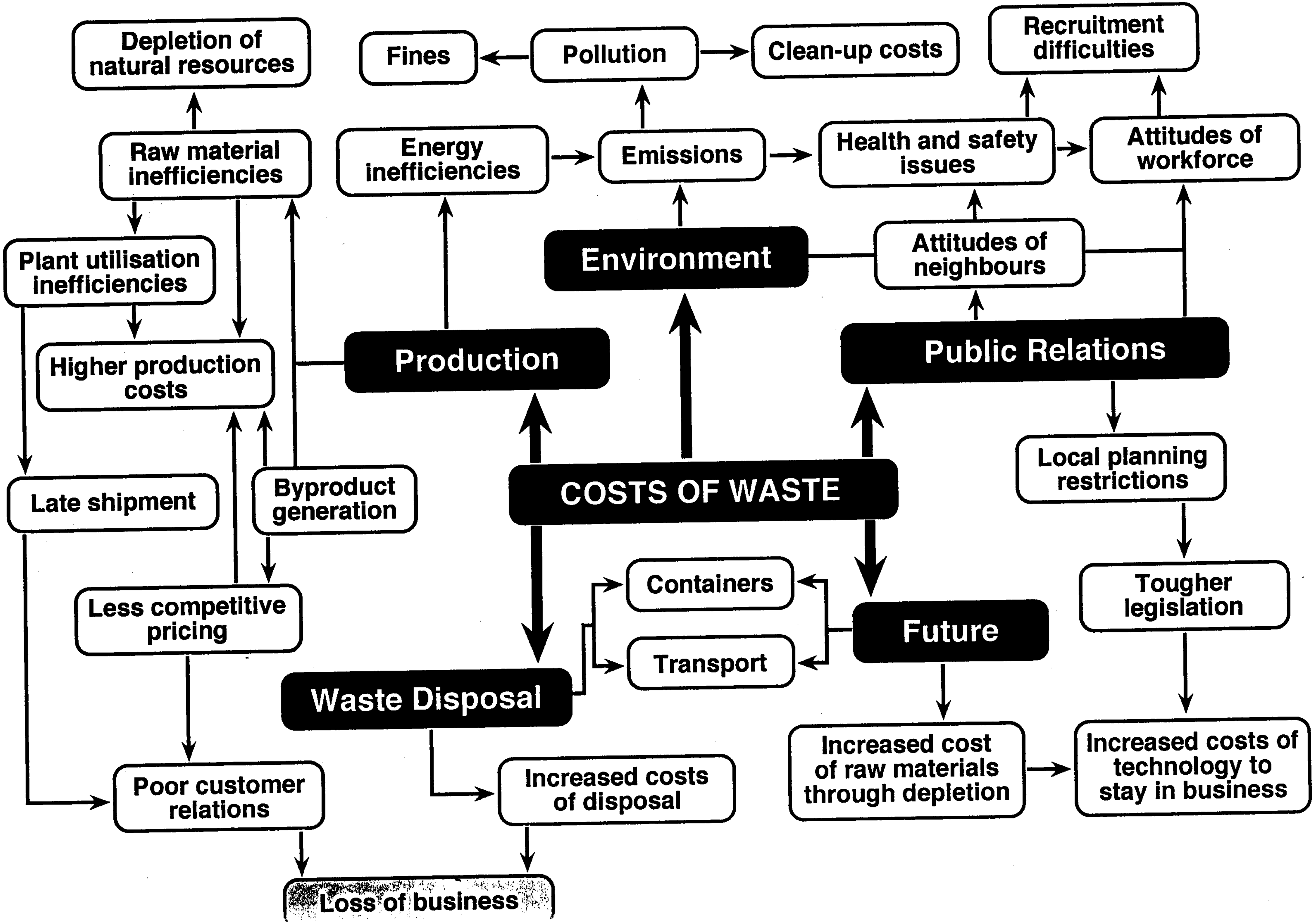

Depletion of natural resources
Fines
Pollution
Clean-up costs
Recruitment difficulties
Raw material inefficiencies
Energy inefficiencies
Emissions
Health and safety issues
Attitudes of workforce
Plant utilisation inefficiencies
Environment
Attitudes of neighbours
Higher production costs
Production
Public Relations
Late shipment
Byproduct generation
COSTS OF WASTE
Local planning restrictions
Less competitive pricing
Containers
Transport
Future
Tougher legislation
Waste Disposal
Poor customer relations
Increased costs of disposal
Increased cost of raw materials through depletion
Increased costs of technology to stay in business
Loss of business

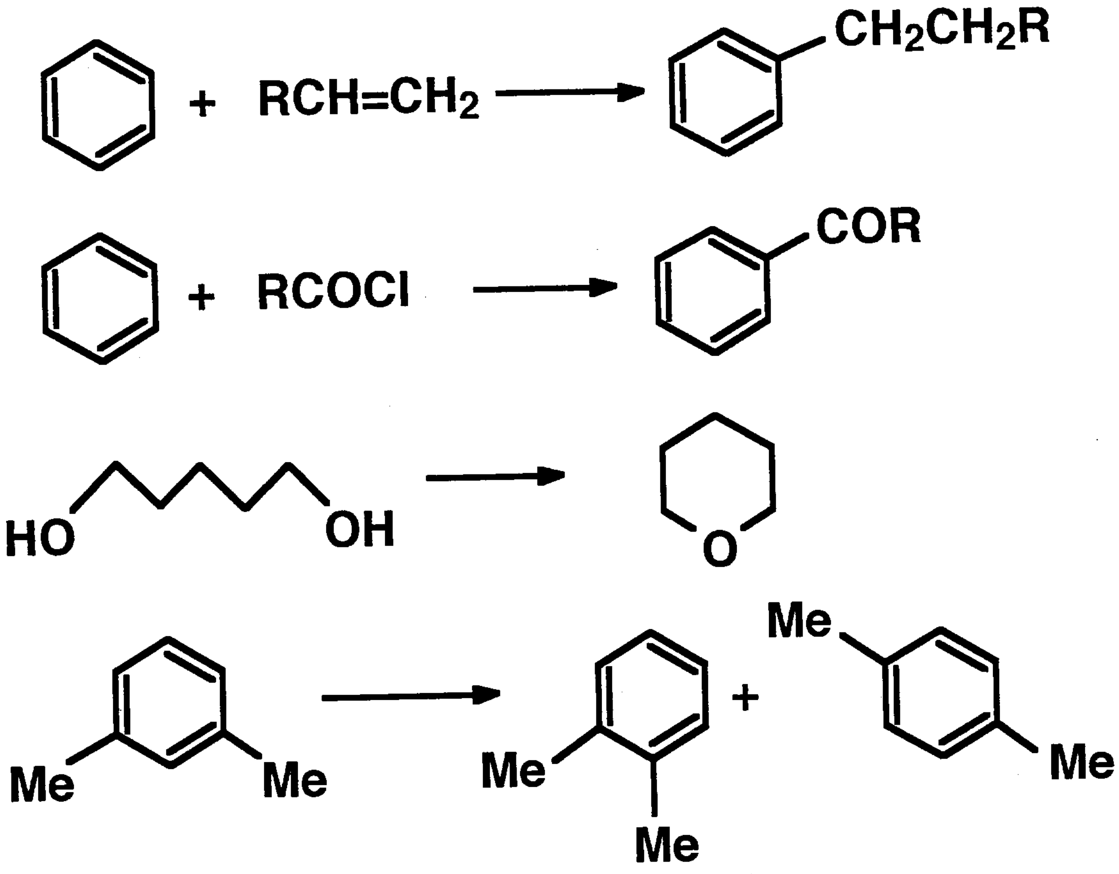
# ADVANTAGES OF SUPPORTED REAGENT CATALYSTS

- non-toxic
- easy to handle
- genuinely catalytic
- no solvent/hydrocarbon solvent
- different phase to organics
- may be reusable
- can offer enhanced selectivity
- waste minimising

# ACID-CATALYSED REACTIONS

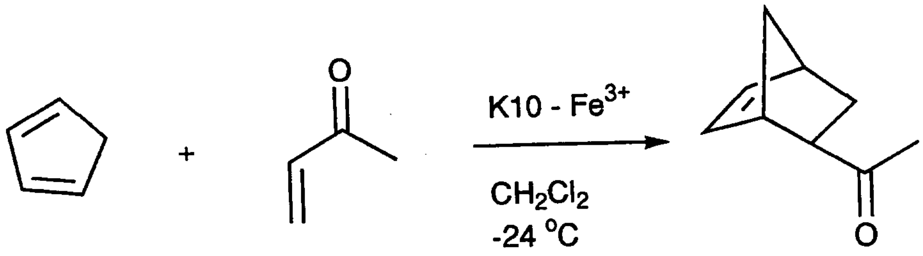
- most widely used type of catalysis
- applications in all sectors of the chemical, pharmaceutical and allied industries
- largely based on inexpensive Bronsted and Lewis acids

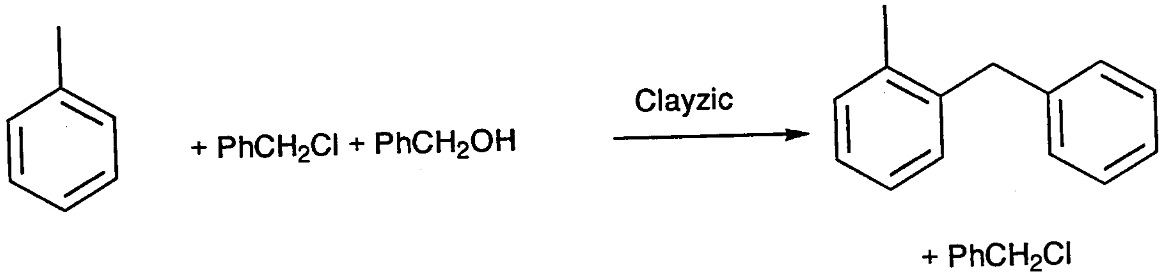
  - $H_2SO4$ - HF - $AlCl_3$ - $BF_3$
- larger scale continuous vapour phase processes moving towards solid acids
- diverse chemistry:

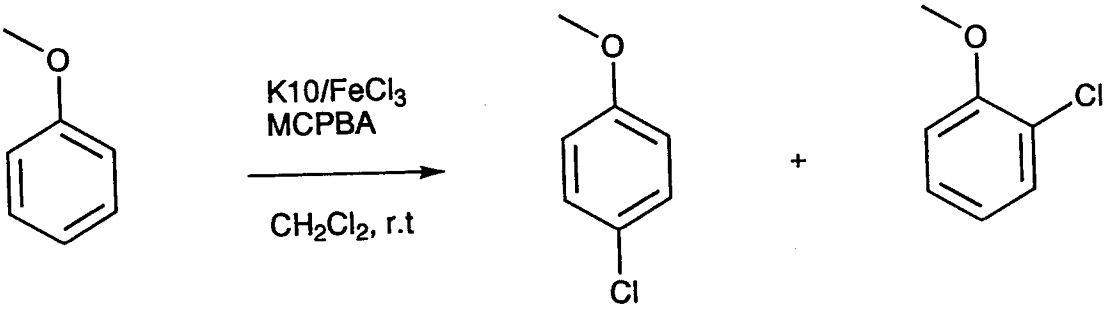


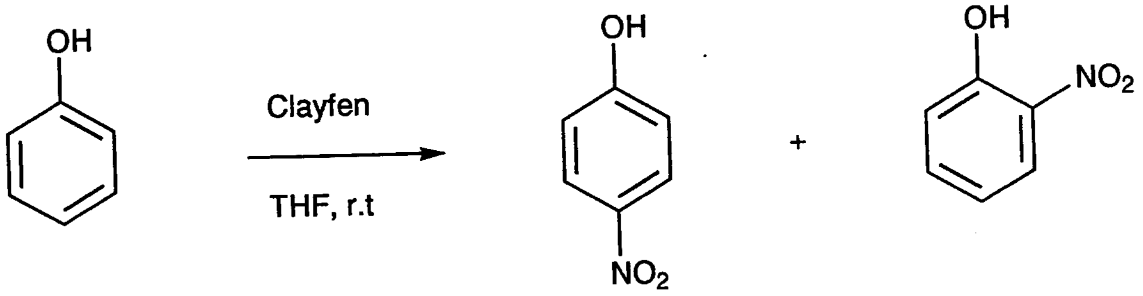
# Traditional Applications for Clay-Based Catalysts

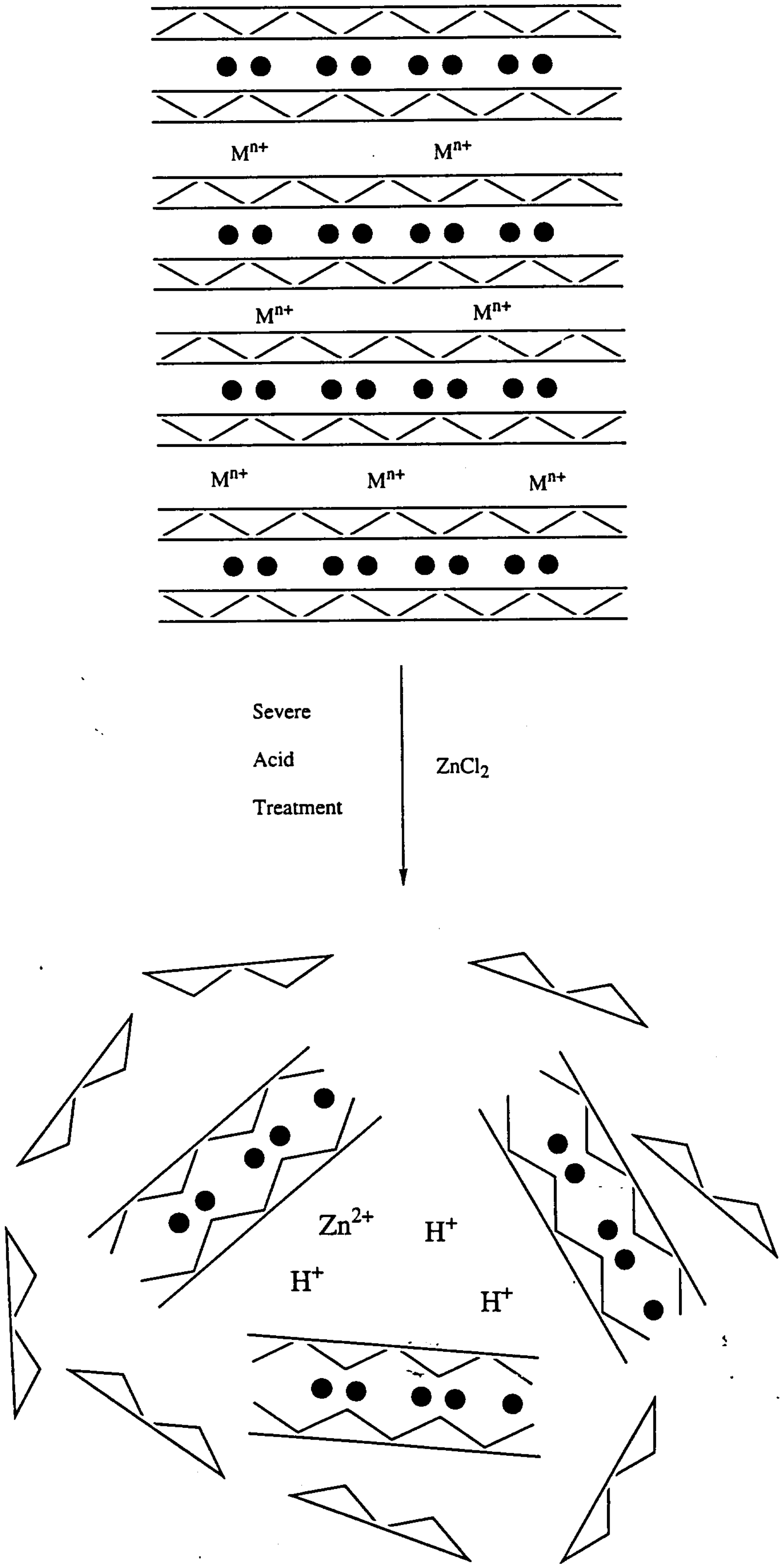
( Geol. Carp. Series Clays, 1994, 45; Acc.Chem.Res., 1993,607; J. Chem. Soc. Perk II, 1994,1117; Synlett, 1994,155)



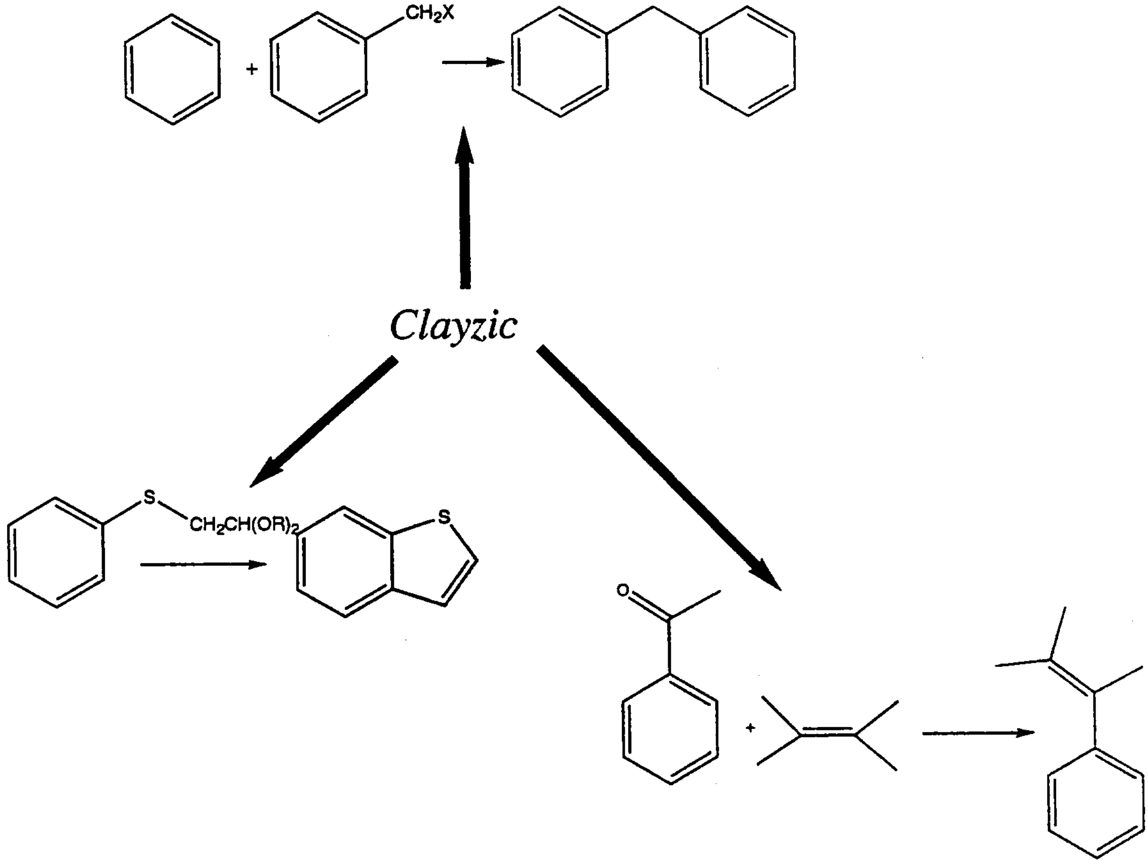







M$^{n+}$
M$^{n+}$
M$^{n+}$
M$^{n+}$
M$^{n+}$
M$^{n+}$
M$^{n+}$
Severe
Acid
Treatment
ZnCl$_2$
Zn$^{2+}$
H$^+$
H$^+$
H$^+$

# Clay-supported zinc chloride (Clayzic)

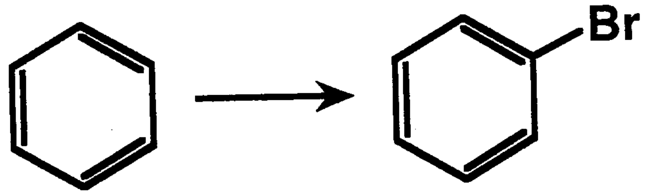


# BROMINATION

- international speciality chemical industry
- photographic chemicals and chemical and pharmaceutical intermediates
- largely based on use of bromine
- diverse chemistry:

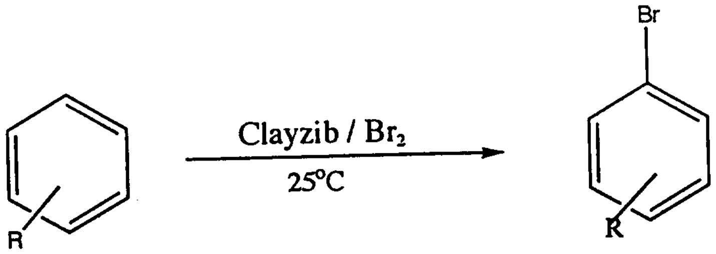
$$\mathrm{ROH} \longrightarrow \mathrm{RBr}$$

$$\mathrm{RCH_2COOH} \longrightarrow \mathrm{RCHBrCOOH}$$



- most of bromine does not end up in final product

# CATALYTIC AROMATIC BROMINATION



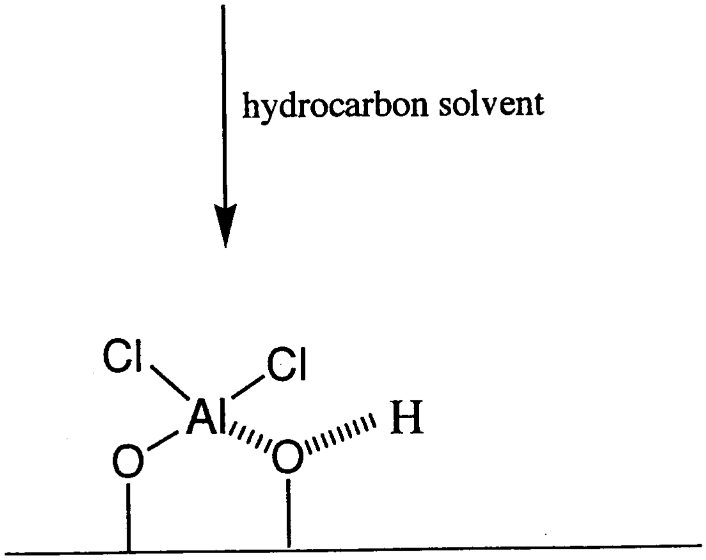
R = alkyl, halo

| *Catalyst* | *% bromination (hours)* | *p/o* |
|---|---|---|
| none ($CCl_4$) | 10 (24) | 4.1 |
| clayzib ($CCl_4$) | 100(8) | 9.6 |
| silizib ($CCl_4$) | 94(7) | 9.7 |
| clayzib (hexane) | 100(7) | 8.5 |
| silizib (hexane)* | 100(7) | 8.7 |

* reusable for 4 runs with no significant loss in activity/selectivity

# *Immobilised aluminium chloride*

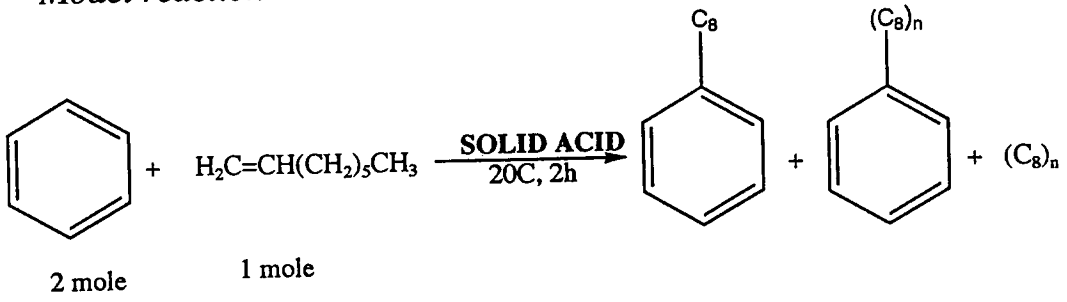
$AlCl_3$ + dry hydroxylated support material



Supported Lewis acid and Bronsted acid

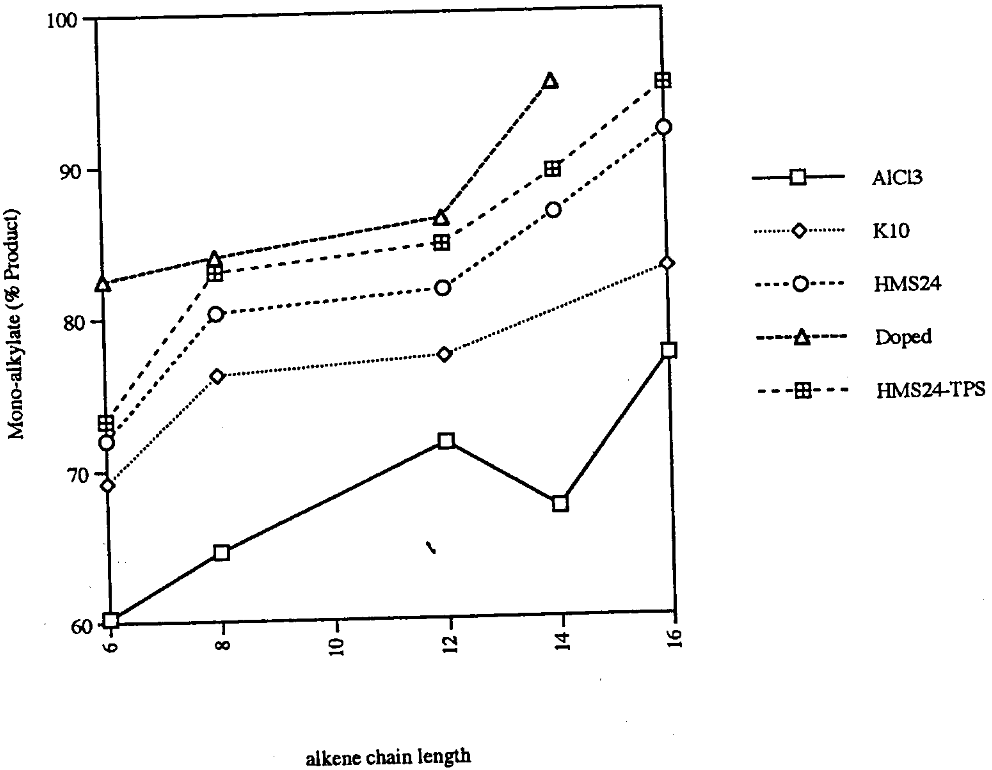
# SOLID ACID CATALYSED ALKYLATION OF AROMATICS USING ALKENES

*Model reaction*

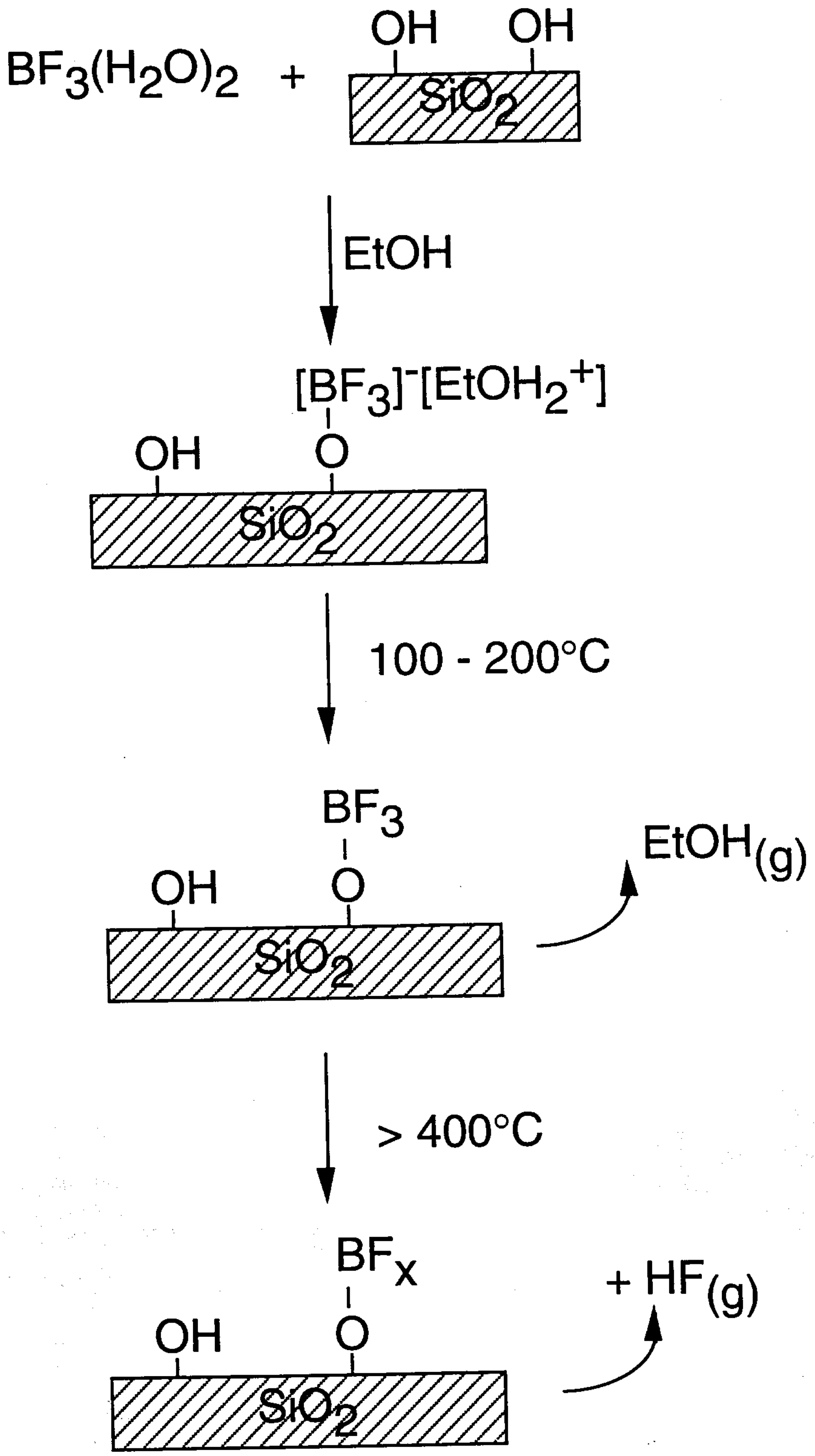


| | | | |
|---|---|---|---|
| **$AlCl_3$** | **62** | **21** | **17** |
| **K10 (24h)** | **33** | **4** | **0** |
| **Clayzic (80C)** | **40** | **18** | **25** |
| **$SiO_2$-$AlCl_3$** | **80-60** | **30-20** | **10-0** |
| **K10-$AlCl_3$** | **76** | **24** | **0** |

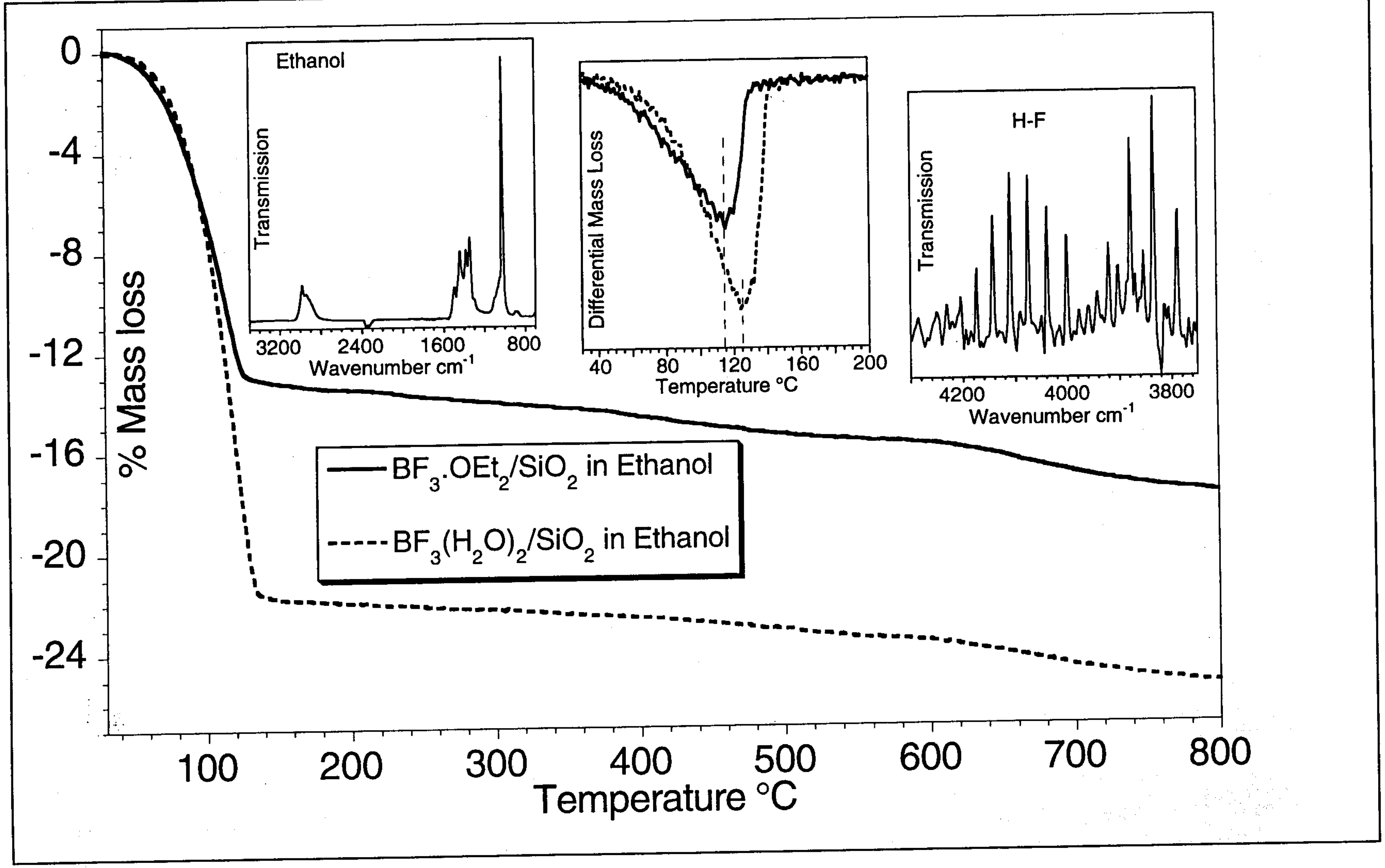
Comparison of selectivities using various alkenes



## • Preparation and thermal processing of $BF_3(H_2O)_2/SiO_2$

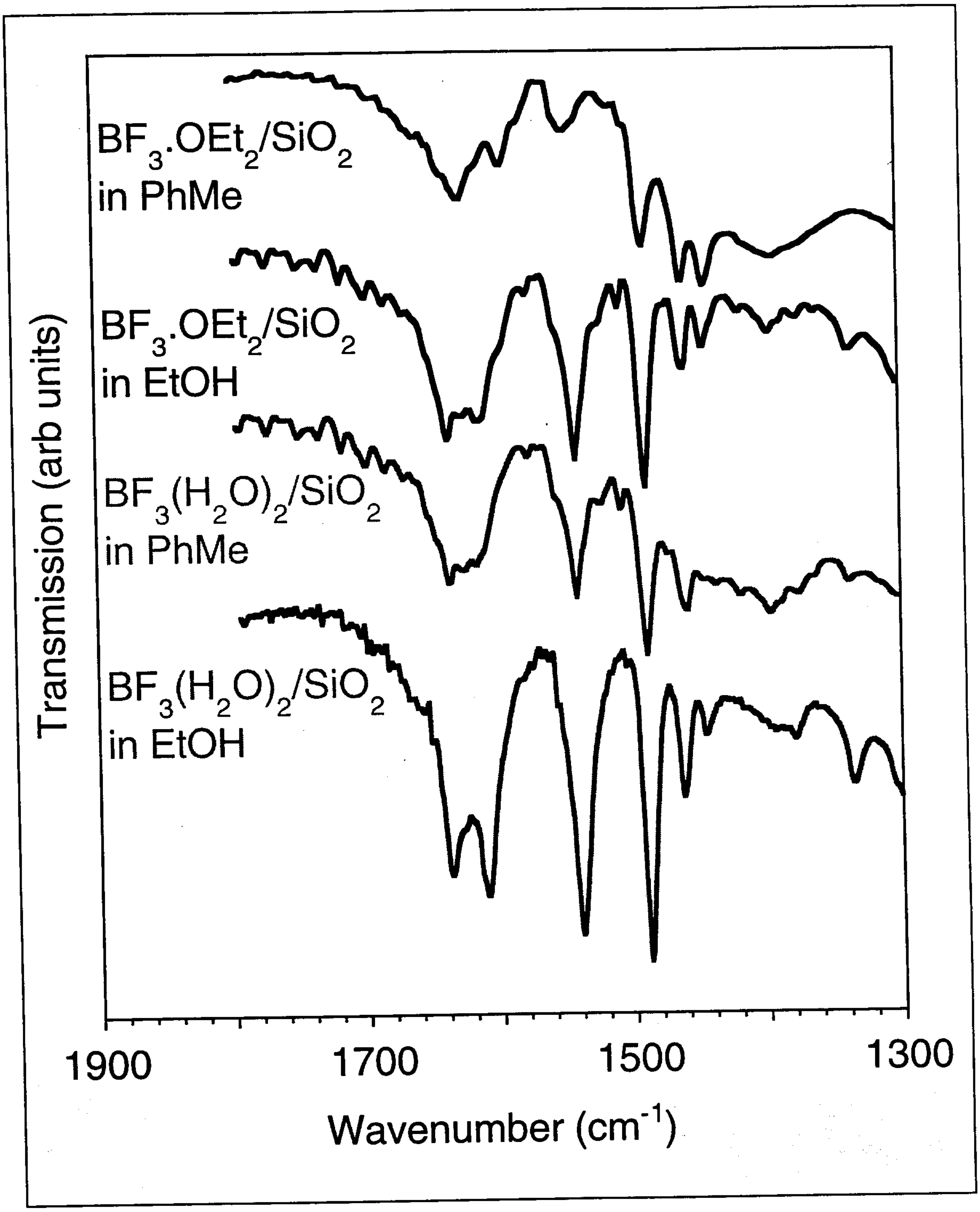


- TGIR shows evolution of EtOH, and HF as catalyst is thermally decomposed



- Stronger acid sites have higher EtOH desorption temperature

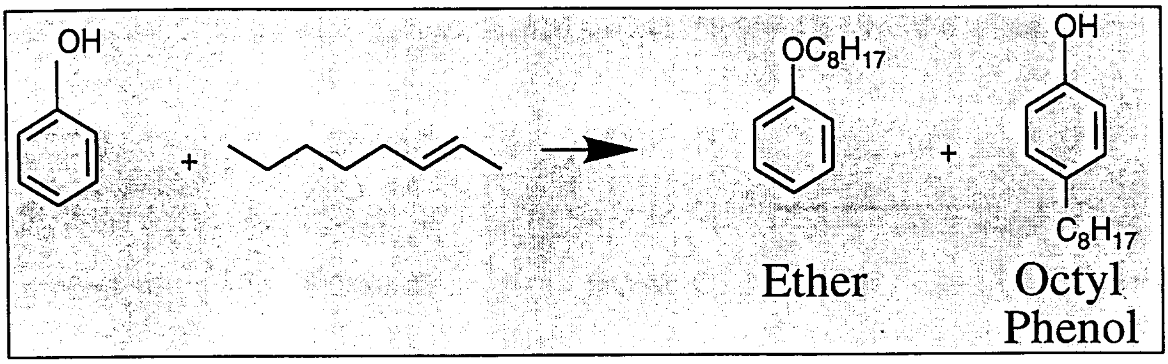
- Pyridine titration of supported $BF_3$ catalysts



- $BF_3/(H_2O)_2/SiO_2$ prepared in EtOH exhibits greater Brønsted acidity

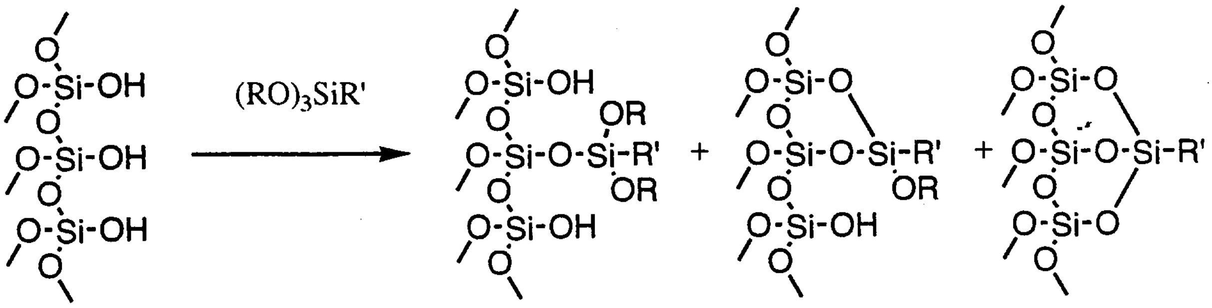
- $^1H$ MAS-NMR reveals protonated EtOH → formation of $[BF_3]^-[EtOH_2]^+$ complex

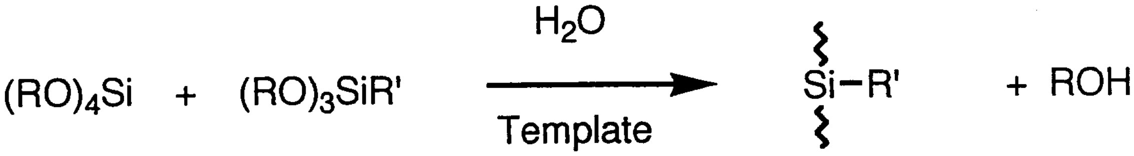
# Alkylation of Phenol by 1-Octene

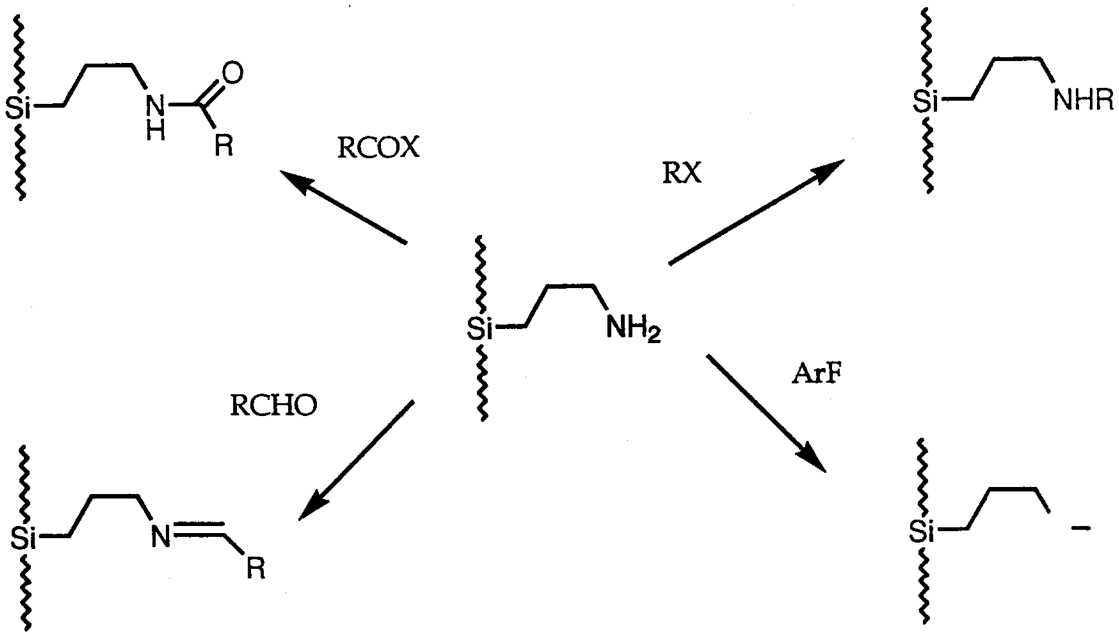


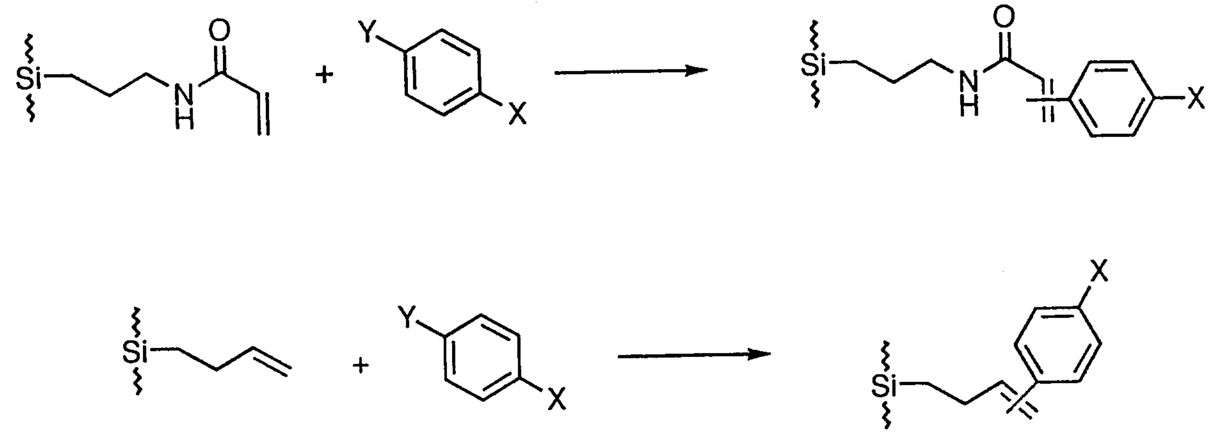
| Catalyst | Phenol Conversion | Ether Selectivity |
|---|---|---|
| $BF_3(H_2O)_2/SiO_2$ (EtOH) | 30 % | 61 % |
| $BF_3(H_2O)_2/SiO_2$ (EtOH)-recycled | 6 % | 97 % |
| $BF_3(H_2O)_2/SiO_2$ ($PhCH_3$) | 4 % | 78 % |
| $BF_3(OEt_2)/SiO_2$ (EtOH) | 3 % | 85 % |
| $BF_3(OEt_2)/SiO_2$ ($PhCH_3$) | <1 % | 92 % |

- Conversion of phenol and selectivity towards octyl phenol increases with catalyst Brønsted acidity.


(RO)₃SiR'
O-Si-OH
OR
O-Si-O-Si-R'
OR
+
O-Si-O
O-Si-O-Si-R'
+
O-Si-O-Si-R'

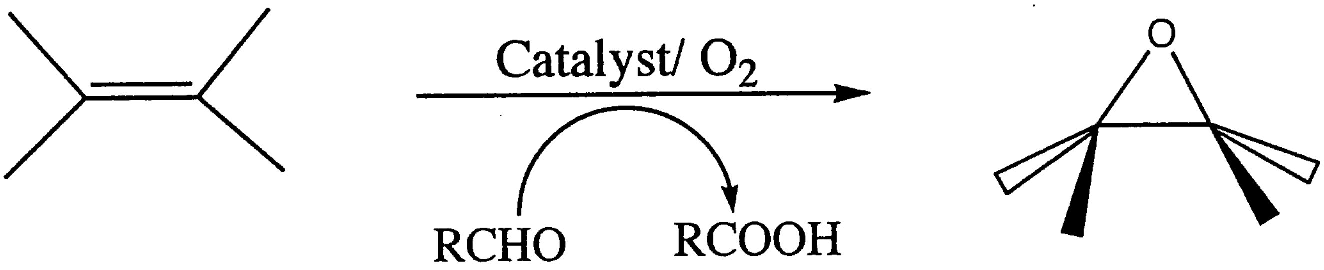

(RO)₄Si
+
(RO)₃SiR'
H₂O
Template
Si–R'
+ ROH

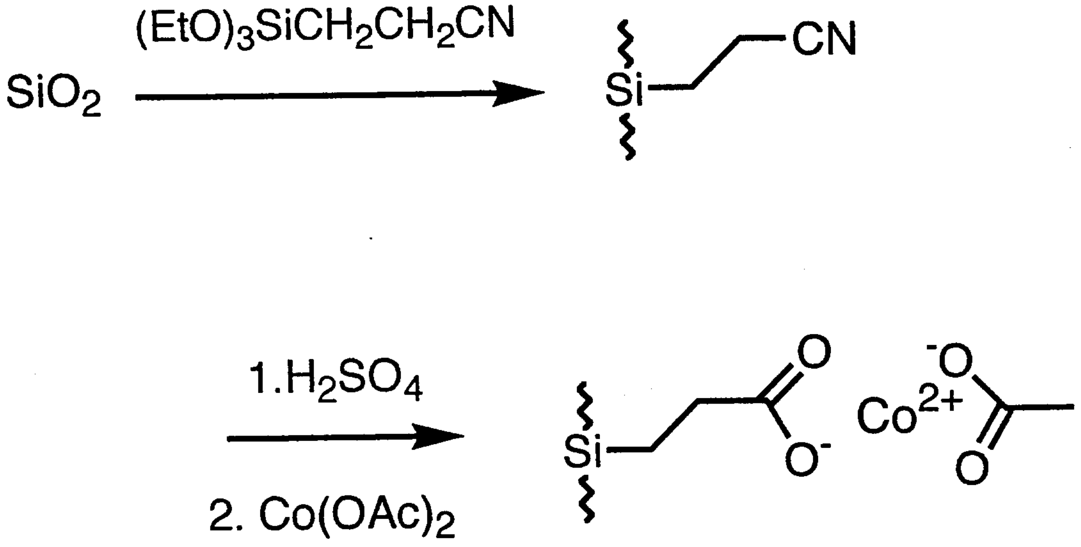

RCOX
RX
RCHO
ArF
Si
NH₂
NHR
N
H
O
R
N
R
–



$X = H, CHO, CO_2H, CN; \quad Y = Br, I$

# EPOXIDATION OF ALKENES CATALYSED BY SILICA-SUPPORTED Co(II)



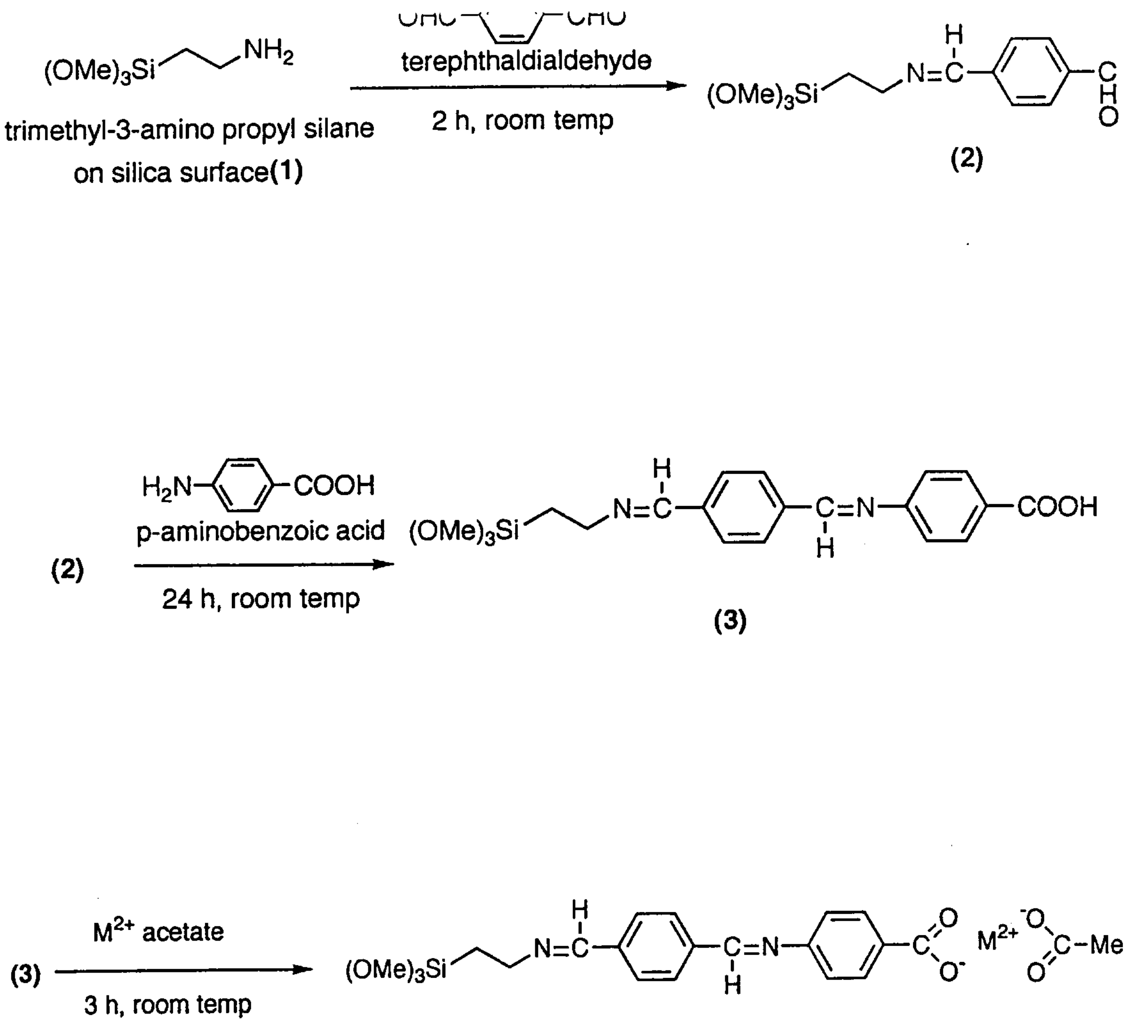


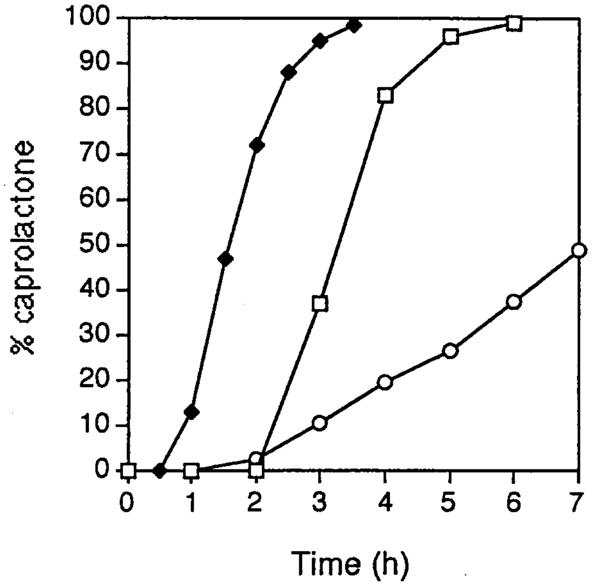
## Epoxidation of alkenes using supported cobalt acetate.

| Alkene | time (h) | Yield of epoxide[a] |
|---|---|---|
| cyclohexene | 5 | 85 |
| oct-1-ene | 5 | 45 |
| octa-1,7-diene | 24 | 48[b] |
| 2,4,4-trimethylpentene | 5 | 95 |
| hex-1-ene | 24 | 30 |
| styrene | 3 | 32[c] |

All reactions were carried out at 19°C in dichloromethane with isobutyraldehyde as sacrificial aldehyde.

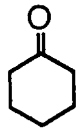
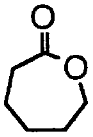
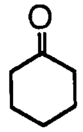
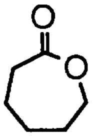
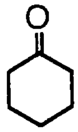
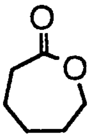
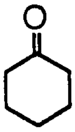
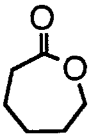
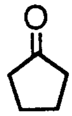
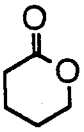
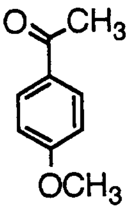
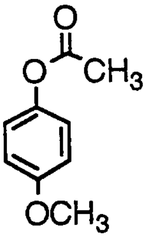
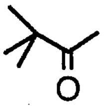
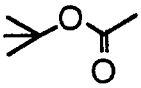
a) Gc yield with internal standard; b) monoepoxide; 7% of diepoxide was also formed; c) 5% PhCHO and 21% polymer also formed.





Percentage conversion of cyclohexanone to ε-caprolactone with no catalyst (○), catalyst activated at 105 °C for 24 h (♦) and catalyst used without activation (□).

Baeyer-Villiger oxidation of ketones using an immobilised nickel catalyst in the presence of molecular oxygen and benzaldehyde[a]

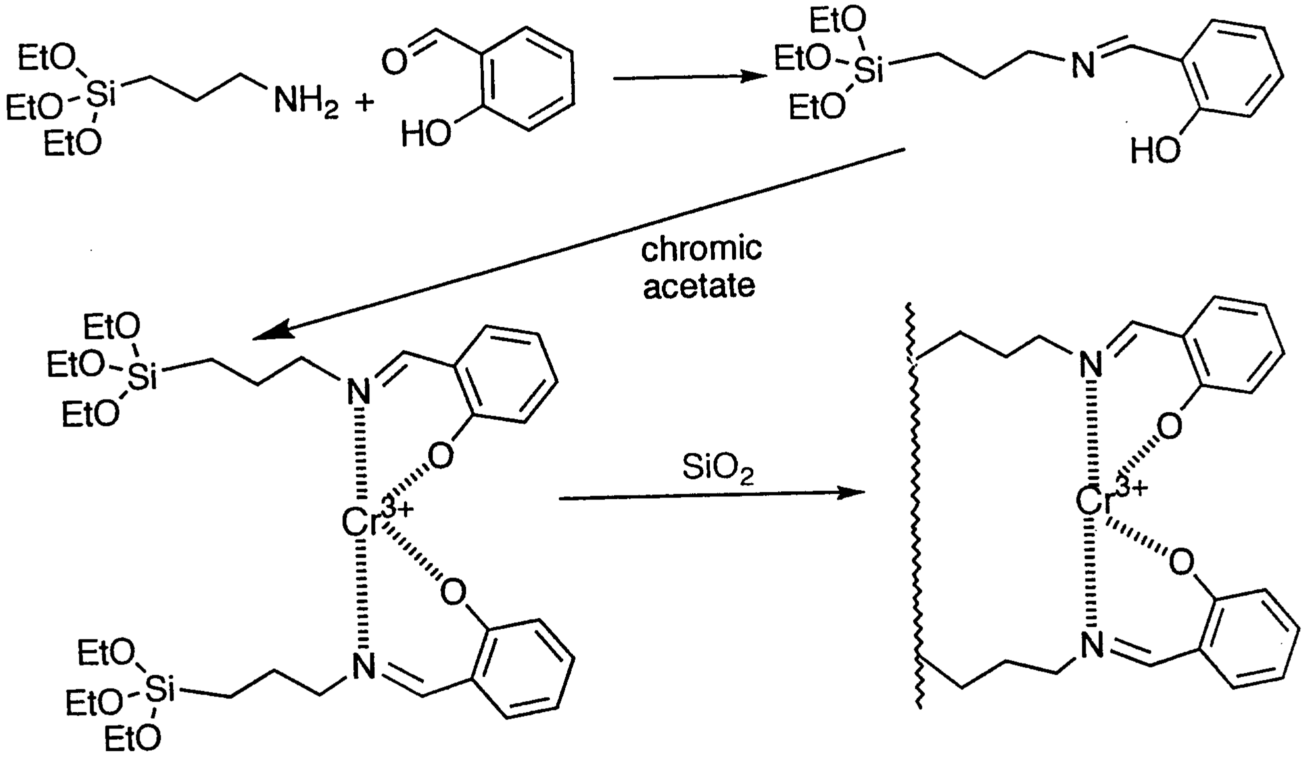
| Substrate | Solvent | Time / h | Product[d] | GC Yield / % |
|---|---|---|---|---|
|  | benzene | 3.5 |  | 98 |
|  | DCM[b] | 7 |  | 95 |
|  | DCE[c] | 8 |  | 91 |
|  | toluene | 24 |  | 15 |
|  | benzene | 7 |  | 91 |
|  | benzene | 24 |  | 81 |
|  | benzene | 24 |  | 76 |

[a] reaction conditions: catalyst 0.5 g, substrate 20 mmol, benzaldehyde 60 mmol, solvent 120 mL, 16 - 18 °C

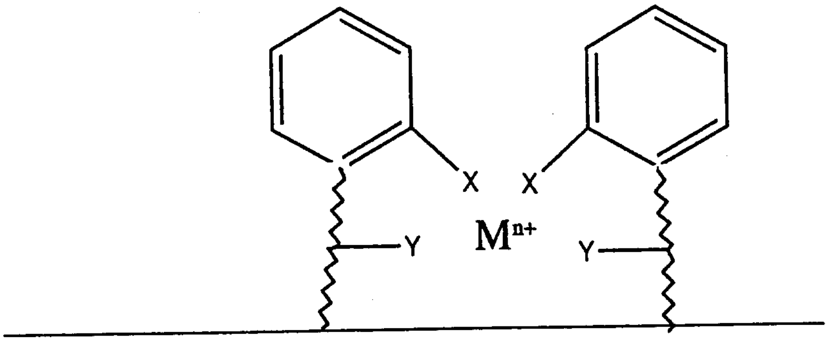
[b] dichloromethane

[c] 1,2-dichloroethane

[d] as confirmed by GC-MS



# NEW OXIDATION CATALYSTS



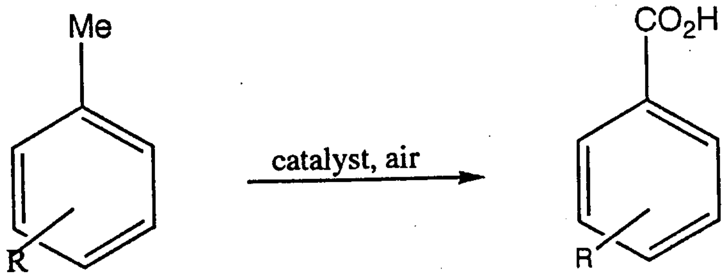
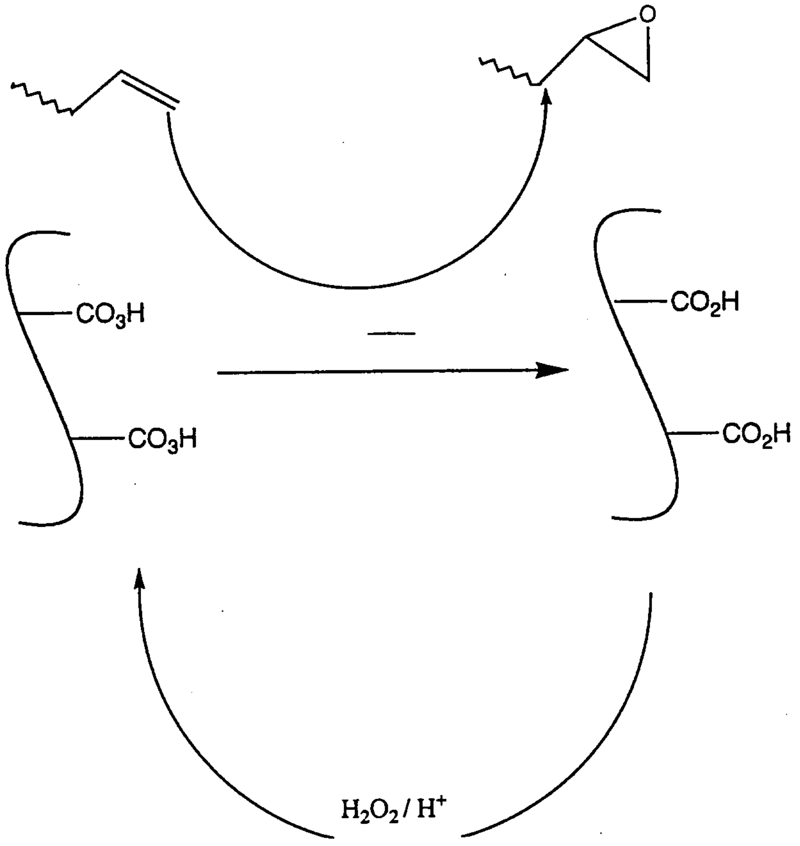


Table 1 Oxidation of alkylaromatics using the supported chromium catalyst[a]

| **Substrate** | **Temp. / °C** | **Product(s)** | **Isolated product yield / %** |
|---|---|---|---|
| ethylbenzene | 130 | acetophenone | 50 |
| *p*-xylene | 145 | *p*-toluic acid | 29 |
| | | terephthalic acid | 5 |
| *o*-xylene | 145 | *o*-toluic acid | 7 |
| *p*-chlorotoluene | 130 | *p*-chlorobenzoic acid | 12 |

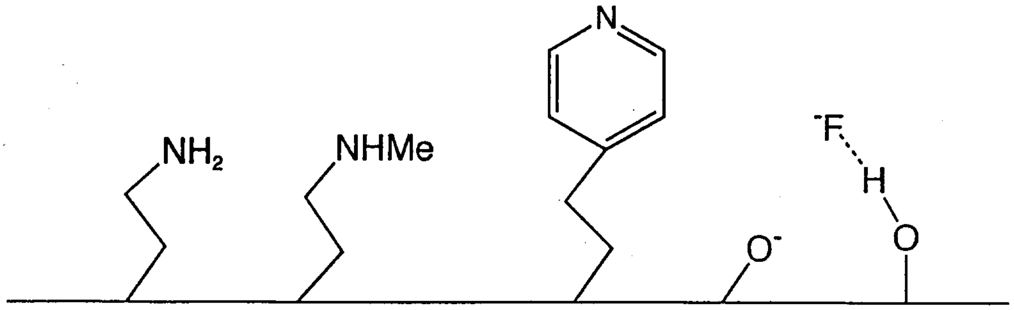
[a] Reactions were carried out using the *supported chromium catalyst* (1.5 g) in *neat substrate* (4.1 mol) with an *air* feed rate of 800 mL $\text{min}^{-1}$ and an agitation rate of 1500 rpm, for a period of 24 h.

# SUPPORTED PERACIDS

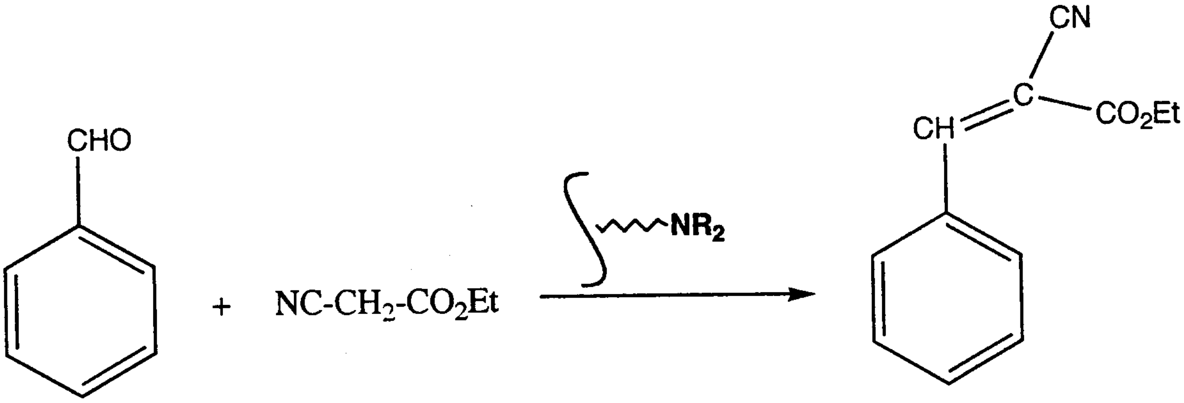


* structured and amorphous materials
* loadings comparable to soluble reagents
* high activities and oxygen utilisation
* improved stability and easier use

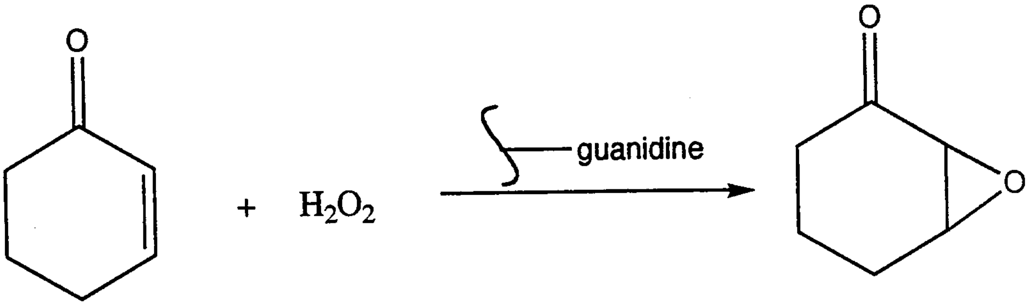
# SOLID BASES

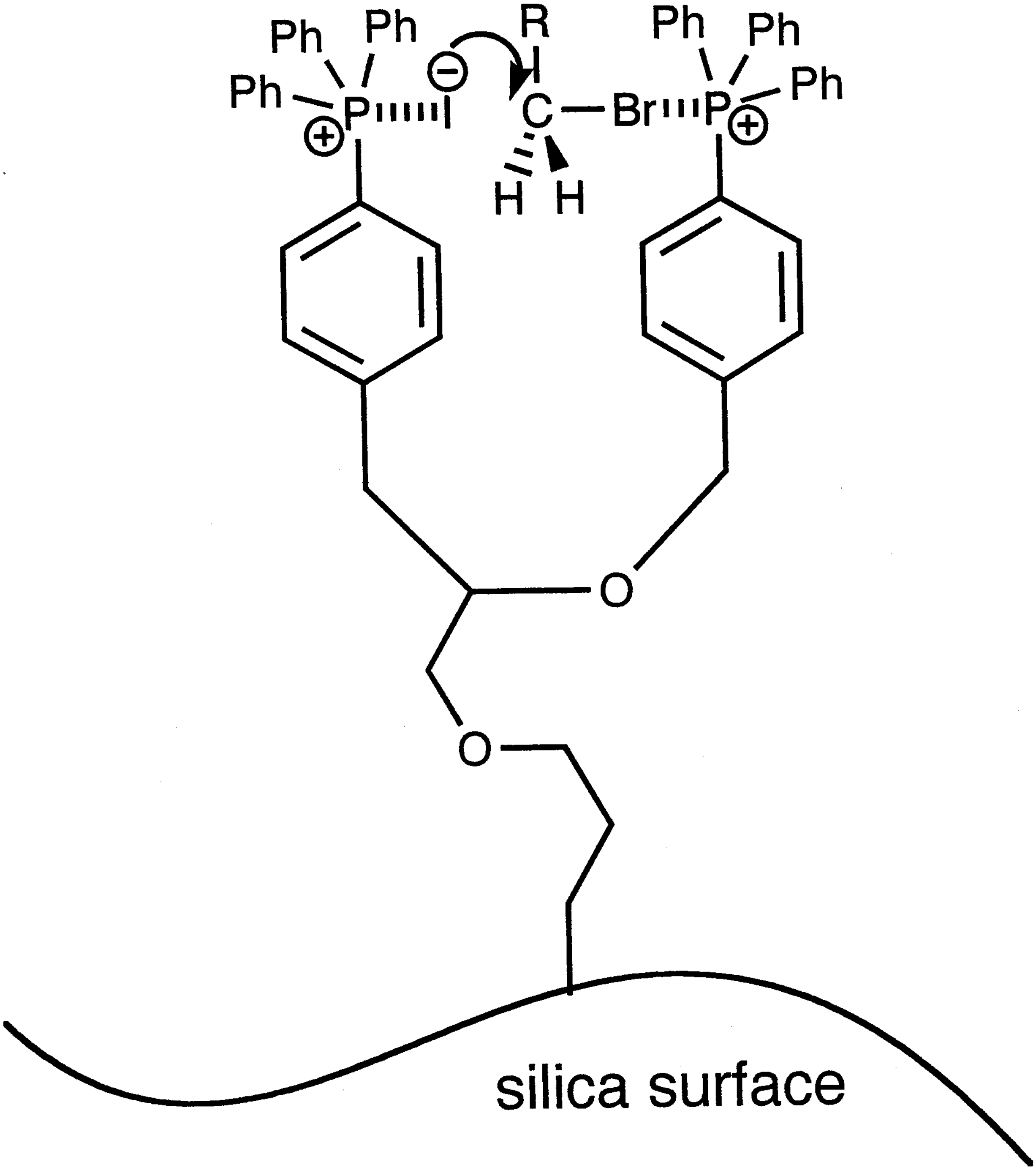


# Reactions catalysed by solid bases



$$\mathrm{RCOCH{=}CH_2} + \mathrm{RCH_2NO_2} \xrightarrow{\text{KF-alumina}} \mathrm{RCOCH_2CH_2CH(R)NO_2}$$




Ph
Ph
Ph
P
I
R
C
H
H
Br
P
Ph
Ph
Ph
O
O
silica surface

# *The York Green Chemistry Group*

Works at the frontiers of modern chemical resarch and seeks to:

- develop new chemical processes to replace environmentally unacceptable methods
- apply innovative catalyst technology to established industrial processes
- reduce waste through increased reagent and solvent efficiency
- design new environmentally friendly materials

In working towards these goals The York Green Chemistry Group:

- works closely with industry
- promotes the concepts of clean technology
- fosters interdisciplinary research
- develops international programmes of research

*Thanks to:* EPSRC, RAEng, Royal Society, EU, Industry............
and many researchers and collaborators