Modern Methods in Heterogeneous Catalysis Research

Acid-Base Catalysis

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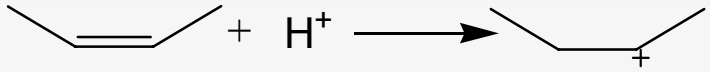
Outline

1. Introduction - basic principles
2. Substrates and products
3. Types of acid / base catalysts - examples
4. Characterization of surface acidity / basicity - examples
5. Acid catalyzed reactions
6. Base catalyzed reactions
7. Acid-base bifunctional catalysis
8. Summary and outlook

1. Introduction - Basic definitions

concept	acid	base
Brønsted	H_2O OH^- + H^+ proton donor	proton acceptor
Lewis	$FeCl_3$ + Cl^- $[FeCl_4]^-$ electron pair acceptor	electron pair donator

Hydrogen transfer reactions

		intermediates
acid-catalyzed		carbenium ions
base-catalyzed		carbanions

1. Introduction - Basic definitions

	specific acid / base catalysis	**general acid / base catalysis**
active species	H_3O^+ or OH^-	undissociated acid or base groups; a variety of species may be simultaneously active
reaction medium / conditions	•in solution •on the surface of a hydrated solid	•gas phase reactions •high reaction temperatures

1. Introduction - Basic definitions

Advantages of **solid** acid-base catalysts:

- Easier separation from the product
- Possible reuse and regeneration
- Fewer disposal problems
- Non-corrosive and environmentally friendly (but not always!)

2. Substrates and products

	solid acid catalysis	solid base catalysis
substrates	•Alkanes, aromatics (components of crude petrolium) •Alkenes (products of petrolium cracking (FCC, steam cracking))	•Alkenes •Alkynes •Alkyl aromatics •Carbonyl compounds
products	•Gasoline components •Chemical intermediates •Fine chemicals	•Chemical intermediates •Fine chemicals

K.Tanabe, W.F.Hölderich, Applied Catalysis A 181 (1999) 399.

3. Types of acid / base catalysts

Industrial processes in 1999:

103	solid acids	worldwide production by catalytic cracking: 500×10^6 tonnes/y
10	solid bases	
14	solid acid-base bifunctional catalysts	

K. Tanabe, W.F. Hölderich, Applied Catalysis A 181 (1999) 399.

3. Types of acid / base catalysts

Solid acids	Solid bases
•Zeolites ZSM-5, Mordenite, Y-zeolite, US-Y, Beta •Oxides, phosphates SiO_2-Al_2O_3, Al_2O_3-BF_3, SO_4^{2-}(Mn,Fe)/ZrO2, $SrHPO_4$, $FePO_4$, Li_3PO_4, phosphoric acid, SAPO-11, SAPO-34 1.Ion-exchange resins Amberlyst®, Nafion® •Clays Kaolinite, Montmorillonite, pillared clays	•Oxides and modified oxides Al_2O_3-NaOH-Na, Al_2O_3-KOH-K, ZrO_2-KOH, ZrO_2-K_2O, MgO, MgO-Al_2O_3, hydrotalcites •Zeolites CsNaX, CsNaY, microporous titanosilicate ETS-10 •Mesoporous silicas modified with amino groups •Cs/NPC •Oxynitrides AlPON, AlGaPON, ZrPON

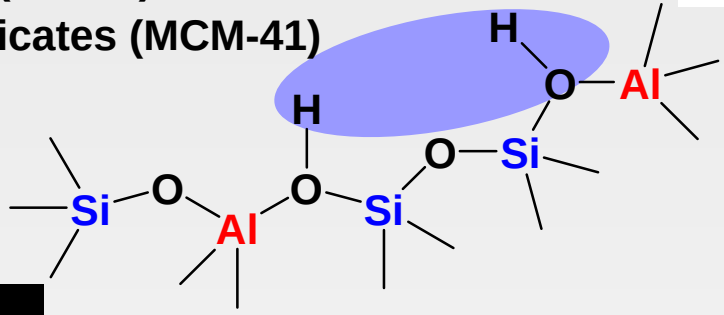
K. Tanabe, W.F. Hölderich, Applied Catalysis A 181 (1999) 399.

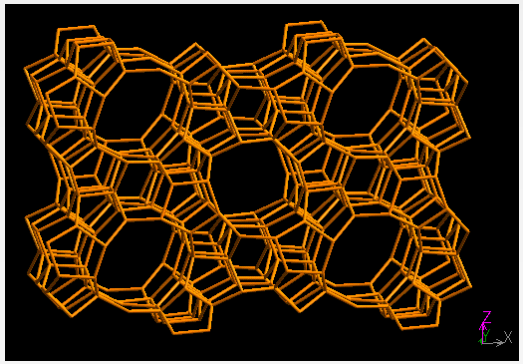
Alumosilicates

- Amorphous alumosilicates
- Microporous zeolites (ZSM-5)
- Mesoporous alumosilicates (MCM-41)

Brønsted acid site

in H-exchanged zeolites

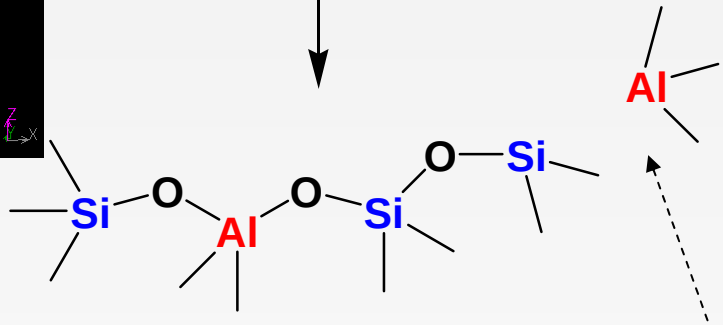




MFI viewed along [010]

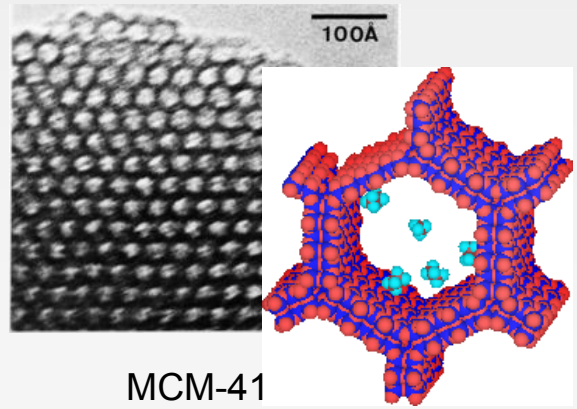
d = 5.3x5.6 Å

- H_2O



or extraframework Al^{3+}

Lewis acid sites

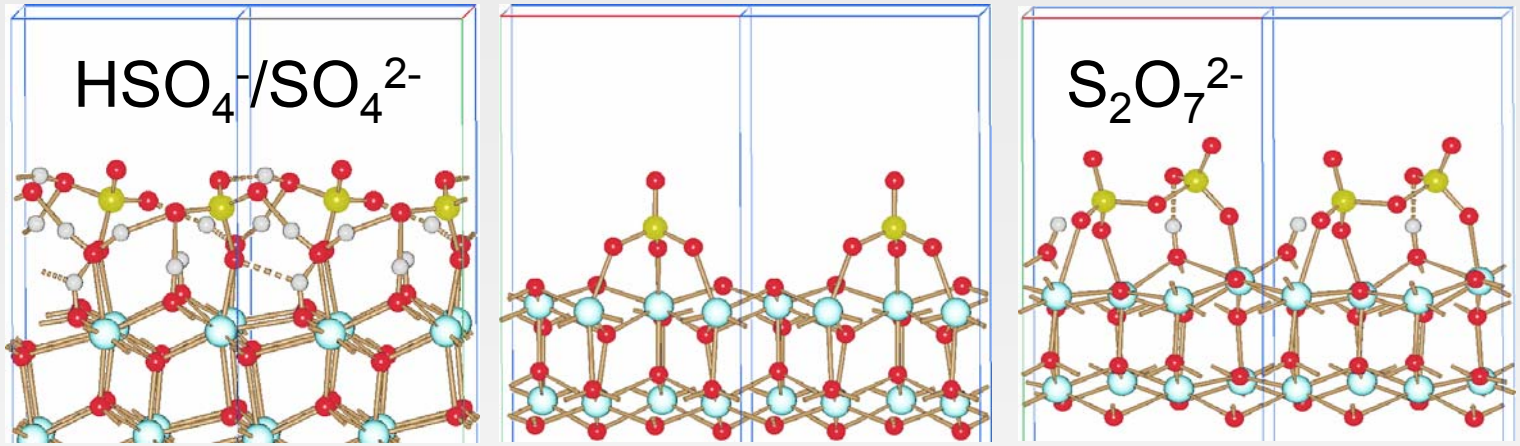


MCM-41

www.iza-structure.org/databases/

Sulfated zirconia

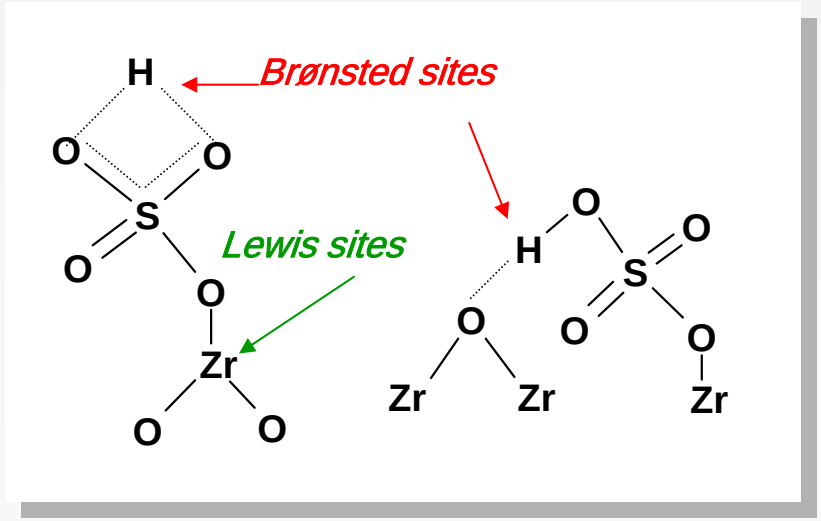
Structure of surface sulfates



A. Hofmann, J. Sauer, J. Phys. Chem B 108 (2004) 14652.

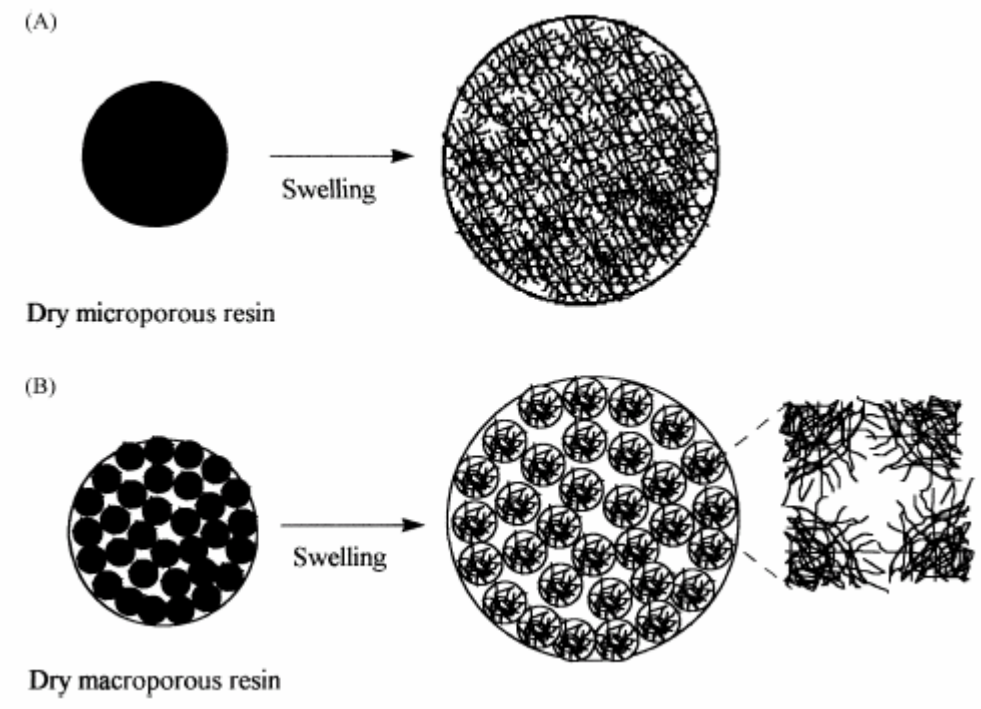
Surface acid sites

L.M. Kustov, V.B.Kazansky, F.Figueras, D. Tichit, J. Catal. 150 (1994) 143.

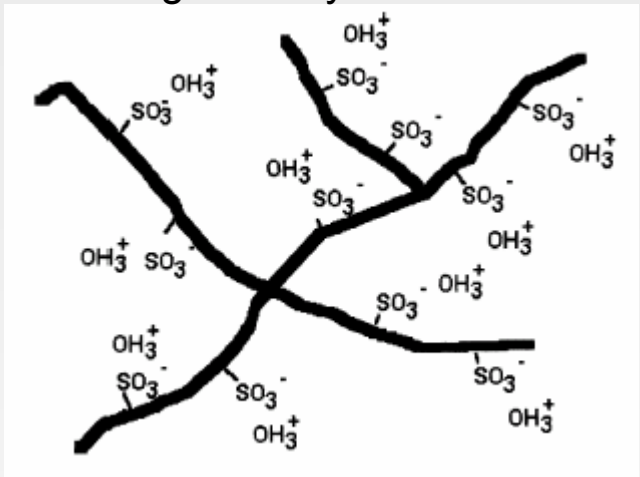


Resins

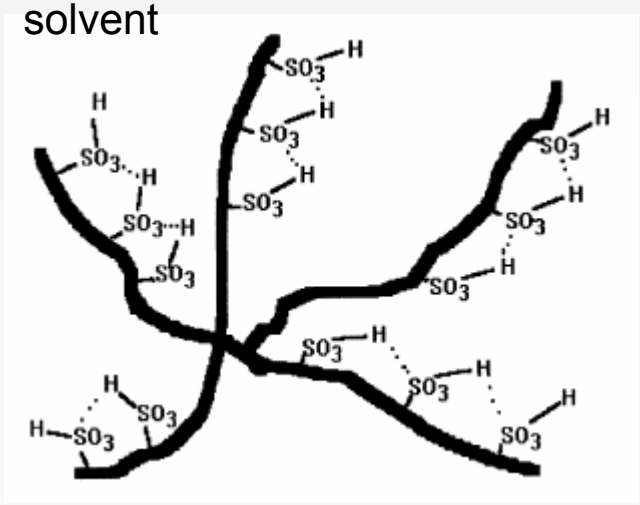
Morphology of styrene-based sulfonic acids



Hydrated protons in water-swollen ion exchanger catalyst

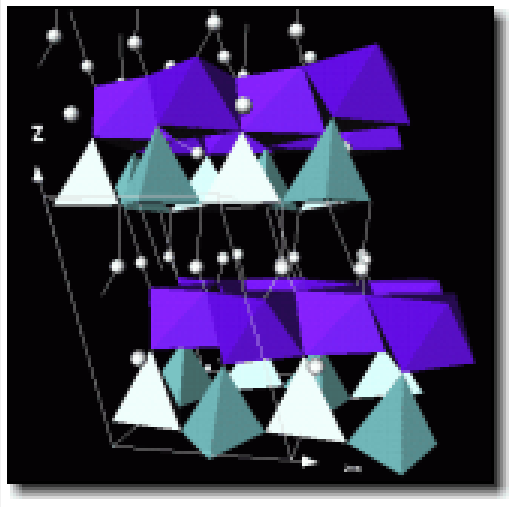


Undissociated acidic protons in a catalyst swollen in non-aqueous solvent



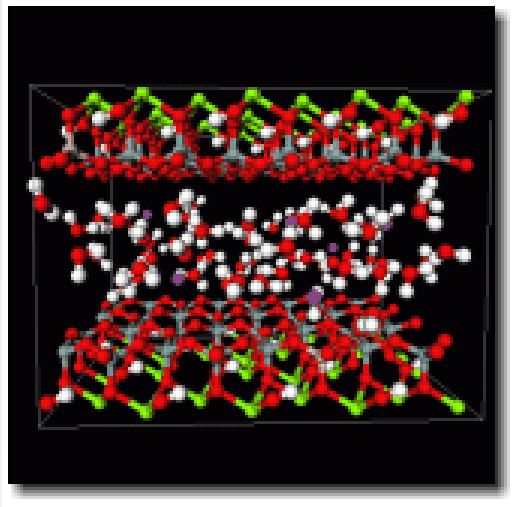
B. Corain, M. Zecca, K. Jeřábek, J. Mol. Catal. A 177 (2001) 3.

Clays and pillared clays



$Al_2[Si_2O_5](OH)_4$

Kaolinite



$Al_2[Si_4O_{10}](OH)_2$

Montmorillonite

Acid sites: Brønsted (protons) and Lewis (metal ions)

Z. Ding, J.T. Kloprogge, R.L. Frost, G.Q. Lu, H.Y. Zhu, Journal of Porous Materials 8 (2001).

http://www.ill.fr/dif/3D-crystals/layers.html

MgO

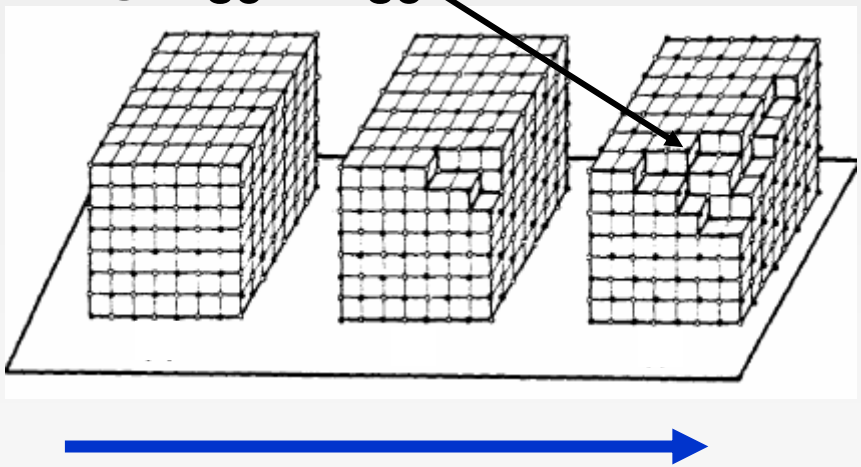
- Basic sites:
  - hydroxyl group
  - surface oxygen anions
- Anionic charge of the oxygen is associated to the ionicity of the M-O bond and, therefore, always also to Lewis acidity

ions pairs $Mg^{2+}_{3c}O^{2-}_{3c}$

Sites:

- five coordinated sites on flat (001) faces (M^{2+}_{5c} and O^{2-}_{5c})
- four coordinated sites on steps and edges (M^{2+}_{4c} and O^{2-}_{4c})
- three coordinated sites on corners (M^{2+}_{3c} and O^{2-}_{3c})

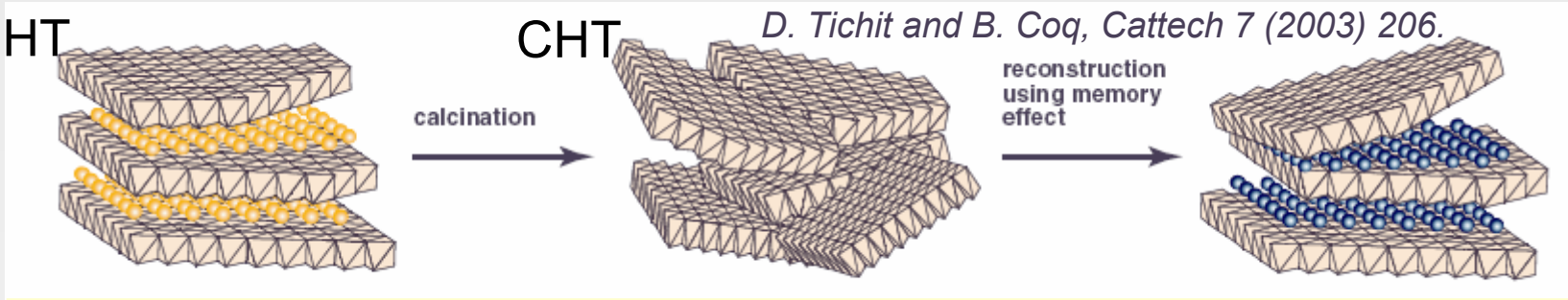
(c = coordinatively unsaturated).



progressive water attack on MgO

G. Spoto, E.N. Gribov, G. Ricchiardi, A. Damin, D. Scarano, S. Bordiga, C. Lamberti, A. Zecchina, Progress in Surface Science 76 (2004) 71.
S. Coluccia, Stud. Surf. Sci. Catal. 21 (1985) 5.

Hydrotalcites and $MgO\text{-}Al_2O_3$

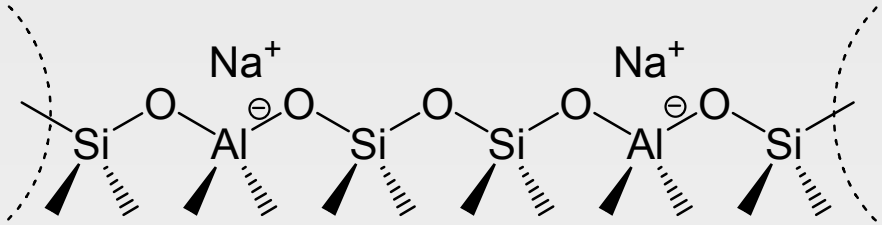


$[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}[A_{x/n}]^{n-1}\cdot mH_2O$; M^{2+}= Mg^{2+}; M^{3+}=Al^{3+}, A= CO_3^{2-}, OH^-

Sample	Theor. ratio Al/(Al + Mg)	Mg/Al molar ratio			S_{BET} (m^2/g)	V_p (cm^3/g)	d_p[a] (Å)	C[b] (wt%)	Weight loss[c] (wt%)
		Theor.	Bulk (ICP)	Surface (XPS)					
HT0.6 (MG30)	0.67	0.5	0.6	n.d.	163	0.32	76	1.42	n.a
HT1.4 (MG50)	0.44	1.25	1.4	n.d.	13	0.05	167	1.19	n.a
HT2.2 (MG61)	0.33	2.0	2.2	n.d.	15	0.05	128	2.42	n.a.
HT3.0 (MG70)	0.25	3.0	3.0	n.d.	20	0.10	205	2.27	n.a.
CHT0.6	0.67	0.5	0.6	0.8	257	0.52	81	-	31
CHT1.4	0.44	1.25	1.4	1.4	201	0.23	45	-	36
CHT2.2	0.33	2.0	2.2	2.0	114	0.13	46	-	42
CHT3.0	0.25	3.0	3.0	2.0	203	0.22	52	-	44
MgO	-	-	-	-	75	0.96	258	-	-
Al_2O_3	-	-	-	-	234	0.54	45	-	-

Basic zeolites

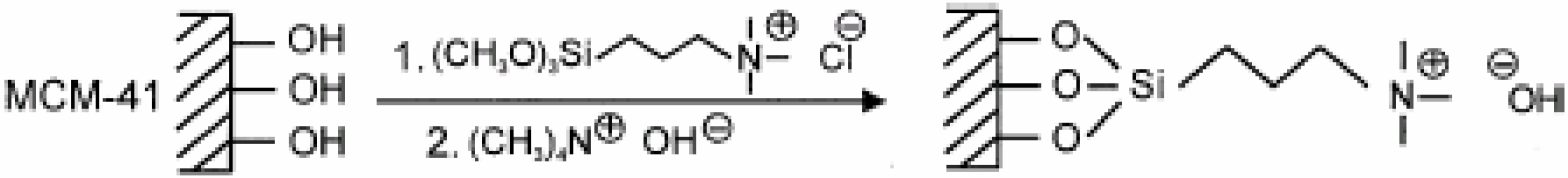
•Basicity is related to framework oxygen



•Exchanging zeolites with a less electronegative charge balancing cation such as Cs^+ creates a more basic zeolite (shift to lower O_{1s} binding energies)

•Occlusion of alkali metal oxide clusters or alkali metal clusters in zeolite cages

•Anchoring organic bases at silanol groups of mesoporous alumosilicates (e.g. 3-trimethyloxysilyl-propyl(trimethyl)ammonium chloride) – wide distribution of base sites



I. Rodriguez, S. Iborra, A. Corma, F. Rey, J.L. Jordá, Chem. Commun. (1999) 593.

4. Characterization of acid / base properties

Indicator methods

The color change of an indicator B^- is determined by the reaction

$$B^- + H^+ \rightleftharpoons BH$$

B^- base indicator
BH conjugated acid

$$H_- = pK_{BH} + \log \frac{[B^-]}{[BH]}$$

Hammett acidity function

Louis P. Hammett, Alden J. Deyrup, J. Am. Chem. Soc. 54(7) (1932) 2721.

Tanabe et al., Stud. Surf. Sci. Catal. 51 (1989) 21:

H_- is equal to the highest among the pK_{BH} values of adsorbed indicators from which the basic site is able to abstract a proton (i.e., which can be protonated by the acid site).

$H_- < -12$ „superacid“

$H_- > 26$ „superbase“

4. Characterization of acid / base properties

Hammett Indicators

TABLE 2–3 Basic indicators used for spectrophotometric determination of acid strength

Indicators	pK_a
Phenylazonaphthylamine	+4.0
p-Dimethylaminoazobenzene	+3.3
Aminoazobenzene	+2.8
Benzeneazodiphenylamine	+1.5
p-Nitroaniline	+1.1
o-Nitroaniline	−0.2
p-Nitrodiphenylamine	−2.4
2,4-Dichloro-6-nitroaniline	−3.2
p-Nitroazobenzene	−3.3
2,4-Dinitroaniline	−4.4
Benzalacetophenone	−5.6
p-Benzoyldiphenyl	−6.2
Anthraquinone	−8.1
2,4,6-Trinitroaniline	−9.3
3-Chloro-2,4,6-trinitroaniline	−9.7
p-Nitrotoluene	−10.5
Nitrobenzene	−11.4
2,4-Dinitrotoluene	−12.8

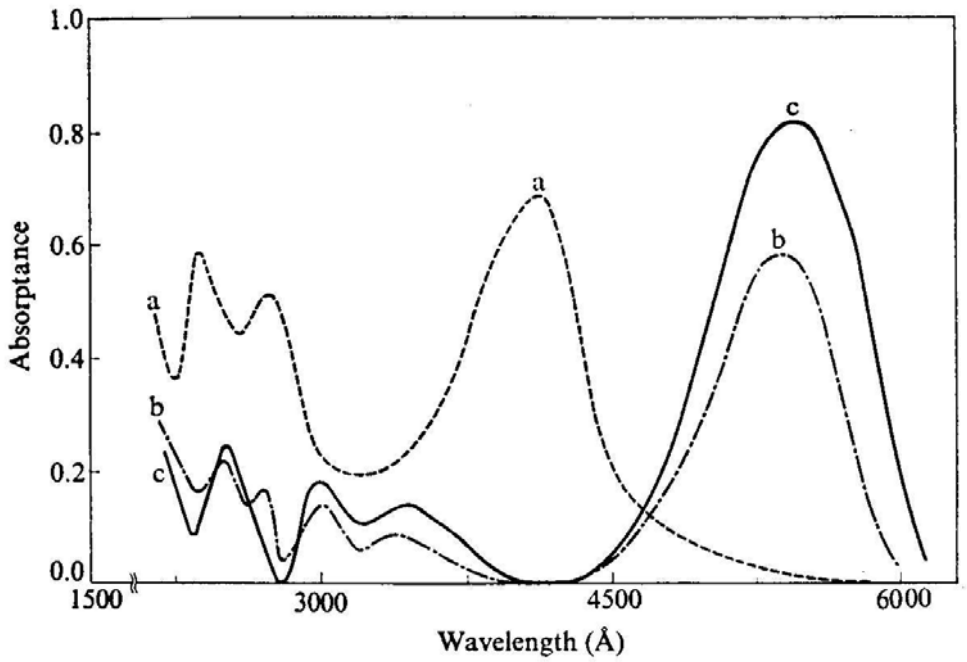


Fig. 2–1 Absorption spectra for phenylazonaphthylamine
a: in isooctane solution, b: in ethanolic HCl, c: adsorbed on silica-alumina

- Approach is only applicable to **Brønsted** acid and bases of **uniform** strength.
- Color change is not always related to the acid-base reaction, e.g., formation of charge-transfer complexes, colorless catalyst required

4. Characterization of acid / base properties

Gas Phase Acidity – Electron Affinity

$$M^{x+}\ (g) + e^{-}\ (g) \rightarrow M^{(x-1)+}\ (g)$$

Electron affinity [kJ/mol]

low ionization energy, i.e. high electron affinity = high acidity

	kJ/mol
K^{+}	419
Mn^{2+}	1509
Pt^{3+}	1791
Co^{3+}	3232

4. Characterization of acid / base properties

Gas Phase Basicity – Proton Affinity

$$B\ (g) + H^+\ (g) \rightarrow BH^+\ (g)$$

$$B^-\ (g) + H^+\ (g) \rightarrow BH\ (g)$$

Proton affinity [kJ/mol]

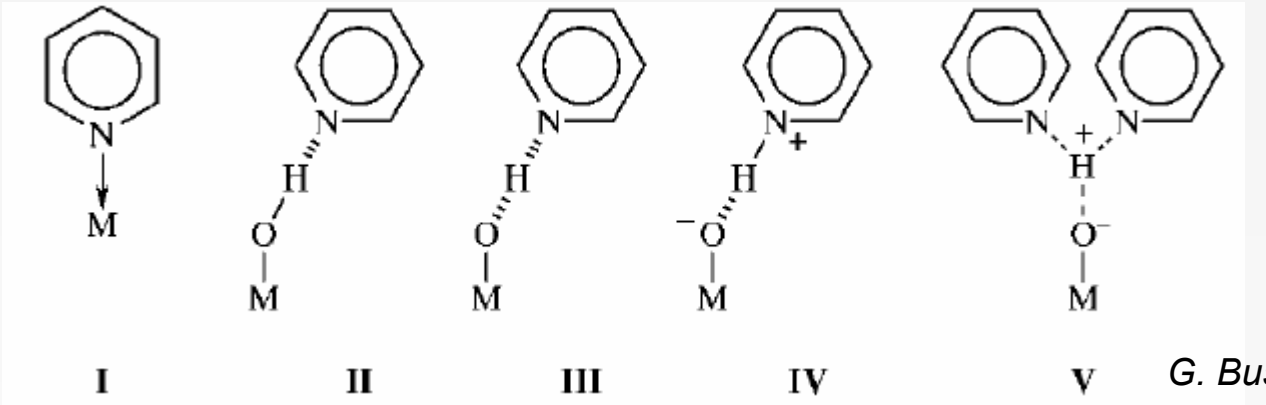
the negative enthalpy of the protonation reaction,
i.e. high proton affinity = high basicity

	kJ/mol
CO	594
H2O	697
NH3	872
C5H5N Pyridine	953

FTIR of adsorbed bases

Base		Conjugated acid	Basic strength		Sensitive bands (base) Lewis acidity		Diagnostic band (acid) Brønsted acidity	
			pK_a	PA[a]	Mode	Position[b]	Mode	Position[b]
Piperidine	$C_5H_{10}NH$	$C_5H_{10}NH_2^+$	11.1	933			$\delta\ NH_2^+$	~1650
n-Butylamine	n-C_4H_9—NH_2	n-C_4H_9—NH_3^+	10.9				$\delta_{sym}\ NH_3^+$	~1540
Ammonia	NH_3	NH_4^+	9.2	846	$\delta_{sym}\ NH_3$	1300–1000	$\delta_{as}\ NH_4^+$	~1440
Pyridine	C_5H_5N	$C_5H_5NH^+$	5.2	912	ν8a	1632–1580	ν8a	~1640
					ν19b	1455–1438	ν19b	~1540
					ν1 (ring)	1020–990		
Acetone	$(CH_3)_2C{=}O$	$(CH_3)_2C{=}OH^+$	−7.2	816	$\nu C{=}O$	1730–1650		
Pyvalonitrile	t-C_4H_9—$C{\equiv}N$	t-$C_4H_9C{\equiv}NH^+$	~ −10		$\nu C{\equiv}N$	2310–2235		
Acetonitrile	CH_3—$C{\equiv}N$	CH_3—$C{\equiv}NH^+$	−10.4	783	$\nu C{\equiv}N$	2340–2290		
					F.R.[c]	2315–2250		
Nitric oxide	NO	$[HNO]^+$			$\nu N{\equiv}O$	2100–1875		
Carbon monoxide	CO	$[HCO]^+$		598	$\nu C{\equiv}O$	2240–2150		

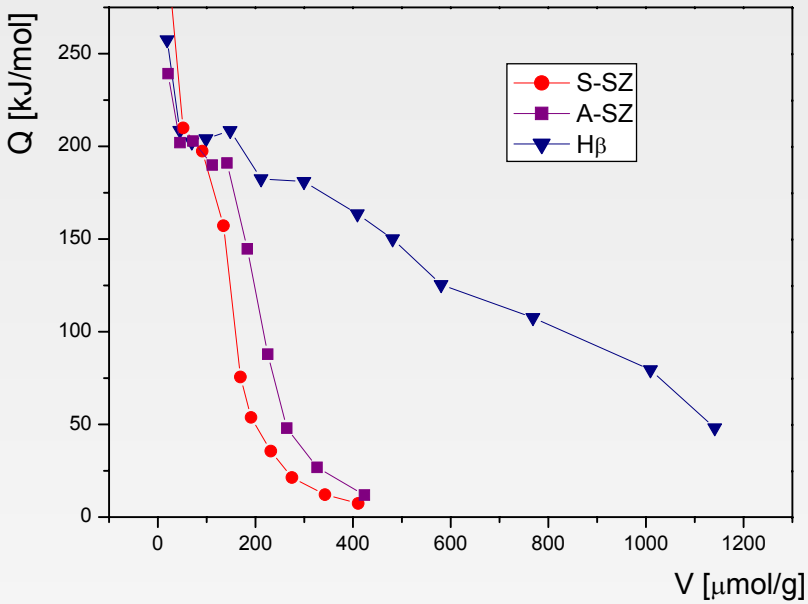
[a] PA = proton affinity (kJ mol^{-1}). [b] Range (cm^{-1}). [c] Fermi resonance doublet.

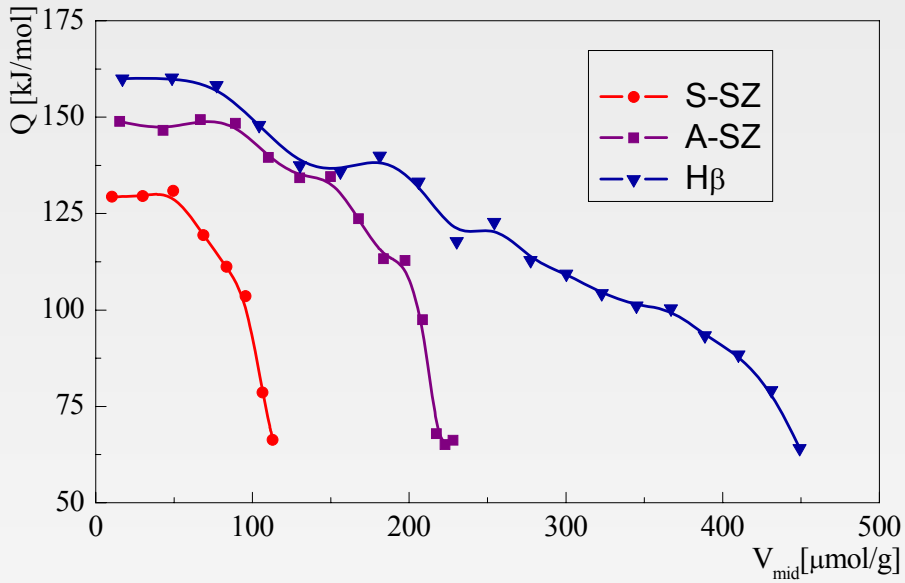


G. Busca, PCCP 1 (1999) 723.

Microcalorimetry

Pyridine adsorption





150°C, gas phase

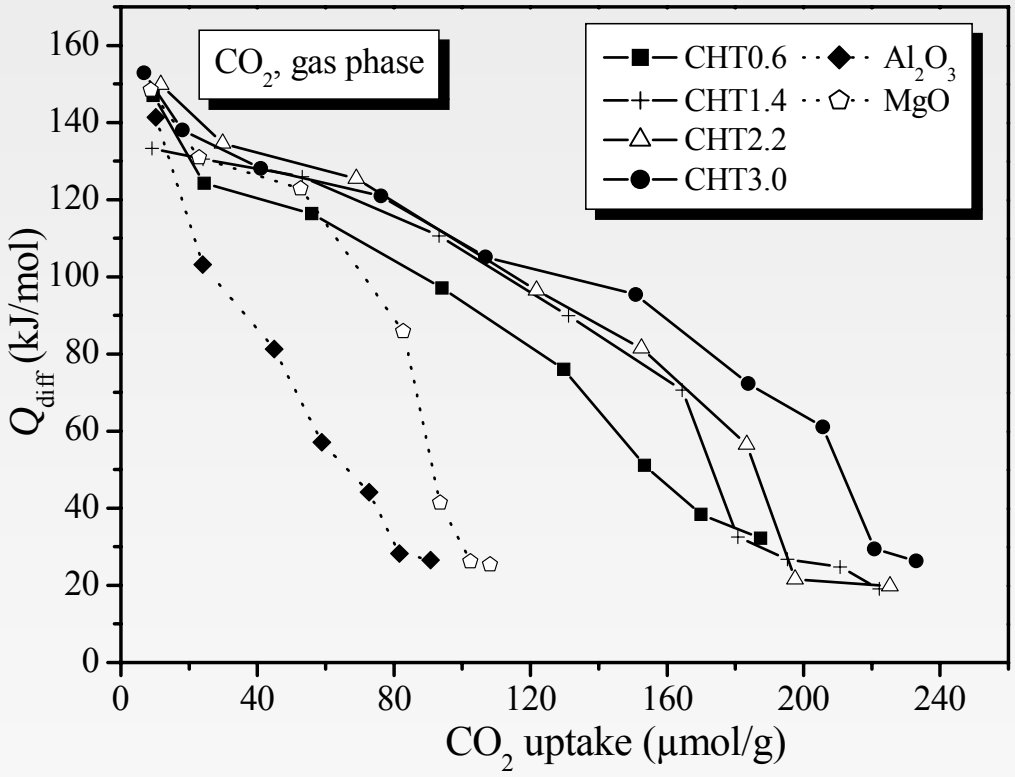
70°C in anisole

SZ=sulfated zirconia, preparation:

S-SZ precipitation of zirconia, sulfation
A-SZ sol-gel procedure + S, supercritical drying

Microcalorimetry

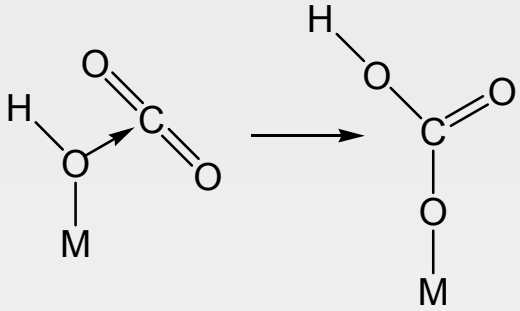
CO_2 adsorption, 40°C, gas phase



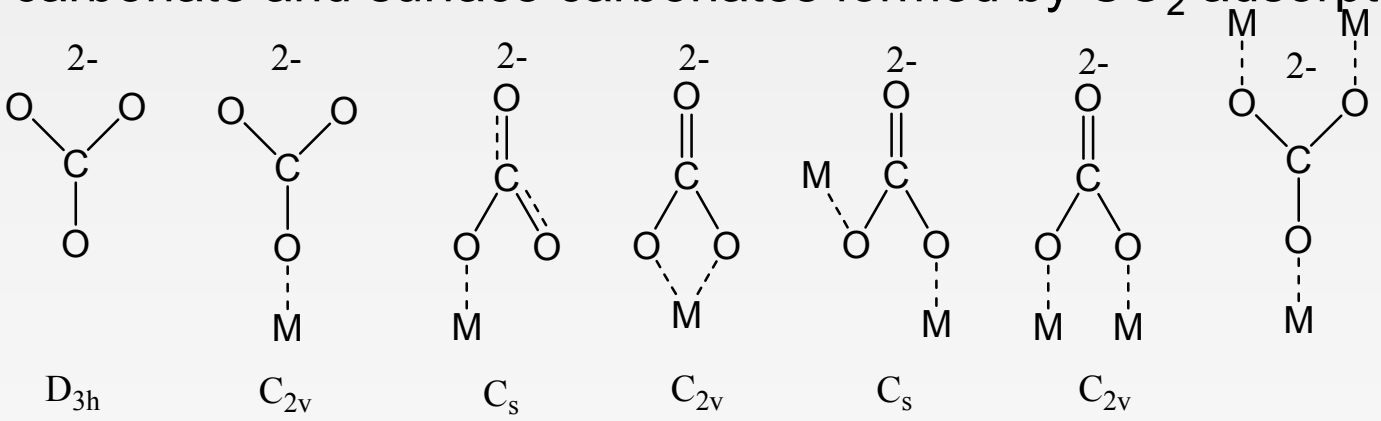
CHT = calcined hydrotalcites with Mg/Al ratios from 0.6 to 3

CO_2 as probe for basic sites

Formation of bicarbonates by reaction of CO_2 with basic OH groups



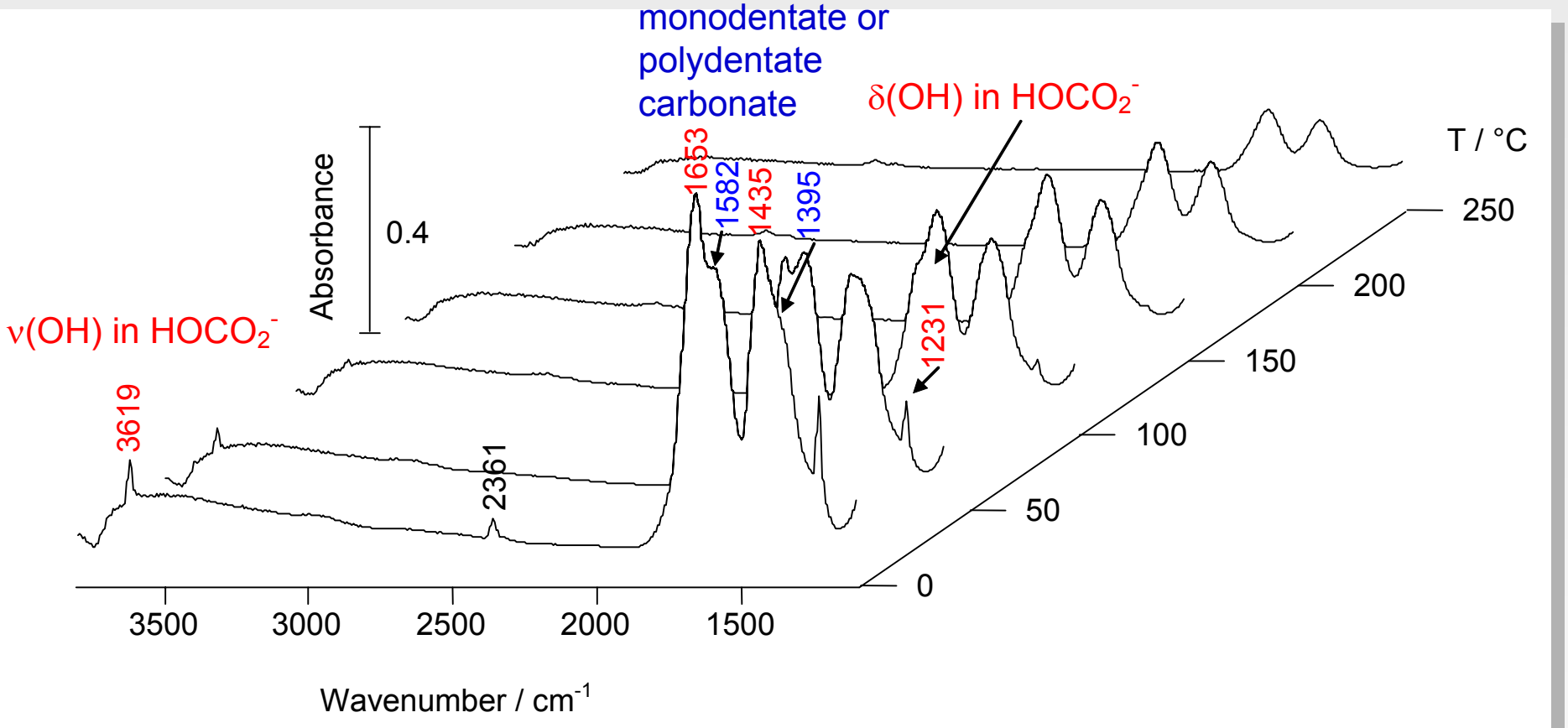
Free carbonate and surface carbonates formed by CO_2 adsorption



Other probes: e.g., SO_2, pyrrole, $CHCl_3$, CH_3CN, $B(OCH_3)_3$

J.C. Lavalley, Catal. Today 27 (1996) 377.

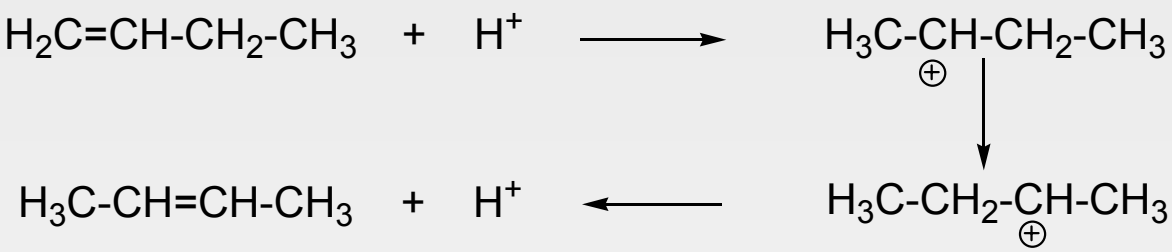
CO_2 TPD



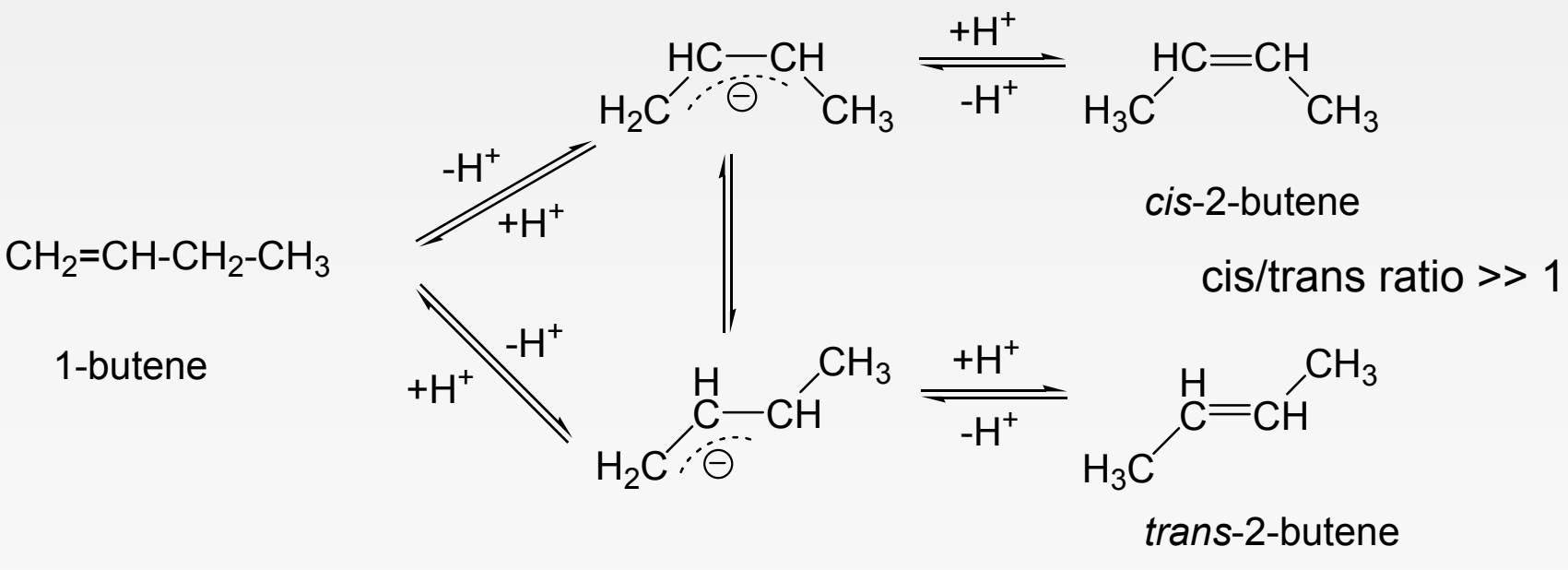
Adsorption and temperature-programmed desorption of CO_2 on $MgO\text{-}Al_2O_3$ (Mg/Al=0.6)

Catalytic test reactions

Double bond migration – 1-butene isomerization



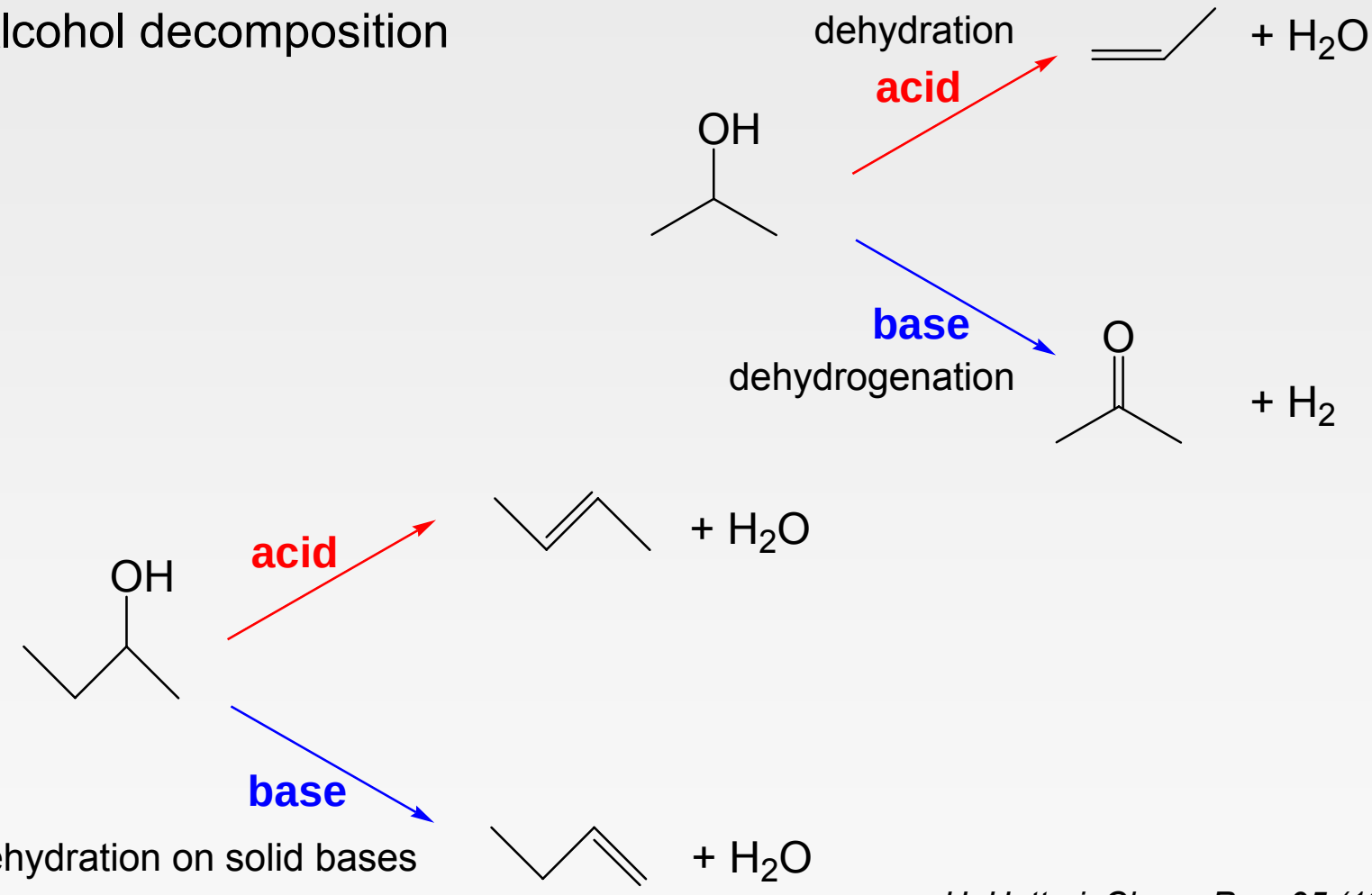
cis/trans ratio = 1



H. Hattori, Chem. Rev. 95 (1995) 537.

Catalytic test reactions

Alcohol decomposition



H. Hattori, Chem. Rev. 95 (1995) 537.

5. Acid catalyzed reactions

cis-trans-isomerization < **double bond shift** < **skeleton isomerization** < **aromatic alkylation** < **xylene isomerization** < **cracking**

acid strength of active sites

Carbocation chemistry in superacid solutions:

HF/SbF_5 or FSO_3H/SbF_5 in aprotic solvents

$$2\ FSO_3H + SbF_5 \rightleftharpoons [FSO_3H_2]^+ + [SbF_5(FSO_3)]^-$$

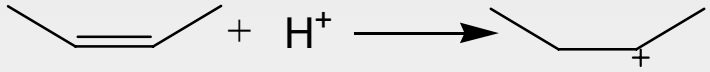
$$2\ HF + SbF_5 \rightleftharpoons [H_2F]^+ + [SbF_6]^-$$

$$RCH{=}CHR' + H^+ \rightleftharpoons R\text{-}\overset{\oplus}{C}H_2\text{-}CH\text{-}R'$$

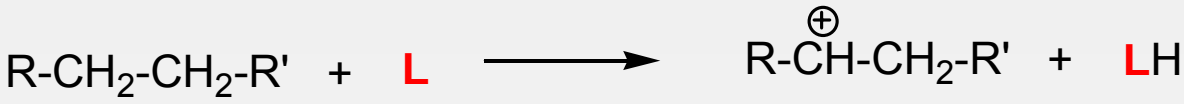
Carbocations: Intermediates in hydrocarbon reactions

Formation of Carbenium Ions

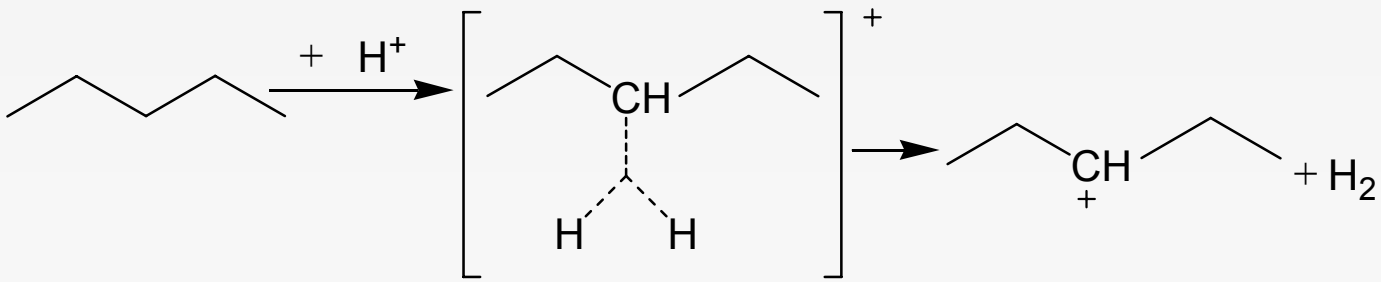
- Proton addition to an alkene or aromatic molecule



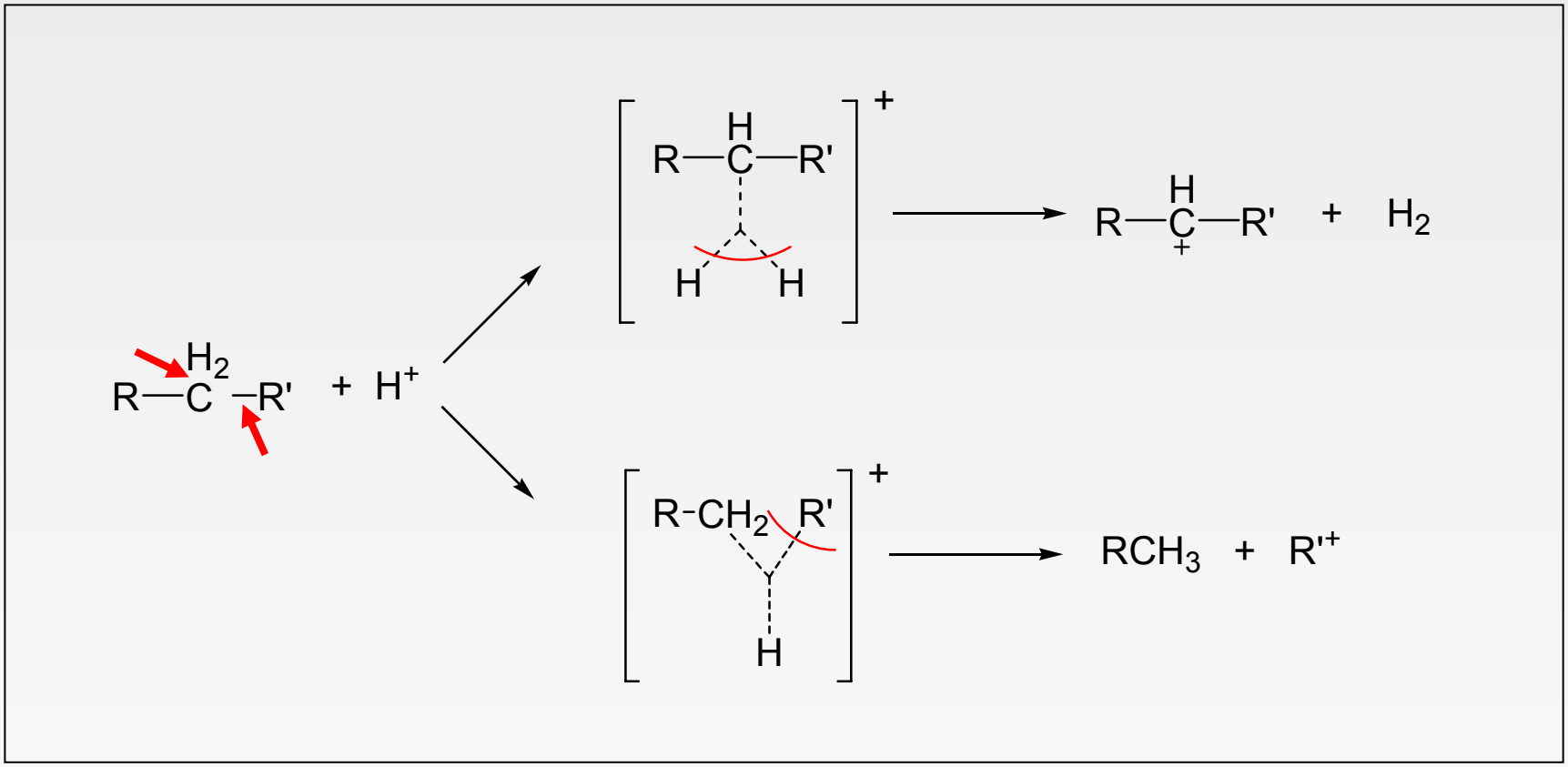
- Hydride abstraction from an alkane



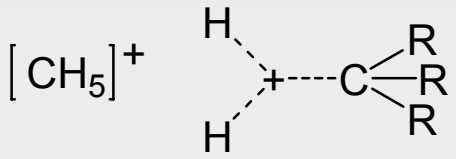
- Formation via carbonium ion intermediate from an alkane
  - Proton addition to an alkane



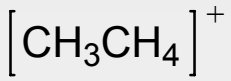
Formation of carbenium ion via carbonium ion intermediate



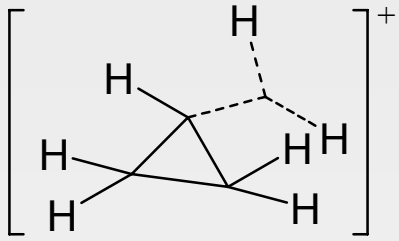
Examples of alkylcarbonium ions



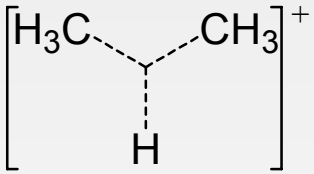
Methoniumion



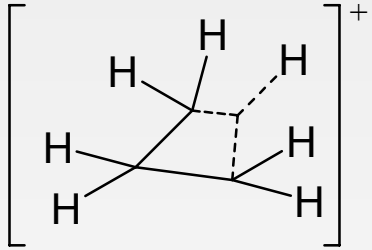
H-Ethoniumion



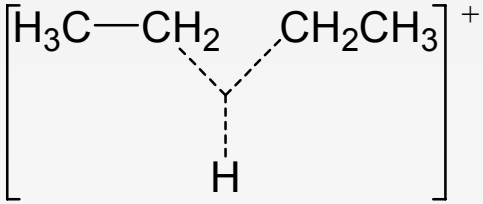
H-Cycloproponiumion



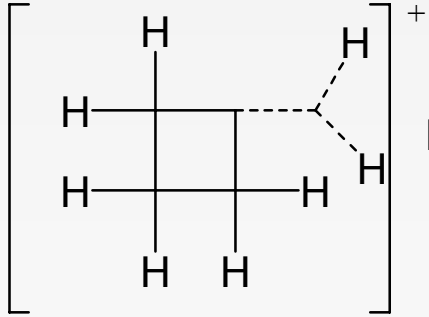
C-Ethoniumion



C-Cycloproponiumion



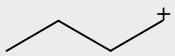
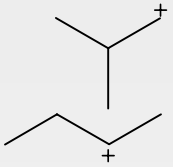
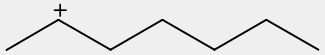
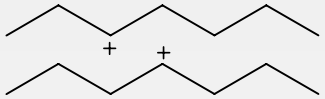
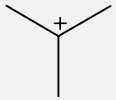
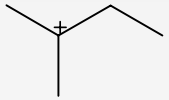
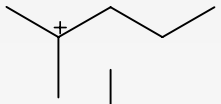
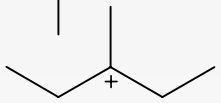
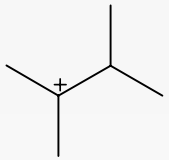
2-C-Butoniumion



H-Cyclobutoniumion

studied in MS, never isolated

Stability of carbenium ions

Strukture	ΔH^o (kJ mol^{-1})
	+138
	+130
	+67
	+6.3
	+2.5
	0
	0
	-12
	-16
	-19
	-21

Enthalpy differences between aliphatic alkylcarbenium ions in the gas phase at 298 K

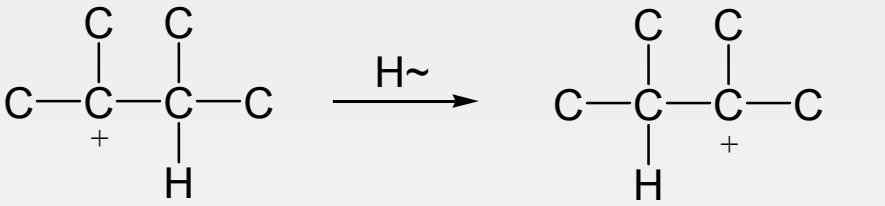
Stability:

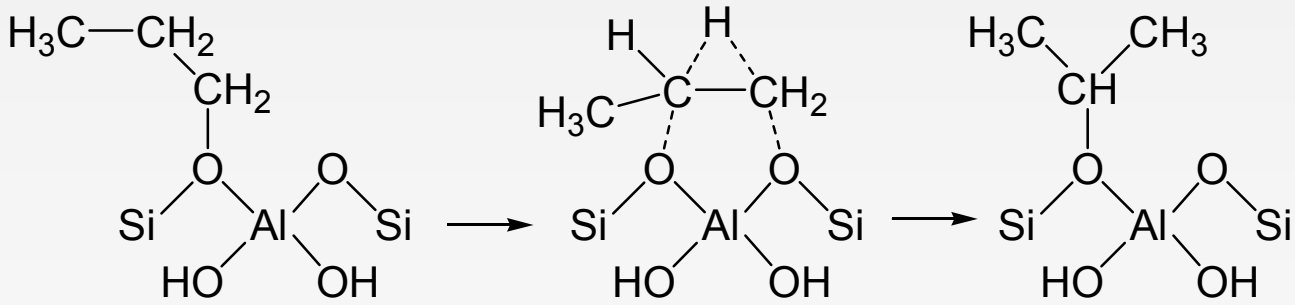
tertiary > secondary > primary

G.A. Olah, P.v.R. Schleyer, Carbonium Ions, Wiley, NY, 1968, p. 162.;
A. Corma et al., J.Catal. 77 (1982) 159.

Intramolecular reactions of carbenium ions

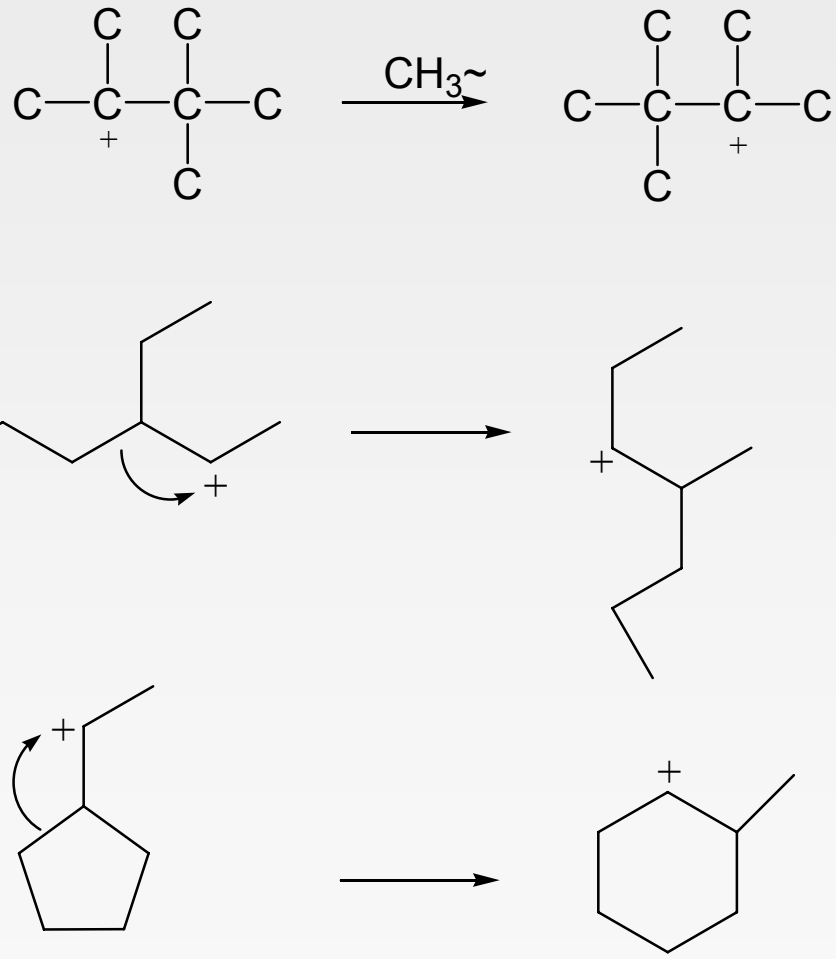
Hydride Shift



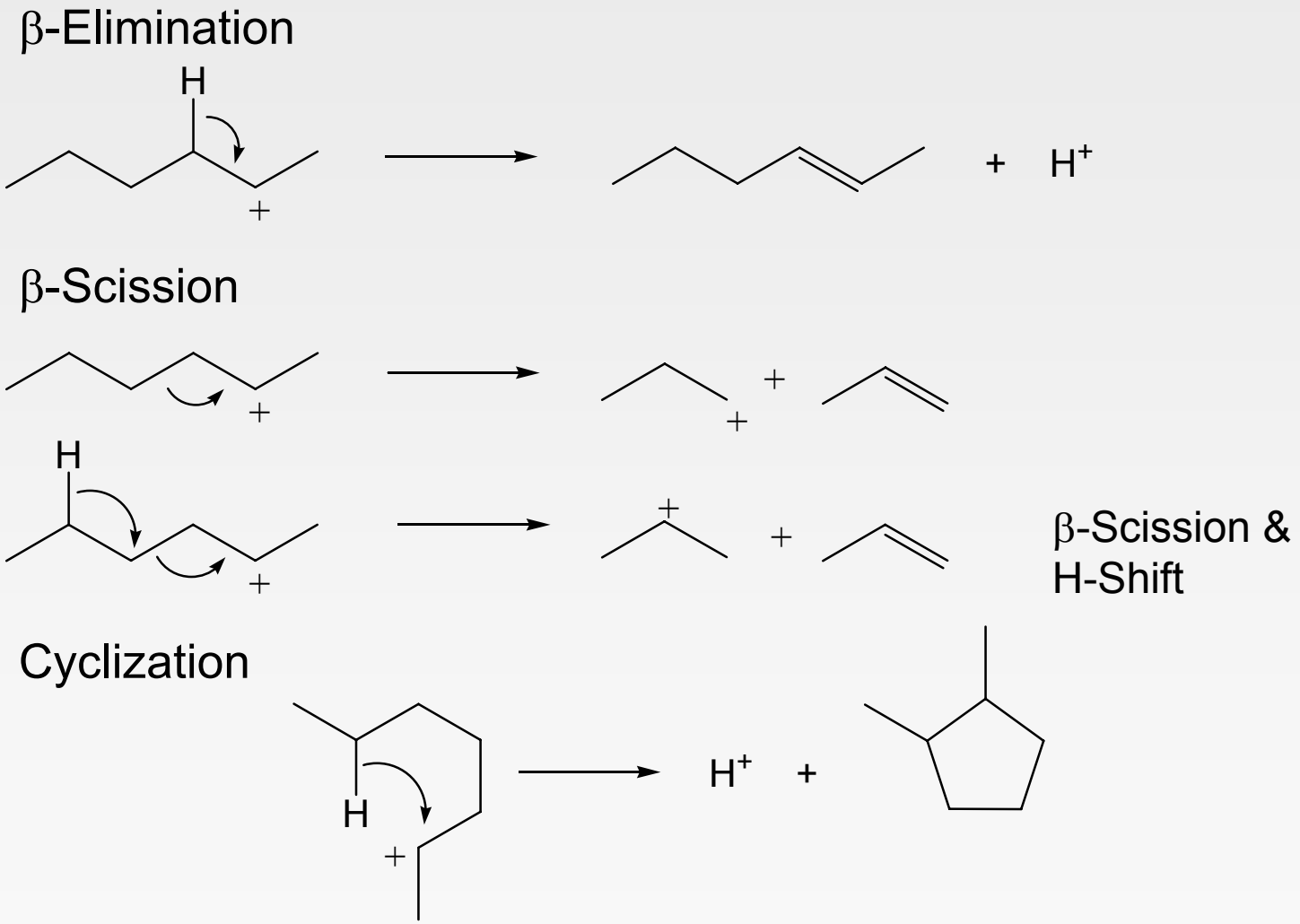


Intramolecular reactions of carbenium ions

Alkyl Shift

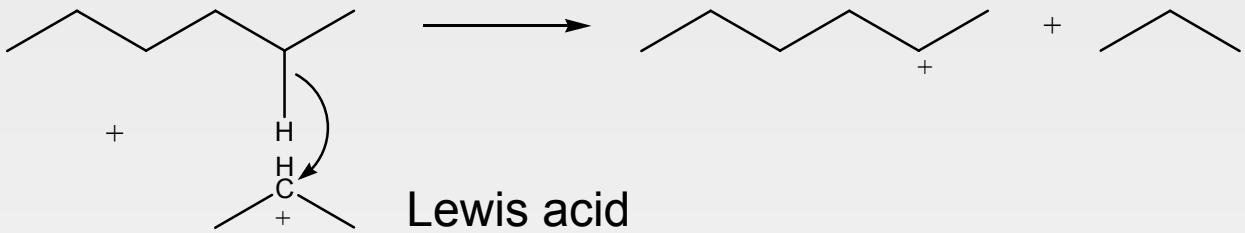


Intramolecular reactions of carbenium ions



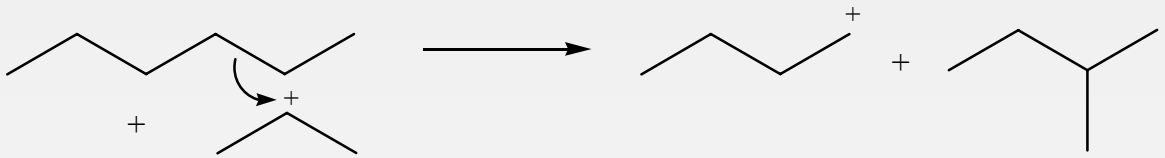
Intermolecular reactions of carbenium ions

Hydride Transfer

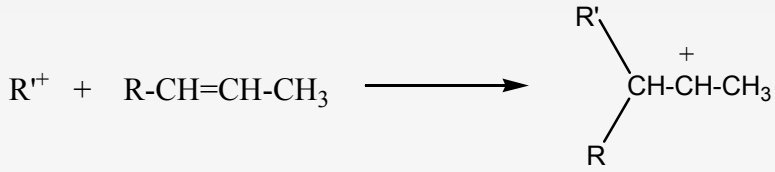


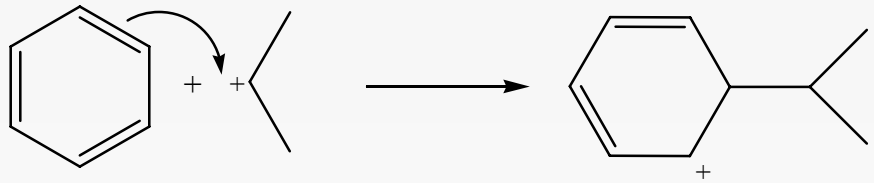
Lewis acid

Disproportionation

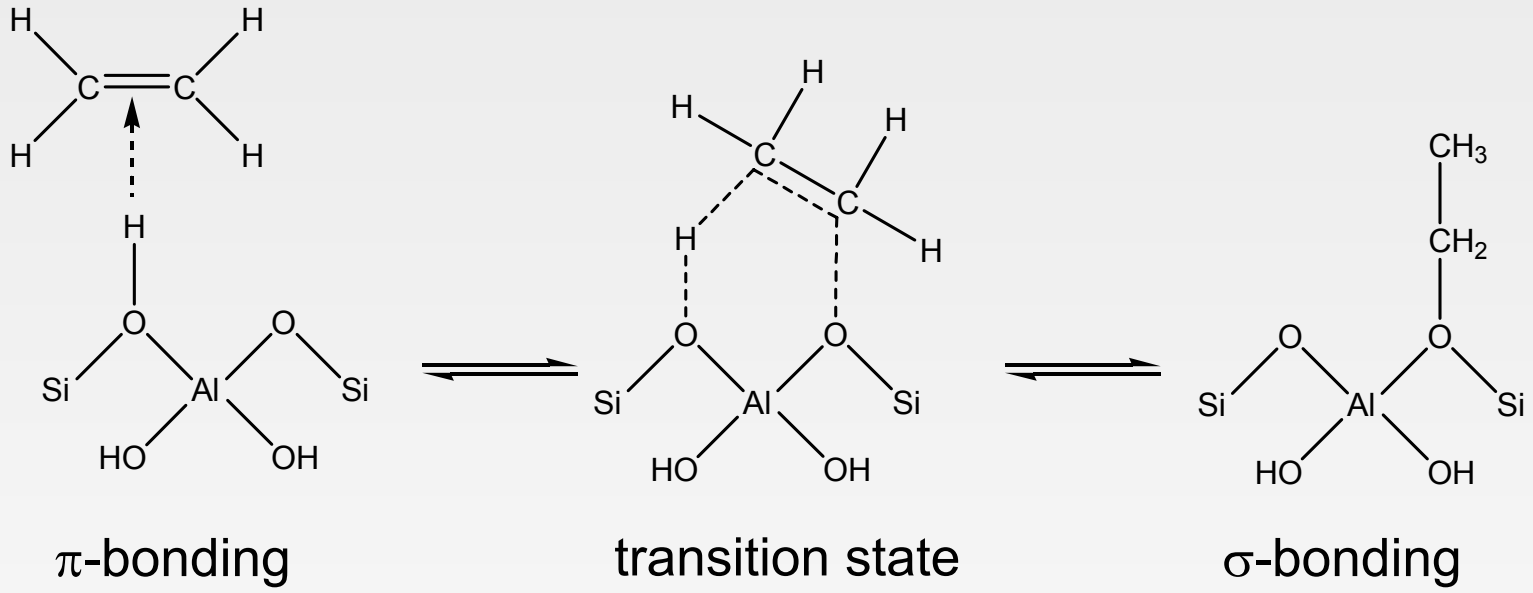


Addition of alkenes / aromatics (alkylation)





Carbocations on the catalyst surface

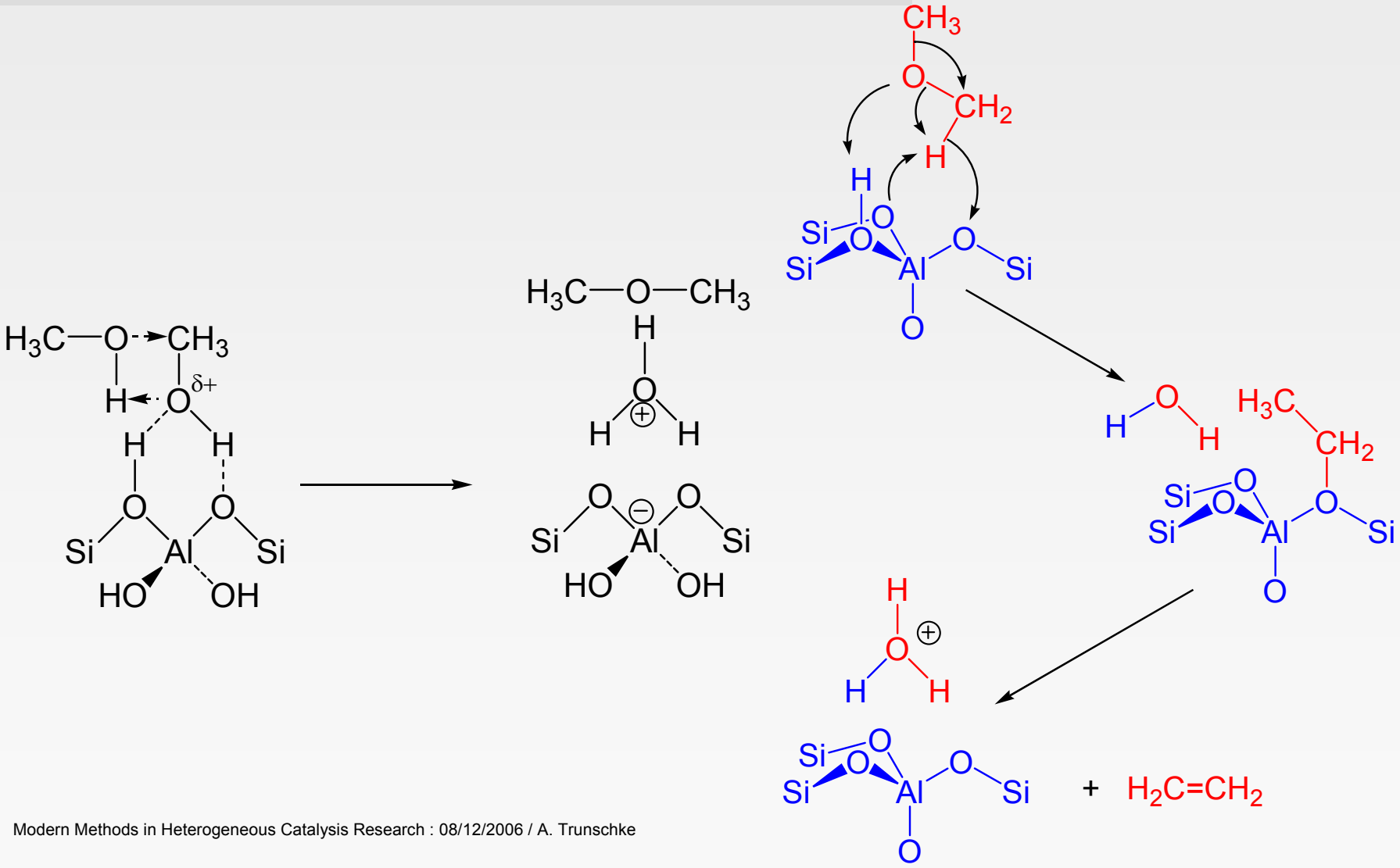


π-bonding transition state σ-bonding

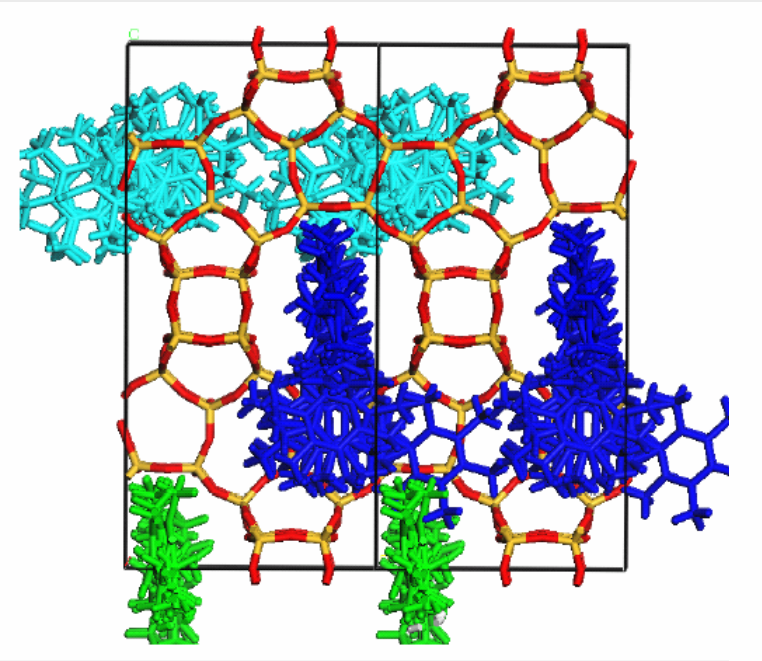
V.B. Kazanskii, I.W. Senchenya, J. Catal. 119 (1989) 108.

Proton catalyzed ethylene formation from methanol / DME

$$n/2\ [2\ CH_3OH \rightleftharpoons CH_3OCH_3 + H_2O] \xrightarrow{-n\ H_2O} C_nH_{2n} \longrightarrow n[CH_2]$$

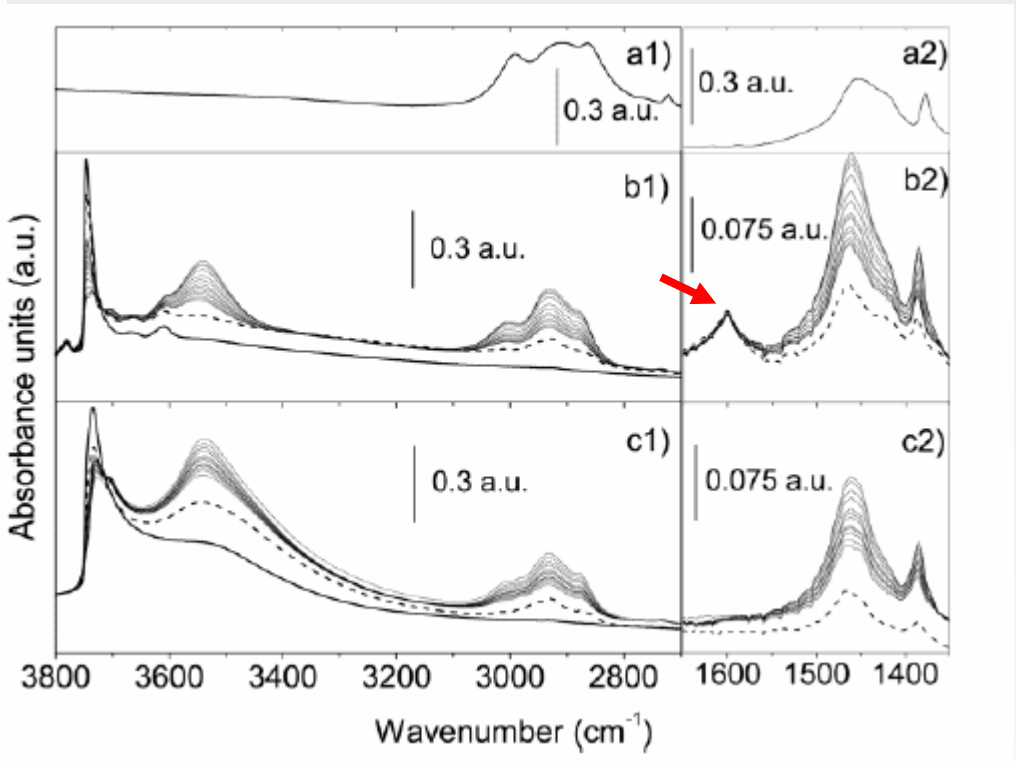


Stabilization of carbenium ions on/in solid acids



Low energy adsorption sites for HMB in H-Beta ([100] direction)

M. Bjørgen, F. Bonino, S. Kolboe, K.-P. Lillerud, A. Zecchina, S. Bordiga, J. Am. Chem. Soc. 125 (2003) 15863.

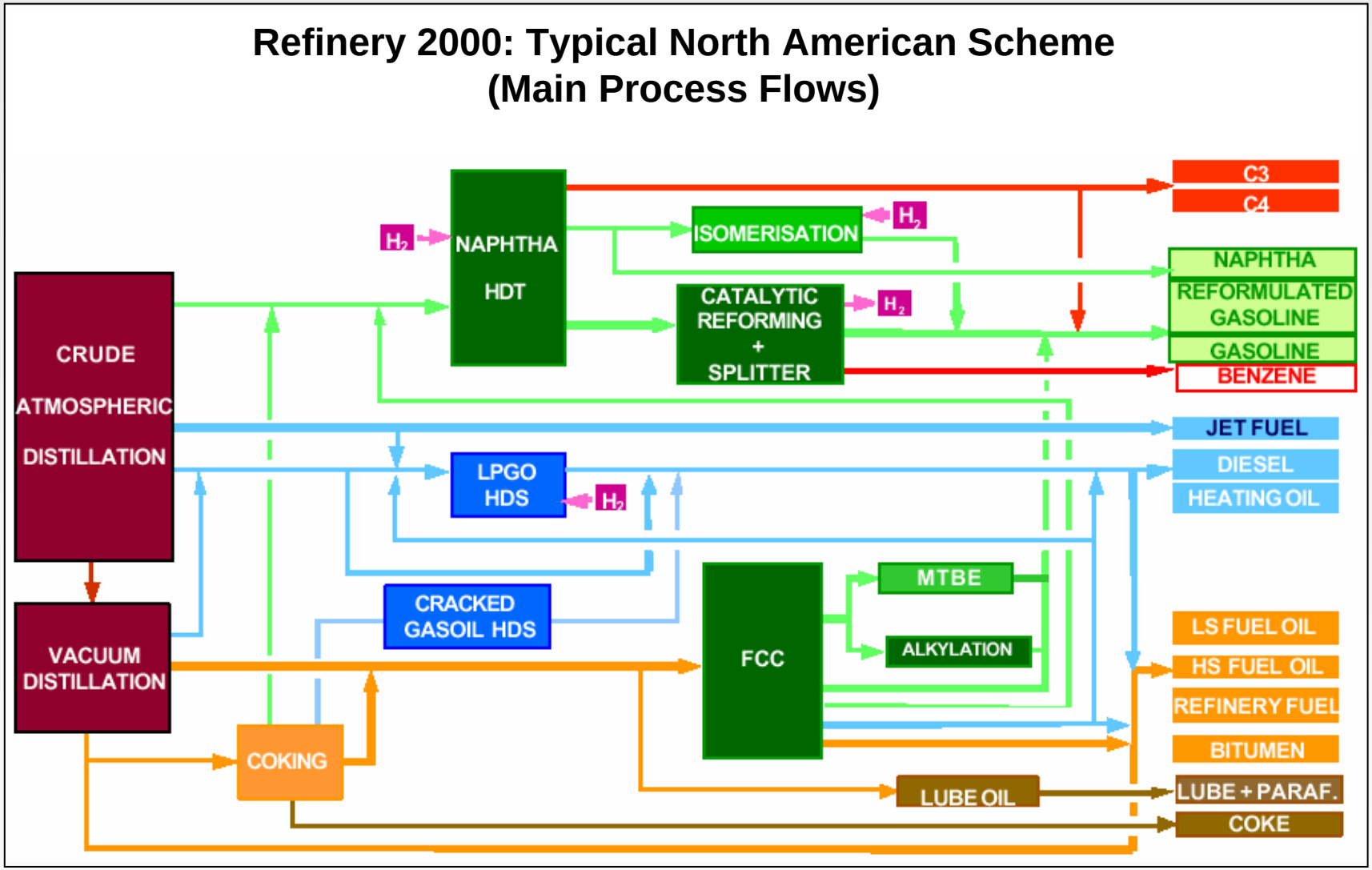


FTIR-spectra of **h**exa**m**ethyl**b**enene

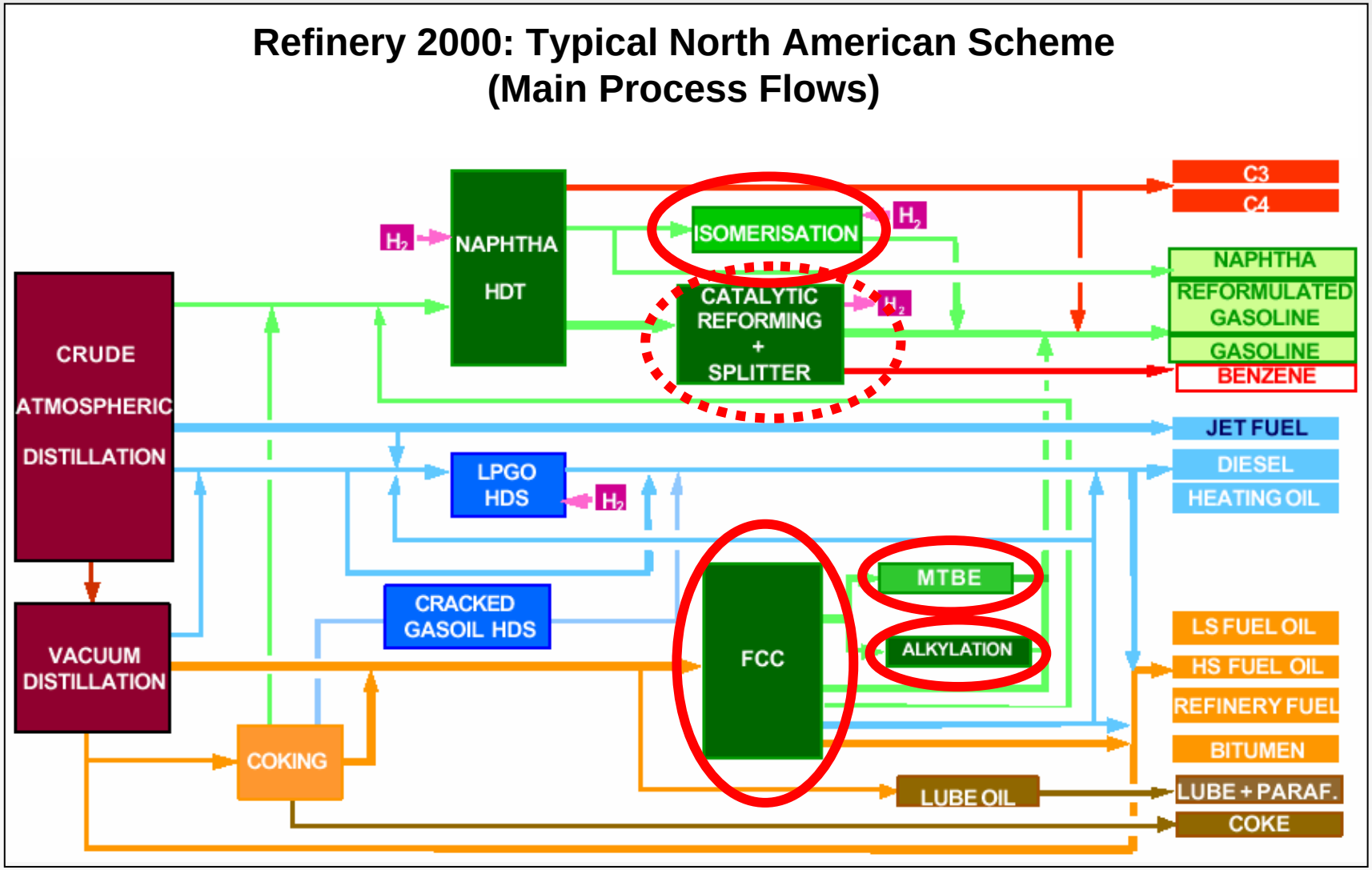
a) in KBr
b) adsorbed on H-Beta
c) adsorbed on dealuminated H-Beta (free from protons)

See also: A.Corma, Topics in Catal. 6 (1998) 127.

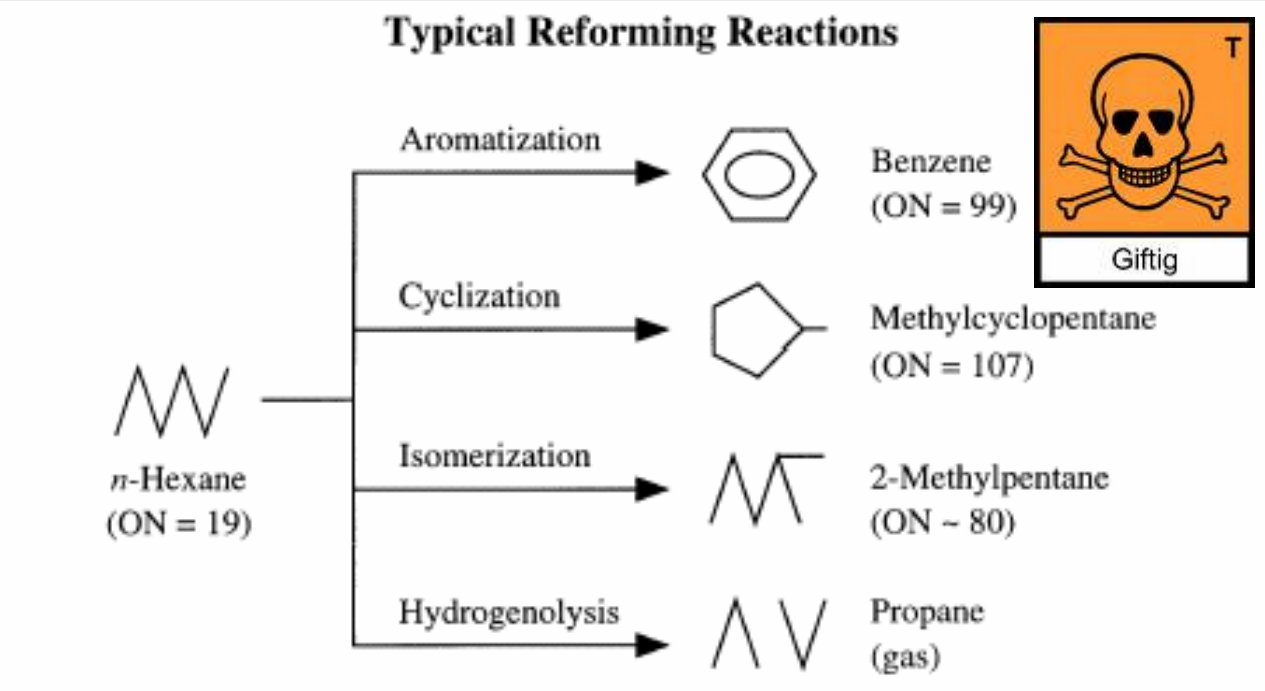
Acid-base catalysis in a refinery



Acid-base catalysis in a refinery



Catalytic reforming

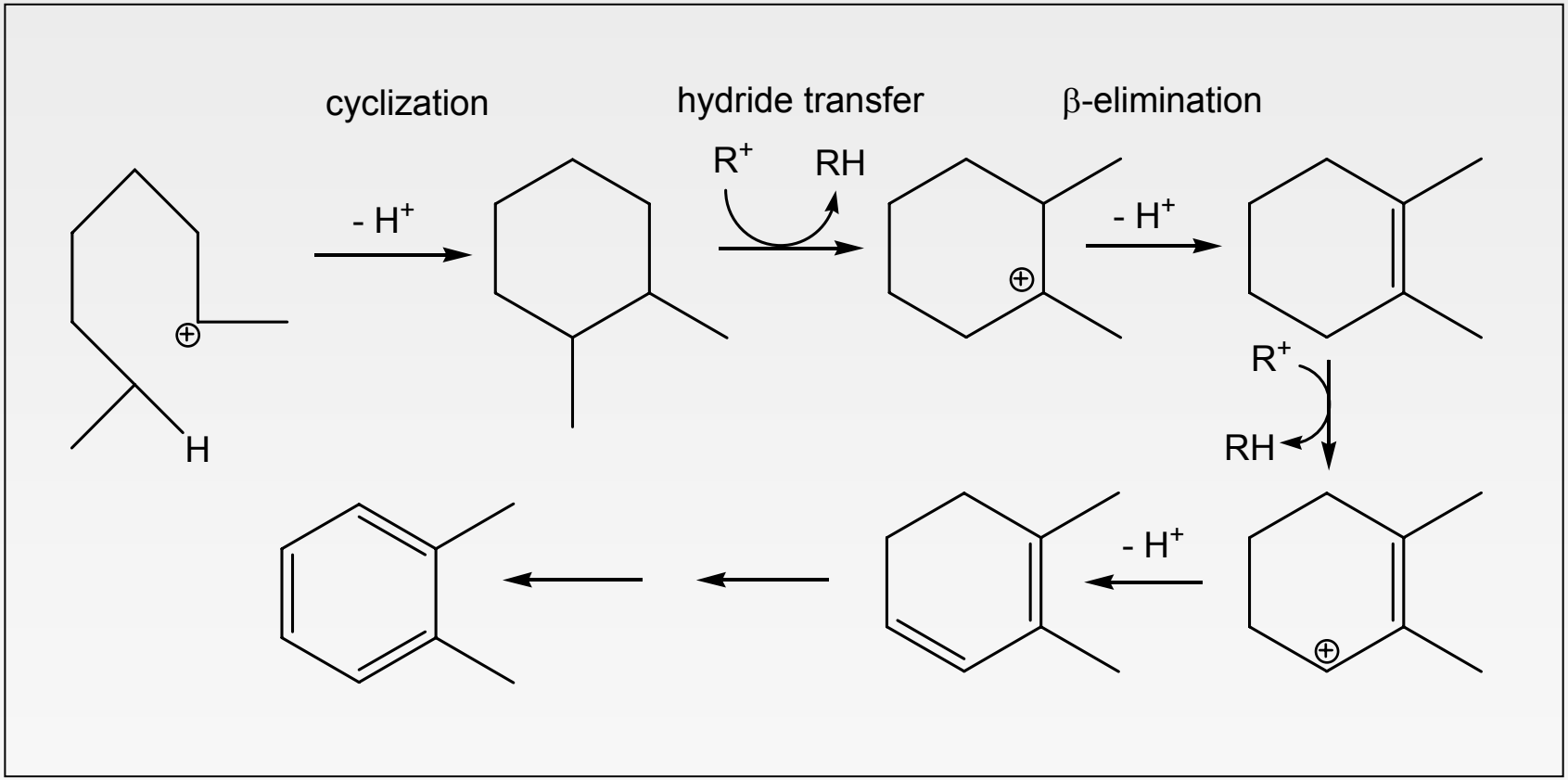


Bifunctional catalysis:

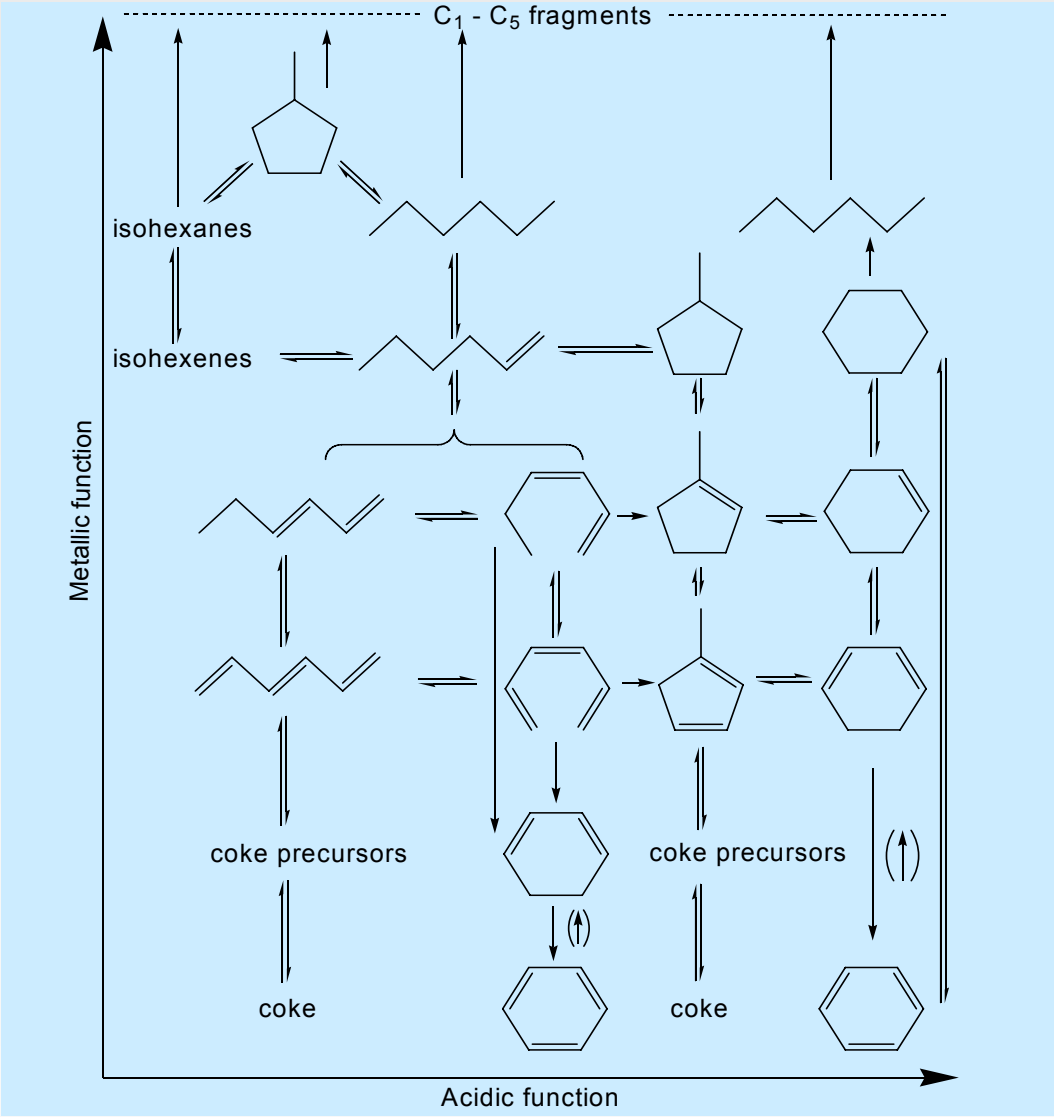
Metal: dehydrogenation / hydrogenation

Support: carbenium ion reactions

Aromatization

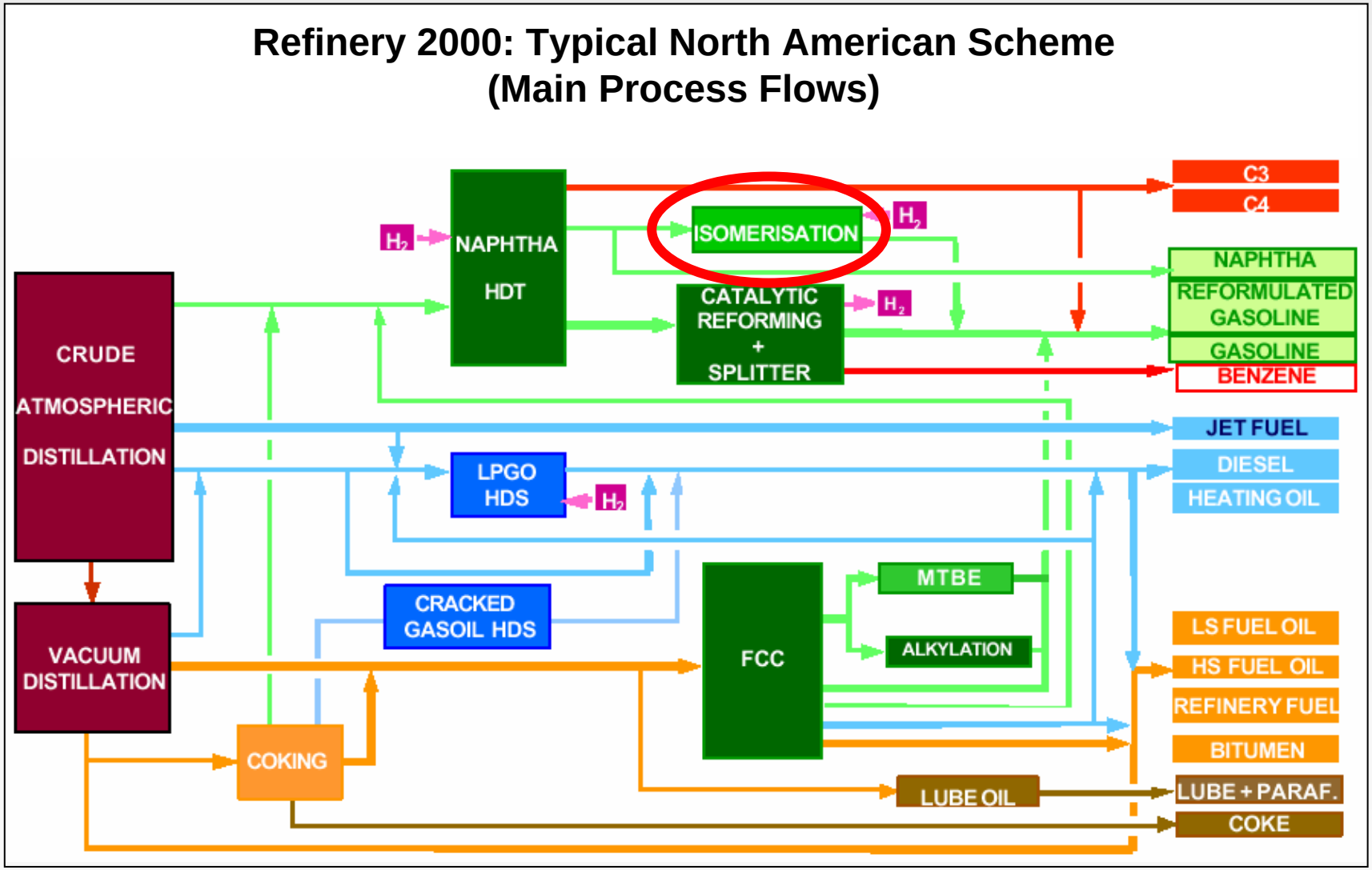


Two-dimensional reaction scheme over bifunctional catalysts

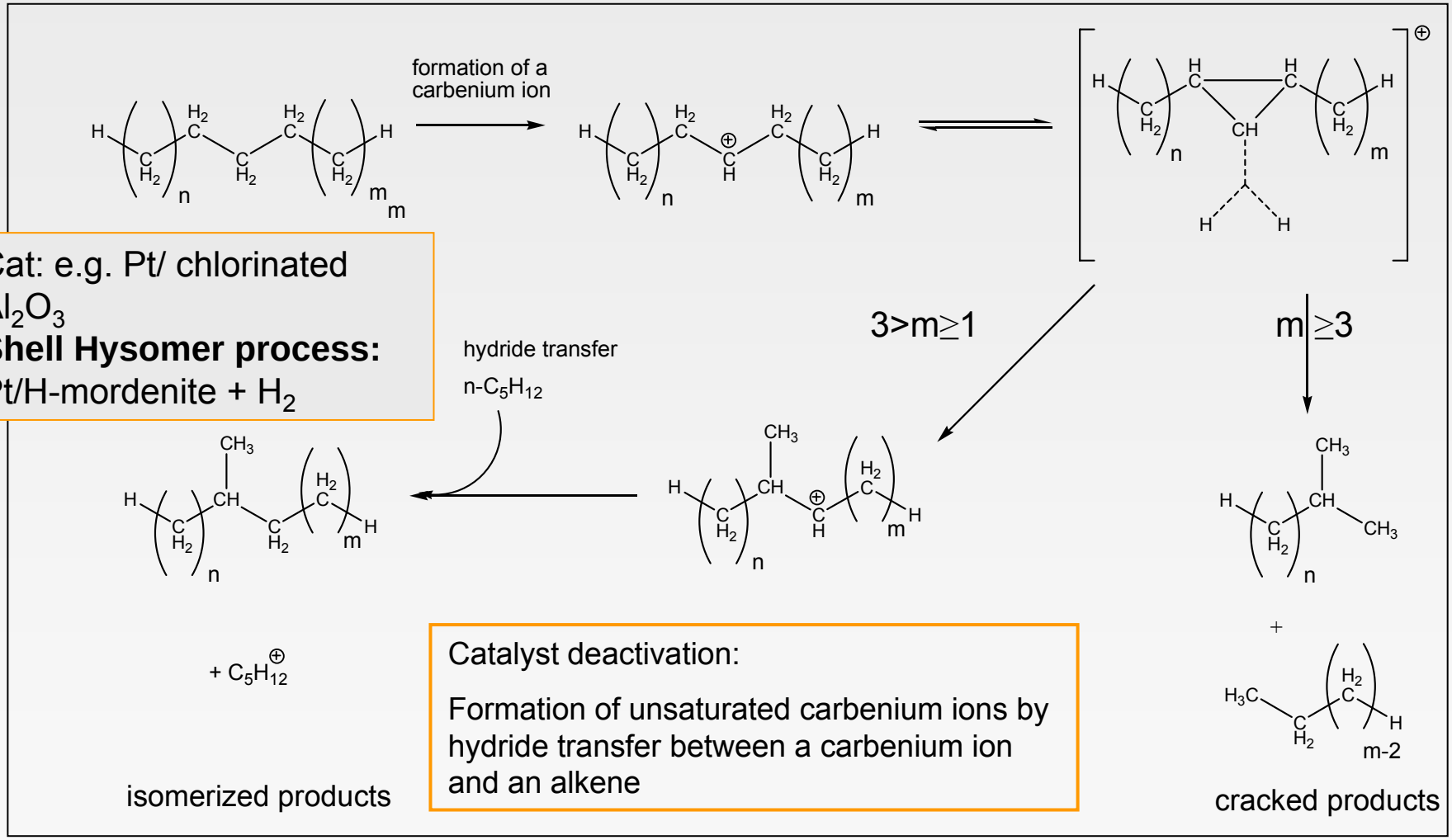


Z. Paál. J. Catal. 105 (1987) 540.

Acid-base catalysis in a refinery

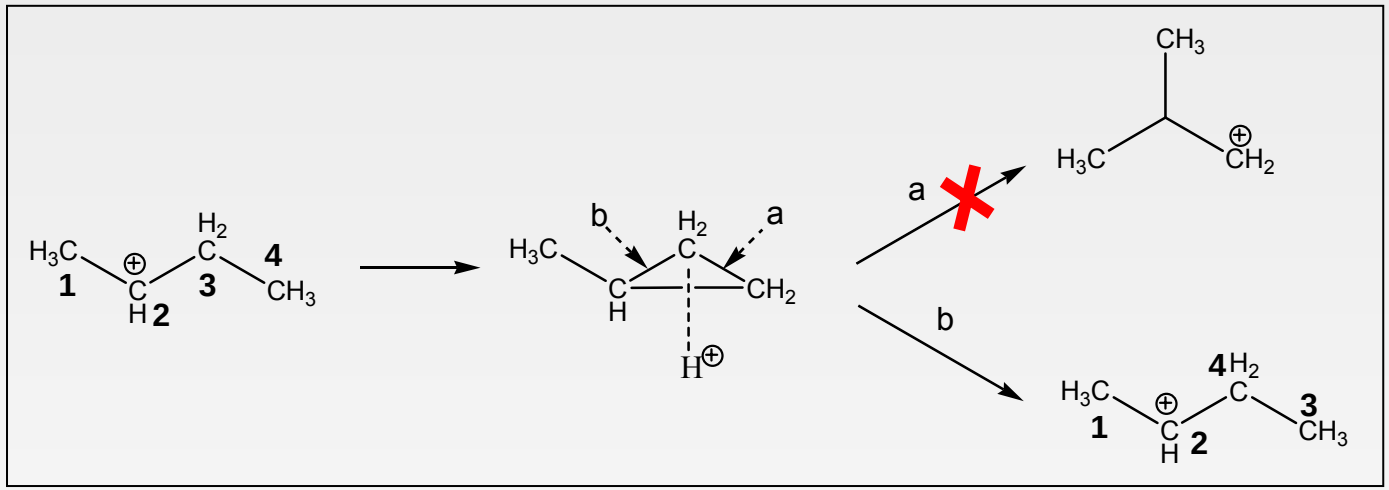


Skeletal isomerization of C_{5+}-alkanes



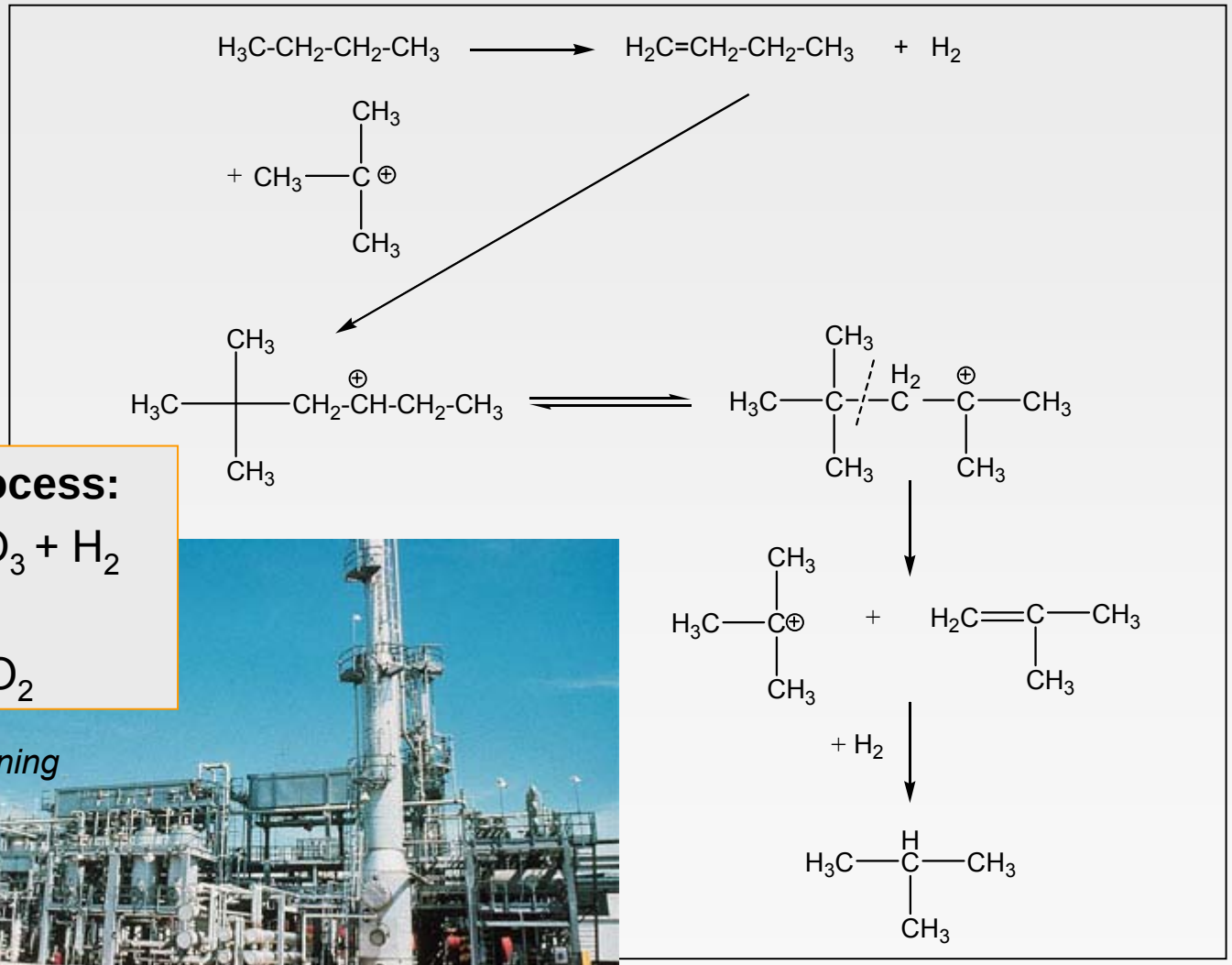
n-Butane isomerization

Possible and forbidden rearrangements of the sec-butyl cation



Investigation of n-C_4; n-C_5; n-C_6 isomerization in HF/SbF_5

n-Butane isomerization



UOP Butamer process:

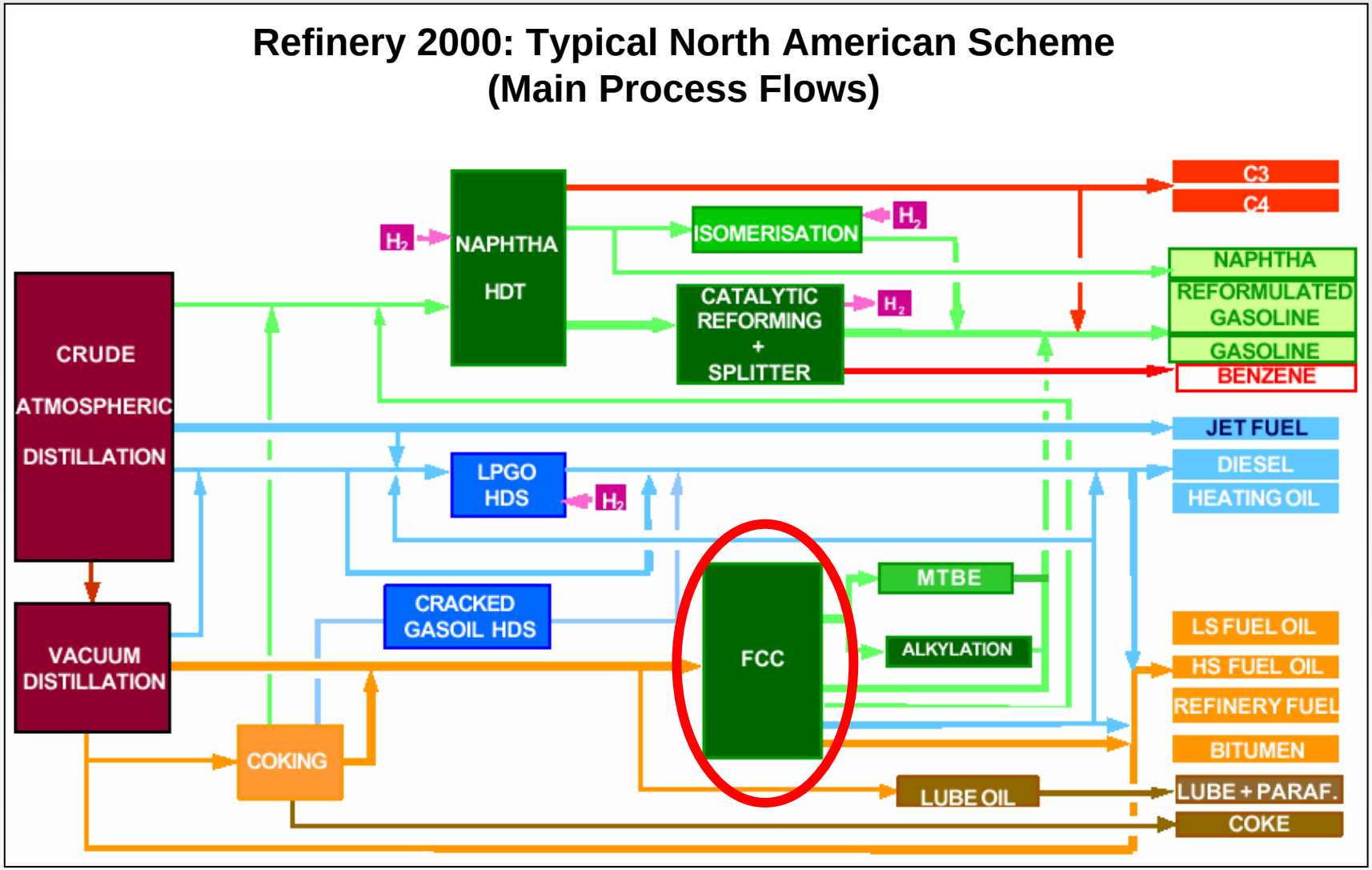
Pt/chlorinated Al_2O_3 + H_2

Sun Refining:

Fe/Mn/sulfated ZrO_2

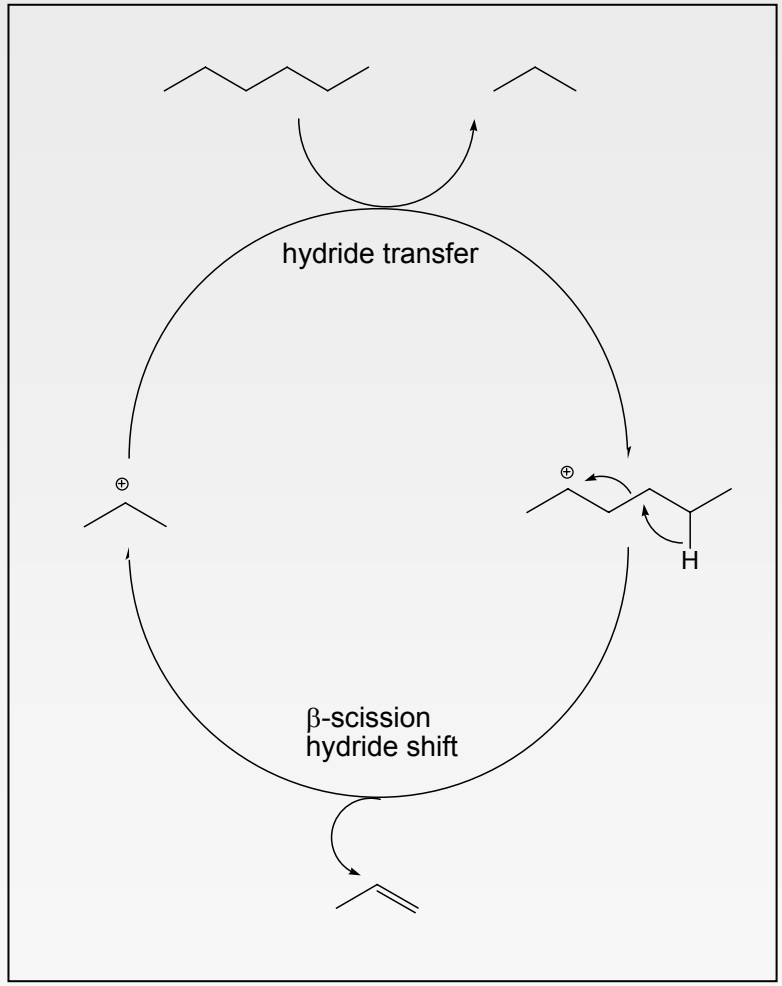
http://www.uop.com/refining

Acid-base catalysis in a refinery



Cracking

Catalysts, e.g.:
5-40% HY or rare earth exchanged Y
+ silica/alumina binder
+ clay filler
(UOP)



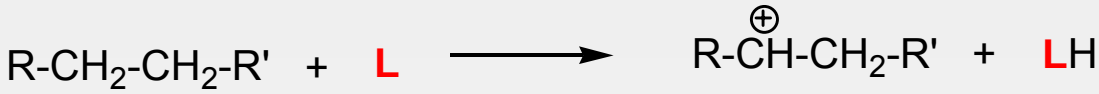
Schematic catalytic cycle for the bimoleculare cracking of alkanes

Cracking

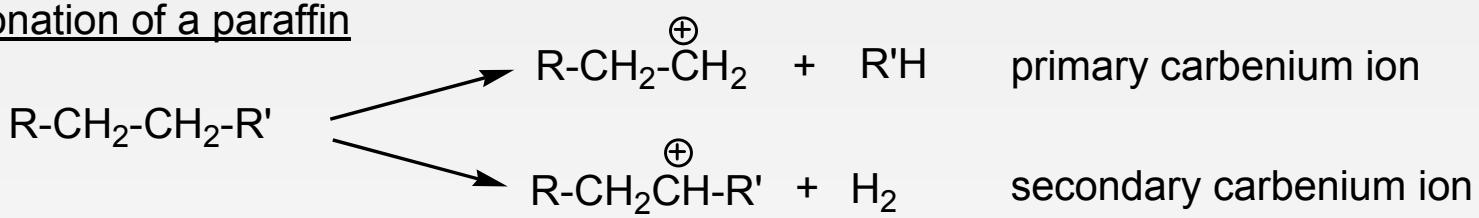
1. Carbenium ion generation

protonation of an olefin

hydride ion abstraction from a paraffin



protonation of a paraffin



decomposition of thermally produced radicals

Predominating mechanism depends on:

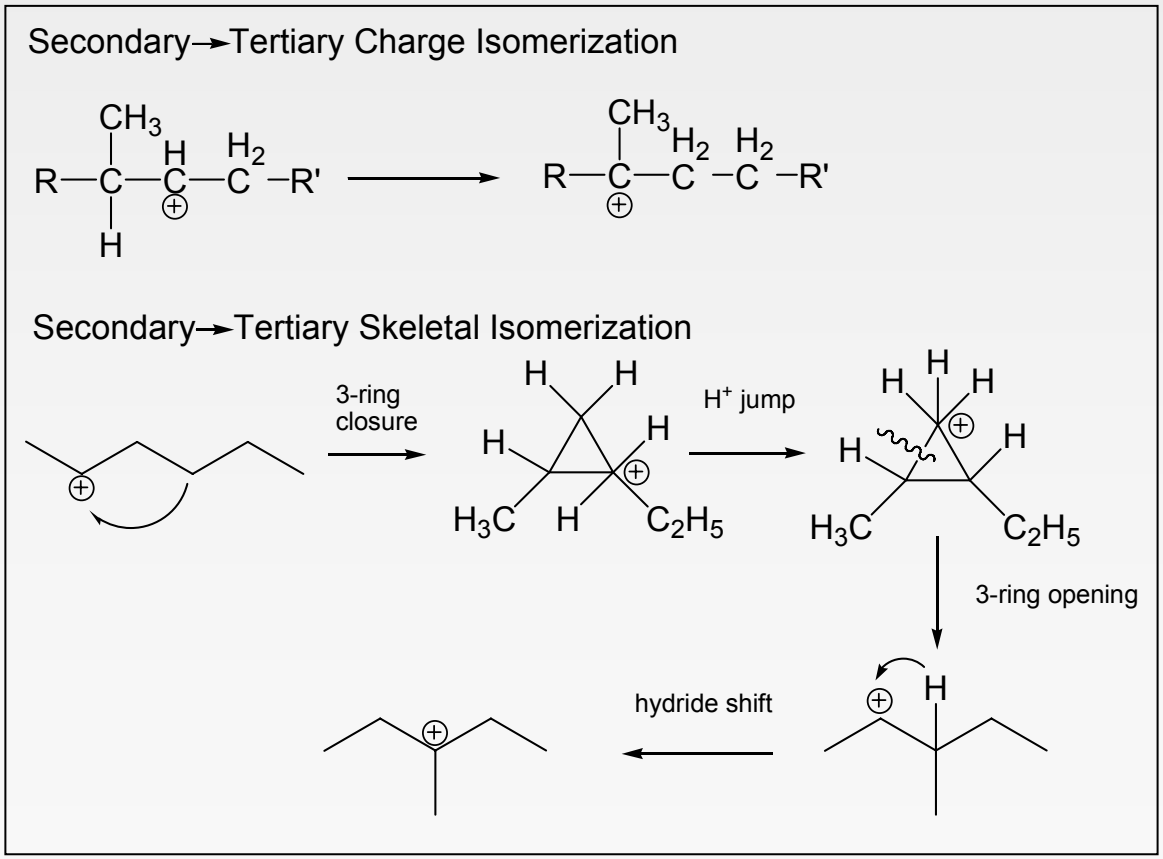
- Reaction conditions
- Feed composition
- Brønsted- / Lewis site ratio

Cracking

2. Carbenium Ion Rearrangement

Carbenium ion stability:

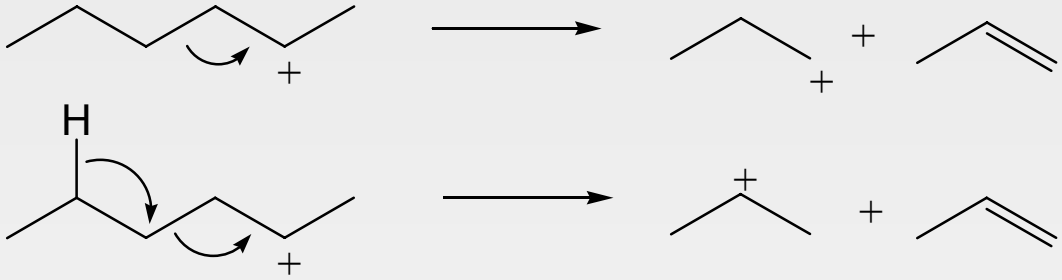
Tertiary > Secondary >Primary



In catalytic cracking reactions there will be always a higher degree of branched products than for thermal cracking

Cracking

3. Cracking of C-C-Bonds via β-scission



β-Scission &
H-Shift

4. Hydride Transfer Propagation Reaction

$$CH_3\text{-}\overset{\oplus}{C}H\text{-}CH_2\text{-}CH_2\text{-}CH_3 + RH \longrightarrow CH_3\text{-}CH_2\text{-}CH_2\text{-}CH_2\text{-}CH_3 + R^{\oplus}$$

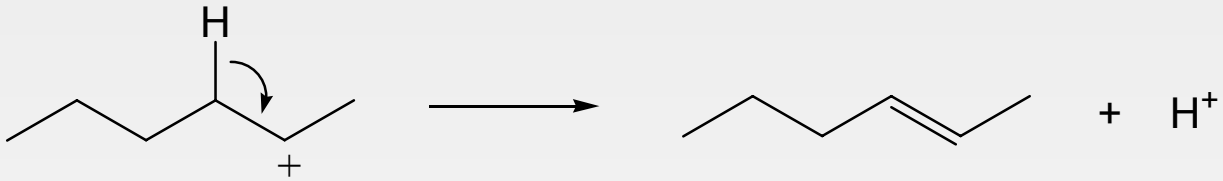
Ratio of hydride transfer to β-Scission (= product selectivity) can be controlled by catalyst composition:

- Addition of rare earth to zeolite (REY) increases hydride transfer and cracking products will be predominantly paraffinic.
- If USY is used, hydride transfer is diminished and there will be more olefins in the product.

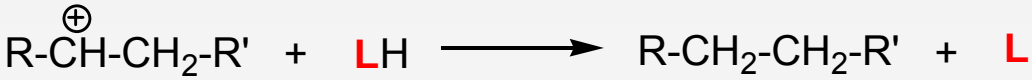
Cracking

5. Termination Reactions

β-Elimination

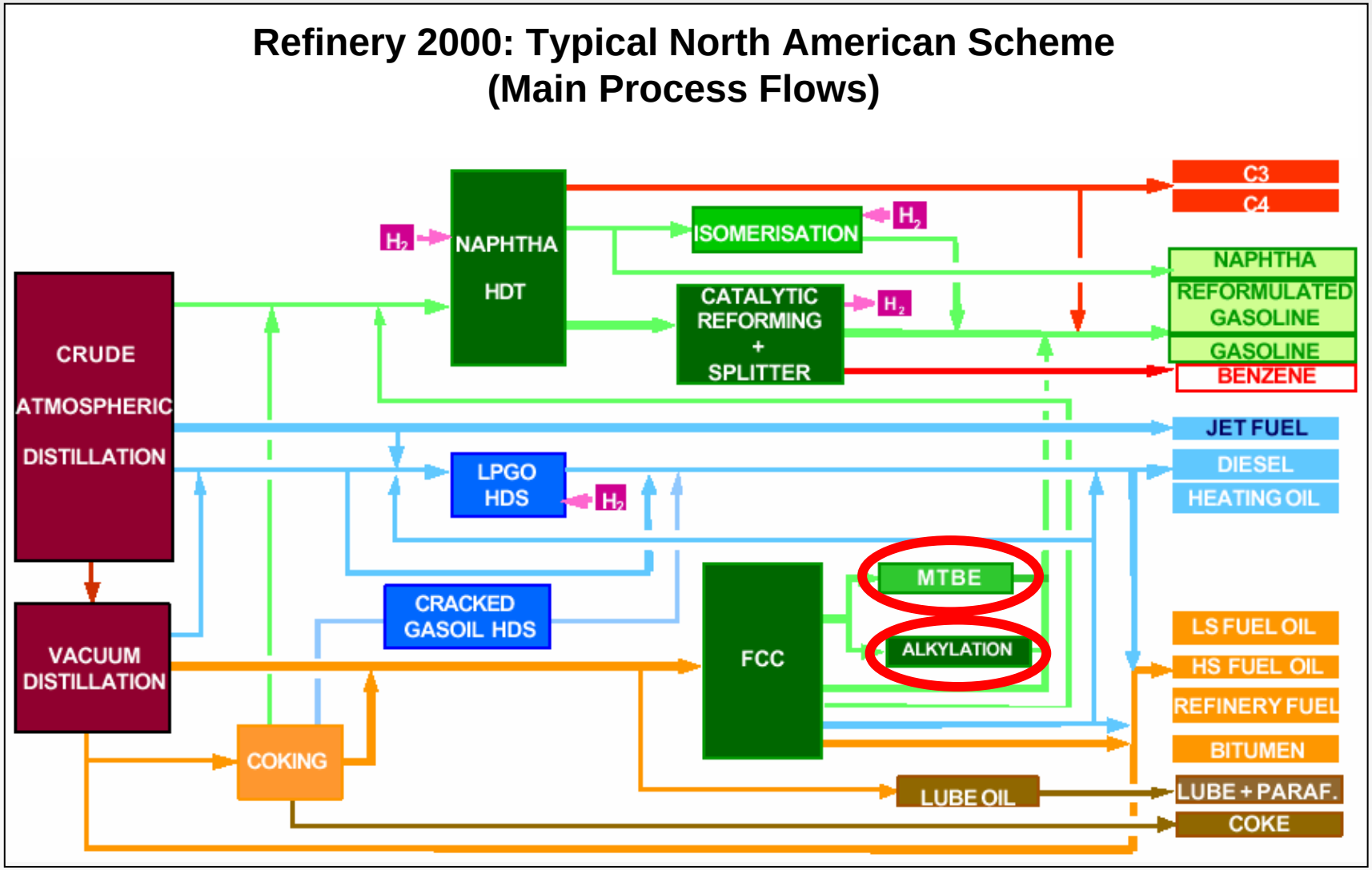


Hydrid transfer to the carbenium ion

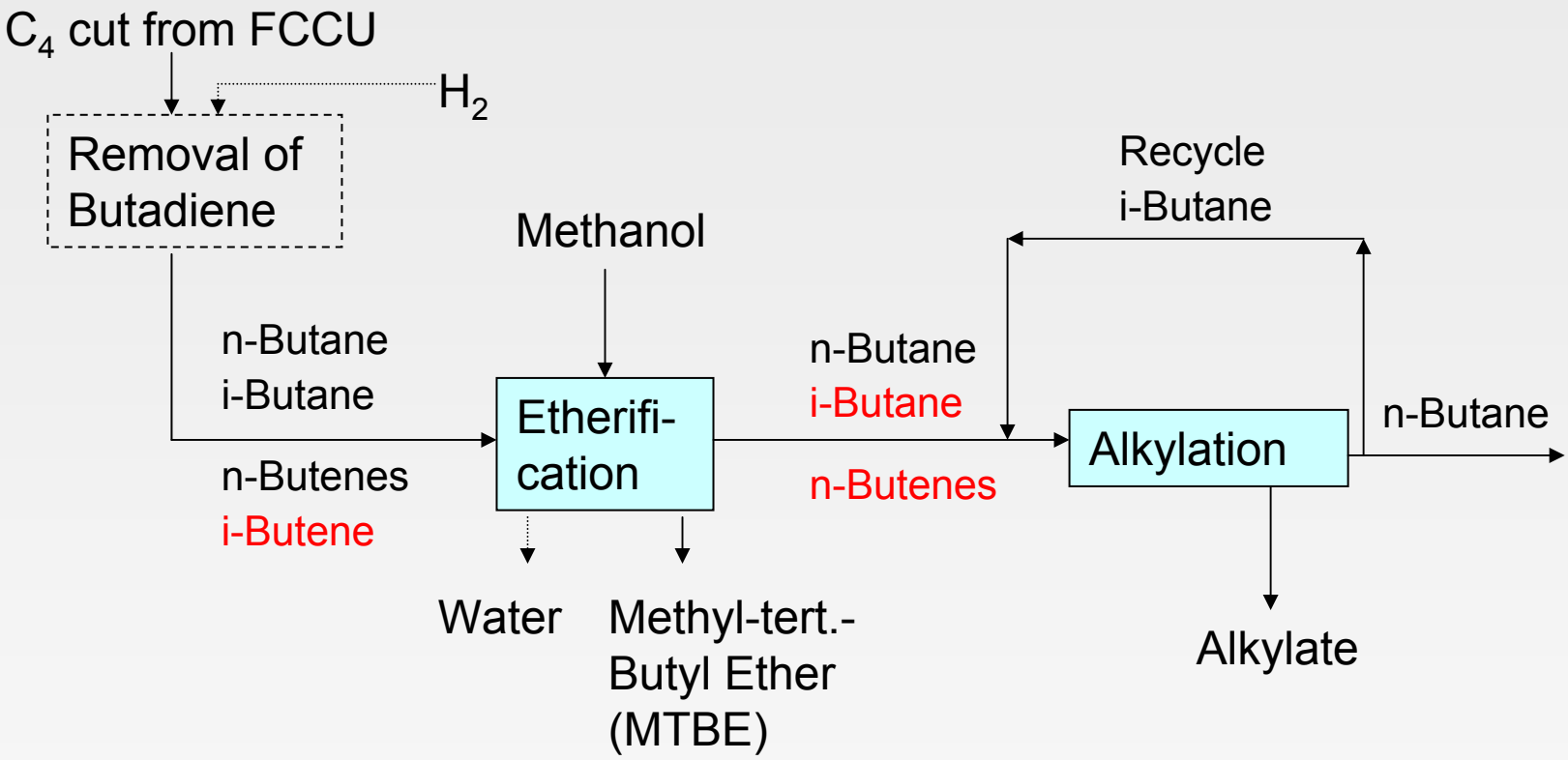


everything is much more complicated in reality!

Acid-base catalysis in a refinery



Alkylation of isobutane with alkenes

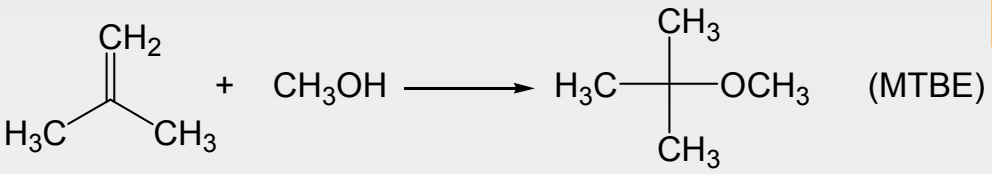


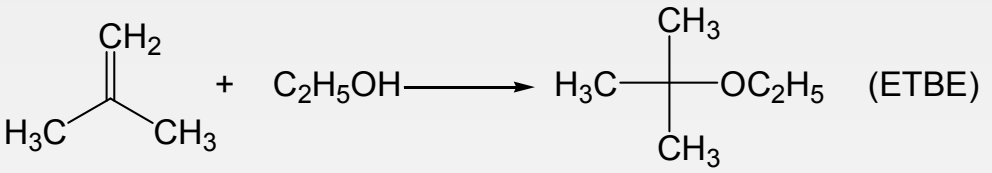
Typical position of an alkylation unit in a modern refinery (FCCU: Fluid catalytic cracking unit)

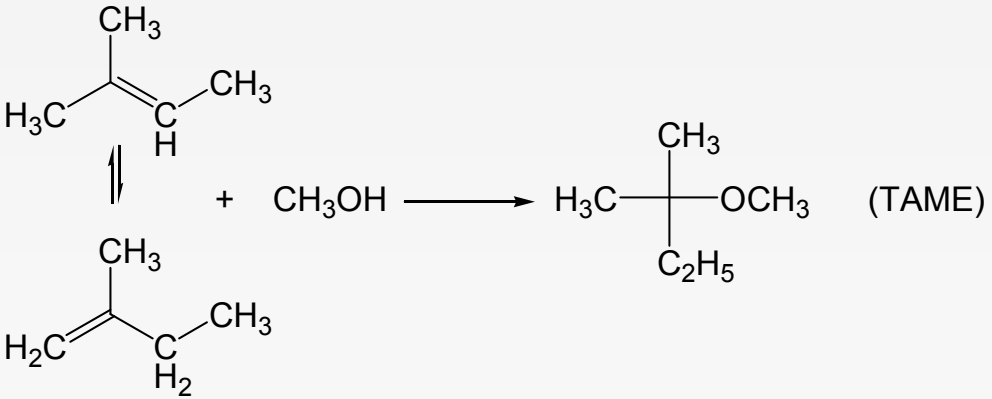
J. Weitkamp, Y. Traa in Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997, Vol. 4, p. 2049.

Synthesis of MTBE/TAME

Chemical reactions to ethers

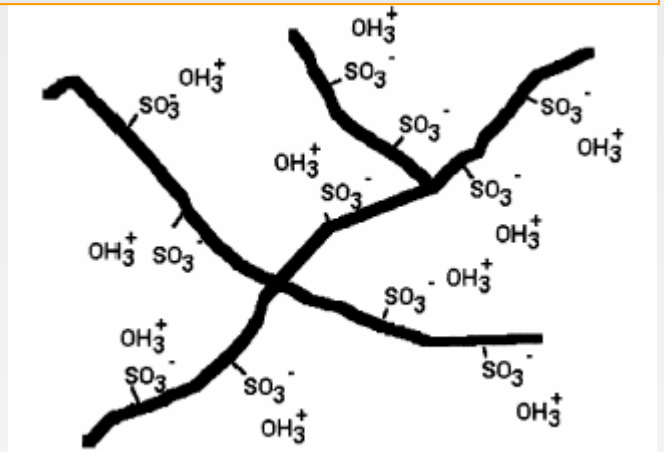


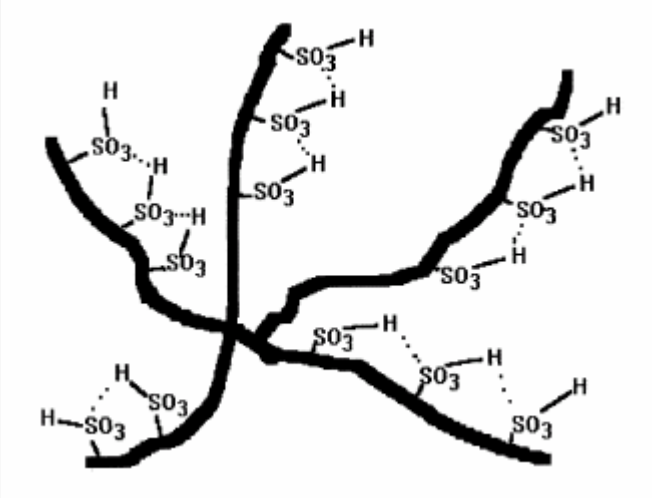




p=15-20 bar, T=60-80°C

macroporous sulfonic acid resin catalyst
e.g. Amberlyst®-15, Dowex® M32

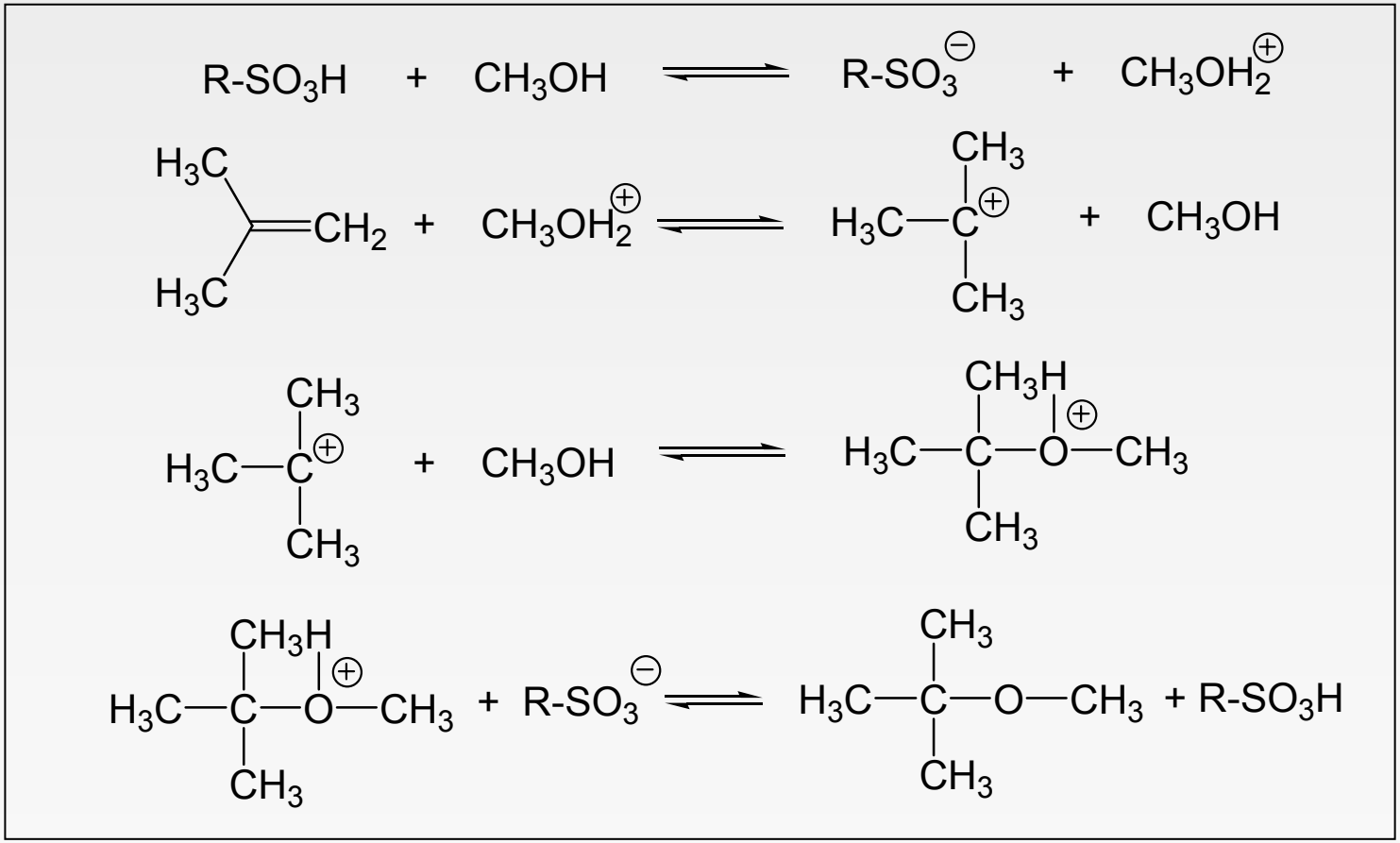




Synthesis of MTBE/TAME

Reaction steps in etherification

Specific acid catalysis



Alkylation of isobutane with n-alkenes

Isobutane + C_3-C_5 alkenes = mixture of branched alkanes (alkylate)

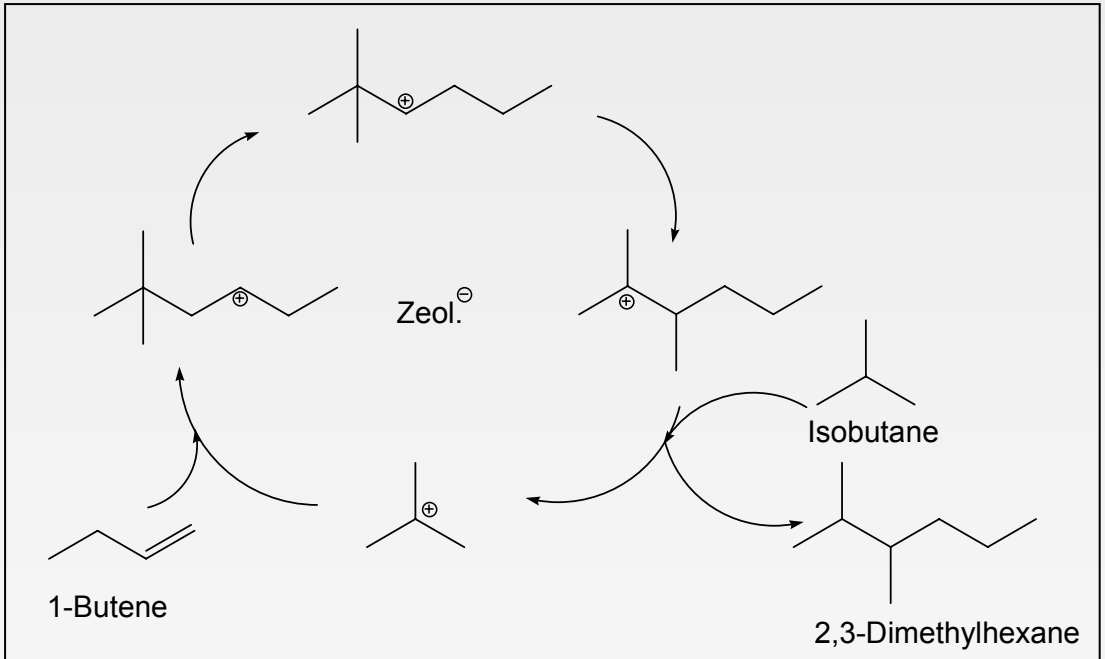
Conventional catalysts:

HF: toxic

H_2SO_4: consumption of 70-100 kg acid/ton alkylate

New processes under development:

- CF_3SO_3H/SiO_2: Haldor Topsoe / Kellog FBA process
- $AlCl_3/Al_2O_3$ promoted by alkali metal ins + Ni, Pd, Pt (?) = HAL-100™: UOP Alkylene process
- Faujasite-derived catalyst: Lurgi Eurofuel Process



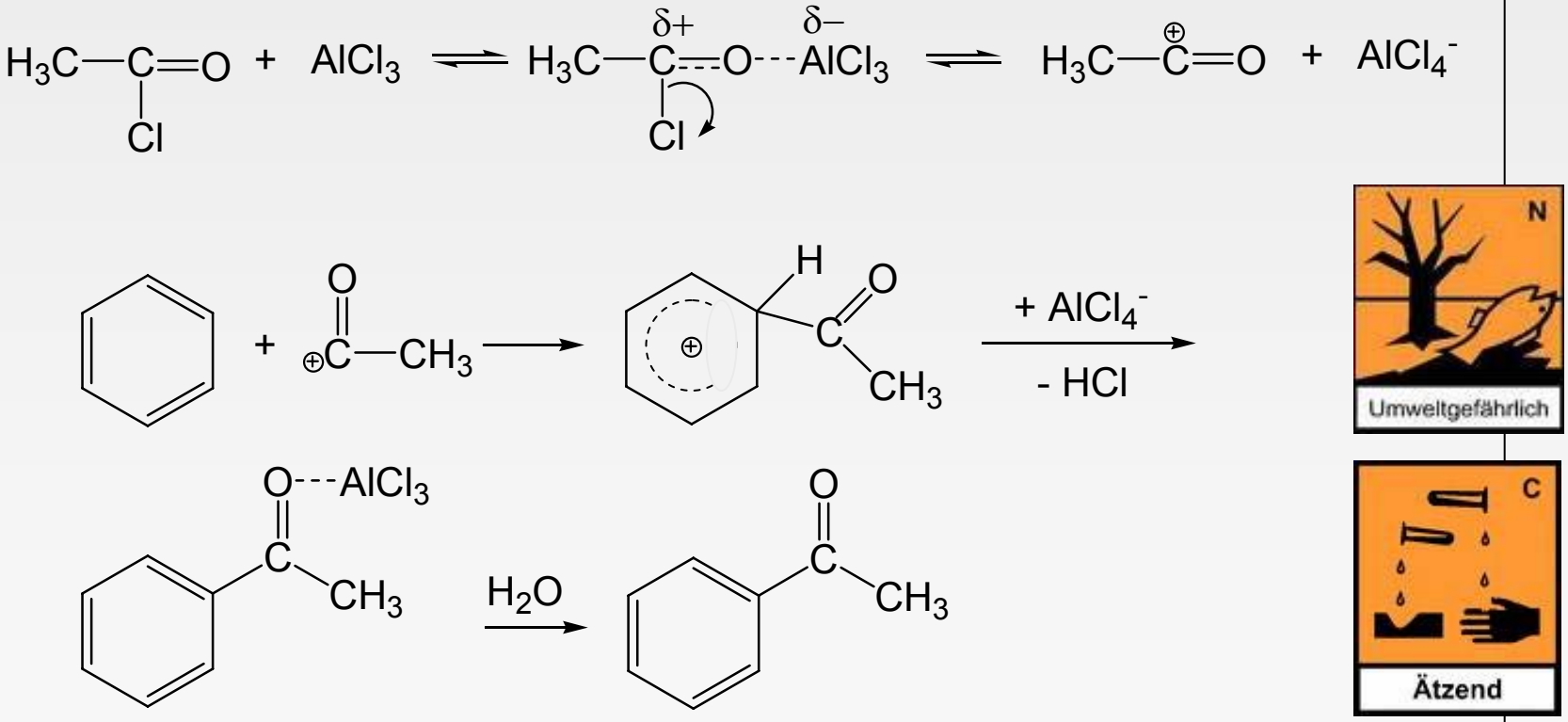
Simplest mechanism for the formation of a dimethylhexane

J. Weitkamp, Y. Traa in Handbook of Heterogeneous Catalysis, VCH, Weinheim, 1997, Vol. 4, p. 2049.

A. Feller, J. A. Lercher, Adv. Catal. 48 (2004) 229.

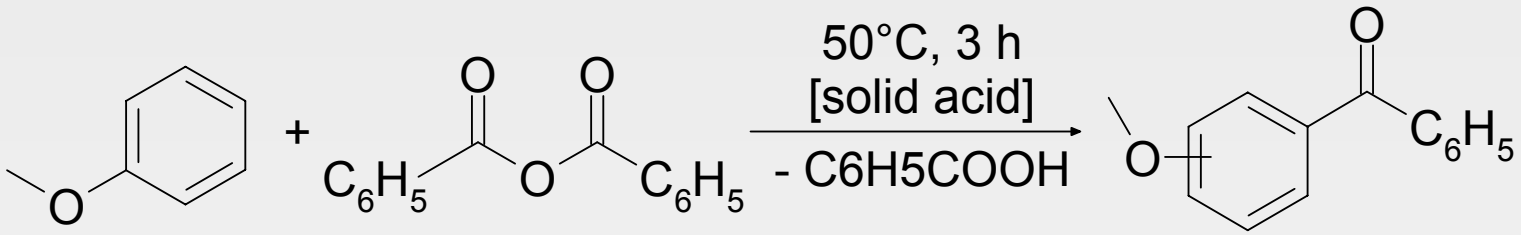
Petrochemistry / Fine chemistry

Stochiometric Friedel-Crafts acylation of aromatics

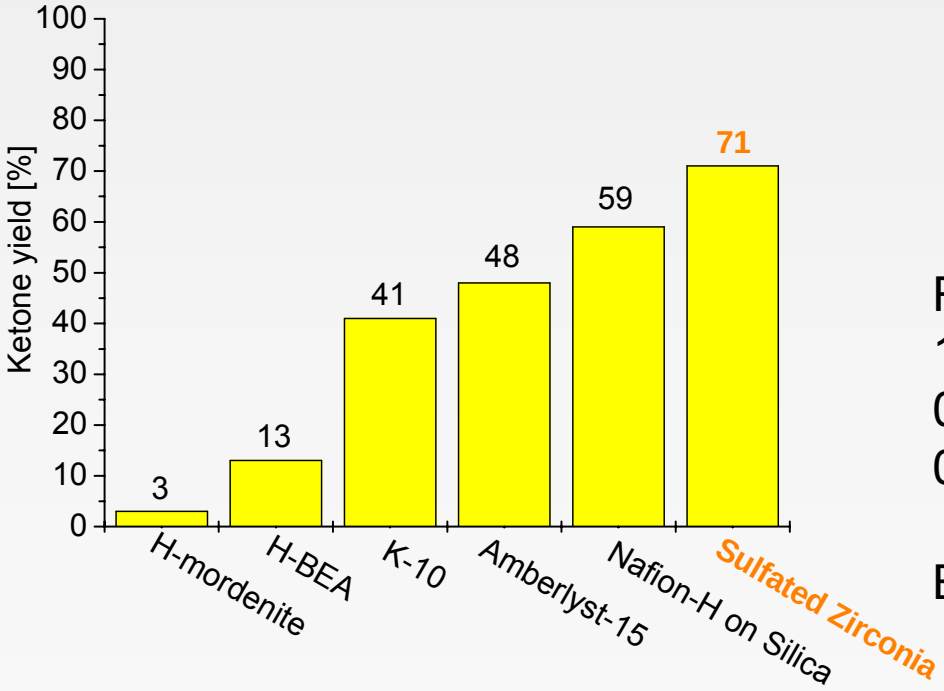


Solid acids in the acylation of aromatics

Test reaction: Benzoylation of anisole



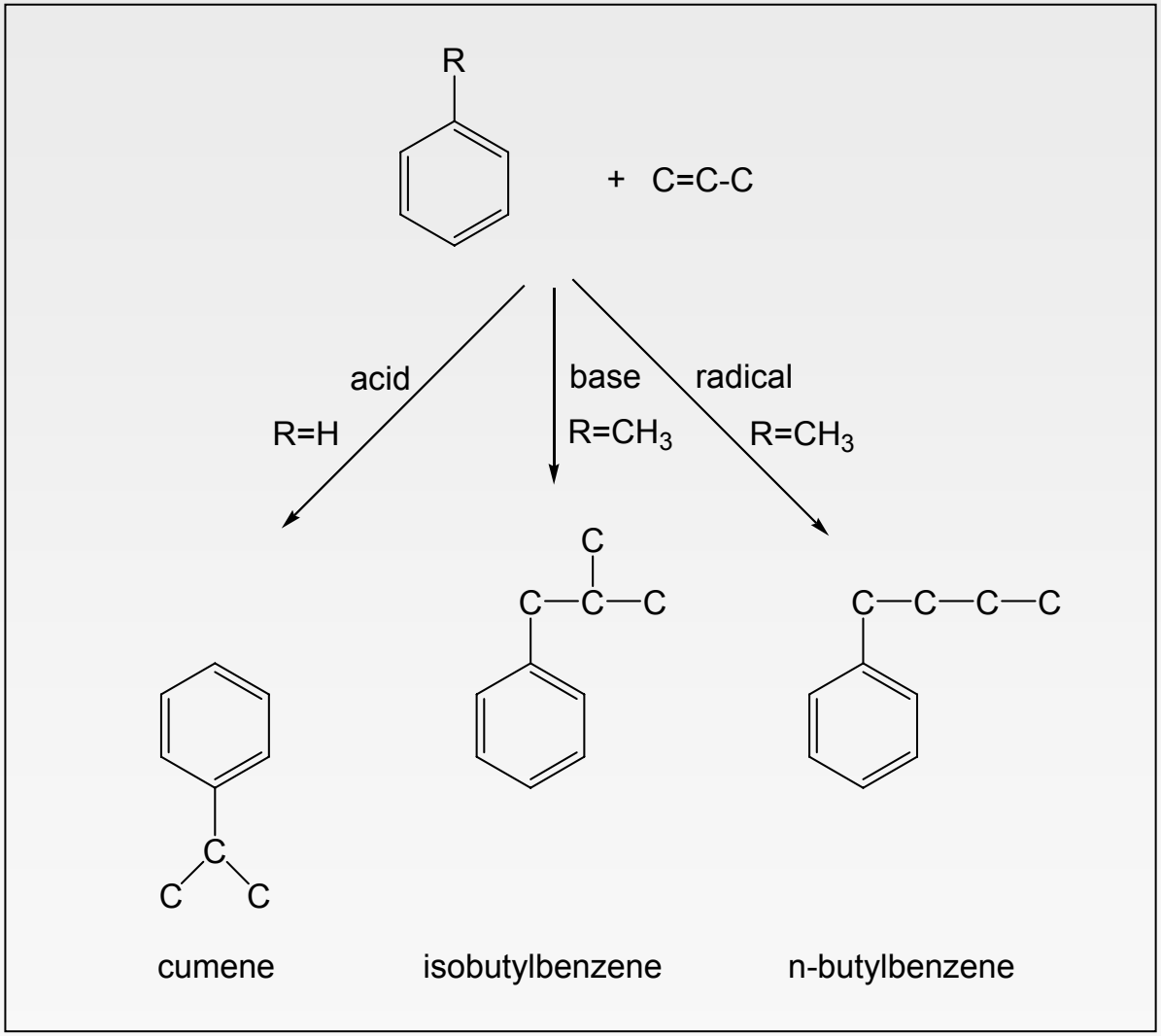
4- and 2-methoxy-benzophenone (96 / 4)



Reaction mixture:
12 ml anisole
0.6 g benzoic anhydride
0.2 g solid acid

Batch mode

Alkylation of aromatics



Alkylation of benzene with ethylene

Acid Catalyzed Synthesis of Alkylbenzenes

$$CH_2{=}CH_2 + HA \rightleftharpoons CH\text{-}CH_3^{\oplus}A^{\ominus} \xrightleftharpoons{+\ ArH} [CH_3\text{-}CH_2\text{-}ArH]^{\oplus}A^{\ominus} \rightleftharpoons CH_3\text{-}CH_2\text{-}Ar + HA$$

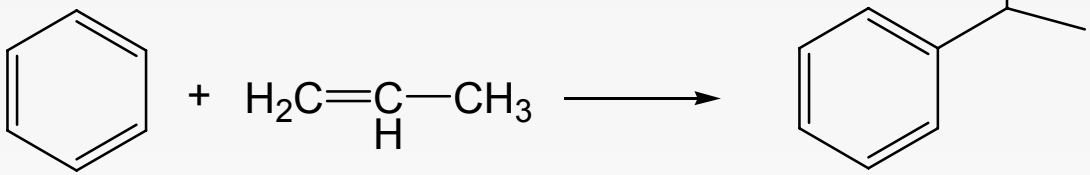
Alkylation of benzene with ethylene

Conventional catalysts:

- Metal chlorides (liquid phase) Friedel-Crafts-catalysts BF_3, $\underline{AlCl_3}$ (Monsanto-Lummus)
- Mineral acids HF, H_2SO_4

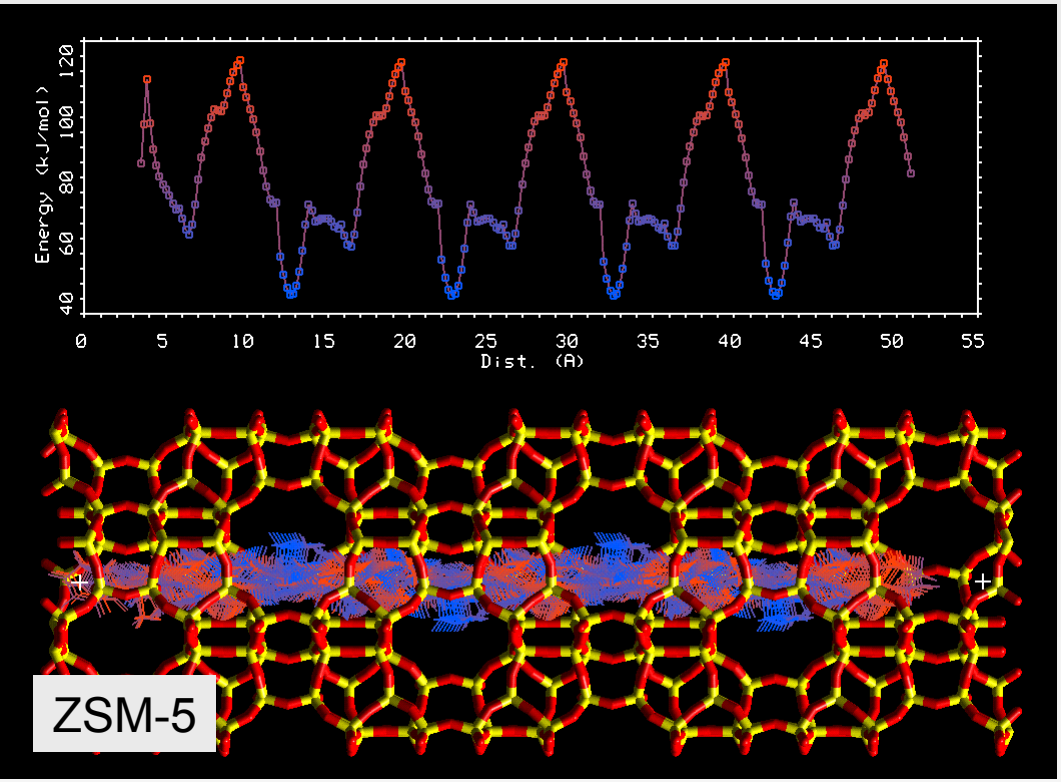
New processes:

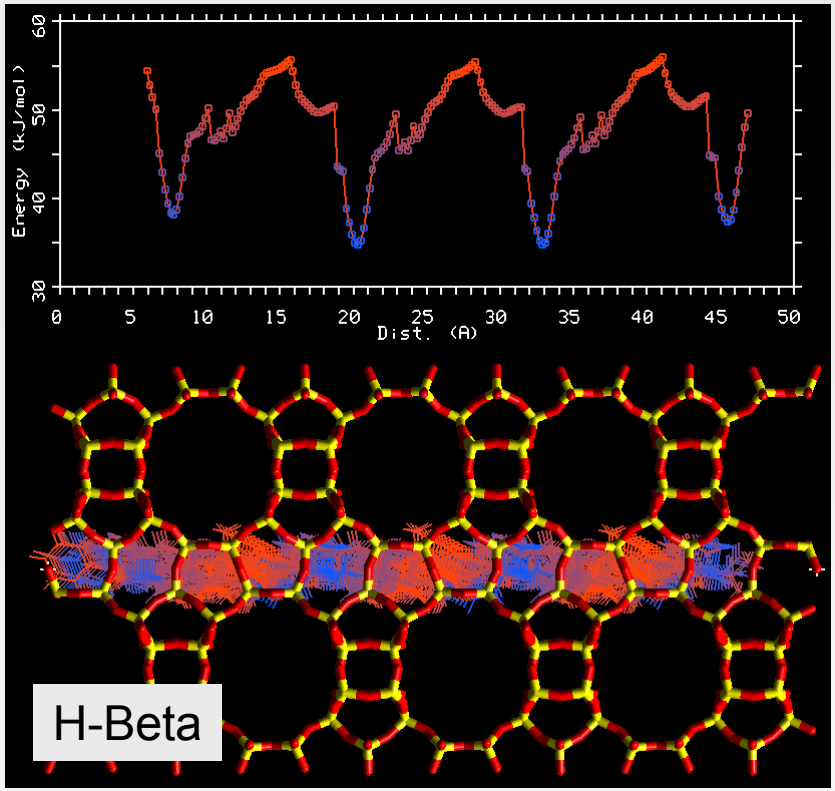
- H-ZSM-5 vapour phase (Mobil-Badger)
- EBZ 500 zeolite liquid phase (UOP/Lummus)



- High silica zeolite (Mobile-Badger/Raytheon
- H-Beta (Enichem)

Alkylation of benzene with propylene

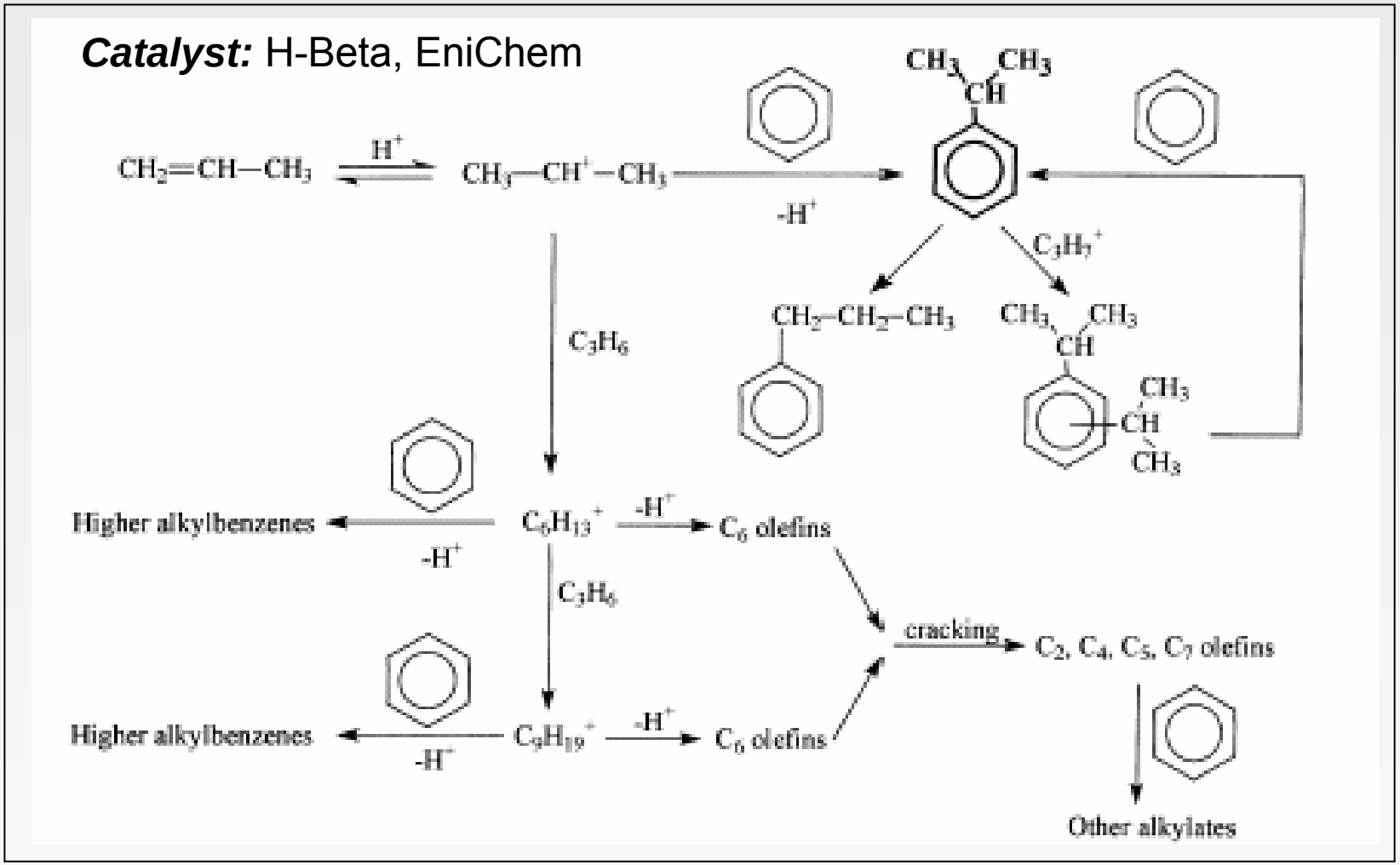




www.accelrys.com/ cases/eniricerche.html

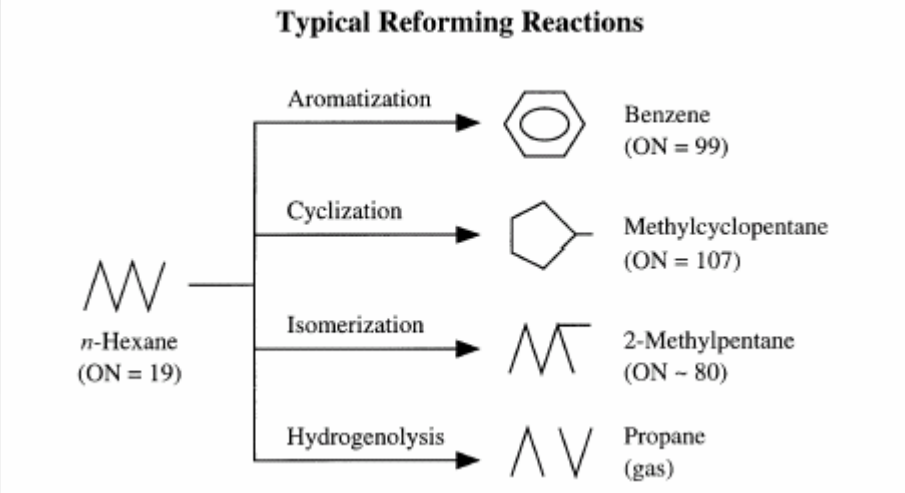
In ZSM-5, the bulkier cumene tends to isomerize to the less bulky n-propylbenzene.

Alkylation of benzene with propylene

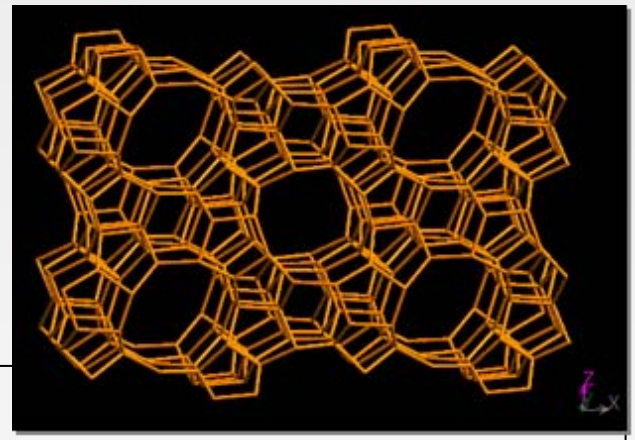


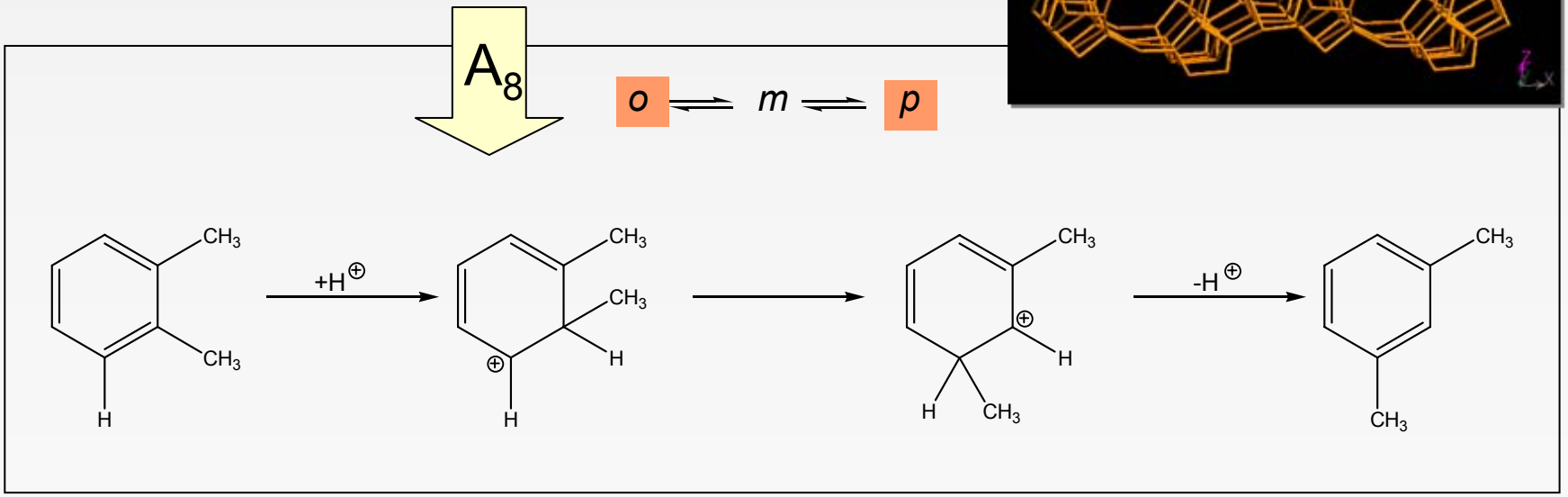
C. Perego, P. Ignallina, Catalysis Today, 73 (2002) 3.

Isomerization of xylenes



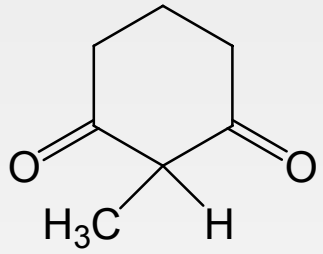
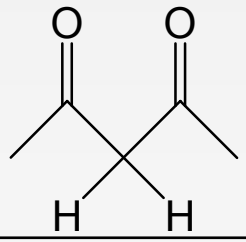
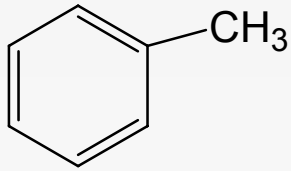
Mobil Oil:
H-ZSM-5





6. Base catalyzed reactions

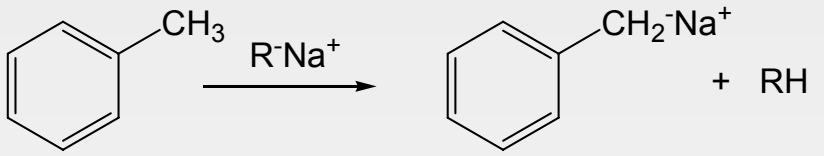
$$RH + H_2O \rightarrow R^- + H_3O^+$$

Acid	pK_a	Acid	pK_a
	7	CH_3OH	16
	9	CH_3CN	25
CH_3COCH_3	20		36

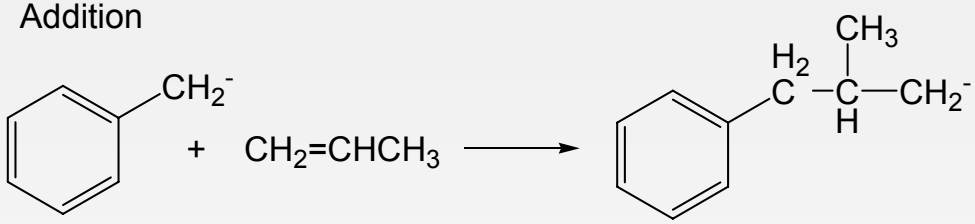
Side-chain alkylation of aromatics

Mechanisms of base catalyzed side-chain alkylation of toluene with propylene via a carbanion chain reaction

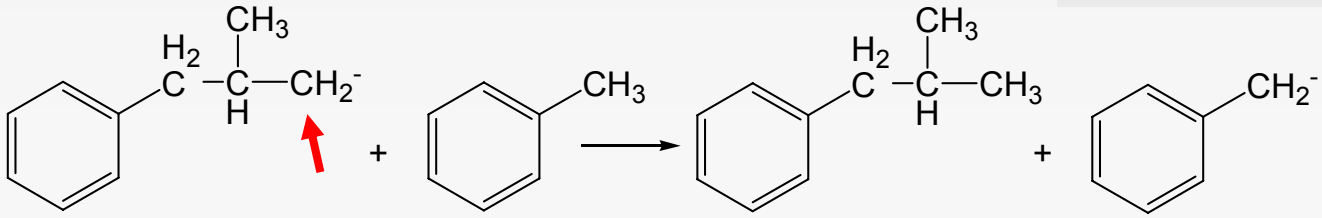
Initiation



Addition

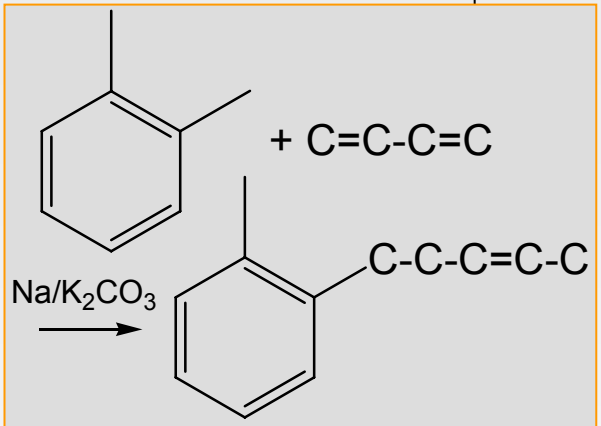


Addition



Isobutylbenzene

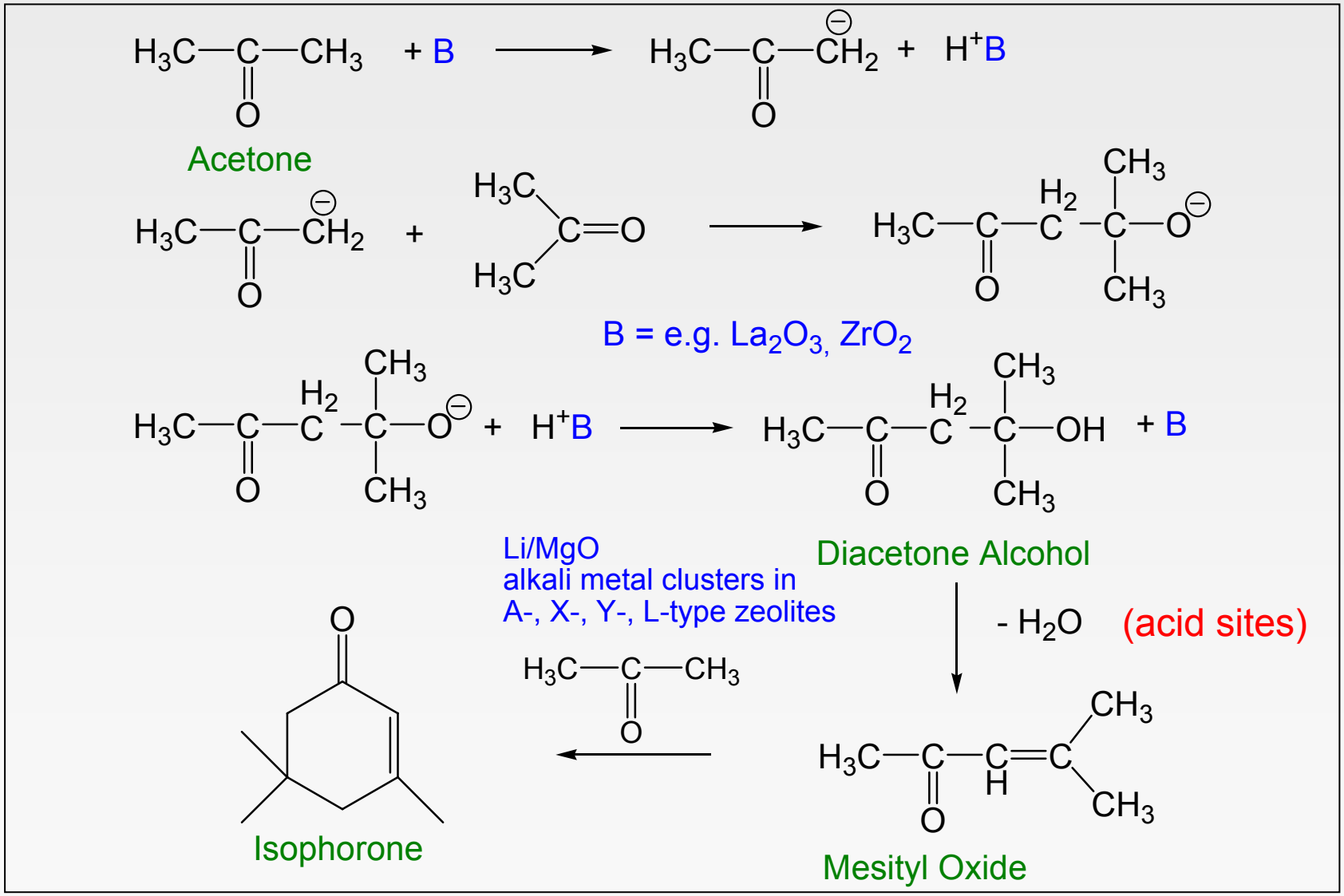
Stability of carbanions:
benzylic ≈ allylic >primary > secondary



AMOCO Chemical, Teijin

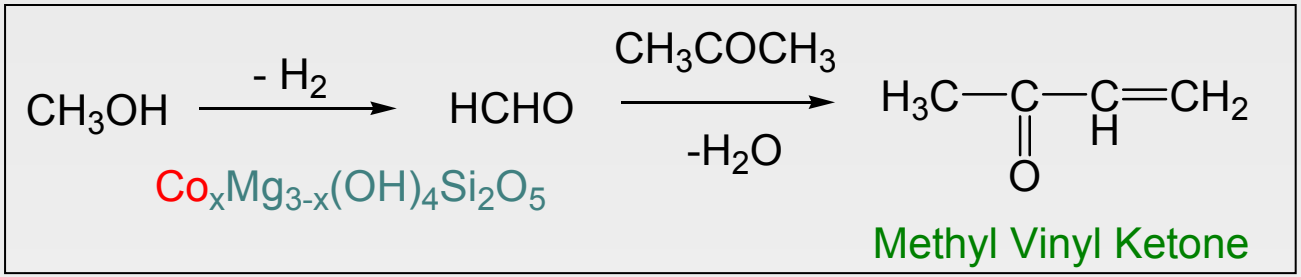
K.Tanabe, W.F.Hölderich, Applied Catalysis A 181 (1999) 399.

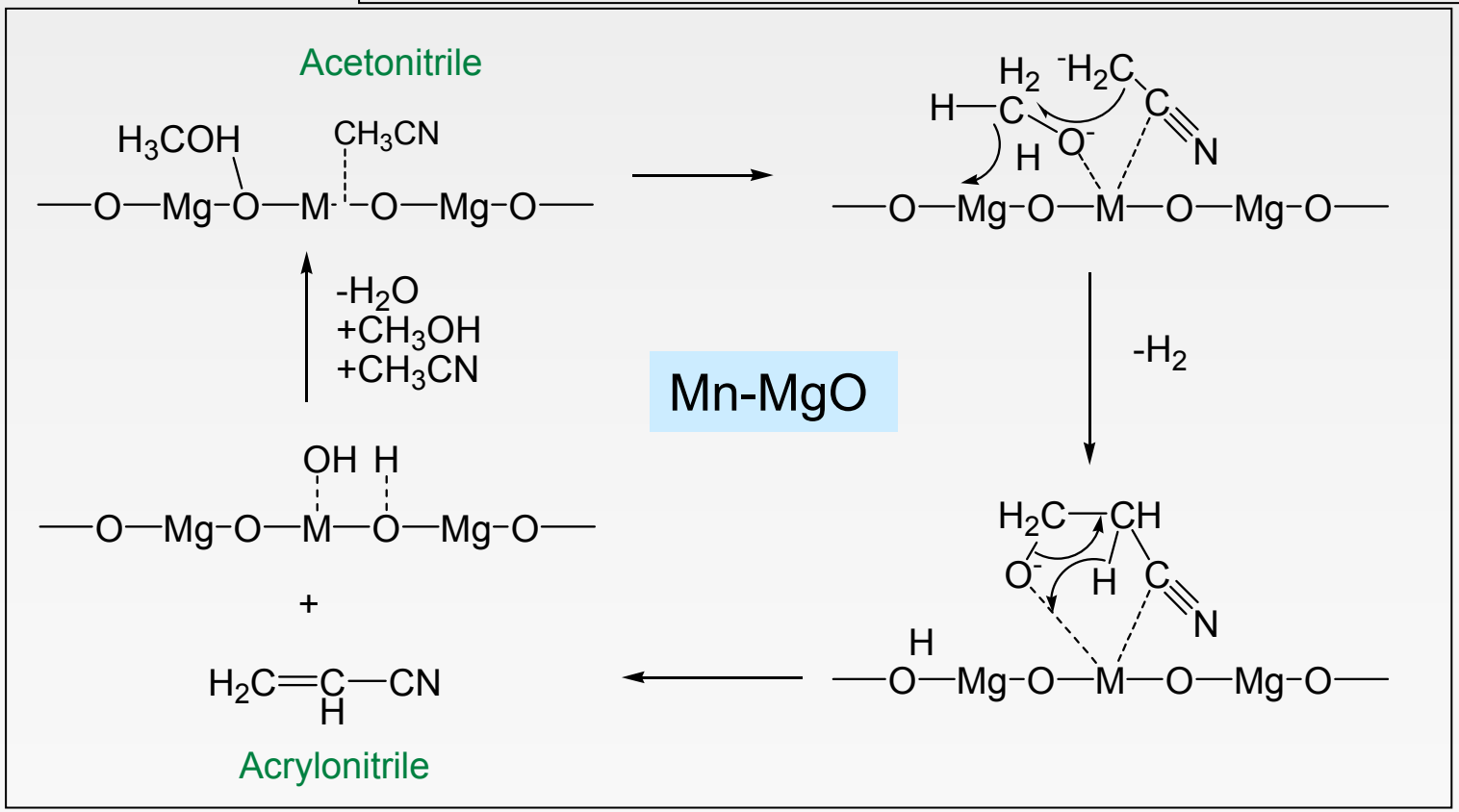
C-C Bond Formation – Aldol Condensation



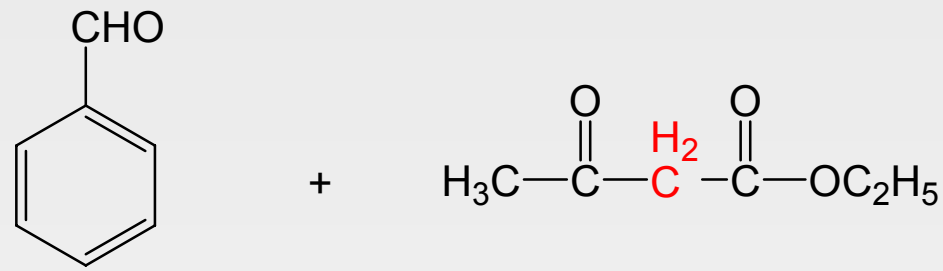
Formation of α-β unsaturated compounds

Using methanol:

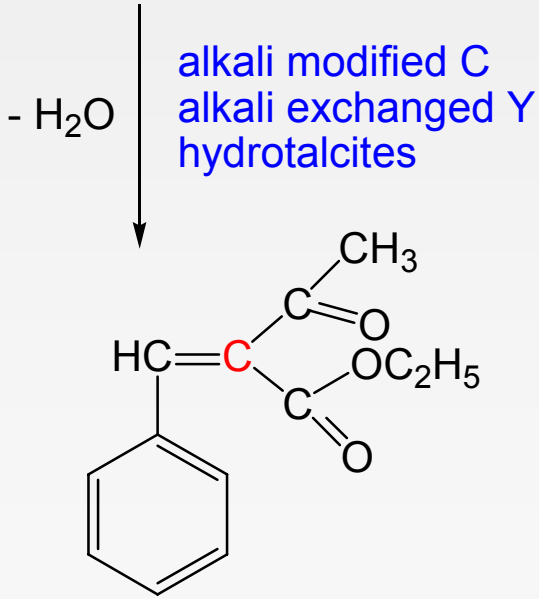




C-C Bond Formation – Knoevenagel Condensation

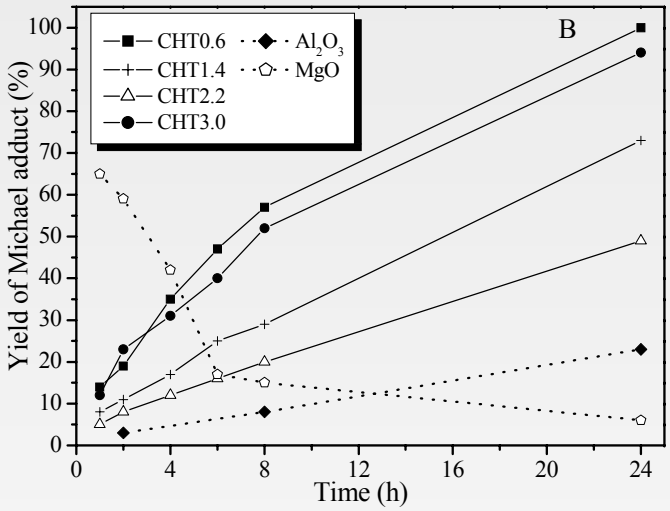


Reaction of an aldehyde or ketone with an methylene group activated by electron-withdrawing moieties

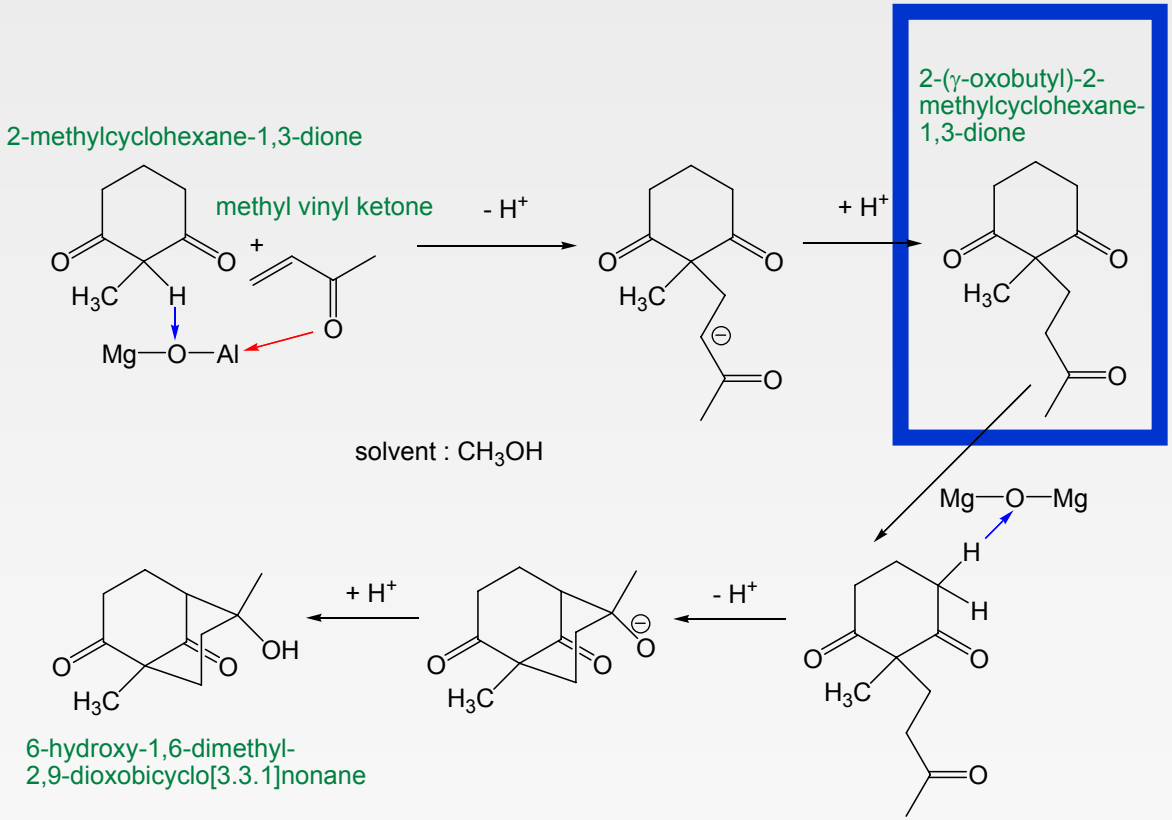


C-C Bond Formation – Michael Addition

Nucleophilic addition of carbanions to α-β unsaturated carbonyl compounds

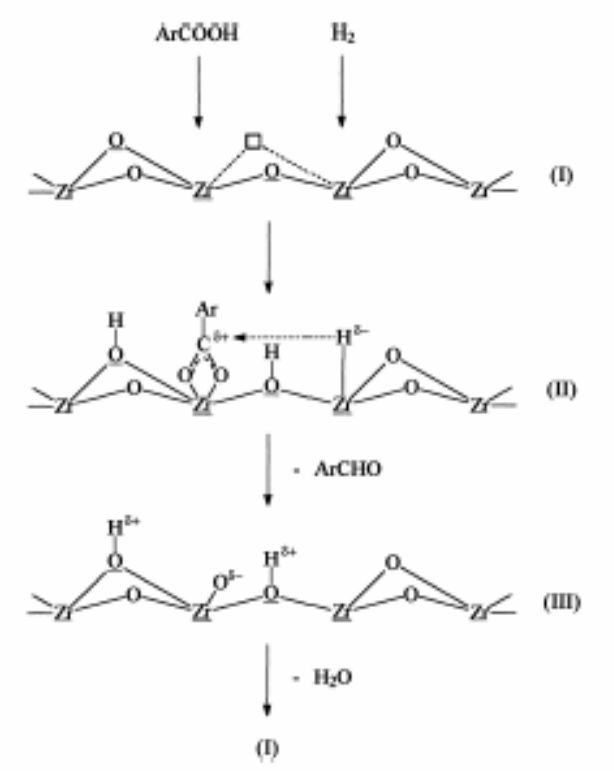


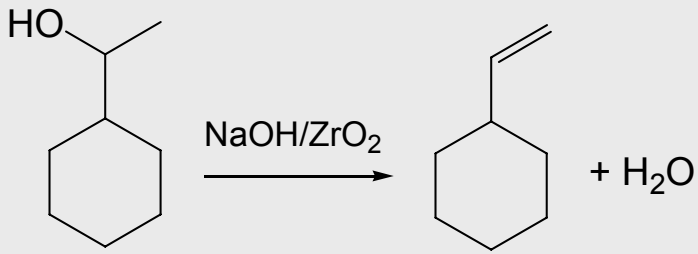
Michael addition of 2-methylcyclohexane-1,3-dione to methyl vinyl ketone over calcined hydrotalcites (CHT) with Mg/Al ratios from 0.6 to 3.0, Al_2O_3 and MgO; T=21°C.



7. Acid-base bifunctional catalysis

Hydrogenation of benzoic acid to benzaldehyde





Sumitomo

Mitsubishi Kasai
ZrO_2,doped with
Cr_2O_3
350°C

Acid / base bifunctional mechanism over a zirconia catalyst (Zr^{4+}: acid site; O^{2-} base site)

8. Summary and outlook

•Fine and speciality chemicals will be manufactured in the future to a greater extent using solid acid-base catalysts

•Solid acid-base bifunctional catalysis is expected to become more important in the future

Problems and needs:

•New bases resistant to deactivation (CO_2 and water poisoning) need to be developed

•Deactivation of catalysts

•Development of catalysts other than acidic resins which can be used in aqueous solutuins

•Universal acidity / basicity scale for solids

Acknowledgements

Thanks for data and material for illustration to

Dr. Jens Deutsch, ACA

Zhi-Jian Li , HU Berlin

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Dr. Veronika Quaschning, BASF AG

Prof. Aline Auroux, Institut de Recherches sur la Catalyse, Villeurbanne

Dr. Alexander Hofmann, HU Berlin

Dr. Friederike Jentoft