Clean Conversion of Waste Cooking Oil

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Shanghai

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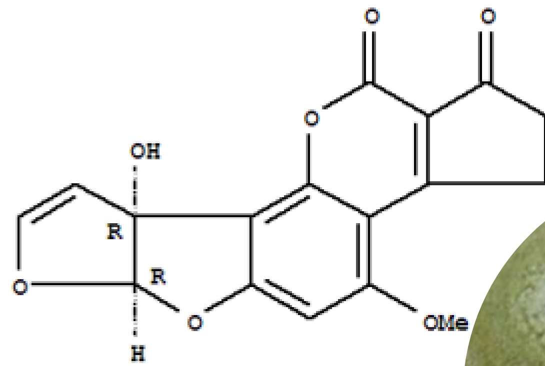
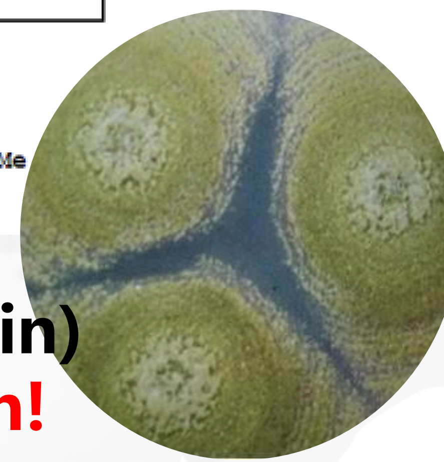
BACKGROUND


Fried oil
Palm oil Residue
Leftover food oil
Waste Oils
Acidized oil
Drainage Oil

BACKGROUND

10 Millions tons per year





AFT(aflatoxin)

Carcinogen!

Great threaten to the food safety if returning to our dining table !

HOW TO UTILIZE THEM

Food and environment safety

10 million tons of waste oils

Green Conversion

Biodiesel (BD)
Bio-Jet fuel

Reduce CO_2 emission

BIODIESEL 10 million tons
Or JET-FUEL 6 million tons
50 billion CNY

BIO-plasticizer
3 million tons
21 billion CNY

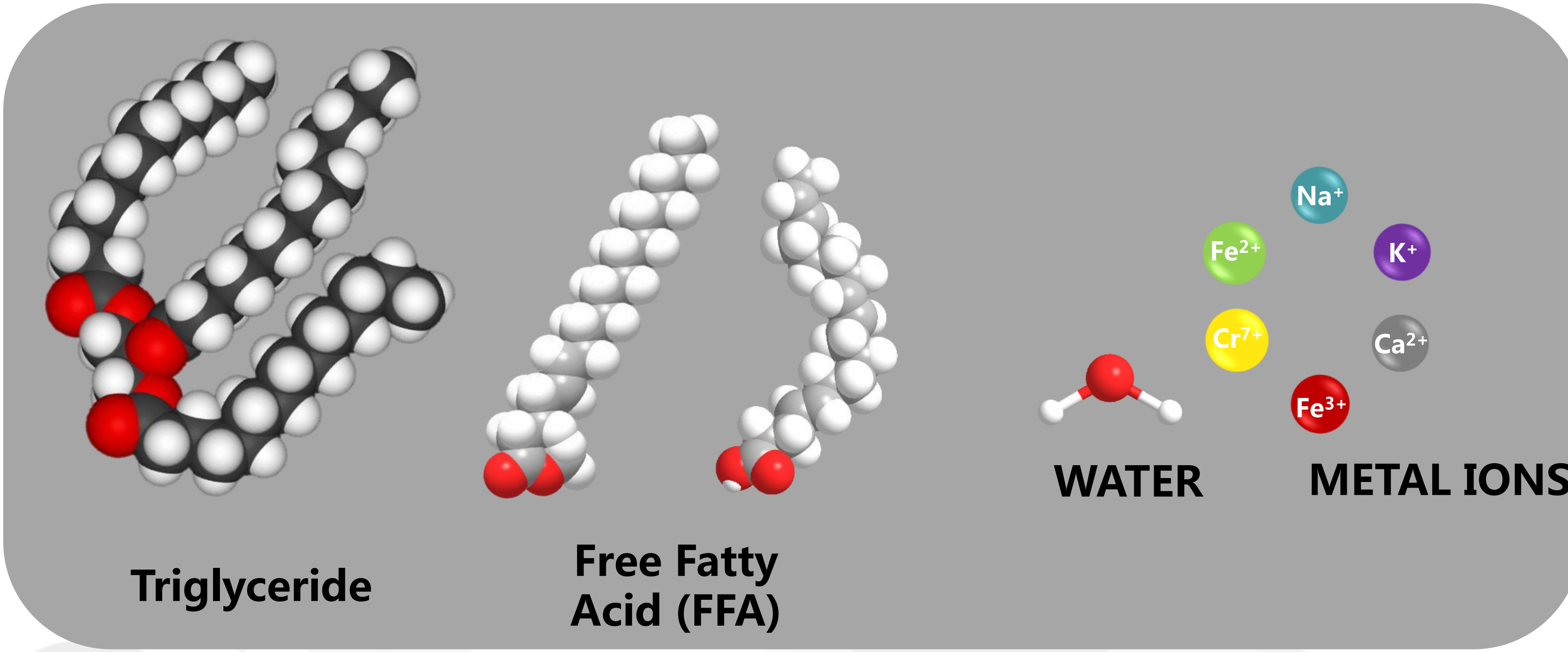
147.4
BILLION
CNY

60 million
tons
cooking
wastes
30.8 billion
CNY

BIO-surfactant
1.9 million tons
45.6 billion CNY

Contents

Composition of waste cooking oil



Main components

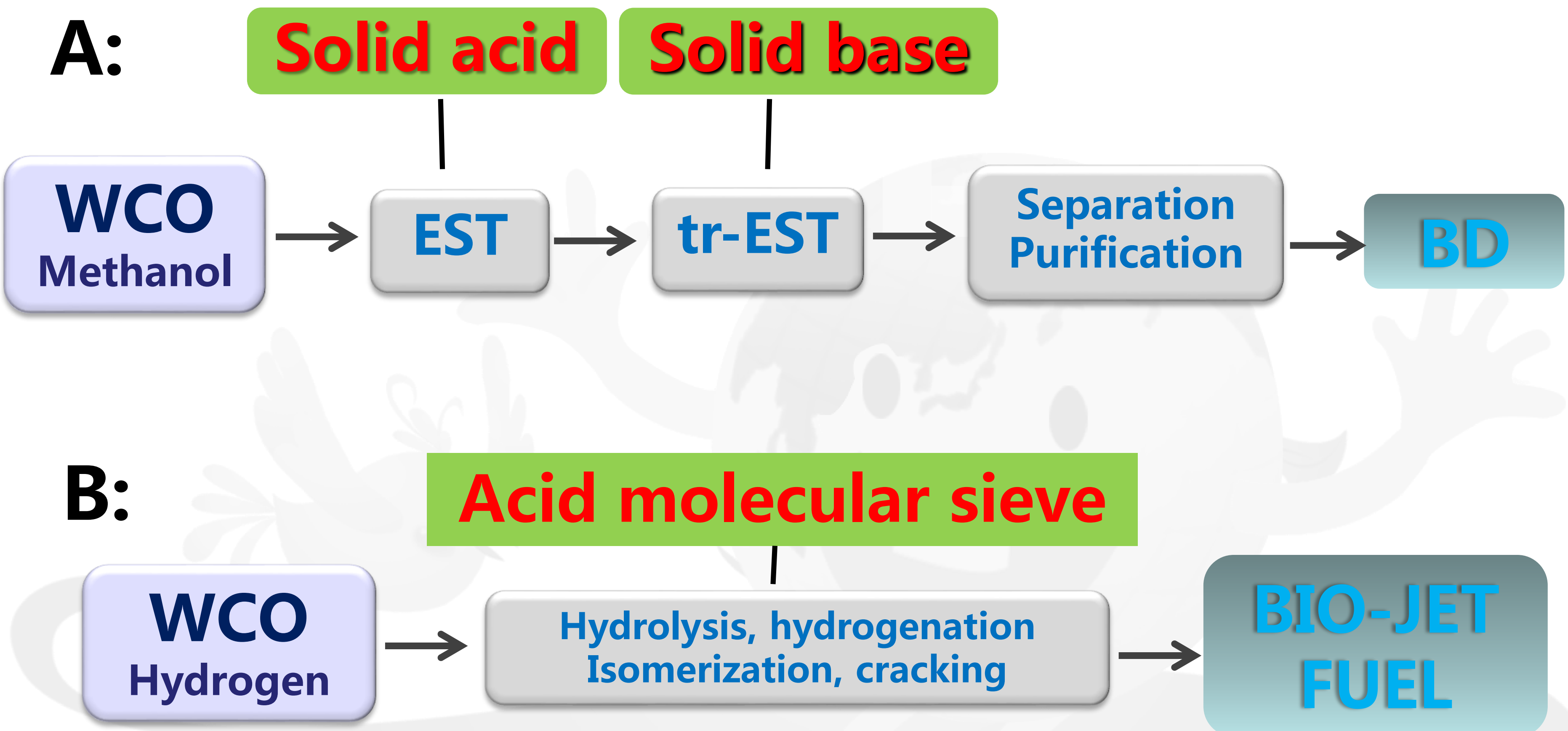
Impurities

Special properties of wastes cooking oil

- Large molecular size，4.4nm
- High viscosity
- Not polar
- Complex composition of FFA

- Varied carbon chain length (C4-C22)
- FFA includes Saturated Fatty Acid，SFA and Unsaturated fatty acid， USAF.
- USFA includes monoenoic acid (Oleic acid)、dienoic acid (Linoleic acid)、trienic acid (Linolenic acid) ，etc. Also including FFAs with double bonds, isomers.

TWO CLEAN PROCESSES

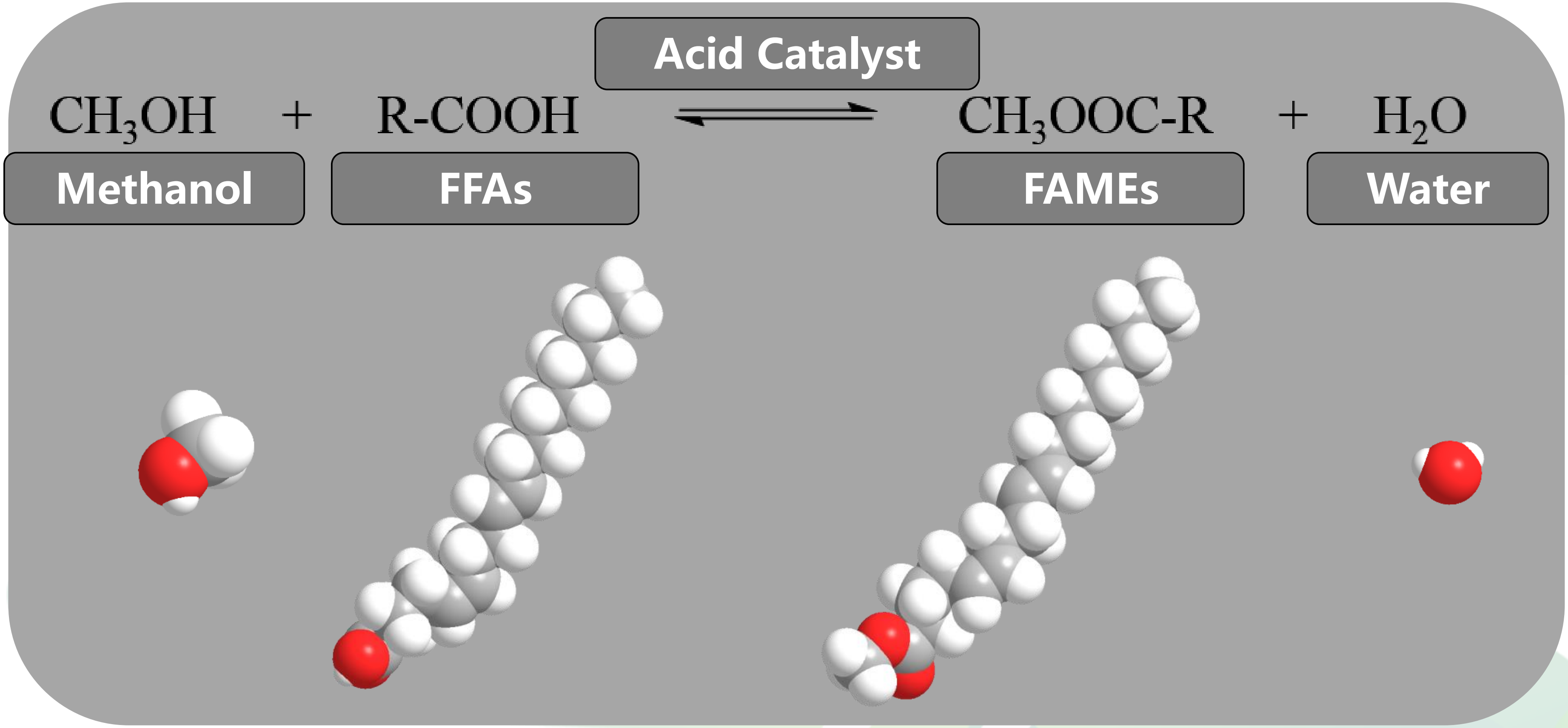


Core technologies

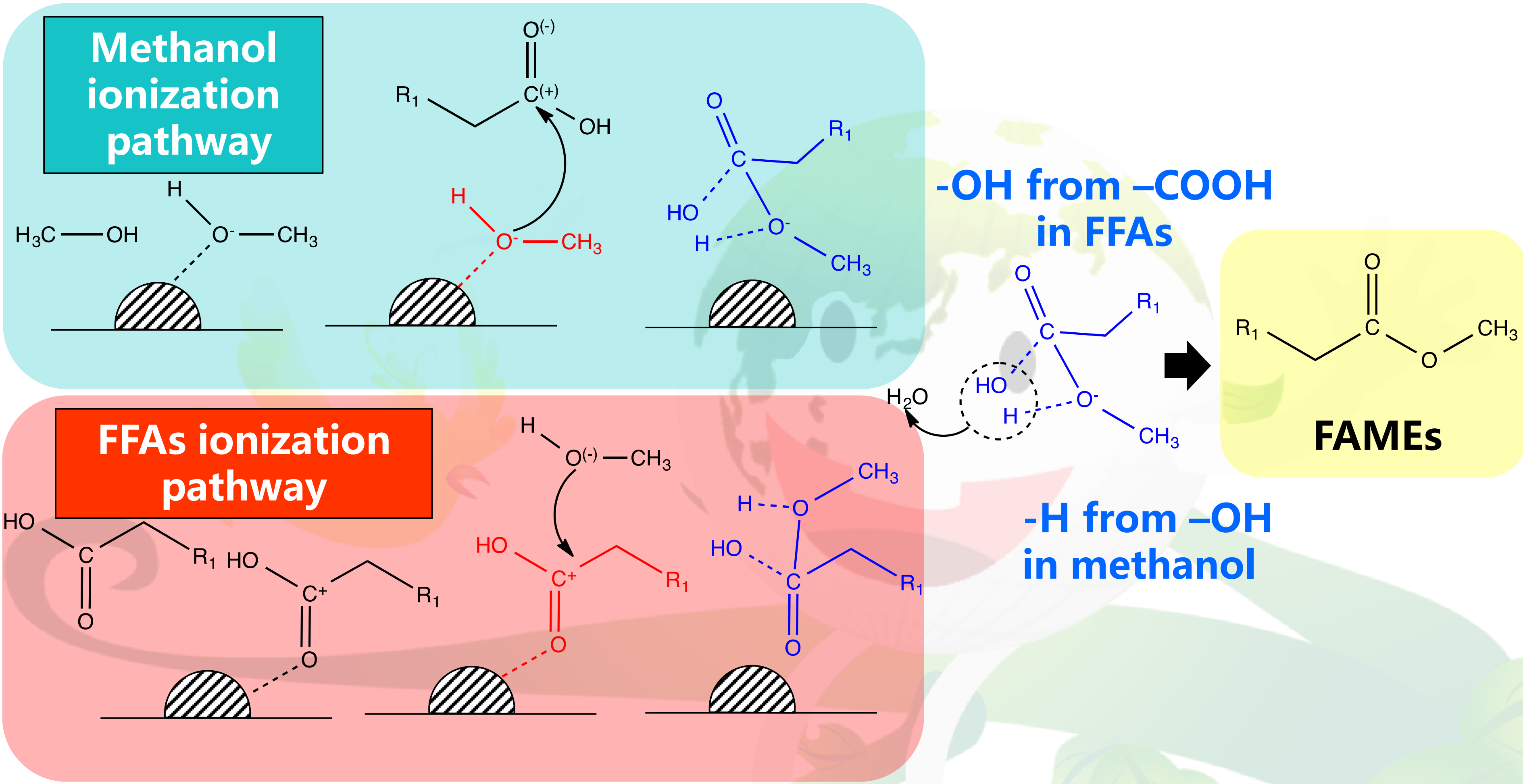
1. SOLID ACID
2. SOLID BASE
3. ACID MOLECULAR SIEVE

Contents

Solid acid catalyzed esterification reaction



Mechanism of solid acid catalyzed esterification reaction

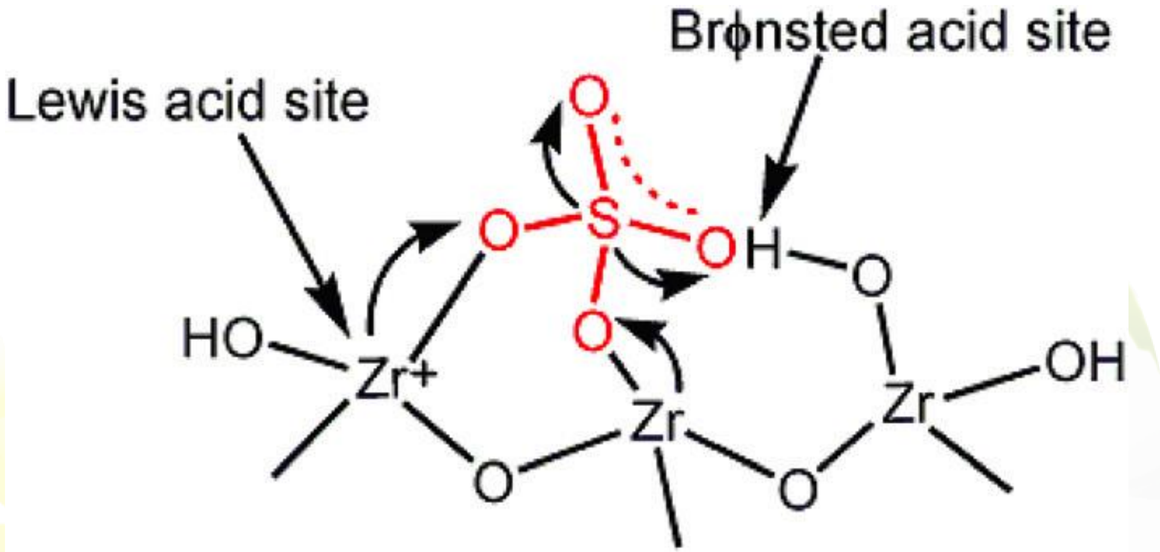


Solid acid category

(1) Solid superb acid	H_0<11.9	SO_4^{2-}/M_xO_y	L/B
(2) Acid molecular sieve	Ordered Structure	M@Si/Al	L/B
(3) Carbon based solid acid	Biomass based	cH_2SO_4 sulfonation	B/L
(4) Polyoxometalates, POMs	Condensation of metal oxyacid	HPW series Slightly soluble in polar solution	B
(5) Cation exchange resin	Polymer network	cH_2SO_4 sulfonation	B

(1) Solid superb acid (SO_4^{2-}/M_xO_y)

Hammett acidity indicator, $H_0<-11.9$, stronger than 100% cH_2SO_4



- The L-acid is site formed by the coordination adsorption of SO_4^{2-} on the metal oxide.
- The B-acid site is formed in the drying and calcination of the catalyst as the structural water detached from the surface.

✓ SO_4^{2-}/ZrO_2

170℃，Methanol/acid20:1，catalyst loading=3 wt. %，1h，86%

✓ Fe_2O_3-MnO-SO_4^{2-}/ZrO_2

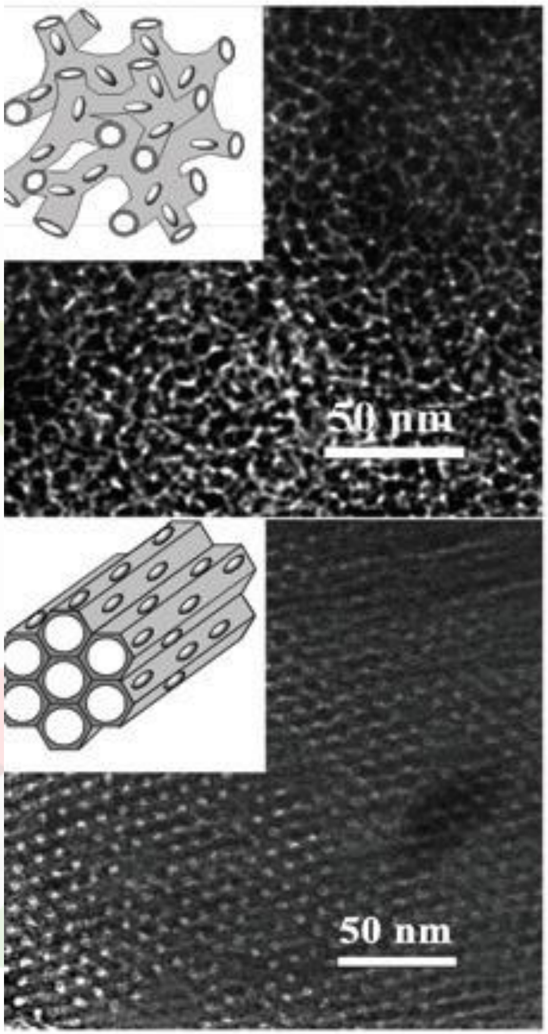
180℃，Methanol/oil20:1，catalyst loading=4 wt. %，4h，96.5%，After 7-times reuse-85%

✓ $HClSO_3$-ZrO_2

100℃，Methanol/acid8:1，3 wt. %，12h，100%

(2) Acid molecular sieve

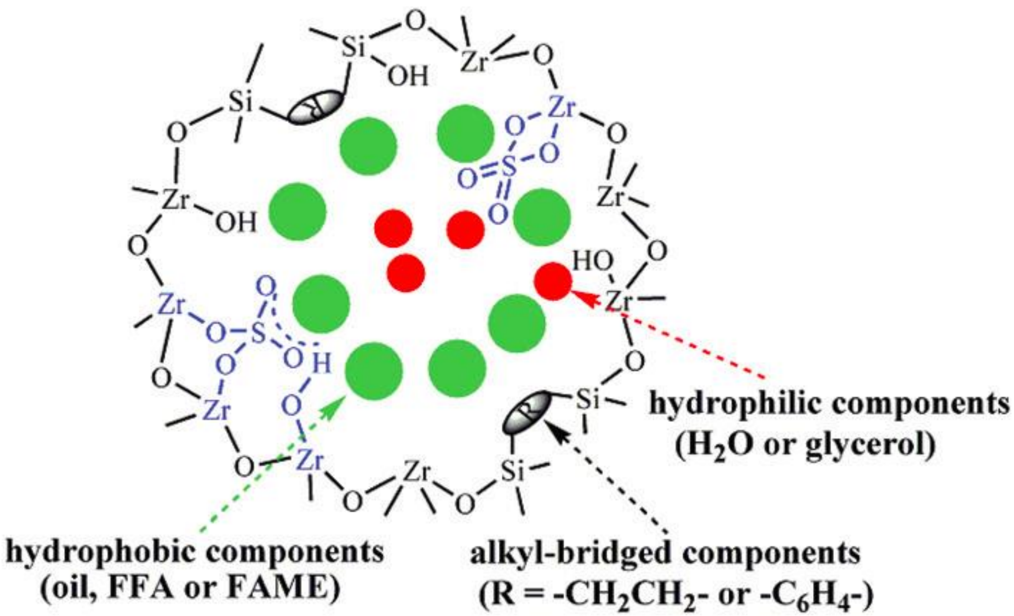
High surface area ($1000 m^2 g^{-1}$) , ordered structure , stable structure



Acid sites can be formed :

- Structural Si/Al (L)
- Covalent loaded by other acids (solid superb acid , POMs , Ionic liquid, etc.)
- $-SO_3H$ covalent carried (by cH_2SO_4, $HClSO_3$)

SO_4^{2-}/Zr/Si-MS



65℃, 1 atm. , methanol/oil=90:1 , 24h , 5wt. % , 90%

SO_3H@SBA-15

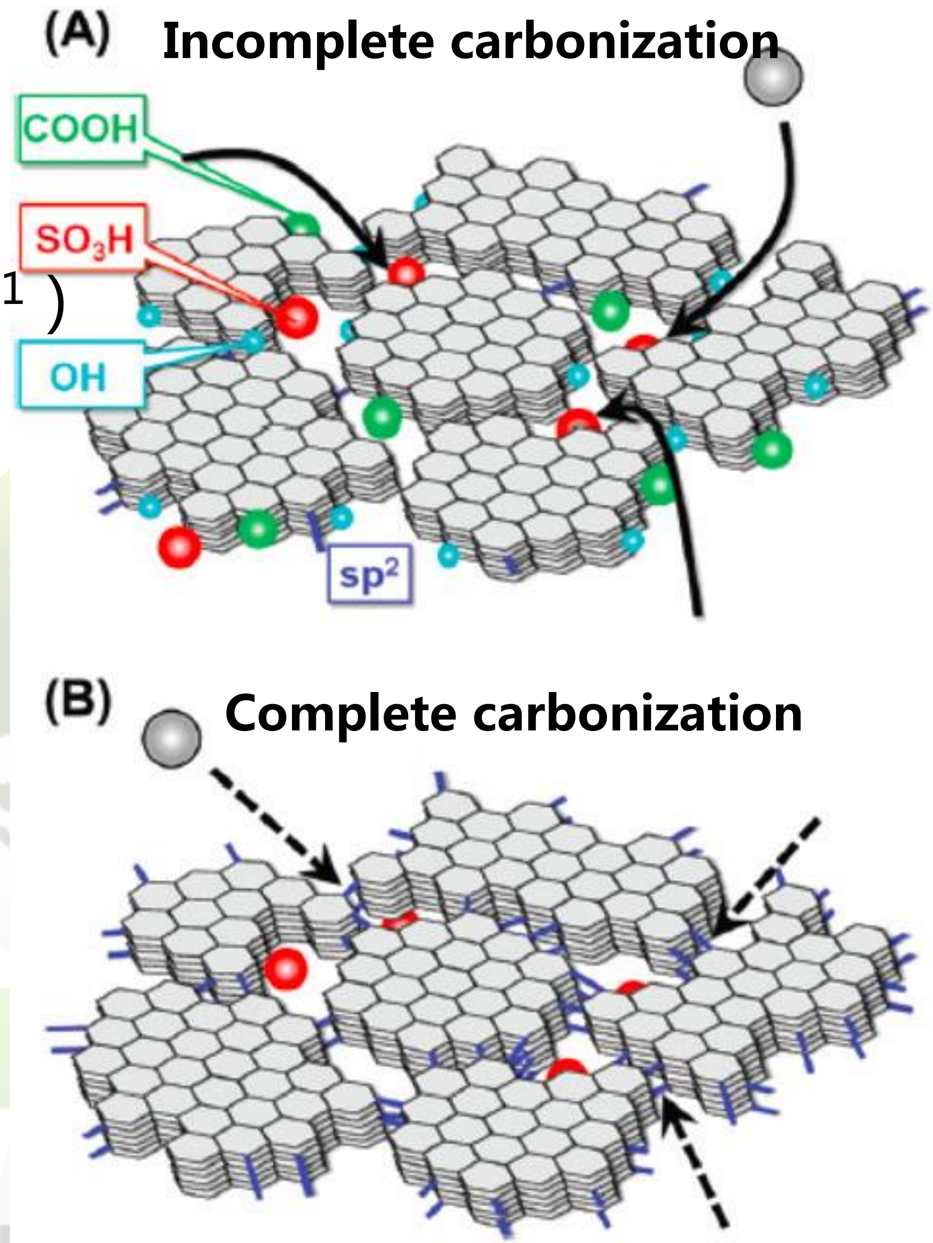
150℃ , methanol/oil=24:1 , 15 wt. % , continuous reaction 75h , 78%

(3) Carbon based solid acid

- High surface area ($500 m^2 g^{-1}$)
- Based on biomass, greener synthesis procedure

Acid sites can be formed :

- -COOH
- -OH
- $-SO_3H$



✓ **Incomplete carbonized cassava residue**

90℃，methanol/oil=18:1，

catalyst loading=5 wt. %，

94%，5-times-reuse

✓ **Incomplete pyrolysis husk**

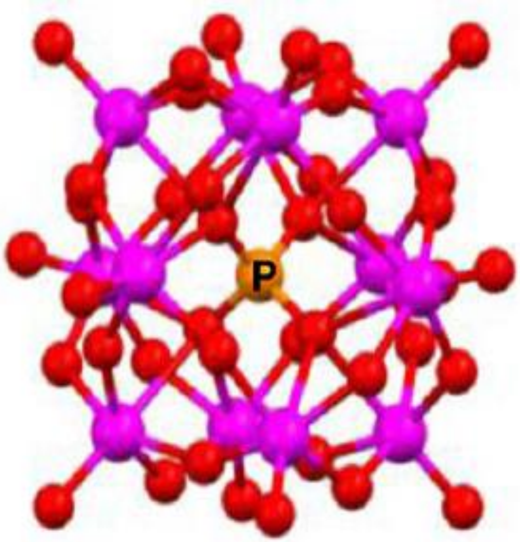
110℃，methanol/oil=20:1，

catalyst loading=5 wt. %，

98%，5-times-reuse

（4） Polyoxometalates，POMs

POM is a kind of oxyacid that is formed by **heteroatom (such as P, Si, Fe, Co, etc.) and multi-atom (such as Mo, W, V, Nb, Ta)** with certain structure through oxygen atom coordination.



Water soluble
Slightly soluble in non-polar solution

Acid sites can be formed：

① H+ from POM salts

② Hydrolysis of negative group in POMs preparation

$$PW_{12}O_{40}^{3-}+H_2O \rightarrow PW_{12}O_{39}^{2-}+WO_4^{2-}+6H^+$$

③ Clathrate water（with metal core）hydrolysis

$$Ni(H_2O)m^{2+} \rightarrow Ni(H_2O)_{m-1}(OH)^{+}+H^+$$

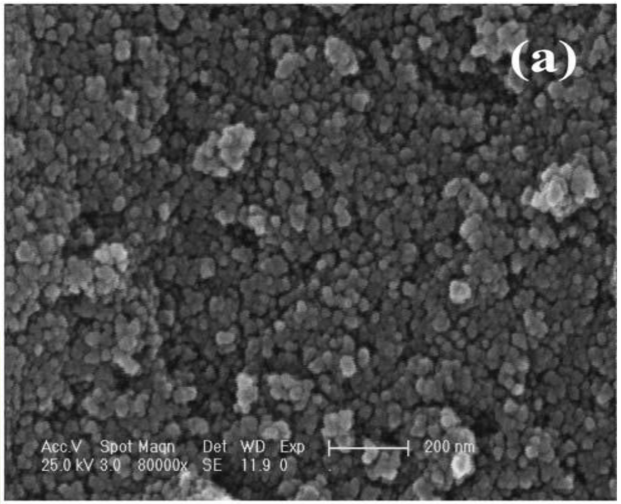
④ L-acid sites from cationic group

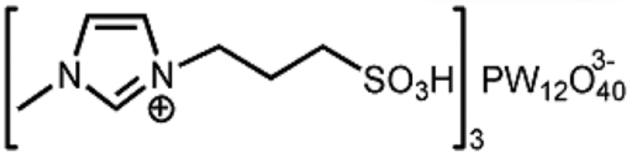
⑤ Reduction of metal ions（with H_2）

$$Ag^{+}+1/2H_2 \rightarrow Ag+H^+$$

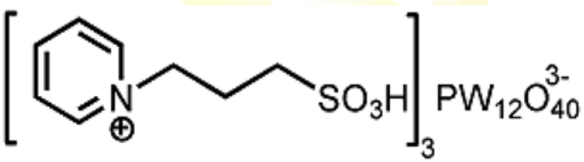
✓ SiO_2-HPA

65℃ , methanol/acid=8:1 , 8.2 wt. % , 2h , 90.4% , 5-times-reuse

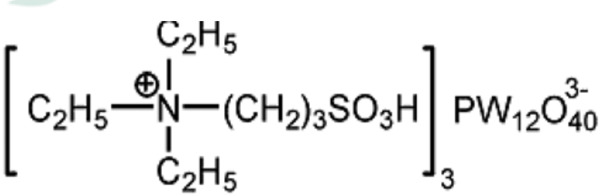




$[MIMPS]_3PW_{12}O_{40}$



$[PyPS]_3PW_{12}O_{40}$



$[TEAPS]_3PW_{12}O_{40}$

✓ $[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$

65℃ , methanol/acid=13:1 , 30 wt. % , 0.8h , 96% , 6-times-reuse

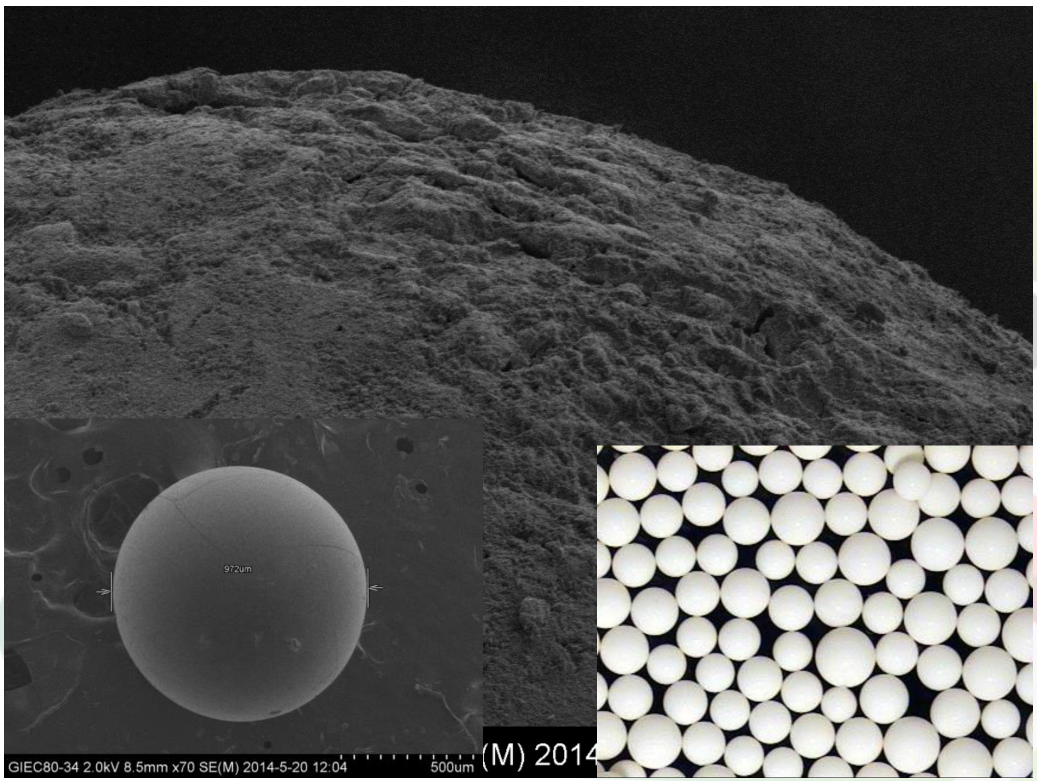
Limitations of the above 4 kinds of catalysts

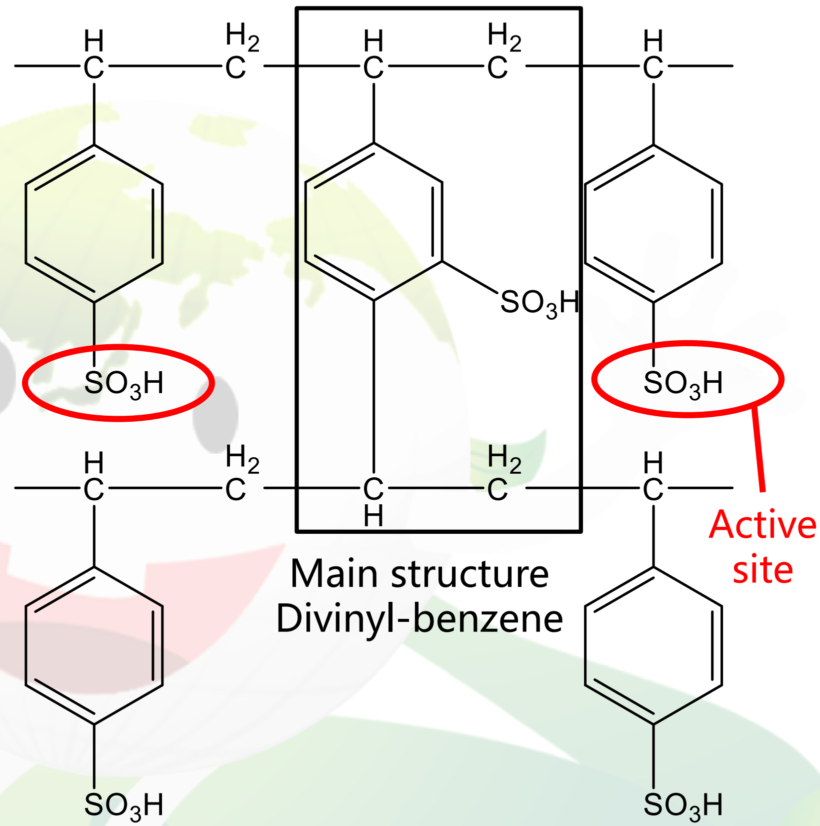
- x **Limited activity**
- x **Severe reaction condition**
- x **Short service life**
- x **In powder form, hard to be recycled**
- x **High preparation cost**

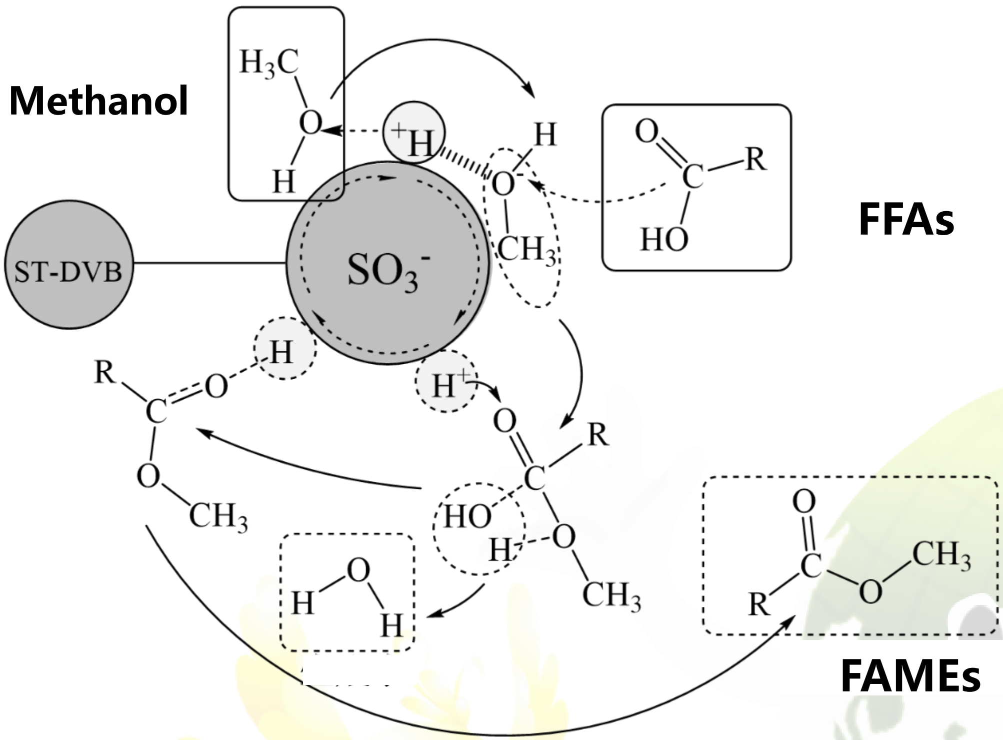
Scale up
Application
unable

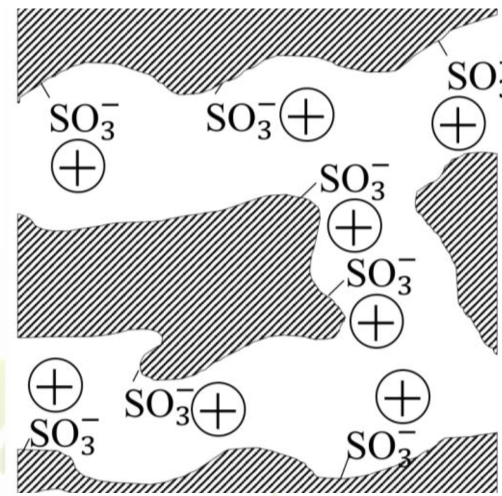
(5) Cation exchange resin

Network structure , large pore size , -SO_3H acid sites



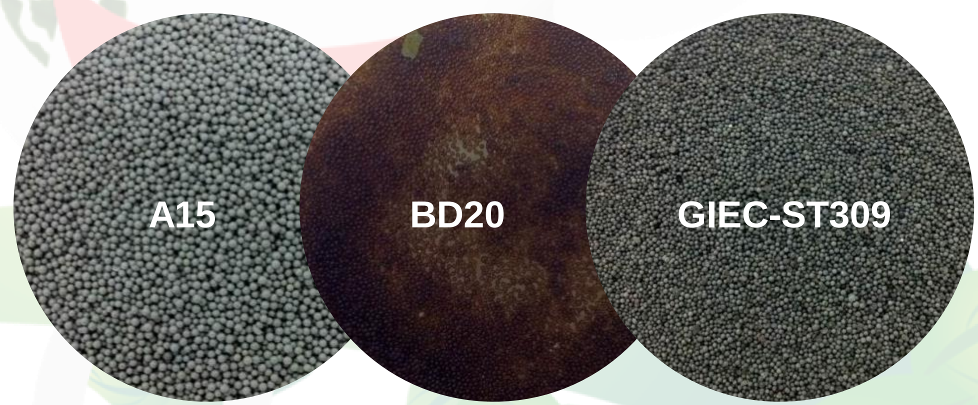


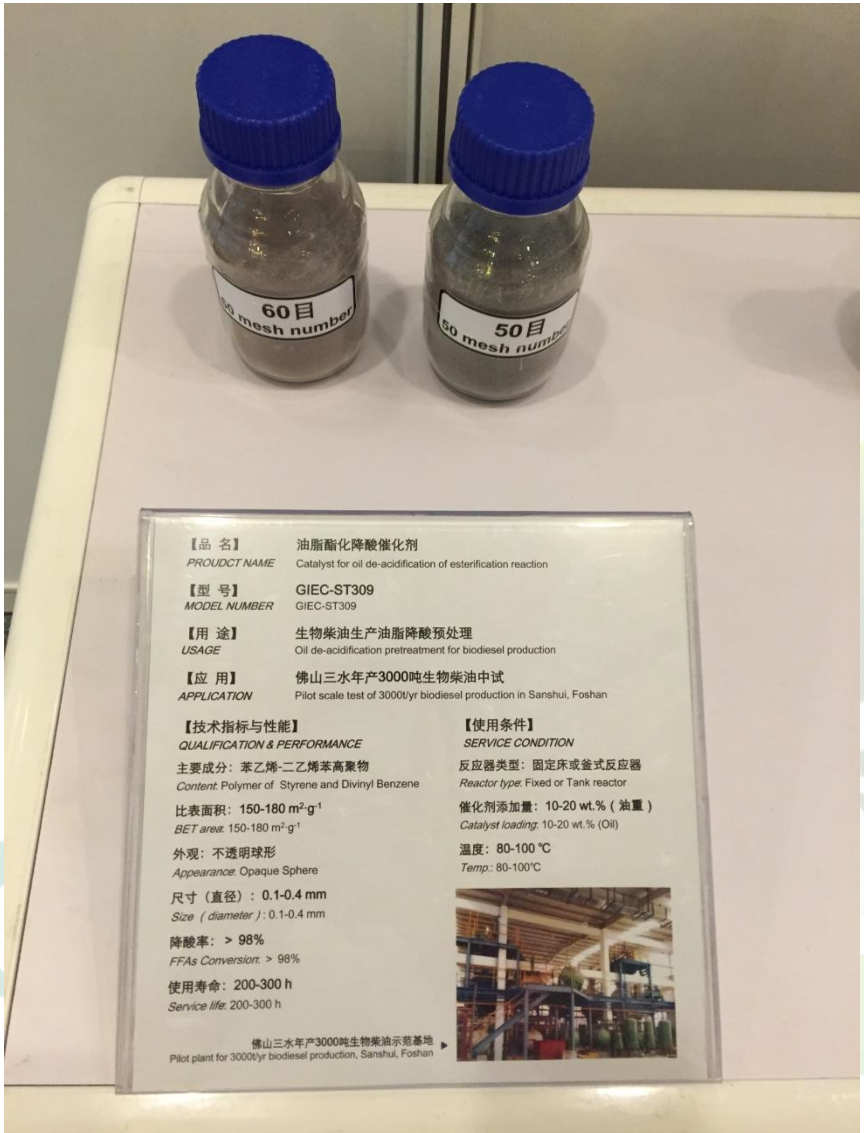




Macroporous : Amberlyst 15, GIEC-ST309

Gel-type : BD20





GIEC-ST309

$150\text{-}180\ m^2\ g^{-1}$

100℃ , 10 wt.%

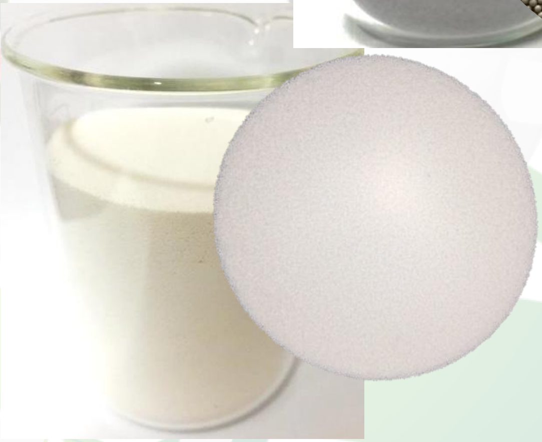
Methanol/acid=18:1

Higher than 98%

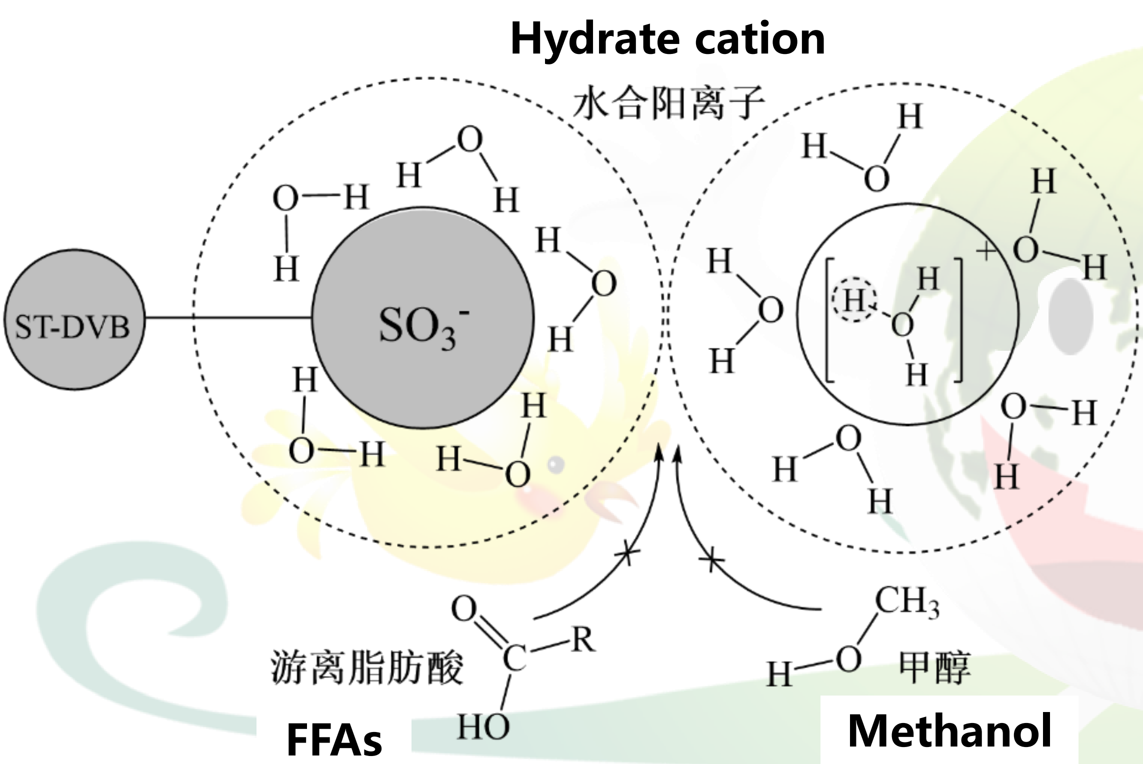
Service life 200-300h

CATION EXCHANGE RESIN
A promising catalyst for biodiesel production

- □Stable structure，
- □Highly active，long service life
- □Easy-recycled-form (0.3-0.4 mm sphere)
- □Cost-efficient



Cation exchange resin-Problem to be solved

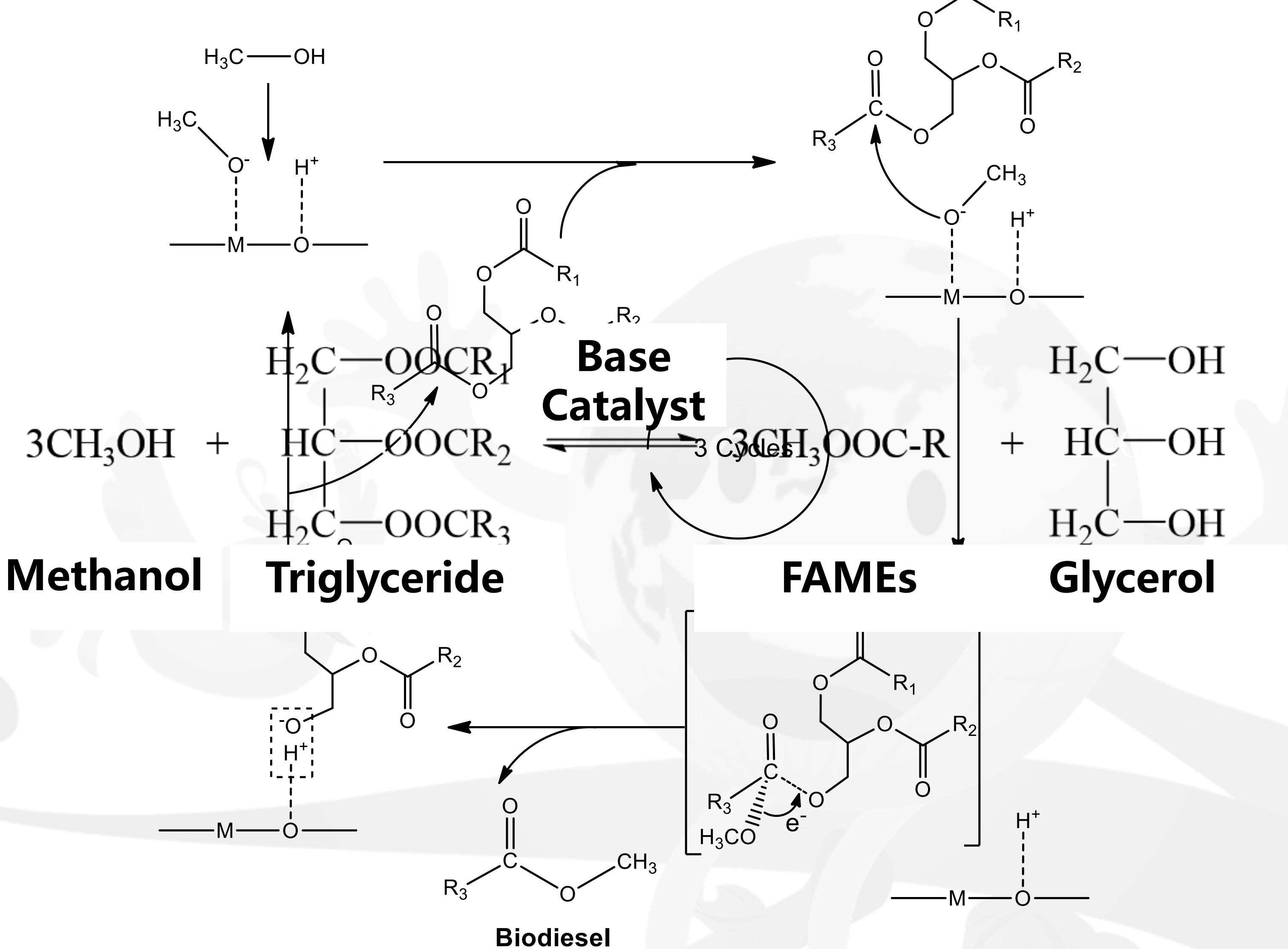


WATER ADSORPTION

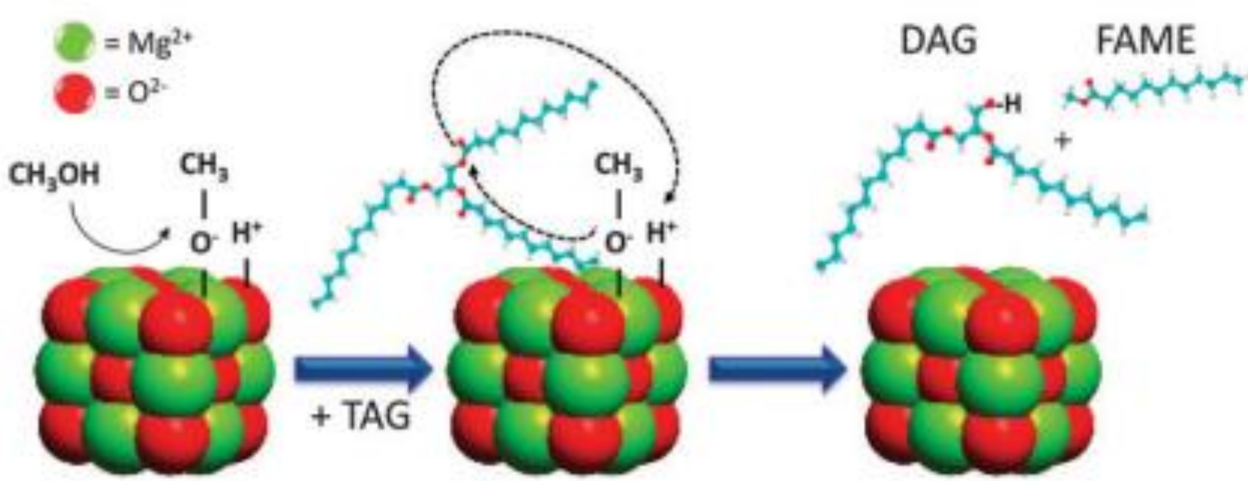
$-SO_3H$ is hydrophilic enough to absorb generated H_2O to form hydrate cation that prevent the substrates from approaching the active cites

Contents

Trans-esterification



Mechanism of solid base catalyzed transesterification reaction



(a)Methanol splits into $–CH_3O^-$ and $-H^+$ on surface of -M-O-;

(b)$-CH_3O^-$ then attacks the –COOH to form an unstable intermediate;

(c)The intermediate then decomposes into a FAME and diglyceride anion;

(d) Diglyceride anion then reacts with the H+ from methanol to form a diglyceride to finish the first cycle of transesterification reaction.

Category of solid base

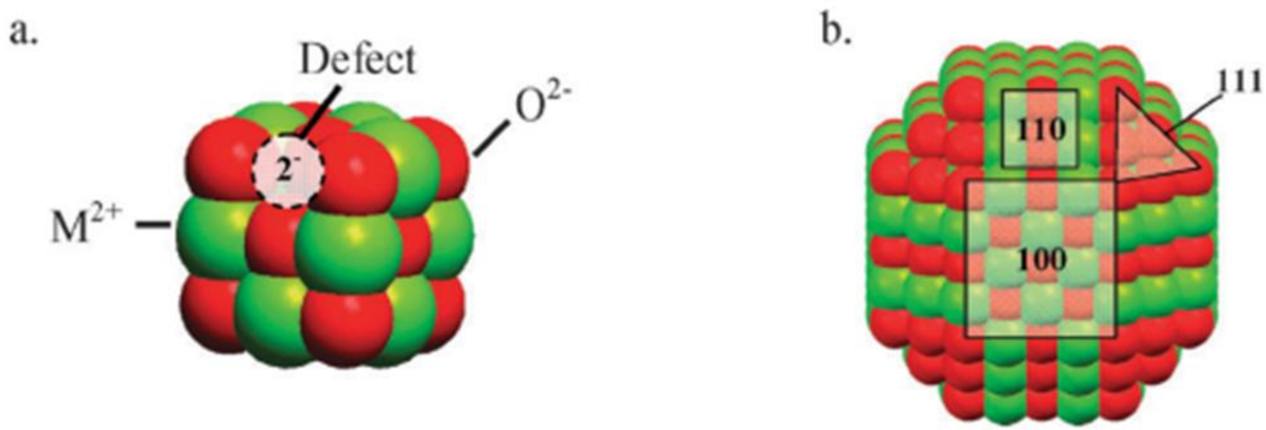
(1) alkaline metal/alkaline earth metal oxides

(2) alkaline metal oxides loaded transition metal

(3) hydrotalcite

(4) base molecular sieve

(1) Alkaline metal/alkaline earth metal oxides



- **The base sites can be formed:**

(a) Cation defect;

(b) Crystal corner/ edge/ defect of low coordination atoms and high Miller-index surface turn to have stronger basicity;

Alkaline metal/alkaline earth metal oxides

Metal oxides	Substrate Oil	Temp. /℃	Time/h	Methanol to Oil (mol)	FAME yield (%wt)
CaO	Vegetable oil	75	0.75	4:1	>80%
CaO·ZnO (Ca/Zn=0.25)	Palm oil	60	1	30:1	94%
Li/Na/K·CaO Li·MgO	Rapeseed oil	60	3	6:1	90%

- Compared to single metal oxide, co-doping/mixed metal oxides shows higher activity

(2) Alkaline metal oxides loaded transition metal

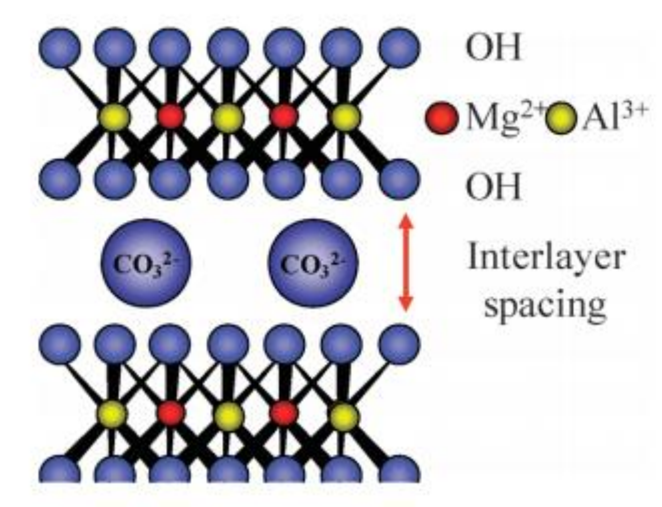
Metal oxides	Substrate Oil	Temp. /℃	Time/h	Methanol to Oil (mol)	FAME yield (%wt)
$NaO\cdot ZrO_2$	Soybean Oil	65	3	30:1	98%
TiO_2	Soybean Oil	65	8	40:1	>97%

◆Transition metal can catalyze EST and t-EST reaction simultaneously.

(3) Hydrotalcite

- **Hydrotalcite or**

hydrotalcite lamellar double metal hydroxides:



$[M^{2+}_{(1-x)}M^{3+}\ x(OH)_2]^{x+}\ (A_{x/n})^{n-}\bullet yH_2O$

where , M^{2+} = Mg^{2+} , Mn^{2+} , Zn^{2+} , etc. ；

M^{3+} = Al^{3+} , Fe^{3+} , Cr^{3+} , etc. ；

A = CO_3^{2-} , Cl^- , NO_3^- , OH^- , etc.。

Category of hydrotalcite

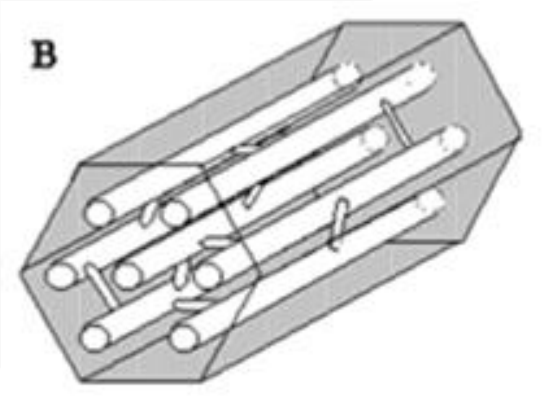
Hydrotalcites	Substrate Oil	Temp ./℃	Time/h	Methanol to Oil (mol)	FAME yield (%wt)
Mg–Al–CO_3 hydrotalcite catalyst (HT2)	Cotton seeds oil	200	3	6：1	99%
$[Al_2Li(OH)_6]_2CO_3 \cdot nH_2O$	Soybean oil	60	2	15：1	83%
CaO-La_2O_3 catalyst	Rapeseed oil	58	1	20：1	94.3%

- **Highly active and tolerable in high water or FFAs content**
- **Metal ions leaching**

(4) Base molecular sieve

Catalysts	Substrate Oil	Temp ./℃	Time/h	Catalyst loading (%wt.)	FAME yield (%wt.)
MgO/MCM-41	Vegetable oil	220	5	2	68%
MgO/Kit-6					82%
MgO/SBA-15					96%
K/SBA-15	Palm oil	70	5	4	93%

- **With larger pore size, thicker wall, higher thermal stability, SBA-15 is more suitable solid base carrier compared to MCM-41.**

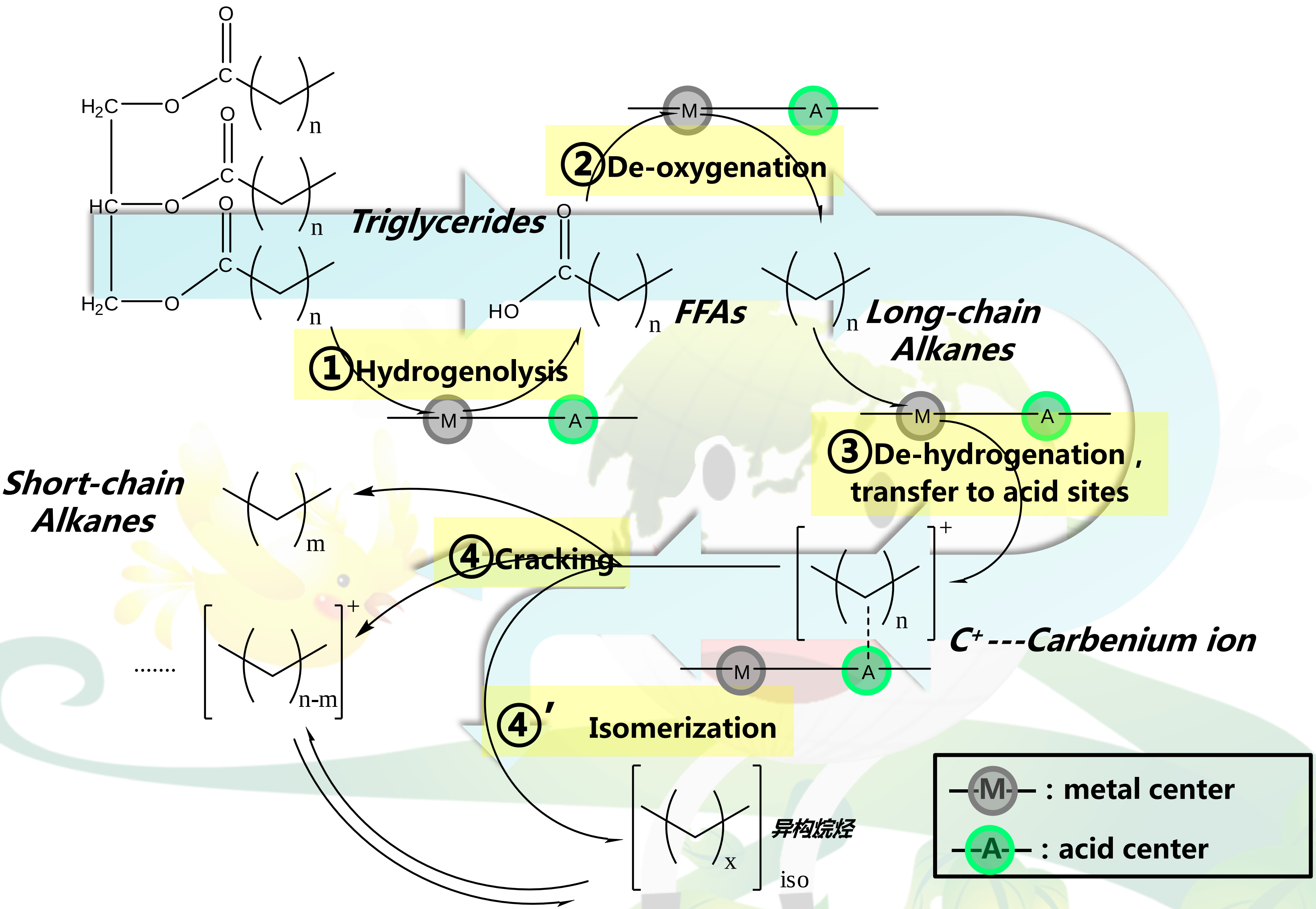


Problems to be solved for solid-base

- **Active sites of alkaline metal oxides (such as CaO) can be poisoned by CO_2, H_2O in air easily.**
- **The metal ions are likely to run off into the liquid reaction system, then the catalyst service life is shorten.**

Contents

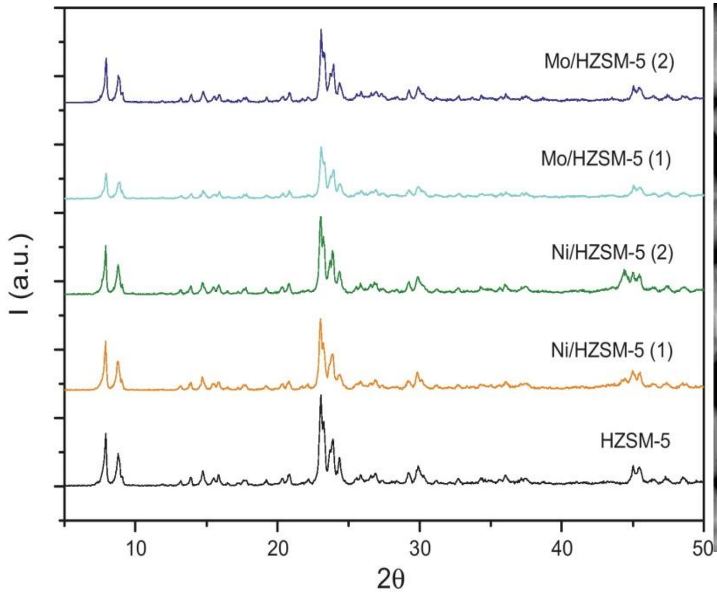
MS catalyzed oil to alkanes mechanism

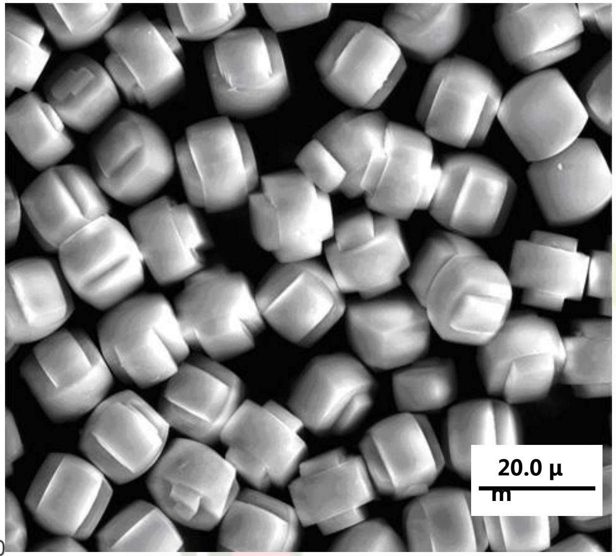


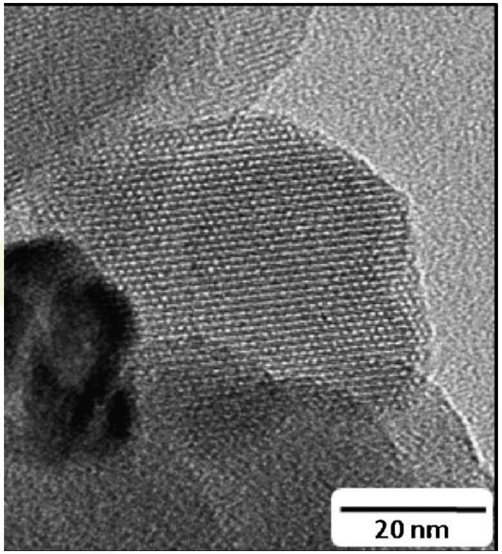
- **Microporous MS (d < 2 nm)**
  - **HZSM-5**
  - **SAPO-11**
  - **Hβ-MS**
- **Mesoporous MS (d: 2~50 nm)**
  - **Al-MCM-41**
  - **Al-SBA-15**
- **Hierarchical MS (d: 0~50 nm)**

➢ HZSM-5

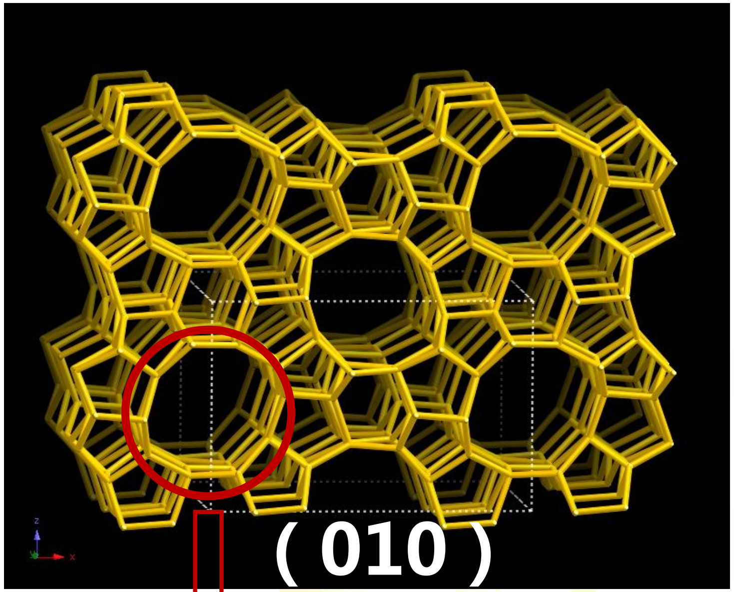
MFI framework





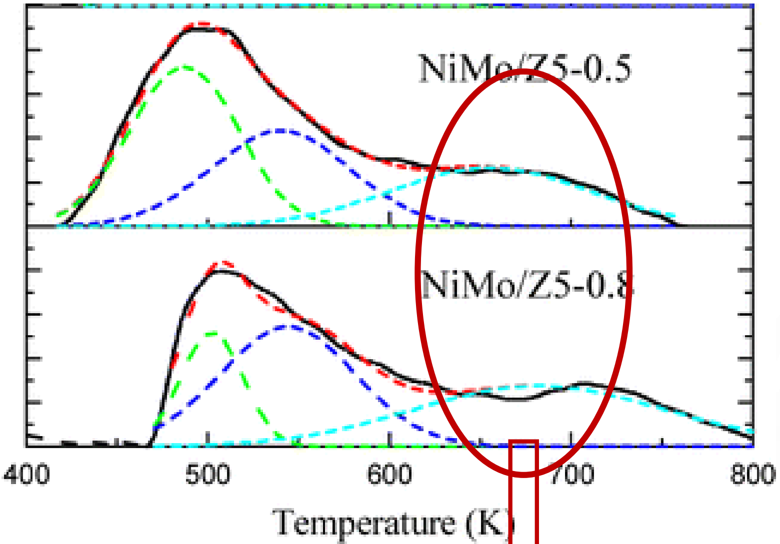


XRD **SEM** **TEM**



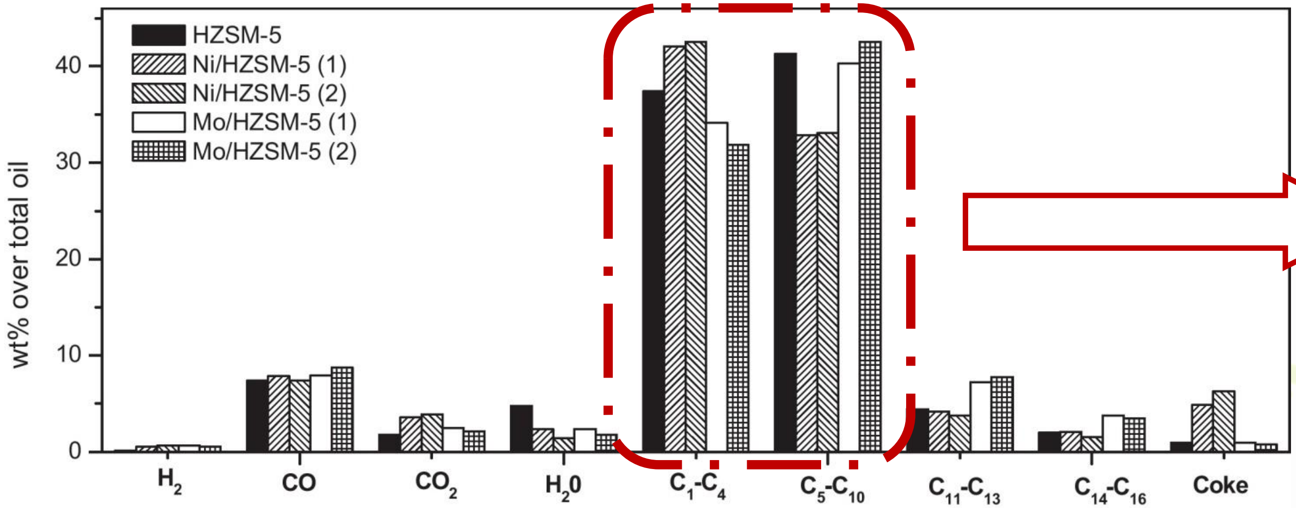
Pore size 0.56*0.53 nm

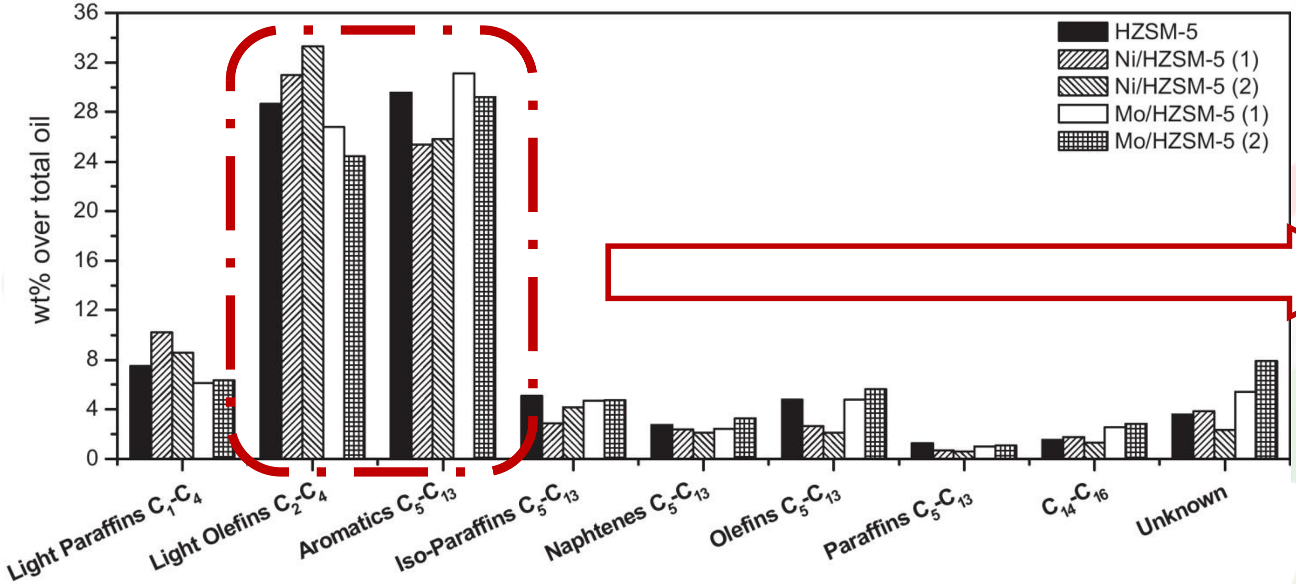
NH$_3$-TPD



Over-amount strong acid sites

➤ HZSM-5: Product Distribution





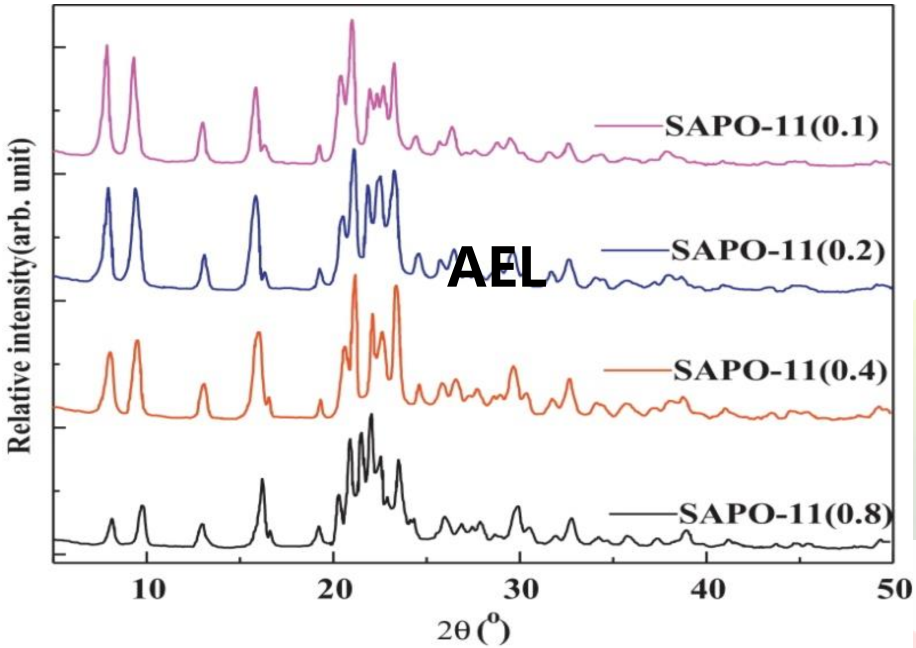
Gas: C1-C4

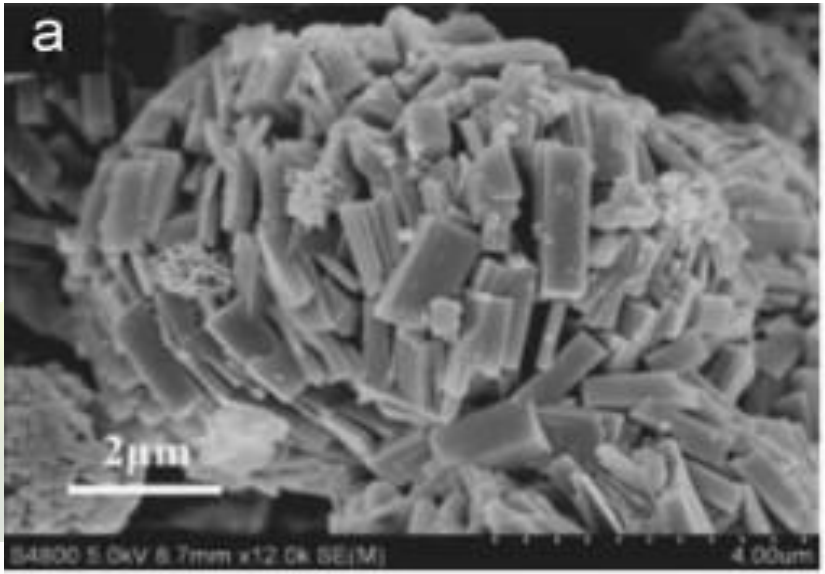
Liquid: C5-C10

C2-C4 Olefins

C5-C13 Arenes

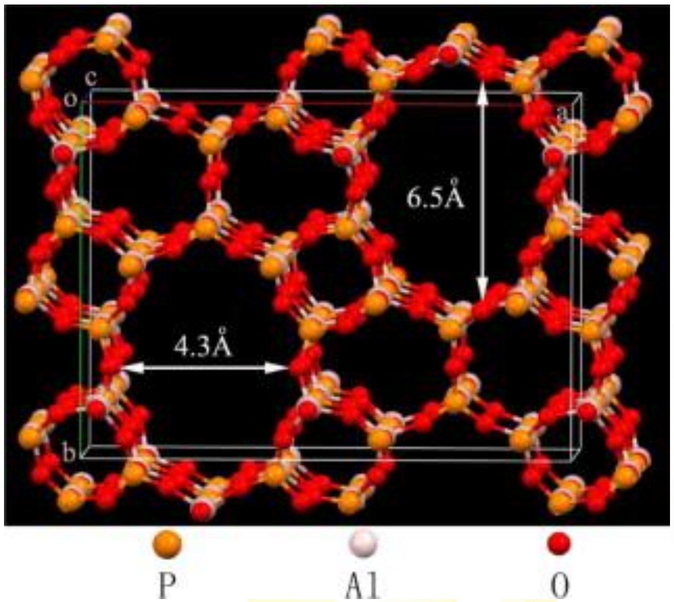
➢ SAPO-11

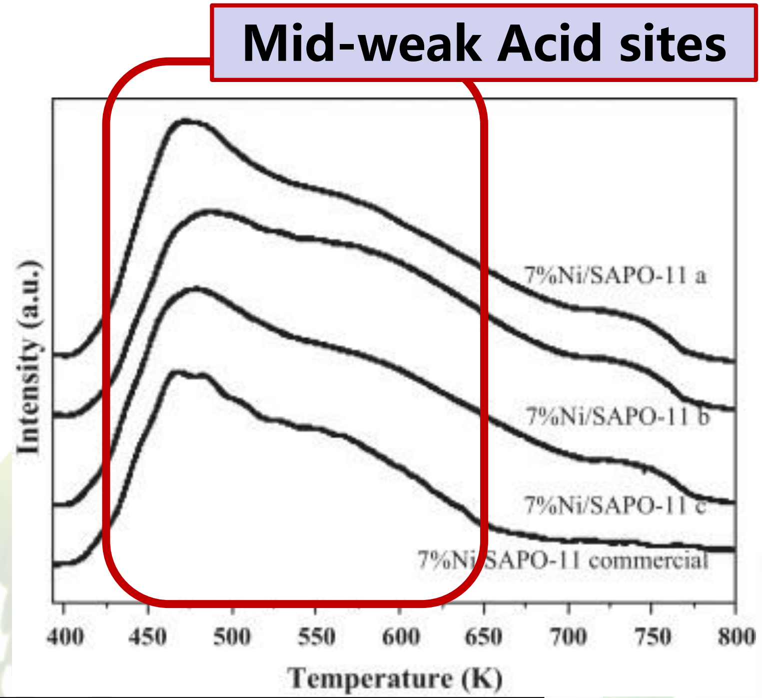




XRD **SEM**

Highly crystallized AEL structure

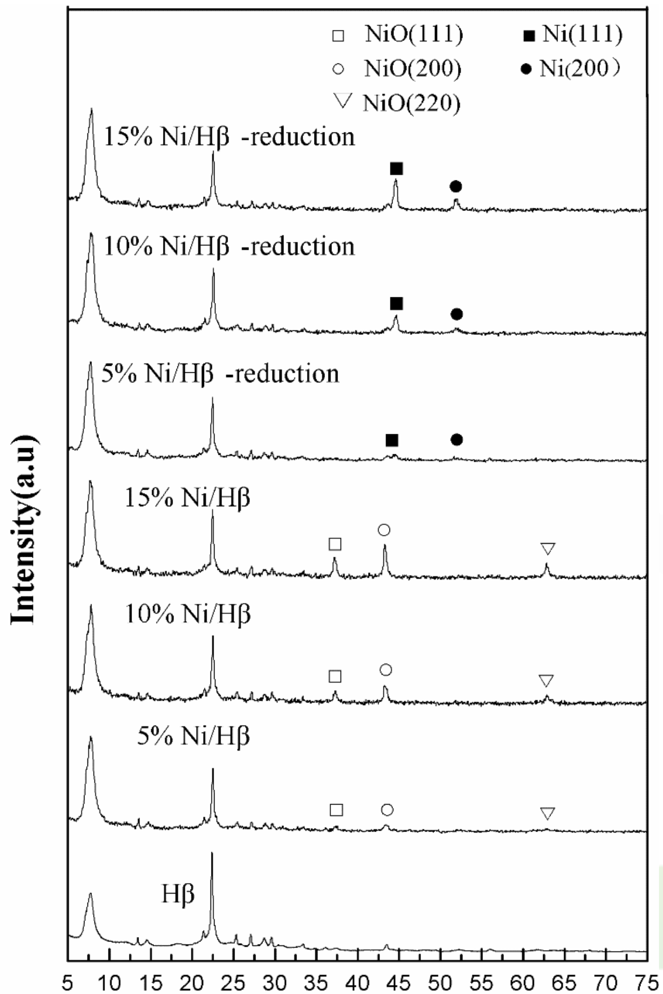




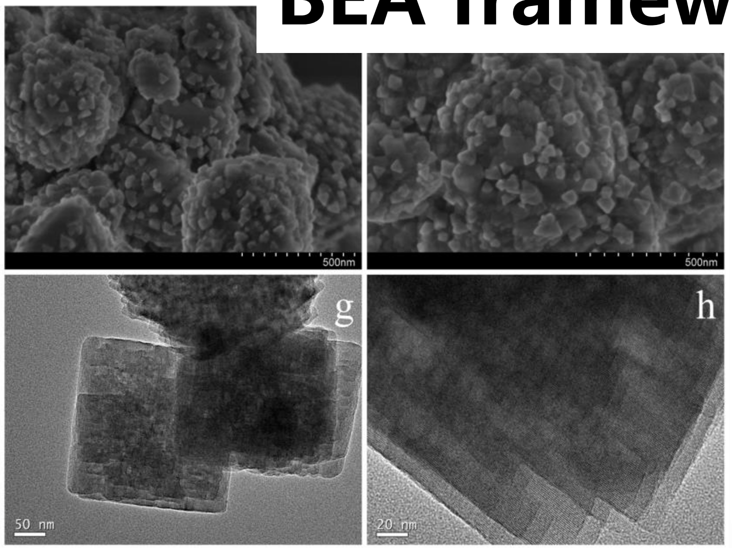
	NiMo/MSP-1	NiW/MSP-1	NiMo/MSP-2	NiW/MSP-2
<C15	25.32	13.7	13.6	12.13
C15	6.37	11	3.61	9.07
C16	12.51	6.6	13.9	8.8
C17	22.4	51	27.7	40
C18	33.4	17.7	41.19	30
C15/C16	0.51	1.67	0.26	1.03
C17/C18	0.67	2.88	0.67	1.33

➢ Hβ-MS

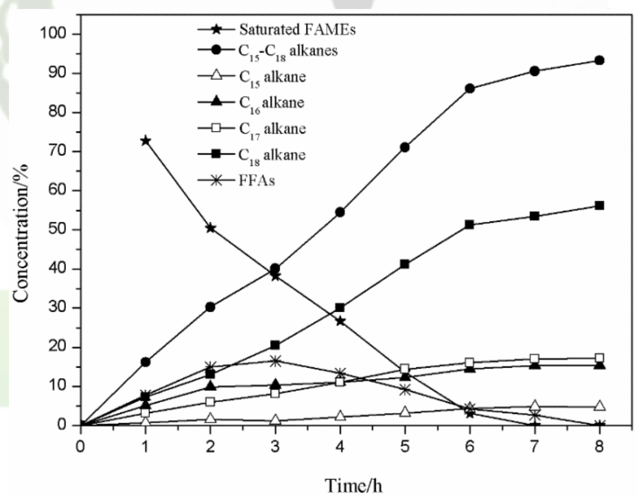
BEA framework



XRD



SEM/TEM



DRAWBACKS for MICROPOROUS MS

□HZSM-5

Much small pore size 0.56*0.53 nm -> low activity
Strong acid sites -> over-amount cracking

□SAPO-11

Much small pore size: 0.65*0.43 nm -> low activity
Lack of strong acid sites ->almost no cracking

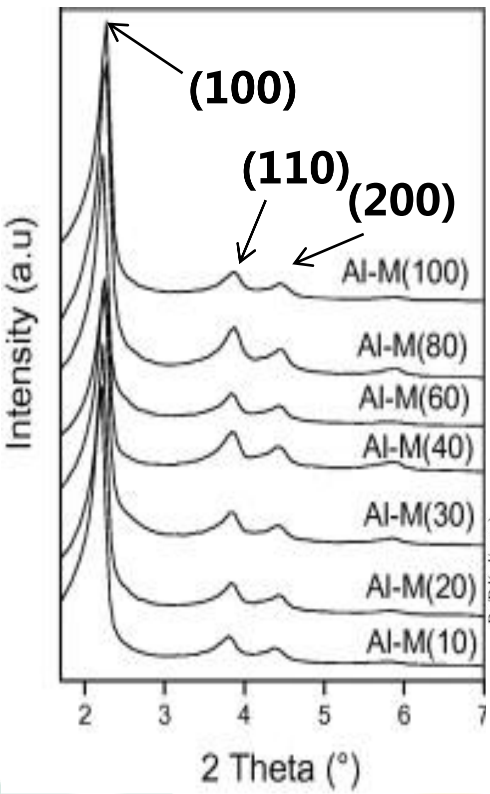
□Hβ

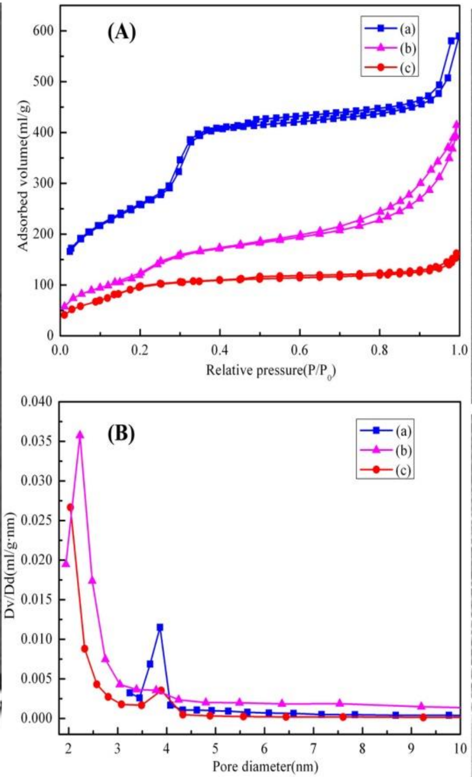
Much small pore size: 0.67*0.60 nm -> low activity
Not matched acid strength -> no isomerization

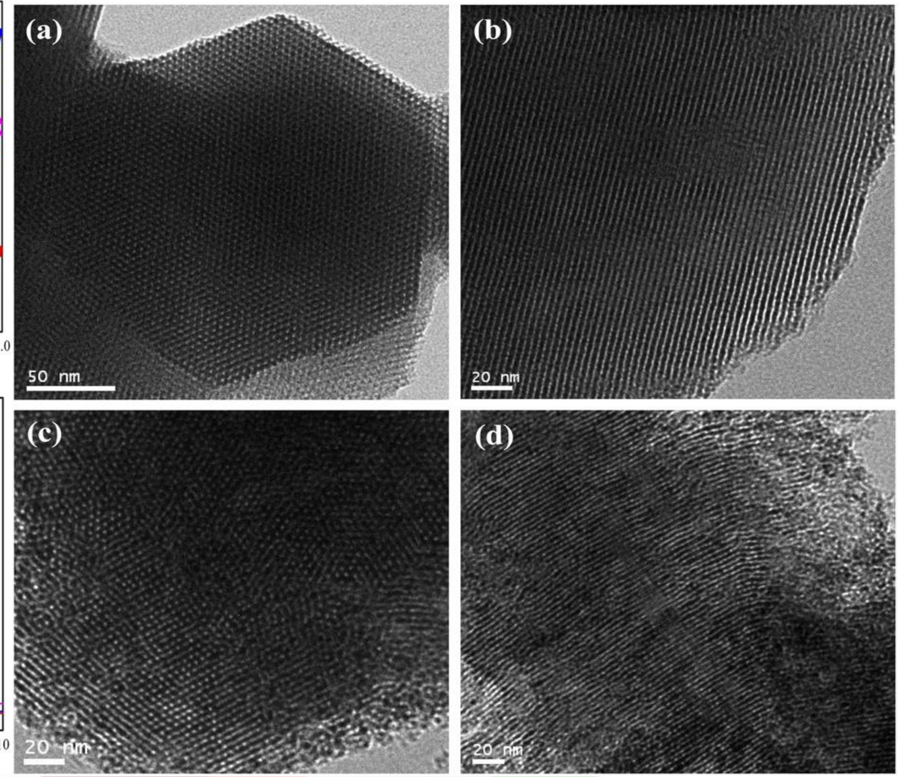
Mesoporous MS
(d: 2~50 nm)

- Al-MCM-41
- Al-SBA-15

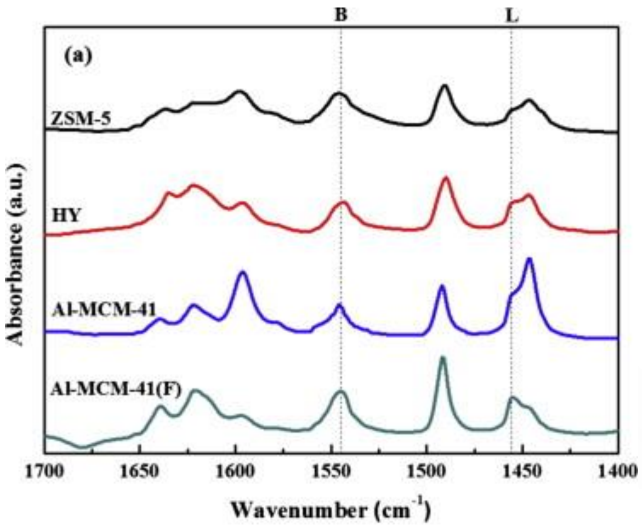
➢ Al-MCM-41

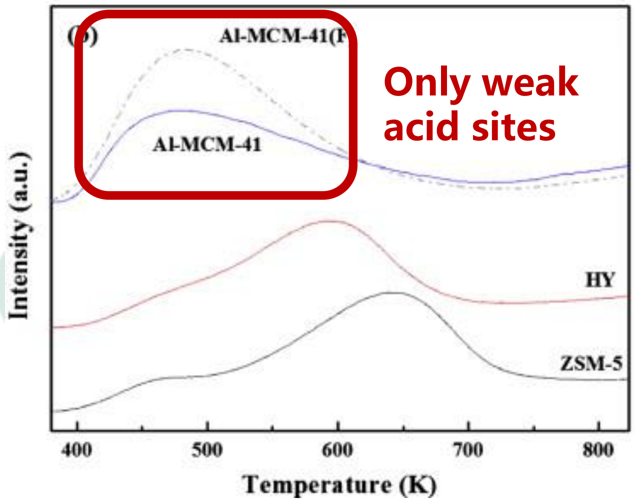






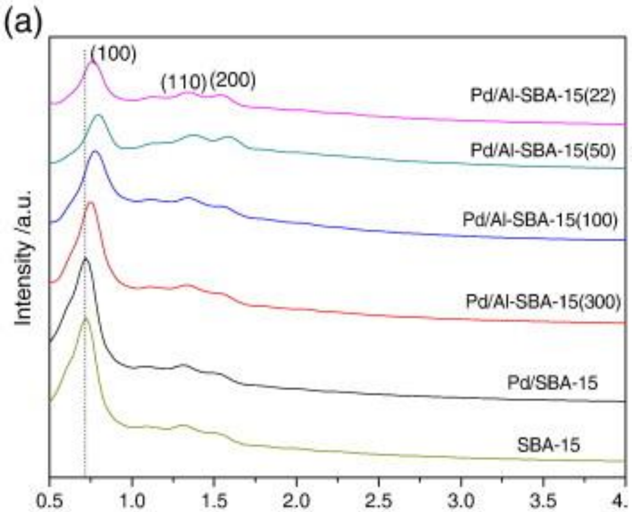
- Highly ordered hexagonal structure
- Hydro-thermostable
- Pore size 2-4 nm
- Surface area high as 1000 m^2/g

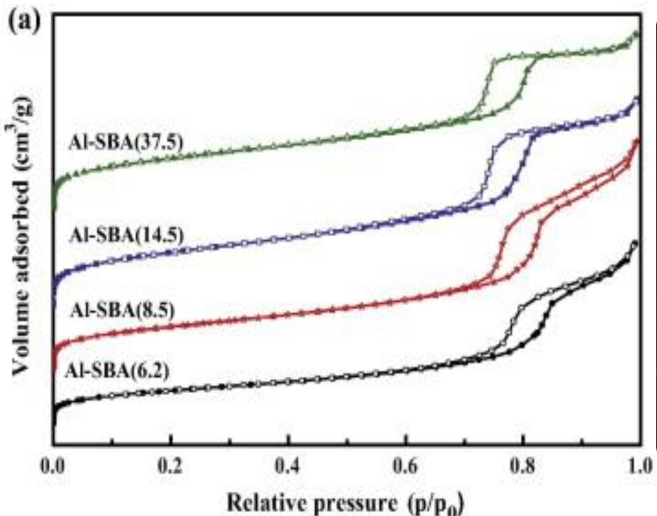


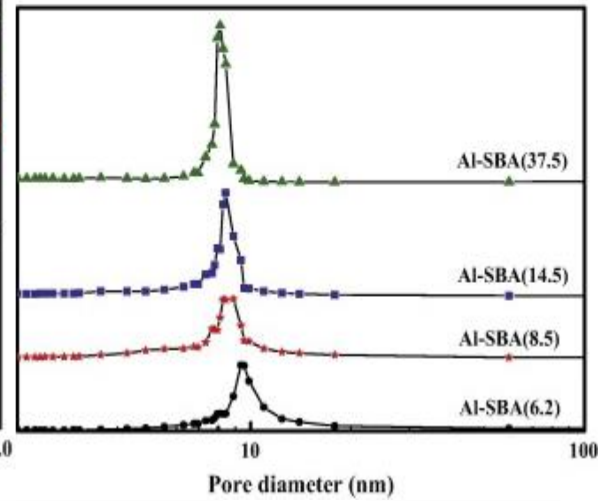


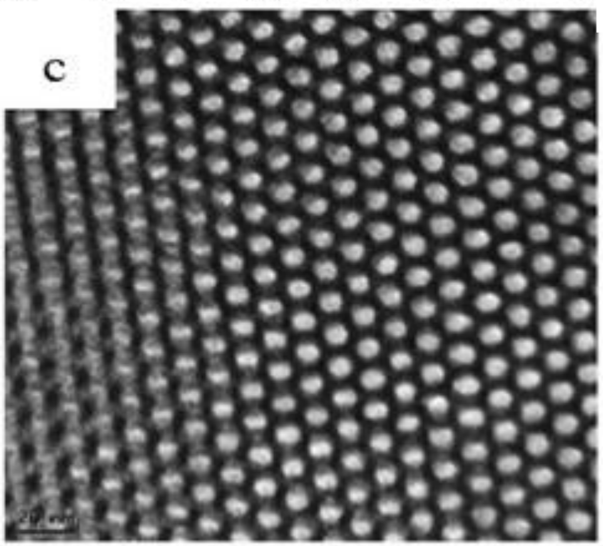
	HZSM-5	Hβ	Al-MCM-41
Pore size (nm)	0.51 × 0.55 0.53 × 0.56	0.55 × 0.65 0.64 × 0.76	2.73
Area BET (m^2/g)	330	519	1007
External surface (m^2/g)	38	183	85
Pore volume (cm^3/g)	0.18	0.17	0.83
Si/Al ratio	22	25	119
Acidity (mmol/g)	2	2.1	0.3
Acidity (weak acid sites) (mmol/g)	1.2	1.1	0.3
Acidity (strong acid sites) (mmol/g)	0.8	1	0

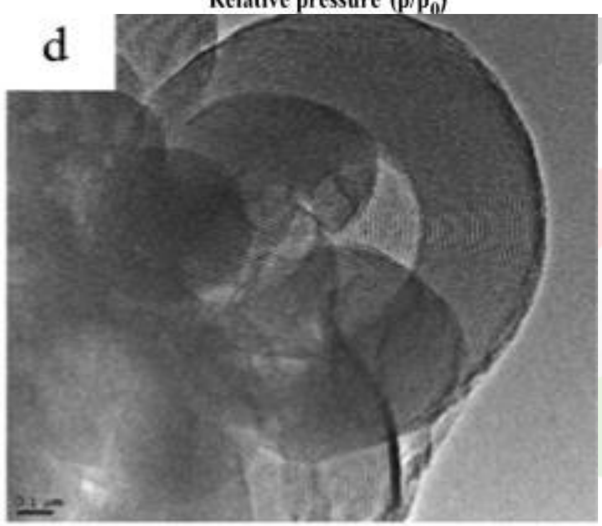
➢ Al-SBA-15











Hexagonal structure

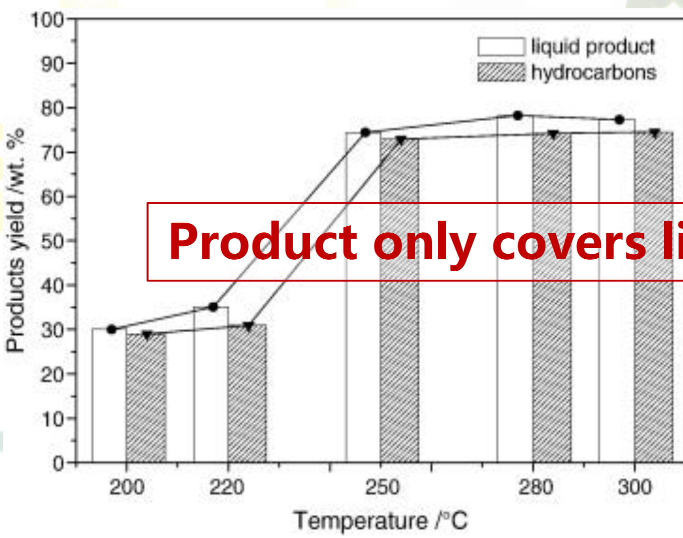
Surface area > 500 m^2/g

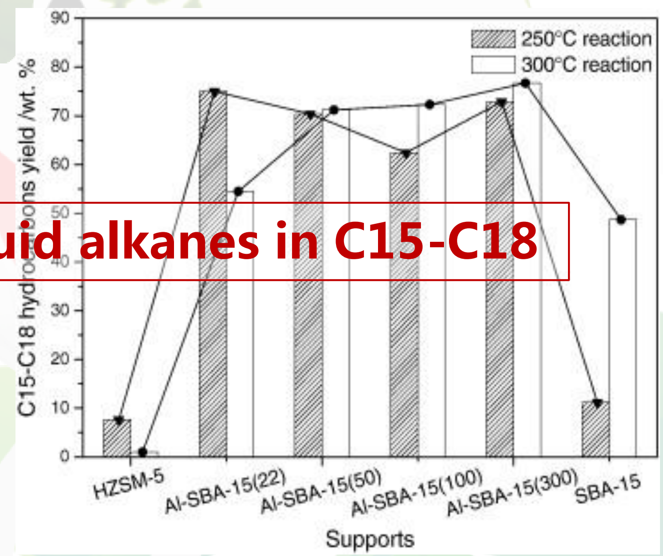
Pore size 8~9 nm

Wall thick 6 nm

Hydro-thermostable

Catalyst	S_{BET} (m^2/g)	Mean pore (nm)	D_{PdO}(nm)	Acid sites distribution		
				Weak	Medium + strong	Total
Pd/SBA-15	817	5.9	19.5	1	–	1
Pd/Al-SBA-15(300)	766	5.7	16.1	0.78	–	0.78
Pd/Al-SBA-15(100)	671	6	16.1	0.81	–	0.81
Pd/Al-SBA-15(50)	708	5.8	16.1	0.85	0.05	0.9
Pd/Al-SBA-15(22)	675	6.8	15.5	0.73	0.49	1.22
Pd/HZSM-5(22)	**329**	**0.55**	–	**1.89**	**1.57**	**3.46**





Product only covers liquid alkanes in C15-C18

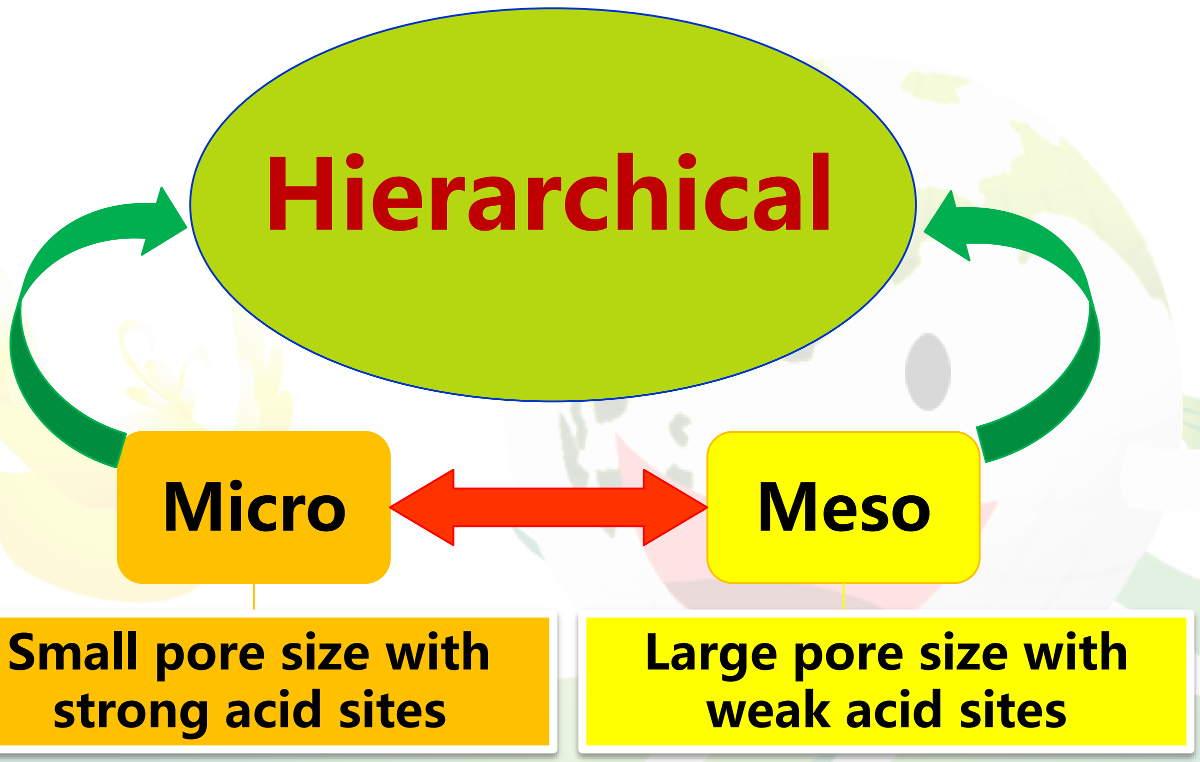
DRAWBACKS for MESOPOROUS MS

Al-MCM-41 and Al-SBA-15

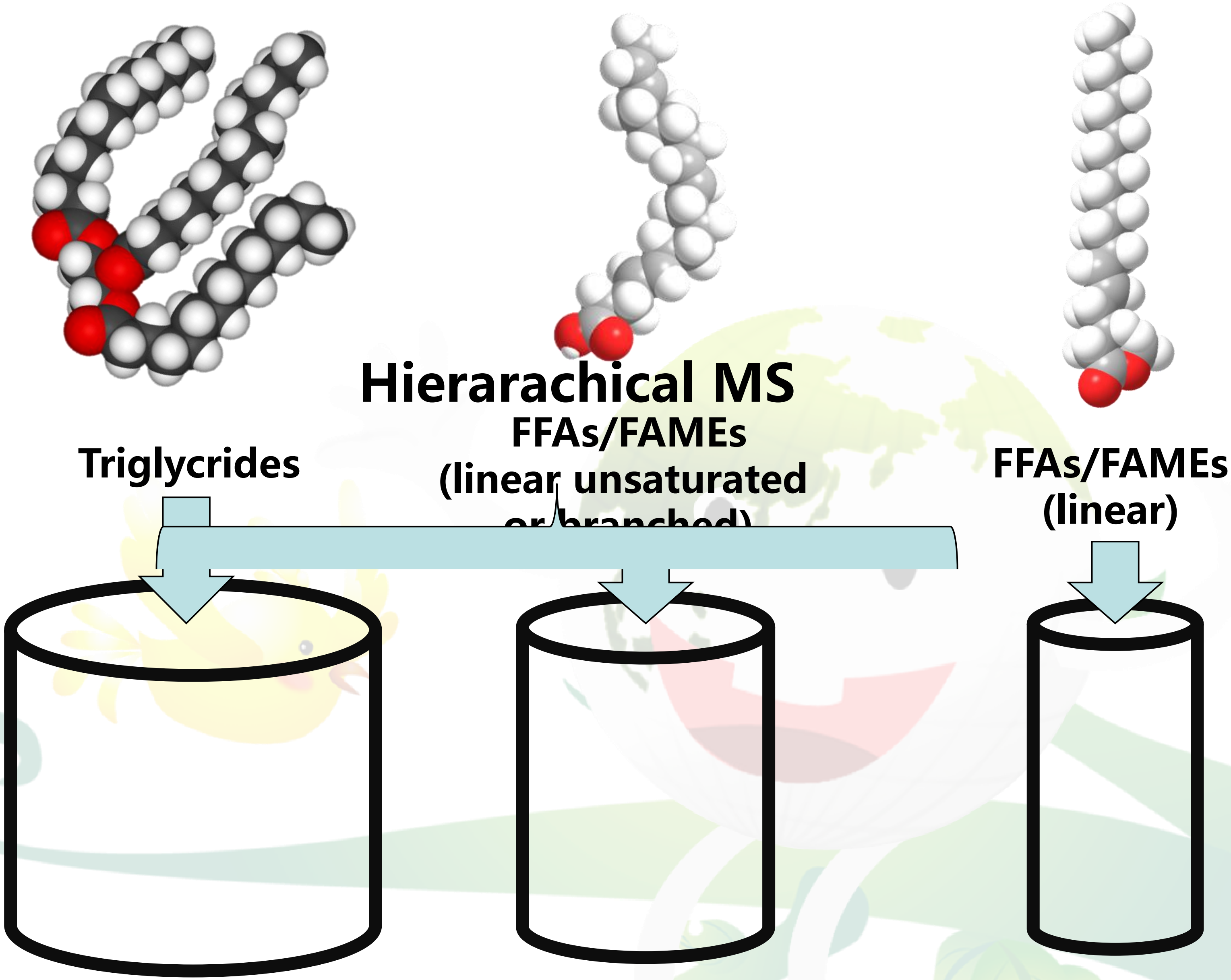
- **Enough surface area and pore size but low total acid amount.**
- **Not enough acid sites (weak acid sites and mid-strong acid sites)**

Hierarchical MS

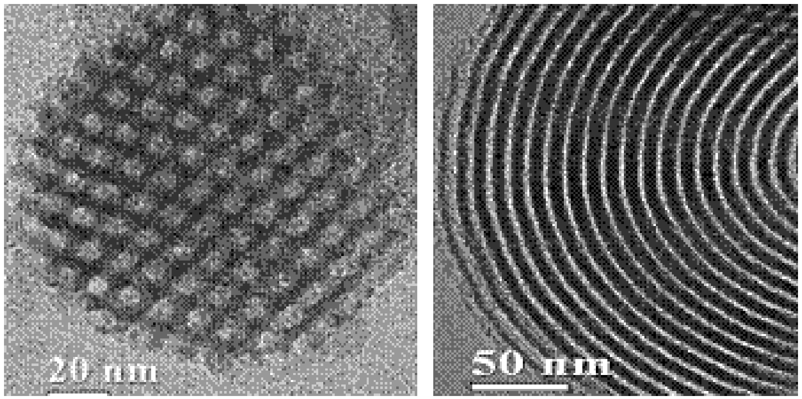
(d: 0~50 nm)

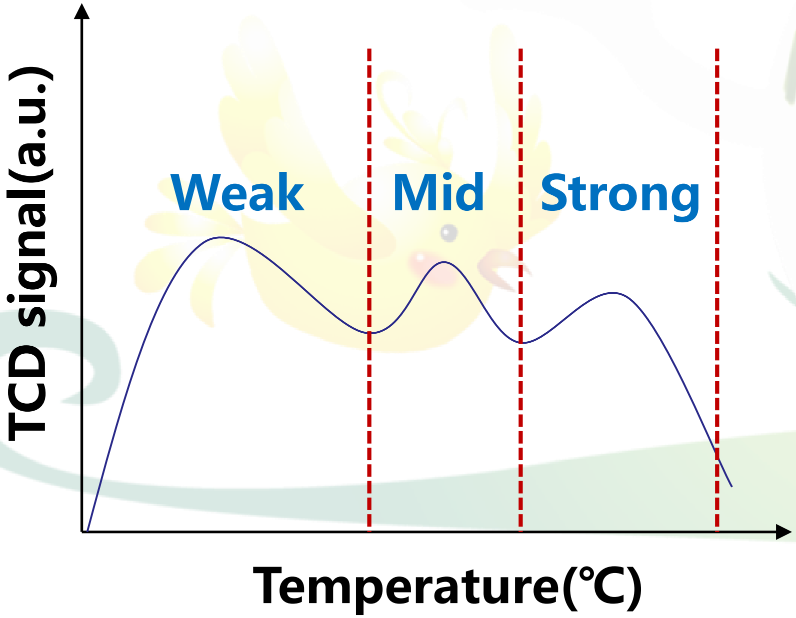


Hierarachical MS



Prospective MS for oil to jet-fuel





□Pore size

- To reduce mass transfer resistance.
- To make in-pore active acid sites more accessib le to the substrates.

□ Active acid sites

- The **strength and amount** of acid sites should be compatible to the three reactions in order to **balance Cracking** (Strong acid) **and Isomerization** (Weak acid).

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Xing Shiyou, Dr. candidate

Wang Jiayan, Master degree candidate

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Thanks for your attention!