Temperature-Controlled Catalyst Recycling: New Protocols Based upon Temperature-Dependent Solubilities of Fluorous Compounds and Solid/Liquid Phase Separations

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1 Introduction .................................. 68
2 General Considerations ....................... 70
3 First Test System: Thermomorphic Lewis Base Catalysis ............... 71
4 First Test System with Fluorous Support: Leaching Data .................. 74
5 Second Test System: Thermomorphic Metallacycle Catalysts ........... 76
6 Third Test System: Thermomorphic Rhodium Catalysts .................. 80
7 Results from Other Investigators .......... 83
7.1 Recycling Without Supports ................. 83
7.2 Recycling With Supports .................... 86
8 Summary ...................................... 87
References ..................................... 88

Abstract The absolute solubilities of fluorous compounds can be tailored by varying the lengths of the \((\text{CF}_2)_{n-1}\text{CF}_3 (\text{R}_m)\) segments. Many such compounds exhibit immense solubility increases in organic solvents or neat liquid reactants upon heating. Suitably designed fluorous catalysts can therefore be employed under homogeneous conditions at elevated temperatures, and recovered by solid/liquid phase separation at lower temperatures. Expensive fluorous solvents are avoided. Fluorous supports can be used to aid the recovery of small catalyst quantities, and render phase separation more efficient. Other design considerations, such as the nature of the catalyst rest state, are analyzed. Examples from the authors' laboratory arising from a multi-investigator project on multiphase catalysis are emphasized. These include phosphine-catalyzed additions, metallacycle syntheses and reactions, and rhodium-catalyzed hydrosilylations. Results from other laboratories are briefly described.

Keywords Fluorous · Hydrosilylation · Palladacycles · Phosphines · Recycling · Rhodium · Teflon® · Thermomorphic
1 Introduction

Following the publication of the first example of fluorous biphase catalysis by Horváth and Rábai in 1994 [1], the immediate focus was to develop catalysts that would exhibit very biased partition coefficients with respect to fluorous and organic solvents. Such liquids are normally immiscible at room temperature. This was done by attaching “ponytails” of the formula \( (\text{CH}_2)_m(\text{CF}_2)_{n-1}\text{CF}_3 \) (abbreviated \((\text{CH}_2)_m\text{Rf}_n\)), including arrays emanating from silicon atoms [2]. Catalysis was then effected at elevated temperatures, where fluorous and organic solvents are commonly miscible, with product/catalysis separation at the low-temperature two-phase limit.

In this initial burst of activity, Hughes synthesized the fluorous ferrocenes \( (\eta^5-\text{C}_5\text{H}_4(\text{CH}_2)_2\text{Rf}_n)_2\text{Fe} \) \( (1-\text{Rf}_n; \ n = 6, 8, 10) \), and commented on their solubilities [3]. The complex with the shortest ponytail, \( 1-\text{Rf}_6 \), dissolved readily in common nonpolar organic and fluorous solvents. Complex \( 1-\text{Rf}_8 \) was less soluble, but appreciable concentrations could still be achieved. The complex with the longest ponytail, \( 1-\text{Rf}_{10} \), “dissolved easily in diethyl ether, moderately in hexanes, and sparingly in chloroform, acetone, and toluene at room temperature, although it dissolved easily in these solvents hot”. A 0.1 M solution of \( 1-\text{Rf}_{10} \) in \( \text{CF}_3\text{C}_6\text{F}_{11} \) (perfluoro(methylcyclohexane)) could be realized at 40 °C, but only a 0.003 M solution at room temperature. This represents a ca. 33-fold concentration increase over less than 20 °C. The corresponding solubilities of \( 1-\text{Rf}_8 \) and \( 1-\text{Rf}_6 \) at room temperature were 0.06 and > 0.09 M.

The solubilities of other fluorous compounds were subsequently noted to greatly depend upon the lengths of the perfluoroalkyl segments. A few researchers remarked on the highly temperature-dependent solubilities, which in at least some cases were discovered during efforts to acquire NMR spectra. However, extended discourses on solubility properties do not normally make for gripping reading, and are avoided by many authors. Therefore, wide general recognition of these properties remained “off the radar screen”, delaying possible applications.

\[
\begin{align*}
\text{Fe} & \\
(\text{CH}_2)_2\text{Rf}_n & \\
\text{P}((\text{CH}_2)_m\text{Rf}_n)_3 & \\
\xi^{[36]} & \\
\text{Rf}_n = (\text{CF}_2)_{n-1}\text{CF}_3 & \\
\text{m/n} = 2/8, \ a & \\
\text{m/n} = 3/8, \ b
\end{align*}
\]