

Last words of Raney before death
"I was just lucky...I had an idea for a
catalyst and it worked the first time."



Murray Raney

The man behind the

Skeletal Catalyst

Laboratory of Nano Green catalysis

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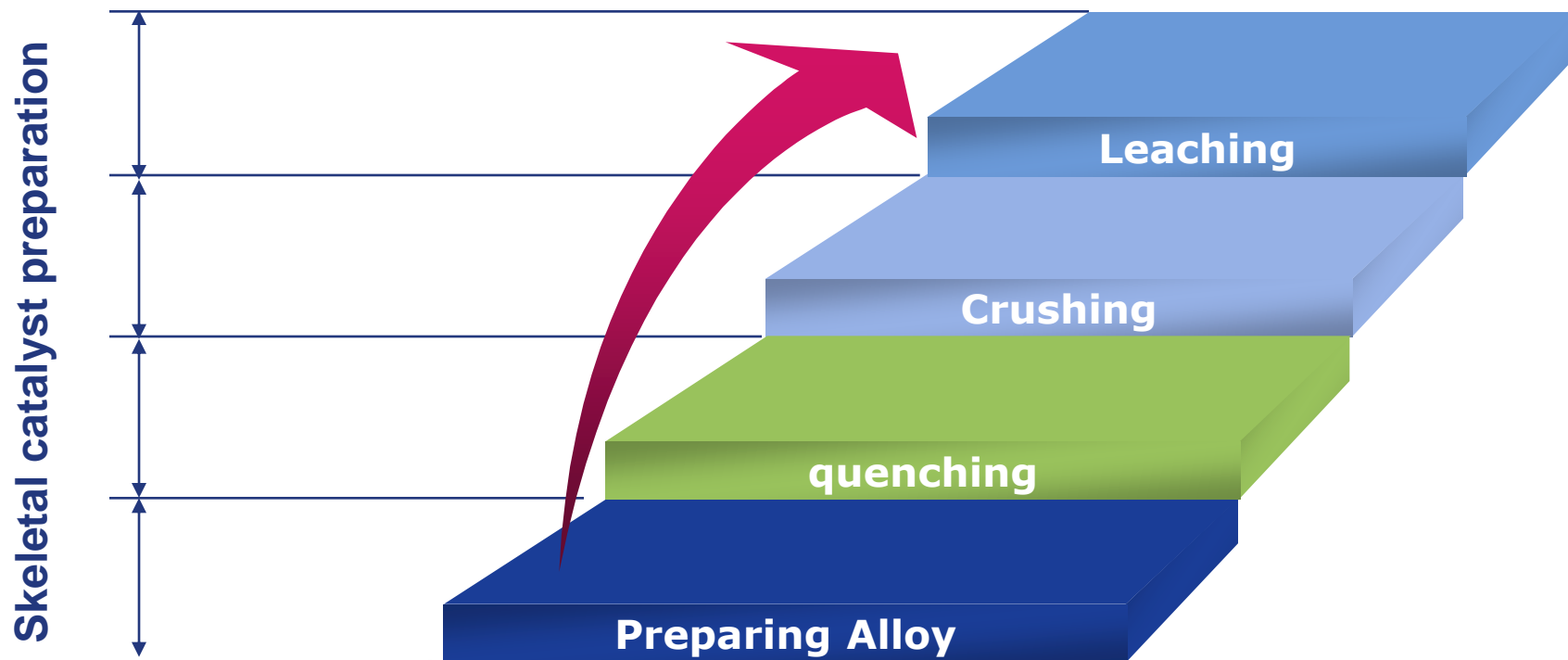


A glance on history of skeletal catalyst

- ◆ In 1939, Murray Raney and Adolph Butenandt shared the Nobel prize in chemistry for the discovery.
- ◆ Between 1925 and 1961 he was granted six US and five European patents covering the preparation of his catalyst.
- ◆ Murray Raney responsibility for the production of hydrogen and its use in the catalytic conversion of liquid vegetable oil to solid fats at Lookout Refining Co., led him to his interest in catalysts.
- ◆ Raney's first patent was for alloy of approximately 50/50 wt % of Nickel and Silicon subsequently leached in concentrated hydroxide solution

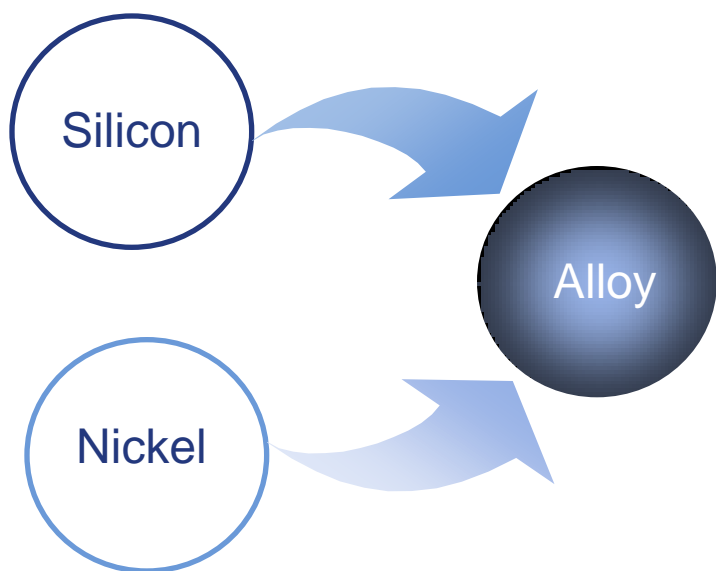


Skeletal catalyst Preparation



Preparation of skeletal catalyst

Step 1 Formation of alloy.



- ◆ Based on the utility Metal is chosen for preparation of alloy and mixed with either silicon or aluminum ; how ever aluminum gives higher activity
- ◆ The exact composition of the precursor alloy depend on which metals are being alloyed
- ◆ Different intermetallic phases provide different characteristics to the final catalyst
- ◆ The activity and stability of catalyst can be improved with the use of additives often referred as promoters



Preparation of skeletal catalyst

Step 2 Alloy quenching and crushing

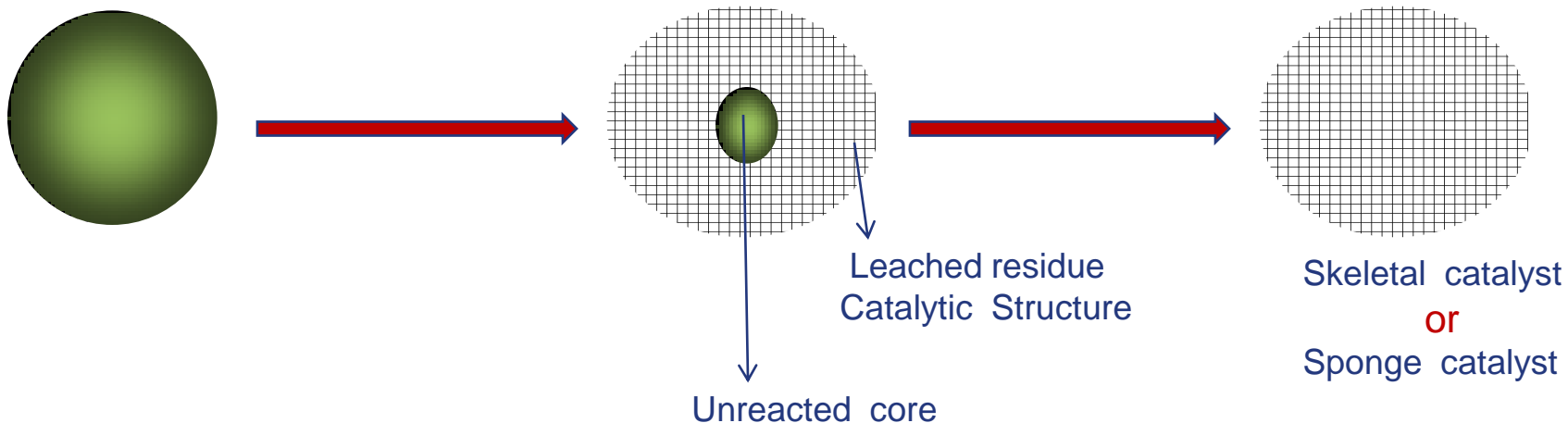


- ◆ Quenching refers to phenomenon in which molecule is heated to high temperature
- ◆ The quenched alloy is crushed or ground and screened to a specific particle size range
- ◆ Ostgard et al. first proposed the manufacture of hollow skeletal catalyst spheres. Precursor alloy is deposited on an organic polymer sphere that is later oxidized completely by heating in air



Preparation of skeletal catalyst

Step 3 Leaching



- ◆ Leaching is a phenomenon in which Aluminum and silicon are removed by using base or acid (leaching solution = Lixiviant)
- ◆ Usually bases are used as it has been found that acidic leaching is reducing the activity of catalyst



Table

Raney Metal	Reaction type	Raw material	Product
Ni	Hydrogenation Methanation Dehydrogenation	Linolenate Syngas(CO/CO ₂ /H ₂) Cholesterol	Oleate Methane Cholestene3one
Cu	Water gas shift Dehydrogenation Hydrogenation	CO+H ₂ O Diethanolamine Butyronitrile	CO ₂ +H ₂ Iminodiacetic acid Butyl amine
Ru	Hydrogenation Ammonia	Phenol N ₂ + H ₂	Cyclohexanol Ammonia
Co	Hydrogenation	Cinnamonitrile	3-Phenylallylamine
Fe	Fisher-Tropsch	Syngas(Co/Co ₂ /H ₂)	Click to add text
Pt	Hydrogenation	Isopropanol	Ethane + Propane



Leaching Kinetics

- Till now best understood leaching kinetic system is copper system.
- Leaching kinetics can be measured in two ways either by evolved hydrogen or by dissolved aluminum.



- The leaching rates increases with increase in temperature.
- The kinetics have been fitted to Levenspiel's shrinking core model which describes the fractional conversion over time for spherical particles reacting with a sharp reaction front under either reaction – or diffusion controlled kinetics.
- Parallels between dealloying theory and skeletal copper formation have been drawn that allow a better understanding of the mechanism of formation of the residual catalytic meta during leaching.



Promoters

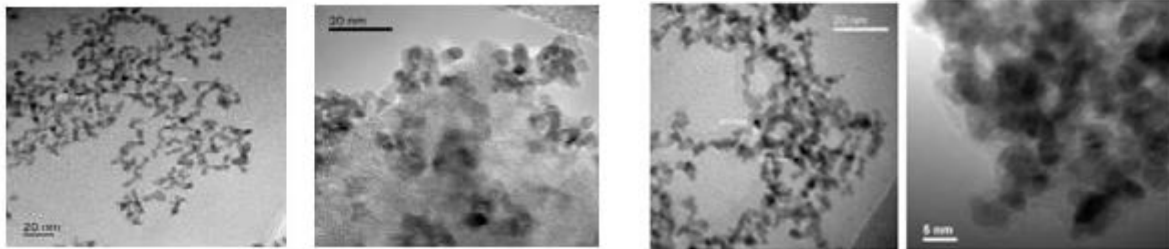
- ❖ These are additional metals or organic compounds added in lixiviant or original alloy.
- ❖ Promoter species increases the activity of the final catalyst without showing catalytic activity by themselves. The effect can be chemical in nature or structural .
- ❖ Promoter deposition through different mechanisms can account for different catalyst properties. This implies the catalytic activity of these materials depends on the preparation conditions
- ❖ Addition of different type of promoter show different activity upon catalyst . (Skeletal Nickel catalyst , Hydrogenation of organic substrates)

Promoter Metal	Butyronitrile	Acetone	Nitro Phenol
Molybdenum	6.5	2.9	1.7
Chromium	3.8	1.5	1.6
Copper	2.9	1.7	1.3
Iron	3.3	1.3	2.1



Structural Determination

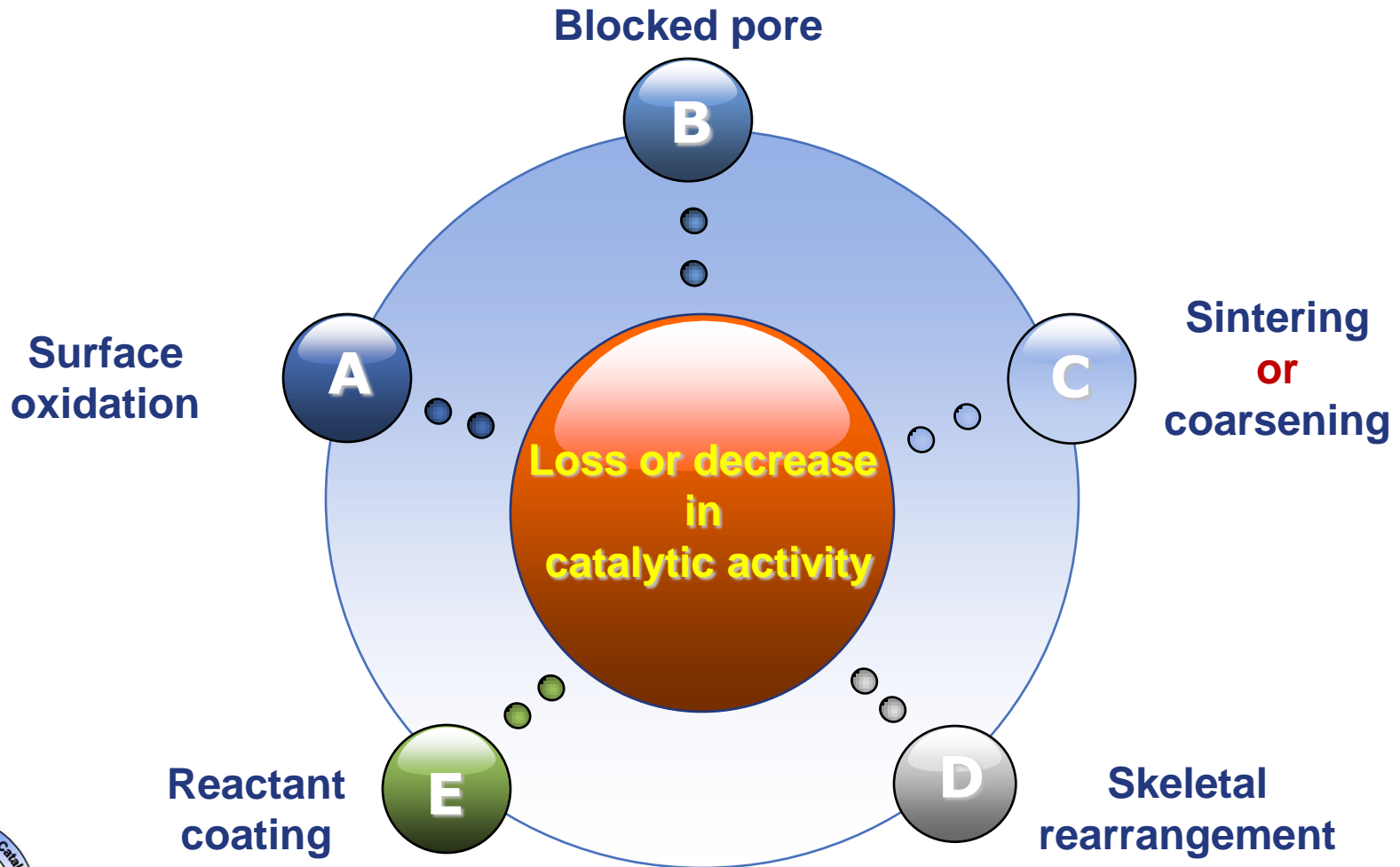
- ❖ Dissolution of the aluminum or silicon causes removal of atoms from the alloy structure.
- ❖ The structural elucidation can be carried by following methods
 - X-ray diffraction
 - X-ray absorption spectroscopy
 - X-photo electron spectroscopy
 - Electron diffraction
 - Auger spectroscopy
 - Pore size and Surface area measurement
 - SEM and TEM with focused ion beam



Ru SEM Images

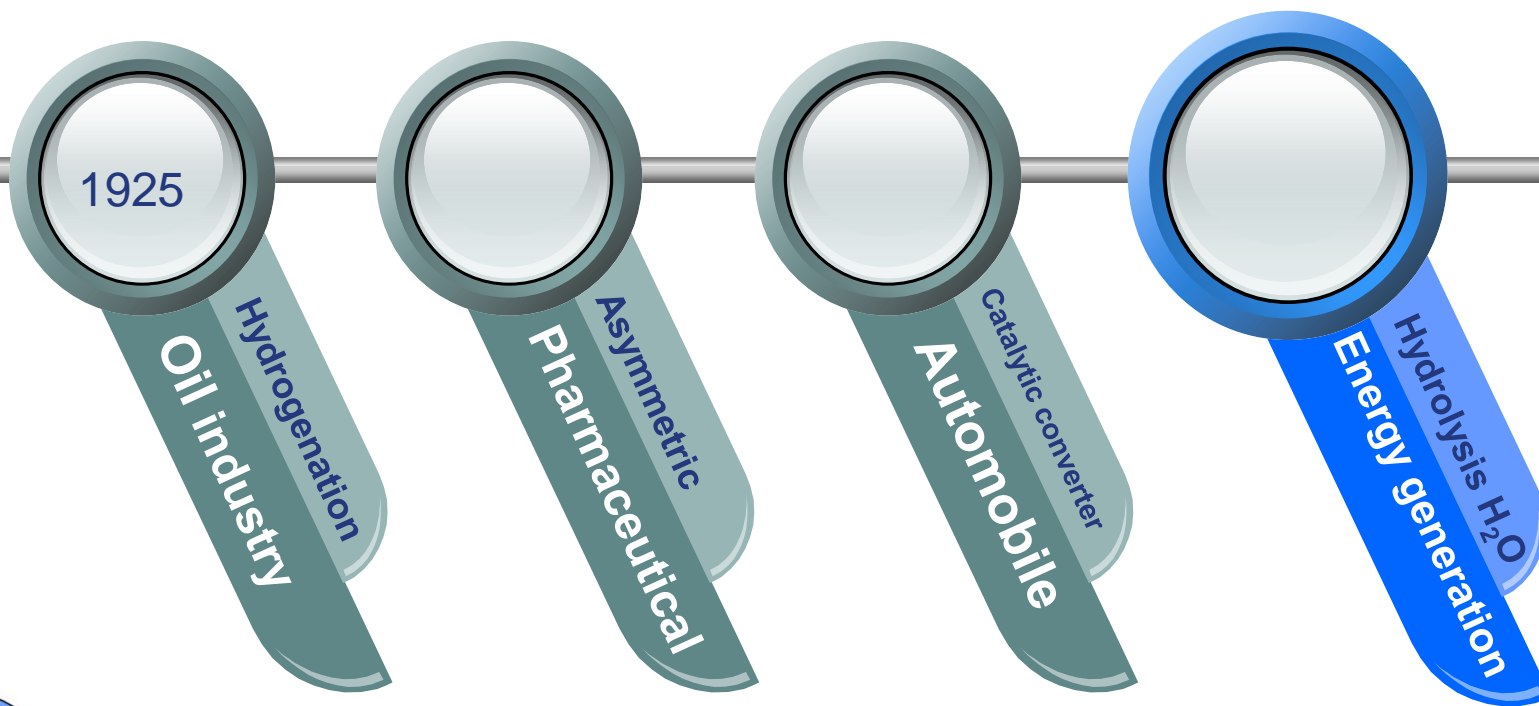
Ni SEM images

Deactivation / Aging



Application

Almost **nine decades** since their first discovery, skeletal catalysts have progressed considerably from the era of vegetable oil hydrogenation to a new era of fuel cell.





Any Clarifications

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Thank You !

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