Chem. Rev. **2002,** *102,* 3579–3588

Nano-Organometallics: Heterogenizing Homogeneous Catalysts via Thin Film Methodology

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Received January 9, 2002

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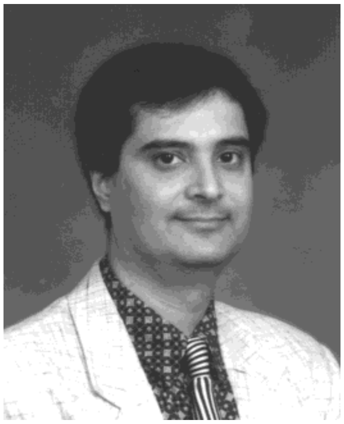

Ashok K. Kakkar obtained his Ph.D. degree in Chemistry in 1990 from University of Waterloo, Waterloo (Canada), and he was an NSERC postdoctoral fellow at University of Cambridge (England) and Northwestern University from 1990 to 1993. He joined the Department of Chemistry at McGill University in 1993, where he is now an Associate Professor of Chemistry. His research interests include fabrication of nanomaterials, molecular self-assembly, interfacial phenomenon, dendrimers, sol–gel processing, and functionalized polymers, for applications in areas such as heterogenized homogeneous catalysis, drug delivery, and nonlinear optics.

I. Introduction

Nanotechnology offers significant potential in building new types of devices with atomic or molecular precision,[1] and nanoscale strategies are being currently developed in an overdrive mode to make smart materials where the parallels from biological life play a crucial role in directing the need and incentives for molecular-scale machines.[2] Chemical knowledge or what we classify as chemistry is the essential tool and life support in constructing nanodevices. To manipulate molecules into desired structures, novel chemical methodologies are required. An intriguing route to construct such nanosystems is by molecular self-assembly on surfaces.[3] Applications of these nano-assemblies are tremendous, and catalysis is no exception.[4] Catalysis plays a key role in carrying out chemical reactions efficiently. The latter can be attributed to the structure–property relationship of the catalyst and substrate, and it is essential to have a detailed understanding of the molecular details of the process.[5] A catalyst accelerates a chemical reaction by providing an alternative pathway for the reactants en route to products without being consumed in the reaction. In the design of transition metal based catalysts, much emphasis is placed on their activity and selectivity.[6] However, catalyst recovery and recycling are equally important issues, and more so for industrial chemical processes when cost of the metal involved becomes an economic factor, and the distribution of the residual catalyst in the product may affect the properties of the desired product. Such issues are addressed in the development of the field referred to as supported metal catalysis or heterogenized homogeneous catalysis.[7] The purpose of this review is to probe the role of molecular self-assembly of organometallic complexes in catalysis, and to consider the viability of nano-organometallics in engineering surfaces at the molecular level to yield ultrathin films for enabling active, selective, and recoverable catalysis. Such supramolecular structures are held together by noncovalent molecule–molecule interactions called the van der Waals forces of attraction. The latter are quantum mechanical in origin, and act from interatomic distances at 0.2 to about 10 nm to bring molecules together, and align and orient them at the interfaces. An understanding of the effect of packing and order in these thin film materials on catalytic activity could prove highly beneficial in developing efficient catalytic molecular nanotechnology.

II. Molecular Organization

A. Langmuir–Blodgett and Molecular Self-Assembly

Langmuir–Blodgett and molecularly self-assembled thin films offer potential in engineering micron scale

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10.1021/cr010360k CCC: $39.75

surfaces,[3,8] and can be considered as the closest resemblance to molecular nanotechnology. Langmuir–Blodgett (LB) films are two-dimensional solid structures of amphiphilic molecules that are constructed in a predetermined and controllable fashion.[9] In the preparation[2,10] of LB thin films, the desired molecules are spread on the surface of a liquid (most commonly water) containing the required substrate to yield a monolayer. The substrate is then pulled out at a particular speed to transfer the monolayer to its surface. The amphiphilic molecules used for the preparation of LB thin films contain the long hydrocarbon chain as the hydrophobic tail (T) terminated with a polar headgroup (H). The LB assemblies of such molecules can lead to three types of structures[11] that are shown in Figure 1: **A**: HTHTHT... the orientation in which the polar headgroup is at the surface of the substrate exposing the hydrophobic tail to the top, and the subsequent layers are deposited in a similar manner. Such structures are referred to as Z-type structures; **B**: THTHTH... This type of structure is reverse of **A** with the hydrophobic tail at the surface and the polar headgroup on top, leading to X-type thin films; and **C**: HTTHHT... This arrangement contains a head bound first layer, followed by a tail down layer, and then a head down layer, yielding a Y-type LB film.

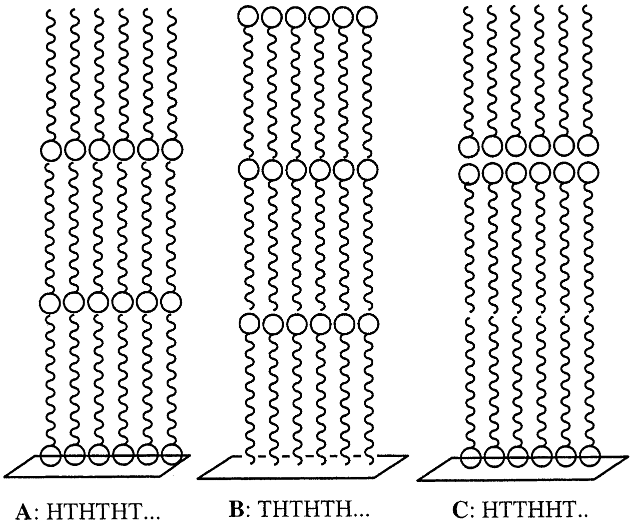
A: HTHTHT... **B**: THTHTH... **C**: HTTHHT..

Figure 1. Langmuir-Blodgett assemblies of amphiphilic molecules with a hydrophobic tail (T) and a terminal polar head group (H).

When molecules that are used to create densely packed structures on solid substrates combine at one end with the surface leading to the formation of a chemical bond, the process is referred to as chemisorption. The latter is a first step in the methodology called molecular self-assembly that yields densely packed and highly ordered self-assembled monolayers.[12] The commonly used inorganic oxide substrates for molecular self-assembly are silica, quartz, and single crystal silicon with a definitive measured layer of silica on top. The surfaces of these substrates are terminated with OH groups that are weakly acidic, and offer extensive chemistry in anchoring a variety of structures. The typical molecules used in molecular self-assembly are long chain hydrocarbons with terminal -$SiCl_3$ or $Si(OR)_3$ groups. The latter react with the surface hydroxyl groups leading to their chemisorption (Figure 2). It is now well understood that the length of the molecules used for assembly construction plays a significant role in their packing and orientation on surfaces. In the self-organization of long chain alkanes, a length of 10–18 carbons is essential to yield densely packed thin films.

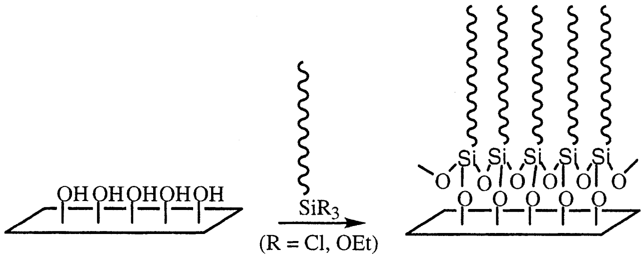

Figure 2. Construction of self-assembled thin films on silica based surfaces using long chain alkanes terminated with trichloro- or trialkoxysilane groups.

B. Surface Structure Characterization

An understanding of the macroscopic properties of the newly formed thin films that include their surface and bulk characteristics is essential to evaluate the packing of the molecules in these assemblies. There are numerous analytical tools that are currently available to characterize assemblies of molecules at interfaces, and most are common to both LB and self-assembled thin films. Some of the relevant and routinely used techniques are described here, and for a more complete and detailed description, the reader is referred to appropriate references.[3,8]

The surface characteristics of a thin film can be easily evaluated using contact angle goniometry (Figure 3) that can provide information about its wetting properties, uniformity, and order.[3] A measured volume of a liquid (water, hexadecane) is lowered on top of the thin film until it comes into contact with the derivatized surface in a vibration free environment. Depending on its wetting properties, the liquid spreads on the surface and forms an angle, the contact angle. The latter depicts a balance between the cohesive and adhesive interactions of the liquid molecules and the substrate, and is dependent on the relative hydrophobicity or hydrophilicity of the thin film surface and the liquid. A clean glass surface produces a contact angle of 18–20° with water, and ~85° with a nonpolar liquid such as hexadecane. The higher contact angle of hexadecane on a hydrophilic surface is due to an increase in the forces of repulsion

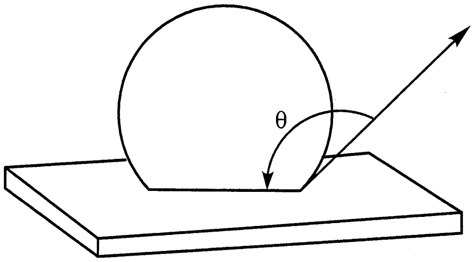

Figure 3. Determination of wetting behavior of a newly formed thin film using contact angle goniometry.

at the solid−liquid interface. Typical contact angles on an ordered thin film of a hydrophobic long chain hydrocarbon exposing methyl groups on top are 112−115° for water and 43−45° for hexadecane.[13] For a disordered liquidlike thin film exposing methylene groups on the surface, contact angles of 102−104° for water and ~0° for hexadecane are obtained.[14] Thus, a simple measurement yielding wetting characteristics of a newly formed thin film can provide very useful information about its surface composition and the related structure.

An analysis of the thin film bulk properties can be achieved using techniques such as ellipsometry and Fourier transform infrared spectroscopy (FT-IR) in the attenuated total reflection (ATR) or grazing angle incidence modes.[3] Ellipsometry is an optical technique that is used to estimate thickness and uniformity of the thin films.[15,16] In a typical measurement, plane polarized light from a laser source is used to interact with the surface at a desired angle. Upon interaction, it is resolved into its parallel (s) and perpendicular (p) components that are reflected from the surface. The combination of the reflected s and p components yields elliptically polarized light, and hence the name ellipsometry. The elliptically polarized light is changed back to plane polarized light. By measuring the angles of polarization of incident and reflected plane polarized lights, one can determine the phase shift between the parallel and perpendicular components (Δ), and the change in the ratio of the amplitudes of the two components (ψ). By a simple mathematical reflection using an estimated value for the refractive index of the organic phase,[17] this information is then translated into the thickness of the deposited thin film.

Fourier transform infrared spectroscopy in the attenuated total reflection (ATR) or grazing angle incidence (GAI) modes is a simple and most commonly employed method to obtain useful information about the orientation of the molecules in thin films, i.e., their packing order and surface coverage.[3,18,19] The characteristic frequencies for each chemical group can also provide their definitive identification, especially so for surface bound organometallic moieties. For an FTIR-ATR experiment, there are several ways to prepare a setup, and the one mentioned here has been more particularly employed by the author. A thallium bromo-iodide (KRS-5) crystal is sandwiched between the functionalized Si ⟨111⟩ wafers with a miniature pressure device to maximize optical contact. It is then placed in the path of polarized infrared radiation at a particular incidence angle (45°). The excitation of the molecular components at the interface with this light is dependent on their alignment and the polarization vector. By using s and p polarized light, one can obtain information about the preferential orientation of the molecules aligned on the surface.

Solid-state NMR spectroscopy has been widely used to characterize organic molecules chemisorbed on high-surface-area substrates such as zeolites and silica gels.[20] The solid-state ^{29}Si NMR spectra of functionalized silica gels, obtained using cross-polarized magic-angle spinning (CP/MAS) technique, can provide important information related to the overall structure of these network materials. The application of solid-state ^{29}Si, ^{13}C, and ^{31}P NMR spectroscopy to characterize self-assembled monolayers is relatively recent; however, these are proving to be powerful tools to determine the binding properties of molecules to the surface, and to evaluate the conformation of the alkyl chains in SAMs.[21] Some of the additional techniques that are employed for the characterization of the newly formed thin films include UV−visible spectroscopy,[22a,b] X-ray reflectivity,[22c,d] X-ray photoelectron spectroscopy,[22e,f] and X-ray diffraction.[22g] A combination of the surface characterization techniques by choice can lead to a detailed and definitive examination of the structure and packing in LB and self-assembled thin films.

III. Nano-Organometallic Langmuir−Blodgett Thin Films

One of the examples of LB organometallic thin films in catalysis that demonstrates the effect of molecular order on catalytic activity was reported by Milstein et al. in 1997.[23] They prepared three types of LB films of an amphiphilic rhodium complex, [4,4′-diheptadecyl-2,2′-bipyridine)rhodium-(hexadiene)]$^+$PF$_6^-$ on glass. A monolayer of this rhodium complex was first obtained on the air−water interface, and then transferred to the hydrophilic or hydrophobic glass slides. Using this procedure, they prepared (i) a monolayer of the rhodium complex in which its tail hydrocarbon end was at the hydrophobic glass surface and the organometallic headgroup on top; (ii) a triple layer of the complex in which the first layer had its organometallic head (H) group on the hydrophobic glass, and the hydrocarbon tail (T) on top. The second layer was deposited with the hydrocarbon tail on the hydrophobic surface of the monolayer and organometallic headgroup on top, followed by a third layer with the rhodium complex head on the surface exposing the hydrophobic tail on the top; and (iii) a quadruple layer on hydrophobic glass with HTTHHTTH type of combination (Figure 4). The tail-to-glass type LB films of this rhodium complex were found to be stable only under water.

The LB films were characterized by infrared and ultraviolet spectroscopies, and synchrotron grazing incidence X-ray diffraction measurements. The monolayer was found to be relatively less ordered, and the degree of order and packing seemed to have improved with the increase in the number of layers. The catalytic activity of these LB films were examined for the hydrogenation of acetone in a 0.6% or 0.1 M aqueous solution, at ambient temperature, 72 psi hydrogen pressure with no stirring of the mixture for 48 h. The product mixture was analyzed using gas chromatography (GC) or GC-mass spectrometry (GC-MS).

The organometallic LB monolayer was found to be an active catalyst for the hydrogenation of acetone yielding 2-propanol as the only product with a turnover number of 60 000. The LB-triple layer, that exposed the hydrocarbon tail and had its organometallic headgroups buried inside, showed no reduction of acetone. The dense packing in this triple layer

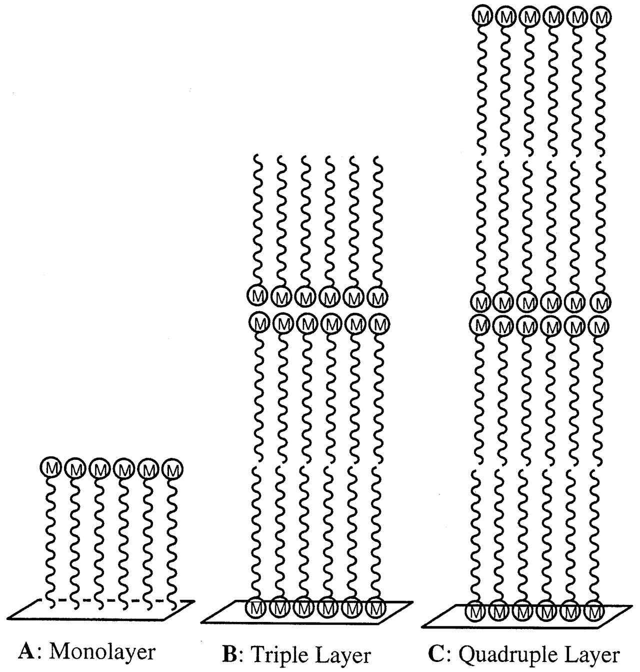

Figure 4. Mono- and multilayer Langmuir–Blodgett thin film assemblies of [4,4′-diheptadecyl-2,2′-bipyridine)rhodium-(hexadiene)]$^+$PF6$^-$ on glass.

prevented any substrate molecules from reaching the active metal centers, and thus no conversion of acetone to its hydrogenated products was observed. The LB-quadruple layer was found to be a better catalyst than the monolayer with a turnover number of 70 000. This increase in activity was attributed to the higher degree of order and packing as a result of increase in number of layers.

To eliminate the possibility that the reaction was not catalyzed by structures other than the LB films, they examined the activity of the solution from which the catalytic films were removed after one batch of successful hydrogenation of acetone. No further activity was observed indicating that the organometallic complex intact on the surface was necessary for the catalysis.

The catalytic activity of the LB films was compared with that for its homogeneous analogue. The rhodium complex in acetone under similar conditions as those used for the LB films was found to be a very poor catalyst for the hydrogenation of acetone, and gave a much lower turnover number (500). In addition, when the complex was suspended in water, it was found to be completely inactive. The LB films also showed a very high selectivity for the substrate. The thin films were active catalysts for the hydrogenation of acetone but showed no or little activity for butanone. The rhodium complex under homogeneous reaction conditions showed no selectivity, and reduced both of them without any noticeable difference in turnover numbers.

It is known that the degree of order in LB films is significantly influenced by temperature, and the densely crystalline thin films become disordered fluidlike when the temperature is increased. The effect of temperature on the catalytic activity of the organometallic LB films was found to follow a similar pattern. The catalytic activity was found to be at its maximum at 30 °C, and decreased significantly with an increase in temperature. This effect was reversible, and the activity could be restored by cooling the reaction mixture. These results clearly demonstrate the effect of molecular order on catalytic activity and selectivity, and indicate that supporting transition metal complexes on organized LB films offers potential in the design of tailor-made catalysts.

IV. Molecularly Self-Assembled Nano-Organometallic Thin Films

Molecular self-assembly is an intriguing process that leads to the spontaneous formation of robust and highly organized interfaces on a variety of substrates.[24] There is large body of work that has been devoted to the study of long chain alkane thin films,[3] and it is now well-known that such supramolecular structures are tightly packed and highly ordered due to strong interchain van der Waals forces of attraction. Inorganic oxides such as glass, quartz, mica, single crystal silicon are commonly employed substrates since their surface hydroxyl groups offer rich chemistry[25] to covalently bind desired molecules at the interfaces. Silica is also a commonly used support for heterogenizing homogeneous catalysis.[4] In the latter, surface modification of silica and related inorganic oxides that contain weakly acidic OH groups has traditionally been achieved by reacting them with molecules containing terminal trialkoxy groups, e.g., $(C_2H_5O)_3Si(CH_2)_nER_2$ (E = N, P). The condensation of the latter with the Si–OH groups leads to the formation of a strong covalent bond on the surface with the release of C_2H_5OH. This methodology has been extensively used[26,27] for the preparation of thin films containing donor ligands on silica that are subsequently used to bind organometallic fragments for supported metal catalysis.

The functionalization of silica using trialkoxy terminated silicon compounds requires synthesis of target molecules with appropriate donor ligands. In addition, this methodology has been a subject of much scrutiny lately, and there are significant issues related to this chemistry. It has now been established that when $(C_2H_5O)_3Si(CH_2)_3PPh_2$ is employed for the surface modification, there is unwanted preoligomerization of the silane compound in solution, its reaction with the surface hydroxyl groups on silica is not quantitative, and more importantly, the terminal phosphine in the above compound is prone to oxidation by Si–OH groups, leading to significant amounts of immobilized P^V species that do not bind tightly to the transition metals. The latter will contribute to the leaching of the metal from the surface, and make the process of heterogenization of homogeneous catalysts inefficient. This route is not particularly suited for molecular self-assembly that dictates a clean transfer of the desired molecules from solution to the surface by exclusive chemisorption without any side reactions. Some of the above-mentioned issues can be resolved using a new methodology that utilizes acid–base hydrolysis of amino-silanes with terminal OH groups,[28] a well-known chemical reaction that leads to quantitative conversions.[29]

The surfaces of silica based substrates (glass, quartz, and single-crystal silicon with an oxide layer on top) contain Si$-$OH groups with a packing density of $\sim$4.70 OH/100 Å.[30] The availability of these hydroxyl groups is enhanced by a cleaning process[31] that involves (i) soaking of the substrates in soap solution and sonication for 30 min; (ii) treatment with a mixture of 70% H_2SO_4 and 30% H_2O_2 (a highly potent piranah solution); (iii) rinsing copiously with deionized water; and (iv) drying over a stream of nitrogen. The appropriate clean substrate is then treated with a toluene solution of $SiCl_4$ followed by dry NR_2H that leads to the formation of a thin film of Si$-NR_2$ with no residual Si$-$OH groups. The same reaction can also be carried out by presynthesizing $Si(NR_2)_{4-n}Cl_n$ or $Si(NR_2)_4$ in solution, and then reacting the latter with surface Si$-$OH groups. The thin film is then treated with a solution of desired species containing terminal OH and PPh_2 groups, e.g., HO-$(CH_2)_3PPh_2$ in toluene (Figure 5).[32] Since there are no Si$-$OH groups on the surface, the reaction leads to thin films containing terminal phosphine groups without any surface bound phosphine oxide (P^V). This was confirmed by obtaining a solid-state cross-polarized $^{31}P\{^1H\}$ NMR spectrum of the thin film on silica [Si]-O$-(CH_2)_3PPh_2$ that showed a single resonance at -16.01 ppm. The latter was comparable to the high resolution $^{31}P\{^1H\}$ NMR spectrum of Me_3-Si$-$O$-(CH_2)_3PPh_2$ with a peak at -14.05 ppm, and also to that for a thin film prepared by condensation of $(C_2H_5O)_3Si(CH_2)_3PPh_2$ on silica (-16.3 ppm).[26b] It should be noted that the reaction of $(C_2H_5O)_3Si(CH_2)_3$-PPh_2 with silica also leads to the formation of the surface bound pentacoordinate phosphine oxide species, $Ph_2P(\text{-O-}[SiO_2]_2)_2(CH_2)_3Si\text{-O-}[SiO_2]$ that showed a spectral resonance at 25.9 ppm. The acid$-$base hydrolytic methodology thus eliminates a major side reaction, and is an efficient procedure to functionalize supports that are free from any bound phosphine-oxide. These thin films of the donor ligands are then used to covalently anchor organometallic complexes on the surface by ligand displacement[33] or bridge-splitting[34] reactions: [Si]-O-$(CH_2)_3PPh_2Ni(CO)_2PPh_3$, [Si]-O-$(CH_2)_4PEt_2Ni(CO)_2PPh_3$, [Si]-O-$(CH_2)_3PPh_2$-$RhCl(CO)_2$, [Si]-O-$(CH_2)_3PPh_2RhCl(CO)PPh_3$, [Si]-O-$(CH_2)_3PPh_2Pd(PPh_3)_3$, and [Si]-O-$(CH_2)_3PPh_2RuCl_2$-$(CO)_2PPh_3$.[32]

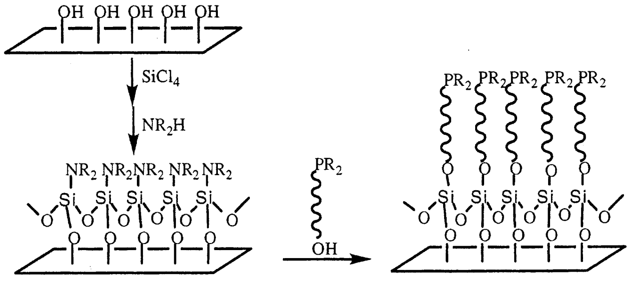

Figure 5. Functionalization of glass, quartz, or single crystal silicon surface with a self-assembled monolayer exposing terminal phoshine donor groups.

The characterization of the newly formed thin films was achieved using surface analytical tools such as contact angle goniometry, X-ray photoelectron spectroscopy, solid-state NMR, UV$-$Visible and FT-IR spectroscopies. The combined results obtained from these techniques provided a useful estimation of the surface composition and their structure. Contact angle goniometry also provided some insight into the packing of the thin films of the donor molecules on flat surfaces. Thin films containing terminal phosphine ligands showed contact angles of 8$-$10° with hexadecane and an average of 95° with water. These values were in agreement with those expected for the surfaces exposing phenyl groups attached to small hydrocarbon chain alkanes, and suggested that the thin films were densely packed.[35]

The analysis of the thin films using X-ray photoelectron spectroscopy indicated that the deposition process using a three-step methodology of treating the substrates with $SiCl_4$, NEt_2H, and finally with HO-$(CH_2)_nPPh_2$, was highly efficient. No residual chlorine or nitrogen were detected in a thin film of [Si]-O-$(CH_2)_nPPh_2$, and only the expected elements (Si, O, C, and P) at appropriate binding energies were present. Similar presence of only the elements of molecules making the organometallic thin films were observed in monolayers of [Si]-O-$(CH_2)_nPPh_2ML_n$.

FT-IR spectroscopy in the attenuated total reflection mode is an extremely useful technique in the characterization of organometallic thin films, and can also provide insight into the environment of the metal center on the surface and its packing arrangement on the flat surfaces. An FTIR-ATR spectrum of a thin film of [Si]-O-$(CH_2)_3PPh_2Ni(CO)_2PPh_3$ on a $\langle 111 \rangle$ surface of a single-crystal silicon wafer showed two peaks for the carbonyl stretching frequencies that were comparable in their peak positions to that for its solution model, $Ni(CO)_2(PPh_3)_2$. However, a comparison of the peak intensities indicated a difference in the structure of the organometallic complexes. The surface bound species showed two peaks that were almost equal in their intensities while the one in solution had unequal intensities for their stretching frequencies. The latter were attributed to the symmetric and antisymmetric dipole moment changes in the tetrahedral complex, $Ni(CO)_2(PPh_3)_2$.[36] The surface imposes some steric constraints, and might force the complex to assume a distorted tetrahedral geometry, which may be responsible for the change in the intensities of the carbonyl stretching frequencies.

An estimation of the packing density in an organometallic thin film can be made using UV$-$Vis absorption spectroscopy and Beer Lambert's law.[37] This evaluation is based on the comparison of the solution and surface absorption spectra of the organometallic complex. For a thin film of [Si]-O-$(CH_2)_3$-$PPh_2Ni(CO)_2PPh_3$ on quartz, surface coverage was estimated to be 3×10^{-9} mol cm^{-2} based on the extinction coefficient of its solution model $Ni(CO)_2$-$(PPh_3)_2$. This surface density suggested a highly close packed thin film.

The organometallic thin films were then used for the catalytic oligomerization of phenylacetylene, a reaction that had been extensively studied earlier[38] using $Ni(CO)_2(PPh_3)_2$ as a catalyst in solution. In a similar reaction in the homogeneous phase, the Ni-(0) solution model complex, $Ni(CO)_2(PPh_3)[PPh_2(CH_2)_3$-

Table 1. Oligomerization of Phenylacetylene

complex/thin film	catalyst:substrate ratio/surface density	1,2,4-triphenylbenzene (%)	1,3,5-triphenyl benzene (%)	linear product (%)
$[Ni(CO)_2(PPh_3)_2]$[38] or	1:250	70	<1	30[a]
$[Ni(CO)_2(PPh_3)(PPh_2(CH_2)_3OSiMe_3]$[32]	1:24000			
$\{[Si]\text{-}O\text{-}(CH_2)_3PPh_2Ni(CO)_2(PPh_3)\}$[32]	3×10^{-9} mol/cm^2 (roughly equivalent to 1:24000 ratio)	23	56	21[b]

[a] 1,3,6-triphenyl-1-yne-3,5-diene. [b] 1,4,6-triphenyl-1-yne-3,5-diene

Table 2. Hydrogenation of Diphenylacetylene (tolan)[40]

complex/thin film	hydrogen pressure (bar)	*cis*-stilbene (%)	*trans*-stilbene (%)	bibenzyl (%)
$[(CH_3)_3Si\text{-}O\text{-}(CH_2)_{12}PPh_2RhCl(1,5\text{-}COD)]$	5	60	37	<4
	20		25	75
$[Si]\text{-}O\text{-}(CH_2)_{12}PPh_2RhCl(1,5\text{-}COD)$	5	83	5	12
	20			100

$OSiMe_3$] in a 1:250 catalyst-to-monomer ratio, oligomerized phenylacetylene to give the cyclic and acyclic products, 1,2,4-triphenylbenzene (70%), 1,3,5-triphenylbenzene (less than 1% yield), and 1,3,6-triphenyl-1-yne-3,5-diene (30%). In the catalyst-to-monomer ratio of 1:24 000, the catalyst was found to be inefficient for the oligomerization of phenylacetylene (Table 1). The latter ratio is comparable to the expected catalyst concentration on a 1 × 1-in. glass slide utilized in this study.

The surface anchored Ni(0) complex, $[Si]\text{-}O\text{-}(CH_2)_3\text{-}PPh_2Ni(CO)_2(PPh_3)$, was found to be a highly active catalyst for the oligomerization of phenylacetylene, and yielded a product distribution that was different from that in the homogeneous phase: symmetric 1,3,5-triphenylbenzene, 56%; asymmetric 1,2,4-triphenylbenzene (23%), and a linear product 1,4,6-triphenyl-1-yne-3,5-diene, 21%. The catalyst activity was found to be significantly enhanced by surface immobilization on a flat surface, and the turnover number using the surface anchored organometallic complex was much higher than that in solution. The turnover frequency (number of moles of the product/moles of the catalyst/h) for the surface bound catalyst was found to be 1656 h^{-1}. For the catalytic reaction in solution using a monomer-to-catalyst ratio similar to that for the surface anchored Ni(0) complex, the turnover frequency was calculated to be 1.16×10^{-3} h^{-1}. These results suggest that the immobilization of the organometallic complexes in nanosize thin films leads to an advantageous difference in their catalytic activity and selectivity.

To examine the possible cause for the difference in catalyst activity and selectivity upon heterogenization, a detailed time-evolved FT-IR spectroscopic evaluation of the above reaction was undertaken. The results indicate that the above reaction might have proceeded by an initial loss of a triphenylphosphine and a carbonyl ligand, followed by an attack with phenylacetylene. A detailed evaluation of the reaction in solution done earlier had suggested that the active catalyst in this reaction was the coordinatively unsaturated complex created by the loss of both carbonyl ligands.[39] It is possible that the surface anchoring of the complex imposes specific constraints on the complex, and creates an active pocket directing it to follow a different reaction pathway. The addition of phenylacetylene at the metal center then takes place in an orientation that is favorable for the formation of the symmetric product, 1,3,5-triphenylbenzene. The linear product formed on the surface was also different (1,4,6-triphenyl-1-yne-3,5-diene) than the one obtained in the solution reaction, 1,3,6-triphenyl-1-yne-3,5-diene.

The acid−base hydrolytic methodology had resolved some of the pertinent issues related to the functionalization of the inorganic oxide surfaces with thin films containing terminal phosphine donor ligands that are essential in surface anchoring of a variety of transition metal based catalysts. The above study had also demonstrated that anchoring of organometallic complexes in thin films led to an enhancement of catalytic activity and selectivity. The molecules that were employed in this study had a small hydrocarbon chain, and it is known that long chain alkane molecules with a chain length of 10−18 CH_2 groups form highly ordered structures.[3] Thus, the potential of the above methodology may be further enhanced by constructing molecularly self-assembled organometallic thin films of phosphine terminated long chain alkanes of controlled structure that are robust, and are advantageously oriented. The latter will help in strengthening the definitive role played by self-organization in designing smart and recoverable catalysts by nanotechnology.

The long alkane chain phosphines that were needed for the self-organization process were prepared from the commercially available alcohols, $HO\text{-}(CH_2)_n\text{-}X$ ($n = 10-12$, X = Cl, Br) by first protecting the alcohol moiety with Me_3Si group, reacting the resulting silylated alcohol with $KPPh_2$, and finally deprotecting the alcohol group with citric acid. The molecular self-assembly of the resulting phosphines ($HO\text{-}(CH_2)_n\text{-}PPh_2$) on silica based substrates (glass, quartz, single-crystal silicon), was achieved by a similar three-step acid−base hydrolytic methodology as described above.[40] The resulting thin films containing terminal donor phosphines were then metalated using a bridge-splitting reaction with μ-chloro-(1,5-cyclooctadiene)rhodium(I) dimer (Figure 6). The organometallic thin films could also be prepared by first reacting the desired phosphine in solution with the

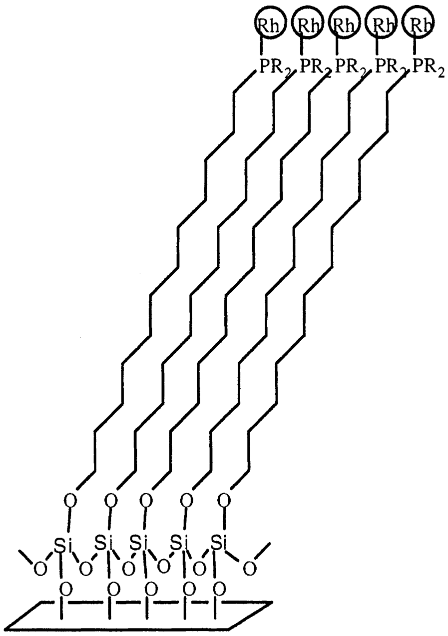

Figure 6. Organometallic self-assembled monolayer with terminal phosphine bound RhCl(1,5-cyclooctadiene) groups.

rhodium dimer, and then subjecting the metalated phosphine to molecular self-assembly on the desired substrate.

The characterization of the thin films was once again achieved by using techniques including contact angle goniometry, ellipsometry, XPS, and FTIR-ATR spectroscopy. The contact angles on thin films exposing PPh_2 groups on top were ~90° with water and ~20° with hexadecane. These values suggested a high packing density and that the thin films were well ordered. Ellipsometry is a commonly used technique to evaluate the thickness of the thin films, and help establish if the chemisorption process is yielding the desired monolayers. To calculate the thickness, data from the same substrate before and after functionalization was compared, and an assumption for the refractive index of the organic phase was made. For long chain alkane phosphines, [Si]-O-$(CH_2)_n$-PPh_2 ($n = 10-12$), thickness values of 26, 28, 32 Å, respectively, were obtained, and were found to be in accord with the expected values of 28, 30, 31 Å, respectively. These results clearly demonstrated that the acid–base hydrolytic chemisorption process yields well-packed and ordered self-assembled monolayers. Upon complexation with rhodium complex, the thicknesses increased, as expected, to 35, 38, 40 Å.

The binding energies of elements in the thin films were obtained using XPS, and were found to be consistent with those for their homogeneous analogues, and confirmed the composition of the thin film structures.

FT-IR spectroscopy in the attenuated total reflection mode was found to be a highly valuable technique to evaluate the degree of order in newly formed thin films. An extensive literature now exists on the CH_2 stretching frequencies, and it is concluded that for highly ordered self-assembled thin films, the typical values for the symmetric and antisymmetric CH_2 stretching frequencies are 2850 and 2920 cm^{-1}, respectively.[3] An increase in these peak positions is indicative of disorder, and a liquidlike thin film structure yields $\nu_s(CH_2)$ at 2856 and $\nu_{as}(CH_2)$ at 2928 cm^{-1}. The FTIR-ATR spectra of [Si]-O-$(CH_2)_n$-PPh_2 ($n = 10-12$) thin films showed $\nu_s(CH_2)$ and $\nu_{as}(CH_2)$ peaks at ~2851 and ~2922 cm^{-1}. The latter were characteristic of tightly packed and highly ordered thin films. Upon complexation with rhodium, these values showed no noticeable change in their peak positions. The latter strongly suggested that the monolayers were solidlike, and metalation did not disturb this densely packed arrangement.

The nano-organometallic thin films were evaluated for their catalytic ability in hydrogenation of diphenylacetylene (tolan). The choice of this substrate was ideal since its hydrogenation could afford three products, *cis*-stilbene, *trans*-stilbene, and bibenzyl, and thus this reaction could help establish selectivity criteria for homogeneous[41] and heterogenized homogeneous catalysts. Solution models of the surface bound complexes, Me_3SiO-$(CH_2)_n$-$PPh_2RhCl(1,5\text{-}C_8H_{12})$, were found to be active catalysts for the hydrogenation of tolan, and at 5 bar of hydrogen pressure, typically afforded a mixture of 60% *cis*-stilbene, 36% *trans*-stilbene, and 4% bibenzyl. As the pressure was increased, *cis*-stilbene was preferentially hydrogenated further to bibenzyl, and at 20 bar of hydrogen pressure, the product mixture consisted of ~75% bibenzyl, 24% *trans*-stilbene, and 1% *cis*-stilbene (Table 2).

The organometallic self-assembled monolayers, [Si]-O-$(CH_2)_nPPh_2RhCl$(1,5-COD), were found to be highly active in the catalytic hydrogenation of tolan. However, there was a significant difference in the product distribution. At 5 bar of hydrogen pressure, ~83% *cis*-stilbene, ~5% *trans*-stilbene, and ~12% bibenzyl were obtained. When the hydrogen pressure was increased to 20 bar, there was an almost exclusive formation of bibenzyl. It suggested that the surface bound organometallic complex shows a strong preference for *cis*-stilbene at low pressures, and upon increasing the hydrogen pressure it gets converted completely to bibenzyl. The latter being the only product at high pressures. It is also interesting to note that the catalyst in the homogeneous phase decomposed during the conversion. However, the organometallic thin films were found to be stable, and could be recycled. The thin films were easily removed from the reaction mixture after the first batch of hydrogenation at a particular pressure, washed with the appropriate solvent, and reintroduced into the reaction mixture with retention of catalytic activity. The recycled catalytic thin films produced a product distribution indistinguishable from the one obtained in the first batch.

V. Concluding Remarks

Catalysis plays a pivotal role in carrying out important organic transformations, and in designing new generation of catalysts it is essential to consider three important features: activity, selectivity, and recovery and recycling ability. It is clear that heterogenization of homogeneous catalysts is an obvious choice to come close to achieving these goals in one system. This review has highlighted a tantalizing and promising support for transition metal catalysts, i.e., well-ordered and densely packed thin films. These nanostructured materials are at the cutting edge of designing new technologies with maximum desired output. The results obtained with LB and self-assembled thin films have demonstrated that the catalyst's activity and selectivity is significantly influenced by anchoring the desired metal complexes at these interfaces. Another very important feature of these nanosystems is their ability to stabilize the catalyst, recover it intact, and recycle it with retention of its activity and selectivity. Molecularly self-assembled thin films that are chemisorbed are particularly suited for this purpose, and have yielded very encouraging results in this regard. Considering the two assembly methodologies discussed in this review, it is the view of the author that LB organometallic thin films provide a useful medium to carry out fundamental studies related to the understanding of nano-catalytic materials. However, for all practical purposes, molecular self-assembly will lead the way in the design of high performance catalysts. Self-assembly process initiated by chemisorption yields highly robust thin films, a very important factor of significant industrial relevance. Heterogenized homogeneous catalysis using nano-organometallics at interfaces is a powerful tool, and offers potential in building smart catalysts by molecular design. We need to put more effort now in understanding the environment of metals at these interfaces, and its role in influencing the catalytic behavior. The study of nano-organometallic thin films using additional surface characterization tools such as atomic force and scanning tunneling microscopies in combination with characterization techniques discussed in this review will prove highly beneficial in providing molecular level understanding of the reactions at these interfaces. Silica based substrates are environmentally friendly, and offer advantages in building cheap and viable technology. However, it may also be important to explore the use of other substrates such as gold and silver that are well-known in the self-assembly of thiol and carboxylic acid terminated molecules. A comparison of the catalytic activity at different interfaces may help discern the role played by the substrate itself in the design of nanomaterials for catalysis.

VI. Acknowledgments

I would like to thank Natural Sciences and Engineering Research Council of Canada and Fonds pour la Formation de Chercheurs et l'Aide a la Recherche (FCAR, Quebec, Canada) for their financial assistance, and very dedicated students especially Dr. Maria G. L. Petrucci who contributed significantly in getting some of the results discussed in this review.

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CR010360K