

## 10

### Environmental Catalysis and Green Chemistry

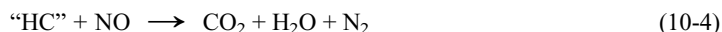
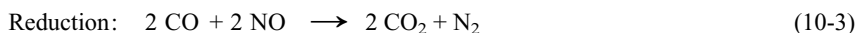
Traffic and industry are the most important sources of air pollution. They are responsible for the emission of CO, nitrogen oxides (NO<sub>x</sub>), sulfur oxides (SO<sub>x</sub>), and all sorts of volatile organic compounds (VOCs). Therefore, environmental catalysts are necessary for cleaning flue gases. Here we concentrate only on some topics, namely

- Automotive exhaust catalysis
- NO<sub>x</sub> removal systems
- Catalytic afterburning of VOCs

#### 10.1

##### Automotive Exhaust Catalysis [2, 3]

For the conversion of automotive exhaust gases the three-way catalyst (TWC) enables the removal of the three pollutants CO, NO and hydrocarbons („HC“) in the following manner (Eqs. 10-1 to 10-4):



The three-way catalyst allows the treatment of the two reducing pollutants, CO and „HC“ (C<sub>x</sub>H<sub>y</sub>), and the oxidizing pollutant, NO<sub>x</sub>, it has been in use since 1979. All reactions are running simultaneously, therefore, the composition of the exhaust gas must be carefully adjusted to an air-to-fuel ratio of 14.7 using an oxygen sensor (the so-called lambda-probe). At higher oxygen content, that means under lean-burning conditions with air-to-fuel ratios of about 20:1, the NO<sub>x</sub> reduction is extremely difficult. This negative effect is reasonable, because the CO oxidation reaction consumes too much CO and hence the NO conversion fails. On the other hand, if the oxygen content is too low all of the NO<sub>x</sub> is converted, but hydrocarbons and CO

are not completely oxidized. The actual support of a monolith is called „washcoat“, which provides a high surface area for the active catalyst.

The three-way catalyst compositions is 70% cordierite substrate ( $\text{MgAl}_2\text{O}_4$ ) and the washcoat:

20–25%  $\gamma\text{-Al}_2\text{O}_3$  (or  $\alpha\text{-Al}_2\text{O}_3$ ,  $\text{ZrO}_2$ )  
 < 10%  $\text{CeO}_2$ ,  $\text{BaO}$ , etc. (oxygen storage, stabilizer)  
 0.2–0.6% Pt, Pd (CO, HC conversion)  
 0.04–0.06% Rh ( $\text{NO}_x$  activity)

The three-way catalyst represents a remarkably successful area of catalytic technology. The main shortcoming of the three-way catalyst is only, that it is not good enough under lean (oxygen-rich) conditions.

## 10.2

### $\text{NO}_x$ Removal Systems

The main technologies to remove  $\text{NO}_x$  are as follows:

- The selective catalytic reduction (SCR) (Eq. 10-5):



- The catalytic decomposition to elements (Eq. 10-6):



#### 10.2.1

##### Selective Catalytic Reduction of Nitrogen Oxides [8]

Selective catalytic reduction (SCR; DENOX process) is the reduction of NO and  $\text{NO}_2$  ( $\text{NO}_x$ ) by ammonia in the presence of oxygen to give molecular nitrogen. Since the 1970s SCR processes have been used to an increasing extent for the catalytic after-treatment of flue gases from power stations and furnaces. In Germany the limiting  $\text{NO}_x$  value for new coal-fired plants with a power output of 300 MW is  $200 \text{ mg/m}^3$ . Such low  $\text{NO}_x$  levels can only be achieved by applying secondary measures. The 3–12 % oxygen in the flue gas also takes part in the reaction, as shown for NO in Equation 10-7.



It can be assumed that in the presence of an excess of oxygen, NO reacts with an equimolar quantity of  $\text{NH}_3$  to give  $\text{N}_2$  and  $\text{H}_2\text{O}$ .

The catalysts must be designed so that side reactions such as the oxidation of ammonia by oxygen (Eq. 10-8) and the formation of  $\text{N}_2\text{O}$  (Eq. 10-9) are suppressed. The oxidation of  $\text{SO}_2$  to  $\text{SO}_3$  must also be avoided.



Transition metal oxides on ceramic supports have proved to be particularly suitable as catalysts; for example: support: TiO<sub>2</sub> (ca. 90 %), active components: V<sub>2</sub>O<sub>5</sub> (1.5–5 %), WO<sub>2</sub> (5–10 %), MoO<sub>3</sub>, GeO<sub>2</sub>. Sheet or honeycomb catalysts are used industrially, and the usual operating temperature is 350–400 °C. Figure 10.1 shows honeycomb catalysts for air purification.

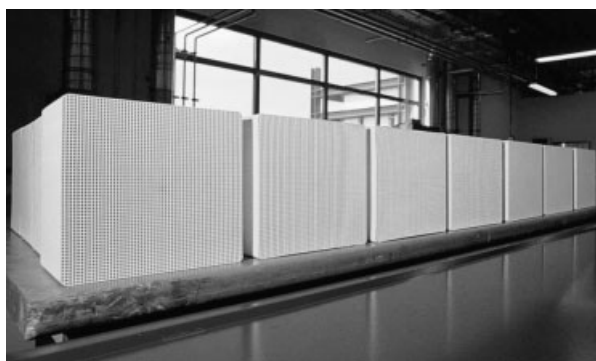


Fig. 10-1 Honeycomb catalysts for air purification (Süd-Chemie AG, Heufeld, Germany)

A mechanistic proposal (Fig. 10-2) explains the formation of N<sub>2</sub> besides N<sub>2</sub>O and H<sub>2</sub>O [12]. On the hydroxyl-group-containing surface of the oxide, ammonia is adsorbed on Brønsted acid centers with formation of an ammonium structure (step 1). In step 2, NO undergoes addition to the ammonium complex according to the Eley–Rideal mechanism. The resulting complex has two possible decomposition routes. In the major route (step 3a), an N≡N bond is formed and N<sub>2</sub> and H<sub>2</sub>O are cleaved off. In the following reaction (step 4a), oxygen is filled up and water is released by the catalyst surface. In the minor route (step 3b), lattice oxygen is abstracted from the catalyst, and N<sub>2</sub>O and H<sub>2</sub>O are formed. In step 4b the oxygen vacancy is filled and water is cleaved off to regenerate the original catalyst.

In industry, two variants of the process compete with one another [7]. In the first variant, the SCR reactor is located in the high-dust high-temperature region directly after the boiler on the raw-gas side. The flue gas enters with a temperature of 300–450 °C and a dust content of 10–30 mg/m<sup>3</sup> (high-dust configuration). Since this variant involves strong abrasion and more rapid poisoning of the catalyst, bulk catalysts on the basis of V, W, or Ti oxides are used. In the second variant, the SCR reactor is located after the flue gas purification and desulfurization stages (low-dust configuration). Since abrasion and poisoning are much lower in this case, honeycomb and sheet catalysts can also be used. A disadvantage is that the flue gas leaving the desulfurization stage at 50–70 °C must be heated to the reaction temperature of 300–350 °C.

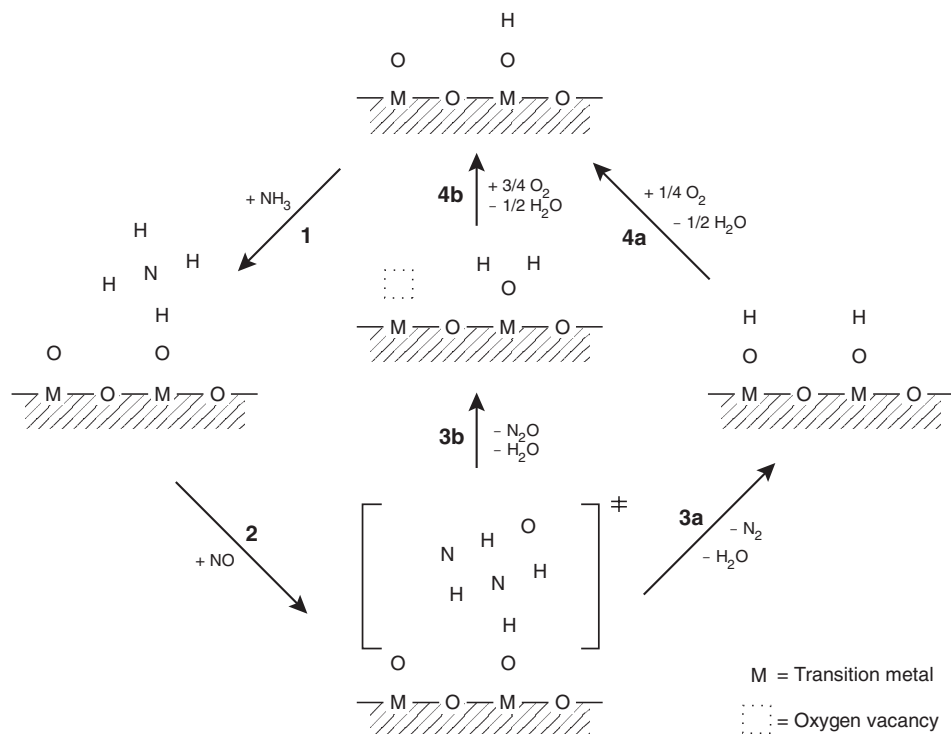


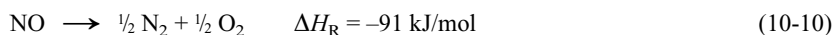
Fig. 10-2 Mechanism of the selective catalytic reduction of NO by NH<sub>3</sub> [12]

The SCR processes have become established in Western Europe, and the required TiO<sub>2</sub>/V<sub>2</sub>O<sub>5</sub> based honeycomb catalysts are produced by various European catalyst producers under a Japanese license.

### 10.2.2

#### NO<sub>x</sub> Storage-Reduction Catalyst for Lean-Burning Engines

The NO<sub>x</sub> abatement in Diesel and lean-burn Otto engine exhaust gases is of special interest. The direct decomposition of NO into N<sub>2</sub> and O<sub>2</sub> (Eq. 10-10) is a dream reaction for catalyst researchers:



The reaction is strongly exothermic, hence the equilibrium constant favors the reaction at low temperatures. It is well-known that Cu-zeolites can decompose NO directly to molecular oxygen and nitrogen, but unfortunately the zeolite is not stable under humid conditions. The main features of the Cu-ZSM-5 catalyst are:

- The reaction is a true decomposition and under controlled conditions a good material balance is achieved
- The decomposition passes through a reversible maximum with rising temperature at 500–600 °C
- The reaction order in NO is 1.0–1.2 and it may change with NO concentration
- Oxygen inhibits the reaction but the inhibition decreases with rising temperature
- Excess Cu loading in zeolite enhances the activity
- Sulfur compounds in the gas phase suppress the decomposition activity

Toyota has developed 1994a NO<sub>x</sub>-storage-reduction (NSR) catalyst based on a two step process. The engine switches periodically between a long lean-burn stage and a very short fuel-rich stage. The NSR catalyst used in this process consists of two compounds: the active oxidation catalyst Pt and the NO<sub>x</sub> storage compound based on BaO.

In the lean-burn stage all exhaust components are oxidized by the Pt catalyst and NO is oxidized to NO<sub>2</sub>. The latter reacts with the basic storage compound BaO to yield Ba(NO<sub>3</sub>)<sub>2</sub>. In the fuel-rich stage which only lasts for seconds, the reducing agents CO, H<sub>2</sub>, and hydrocarbons in the exhaust stream are able to reduce the Ba(NO<sub>3</sub>)<sub>2</sub> to give N<sub>2</sub>, CO<sub>2</sub> and H<sub>2</sub>O. Figure 10-3 illustrates the overall process.

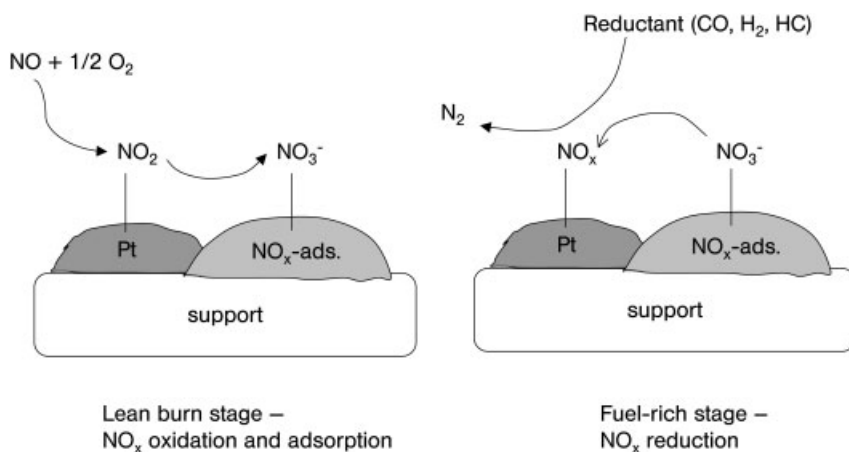


Fig. 10-3 Action of a NO<sub>x</sub>-storage-reduction catalyst

Note that BaO is not a catalyst but reacts only in a stoichiometric manner with NO<sub>2</sub>. A major difficulty limiting the general applications of the NSR catalyst is the sulfur sensitivity. Therefore, up to now this concept is only applicable in markets where low-sulfur fuels (< 30 ppm S) are available, such as in Japan and Sweden. The NSR technology claims to meet future standards and will find wider application all over the world.

### 10.3

#### Catalytic Afterburning [5, 11]

Afterburning processes enable the removal of pollutants such as hydrocarbons and volatile organic compounds (VOCs) by treatment under thermal or catalytical conditions. Combinations of both techniques are also known. VOCs are emissions from various sources (e.g. solvents, reaction products etc. from the paint industry, enamling operations, plywood manufacture, printing industry). They are mostly oxidized catalytically in the presence of Pt, Pd, Fe, Mn, Cu or Cr catalysts. The temperatures in catalytic afterburning processes are much lower than for thermal processes, so avoiding higher  $\text{NO}_x$  levels. The catalysts involved are ceramic or metal honeycombs with washcoats based on cordierite, mullite or perovskites such as  $\text{LaCoO}_3$  or Sr-doped  $\text{LaCoO}_3$ . Conventional catalysts contain Ba-stabilized alumina plus Pt or Pd.

Both thermal and catalytical exhaust gas purification systems operate at pollutant concentrations  $>1.5\text{--}3 \text{ g/Nm}^3$  autothermally. Since the efficiency of internal heat recovery is 80–90%, no additional energy is required for heating the exhaust gas. Thus both processes are environmentally sound and economical in operation. In Table 10-1 are some working temperatures compared for both processes. Limitations for catalytical processing are the catalyst sensitivity towards poison and overheating.

**Table 10-1** Comparison of process temperatures for the oxidation of VOCs in afterburning processes

Pollutant	Temperature Catalytical processing (°C)	Temperature Thermal processing (°C)
Formaldehyde	300	800
CO	250	760
Styrene	250	760
Solvents	350	760
Phenol/formaldehyde	350	800
Phenol/creosol	400	800
Ethylacetate	350–400	760

Figure 10-4 illustrates schematically a typical course of an afterburning process.

The curve shows the dependence of conversion on process temperature. There can be defined typical conversion values and areas:

T 50: 50% of the initial concentration is to be oxidized (ignition temperature)

T 90: 90% of the initial concentration is to be oxidized

Conversion at maximum process temperature (which may be fixed before)

Area I: kinetic region

Area II: diffusion region

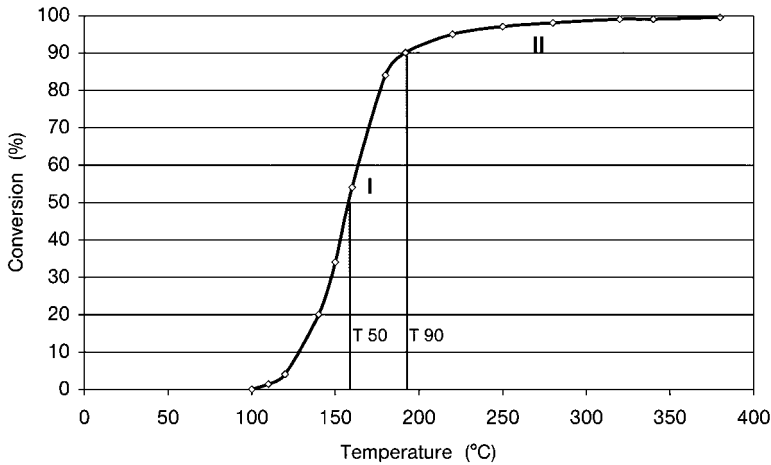


Fig. 10-4 Typical afterburning process of a hydrocarbon

*Example* [11]:

In formaldehyde processes the exhaust gas consists of 1.2–1.6 vol.% pollutants:

CO	0.7–1.2%
Dimethylether	0.1–0.4%
Methanol	0.1–0.2%
Formaldehyde	0.005–0.1%

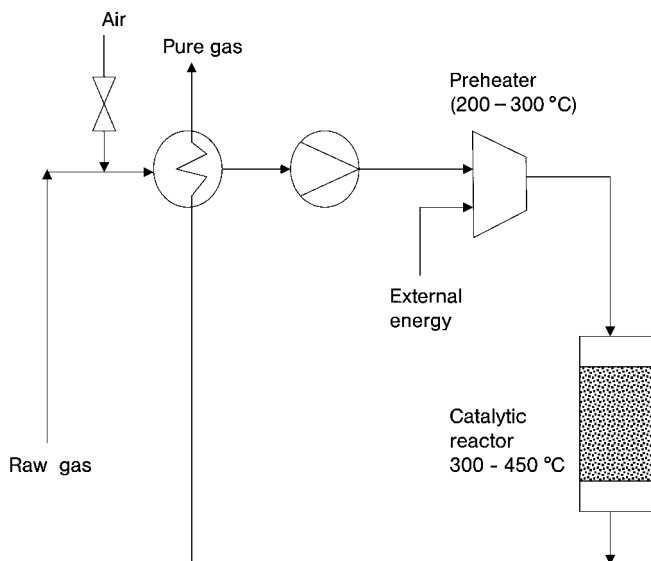
The feed gas is heated up to ca. 200 °C and can completely be oxidized by the catalyst. During this process the temperature rises up to 300–450 °C, dependent to the heat recovery system applied in the plant. The degree of conversion depends to the process temperature and the catalyst age. The following approximate results can be obtained:

Catalyst temperature (°C)	Conversion of the pollutants [%]
300	90%
350	99.0%
450	99.9%

With process temperatures of about 400 °C the following purification levels of the clean gas can be achieved over some years:

Formaldehyde	10 mg/m <sup>3</sup>
Organic carbon	20 mg/m <sup>3</sup>

Figure 10-5 shows schematically a catalytic afterburning plant.



**Fig. 10-5** Scheme of a catalytic afterburning plant

Finally, the catalyst design procedure for an afterburning process can be described as follows:

- Determination of pollutants, concentrations, limiting values (clean gas composition), poisons etc.
- Rough estimation: possible – yes or no
- Determination GHSV (gas hourly space velocity)
- Selection: pellets or monolith
- Estimation of the pressure drop
- Estimation of feed temperature,  $\Delta T$  in the catalyst bed
- Catalyst weight (pellet height)
- Recommendation for a suitable catalyst
- Eventual test or new calculation

Advanced catalyst systems together with optimized engine management and process control can aid the achievement of the future low emission standards.

#### 10.4

##### Green Chemistry and Catalysis [9]

Green chemistry, also called sustainable chemistry, was formally delineated in 1990 in the United States with the aim of preventing pollution through better process design rather than by managing emissions and waste – the “end of the pipe” solution. Catalysis is one of the fundamental pillars of green chemistry, the design of



chemical products and processes that reduce or eliminate the use and generation of hazardous substances. The design and application of new catalysts and catalytic systems are simultaneously achieving the dual goals of environmental protection and economic benefit [10].

Catalysis offers numerous green chemistry benefits including:

- Lower energy requirements
- Catalytic versus stoichiometric amounts of materials
- Increased selectivity
- Decreased use of processing and separation agents and
- Allows for the use of less toxic materials

Heterogeneous catalysis, in particular, addresses the goals of green chemistry by providing the ease of separation of product and catalyst, thereby eliminating the need for separation through distillation or extraction. In addition, environmentally benign catalysts such as clays and zeolites, may replace more hazardous catalysts currently in use.

Mass balances of alternative routes in chemical processing can be compared using measures such as the  $E$  factor and mass index  $S^{-1}$ . The  $E$  factor (ratio of waste [kg] to product unit [kg]) is an output orientated indicator, whereas the mass index  $S^{-1}$  (ratio of all raw materials [kg] to the product [kg]) is an input oriented indicator. These measures and the cost index CI (currency unit per kg product) clarify the benefits and drawbacks of changes in synthesis design, i.e. the strong and weak points, which must be addressed [6].

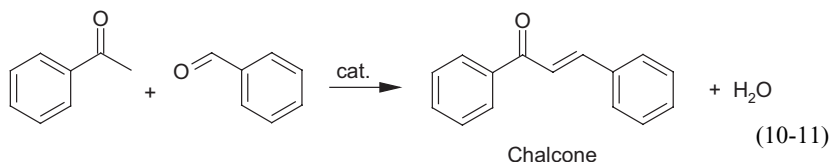
Waste is defined as everything that is produced during operation of the process, except the desired product. There is a substantial increase in  $E$  factors on going downstream from bulk chemicals ( $<1-5$ ) to fine chemicals ( $5 - >50$ ) and specialties ( $25 - >100$ ). This reflects the more widespread use of stoichiometric reagents and multi-step syntheses in the latter sectors. Therefore, the longer term trend in fine chemicals manufacture is towards the use of the simplest raw materials –  $H_2$ ,  $O_2$ ,  $H_2O$ ,  $H_2O_2$ ,  $NH_3$ ,  $CO$ ,  $CO_2$  – in low-salt, atom efficient processes employing homogeneous, heterogeneous, or biocatalysts.

#### 10.4.1

##### Examples of Catalytical Processes

##### 10.4.1.1 Aldol Condensation

The aldol condensation of benzaldehyde and acetophenone yields chalcone (Eq. 10-11) [6].



The aldol reaction is usually base-catalyzed, the results of the synthesis using different catalysts are demonstrated in Table 10-2.

**Table 10-2** Results of the aldol condensation with various catalysts [6]

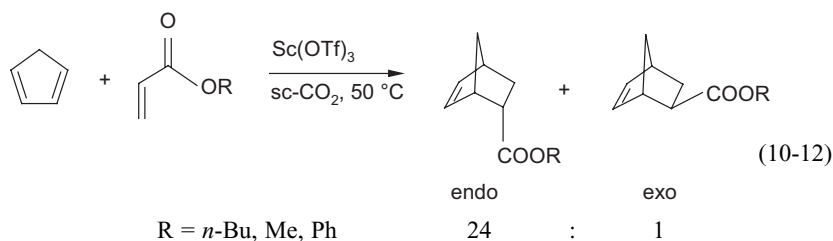
Catalyst	Yield (%)	Mass index $S^{-1}$ (kg/kg)	E factor (kg/kg)
(a) KOMe	75	5,6	4,6
(b) NaOMe	71	7,8	7,0
(c) NaOH	85	6,8	5,8
(d) Nafion H	78	2,7	1,7 (1,5) <sup>a)</sup>

a) cat. d is reused (at least ten times)

The base catalysts must be neutralized and/or washed out during the work-up procedure. The solid-acid Nafion H, on the other hand, can be reused. Table 10-2 shows that the most effective procedure with regard to mass efficiency and E factor can be carried out with catalyst d. Not only solvents and auxiliary materials can be saved, but the catalyst too, is reusable without having a negative effect on the yield. This leads to a further decrease in the *E* factor. In conclusion, Nafion H seems to be an efficient catalyst for performing aldol condensation to yield chalcone in an environmentally friendly manner, i.e. avoiding the use of water and reducing the amount of solvent.

#### 10.4.1.2 Diels-Alder Reaction [1]

Supercritical carbon dioxide (sc-CO<sub>2</sub>) is an environmentally benign solvent that is providing a viable alternative to the traditional organic solvents. A Diels-Alder reaction between *n*-butyl acrylate and cyclopentadiene was investigated with the Lewis acid catalyst scandium tris (trifluoromethanesulfonate), primarily due to its solubility in sc-CO<sub>2</sub> (Eq. 10-12):

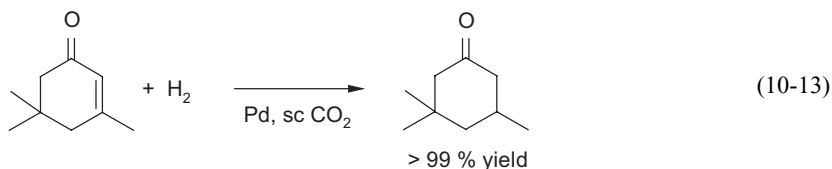


By varying the pressure of the solvent, endo:exo selectivity was maximized at 24:1, a significant improvement over selectivity achieved in conventional solvents (11:1). Green chemistry benefits of a less hazardous solvent, reduced energy usage,

ease of separation, and selectivity for waste minimization, as can be seen in this example [1].

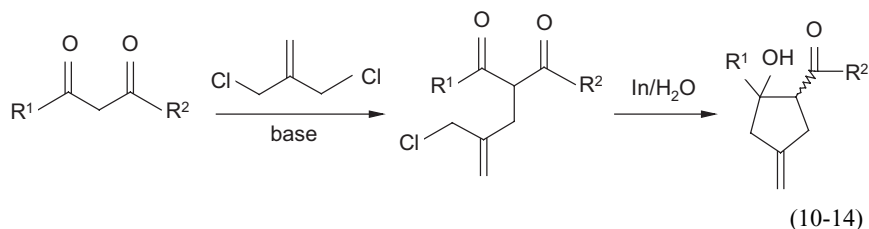
#### 10.4.1.3 Hydrogenation [10]

The selective hydrogenation of an unsaturated cyclic ketone can be carried out successfully with Pd catalyst in supercritical CO<sub>2</sub> (Eq. 10-13):



#### 10.4.1.4 Cyclization in Water [1]

A variety of reactions can be carried out in an aqueous environment given the right choice of catalyst. Water is an extremely attractive solvent choice. Allylation of 1,3-dicarbonyl compounds, for example, is efficiently promoted in water using an indium catalyst (Eq. 10-14).



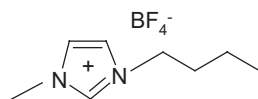
Metal mediated reactions in water have found applications in cyclization, ring expansion, and isomerization reactions.

#### 10.4.1.5 Use of Ionic Liquids [1]

Ionic liquids (IL) are also gaining acceptance as alternatives to traditional organic solvents.

Ionic liquids are salts that are liquid at low temperatures. Unlike traditional solvents that can be described as molecular liquids, ionic liquids are composed of ions. This creates the potential to behave quite differently from conventional solvents. Due to the unique chemical physical properties of ionic liquids, they have been called „green solvents“.

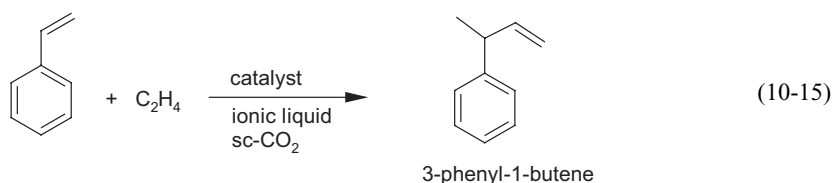
Especially room temperature ionic liquids (RTILs), such as those based on *N,N*-dialkylimidazolium ions, are interesting solvents for catalytic reactions, for example:



1-butyl-3-methylimidazolium-tetrafluoroborate

Ionic liquids are non-volatile and non-flammable, eliminating the hazards associated with volatile organic compounds (VOCs). In addition, the properties of ionic liquids may be tuned by varying the identities of the cations and anions, thereby tailoring the solvent to a specific application.

The ionic liquids show excellent extraction capabilities and allow catalysts to be used in a biphasic system for convenient recycling. For example, the hydrovinylation of styrene with ethene can be carried out successfully using an ionic liquid and supercritical  $\text{CO}_2$  as solvent (Eq. 10-15). The ionic liquid dissolves the metal organic complex catalyst and  $\text{sc-CO}_2$  facilitates mass transfer and continuous processing.



IFP France has developed dimerization, hydrogenation, isomerization, and hydroformylation reactions without conventional solvents. For butene dimerization a commercial process exists. There is formed a biphasic system with the catalyst in the IL phase, which is immiscible with the reactants and products. This system can be extended to a number of organometallic catalysts.

A variety of other reactions such as acylation of toluene, anisole, and chlorobenzene to give selectively *p*-isomer, alkylations, etc. have been conducted with ionic liquids.

## ► Exercises for Chapter 10

### Exercise 10.1

Why is the automotive exhaust catalyst called a three-way catalyst?

### Exercise 10.2

Which metals are used in the automotive catalyst and what reactions do they catalyze?

### Exercise 10.3

What are the major compounds of exhaust gases?

**Exercise 10.4**

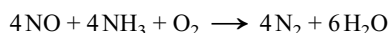
Describe how  $\text{NO}_x$  can be removed from the exhaust when a car operates under lean-burn conditions (i.e. oxygen rich). Why is it attractive to drive cars under lean-burn conditions?

**Exercise 10.5**

Explain the common characteristics of the NSR catalytic system for  $\text{NO}_x$  abatement based on the principle „oxidation before reduction“ employing the oxidation states of all stages.

**Exercise 10.6**

A BASF process proceeds according to the following equation:



- a) What is the significance of the process and what is it called?
- b) Catalysts and temperature range?

**Exercise 10.7**

You can select a suitable catalyst for a catalytic afterburning process from monoliths or pellets. Which process parameters are mainly influenced by your choice?

**Exercise 10.8**

Explain the atom efficiency concept by comparing the classical chlorohydrin route and the newer petrochemical ethylene oxide manufacture.

**Exercise 10.9**

What is an *E*-factor? Which processes usually have the highest *E*-factors?

**Exercise 10.10**

In the nitration of aromatic compounds, solid acid catalysts such as clays and zeolites are an alternative to the conventional process employing a mixture of  $\text{HNO}_3/\text{H}_2\text{SO}_4$ . List some reasons in view of green chemistry.

**Exercise 10.11**

Which advantages for process development can be offered by ionic liquids?