Synthesis of Coal-based Clean Fuel and Chemicals

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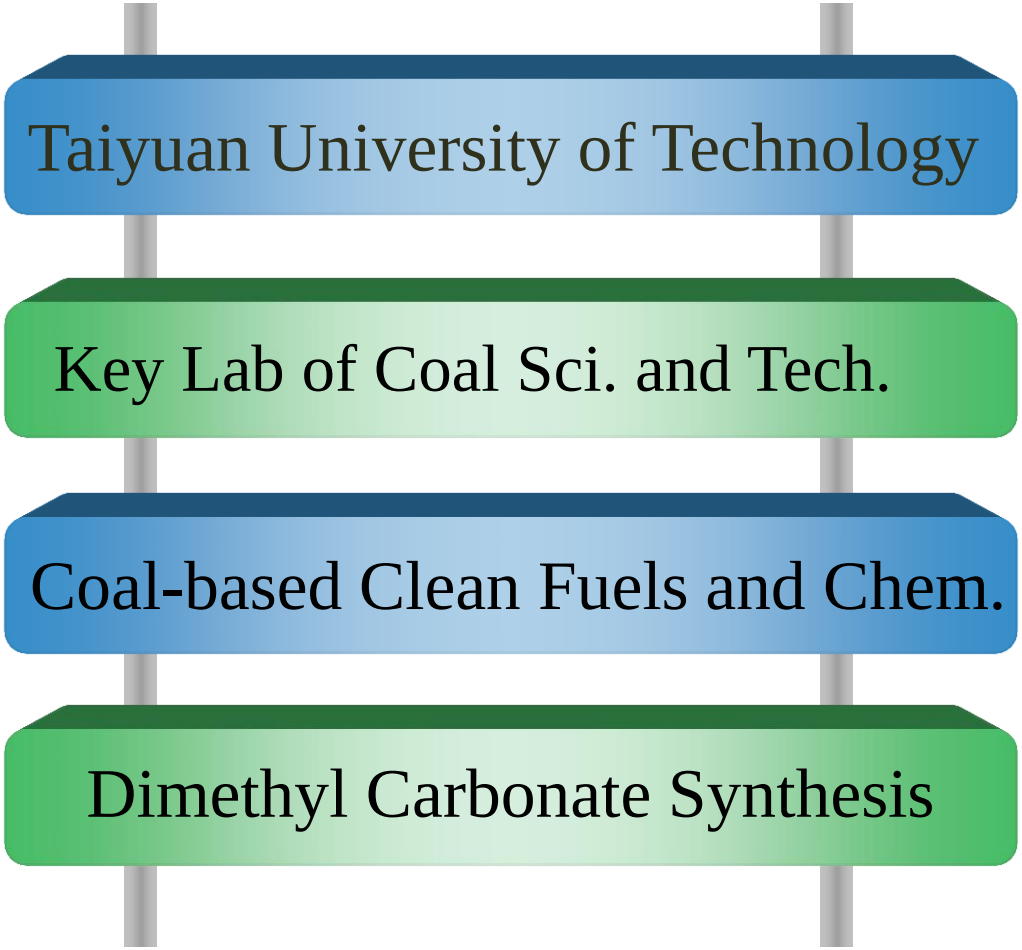
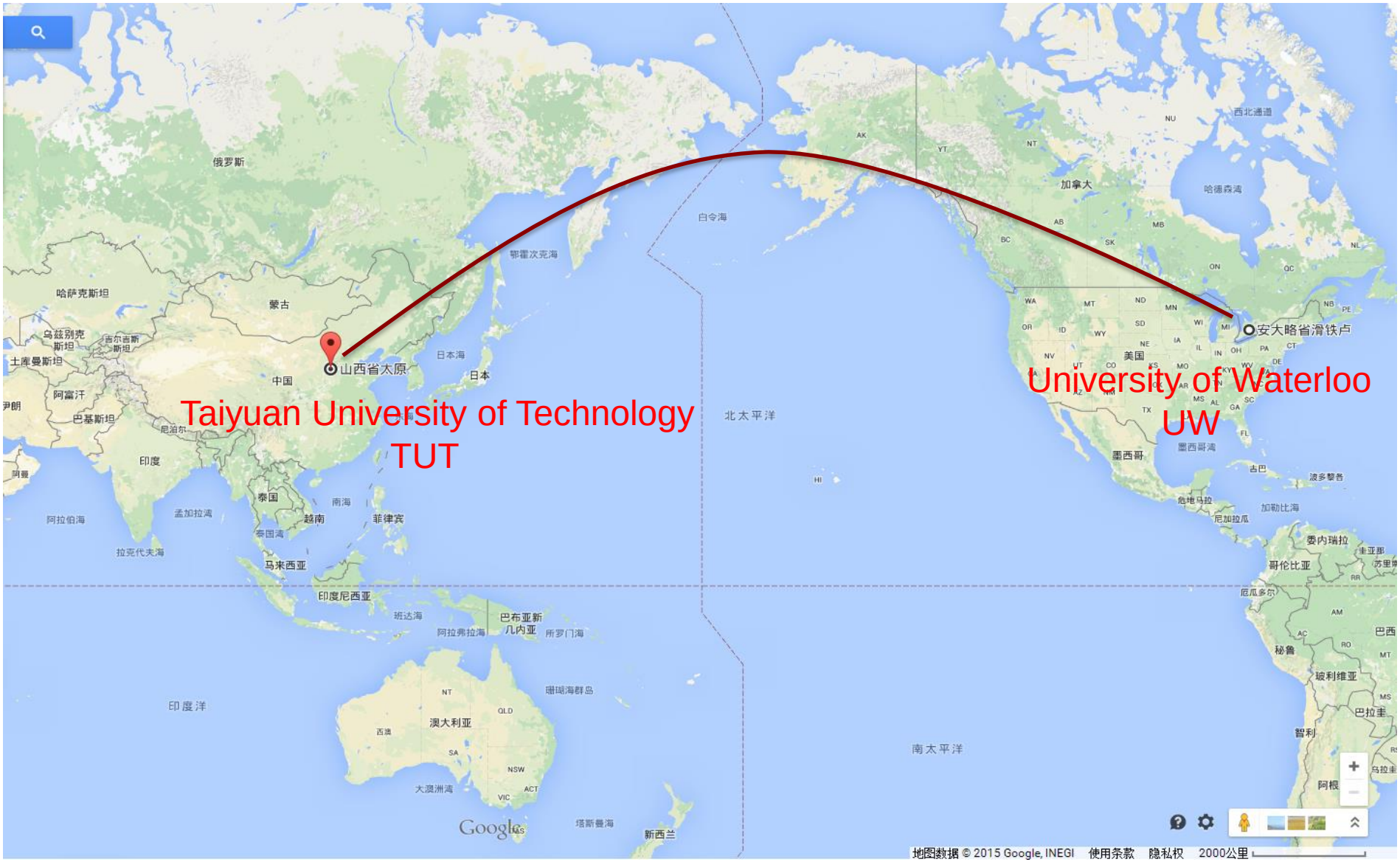
Introduction

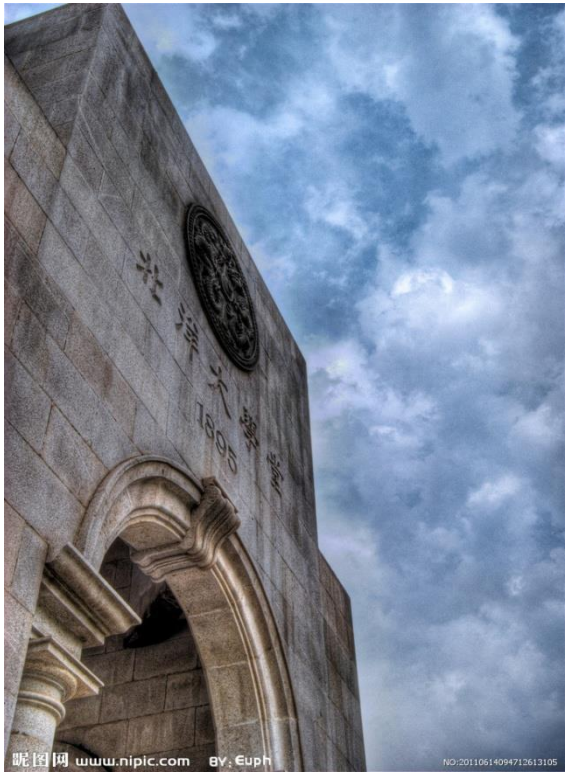


Where We Are

太原理工大学
TAIYUAN UNIVERSITY OF TECHNOLOGY



One of the oldest three national University in China



Peiyang University

(1895~)

Western learning College, Shanxi University

(1902~)

Imperial University of Peking

(1898~)

Basic Information

太原理工大学
TAIYUAN UNIVERSITY OF TECHNOLOGY

20 Colleges
67 Undergraduate majors
169 Master's degree programs
49 Doctorate programs

Employees	3976
Teaching staff	1941
Professors	311
Associate professors	589
Full-time undergraduates	25000
Ph.D.& Master's Degree Students	5930

Located in Shanxi

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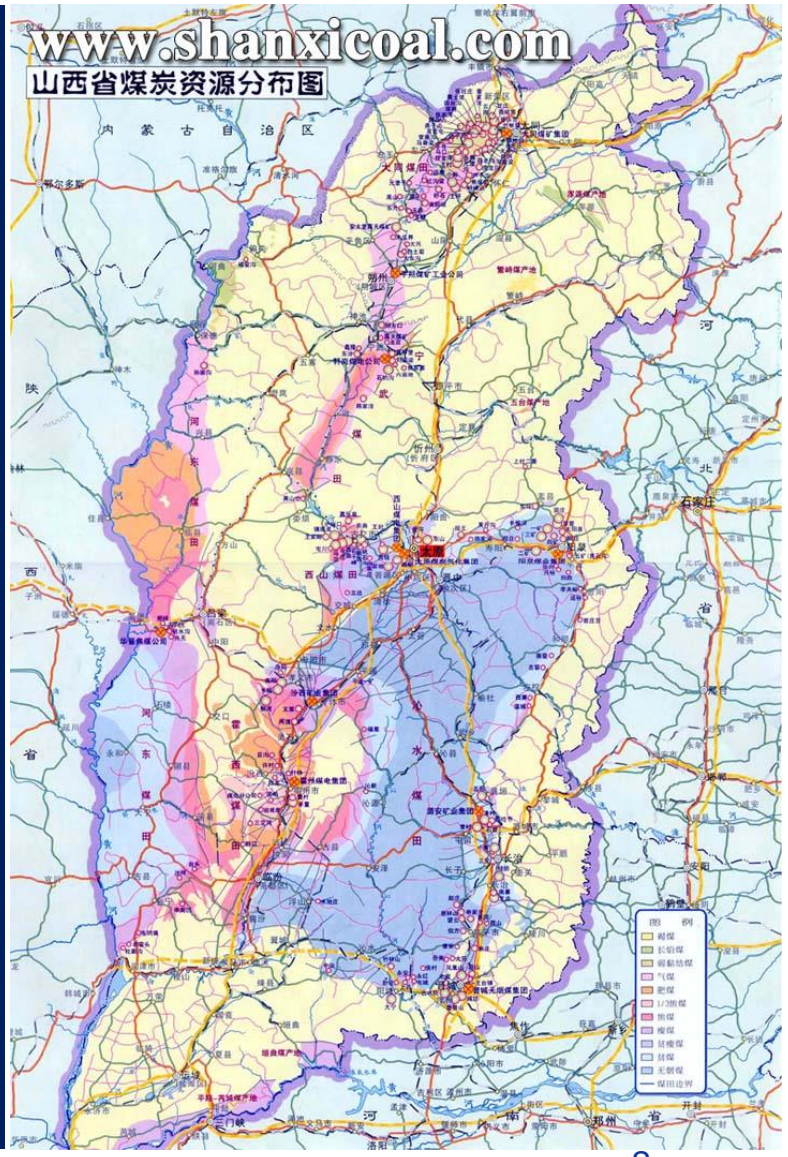
TAIYUAN UNIVERSITY OF TECHNOLOGY

- ✓The Yellow River flows through Shanxi province
- ✓The geographic constructions are mainly mountain, plateau or basin.
- ✓One of the birthplaces of the Chinese people with a long history,
- ✓Brilliant civilization and a large amount of historical and cultural heritage

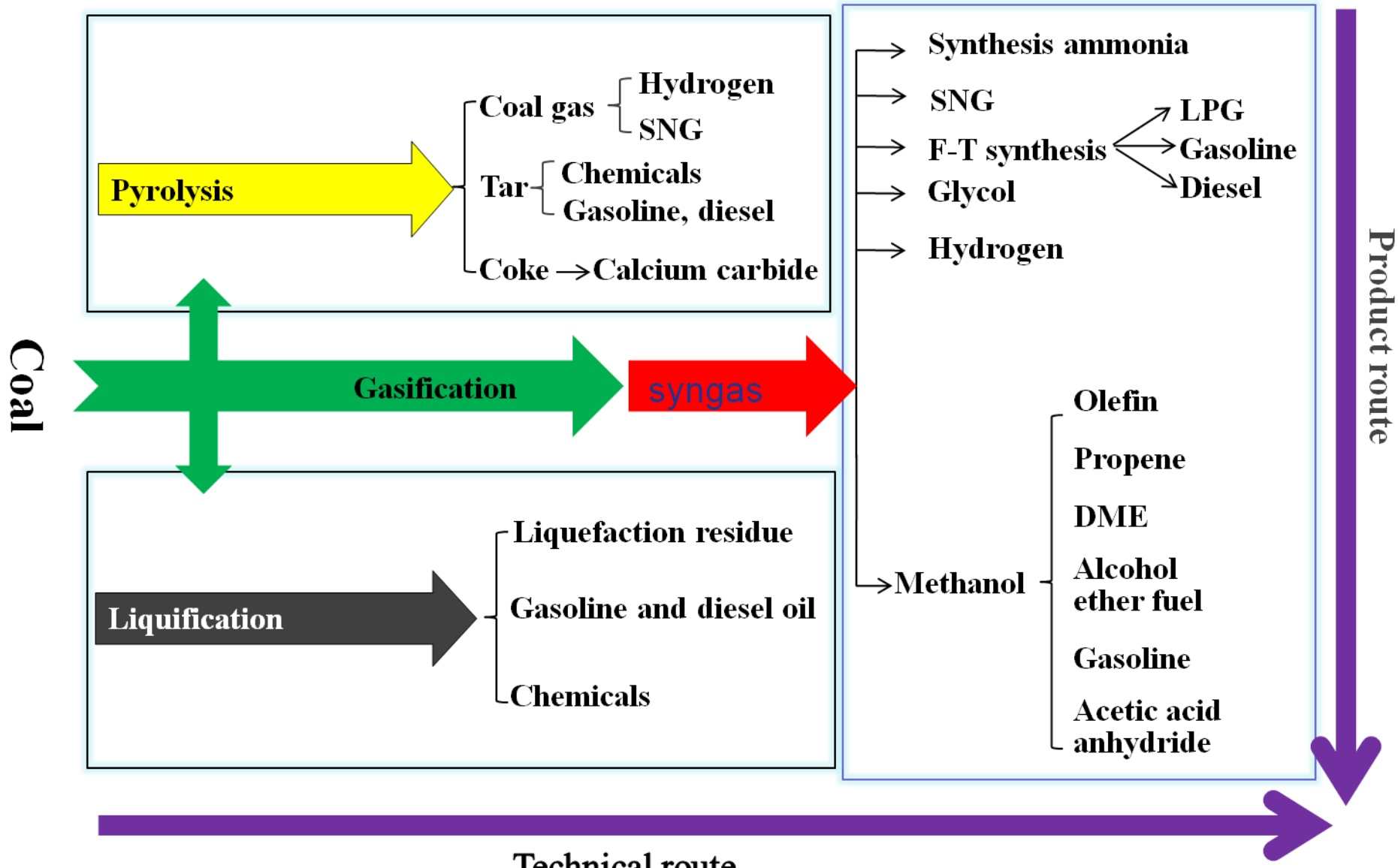
Historical and Cultural Heritage

Coal in Shanxi 2014

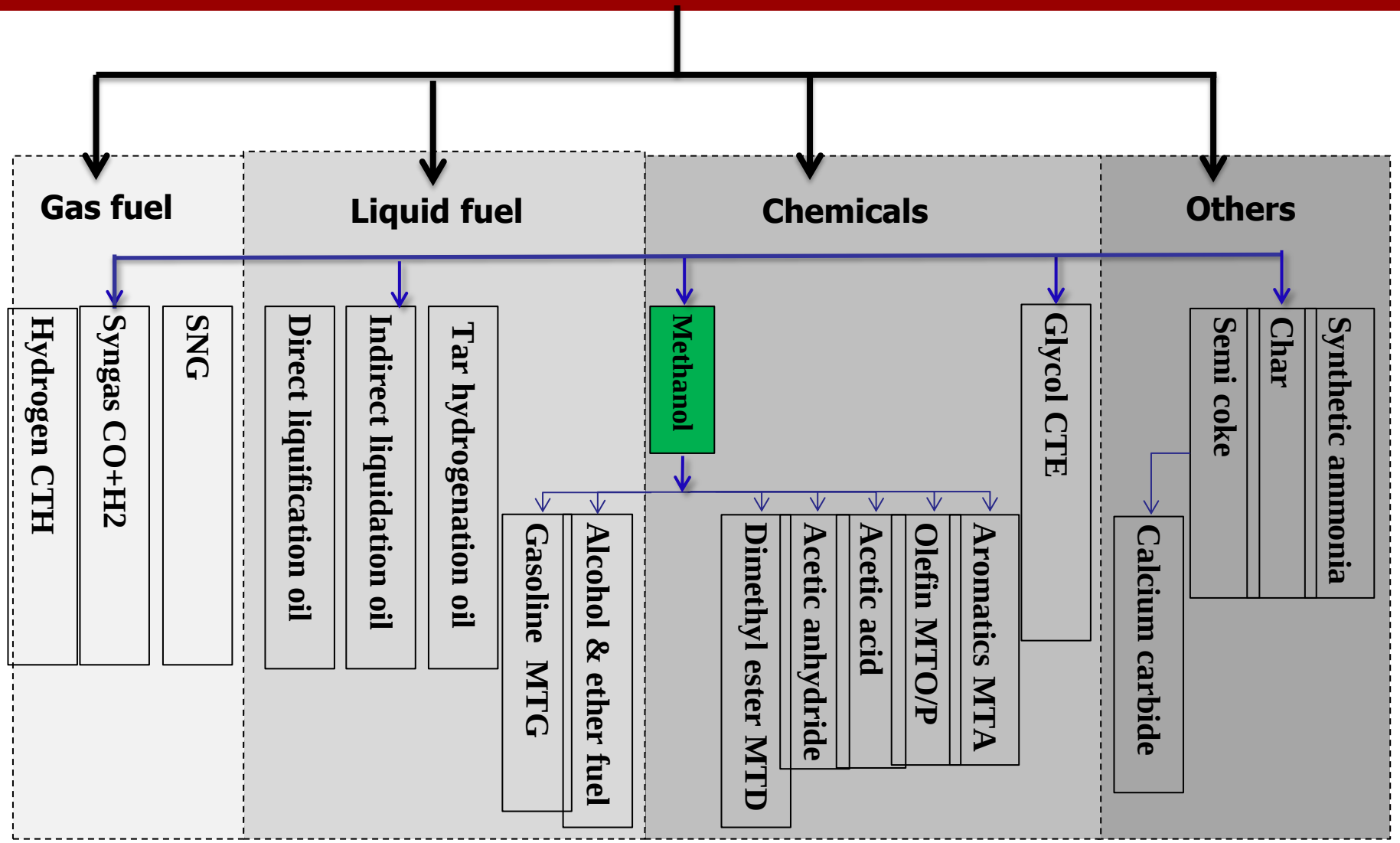
- ✓ The production of coal 0.9 billion tons
- ✓ Export sales 0.56 billion tons.
- ✓ Coal power electricity 20 million KV
- ✓ Coke production 50 million tons
- ✓ Synthetic ammonia and urea 15 million tons
- ✓ Methanol and alkene 4 million tons
- ✓ Synthetic oil 2 million tons



Coal Chemical Industry

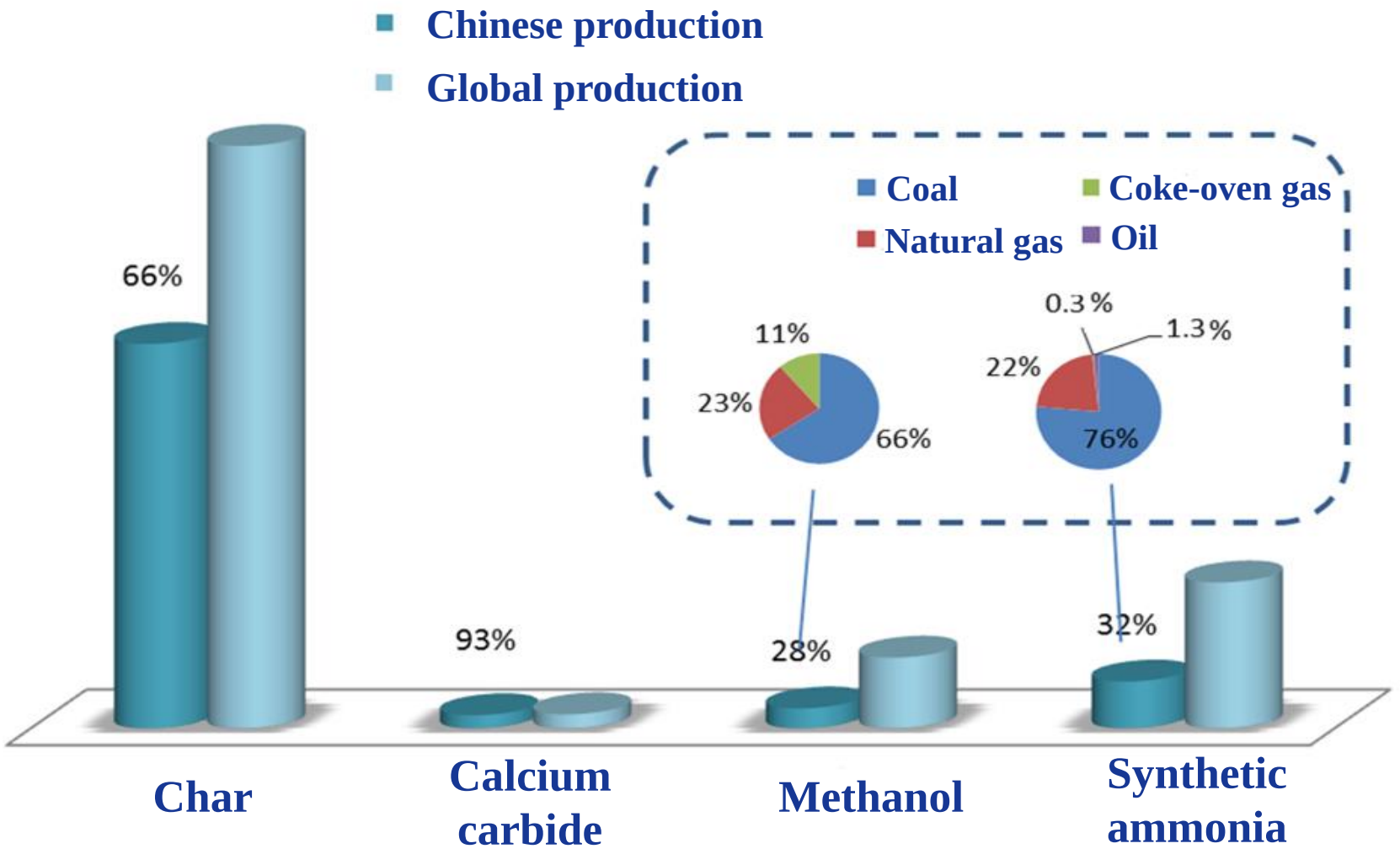


Coal-based fuels and Chemicals



Four categories, Twenty products

Chinese VS. Global



Coal Chemical Industry in China

Product	Capacity (10,000 tons)	Yield (10,000 tons)	Rate of operation(%)
Char	72699	47691	65.6
Semi coke	3500	2000	57.1
Synthetic ammonia	4881	4003	82.0
Calcium carbide	2963.5	2547.9	86.0
Methanol	6860	3740	54.5
MTO	326	581.5	86.8
MTP	465.3	391.8	84.2
MTD	726	290	39.9
CTE	717.6	440	61.3
Acetic acid	572	328	57.3
Anhydride	76	—	—
Direct liquification oil	108	—	—
Indirect liquification oil	50	—	—
MTG	170	106.8	62.4
SNG	30 billion m^3		
CTH	50	—	—
Hydrogenation of coal tar	400	273	68.3
Alcohol ether fuel	—	300 (methanol)	—
Note: Capacity of coal tar hydrogenation refer to the raw material quantity			

Coal Chemical Projects

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SNG

CTL

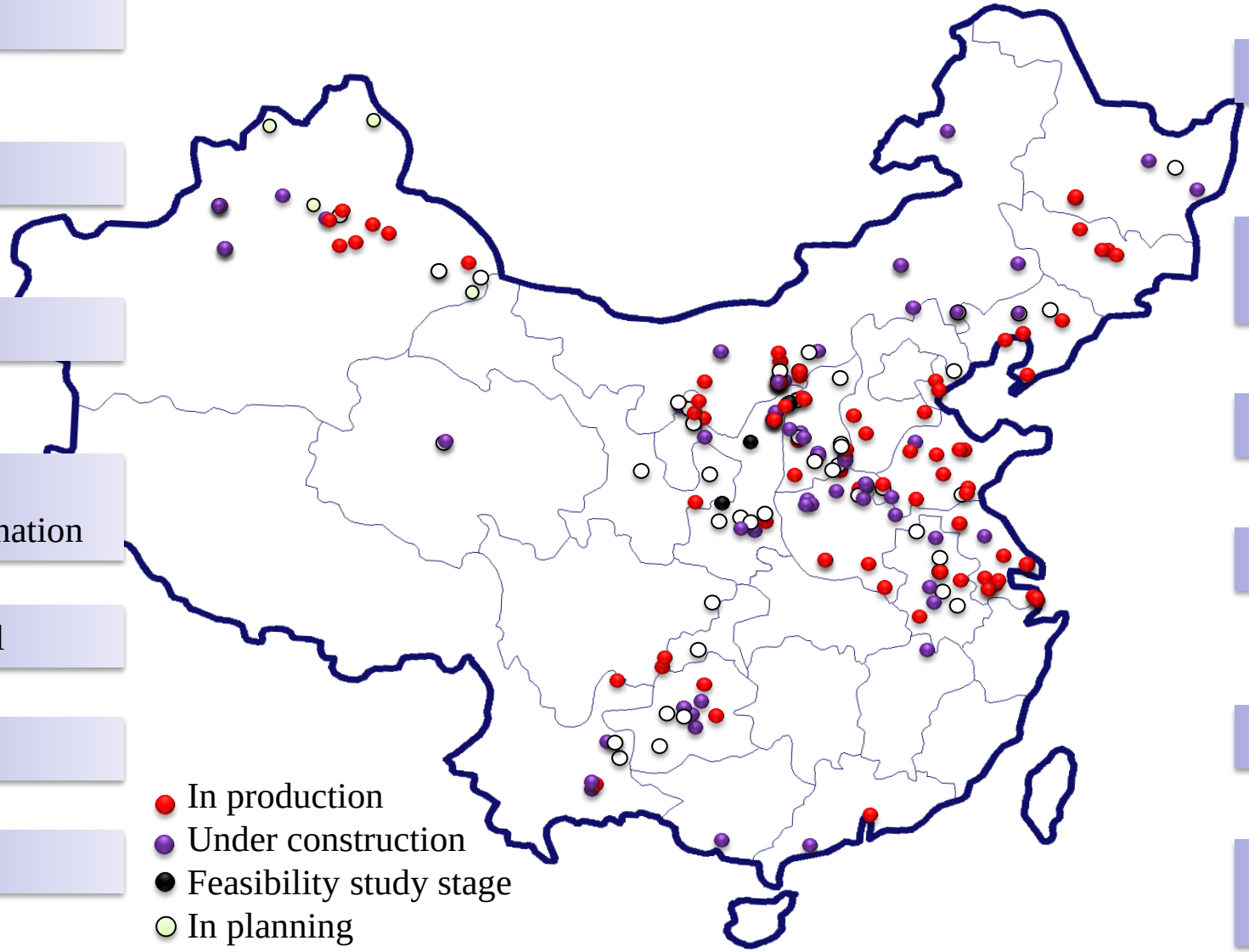
MTG

Tar Hydrogenation

Methanol

DME

MTO/P



MTA

Synthetic ammonia

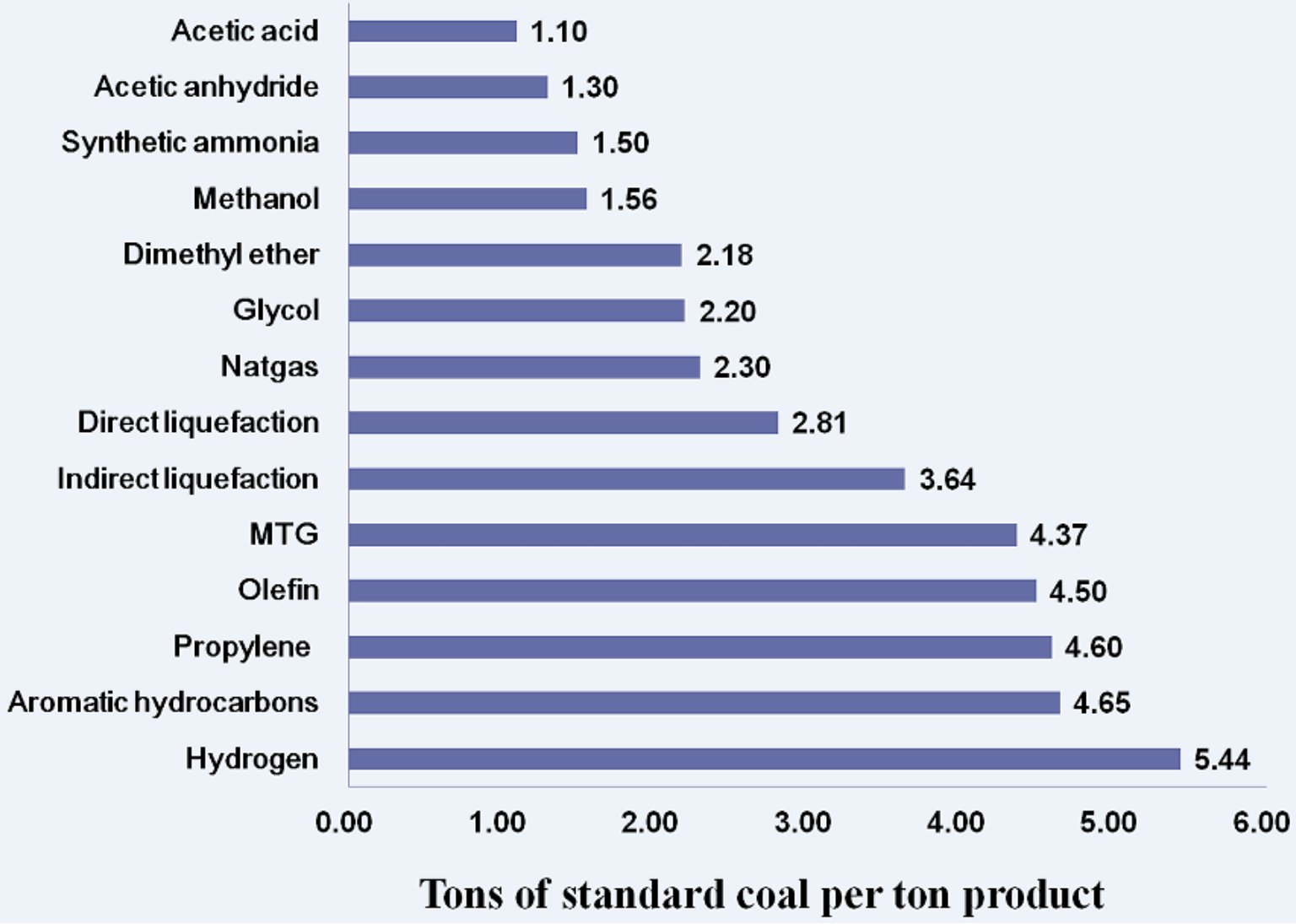
semi coke

MTE

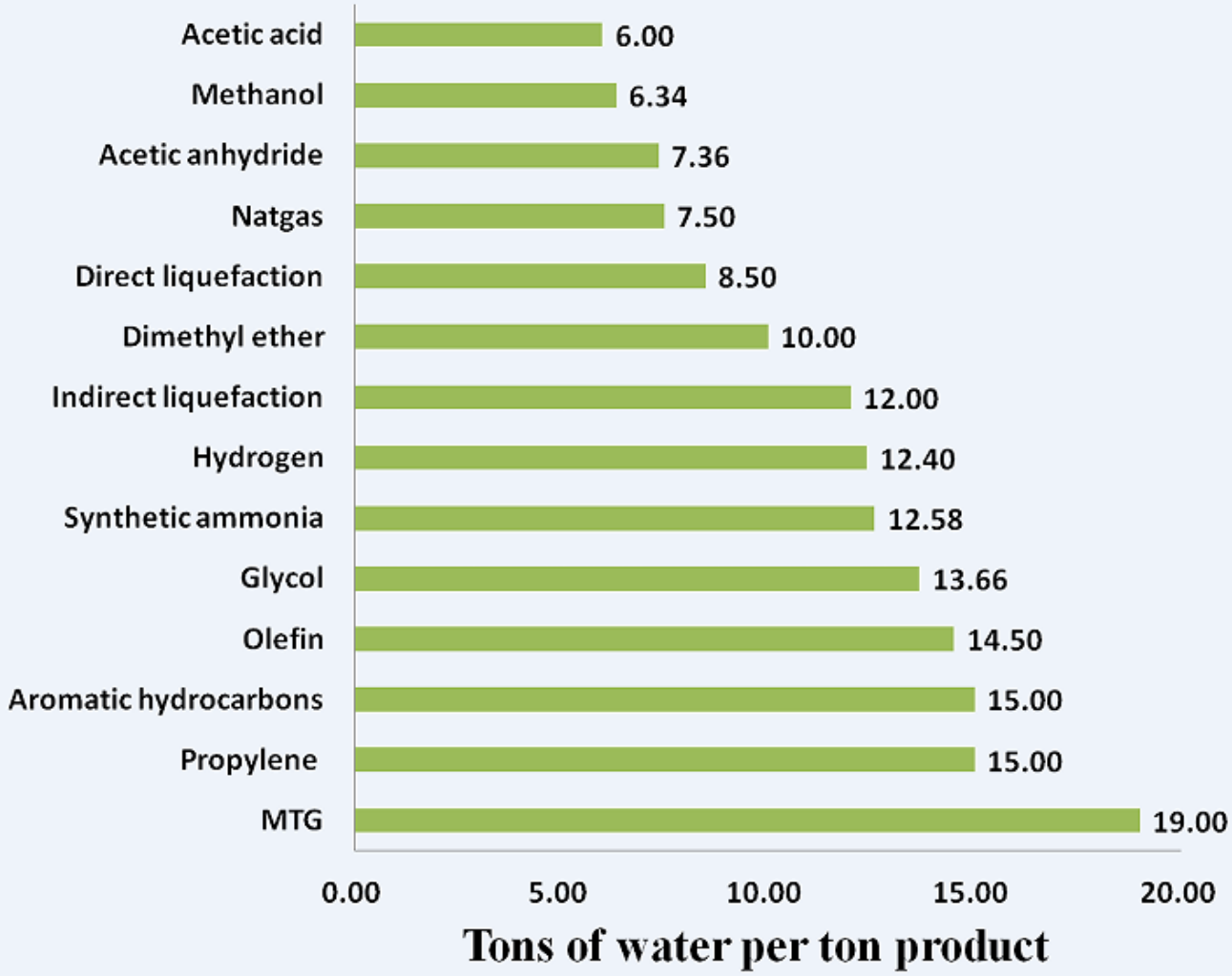
MTH

Acetic Anhydride

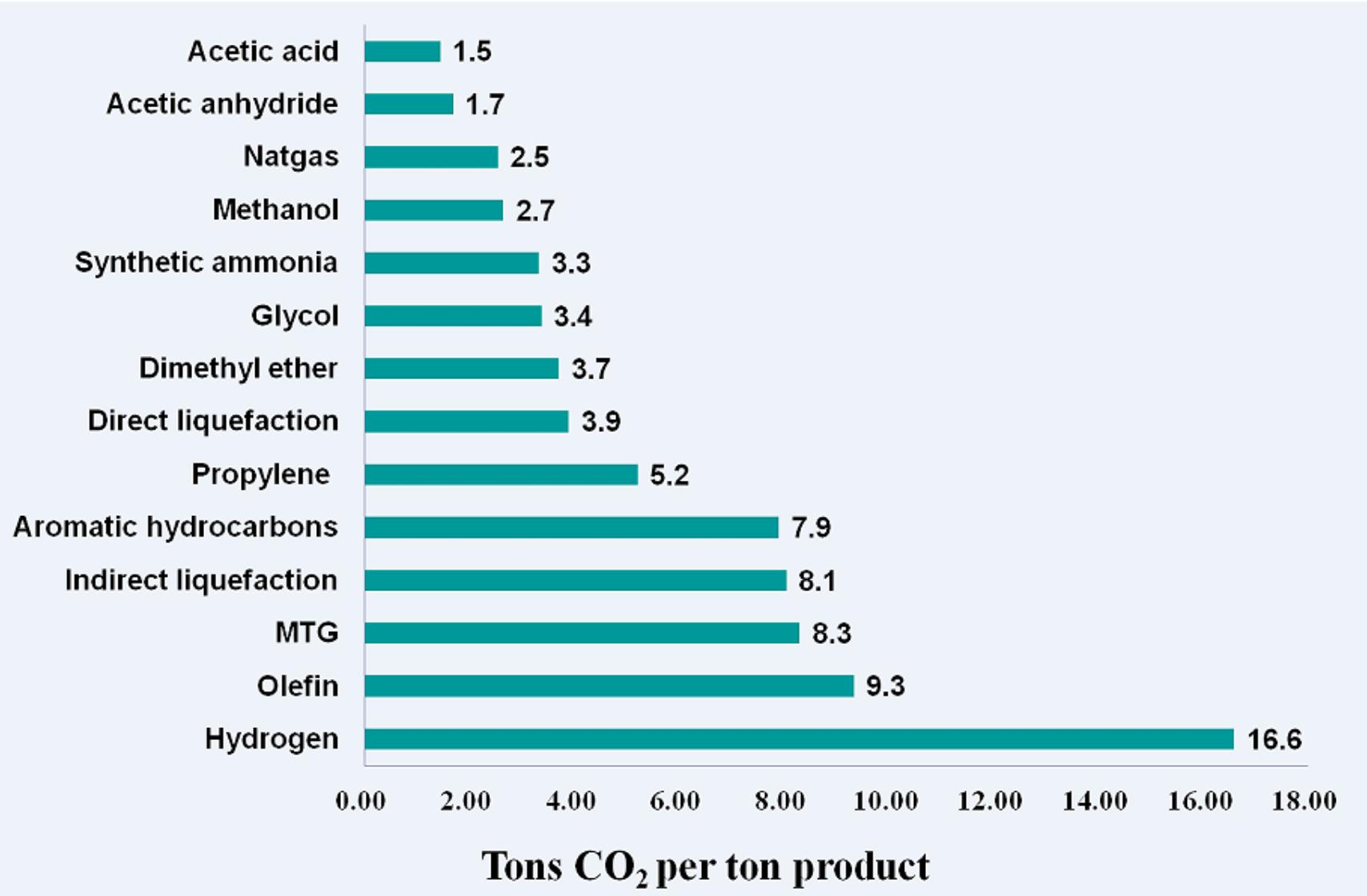
Coal Consumption

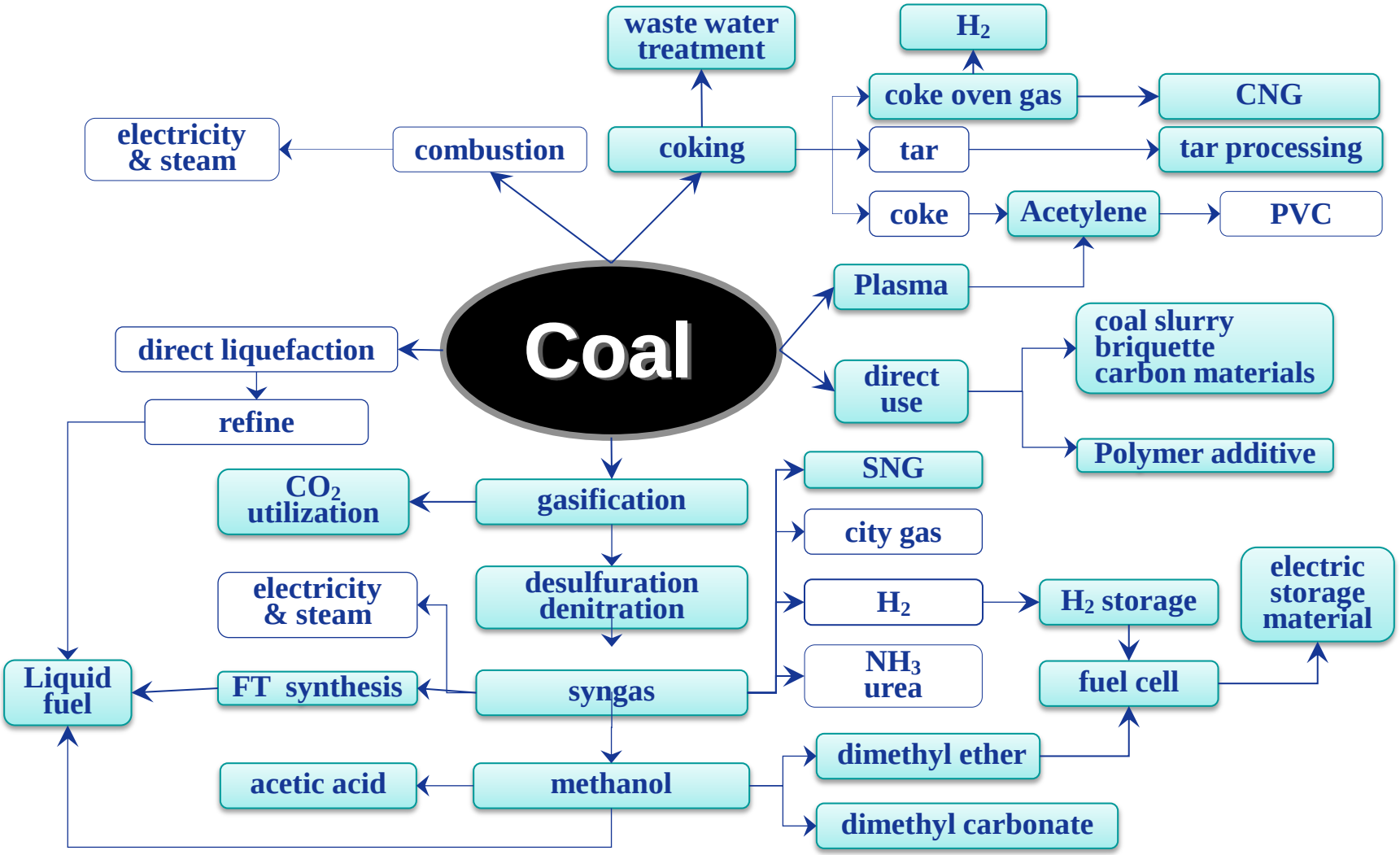


Water Consumption



CO_2 Emissions




Coal
waste water treatment
H2
coke oven gas
CNG
electricity & steam
combustion
coking
tar
tar processing
coke
Acetylene
PVC
Plasma
direct liquefaction
direct use
coal slurry briquette carbon materials
refine
Polymer additive
CO2 utilization
gasification
SNG
city gas
electricity & steam
desulfuration denitration
H2
H2 storage
electric storage material
Liquid fuel
FT synthesis
syngas
NH3 urea
fuel cell
acetic acid
methanol
dimethyl ether
dimethyl carbonate

Research direction

太原理工大学
TAIYUAN UNIVERSITY OF TECHNOLOGY

- Coal Science and Processing Technology
- Gas Purification and Pollutants control
- C_1 Chemistry and Technology
- Novel Inorganic Porous Materials
- Clean Separation Techniques for Coal

Research direction

太原理工大学 TAIYUAN UNIVERSITY OF TECHNOLOGY

➢ C_1 Chemistry and Technology

- Reaction and mechanism of $CO+H_2$ to alcohol, ether, ester and etc.
- Conversion of methanol
- Methanol fuel substituted petroleum from coal
- Environmental friendly catalyst



Our works

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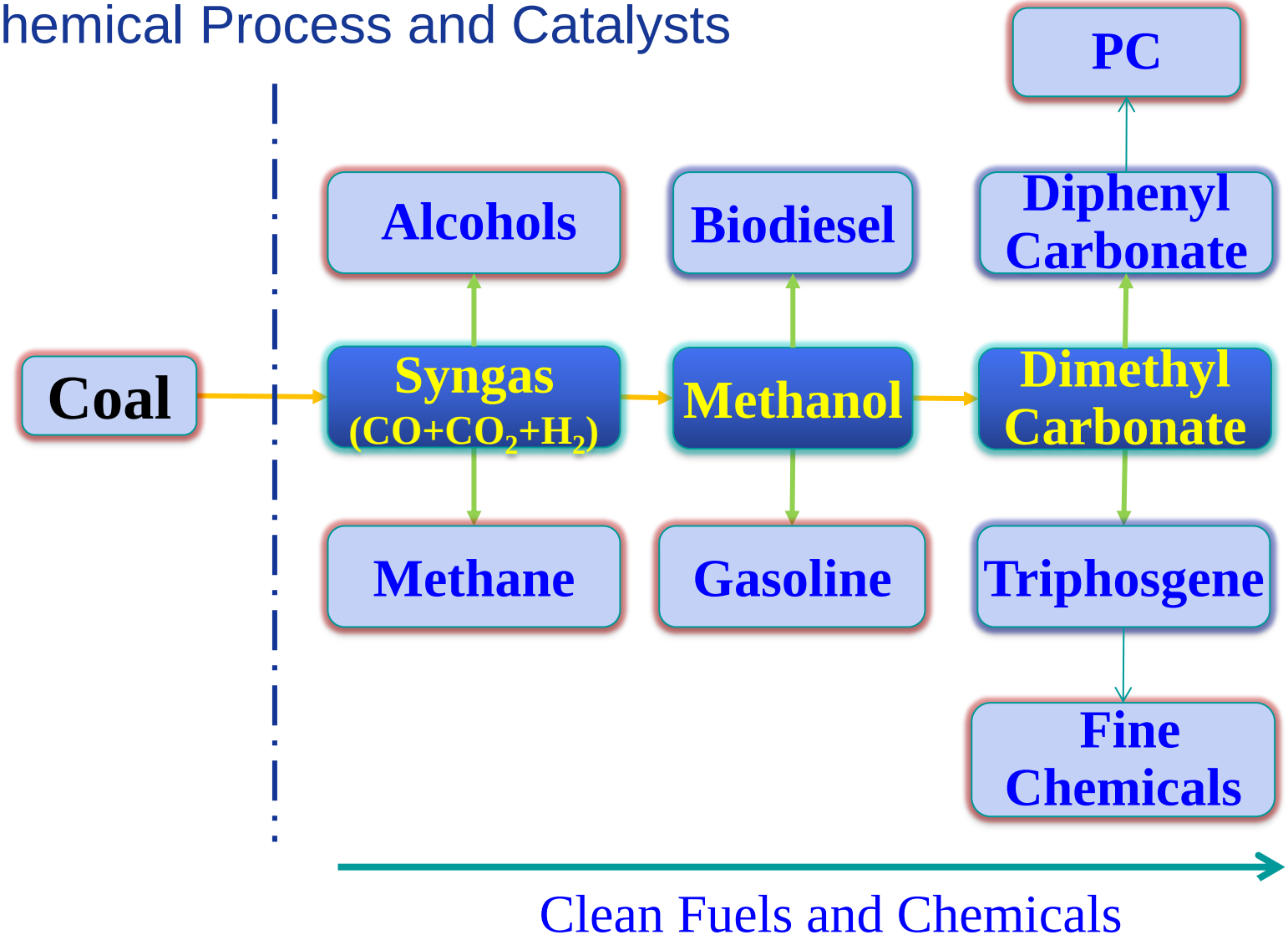
Chemical Process and Catalysts



Dimethyl Carbonate (DMC) Synthesis

Dr. Zhong Li

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2015.06.12

Dimethyl Carbonate (DMC)

Green Chemicals

Organic intermediate

Substitution of halogenated hydrocarbons &phosgene

Nontoxic solvent

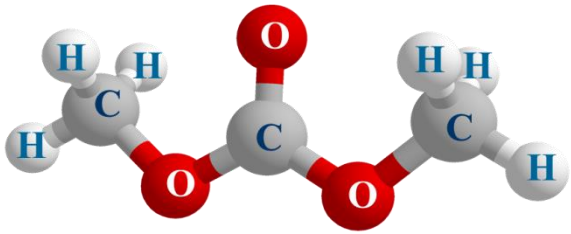
Oil additive

Organic carbonate

Polycarbonate(PC)

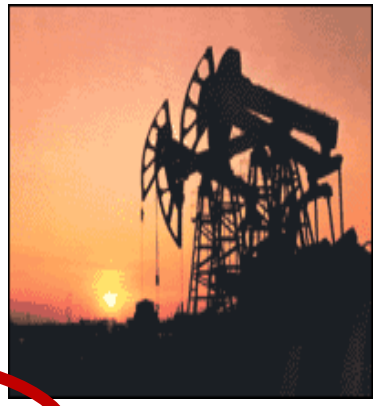
Dimethyl Carbonate(DMC)

Diphenyl carbonate(DPC)



Industry Technology

➢ Petrochemical route



- Raw materials are petrochemical products which great influence by the oil price.
- Production scale and cost are limited by the market of ethylene glycol and propylene glycol.

Industry Technology

➢ Coal Chemical route

- High atom economy.
- The byproduct is only water.
- Green chemical process.

$$2CH_3OH + CO + 0.5O_2 \longrightarrow CH_3O{-}\overset{\overset{O}{\|}}{C}{-}OCH_3 + H_2O$$

DMC production in China (2012)

Manufacturer	Capacity (tons/a)	Technique
Tongling Jintai Chemical industrial CO.,Ltd.	90,000	Transesterification
Tangshan Chaoyang Chemical Co.,Ltd.	30,000	
Shandong Shida Shenghua Chemical Group	110,000	
Dongying Hi-Tech Spring Chemical Industrial Co.,Ltd.	50,000	
Jinxi Huayi Industrail Corparation	10,000	
Hebei Chaoyang Chemical Industrail	30,000	
Shandong Wells Chemicals Co.,Ltd.	55,000	
Liaohe Dali Group	16,000	
Xingshan Xinglihua Chemical Industrial Co.,Ltd	4,000	Oxycarbonylation
Heilong Heihua Group Co.,Ltd	15,000	
Others	102,000	
SUM	512,000	

Oxidative Carbonylation of Methanol

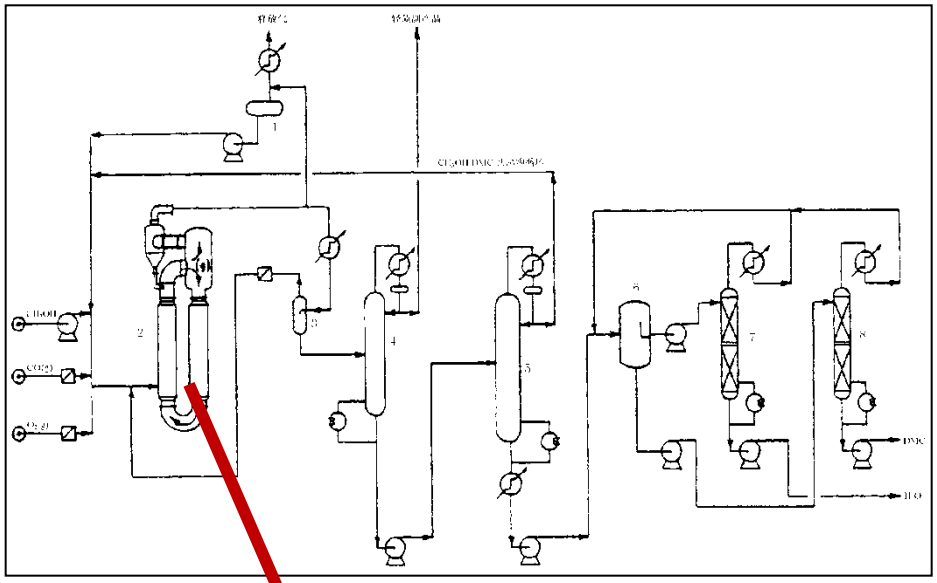


Fig. **Reaction process flow chart of ENIChem Inc.**

- **Liquid phase**
- **Enichem Inc. (Italy)**

1983, 5500 t/a.

1988,up to 8800 t/a.

1993, up to 12600 t/a.

- **Japan Daicel Chem Inc.**

1991, 6000 t/a.

CuCl Catalyst
(Cu:Cl=1:1)

Forming HCl
Cl^- loss

- ✓ **Catalyst deactivation.**
- ✓ **Equipment corrosion.**
- ✓ **Environment pollution.**

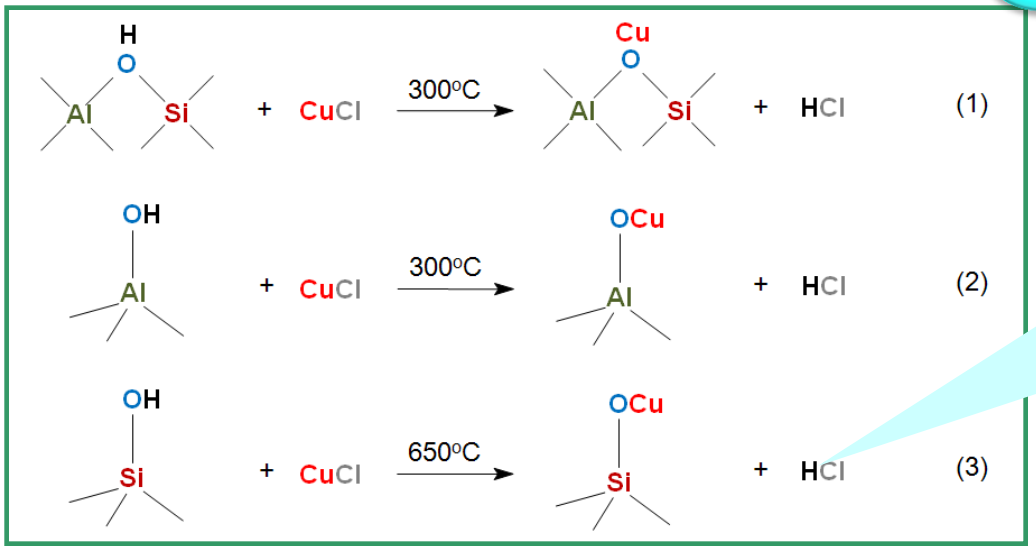
Similar environment around the active center Cu^+

Cu^{+}-SSIE catalyst

$$CuCl + H^{+}Ze^{-} \longrightarrow Cu^{+}Ze^{-} + HCl$$

（H^{+}: Brønsted acid）

Solid state ion exchange (SSIE)

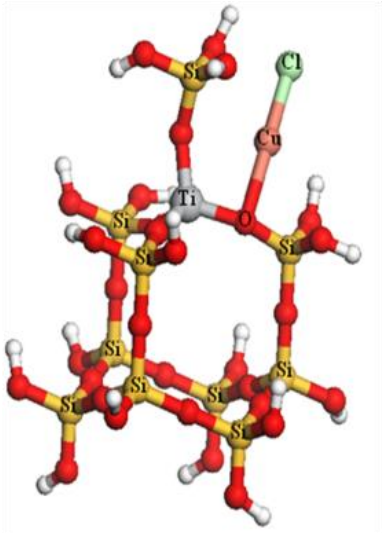


Preparation theory of Cu^{I} catalyst via solid state ion exchange

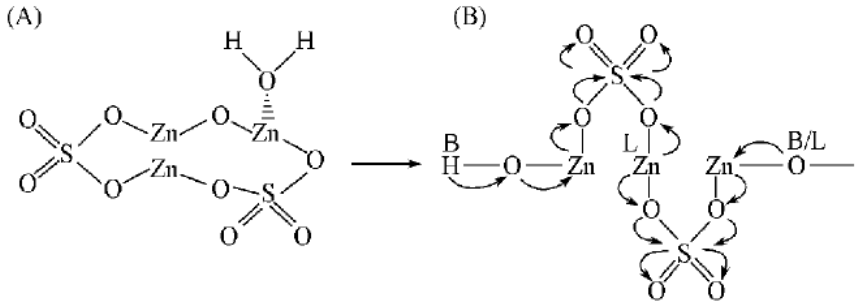
- Excess CuCl can be removed due to easy sublimation when heated， thus obtained supported Cu^{I} catalyst

- Li Z, Xie K, Slade R C T. *Appl Catal A: Gen*, 2001, 205(1-2): 85-92
- Li Z, Xie K, Slade R C T. *Appl Catal A: Gen*, 2001, 209(1-2): 107-115

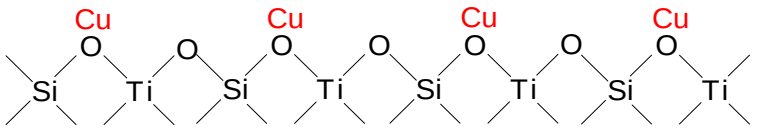
Cu^{+}-SSIE catalyst



Adsorption complex of CuCl with silica–titania support via coordination mechanism



Structural models of SO_4^{2-}/ZnO和$S_2O_8^{2-}$/ZnO solid acid



Structural model of Cu-SiO_2-TiO_2 catalyst

- Other solid acids, such as SiO_2/TiO_2, SiO_2/ZrO_2, SiO_2/Al_2O_3, SO_4^{2-}/M_xO_y and $S_2O_8^{2-}/M_xO_y$ can also be used as support to prepared Cu-based catalyst *via* SSIE.

- **Li Z, Wang R, Zheng H, et al. Fuel, 2010, 89(7): 1339-1343**
- **Li Z, Liu S, Ren J, *et al. Chin J Catal*, 2010, 31(6): 683-688**
- **Ren J, Li Z, Liu S, *et al. Kinet Catal*, 2010, 51(2): 250-254**
- **Ren J, Liu S, Li Z, *et al. Catal Commun*, 2011, 12(5): 357-361**
- **Li Z, Meng F, Ren J, *et al. Chin J Catal*, 2008, 29(7): 643-648**
- **Li Z, Huang H, Xie K. *Chem J Chin U*, 2008, 29(8): 1609-1615**
- **Ren J, Li Z, Liu S, *et al. Catal Lett*, 2008, 124(3-4): 185-194**
- **Ren J, Liu S, Li Z, *et al. Appl Catal A: Gen*, 2009, 366(1): 93-101**

Cu^+-SSIE catalyst

✓ **Cu^+/Y zeolite exhibits good catalytic performance.**

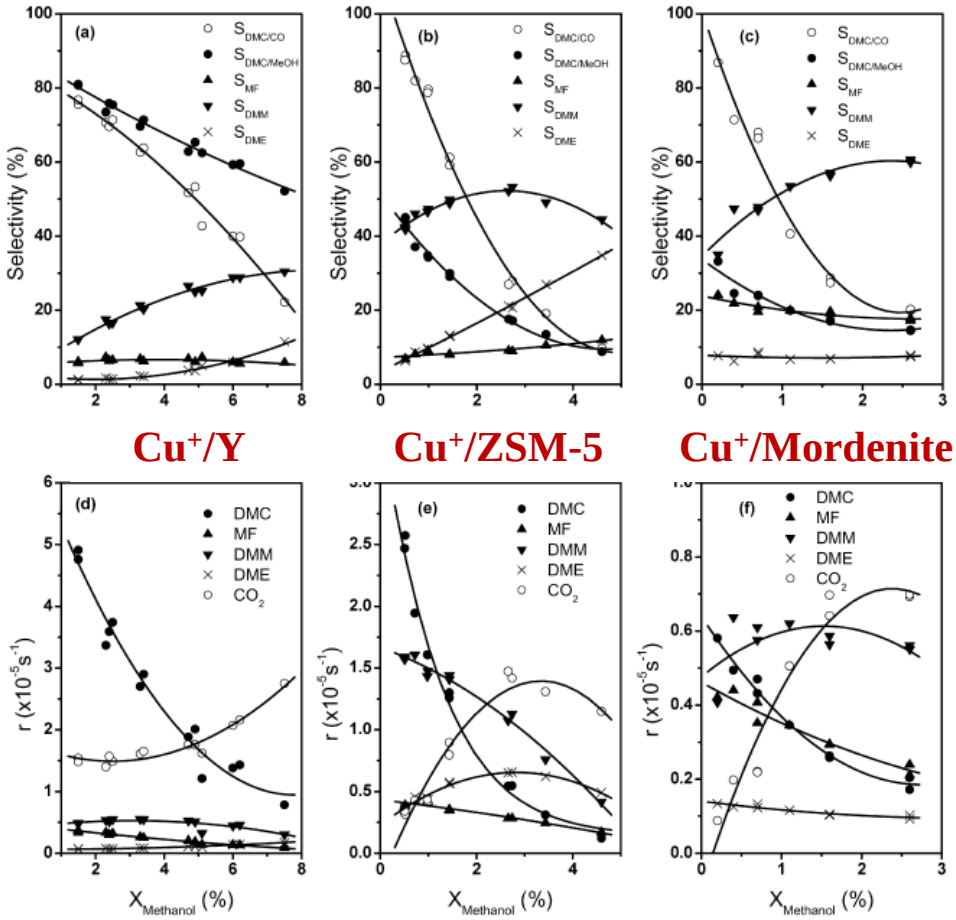


Fig. 9. Selectivities and production rates as a function of methanol conversion (achieved by varying the feed residence time) on Cu-Y (a, d), Cu-ZSM-5 (b, e), Cu-MOR (c, f) at 403 K under $CH_3OH/CO/O_2$ (12.12/20.2/2.02 kPa).

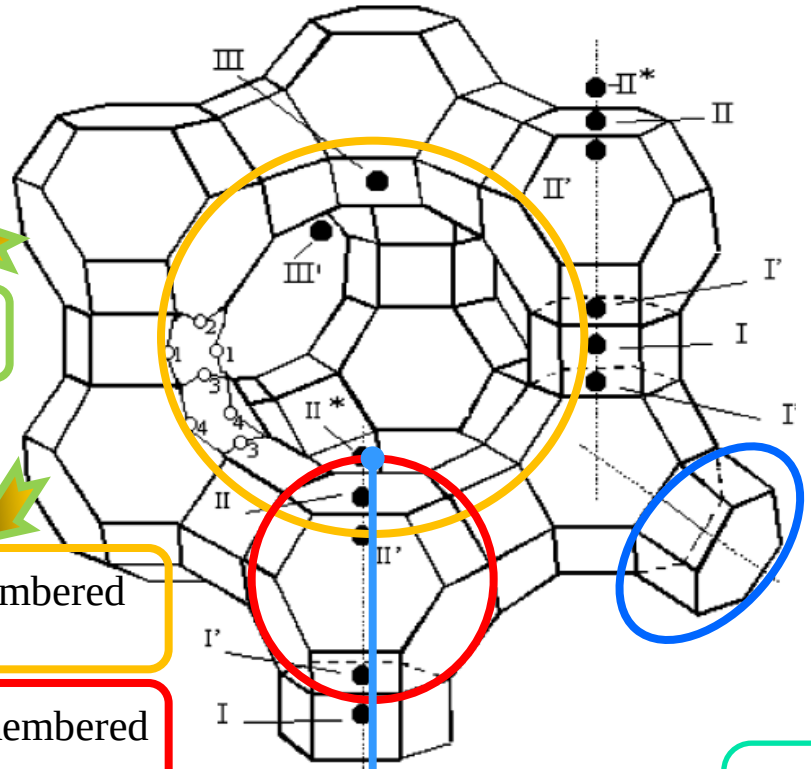
◆ *Zhang, Y.H., et al., **J. Catal.**, 2007, 251(2): 443-452*

Cu^{+}-SSIE catalyst

big pore volume

high surface area

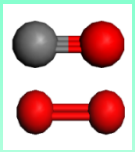
hydrothermal stability



supercage with 12 membered ring (7.4 Å)

sodalite cages with 6 membered ring (2.3 Å)

hexagonal prisms with double 6 membered ring (2.3 Å)



kinetic diameter:
CO 3.76 Å; O_2 3.46 Å

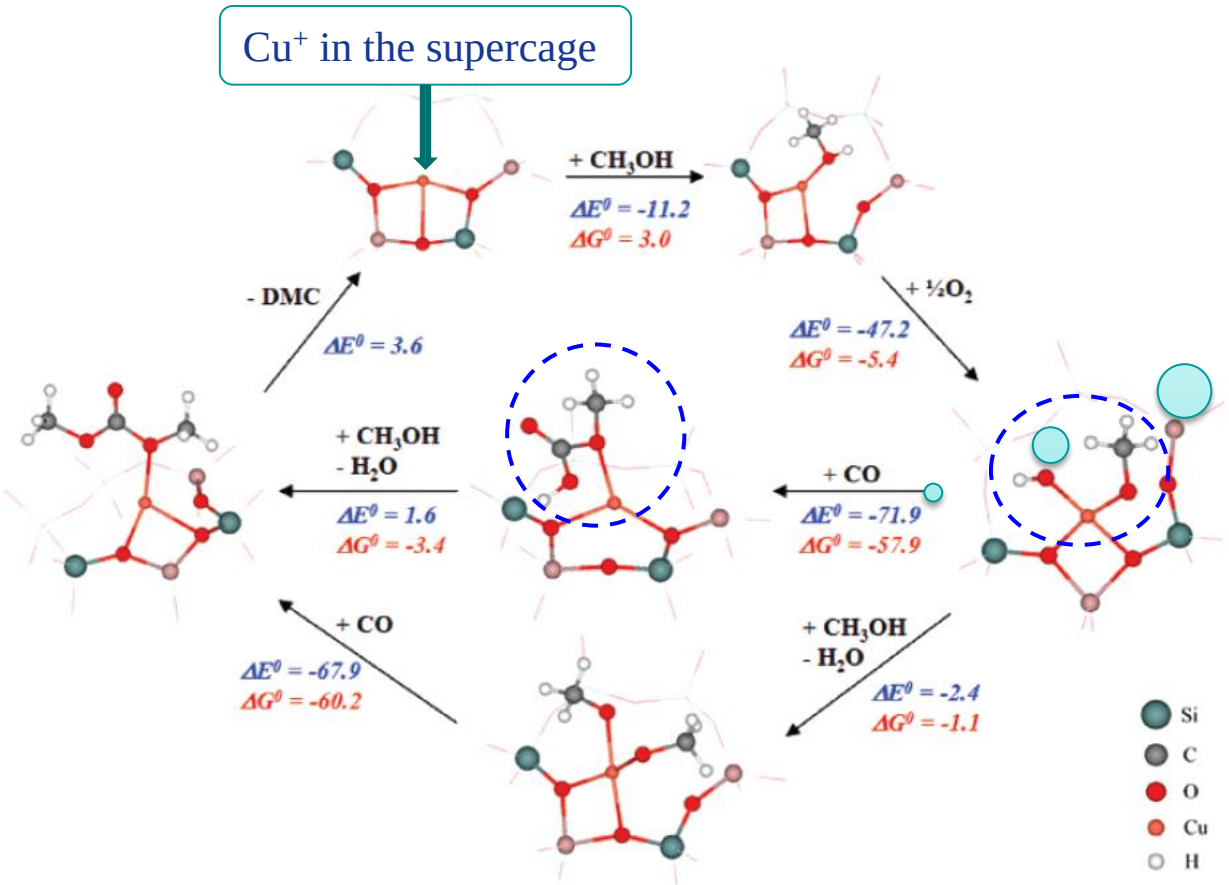
Reactant can not enter into the sodalite cage or hexagonal prism.

Cu^{+} in the supercage shows the best catalytic activity.

- *Angew Chem int Ed. 2005, 44: 4774.*
- *Appl Catal A: Gen. 2010, 382: 303.*
- *Phys Chem Chem Phys. 2012, 14: 2183.*
- *Catal Rev. 2006, 48: 269.*

Cu^+-SSIE catalyst

✓ **The mechanism of DMC synthesis on Cu-exchanged zeolite Y**



CO insertion is the rate-determining Step.

- *Zhang, Y.H., A.T. Bell, J.Catal., 2008, 255(2): 153-161*
- *Zheng, X.B., A.T. Bell, J.Phys. Chem. C, 2008, 112(13): 5043-5047*

Cu^{+}-SSIE catalyst

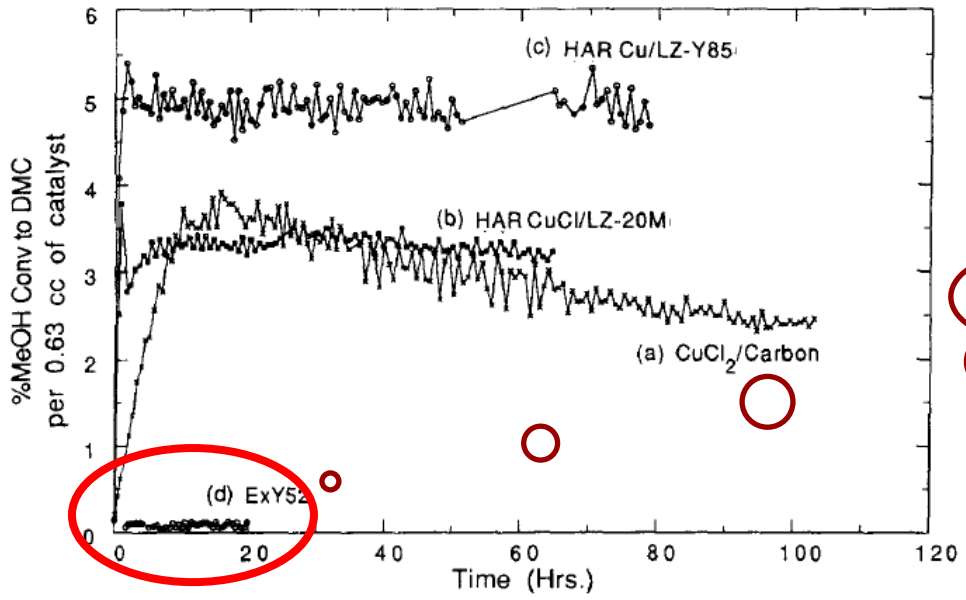
Problems:

- CuCl refining process is complicated.
- Pipe blocked and low-efficiency because CuCl is easy to sublimate, solid reaction is insufficient.
- **CuCl can not be removed completely**, still leading to catalyst deactivation and corrosion of equipment.

☼ **Cu-based catalyst prepared with chlorine-free copper salt could solve the problems.**

Chlorine-free CuY catalyst

The chlorine-free CuY catalyst is prepared by **solution phase ion exchange** of **copper nitrate** solution with the NaY zeolite.



Cu^{2+} in Y zeolite shows low catalytic performance.

✓ **Introducing high temperature activation to achieve high catalytic activity.**

◆ *King, S.T., J. Catal., 1996, 161(2): 530-538*

CuY catalyst

➢ High temperature activation

Effect of activation temperature on CuY catalytic performance

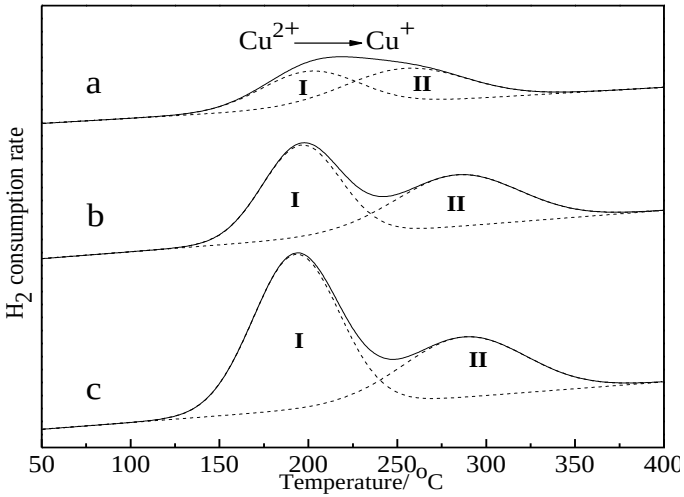
Catalysts	Calcination Temperature /°C	STY_{DMC}/ $mg \cdot g^{-1} \cdot h^{-1}$	S_{DMC}/%	X_{CH3OH}/%
CuY	-	19.77	46.75	1.38
CuY500	500	98.95	69.67	4.73
CuY600	600	131.44	68.53	6.50
CuY700	**700**	**134.02**	**68.61**	**6.65**
CuY750	750	89.43	69.40	4.27

➢ CuY Catalyst shows good catalytic performance after activated between **600 ~ 700°C**

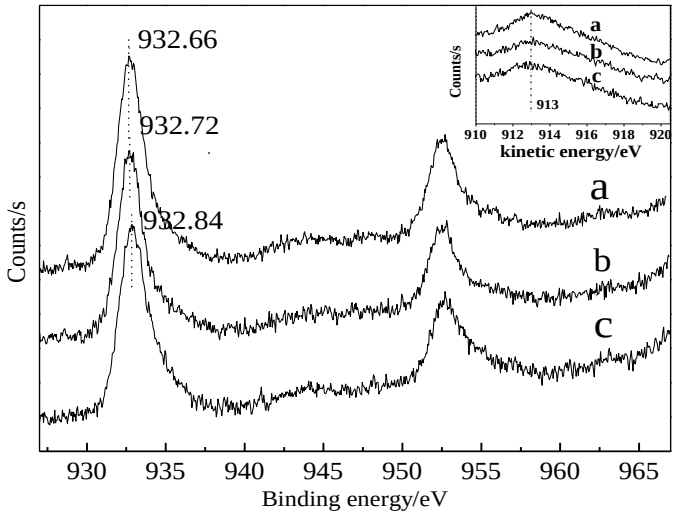
- **Li Z*, Fu T, Wang R, *et al. Chem J Chin U*, 2011, 32(6): 1366-1372**

CuY catalyst

- **High temperature activation**



H_2-TPR profiles of CuY catalyst



XPS spectra of CuY catalyst

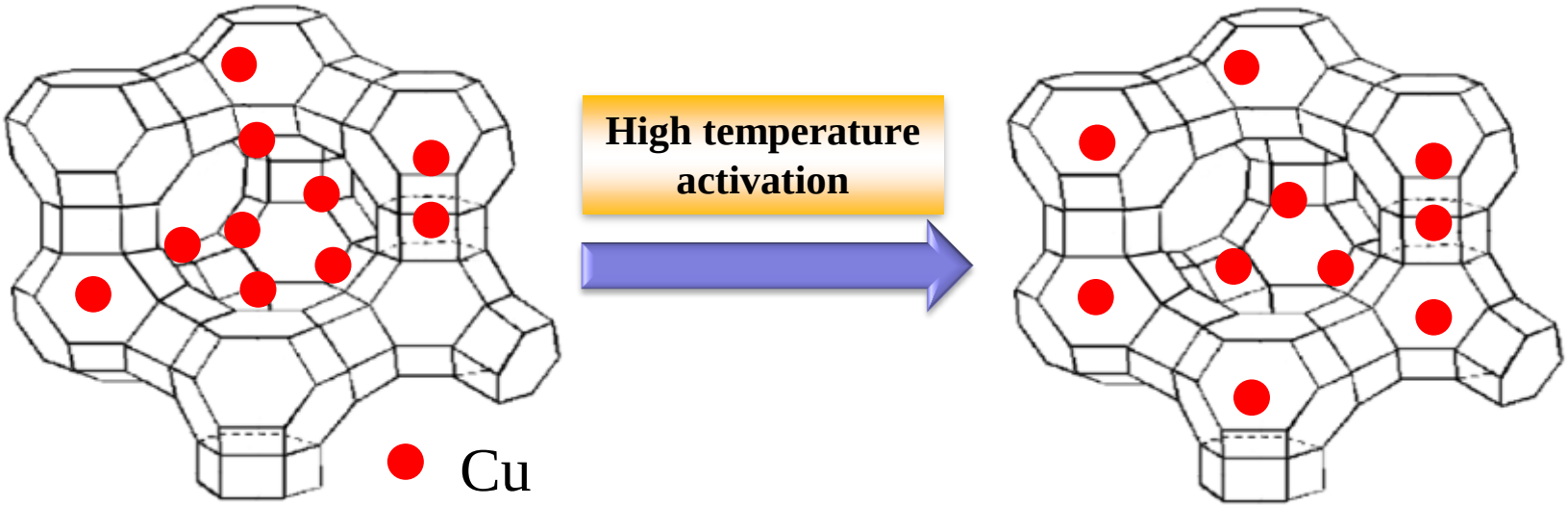
a.CuY700； b. CuY500； c. CuY400

- Cu^{2+} in the supercage would be easily auto-reduced to Cu^{+} in the activation process.
- High activation temperature promote Cu^{2+} migrated into the sodalite cages and hexagonal prisms.
- Auger kinetic energy of Cu^{+} is lower 3eV than pure Cu_2O.

- **Li Z*, Fu T, Wang R, *et al. Chem J Chin U*, 2011, 32(6): 1366-1372**

CuY catalyst

Principle of Cu location Controlling



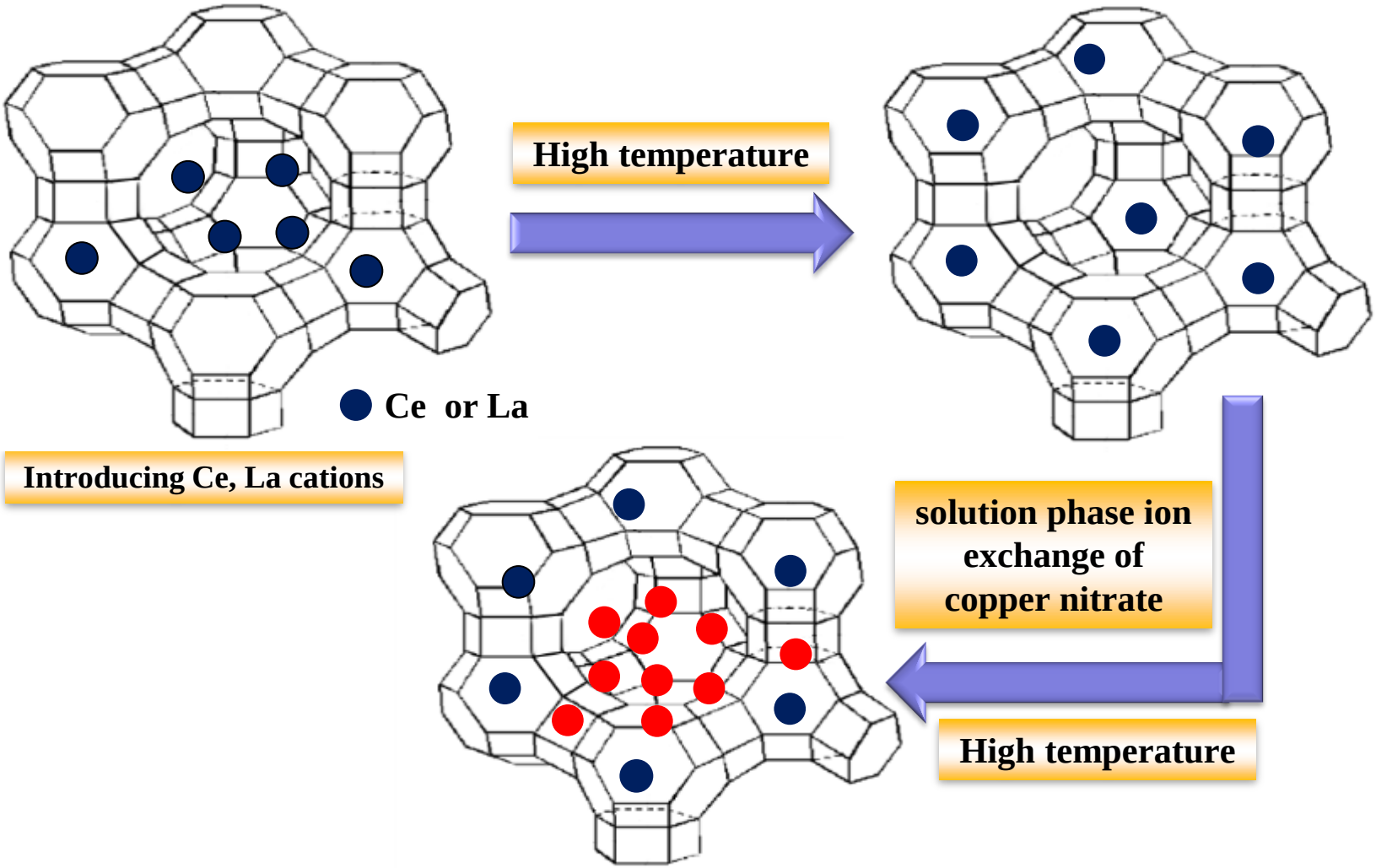
- Cu^{2+} is auto-reduced to Cu^{+}.
- Cu migrates into small cage.

How to hinder Cu migrate into the small cage ?

- Li Z*, Fu T, Wang R, *et al. Chem J Chin U*, 2011, 32(6): 1366-1372

CuY catalyst

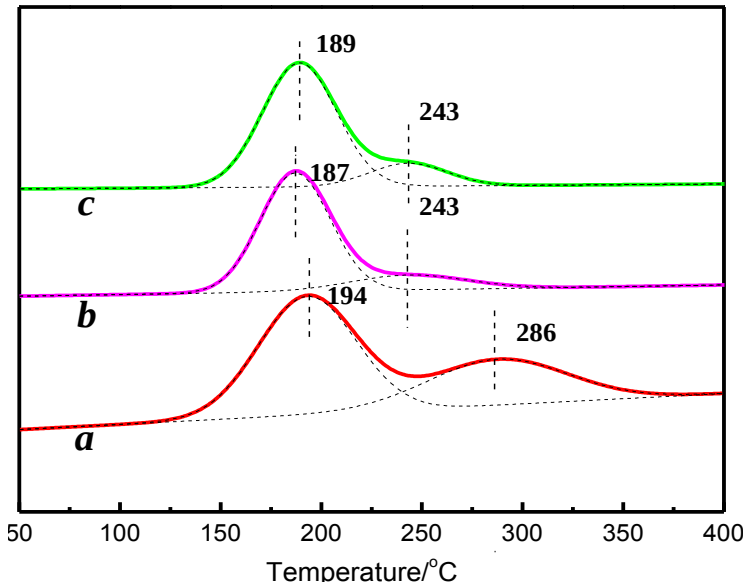
Principle of Cu location Controlling



Fu T, Zheng H, Niu Y, Li Z*. *Acta Chim Sinica*, 2011, 69(15): 1765-1772

CuMY catalyst

Effect of metal cation on Cu location



H_2-TPR profiles and gaussion fitting of the catalysts (a) CuY; (b) CuLaY; (c) CuCeY

Quantitative analysis of H_2-TPR profiles

Catalysts	T_m[a](°C)		Cu_{sup}/(Cu_{sod}+Cu_{hex})
	Supercage	Sodalite cavity and hexagonal prism	
CuY	194(62.0)[b]	286(38.0)	1.63
CuLaY	187(82.9)	243(17.1)	4.85
CuCeY	189(83.8)	243(16.2)	5.17

[a] Temperature at which the Cu^{2+}→Cu^{+} reduction rate is maximum.

[b] The percentage of Cu^{2+} ions located in the cage is given in brackets.

- The Cu located in the supercage is promoted by introducing Ce or La into small cage.

- Fu T, Zheng H, Niu Y, Li Z*. *Acta Chim Sinica*, 2011, 69(15): 1765-1772

CuMY catalyst

Effect of metal cation on CuY catalytic performance

Catalysts	Cu mass[a]/%	Cu mass[b]/%	X_{CH3OH}/%	S_{DMC}/%	STY_{DMC}/mg·g^{-1}·h^{-1}
CuY	6.77	5.85	6.50	68.53	131.4
CuCeY	6.63	5.05	7.43	65.86	145.1
CuLaY	6.59	4.88	8.62	64.79	166.3

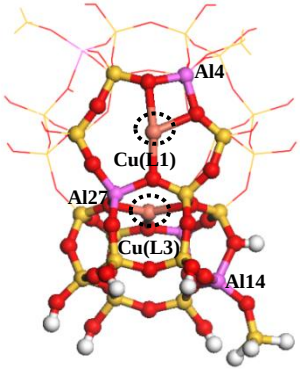
a Cu mass percent of bulk phase measured by AAS.
b Cu mass percent of epiphase measured by XPS.

- Cu content are similar among the catalysts, which implies that introducing Ce or La doesn't influence the exchange degree of Cu cation and Y zeolite.
- The catalytic performance of CuY catalyst are improved by introduction of Ce or La cation.

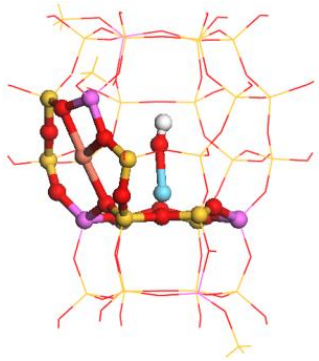
- **Fu T, Zheng H, Niu Y, Li Z*.** ***Acta Chim Sinica*****, 2011, 69(15): 1765-1772**

CuMY catalyst

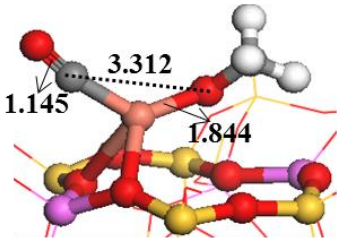
Effect of metal cation on Cu location



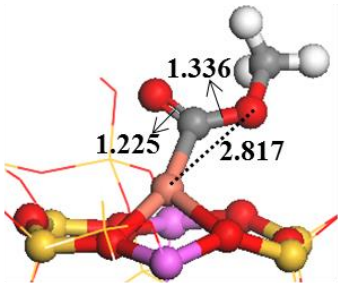
(a) CuCuY-I′^{A}



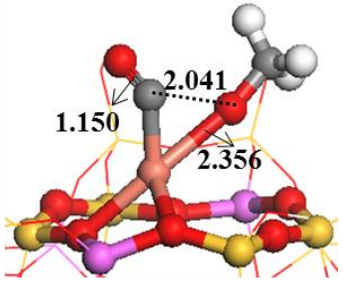
(b) CuMY-I′^{B}(La, Ce)



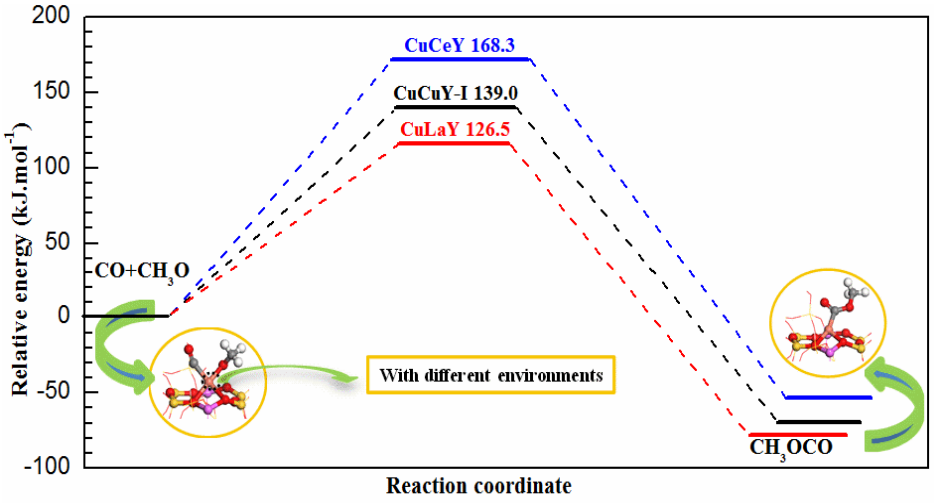
(a) CO/CH_3O on CuCuY-I′^{A}



(b) CH_3OCO on CuCuY-I′^{A}



(c) TS on CuCuY-I′^{A}



✓ **Introducing metal cation not only adjusts more Cu located in the supercage, but also changes the environment around the active center Cu^{+}.**

Zheng H, Qi J, Zhang R, **Li Z***, Wang B, Ma X. *Fuel Process Technol*, 2014, 128: 310-318

CuMY catalyst

➢ Effect of metal cation on environment around Cu^+

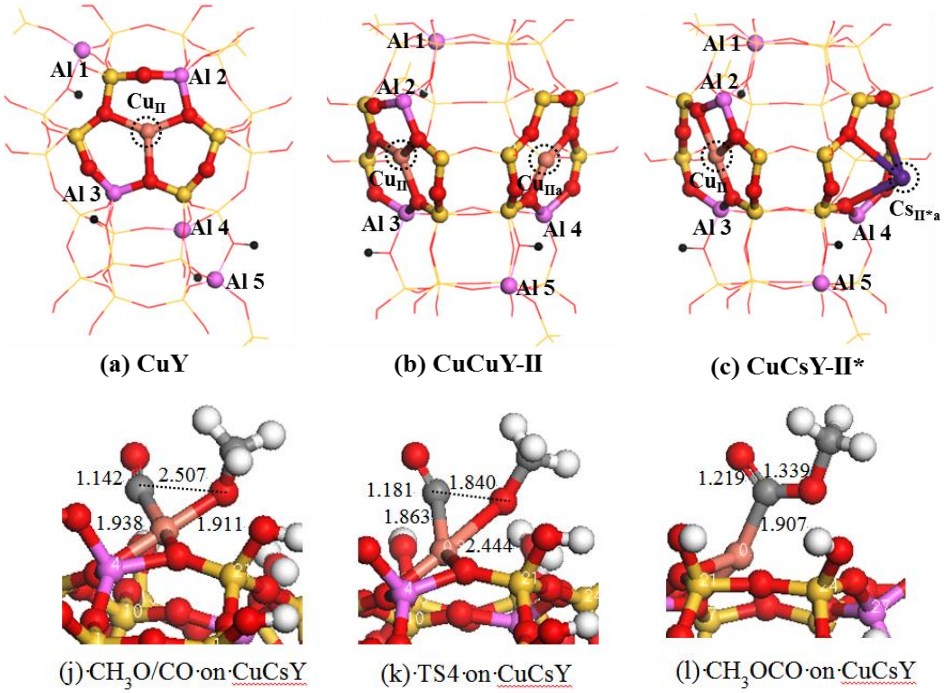
Catalysts	T_M[a] /°C		Cu_{sup}/ (Cu_{sod}+Cu_{hex})	STY_{DMC}/mg •g^{-1}•h^{-1}
	Supercage	Sodalite and hexagonal prism		
CuY	194(62.0)[b]	286(38.0)	1.63	131.4
CuCsY	191(54.7)	276(45.3)	1.21	176.5

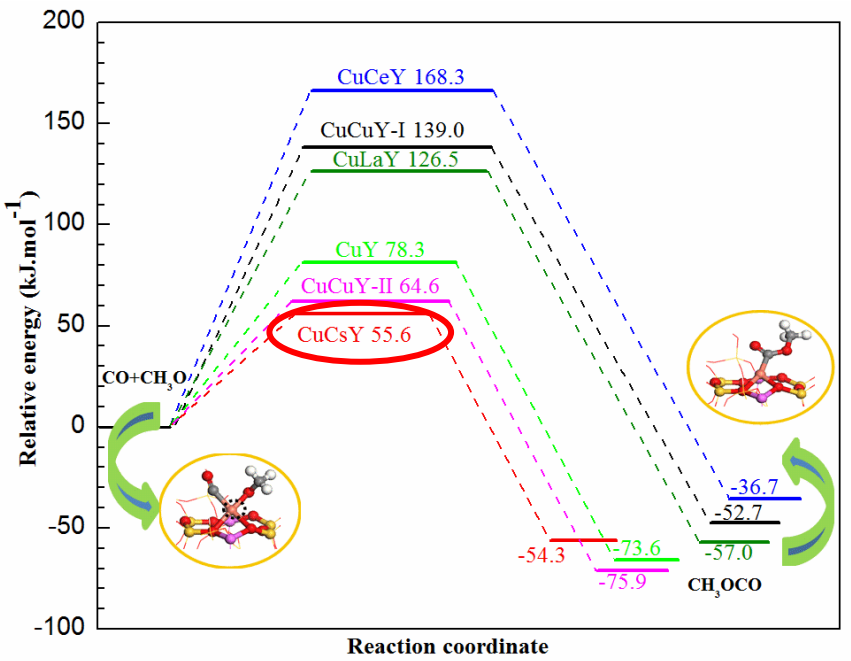
◆ Introduction of Cs cation decreases the ratio of Cu located in the supercage. However, CuCsY catalyst shows the best activity.

➢ Fu T, Zheng H, Niu Y, **Li Z*.** *Acta Chim Sinica*, 2011, 69(15): 1765-1772

CuMY catalyst

➢ Effect of metal cation on Cu location





✓ Introducing Cs species into the supercage of CuY zeolite significantly improves the adsorption energy of co-adsorbed CO and the stability of transition state configuration for CO insertion reaction.

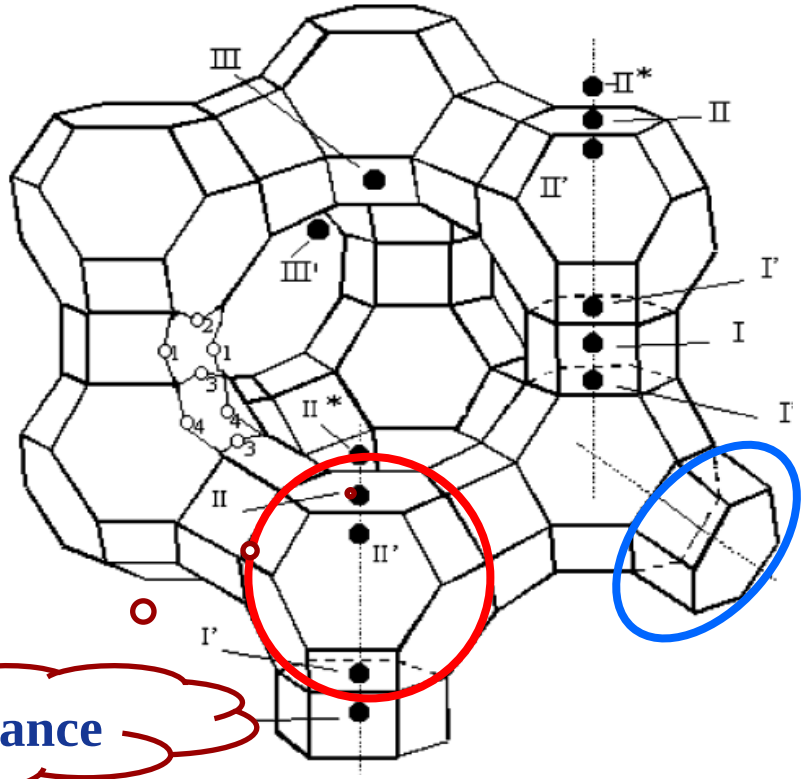
➢ Zheng H, Qi J, Zhang R, **Li Z***, Wang B, Ma X. *Fuel Process Technol*, 2014, 128: 310-318

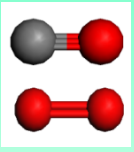
CuY catalyst

supercage (7.4 Å)

sodalite cages (2.3 Å)

hexagonal prisms (2.3 Å)





kinetic diameter:
CO 3.76 Å; O_2 3.46 Å

Steric hindrance

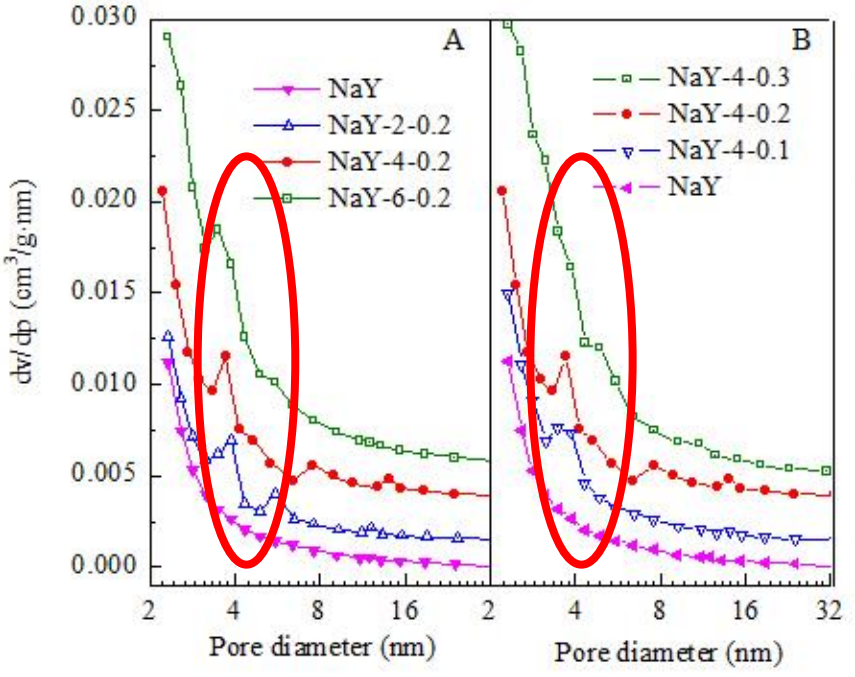
Reactant can not enter into the solid cage or hexagonal prism.

✓ **Mesopores formed by acid or alkali treatment can promote the accessibility of active sites.**

➢ Li J, Zheng H, Li Z*. *Chin. J Inorg. Chem.*, 2015, accepted

CuY catalyst

NaY zeolite treated with oxalic acid

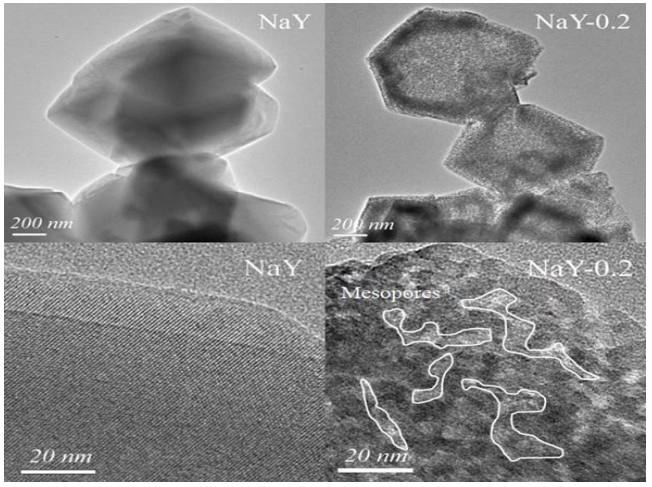


Mesopore size distribution of NaY zeolites

Textural properties for NaY zeolites

Zeolites	S_{BET} (m^2/ g)	S_{micro} [a] (m^2/ g)	S_{ext} [a] (m^2/g)	V_{micro} [b] (cm^3/g)	V_{meso} [b] (cm^3/g)
NaY	517	486	30	0.251	0.012
NaY-2-0.2	549	489	59	0.261	0.041
NaY-4-0.2	440	314	125	0.164	0.079
NaY-6-0.2	513	413	99	0.183	0.061
NaY-4-0.1	491	422	68	0.195	0.038
NaY-4-0.3	298	249	49	0.102	0.020

[a] :calculated by t-plot method. [b] :volume adsorbed at p/p=0.99



TEM

✓ **About 4nm Mesopores are formed by acid treatment.**

➢ Li J, Zheng H, Li Z*. *Chin. J Inorg. Chem.*, 2015, accepted

CuY catalyst

NaY zeolite treated with oxalic acid

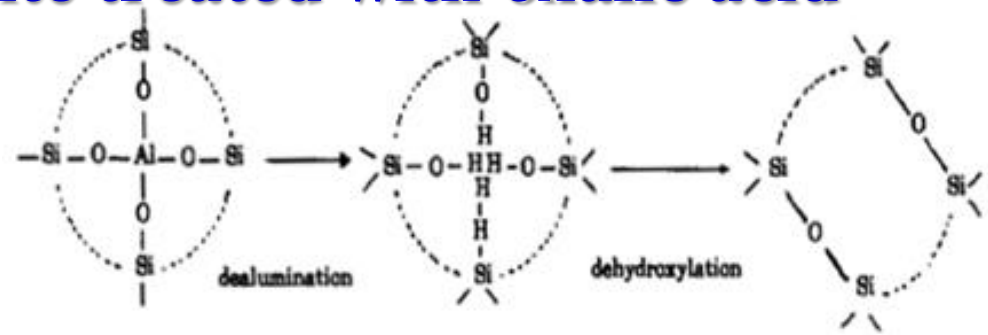
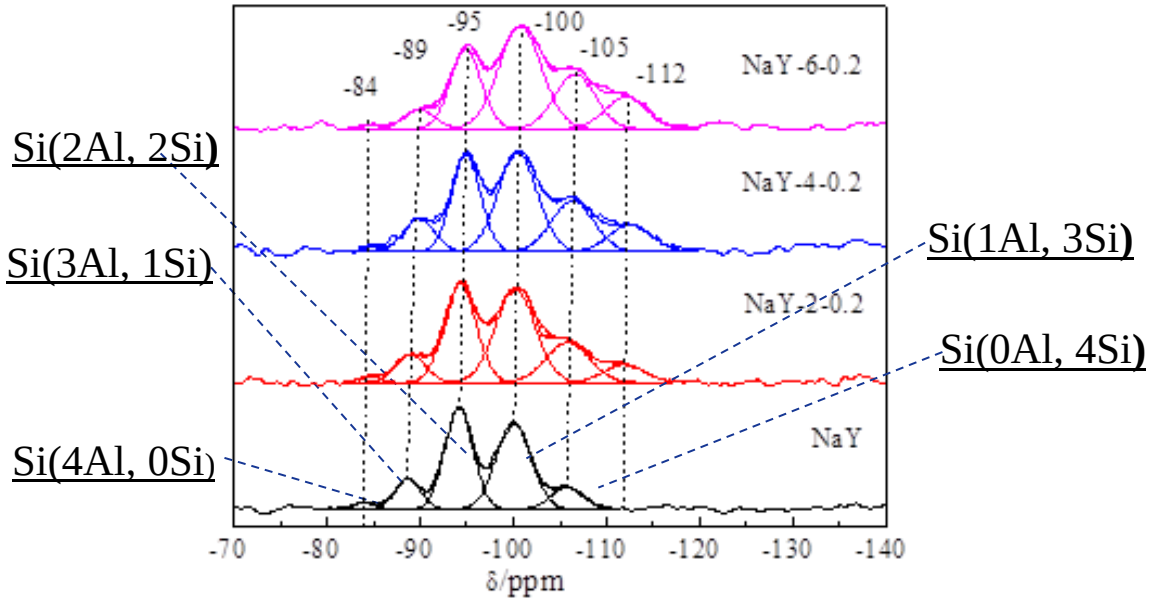
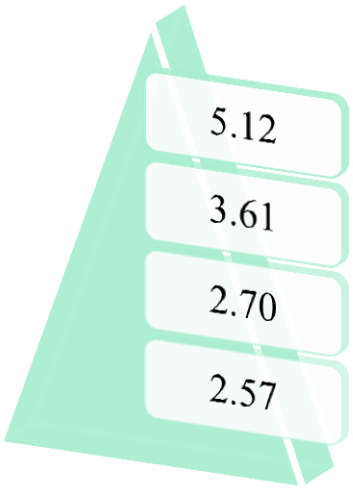


Diagram of the formation of hydroxyl nests and aluminum vacancies



^{29}Si MAS NMR patterns of NaY zeolites

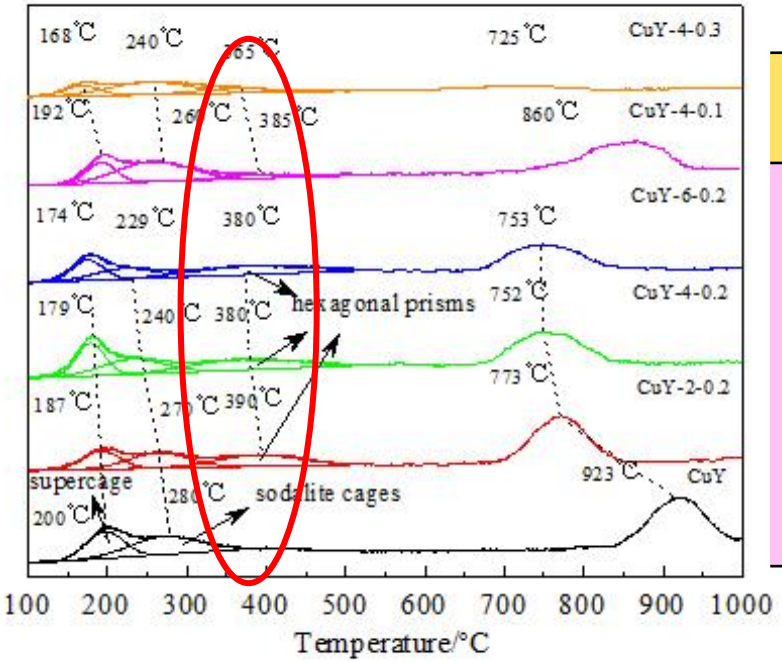


The framework Si/Al of NaY

- Li J, Zheng H, Li Z*. *Chin. J Inorg. Chem.*, 2015, accepted

CuY catalyst

NaY zeolite treated with oxalic acid

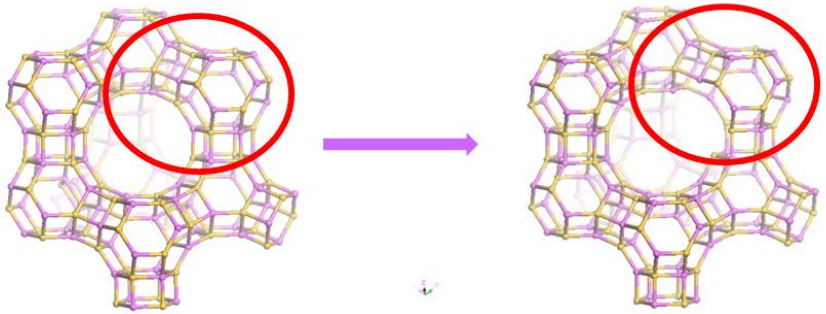


H_2-TPR profiles and gaussion fitting of the catalysts

Catalysts	Cu wt%	X_{CH_3OH} mol%	STY_{DMC} $mg \cdot g^{-1} \cdot h^{-1}$	DMC selectivity
CuY	5.6	6.3	103.6	63.1
CuY-2-0.2	5.4	6.4	127.8	65.9
CuY-4-0.2	5.4	10.2	184.9	61.3
CuY-6-0.2	5.2	7.8	155.3	66.2
CuY-4-0.1	5.3	6.4	119.5	61.7
CuY-4-0.3	2.6	1.6	38.7	76.3

Reaction conditions: 26.7% MeOH, 66.7% CO, 6.7%O_2, SV=5600 h^{-1}, m(cat) =0.45g, T =140℃, t =10h.

- ✓ The sodalite cages are partially broken.
- ✓ Cu species in the smallcage can contact with the reactant, increasing the catalytic activity.

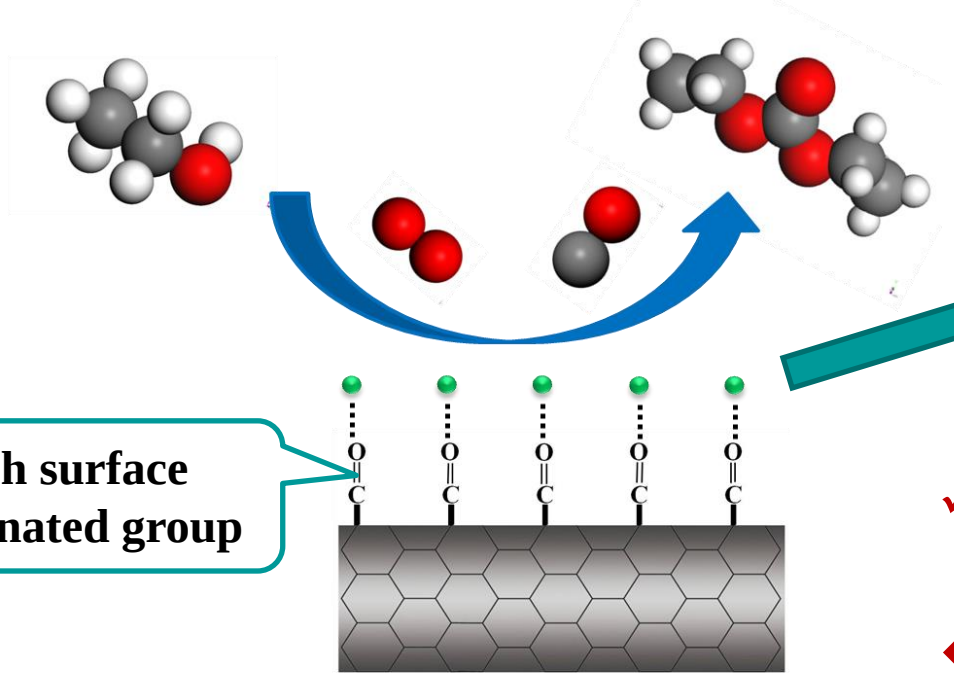


- Li J, Zheng H, Li Z*. *Chin. J Inorg. Chem.*, 2015, accepted

Summary

- ✓ **Cu^{+}-SSIE catalyst provides similar environment around the active center Cu^{+} with CuCl, showing a good catalytic activity.**
- ✓ **Cu^{+} in the supercage is the active center of oxidative carbonylation reaction.**
- ✓ **Cu^{2+} in the CuY catalyst is auto-reduced to Cu^{+} during the high temperature activation process.**
- ✓ **Introducing metal caution, not only adjusts more Cu located in the supercage, but also changes the environment around the active center Cu^{+},**
- ✓ **Mesopores in Y zeolite make the reactant molecular easily access the active sites,resulting in the improvement of catalytic activity.**

Cu/AC catalyst



Rich surface oxygenated group

Activated Carbon

$CuCl_2/AC$

$Cu_2(OH)_3Cl/AC$

✓ **Good activity.**

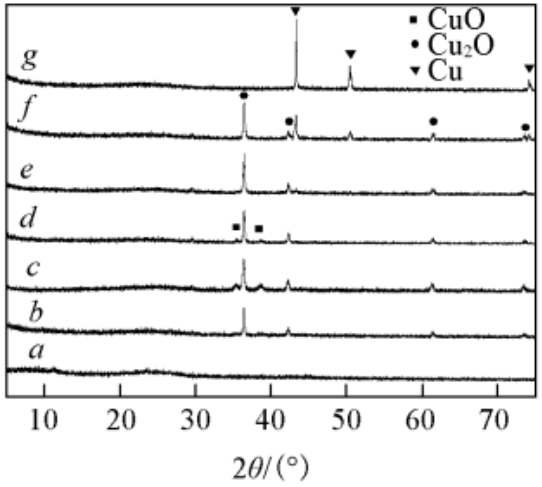
◆ **Cl^- loss**
- Catalyst deactivation.
- Equipment corrosion.
- Environment pollution.

✓ The chlorine-free Cu/AC catalyst is prepared by **pyrolysis of $Cu(CH_3COO)_2$ /AC**.

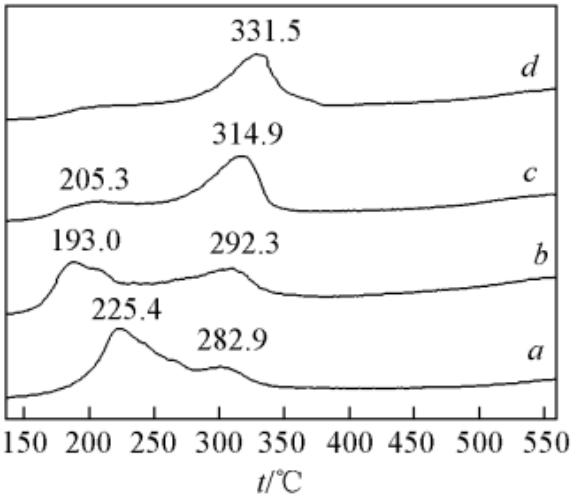
- *AIChE J. 2013, 59(10): 3797-3805.*
- *Angew Chem int Ed. 2005, 44: 4774.*
- *J Catal. 2010, 276(2): 215-228.*
- *Chem Eng J. 2010, 165(1): 78-88.*

Cu/AC catalyst

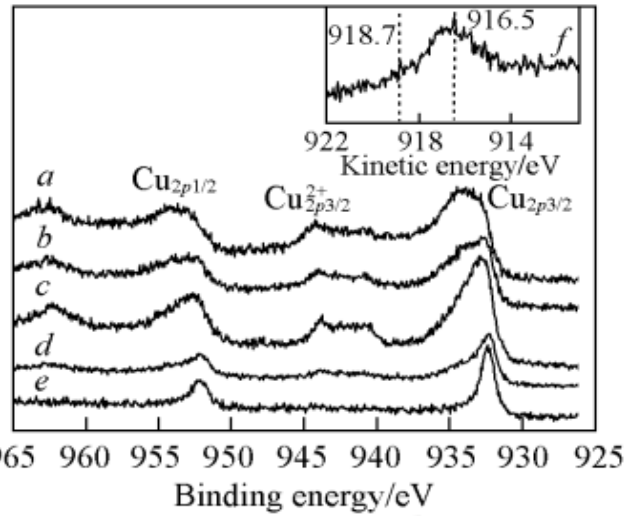
- **Cu/AC catalyst was prepared *via* pyrolysis of $Cu(CH_3COO)_2$ /AC.**



XRD patterns of $Cu(CH_3COO)_2 \cdot H_2O$/AC heat-treated for 4h
a 150 °C, b 200 °C, c 250 °C, d 300 °C, e 350 °C, f 400 °C, g 450 °C



H_2-TPR patterns of $Cu(CH_3COO)_2 \cdot H_2O$/AC heat-treated for 4h
a 200 °C, b 250 °C, c 300 °C, d 350 °C,



Cu $_{2p}$ patterns of $Cu(CH_3COO)_2 \cdot H_2O$/AC heat-treated for 4h
a 150 °C, b 200 °C, c 250 °C, d 300 °C, e 350

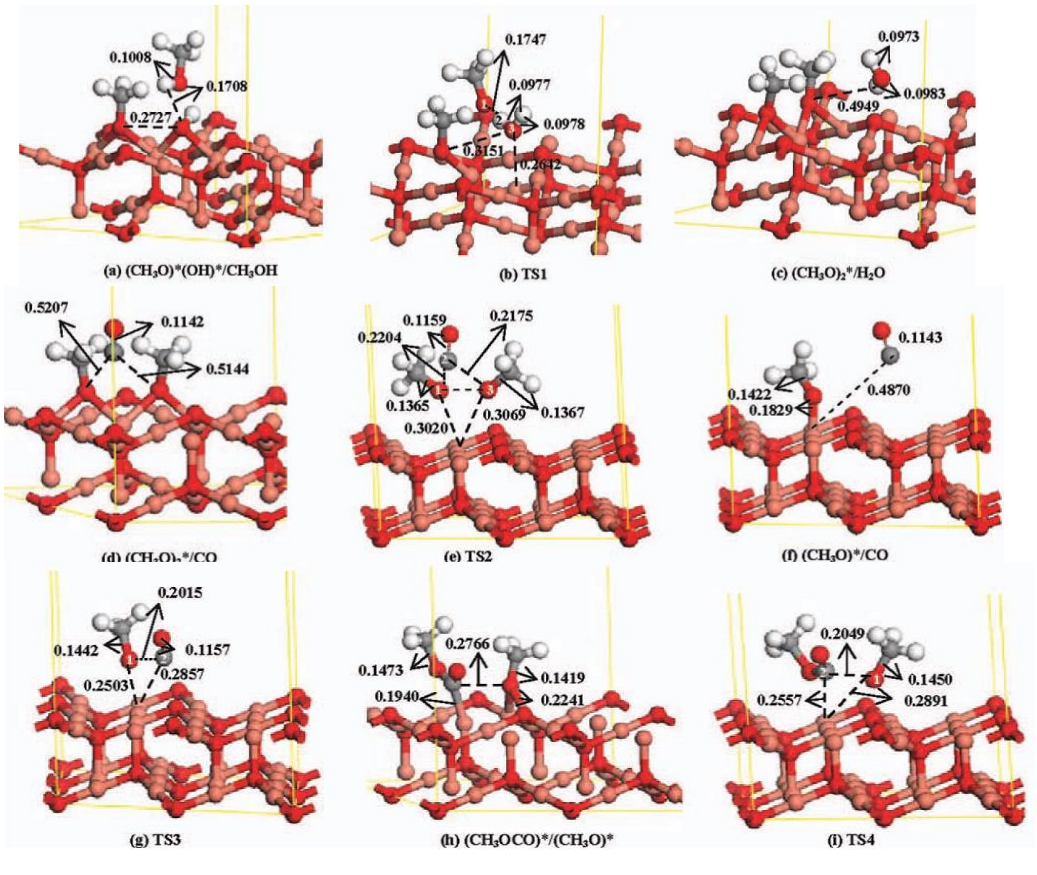
Treatment temperature(° C)	STY_{DMC}/mg·g^{-1}·h^{-1}	C_m/%	S_{DMC}/%	S_{DME}/%	S_{DMM}/%	S_{MF}/%
150	47.83	2.82	35.11	2.57	4.81	57.51
200	76.34	4.15	60.07	0.67	1.68	37.58
250	107.28	5.70	62.38	1.56	3.15	32.91
300	128.16	6.21	64.26	2.24	3.42	30.08
350	123.64	6.29	58.42	4.97	3.73	32.88
400	110.85	6.61	57.55	2.53	3.54	36.38
450	22.53	2.05	52.09	0.94	3.03	43.94

- Cu_2O was main active species.

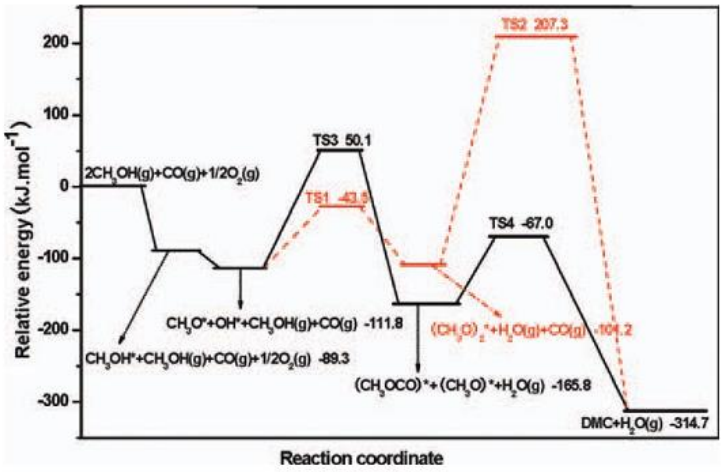
- **Li Z*, Wen C, Wang R, Zheng H, Xie K. *Chem J Chin U*, 2009, 30: 2024-2031**

Cu/AC catalyst

➢ Catalytic mechanism over Cu_2O surface



Optimized coadsorbed structures and transition states over $Cu_2O(111)$ surface

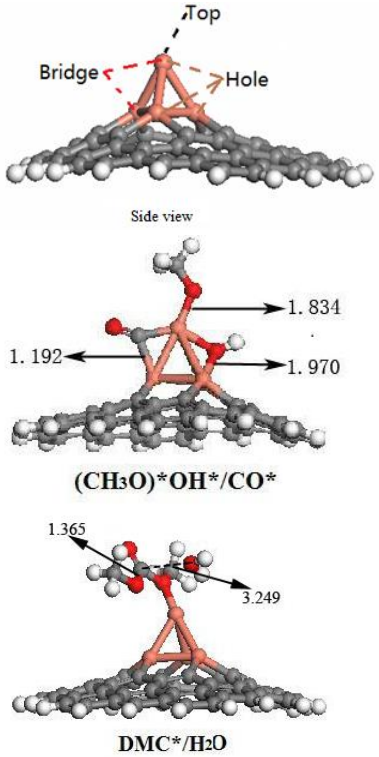


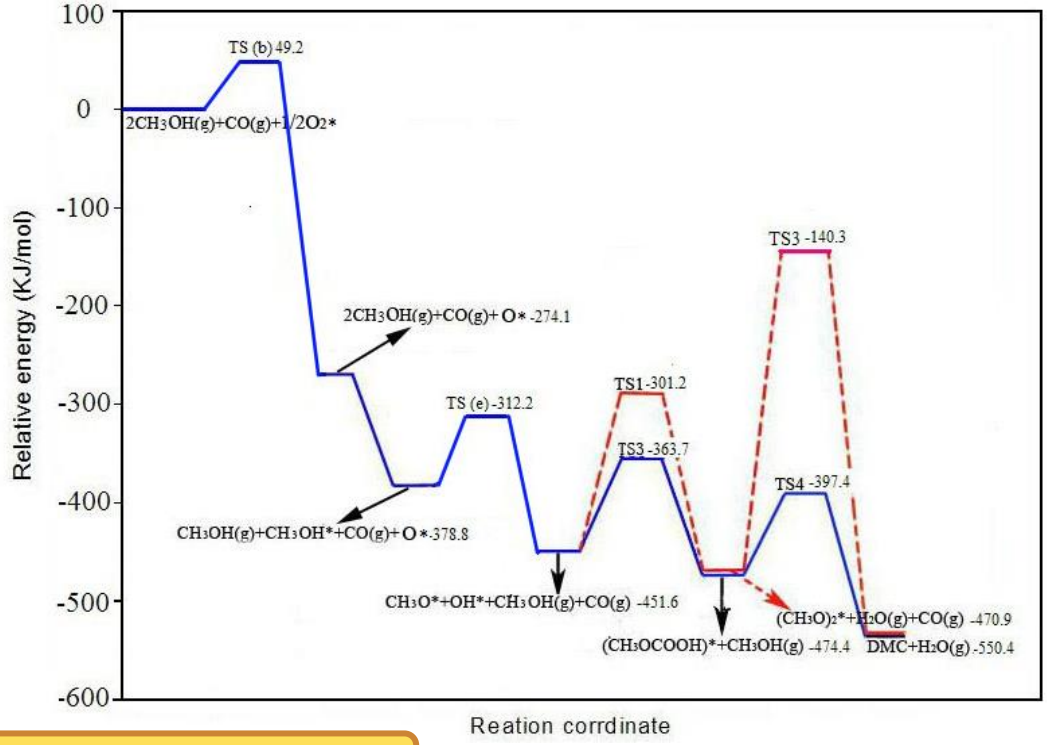
- ✓ O_2 is adsorbed on the surface of $Cu_2O(111)$ with oxygen vacancy defects, and easy to decompose to lattice oxygen, which is conducive to the formation of CH_3O species.
- ✓ CO and CH_3O are co-adsorbed on the surface of $Cu_2O(111)$ to produce monomethyl carbonate species.

- ➢ Zhang R, Song L, Wang B, **Li Z***. ***J Comput Chem,*** 2012, 33: 1101-1110
- ➢ Zhang R, Ling L, **Li Z***, Wang B. ***Appl Catal A-Gen***, 2011, 400: 142

Cu/AC catalyst

➢ Catalytic mechanism over Cu/AC catalyst





✓ **The proposed reaction mechanism:**

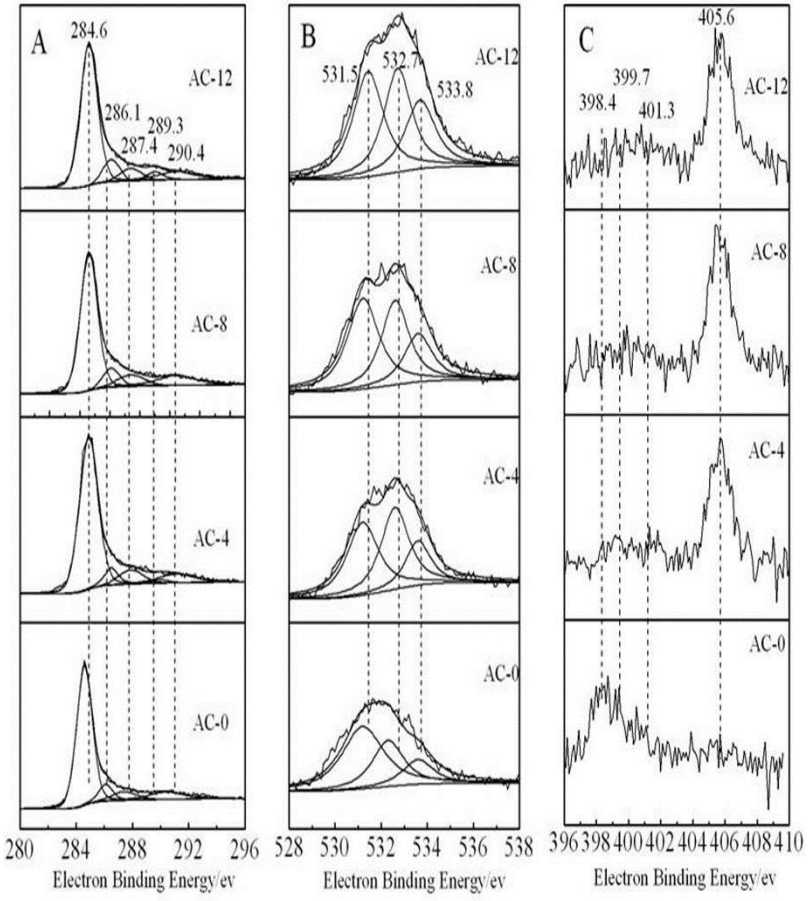
$$(CH_3O)^*(OH)^* + CO \rightarrow (CH_3OCOO\ H)^*$$

$$(CH_3OCOO\ H)^* + (CH_3OH)^* \rightarrow CH_3OCOOCH_3^* + H_2O$$

➢ Ren J, Wang W, Wang D, Zuo Z, Lin J, **Li Z***. ***Appl Catal A: Gen***, 2014, 472: 47-52

Cu/AC catalyst

➢ AC surface modification



XPS spectra of C1s (A), O1s (B), and N1s (C) of the AC samples

Carbon、oxygen and nitrogen contents of the AC samples obtained by XPS

AC Samples	Carbon (wt.%)	Oxygen (wt.%)	Nitrogen (wt.%)
AC-0	91.0	8.0	1.0
AC-4	88.4	10.5	1.1
AC-8	87.1	11.8	1.1
AC-12	84.2	14.7	1.1

surface oxygenated groups of the AC samples determined by Boehm titration

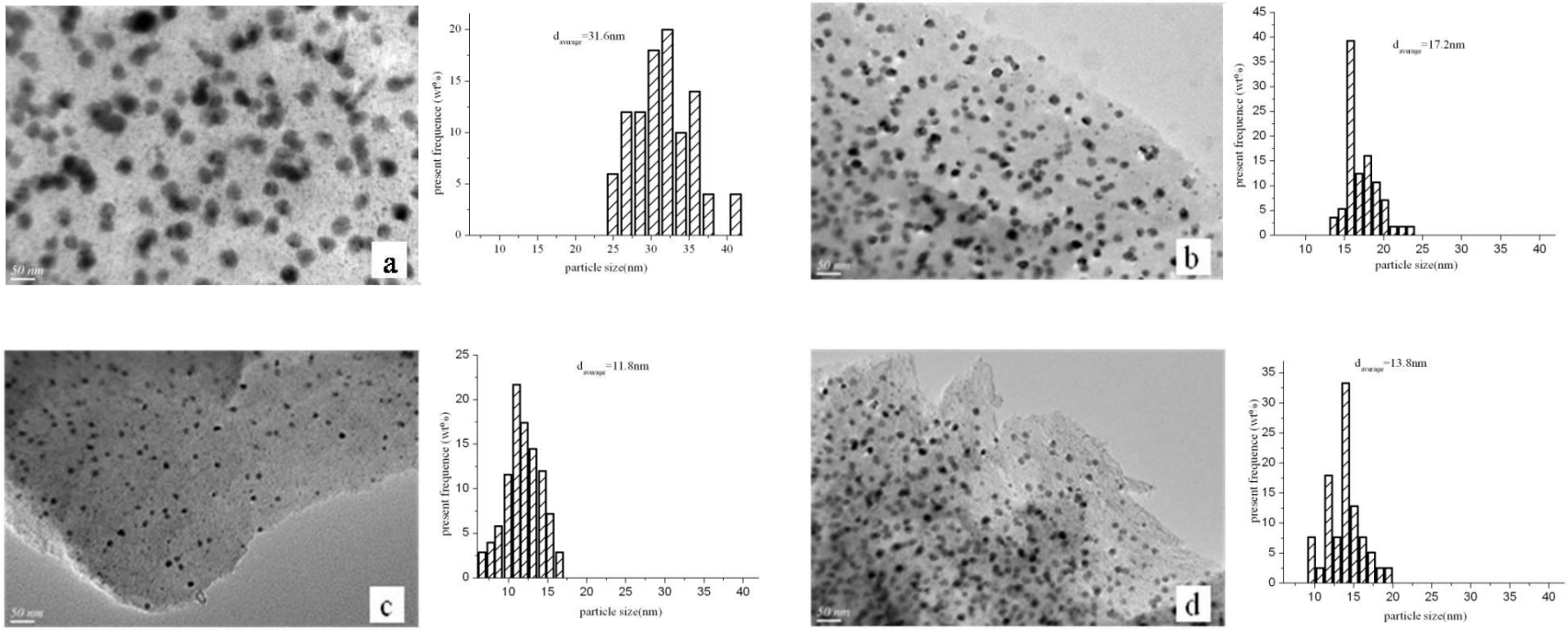
AC samples	Carboxyl group (mmol/g)	Lactonic group (mmol/g)	Phenol group (mmol/g)	Total acidity (mmol/g)
AC-0	0.22	0.03	0.08	0.33
AC-2	0.37	0.12	0.25	0.74
AC-4	0.48	0.14	0.25	0.87
AC-8	0.71	0.15	0.34	1.20
AC-10	0.84	0.29	0.38	1.51
AC-12	1.05	0.32	0.41	1.78

✓ **Acid treatment effectively modify the surface oxygenated groups on AC.**

➢ Zhang G, **Li Z***, Zheng H, Fu T, Ju Y, Wang Y. ***Appl Catal B: environ***, 2015, 179: 95-105

Cu/AC catalyst

➢ AC surface modification



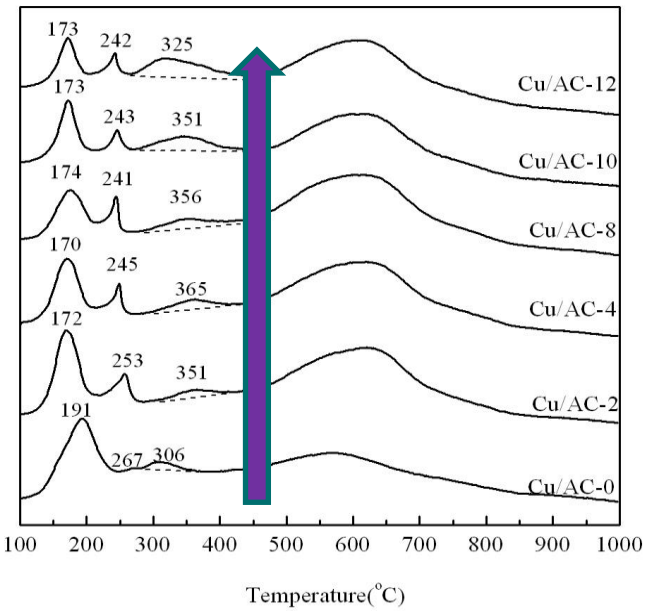
TEM images of catalysts a Cu/AC-0，b Cu/AC-2，C Cu/AC-4，d Cu/AC-8，

✓ **The surface oxygenated group is conducive to the dispersion and valence distributions of copper species.**

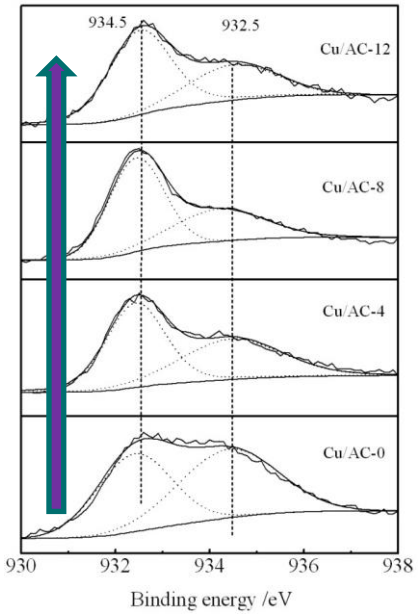
➢ Zhang G, **Li Z***, Zheng H, Fu T, Ju Y, Wang Y. ***Appl Catal B: environ***, 2015, 179: 95-105

Cu/AC catalyst

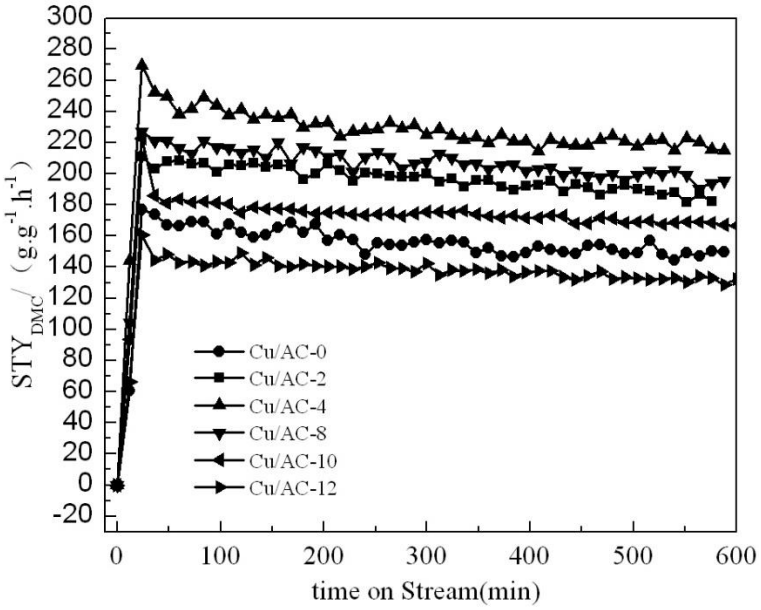
➢ Oxidation state and catalytic activity of Cu/AC catalyst



TPR profiles of Cu/AC catalysts



$Cu2p_{3/2}$ XPS spectra of Cu/AC catalysts



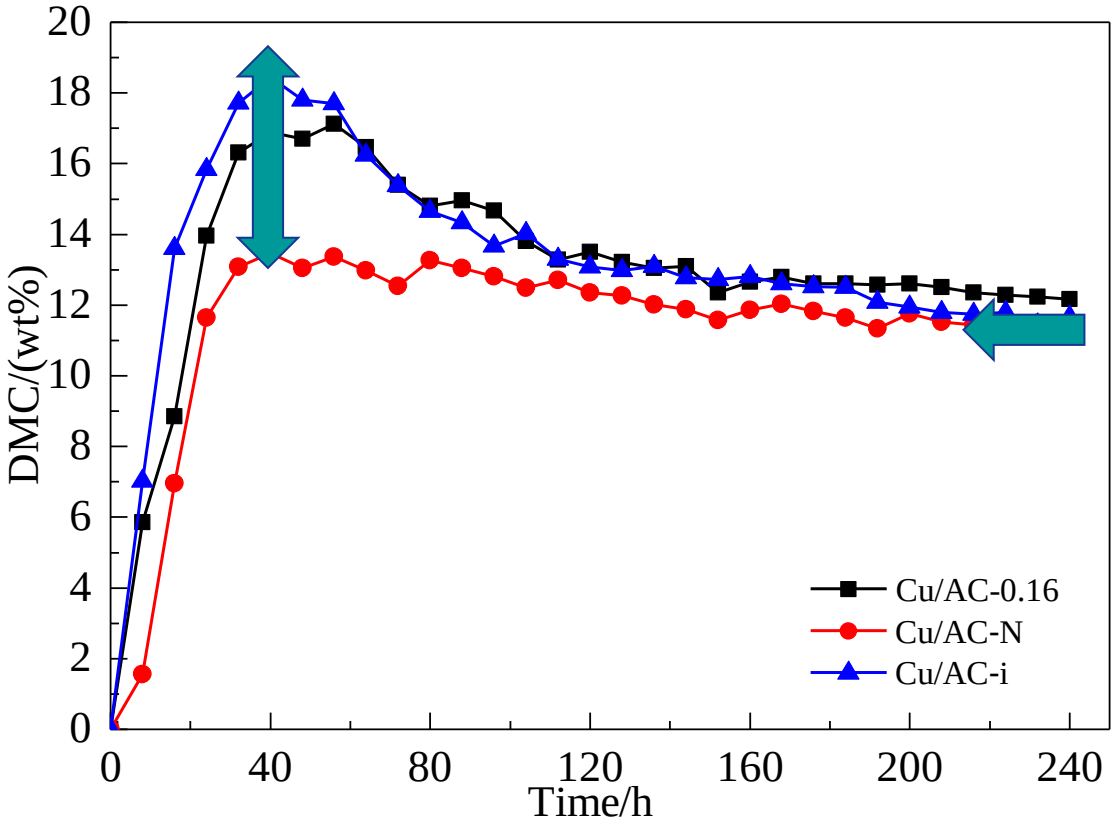
Variation of STY_{DMC} with time on stream on different Cu/AC catalysts

✓ **The optimal catalytic performance is due to the highest dispersion of Cu^+ and Cu^0 species.**

➢ Zhang G, **Li Z***, Zheng H, Fu T, Ju Y, Wang Y. ***Appl Catal B: environ***, 2015, 179: 95-105

Cu/AC catalyst

➢ Cu/AC catalyst applied in liquid phase reaction



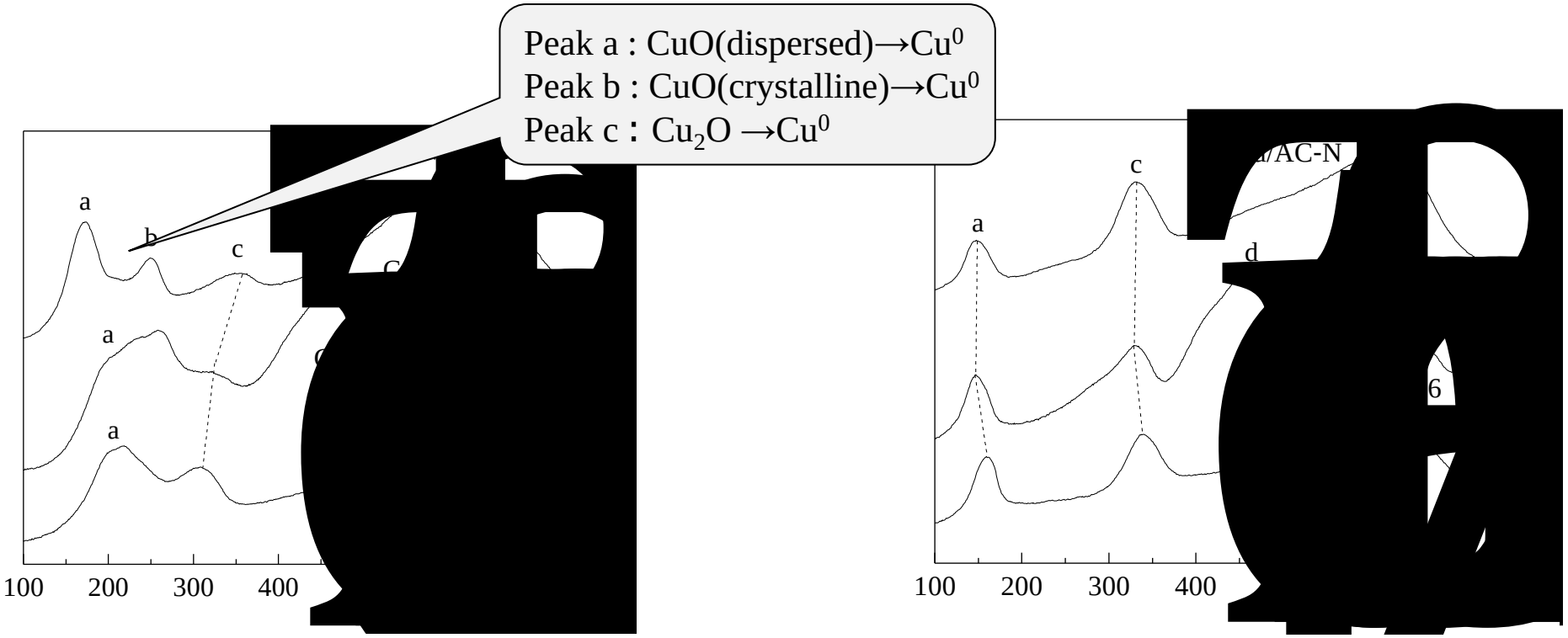
DMC yield of three types of Cu/AC catalysts

- ✓ **The catalytic activities are different in the initial stage.**
- ✓ **Interestingly, they are similar in the stable stage.**

➢ **Li Z***, Ju Y, Zheng H. ***J Catal***, under review.

Cu/AC catalyst

➢ H_2-TPR patterns of Cu/AC catalyst before and after reaction

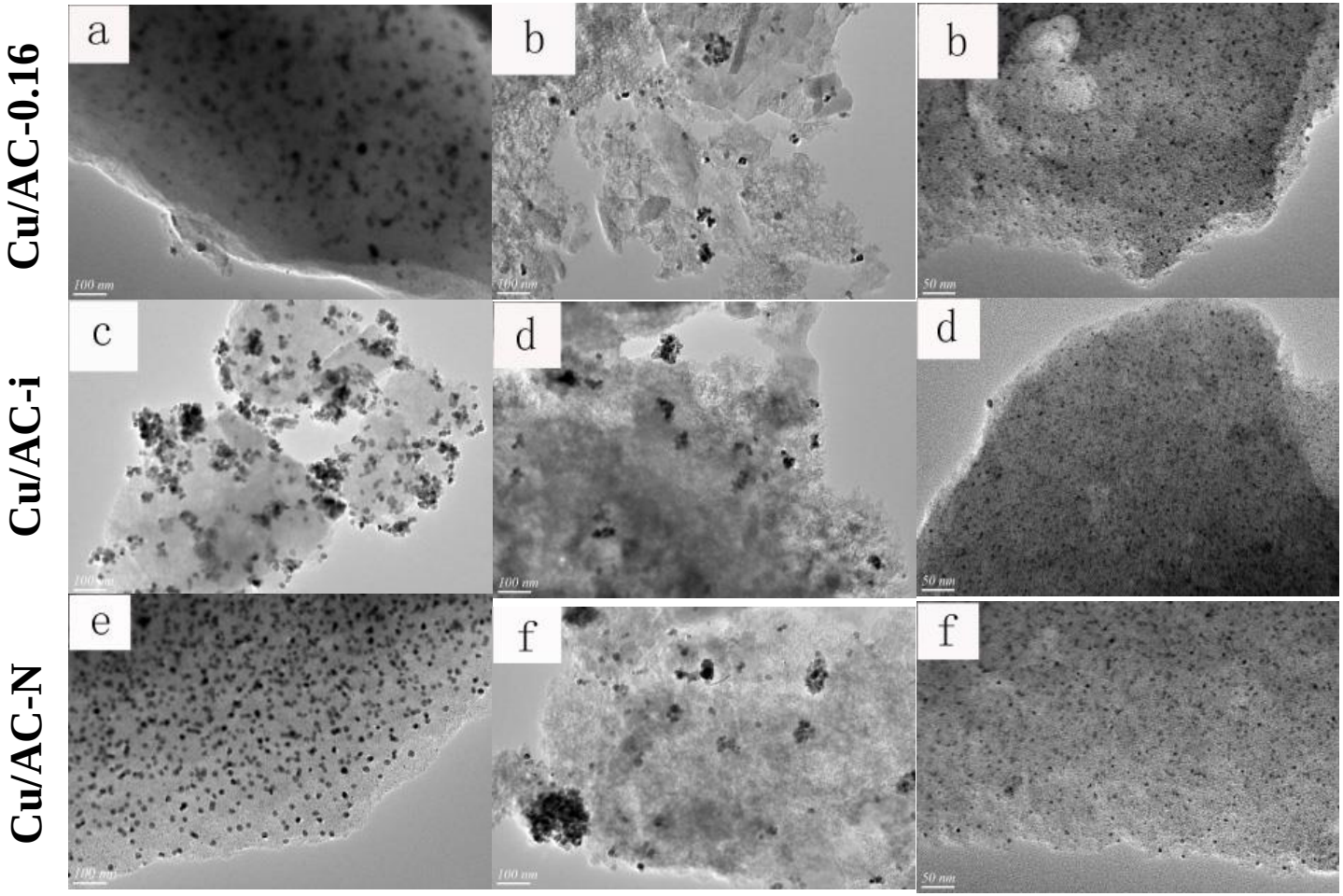


✓ **After reaction, the oxidation and dispersive states of Cu species are similar.**

➢ **Li Z***, Ju Y, Zheng H. ***J Catal***, under review.

Cu/AC catalyst

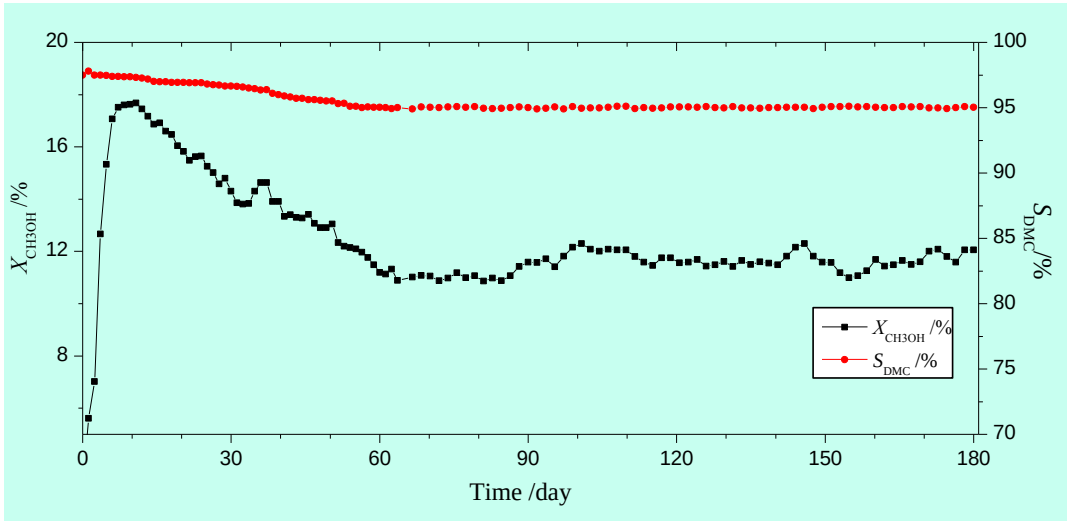
- **TEM of Cu/AC catalyst before and after reaction**



- **Li Z***, Ju Y, Zheng H. ***J Catal***, under review.

Dimethyl Carbonate synthesis

➢ Catalytic activity and stability in 180 day



- Methanol conversion >12%
- DMC selectivity ≈ 95%
- Activity better than CuCl catalyst
- No equipment corrosion & environment pollution problem
- The project is being conducted in pilot scale.

Summary

- Cu_2O was main active species of Cu/AC catalyst for oxidative carbonylation reaction.
- O_2 adsorbed on $Cu_2O(111)$ is easily to promote the formation of CH_3O species. With CO adsorbed on $Cu_2O(111)$, monomethyl carbonate species are formed.
- The surface oxygenated group is favor to the reduction of Cu^{2+} to active Cu^{+} species.
- Cu/AC catalyst applied in liquid phase reaction exhibits excellent catalytic activity and stability.

Acknowledgement

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Prof. Riguang Zhang

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Dr. Fanhui Meng

Dr. Tingjun Fu,

Dr. Hanqing Zhao

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Thanks!

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