mechanism by which disorder can be introduced in this direction that also accounts for the observed niobium deficiency. If all of the Nb(1) atoms in a (101) "layer" are removed, the remaining structural motifs can be connected through corner-shared Nb(2) and Si(Ge) polyhedra to form structures containing six-membered channels along the [010] direction. Modeling studies suggest that if such layers of Nb(1) atoms are removed at random, order is lost along the [101] direction but maintained in the [011] direction.

Thermal analysis of NSH-1 and NGH-1 revealed that loss of the template occurs between about 200 and 520 °C. Powder X-ray diffraction patterns of samples of NSH-1 and NGH-1 heated for 1–2 h at 350 and 440 °C, respectively, indicated that the frameworks remain intact following loss of the template, although a substantial loss of crystallinity was evident. IR spectroscopy confirmed complete loss of the template from the calcined materials. Heating at substantially higher temperatures produced amorphous materials.

Ion-exchange experiments revealed that the piperazinium cations in NSH-1 and NGH-1 could be successfully exchanged for Na^+ and K^+ ions, as demonstrated by small changes in the powder X-ray diffraction patterns and the diminution in the intensity of the carbon–carbon and carbon–nitrogen stretches in the IR spectra. The materials largely retained their crystallinity following the exchange procedure, although some line broadening was observed.

In summary, we have described the low-temperature hydrothermal synthesis and structure of the first examples of organically templated open-framework niobium silicates and germanates. The materials display thermal stability and ion-exchange capability. Given the large variety of organic templates that could be used in this synthetic regime, and the range of compositions seen in condensed niobium silicates and germanates, the scope for the synthesis of further novel materials in this class appears to be very large.

Experimental Section

Syntheses were conducted hydrothermally in a Teflon-lined autoclave (23 mL).

NSH-1: Nb_2O_5 (0.089 g,99.5 %, Aldrich) was dissolved in aqueous HF (0.167 g 48 wt %, Aldrich) and heated to 110 °C for 4 h. After cooling, this solution was combined with SiO_2 (0.120 g, fumed, 99.8 %, Aldrich), piperazine (0.459 g, 99 %, Aldrich), H_2O (2.88 g), and ethylene glycol (5 g) and heated at 160 °C for 25 days. A fine white powder (particle size ca. 0.2 μm) of NSH-1 was recovered. NGH-1 was synthesized following the same procedure, by using 0.209 g of GeO_2 (99.99 %, Aldrich) instead of the SiO_2. A fine white powder of NGH-1 (ca. 0.4 μm) was obtained after heating at 160 °C for six days.

Ion-exchange reactions were performed by stirring 100 mg samples in 2 M aqueous solutions (10 mL) of either NaCl or KCl at 60 °C for 12 h. Thermogravimetric analyses were performed in flowing dry air on a Thermal Instruments TGA 2950 instrument at a ramp rate of 5 K min^{-1}. IR spectra were collected on a Mattson FTIR 5000 spectrometer (KBr method).

Received: March 12, 2001 [Z 16758]

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A Lewis Acid Catalyst Anchored on Silica Grafted with Quaternary Alkylammonium Chloride Moieties**

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The development of novel catalytic materials based on mesoporous supports by chemically binding the active species on their surfaces has become of profound importance in recent years owing to the benefits of catalyst heterogeniza-

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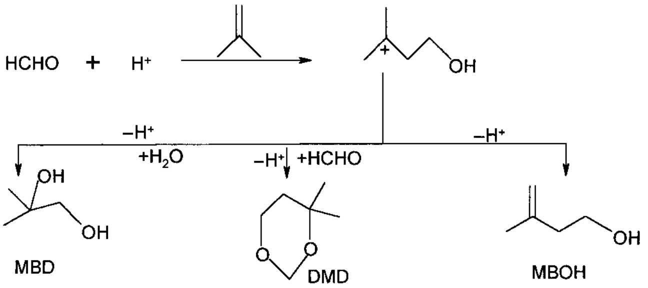
[**] T.M.J. is grateful to the Blechner fund for a postdoctoral fellowship.

tion.[1] This can potentially lead to enhanced activity and/or product selectivity while avoiding the drawbacks of catalyst instability and limited reusability. Although polymer-supported catalysts have been widely used in synthesis, catalysts based on high-surface-area inorganic supports are preferred due to their higher thermal stability and better rates of molecular diffusion.[2] The corrosivity and potential environmental hazards associated with common Lewis acid catalysts such as $AlCl_3$, BF_3, and $SnCl_4$, as well as difficulties in catalyst recycling, have aroused great interest in finding alternatives. Direct immobilization of such catalysts on inorganic supports appears to be easy, but their application is rather limited due to possible leaching of the supported species during the reaction.[2b,3] Also, the mineral acid evolved in the reaction of surface hydroxy groups with the Lewis acid is sometimes retained on the catalyst and can even change the nature of the support.[4]

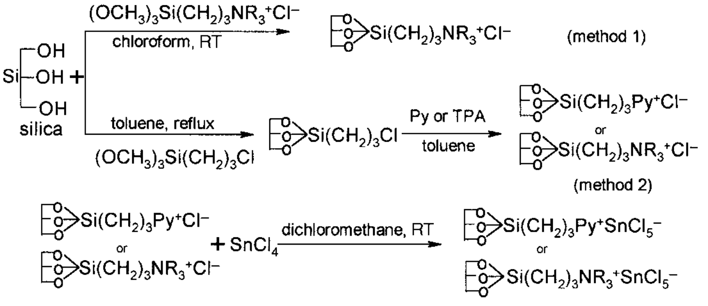
In connection with our ongoing research on the Prins condensation of alkenes and formaldehyde to give valuable unsaturated alcohols (Scheme 1), we developed a new catalyst by anchoring the active $SnCl_4$ catalyst on silica functionalized with organic quaternary ammonium chloride moieties. Our methodology is based on the fact that the nucleophilic addition of tetraalkylammonium halides to $SnCl_4$ leads to the formation of pentacoordinate anionic tin species.[5] Such complexes of general formula $[NR_4]^+[SnCl_5]^-$ resemble ionic liquids or molten salts.[6] Ionic liquids, which can be prepared by the reaction of a tetraalkylammonium halide $NR_4^+X^-$ with a Lewis acid MX, are effective Friedel–Crafts catalysts. Holderich et al. immobilized such ionic liquids directly on various inorganic supports and used them in alkylation reactions.[7]



Scheme 1. Prins condensation of isobutene with formaldehyde. MBD = 3-methylbutane-1,3-diol, DMD = 4,4-dimethyl-1,3-dioxane, MBOH = 3-methyl-3-buten-1-ol.

A recent patent described the use of $SnCl_4$ anchored to an ion-exchange resin containing tetraalkylammonium chloride substituents in the Prins condensation of isobutene and formaldehyde for the selective synthesis of 3-methyl-3-buten-1-ol (MBOH), which is an important synthesis block for industrially valuable terpenes.[8] Zeolite catalysts such as ZSM-5 and FeMCM-22 were used in the selective synthesis of MBOH, but the yield was unsatisfactory.[9] Also, MBOH was prepared from isobutene and formaldehyde by using metal chlorides such as $SnCl_4$ and $ZnCl_2$ under mild conditions, but the yield was low due to the formation of many side products.[10]

Preliminary experiments on the Prins condensation of isobutene with formaldehyde indicated that complexation of $SnCl_4$ with a tetraalkylammonium chloride leads to improved selectivity for the unsaturated alcohol MBOH. Such complexes were grafted onto silica by two methods (Scheme 2).



Scheme 2. Preparation of $SnCl_4$ anchored on tetraalkylammonium chloride functionalized silica. Py = pyridine, TPA = tetrapropylammonium chloride, R = alkyl.

Formation of a complex between $SnCl_4$ and the tetraalkylammonium chloride moiety was confirmed by ^{119}Sn NMR spectroscopy. A shift in the NMR signal from $\delta = -665.0$ to -725.2 after the reaction with tetraalkylammonium chloride reflects the change in the coordination number of tin. Moreover, the tin/chlorine atomic ratio, determined by elemental analysis, was in accordance with formation of such a complex.

The results of the Prins condensation of isobutene and formaldehyde on various complexes are summarized in Table 1. Clearly, complexation of $SnCl_4$ with tetraalkylammonium chloride improves the selectivity for the unsaturated alcohol. Tin(IV) chloride alone under anhydrous conditions displayed high activity, but the selectivity for MBOH was poor. The solvent (acetonitrile, chloroform, or dichloromethane) had little influence on formaldehyde conversion and MBOH selectivity. However, the use of an aqueous formaldehyde solution instead of paraformaldehyde adversely

Table 1. Prins condensation of isobutene and formaldehyde over NR_4Cl–$SnCl_4$ complexes.[a]

Entry	Catalyst	Solvent/ HCHO	Conversion of formaldehyde [%]	MBOH selectivity [%][g]	MBOH yield [%][h]
1	$SnCl_4$	$CHCl_3$/pf[b]	97.4	54.6	53.0
2	$SnCl_4$-TPAC[c]	$CHCl_3$/pf	77.1	89.0	68.7
3	$SnCl_4$-TPAC	CH_2Cl_2/pf	77.3	88.5	68.4
4	SnCl4-TPAC	CH_3CN/pf	75.9	87.7	66.7
5	$SnCl_4$-TPAC	CH_3CN/aq[d]	59.7	40.0	22.0
6	$SnCl_4$-BTEAC[e]	$CHCl_3$/pf	76.6	87.1	66.7
7	$SnCl_4$-TMSPAC[f]	$CHCl_3$/pf	70.3	89.4	62.8
8	No catalyst	$CHCl_3$/pf	–	–	–

[a] 56 g isobutene, 3 g paraformaldehyde, catalyst containing 4 mmol of $SnCl_4$, and 40 g of chloroform solvent were introduced into the reactor and stirred for 2 h at 60 °C. [b] Paraformaldehyde. [c] Tetrapropylammonium chloride–$SnCl_4$ complex. [d] 30% aqueous solution of formaldehyde. [e] Benzyltriethylammonium chloride–$SnCl_4$ complex. [f] Complex prepared from [3-(trimethoxysilyl)propyl]octadecyldimethylammonium chloride and $SnCl_4$. [g] Other products included 4,4-dimethyl-1,3-dioxane and traces of polycondensation products. [h] Yield was determined by using 2-butanol as an internal standard.

affected the conversion and MBOH selectivity. Under these conditions, larger amounts of side products such as 4,4-dimethyl-1,3-dioxane (DMD) and 3-methylbutane-1,3-diol (MBD) were formed. Hence, to maximize the yield of MBOH, anhydrous conditions were maintained in all other experiments.

Various silica-based catalysts were tested in the selective synthesis of MBOH (Table 2). For comparison, the $NR_4^+SnCl_5^-$ complex immobilized directly on silica and silica-supported $SnCl_4$ were also tested. The catalysts immobilized on silica that was functionalized with organic quaternary ammonium moieties showed the highest selectivity for MBOH (88–93 %). X-ray fluorescence (XRF) analysis of the filtrate after the reaction (detection limit: >0.5 ppm of Sn) indicated no leaching of tin from the catalyst. Furthermore, when a subsequent reaction was performed with the filtrate after separating the catalyst no formaldehyde conversion occurred. Recycling of the catalyst led to no appreciable loss in activity. Increasing the reaction time to 3.5 h increased the MBOH yield to 76 % (entry 7) and 81 % (entry 9). The catalyst prepared by treating a solution of $SnCl_4$ in chloroform with silica (silica/$SnCl_4$) is prone to leaching during the reaction. Analysis of the filtrate after the reaction showed that around 39 % of the tin chloride had been leached out. Moreover, the performance of this catalyst in the selective synthesis of MBOH is poor (entry 3) compared to immobilized complexes. Direct immobilization of the complex on silica (SIL/TPA$^+$-SnCl$_5^-$) also resulted in lower catalytic activity and MBOH yield relative to the pure complex $SnCl_4$–TPAC and the SIL-TPA$^+$SnCl$_5^-$ catalyst. The turnover number (TON), that is, the number of moles of formaldehyde converted per mole of catalyst per unit time, for the SIL-TPA$^+$SnCl$_5^-$ catalyst (TON = 8.0) was 83 % of that obtained in a homogeneously catalyzed reaction (TON = 9.6, Table 1, entry 2) at similar MBOH selectivities. Direct immobilization of the complex reduced the relative TON to 74 % (TON = 7.3).

Table 2. Condensation of isobutene and formaldehyde to give 3-methyl-3-buten-1-ol (MBOH) over silica-based catalysts and with catalyst recycling.[a]

Entry	Catalyst	$SnCl_4$ loading [mmol g^{-1} support]	Conversion of formaldehyde [%]	MBOH selectivity [%]	MBOH yield [%]
1	SIL-TPA$^+$SnCl$_5^-$[b]	0.32	64.1	88.1	56.4
2	SIL/TPA$^+$SnCl$_5^-$[c]	0.32	57.0	79.8	45.5
3	Silica/$SnCl_4$	0.95	77.9	63.2	49.2
4	SIL-NR$_4^+$SnCl$_5^-$[d]	0.78	64.6	92.8	59.9
5	recycle 1[e]	0.78	63.3	91.1	57.6
6	recycle 2	–	61.9	91.0	56.3
7	SIL-NR$_4^+$SnCl$_5^-$[f]	0.78	100	76.1	76.1
8	SIL-Py$^+$/SnCl$_5^-$[g]	0.48	66.3	91.9	60.9
9	SIL-Py$^+$/SnCl$_5^-$[f]	0.48	97.8	82.6	80.7

[a] Reaction conditions were as in Table 1, and in all cases the amount of catalyst containing 4 mmol of $SnCl_4$ was used. [b] Tetrapropylammonium chloride functionalized silica complex. [c] Direct immobilization of complex on silica. [d] Catalyst prepared by method 1. [e] Recycling of SIL-NR$_4^+$SnCl$_5^-$ after exhaustive washing with dichloromethane. [f] Reaction continued for 3.5 h. [g] Pyridinium chloride functionalized silica complex.

The present methodology of immobilizing a Lewis acid is of wide practical utility due to the possibility of anchoring various metal halides to give novel supported catalysts for different organic reactions. This type of anchoring could be advantageous for obtaining catalysts with high stability and longer lifetime. Unlike catalysts with a directly attached Lewis acid, prepared by the reaction of surface hydroxy groups of the support with hydrolyzable groups in the Lewis acid, the present catalyst is stable under the experimental conditions due to the formation of strong Si–O–Si bonds on the catalyst surface. Moreover, we believe that the the active sites will be more readily accessible to the reactants, since they are further from the silica surface.

In conclusion, we have demonstrated a new supported Lewis acid catalyst which is resistant to leaching and shows high selectivity in the synthesis of 3-methyl-3-butene-1-ol by the Prins condensation of isobutene and formaldehyde. Further work is underway to exploit these supported Lewis acid catalysts for developing clean technology in fine-chemical synthesis.

Experimental Section

All manipulations were performed under dry and inert conditions in a glove box, and all solvents were dried by standard procedures. $SnCl_4$–TPAC complex was prepared by the dropwise addition of anhydrous $SnCl_4$ (4 mmol) to a solution of tetrapropylammonium chloride (4 mmol) in dichloromethane (40 g) with constant stirring. The mixture was stirred overnight at ambient temperature, and the solution was concentrated in vacuum to give a white crystalline material, which was recrystallized from dichloromethane/hexane and stored under moisture-free conditions. Elemental analysis (%): calcd: Sn 24.61, Cl 36.74; found: Sn 24.78, Cl 36.40.

Silica gel (surface area: 500 m^2 g^{-1}) with an average pore diameter of 6 nm and particle size between 0.063 and 0.20 mm (Aldrich), preheated at 473 K for 6 h, was used as support. In method 1, silica (5 g) was treated with a solution of [3-(trimethoxysilyl)propyl]octadecyldimethylammonium chloride (4.82 g, 7 mmol, Aldrich) in chloroform to give tetraalkylammonium chloride functionalized silica. The excess of the reagent was removed by exhaustive Soxhlet extraction with dichloromethane and finally dried in vacuum. In method 2, silica support (5 g) was first treated with a solution of trimethoxysilylpropyl chloride (3 g, 14.64 mmol, Aldrich) in toluene under reflux for 5 h. The excess of the reagent was removed as explained above, and the propylated silica was treated with an excess of pyridine or tripropylamine (6–7 g) in toluene for 24 h under reflux to give pyridinium chloride functionalized and tetrapropylammonium chloride functionalized silica, respectively.

The amount of chloride ions present on the functionalized silica was determined by treating the solid with 0.1N nitric acid, followed by titration with a standard $AgNO_3$ solution and potassium chromate indicator.

The tin chloride was anchored on functionalized silica by treating a suspension of the amount of modified silica containing 4 mmol of chloride anion in dicholoromethane with a solution of anhydrous $SnCl_4$ (1.04 g, 4 mmol) with stirring for 12 h (Scheme 2). After the reaction, the catalyst was collected by filtration and subjected to Soxhlet extraction to remove loosely bound species.

Silica/TPA-$SnCl_4$ catalyst was prepared by adding a chloroform solution of the complex prepared as mentioned above to 4 g of predried silica support suspended in chloroform with constant stirring. The excess solvent was removed after stirring overnight, and the material was extracted with chloroform for 12 h in a Soxhlet apparatus. The material was finally dried and kept under moisture-free conditions before use.

The Prins condensation of isobutene and formaldehyde was carried out at 60 °C under autogenous pressure by introducing isobutene (56.1 g, 1.0 mol), paraformaldehyde (3 g, 0.1 mol), the solvent (40 g), and the amount of catalyst containing 4 mmol of $SnCl_4$ into a 250-mL Büchi autoclave. After stirring the mixture for 2 h, isobutene was released, the solid catalyst was separated, and the filtrate was analyzed on a gas chromatograph equipped with a capillary column (DB WAX) and thermal conductivity detector.

Received: February 23, 2001 [Z16673]

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Molecular Models of Titania – Silica Systems and a Late Transition Metal Complex Grafted Thereon**

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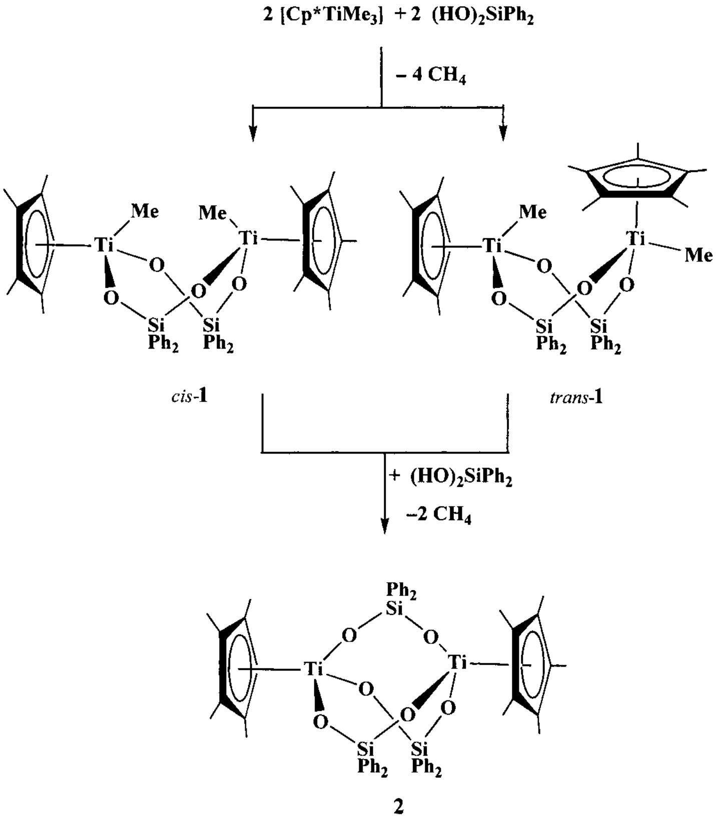
Titania – silica materials are the focus of much attention on account of their unique properties:[1, 2] 1) they can act as catalysts for a wide variety of processes; 2) they are suitable supports for late transition metal catalysts because they improve the mechanical strength, thermal stability, and surface area relative to TiO_2 supports.[3] Although titania – silica materials have been extensively used as catalysts and supports for a great variety of reactions, and several well-defined soluble metallasiloxanes[4, 5] have been used to mimic and facilitate the understanding of the situation in solid materials, until now no molecular models have been reported for late transition metal catalysts supported on titania – silica. We previously reported[6] the synthesis of the complex $[Cp^*Ti(\mu_3\text{-}O)_3\{Rh(cod)\}_3]$ (cod = 1,5-cyclooctadiene, $Cp^* = \eta^5\text{-}C_5Me_5$), which can be regarded as a model of rhodium supported on titania. We have now extended our studies to modeling a rhodium complex supported on titania – silica. Here we report on the synthesis of the dimetallic titanium alkyl siloxide complexes $[\{Cp^*TiMe(O_2SiPh_2)\}_2]$ (**1**) and $[Cp^*Ti(O_2SiPh_2)_3TiCp^*]$ (**2**), which can be regarded as models for the above-mentioned titania – silica systems. The reaction of **1** with $[\{Rh(\mu\text{-}OH)(cod)\}_2]$ leads to the formation of $[\{Cp^*Ti(O_2SiPh_2)(\mu_3\text{-}O)Rh(cod)\}_2]$ (**3**), which can be regarded as an unprecedented molecular model of a late transition metal supported on titania – silica.

The titanium complex $[Cp^*TiMe_3]$ reacts with diphenylsilanediol to afford the yellow solid **1** (Scheme 1), which was isolated in good yield (76 %) as a mixture of two isomers. By comparison with the previously reported analogous titanium complexes,[7] we propose that **1** is a dimer in which the siloxide ligands act as bridges between two titanium atoms, and the two isomers are the *cis* and *trans* forms.[8] According to variable-temperature (VT) NMR experiments in $[D_8]$toluene, the ratio of the two isomers does not change up to 353 K. It is also independent of the concentration of the sample and the solvent ($[D_8]$toluene, C_6D_6, $CDCl_3$, $[D_8]$THF). According to



Scheme 1. Synthesis of **1** and **2**.

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[**] Financial support from the Dirección General de Enseñanza Superior e Investigación, Spain (Grant. No. D.G.E.S. PB98-0159-C02-01) is gratefully acknowledged. We thank Prof. Dr. J. L. G. Fierro, Instituto de Catálisis y Petroleoquímica, for XPS measurements.