the five consecutive reactions (representative example: Table 3, entry 8, $t_{1/2}$ = 32 h) above the level associated with that of blank solutions (Table 3, entry 9, $t_{1/2}$ = 39 h).

For MTS oxidation by TBHP catalyzed by both (pdt)Re(O)(Me)(PPh_3) and (SiO_2-RTA)Re(O)(Me)(PPh_3), a substantial rate increase was observed when the reactions were run at 50 °C in toluene, rather than 20 °C. With (pdt)Re(O)(Me)(PPh_3) at 20 °C, ∼100 catalytic turnovers could be achieved in 4 h (Table 3, entry 2), while ∼1000 turnovers were achieved at 50 °C after only 16 min (Table 6, entry 1). Likewise, (SiO_2-RTA)Re(O)(Me)(PPh_3) at 20 °C took 6 h for 30 turnovers (Table 3, entry 4) but only 40 min for 300 turnovers at 50 °C (Table 6, entry 2). Furthermore, at 50 °C, all 3000 equivalents of MTS could be cleanly oxidized in 18 h with (SiO_2-RTA)Re(O)(Me)(PPh_3) (Table 6, entry 4).

It should be noted that silica alone has been reported to catalyze the oxidation of sulfides to sulfoxides and sulfones at 25 °C with TBHP or OXONE [51] or with H_2O_2 at 25 or 40 °C [52] as the oxidants. However, for the reactions at 20 °C in this paper, the silica-catalyzed oxidation of methyl(*p*-tolyl)sulfide by TBHP (Table 3, entry 7, $t_{1/2}$ = 25 h) is only slightly faster than the oxidation that occurs (Table 3, entry 9, $t_{1/2}$ = 39 h) in the presence of only solvent and reactants; both are an order of magnitude slower than the rhenium-catalyzed reactions (Table 3, entries 1–4). In contrast, the oxidation of MTS by TBHP with SiO_2 at 50 °C is much faster than at 20 °C (compare Table 3, entry 7 with Table 6, entry 5); more than 95% of the MTS in 1.0 mL of a 0.60 M solution in toluene is oxidized by TBHP in the presence of 10.0 mg of SiO_2 within 10 h at 50 °C.

Table 6
Catalyst activities for MTS oxidation by TBHP at 50 °C[a]

Entry	Catalyst	Catalyst[b] (mol%)	$t_{1/2}$ (h)[c]	TO at 0.1 h[d]
1	(pdt)Re(O)(Me)(PPh_3)	0.10	0.067 (1)	645
2	(SiO_2-RTA)Re(O)(Me)(PPh_3)[e]	0.30	0.156 (5)	120
3	(pdt)Re(O)(Me)(PPh_3)	0.010	14 (2)	NA[i]
4	(SiO_2-RTA)Re(O)(Me)(PPh_3)[f]	0.030	4.5 (3)	47.6
5	SiO_2[e]	0	2.3 (2)	NA[g]
6	SiO_2[f]	0	21 (3)	NA[g]
7	Blank[h]	0	15 (2)	NA[g]

[a] Reaction conditions: 1.0 mL of toluene solvent, 0.60 M MTS, 0.66 M TBHP, 50 °C.
[b] Ratio of rhenium to substrate (MTS) expressed as a percentage. Amount of rhenium: 0.30 mol% = 1.8 μmol Re, 0.10 mol% = 0.6 μmol Re, 0.030 mol% = 0.18 μmol Re, 0.010 mol% = 0.06 μmol Re.
[c] Table 3, footnote c.
[d] Catalytic turnover (mol MTS reacting/mol Re) after 0.1 h of reaction.
[e] Ten milligrams of solid catalyst.
[f] 1.0 mg of solid catalyst.
[g] Table 3, footnote h.
[h] No catalyst.
[i] Table 3, footnote g.

The high activity of (SiO_2-RTA)Re(O)(Me)(PPh_3) (Table 3, entry 4, $t_{1/2}$ = 1.4 h) as compared to that of its filtered mother liquor (Table 3, entry 8, $t_{1/2}$ = 32 h) or SiO_2 with no rhenium (Table 3, entry 7, $t_{1/2}$ = 25 h) clearly shows that the tethered rhenium complex is required for catalytic activity of (SiO_2-RTA)Re(O)(Me)(PPh_3). One might consider the possibility that a non-tethered rhenium species is formed during the reaction of $(PhS)_4Re(O)_2(Me)_2/(PPh_3)$ with SiO_2-$RTAH_2$ (Fig. 2, path b). However, the reaction of $(PhS)_4Re(O)_2(Me)_2/(PPh_3)$ with SiO_2 without the tethering ligand gives a catalyst (Table 3, entry 6, $t_{1/2}$ = 11 h) that is much less active than (SiO_2-RTA)Re(O)(Me)(PPh_3). These observations and the recyclability (Table 5) of (SiO_2-RTA)Re(O)(Me)(PPh_3) indicate that the tethered dithiolate rhenium complex is the active catalyst in (SiO_2-RTA)Re(O)(Me)(PPh_3).

3.5. Catalytic oxidation of DBT and 4,6-Me_2DBT

The less reactive dibenzothiophene (DBT) was oxidized by TBHP in toluene at 50°C using 0.1 mol% of the homogeneous (pdt)Re(O)(Me)(PPh_3) catalyst (Table 7, entry 1, $t_{1/2}$ = 0.8 h). However, at 0.01 mol% catalyst, this (pdt)Re(O)(Me)(PPh_3) catalyst was incapable of oxidizing all 10,000 equivalents of DBT, losing activity after approximately 1000 turnovers (Table 7, entry 2). Using 0.3 mol% of the immobilized (SiO_2-RTA)Re(O)(Me)(PPh_3), 300 equivalents of DBT were oxidized in 2 h (Table 7, entry 3, $t_{1/2}$ = 0.48 h); and 0.03 mol% catalyst was capable of oxidizing all 3000 equivalents of DBT (Table 7, entry 4, $t_{1/2}$ = 2.5 h).

When (SiO_2-RTA)Re(O)(Me)(PPh_3) was used as the catalyst for the oxidation of a mixture of 0.60 M MTS (300 equivalents) and 0.60 M (300 equivalents) DBT in toluene at 50 °C with 1.2 M (600 equivalents) TBHP, the MTS was completely converted to the sulfoxide (MTS(O)) in less than 1 h (Fig. 5). Thereafter, the oxidation of DBT to DBT(O) and MTS(O) to the sulfone ($MTS(O)_2$) occurred concurrently with DBT oxidation being slightly faster than the MTS(O) oxidation. The reaction proceeded for 6 h until all of the TBHP had been consumed. Complete oxidation of all of the DBT to DBT(O) and MTS to $MTS(O)_2$ could be achieved by addition of excess TBHP (not shown).

Table 7
Catalyst activities for DBT oxidation by TBHP at 50 °C[a]

Entry	Catalyst	Catalyst[b] (mol%)	T	$t_{1/2}$ (h)[c]	TO at 0.5 h[d]
1	(pdt)Re(O)(Me)(PPh_3)	0.10	50	0.8 (2)	341
2	(pdt)Re(O)(Me)(PPh_3)	0.010	50	NA[e]	NA[e]
3	(SiO_2-RTA)Re (O)(Me)(PPh_3)[f]	0.30	50	0.48 (4)	172
4	(SiO_2-RTA)Re (O)(Me)(PPh_3)[g]	0.030	50	2.5 (4)	428
5	(SiO_2-RTA)Re (O)(Me)(PPh_3)[g]	0.030	100	0.60 (8)	1471
6	SiO_2[f]	0	50	NR[h]	
7	Blank[i]	0	50	NR[h]	

[a] Reaction conditions: 1.0 mL of toluene solvent, 0.60 M DBT, 0.66 M TBHP, 50 °C.
[b] Ratio of rhenium to substrate (DBT) expressed as a percentage. Amount of rhenium: 0.30 mol% = 1.8 μmol Re, 0.10 mol% = 0.6 μmol Re, 0.030 mol% = 0.18 μmol Re, 0.010 mol% = 0.06 μmol Re.
[c] Table 3, footnote c.
[d] Catalytic turnover (mol DBT reacting/mol Re) after 0.5 h.
[e] Catalyst loses activity after 1000 TO (10% reaction).
[f] Ten milligrams of solid catalyst.
[g] 1.0 mg of solid catalyst.
[h] No reaction observed over 12 h.
[i] No catalyst.

For the oxidation of DBT (0.60 M) with TBHP in toluene at 20 °C using 0.03 mol% (SiO_2-RTA)Re(O)(Me)(PPh_3), no reaction was observed even after 3 days (not shown). However, at 50 °C, as mentioned above, DBT oxidation was facile (Table 7, entry 4, $t_{1/2}$ = 2.5 h), and the reaction was almost five times faster at 100 °C (Table 7, entry 5, $t_{1/2}$ = 0.6 h). Control experiments at 50 °C showed that DBT was not oxidized by TBHP (Table 7, entry 7) in solution or by TBHP in the presence of silica (entry 6) when rhenium was not present. This is in contrast to MTS oxidation (Table 3, Section 3.3) where slow oxidation was observed even in the absence of rhenium.

3.6. Oxidation of dibenzothiophenes in simulated petroleum feedstocks

In order to determine whether the (SiO_2-RTA)Re(O)(Me)(PPh_3) catalyst could facilitate the oxidation (Eq. (1)) of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-Me_2DBT) in a simulated petroleum feedstock, a 45:55% (v/v) solution of toluene:hexane containing 9.45 mM DBT or 4,6-Me_2DBT was oxidized with TBHP in the presence of the catalyst. (The 9.45 mM concentration corresponds to 374 ppm of sulfur, which is just below the current EPA limit (400 ppm) on sulfur content in gasoline [1].) The oxidation of DBT at these low concentrations (Table 8, entry 1), using 2.0 mol% of (SiO_2-RTA)Re(O)(Me)(PPh_3) at 50 °C with three equivalents of TBHP occurred with a half-life of 0.28 h. By lowering the catalyst amount to 0.50 mol%, a four-fold reduction in catalyst, reaction times and half-lives were extended by slightly more than four-fold (Table 8, entry 2, $t_{1/2}$ = 1.3 h). The sterically hindered, 4,6-Me_2DBT was

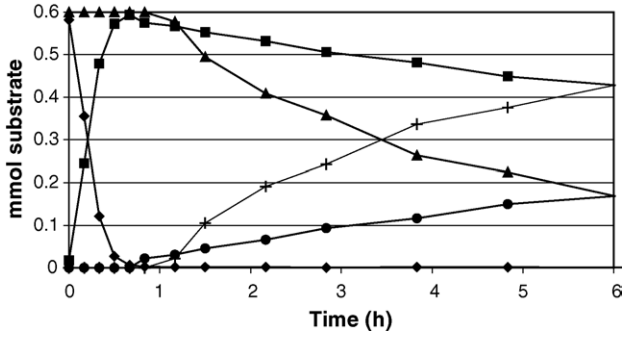


Fig. 5. (SiO_2-RTA)Re (O)(Me)(PPh_3)-catalyzed oxidation of MTS and DBT with TBHP at 50 °C[a] (a) reaction conditions: 0.60 M DBT and 0.60 M MTS in 1.0 ml toluene, 50 °C, 1.2 M TBHP, 10.0 mg (SiO_2-RTA)Re (O)(Me)(PPh_3), 0.3 mol% Re. Reaction stopped after 6 h due to total consumption of TBHP; addition of excess TBHP led to complete oxidation of both MTS and DBT. (▲) DBT, (♦) MTS, (■) MTS(O), (●) MTS($O)_2$, (+) DBTO.

Table 8
(SiO_2-RTA)Re (O)(Me)(PPh_3)-catalyzed oxidation of DBT and 4,6-Me_2DBT by TBHP at 50 °C[a]

Entry	Substrate	Catalyst[b] (mol%)	$t_{1/2}$ (h)[c]	TO at 0.5 h[d]
1	DBT	2.0	0.28 (1)	35
2	DBT[e]	0.50	1.3 (1)	47
3	4,6-Me_2DBT[f]	2.0	0.33 (3)	33
4	4,6-Me_2DBT[g]	2.0	0.24 (2)	38
5	4,6-Me_2DBT[h]	2.0	0.30 (1)	34
6	4,6-Me_2DBT[i]	2.0	0.31 (3)	34

[a] Reaction conditions: 1.0 mL of toluene:hexane (45:55) solvent mixture, 9.45 mM DBT or 4,6-Me_2DBT, 28.4 mM TBHP, 50 °C, 1.0 mg (0.18 μmol Re) of solid catalyst.
[b] Ratio of rhenium to substrate (DBT or 4,6-Me_2DBT) expressed as a percentage. Amount of rhenium: 2.0 mol% = 0.18 μmol Re, 0.50 mol% = 0.045 μmol Re.
[c] Table 3, footnote c.
[d] Table 7, footnote d.
[e] [DBT] = 4.75 mM.
[f] First use.
[g] Second use.
[h] Third use.
[i] Fourth use.

oxidized by (SiO_2-RTA)Re(O)(Me)(PPh_3) (with 2.0 mol% catalyst) at a rate (Table 8, entry 3, $t_{1/2}$ = 0.33) that was only slightly slower than that for DBT (entry 1). A series of reuse experiments (Section 2.3) showed that the catalyst does not lose activity in the oxidation of 4,6-Me_2DBT through four cycles (Table 8, entries 3–6, $t_{1/2}$ = 0.33, 0.24, 0.30 and 0.31 h) and the rates of 4,6-Me_2DBT oxidation are nearly the same as that of DBT (Table 8, entry 1, $t_{1/2}$ = 0.28 h). Thus, this catalyst converts the 400 ppm of sulfur present in the 9.45 mM DBT or 4,6-Me_2DBT solution to the corresponding oxides in greater than 95% yield within 1.2 h using 2 mol% catalyst at 50 °C, and this catalyst remains active for at least four uses.

3.7. Catalyst lifetime and reuse

In order to determine the catalyst lifetime of (SiO_2-RTA)Re(O)(Me)(PPh_3), a series of 0.60 M DBT oxidations at 100 °C in toluene were performed using different ratios of catalyst to substrate (mol% catalyst). In five consecutive reactions with 0.3 mol% of (SiO_2-RTA)Re(O)(Me)(PPh_3), where the catalyst was recycled and re-used, the catalyst showed no decrease in activity. This corresponds to approximately 1500 catalyst turnovers. However, using 0.03 mol% of (SiO_2-RTA)Re(O)(Me)(PPh_3), the catalyst was only fully active for DBT oxidation during its first use; a second use of the catalyst provided less than 300 turnovers after a day of reaction. Thus, (SiO_2-RTA)Re(O)(Me)(PPh_3) has a lifetime of just over 3300 turnovers for the oxidation of DBT at 100 °C. Since (pdt)Re(O)(Me)(PPh_3) loses activity after 1000 turnovers (Section 3.4) and (SiO_2-RTA)Re(O)(Me)(PPh_3) remains active through 3300 turnovers, the tethered catalyst is approximately three times more productive than the homogeneous pdt catalyst.

The effect of the TBHP oxidant on the catalyst activity was probed by a series of catalyst pretreatments where the catalyst was stirred with TBHP in toluene at 50 °C prior to the addition of the 4,6-Me_2DBT substrate (Table 9). As compared with no TBHP pretreatment (Table 9, entry 1, $t_{1/2}$ = 0.33 h), a 3 h pretreatment caused a significant increase in rate (entry 2, $t_{1/2}$ = 0.121 h). A 5 h pretreatment, caused the rate to decrease to that of the untreated catalyst (entry 3, $t_{1/2}$ = 0.33 h). Pretreatment for 30 h greatly reduced the catalyst activity (entry 4, $t_{1/2}$ = 1.3 h) to approximately 25% of that exhibited by the untreated catalyst. Treatment with TBHP for 46 h at 50 °C left the system inactive (entry 5); however, this deactivation was due to TBHP decomposition because the oxidation of the 4,6-Me_2DBT proceeded smoothly (entry 6, $t_{1/2}$ = 0.3 h) and as rapidly as a non-pretreated sample (entry 1, $t_{1/2}$ = 0.33 h) when fresh TBHP was added to the reaction solution. However, upon filtration of the 46 h pretreated sample, it was discovered that the solid catalyst retained no activity for 4,6-Me_2DBT oxidation even with fresh TBHP (entry 7). Instead, the mother liquor was responsible for all of the observed activity, as the rate using the mother liquor (entry 8, $t_{1/2}$ = 0.31 h) as the catalyst was nearly identical to that observed for the sample that had not been filtered (entry 6, $t_{1/2}$ = 0.3 h). Thus, prolonged exposure of (SiO_2-RTA)Re(O)(Me)(PPh_3) to TBHP at 50 °C removes the rhenium catalyst from the surface. This could occur at the ester linkage, perhaps by transesterification (*t*-BuOH) of the ester bond or by removal of some form of the rhenium that is still active. It should be noted (Sections 3.3, 3.5, 3.6) that this cleavage is negligible during normal catalytic reactions, which do not involve long TBHP pretreatments.

Table 9
Effect of 50 °C TBHP pretreatments on (SiO_2-RTA)Re (O)(Me)(PPh_3)-catalyzed oxidation of 4,6-Me_2DBT by TBHP at 50 °C[a]

Entry	Pretreatment (h)	$t_{1/2}$ (h)[b]	TO at 0.5 h[c]
1	0	0.33 (3)	33
2	3	0.121 (1)	47
3	5	0.33 (3)	33
4	30	1.3 (1)	12
5	46	NR[d]	NA
6	46[e]	0.3 (1)	34
7	46[f]	slow[g]	NA
8	46[h]	0.31 (3)	34

[a] Reaction conditions: 1.0 mL of toluene:hexane (45:55) solvent mixture, 9.45 mM 4,6-Me_2DBT, 28.4 mM TBHP, 50 °C, 1.0 mg of solid catalyst, 2.0 mol% catalyst (0.18 μmol Re).
[b] Table 3, footnote c.
[c] Table 7, footnote d.
[d] No reaction observed in 1 day.
[e] 28.4 mM fresh TBHP added to catalyst from entry 5.
[f] Immobilized catalyst from entry 5 washed after pretreatment prior to use with 28.4 mM fresh TBHP.
[g] Less than 1% reaction in 1 day.
[h] Mother liquor from the washed catalyst (entry 7) with 28.4 mM fresh TBHP.

4. Conclusion

An immobilized oxorhenium(V) dithiolate catalyst, (SiO_2-RTA)Re(O)(Me)(PPh_3), that oxidizes a sulfide and dibenzothiophenes has been synthesized and characterized. The catalyst activity and selectivity mirror those exhibited by its solution analog, (pdt)Re(O)(Me)(PPh_3). In addition, the supported catalyst is recyclable and displays a longer lifetime (TO ∼3300) for DBT oxidation at 100 °C than the homogeneous analog (pdt)Re(O)(Me)(PPh_3) (TO ∼1000). Furthermore, the catalyst easily converts the refractory sulfur compounds DBT and 4,6-Me_2DBT in simulated petroleum feedstocks to their sulfoxides or sulfones.

Acknowledgments

This research was supported at Ames Laboratory by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, Division of Chemical Sciences, under Contract W-7405-Eng-82 with Iowa State University. We thank Mr. J. Messerly and Dr. R.S. Houk for the ICP-MS Re analyses.

References

[1] M. Borushko, Fed. Regist. 66 (2001) 5001.
[2] (a) D.D. Whitehurst, T. Isoda, I. Mochida, Adv. Catal. 42 (1998) 345;
(b) B.C. Gates, H. Topsøe, Polyhedron 16 (1997) 3213;
(c) H. Topsøe, B.S. Clausen, F.E. Massoth, Hydrotreating Catalysis Science and Technology, Springer, Berlin, 1996, pp. 7;
(d) T.C. Ho, Catal. Today 98 (2004) 3.
[3] (a) C. Song, X. Ma, Appl. Catal. B: Environ. 41 (2003) 207;
(b) X. Ma, S. Velu, J.H. Kim, C. Song, Appl. Catal. B: Environ. 56 (2005) 137;
(c) A.J. Hernández-Maldonado, F.H. Yang, G. Qi, R.T. Yang, Appl. Catal. B: Environ. 56 (2005) 111.
[4] (a) I.V. Babich, J.A. Moulijn, Fuel 82 (2003) 607;
(b) Refs. 84–86 in above.
[5] (a) V.P. Nero, R.E. Levy, A.S. Rappas, S.P. Clark, F.-M. Lee, K. Bowers, Hydrocarbon Eng. 8 (2003) 51;
(b) R.E. Levy, A.S. Rappas, F.-M. Lee, V.P. Nero, S.J. Decaino, Hydrocarbon Eng. 7 (2002) 25.
[6] K. Ryu, J. Heo, I.-K. Yoo, Biotech. Lett. 24 (2002) 143.
[7] F.M. Collins, A.R. Lucy, C. Sharp, J. Mol. Catal. A: Chem. 117 (1997) 397.
[8] Y. Wang, G. Lente, J.H. Espenson, Inorg. Chem. 41 (2002) 1272.
[9] N. d'Alessandro, L. Tonucci, M. Bonetti, M. Di Deo, M. Bressan, A. Morvillo, New J. Chem. 27 (2003) 989.
[10] K. Yazu, Y. Yamamoto, T. Furuya, K. Miki, K. Ukegawa, Energy Fuels 15 (2001) 1535.
[11] (a) K. Yazu, T. Furuya, K. Miki, K. Ukegawa, Chem. Lett. 32 (2003) 920;
(b) K. Yazu, T. Furuya, K. Miki, K. Ukegawa, J. Jpn. Pet. Inst. 46 (2003) 379.
[12] P.D. Filippis, M. Scarsella, Energy Fuels 17 (2003) 1452.
[13] (a) Y. Shiraishi, K. Tachibana, T. Hirai, I. Komasawa, Ind. Eng. Chem. Res. 41 (2002) 4362;
(b) Y. Shiraishi, T. Hirai, Energy Fuels 18 (2004) 37.
[14] M. Te, C. Fairbridge, Z. Ring Appl. Catal. A: Gen. 219 (2001) 267.
[15] V. Hulea, F. Fajula, J. Bousquet, J. Catal. 198 (2001) 179.
[16] Y. Shiraishi, T. Hirai, I. Komasawa, J. Chem. Eng. Jpn. 35 (2002) 489.
[17] Y. Shiraishi, T. Hirai, I. Komasawa, J. Chem. Eng. Jpn. 35 (2002) 1305.
[18] Y. Shiraishi, T. Naito, T. Hirai, Ind. Eng. Chem. Res. 42 (2003) 6034.
[19] J. Palomeque, J.-M. Clacens, F. Figueras, J. Catal. 211 (2002) 103.
[20] D. Wang, E.W. Qian, H. Amno, Z. Okata, A. Ishihara, T. Kabe, Appl. Catal. A: Gen. 253 (2003) 91.
[21] S. Murata, K. Murata, K. Kindena, M. Nombra, Energy Fuels 18 (2004) 116.
[22] K. Yatsu, H. Miki, K. Ukegaw, N. Yamamoto, Jpn. Kokai Tokkyo Koho 2001, Patent No. JP2001/29376, p. 12 to Ministry of Economy, Trade and Industry; National Industrial Research Institute, Japan.
[23] S. Otsuki, T. Nonaka, W. Qian, A. Ishihara, T. Kabe, Sekiyu Gakkaishi 42 (1999) 315.
[24] (a) R. Hille, Chem. Rev. 96 (1996) 2757;
(b) R.H. Holm, J.M. Berg, Acc. Chem. Res. 19 (1986) 363;
(c) R.H. Holm, Chem. Rev. 87 (1987) 1401;
(d) S.J. Lippard, J.M. Berg, Principles of Bioinorganic Chemistry, University Science Books, Mill Valley, CA, 1994;
(e) A. Ishihara, D. Wang, F. Dumeignil, H. Amano, E.W. Qian, T. Kabe, Appl. Catal. A: Gen. 279 (2005) 279;
(e) C. Li, Z. Jiang, J. Gao, Y. Yang, S. Wang, F. Tian, F. Sun, X. Sun, P. Ying, C. Han, Chem. Eur. J. 10 (2004) 2277.
[25] (a) G.N. George, J. Hilton, C. Temple, R.C. Prince, K.V. Rajagopalan, J. Am. Chem. Soc. 121 (1999) 1256;
(b) K.-M. Sung, R.H. Holm, J. Am. Chem. Soc. 123 (2001) 1931;
(c) L.J. Laughlin, C.G. Young, Inorg. Chem. 35 (1996) 1050;
(d) P.D. Smith, A.J. Millar, C.G. Young, A. Ghosh, P.J. Basu, J. Am. Chem. Soc. 122 (2000) 9298;
(e) P.D. Smith, D.A. Slizys, G.N. George, C.G. Young, J. Am. Chem. Soc. 122 (2000) 2946.
[26] D.E. DeVos, B.F. Sels, P.A. Jacobs, Adv. Catal. 46 (2001) 1.
[27] (a) J.D. Morrison (Ed.), Asymmetric Synthesis, Chiral Catalysis, vol. 5, Academic Press, Orlando, 1985;
(b) D.E. Vos, I.F.J. Vankelecom, P.A. Jacobs (Eds.), Chiral Catalyst Immobilization and Recycling, Wiley-VCH, New York, 2000;
(c) E.N. Jacobsen, A. Pfaltz, H. Yamamoto (Eds.), Comprehensive Asymmetric Catalysis, vol. I–III, Springer, New York, 1999.
[28] (a) M.H. Valkenberg, W.F. Hölderich, Catal. Rev. 44 (2002) 321;
(b) J.A. Gladysz (Ed.), Chem. Rev., 102, 2002, p. 3215;
(c) I. Toth, P. Van Geem, in: I.T. Horvath (Ed.), Encyclopaedia of Catalysis, vol. 4, Wiley & Sons, 2003, p. 164.
[29] J. Jacob, J.H. Espenson, Chem. Commun. (1999) 1003.
[30] J. Jacob, I.A. Guzei, J.H. Espenson, Inorg. Chem. 38 (1999) 1040.
[31] J. Jacob, G. Lente, I.A. Guzei, J.H. Espenson, Inorg. Chem. 38 (1999) 3762.
[32] G. Lente, J. Jacob, I.A. Guzei, J.H. Espenson, Inorg. React. Mech. (Amsterdam) 2 (2000) 169.
[33] G. Lente, I.A. Guzei, J.H. Espenson, Inorg. Chem. 39 (2000) 1311.
[34] G. Lente, X. Shan, I.A. Guzei, J.H. Espenson, Inorg. Chem. 39 (2000) 3572.
[35] G. Lente, J.H. Espenson, Inorg. Chem. 39 (2000) 4809.
[36] D.W. Lahti, J.H. Espenson, J. Am. Chem. Soc. 123 (2001) 6014.
[37] J.H. Espenson, X. Shan, Y. Wang, R. Huang, D.W. Lahti, J. Dixon, G. Lente, A. Ellern, I.A. Guzei, Inorg. Chem. 41 (2002) 2583.
[38] J. Dixon, J.H. Espenson, Inorg. Chem. 41 (2002) 4727.
[39] A.B. Pangborn, M.A. Giardello, R.H. Grubbs, R.K. Rosen, F.J. Timmers, Organometallics 15 (1996) 1518.
[40] (a) B.L. Booth, G.C. Ofunne, C. Stacey, P.J.T. Tait, J. Organomet. Chem. 315 (1986) 143;
(b) G. Dupas, P. Tintillier, T. Trefouel, J. Cazin, D. Losset, J. Bourguignon, G. Queguiner, New J. Chem. 13 (1989) 255.
[41] J. Takacs, M.R. Cook, P. Kiprof, J.G. Kuchler, W.A. Herrmann, Organometallics 10 (1991) 316.
[42] X. Shan, A. Ellern, J.H. Espenson, Angew. Chem. Int. Ed. 41 (2002) 3807.
[43] A. Pines, M.G. Gibby, J.S. Waugh, J. Chem. Phys. 59 (1973) 569.
[44] O.B. Peersen, X. Wu, I. Kustanovich, S.O. Smith, J. Magn. Reson. A 104 (1993) 334.
[45] J. Gulinski, H. Maciejewski, I. Dabek, M. Zaborski, Appl. Organomet. Chem. 15 (2001) 649.
[46] J.A. Davis, S. Dutramez, A.A. Pinkerton, Inorg. Chem. 30 (1991) 2380.
[47] (a) A. Bielecki, D.P. Burum, J. Magn. Reson. A 116 (1995) 215;
(b) A.-R. Grimmer, A. Kretschmer, V.B. Cajipe, Magn. Reson. Chem. 35 (1997) 86.
[48] J.V. Paukstelis, E.F. Byrne, T.P. O'Connor, T.E. Roche, J. Org. Chem. 42 (1977) 3941.
[49] J.P. Osegovic, R.S. Drago, J. Catal. 182 (1999) 1.
[50] J.H. Espenson, Coord. Chem. Rev. 249 (2005) 329.
[51] P.J. Kropp, G.W. Brenton, J.D. Fields, J.C. Tung, B.R. Loomis, J. Am. Chem. Soc. 122 (2000) 4280.
[52] E.N. Kadnikova, N.M. Kostić, J. Non-Cryst. Solids 283 (2001) 63.