1 Introduction and task

Olefins, particularly ethylene, propene and butenes, are the basic building blocks of the petrochemical industry. They are easily available, cheap, reactive and readily transferable into a range of useful products, e.g. biodegradable detergents, different kinds of polymers, lubricants, and many other industrially useful chemicals. Nowadays using catalytic reactions, olefins, especially ethylene, have also become important in the oleo- and pharma-chemistry. By applying ethylene as one of the reactants, a lot of catalytic reactions have been studied and some of them have been developed for the industrial productions. Among them, cooligomerization of ethylene with conjugated diene is one of the most important reactions.

The early studies of Alderson and Cramer [1, 2] showed that in the presence of rhodium catalysts, the reactions of **ethylene with 1,3-butadiene**, isoprene or 2,4-hexadiene afforded products of great importance in polymer chemistry, e.g. ethylene-propylene-diene monomer (EPDM) . Later Su etc. [3, 4, 5] have also made an intensive study on the rhodium catalyzed cooligomerization of ethylene with 1,3-butadiene. As rhodium catalyzed reactions favored the production of trans-1,4-hexadiene, the molar ratio of trans- to cis-1,4-hexadiene was generally between 2:1 to 4:1. Higher ratios have been also reported by Su [3], but no recycling runs were discussed.

Behr et al. were the first who studied the cooligomerization of **ethylene with conjugated fatty dienes**. Using rhodium(III)trichloride trihydrate ($RhCl_3 \cdot 3H_2O$) as the catalyst precursor, phosphines and phosphites as ligands and the conjugated methyl linoleate (CML) as the fatty substance, yields over 90% were achieved in a single phase reaction after 20 hours with chloroform as solvent [6, 7]. The reaction gave branched fatty substances, either mono-, di- or tri-substituted. The saturated derivatives of these fatty compounds were found to possess low pour points, low melting points and high biodegradabilities [8, 9], and are of great interest for the lubricant chemistry because of their sustainable resources.

Cooligomerization of **ethylene with styrene** or hydrovinylation of styrene gives important intermediates for the production of α-aryl-propionic acids. However according to early results of Alderson et al. [1] and Umezaki et al. [10], rhodium(III) catalysts were found to have very low catalytic activities and rhodium(I) catalysts were found inactive in the hydrovinylation of styrene.

In this doctoral thesis the above discussed reactions, the rhodium catalyzed cooligomerizations of ethylene with 1,3-butadiene, with conjugated methyl linoleate and with styrene, were studied. The tasks were to achieve a stable and high molar ratio of trans-/cis-1,4-hexadiene by conditioning the reaction solvents, to enhance the activity of the rhodium catalyst in the hydrovinylation of styrene and to improve the catalyst recycling process in the cooligomerization of ethylene and conjugated fatty dienes.

The catalyst recycling is actually another important point of this work. For homogeneously catalyzed reactions, catalyst separation has been one of the most urgent tasks. Due to the catalyst leaching and the contamination of the products, many reactions are still limited to the lab scale, although they offer high reaction rates and high selectivity. As rhodium is very expensive in price, the recovering and recycling of the rhodium catalyst are taken as the decision factors in industrializing these reactions. On the other hand, a good separation of the catalysts and the products also helps to match the requirements on limited metal concentrations especially in pharma-chemistry.

Various existing catalyst recycling concepts were generally reviewed in this paper. Based on these recycling concepts, different techniques were developed and applied in the above discussed reactions, with respect to the reaction conditions and the properties of the products. To separate the products with low boiling points, a chemical recovery by distillation was used; to separate the products with high boiling points, temperature-dependent multi-solvent systems and also the extraction technique were used. The separated catalysts were retreated and recycled into the next run and the activities of recycled catalysts were evaluated. Inductively coupled plasma - Optical emission spectrum (ICP-OES) analysis was applied to determine the leaching degree of the rhodium catalyst for the estimation of the recycling efficiency.

2 General part

2.1 Cooligomerization

The catalytic transformation of olefins by transition metal complexes has received a great deal of attention during the last two decades. Some of these catalytic reactions are industrially important, because they represent one of the most economical ways to synthesize olefinic monomers or polymers. The more common types of these transformation reactions are: (a) dimerization or polymerization of α-olefins; (b) dimerization, oligomerization, cyclooligomerization or polymerization of conjugated dienes; (c) codimerization or cooligomerization of α-olefins and conjugated dienes. The main reaction discussed in this dissertation is the last type, the cooligomerization of α-olefins and conjugated dienes. The α-olefin used here is ethylene whereas the conjugated dienes varied from aliphatic dienes, aromatic dienes to conjugated fatty dienes. More detailed examples are the cooligomerization of ethylene and 1,3-butadiene, the cooligomerization of ethylene and styrene and the cooligomerization of ethylene and conjugated methyl linoleate. This catalytic cooligomerization of olefins with dienes provides an interesting and powerful tool for selective C-C coupling reactions [11, 12] and has already been applied as an effective synthesis method in the fields of petrochemistry, oleochemistry and pharmachemistry.

2.1.1 Synthesis methods in petrochemistry

The reactions between aliphatic dienes and α-olefins are widely studied, e.g. the cooligomerizations of ethylene with 1,3-butadiene, isoprene and pentadiene or the cooligomerizations of 1,3-butadiene with acryl compounds. All these reactions give valuable products, which can be treated for further applications. For example, 1,4-hexadienes from the reaction of ethylene with 1,3-butadiene are very important in the synthesis of EPDM terpolymers, which are excellent monomers for producing rubbers with good ozone resistance and rapid curability.

2.1.2 Synthesis methods in oleochemistry

About 1.15 million tonnes of lubricants are used every year in Germany [13]. 53% of this amount are collected as waste oils, which are then recycled or used as a source of heating energy. The rest, about 540.000 tonnes, is lost in the environment as a result of leakage, total loss applications or system specific reasons where they can cause pollution of the environment [13]. The use of rapidly biodegradable lubricants could significantly reduce this environmental pollution. In Germany, ecologically friendly lubricants currently account for about 4-5% of all lubricants consumed so far.

Natural products as well as modified renewable oil esters can be used as a base stock for the preparation of environmentally friendly, rapidly biodegradable lubricants. Some of the rapidly biodegradable lubricants are based on pure, unmodified vegetable oils. In Europe predominantly rapeseed and sunflower oil are used. Chemically these are esters of glycerine with long chain fatty acids, while the fatty acid components are plant-specific and therefore variable. However, their thermal oxidation and hydrolytic stability is limited [14, 15, 16]. Therefore pure vegetable oils are only used in applications with lower thermal stress.

An improvement of the thermal, oxidative and hydrolytic stability of vegetable oils can be primarily achieved by chemical modifications, the modification on the carboxylic group or the modification of the double bonds on the fatty acid chain. In the field of lubricant base fluids, reactions at the double bonds are used to increase the product stability. At the same time, the introduction of functional groups and branches changes the physical properties of those newly-created fluids considerably. Generally speaking the chemical structure of the substances influence the physical properties as summarized in Table 2.1.

Table 2.1: Physical properties of different fatty substances

High degree of branching	Outstanding low-temperature characteristics, high hydrolytic stability, low viscosity index
High linearity	High viscosity index, relatively poor low-temperature characteristics
Low saturation	Outstanding low-temperature characteristics, limited oxidation stability
High saturation	Outstanding oxidation stability, poor low-temperature characteristics

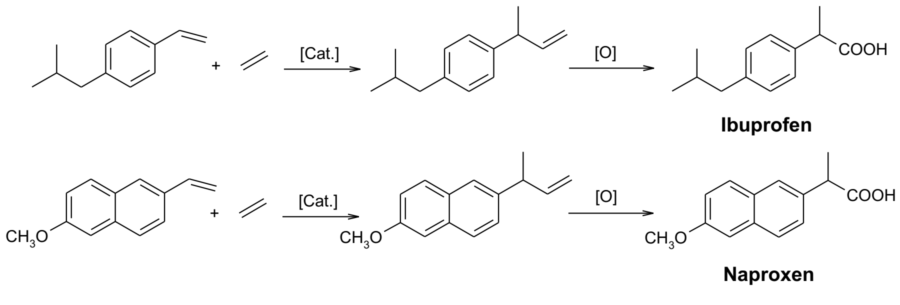
At present less than 10% of the known reactions of fatty acid chains are industrially applied. These possibilities represent a great potential for expanding the oleochemical product lines in the future and the greater economic exploitation of vegetable oils and fats.

The cooligomerization of ethylene with fatty dienes plays an important role in developing some novel fatty substances with interesting properties. For instance, cooligomerization of ethylene with conjugated methyl linoleate gives branched fatty compounds. Further modifications of these branched fatty compounds afford some new and interesting properties. One example is that the saturated derivatives by hydrogenation have excellent physical properties, e.g. low melting points, low pour points and also improved bio-degradabilities, which featured these compounds as favorite alternatives in developing a novel generation of lubricants and cosmetics.

Besides the reaction between ethylene and conjugated methyl linoleate, other cooligomerizations with fatty dienes as substrates have also been studied. For examples, the cooligomerization of propylene with conjugated methyl linoleate [6],or the cooligomerization of acrylic compounds with fatty dienes.

2.1.3 Synthesis methods in pharmachemistry

α-Arylpropionic acids (Fig.2.1) have emerged as an important class of non-steroidal anti-inflammatory agents over the past two decades. There are several reports showing considerable efforts in order to synthesize this class of drugs [17, 18]. In particular, cooligomerization of ethylene with vinylarenes, or hydrovinylation reactions of vinylarenes have been investigated most extensively because of the importance of 3-aryl-1-butenes as potential intermediates for the drugs, e.g. Ibuprofen and Naproxen [19, 20].



O = oxidation

Figure 2.1: Ibuprofen and Naproxen

Serving as a model reaction for the synthesis of compounds with pharmacological activity, the cooligomerization of ethylene with styrene to give 3-phenyl-1-butene is of particular interest and has been widely studied.

2.2 Catalysts

The cooligomerization reaction has a long history. The first reference in the open literature to transition-metal catalyzed codimerization of reactions involving ethylene can be traced to Alderson, Jenner, and Lindsey [1] who used hydrated Rh and Ru chlorides to effect cooligomerization of ethylene at high pressures with a variety of olefins including styrene and butadiene. As much more attention on the cooligomerization of ethylene and other olefins was developed, catalysts other than Rh and Ru were also extensively studied.

2.2.1 Nickel catalysts

Nickel complexes are the most common group of the olefin cooligomerization catalysts exhibiting the highest activity and selectivity to linear α-olefins. The nickel catalyst complexes can be divided into two groups: nickel(II) compounds modified with alkyl or hydride main-group metal derivatives (Ziegler-Natta type catalysts) and chelate nickel compounds with a Ni-C bond.

2.2.2 Cobalt catalyst

Another widely studied group of catalysts are cobalt complexes. The cobalt salts, together with phosphine ligands and organoaluminum compounds, showed their high activities and selectivity in cooligomerization reactions. For example, Hendriksen et al. reported that in the presence of a catalyst system of $Co(acac)_2$, 1,3-bis(diphenylphosphino) propane (DPPP) and diethylaluminum chloride (DEAC), the reaction between ethylene and butadiene resulted in a 99% conversion and a 99.9% selectivity to cis-1,4-hexadiene [21].

2.2.3 Rhodium catalysts

Other than nickel and cobalt complexes, rhodium compounds are also active catalysts in some cooligomerization reactions. As mentioned above, the hydrated rhodium chloride as catalyst in cooligomerizations of ethylene and olefins was first reported by Alderson et al [1]. Later Behr and his coworker have developed rhodium catalyzed cooligomerizations of α-olefins with fatty dienes [6, 7]. Except the high catalytic activity, rhodium catalysts have also showed their special orientation in the selectivity of some products. One example is the cooligomerizaition of ethylene and butadiene. Rhodium catalyzed reactions selectively give trans-1,4-hexadiene while those reactions catalyzed by nickel or cobalt catalysts give in favor the cis-1,4-hexadiene.

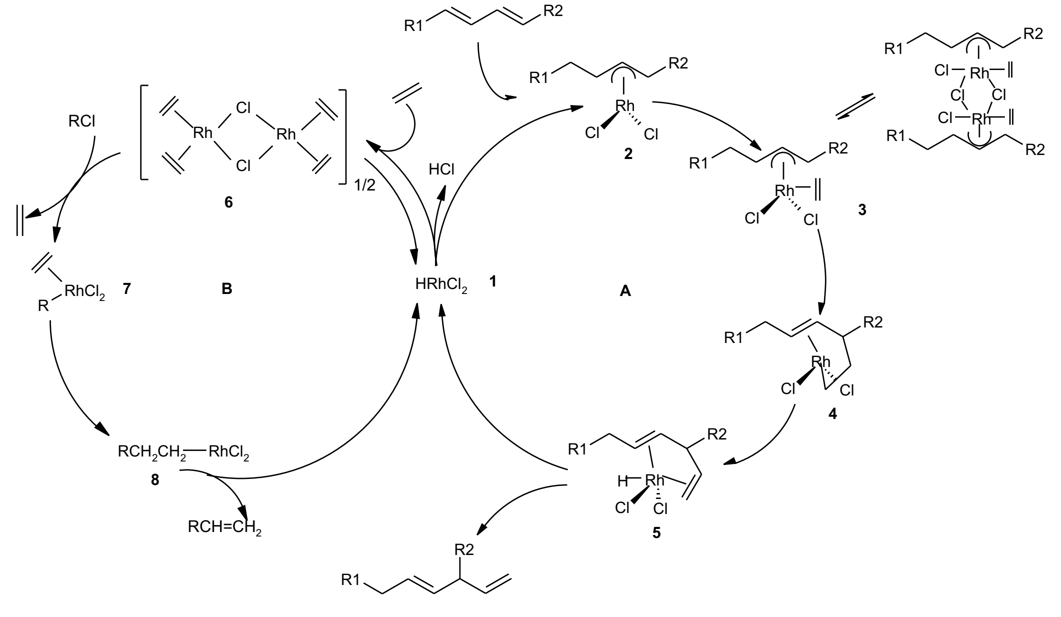


Figure 2.2: Mechanism of rhodium catalyzed cooligomerization of ethylene and conjugated dienes

$RhCl_3 \cdot 3H_2O$ is used as the catalyst precursor. The intermediate species is a Rh^{III} hydride, $HRhCl_2$, which reacts with butadiene to give a dimeric η^3-crotyl complex. Insertion of ethylene into this η^3-crotyl-Rhodium bond results in the formation of an η^2-η^2-1,4-complex. A β-elimination regenerates the hydride species and the 1,4-diene. The preferential formation of the 1:1 adduct is a consequence of the favored stability of the η^3-crotyl-Rh complex compared with an ethyl-Rh complex.

The olefin coordination reduced the Rh^{III} into Rh^{I} (see cycle B, Fig.2.2). The insertion of organic chlorides can regenerate the Rh^{III}.

2.2.4 Other transition metal catalysts

Other transition metals like Fe, Ru and Pd are also studied as the cooligomerization catalysts. For example, Myers et al. studied a catalyst system of a ruthenium salt and an aluminum halide for the codimerization of α-monoolefins and conjugated diolefins[22].

2.3 Recycling concepts

The techniques and processes for the recycling of homogeneous catalysts have been developed for many years since the first documented catalytic reaction. Some of the recycling concepts are catalogued in Fig.2.3.

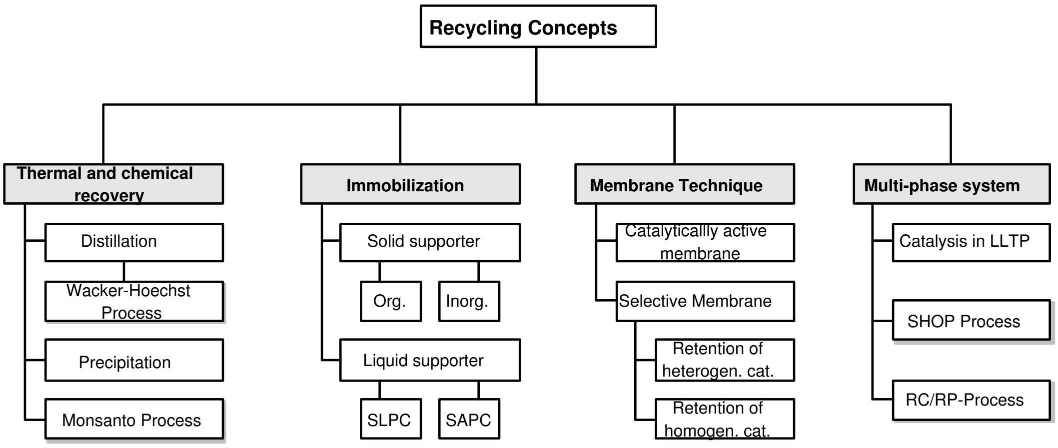


Figure 2.3: General classification of existing recycling concepts

2.3.1 Catalyst recycling in homogeneous catalysis

Homogeneous catalysis is of great importance in modern synthetic chemistry. Many transition metals have been studied as homogeneous catalysts in different reactions and plenty of studies were published in the last decades. However, most of these studies are still only limited to the lab scale because of their economical and ecological disadvantages. These drawbacks are mostly due to the inefficiency in the recovering of catalysts from products. In order to overcome these problems, some recycling concepts have been developed.

2.3.1.1 Thermal or chemical recovery

The concept of thermal recovery uses the distillation to separate the products with low boiling points from the homogeneous mixtures after the reaction. The catalysts and the rest heavy ends can be directly recycled. Since late 1950s this concept has been applied in the Wacker-Hoechst-Process (the palladium/copper catalyzed oxidation of ethene to acetaldehyde) [23] and it is now still a worldwide important industrial process for the production of acetaldehyde. Ethylene is oxidized in the gas-fluid reactor by using Pd(II) salt as catalyst and during the reaction, the formed products are distilled off and the rest Pd(0) species can be regenerated by oxidation using Cu^{2+}/Cu^{+}, together with oxygen or air [24].

In late 1960s Monsanto developed a low-pressure process for the production of acetic acid by the homogeneously rhodium catalyzed carbonylation of methanol. After many modifications and improvements this process is up to now still competitive in production [25]. In 2000 however, the iridium catalyzed Cativa^{TM}-Process was developed and compared to the older Monsanto-Process, this new-developed process showed its advantage in the aspects of both the technique and the environmental-benignity [26].

Chemical recovery by catalyst precipitation or decomposition was practiced in the early processes of hydroformylation of high olefins [27]. For example, the active catalyst species $HCo(CO)_4$ can be firstly precipitated in the form of its sodium salts and then regenerated by acidification of the salts. The alternatives to this method are the thermal or oxidation decompositions of the cobalt carbonyl compound. The disadvantage of this recycling method is the production of large amount of salts.

2.3.1.2 Immobilization

The definition of immobilization or heterogenization can be understood as the impregnation or anchoring of homogeneous soluble catalysts onto or into the solids or the liquids, the organic or the inorganic supporters[28, 29]. And the contact between the stationary phase (supporter) and the mobil phase (reaction medium) is defined as the ”Interphase” [30, 31]. The most often used organic supporter is cross-linked polystyrene and recently the Nafion material is also becoming popular as organic supporter [32]. Meanwhile variously modified silica are used most frequently as inorganic supporters. Examples of fluid supporters are those organic solvents with high boiling points (supported liquid phase catalysis **SLPC**) or water (supported aqueous phase catalysis **SAPC**). Till now