

# Factors Influencing the Activity, Selectivity, and Stability of Rh-Based Supported Ionic Liquid Phase (SILP) Catalysts for Hydroformylation of Propene

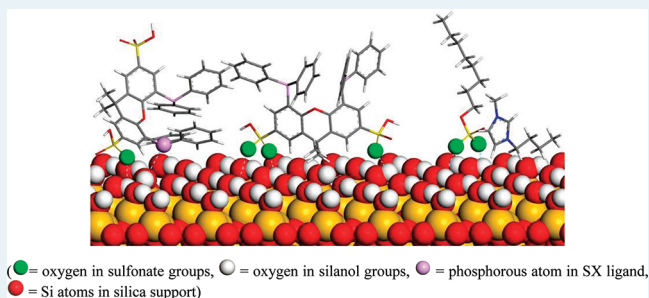
Sankaranarayananpillai Shylesh, David Hanna, Sebastian Werner, and Alexis T. Bell\*

Department of Chemical and Biomolecular Engineering, University of California, Berkeley, California 94720, United States

## Supporting Information

**ABSTRACT:** An investigation has been carried out on the effects of catalyst preparation on the activity and stability of supported ionic liquid phase (SILP) catalysts for propene hydroformylation. Catalyst activity and stability were found to be strongly influenced by ligand and ionic liquid composition, ligand-to-rhodium ratio, and the surface density of silanol groups on the silica support. Highest activity was achieved using rhodium sulfoxantphos (SX) complexes in the presence of [bmim][OctSO<sub>4</sub>]. In situ FT-IR and solid-state <sup>31</sup>P and <sup>29</sup>Si MAS NMR characterization suggest that active Rh centers are not present as homogeneous complexes dissolved in an ionic liquid film, instead are present as HRh(CO)<sub>2</sub>SX complexes bound to the support by interactions of the sulfonate groups of SX with silanol groups of the support. The function of the ionic liquid is to inhibit undesired interactions of SX ligands, since such interactions render the phosphine groups unavailable for interaction with the Rh<sup>+</sup> cations. Catalyst deactivation is attributed mainly to the formation of catalytically inactive [Rh(CO)(μ-CO)SX]<sub>2</sub> or HRh(SX)<sub>2</sub> complexes when the SX/Rh ratio is too low or high, respectively.

**KEYWORDS:** SILP catalysts, rhodium, ionic liquids, sulfoxantphos, hydroformylation



## INTRODUCTION

The hydroformylation of alkenes using homogeneous Rh complexes has received extensive interest because such catalysts can operate under relatively mild conditions (typically 80–120 °C, 10–30 atm).<sup>1–3</sup> For practical application, the products need to be separated from the catalyst, a challenge that continues to be subject of ongoing research. A particularly appealing approach is immobilization of the Rh complex onto a solid support.<sup>4–8</sup> Davis and co-workers have reported the preparation of supported aqueous-phase (SAP) catalysts by forming a thin layer of Rh-tppts (tppts = tri(*m*-sulfonyl)-triphenyl phosphine trisodium salt) dissolved in water onto high-surface-area hydrophilic silica.<sup>9,10</sup> <sup>31</sup>P NMR spectra of the catalyst were consistent with the presence of mobile Rh species in the aqueous phase. Liquid-phase hydroformylation of oleyl alcohol and several other high molecular weight alkenes was demonstrated at 100 °C. In related studies, Horvath reported that similar SAP catalysts exhibited good activity for hexene, octene, and decene hydroformylation but deactivated via the loss of water.<sup>11</sup> The concept of supported ionic liquid catalysis (SILC) was introduced by Mehnert and co-workers.<sup>12,13</sup> Catalysts were prepared by impregnating a solution of Rh-tppts in [bmim][BF<sub>4</sub>] or [bmim][PF<sub>6</sub>] into a 1-*n*-butyl-3-methyl imidazolium modified silica gel support. SILC catalysts were found to be more active for the liquid-phase hydroformylation of 1-hexene than SAP catalysts. However, a loss of

Rh was observed at high conversion because of depletion of the supported ionic liquid layer into the reaction medium. Most recently, Wasserscheid and co-workers have reported very stable supported ionic liquid-phase (SILP) Rh catalysts for the vapor-phase hydroformylation of propene.<sup>14–16</sup> In this case, silica dehydrated at 500 °C was impregnated with a solution of Rh sulfoxantphos (SX) dissolved in [bmim][OctSO<sub>4</sub>]. IR and <sup>31</sup>P NMR characterization of SILP catalysts suggested that the active form of the catalyst were Rh(H)(CO)<sub>2</sub>SX complexes dissolved in a thin layer of the ionic liquid.

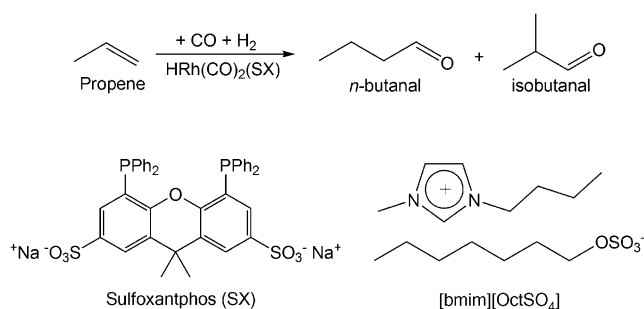
The aim of the present study was to investigate the effects of catalyst synthesis on the activity, selectivity, and stability of Rh SILP catalysts for the hydroformylation of propene (Scheme 1). Particular attention was given to the effects of (a) ligand composition, (b) ligand/rhodium ratio, (c) ionic liquid composition, (d) ionic liquid loading, and (e) temperature of silica pretreatment. The structure of the catalyst was characterized by in situ FT-IR and by <sup>31</sup>P and <sup>29</sup>Si MAS NMR. The effects of catalyst formulation on the activity and stability of Rh-based SILP hydroformylation catalysts are interpreted in terms of the observed interactions between the various components and the interaction of each component

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### Scheme 1. Bidentate Phosphine Ligand and Ionic Liquid Used in the Hydroformylation of Propene



with silanol groups of the silica support. The results of the present study suggest that the active Rh centers are not present as homogeneous complexes dissolved in ionic liquid, but instead as complexes bound to the support by interactions of the sulfonate groups associated with the sulfoxantphos ligand and the silanol groups of the support. The ionic liquid, rather than serving as a solvent, inhibits the undesired interaction of sulfoxanthos ligands via interactions of the phosphines groups of the ligands with the acidic silanol groups of the support.

### EXPERIMENTAL SECTION

Silica (Silicycle, surface area: 300 m<sup>2</sup> g<sup>-1</sup>, pore volume = 1.15 cm<sup>3</sup> g<sup>-1</sup>) was used as the support. One gram of this material was dried in vacuum at 100 °C for 24 h, or at 550 and 750 °C for 15 h, and then stored in vacuum prior to use. Catalysts were also prepared on silica that had been silylated according to the following procedure. Silylation was performed by dispersing 0.5 g of the silica in 25 mL of dry toluene followed by the addition of 3.75 mmol of methyl trimethoxysilane (Strem) and stirring at 100 °C for 12 h under an inert atmosphere. The material was then cooled down to room temperature, filtered, washed with copious amounts of ethanol, and vacuum-dried. The final material is referred to as SiO<sub>2</sub>-100 °C-Me. SILP catalysts were synthesized according to the procedure described in ref 15. The dried silica support or SiO<sub>2</sub>-100 °C-Me was impregnated with an anhydrous methanolic solution (10 mL, Aldrich) of the ionic liquid bmim[OctSO<sub>4</sub>] (0.52 mmol) containing the catalyst precursors Rh(acac)(CO)<sub>2</sub> (0.02 mmol, Aldrich) and the bidentate sulfoxantphos<sup>17</sup> ligand (0.19 mmol). A light red colored, free-flowing powder was obtained upon removal of methanol by vacuum evaporation followed by drying at 80 °C for 12 h.

Gas-phase hydroformylation of propene was performed in a 6.35 mm OD quartz tube with an expanded section (~12.7 mm OD, ~20 mm length). The reactor was packed with quartz wool above and below the catalyst bed to hold the catalyst in place. The feed to the reactor consisted of propene (Praxair, 3.0 grade), CO (Praxair, 4.0 research grade), and H<sub>2</sub> (Praxair, 5.0 UHP grade). A reactant ratio of C<sub>3</sub>H<sub>6</sub>/CO/H<sub>2</sub> of 1:1:1 was used unless specified otherwise. Experiments were carried out at a temperature of 120 °C, total gas pressures of 2 atm, total gas flow rate of 120 cm<sup>3</sup> min<sup>-1</sup> at standard temperature and pressure (STP) to maintain a constant volumetric flow rate of 60 cm<sup>3</sup> min<sup>-1</sup> at pressure. Under these conditions, the conversion of propene was always less than 1%. Reaction products were analyzed using an Agilent 6890N gas chromatograph containing a bonded and cross-linked (5%-phenyl)-methylpolysiloxane capillary column (Agilent, HP-1) connected to a flame ionization detector.

Infrared spectra were acquired using a Thermo Scientific Nicolet 6700 FTIR spectrometer equipped with a liquid nitrogen cooled MCT detector. Each spectrum was obtained by averaging 32 scans taken with 1 cm<sup>-1</sup> resolution. A 0.05 g portion of SILP catalyst was pressed into a 20 mm-diameter pellet (<1 mm thick) and placed into a custom-built transmission cell equipped with CaF<sub>2</sub> windows, a K-type thermocouple for temperature control, and resistive cartridge heaters. All scans were acquired at 120 °C. Experiments at elevated pressure were carried out by throttling a needle valve located downstream from the reactor. Pure CO was passed through a trap packed with 3.2 mm pellets of 3 Å molecular sieve to remove iron pentacarbonyl formed within the cylinder. All absorption spectra were referenced to the empty transmission cell. The spectrum of the catalyst under He flow was subtracted from all the results reported.

Solid-state <sup>31</sup>P MAS NMR and <sup>29</sup>Si MAS NMR experiments were performed on a Bruker Avance I-500 MHz spectrometer. <sup>31</sup>P MAS NMR spectra were obtained at 202.5 MHz, using 90° pulses of 4.2 μs duration, a recycle delay of 60 s relative to 85% H<sub>3</sub>PO<sub>4</sub>, and a spinning rate of 10 kHz at room temperature. Samples were sealed into zirconia rotors under nitrogen atmosphere to avoid the possible oxidation of phosphorus in SX ligand. <sup>29</sup>Si MAS NMR were acquired at 80 MHz, using 90° pulses of 8.1 μs duration, a recycle delay of 360 s relative to TMS, and a spinning rate of 10 kHz. The resolution obtained in the <sup>29</sup>Si NMR spectra was sufficient for accurate peak assignments, and the relative peak area of each site was obtained by the curve-fitting, using a series of Gaussian peaks.<sup>8</sup>

### RESULTS AND DISCUSSION

**Choice of Ligand and Ionic Liquid.** It is well-known that the activity, stability, and selectivity of homogeneous rhodium-phosphine complexes used for hydroformylation are sensitive to the structure and concentration of the ligand.<sup>2,16</sup> The effect of various phosphine ligands was investigated using monodentate triphenylphosphine (tpp), sulfonated triphenyl phosphine (tppts), and bidentate xantphos (X) and sulfonated xantphos (SX). Each of these ligands was mixed with [bmim][OctSO<sub>4</sub>] and immobilized on silica pretreated at 550 °C (SiO<sub>2</sub>-550 °C). Experiments conducted in the absence of ligands showed negligible catalytic activity. Table 1 shows that

**Table 1. Results from the Hydroformylation of Propene Using Various SILP Catalysts<sup>a</sup>**

ligand-IL	L/Rh ratio <sup>b</sup>	α <sup>c</sup>	TOF (hr <sup>-1</sup> ) <sup>d</sup>	n/iso <sup>e</sup>
tppts-bmim[OctSO <sub>4</sub> ]	10	0.2	15	2.3
tppts-bmim[OctSO <sub>4</sub> ]	20	0.2	8	3.8
tpp-bmim[OctSO <sub>4</sub> ]	10	0.2	11	8
SX-bmim[OctSO <sub>4</sub> ]	10	0.2	84	12
SX-bmim[OctSO <sub>4</sub> ] <sup>f</sup>	10	0.1	100	13
X-bmim[OctSO <sub>4</sub> ] <sup>f</sup>	10	0.1	40	11

<sup>a</sup>Reaction conditions: C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/CO = 1:1:1, P<sub>Total</sub> = 2 bar, T = 120 °C, t = 8 h, 0.2 wt % Rh metal loading, SiO<sub>2</sub> pretreated at 550 °C.

<sup>b</sup>Molar ligand to metal ratio. <sup>c</sup>Pore filling degree of the support as the ratio of IL volume/support pore volume. <sup>d</sup>Turn over frequency in moles aldehyde per mole of Rh per hour. <sup>e</sup>Linear to branched ratio. <sup>f</sup>SiO<sub>2</sub> pretreated at 100 °C.

under identical reaction conditions, Rh-SX complexes are about 5-fold more active than Rh-tppts complexes, as well as exhibiting a nearly 6-fold higher n/iso product selectivity.

The higher activity of Rh complexes involving SX over monodentate phosphines can be attributed to the chelating ability of SX, which yields a higher concentration of the coordinated Rh species. Consistent with this interpretation, the molar ratio of *n*-butanal to *iso*-butanal (*n*/*iso*) is higher when SX is used as the ligand because of the wider bite angle.<sup>2</sup> This in turn results in increased complexation of the rhodium center by the diphosphine SX ligand, and the rigid backbone of the ligand compels the phenyl groups of SX to exert a greater degree of steric hindrance on the alkene entering the coordination sphere, thereby favoring linear products.<sup>18,19</sup> Table 1 also shows that Rh-*tpp* and Rh-*tppts* complexes have comparable activity; the higher *n*/*iso* ratio observed for the Rh-*tpp* system relative to the Rh-*tppts* system is due to the formation of HRh(CO)<sub>2</sub>(*tpp*)<sub>2</sub> versus HRh(CO)<sub>3</sub>(*tppts*) complexes.<sup>20</sup> Table 1 also shows that the activity of Rh-SX system is 2.5 times more active than the Rh-X system. As discussed below, the presence of the sulfonate groups on SX enables the Rh-SX complex to interact with the silanol groups of the support, thereby stabilizing the complex in an active form.

The effects of IL composition on the activity and selectivity of SILP catalysts for propene hydroformylation are presented in Table 2. The choice of anion associated with [bmim]<sup>+</sup> cations

**Table 2. Results from the Hydroformylation of Propene Using Different Ionic Liquids Containing Rh-SX SILP Catalysts<sup>a</sup>**

IL	L/Rh ratio <sup>b</sup>	$\alpha^c$	TOF (hr <sup>-1</sup> ) <sup>d</sup>	<i>n</i> / <i>iso</i> <sup>e</sup>
[bmim][OctSO <sub>4</sub> ]	10	0.2	84	12
[bmim][MeSO <sub>4</sub> ]	10	0.2	32	13
[bmim][HSO <sub>4</sub> ]	10	0.2	3	11
[bmim][NTf <sub>2</sub> ]	10	0.2	26	16
[emim][MeSO <sub>4</sub> ]	10	0.2	15	13

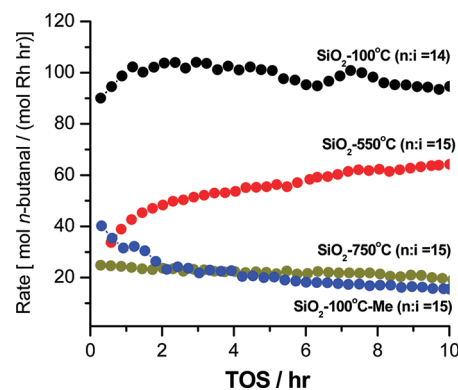
<sup>a</sup>Reaction conditions: C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/CO = 1:1:1,  $P_{\text{Total}} = 2$  bar,  $T = 120$  °C,  $t = 8$  h, 0.2 wt % Rh metal loading, SiO<sub>2</sub> pretreated at 550 °C.

<sup>b</sup>Molar ligand to metal ratio. <sup>c</sup>Pore filling degree of the support as the ratio of IL volume/support pore volume. <sup>d</sup>Turn over frequency in moles aldehyde per mole of Rh per hour. <sup>e</sup>Linear to branched ratio.

had a strong effect on the catalyst activity but relatively little effect on the *n*/*iso* ratio. Highest activity was achieved using [OctSO<sub>4</sub>]<sup>-</sup> anions and the lowest, with [HSO<sub>4</sub>]<sup>-</sup> anions. Changing the composition of the cation from [bmim]<sup>+</sup> to [emim]<sup>+</sup>, while maintaining [MeSO<sub>4</sub>]<sup>-</sup> as the anion, caused a 2-fold reduction in the catalyst activity.

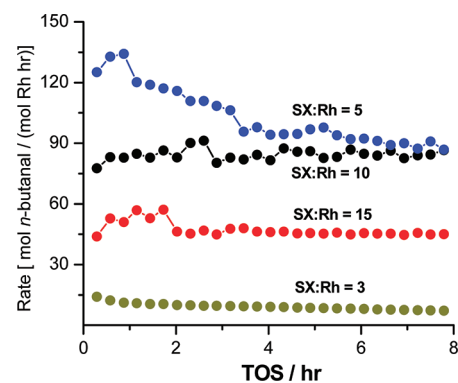
**Effect of Silica Pretreatment.** The results presented in Figure 1, show that SiO<sub>2</sub> pretreated at 100 and 550 °C (SX/Rh = 10) produces very stable catalysts, whereas pretreatment at 750 °C (SiO<sub>2</sub>-750 °C) results in a less active catalyst that loses activity with time on stream. Interestingly, irrespective of pretreatment conditions the *n*/*iso* ratio remained the same throughout each run. These experiments suggest that silanol groups are required to stabilize the active form of the catalyst. To test this hypothesis, the silanol groups were passivated by silylation (SiO<sub>2</sub>-100 °C-Me) prior to formation of the SILP catalyst (see Experimental Section). While the SILP catalyst prepared on SiO<sub>2</sub>-100 °C-Me was initially nearly twice as active as that prepared on SiO<sub>2</sub>-750 °C, this catalyst rapidly lost activity and became comparable in activity to that prepared on SiO<sub>2</sub>-750 °C.

**Effect of Ligand and Ionic Liquid Concentrations.** The effects of SX/Rh ratio and IL concentration were explored for



**Figure 1.** Effects of silica pretreatment temperature and silica passivation on the activity and stability of SILP catalysts (SX/Rh = 10,  $\alpha = 0.1$ , Rh = 0.2 wt %) for the hydroformylation of propene.  $T = 120$  °C,  $P_{\text{Total}} = 2$  atm, C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/CO = 1:1:1, catalyst mass = 0.3 g, total gas flow rate = 120 cm<sup>3</sup> min<sup>-1</sup> at STP.

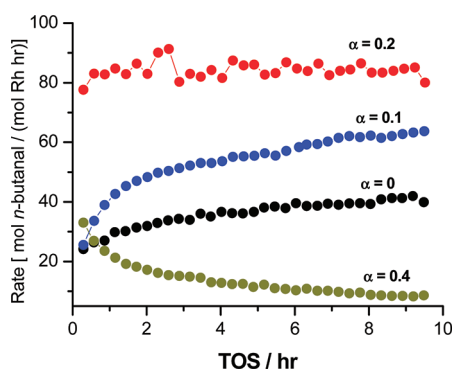
SILP catalysts prepared with SiO<sub>2</sub>-550 °C. Figure 2 shows the effects of varying the SX/Rh ratio from 3 to 15, at a constant



**Figure 2.** Effects of SX/Rh ratio on the activity and stability of SILP catalysts (SiO<sub>2</sub>-550 °C,  $\alpha = 0.2$ , Rh = 0.2 wt %) for the hydroformylation of propene.  $T = 120$  °C,  $P_{\text{Total}} = 2$  atm, C<sub>3</sub>H<sub>6</sub>/H<sub>2</sub>/CO = 1:1:1, catalyst mass = 0.3 g, total gas flow rate = 120 cm<sup>3</sup> min<sup>-1</sup> at STP.

Rh loading of 0.2 wt %. The hydroformylation activity increases with increasing SX/Rh ratio, reaching a maximum for SX/Rh = 5 and then decreasing for higher SX/Rh ratios. While the initial activity for SX/Rh = 5 is higher than that for SX/Rh = 10, the activities of these two catalysts approach a common value after 8 h of time on stream. These results differ from Rh-SX systems investigated in homogeneous biphasic systems, for which very stable catalytic activity was observed for SX/Rh ratios of 2–5.<sup>21–23</sup>

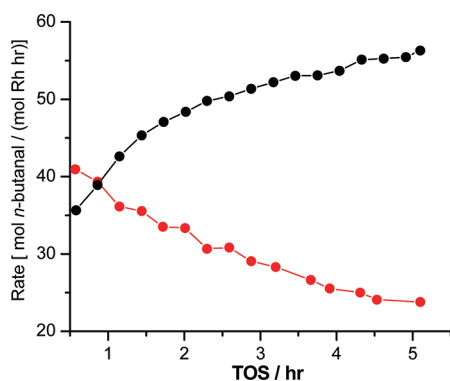
The degree of pore filling by IL,  $\alpha$ , (defined as the ratio between the volume of ionic liquid used and the pore volume of the support) also had a significant effect on the activity and stability of the SILP catalysts. Figure 3 shows that with no added IL, the catalyst increases in activity over 9.5 h of time on stream. The activity of the catalyst increases with  $\alpha$  up to 0.2, but then decreases rapidly falling below that observed for no addition of IL. It is also notable that for  $\alpha \leq 0.2$  the selectivity of propene to butanal was 100%; however, for  $\alpha = 0.4$  the selectivity to butanals dropped and large concentrations of aldol condensation products were observed. The value of  $\alpha$  influenced catalysts stability in addition to activity. For catalysts



**Figure 3.** Effect of  $\alpha$  on the activity and stability of SILP catalysts ( $\text{SiO}_2$ -550 °C, SX/Rh = 10, Rh = 0.2 wt %) for the hydroformylation of propene.  $T = 120$  °C,  $P_{\text{Total}} = 2$  atm,  $\text{C}_3\text{H}_6/\text{H}_2/\text{CO} = 1:1:1$ , catalyst mass = 0.3 g, total gas flow rate =  $120 \text{ cm}^3 \text{ min}^{-1}$  at STP.

with  $\alpha \leq 0.1$  the activity increased with time on stream, was stable for  $\alpha = 0.2$ , and decreased with time on stream for  $\alpha = 0.4$ .

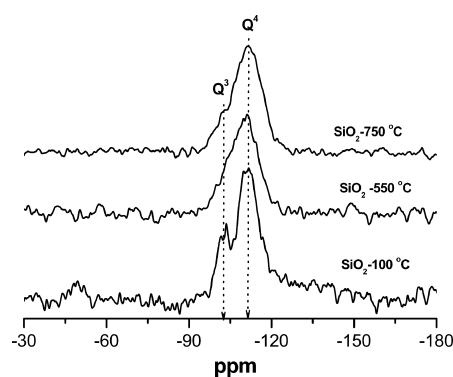
To further understand how the IL interacts with the support, the support was first contacted with the IL ( $\alpha = 0.1$ ) after which the rhodium precursor and SX dissolved in methanol (SX/Rh = 10) were introduced. Figure 4 shows that in contrast



**Figure 4.** Effects of the manner of catalyst preparation on the activity and selectivity of SILP catalyst ( $\text{SiO}_2$ -550 °C, SX/Rh = 10,  $\alpha = 0.1$ , Rh = 0.2 wt %) for the hydroformylation of propene: (red solid circles) silica support treated with IL followed by the addition of rhodium precursor and SX; (black solid circles) simultaneous addition of IL, rhodium precursor and SX to the silica support.  $T = 120$  °C,  $P_{\text{Total}} = 2$  atm,  $\text{C}_3\text{H}_6/\text{H}_2/\text{CO} = 1:1:1$ , catalyst mass = 0.3 g, total gas flow rate =  $120 \text{ cm}^3 \text{ min}^{-1}$  at STP.

to the steady increase in hydroformylation activity observed when the Rh precursor, SX, and IL are introduced together, initial introduction of the IL leads to a progressive loss in activity. These results suggest that initial contact of the IL with the silanol groups of the support inhibits the interaction of the catalyst with the support.

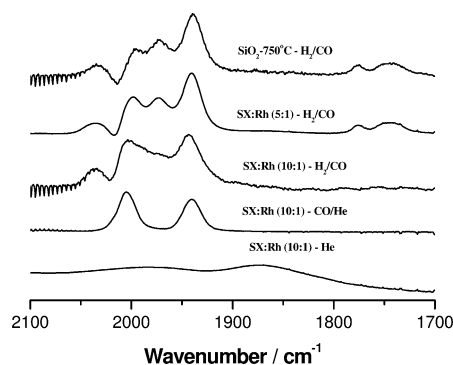
**Characterization of SILP Catalysts.** The influence of silica dehydration on the structure of the support was probed by  $^{29}\text{Si}$  MAS NMR. Figure 5 shows spectra for silica dehydrated at 100 °C, 550 °C, and 750 °C. These spectra show  $Q^3$  and  $Q^4$  peaks at  $-100$  and  $-110$  ppm, respectively. The  $Q^3$  feature is due to silanol groups whereas the  $Q^4$  feature is due to Si atoms coordinated to four other Si atoms via Si–O–Si bonds. With increasing temperature of dehydration the ratio of Si in silanol groups decreases relative to the concentration of Si in siloxane bonds.<sup>15</sup> The apparent surface concentration of silanol groups



**Figure 5.** Solid-state  $^{29}\text{Si}$  MAS NMR spectra of  $\text{SiO}_2$  pretreated at different temperatures. ( $\text{SiO}_2$ -100 °C shows  $Q^3/Q^4 = 0.25$ ,  $\text{SiO}_2$ -550 °C shows  $Q^3/Q^4 = 0.17$  and  $\text{SiO}_2$ -750 °C shows  $Q^3/Q^4 = 0.11$ ).

determined from these measurements and the corresponding Brunauer–Emmett–Teller (BET) surface areas show that the concentration of silanol groups decreases from 4 OH/nm<sup>2</sup> for  $\text{SiO}_2$ -100 °C, to 3 OH/nm<sup>2</sup> for  $\text{SiO}_2$ -550 °C, and to 1.6 OH/nm<sup>2</sup> for  $\text{SiO}_2$ -750 °C, in agreement with values reported previously for silica treated at similar temperatures.<sup>24</sup>

SILP catalysts were characterized by in situ IR and ex-situ  $^{31}\text{P}$  MAS NMR. Unless otherwise specified, these experiments were carried out using a SILP catalyst prepared on  $\text{SiO}_2$ -550 °C with SX/Rh = 10 and  $\alpha = 0.1$ . IR spectra of the catalyst taken at 1 atm in He, CO/He, and CO/H<sub>2</sub> are shown in Figure 6. The

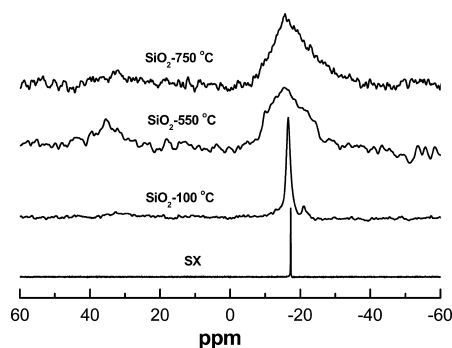


**Figure 6.** In situ FT-IR spectra of SILP catalysts showing the formation of monomeric and dimeric complexes ( $\alpha = 0.1$ ,  $\text{SiO}_2$ -550 °C, 120 °C, after 30 min in synthesis gas).

spectrum recorded in He at 120 °C is devoid of features in the carbonyl stretching region, suggesting the CO ligands associated by the Rh precursor,  $\text{Rh}(\text{acac})(\text{CO})_2$  were replaced by coordination with the phosphine groups of SX.<sup>25</sup> As noted below, evidence for coordination of SX with Rh at this stage was obtained from  $^{31}\text{P}$  MAS NMR spectra. Upon contacting the catalyst with 0.5 atm CO in He, carbonyl bands appeared at 2007 and 1940  $\text{cm}^{-1}$ . The positions of these bands are attributed to the formation of the cationic complex  $[\text{SXRh}(\text{CO})_2]^+$ . Addition of H<sub>2</sub> to CO in the gas stream resulted in the appearance of four carbonyl bands at 2035, 2000, 1973, and 1943  $\text{cm}^{-1}$ . These features are identical to those observed for Rh complexes formed with SX dissolved in organic solvents and in ILs.<sup>21,22</sup> The bands at 2035 and 1973  $\text{cm}^{-1}$  are attributable to ee-HRh(CO)<sub>2</sub>SX, in which both phosphorus atoms occupy equatorial coordination sites, and the bands at 2000 and 1943  $\text{cm}^{-1}$  are attributable to ea-HRh(CO)<sub>2</sub>SX, in which one

phosphorus atom is equatorial and the other is apical. No bands were observed in the region characteristic of CO bridging ligands ( $1800\text{--}1700\text{ cm}^{-1}$ ) for SILP catalysts prepared with SX/Rh = 10 on  $\text{SiO}_2@550\text{ }^\circ\text{C}$ . However, bands at  $1775$  and  $1745\text{ cm}^{-1}$  were observed for SILP catalysts prepared on  $\text{SiO}_2@550\text{ }^\circ\text{C}$  with SX/Rh = 5 and on  $\text{SiO}_2@750\text{ }^\circ\text{C}$  with SX/Rh = 10. These features can be attributed to  $[\text{Rh}(\text{SX})(\text{CO})(\mu\text{-CO})]_2$ .<sup>26–28</sup>

$^{31}\text{P}$  MAS NMR spectra of SILP catalysts prepared on  $\text{SiO}_2$ -100  $^\circ\text{C}$ ,  $\text{SiO}_2$ -550  $^\circ\text{C}$ , and  $\text{SiO}_2$ -750  $^\circ\text{C}$  with SX/Rh = 10 and  $\alpha = 0.1$  are presented in Figure 7. Also shown is the spectrum for



**Figure 7.** Solid-state  $^{31}\text{P}$  MAS NMR spectra of SILP catalysts (SX/Rh = 10) under different silica pretreatment conditions. SILP- $\text{SiO}_2$ -100  $^\circ\text{C}$  shows peaks for free SX ligand ( $\delta = -16$  ppm, 76%), surface bound ligand ( $\delta = -22$  ppm, 10%) and to the complexed ligand ( $\delta = 30$  ppm, 14%); SILP- $\text{SiO}_2$ -550  $^\circ\text{C}$  shows peaks for free SX ligand ( $\delta = -16$  ppm, 54%), surface bound ligand ( $\delta = -22$  ppm, 23%) and to the complexed ligand ( $\delta = 30$  ppm, 23%); SILP- $\text{SiO}_2$ -750  $^\circ\text{C}$  shows peaks for free SX ligand ( $\delta = -16$  ppm, 47%), surface bound ligand ( $\delta = -22$  ppm, 33%) and to the complexed ligand ( $\delta = 30$  ppm, 10%).<sup>15</sup>

pure SX in  $\text{CDCl}_3$ , which exhibits a single peak at  $-16$  ppm. For the catalyst prepared on  $\text{SiO}_2$ -100  $^\circ\text{C}$ , this feature is accompanied by a feature at  $-21$  ppm. We attribute the peak at  $-16$  ppm to SX weakly physisorbed on silica, and attribute the peak at  $-21$  ppm to phosphorus atoms in either singly protonated or nonprotonated, strongly physisorbed SX groups. These assignments are fully consistent with  $^{31}\text{P}$  MAS NMR observation reported by Grey and co-workers for bidentate  $\text{PPh}_2(\text{CH}_2)_n\text{PPh}_2$  ( $n = 1$ ) adsorbed on HY zeolite.<sup>29</sup> The weak band at 30 ppm is assigned to the phosphine groups of SX

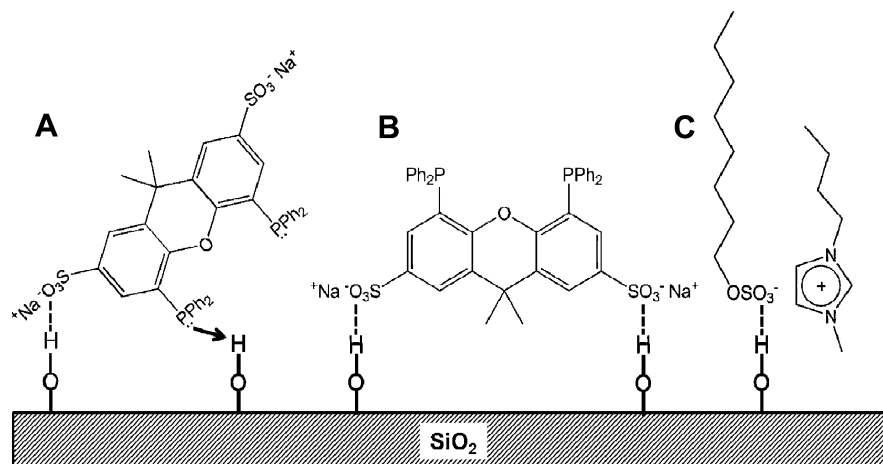
interacting with Rh.<sup>15</sup> As the temperature of silica dehydration increases, the peaks attributed to “free” SX and SX interacting with silanol groups meld into one broad feature, whereas the peak due to SX-Rh interactions increases and passes through a maximum for  $\text{SiO}_2$ -550  $^\circ\text{C}$ . The distribution of SX between “free” and interacting with silanol groups is also dependent on the SX/Rh ratio. Decreasing the SX/Rh ratio from 10 to 5, decreased the ratio of “free” to silanol-interacting SX from 2.5 to 1.3. The strong broadening in both the “free” to silanol-interacting SX with increasing temperature of silica dehydration suggests that the component described as “free” may be better described as SX interacting with silanol groups via the sulfonate groups. Illustrations of the two forms of SX interaction with silanol are presented in Figure 8 (Structures A and B). More detailed representations of these structures are presented in the Supporting Information.

#### Effects of Catalyst Formulation on Catalyst Activity and Selectivity.

The results of the present study demonstrate that the activity and stability of Rh-based SILP catalyst are highly sensitive to their formulation. Silanol groups on the surface of the support are required to achieve high activity and stability. Dehydration of the support at 750  $^\circ\text{C}$  or removal of silanol groups by silylation reduces the propene hydroformylation activity by a factor of 5. Highest activity and stability are attained for an SX/Rh ratio of 10, and both lower and higher ratios lead to less active catalysts. The IL loading also has an effect on catalyst activity and stability; catalysts with  $\alpha = 0.2$  are most active. A qualitative interpretation of the effects of catalyst composition on catalyst performance can be developed on the basis of the observed interactions of SX and  $[\text{bmim}][\text{OctSO}_4]$  with the support.

$^{31}\text{P}$  MAS NMR spectra of the SILP catalysts indicate that SX interacts with the silanol groups of silica via the modes shown in Figure 8 (structures A and B). The resonance observed at  $-16$  ppm, previously attributed to free SX can be better assigned to SX interacting with silanol groups via their sulfonate groups (species B in Figure 8); however, consistent with previous studies, the resonance observed at  $-22$  ppm is attributed to SX interacting with silanol groups via their phosphine groups (species A in Figure 8).<sup>15,29</sup>

The concentration of silanol groups decreases from 4  $\text{OH}/\text{nm}^2$  for silica dehydrated at 100  $^\circ\text{C}$  to 1.6  $\text{OH}/\text{nm}^2$  as the dehydration temperature was increased to 750  $^\circ\text{C}$ . Dehydration increases the fraction of isolated silanol groups and their



**Figure 8.** Possible interaction of sulfoxantphos ligand (A and B) and  $[\text{bmim}][\text{OctSO}_4]$  ionic liquid (C) on silica support.

Brønsted acidity.<sup>30,31</sup> Consequently, the Lewis acid–base interaction between the silanol groups and the phosphine groups of SX is enhanced. For a Rh loading of 0.02 mmol g<sup>-1</sup> and an SX/Rh ratio of 10, the apparent surface density of SX is always lower (~0.4 SX/nm<sup>2</sup>) than that of silanol groups. The <sup>31</sup>P MAS NMR spectra suggest that as the surface concentration of silanol groups decreases, an increasing fraction of SX is bound via its phosphine groups, making these groups unavailable for coordination with Rh<sup>+</sup> cations. By contrast, SX interacting with silanol groups via their sulfonate groups can form complexes with Rh<sup>+</sup> cations. Unbound SX would also coordinate with Rh<sup>+</sup> cations; however, since the concentration of Rh is high in the liquid composed of SX and IL, it is likely that free HRh(CO)<sub>2</sub>SX dimerize to form [Rh(CO)(μ-CO)-SX]<sub>2</sub> complexes or HRh(SX)<sub>2</sub> complexes, which are inactive for propene hydroformylation.<sup>25,26</sup> The proposal that HRh(SX)<sub>2</sub> complexes may result in less active catalysts is supported by observations of van Eldik and co-workers, who demonstrated the low catalytic activity of HRhL<sub>4</sub> type species in hydroformylation reactions.<sup>32</sup> Therefore, it is proposed that the role of silanol groups on silica is to stabilize SX mainly in the form of species B (Figure 8), thereby producing isolated HRh(CO)<sub>2</sub>SX complexes. The in situ IR spectra presented in Figure 6 provide evidence for the formation of such complexes.

The dependence of propene hydroformylation activity on SX/Rh ratio seen in Figure 2 can be interpreted in the following manner. For SX/Rh = 0, no catalytic activity was observed, indicating an SX-Rh complex is necessary to initiate the hydroformylation of propene. For SX/Rh = 3, a very low activity is observed, because a large fraction of the SX interacts with the support via its phosphine groups, that is, species A in Figure 8. As the SX/Rh ratio is raised a greater fraction of SX is bound to the support in the form of species B, enabling the formation of catalytically active HRh(CO)<sub>2</sub>SX complexes. Above SX/Rh = 5, it is conceivable that free SX now interacts with the isolated complexes to form HRh(SX)<sub>2</sub> complexes, which are expected to be less active for propene hydroformylation.<sup>30,31</sup> It is important to note that an optimal concentration of SX/Rh has also been reported in studies of HRh(CO)<sub>2</sub>SX complexes dissolved in various solvents.<sup>22–24</sup> The near constancy of the n/iso ratio as the concentration of SX varied suggests that CO dissociation from both the ee and ea isomers of HRh(CO)<sub>2</sub>SX result in the same reactive four coordinate HRh(CO)SX intermediates in the hydroformylation cycle.<sup>19</sup>

While previous studies of Rh-based SILP propene hydroformylation catalyst have suggested that the IL acts as a solvent for homogeneously dispersed HRh(CO)<sub>2</sub>SX complexes, we propose an alternative interpretation.<sup>14–16</sup> Figure 3 and 4 demonstrate that there is an optimal loading of IL necessary for achieving high catalyst activity and stability, and that introduction of IL prior to introducing Rh(CO)<sub>2</sub>(acac) and SX results in a less active catalyst. As noted above, this suggests that the IL interacts with the silanol groups of the support, thereby interfering with the interaction of SX to form species B. Evidence for interactions of [bmim][OctSO<sub>4</sub>] was obtained from IR spectra taken before and after treatment of SiO<sub>2</sub>-550 °C with IL (α = 0.2). Prior to introduction of the IL, the only feature observed was a sharp silanol band at 3740 cm<sup>-1</sup>. After contacting the support with IL, the intensity of this band decreased significantly, and a broad band appeared at 3650 cm<sup>-1</sup>. A similar pattern was observed when SX/SiO<sub>2</sub> was contacted with IL. We attribute the observed changes in the

spectrum to interactions of the sulfonate groups of [bmim]-[OctSO<sub>4</sub>] with the silanol groups of the support.<sup>6</sup> We note that evidence for such interaction has been reported by Antonietti and co-workers who showed that [BF<sub>4</sub>]<sup>-</sup> anions of [bmim]-[BF<sub>4</sub>] IL form hydrogen bonds with the silanol groups of mesoporous silica.<sup>33</sup> It is quite possible that the higher catalytic activity observed using [bmim][OctSO<sub>4</sub>] compared to other anions is attributable to the strength of anion interaction with the support.<sup>34</sup> For RSO<sub>4</sub><sup>-</sup> anions (R = H, Me, Oct) the strength of interaction of the anion with silanol groups of the support would be expected to increase with an increase in the pK<sub>a</sub> of the conjugate Brønsted acid. Thus, the low activity observed in Table 2 when [bmim][HSO<sub>4</sub>] was used as the IL could be ascribed to excessive interaction of the IL with the support, thereby inhibiting the association of SX with the support to form species B.

All these observations lead to the hypothesis that IL molecules spatially distribute HRh(CO)<sub>2</sub>SX complexes on the support surfaces at lower α values while they compete with SX ligands for silanol groups at high α values (see Supporting Information). We note that for SX/Rh = 10, α = 0.1 to 0.4 corresponds to IL/SX = 1 to 4. Since an optimal hydroformylation activity is achieved for α = 0.2 for a SILP catalyst prepared on SiO<sub>2</sub>-550 °C with SX/Rh = 10, this indicates that the optimum IL/SX ratio in this case is 2. For higher IL/SX ratios, it is likely that the excess IL displaces SX attached to the support in the form of species B. Further evidence for the interaction of IL with the support is suggested by the dependence of catalyst activity on IL composition. As noted in Table 2, propene hydroformylation activity depends primarily on the composition of the IL anion, and to a lesser extent the composition of the cation.

The mechanism of catalyst activity loss observed in Figures 1–3 can be explained as follows. Greatest evidence for a decline in activity with time on stream is seen for SILP catalysts prepared on SiO<sub>2</sub>-750 °C with SX/Rh = 10 and α = 0.1, SiO<sub>2</sub>-550 °C with SX/Rh = 5 and α = 0.1, and SiO<sub>2</sub>-550 °C with SX/Rh = 10 and α = 0.4. These examples suggest that deactivation most likely occur when catalysts are prepared with a low concentration of SX in the form of species B. The gradual loss of HRh(CO)<sub>2</sub>SX complexes on the support could lead to the formation of [Rh(CO)(μ-CO)SX]<sub>2</sub> dimer complexes that are inactive for propene hydroformylation. Evidence for bridging CO, characteristic of such complexes, was observed in in situ IR spectra taken of SILP catalysts prepared on SiO<sub>2</sub>-750 °C with SX/Rh = 10 and α = 0.1 and on SiO<sub>2</sub>-550 °C with SX/Rh = 5 and α = 0.1.

## ■ CONCLUSIONS

The results of this study provide important insights into the factors influencing the activity and stability of Rh-based SILP catalysts for the hydroformylation of propene prepared on high surface area silica. Catalyst activity and stability are found to be strong functions of ligand and IL composition, as well as ligand-to-Rh ratio, IL loading, and temperature of support pretreatment. Highest activity is achieved with SX as the ligand and [bmim][OctSO<sub>4</sub>] as the IL supported on silica pretreated at 100 °C and using an SX/Rh ratio of 10 and IL loading corresponding to α = 0.2. Characterization of SILP catalysts by various techniques suggests that the active form of the catalyst consists of HRh(CO)<sub>2</sub>SX complexes stabilized by the support through interactions of the sulfonate groups of the SX ligand with silanol groups of the support. Pretreatment of the support

at temperatures above 100 °C decreases the surface density of silanol groups and increases the acidity of these groups. This results in an increasing fraction of SX binding to the support through its phosphine groups, thereby reducing the availability of these groups to coordinate Rh<sup>+</sup> cations. High IL loadings are undesirable, since the interaction of IL with the silanol groups of the support can inhibit interaction of silanol groups with the sulfonate groups of SX, resulting in the formation of [Rh(CO)(μ-CO)SX]<sub>2</sub> species that are catalytically inactive. The SX/Rh ratio also has a large effect on the catalytic activity and stability. If SX/Rh is much less than 10, the fraction of SX bound to the surface via phosphine groups is high and therefore the concentration of HRh(CO)<sub>2</sub>SX complexes stabilized by the support through interactions of the sulfonate groups of the SX ligand is low. By contrast for SX/Rh ratios greater than 10, the excess SX may form HRh(SX)<sub>2</sub> complexes that are less active for propene hydroformylation

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Textural properties of SILP catalysts, TEM images, schemes for the interaction of sulfoxantphos, ionic liquid with silica support. This material is available free of charge via the Internet at <http://pubs.acs.org>.

## ■ AUTHOR INFORMATION

### Corresponding Author

\*E-mail: [bell@cchem.berkeley.edu](mailto:bell@cchem.berkeley.edu). Phone: +1 510 642 1536. Fax: +1 510 642 4778.

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### Notes

The authors declare no competing financial interest.

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