Founded in 1912 as "Kaiser Wilhelm Institute for Coal Research"
Most important influencers: Emil Fischer, first german chemistry Nobel Prize winner (1902) and Hugo Stinnes (big industrialist)
The primary goal was the direct conversion of coal to electricity
4 days after the opening, WWI started

The presentation will be divided into 3 eras represented by 3 directors:

1. Director (1913-1943): Franz Fischer (not related to Emil Fischer), 437 publications, 71 patents
research was plagued by two world wars and many publications fell into the Ziegler era because they were delayed by the second world war (e.g. Koch synthesis)
1925: patent for the Fischer-Tropsch Process (catalytic production of liquid hydrocarbons from coal); production volume in the 1940s about 600,000 tonnes/year
Despite the wars he published 12 Volumes of "Summarized essays about the knowledge of coal" which can be understood as his lifework

2. Director (1943-1969): Karl Ziegler, shifted the institute’s work to organometallic chemistry
1949: changed the name to Max Planck Institut für Kohlenforschung
1952: patent for "Koch Reaction"
1953: patent for atmospheric pressure polymerization of ethylene at rt; today: 150 mio. tonnes / year
1954: patent for the direct synthesis of Al(El)_3
1954: patent for the synthesis of primary alcohols
1956: patent for cyclodimerization & -trimeration of butadien to COD & CDT (Wilke)
1963: Nobel Prize for Ziegler together with Natta (Mailand) For their discoveries in the field of the chemistry and technology of high polymers

1970: patent for the decaffeination of green coffee beans called "Destraction" (Zosel)
1973: patent for the enabling process for the electrochemical industrial Ferrocene production (Wilke)
1979: patent for the synthesis of magnesiumhydrides used as energy storage (Bogdanovic)

The contributions after 1993 will be covered in a later second topic presentation.
Franz Fischer (1877-1947), Director 1913-1943
Curiously became the first director because Hugo Stinnes was on the founding-board and had rich influence as a big industrialist and co-founder of RWE (big german energy provider). He heard about the possibility to convert coal directly into electricity (contemporary means was to burn coal in a steam engine to generate electricity). This provided an incentive for the electrochemist Fischer to become director of the institute for coal resarch.

Fischer started with work on methane because it was a very abundant sideproduct in the coal industry:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2
\]

\[
\text{CH}_4 \rightarrow 1200 \degree \text{C} \rightarrow \text{C} \rightarrow \text{HC}≡\text{CH} + \text{H}_2
\]

\[
5\text{CH}_4 + 3\text{O}_2 \rightarrow 1500 \degree \text{C} \rightarrow \text{H}_2\text{C}≡\text{CH}_2 + 3\text{CO} + 6\text{H}_2 + 3\text{H}_2\text{O}
\]

The desire for liquid fuel began to rise and many processes with various catalysts and various products were developed. The general process became famous as Fischer-Tropsch synthesis for liquefication of coal.

\[
\text{C} + \text{O}_2 + \text{H}_2\text{O} \rightarrow > 900 \degree \text{C} \rightarrow \text{nCO} + (2\text{n}+1)\text{H}_2
\]

\[
\text{"syngas"}
\]

\[
\text{Cat. e.g. Fe/ZnO or Co/Co}_2\text{O}_3 \rightarrow 1\text{bar, 190-350 }\degree \text{C} \rightarrow \text{C}_n\text{H}_{2n+2} + \text{H}_2\text{O}
\]

The products were wild mixtures of all chainlength, which could be controlled to a certain extent. A table by Fischer shows the composition differences depending on the reaction conditions:

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Pressure (bar)</th>
<th>cat.</th>
<th>product description</th>
<th>gas prod.</th>
<th>liquid prod.</th>
<th>solid prod.</th>
</tr>
</thead>
<tbody>
<tr>
<td>190 (Co)</td>
<td>1</td>
<td>Ni/Co/Fe</td>
<td>paraffines &amp; olefines</td>
<td>little</td>
<td>much</td>
<td>little</td>
</tr>
<tr>
<td>&gt; 200</td>
<td>100</td>
<td>?</td>
<td>aromatic carbohydrides</td>
<td>much</td>
<td>much</td>
<td>none</td>
</tr>
<tr>
<td>190</td>
<td>5-20</td>
<td>Co</td>
<td>paraffines &amp; few olefines</td>
<td>little</td>
<td>much</td>
<td>much</td>
</tr>
<tr>
<td>240</td>
<td>5-20</td>
<td>Fe</td>
<td>paraffines &amp; many olefines</td>
<td>little</td>
<td>much</td>
<td>little</td>
</tr>
</tbody>
</table>

For a summary by Fischer see:
Oel und Kohle, 1943, 517
9 Fischer Tropsch plants were built by the Nazis with a yearly production of 600,000 tons. Unsatisfactory results were obtained because the sulfur containing synthesis gas from brown coal deactivated the catalysts on industrial scale. Therefore the Bergius Process (Hydrogenation of coal, Nobel Prize 1931), which delivered higher quality, was mostly used to provide liquid fuel for the war. The Fischer Tropsch process was, however, continually used to a small degree since its discovery. Today there are 2 production plants in South Africa (covering 28% of RSA-need). Several plants are using natural gas (methane, cheaper!) and a reforming process to make syngas: "GTL" (gas to liquid) plants in Malaysia, RSA, Qatar, more plants in planning.

Ben List about the Fischer-Tropsch Process: Organic chemistry can always continue, even after the oil is consumed. There will always be a way to make hydrocarbons.

Important Co-Workers of Fischer:
1. Herbert Koch, inventor of the Koch Synthesis for tertiary carboxylic acids from olefins and CO

![Chemical reaction diagram](image)

Justus Liebig's Annalen der Chemie, 1958, 251

Alcohols and sometimes alkyl chlorides and alkyl esters can also function as starting materials.
The reaction is used on an industrial scale for the production of pivalic acid.

2. Otto Roelen, head of the pilot plant at the institute, changed to Ruhrchemie AG in 1934 where he developed the hydroformylation of olefins known as the Roelen-Reaction, hydroformylation or Oxosynthesis. He was not really interested in publications, but more in patents. He owned more patents than publications (around 100)

Roelen did further developments of the Fischer-Tropsch synthesis and also tried to incorporate NH₃ into the product. During a disturbance of the reactor, he noticed a white solid:

![Chemical reaction diagram](image)

His suggestion that the NH₃ only functioned as a reactant after the actual reaction was found to be right. He never made a lot of money from this patent, because German patents in other countries were declared invalid after WW2. Therefore only the small German companies paid him for this patent.

This protocol is nowadays used as a huge industrial process. The employed catalysts are usually metalcarbonylhydrides of Rh or Co. The iso-/n-product distribution can be controlled by the choice of ligands.
Karl Ziegler (1898-1973), Director 1943-1969, ~200 publications, Nobel Prize 1963
It is known, that he was against Hitler, but was still offered this important position, because he was too good to expulse him from Germany. They hoped the position as a director would limit his influence on students, but would still yield productive results.
Ziegler restricted the acceptance of the position as a director to the same condition as Fischer (freedom of his research). He was concered about the name of the institute that included the purpose and direction of the research.

Ziegler tried to distill EtLi:

\[
\text{Et-Li} \quad > 100^\circ C \quad \xrightarrow{\text{reversible?}} \quad \text{LiH} + \text{H}_2\text{C}==\text{CH}_2 + \text{H}_3\text{C}==\text{CH}_2
\]

(known)

(new!)

if yes, it would be a polymerization method

This reaction might also be the first known carbometallation

Side reaction:

\[
\text{Et-Li} + \text{H}_2\text{C}==\text{CH}_2 \rightarrow \text{H}_3\text{C}==\text{CH}_2\text{Li}
\]

Many, many reactions later, in a desperate fashion (1949):

\[
\text{H}_2\text{C}==\text{CH}_2 + \text{LiAlH}_4 \xrightarrow{\text{Ether}} \text{C}_4 - \text{C}_{12}
\]

180-200°C

100 bar (developed 1947)

active catalyst: LiAl(Et)_4

After deep investigations, they found the cheap and abundant Al was the important species and not the rare and expensive Li

\[
\text{Et} \quad \xrightarrow{\text{Et}} \quad \text{H}_2\text{C}==\text{CH}_2 \quad \xrightarrow{\text{100-120^\circ C}} \quad \text{100 bar} \quad \text{CH}_2\text{(CH}_2)_n\text{CH}_3 \quad \text{Al}-\text{CH}_2\text{(CH}_2)_m\text{CH}_3 \quad \text{CH}_2\text{(CH}_2)_o\text{CH}_3
\]

n, m, o = ~100

Why did \( n, m, o \) never exceed beyond ~100?

\[
\text{H}_2\text{C}==\text{CH}_2 + \text{CH}_2\text{(CH}_2)_n\text{CH}_3 \xrightarrow{\text{Et}} \text{Al-X} + \text{H}_2\text{C}==\text{CH}(\text{CH}_2)_{n-1}\text{CH}_3
\]

"Verdrängungsreaktion" displacement reaction

Even tough the reaction was never "good enough" to yield polymers, by carefully choosing the reaction conditions, the chainlength of the alpha olefins could be controlled. This was benefical for a different industrial application:

\[
\text{CH}_2\text{(CH}_2)_n\text{CH}_3 \xrightarrow{\text{O}_2} \text{OCH}_2\text{(CH}_2)_n\text{CH}_3 \xrightarrow{\text{H}_2\text{O}} \text{OH} \quad \text{CH}_2\text{(CH}_2)_n\text{CH}_3
\]

Primary C_{12} - C_{16} alcohols are used as biodegradeable detergents and find worldwide application. The Al(OH)_3 sideproduct has several other applications. Thanks to Ziegler, pictures like these belong to the past:

Non biodegradeable detergents in the river Ruhr built foam on the surface.

1964 dpa picture alliance
The build-up reaction is much slower with α-olefins (e.g. propylene) and is stopped after dimerization by the displacement reaction (steric reasons). In the case of propylene this reaction is also used for an industrial process (Goodyear-Scientific-Design-Process):

\[
\begin{align*}
\text{H}_2\text{C} = \text{CH}_2 & \quad \text{build-up} \\
\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{CH}_2\text{CHCH}_3 \\
\text{Al}-\text{X} & \quad \text{Al}-\text{X} \\
\text{CH}_2\text{CH}_2\text{CH}_3 & \quad \text{only product} \\
\text{H}_2\text{C} = \text{CH}_2 & \quad \text{displacement} \\
\end{align*}
\]

The serendipity and tenacity that led to the Nobel prize:

\[
\begin{align*}
\text{Al}(\text{Et})_3 & + \quad \text{H}_2\text{C} = \text{CH}_2 & \quad ? \\
\quad & \quad 100 \ ^\circ\text{C} \quad 100 \ \text{bar} \\
\quad & \quad \text{only product} \\
\end{align*}
\]

After weeks of investigations a small amount of poorly soluble nickelphosphate was identified as the reason for the fast displacement reaction. The reactor was previously used for a hydrogenation reaction and some nickel remained in little cuts in the wall. The reactor was cleaned with HNO_3 and a phosphor containing detergent which left small amounts of nickelphosphates in the reactor. The aluminumalkyls reduced the nickel, which enhanced the displacement reaction. The enhancement of the displacement to only form dimers became known as the nickel effect.

Now, what does any other metal do?

Investigations into chromium, platinum, gold, copper...(insert most metals)...uranium and thorium revealed titanium as a very reactive catalyst for the elusive polymerization. Dr. Heinz Martin found a way to polymerize at atmospheric pressure and rt by employing TiCl_4 and Al(\text{Et})_2Cl as “mixed catalyst.”

A 5 liter preserving jar from Ziegler’s wife was used as a reactor:

\[
\begin{align*}
\text{Me} & \quad \text{cis-1,4-polyisoprene} \\
\text{Me} & \quad \text{trans-1,4-polyisoprene} \\
\text{widely used e.g. tires,} & \quad \text{not widely used, but} \\
\text{shoe soles, seals} & \quad \text{e.g. golf balls}
\end{align*}
\]
The first patent was submitted only 3 weeks after the discovery and recognized Erhard Holzkamp, Heinz Brei, Heinz Martin and Karl Ziegler as inventors.

Patent fights over more than 30 years were all won by the Max Planck institute and therefore supplied enough money to finance the institute for 40 years. Heinz Martin was the main defender of these patents and wrote a book *Polymers, Patents, Profits* about this journey.

Ziegler-Hafner Azulene Synthesis:

\[
\begin{align*}
\text{NO}_2\text{Cl} & \xrightarrow{1) \text{Pyridine}} \text{NO}_2\text{NO}_2 \xrightarrow{2) \text{Me}_2\text{NH} \text{NaOMe}} \\
\text{Me}_2\text{N}\text{NH} \text{NMe}_2 & \xrightarrow{\text{Me}_2\text{N}+\text{NMe}_2} \text{Me}_2\text{N}H\text{NMe}_2 \\
\text{Me}_2\text{N}H\text{NMe}_2 & \xrightarrow{\text{Me}_2\text{N}H\text{NMe}_2} \text{Azulene}
\end{align*}
\]

Important work by Ziegler that was not done in Mühlheim:

Total Synthesis of Ascardiol:

\[
\begin{align*}
\text{Me} & \xrightarrow{\text{Chlorophyll, O}_2 \text{ high dilution, light}} \text{Naturally occurring peroxide} \\
\text{Naturwissenschaften, 1944, 157}
\end{align*}
\]

Wohl-Ziegler Bromination of the allylic position:

\[
\begin{align*}
\text{Br} & \xrightarrow{\text{NBS has to contain Br}_2 \text{ as impurity, to get the radical reaction started}}
\end{align*}
\]

Thorpe-Ziegler Reaction (makes use of the Ziegler-Ruggli dilution principle)

\[
\begin{align*}
\text{CN} & \xrightarrow{1) \text{base}} \text{CN} \xrightarrow{2) \text{H}_3\text{O}^+} \text{CO} \\
\text{Good for rings that are bigger than 13 and smaller than 9}
\end{align*}
\]

Simplification of the BuLi synthesis:

\[
\begin{align*}
\text{Bu-Cl} & \xrightarrow{\text{Li}} \text{Bu-Li} + \text{LiCl}
\end{align*}
\]
Günther Wilke, 1925-2016, Director 1969-1993, “He is the man who brought sex into chemistry” (Robert A. Welch, 1965)
Wilke already worked several years under Ziegler and some of the reactions presented here were discovered in the Ziegler era.
He renovated the old "director’s house" and made a canteen out of it. Ziegler’s comment after seeing this: "Well that’s how it is. I earned the money with hard work and you are throwing it out."

Wilke found the following two reactions:

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 + \text{Ti(OBu)}_4 & \rightarrow \text{CH}_2=\text{CH}_2 + \text{Al}(\text{Et})_3 \\
\text{H}_2=\text{C} &= \text{CH}_2 + \text{Ti(OBu)}_4 & \rightarrow \text{H}_2=\text{C} &= \text{CH}_2 + \text{Al}(\text{Et})_3
\end{align*}
\]

Then he questioned, what a classical ethylene-polymerization-catalyst would do in the case of butadiene?

\[
\begin{align*}
\text{CH}_2=\text{CH}_2 + \text{TiCl}_4 & \rightarrow \text{CH}_2=\text{CH}_2 + \text{Al}(\text{Et})_3 \\
\end{align*}
\]

The E/Z configuration of the double bond in the trimerization product could be controlled by the employed transition metal. Nickel was suited best for the all trans product (>80%). It was also revealed that Nickel forms complexes with these olefins as ligands. These complexes became famous as "nacked nickel".

Wilke about the Ni(COD)_2 synthesis: "We handled the synthesis in our pilot plant on a 10 kg scale without any interference. The synthesis belongs to the indispensable practice-tasks for new students."

Mechanism:

\[
\begin{align*}
&\text{NiBr}_2 + \text{MgCl} \rightarrow \text{NiCl} + \text{MgBr} \\
\text{NiCl} + \text{CH}_2=\text{CH}_2 \rightarrow \text{NiCDT} + \text{CH}_2=\text{CH}_2
\end{align*}
\]

When one coordination site in the nickel was blocked by a phosphor-ligand, which could not be displaced by butadien, the trimerization would be prohibited and the dimerized product Ni(COD)_2 was formed. NICDT is a trimerization catalyst itself.
Two of the many industrial applications of CDT:

- 1) H₂
- 2) Ox.

\[
\text{CDT} \quad \xrightarrow{\text{H}_2} \quad \xrightarrow{\text{Ox.}} \quad \text{HOOC-(CH}_2\text{)}_{10}\text{-COOH}
\]

used for polyamides

- Vestamid
- Polyamide 12

Wilke’s contribution to Germany winning the WC 1974: the pins under the shoes are made out of Vestamid.
The picture shows the winning goal for the 2:1 victory over the Netherlands.

"Hydrogen storage" by Bogdanovic

\[
\text{MgH}_2 \quad \xrightarrow{\text{cat.}} \quad \text{Mg} + \text{H}_2 \quad 7 \text{ w\% storage capacity}
\]

\[
\text{NaAlH}_4 \quad \xrightarrow{\text{Ti, 100 °C}} \quad \text{NaH} + \text{Al} + \text{H}_2 \quad 5 \text{ w\% storage capacity}
\]
goal for use in cars: 10 w\% storage and use under 80 °C

Cyclopropene and Methylene-cyclopropane chemistry by Binger

\[
\text{R} + \text{R} \quad \xrightarrow{[\text{Pd}^0]} \quad \text{R} + \text{R}
\]

no ligand!

with phosphine ligands the trimer and tetramer are also accessible

Chiral P-Ligands were able to add ethylene enantioselective:

\[
\text{CH} = \text{CH}_2 \quad \xrightarrow{\text{P}^*\text{R}_3} \quad \text{95\% ee}
\]

Industrial Ferrocene production by electrolysis:

\[
\text{Fe} + 2 \text{EtOH} \quad \xrightarrow{-2 \text{e}^-} \quad \xrightarrow{-\text{H}_2} \quad \text{Fe(OEt)}_2
\]

(simple filtration)

\[
\text{H}_2\text{C} = \text{CH}_2 \quad \xrightarrow{\text{K}} \quad \text{K}^+ \quad \xrightarrow{\text{H}_2\text{C} = \text{CH}_2} \quad \text{easy derivatisation from here}
\]

Metalloocene chemistry by Jonas

\[
\text{2 CH} = \text{CH} + \text{Ni} \quad \xrightarrow{\text{cat.}} \quad \text{N} \quad \text{via:}
\]

cat:
Unusual polymerization by Fink:

\[
\begin{align*}
&\text{Recent Advances in Mechanistic and Synthetic Aspects of Polymerization, 515} \\
&\text{proved for } C_4 \text{ to } C_{20} \\
&\text{Basic resarch: interesting structures without any application?!}
\end{align*}
\]

Hydrogenation without catalysts by Köster:

\[
\begin{align*}
&RCH_2 \xrightarrow{H-\text{BR}_2} R\text{BR}_2 \\
&R\text{BR}_2 \xrightarrow{H_2, > 140 \degree C} R\text{Me} \\
&\text{Used for hydrogenation of polymers. Studies on hydrogenation of coal were conducted but failed due to deactivation of the boron compound}
\end{align*}
\]

Is NiCDT chiral? Yes it is! The fourth free coordination site was used to separate the two enantiomers (by Wilke)

\[
\begin{align*}
&[\eta^3-C_3H_6-NiBr]\_2 \\
&\text{without:} \\
&[\alpha]_D^{30} = +104^\circ \\
&\text{Now the two diastereoisomers, can be seperated by crystallization}
\end{align*}
\]
The first "side-on" complexes of N₂ by Jonas:

Convenient preparation of Boroalkyls by Köster:

\[
\begin{align*}
\text{Me}_3\text{AlCl}_3 + (n\text{BuO})_3\text{B} & \rightarrow \text{Me}_3\text{B} + \text{AlCl}_3 + \text{Al}(n\text{BuO})_3, \\
\text{Et}_2\text{O} & \rightarrow 2 \text{Et}_2\text{BF}_3 + 3 \text{Et}_2\text{O} - \text{AlEt}_3 & \rightarrow 2 \text{BEt}_3 + 3 \text{EtAlF}_2 + 5 \text{Et}_2\text{O} & \text{recommended for up to 500 g} \\
\text{Et}_3\text{Al} + \text{KBF}_4 & \rightarrow \text{Et}_3\text{B} + \text{KAIF}_4 & \text{recommended for } > 1 \text{ kg} \\
\text{hydrocarbons} & \rightarrow 160 ^\circ \text{C}
\end{align*}
\]

DOI: 10.1080/00945717308057281

Turnover per seconds WR by Bogdanovic:

\[
\begin{align*}
\text{H}_2\text{C} = / \pi\text{C}_3\text{H}_6\text{NiBrPCy}_3 (1 \text{ mol}) & \rightarrow \text{dimers and higher olefins} \\
\text{EtAlCl}_2, \text{PhCl} & \text{Tps:} \\
-75 ^\circ \text{C}: 60 & -65 ^\circ \text{C}: 130 \\
-55 ^\circ \text{C}: 230 & \text{extrapolation to } 25 ^\circ \text{C}: \sim 60,000 \text{ tps} \\
\text{Meaning: 150 tons of product per hour and per 1 g of Ni capable of competing to enzymes!}
\end{align*}
\]

Reactions of alkenes & alkynes with CO₂ by Hoberg:

\[
\begin{align*}
\text{NICDT} + \text{R} & \rightarrow \text{Ligand} \\
\text{Et}_2\text{BF}_3 & \rightarrow \text{2 BEt}_3 + 3 \text{EtAlF}_2 + 5 \text{Et}_2\text{O} & \text{recommended for up to 500 g} \\
\text{Et}_3\text{Al} & \rightarrow \text{Et}_3\text{B} + \text{KBF}_4 & \text{recommended for } > 1 \text{ kg} \\
\text{hydrocarbons} & \rightarrow 160 ^\circ \text{C}
\end{align*}
\]


Discovery of CO₂ as a solvent by Zosel:

Supercritical CO₂ dissolves highly selectively the caffeine in green coffee beans. Called “Destruction”. Industrial process for producing caffeine free coffee. Much better than the prevailing extraction with DCM or EtOAc...