

Organorhodium Complex on Smectite Clay: Preparation, Characterization, and Catalytic Activity for the Hydroformylation of Vinylsilanes

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Sodium montmorillonite reacts with the dimer of chloro(1,5-cyclooctadiene)rhodium(I) in dichloromethane to form a material (Rh–clay) in which rhodium is covalently attached to the silicate sheets of montmorillonite. Linear silylaldehydes were obtained, as the major or only product, in excellent yield by the hydroformylation of trialkylvinylsilanes or triphenylvinylsilane catalyzed by Rh–clay.

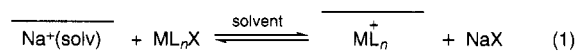
Introduction

There has been considerable interest in recent years in converting homogeneous transition-metal complexes into heterogeneous catalysts by anchoring the complexes to insoluble supports such as organic polymers or metal oxides.¹ One of the objectives of such research is to study the elementary steps of heterogeneous catalysis. Reaction of organometallic complexes with solid surfaces may lead to stable solid catalysts, in which an organometallic fragment remains hooked or anchored to the surface atoms. In other words, by analysis of these anchored organometallic species, one can gain insight into the reactivity and active sites of the supported catalysts.

Clay minerals served as excellent solid supports in the past decade, and among the smectite clays, montmorillonite was studied extensively due to its natural abundance, ready availability and good swelling ability.^{1,2} Under appropriate conditions of swelling by adsorbed solvents, the interlayers occupied by the organometallic species are accessible to substrates and catalytic reactions analogous to those that occur in homogeneous solution can be achieved in the solid state.

The objective of the present study was to synthesize and examine the properties of a clay-intercalated rhodium catalyst and test its activity toward the hydroformylation of vinylsilanes. Hydroformylation catalyst precursors are usually neutral species that can be immobilized on supports by covalent attachment mechanisms.^{3,4} The mechanism of catalyst intercalation or anchoring in layered silicates involves either a cationic

exchange reaction or elimination of interlayer cations (Na⁺) as a neutral species (eq 1, horizontal line indicates



the interlayers of montmorillonite).

Cationic complexes of the type Rh(COD)(PPh₃)₂⁺, where COD is 1,5-cyclooctadiene intercalated into hectorite by a cation-exchange mechanism, have been reported by Pinnavaia and co-workers⁵ to have hydroformylation activity.

Results and Discussion

Intercalation of [Rh(COD)Cl]₂ between the Interlayers of Montmorillonite. [Rh(COD)Cl]₂ was reacted with Na⁺-exchanged montmorillonite in dichloromethane at room temperature for 5 h to form a rhodium-intercalated montmorillonite material [Rh–clay (1)]. The driving force of the reaction may be the elimination of neutral NaCl as described in Scheme 1.

Scheme 1 shows a possible structure of 1. Palyi and co-workers⁶ reported a similar reaction under homogeneous reaction conditions using Ph₃SiO[−]Na⁺ and [Rh(COD)Cl]₂ and proposed the formation of a similar species with solid oxide supports. Also, Shore et al.⁷ described the surface species, resulting when tris(allyl)rhodium was reacted with silica, alumina, titania, and magnesia, based on the nature and degree of hydroxylation of the support. Elemental analysis of the Rh–clay indicated the presence of 0.03 mmol of rhodium/g of the clay (the calculated value for 100% exchange is 0.05 mmol/g, based on the cation-exchange capacity of Na⁺–montmorillonite). The observed 001 X-ray reflection of Rh–clay corresponds to a spacing of 21.4 Å, since the silicate sheets are 9.6 Å thick,⁵ the average Δd₀₀₁ value, which is a measure of the thickness of the interlayer region occupied by the Rh complex is 11.8 Å.

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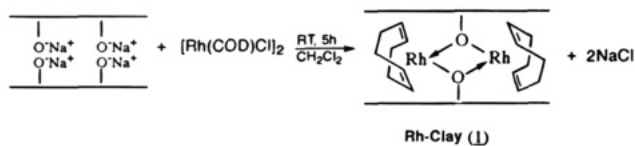
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Scheme 1^a

^a Horizontal line indicates the interlayers of montmorillonite.

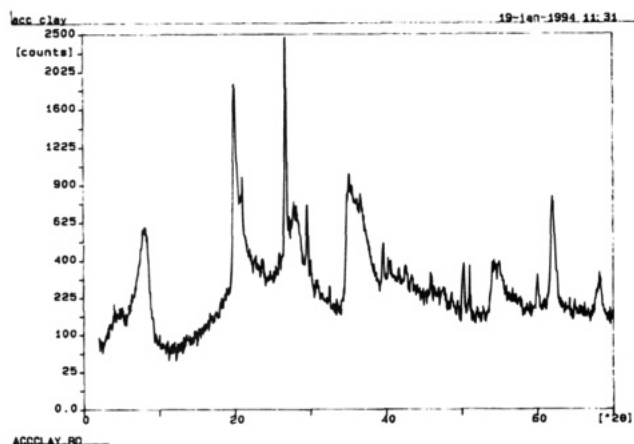


Figure 1. X-ray powder diffractogram of Rh-clay.

Figure 1 shows a well-ordered X-ray powder diffractogram of Rh-clay indicating a uniform distribution of rhodium species between the interlayers in the 00 l direction. The large expansion of interlayers can be ascribed to the presence of bulky COD (cyclooctadiene) ligands.

FTIR spectroscopy recorded on Rh-clay, after subtracting Na⁺-montmorillonite as the reference, indicated the presence of a [Rh(COD)] stretching frequency at 1492 cm⁻¹ and weak, low-frequency absorptions associated with Rh-O stretching motions⁸ were observed at 469 and 526 cm⁻¹. After calcinating for 5 hours at 600 °C, the interlayer distance was found to be 14.8 Å indicating the elimination of COD and probably forming colloiddally dispersed Rh on montmorillonite. Bradley and co-workers⁹ have extensively studied the properties as well as the behavior of various metal clusters and colloids using FTIR and high-resolution NMR and TEM techniques. FTIR spectroscopy on calcinated Rh-clay showed strong bands due to Rh-O stretching, while a spectrum recorded on Rh-clay treated with carbon monoxide gave a strong band at 2030 cm⁻¹ due to the formation of Rh(CO) upon the elimination of the labile COD ligand. Analysis of gases evolved on heating a solid sample of Rh-clay in a mass spectrometer revealed the presence of COD.

A thermogravimetric analysis of Rh-clay (Figure 2) indicated the replacement of interlayer water by Rh complex and showed a weight loss of up to 11% at 700 °C. When considered with the mass spectrum, it is evident that the loss in weight of the Rh-clay from the TGA experiment is due to the loss of the COD ligand.

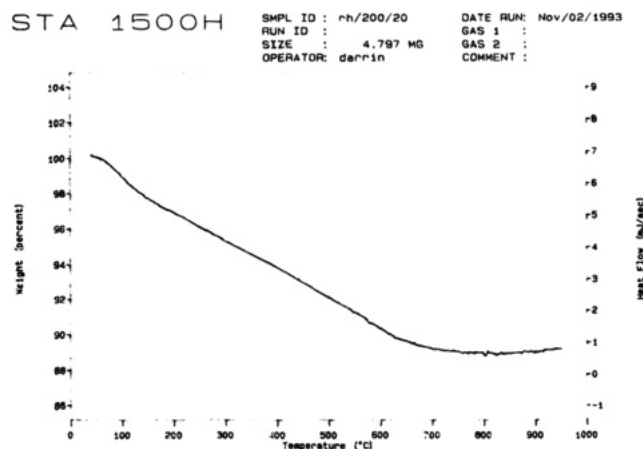


Figure 2. Thermogravimetric analysis of Rh-clay.

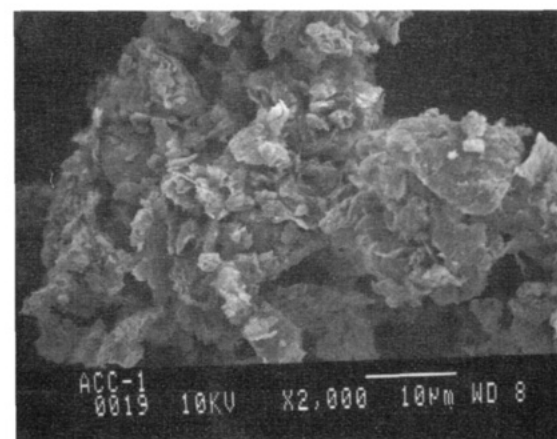
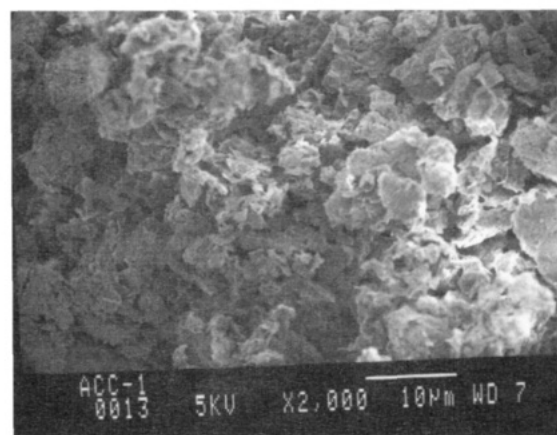


Figure 3. Scanning electron micrographs (SEM) of Rh-clay (ACC-1).

An SEM¹⁰ recorded on Rh-clay, in comparison to Na⁺-montmorillonite, did not show much difference on a macroscopic scale. However, microscopically on a 10 µm scale, the layers of Na⁺-montmorillonite appear to be more compact and the material appears less porous. An increase in the surface area due to the lifting of two dimensional silicate layers was observed from the Rh-clay sample (Figure 3). These studies suggest 1 as the structure for the Rh-clay described in Scheme 1 and

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Table 1. Hydroformylation of Vinylsilanes Catalyzed by Rh-Clay^a

entry	catalyst	solvent	time (h)	2, R =	yield ^b (%)	product distribution ^c 3:4:1,3-Si shifted
1	Rh-clay	C ₆ H ₆	36	Me	95	96:4:0
2	Rh-clay	PhCH ₃	36	Me	88	95:5:0
3	[Rh(COD)Cl] ₂	C ₆ H ₆	36	Me	76	42:44:14
4	[Rh(COD)Cl] ₂ Na ⁺ -clay ^d	C ₆ H ₆	36	Me	91	62:23:15
5	Na ⁺ -clay ^d	C ₆ H ₆	48	Me	0	
6	Rh-clay calcinated ^e	C ₆ H ₆	48	Me	11	100:0:0
7	Rh-clay	C ₆ H ₆	36	Et	98	100:0:0
8	Rh-clay	PhCH ₃	36	Et	93	100:0:0
9	Rh-clay	C ₆ H ₆	18	Ph	99	100:0:0
10	Rh-clay	C ₆ H ₆	24	OMe	89	8:92:0

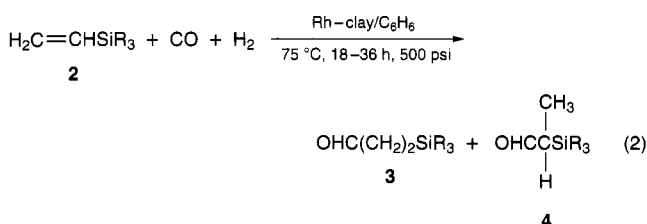
^a Conditions: vinylsilane (2 mmol), solvent (8 mL), Rh-clay (15 mg, contains 4.5×10^{-4} mmol of Rh), CO/H₂ (1:1, 500 psi). ^b Isolated yield. ^c Determined by ¹H NMR. ^d Na⁺-montmorillonite. ^e Calcinated at 600 °C for 5 h.

the possibility of a cation-exchange mechanism is not certain in this case. Leaching of Rh was not observed during the course of catalysis; however, the labile COD ligand was lost when Rh-clay was calcinated during catalysis. Thus, to obtain an active catalyst for hydroformylation reactions, the method of drying the Rh-clay plays an important role. The activity of Rh-clay toward the hydroformylation of vinylsilanes was markedly affected when Rh-clay was dried by vacuum or oven-drying techniques (Table 1).

Regioselective Hydroformylation of Trialkylvinylsilanes and Triphenylvinylsilane Using 1. One of the principal objectives of preparing Rh-clay is to determine its potential as a heterogeneous catalyst for hydroformylation reactions. Hydroformylation is of demonstrated value for the synthesis of aldehydes¹¹ from alkenes. However, little is known about the hydroformylation of vinylsilanes.^{12a} The product organosilicon aldehydes are potential building blocks in organic synthesis, and conventional preparative methods have some disadvantages including low selectivity and irreproducibility in some cases.¹³ Takeuchi and co-workers^{12b} have extensively studied the hydroformylation of trialkylvinylsilanes using homogeneous transition-metal catalysts. Although the activity of homogeneous catalysts was high, low regioselectivities were obtained. To achieve improved regioselectivity to the linear aldehyde, the addition of a large excess of phosphine is necessary. Recently, one of us^{12a} reported the hydroformylation of vinylsilanes using various homogeneous transition-metal complexes including Rh(COD)BPh₄ and [Ir(COD)]⁺BPh₄⁻. The practical difficulty of homogeneous catalysis, i.e., the purification of the product aldehydes and recovery of the catalyst were encountered with the resultant reduction in product yields.

The hydroformylation of trimethylvinylsilane (**2**, R = CH₃) proceeds in the presence of Rh-clay affording

linear aldehydes, **3** (eq 2) as the exclusive products in high yields. The reaction was simple in execution and workup. The results for the hydroformylation reaction of several vinylsilanes, catalyzed by **1**, are summarized in Table 1.



Since the interlayer expansion of the Rh-clay is large, the selectivity obtained in the hydroformylation reactions may be due not to the spacial requirements but to the electronic factors associated with the interlamellar space of montmorillonite. For example, in the case of trimethoxyvinylsilane, the regioselectivity was opposite (branched aldehyde, **4**, R = OMe as the main product) to that of vinyltrimethylsilane and may be due to electronic factors.

The enol silylether product, which would be formed by a 1,3-silicon shift from carbon to oxygen was not detected using Rh-clay. However, the corresponding homogeneous catalyst analogue, [Rh(COD)Cl]₂, afforded **3** and **4** in poor regioselectivity along with 14% of the product arising from a 1,3-silyl shift (entry 3, Table 1). An experiment done using a mixture of [Rh(COD)Cl]₂ and Na⁺-montmorillonite with the idea of forming an in situ Rh-supported catalyst gave the linear product **3**, R = Me, in 62% yield, together with 23% of **4** and 15% of the Si shift product. Na⁺-montmorillonite alone was inactive for the hydroformylation of trimethylvinylsilane and starting material was recovered in 92% yield. Rh-clay is active for three cycles, and metal leaching was not observed during each cycle. However, the presence of a COD ligand was not observed in the IR spectrum for the recovered Rh-clay. Instead, a strong Rh(CO) stretching band was present at 2030 cm⁻¹. An X-ray powder diffractogram recorded on the recovered catalyst showed an interlayer expansion of 12.9 Å. The mechanism for the hydroformylation of **2** may be that illustrated in Scheme 2, analogous to the pathway proposed for the homogeneous reaction.¹¹

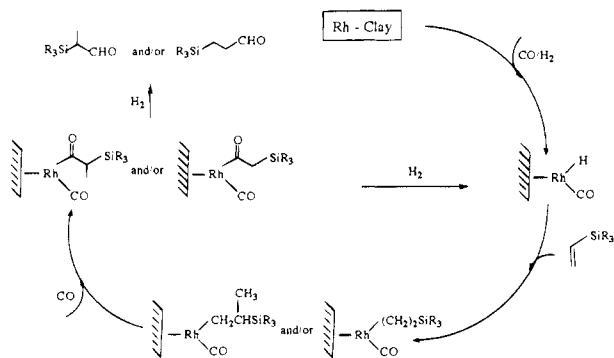
Unsaturated substrates containing aromatic rings were subjected to hydroformylation using Rh-clay. Triphenylvinylsilane give the linear aldehyde in quantitative yield (Table 1, entry 9). Use of styrene as reactant, in which the phenyl group is attached to an unsaturated carbon atom, afforded only the branched

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Scheme 2. Proposed Mechanism of Rh–Clay Catalyzed Hydroformylation of Vinylsilanes



aldehyde (in 97% isolated yield) with 100% selectivity. The hydroformylation of 3,3-dimethyl-1-butene, the carbon analog of **2**, R = Me, was performed using Rh–clay under the standard experimental conditions, giving only the linear aldehyde in 91% isolated yield.

Conclusion

In conclusion, the reaction of $[\text{Rh}(\text{COD})\text{Cl}]_2$ with silicate layers of Na^+ -exchanged montmorillonite afforded a new organometallic Rh complex attached to the interlayers of montmorillonite. On the basis of the spectroscopic evidence, it was proposed that Rh atoms are covalently attached to the silicate sheets of the montmorillonite. The Rh–clay was shown to be an active catalyst for the regioselective hydroformylation of trialkylvinylsilanes, giving linear silyl aldehydes as the major products in good-to-excellent yields. This methodology compares favorably to the use of homogeneous catalysis in terms of regioselectivity and yield, with the added advantage of product and catalyst recovery.

Finally, as the interlayer expansion of Rh–clay is high (21.4 Å), the choice of solvent and its polarity for the hydroformylation reaction are not crucial as swelling is not an important criteria. The tendency for the intercalated catalysts to increase the ratio of normal-to-branched chain silyl aldehydes and to decrease the extent of silyl-shifted product relative to the homogeneous case suggests that the relative stabilities of primary and secondary metal silylalkyl intermediates may be influenced by the Lewis and Bronsted acid sites, thereby creating an electronically different environment in the interlamellars of montmorillonite. Also, the presence of Lewis and Bronsted acidic sites can polarize

the carbon monoxide and enhance the reactivity toward hydroformylation. Thus, in comparison to Pinnavaia's⁵ intercalated cationic $\text{Rh}(\text{COD})(\text{PPh}_3)_2^+$ –hectorite system, the behavior of Rh–clay is different as far as the hydroformylation reaction is concerned. The consequence of regioselectivity in the case of Rh–clay is not the result of spatial restriction as in the case of the cationic $\text{Rh}(\text{COD})(\text{PPh}_3)_2^+$ –hectorite system, but may be due to electronic factors.

Experimental Section

General Methods. The following spectrometers were used to obtain spectral data: Bomem MB100-C15 (FT-IR), Varian XL-300 and/or Gemini 200 (NMR), and VG 7070E (MS). X-ray basal spacings of Rh–clay were determined with a Philips PW 3710 based analytical diffractometer using Ni-filtered Cu K α radiation. TGA experiments were performed with a STA 1500H thermoanalysis dual system (version V5.32, Polymer Lab Instrumentation). SEM measurements were done on a JEOL JSM840 instrument using 10 keV accelerating voltage at a working distance of 8 mm. Beam current is fixed at 6×10^{-11} A and the objective aperture is 70 μm . The samples were coated with 400 Å of gold.

Preparation of Rh–Clay (1). A mixture of $[\text{Rh}(\text{COD})\text{Cl}]_2$ (24.65 mg, 0.05 mmol), Na^+ –montmorillonite (1 g, from Crook Country, WY, was purchased from Clay Minerals Society, Columbia, MO; further purified by sedimentation prior to use) in dry dichloromethane (25 mL) under nitrogen atmosphere was subjected to vigorous stirring for 5 h at room temperature. The resulting pale yellow solid material (Rh–clay) was filtered and washed thoroughly with dry dichloromethane and dried by blowing with air or nitrogen.

General Procedure for the Hydroformylation Reactions. A mixture of **2** (2.0 mmol), Rh–clay (15 mg, contains 4.5×10^{-4} mmol of Rh) and dry benzene (10 mL) was placed in a 30 mL autoclave. The autoclave was flushed thoroughly with carbon monoxide, subsequently pressurized with a mixture of carbon monoxide and hydrogen (1:1, 500 psi), and subjected to heating at 75 °C for 18–36 h. The reaction mixture was cooled to room temperature, filtered to remove Rh–clay and concentrated affording the aldehydes in 95% purity (by NMR and GC using internal standard). The products were further purified by vacuum distillation and structures were established by comparison of spectral results with literature data.¹¹

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