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A New Method for Enhancing Site Isolation on Silica Gel and for Improving the Lifetime of Site-Isolated Catalysts

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Cofunctionalization of silica gel with trialkylchlorosilanes and $(CH_3O)_3SiCH_2CH_2CH_2SRh(CO)_2$ produces a catalyst for the oxidation of 1-hexene that can be compared with a catalyst that does not have an R_3Si- covering. Physical methods are used to determine the concentration of groups on the silica surface and also to determine the loading at which site separation occurs. The alkylated supports can be loaded with a greater concentration of the site-isolated rhodium complex, producing catalysts that have greater activity per gram of catalyst and longer lifetimes than the corresponding catalysts produced with nonalkylated silicate gels. Increasing the length of the alkyl group used to cover the surface decreases the effectiveness of the silica as a catalytic support and eventually leads to a catalyst surface that is not wetted by ethanol solvent.

Introduction

Site isolation is one of the primary advantages associated with the use of hybrid catalysts.[1] This feature can lead to stable coordinatively unsaturated or weakly coordinated species and stabilize catalysts by inhibiting their decomposition by multiordered or aggregation pathways. The factors that mitigate against attaining these objectives include flexible supports, migration of the attached reagent over surface sites, and the probability that near neighbors will exist as the concentration of material added to the support increases. The flexibility of the support can be controlled by proper selection of material. Silica gel has the desirable property of rigidity, and it was our goal to determine if alkylation of this surface with R_3SiCl would inhibit migration and enhance the amount of reagent that could be attached under site-isolated conditions.

In recent work from this laboratory,[2] we reported an ideal system to probe site separation from both the standpoint of a spectroscopic examination of the catalyst precursor and the catalytic reactivity of the supported compound. The reaction involves the catalytic oxidation of 1-hexene to 2-hexanone.[3,4] The catalyst is prepared by introducing an organosulfide functionality onto silica gel, producing $[SG]-OSi(OCH_3)_2CH_2CH_2CH_2SH$, abbreviated as [SG]–SH. Reactions of this material with $Rh(CO)_2{}^+BF_4{}^-$ produce solvent-stabilized organosulfide rhodium carbonyl complexes (abbreviated $[SG]-SRh(CO)_2$) on this support only under site-isolated conditions. (For simplicity in representation, the stabilizing, weakly coordinated solvent molecules will not be indicated in this paper.) These monomeric thiol complexes do not have a solution counterpart. Bimetallic, thiol-bridged species $[(CO)_2RhSR]_2$ are formed in solution and are obtained at higher extents of functionalization of silica gel. The infrared spectra of these materials enable one to readily distinguish the two compounds. Furthermore, the bridged bimetallic species lead to materials that are inactive in the catalytic oxidation of alkenes while the monomeric species is a precursor to an effective catalyst.

Our objective in this work is to use the spectral properties of the monomeric species as well as the catalytic behavior of this system to provide a means of determining how effective various procedures are for enhancing site separation. In this article, we show that isolating the functionalized [SG]-SH groups with $[SG]-SiR_3$ (where R is alkyl) causes some very pronounced changes in stability. Furthermore, significantly larger amounts of the rhodium reagent can be added to the support under site-isolated conditions.

Experimental Section

General Procedures. All solvents and reagents were of reagent grade and were used without further purification unless otherwise specified. $[Rh(CO)_2Cl]_2$[5] and $[Rh(CO)_2S'_n]BF_4$[6] (S′ = solvent) were prepared as reported in the literature or purchased from Aldrich and recrystallized from *n*-hexane. $(CH_3O)_3SiCH_2CH_2CH_2SH$ and $ClSi(CH_3)_3$ were obtained from Aldrich and $ClSi(C_2H_5)_3$ and $ClSi(C_3H_7)_3$ from Petrarch Systems. Silica gel was grade 62 from Davison Chemical.

Infrared spectra were recorded on a Perkin-Elmer Model 283B infrared spectrometer. GLC's were obtained with a Varian Model 940 FID instrument using a 3-m length, $^1/_{16}$-in. i.d. copper column packed with Chromasorb P supported diethylene glycol adipate or with a Varian Model 3700 FID chromatograph using an 8-ft length, $^1/_8$-in. i.d. column of the same material. 2-Hexanone production was quantified with use of 2-heptanone as an internal standard. Electronic absorption spectra were taken on a Cary 14; all samples were run in air at ambient temperatures and pressures.

Preparation of Silica Gel Supports. All reactions of functionalizing silanes with silica gel were done under argon with xylenes as solvent. Silica gel was stirred in xylenes under argon, followed by heating, and then a solution of one or more silanes in xylenes was added dropwise to the hot silica gel slurry. The nonalkylated [SG]–SH gel was made by adding $(CH_3O)_3SiCH_2CH_2CH_2SH$ to the gel. The [SG]–SH alkylated gels were made by adding a solution of the mercaptosilane mixed with R_3SiCl (R = CH_3, C_2H_5, C_3H_7). This technique is preferable to adding each silane in separate steps. After they were refluxed for 24 h, the silica gels were thoroughly washed with xylenes and ethanol and then dried at ~90 °C. The silica gels remain white in appearance.

Determination of –SH on Silica Gel. Silica gel and its surface silanol groups were reacted with $(CH_3O)_3SiCH_2CH_2CH_2SH$ to produce [SG]–SH. R_3SiCl (R = methyl, ethyl, propyl) was used to complete reaction of the Si–OH groups and cover the silica gel surface with alkyl groups. Evidence that trialkylsilyl groups are bound to the surface includes a substantial increase in the percent carbon found in the elemental analyses and an increase in the lifetime of the functionalized catalyst.

Electronic absorption was used to determine the amount of sulfide on each silica gel sample ([SG]–SH). [SG]–SH samples were stirred with freshly prepared $[Rh(CO)_2S'_n]BF_4$ (S′ = solvent), the solid was filtered off, and the electronic absorption spectrum of the filtrate was taken. From a calibration curve of the rhodium complex concentration vs. its absorbance at 390 nm the amount of rhodium in the filtrate is measured. The amount of rhodium on the gel is determined by the difference of the known initial amount of rhodium and the amount of rhodium in the filtrate. Assuming complete reaction of one rhodium per sulfide, the amount of rhodium is equal to the amount of sulfide on the silica surface. An analysis of this type was done for all samples.

Samples were prepared that varied in surface sulfide concentration and in percent of available surface silanol groups that were "alkylated" (reacted with trialkylchorosilane). Assuming tetrahedral coordination around silicon and oxygen atoms with an approximate silicon–oxygen bond distance of 2 Å, and assuming that as an upper limit a flat surface exists with all surface groups being Si–OH, a separation of 6.5 Å exists between the oxygens of surface hydroxyl groups. This corresponds to one surface hydroxyl per 4.3×10^{-19} m^2 of surface, so it can be calculated

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that as an *upper limit* there is about 1 mmol of surface Si–OH groups per gram of [SG]. With this value it can be determined that the [SG]–SH samples prepared contain approximately 1/40, 1/20, 1/10, and1/5 mmol of sulfide/mmol surface Si (S/Si), which correspond to 0.025, 0.05, 0.10, 0.20, and 0.40 mmol of S/g of [SG]. Silica gel samples used as catalytic supports will be referred to by a S/Si ratio and by a number of mmol of S/g of [SG]. In some instances the percent alkylation (methylation, ethylation, or propylation) of the surface silicon sites will also be used.

Catalytic Oxidations of 1-Hexene. All catalytic 1-hexene oxidations were run in 250-mL Parr pressure bottles equipped with brass Swagelok pressure heads. These were constructed to allow purging with O_2, as well as sampling of the solution under reaction conditions during the course of the reactions. 2-Hexanone production was measured by GLC. Since these mixtures are potentially explosive, care should be taken to protect workers. The samples should be cooled before venting and dishcarged in a flame-free and spark-free environment.

All catalytic reactions were run with use of 0.074 mmol of $[Rh(CO)_2S'_n]BF_4$ (prepared as reported earlier and used immediately) and 0.0179 g of $Cu(NO_3)_2 \cdot 3H_2O$ (0.074 mmol). The amount of silica gel employed was varied to provide enough –SH sites to bind all of the rhodium and copper with a 10% excess (e.g. 4.9 g of 1/20 S/Si 80% Et [SG]–SH). Both metal ions are attached to the [SG]–SH samples through the –SH moiety, producing a lemon yellow to yellow-green supported catalyst. The catalyst was added to a 250-mL Parr bottle along with 0.32 mL of 0.47 M $HClO_4$ (0.150 mmol, as an ethanol solution prepared from aqueous concentrated $HClO_4$), 1.136 mmol of 2-heptanone, 15 mL of absolute ethanol, and 15 mL of 1-hexene (purged through alumina to remove peroxides). This mixture was purged five times with 60 psi O_2, set to 40 psi O_2, and the reaction initiated by placing the system in a 70 °C oil bath.

Results and Discussion

The functionalization of silica gel is accomplished via the reactivity of R_3SiCl and $(CH_3O)_3SiCH_2CH_2CH_2SH$ with silanol groups on the surface. The reaction of the former reagent is described as

$$[SG]\text{–}OH + R_3SiCl \rightarrow [SG]\text{–}O\text{–}SiR_3 + HCl \qquad (1)$$

Reaction of the (3-mercaptopropyl)trimethoxysilane with the surface would occur similarly, except that one or more of the methoxy groups would react forming CH_3OH instead of HCl. The natures of the species formed when more than one group reacts with the silica surface (as for the trimethoxysilane) have been described.[8]

Electronic absorption (as described in the Experimental Section) was used to quantify the amount of sulfide on the silica surface. If it is assumed that all of the added $(CH_3O)_3SiCH_2CH_2CH_2SH$ reacts completely, one gets values of 0.025, 0.050, and 0.100 mmol of S/g of [SG] corresponding to 1/40, 1/20, and 1/10 S/Si, respectively. The analysis for sulfide (using rhodium as described in the Experimental Section) for a series of [SG]–SH gave values of 0.020, 0.041, and 0.076 mmol of S/g of [SG]. These values are reasonably close to those expected for complete reaction of the functionalizing agent. For a series of 1/40, 1/20, and 1/10 S/Si gels with 50% methylation of the surface, values of 0.019, 0.039, and 0.077 mmol of S/g of [SG] were obtained, respectively. An analysis of this type was done for most of the samples that were prepared. The 1/20 S/Si sample in any one series contained approximately twice the number of –SH groups as the 1/40 S/Si sample and half that of the 1/10 S/Si sample. The amount of functionalized silica gel necessary to give the same amount of rhodium and copper for use in each catalytic oxidation was determined from these analyses.

Infrared spectroscopy was employed to help characterize rhodium carbonyl species bound to the [SG]–SH silica gels. In each case freshly prepared $[Rh(CO)_2S'_n]BF_4$ (S′ = solvent) was reacted with a [*S*G]–SH sample under nitrogen and an infrared spectrum (mull) of the gel quickly taken in the CO region. When the supported rhodium complex is essentially monomeric $[SG]\text{–}SRh(CO)_2$ (e.g. 1/10 S/Si 50% Me), a two-band infrared spectrum (2055 and 2005 cm^{-1}) is obtained. A three-band spectrum (2075 (m), 2055 (s), and 2005 (s) cm^{-1}) is indicative[9] of a supported dimer, $([SG]\text{–}S)_2Rh_2(CO)_4$, and is obtained when a sample of 1/2.5 S/Si gel is reacted. Since the rhodium complex is attached to a chain of atoms, there is a relatively large area over which the rhodium may move even while attached to the silica surface. With use of typical bond distances and angles, a SiC–C–C–S–Rh chain is estimated to be 11 Å long and can rotate to sweep a 380 $Å^2$ area. With about 1 silicon atom/43 $Å^2$ of surface, the surface must be on the average about 1/9 S/Si or more dilute to produce a system in which most of the rhodium is site isolated. A sample of 1/5 S/Si 80% methylated silica gel has an infrared spectrum when functionalized with $Rh(CO)_2^+$ that indicates the presence of both monomer and dimer.

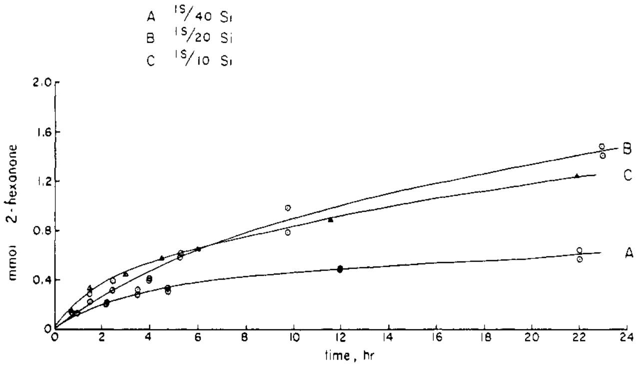

Figure 1. Amount of 2-hexanone produced vs. time for catalyst systems with (A) 0.025 mmol of S/g of [SG], (B) 0.05 mmol of S/g of [SG], and (C) 0.10 mmol of S/g of [SG]. Each [SG] is nonalkylated. All reactions were run with use of the following: 0.074 mmol of $[Rh(CO)_2S'_n]BF_4$ (as a freshly prepared ethanol solution, S′ = solvent), 0.074 mmol of $Cu(NO_3)_2 \cdot 3H_2O$, 0.16 mmol of S (as [SG]–SH), 0.015 mmol of $HClO_4$ as an ethanol solution, 1.136 mmol of 2-heptanone (as an internal standard), 45 mL of ethanol, and 15.0 mL of 1-hexane. All reactions were run at 70 °C under 40 psi O_2 after components were mixed at room temperature.

Many rhodium–copper-catalyzed oxidations of 1-hexene were carried out with use of a variety of functionalized silica gel supports. In all instances where the infrared spectrum indicated a significant concentration of monomer, an active catalyst system resulted. When the supported reagent is essentially a dimer, the catalyst is virtually inactive. The results of several of these experiments will be discussed below and are displayed in the figures as graphs of millimoles of product (2-hexanone) vs. time (in hours). All of the oxidations use the same amount of rhodium and copper (0.074 mmol each) along with a 10% excess of the amount of silica gel necessary to bind all of the rhodium and copper. Silica gels that have only sulfide but no alkylsilane on the surface (gels functionalized with only (3-mercaptopropyl)trimethoxysilane) will be referred to as nonalkylated.

Oxidations of 1-hexene using the rhodium–copper catalyst supported on nonalkylated [SG]–SH produce the results shown in Figure 1. If all of the rhodium and copper is effectively site isolated on these samples, then very similar activity should result from each of the catalysts. The 1/40 S/Si (0.025 mmol of S/g of [SG]) sample (curve A) is less active for 2-hexanone production than the 1/20 and 1/10 S/Si gels (0.05 and 0.10 mmol of S/g of [SG]), which is due to diffusion problems associated with the large amount of 1/40 S/Si catalyst needed (vide infra) to provide 0.074 mmol of copper and rhodium. When half the amount of this particular catalyst is used, the system is more than half as active. If diffusion were not rate controlling, the rate of this oxidation should have been half of the original rate since the oxidation is first order in rhodium concentration.[10]

Figure 2 shows the oxidations run by using catalysts supported on gels with approximately 50% of their surface covered with trimethylsilyl groups. Not only do they demonstrate much greater

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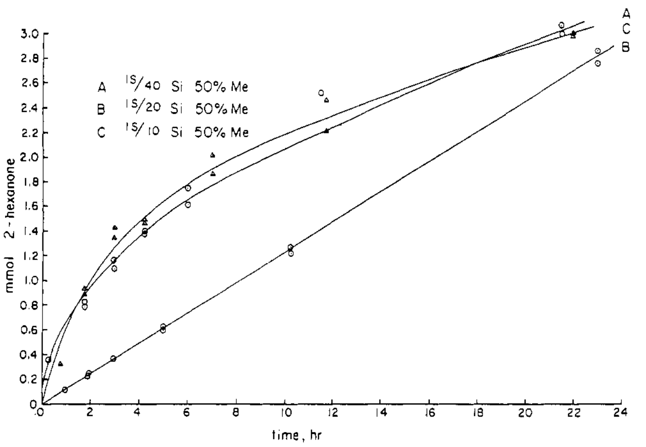

Figure 2. Amount of 2-hexanone produced vs. time for catalyst systems with (A) 0.025 mmol of S/g of [SG], 50% of the silica surface methylated, (B) 0.05 mmol of S/g of [SG], 50% methylated, and (C) 0.01 mmol of S/g of [SG], 50% methylated. All reaction systems were prepared as in Figure 1.

initial activity in some instances than their unmodified counterparts (Figure 1) but they are also still more active after 24 h. The 1/20 S/Si (0.05 mmol of S/g of [SG]) 50% methylated gel (curve B) shows virtually linear 2-hexanone production over 24 h. In comparison to the case for nonalkylated catalyst (Figure 1), an almost twofold increase in product has been obtained after 24 h and a very active catalyst remains. At the end of 4 h essentially the same amount of 2-hexanone had been produced by catalyst B (Figures 1 and 2). Infrared spectra indicated that in both catalysts the major species were monomeric [SG]-SRh$(CO)_2$ after reaction. Thus alkylation of silica gel in this instance greatly enhanced the catalyst lifetime.

Comparison of the 1/10 S/Si based catalyst systems reveals that the methylated catalyst is superior almost from the very start of the reaction (see curves C of Figures 1 and 2). This result correlates with the observation that dimer is detected after reaction with $Rh(CO)_2^+$ in the nonalkylated gel but not in the alkylated one. With this result we have demonstrated that higher loading of complex can be obtained under site-isolated conditions by diluting the functionalized reagent in the hydrocarbon matrix formed by $-Si(CH_3)_3$. A very active catalyst still exists after 24 h.

Curves A in Figures 1 and 2 present a very surprising result. Site isolation exists in both systems. The diffusion problem described in the discussion of Figure 2 apparently has been decreased by the greater affinity of alkene for the alkylated surface than for solvent. Such a rationalization explains the greater initial activity of curve A in Figure 2 vs. that in Figure 1 as well as the increased activity after 24 h.

Figure 3 allows a comparison of 80% methylation with the 50% shown in Figure 2. The more highly methylated gel is about as active as the 50% methylated material. This catalyst continues to be active after 140 h. A decrease in the activity of the catalyst is seen when $(C_2H_5)_3SiCl$ and $(C_3H_7)_3SiCl$ are used to block surface sites. The 80% propylated silica gel samples yield results similar to those of the unmodified gels in Figure 1. These silica gels are markedly slow in "wetting" by ethanol. Perhaps it is this increased hydrocarbon-like nature of the surface that accounts for their decreased efficiency as catalytic supports, relative to that of the methylated silica gels. Thus, even though enhanced solubility of the alkene in the surface layer may occur, exclusion of the solvent inhibits the reaction. Furthermore, the catalyst system selected is a bimetallic system, and if the surface composition is very effective at isolating the copper and rhodium, decreased activity would result.

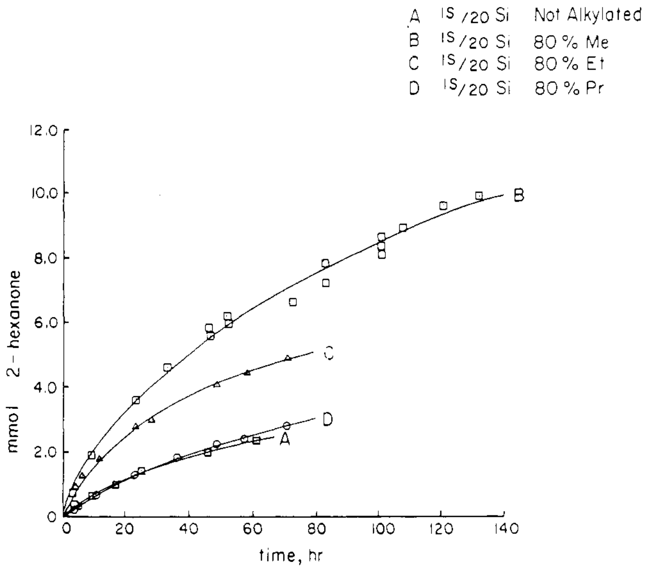

Figure 3. Amount of 2-hexanone produced vs. time for catalyst systems with (A) 0.05 mmol of S/g of [SG], nonalkylated surface, (B) 0.05 mmol of S/g of [SG], 80% of silica surface methylated, (C) 0.05 mmol of S/g of [SG], 80% of silica surface ethylated, (D) 0.05 mmol of S/g of [SG], 80% of silica surface propylated. All reaction systems were prepared as in Figure 1.

We can speculate on a model to account for the enhanced long-term stability of the methylated gels. On nonalkylated [SG]-SH the derivatized silanol groups may exchange with protons on nearby silanol groups, transferring the derivatized group. This provides a mechanism whereby the functionality can migrate along the surface, aggregate, and become inactive. The alkylated gels cap these -OH groups and would be expected to effectively suppress such a process, leading to a longer lifetime for site-isolated conditions. The mixing of reagents prior to functionalization also ensures a better distribution of functional group over the surface under site-isolated conditions and enables one to attain a more concentrated site-isolated catalyst. This approach should find general application and utility in stabilizing hybrid catalysts where site isolation is a desired feature.

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Registry No. Rh, 7440-16-6; SiH_4, 7803-62-5; $(CH_3O)_3SiCH_2CH_2CH_2SRh(CO)_2$, 96413-87-5; 1-hexene, 592-41-6.