Zeiolites Modificatiom

- Cation exchange-replace cationic sites with other ions- such as H^+ or other cations.
- Liquid phase supported catalyst-replace homogeneous catalyst inside zeolitic cavity.

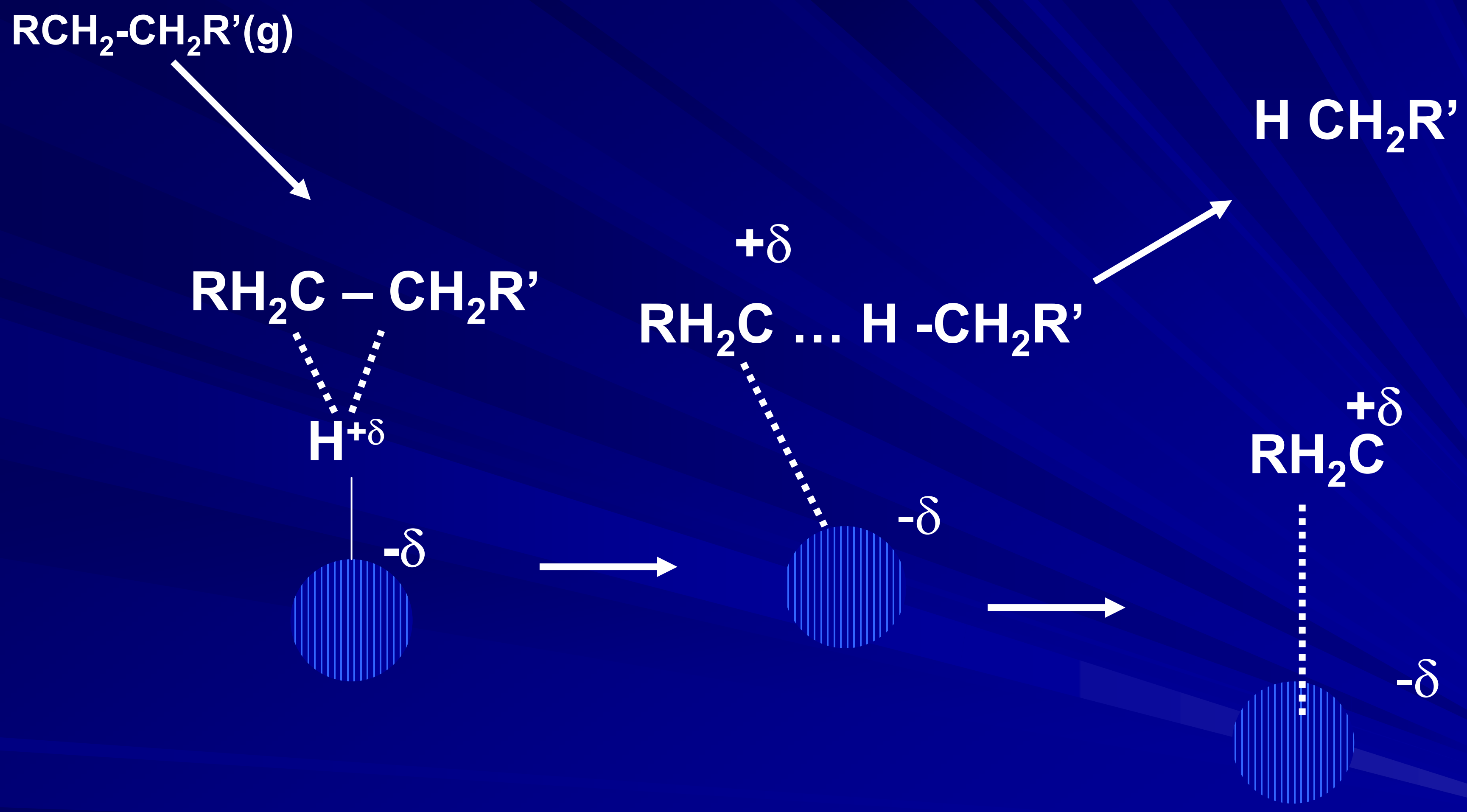
  e.g. ethylene hydrogenation using $RhCl(CO)(PPh_3)_2$ catalyst dissolved in dioctylphthalate.
- Introduce metal oxides and phosphates into the framework, e.g. introduction of phosphates using $P(OH)_4^+$

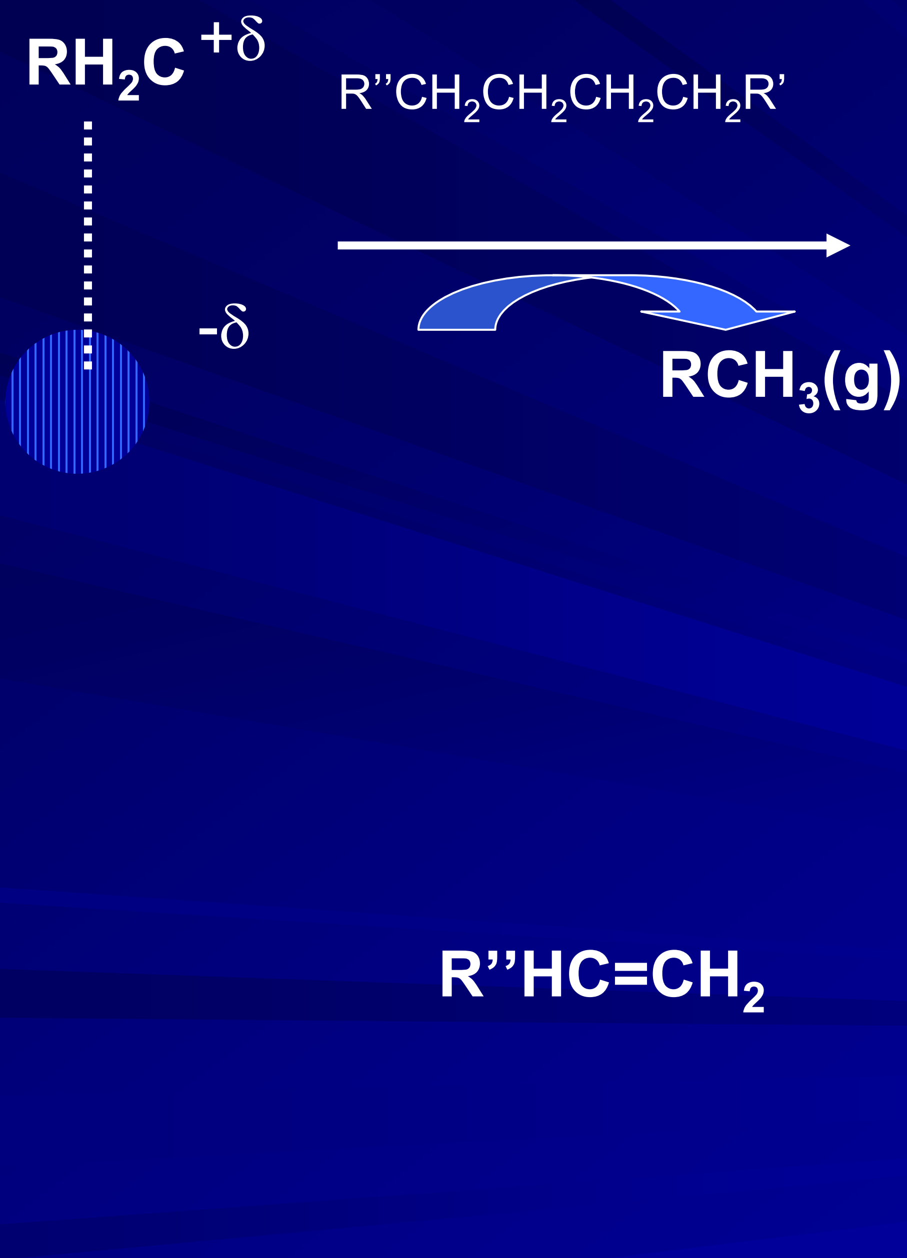
  therefore introducing cationic sites in the framework.
- If all alumina are replaced with phosphates then we have cationic framework, with labile anions, good for anion exchange applications.

  $[(AlO_4)_a(PO_4)_b]yR.nH_2O$ alumino-phosphate M. S.

  [(SiO4)x(PO4)y(AlO4)z]n+.R.nH2O
- Molecular sieves

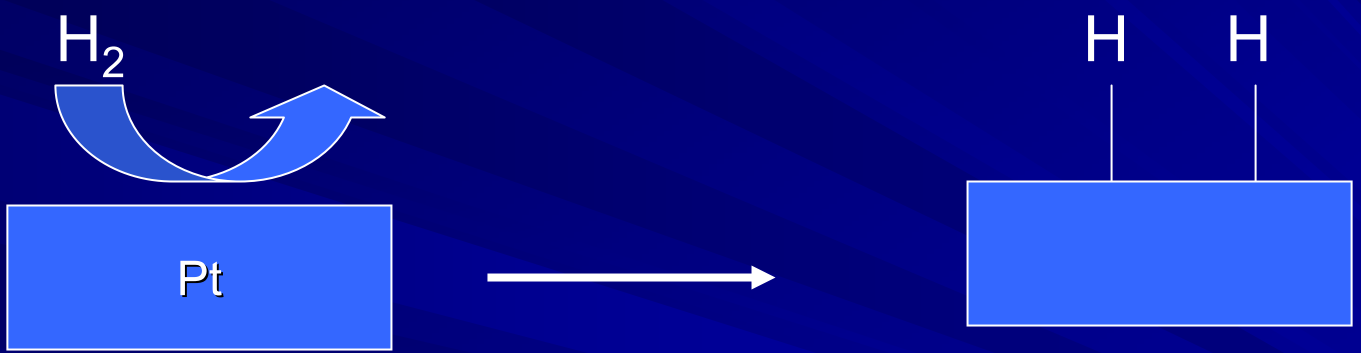
Catalysis by zeolites



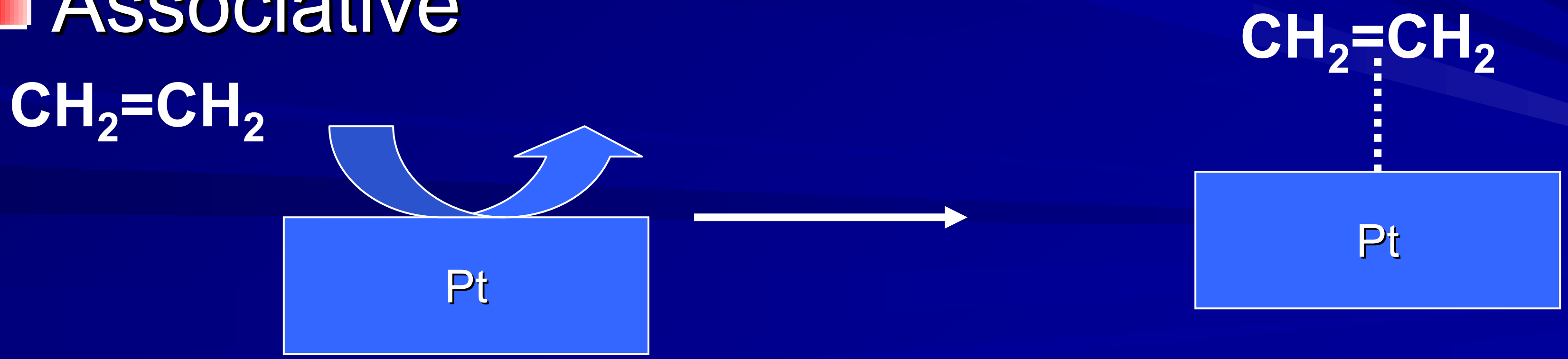

RH2C +δ
-δ
R''CH2CH2CH2CH2R'
RCH3(g)
R''H2CCH2βCH2 αCHR'
+δ
-δ
β-scission
R'H2C+δ
-δ
R''HC=CH2

Reactions at Surfaces

- Dissociative adsorption
- E.g.



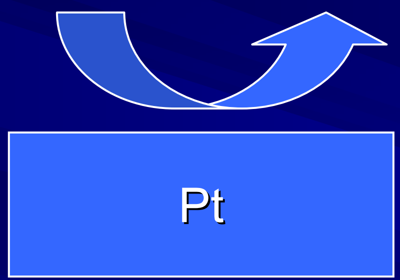
- Associative

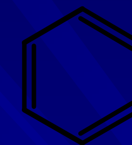


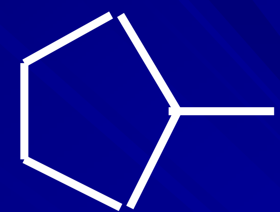
Reactions @ Surfaces

CH_3-CH_2-CH_2-CH_2-CH_2-CH_3

+ H_2



Aromitization  **+ H_2**

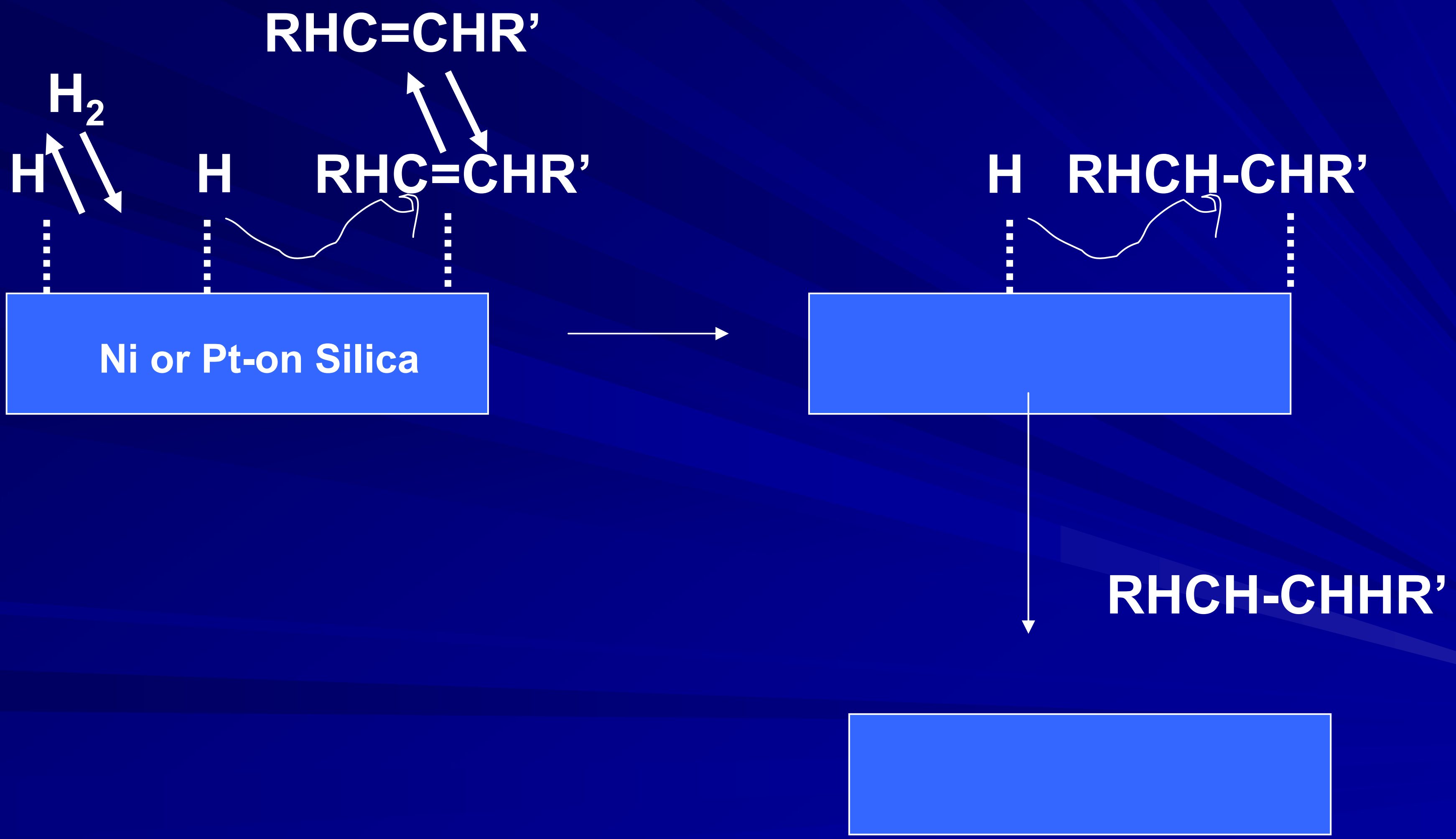
Cyclization  **+ H_2**

Isomerization **CH_3-$CH(CH_3)$-CH_2-CH_2-CH_3**

Hydrogenolysis **$2CH_3CH_2CH_3$**

Hydrogenation

Hydrogenation of Vegetable oil on Ni



Hydrogenolysis

- C-C bond scission
- Pt- induce C-C in a primary act
- Mo induce single and multiple C-C bond cleavage
- Fe induce multiple hydrogenolysis of higher alkanes to yield methane
- Pd & Ni favor terminal action
- Ir favor medial bond cleavage
- Mo & Rh are less selective

Hydrogenolysis

- The carbon chain must be attached to the surface in the form of a bridge across the metal atoms. When the electron density across the C-C bonds are depleted due to electron withdrawal to surface bond cleavage occurs.
- Hydrogenolysis: requires an ensemble of metal atoms @ the surface, therefore dilution of metal sites may result in decreasing hydrogenolysis;
- i.e. metal dispersion may decrease hydrogenolysis. At high degree of dispersion metal particles are too small to create the required ensemble.

Solid Acids

- Hydrocarbons are chemisorbed on acidic sites as positively charged species which may catalyze processes such as
  - Isomerization
  - Cracking
  - And polymerization
- Kinetic factors are not limiting in these conversions processes
- i.e. thermodynamics is very important in these conversions.

Adsorption of Alkene: Cracking & Polymerization

- Protonation gives carbonium ion of the following stability
- 3 ° >2 ° >1°
- $(CH_3)_3C^+ > CH_2CH_2CH^+CH_3 > CH_2CH_2CH_2CH_2^+$
- The process is sensitive to temperature

Isomerization

- Gas Phase
- CH_3-CH_2-CH=CH_2 CH_3CH=CH-CH_3
- CH_3-CH_2-CH^+-CH_3

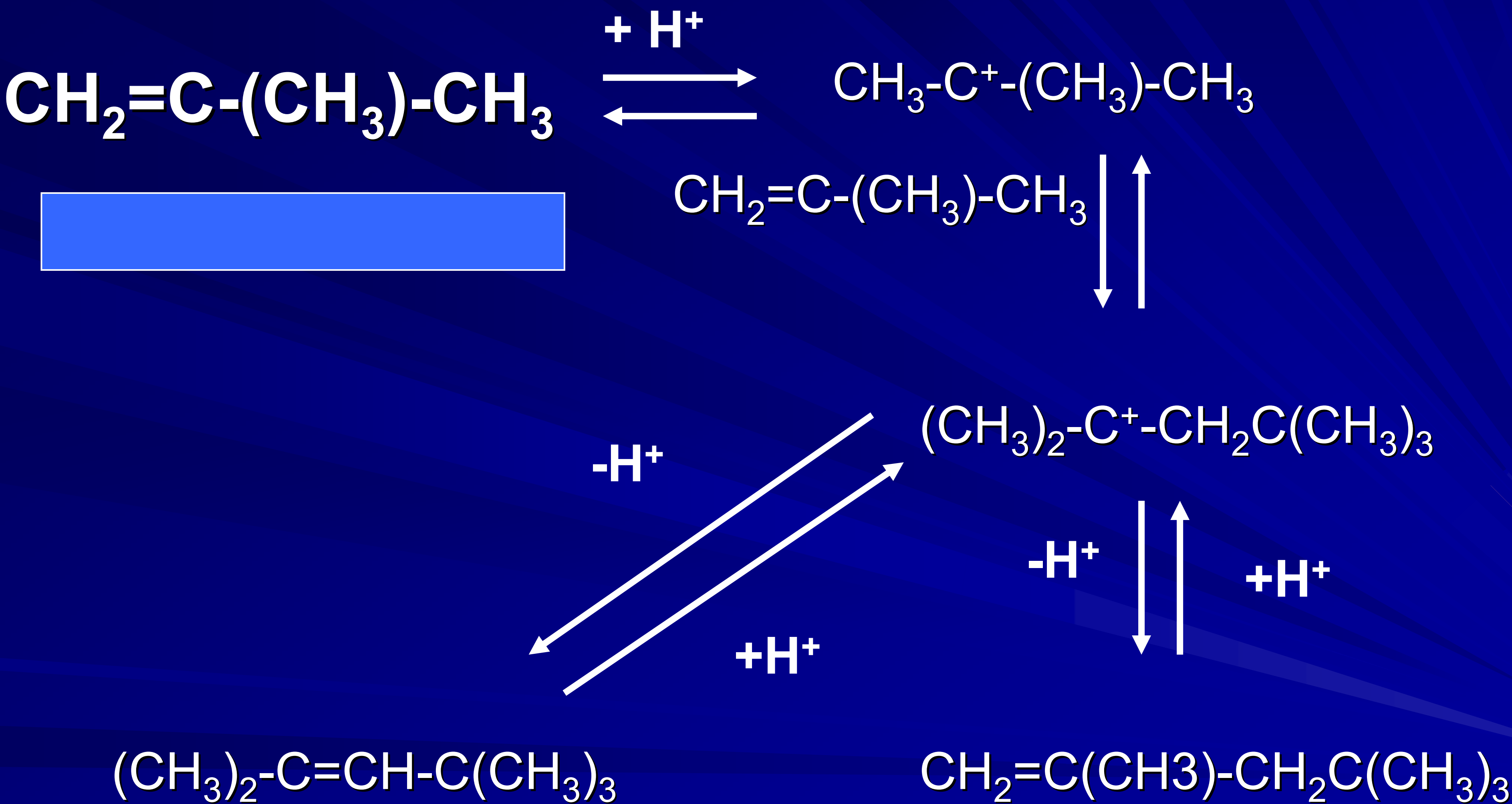
Surface

CH_3-C^+-(CH_3)-CH_3

-H^+ -H^+

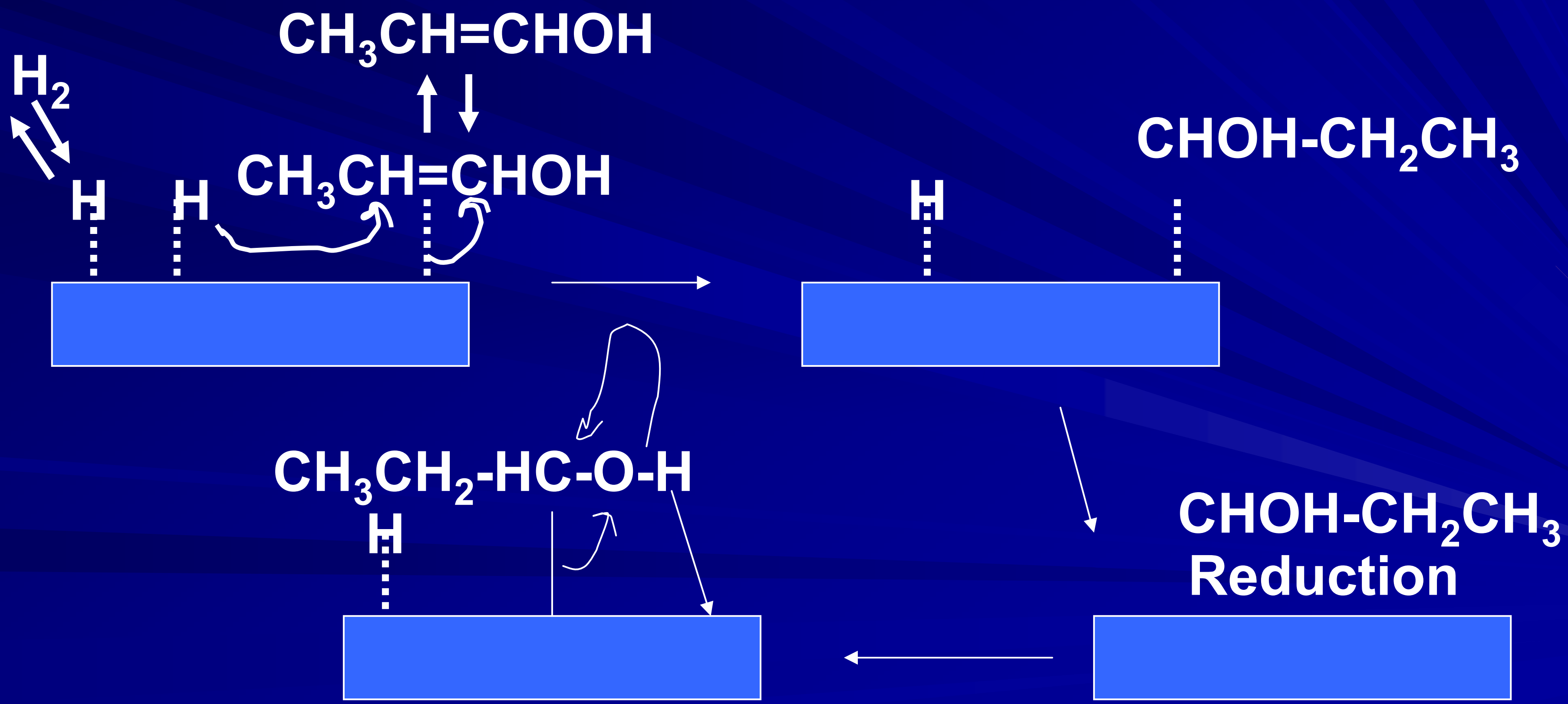
CH_2=C-(CH_3)-CH_3

Oligomirization

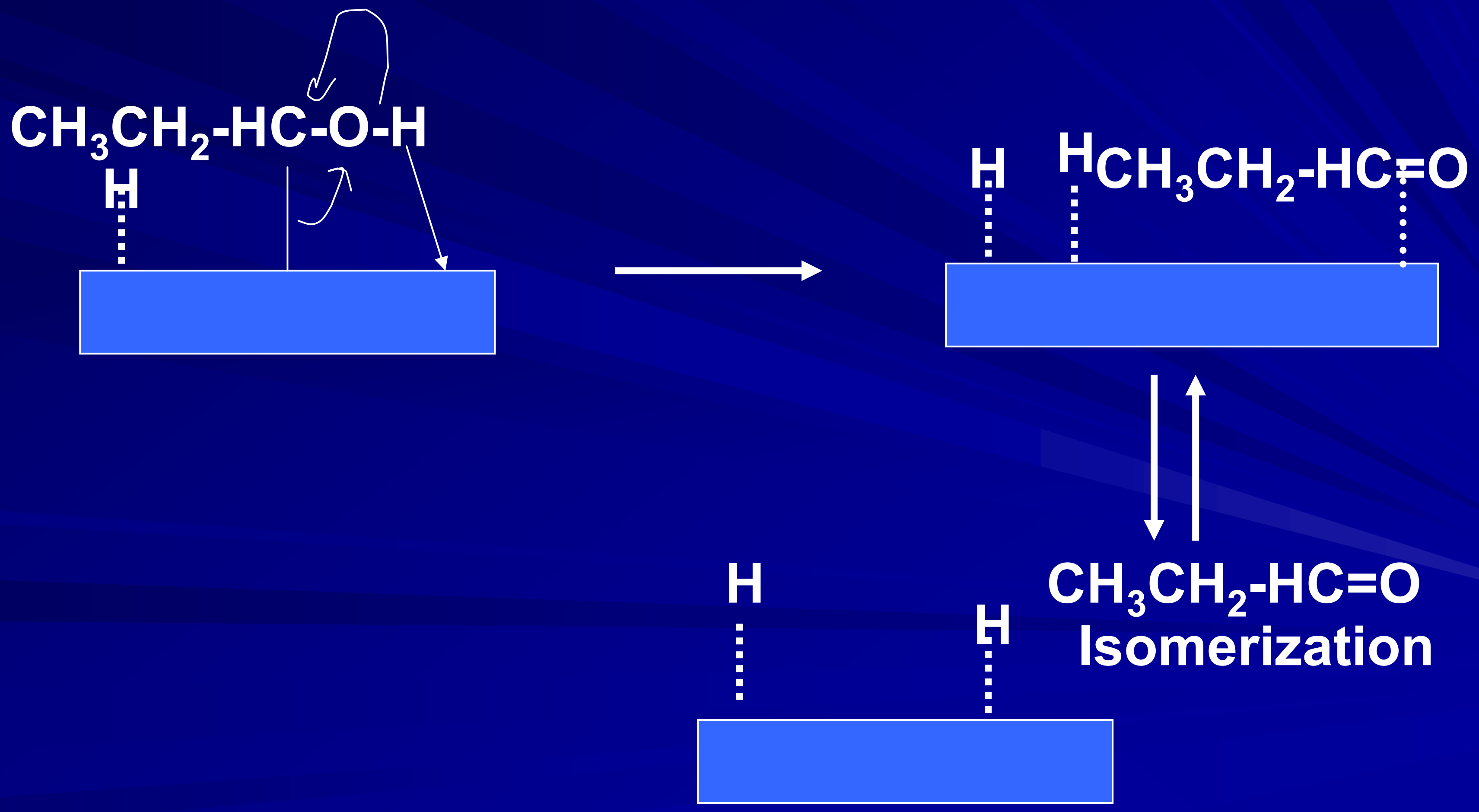


Hydrogenation & Dehydrogenation

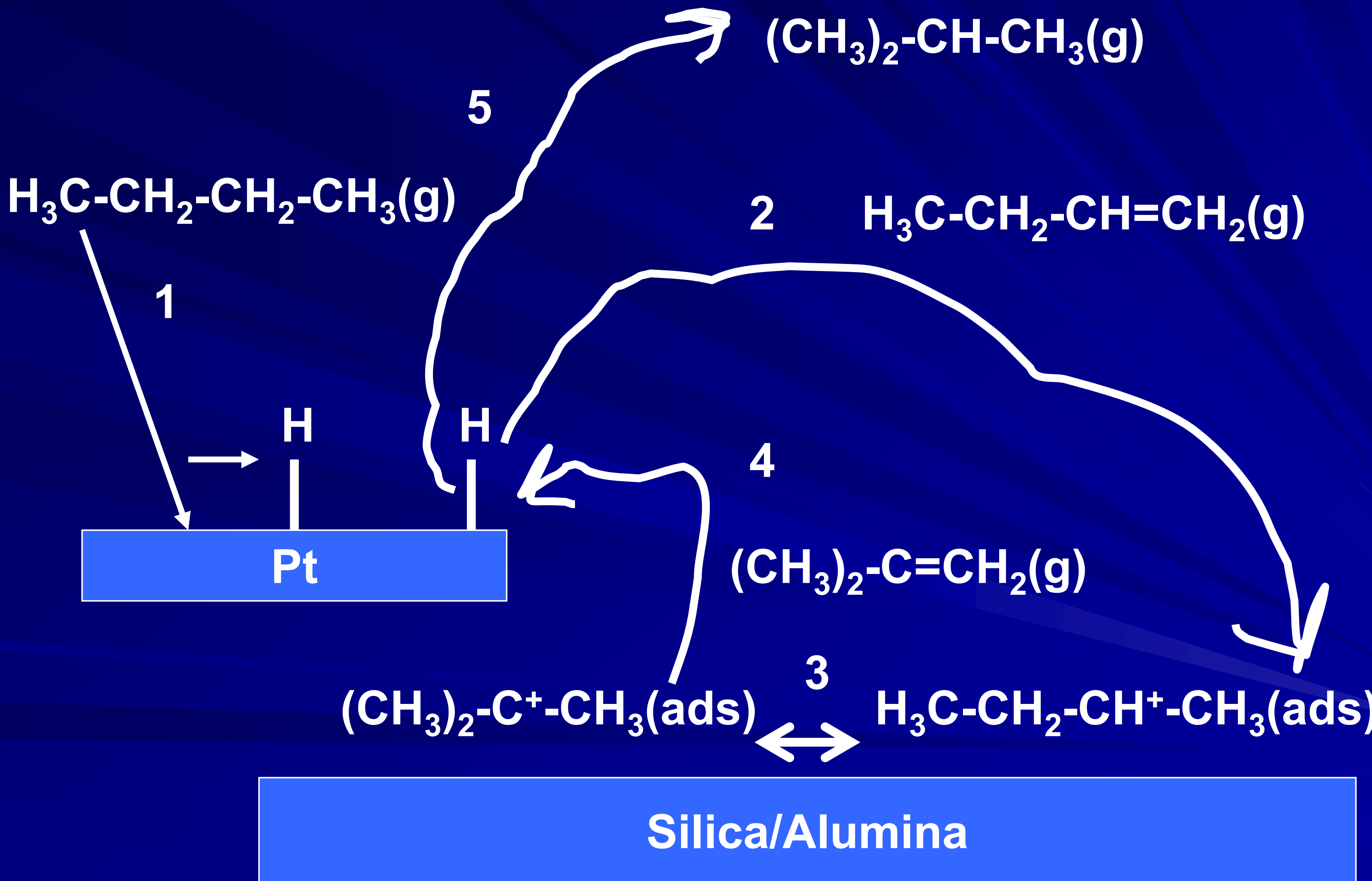
- Hydrogenation of 1-propene-1-ol on Rh/Al phosphate support



Isomerization



Reforming/Dual Catalysts



Oxidation Reactions on Redox Catalysts

- **Most selective oxidation catalyst are cations with an empty or full outermost d-orbitals, *e.g.* Mo^{VI} ($4d^0$) or V^V($3d^0$) and Sb^V and Sn^{IV} ($4d^{10}$)**
- **The oxides from these species have the ability to release associated lattice oxygen (O^{2-}) for incorporation into organic compounds, followed by reduction of the metal center to preserve electrical neutrality.**

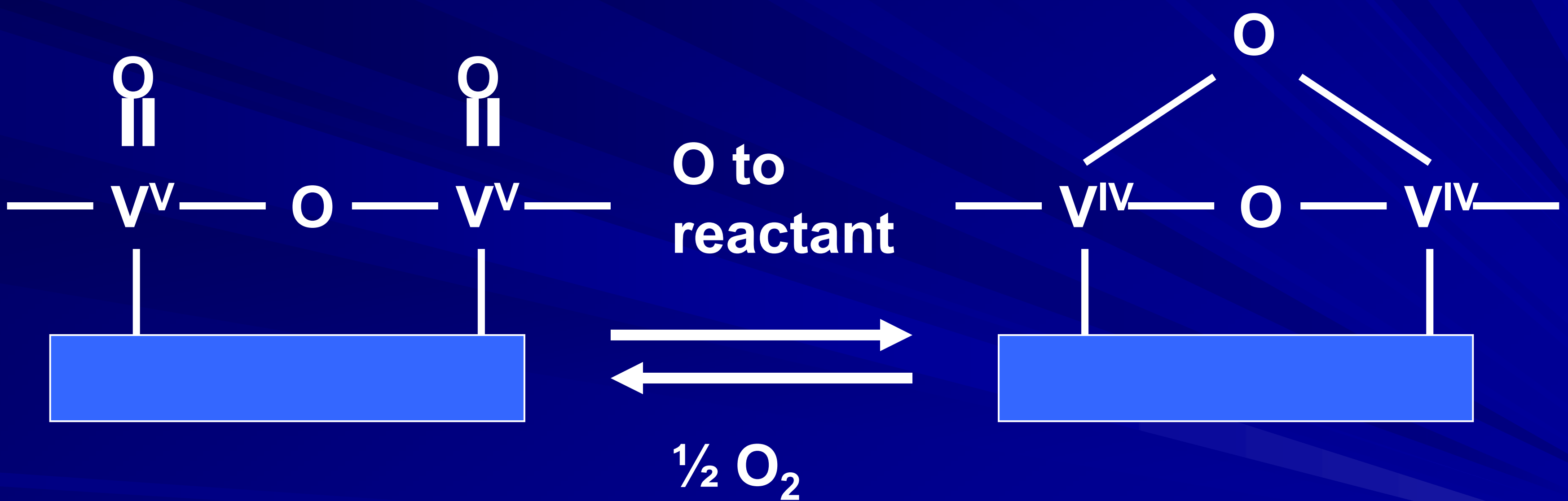
Oxidation Reactions on Redox Catalysts

- Two mechanisms
- A. $\frac{1}{2} O_2(g) \rightarrow O(ads)$

  $X(ads) + O(ads) \rightarrow$ product
- B $X (ads) + O(lattice) \rightarrow$ product + lattice vacancy

  $\frac{1}{2} O_2(g)$ + lattice vacancy $\rightarrow$ O (lattice)
- When X is an organic molecule, deep oxidation occur using mechanism a.
- Mechanism B results in selective oxidation.

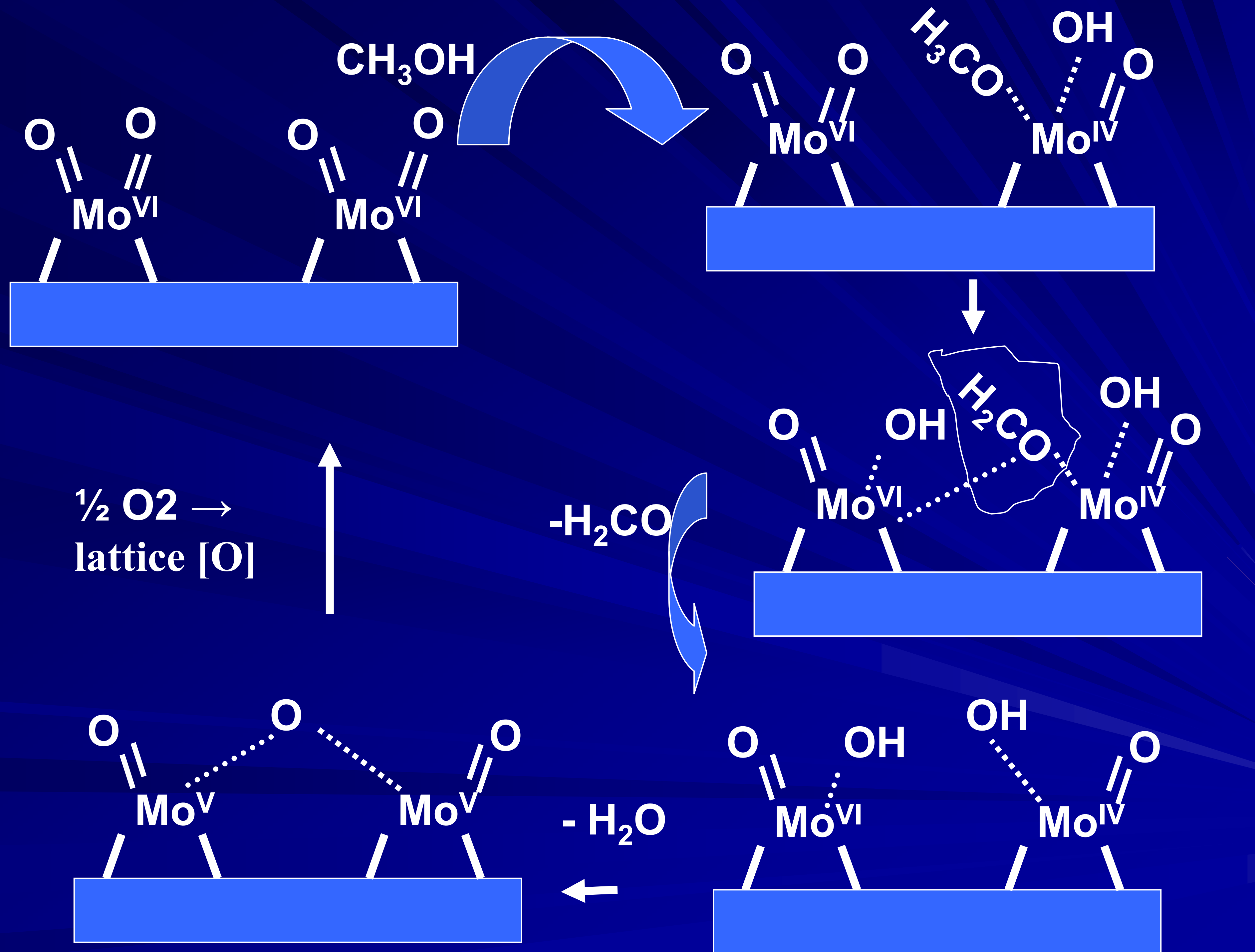
Redox Catalysis



- Many of the most selective oxidation catalysts are a mixture of metals from groups V, VI or VII and metalloids such as Bi_2O_3, SnO_2 and UO_2.

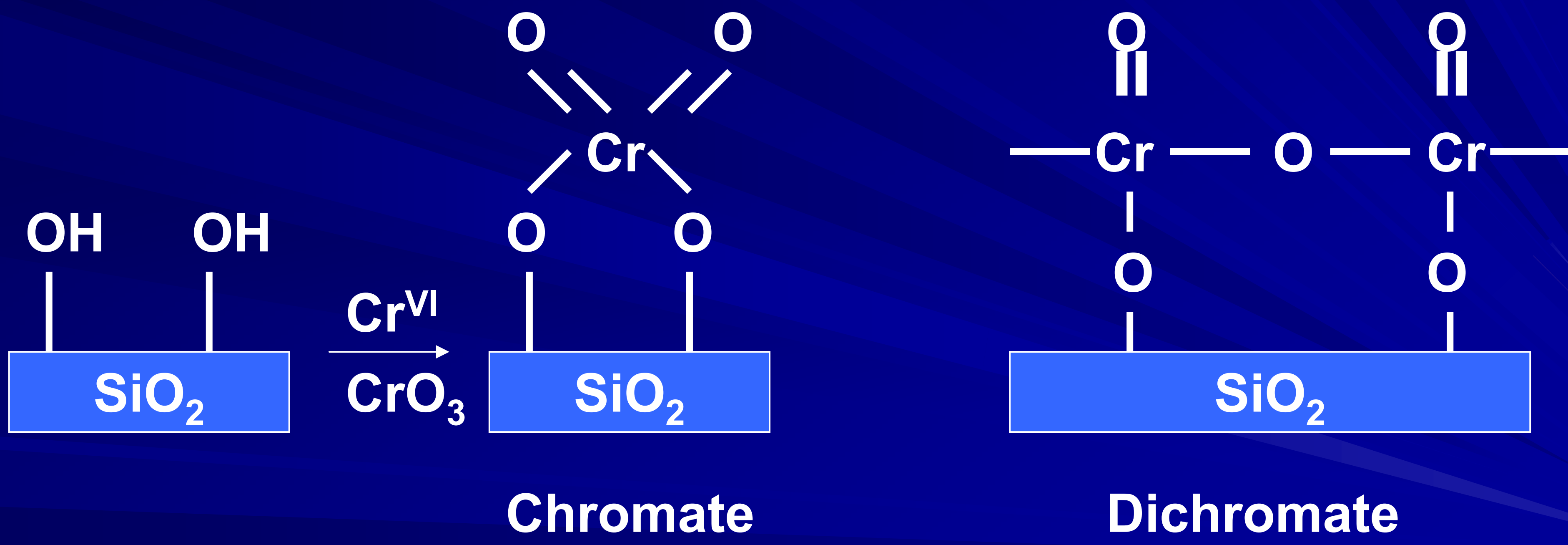
Redox Catalysis

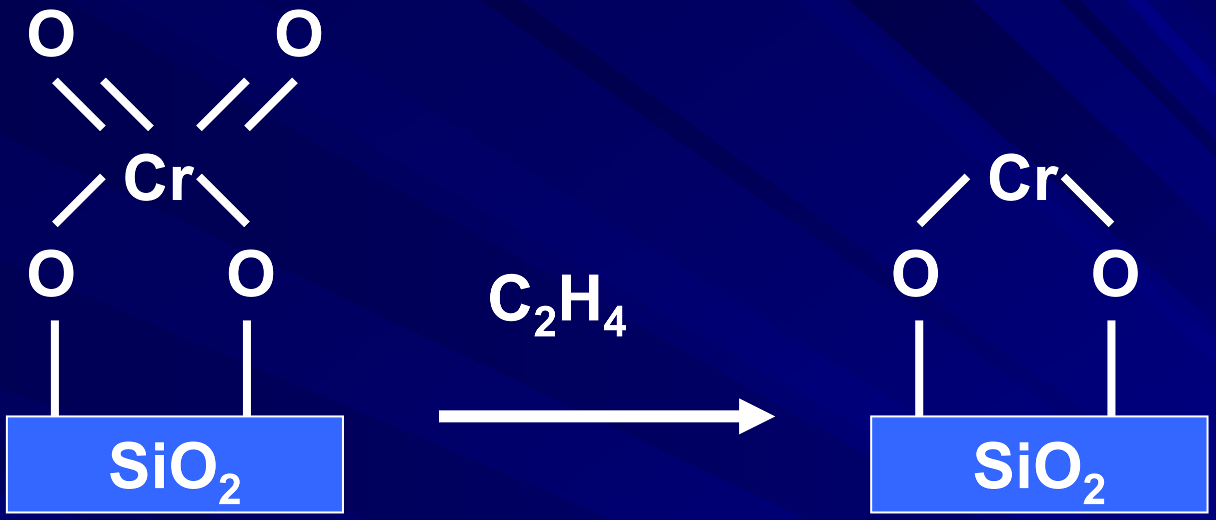
- e.g. $CH_3OH \rightarrow CH_2O$ on Vanadia or Mo-oxide molybdena surface.
- K_2SO_4 is a promotor. Donate electron density to the oxide, reduces the strength of the V=O bond.


CH3OH
O
O
MoVI
O
O
MoVI
O
O
MoVI
H3CO
OH
O
MoIV
½ O2 → lattice [O]
-H2CO
O
OH
MoVI
H2CO
OH
O
MoIV
O
O
O
MoV
MoV
- H2O
O
OH
MoVI
OH
O
MoIV

Linear Polyethylene Production

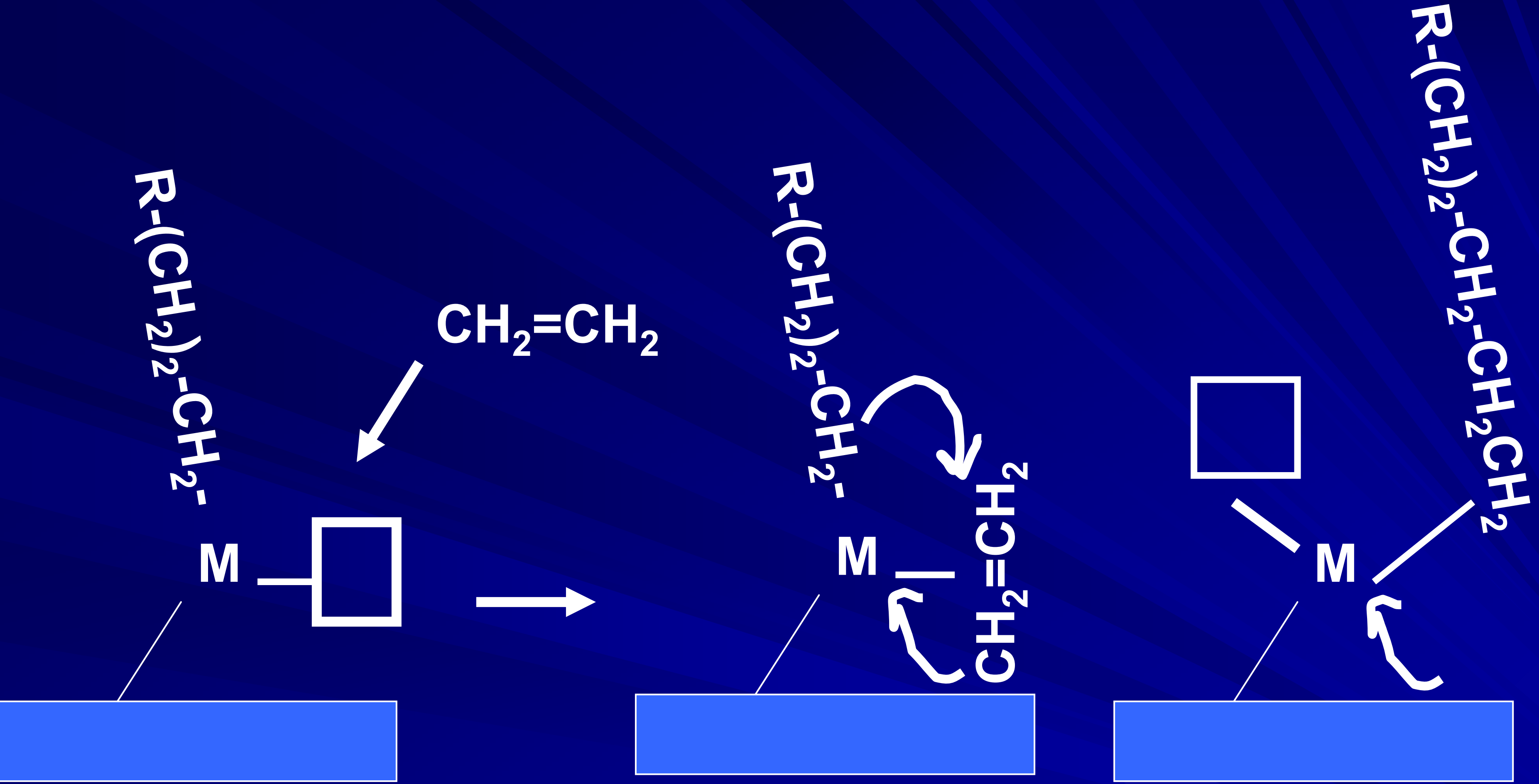
- Oxidized Ti (Ziegler-Natta catalysts $TiCl_4/AlEt_3$) and Cr (Phillips catalysts) are effective for the polymerization of alkene under mild conditions.





+ HCHO
Detected
product

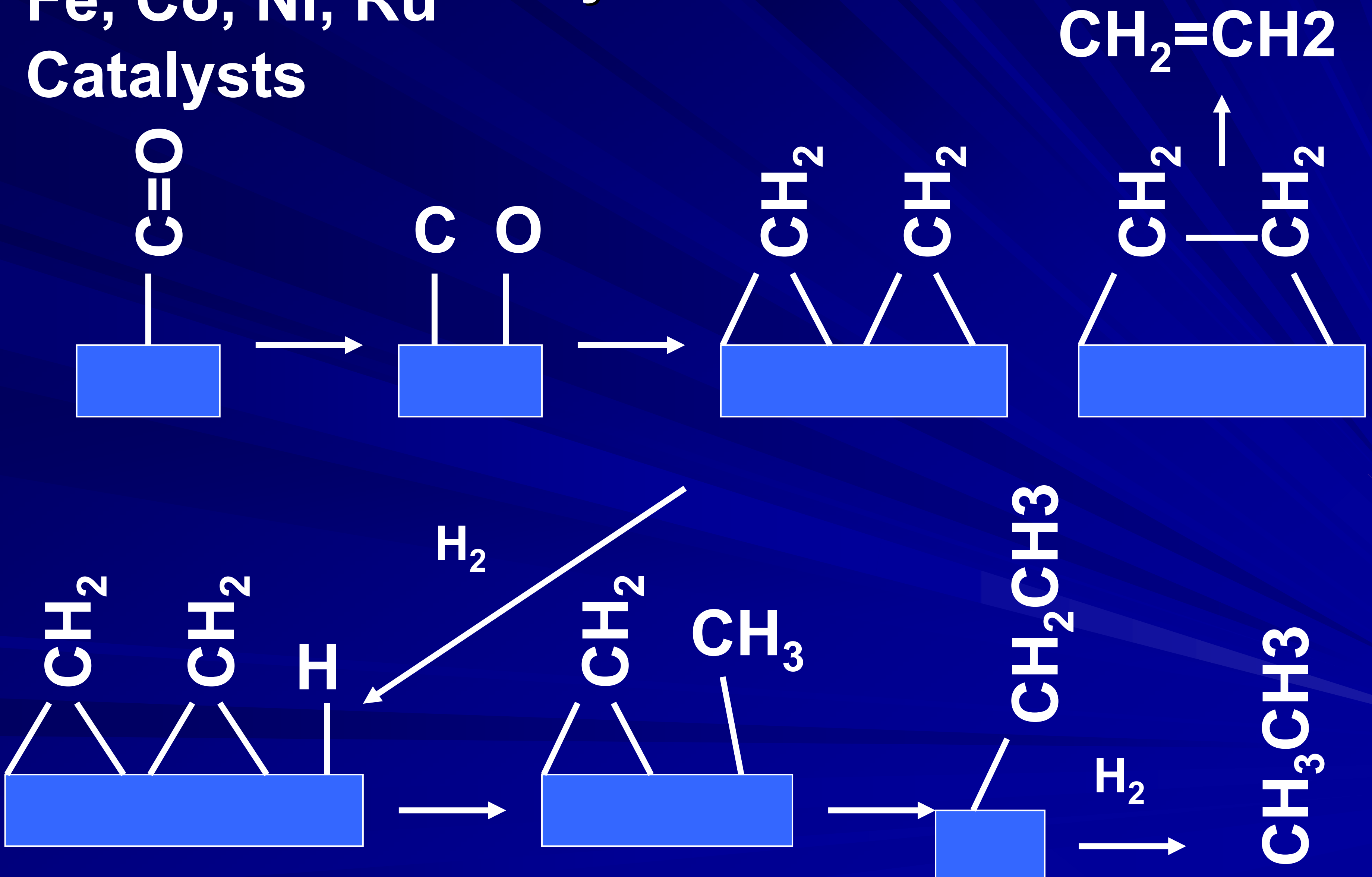
Active catalyst
Coordinatively unsaturated CrIII



R-(CH2)2-CH2-
M
CH2=CH2
R-(CH2)2-CH2-
M
CH2=CH2
R-(CH2)2-CH2-CH2CH2
M

Reduction of CO by H_2: The Fisher-Tropsch synthesis

Fe, Co, Ni, Ru Catalysts



Formation of HNO_3 & H_2SO_4

- $N_2 + 3H_2 \rightarrow 2NH_3$
- $SO_2 + \frac{1}{2} O_2 \rightarrow SO_3$