

*Title:* **Heterogenization of Homogeneous Catalysts: The Effect of the Support**

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*Submitted to:* DOE Office of Scientific and Technical Information (OSTI)

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## Heterogenization of Homogeneous Catalysts: The Effect of the Support

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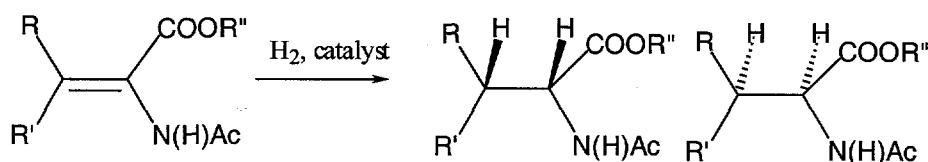
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### Abstract

We have studied the influence of placing a soluble, homogeneous catalyst onto a solid support. We determined that such a 'heterogenized' homogeneous catalyst can have improved activity and selectivity for the asymmetric hydrogenation of enamides to amino acid derivatives. The route of heterogenization of  $\text{RhDuPhos}(\text{COD})^+$  cations occurs via electrostatic interactions with anions that are capable of strong hydrogen bonding to silica surfaces. This is a novel approach to supported catalysis. Supported  $\text{RhDuPhos}(\text{COD})^+$  is a recyclable, non-leaching catalyst in non-polar media. This is one of the few heterogenized catalysts that exhibits improved catalytic performance as compared to its homogeneous analog.

### Background and Research Objectives

Our goal was to study the influence of a surface as a ligand for a homogeneous catalyst. We began by studying a variety of "heterogenized" homogeneous hydrogenation catalysts, and arrived at the discovery of a catalyst system that has improved reactivity, and in some cases, improved selectivity for the asymmetric hydrogenation of enamides to prepare chiral amino acid derivatives:

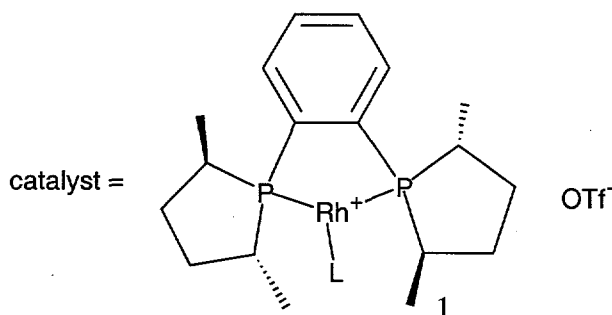


I

II

Addition of  $\text{H}_2$  across the double bond of the enamide can occur on either the lower or upper face, producing the two enantiomers I and II shown above. It is known that an asymmetric catalyst can alter the facial preference for addition of  $\text{H}_2$  resulting in an excess of one enantiomer over the other, termed the enantiomeric excess, ee (see table below). This is

desirable for the production of optically active, chiral precursors for the synthesis of biomolecules or pharmaceuticals.



Asymmetric catalysts such as diphosphenorhodium cations as shown above are known to catalyze the enantioselective hydrogenation of a variety of unsaturated substrates. In general, when these soluble catalysts are anchored to a support, either their activity, or their enantioselectivity, or usually both, declines precipitously. The focus of this project was to investigate the influences of the support on this chemistry, and use these effects as a probe of the local structure of surface-bound catalysts.

### **Importance to LANL's Science and Technology Base and National R&D Needs**

This proposal has helped to maintain and further develop our capabilities in the synthesis and characterization of complex materials, and the study of reactions in interfacial systems. These areas of research are important to the Laboratory and its missions. In addition, research in this area is important to the chemical process and pharmaceutical industries.

### **Scientific Approach and Accomplishments**

Approaches to the problem of "heterogenizing" homogenous catalysts have varied widely. Some approaches to this problem range from the heterogenization on solid supports by covalent attachment of a ligand to a solid support, [1] to the use of fluorous biphasic systems [2] and supporting catalysts on thermomorphic polymers [3]. The discovery seven years ago of the M41S class of mesoporous materials [4], set off an explosion of research on these versatile materials, as evidenced by the many reviews in this area [5].

The M41S materials have been featured in acid catalysis, polymerization catalysis, oxidation and palladium cross coupling schemes, to name a few catalytic applications [6]. Our initial studies were directed at covalent attachment of ligands to silicate surfaces such as MCM-41. Then by varying the diameter of the pore in a systematic fashion, we hoped to be able to learn much about the interactions of a catalyst with its support. We were unable to observe any enantioselective catalysis using this approach, and so we began to investigate other approaches using a surface as a replacement for 'L' in the figure above.

We have found an unusual mode of heterogenizing homogeneous catalysts. Good hydrogen bond acceptors, such as triflate anion (trifluoromethanesulfonate, OTf<sup>-</sup>), bind quite strongly to the Si-OH groups present on silica surfaces, such as those of MCM-41, or of ordinary silica. We have bound catalytically active RhDuPhos(COD)<sup>+</sup> (COD= cyclooctadiene) to the surface by electrostatic interactions with surface-bound triflate anion. We describe below a few of the details regarding the properties and catalysis of the heterogenized catalyst RhDuPhos(COD)OTf on MCM-41 and silica. In addition to the information reported herein, we have characterized these materials using x-ray diffraction, porosimetry, and elemental analysis.

The use of relatively poor hydrogen bond acceptors, such as  $\text{BAR}_F^-$  (tetrakis(pentafluorophenyl)borate) result in catalysts that are less strongly bound to the catalyst. Indeed, the rhodium cation may be removed from the surface-bound triflate by anion exchange of the triflate with  $\text{BAR}_F^-$ . The influence of hydrogen bonding of surface-bound  $\text{RhDuPhos(COD)}^+ \text{OTf}^-$  with and without added  $\text{BAR}_F^-$  are supported by P-31 (figure 1) and F-19 (figure 2) nuclear magnetic resonance spectroscopic studies shown below:

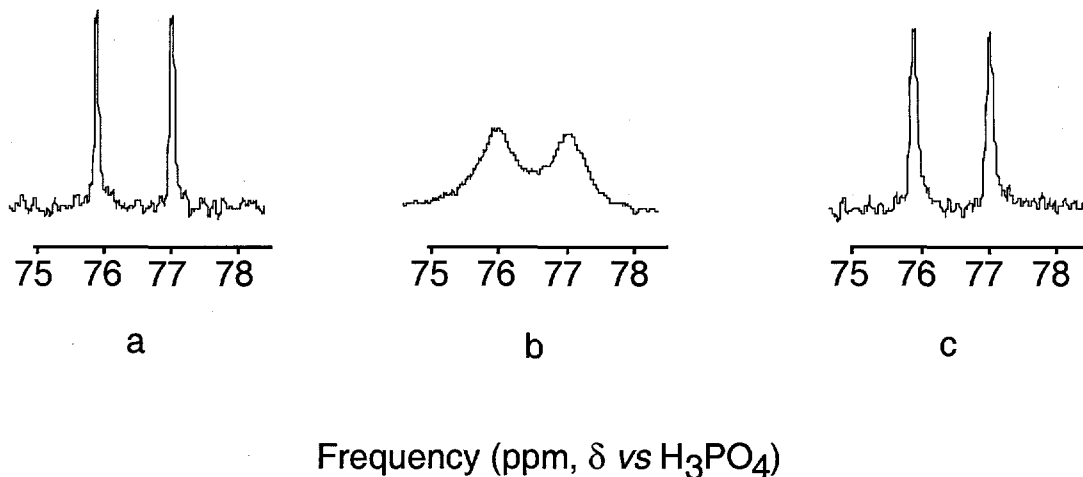


Figure 1.  $^{31}\text{P}$ NMR (a)  $[(R,R)\text{-Me-(DuPHOS)Rh(COD)}]\text{OTf}$  in  $\text{CH}_2\text{Cl}_2$  (b) after addition of MCM-41 (c) after addition of  $\text{NaBAR}_F^-$

The P-31 spectrum of  $\text{RhDuPhos(COD)}^+ \text{OTf}^-$  in solution (a) exhibits narrow resonances because of rapid tumbling in solution. When MCM-41 is introduced to this sample, the orange rhodium complex is adsorbed to the surface, reducing its ability to tumble freely, resulting in the broadening of the resonances (b). When  $\text{NaBAR}_F^-$  is introduced,  $\text{RhDuPhos(COD)}^+$  is released from the surface-bound triflate, the solution becomes orange above the white solid, and the narrow NMR lineshapes (c) indicate the cation is free in solution.

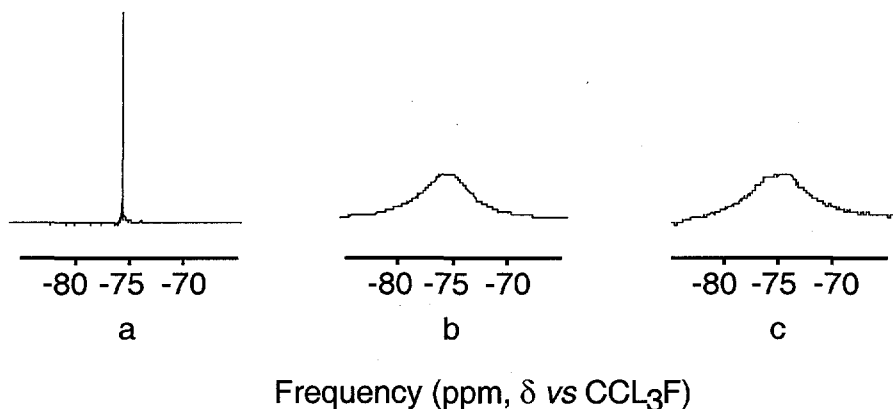


Figure 2:  $^{19}\text{F}$  NMR (a)  $[(R,R)\text{-Me-(DuPHOS)Rh(COD)}]\text{OTf}$  in  $\text{CH}_2\text{Cl}_2$  (b) after addition of MCM-41 (c) after addition of  $\text{NaBAR}_F^-$ .

The F-19 NMR spectra of these solutions is shown in Figure 2, and is consistent with this interpretation. The fluorine spectrum of RhDuPhos(COD)<sup>+</sup> OTf in solution is narrow, but upon introduction of the solid MCM-41, the lineshape broadens substantially, indicating the triflate is bound to the support. Upon introduction of BAr<sub>F</sub>, a poorer hydrogen bond acceptor, the triflate spectrum remains broad, indicating the triflate remains bound to the surface.

The heterogenized catalyst [(R,R)-Me-(DuPHOS)Rh(COD)]OTf/MCM-41 shows high selectivity in the hydrogenation of enamines (Table 1). In hexane, the homogeneous catalyst [(R,R)-(DuPhos)Rh(COD)]OTf hydrogenated substrates more slowly, often with poorer selectivity under the same conditions. This points to a positive influence of the support on the activity and selectivity of the catalysis. One report of such a positive influence on activity and selectivity for heterogenized catalysts has appeared since we began our research [7], but, in general the opposite is true [8]. The catalyst also shows a similar enhancement, but the loading of the catalyst on this silica that has a much lower surface area and number of surface silanol sites so that a larger amount of [(R,R)-Me-(DuPhos)Rh(COD)]OTf/SiO<sub>2</sub> must be used to achieve a similar Rh loading as the MCM-41 supported material.

Table 1: Hydrogenation Results. Enantiomeric excess (ee) is the quantity (I-II/I+II)

Substrate	Support	Solvent	Temp	Time	Conv.	ee
<b>A</b>	MCM-41	Hexanes	R.T. <sup>a</sup>	0.5 hr	>99%	99%
<b>A</b>	SiO <sub>2</sub> <sup>c</sup>	Hexanes	R.T.	0.5 hr	>99%	>99%
<b>A</b>	none	Hexanes	R.T.	0.5 hr	7%	>99%
<b>A</b>	none	MeOH	R.T.	0.5 hr	>99%	>99%
<b>B</b>	MCM-41	Hexanes	R.T.	24 hr	>99%	99%
<b>B</b>	MCM-41	Hexanes	40 °C	24 hr	>99%	99%
<b>B</b>	SiO <sub>2</sub>	Hexanes	R.T.	24 hr	>99%	>99%
<b>B</b>	none	Hexanes	R.T.	24 hr	62%	45%
<b>B</b>	none	Hexanes	R.T.	24 hr	1%	92% <sup>c</sup>
<b>B</b>	none	MeOH	R.T.	24 hr	>99%	99%
<b>C</b>	MCM-41	Hexanes	R.T.	24 hr	>99%	79%
<b>C</b>	SiO <sub>2</sub>	Hexanes	R.T.	24 hr	>99%	77%
<b>C</b>	none	Hexanes	R.T.	24 hr	60%	71%

The results indicate that there is little or no difference for the hydrogenation of enamides using either MCM-41 or silica bound catalysts. This suggests that the size of the pore (20 Å for MCM-41, ca. 100 Å for the silica we used) is not important. The observation that the rates of hydrogenation of supported catalyst in hexane are higher than those found for the homogeneous case indicate that the surface has a positive influence on the reaction. The enhancement of rate and enantioselectivities suggest that this is due either to the presence of the surface influencing substrate binding, or enhancement of the rate of hydrogenation of bound substrate. Additional experiments at different temperatures and at different hydrogen pressures are in progress that may lead to a description of how the surface is influencing the rates of the catalytic reactions, and this may lead to a better description of how the catalyst interacts with the silica surface.

We have demonstrated that the MCM-41 bound catalyst does not leach under these conditions, and so the activity we observe is only from surface bound catalyst. We also demonstrated that the catalyst is recyclable. After three or four cycles, the rate of reaction slows appreciably. P-31 NMR spectroscopy indicated that the RhDuPhos(COD) cation was intact, and so the deactivation was not due to catalyst decomposition. Thermal analysis indicated that the pores of the MCM-41 catalyst had become filled with organics. Extraction of the catalyst with methanol proved that the catalyst contained 65 wt. percent hydrogenation product.

Washing of the catalyst with hexane was ineffective in removing the product from the pores, and so was ineffective in reactivating the catalyst. Washing with toluene did remove the material from the pores without leaching the catalyst, and the catalyst recovered its activity.

Our results indicate that cationic asymmetric hydrogenation catalysts such as RhDuPhos(COD) cation can be bound to silanol surfaces by way of hydrogen bond accepting counterions. These catalysts can be more active than the homogeneous analogs, and more selective. These catalysts are recyclable and do not leach RhDuPhos(COD)<sup>+</sup> in non-polar solvents that cannot compete with triflate for hydrogen bonding sites on the silica. The heterogenized homogeneous catalysts RhDuPhos(COD)OTf/MCM-41 (or supported on silica) is one of the first examples of a recyclable catalyst that exhibits better activity and selectivity than its homogeneous counterpart.



## Publications

1. de Rege, F. M.; Morita, D. K.; Tumas, W.; Ott, K. C. Transition metal catalysts supported on mesoporous materials. Book of Abstracts, 216th ACS National Meeting, Boston, August 23-27 (1998).
2. de Rege, F. M.; Morita, D. K.; Tumas, W.; Ott, K. C. Asymmetric hydrogenation catalysts supported on mesoporous materials. Organometallic Chemistry Gordon Research Conference, Salve Regina University, Newport, Rhode Island, July 26-31, 1998. "[*(R, R)*-Me-DuPHOSRh(COD)]OTf/MCM-41: A Heterogenized Asymmetric Catalyst", F. M. de Rege, D. K. Morita, G. H. Brown, R. D. Broene, W. Tumas, and K. C. Ott, (to be submitted to *J. Am. Chem. Soc.*).
3. "Heterogenization of RhDuPHOS(COD)<sup>+</sup> for Asymmetric Hydrogenation of Enamides", F. M. de Rege, D. K. Morita, G. H. Brown, R. D. Broene, W. Tumas, and K. C. Ott, (to be submitted to *Proc. Organic Reactions Soc.*).

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