

ALKANE METATHESIS AND RELATED REACTIONS

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INTRODUCTION

Alkanes are the major constituents of petroleum and the most important components of fuel. For example, C₉-C₂₀ *n*-alkanes constitute the ideal fuel composition for a diesel engine. As the global petroleum reserves decrease, the Fischer-Tropsch process has become more important in the production of liquid hydrocarbons, especially *n*-alkanes. However, neither natural sources nor the Fischer-Tropsch production yield alkane mixtures with tight control of molecular weight distribution. It represents a continuing scientific challenge to convert light alkanes into higher molecular weight homologs.¹ To solve the problem, alkane metathesis reaction, which is the transformation of alkanes to homologs of different chain lengths, has been developed during the past decade. Two catalyst systems have been established based on distinct mechanisms: the single-site catalyst system and the dual catalyst system. This seminar will focus on the general development of alkane metathesis, including insight into both catalyst systems.

SINGLE-SITE CATALYST SYSTEM FOR ALKANE METATHESIS

The discovery of alkane metathesis on single-site catalyst systems arose from the development of surface organometallic chemistry of zirconium, tantalum, and tungsten.² In 1997, Basset and coworkers reported a heterogeneous catalyst system in which silica-based tantalum monohydride is utilized as the catalyst.³ With this catalyst system, alkanes can be transformed under mild conditions (<150°C) into homologs with higher and lower molecular weight, as described by the general equation: $C_nH_{2n+2} \longrightarrow C_{n+i}H_{2(n+i)+2} + C_{n-i}H_{2(n-i)+2}$. In addition, the silica/alumina-supported tungsten hydride complexes were demonstrated to be active in alkane metathesis.^{4,5} In these systems, Silica/alumina supported metal hydrides are the active catalyst species that perform C-H activation of alkanes to yield alkyl metal complexes and hydrogen. The alkyl metal complexes are the active species of metathesis process. However, low selectivity and moderate turnover number (TON) remain limitations for the single-site catalyst system.

DUAL CATALYST SYSTEM FOR ALKANE METATHESIS

The dual catalyst system for alkane metathesis was developed from the combination of C-H activation and olefin metathesis. The earliest example was reported by Burnett and Hughes in 1973.⁶

They employed alumina-supported platinum as hydrogenation/dehydrogenation catalyst and silica-supported tungsten trioxide as olefin metathesis catalyst to convert butane into C1-C8 hydrocarbons. However, the disadvantages of the system were harsh conditions (temperatures as high as 399°C), poor selectivity, and low yield. In 2006, Goldman and Brookhart reported a homogeneous dual catalyst system for alkane metathesis that utilized an iridium-based pincer complex and a Schrock-type catalyst to catalyze hydrogenation/dehydrogenation and olefin metathesis respectively.¹ Dual catalyzed alkane metathesis undergoes tandem reactions of “dehydrogenation-olefin metathesis-hydrogenation”. The dual catalyst system was also applied into ring-expansion and metathesis cyclo-oligomerization of cycloalkanes.⁷

More recently, a heterogeneous dual catalyst system with much higher TONs was reported by Goldman and Brookhart.⁸ In the system, Alumina-supported catalysts showed significantly higher activity and stability than homogeneous catalysts. It is proposed that alumina adsorbs the two catalysts and separates them to prevent unfavorable interactions between different catalysts that lead to decomposition or inhibition.

SUMMARY

Alkane metathesis is a fascinating area of great significance for the utilization of alkanes and natural gas.² It is successful in converting lower molecular weight alkanes to higher molecular weight homologs, important in helping with the energy crisis and environment protection. Numerous applications for alkane metathesis are still under investigation. While the improvement of TONs and selectivity remain challenging, alkane metathesis has proven to be a useful strategy for the production of medium to long chain alkanes.

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