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Immobilized Transition-Metal Carbonyls and Related Catalysts

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Contents

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Stanley H. Langer is Professor of Chemical Engineering at the University of Wisconsin—Madison where he has been since the mid-60s. He came there from the Research Laboratories of American Cyanamid in Stamford, CT, where he was a group leader in exploratory fuel cell research. In addition to kinetics, catalysis, and areas described in this article, his present research interests include electrochemical energy generation, physicochemical applications of chromatography, and hydrometallurgy.

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I. Introduction

The preparation of catalysts by immobilizing active transition-metal complexes on solid supports such as organic polymers, inorganic oxides, and related materials has recently attracted widespread attention. Serious interest in these catalysts originated with efforts to develop industrially competitive homogeneous catalysts. These attempts to supplant heterogeneous catalysts met with only limited success due to the separation problem associated with homogeneous systems. In addition to providing a solution to this problem, the new hybrid catalysts have the attractive features of being reproducible and allowing control and knowledge of the nature of the incipient species immobilized on the support. There is the further promise, yet unfulfilled, of identifying important catalyst features through synthesis and experiment. In addition, immobilized metal carbonyls can be decomposed to produce highly dispersed supported metal or metal oxide particles.

This review is concerned primarily with immobilized transition-metal carbonyls and derived materials. Emphasis is placed on their syntheses, structures, and catalytic properties. This discussion also covers immobilized carbonyls serving as precursors of supported metals or metal oxides. The immobilization and catalytic properties of other types of transition-metal complexes have been the subject of earlier reviews.[1-20]

The renewed interest in the catalytic properties of transition-metal carbonyls stems mainly from their potential for catalyzing olefin and carbon monoxide reactions wherein desired more complex organic molecules are produced.[21,22] With the diminishing supply of available petroleum feedstocks, the viable production of these useful molecules has become an urgent priority of the industrialized world. Transition-metal carbonyls are of further interest because the carbonyls of many catalytically active metals are known, and commercially available or readily synthesized.[22] Their bonding and structure are now well characterized.[23] The carbonyl clusters are candidate catalysts for reactions requiring multiple metal sites. Furthermore, after the synthesis and activation of these catalysts, the gaseous nature of carbon monoxide makes it a renewable as well as labile ligand.

The potential advantages to be gained from employing the new hybrid catalyst systems are best appreciated by comparing them with traditional heterogeneous and homogeneous catalysts. Heterogeneous catalysts have several advantages, including (1) acceptable thermal and mechanical stability, (2) high activity for a wide range of reactions, and (3) capacity for use in packed and fluidized beds as well as ready separation from reaction products. Disadvantages may include (1) design and improvement limits due to frequently ill-defined active sites, (2) limited accessibility and effectiveness of the catalytic components, and (3) severe and costly reaction conditions (i.e., high temperatures and pressures). In contrast, homogeneous systems are characterized by (1) well studied and interpreted catalytic activity, (2) reported activity under mild reaction conditions, (3) efficient and reproducible use of metal atoms, and (4) electronic and steric properties that can be varied and frequently controlled. A major disadvantage lies with the separation problem. Additional advantages stemming from the attachment process per se include[1,9a] (1) the introduction of preferred orientations, (2) an altered stereochemistry about the metal atom, (3) a changed equilibrium between the metal atoms and their ligands, and (4) advantageous stabilization of catalytically active but normally unstable structures.[11b] The hope is that the immobilization of transition-metal complexes on solid supports eventually will give superior hybrid catalysts possessing the advantages of both traditional catalyst systems with few disadvantages.

Components of the hybrid catalyst system must each be tailored to reaction requirements. The support should be inert to the reaction mixture, withstand the required reaction conditions, and possess an acceptable surface area. Typical organic supports include styrene polymers, poly(amino acids), acrylic polymers, and cross-linked dextrans.[9b,11b] Among acceptable inorganic supports are glass, silica, alumina, zeolites, and clays.[9b,11b] The active portion of the catalyst must be stable under reaction conditions while being solvated and "soluble" in the reaction medium. To enhance activity it may be preferable to anchor the metal complex to the support through a chemical chain rather than directly bond it to the support surface. Anchoring ligands can be employed which coordinate strongly and give thermally stable complexes.[1] The remaining ligands should impart good local solubility without sterically hindering interaction between the metal atom and reactive substances. The most important identified feature of an active catalyst is the presence of a coordinately unsaturated metal atom having one or more orbitals where facile substrate coordination or adsorption can occur. This may be inherent or created through ligand dissociation.

Interest also has grown in the decarbonylation of immobilized transition-metal carbonyls to prepare supported dispersed metallic particles on both organic[24] and inorganic[25-27] supports because this route offers the promise of increased control of the particle structure.[26] These materials are also potential precursors for the production of supported metal oxides, especially for those metals having lower oxidation states not readily accessible through reduction of the supported metal oxide (e.g., molybdenum).[28]

II. Organic Supports

A. Introductory Discussion

The primary requirement for a useful organic polymer support is the incorporation of functional groups which are potential ligands. Many polymers contain characteristic groups which can act as ligands (e.g., polystyrenes and polyamides).[29] Some groups can serve as a starting point for further modification and attachment of ligands, limited only by the organic chemistry of the polymers.[29]

Desired support characteristics include (1) good mechanical properties, such as attrition resistance, porosity and adequate thermal stability, (2) readily accessible sites for anchoring potential active centers, and (3) limited solubility in the reaction medium.

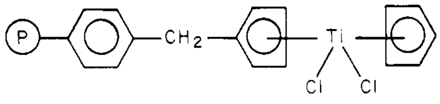
Mechanical and thermal stability are generally governed by the intrinsic nature of the polymer and, to a lesser degree, by the extent of cross-linking and network formation (reticulation). Thermal stability further implies a strong linkage between the support and the metal carbonyl to prevent metal leaching in a flow process or recycling operation. It does not imply that all metal–ligand bonds be stable, a property generally in conflict with acceptable catalytic activity, but only that the complex–support interaction be secure.[5]

Readily accessible catalytic sites are also desirable. The immobilized catalyst may be viewed as a combination of a "soluble" part, which bears catalytic sites, and an "insoluble" polymeric support, inert toward the substrate. This inertness presupposes minimal steric restriction to substrate and product transport near the active site. However, free and equivalent diffusion of all components may not always be desirable. Occasionally diffusion effects may be employed to enhance selectivity for smaller reactants.[5]

Diffusion in a polymer depends on the nature of its porous structure, which in turn is usually determined by the extent of swelling of the polymer lattice. This is governed by the degree of cross-linking as well as the nature of the substrate and/or solvent used in the reaction. For example, when solvents used with polystyrene-immobilized catalysts are more polar than benzene, two processes occur: (1) pore width decreases due to decreased resin swelling and (2) polar gradients between the bulk solvent and the local environment of the active site are created.[30] The former decreases the diffusion rate of larger reactants; the latter selectively increases the diffusion rate of nonpolar reactants. In fact, with increased ethanol content of a benzene–ethanol solvent system used with an immobilized hydrogenation catalyst, the rate of reduction of nonpolar olefins increased until high concentrations of ethanol acted to shrink the pores so that molecular size dominated selectivity. For cyclohexene, the rate of hydrogenation increased by a factor of 2.4 with a change from pure benzene to 1:1 benzene–ethanol.[30] Although the porous nature of the polymer generally is not well defined, a proper choice of a solvent–polymer system can result in some control of the porosity to give a "shape-selective" catalyst.[1,30]

The inert nature of the support presupposes a compatibility between the support, the solvent, and the substrate which is determined by ill-defined physical characteristics including the resin's hydrophobic or hydrophilic nature as well as localized electrostatic and dipolar interactions. The system components may not be chosen independently since solvent choice can be dictated by the nature of the metal complex, especially in those instances where a particular solvent is required to stabilize a reactive form of the metal complex.[5]

The degree of cross-linking may affect the nature of the catalyst. Although most workers have employed polymers with 1 or 2% cross-linking, some have used resins which contain 20%[31,32] to 60%[33] cross-linking. The increased rigidity can enhance catalytic activity by limiting the likelihood of interaction between those active centers which tend to dimerize with subsequent deactivation.[31,32] For example, the stable but catalytically inactive titanocene dichloride complex yields, upon reduction, catalysts active for the hydrogenation of alkenes, alkynes, and molecular nitrogen. However, the active species readily polymerizes with deactivation. When immobilized on a 20% cross-linked polystyrene support (1), a stable catalyst is obtained which is 25–120 times more active than the unattached complex for cyclohexene hydrogenation.[31,32] However, lower resin flexibility may hinder transport of the reagents and metal complexes which functionalize the support[34,35] as well as the reactants and products of the catalytic reaction itself.[30-32,36] In addition, the metal–ligand equilibria for supported metal complexes may be quite different from those for similar concentrations of comparable metal complexes and ligands in homogeneous systems.[37]



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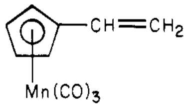
For this discussion, polymer-immobilized metal carbonyls are divided into two groups: those with hydrocarbon backbones and those with some heteroatom or functionalization incorporated into the support. A summary of polymer-immobilized metal carbonyl studies is given in Table I.

B. Metal Carbonyls Immobilized on Hydrocarbon Polymers

1. Preparation

One approach to preparing immobilized metal carbonyls involves polymerization of metal carbonyl containing monomers incorporating groups which undergo vinyl polymerization,[38,39] such as 2–6. These monomers are readily synthesized from available materials, as demonstrated for 4[40] (eq 1 and 2). The monomers then



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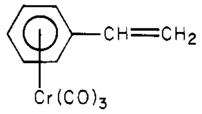

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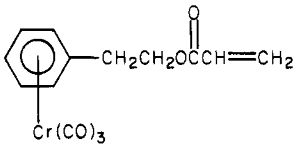

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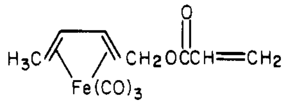

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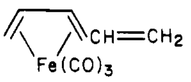

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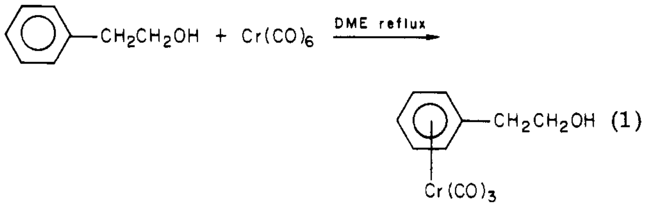

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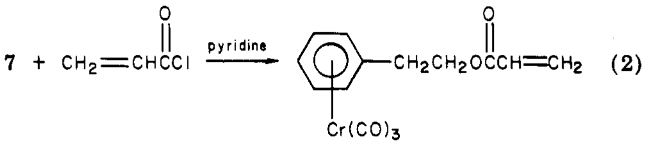

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Table I. Selected Studies of Polymer-Immobilized Transition Metal Carbonyls and Related Materials

Initial Carbonyl	Support	Proposed Structure of Supported Complex[a]	Reaction Studied	Comments[b]	Ref.
VANADIUM					
V(CO)$_6$	poly(diphenylstyrylphosphine)				88
CHROMIUM					
Cr(CO)$_6$	η^6-(2-phenylethyl acrylate)tricarbonylchromium homo- and copolymers			thermal decomposition to supported Cr$_2$O$_3$	40
Cr(CO)$_6$	polystyrene; styrenetricarbonylchromium copolymers				42,58
Cr(CO)$_6$	polystyrene				44
Cr(CO)$_6$	poly(styrylmethylenecyclopentadienyl anion)	Ⓟ-CH$_2$-Cp-Cr(CO)$_3$H Ⓟ-CH$_2$-Cp-Cr(CO)$_3$Cl Ⓟ-CH$_2$-Cp-Cr(CO)$_2$NO [Ⓟ-CH$_2$-Cp-(CO)$_3$Cr]$_2$		infrared data; thermal stability	46
Cr(CO)$_6$	polystyrene	Ⓟ-C$_6$H$_5$-Cr(CO)$_3$	methyl sorbate hydrogenation	infrared data	49
Cr(CO)$_6$	polystyrene; poly(vinyl benzoate)	Ⓟ-C$_6$H$_5$-Cr(CO)$_3$	methyl sorbate hydrogenation	infrared spectra; thermal stability	50
Cr(CO)$_6$	η^6-(2-phenylethyl methacrylate)tricarbonylchromium homo- and copolymers			thermal decomposition to supported Cr$_2$O$_3$	57
Cr(CO)$_6$	π-(benzyl acrylate)tricarbonylchromium homo- and copolymers				59
Cr(CO)$_6$	linear and crosslinked phosphinated polystyrene			infrared spectra	63
Cr(CO)$_6$	carbonyl polymerized with 4-pyridylethylene			infrared data	73a
Cr(CO)$_6$	poly(2-pyridylethylene)				76
Cr(CO)$_6$	poly(methyl methacrylate)			infrared data; electron spin resonance spectrum	244
Cr(CO)$_6$	poly(diphenylbenzyl phosphine)			infrared data	245
MOLYBDENUM					
Mo(CO)$_6$	poly(styrylmethylenecyclopentadienyl anion)	Ⓟ-CH$_2$Cp-Mo(CO)$_3$H		thermal stability	46
Mo(CO)$_6$	polystyrene	Ⓟ-C$_6$H$_5$-Mo(CO)$_3$	benzyl chloride polymerization; anisole alkylation; anisole acylation	infrared data; solvent leaching	51
Mo(CO)$_6$	linear and cross-linked phosphinated polystyrene			infrared data	63
Mo(CO)$_6$	phosphinated polystyrene; poly(styrylbipyridine)	Ⓟ-C$_6$H$_4$-bipy-Mo(CO)$_4$ [Ⓟ-C$_6$H$_4$-PPh$_2$]$_x$ Mo(CO)$_{6-x}$ x = 1,2	2-pentene metathesis	infrared data; effect of oxygen	77
Mo(CO)$_6$	poly(styrene-difluorobutenoate) with fluoroacetate ligands	Ⓟ-CF$_2$COOMo(C$_3$H$_5$)(CO)$_{6-n}$L n = 3 L = THF n = 4 L = DME	1,3-butadiene polymerization		78
Mo(CO)$_6$	Amberlite IRA-45	Ⓟ-NR$_2$-Mo(CO)$_5$	propylene epoxidation		79
Mo(CO)$_6$	phosphinated polystyrene	Ⓟ-CH$_2$-PPh$_2$-Mo(CO)$_5$	2-pentene metathesis	EtAlCl$_2$/O$_2$ cocatalyst employed	80
Mo(CO)$_6$	phosphinated polystyrene				244
Mo(CO)$_6$	poly(diphenylbenzylphosphine)			infrared data	245
Mo(CO)$_6$	phosphinated polystyrene				246

Table I. cont.

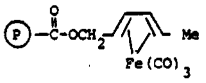
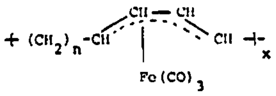
Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
TUNGSTEN					
$W(CO)_6$	poly(styrylmethylene-cyclopentadienyl anion)	$\textcircled{P}-CH_2Cp-W(CO)_3H$		thermal stability	46
$W(CO)_6$	linear and crosslinked phosphinated polystyrene			infrared data	63
$W(CO)_6$	carbonyl polymerized with 4-pyridylethylene				74
$W(CO)_6$	phosphinated polystyrene; poly(styrylbipyridine)	$\textcircled{P}-C_6H_5-bipy-W(CO)_4$ $[\textcircled{P}-C_6H_5-PPh_2]_x W(CO)_{6-x}$ $x = 1,2$	2-pentene metathesis	infrared data	77
$W(CO)_6$	phosphinated polystyrene	$\textcircled{P}-CH_2-PPh_2W(CO)_5$ $\textcircled{P}-CH_2-W(CO)_3(\eta-C_5H_5)$	3-heptene metathesis	solvent leaching; $\underline{i}$-$BuAlCl_2/O_2$ Co-catalyst employed	81
$W(CO)_6$	poly(vinylpyridine)	$\textcircled{P}-py-W(CO)_5$		photoacoustic spectra	95b
$W(CO)_6$	poly(methyl methacrylate)				244
$W(CO)_6$	poly(diphenylbenzylphosphine)			infrared data	245
MANGANESE					
$[Mn(CO)_5]^-$	linear and crosslinked chloromethylated polystyrene	$\textcircled{P}-CH_2-Mn(CO)_5$		thermal decomposition to entrapped $Mn_2(CO)_{10}$	35
$Mn_2(CO)_{10}$	(vinylcyclopentadienyl)-tricarbonylmanganese copolymers				43
$Mn_2(CO)_{10}$	linear and cross-linked phosphinated polystyrene			infrared data	63
$Mn_2(CO)_{10}$	carbonyl polymerized with 4-pyridylethylene				74
$Mn_2(CO)_{10}$	poly(1-vinyl-2-pyrrolidinone)				75
$Mn_2(CO)_{10}$	poly(diphenylstyrylphosphine)				88
$[Mn(CO)_5]^-$	poly(diphenylbenzylphosphine)			infrared data	245
$[Mn(CO)_5]^-$	carbonyl polymerized with fluoro-alkenes				247
$Mn_2(CO)_{10}$	vinylcymantrene copolymers				248
RHENIUM					
$Re_2(CO)_{10}$	phosphinated polystyrene				246
IRON					
$Fe(CO)_5$	π-(2,4-hexadiene-1-yl acrylate)-tricarbonyliron			thermal decomposition to supported Fe_2O_3	41
$Fe_2(CO)_9$	$CpCH_2$-substituted polystyrene	$\textcircled{P}-CH_2-Cp-Fe(CO)_2H$			47
$Fe(CO)_5$	methacrylate copolymers			thermal decomposition to supported Fe metal	55a,56
$Fe_3(CO)_{12}$	polybutadiene; styrene-butadiene copolymer			thermal decomposition to supported Fe_3O_4	60-62
$Fe(CO)_5$	linear and crosslinked phosphinated polystyrene	$(\textcircled{P}-C_6H_4-PPh_2)_2Fe(CO)_3$			63

Table I. cont.

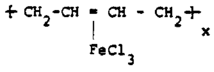
Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
$Fe(CO)_5$	phosphinated polystyrene				64
$Fe(CO)_5$ $Fe_3(CO)_{12}$	phosphinated polystyrene	$[\textcircled{P}-PPh_2]_{5-n}Fe(CO)_n$ $n = 3,4$ $[\textcircled{P}-P(Ph)CH_2CH_2PPh_2]_x[Fe(CO)_n]_y$ $x = 1,2;\ n = 3,4;\ y = 1,2$	1-pentene isomerization; 1-pentene hydrosilylation	photogeneration of active species; infrared data	70
$Fe(CO)_5$	poly(4-pyridylethylene)				73b
$Fe(CO)_5$	poly(1-vinyl-2-pyrrolidinone)			infrared data	75
$Fe(CO)_5$	phosphinated polystyrene	$[\textcircled{P}-PPh_2]_{5-n}-Fe(CO)_n$ $n = 3,4$	1-pentene isomerization; 1-pentene hydrosilylation	photogeneration of active species; infrared data	82
$Fe(CO)_5$ $[Fe(CO)_4]^{2-}$	carbonyl polymerized with fluoroalkenes				247
$Fe(CO)_5$	carbonyl polymerized with dichlorobutene or dichloroxylene	 $\left[CH_2-\underset{FeCl_3}{\underset{\vert}{CH}}=CH-CH_2\right]_x$			249
$Fe(CO)_5$	poly(*p*-vinylphenyldiphenylphosphine); poly(vinyldiphenylphosphine); poly(*p*-vinylphenoxydiphenylphosphine)				250
$Fe(CO)_5$	teflon; polyethylene				251
RUTHENIUM					
$H_4Ru_4(CO)_{12}$	phosphinated polystyrene	$\textcircled{P}-PPh_2-[H_4Ru_4(CO)_{11}]$ $(\textcircled{P}-PPh_2)_3-[H_4Ru_4(CO)_9]$ $(\textcircled{P}-PPh_2)_4-[H_4Ru_4(CO)_8]$	ethylene hydrogenation	infrared spectra	83
$Ru_3(CO)_{12}$	poly(2-vinylpyridine)		hydroformylation		86
$Ru_3(CO)_{12}$ $RuH_2(CO)(PPh_3)_3$	poly(acrylic acid); poly(methacrylic acid); ethylene-maleic acid copolymer		1-pentene isomerization; 1-pentene hydrogenation	infrared data	252
COBALT					
$Co_2(CO)_8$	$(C_5H_5)CH_2$-substituted polystyrene	$\textcircled{P}-CH_2-C_5H_4-Co(CO)_2$ $\textcircled{P}-CH_2-C_5H_4-Co-(C_6H_5-\textcircled{P})_n$ $n = 1,2$			47
$Co_2(CO)_8$	$(C_5H_5)CH_2$-substituted polystyrene	$\textcircled{P}-CH_2-C_5H_4-Co(CO)_2$	ethyl propiolate cyclooligomerization		48
$Co_2(CO)_8$	$(C_5H_5)CH_2$-substituted polystyrene		1-pentene hydroformylation		52
$Co_2(CO)_8$	polyethylene with polar ligands			thermal decomposition to supported Co particles	54
$Co_2(CO)_8$	poly(ethylene glycol); methyl methacrylate copolymers			thermal decomposition to supported Co particles	55
$Co_2(CO)_8$	polybutadiene; natural rubber; styrene-butadiene copolymer			thermal decomposition to supported CoO	61,62
$Co_2(CO)_8$	linear and crosslinked phosphinated polystyrene	$[(\textcircled{P}-C_6H_4-CH_2-PPh_2)_2-Co(CO)_3]^+[Co(CO)_4]^-$ $[\textcircled{P}-C_6H_4-CH_2-PPh_2-(CO)_3Co]_2$	1-pentene hydroformylation; allylbenzene isomerization	infrared data	63

Table I. cont.

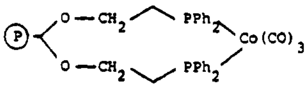
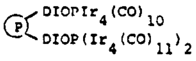
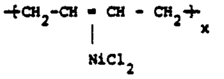
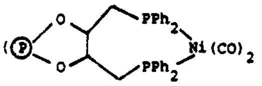
Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
$Co_2(CO)_8$	phosphinated polystyrene				64
$Co_2(CO)_8$	poly(p-styryldiphenylphosphine)		2-hexene hydroformulation		65
$Co_2(CO)_8$	poly(4-pyridylethylene); carbonyl polymerized with 4-pyridylethylene				73b,74
$Co_2(CO)_8$	poly(1-vinyl-2-pyrrolidinone)				75
$Co_2(CO)_8$ $HCo(CO)_4$	poly(2-vinylpyridine)		2-hexene hydroformylation		84,85
$Co_2(CO)_8$	poly(2-vinylpyridine); poly(4-vinylpyridine)		hydroformylation	photoactivation of active sites	86,87, 95a
$Co_2(CO)_8$	poly(diphenylstyrylphosphine		1-hexene hydroformylation		88
$Co_2(CO)_8$	polybutadiene		1-hexene hydroformylation		89
$Co_2(CO)_8$	poly(vinylpyridine)		2-hexene hydroformylation		90
$Co_2(CO)_8$	DOWEX MWA-1		1-hexene hydroformylation		100
$[Co(CO)_4]^-$	poly(4-vinylpyridine)		1-hexene hydroformylation		253
$Co_2(CO)_8$	styrene-vinylpyridine copolymers		2-hexene hydroformylation		254
$Co_2(CO)_8$	poly(vinyl alcohol)				255
$Co_2(CO)_8$	phosphinated polystyrene		hydroformylation; hydrogenation	infrared data	256
RHODIUM					
$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	phosphinated polystyrene			preparation of supported Rh aggregates	24a
$Rh_6(CO)_{16}$	phosphinated polystyrene			production of supported Rh aggregates	24b
$RhH(CO)(PPh_3)_3$	phosphinated polystyrene	$(\textcircled{P}\text{-}C_5H_4\text{-}PPh_2)_xRhH(CO)(PPh_3)_{3-x}$	1-pentene hydroformylation		36,98, 99, 255
$Rh_6(CO)_{16}$	Amberlyst A-21		hydrogenation of α,β-unsaturated compounds		72
$Rh_4(CO)_{12}$	poly(2-vinylpyridine); poly(4-vinylpyridine)		hydroformylation	photoacoustic spectra	86,95
$Rh_4(CO)_{12}$	polystyrene		arene hydrogenation		91
$Rh_6(CO)_{16}$	phosphinated polystyrene	$(\textcircled{P}\text{-}PPh_2)_3[Rh_6(CO)_{13}]$	ethylene and cyclohexene hydrogenation	preparation of Rh aggregates; infrared spectra	92,93
$Rh_6(CO)_{16}$	Amberlyst A-21	$\textcircled{P}\text{-}C_6H_4\text{-}CH_2N^+Me_2H[Rh_x(CO)_y]^-$ $\textcircled{P}\text{-}C_6H_4\text{-}CH_2NMe_2Rh_x(H)(CO)_y$	nitrobenzene hydrogenation		94,258
$Rh_4(CO)_{12}$	DOWEX MWA-1		1-hexene hydroformylation		100
IRIDIUM					
$Ir(CO)_2$(p-toluidine)Cl	phosphinated polystyrene	$\textcircled{P}\text{-}PPh_2Ir_4(CO)_{11}$ $\textcircled{P}\text{-}DIOP(Ir_4(CO)_{11})_2$  $\textcircled{P}\begin{cases}DIOPIr_4(CO)_{10}\\DIOP(Ir_4(CO)_{11})_2\end{cases}$ $(\textcircled{P}\text{-}PPh_2)_yIr_4(CO)_9(PPh_3)_{3-y}$ $(\textcircled{P}\text{-}PPh_2)_2Ir_4(CO)_{10}$	ethylene and cyclohexene hydrogenation	infrared spectra; thermal stability	67,71,96

Table I. cont.

Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
NICKEL					
$Ni(CO)_2(PPh_3)_2$	phosphinated polystyrene	$(\textcircled{P}-C_6H_4-PPh_2)_2Ni(CO)_2$	butadiene cyclo-oligomerization	used in bifunctional catalyst system	36,97-99, 257
$Ni(CO)_4$	methyl methacrylate copolymers			preparation of supported Ni particles	55a
$Ni(CO)_4$	polybutadiene; natural rubber; styrene-butadiene copolymer			preparation of supported NiO particles	61,62
$Ni(CO)_2(PPh_3)_2$	phosphinated polystyrene	$(\textcircled{P}-C_6H_4-PPh_2)_2Ni(CO)_2$	ethyl propiolate cyclooligomerization	infrared data	63
$Ni(CO)_4$	phosphinated polystyrene	$\textcircled{P}-C_6H_4-PPh_2Ni(CO)_3$ $(\textcircled{P}-C_6H_4-PPh_2)_2Ni(CO)_2$			64
$Ni(CO)_4$	poly(4-pyridylethylene) |				73b
$Ni(CO)_4$	poly(1-vinyl-2-pyrrolidinone) |				75
$Ni(CO)_4$ $Ni(CO)_3PPh_3$ $Ni(CO)_2(PPh_3)_2$	poly(diphenylbenzylphosphine) |			infrared data	245
$Ni(CO)_4$	carbonyl polymerized with dichlorobutene or dichloroxylene	 $\left[CH_2-\underset{NiCl_2}{\underset{\vert}{CH}}=CH-CH_2\right]_x$			249

$Ni(CO)_4$	poly(p-vinylphenyldiphenylphosphine);
	poly(vinyldiphenylphosphine);
	poly(p-vinylphenoxydiphenylphosphine) |
					250

$Ni(CO)_4$	phosphinated polystyrene		alkyne cyclo-oligomerization		256
$Ni(CO)_4$	poly(p,p'-isopropylidenediphenol) |		1,3-butadiene cyclooligomerization		259
BIMETALLIC CLUSTERS					
$Co_2Rh_2(CO)_{12}$	DOWEX MWA-1		1-hexene hydroformylation		100
$Fe_2Pt(CO)_9PPh_3$ $RuPt_2(CO)_5(PPh_3)_3$ $HAuOs_3(CO)_{11}$	phosphinated polystyrene	$(\textcircled{P}-PPh_2)_2[Fe_2Pt(CO)_8]$ $(\textcircled{P}-PPh_2)_3[RuPt_2(CO)_5]$ $\textcircled{P}-PPh_2-[HAuOs_3(CO)_{10}]$	1-butene hydrogenation	infrared data	101

Key to Table I:

bipy - bipyridine
Cp - cyclopentadienyl
DIOP - 2,3-dihydroxy-1,4-bis(diphenylphosphino)butane
Me - methyl
$\textcircled{P}$ - polymer backbone
Ph - phenyl
py - pyridine

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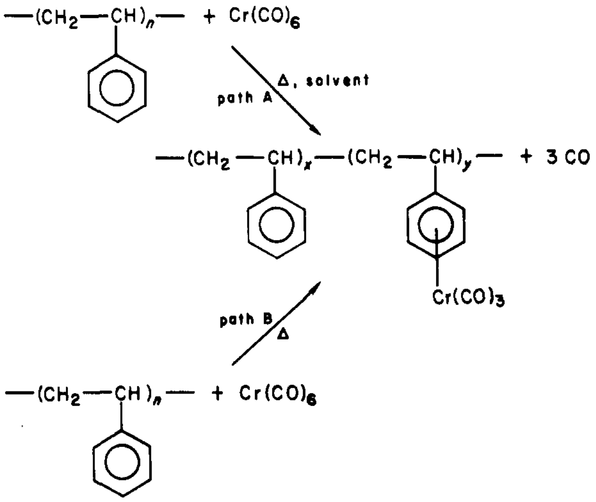
[a] Structures are given only in those instances where supporting evidence is available.

[b] Only studies other than simple preparations are indicated.

undergo either homopolymerization or copolymerization with styrene, methyl acrylate, acrylonitrile, 2-phenylethyl acrylate, or other monomers in degassed benzene or ethyl acetate solvents at mild temperatures (328–358 K) with azobis(isobutyronitrile) (AIBN) or other azo initiators.[39] The nature of the compounds obtained varies with the organometallic group.[39] For example, **2**, **4**, and **5** readily homopolymerize; **3** will not homopolymerize but will copolymerize; **6** undergoes neither radical-initiated homopolymerization nor copolymerization.[38,39] This is due to the stable radical that results from chain attack at the vinyl moiety interrupting chain propagation.[41] The majority of these vinyl monomers contain first row transition elements.[38,39] The formation of monomers containing second and third row transition elements is often not possible.[40]

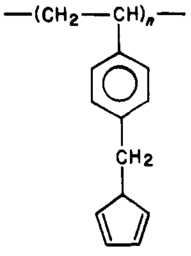
Similar catalysts can be obtained by reacting metal carbonyls with polymers containing arene π electrons in two ways (eq 3). The first (path A) involves re-



(3)

fluxing the polymer with the metal carbonyl in a suitable solvent.[42,43] Alternatively (path B), one can heat a mixture of the polymer and carbonyl under pressure to give immobilized metal carbonyls.[44]

Metal carbonyls can also be immobilized on polymers through cyclopentadienyl linkages by two methods.[32,45] The first involves treating chloromethylated polystyrene with SnCl$_4$ followed by reaction with sodium cyclopentadienide in THF at room temperature to produce the functionalized polymer 8.[32] The identical product



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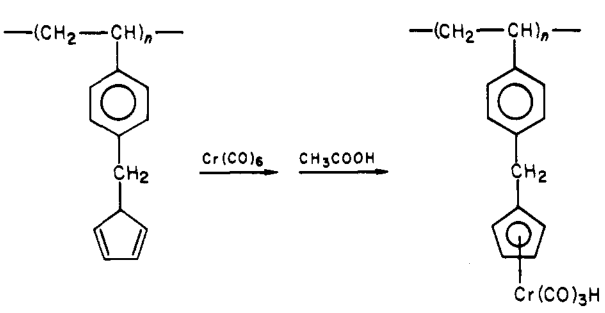
can be obtained by brominating polystyrene, treating it with butyllithium, and reacting the product with cyclopentenone in THF.[45] Group 6 metal carbonyls are immobilized by reacting the carbonyl with support followed by acidification[46] (eq 4). Subsequent treatment can yield a dimer or further substituted products[46] (eq 5–7). Treatment of the functionalized polymer with Fe$_2$(CO)$_9$ yields a stable hydride compound[47] (13).



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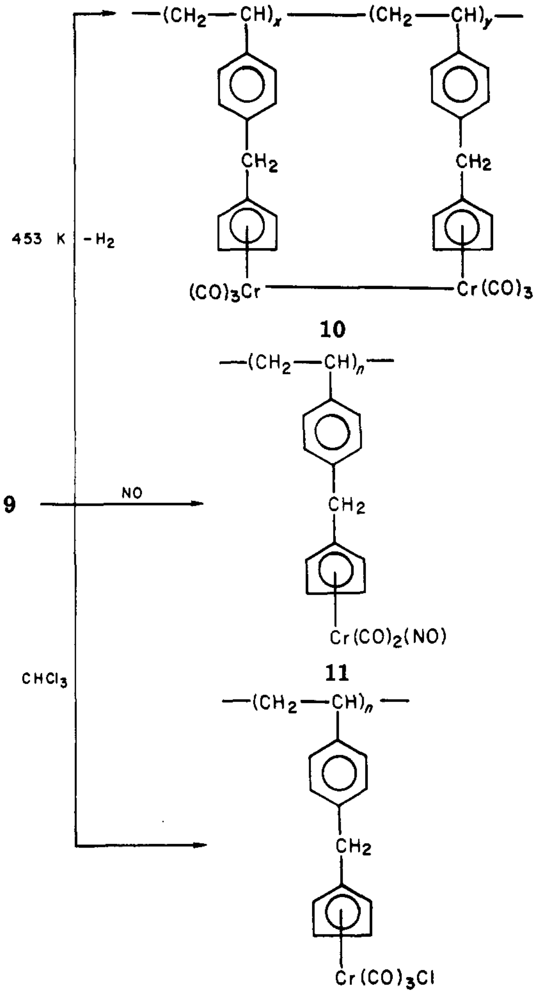

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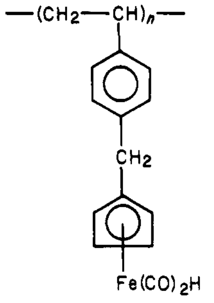

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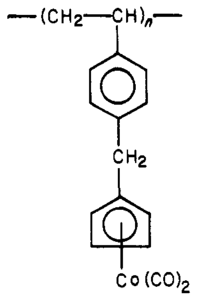
As expected from the equivalent atomic number (EAN) rule, Co$_2$(CO)$_8$ does not form a hydride when reacted with the polymer.[47,48] Upon irradiation, the unsaturated cobalt centers of 14 may react with aromatic rings of the polymer support in the absence of neighboring metal atoms,[47] producing 15. These materials are stable for several weeks in an inert atmosphere in the dark.[47]



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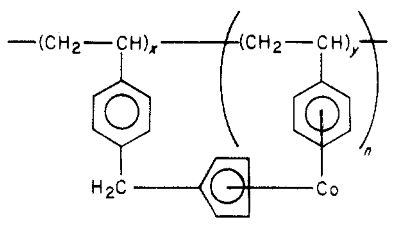
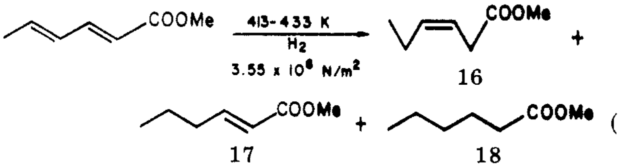


15, $n = 1$ or 2

2. Catalytic Properties and Reactions

Pittman, Kim, and Douglas[49] treated swollen 1% divinylbenzene–styrene resin in dimethoxyethane with $Cr(CO)_6$ under nitrogen to produce a catalyst with $Cr(CO)_3$ moieties complexed to 20–25% of the aryl rings of the support. This material catalyzed the hydrogenation of methyl sorbate in cyclohexane or DMF (eq 8).



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The product distribution was a function of temperature. At 413 and 433 K, the selectivity for **16** was >95%; at 423 K, the selectivity was significantly lower (74–81%). Recycling the catalyst gave a different steady-state product distribution which was stable with subsequent recyclings. Infrared spectra and elemental analysis indicated that this was due to chemical binding of methyl sorbate or a reaction product to the resin rather than leaching of chromium from the polymer. Lower reaction rates were observed with polymer-immobilized catalyst than with its homogeneous analogue, η^6-(ethylbenzene)tricarbonylchromium. This was attributed to mass-transfer limitations.[49]

Although initial activities were in substantial agreement, Awl et al.[50] found a greater loss in activity with recycling than Pittman and co-workers.[49] They ascribed it to leaching of arene–$Cr(CO)_3$ moieties. None of the catalysts studied could be recycled more than twice. Higher initial activities were obtained when a poly(vinyl benzoate) support was employed. None of the catalysts studied were stable to air or heat.[50]

A catalyst prepared by refluxing $Mo(CO)_6$ and polystyrene beads in heptane was used by Tsonis and Farona[51] in the alkylation and acylation of aromatic substrates. The polymer-immobilized catalyst tended to be less active than its homogeneous (toluene)tricarbonylmolybdenum counterpart for alkylation reactions. Acylation of anisole promoted by the heterogeneous system was comparable to that observed with the homogeneous catalyst; the heterogeneous catalyst did not effectively catalyze toluene acylation. As with its homogeneous analogue, the immobilized catalyst gave predominantly para isomers when the aromatic substrates contained ortho/para directing substituents. Leaching experiments indicated no metal loss during reaction.

Polymer-immobilized (η^5-cyclopentadienyl)cobalt dicarbonyl catalysts recently have been employed in olefin hydroformylation.[48,52] Chang, Grubbs, and Brubaker[48] found the cobalt catalyst to be inactive for hydroformylation at 383 K and 120×10^5 N/m² ($CO:H_2$ = 1:1). Brintzinger[52] found the same catalyst to be active for the hydroformylation of 1-pentene at 408 K and 200×10^5 N/m² ($CO:H_2$ = 1:1) with 98% selectivity for primary product formation. Preliminary results indicated this catalyst to be inactive for olefin hydrogenation and olefin isomerization, but moderately active for the cyclotrimerization of ethyl propiolate.[48]

Perkins and Vollhardt[53] employed (η^5-cyclopentadienyl)cobalt dicarbonyl supported on cross-linked macroporous polystyrenes as a Fischer–Tropsch catalyst at 463–473 K ($CO:H_2$ = 3:1, 5.2×10^5 N/m²). After an initial induction period, steady-state turnover numbers of 0.01 mmol/mol of Co per h for CO were observed. Exposure to air destroyed catalytic activity. The reproducibility of catalytic activity, regenerability of active sites, and observed product distribution suggested that the activity was attributable to immobilized cobalt complexes rather than metal crystallites. Homogeneous $CpCo(CO)_2$ was inactive under similar conditions. The bound catalyst was active for alkyne cyclizations, but deactivated rapidly. Limited activity for 1-pentene isomerization and hydroformylation was observed.

Immobilized (η^5-cyclopentadienyl)rhodium dicarbonyl prepared by Chang, Grubbs, and Brubaker[48] was active for hydrogenation of olefins, ketones, and aldehydes, isomerization of allylbenzene, disproportionation of 1,4-cyclohexadiene, and cyclotrimerization of ethyl propiolate. However, in all but the last case infrared spectra indicating diminished CO stretching intensities suggested that the active species was actually Rh(0). This catalyst was very active for the hydroformylation of 1-pentene and 1-hexene at 293–383 K. The linear/branched selectivity was approximately 1 with the H_2/CO equal to 1; it increased with increasing temperature or pressure. Used catalysts produced infrared spectra identical with those for fresh samples and retained the original activity.

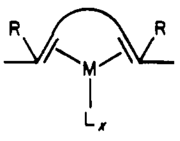
3. Production of Dispersed Metals and Metal Oxides

Hess and Parker[54] and Thomas[55] described the preparation of uniform metallic particles of cobalt in the 10–1000-Å range by thermally decomposing $Co_2(CO)_8$ in solutions of dispersant polymers. Linear addition polymers of high molecular weight with relatively nonpolar backbones and more polar pendant groups attached at intervals between 100 and 200 backbone atoms were most effective.[54] The size of the cobalt particles could be controlled to some extent by varying the concentration of polar groups in the polymer. Smaller metal particles were favored by higher concentrations of polar pendant groups.[54] In these systems, the polymer is believed to preferentially adsorb on the metal particle, forming a protective envelope, preventing metal aggregation while permitting particle growth.[55a] Similar crystallites are reported to be formed from $Ni(CO)_4$[55a] and $Fe(CO)_5$.[56]

Much of the work of Pittman and his co-workers has involved the synthesis and polymerization of a variety of tricarbonylchromium monomers. These monomers undergo copolymerization with materials such as acrylonitrile, styrene, and methyl acrylate at low temperatures, typically 343 K, with azo initiators.[40,42,57–59] Some complexes may also undergo homopolymerization under similar conditions.[40,57] These polymer-immobilized compounds can be decomposed thermally or with light to produce dispersed metal oxide particles. Photodecomposition typically leads to the formation of

Cr_2O_3 dispersed throughout the polymer.[40] Thermal decomposition both in air and under N_2 results in the slow destruction of the tricarbonylchromium units with CO evolution and formation of uncharacterized chromium oxides imbedded in highly cross-linked polymers.[40,57] Thermal decomposition of similar $Mn(CO)_5$-containing polymers resulted in $Mn_2(CO)_{10}$ entrapped throughout the matrix.[35]

Manuel and Berger described polybutadiene-immobilized metal carbonyls, **19**, prepared by refluxing the carbonyl with polymer in suitable solvents.[60-62] Here M is iron, cobalt, or nickel, L is carbon monoxide, x = 1–4, and R can by hydrogen or hydrocarbon groups. These materials self-cure or can be vulcanized with proper reagents. Extensive thermal decomposition studies on these materials showed that heating the polymers between 423 and 1273 K gave small, finely divided metal or metal oxide particles throughout the polymer. These particles apparently are intertwined with the polymer chain and not separated by ordinary magnetic separation methods. The particles commonly have an average particle or cluster size of about 10–150 Å, with growth and ultimate size governed by the heating rate. Specifically when polybutadiene-immobilized iron carbonyl is heated at elevated temperatures in air at atmospheric pressure, self-curing occurs with the formation of primarily nonmagnetic Fe_2O_3 crystals. Vulcanization under pressure at elevated temperatures with limited air contact produces fine crystals of Fe_3O_4 and a vulcanizate with magnetic properties.[61]



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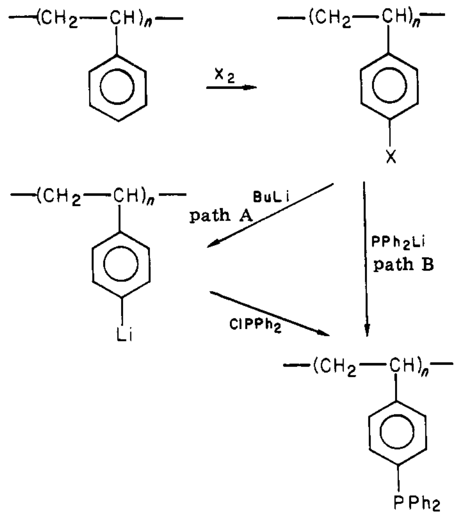
C. Immobilization of Metal Carbonyls with Functionalized Polymers

1. Preparation

Phosphorus, the most common ligand element used to attach metal complexes to polymer supports, can be introduced into polymers via four routes (eq 9). The first involves reacting a halogenated polystyrene with butyllithium (path A), followed by treatment with $ClPPh_2$.[63] Excess butyllithium gives lower yields of phosphinated resin due to formation of Ph_2PBu byproduct.[64] An alternate route to the same product involves treatment of the resin with Ph_2PLi (path B).[64] This support has been used to prepare immobilized complexes and supported metal crystallites from a number of carbonyls and substituted carbonyls, including $Ni(CO)_4$[64] (**21**, **22**), $(PPh_3)_3RhH(CO)$[35] (**23**), and $Rh_6(CO)_{16}$,[24] (**24**). The latter has been used to prepare supported metal crystallites (**25**; eq 10).



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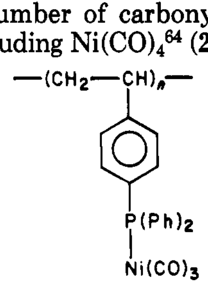

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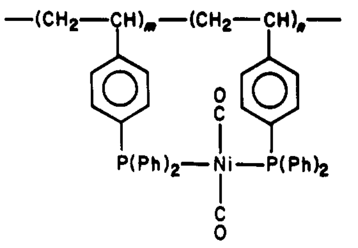

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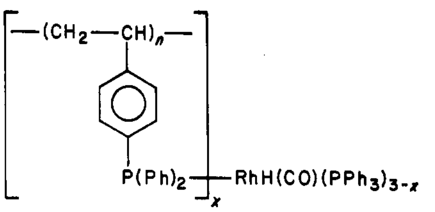

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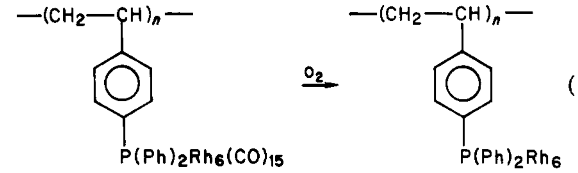
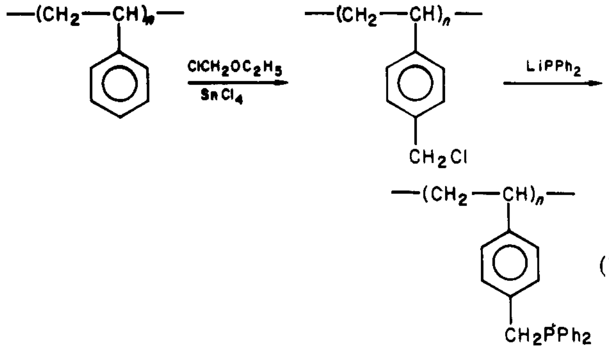


(10)

24 25

A similar functionalized polymer can be prepared by initially chloromethylating the polymer and treating it with $LiPPh_2$[63] (eq 11). Finally, phosphinated polystyrenes can be produced by homo- or copolymerizing *p*-styryldiphenylphosphine with styrene or other suitable monomers.[65]



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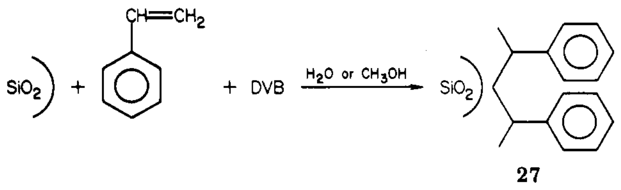
Diffusion limitations for reactants and products in swollen organic polymers may control reaction rates. Arai[66] attempted to eliminate this problem and exploit the mechanical and thermal stability of inorganic sup-



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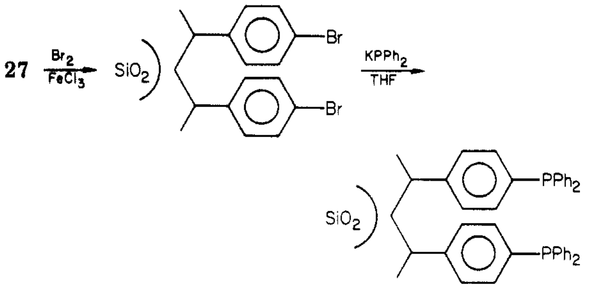
(12)

ports by developing a technique for coating silica gel with phosphinated polystyrene. Copolymers of styrene and divinylbenzene (DVB) are prepared in the presence of AIBN and silica gel (eq 12). The product obtained from brominating **27** is reacted with potassium diphenyl phosphide to give phosphinated polystyrene, **28** (eq 13).



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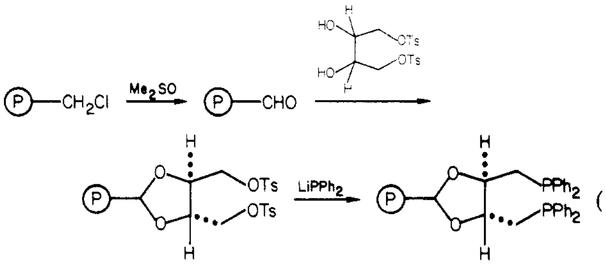
Attachment of metal carbonyls can proceed in the customary manner.

Chelating phosphines such as 2,3-dihydroxy-1,4-bis(diphenylphosphino)butane can be attached to a support, **29**, for use in immobilizing transition-metal carbonyls.[67] The process involves oxidation of a chloromethylated polystyrene resin, treatment with diol to give a ditosylate, and subsequent reaction with lithium diphenylphosphide[68] (eq 14). This is traditionally referred to as Ⓟ-DIOP. DIOP is 2,3-*o*-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.



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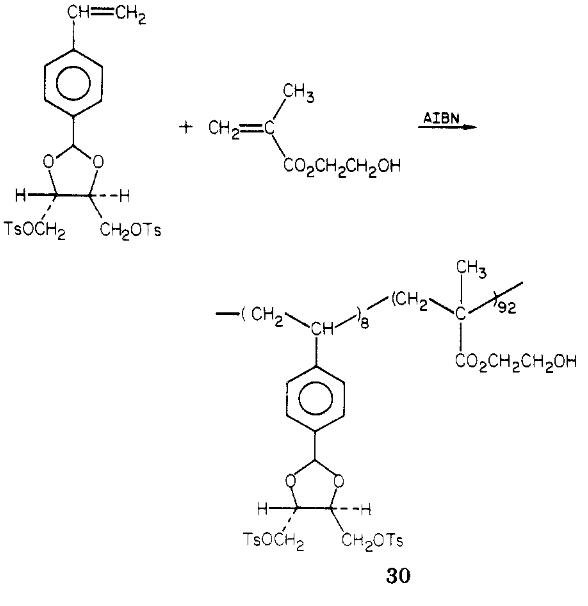
Early experiments with this polystyrene-immobilized chelating phosphine showed it to be effective in asymmetric reactions involving nonpolar solvents.[68a] In polar solvents, the resin collapses and prevents reactant penetration. Attempting to produce an immobilized chelating phosphine ligand for use with polar solvents, Stille et al.[69] copolymerized hydroxyethyl methacrylate and 2-*p*-styryl-4,5-bis(tosyloxymethyl)-1,3-dioxolane (92:8 mole ratio) to produce an immobilized ditosylate, **30**, which can be phosphinated (eq 15, 16). Because the polymer is primarily a hydroxyethyl methacrylate resin, it is easily swollen by polar solvents as demonstrated in the asymmetric hydrogenation of α-acetamidoacrylic acid.[69c]



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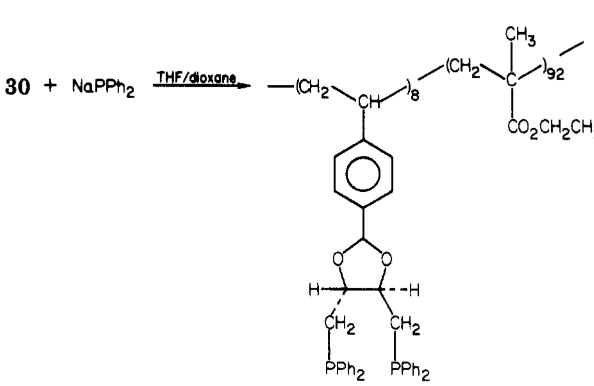

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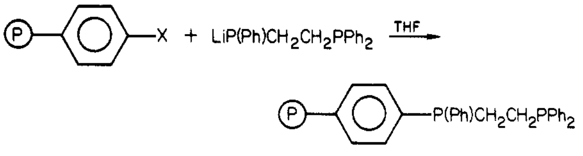
Bis(1,2-diphenylphosphino)ethane (DIPHOS) groups can also be introduced readily into a polymer[70] (eq 17).



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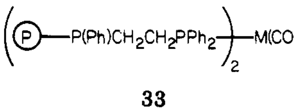
Ⓟ = polymer backbone

Subsequent reaction with metal carbonyls can produce species in which the carbonyl serves as a cross-linking agent (**33**), with few cis-chelated complexes (**34**) being formed.[70]



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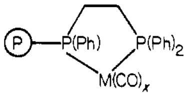

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With preparation of the functionalized resin, immobilization is straightforward. The carbonyl, dissolved in a suitable solvent, is allowed to equilibrate with the resin before the solvent is removed. Alternatively, the mixture is refluxed and the catalyst recovered by filtration. In some instances, the carbonyl can be reacted with a phosphinated resin by using photochemical techniques.[63] With some metal carbonyl clusters, the cluster can be more effectively synthesized in the presence of the functionalized polymer. Gates et al.[67,71] have used this route to prepare phosphine-immobilized derivatives of $Ir_4(CO)_{12}$.

Ligand groups containing nitrogen are also used to anchor metal carbonyls. Commercial Amberlite and Amberlyst resins incorporate these groups.[72] Alternatively they can be prepared by polymerizing nitrogen-containing monomers in the presence of the metal carbonyl,[73-76] with bidentate ligands resulting from use of monomers such as vinylbipyridine.[77] The metal carbonyl is immobilized by using procedures described above for phosphine ligands.

Analogous chemistry can anchor other ligand groups to polymers. An example is the synthesis of resins containing difluoroacetate side chains.[78] First, ethyl 2,2-difluoro-3-butenoate is prepared by the addition of ethyl bromodifluoroacetate to ethylene followed by the free-radical copolymerization or terpolymerization of the unsaturated difluorocarboxylic ester with styrene and divinylbenzene to produce either linear or cross-linked polymers. The ethyl ester groups of the resins are then transformed into acid or allyl ester groups to give supports for immobilizing transition-metal derivatives. The polymer is subsequently reacted with the metal carbonyl at room temperature in a suitable solvent[78] (eq 18).

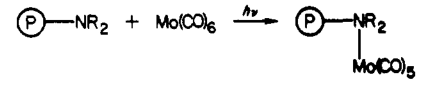
$$\textcircled{P}\!-\!CF_2COOC_3H_5 + Mo(CO)_6 \xrightarrow{\text{THF or DME}} \underset{\textbf{35}}{\textcircled{P}\!-\!CF_2COOMo(C_3H_5)(CO)_{6-n}L} \quad (18)$$

L = THF, $n = 3$
L = DME, $n = 4$

When transition-metal carbonyls are immobilized with functionalized polymers, multiple substitution on the carbonyl may give more than one type of catalytic site.[67] This difficulty may be avoided in the future by selectively controlling the functionalized support. Thus, *p*-styryldiphenylphosphine may be copolymerized with suitable monomers and cross-linking agents to produce polymers with low phosphine concentrations. Reaction of these polymers with metal carbonyls should produce monosubstituted species selectively.

2. Catalytic Properties and Reactions

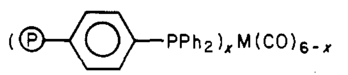
Ivanov, Boeva, and Tanielyan[79] carried out the epoxidation of propene with *tert*-butyl hydroperoxide using a catalyst prepared by irradiating a mixture of $Mo(CO)_6$ and Amberlite IRA-45 (eq 19). The catalytic activity and selectivity of the immobilized complex were essentially equivalent to that of $Mo(CO)_6$ in solution. The friability of the polymer support caused significant deactivation upon recycling.



$$\textcircled{P}\!-\!NR_2 + Mo(CO)_6 \xrightarrow{h\nu} \textcircled{P}\!-\!NR_2\!\!-\!Mo(CO)_5 \quad (19)$$

36

Tamagaki, Card, and Neckers[77] recently compared $Mo(CO)_6$ and $W(CO)_6$ attached to polymers with phenylphosphine (**37**) and bipyridine ligands (**38**) for 2-pentene metathesis (eq 20) at room temperature using ethylaluminum dichloride as a cocatalyst. The polymer-immobilized catalysts were at least an order of magnitude more active than the unattached analogues. Tungsten catalysts were more active than analogous molybdenum catalysts, with bipyridyltungsten catalysts demonstrating the highest activity. The immobilized catalysts could be readily filtered for reuse if kept under argon without drying. Moderate activity loss with reuse was attributed to leaching or destruction of active sites. Oxygen in the reaction mixture dramatically increased the activity of these immobilized catalysts.



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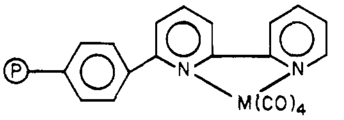


38

M = Mo, W

$$2CH_3CH{=}CHCH_2CH_3 \rightleftarrows CH_3CH{=}CHCH_3 + CH_3CH_2CH{=}CHCH_2CH_3 \quad (20)$$

The catalytic properties of $Mo(CO)_6$ attached to a phosphinated polystyrene–divinylbenzene resin for *cis*-2-pentene metathesis were investigated by Basset et al.[80] Upon treatment with ethylaluminum dichloride and oxygen, this weakly active system gave a conversion of 3.4% in 20 min at room temperature.

Warwel and Buschmeyer[81] studied a similar catalyst based on $W(CO)_6$ for *trans*-3-heptene metathesis. Catalyst treatment with isobutylaluminum dichloride and oxygen caused conversion of 50% of the olefin substrate. Activity decreased dramatically with successive recyclings. The phosphinated polymer acted as a reservoir for coordinately unsaturated tungsten species which were displaced by the alkylaluminum compound. The tungsten complex then performed as a homogeneous catalyst.

Dawans and Morel[78] investigated polymer supports containing fluoroacetate groups where electron-withdrawing properties might strengthen the anchoring linkage of catalytic species. Soluble catalysts prepared according to eq 18 catalyzed 1,3-butadiene polymerization to produce a vinylic microstructure similar to that obtained with unsupported molybdenum complexes. The measured rate with supported catalyst was less than that using unsupported $Mo(CO)_6$. Net activation energies in the range 14.6–19.7 kcal/mol depended on the type of polymer-immobilized η^3-allylic molybdenum catalyst employed. Observed differences were attributed to steric hindrance about the catalytic centers resulting from polymer chain coiling in the reaction mixture.

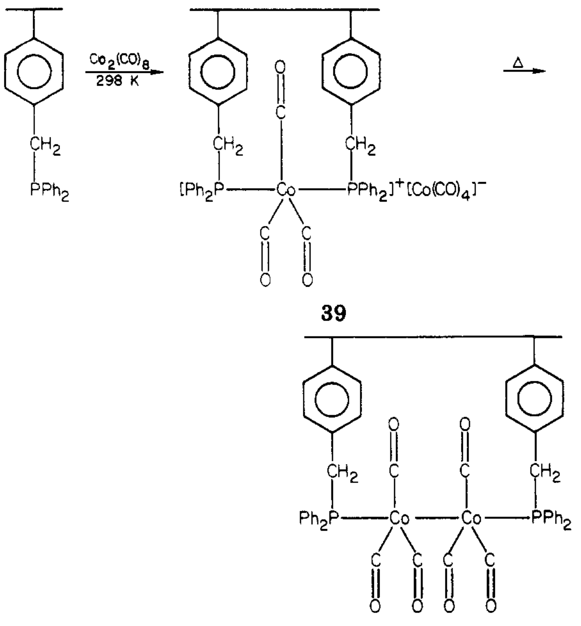
The photocatalytic behavior of $Fe(CO)_5$[70,82] and $Fe_3(CO)_{12}$[70] supported on phosphinated styrene–divinylbenzene resins at 298 K has been investigated by Pittman et al. Irradiation of these compounds creates isolated, coordinatively unsaturated metal atoms which are catalytically active for olefin isomerization and olefin hydrosilylation. In the former reaction, polymer-anchored catalysts provide yields which approximate those for their homogeneous analogues.[82] Little or no activity was observed in the dark, nor was any catalytic activity demonstrated by the nonmetalated polymer.[82] Other points worth noting are the following: (1) solvents in which the resin cell can swell are more effective than those which produce little or no swelling; (2) the number of phosphine substitutions affected the initial activity and selectivity for formation of *cis*- and *trans*-2-pentene;[70] and (3) the photocatalysis requires continuous irradiation. Experiments with homogeneous analogues such as $Fe(CO)_4PPh_3$ and $Fe(CO)_3(PPh_3)_2$ showed the Fe–P bonds to be largely photoinert, so that the catalyst is truly heterogeneous.[82]

Otero-Schipper, Lieto, and Gates[83] prepared polymer-supported derivatives of $[H_4Ru_4(CO)_{12}]$ which were active for ethylene hydrogenation at 325–368 K in a flow reactor system. Reaction of the carbonyl cluster with phosphinated poly(styrene–divinylbenzene) resins resulted in the formation of mono-, tri-, and tetra-substituted clusters. Increasing the number of phosphine substitutions increased the catalyst activity, paralleling observed behavior of the unsupported clusters in solution.[83] The catalysts were stable after 100 h under reaction conditions. Carbon monoxide was a strong catalyst poison.[83]

A. J. Moffat of Phillips Petroleum[84,85] was among the first to study polymer-immobilized group 8 metal carbonyls. Cobalt carbonyls such as $Co_2(CO)_8$ and $HCo(CO)_4$ attached to poly(2-vinylpyridine) were found to be active for hydroformylation. The polymer–cobalt carbonyl system served as a catalyst reservoir for reversibly releasing sufficient cobalt carbonyl to override and/or destroy olefin feed poisons and to catalyze homogeneous hydroformylation at a predictable rate without an induction period. The soluble catalyst concentration was 100 to 300 ppm. Thirty to forty percent of the nitrogen atoms within the resin were available for metal carbonyl complexing.[84] Investigations of metal carbonyl recovery and recycle showed that the poly(2-vinylpyridine) could reversibly complex cobalt carbonyls.[85] In a H_2/CO atmosphere, $HCo(CO)_4$ and $Co_2(CO)_8$ competed for sites within the resin, $Co_2(CO)_8$ being absorbed slowly and to a limited extent while $HCo(CO)_4$ absorbed rapidly and to a greater extent. In a carbon monoxide atmosphere, $HCo(CO)_4$ is released rapidly and converted to $Co_2(CO)_8$ to be returned subsequently to the reaction zone with the olefin feed. Because absorption or release of cobalt carbonyls can be controlled by the presence or absence of hydrogen, a recycle system is feasible for carrying the active catalyst through the cycle without appreciable consumption.

Gray, Rembaum, and Gupta[86,87] have studied the photoactivated immobilization of $Co_2(CO)_8$ on poly(vinylpyridine) and showed that this system can act as a heterogeneous catalyst under specified conditions. When a mixture of the polymer and metal carbonyl is irradiated at 250 nm in solution, an active, air-sensitive hydroformylation catalyst containing immobilized mononuclear radicals is produced.[86] Irradiation of the carbonyl alone leads to formation of the inefficient hydroformylation catalyst $Co_4(CO)_{12}$ in solution.[86]

Pittman and co-workers reacted $Co_2(CO)_8$ with a phosphinated polystyrene having a tendency toward chelation.[63] The initial reaction product, which formed rapidly, was a polymeric analogue of $[Co(CO)_3(PPh_3)_2]^+[Co(CO)_4]^-$, **39** (eq 21). Upon being heated with dimethoxyethane at 343 K this readily converted to a neutral material, **40**, which was active in the hydroformylation of 1- and 2-pentenes.[63] When the immobilized catalysts were recovered by filtration followed by solvent washing and immediate recycle, there was little change in catalytic activity. If washing was not completed rapidly, the polymer oxidized with CO loss. These catalysts were found active at pressures (27×10^5 N/m^2) below those required for homogeneous $Co_2(CO)_8$ activity. They also were active for allylbenzene isomerization.[63] Similar catalyst systems based on $Co_2(CO)_8$ and phosphinated polymers have been shown to possess significant activity for olefin hydroformylation from 443[88] to 723 K[65a] and from 2×10^6[65a] to 3×10^7 N/m^2.[89] In most cases, the catalysts could be recycled[65a,89,90] repeatedly with insignificant metal leaching.



39

40

(21)

Novel polynuclear catalysts were prepared by Collman and co-workers[24a,91] from phosphinated polystyrene treated with $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. Air oxidation resulted in total carbon monoxide loss. Hydrogen reduction (in THF) yielded metal particles of presumed molecular size. The catalyst derived from $Rh_6(CO)_{16}$ catalyzed the hydrogenation of arenes at 298 K and 1×10^5 N/m^2 with activity and selectivity comparable to commercial rhodium on alumina. Incorporation of the metal in the polymer was shown to inhibit metal aggregation. Upon treatment of the $Rh_4(CO)_{12}$ complexed catalyst with carbon monoxide, over 50% of the rhodium was recovered as $Rh_4(CO)_{12}$. Similar treatment of the Rh_6 catalyst yielded small quantities of $Rh_4(CO)_{12}$ and much $Rh_6(CO)_{16}$. Negligible metal carbonyl was produced from the CO-treated commercial catalyst. Similar results were obtained by Iwatate et al.[24b]

Hagihara and co-workers[72] have studied an aminated resin–rhodium catalyst prepared by heating Amberlyst resins with $Rh_4(CO)_{12}$ in an autoclave under carbon monoxide. When used to hydrogenate α,β-unsaturated carbonyl and nitrile compounds, these catalysts exhibited excellent selectivity in that, with the exception of aldehydes, only the alkene double bond was hydrogenated. Furthermore, they were generally more active than their homogeneous analogues.

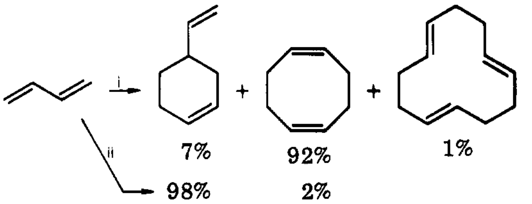
Gates and co-workers investigated $Rh_6(CO)_{16}$ immobilized on phosphinated cross-linked polystyrene as an olefin hydrogenation catalyst.[92,93] The active catalyst contained small rhodium clusters stabilized by the chelating action of the polymer with hydride, hydrocarbon, and polymer-attached phosphine ligands.[92] No carbonyl ligands were present on the active catalyst. Residual metal-bound carbon monoxide was a strong inhibitor. Trace oxygen in the reactant stream oxidized the phosphine groups, leading to rhodium agglomeration.[93] The catalyst retained its activity for up to 75 h on stream.

Ryan et al.[94] used immobilized $Rh_6(CO)_{16}$ on Amberlyst A-21 resin containing *N*,*N*-dimethylbenzylaniline moieties for nitrobenzene reduction and the water-gas shift reaction. The immobilized catalyst performed at lower reaction rates with greater air sensitivity than homogeneous counterparts.

Gates and co-workers[67,71,96] prepared polymer-immobilized analogues of $[Ir_4(CO)_{11}(PPh_3)]$ and $[Ir_4(CO)_{10}$-

$(PPh_3)_2]$ by carbonylating $[Ir(CO)_2(p\text{-toluidine})Cl]$ in the presence of zinc and either Ⓟ $-PPh_2$ or Ⓟ -DIOP.[67] Infrared spectra indicated that reaction with the former polymer resulted in the preparation of Ⓟ $-PPh_2Ir_4(CO)_{11}$. Reaction with Ⓟ -DIOP gives several species. When the phosphorus concentration is low, the DIOP groups act as bridging ligands to form Ⓟ $-DIOP(Ir_4(CO)_{11})_2$. When the concentration of the phosphine groups is increased, some DIOP groups bridge while others act as chelating ligands to produce Ⓟ $-DIOPIr_4(CO)_{10}$.[67] All immobilized iridium carbonyl catalysts were active for ethylene hydrogenation at 313 K and 1×10^5 N/m^2, with acceptable stability upon repeated use.[67,96] One catalyst, Ⓟ $-PPh_2Ir_4(CO)_{11}$, was stable over 5000 turnovers and at 353 K under helium. Upon heating to 393 K under helium there was decarbonylation and metal aggregation.[67] Cyclohexene was also hydrogenated.[96]

Pittman and co-workers studied the catalytic properties of $Ni(CO)_2(PPh_3)_2$ immobilized on a phosphinated polystyrene.[36,97-99] The catalysts were used alone for cyclooligomerization[97] and as part of a cyclooligomerization–hydrogenation bifunctional catalyst system.[36,98,99] The polymer-immobilized material catalyzed reactions 30% faster than the homogeneous analogue.[97] The activity, selectivity, and stability were affected by the nature of the reaction conditions employed (eq 22). In replicate runs (four recycles) the molar turnover with the polymer-immobilized catalyst was >2000 in benzene and 100 in THF. Leaching of Ni from the resin was inhibited with increasing resin cross-linking.[97] Incorporated in a bifunctional catalyst system, the polymer-immobilized $Ni(CO)_2(PPh_3)_2$ was active and stable.[36,98] It also was active for the oligomerization of ethyl propiolate.[63]



(22)

i, tri-*o*-tolyl phosphite, 388 K, C_6H_6
ii, 6.9×10^4 N/m^2 CO, 388 K, THF

Recently, interest has increased in the use of supported bimetallic clusters as potential catalysts which might combine more than one type of catalytic function in a single molecule. Hartwell and Garrou[100] immobilized $Rh_2Co_2(CO)_{12}$ on Dowex MWA-1 (cross-linked polystyrene with pendant benzyldimethylamine groups). When this catalyst was used for hydroformylating 1-hexene at 373 K and 5×10^6 N/m^2, selective alcohol formation was found (96.3%). When employed as a homogeneous catalyst, unattached $Rh_2Co_2(CO)_{12}$ favored aldehyde formation. Neither $Rh_4(CO)_{12}$ nor $Co_4(CO)_{12}$ immobilized on the support gave comparable selectivity.

Several bimetallic clusters active for olefin hydrogenation at atmospheric pressure have been prepared by Gates and co-workers.[101] $[RuPt_2(CO)_5(Ph_2P\text{-}$ Ⓟ $)_3]$ and $[Fe_2Pt(CO)_8(Ph_2P\text{-}$ Ⓟ $)_2]$ were active at 371 and 348 K, respectively. The catalytic activity and infrared spectrum of the fomer remained unchanged after 5 days (~4400 turnovers), indicating a stable catalyst. At higher temperatures (381 K), catalytic activity increases with decarbonylation and metal agglomeration.

III. Inorganic Supports

A. Introductory Discussion

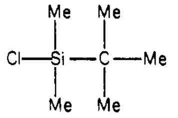
The rigid structure of inorganic supports is an important advantage relative to polymers. Polymeric supports possess enough flexibility to permit interaction of polymer-bound anchoring groups with the metal complex.[102] Polycoordination can either impart increased stability or act to deactivate the catalyst. Polymer flexibility can lead to deactivation through intermolecular condensation reactions as well. The rigid support structure of the inorganic-bound catalyst can prevent such deactivation.

Organic polymer supports typically have an upper thermal stability limit of approximately 433 K, a characteristic of the macroreticular resins. Conversely, the limit of inorganic-bound transition-metal carbonyls is a function of the thermal stability of the complex itself. A limit of more than 573 K is observed for some complexes.[13] In fact, the anchoring process per se may enhance the thermal stability of the complex relative to its homogeneous counterpart.[13]

Another advantage lies in greater control of diffusional factors. Polymer swelling under variable temperature and solution conditions makes practical control of diffusional variables difficult. Inorganic substrates can be preselected for stable diffusional characteristics at most reaction conditions.[13]

Most inorganic oxide supports possess active surface groups for immobilizing metal carbonyls in various ways.[103] Surface silanol groups and siloxane bridges can react directly with carbonyls to immobilize through direct surface bonding. They also can react to produce a support with attached anchoring ligands for catalyst immobilization.

Undesirable side reactions on the support prove to be a frequent disadvantage of oxide-immobilized catalysts. This might be circumvented by modifying the surface hydroxyl groups with a silylating agent to give a lipophilic organic surface layer. This technique, common to gas chromatography, would probably not alter catalytic activity significantly and might increase the rate of desorption of products from the catalyst surface. One particularly effective silylation reagent, *tert*-butyldimethylchlorosilane (41), is 10000 times more stable to hydrolysis than other silylation reagents.[104]



$$Cl{-}\underset{Me}{\overset{Me}{Si}}{-}\underset{Me}{\overset{Me}{C}}{-}Me$$

41

Subsequent sections of this review will discuss metal carbonyls surface bonded to inorganic supports, reacted with functionalized supports, coated onto supports, synthesized within supports, and copolymerized with inorganic monomers. Graphite supports are included here because of their rigid structure. A summary of selected studies of transition metal carbonyls immo-

Table II. Selected Studies of Inorganic-Immobilized Transition Metal Carbonyls and Related Materials

Initial Carbonyl	Support	Proposed Structure of Supported Complex[a]	Reaction Studied	Comments[b]	Ref.
VANADIUM					
$V(CO)_6$	γ-Al_2O_3			hydrocarbon evolution during decomposition	146
CHROMIUM					
$Cr(CO)_6$	γ-Al_2O_3 SiO_2			infrared data; production of supported metal	111
$Cr(CO)_6$	γ-Al_2O_3			temperature programmed decomposition	112
$Cr(CO)_6$	γ-Al_2O_3			infrared data; interaction with NO; production of Cr^{2+}, Cr^{3+}	113
$Cr(CO)_6$	SiO_2		propylene hydrogenation	temperature programmed decomposition; decomposition kinetics	114
$Cr(CO)_6$	SiO_2			electron paramagnetic resonance spectroscopy; production of Cr^{5+}	115
$Cr(CO)_6$	Al_2O_3 SiO_2-Al_2O_3		ethylene polymerization		116,117
$Cr(CO)_6$	γ-Al_2O_3			hydrocarbon evolution during decomposition	146
$Cr(CO)_6$	carbonyl copolymerized with Ph_2PO_2H or $PhSO_2H$				235,236
$Cr(CO)_6$	carbonyl copolymerized with Ph_2PO_2H, Ph_2AsO_2H or PSO_2H			thermal decomposition	239-241
$Cr(CO)_6$	Al_2O_3			production of supported Cr metal; interaction with NO	260
MOLYBDENUM					
$Mo(CO)_6$	γ-Al_2O_3	$Mo(CO)_5$ads, $Mo(CO)_4$ads, $Mo(CO)_3$ads, $(\sigma\text{-}O^-)_2Mo$, $(\sigma\text{-}O^-)_2MoO_2$, $Mo(CO)_2O_2$ads		thermal decomposition; interaction with O_2	28
$Mo(CO)_6$	SiO_2		propene metathesis	infrared data; interaction with NO and CO	108
$Mo(CO)_6$	γ-Al_2O_3 SiO_2			electron paramagnetic resonance spectroscopy; interaction with O_2; production of Mo^{5+}	109
$Mo(CO)_6$	γ-Al_2O_3 SiO_2 SiO_2-Al_2O_3		ethylene, propylene, butene, pentene metathesis; ethylene polymerization; ethylene cyclization		110
$Mo(CO)_6$	γ-Al_2O_3 SiO_2	$Mo(CO)_5$ads; $Mo(CO)_x$ads		infrared spectra	111
$Mo(CO)_6$	γ-Al_2O_3			temperature programmed decomposition	112
$Mo(CO)_6$	γ-Al_2O_3			infrared data; interaction with NO; production of Mo^{2+}	113

Table II. cont.

Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
$Mo(CO)_6$	SiO_2		propene metathesis; propene hydrogenation	temperature programmed decomposition	114
$Mo(CO)_6$	Al_2O_3		acetylene polymerization; propylene, butene, pentene, hexene metathesis; ethylene cyclization; ethylene polymerization		116,117
$Mo(CO)_6$	γ-Al_2O_3 SiO_2 MgO		propene metathesis	infrared spectra; thermal decomposition; interaction with O_2 and CO	118
$Mo(CO)_6$	γ-Al_2O_3 SiO_2 SiO_2-Al_2O_3 MgO		propene metathesis		119
$Mo(CO)_6$	γ-Al_2O_3		propene metathesis	infrared spectra	120
$Mo(CO)_6$	γ-Al_2O_3			x-ray photoelectron spectra; interaction with air	121
$Mo(CO)_6$	γ-Al_2O_3	$Mo(CO)_5ads$; $Mo(CO)_4ads$; $Mo(CO)_3ads$			122
$Mo(CO)_6$	γ-Al_2O_3	$Mo(CO)_3ads$; $Mo(CO)_2O_2ads$	propene metathesis	thermal decomposition; interaction with O_2	123,124
$Mo(CO)_6$	Vycor			Raman spectra	125
$Mo(CO)_6$	γ- + δ-Al_2O_3	$Mo(CO)_xads$; Mo^0ads; $Mo^{2+}ads$; $Mo^{4+}O$; $Mo(CO)ads$	H_2 reduction of CO	preparation of Mo^0 and Mo^{2+}	126
$Mo(CO)_6$	HY zeolite			thermal decomposition; x-ray crystal structure; infrared spectra; production of Mo^{x+}	127,128
$Mo(CO)_6$	HY zeolite			electron spin resonance spectra; interaction with O_2; production of Mo^{1+}, Mo^{5+}	129
$Mo(CO)_6$	Al_2O_3		propylene metathesis		130
$Mo(CO)_6$	γ-Al_2O_3		propylene metathesis	effect of light, air, N_2	131
$Mo(CO)_6$	γ-Al_2O_3		propylene metathesis	interaction with halo-alkenes	132
$Mo(CO)_6$	γ-Al_2O_3 SiO_2	$Mo(CO)_5ads$; $Mo(CO)_4ads$; $Mo(CO)_2O_2ads$; $Mo(CO)_3ads$; $(\sigma\text{-}O^-)_2Mo$	propylene metathesis	production of Mo^0	133
$Mo(CO)_6$	γ-Al_2O_3	$Mo(CO)_3ads$	propylene metathesis; ethylene polymerization	infrared spectra; interaction with NO, CO, propylene	134
$Mo(CO)_6$	SiO_2 ZrO_2		propylene metathesis		135,137
$Mo(CO)_6$	Al_2O_3		octene, cyclopentene metathesis		138,139
$Mo(CO)_6$	γ-Al_2O_3		butene metathesis		140
$Mo(CO)_6$	Al_2O_3	$Mo(CO)_xads$		infrared spectra; interaction with propylene	141
$Mo(CO)_6$	γ-Al_2O_3		pentene, isooctene metathesis		142
$Mo(CO)_6$	γ-Al_2O_3	$(\sigma\text{-}O^-)_nMo^{n+}ads$	propylene hydrogenation	temperature programmed decomposition	143

Table II. cont.

Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
$Mo(CO)_6$	SiO_2			thiol disulphurization reagent	144a
$Mo(CO)_6$	γ-Al_2O_3			hydrocarbon production during decomposition	145,146
$Mo(CO)_6$	carbonyl copolymerized with Ph_2PO_2H				236
$Mo(CO)_6$	carbonyl copolymerized with Ph_2PO_2H, Ph_2AsO_2H, $PhSO_2H$			thermal decomposition	241
$Mo(CO)_6$	Al_2O_3		olefin metathesis		261
$Mo(CO)_6$	SiO_2		propylamine dehydrodimerization	Ph_3Bi cocatalyst also was impregnated on support	262
$Mo(CO)_6$	chloromethylated SiO_2		nonyne metathesis	phenol cocatalyst employed	263,264
$Mo(CO)_6$	SiO_2		olefin metathesis	effect of organic ligands	265
TUNGSTEN					
$W(CO)_6$	Al_2O_3 SiO_2 SiO_2-Al_2O_3		propylene, butene, pentene, hexene metathesis		110
$W(CO)_6$	γ-Al_2O_3			infrared data; production of supported W	111
$W(CO)_6$	γ-Al_2O_3			temperature programmed decomposition	112
$W(CO)_6$	γ-Al_2O_3			infrared data; interaction with NO	113
$W(CO)_6$	SiO_2		propylene metathesis; propylene hydrogenation	temperature programmed decomposition	114
$W(CO)_6$	SiO_2			electron paramagnetic resonance spectra	115
$W(CO)_6$	Al_2O_3		ethylene polymerization; butene, pentene metathesis		116,117
$W(CO)_6$	Al_2O_3			hydrocarbon production during decomposition	126
$W(CO)_6$	Al_2O_3		pentene metathesis		130
$W(CO)_6$	SiO_2 ZrO_2		propylene metathesis		135-137
$W(CO)_6$	γ-Al_2O_3			hydrocarbon production during decomposition	146
$W(CO)_6$ $W(CO)_5PPh_3$ $W(CO)_5PBu_3$	η-Al_2O_3		pentene metathesis	infrared spectra	147,267
$W(CO)_6$	γ-Al_2O_3 η-Al_2O_3	$W(CO)_3ads$ $(\sigma\text{-}O^-)_nW^{n+}ads$		temperature programmed decomposition; effect of support pretreatment	148
$W(CO)_6$	carbonyl copolymerized with Ph_2PO_2H, Ph_2AsO_2H, $PhSO_2H$			thermal decomposition	237-241
$W(CO)_6$	SiO_2		propylene metathesis	effect of organic ligands	265
$W(CO)_6$	Al_2O_3 SiO_2		propylene metathesis		266
MANGANESE					
$Mn_2(CO)_{10}$	γ-Al_2O_3			hydrocarbon formation during decomposition	146
$Mn_2(CO)_{10}$	carbonyl copolymerized with Ph_2PO_2H				236

Table II. cont.

Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
$Mn_2(CO)_{10}$	carbonyl copolymerized with Ph_2PO_2H, Ph_2AsO_2H, $PhSO_2H$			thermal decomposition	237,238, 240,241
$Mn_2(CO)_{10}$	chlorinated Al_2O_3 chlorinated SiO_2		ethylene polymerization	$TiCl_4$ cocatalyst also impregnated on support	268
RHENIUM					
$Re_2(CO)_{10}$	HY zeolite	$Re_2(CO)_7$ads		x-ray crystal structure; infrared spectra; thermal decomposition	127,128
$Re_2(CO)_{10}$	γ-Al_2O_3			hydrocarbon formation during decomposition	146
$Re_2(CO)_{10}$	controlled pore glass		aldehyde hydrogenation	pyrolysis	149,150
$Re_2(CO)_{10}$	Al_2O_3 (impregnated with Pt)		reforming	formation of bimetallic catalyst	151
IRON					
$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	γ-Al_2O_3			formation of hydrocarbons during decomposition	145,146
$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	γ-Al_2O_3			temperature programmed decomposition; CO adsorption; hydrocarbon evolution during decomposition	152-154
$Fe(CO)_5$ $Fe_3(CO)_{12}$	η-Al_2O_3 MgO	$[HFe_3(CO)_{11}]^-M^+$ $M = Al(O-)_x, Mg(O-)_x$		infrared data	155
$Fe(CO)_5$ $Fe_3(CO)_{12}$	γ-Al_2O_3 La_2O_3 MgO SiO_2		H_2 reduction of CO		156
$K_2Fe(CO)_4$	η-Al_2O_3		H_2 reduction of CO	production of promoted catalysts; infrared data; x-ray diffraction; CO chemisorption	157,158
$Fe(CO)_5$ $Fe_2(CO)_9$ $Fe_3(CO)_{12}$	NaY zeolite	$\textcircled{Z}-H_2Fe_3(CO)_{11}$; $\textcircled{Z}-(O^-)_2Fe^{2+}$; $\textcircled{Z}-OH\ldots Fe(CO)_4$	H_2 reduction of CO	infrared data; interaction with NO	159,160
$Fe(CO)_5$	HY zeolite			photochemical and thermal decomposition; production of highly dispersed, pyrophoric iron; transmission	161
$Fe(CO)_5$	graphite			Mössbauer spectra; transmission electron microscopy; production of metallic Fe	162
$Fe_2(CO)_9$	C_5H_5 modified SiO_2	$\textcircled{Si}-OSi(Me)_2-Cp-Fe(CO)_2H$ $[\textcircled{Si}-OSi(Me)_2-Cp]_2Fe_2(CO)_4$ $\textcircled{Si}-OSi(Me)_2-CpFe_2(CO)_4Cp-Si(Me)_2OEt$		infrared data	197
$Fe(CO)_5$	carbonyl copolymerized with Ph_2PO_2H				235
$Fe(CO)_5$	carbonyl copolymerized with Ph_2PO_2H, Ph_2AsO_2H, $PhSO_2H$			thermal decomposition	238-241
$Fe(CO)_5$	Al_2O_3			interaction with NO; production of Fe metal	260
$Fe(CO)_5$	carbon ceramics steel				269
$Fe(CO)_5$	SiO_2 (impregnated with Pt)			preparation of bimetallic catalyst	270
$Fe(CO)_5$	porous glass beads			thermal decomposition; production of Fe metal and metal oxides	271

Table II. cont.

Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
RUTHENIUM					
$Ru_3(CO)_{12}$	HY zeolite	$Ru_3(CO)_9$ads		x-ray crystal structure; infrared spectra; thermal decomposition	127,128
$Ru_3(CO)_{12}$	γ-Al_2O_3			hydrocarbon production during decomposition	146
$Ru_3(CO)_{12}$	γ-Al_2O_3		H_2 reduction of CO		156
$K_2Ru_3(CO)_{12}$	η-Al_2O_3		H_2 reduction of CO	production of promoted catalyst; infrared data; x-ray diffraction; CO chemisorption	157,158
$Ru_3(CO)_{12}$	SiO_2	$Ru_3(CO)_x$ads $\textcircled{Si}_x\text{-}H_yRu_3(CO)_5$	butene hydrogenation	infrared data	163
$Ru_3(CO)_{12}$	η-Al_2O_3 SiO_2 MgO			hydrocarbon formation during decomposition	164
$Ru_3(CO)_{12}$	SiO_2		ethane hydrogenolysis hexane cyclodehydrogenation	x-ray line broadening	165
$Ru_3(CO)_{12}$	MgO			H_2,CO chemisorption	166
$Ru_3(CO)_{12}$	Al_2O_3 SiO_2	$Ru_3(CO)_9$ads		thermal decomposition; production of Ru metal	177
$Ru_3(CO)_{12}$	γ-Al_2O_3 SiO_2				181
OSMIUM					
$H_2Os_3(CO)_{10}$	phosphinated SiO_2	$(\textcircled{Si}\text{-}OSi\text{-}PPh_2)[(H_2Os_3(CO)_9)]$	butene isomerization	infrared data	101
$Os_3(CO)_{12}$	γ-Al_2O_3			hydrocarbon formation during decomposition	146
$Os_3(CO)_{12}$	SiO_2		H_2 reduction of CO		156
$Os_3(CO)_{12}$ $Os_6(CO)_{18}$	η-Al_2O_3			hydrocarbon formation during decomposition	164
$Os_3(CO)_{12}$ $Os_6(CO)_{18}$	Al_2O_3 SiO_2			infrared data; thermal decomposition	177
$Os_3(CO)_{12}$ $H_2Os_3(CO)_{10}$	phosphinated SiO_2	$(\textcircled{Si}\text{-}OSiC_2)[(HOs_3(CO)_9)]$ $(\textcircled{Si}\text{-}OSiC_2H_4PPh_2)[(Os_3(CO)_{11})]$ $(\textcircled{Si}\text{-}OSiC_2H_4PPh_2)[(H_2Os_3(CO)_{10}]$ $(\textcircled{Si}\text{-}OSiC_2H_4PPh_2)[(H_2Os_3(CO)_9)]$		infrared spectra	211
COBALT					
$Co_2(CO)_8$ $Co_4(CO)_{12}$	γ-Al_2O_3			hydrocarbon formation during decomposition	146
$Co_4(CO)_{12}$	ZnO		ethylene, propylene hydroformylation		167,168
$Co_4(CO)_{12}$	γ-Al_2O_3 SiO_2				186
$Co_2(CO)_8$	C_5H_5 modified SiO_2	$\textcircled{Si}\text{-}O\text{-}Si\text{-}Cp\text{-}Co(CO)_2$	olefin hydroformylation	infrared data	197
$Co_2(CO)_8$	phosphinated SiO_2	$[(\textcircled{Si}\text{-}O\text{-}SiC_2H_4PR_2)_2Co(CO)_3]^+[Co(CO)_4]^-$ $[(\textcircled{Si}\text{-}O\text{-}SiC_2H_4PR_2)_2Co(CO)_3]^+$	cyclododecatriene hydrogenation	infrared spectra	212
$Co_2(CO)_8$	carbonyl copolymerized with Ph_2PO_2H				236

Table II. cont.

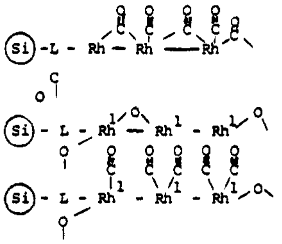
Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
RHODIUM					
$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	γ-Al_2O_3			hydrocarbon formation during decomposition	146
$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	γ-Al_2O_3			hydrocarbon formation during decomposition	156
$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	η-Al_2O_3 SiO_2 MgO			hydrocarbon formation during decomposition	164
$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$ $[Rh_7(CO)_{16}]^{3-}$ $[Rh_{13}(CO)_{23}H_{2-3}]^{2-}$	ZnO MgO TiO_2 La_2O_3 SiO_2 Al_2O_3		ethylene, propylene hydroformylation	temperature programmed decomposition	167,168
$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	γ-Al_2O_3 SiO_2	$Rh_6(CO)_{16-n}(O_2)_m$ads		infrared spectra; interaction with O_2	169
$Rh_6(CO)_{16}$	copper foil SiO_2			ultraviolet photoelectron spectra; infrared spectra; production of Rh metal	170
$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$ $[Rh_7(CO)_{16}]^{3-}$ $[Rh_{13}(CO)_{23}H_{2-3}]^{2-}$	ZnO MgO BeO CaO SiO_2 γ-Al_2O_3 TiO_2 ZrO_2 ThO_2 CeO_2 La_2O_3 activated carbon		H_2 reduction of CO		171-174
$Rh_4(CO)_{12}$ $Rh_6(CO)_{16}$	η-Al_2O_3 γ-Al_2O_3 SiO_2 SiO_2-Al_2O_3 MgO	$Rh^1(CO)_2$ads $Rh^1(CO)_2$ads $Rh^1(CO)_2$ads		infrared spectra; thermal decomposition; interaction with H_2,O_2,H_2O,CO; production of Rh metal	175-178
$Rh_6(CO)_{16}$	Al_2O_3 NaY zeolite HY zeolite			infrared spectra; thermal decomposition; production of Rh metal; interaction with O_2	179
$Rh_6(CO)_{16}$	γ-Al_2O_3 SiO_2			infrared data; electron microscopy; magnetic susceptibility	181
$Rh_6(CO)_{16}$	aminated and phosphinated SiO_2 MgO	(Si)-$L_nRh(CO)_2$ (Si)-$L_mRh(CO)$ (Si)-L_xRhHy L = $(CH_2)_3NH(CH_2)_2NH_2$, $(CH_2)_3NHC_6H_{11}$, $(CH_2)_3PPh_2$	ethylene, propylene, butehydrogenation	infrared spectra; decarbonylation; interaction with H_2; transmission electron microscopy	213-217
$Rh_6(CO)_{16}$	phosphinated SiO_2		cyclohexene, benzene hydrogenation	infrared spectra; interaction with O_2,CO	218-219
——	carbonyl cluster synthesized within NaY zeolite		hexene hydroformylation	infrared spectra	231
——	carbonyl synthesized within NaY zeolite	Ⓩ-Rh^{III}-CO Ⓩ-$Rh^{I}(CO)_2$		infrared spectra; ESCA; interaction with CO	232
——	carbonyl synthesized within NaX zeolite	Ⓩ-$Rh(CO)_x$	methanol carbonylation	infrared spectra; ESCA; interaction with CO	233,234

Table II. cont.

Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
IRIDIUM					
$Ir_4(CO)_{12}$	γ-Al_2O_3			hydrocarbon formation during decomposition	146
$Ir_4(CO)_{12}$	γ-Al_2O_3			hydrocarbon formation during decomposition	156
$KIr(CO)_4$	η-Al_2O_3		H_2 reduction of CO	infrared data; x-ray diffraction; CO adsorption	157,158
$Ir_4(CO)_{12}$	η-Al_2O_3			hydrocarbon formation during decomposition	164
$Ir_4(CO)_{12}$	ZnO		H_2 reduction of CO		171
$Ir_4(CO)_{12}$	γ-Al_2O_3 SiO_2			infrared spectra; decarbonylation; interaction with H_2, CO; electron microscopy; magnetic susceptibility	180-182
$Ir_4(CO)_{12}$	γ-Al_2O_3 SiO_2		ethane, butane, neopentane, neohexane, hydrogenolysis	electron microscopy; interaction with H_2	183
NICKEL					
$Ni(CO)_4$	γ-Al_2O_3			hydrocarbon formation during decomposition	146
$Ni(CO)_4$	Al_2O_3			infrared spectra; interaction with O_2, CO; production of NiO	184
$Ni(CO)_4$	Al_2O_3 fibers γ-Al_2O_3 NaY zeolite HY zeolite			production of Ni crystallites; CNMR	185
$Ni(CO)_4$	γ-Al_2O_3			effect of support pretreatment, thermal decomposition; production of Ni^0, Ni^{2+}	186
$Ni(CO)_4$	MX zeolite M = Li, K, Cs, Ca, Mg, Ba, Na	Ⓩ-Ni(CO)	benzene hydrogenation	effect of exchange cation; thermal decomposition; production of Ni	187-190
$Ni(CO)_4$	γ-Al_2O_3	Ni(π-allyl)ads	olefin digomerization	infrared data; catalyst formed on surface by interaction of $Ni(CO)_4$ and C_3H_5Cl or allene	191,192
$Ni(CO)_4$	phosphinated SiO_2	$\textcircled{Si}-O\overset{\vert}{\underset{\vert}{Si}}(CH_2)_2PPh_2Ni(CO)_3$		infrared data; production of Ni	220
$Ni(CO)_4$	carbonyl copolymerized with Ph_2PO_2H				236
$Ni(CO)_4$	Al_2O_3			infrared spectra; production of Ni; interaction with CO, NO	260
$Ni(CO)_4$	various metals			production of Ni coatings	272
PLATINUM					
$Pt_3(CO)_3(PPh_3)_4$ $[Pt_6(CO)_{12}]^{2-}$ $[Pt_9(CO)_{18}]^{2-}$ $[Pt_{12}(CO)_{24}]^{2-}$ $[Pt_{15}(CO)_{30}]^{2-}$	γ-Al_2O_3 SiO_2		hexane dehydrocyclization	production of supported Pt	27
$[Pt_6(CO)_{12}]^{2-}$ $[Pt_9(CO)_{18}]^{2-}$ $[Pt_{12}(CO)_{24}]^{2-}$ $[Pt_{15}(CO)_{30}]^{2-}$	γ-Al_2O_3 SiO_2 ZnO MgO		H_2 reduction of CO	production of supported Pt	171,193

Table II. cont.

Initial Carbonyl	Support	Proposed Structure of Supported Complex	Reaction Studied	Comments	Ref.
BIMETALLIC CLUSTERS					
$Co_2Rh_2(CO)_{12}$	SiO_2		hexane, methylcyclopentane hydrogenolysis		25,194
$HAuOs_3(CO)_{11}$	phosphinated SiO_2	$[\text{(Si)}-O\overset{\vert}{\underset{\vert}{Si}}(CH_2)_3PPh_2[HAuOs_3(CO)_{10}]$	butene isomerization	infrared data	101
$HFeCo_3(CO)_{12}$ $Co_2Rh_2(CO)_{12}$	Al_2O_3			Mössbauer spectra; ESCA; x-ray emission spectra; reduction in H_2	165
$Co_2Rh_2(CO)_{12}$ $Co_3Rh(CO)_{12}$	ZnO		ethylene, propylene hydroformylation	thermal decomposition; production of mixed-metal crystallites	167,168
$Co_2Rh_2(CO)_{12}$ $Co_3Rh(CO)_{12}$	γ-Al_2O_3 SiO_2			infrared data, electron microscopy, magnetic susceptibility; interaction with H_2,CO	181

Key to Table II

Cp - cyclopentadienyl
Et - ethyl
Me - methyl
Ph - phenyl
R - an organic group
(Si) - silica
(Z) - zeolite

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[a] Structures are given only in those instances where supporting evidence is available.

[b] Only studies other than simple preparations are indicated.

bilized on inorganic supports is given in Table II.

B. Surface Bonding of Metal Carbonyls with Inorganic Oxides

1. Preparation

Surface bonding through impregnation is one of the elementary techniques for immobilizing transition-metal carbonyls on inorganic supports. Impregnating methods have been reviewed;[105-107] only the general procedure will be described here. It commonly involves the following steps: (1) evacuation of the support to expedite total penetration into the pores, (2) contacting the support with impregnating solution, (3) removing excess solution, (4) drying under an inert atmosphere, and (5) calcining and/or activating the catalyst. Critical variables can be contact time, impregnating temperature, and solution pH.

Another preparation method utilizes the volatile nature of many carbonyls. Thus, the metal carbonyl may be sublimed onto the support at a given temperature in a flow of inert gas.[28]

It is also possible to impregnate an inorganic support with metal carbonyl through careful grinding of the carbonyl with the support in an inert atmosphere. This method can give satisfactory results with well-mixed components. However, the heat generated during grinding can lead to some metal carbonyl decomposition.[23] With grinding in air,[108,109] oxidation of the supported complex may occur.[28]

After initial physical adsorption, the carbonyl can react with surface sites, e.g., for $Mo(CO)_6$:[28]

$$Mo(CO)_6 + \sigma\text{-}O^- \rightarrow Mo(CO)_5(\sigma\text{-}O^-) \qquad (23)$$

The supported carbonyl can be heated in a vacuum, inert gas, or oxygen to produce a subcarbonyl or oxidized species on the support surface. Some subcarbonyl species formed during decarbonylation can react further with surface hydroxyls to evolve hydrogen with metal oxidation,[28] e.g.

$$Mo(CO)_3\text{ads} + 2\sigma\text{-}OH \rightarrow (\sigma\text{-}O^-)_2Mo^{2+} + H_2 + 3CO \qquad (24)$$

In the resulting catalyst, the support itself is bonded to the transition metal with Si–O–metal or Al–O–metal interactions often resulting.[2] This leads to some alteration of the molecular character of the carbonyl complex.[110] Surface bonding has been a favored method of deriving heterogeneous catalysts from metal carbonyls because it seems effective for obtaining complete metal atom dispersion.

2. Surface-Bonded Group 6 Carbonyl Catalysts

Early infrared studies by Howe[111] indicated that $Cr(CO)_6$ supported on alumina would undergo complete decarbonylation in vacuo above 283 K to form metal particles on the support surface. Treatment with CO (6.6×10^3 N/m^2) at 318 K partially restored the $Cr(CO)_6$ bands. Subsequent work by Brenner and Hucul[112] using temperature-programmed decomposition demonstrated that under flowing helium, temperatures in excess of 573 K were required for complete decarbonylation. A lower temperature decarbonylation was followed at higher temperatures by a second decarbonylation accompanied by hydrogen evolution, suggesting that the resulting catalyst may not consist of supported zerovalent metal.[112]

Kazusaka and Howe[113] have recently shown that the adsorption of NO on $Cr(CO)_6/Al_2O_3$ results in the formation of species identical with those formed on conventional chromia–alumina catalysts. Infrared and EPR experiments indicate that with catalysts pretreated at 298 K, NO displaces CO and oxidizes the chromium to produce Cr^{2+} and Cr^{3+} species. When the catalysts are pretreated at higher temperatures, the chromium is oxidized by surface hydroxyl groups[112] and the NO adsorbs directly onto oxidized sites to form Cr^{2+} and Cr^{3+} nitrosyl species.

Silica-supported $Cr(CO)_6$ gives somewhat different results. When subjected to temperature-programmed decomposition in flowing helium, a single decarbonylation step over a narrow temperature range is observed.[114] This requires the loss of all six carbonyl ligands in rapid succession. As with an alumina support, hydrogen evolution and metal oxidation accompany the decarbonylation. After treatment at 873 K, the oxidation number of the supported chromium, based on gas evolution, was reported to be 4. Electron paramagnetic resonance studies of $Cr(CO)_6/SiO_2$ catalysts by Howe[115] indicate that treatment in vacuo results in the production of low oxidation states of chromium, most probably Cr^{2+}. Treatment of catalysts activated at 473 K with oxygen at 293 K yields Cr^{5+} ions in square-pyramidal and tetrahedral coordination.

Little study has been directed to the catalytic properties of materials derived from immobilized $Cr(CO)_6$. Banks[116,117] used $Cr(CO)_6$ on alumina or silica–alumina to polymerize ethylene at 394–400 K. Brenner, Hucul, and Hardwick[114] have noted that $Cr(CO)_6/Al_2O_3$ can be used to hydrogenate propylene, with maximum activity being observed at 468 K.

In early studies of support effects, Howe, Davidson, and Whan[118] found that activation of immobilized $Mo(CO)_6$ catalysts involved carbonyl decomposition, the extent of which was a function of the basicity of support hydroxyl groups. Decomposition occurred most readily on silicas which did not stabilize subcarbonyl species. Kinetic and infrared studies indicated that stabilized subcarbonyl species on alumina and magnesia did not catalyze propene metathesis. It was postulated that the $Mo(CO)_6$ acted as a source of molybdenum(0) which could subsequently oxidize to form active speices. This led to the proposing of other organomolybdenum or organotungsten complexes as active metathesis catalysts, a proposition validated for organomolybdenum complexes.[19]

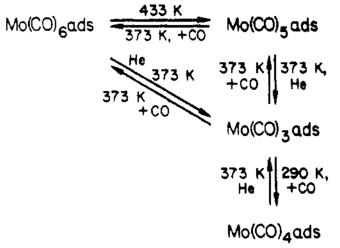
Smith, Howe, and Whan[119] later investigated silica, silica–alumina, alumina, and magnesia supports. In addition to the support per se, support outgassing and activation temperatures were found to influence catalytic activity. All catalysts showed activity for metathesis when fully dehydroxylated supports were used; there were marked differences when the degree of hydroxylation varied. This was explained by an initial reaction of the hexacarbonyl with a surface hydroxyl group to replace one carbonyl ligand, formation of a pentacarbonyl species, and further decomposition leading to maximum metal dispersion. Consistent with this is the fact that silica with its abundant surface hydroxyl groups is the most active support at room temperature.

The surface chemistry of $Mo(CO)_6$ surface bonded catalysts has been pursued with vigor. In 1969, Davie, Whan, and Kemball[120] presented preliminary results from an infrared spectroscopic investigation of the nature of $Mo(CO)_6$ surface bonded to alumina. They noted treatment for 1 h under vacuum at 373 K was required for propene metathesis activity. The first observation of oxygen poisoning of immobilized metal carbonyls was also reported. Infrared spectra of unactivated catalysts displayed a single sharp absorbance at 1985 cm^{-1} corresponding to unchanged metal carbonyl on the alumina. In contrast, in the activated catalyst this sharp peak was replaced by broad peaks at 1880 and 2020 cm^{-1}. The oxygen-treated catalyst showed no absorption in the CO region. For characterization of the catalyst, use was made of complexing agents such as cycloheptatriene. Although results were inconclusive, it appeared that $Mo(CO)_6$ lost two or more likely three carbonyl groups during activation.

Added evidence of carbonyl loss during activation came from Whan, Barber, and Swift[121] in an X-ray photoelectron study of the $Mo(CO)_6/Al_2O_3$ catalyst. Infrared spectra at 173 K showed the carbonyl to be physically adsorbed on the alumina surface. When warmed to room temperature, some $Mo(CO)_6$ sublimed while several different Mo species were retained on the surface. Heating to 373 K resulted in further loss of carbonyl groups. Exposing this catalyst to oxygen resulted in a significant overall shift to higher bonding energies, reflecting further molybdenum oxidation.

Howe and Leith[109] employed electron paramagnetic resonance spectroscopy to characterize the oxidation states of molybdenum hexacarbonyl/alumina catalysts. Results confirmed suggestions[118] that activation of supported molybdenum hexacarbonyl involved metal carbonyl decomposition with some metal oxidation. Initial species formed during activation were interpreted to be molybdenum(V) in a square-pyramidal configuration. Though no correlation existed between catalytic activity and the concentration of this species, it was postulated to be a precursor of either a tetrahedral molybdenum(V) or a molybdenum(IV) reactive intermediate. Some of the conclusions of this early work[108,109,111,118-121] should be viewed with caution since the hydrogen evolution reaction and the deleterious effects of oxygen had not yet been fully recognized.[28]

Brenner and Burwell[122] proposed the scheme shown in eq 25 on the basis of initial results on the thermal decomposition of $Mo(CO)_6$ on γ-alumina. Further study involved a CO mass balance with temperature variation.[123,124] They isolated $Mo(CO)_3$ads which was a moderately active propene metathesis catalyst at 326 K. Treatment of the catalyst at higher temperatures under flowing helium produced additional carbon monoxide loss and a large activity increase. In addition, this species was found to absorb one molecule of oxygen



(25)

at 298 K, ejecting a molecule of carbon monoxide to form adsorbed $\mathrm{Mo(CO)_2O_2}$, a species 15 times more active for metathesis than adsorbed $\mathrm{Mo(CO)_3}$.

Substantiation of the presence of oxidized species[28,122] comes from temperature-programmed decomposition (TPDE) studies of group 6 carbonyls on γ-alumina[112] and silica[114] by Brenner and co-workers. At lower temperatures, decarbonylation occurred without accompanying hydrogen evolution. At these temperatures, a zerovalent subcarbonyl species is presumably bonded to the alumina. At higher temperatures, decarbonylation is accompanied by hydrogen evolution. It was proposed that hydrogen originates as $\mathrm{H^+}$ in the surface hydroxyl groups of the alumina with reduction to hydrogen gas accompanied by an equivalent amount of transition-metal oxidation. Studies with silica demonstrated that it does not stabilize the zerovalent subcarbonyl species adequately for isolation. There are indications that they are in fact formed, some reversibly.

An extensive infrared study of all group 6 metals on silica and alumina was performed by Howe.[111] Results indicated that $\mathrm{Mo(CO)_6}$ vapor is initially physically adsorbed onto the surface. This unstable species immediately decomposes in vacuo to $\mathrm{Mo(CO)_5}$ads which can undergo further decomposition. These steps are reversible (eq 26). Subsequent evacuation at 318 K

$$\mathrm{Mo(CO)_6ads} \xrightleftharpoons[+\mathrm{CO}]{263\ \mathrm{K}} \mathrm{Mo(CO)_5ads} \xrightleftharpoons[+\mathrm{CO}]{283\ \mathrm{K}} \mathrm{Mo(CO)}_x\mathrm{ads} \tag{26}$$

removes some $\mathrm{Mo(CO)_6}$ by sublimation. The spectra after evacuation at 318 K are consistent with the presence of more than one surface species. In similar experiments with $\mathrm{Mo(CO)_6}$ on fully hydroxylated $\mathrm{SiO_2}$ and $\mathrm{W(CO)_6}$ and $\mathrm{Cr(CO)_6}$ on $\mathrm{Al_2O_3}$ and $\mathrm{SiO_2}$ no stable subcarbonyl species were observed. Although it was proposed that the decarbonylation of the group 6 carbonyls was complete and reversible[111] (eq 27), subsequent research[114] has given conflicting results.

$$\mathrm{M(CO)_6ads} \xrightleftharpoons[+\mathrm{CO}]{983\ \mathrm{K}} \mathrm{(M)ads} \tag{27}$$

The results for silica were confirmed by Adams, Gardner, and Parkyns[125] with a Raman spectroscopic study of $\mathrm{Mo(CO)_6}$ surface bonded to a silica surface (porous Vycor glass). Increasing surface loading (up to four layers) resulted only in an increase in absorption intensity without evidence of subcarbonyl formation.

Brenner and Burwell[28] described an extensive study of the $\mathrm{Mo(CO)_6/Al_2O_3}$ catalyst system from 256 to 1273 K. Activation in flowing helium at 373 K of $\mathrm{Mo(CO)_6}$ on partially hydroxylated alumina resulted in the formation of $\mathrm{Mo(CO)_3}$ads, 100% dispersed. Above 473 K, the remaining CO's of $\mathrm{Mo(CO)_3}$ads are liberated; detectable amounts of $\mathrm{Mo(CO)_2}$ads and Mo(CO)ads do not accumulate. It was believed likely that a species labeled as "$(\sigma\text{-O}^-)_2\mathrm{Mo}$" was dominant after activation near 543 K. After heating to 773 K, the average oxidation number of the decarbonylated Mo was about 5.6. The original zerovalent Mo oxidized through reaction with surface hydroxyl groups of the alumina. Mo(VI) also results from heating $\mathrm{Mo(CO)_2O_2}$ads and "$\mathrm{Mo(CO)(O_2)_2}$"ads to 773 K. Use of fully dehydroxylated alumina led to formation of molybdenum mostly in the zerovalent state.

Bowman and Burwell[126] have recently reported studies of Mo clusters formed from $\mathrm{Mo(CO)_6}$ supported on dehydroxylated alumina. When $\mathrm{Mo(CO)_6}$ on alumina partially dehydroxylated at 748 K (approximately 4-$\mathrm{OH^-/nm^2}$) is treated with hydrogen or helium at 573 K, ionic, highly dispersed Mo (primarily $\mathrm{Mo^{2+}}$) is formed on the surface. Initial CO chemisorption studies on catalysts activated in helium at 773 K indicated the presence of Mo clusters of about 4 nm in diameter. The clusters are ascribed to a mixture of $\mathrm{Mo^{2+}}$ and $\mathrm{Mo^0}$ in which the charge is delocalized and balanced by $\mathrm{Al{-}O^-}$ groups at the surface.[126] Some carbon is retained and can be removed as methane by treatment with hydrogen at 923 K.

Howe and co-workers[108,113] have studied the effect of NO on supported $\mathrm{Mo(CO)_6}$ catalysts. Early studies performed to determine the poisoning effect of NO demonstrated that molybdenum was well dispersed on silica.[108] Later investigations showed that a $\mathrm{Mo^{2+}}$–nitrosyl complex was formed by reaction of NO with zerovalent molybdenum subcarbonyl species on alumina activated at low temperatures.[113]

Zeolites have also been used to surface bond $\mathrm{Mo(CO)_6}$. Gallezot et al.[127,128] investigated adsorbed $\mathrm{Mo(CO)_6}$ on HY zeolite with X-ray crystal structure analysis and infrared spectroscopy. As with other supports, $\mathrm{Mo(CO)_6}$ initially physically adsorbed on the zeolite, with one carbonyl per supercage situated in the vicinity of the 12-membered ring of the zeolite framework. On heating, the $\mathrm{Mo(CO)_6}$ loaded zeolite evolves CO without formation of a stable subcarbonyl species. Electron spin resonance studies of $\mathrm{Mo(CO)_6}$ on HY zeolite indicated that at low temperatures (300 K) $\mathrm{Mo^+}$ is formed.[129] At higher temperatures (750 K) $\mathrm{Mo^{5+}}$ predominates.[129]

Surface-bonded group 6 carbonyls have been used extensively for olefin metathesis since Banks and Bailey[130] discovered this chemistry on activated $\mathrm{Mo(CO)_6/Al_2O_3}$. With propene feed at 394 K, the molybdenum catalyst produced 42% ethene, 55% 2-butene, and 3% higher molecular weight olefins at 25% conversion. Feed polymerization was not observed. Ethene was converted in low yield to cyclopropane and methylcyclopropane; this result has gone unduplicated to date. Immobilized tungsten hexacarbonyl produced similar results.

Using $\mathrm{Mo(CO)_6}$ on $\mathrm{Al_2O_3}$ in a static reactor system between 273 and 353 K and propene pressures between 0.5 and 20.0 $\mathrm{kN/m^2}$, Davie, Whan, and Kemball[131] observed virtual equilibrium conversions in periods of 15 min to several hours. No distinction between first- and second-order kinetics was possible with integral rate equations. From infrared spectra and other evidence, they postulated an active species of the form: $\mathrm{(C_3H_6)_2Mo(CO)_4L_{4-x}}$, where x is either 3 or 4 and L is a propene molecule or a part of the alumina surface. The activation energy was 30.5 kJ/mol. These investigators also studied the effect of pretreating immobilized molybdenum carbonyl catalysts with halogenated olefins prior to exposure to reactants.[132] Although halogenated olefin metathesis was not observed, infrared spectra and kinetic studies of the catalyst indicated that the double bond in the activating molecule is bound in some manner to the catalysts.

Brenner and Burwell[133] studied the metathesis activity of several surface species derived from Mo-

$(CO)_6/Al_2O_3$. Catalyst activity strongly depended on the degree of dehydroxylation of the support. Initial catalytic activity when a partially dehydroxylated support is used increased in the order $Mo(CO)_3$ads < $Mo(CO)_2O_2$ads < "$(\sigma\text{-O}^-)_2$Mo" < "$(\sigma\text{-O}^-)_2$Mo" treated with oxygen. Only a small fraction of the surface molybdenum was active.

An in situ infrared study of $Mo(CO)_6/Al_2O_3$ by Olsthoorn and Moulijn[134] confirmed that the metathesis activity depended markedly on the degree of hydroxylation of the alumina. Pretreatment of the catalyst at 523 K, after evacuation at 373 K, produced the most effective catalyst.

Although there have been many investigations of supported $Mo(CO)_6$ catalysts for olefin metathesis,[135–142] little effort has been devoted to the study of other reactions. Surface-bonded $Mo(CO)_6$ exhibits greater activity for olefin hydrogenation than conventional MoO_3/Al_2O_3 catalysts.[114,143] It is also useful in the polymerization of unsaturated hydrocarbons,[116] the desulfurization of thiols,[144a] and the dehalogenation of α-halo ketones.[144b]

During thermal decomposition of all surface-bonded group 6 carbonyls, small quantities of methane are formed, suggesting usefulness in the reduction of CO.[28,145,146] Bowman and Burwell[126] have proven this for catalysts derived from $Mo(CO)_6$ supported on fully dehydroxylated alumina. At 573 K, a turnover frequency of 0.04 s^{-1} was observed. After conditioning for a few minutes, activity remained constant for about 6 h. Catalysts prepared from $Mo(CO)_6$ on partially dehydroxylated alumina also were active, but with lower turnover frequencies.[126]

Surface-bonded $W(CO)_6$ has received less attention than its $Mo(CO)_6$ counterpart. In an early attempt to elucidate the nature of zerovalent metal carbonyls immobilized on an acidic solid, Bilhou et al.[147] investigated $W(CO)_5L$ on η-alumina (L = CO, PPh_3, $P(OPh)_3$, $P(n\text{-}C_4H_9)_3$). Infrared spectroscopy indicated that the first activation step occurs through a W—C═O—Al complexation with a linear carbonyl ligand coordinated to the Lewis center. This serves to increase the ($d\pi$–$p\pi$) back-donation of tungsten $d\pi$ electrons to the π^* orbitals of CO. The net decrease of tungsten electron density favors the departure of ligand, L.

Recently Brenner and Hucul[148] have described the surface chemistry of the $W(CO)_6/Al_2O_3$ system. Although early studies[111] suggested that no stable subcarbonyl species were formed, temperature-programmed decomposition experiments indicate the reversible formation of $W(CO)_3$ads at low temperatures (408 K).[148] At higher temperatures complete decomposition occurs, with W^{6+} being formed on highly hydroxylated supports and W^0 on dehydroxylated supports.[148] Complete decarbonylation generally requires temperatures in excess of 673 K.[148] This behavior is similar to that for the corresponding $Mo(CO)_6$ system.[28] Silica-supported $W(CO)_6$ also resembles $Mo(CO)_6/SiO_2$.[114]

Surface-bonded $W(CO)_6$ generally catalyzes the same reactions as its $Mo(CO)_6$ counterparts. Studies of olefin metathesis,[116,130,134–137] olefin hydrogenation,[114] and polymerization[116] have been reported.

3. *Surface-Bonded Group 7 Carbonyl Catalysts*

Few studies of the surface chemistry of surface-bonded group 7 carbonyls have been reported. Gallezot et al.[127,128] studied $Re_2(CO)_{10}$ surface bonded to HY zeolite with X-ray crystal structure analysis and infrared spectroscopy. Initially, this carbonyl is physically adsorbed onto the zeolite and "stretched" across the supercage. Infrared spectroscopy indicated that the molecular structure was preserved with some weak distortion due to lateral interactions. Thermal decomposition curves show a plateau between 473 and 573 K corresponding to three CO molecules per original molecule evolved. No evidence to date supports the presence of either a single subcarbonyl intermediate or several species. Decomposition is complete at 723 K.

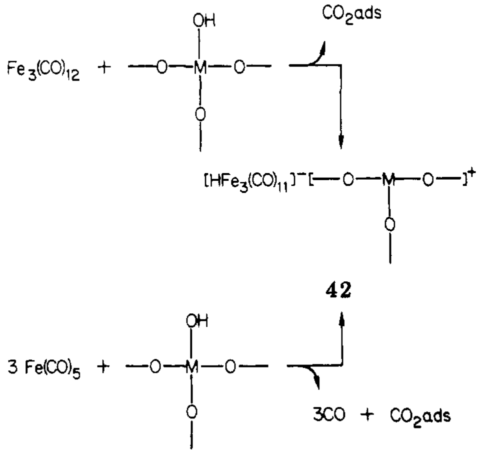
Vanderspurt's[149,150] patents describe partially decomposed $Re_2(CO)_{10}$ on controlled pore glass. The resulting material was used to hydrogenate unsaturated aldehydes selectively to unsaturated alcohols between 323 and 523 K. The decomposition is performed in the presence of hydrogen while air, water, and oxygen, which promote the formation of difficult to reduce oxidized rhenium species,[150] are excluded. "Selective" poisons (CO, CS_2, H_2S) are employed during hydrogenation to inhibit reduction of the double bond. Conventional Re_2O_7 on glass catalysts give generally poorer results.[149]

Antos[151] decomposed $Re_2(CO)_{10}$ on Pt/Al_2O_3 in hydrogen to produce a bimetallic re-forming catalyst. The patent claims a selectivity for hydrocarbons of C_5 or greater that is higher than that of a traditional Pt–Re catalyst.

4. *Surface-Bonded Group 8 Carbonyl Catalysts*

Brenner and Hucul studied iron carbonyls surface bonded to alumina.[152–154] Temperature-programmed decomposition studies of $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ on alumina suggest that the nuclearity of the precursor carbonyl affects the chemistry of the surface-bonded material.[152] Activation below 423 K leads to the formation of primarily zerovalent subcarbonyl species. Although inconclusive, mass balances indicated that $Fe(CO)_2$ads might be formed from $Fe(CO)_5/Al_2O_3$ at 393 K. No other stable subcarbonyl species were evident.[152] Hydrogen evolution above 573 K suggested extensive iron oxidation caused by reaction between the carbonyls and surface hydroxyl groups.[152] Because surface-bonded carbonyls decompose over a wider temperature range than do bulk carbonyls, it was proposed that the alumina acted as a stabilizer of the subcarbonyl species, thus inhibiting metal mirror formation on the surface. Carbon monoxide chemisorption studies indicated that surface-bonded carbonyls could be used to prepare metal catalysts which were at least an order of magnitude more dispersed than those prepared by conventional means.[152] The higher dispersion was attributed to the omission of high-temperature calcination and reduction of Fe^{3+} which could lead to sintering and/or production of difficult to reduce iron compounds on the surface.[154] Preliminary experiments suggested that these catalysts were active for olefin hydrogenation and methanation.[154]

Basset et al.[155] report that the first step in the reaction of $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with supports such as alumina or magnesia involves nucleophilic attack of a support hydroxyl group on a carbonyl ligand with formation of an ionic hydride species, $[HFe_3(CO)_{11}]^-$ (eq 28). The mononuclear species reacted more slowly than



(28)

42

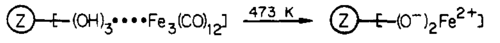
$M = Al^{3+}, Mg^{2+}$

the cluster. The addition of HCl to the supported anionic cluster caused the reappearance of $Fe_3(CO)_{12}$.[155]

Catalysts derived from surface-bonded $Fe(CO)_5$ and $Fe_3(CO)_{12}$ have been successfully employed in the Fischer–Tropsch synthesis between 453 and 543 K.[156] These catalysts generally were more than 50% selective for olefin production, favoring ethylene and propylene. Selectivity declined with time on stream. Catalysts prepared in the customary manner (impregnation with $Fe(NO_3)_3$) exhibited markedly different product distributions with minimum selectivity for ethylene.[156]

McVicker and Vannice[157,158] prepared active Fischer–Tropsch catalysts by impregnating alumina and silica with $K_2Fe(CO)_4$ and decomposing the product under hydrogen. Infrared spectra demonstrated the initial presence of stable surface-bonded carbonyl complexes on partially dehydroxylated alumina in the absence of oxygen. Treatment with air resulted in the irreversible decomposition and oxidation of the iron complexes.[158] Hydrogen reduction produced reduced iron species on the support. Catalysts prepared from these K/Fe complexes had higher surface areas than traditional catalysts, as measured by CO chemisorption. Alumina supports produced a higher degree of dispersion than silica, presumably due to differences in the surface hydroxyl groups.[158] As with catalysts derived from other surface-bonded iron carbonyls,[156] catalysts made from K/Fe carbonyl complexes showed higher activity and higher olefin selectivity than conventionally prepared materials.[158] Because this method of catalyst preparation yields highly dispersed K/Fe particles with intimate contact between the two components the promotional effect of the group 1A metal may be maximized.[158]

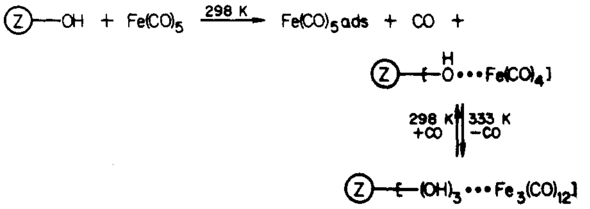
Ballivet-Tkatchenko et al.[159,160] introduced $Fe(CO)_5$, $Fe_2(CO)_9$, and $Fe_3(CO)_{12}$ into NaY and HY zeolites to produce Fischer–Tropsch catalyst precursors. Initial immobilization involved adsorption of the carbonyl complexes within the supercage accompanied by their interaction with surface hydroxyl groups. When $Fe_3(CO)_{12}$/HY zeolite is heated to 333 K, $H_2Fe_3(CO)_{11}$ is formed within the supercage and interacts with the zeolite through hydrogen bonding.[160] Heating to 473 K results in continuous carbon monoxide evolution with iron oxidation (eq 29).



(29)

Ⓩ = zeolite

When NaY zeolite was used as the support, only carbon monoxide was evolved. Because metal oxidation generally is accompanied by hydrogen evolution,[112] use of NaY zeolite may produce supported unoxidized metal particles.[159] The interaction of $Fe(CO)_5$ with HY zeolite follows the chemistry shown in eq 30.[160] These



(30)

materials were active catalysts for the Fischer–Tropsch synthesis at 523 K. Activity depended on (1) the Co/H_2 ratio, (2) the support, and (3) catalyst pretreatment. Unlike catalysts derived from iron carbonyls supported on alumina,[156–158] silica,[157,158] or silica–alumina,[160] zeolite-supported iron catalysts were not selective for olefins.[160]

Nagy, van Eenoo, and Derouane[161] used thermal and photochemical decomposition of $Fe(CO)_5$ adsorbed in HY zeolite to form highly dispersed iron particles. Photochemical decomposition gave smaller particles because of the strong carbonyl–surface interaction due to electronic excitation of the carbonyl during decomposition. This procedure was proposed as a route to highly dispersed, pyrophoric iron.

Recently, Phillips, Clausen, and Dumesic[162] decomposed $Fe(CO)_5$ on graphite (Grafoil) pretreated to maximize the presence of edges and other imperfections. Low-temperature (77 K) Mössbauer experiments showed that the iron carbonyl is physically adsorbed with only slight structural alteration. Heating to 378 K resulted in the formation of supported metallic iron present as "thin rafts" along edges and steps of the graphite. Extended heating at 450 K caused sintering and possible formation of iron carbides.

Robertson and Webb[163] found that $Ru_3(CO)_{12}$ supported on silica was an active olefin isomerization and hydrogenation catalyst between 353 and 415 K. Infrared and radiochemical studies of the thermal decomposition of this carbonyl on silica (298–443 K) indicated that initial physical adsorption is followed by formation of stable subcarbonyl species. These researchers proposed that the carbonyl reacts with surface hydroxyls to form a metal carbonyl hydride with loss of CO, leading to an active complex of the form $L_xH_yRu_3(CO)_5$ where L represents surface O–Si groups.

Since early reports of the production of hydrocarbons during the decomposition of $Ru_3(CO)_{12}$ on alumina,[146,164] catalysts derived from surface-bonded ruthenium carbonyl complexes have been used for the Fischer–Tropsch synthesis. Basset et al.[156] used $Ru_3(CO)_{12}/Al_2O_3$ at 453 K to produce methane with 49% selectivity. McVicker and Vannice[158] impregnated and decomposed $K_2Ru_3(CO)_{12}$ on η-Al_2O_3 to produce highly dispersed ruthenium particles. Their catalysts gave higher conversions of CO than catalysts prepared from comparable iron and iridium complexes; methane selectivity was 32%.

Other studies of surface-bonded ruthenium carbonyls have involved the use of $[H_3Ru_4(CO)_{12}]^+$ to produce small metal crystallites on silica,[165] the use of $Ru_3(CO)_{12}$ to obtain high dispersion of ruthenium oxide on low surface area magnesium oxide,[165] and the thermal decomposition of $Ru_3(CO)_{12}$ on HY zeolite.[127] In the latter study, ruthenium carbonyl was found to adsorb initially in the zeolite supercage and then to decompose to the stable subcarbonyl species $Ru_3(CO)_9$ on heating to approximately 473 K. Decarbonylation was complete at 773 K.[127]

There has been little investigation of catalysts obtained from surface-bonded osmium carbonyls. Thermal decomposition of $Os_3(CO)_{12}$[146,164] and $Os_6(CO)_{18}$[164] on alumina results in hydrocarbon formation. Silica-supported $Os_3(CO)_{12}$ was active in the Fischer–Tropsch synthesis at 473 K with 85.5% selectivity for methane.[156]

Ichikawa employed $Co_4(CO)_{12}/ZnO$ to hydroformylate ethylene and propylene.[167,168] Although it was considerably less active than catalysts derived from rhodium or rhodium–cobalt carbonyl complexes, it exhibited greater selectivity for normal aldehyde formation.[168]

Smith et al.[169] studied the effect of oxygen on rhodium carbonyl clusters immobilized on γ-alumina and silica. Initial treatment of γ-alumina with $Rh_6(CO)_{16}$ results in physical adsorption. In the presence of CO, the infrared spectrum resembles that of solid $Rh_6(CO)_{16}$. Exposure to air or oxygen at room temperature gives carbon dioxide evolution and the formation of small metal aggregates at the surface according to eq 31.

$$Rh_6(CO)_{16}\mathrm{ads} + (m + n/2)O_2 \rightarrow Rh_6(CO)_{16-n}(O_2)_m\mathrm{ads} + nCO_2 \quad (31)$$

Infrared evidence is consistent with the formation of at least one stable subcarbonyl species during this process. When rhodium compounds such as $Rh_4(CO)_{12}$ or $Rh_2(CO)_4Cl_2$ are supported on alumina, decarbonylated, and exposed to carbon monoxide, $Rh_6(CO)_{16}/Al_2O_3$ is formed. No decarbonylation occurred when silica (Vycor) was used as the support for $Rh_6(CO)_{16}$ at room temperature.

Similar results were obtained by Conrad et al.[170] for the $Rh_6(CO)_{16}/SiO_2$ system. At room temperature, $Rh_6(CO)_{16}$ retains its character; rapid heating results in decarbonylation. Infrared data for decarbonylated materials subsequently treated with CO indicate that the Rh_6 structure is retained after decomposition. The rhodium cluster was also supported on copper foil with decomposition occurring only above 473 K.

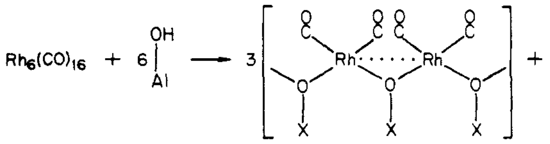
Ichikawa has used catalysts derived from a variety of rhodium carbonyls, including $Rh_4(CO)_{12}$,[171-174] $Rh_6(CO)_{16}$,[171-173] $[Rh_7(CO)_{16}]^{3-}$,[172,173] and $[Rh_{13}(CO)_{23}H_{2-3}]^{2-}$,[171-173] surface bonded to TiO_2,[172,173] ZrO_2,[172,173] ThO_2,[172] CeO_2,[172] La_2O_3,[172,173] ZnO,[171,173] MgO,[173] BeO,[171] Al_2O_3,[171] SiO_2,[171] CaO,[171] and activated carbon[174] for carbon monoxide reduction with hydrogen. These catalysts were prepared by depositing the carbonyls from an organic solution onto the powdered support. After solvent removal, the powder was pressed into a wafer and used for infrared or kinetic experiments. Because the process of making the catalyst wafer can result in some decomposition,[23] the nature of the supported material may be unclear. Under mild reaction conditions of atmospheric pressure and 423–523 K, rhodium crystallites produced from the pyrolysis of these surface-bonded carbonyls in vacuo catalyzed formation of significant quantities of alcohols in addition to paraffinic and olefinic products. Catalysts supported on ZnO, BeO, and CaO selectively favored methanol formation.[171] The relative activity for methanol production varied with the specific rhodium carbonyl initially employed: $[Rh_{13}(CO)_{23}H_{2-3}]^{2-} > Rh_6(CO)_{16} > Rh_4(CO)_{12}$.[171] Selectivities for methanol formation of up to 98.9% could be obtained ($Rh_6(CO)_{16}/ZnO$, $T = 493$ K). The use of La_2O_3, TiO_2, ZrO_2, ThO_2, or CeO_2 supports favored production of ethanol over methanol.[172] Employment of SiO_2 and Al_2O_3 supports resulted in selectivity for methane with traces of alcohols.[171] For most of these catalysts, CO conversion rose and alcohol selectivity declined with increasing reaction temperature.[171-173]

Ichikawa[167,168] also demonstrated the effectiveness of these materials for olefin hydroformylation. Below 363 K $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ on ZnO were inactive; an induction period was required for activity above 363 K.[168] No significant difference in steady-state rates or isomer selectivities was observed with these catalysts after pyrolysis in vacuo or activation under reaction conditions.[167] Infrared studies of the catalyst during reaction suggested that the dispersed rhodium particles formed by pyrolysis recombined to form species similar to partially decarbonylated Rh clusters.[168] When different rhodium clusters were used as precursors (on ZnO), activity at 431 K followed the order[168] $Rh_4(CO)_{12} > Rh_6(CO)_{16} > [Rh_7(CO)_{16}]^{3-} > [Rh_{13}(CO)_{23}H_{2-3}]^{2-}$. Use of other basic supports such as TiO_2 and La_2O_3 also produced effective hydroformylation catalysts.[168] With acidic supports such as Al_2O_3 and SiO_2, ineffective catalysts resulted. This was due, presumably, to formation of different surface species from the strong interactions between the metal carbonyls and the hydroxyl sites.

In their extensive infrared studies of adsorbed and surface-bound rhodium carbonyls, Basset and Smith with others have emphasized geometric and electronic analogies between molecular clusters and very small metal particles.[175-178] When $Rh_4(CO)_{12}$ is initially chemisorbed onto SiO_2 or η-Al_2O_3 at room temperature, the rearrangement[176] shown in eq 32 occurs readily,

$$3Rh_4(CO)_{12} \rightarrow 2Rh_6(CO)_{16} + 4CO \quad (32)$$

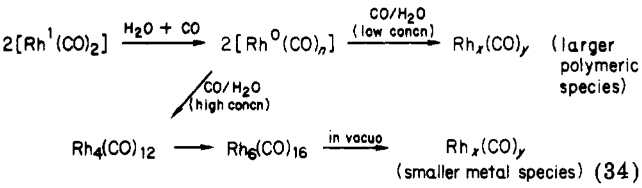
indicating high surface mobility of zerovalent rhodium carbonyl fragments. This reaction is retarded severely by carbon monoxide. Both silica-bonded clusters can be oxidized at 373 K to $[Rh^1(CO)_2]$ species in the absence of water.[175,176,178] Spectroscopic study of the supported Rh^1 species suggested weak metal–metal dimer interactions[175,176] (eq 33).



43, X = Al (also Mg, Si)

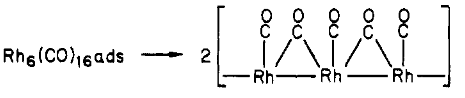
$4CO + 3H_2$ (33)

Reducing the supported rhodium cationic complex with water in the presence of carbon monoxide leads initially to the formation of small rhodium metal clusters followed either by regeneration of adsorbed $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ or supported metal crystallites[176] (eq 34).



(34)

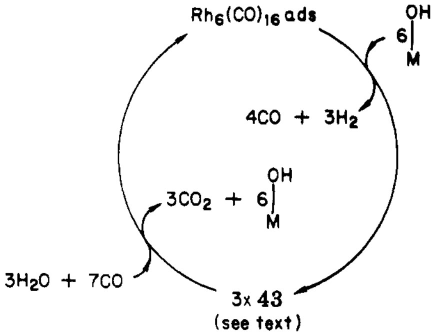
The absence of CO can lead to particle agglomeration. On alumina, the formation of $Rh_6(CO)_{16}$ from $[Rh^1(CO)_2]$ with CO and water is accompanied by regeneration of surface hydroxyl groups and CO_2 evolution.[175] Treatment of silica-supported $Rh_6(CO)_{16}$ with H_2O or H_2 in the absence of CO leads to the formation of species which spectroscopically resemble CO adsorbed on rhodium metal.[178]



44

(35)

While it is not difficult to stabilize $Rh_6(CO)_{16}$ on finely divided silica,[176,178] on alumina and magnesia the original molecular character of the complex is lost with oxidation.[175] On alumina, prior dehydroxylation above 573 K is required for stabilization of the chemisorbed molecular complex.[175] This group has also described the effectiveness of alumina-supported rhodium clusters for the Fischer–Tropsch synthesis[156] and postulated a catalytic cycle for the water gas shift reaction[175] (eq 36).



(36)

Gelin, Ben Taarit, and Naccache[179] determined that $Rh_6(CO)_{16}$ could be immobilized on NaY and HY zeolites and decarbonylated by oxygen or in vacuo at 373 K with substantial retention of molecular structure. In agreement with the studies described above, these supports promoted the fragmentation of the cluster during decarbonylation and the subsequent formation of Rh(I) complexes.

The surface chemistry of $Ir_4(CO)_{12}$ supported on alumina and silica has been investigated by Howe and co-workers.[180–182] The carbonyl is initially physically adsorbed on fully hydroxylated alumina.[180] Heating with evacuation results in gradual decarbonylation, virtually completed after treatment at 623 K for 5 h.[180] The average particle size of the resulting iridium crystallites as measured by gas adsorption was <1 nm.[181,182] Impregnating silica with $Ir_4(CO)_{12}$ initially results in clusters dispersed throughout the support. The cluster becomes sufficiently volatile for adsorption on the silica only after heating to 373 K. After adsorption, decarbonylation proceeds in a manner comparable to that on Al_2O_3.[180] During decarbonylation, hydrocarbons are evolved.[146,164] Catalysts derived from surface-bonded $Ir_4(CO)_{12}$ have been used for the hydrogenolysis of paraffins[183] and the reduction of carbon monoxide with hydrogen.[156,171] Promoted Fischer–Tropsch catalysts were prepared by reducing supported $KIr(CO)_4$.[157,158]

In his pioneering study, Parkyns[184] proposed that at room temperature $Ni(CO)_4$ initially physically adsorbs on alumina, decomposes upon evacuation to small carbonylated metal clusters, and rapidly reacts with oxygen. Silica was less effective in catalyzing this decomposition and oxidation.

Assuming that the Ni atom rather than the CO ligands interacts with the support, Derouane, Nagy, and Vedrine[185] interpreted ^{13}C nuclear magnetic resonance (^{13}C NMR) data to show that the attachment sites on aluminas are acidic electron acceptors. Scanning electron microscopy showed the presence of Ni crystallites on alumina fibers after evacuation. These crystallites were considered to be highly microporous ensembles of tiny spheres of uniform size. They were similar to those formed by vapor codeposition techniques.

Bjorklund and Burwell[186] recently investigated the surface chemistry of $Ni(CO)_4/Al_2O_3$. At low temperatures (298–323 K) $Ni(CO)_4$ vapor reacts with partially dehydroxylated alumina to reversibly form $Ni(CO)_3$ads. The total uptake of $Ni(CO)_4$ increases with increasing dehydroxylation of the support. Heating this material to 373 K results in further decarbonylation and agglomeration of nickel. Subsequent heating to 723 K is accompanied by CO, H_2, and CO_2 evolution and the oxidation of nickel by reaction with surface hydroxyl groups. Thermally treating $Ni(CO)_4$ adsorbed on dehydroxylated alumina gave no hydrogen evolution and presumably little or no nickel oxidation.[112,186] Nickel carbonyl could be adsorbed only slightly on SiO_2 at room temperature.

The interactions between $Ni(CO)_4$ and type Y zeolites seem to depend on the type of zeolite employed. With HY zeolites, ^{13}C NMR data[185] indicate that acidic electron acceptors are the active sites for carbonyl adsorption. Electron donor sites, possibly lattice oxygen anions, are primary attachment sites on NaY zeolites.[185]

Galinskii and co-workers[187–190] investigated the effects of exchange cation and experimental conditions on the reaction between $Ni(CO)_4$ and M-NaX zeolites (M = Li, K, Cs, Ca, Mg, Be). Evidence was presented in support of a stepwise decomposition of the carbonyl to metal with increasing temperature.[187,188] A stable Ni(CO) intermediate was identified.[188] The amount of nickel carbonyl retained on the surface increased with the size of the exchange cation.[189] Dispersion of metallic nickel was maximized by isothermally decomposing the carbonyl in vacuo at 623 K followed by passivation in nitrogen with traces of oxygen.[190] Such catalysts were effective for benzene hydrogenation between 333 and 373 K.[188]

Novel supported Ni–allyl oligomerization catalysts have been prepared by either simultaneously reacting $Ni(CO)_4$ and C_3H_5Cl with γ-Al_2O_3[191] or treating previously adsorbed carbonyl with allene.[192] These catalysts had a monomeric structure in contrast to the dimer formed in solution.[191]

Ichikawa has used platinum carbonyl cluster anions to synthesize supported metal crystallites that are effective in the dehydrocyclization of *n*-hexane[27] and the reduction of carbon monoxide with hydrogen.[171,193] The trigonal prismatic salts $[\{Pt_3(CO)_6\}_n]^{2-}([NEt_4]^+)_2$ (*n* =

1–5) were deposited on silica,[27,193] γ-alumina,[27,193] ZnO,[171] and MgO[171] and decomposed by pyrolysis in vacuo or under He or H_2. Although it was not proven that the resulting Pt metal aggregates contained the same number of atoms as the original clusters, the crystallites were less than 10 Å^2 in area.[27] When tested as dehydrocyclization catalysts, hydrocracking occurred preferentially over Pt crystallites prepared from smaller Pt clusters. This was ascribed to a greater density of lower coordinated corner Pt atoms among the Pt aggregates prepared from these clusters. This favored the formation of adsorbed carbocyclic reaction intermediates.[27] For the Fischer–Tropsch synthesis, these catalysts exhibited a higher CO conversion rate and selectivity for alcohol formation than conventionally prepared Pt catalysts.[171]

5. *Alloy Analogues from Bimetallic Clusters*

Anderson et al.[25,181,194] studied catalysts derived from $Co_2Rh_2(CO)_{12}$ surface bonded to silica and alumina. Compared with materials prepared by support impregnation with cobalt nitrate and rhodium chloride, catalysts derived from carbonyl cluster precursors were more highly dispersed as smaller metal particles (mean particle diameter = 1.1–2.8 vs. 5.8 nm).[181] Alumina promoted the formation of more highly dispersed metal particles from the carbonyl clusters.[181] Decarbonylation in oxygen rather than nitrogen enhances dispersion, indicating oxidative decarbonylation.[181] Infrared studies indicated that $Co_2Rh_2(CO)_{12}$ is initially adsorbed on γ-alumina with loss of bridging carbonyls, followed by the loss of the remaining carbonyl ligands at temperatures greater than 300 K.[181] Evidence was presented suggesting that the crystallites resulting from decarbonylation are surface enriched in cobalt, with silica being more effective than alumina.[181] When used for the hydrogenolysis of *n*-hexane (493–583 K), these catalysts gave higher proportions of dehydrocyclization and isomerization products than either conventionally prepared Co or Rh catalysts.[194] This was attributed to the behavior of a cobalt monolayer on a rhodium-enriched matrix.[194] At 533 and 583 K $Co_2Rh(CO)_{12}/Al_2O_3$ catalysts were more effective for hydrogenolysis than their silica-supported counterparts due to higher surface concentrations of rhodium obtained with alumina.[181,194]

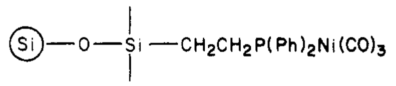
When supported on ZnO and evacuated at 433 K, rhodium–cobalt carbonyl clusters were effective hydroformylation catalysts.[167,168] Specific activity followed the order $Rh_4(CO)_{12} > Rh_2Co_2(CO)_{12} > RhCo_3(CO)_{12} > Co_4(CO)_{12}$.[167,168] In contrast, linear isomer selectivity increased with cobalt content.[168] While the specific activity for hydroformylation by the bimetallic crystallites could be correlated with Rh content, the observed selectivity was attributed to cobalt atoms in the decarbonylated clusters acting to enhance selectivity because of their lower ionization potential.[168]

Kaesz et al.[165] have also used bimetallic clusters to generate supported mixed-metal crystallites. In their study with $HFeCo_3(CO)_{12}$ and $Co_2Rh_2(CO)_{12}$, prior reduction of the support and/or handling under an inert atmosphere were important in bimetallic cluster deposition. Mössbauer studies of $HFeCo_3(CO)_{12}$ on alumina indicated the presence of only oxidized iron on the surface. ESCA studies of $Co_2Rh_2(CO)_{12}$ on alumina showed no surface cobalt.

C. Anchoring Metal Carbonyls on Functionalized Inorganic Oxides

1. *Preparation*

Recent years have witnessed increasing interest in methods for anchoring catalytically active transition-metal complexes to inorganic supports with bifunctional ligands. With one ligand function interacting with the coordination sphere of the metal atom, the other is bonded to the support to anchor the transition-metal complex. Unlike the surface bonding of carbonyls, this immobilization procedure allows significant retention of the molecular character of the initial carbonyl complex. For example, when $Ni(CO)_4$ reacts with phosphinated silica, the structure of the resulting complex is believed to be

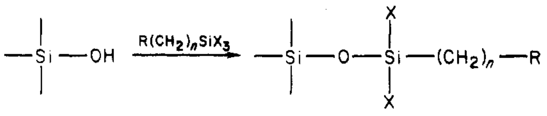


$$\text{Ⓢi}-O-\overset{|}{\underset{|}{Si}}-CH_2CH_2P(Ph)_2Ni(CO)_3$$

45

(see section III.C.2 for further discussion). In contrast, when $Ni(CO)_4$ reacts directly with an inorganic support, interaction with the support can result in alteration of the molecular character of the species through decarbonylation and agglomeration of nickel.[186]

While there are several ways to attach ligand groups to inorganic surfaces, the most useful involves reaction between surface hydroxyl groups and a readily hydrolyzable moiety.[195] This route is preferred because (1)



$$-\overset{|}{\underset{|}{Si}}-OH \xrightarrow{R(CH_2)_nSiX_3} -\overset{|}{\underset{|}{Si}}-O-\overset{X}{\underset{X}{Si}}-(CH_2)_n-R \qquad (37)$$

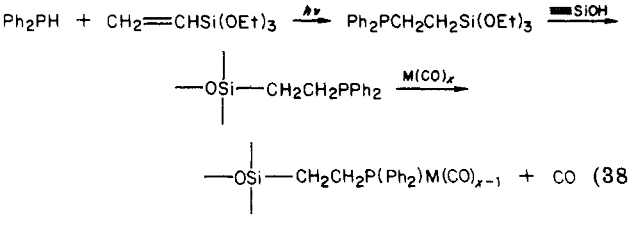
46, *n* = 0, 1, 2 ...

R = an organofunctional group, e.g., PPh_2, NH_2, C_5H_5

X = a hydrolyzable group, e.g., Cl, NH_2, OR, OCOR

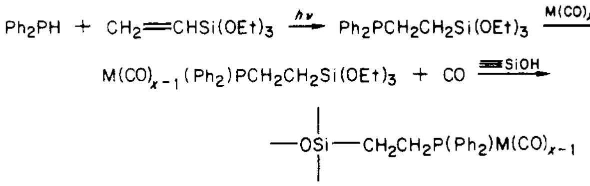
it gives a Si–C bond at the surface which is hydrolytically and thermally stable because of its cross-linking, (2) a wide range of compounds of type $RSiX_3$ are available, and (3) the one-step reaction is simple to perform under mild conditions.[195] Chemistry of this type has been employed successfully to anchor PPh_2,[195] NH_2,[196] C_5H_5,[197] and other ligands.[195,198,199]

Allum et al.[195,200–203] pioneered the use of this technique with their study of silica treated with 2-(diphenylphosphine)ethyltriethoxysilane or related compounds. The silane is prepared under ultraviolet irradiation by diphenylphosphine addition to vinyltriethoxysilane using Niebergall's procedure.[204] The phosphinated silica can be equilibrated with the carbonyl. Ligand displacement by the phosphine anchors it to the surface (eq 38).



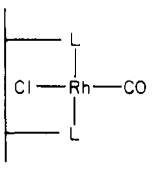
$$Ph_2PH + CH_2{=}CHSi(OEt)_3 \xrightarrow{h\nu} Ph_2PCH_2CH_2Si(OEt)_3 \xrightarrow{\equiv SiOH} -O\overset{|}{\underset{|}{Si}}-CH_2CH_2PPh_2 \xrightarrow{M(CO)_x} -O\overset{|}{\underset{|}{Si}}-CH_2CH_2P(Ph_2)M(CO)_{x-1} + CO \qquad (38)$$

An alternate method for preparing the same catalyst starts with synthesis of a transition-metal complex containing 2-(diphenylphosphino)ethyltriethoxysilane as a ligand. This complex is then reacted with the silica surface (eq 39).



$$Ph_2PH + CH_2{=}CHSi(OEt)_3 \xrightarrow{h\nu} Ph_2PCH_2CH_2Si(OEt)_3 \xrightarrow{M(CO)_x} M(CO)_{x-1}(Ph_2)PCH_2CH_2Si(OEt)_3 + CO \xrightarrow{\equiv SiOH} {-}OSi{-}CH_2CH_2P(Ph_2)M(CO)_{x-1} \quad (39)$$

Murrell[13,205] has reported the results of one illuminating study that compared catalysts prepared by these two methods. Silica pretreated with $Ph_2P(CH_2)_2SiCl_3$ (L) could react with $[Rh(CO)_2Cl]_2$ to give four possible surface complexes. Both *cis*- and *trans*-**47** and **48** could result. Although infrared spectra argue against *cis*-**47**, the other three structures can be present. In contrast, *trans*-$L_2Rh(CO)Cl$ reacts with silica to selectively produce *trans*-**47**. In general, this control of structure is preferred since the catalyst retains any specific configuration found to give desired catalytic behavior.



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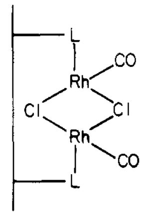

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The two anchoring methods described above can be used to study the effect of bifunctional ligand chain length on catalytic activity. Conceptually this is of interest since adsorbed molecules can block active sites on a metal complex in close proximity to the surface. Anchoring transition-metal complexes to surfaces with long and "flexible" ligand chains may make this type of poisoning less likely, while allowing additional flexibility in tailoring the stereochemical and electronic environments of the metal atom.[205]

Ligand length may be controlled by employment of organosilanes prepared by using the procedure of Oswald, Murrell, and Boucher.[206] The first step involves silane addition to an α,ω-diene in the presence of dipotassium hexachloroplatinate or palladium catalyst (eq 40). The addition is anti-Markovnikov because of the unusual polarization in the silicon-hydrogen bond. Reactive groups, such as esters, may be incorporated in the silane. Addition occurs at terminal double bonds. Excess diene ensures selective production of ω-alkenylsilane monoadducts. With successful organosilane synthesis, the attachment to the silica support can proceed as described earlier.

$$\begin{aligned}&Cl_3SiH + CH_2{=}CH(CH)_nCH{=}CH_2 \xrightarrow{K_2PtCl_6} Cl_3Si(CH_2)_{n+2}CH{=}CH_2\\ &\quad \xrightarrow{Cl_3SiH} Cl_3Si(CH_2)_{n+4}SiCl_3\\ &\quad \xrightarrow[\text{addition}]{\text{further}} Cl_3Si(CH_2)_xCH{=}CH(CH_2)_yCH_3 \quad (40)\end{aligned}$$

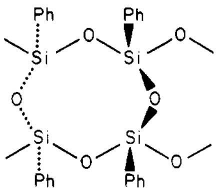
$$x + y = n + 1$$

Because metal carbonyls are usually higher saturated while catalytic action may involve ligand dissociation, metal carbonyls anchored through a single ligand may decompose by dissociation of the attaching ligand. To minimize this problem, it may be possible to employ polydentate groups so that the dissociation of one ligand group is possible while surface anchorage is maintained with the other. Alternatively labile monodentate ligands could be attached to the support at such density that multiple substitution on the metal carbonyl is permitted.

Ligand mobility also may affect catalyst activity. Hydrogen-bonding side groups on an anchoring ligand may interact with nearby silanol groups to reduce catalyst mobility.[207] In liquid-phase reactions, hydrogen-bonding solvents can enhance mobility of the anchored catalyst.[207] Increased mobility may be advantageous in providing multiple anchoring of the catalyst to the support to stabilize the catalyst. Long anchoring ligands may contribute to mass transfer limitations through the "clogging" of very small support pores.

Boucher, Oswald and Murrell[13,205] demonstrated that the nature of X in $RSiX_3$ affects the extent of anchoring. The concentration of phosphine groups anchored to silica decreases with increasing steric requirement of the hydrolyzable group X. This is probably due to the reaction of a single hydrolyzable group with a surface hydroxyl, leaving two groups free to block other sites from reacting with other $RSiX_3$ compounds.

Another type of silica-supported phosphine suitable for immobilizing metal carbonyls was prepared by Guyot et al.[208-210] from polyphenylsiloxane. The inorganic polymer is prepared by hydrolysis of $PhSiCl_3$. After initial formation of a low molecular weight prepolymer, a ladder polymer, **49**, is formed in the presence of KOH catalyst.[209] The polymer is chloromethylated at 333 K with an excess of chloromethyl ether and $ZnCl_2$ catalyst. Phosphination is achieved by reacting the immobilized chloromethylated group with alkyllithium phosphide in THF.[208,209]



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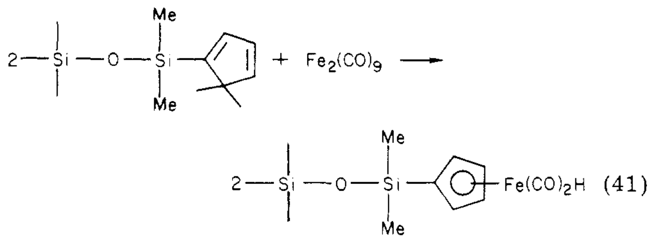
2. *Structures and Catalytic Properties*

Wild, Gubitosa, and Brintzinger[197] have reported that the order in which reactants are combined greatly affects the structure of the resulting anchored cyclopentadienyl iron carbonyl complexes. When $Fe_2(CO)_9$ is reacted with functionalized silica prepared by reaction between $(C_2H_5O)_3Si(CH_3)_2C_2H_5$ and surface hydroxyl groups, mononuclear species (**50**) are formed exclusively (eq 41). As described above, an alternative route to anchoring the carbonyl involves initial reaction between the carbonyl and $(C_2H_5O)_3Si(CH_3)_2C_5H_5$. The resulting dimer reacts with surface hydroxyl groups to form two anchored materials (eq 42). Treatment of the binuclear



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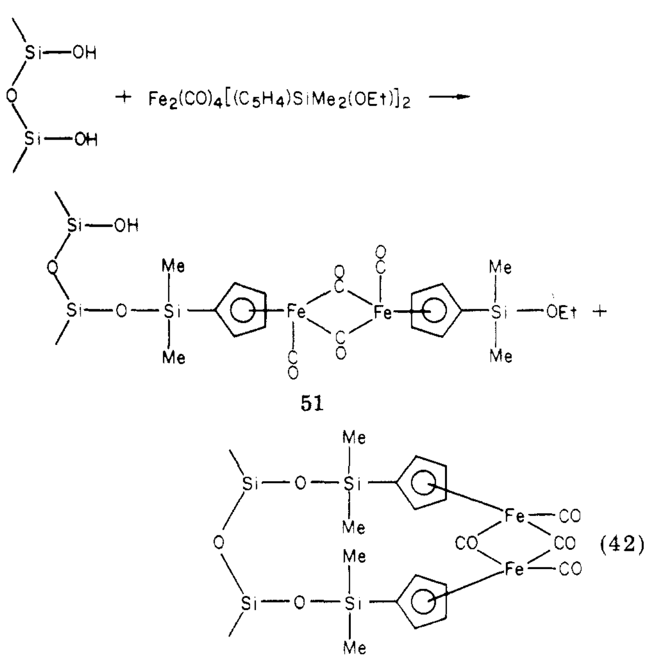

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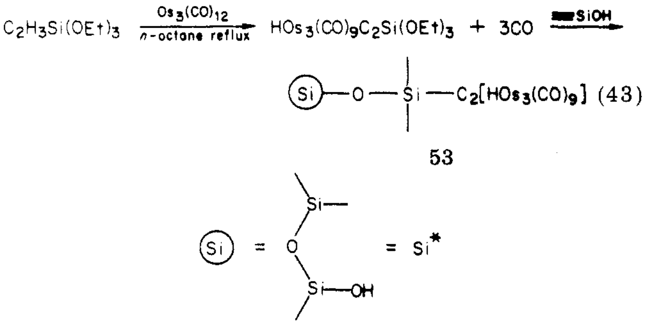
compounds with hydrogen (1×10^7 N/m^2) in benzene at 393 K irreversibly produces the anchored mononuclear iron complex.

When metal carbonyl clusters are immobilized on functionalized inorganic supports, a variety of anchored metal carbonyl structures may be formed, depending on reaction conditions. Brown and Evans[211] illustrated this by anchoring $Os_3(CO)_{12}$ to phosphinated silica. They reported that reaction of vinyltriethoxysilane with $Os_3(CO)_{12}$ followed by treatment with silica resulted in a hydridoosmium cluster attached via an unusual, completely dehydrogenated double bond similar to that in complexes prepared from terminal acetylenes[211] (eq 43). When the silane is phosphinated and reacted with



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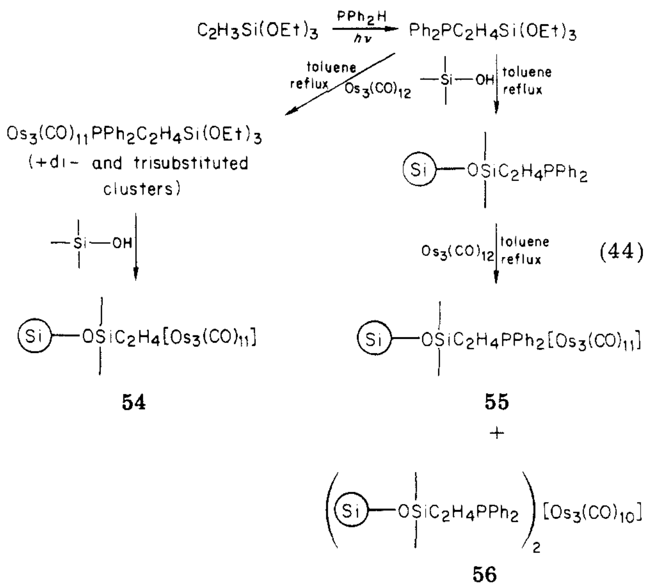
silica and the osmium cluster, several other anchored carbonyl clusters result (eq 44). In all cases, the anchored monosubstituted cluster predominates.

The cluster $H_2Os_3(CO)_{10}$ also reacts with phosphinated silica to form an adduct with anchored phosphine



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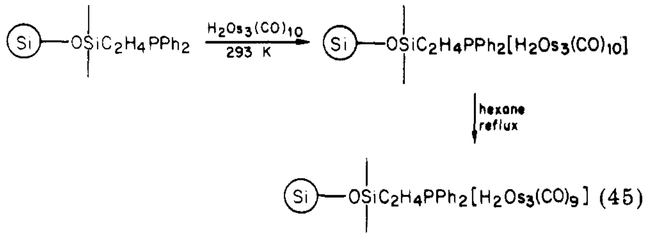

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(eq 45). The anchored cluster, **57**, was inactive for propylene hydrogenation at 373 K but isomerized 1-butene at 383 K.[101]

Dicobalt octacarbonyl reacts according to the EAN rule and forms a mononuclear complex when anchored to silica through a cyclopentadienyl ligand.[197] The order of reaction of carbonyl, cluster and silane does not affect the end product which is active for olefin hydroformylation.[197]

Kuznetsov, Kuznetsov, and Ermakov[212] used anchored cobalt carbonylphosphine complexes to hydrogenate cyclododecatriene (313–343 K). When phosphinated silica, pretreated at 673 K, is reacted at room temperature with $Co_2(CO)_8$ ionic complexes, $[(Si^*—OSi(<)PR_2)_2Co(CO)_3]^+[Co(CO)_4]^-$, (see eq 43 for definition of Si*) similar to those formed on phosphinated polystyrene[93] predominate. Small quantities of $[(Si^*—OSi(<)PR_2)_2Co(CO)_3]^+$ also are present. Heating the mixture to 373 K in toluene completely converts the former to the latter. Employment of silica pretreated at 873 K results in the selective formation of the monomeric product at room temperature. The choice of R in the ligand group $Si^*OSi(<)PR_2$ had a significant effect on hydrogenation selectivity. Butyl and cyclohexyl groups enhance monoene formation (93–96%). Phenyl groups produce unselective catalysts.

The surface chemistry and activity of anchored $Rh_6(CO)_{16}$ have been investigated by Knözinger and co-workers.[213-217] Initial infrared studies of $Rh_6(CO)_{16}$ anchored to $Si^*OSi(<)(CH_2)_3PPh_2$, $Si^*OSi(<)(CH_2)_3NHC_6H_{11}$ and $Si^*OSi(<)(CH_2)_3NH(CH_2)_2NH_2$ at 333 K suggested that the supported cluster retained the structure of the metal framework.[213] Subsequent infrared studies using amine ligand groups[214,215] showed that in reality the materials contained $L_xRh(CO)_2$ groups when fully carbonylated and $L_yRh(CO)$ species after decarbonylation, where L are ligand groups and x and y are undefined. The angle between the CO ligands in the former was approximately 100°.[214] X-ray photoelectron spectra supported the assignment of a +1 oxidation state to Rh in these complexes.[214] Exposure of the anchored mononuclear Rh complexes to hydrogen above 370 K caused reduction and aggregation of the metal.[215,216] Aggregation was more rapid when phosphine ligand groups were employed.[216] The rhodium crystallites formed during aggregation were 16–17 and 12–15 Å in diameter on amine-modified and phosphine-modified silica, respectively.[216] These catalysts were active for olefin and alkyne hydrogenation as well as for isomerization at 329–373 K.[215,216] The activity remained essentially constant for several weeks.[215]

Basset et al.[218,219] also studied $Rh_6(CO)_{16}$ anchored to monophosphine-modified silica. When anchored at 353 K in benzene two types of complexes were formed.[218,219] One was identified as consisting of partially oxidized (Rh^+) species of unknown nuclearity with two terminal CO ligands per Rh. This corresponds to the complex of Knözinger.[214,215] The other surface complexes were believed to be rhodium aggregates of unknown nuclearity in a metallic state which when carbonylated had an infrared spectrum which resembled that of the product of $Rh_6(CO)_{16}$ surface bonded to silica, **43**.[176] Anchoring under vacuum at 423 K produced similar results.[218,219] In contrast, anchoring at 298 K gave zerovalent Rh particles which retained the Rh_6 cluster structure.[219] This behavior is similar to that of $Rh_6(CO)_{16}$ on phosphinated polystyrene.[24] Carbonylation of the Rh aggregates produced a complex with an infrared spectrum consistent with the structure $(Si*OSi(<)PPh_2)_3Rh_6(CO)_{13}$.[218,219] Reaction of $Rh_6(CO)_{16}$ with silica containing a tridentate ligand, $Si*OSi(CH_2CH_2PPh_2)_3$, at 298 K produced a similar compound, $Si*OSi(CH_2CH_2PPh_2)_3Rh_6(CO)_{13}$.[218] Catalysts prepared from monophosphine-modified silica were active for benzene hydrogenation, with the catalyst prepared in refluxing benzene 10 times more active than that prepared at 298 K.[218]

Nickel carbonyl was successfully anchored to phosphinated silica by Smith, Basset, and Maitlis.[220] Reaction between carbonyl and support at room temperature produced a monosubstituted $Ni(CO)_3L$ complex, **45** (L is the phosphinated silica), regardless of phosphine group concentration. Heating under vacuum causes loss of all carbonyl ligands at 423 K. During decarbonylation, nickel atoms migrate to the silica surface where they react at room temperature with low pressures of CO to give $Ni(CO)_4$ which combines with the phosphinated silica to regenerate $Ni(CO)_3L$. Anchored $Ni(CO)_2L_2$ could be prepared by reaction of $Ni(CO)_2[PPh_2(CH_2)_2Si(OC_2H_5)_3]_2$ with silica. Heating to 493 K was required for complete decarbonylation, demonstrating the enhanced stability imparted by polydentate anchoring.

Attempts at anchoring bimetallic clusters to silica have been, with one exception, unsuccessful to date. When Gates et al.[101] reacted $[H_2FeRu_3(CO)_{13}]$ with phosphinated silica, $[Ru(CO)_4PPh_2Si(<)OSi*]$ was formed. Contacting $[Fe_2Pt(CO)_8(PPh_3)_2]$ with the same support resulted in decomposition and metal aggregation.[101] Anchored $[HAuOs_3(CO)_{10}Ph_2PSi(<)OSi*]$ was inactive for propylene hydrogenation at 373 K, while isomerizing 1-butene at 383 K.[101]

D. Coating Supports with Liquid-Phase Catalysts

A third method of immobilizing transition-metal carbonyl complexes on inorganic oxides involves dispersing or dissolving the carbonyl in a high-boiling solvent before applying the solution to the support as is done with gas–liquid chromatographic packings. Despite precedents as early as 1939–1948, when sulfuric acid on porous carbon or silica gel was used to polymerize olefin–paraffin mixtures in both gas and liquid phases,[221-224] the extension of the supported liquid-phase catalyst (SLPC) concept to dissolved metal complexes has been relatively neglected. Acres et al.[225] reported the first application of a supported liquid-phase metal complex when they isomerized 1-pentene over ethylene glycol solutions of rhodium trichloride dispersed on Chromosorb W. Noticeable catalyst deactivation was believed due to reduction of the rhodium trichloride (or the active species formed therefrom) by either solvent or reactant.

A supported liquid-phase metal carbonyl catalyst can be prepared by dissolving the metal carbonyl and a desired liquid phase in a volatile solvent. This mixture is then introduced onto the support and allowed to equilibrate. The solvent can then be removed with gentle heating in the presence of flowing inert gas. Careful choice of liquid phase could result in the selective retention of reactants or stabilization of reactive intermediates, enhancing catalytic activity.[226]

Although metal carbonyls have yet to be immobilized in this manner, the general range of behavior of SLPC's has been described by Rony:[227,228] (1) some metal complexes exhibit similar catalytic properties with or without a liquid phase present, (2) in situations where the catalyst is active both with and without a liquid phase, the SLPC generally displays greater activity, (3) in some instances, the liquid phase is necessary for any catalytic activity to be observed, and (4) there is some correlation between optimum liquid loading and intrinsic activity. The question of whether the catalyst is actually composed of a transition-metal complex dissolved in solvent coated on the support or a transition-metal complex chemically attached to the support with a thin film of liquid on the surface has not been resolved.[227] This could be a problem with metal carbonyls which do react with surface hydroxyl groups.[28,122]

The presence of a liquid phase may increase transport limitations, resulting in diffusion-limited reaction rates. Rony[229] suggested that the catalyst activity depends on whether the dispersed liquid forms thin films or liquid plugs in the pores. For a given system, as higher liquid loadings are employed, diffusion limitations begin to counteract increases in catalyst concentration, resulting in specific catalytic activity maxima. Higher liquid loading eventually leads to pore flooding with diminished activity due to long liquid diffusion paths. Because this model did not explain how diffusivities are affected by liquid loading and pore structure for nonideal porous supports, Chen and Rinker[230] proposed a model based on the dusty gas equation which treats the pore-size distribution of the dry support with nonuniform liquid-phase distribution.

E. Synthesizing Metal Carbonyls within the Porous Structure of the Support

A logical extension to immobilizing techniques involves synthesis of metal carbonyls in zeolite supercages. Equilibration of the zeolite with an aqueous solution of a salt of the metal of interest is followed by washing to remove excess electrolyte and drying. The carbonyl is generated by treatment in an autoclave with carbon monoxide and hydrogen (1:1).[231,232] Hydrogen facilitates the formation of a stable complex between carbon monoxide and the metal atoms in the zeolite framework.[231] Similar results can be obtained by pretreating the ion-exchanged zeolite with acetic acid followed by CO treatment.[233,234]

Attempts to entrap rhodium carbonyl complexes to date have not given an unambiguous identification of the resulting carbonyl complex. Although early infrared spectra indicated the presence of terminal and bridging carbonyl groups,[231] later infrared and ESCA studies suggest formation of a multicarbonyl complex, $Rh(CO)_x$, where x is probably 2.[232-234] The overall reaction mechanism for Rh^{3+} reduction by carbon monoxide in solution appears to be operative in zeolites[232] (eq 46).

$$Rh^{3+} + CO \rightarrow [Rh(CO)]^{3+}$$

$$[Rh(CO)]^{3+} + 2CO + H_2O \text{ (or OH groups)} \rightarrow [Rh(CO)_2]^+ + CO_2 + 2H^+ \quad (46)$$

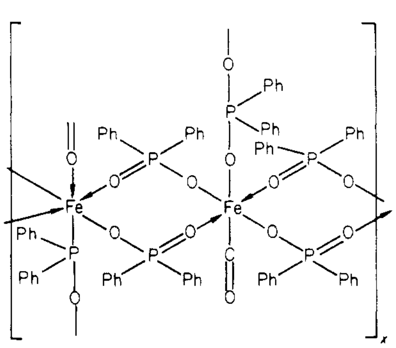
The second step is slow, hindered at low temperature, and does not occur in the absence of water or OH groups.[232]

Mantovani, Palladino, and Zanobi[231] described the effectiveness of a $Rh^I(CO)_2/NaY$ catalyst for liquid-phase hydroformylation. With an α-olefin substrate, a high selectivity for aldehyde formation (~95%) and a normal:branched ratio (1:1.2) similar to that for the homogeneous hydroformylation of olefins using rhodium carbonyl clusters were observed. With an α,ω-diolefin substrate the zeolite-entrapped catalyst produced monoaldehydes (60%) in preference to dialdehydes (40%). Dialdehyde production is favored with homogeneous rhodium catalysts. Catalyst stability was acceptable, with little loss of metal or change in metal carbonyl composition on repeated use.

F. Copolymerizing Metal Carbonyls with Inorganic Monomers

Podall and Iapalucci[235] found that the metal carbonyls could be copolymerized with inorganic monomers such as diphenylphosphinic acid to yield soluble and insoluble transition-metal coordination polymers. Carbonyls of groups 6,[235,236] 7,[236] and 8[235,236] were used in this procedure. Phenylsulfinic acid also could be used as a monomer.[236]

The structure and thermal decomposition of metal carbonyl copolymers was investigated by Korshak and co-workers. Infrared data[237] suggested that insoluble copolymers of $Fe(CO)_5$ and diphenylphosphinic acid had a three-dimensional structure, **58**. Polymers synthesized from this monomer and group 6 or 7 metal carbonyls were linear and lost all carbonyl ligands, **59**.



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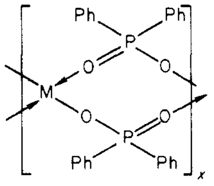
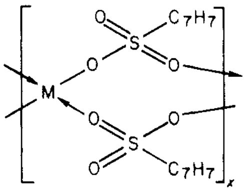


59, M = Co, Mo, W, Mn

Copolymers of p-toluenesulfonic acid and metal carbonyls had similar structures, with $(C_7H_7)SO_3$ replacing Ph_2PO_2 in the matrix **60**.[238] Polymers made with diphenylarsenic acid are comparable to their phosphinic acid counterparts.[239,240] Thermal stability depends on both the carbonyl and inorganic monomer used.[241] For any given metal carbonyl, thermal stability follows the order S > P > As with respect to acid-forming elements. These materials have yet to be tested for catalytic activity.



60, M = Mn, W, Fe

IV. Concluding Remarks

Immobilized transition-metal carbonyls and derived materials catalyze a wide variety of reactions. Originally conceived as a solution to the separation problem associated with homogeneous catalyst systems, metal carbonyl immobilization can lead to the preparation of novel species having unusual catalytic properties of their own. To date, a few systems have been studied extensively; others have received only cursory treatment. The interest in olefin and carbon monoxide reactions together with the fundamental nature of the approach reinforces expectations that the study of these hybrid catalysts will continue to grow.

Methods have been developed whereby catalytically active carbonyl complexes can be anchored with retention of their molecular nature. These techniques also are useful for stabilizing catalytically active but unstable species generated in situ. In addition, unique carbonyl complexes having no known unsupported counterparts can be prepared, studied, and utilized. Heretofore the majority of anchoring systems employed phosphine linkages; further development of macrocyclic chelating and other nonlabile ligands for immobilization will enhance the usefulness of these materials.

Decarbonylation and/or oxidation of metal carbonyls bound directly to the support provides a new, convenient route to highly dispersed metals and metal oxides. This preparative method is particularly attractive because low temperatures are employed and materials which could adversely affect the catalyst (e.g., Cl^-, H_2O) are absent from the procedure. Bimetallic clusters can be used to prepare selectively promoted metals or alloy analogues on the surface.

Work currently in progress with immobilized metal carbonyls will do much to identify the salient features which govern their catalytic activity for a number of reactions. While infrared spectroscopy will continue to be the most widely employed technique in this effort, other sophisticated methods of investigating surface species will be used with increasing frequency.[242,243] The emerging understanding of immobilized transition-metal carbonyls raises the possibility of employing them as one means of realizing the perennial aspirations of catalytic chemists and engineers to develop the capability of designing reproducible and efficient catalysts.

V. Addendum (November 1980)

Since the original submission of this manuscript, a number of new, pertinent studies have come to our attention. These are summarized below to indicate recent developments and current research directions.

Whitehurst[273] recently reviewed catalysis by immobilized transition-metal complexes. General synthetic principles are discussed and areas for further research are suggested.

A. Polymer Supports

Tatarsky, Kohn, and Cais[274] immobilized (phenanthrene)chromium tricarbonyl on phosphinated polystyrene to give Ⓟ $-1,4-C_6H_4CH_2PPh_2Cr(CO)_2$phen. Scanning electron microscopy studies showed uniform distribution of chromium in beads with large pores (1.3×10^4 nm), with only limited penetration into beads with smaller pores ($<5 \times 10^2$ nm).

Vatanatham and Farona[275,276] reacted $Mo(CO)_6$ with cross-linked polystyrene to obtain a heterogeneous molybdenum catalyst with no carbonyl ligands. The product catalyzed [2 + 2] cycloadditions of phenylacetylene in the presence of CO (523 K, 3.4×10^6 N/m^2) to give isomers of triphenyl(Dewar benzene) as well as bicyclo and tetracyclo compounds containing carbonyl groups.

Using polymer-anchored $RuCl_2(CO)_2(PPh_3)_2$ in the hydrogenation of (*Z,Z*)-1,5-cyclooctadiene, Pittman and Wilemon[277] found the selectivity for cyclooctene over cyclooctane increased with the P/Ru ratio for a given phosphine loading (PL). At lower P/Ru ratios, the selectivity increased with PL (for P/Ru = 3–6; PL = 14, 82.4% selectivity; PL = 82.8, 53.2%). Presumably this reflects hindered chain mobility due to metal-centered cross-links and decreased concentration of "effective" phosphine ligands.

Tang, Paxson, and Kim[278] immobilized $Co_2(CO)_8$ on a macroreticular sulfonated styrene–divinylbenzene resin which had been previously reacted with bifunctional aminophosphines (e.g., $[Me_2N]_3P$, $[Me_2NCH_2CH_2O]_3P$). In the hydroformylation of 1-hexene (393 K, 8.37×10^6 N/m^2, CO/H$_2$ = 1) aldehydes (~99%) were the primary products. The normal-to-branched ratio was approximately 2.5.

Pittman, Honnick, and Yang employed polymer-anchored $RhH(CO)(PPh_3)_2$ catalysts for the hydroformylation of methyl methacrylate[279] and allyl alcohol.[280] In methyl methacrylate hydroformylation, the bound catalysts were less active but more selective for branched product formation (75% vs. 57% at 353 K, 1.38×10^6 N/m^2) than their homogeneous counterparts at comparable temperatures, pressures, and P/Rh ratios.[279] At similar P/Rh ratios, catalysts with higher phosphine loadings gave more branched products (at P/Rh ~20; PL = 40, 84% branched product; PL = 29, 68%).[279] In the hydroformylation of allyl alcohol, the normal-to-branched ratio was relatively insensitive to P/Rh ratio changes as well as pressure for both homogeneous and bound catalyst; increases in temperature favored normal aldehyde production.[280] Anchoring the complex favored hydroformylation over hydrogenation at high H_2/CO ratios.[280]

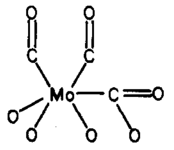
Gates and co-workers[281,282] have continued their study of anchored bimetallic clusters. Polymer-immobilized tetranuclear clusters with open butterfly structures (e.g., [$ClAuOs_3(CO)_{10}Ph_2P$–Ⓟ] and [$Co_2Pt_2(CO)_8(Ph_2P$–Ⓟ$)_2$]) were active for ethylene hydrogenation (≤373 K, 1×10^5 N/m^2); polymers incorporating clusters with closed tetrahedral structures (e.g., [$HAuOs_3(CO)_{10}Ph_2P$–Ⓟ] and [$H_2PtOs_3(CO)_{10}(Ph_2P$–Ⓟ $)_2$]) were inactive.[281] This difference was attributed to the inherent presence of active sites with coordinative unsaturation in the former. Bond cleavage would be required to induce such catalytic activity in clusters of the latter type.[281] Polymer-bound [$RuPt_2(CO)_5(Ph_2P$–Ⓟ $)_3$] and [$Fe_2Pt(CO)_8(Ph_2P$–Ⓟ $)_2$] were active for ethylene hydrogenation (343–373 K, 1×10^5 N/m^2). The former was stable for ~4400 turnovers, while the latter decomposed into mononuclear and/or aggregated metal species.[282]

B. Inorganic Supports

1. Surface-Bonded Carbonyls

Infrared and EPR studies of surface-bonded $Cr(CO)_6/Al_2O_3$ (pretreated at 723 K) performed by Kazusaka and Howe[283] showed formation of only monomeric subcarbonyl species during decarbonylation. Outgassing at 373 K for 1 h essentially completed decarbonylation.

The surface structure and catalytic chemistry of $Mo(CO)_6/Al_2O_3$ continue to attract interest. Laniecki and Burwell[284] showed that $Mo(CO)_6$ initially physically adsorbs on hydroxylated Al_2O_3 (HA, pretreated at 423 K), partially dehydroxylated Al_2O_3 (PDA, 723 K), and dehydroxylated Al_2O_3 (DA, 1273 K) at 298 K and subsequently reacts with the surface of PDA and DA to form $Mo(CO)_5$ads. The structure of $Mo(CO)_3$ads on PDA and DA was hypothesized to include contributions of the form



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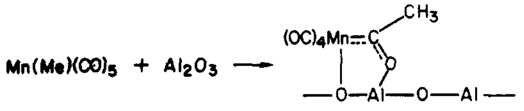
or related surface structures with carboxylate groups.[284]

The proposed structure on HA was $(\sigma\text{-OH})_3Mo(CO)_3$.[284] Kazusaka and Howe[285] reported an infrared study of $Mo(CO)_6/Al_2O_3$ under various conditions. They suggested that the $Mo(CO)_3$ surface species was a mixture of a mononuclear complex, $(X)(CO)_2Mo(CO)Al$, and a binuclear entity containing two bridging carbonyl ligands interacting with Lewis acid sites, $(X)(CO)_2Mo[(CO)Al]_2Mo(CO)_2(X)$. Here (X) represents surface oxide or hydroxyl groups. At present, it is not possible to choose between the two proposed structures for $Mo(CO)_3$ads. Defosse, Laniecki, and Burwell[286] found catalysts derived from $Mo(CO)_6$/PDA to be more catalytically active for isotopic exchange between alkanes and deuterium than any previously reported oxide-type materials. Metal-like Mo generated from $Mo(CO)_6$/DA was also active.[286] Gallezot et al.[287] decomposed $Mo(CO)_6$ in 10.9% PtNaHY zeolite to produce a very active hydrogenolysis catalyst for which there was evidence of Pt–Mo associations.

Surface-bonded tungsten carbonyl studies have also been pursured. Kazusaka and Howe[283] found the surface chemistry of $W(CO)_6$/PDA to resemble that of $Mo(CO)_6$/PDA. Bimolecular species in which bridging carbonyls were presumed to coordinate to support Lewis acid sites were proposed. Shapley et al.[288] found $(\eta^5\text{-}C_5H_5)_2W_2(CO)_6/Al_2O_3$ inactive for CO reduction.

Surface-bonded group 7 carbonyls have been the subject of several recent studies. Burwell et al.[289] found methyl migration to be involved in the initial adsorption of $Mn(Me)(CO)_5$ on Al_2O_3 (eq 47). Vanderspurt[290] has discussed the $Re_2(CO)_{10}$/glass hydrogenation catalyst.



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The properties of surface-bonded iron carbonyls have received further investigation. Basset and co-workers[291-293] decomposed (473 K) $Fe(CO)_5$ or $Fe_3(CO)_{12}$ on dehydroxylated inorganic supports to produce catalysts active in the Fischer–Tropsch reaction. A high selectivity for low molecular weight olefins was observed. The selectivity was associated with low activity, was not constant with time, and was attributed to the initial small, zerovalent metal particles (<150 nm) deposited from the precursor carbonyls.[291,292] On hydroxylated supports, oxidation accompanied decarbonylation.[291] Alper and Gopal[294] found $Fe_3(CO)_{12}/Al_2O_3$ to be active for reducing nitroamines. Guczi et al.[295] found $Fe_3(CO)_{12}/SiO_2$ (decarbonylated at 370 K in He or H_2) to be active for CO reduction. Bimetallic catalysts were prepared by simultaneous decomposition (above 370 K) of $Fe_3(CO)_{12}$ and $Ru_3(CO)_{12}$.[295] Ballivet-Tkatchenko et al.[296] demonstrated that while $Fe_3(CO)_{12}$ entrapped within Y-type zeolites is inactive for CO reduction, it is a precursor for the formation of small, active metal particles in the zeolite supercage.

Guczi et al.[295] found that decarbonylating $Ru_3(CO)_{12}/SiO_2$ (or a mixture of $Ru_3(CO)_{12}$ and $Fe_3(CO)_{12}$) in helium produced highly dispersed metal crystallites which were more active for CO reduction than those produced from hydrogen reduction of the supported clusters. This was ascribed to the carbon content of the catalysts decomposed in helium which acted to prevent metal agglomeration. Kaesz et al.[297] described the decarbonylation of $Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, and $[NEt_4][H_3Ru_4(CO)_{12}]$ on Cab-O-Sil. Kuznetsov, Bell, and Yermakov[298] found the extent of adsorption of $Ru_3(CO)_{12}$, $\alpha\text{-}H_4Ru_4(CO)_{12}$, and $Ru_6C(CO)_{17}$ on Al_2O_3 depended on the degree of support hydroxylation. Interactions between the carbonyl ligands and surface hydroxyl groups and/or Lewis acid sites were proposed. Three surface structures, independent of original cluster, were hypothesized: $[Ru(CO)_2X_2]_n$, $[Ru(CO)_3X_2]_n$, and $[Ru(CO)_4X_2]_n$. Here X is a surface oxygen atom and n is undefined. Complete decarbonylation was believed to lead to possible formation of surface aluminates. Ballivet-Tkatchenko et al.[296] found $Ru_3(CO)_{12}$/Y-type zeolite to be a precursor for Fischer–Tropsch catalysts.

Basset et al.[299] described the oxidative addition of surface (SiOH) groups to $Os_3(CO)_{12}$ to give $[HOs_3(CO)_{10}(OSi{\equiv})]$ at 423 K. At 473 K, physically adsorbed $Os_3(CO)_{12}$, $H_2Os_3(CO)_{10}$, and $Os_6(CO)_{18}$ form Os^{2+} species of the type $[Os(CO)_2(OSi{\equiv})_2]_n$ or $[Os(CO)_3(OSi{\equiv})_2]_n$ (stable to 573 K) resembling those proposed for Ru.[298] Similar behavior was observed for these clusters on alumina[299] and for $Os_3(C_6H_8)(CO)_{10}/Al_2O_3$.[300] The latter catalyzed ethylene hydrogenation (313–363 K, 1×10^5 N/m^2).[300] Surface-bonded $Os_3(CO)_{12}/Al_2O_3$ was shown active for the reduction of CO.[288]

As with other metal carbonyls,[28,152,180] Watters, Schneider, and Howe[301] found alumina to be a more reactive support for the decarbonylation of $Co_3(CO)_4CCH_3$ than silica or NaY zeolite.

Ichikawa and Shikakura[302,303] decarbonylated (423–473 K) $Rh_4(CO)_{12}$, $Rh_6(CO)_{16}$, $Ir_4(CO)_{12}$, and $[Pt_3(CO)_3(\mu\text{-}CO)_3]_n{}^{2-}$ (n = 3–5) on MgO, La_2O_3, and ZrO_2 to produce catalysts more active and selective for methanol and ethanol production from CO/H_2 (473 K, 1×10^5 N/m^2) than those prepared from salt impregnation. Infrared spectra suggested interactions between the carbonyl ligands and surface hydroxyl groups to form $CO_2{}^{2-}$ and $CO_3{}^{2-}$ species.

Surface bonded $(\eta^5\text{-}C_5H_5)WOs_3(CO)_{12}H$ and $(\eta^5\text{-}C_5H_5)MoOs_3(CO)_{12}H$ were compared with $Os_3(CO)_{12}/Al_2O_3$ for CO reduction with no observable differences.[288] This was explained by fragmentation of the surface-bonded clusters during activation or poisoning of the group 6 metal atom by carbon from the cyclopentadienyl ligands.

2. Anchored Carbonyls

Metal carbonyls anchored to inorganic supports with bifunctional ligands have received further study. Awl et al.[304] anchored $Cr(CO)_6$ to the ladder polymer polyphenylsilsequioxane, **49**, to prepare $[{\equiv}Si\text{-}1,4\text{-}C_6H_4Cr(CO)_3]$. The catalyst was more stable at 453–473 K than $Cr(CO)_6$/polystyrene and active for the stereoselective hydrogenation of methyl sorbate to *cis*-3-hexenoate (equation 8). Loss of activity associated with leaching of $Cr(CO)_3$ moieties occurred with recycling.

Evans and Gracey[305] anchored metal clusters containing bridging ligands (e.g., $(\mu\text{-H})M_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2Si(OMe)_3]$, M = Ru, Os) to SiO_2, $\gamma\text{-}Al_2O_3$, TiO_2, SnO_2, ZnO, and MgO in an attempt to preserve the metal framework during immobilization. The resulting compounds, $(\mu\text{-H})M_3(CO)_{10}[\mu\text{-}SCH_2CH_2CH_2Si(OMe)_{3-x}(\text{oxide})_x]$, also could be prepared from $M_3(CO)_{12}$ and supports pretreated with

$HSCH_2CH_2CH_2Si(OMe)_3$. Similar results were observed for $Co_3(CO)_9(\mu_3\text{-}CSiCl_3)$.

Gates et al.[282] found $H_2Os_3(CO)_{10}$ anchored to phosphinated silica active for 1-butene and 1-hexene isomerization (298–373 K, 1×10^5 N/m^2). The catalyst was unstable due to presumed formation of an olefin complex, $[HOs_3(CO)_9(vinyl)PPh_2Si^*]$.

Studer and Schrader[306] used $[Ir_4(CO)_{11}PPh_2Si^*]$ and $[Ir_4(CO)_{10}(PPh_2Si^*)_2]$ to hydrogenate ethylene (298–473 K, (1–1.5) $\times 10^5$ N/m^2). The former was inactive in the Fischer–Tropsch synthesis (298 K, 1×10^5 N/m^2).

3. Carbonyls Synthesized within Zeolites

Verdonck, Schoonheydt, and Jacobs[307] treated $Ru(NH_3)_6^{3-}$-exchanged faujasite-type zeolites in synthesis gas (523 K, 1×10^5 N/m^2, $CO/H_2 = 1$) to obtain a water gas shift catalyst active at low temperatures (473–573 K). Infrared spectra indicated the presence of two Ru-CO species: $Ru^{II}(NH_3)(CO)$ and $Ru^{I}(NH_3)(CO)_2$.

Gelin, Ben Taarit and Naccache[308] entrapped $Rh^{I}(CO)_2$ and $Ir^{I}(CO)_3$ species within zeolites by CO treatment of RhY and IrY at 433 K. The products catalyzed methanol carbonylation in the presence of a CH_3I promoter (403–433 K).

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