中国科学院大连化学物理研究所
DALIAN INSTITUTE OF CHEMICAL PHYSICS,CHINESE ACADEMY OF SCIENCES

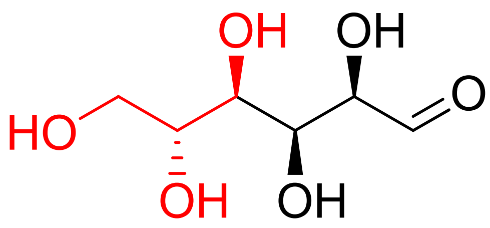
大连化物所第十届青年学术报告会

催化转化丙三醇制备高附加值化学品

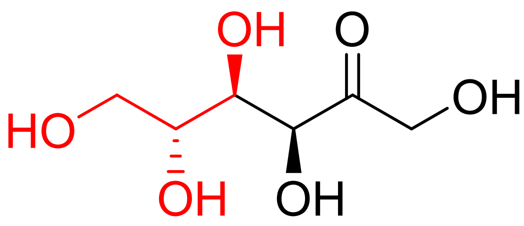
王峰

September 29, 2010

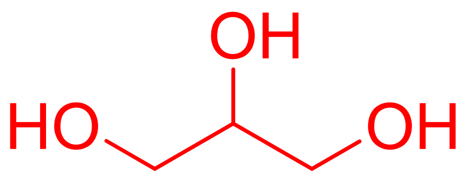
丙三醇是多元醇的基本结构单元



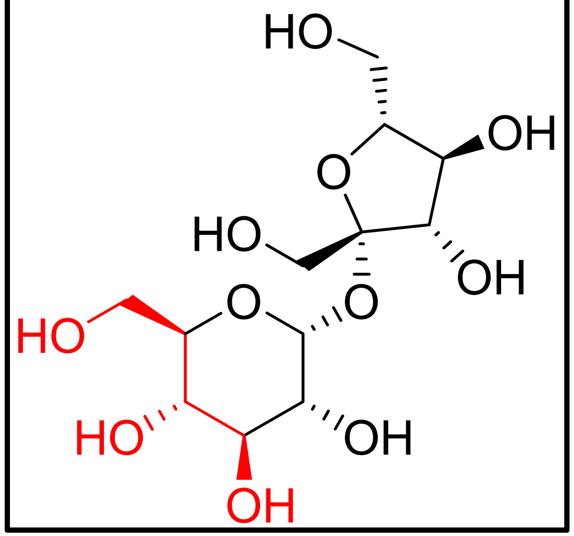
glucose

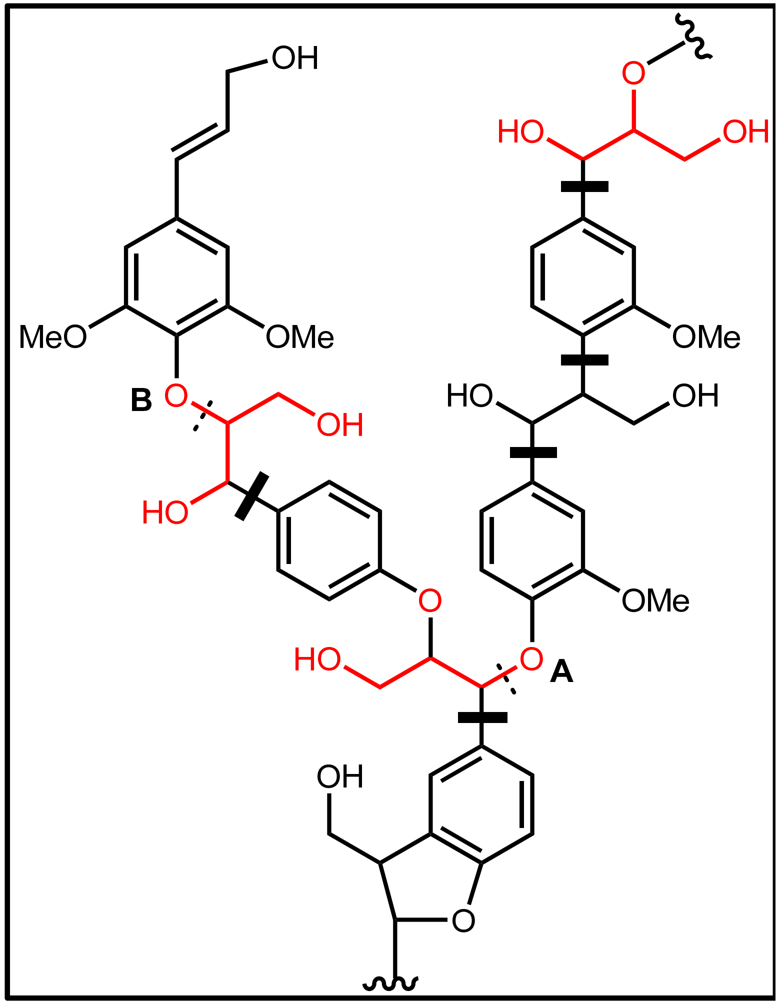


fructose



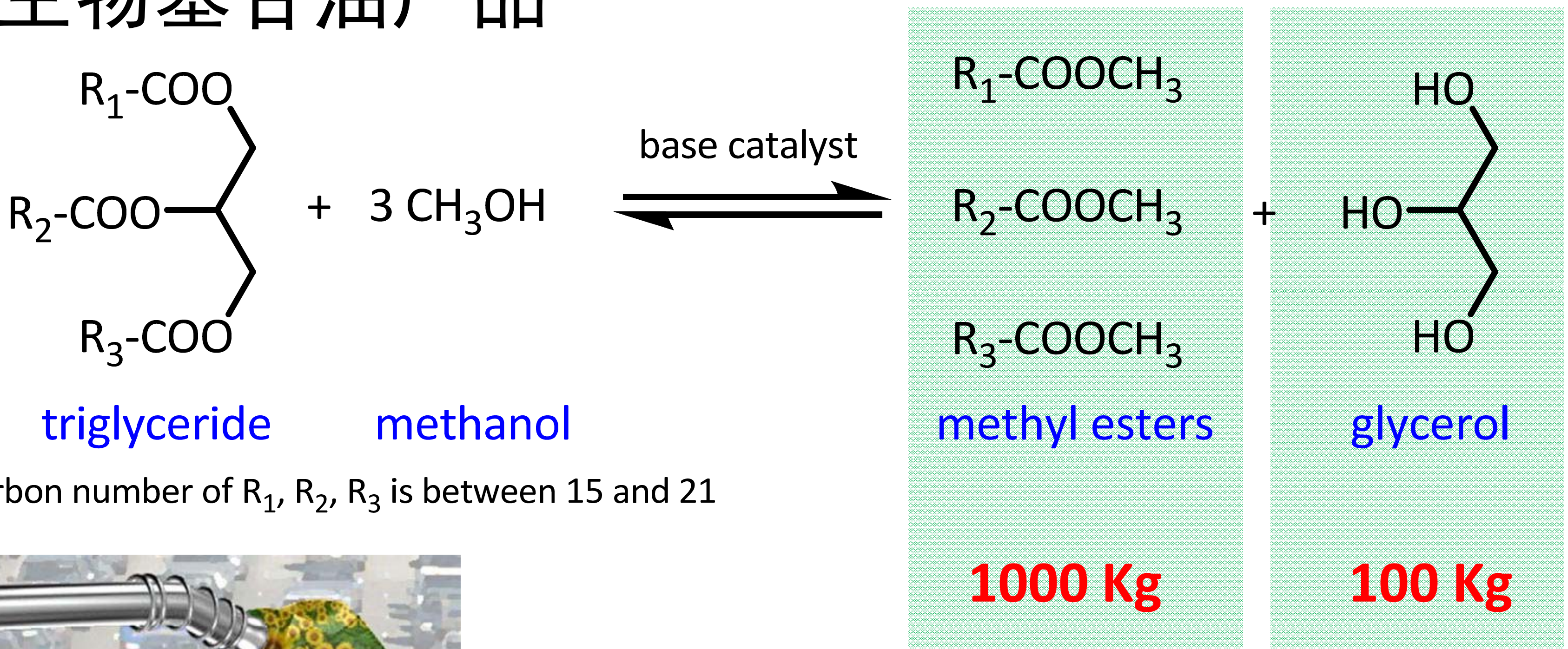
glycerol





丙三醇是生产生物柴油的副产物

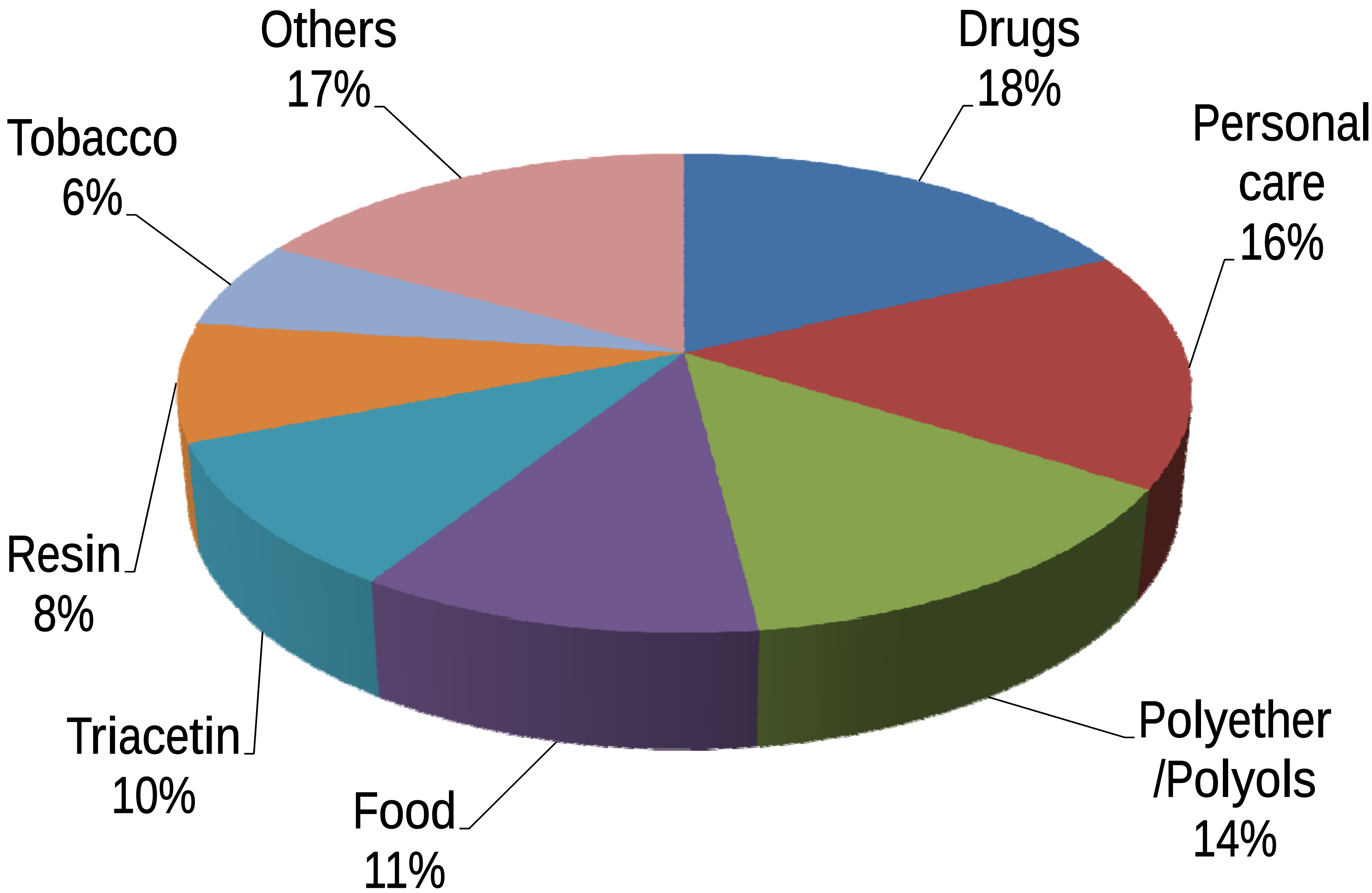
- 生物基甘油产品



Carbon number of R_1, R_2, R_3 is between 15 and 21

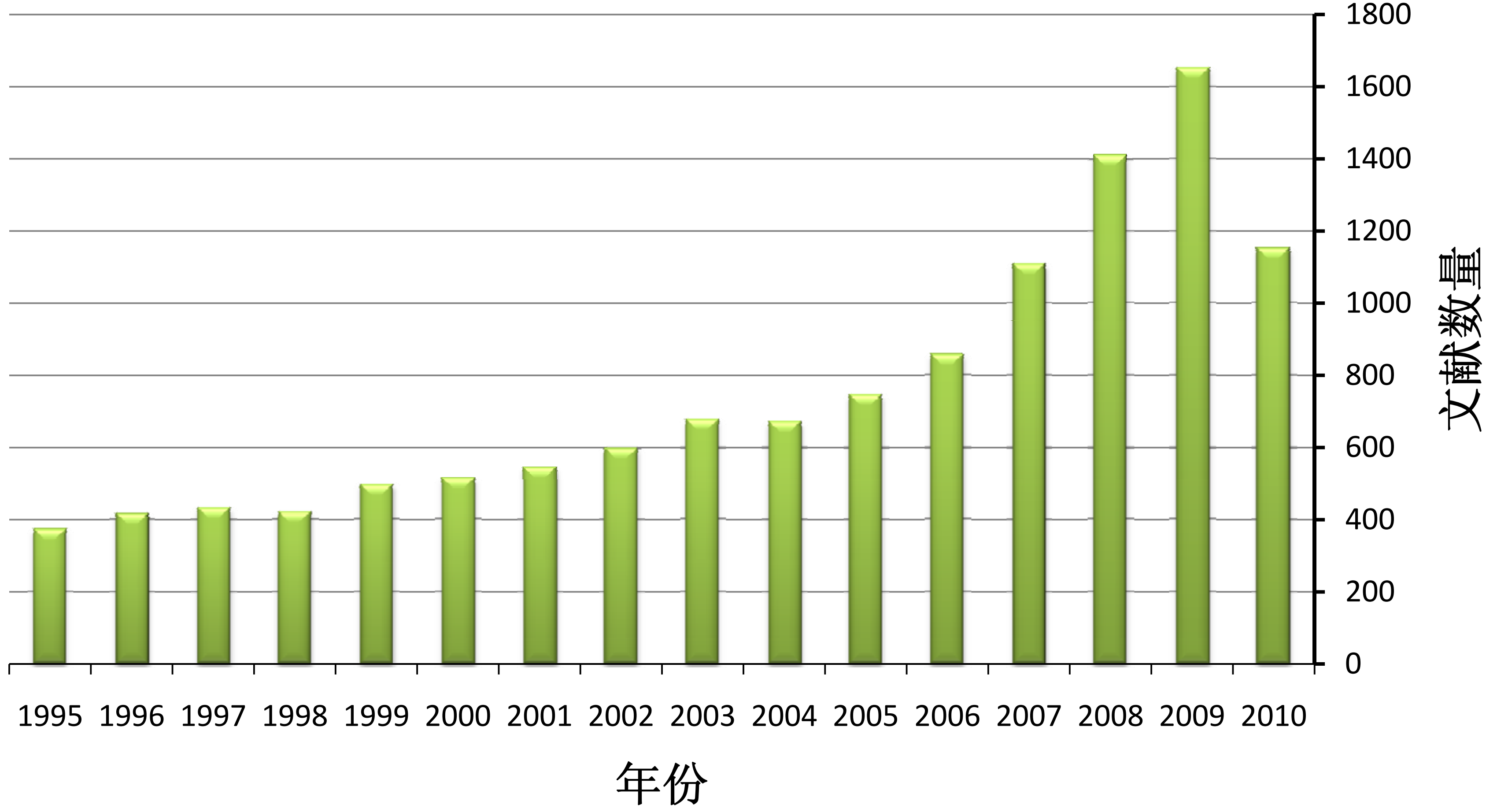
M. McCoy, *Chem. Eng. News*, 2006, **84**, *7*.

精制丙三醇的用途



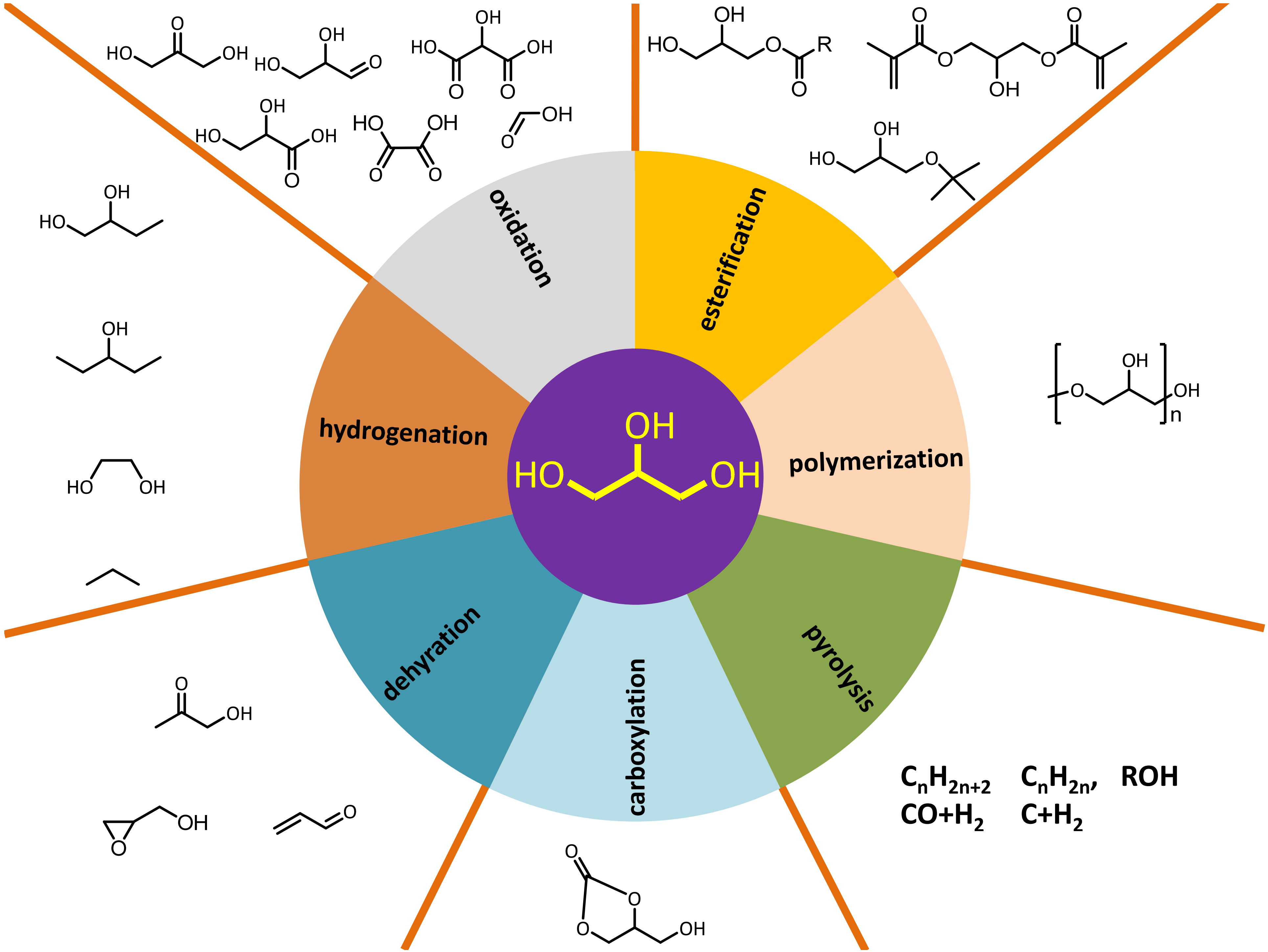
Others 17%
Drugs 18%
Tobacco 6%
Personal care 16%
Resin 8%
Triacetin 10%
Food 11%
Polyether /Polyols 14%

催化转化甘油已成为研究热点



数据来自 SciFinder，关键词：glycerol and catalysis

丙三醇制备化学品



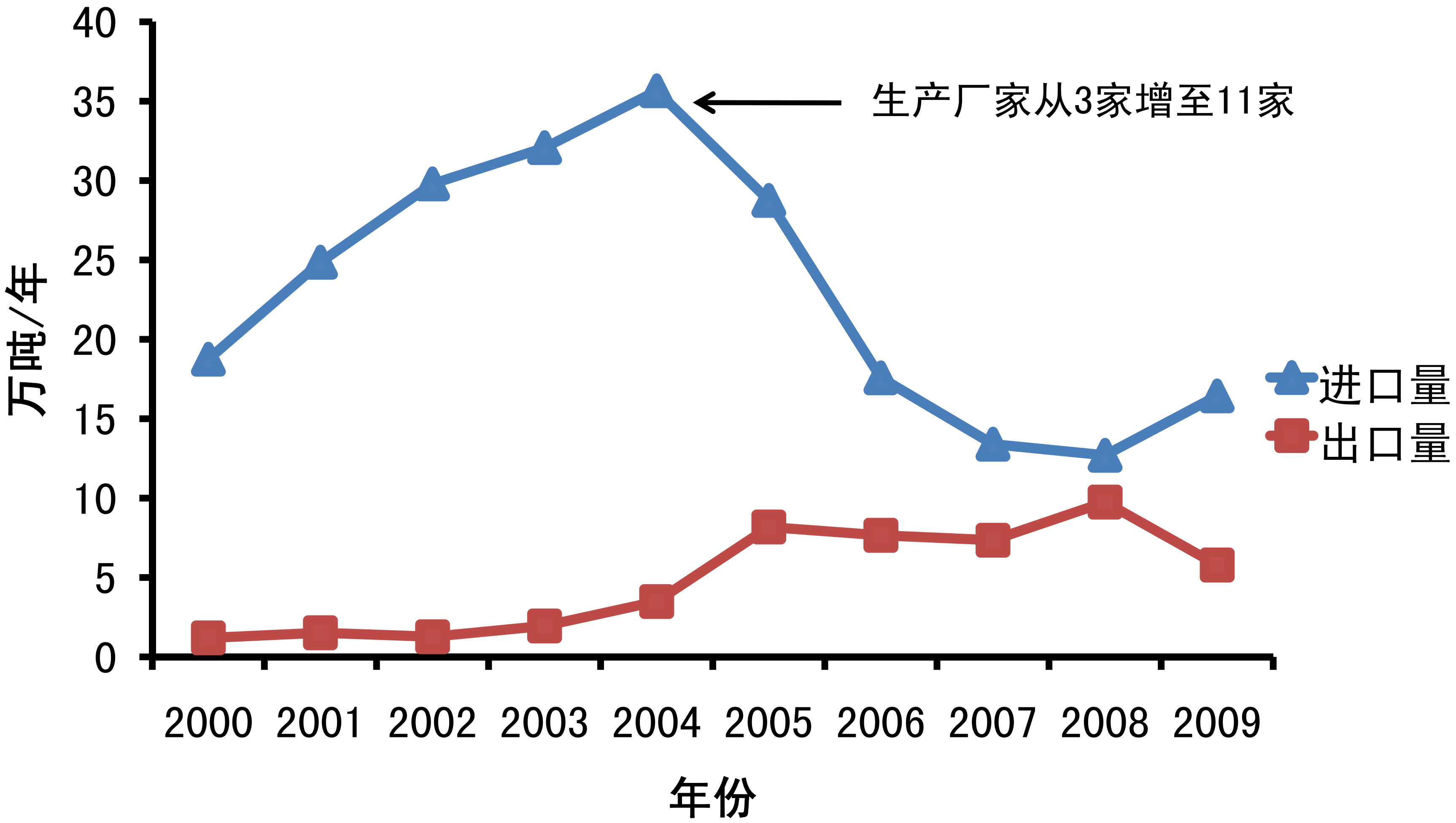
oxidation
esterification
polymerization
pyrolysis
carboxylation
dehyration
hydrogenation
C_nH_{2n+2} C_nH_{2n}, ROH
$CO+H_2$ $C+H_2$

国内丙烯酸年总产约250万吨

企业名称	地点	丙烯酸 （万吨/年）	丙烯酸酯 （万吨/年）
北京东方	北京市	8.0	8.0
浙江卫星	浙江嘉兴	4.0	4.5
沈阳蜡化	沈阳市	8.0	12.0
江苏裕廊	江苏盐城	20.5	25.0
吉林石化	吉林市	3.3	3.0
上海华谊	上海市	18.6	22.0
扬子-巴斯夫	南京市	16.0	15.5
台塑(宁波)	浙江宁波	16.0	20.0
开泰实业	山东淄博	4.0	0.6
正和集团	山东广饶	6.0	6.0
兰州石化	兰州市	8.0	10.0

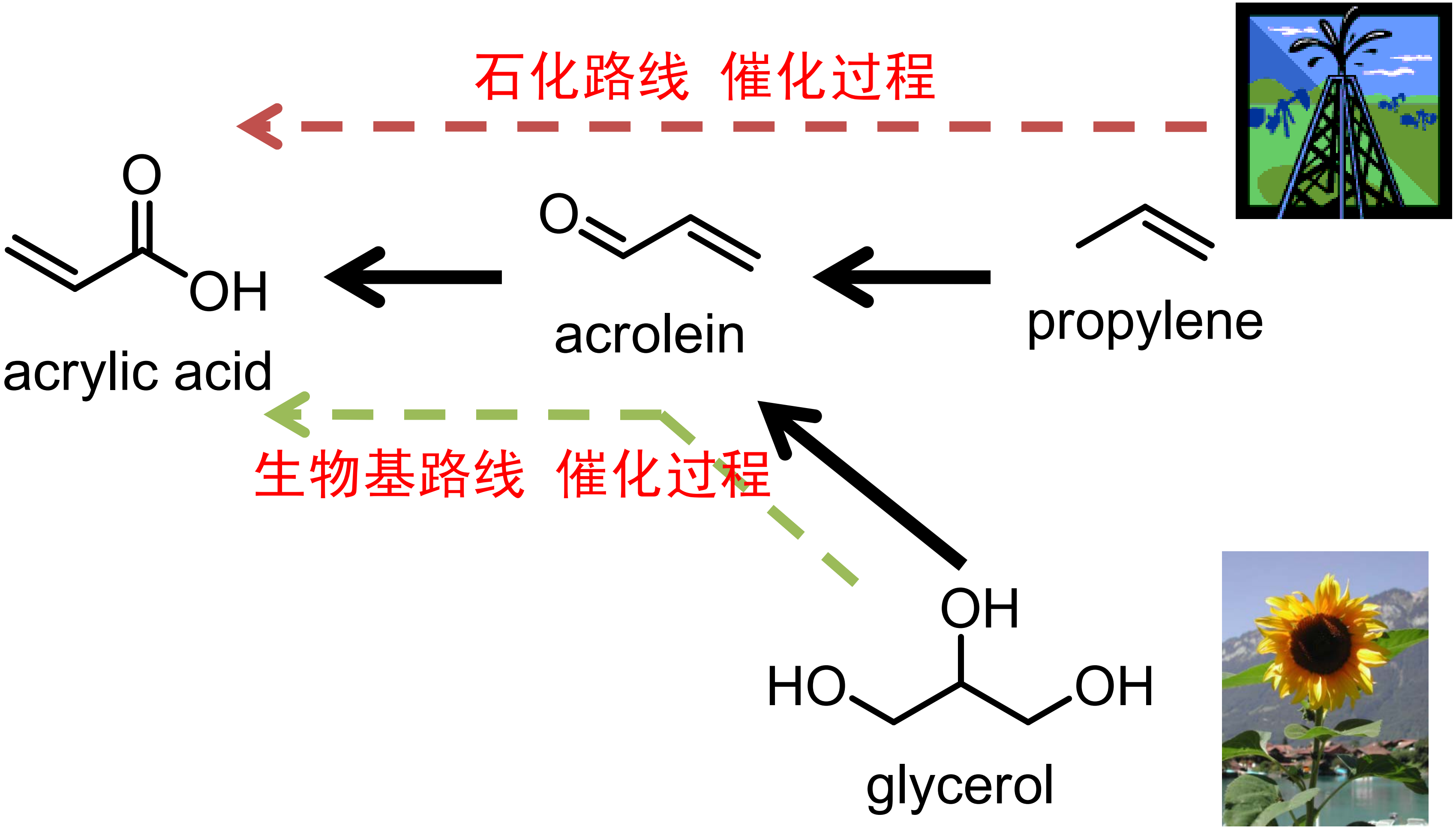
2010年第31期《中国化工信息》

进口>出口

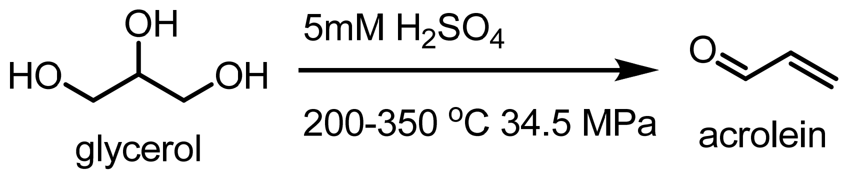


2010年第31期《中国化工信息》

从可再生资源生产丙烯酸

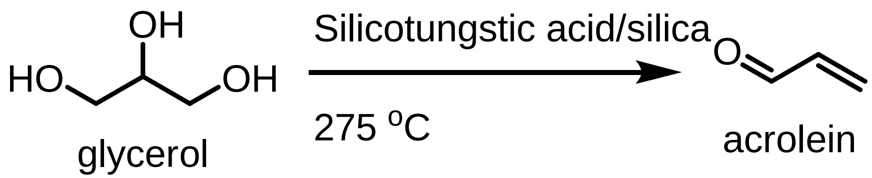


丙三醇脱水制备丙烯醛



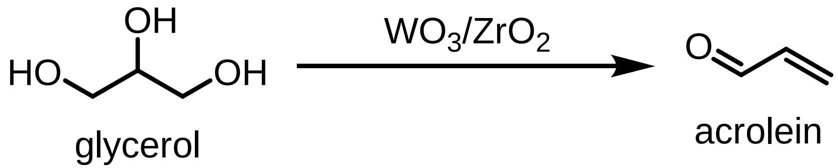
Conv. 40%　　Sel. 84%

S. Ramayya, A. Brittain, C. Dealmeida, W. Mok, M.J. Antal, *Fuel*. 66 (1987) 1364.



Conv. 98%　　Sel. 86%

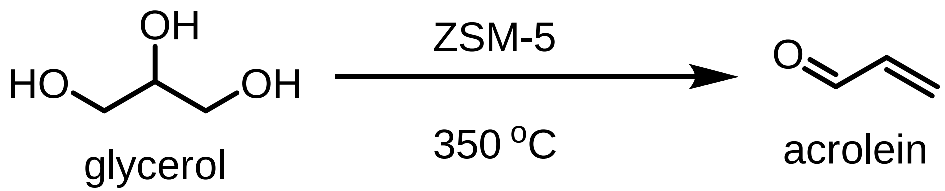
E. Tsukuda, S. Sato, R. Takahashi, T. Sodesawa, *Catal. Commun*. 8 (2007) 1349 .



Conv. 100%　　Yield 73-80%

Dubois JL, et al. Arkema SA, WH (2005) F Patent 2,882,052; WH (2005) F Patent 2,882,053; WH (2005) F Patent 2,884,817; WH (2006) F Patent 2,884,818

脱水路线积碳严重

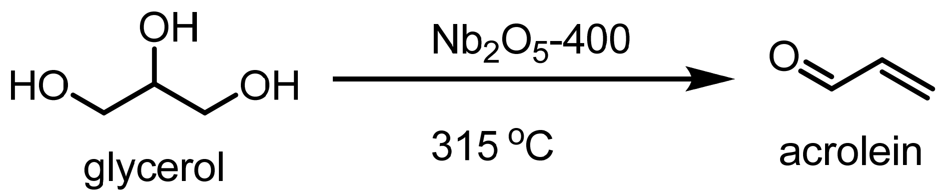


Conv. 100%

Yield 55-61%

coke sel. 7-20%

A. Corma, G.W. Huber, L. Sauvanauda, P. O'Connor, *J. Catal.* 257 (2008) 163



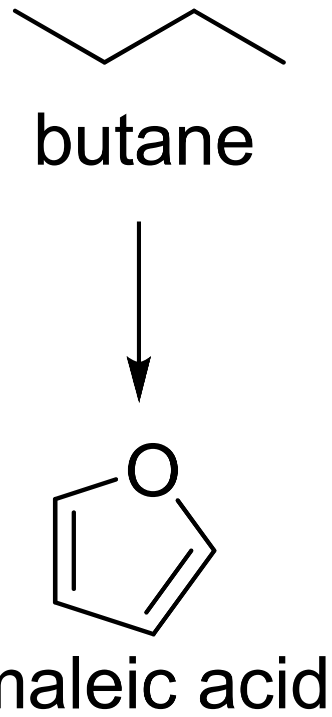
Conv. 100%

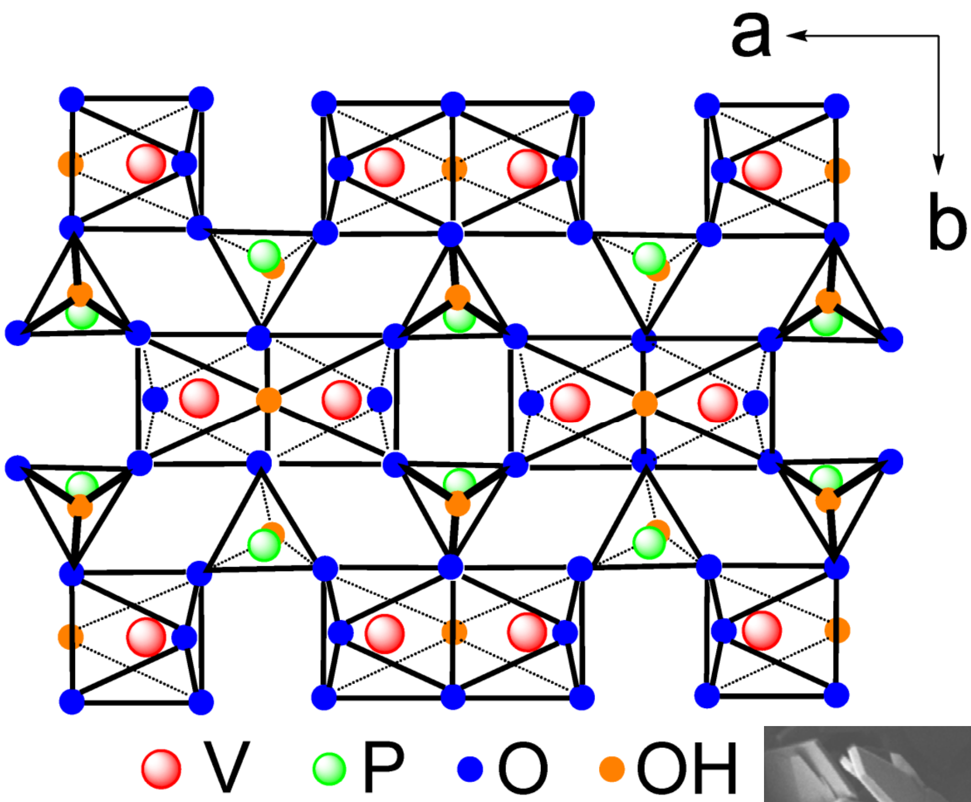
Sel. 37%

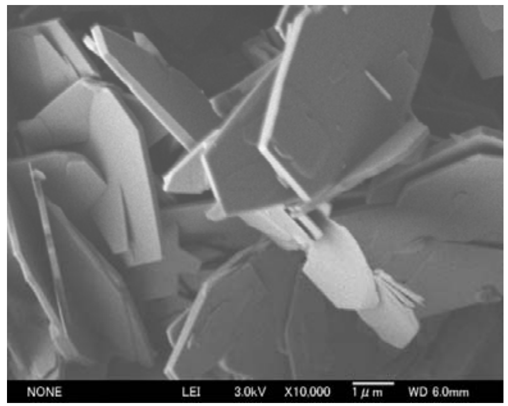
coke formation:10% cat weight

S.H. Chai, H.P. Wang, Y. Liang, B.Q. Xu, *J. Catal.* 250 (2007) 342

V-P-O催化剂：丁烷制备马来酸酐

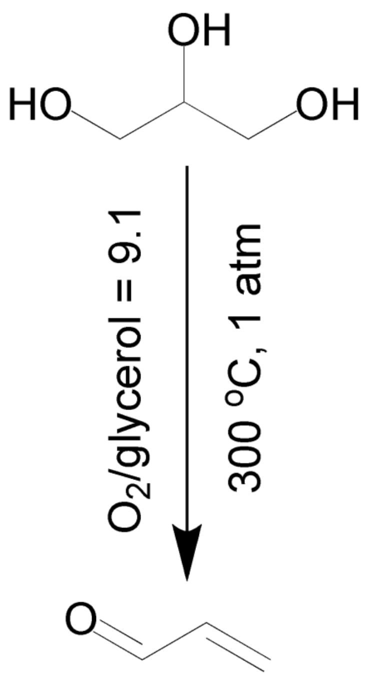


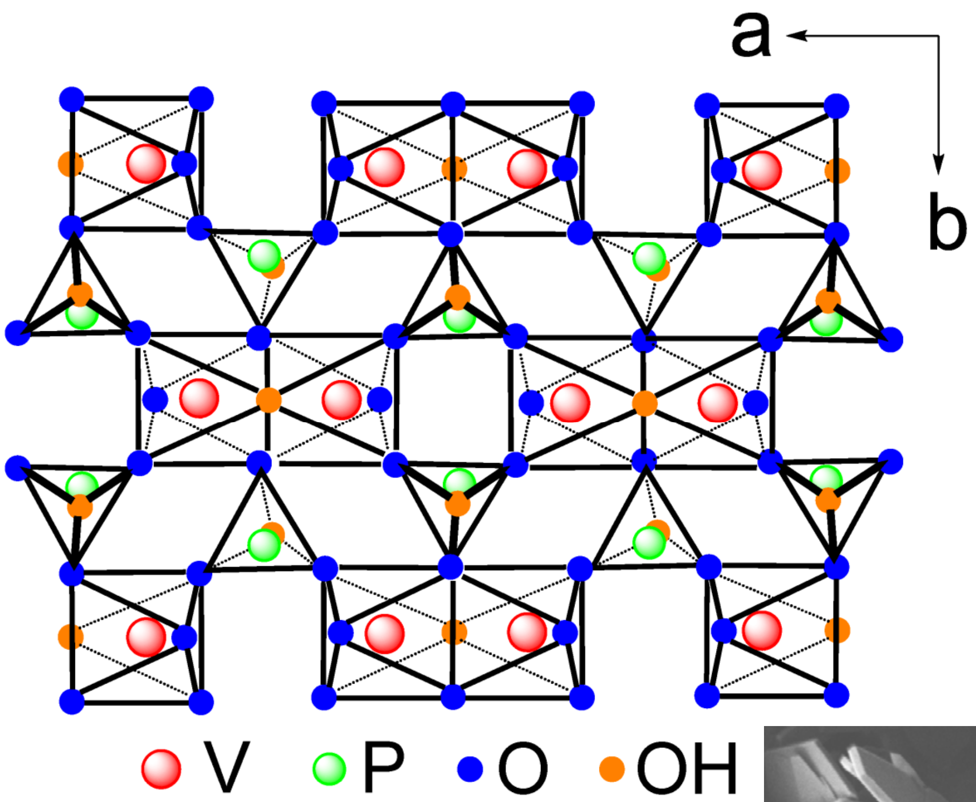


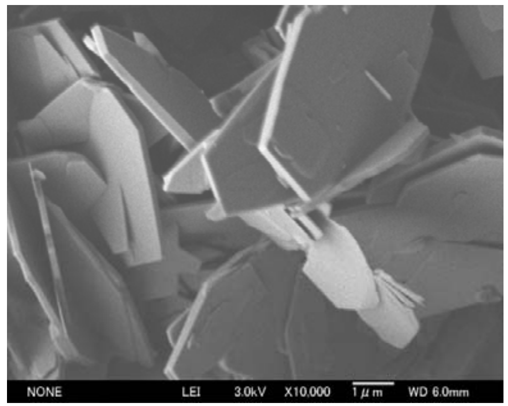


结构敏感反应

V-P-O催化剂：氧化脱水反应



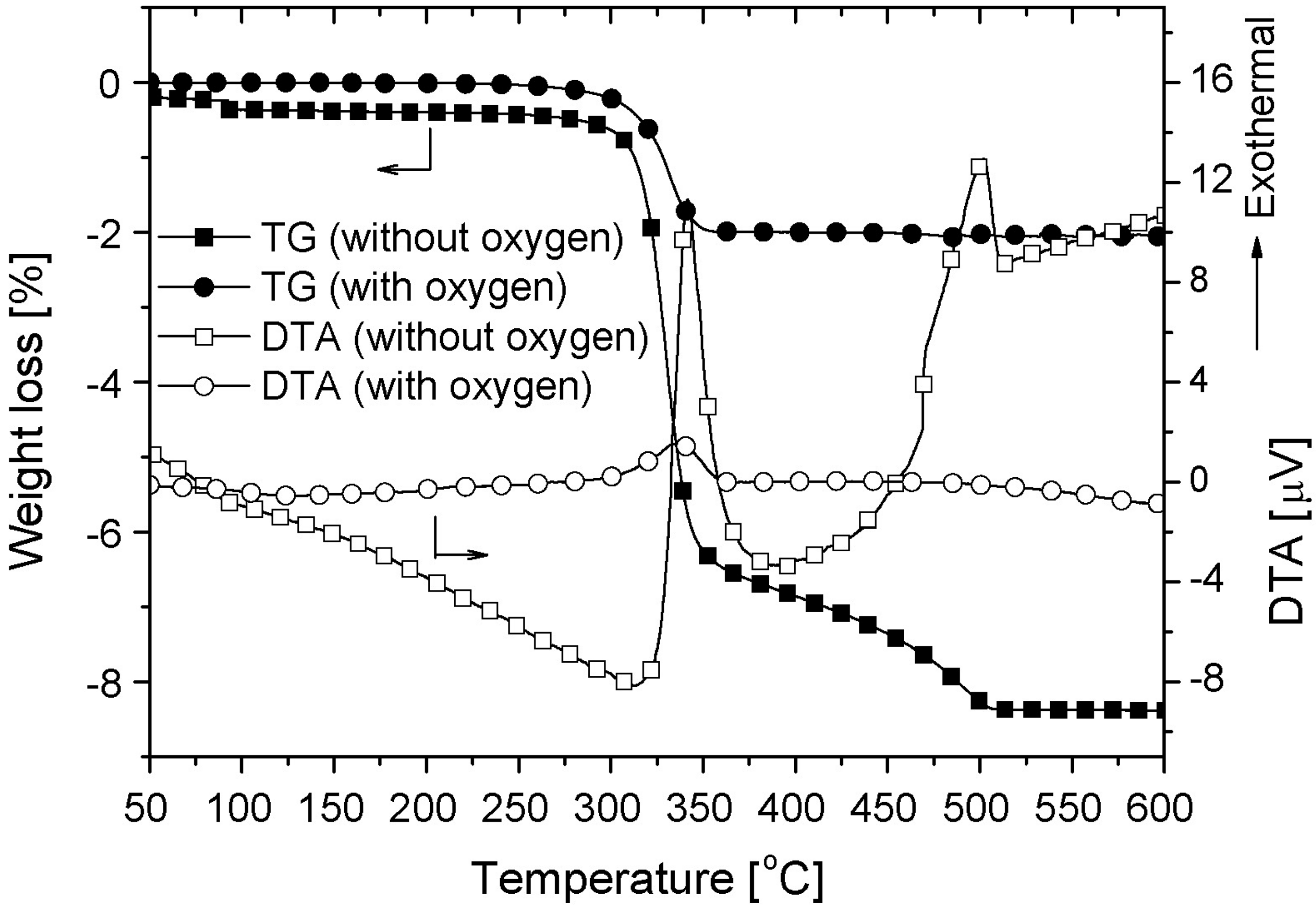




Glycerol conversion 100%, acrolein selectivity 66%,
acetaldehyde and acetic acid 20%

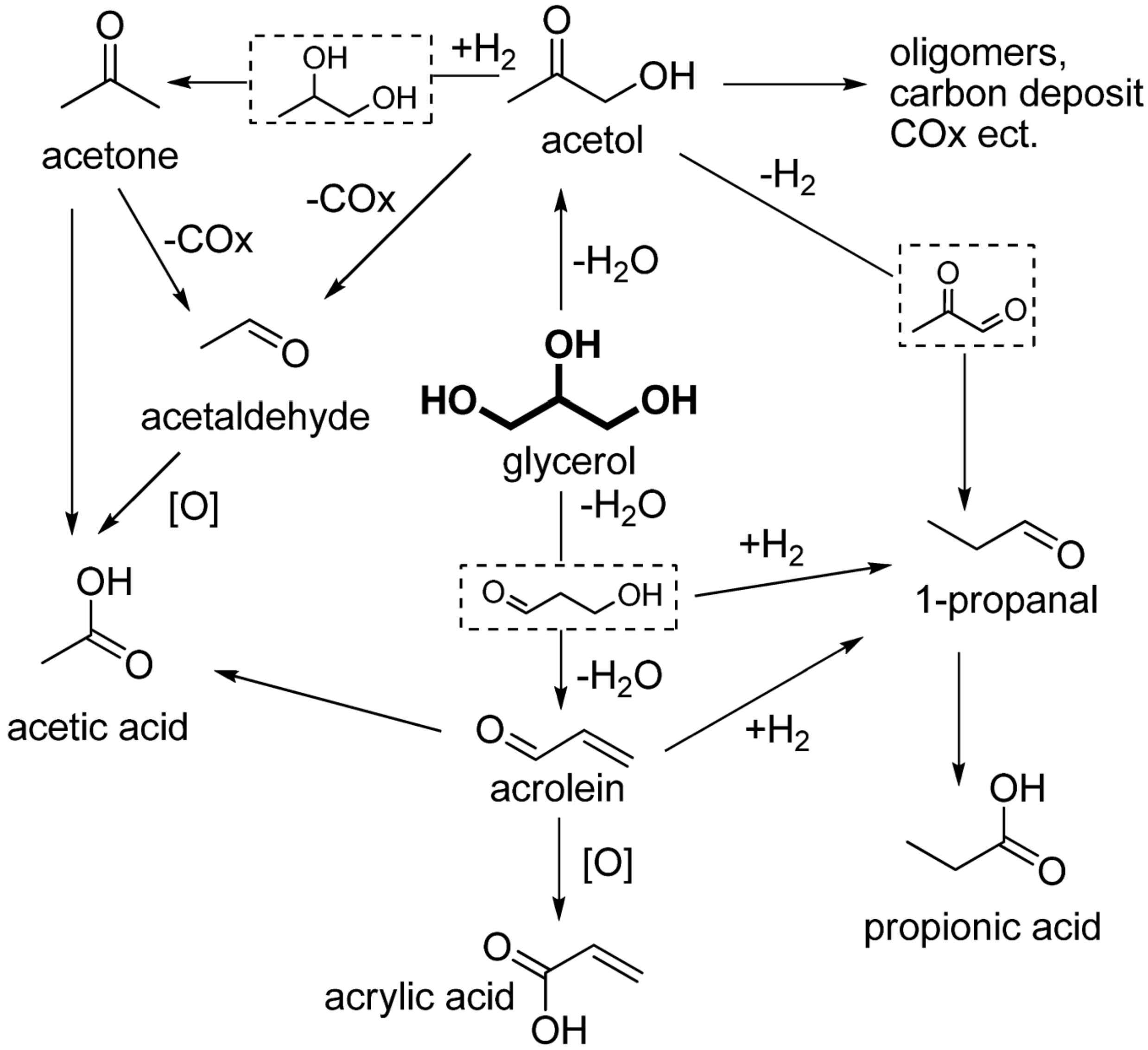
Feng Wang et al, J. Catal. 2009, 268, 260-267;
Appl. Catal. A 2010, 376, 25-32

氧化气氛(O_2/gly=9.1)减少积碳



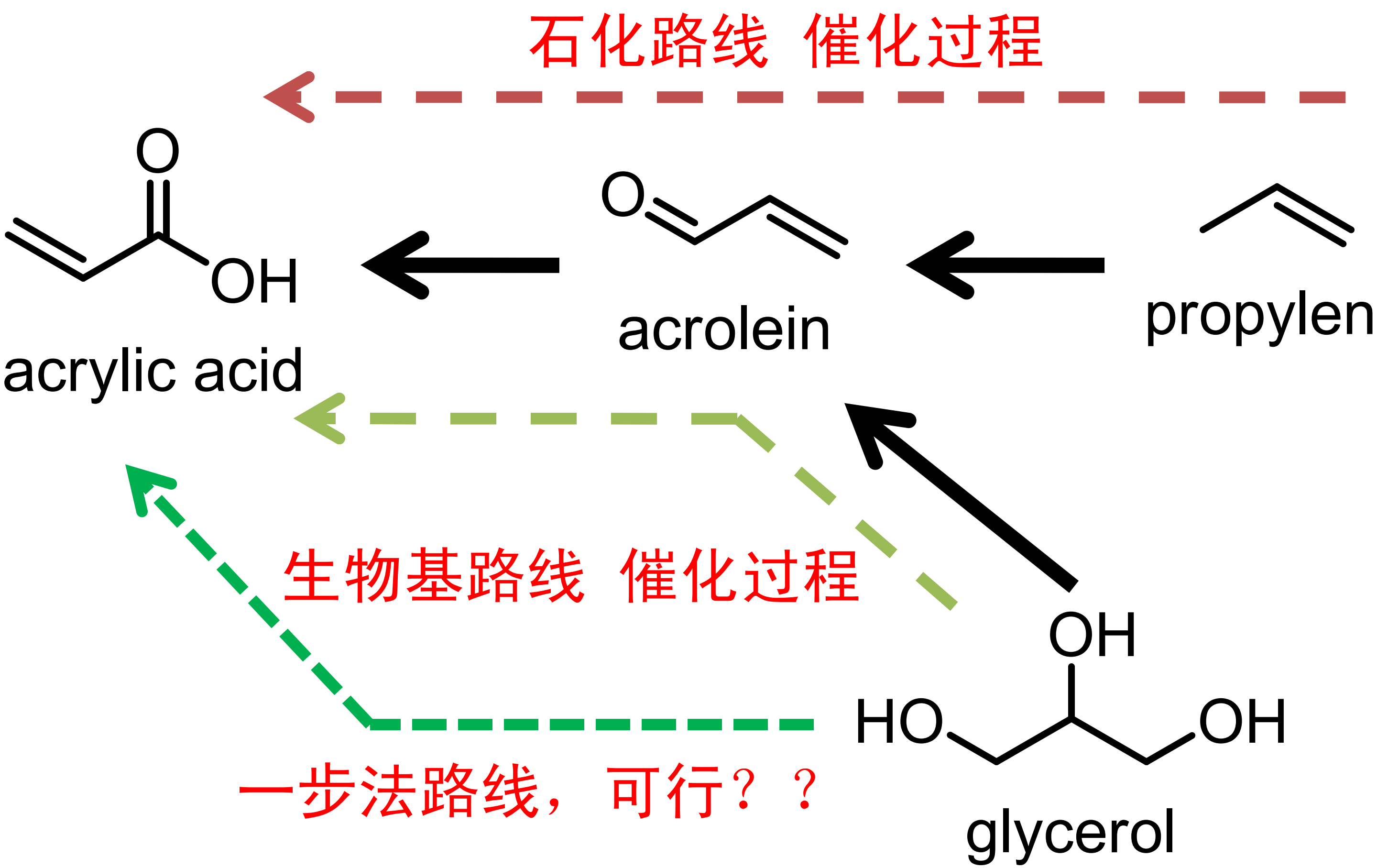
反应时间:10 h, 重时空速(WHSV): 2.5 h^{-1}

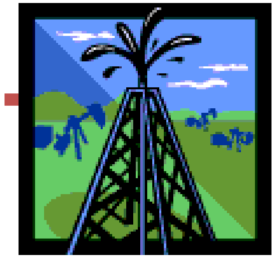
复杂的反应路径



+H2
OH
OH
O
OH
acetone
acetol
oligomers,
carbon deposit
COx ect.
-COx
-COx
-H2
-H2O
O
O
acetaldehyde
OH
HO
OH
glycerol
[O]
-H2O
+H2
1-propanal
O
OH
-H2O
+H2
acetic acid
acrolein
[O]
OH
propionic acid
acrylic acid

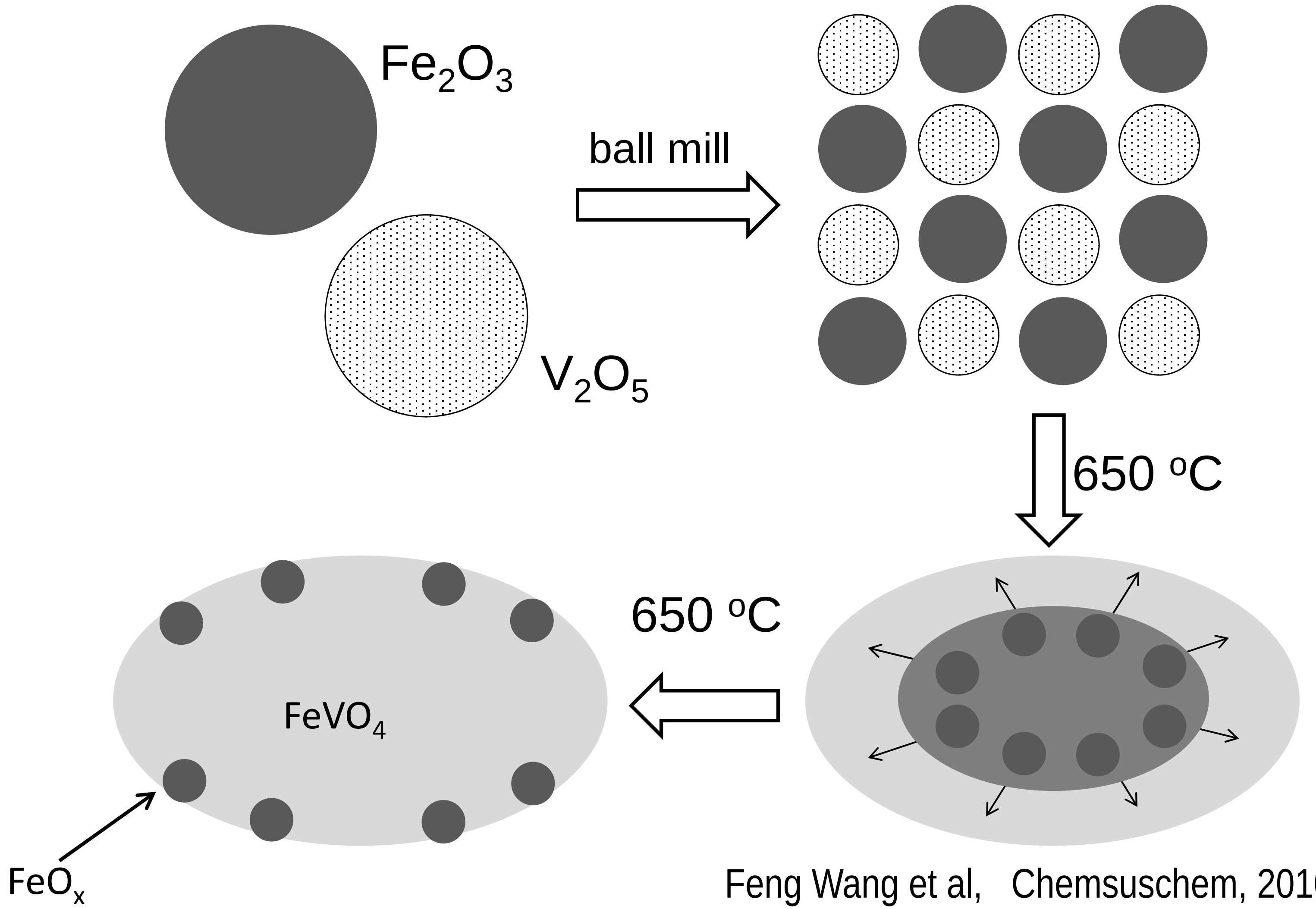
一步法从丙三醇制备丙烯酸





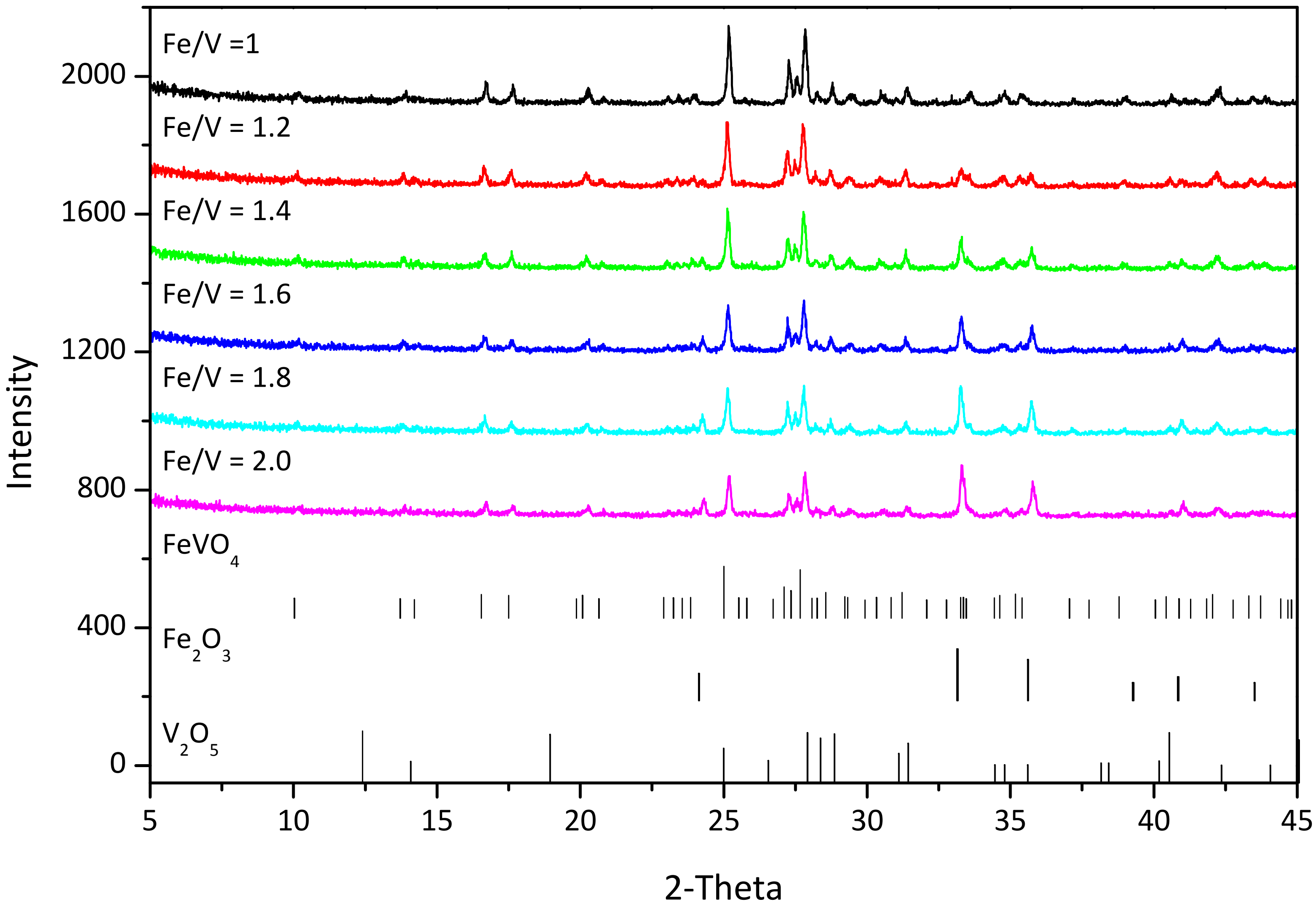
关键科学问题：具有氧化和脱水双功能的催化剂

嵌入式催化剂FeO_x@$FeVO_4$的制备



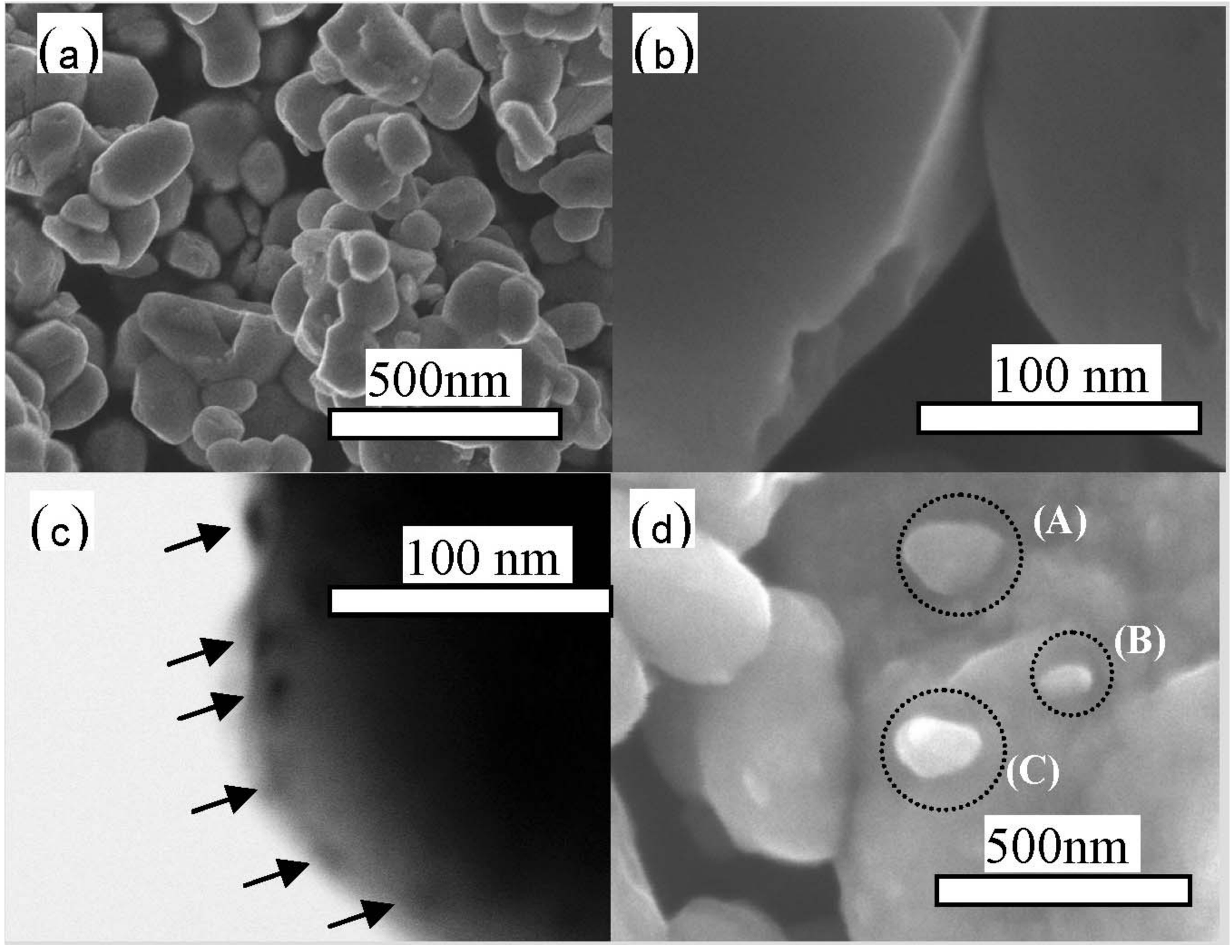
Feng Wang et al,   Chemsuschem, 2010, in print

催化剂的结构与形貌

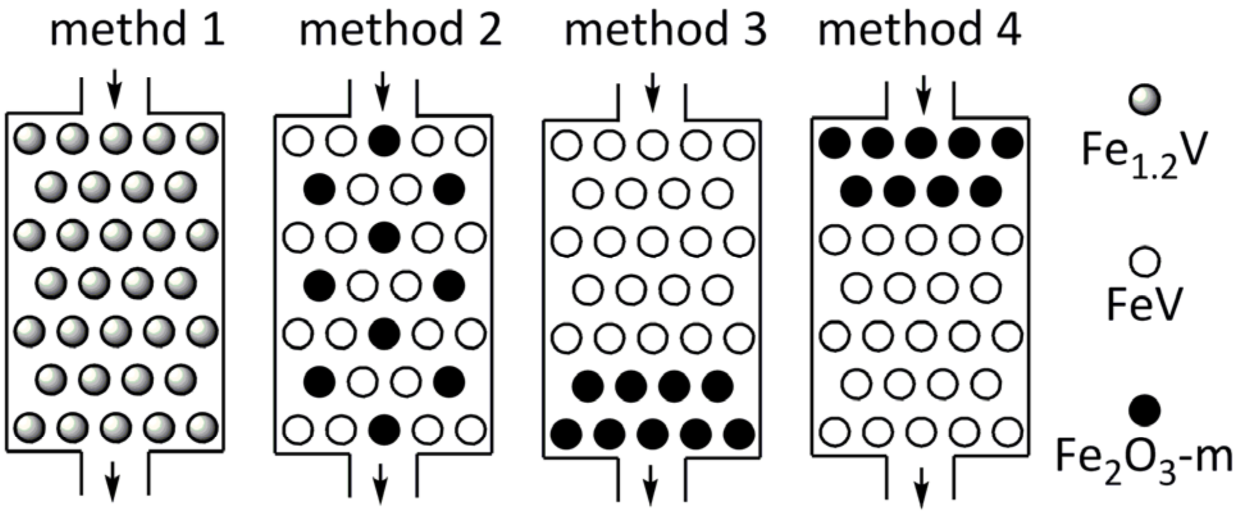


Fe/V =1
Fe/V = 1.2
Fe/V = 1.4
Fe/V = 1.6
Fe/V = 1.8
Fe/V = 2.0
FeVO4
Fe2O3
V2O5
Intensity
2000
1600
1200
800
400
0
5
10
15
20
25
30
35
40
45
2-Theta

催化剂的结构与形貌

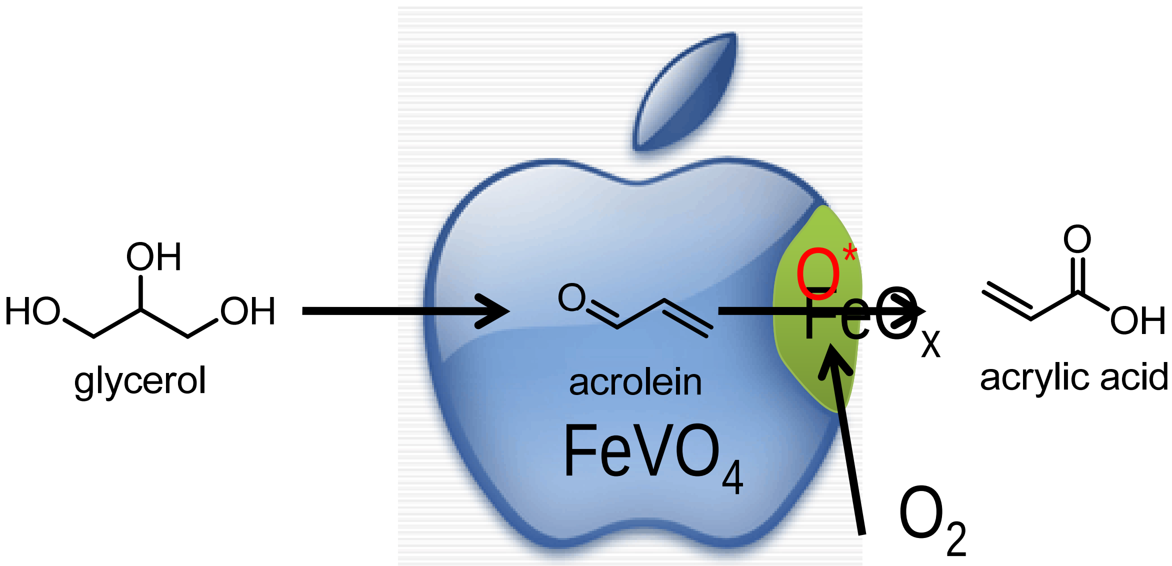


嵌入FeO_X活性相催化性能优越



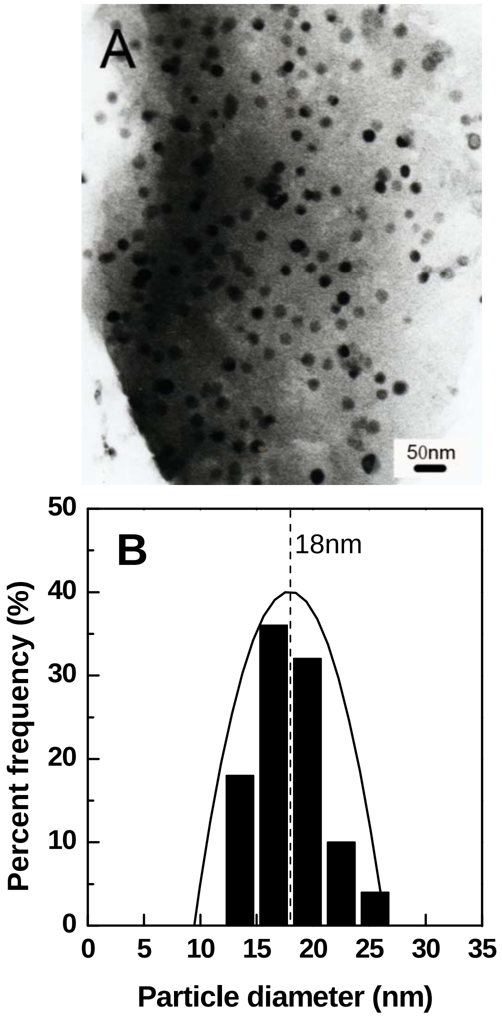
	Method1	Method2	Method3	Method4	负载催化剂
甘油转化率	100	93	89	100	100
丙烯醛	28	30	50	40	5
丙烯酸	26	3	6	1	0
乙酸	24	21	10	13	64

可能的反应历程

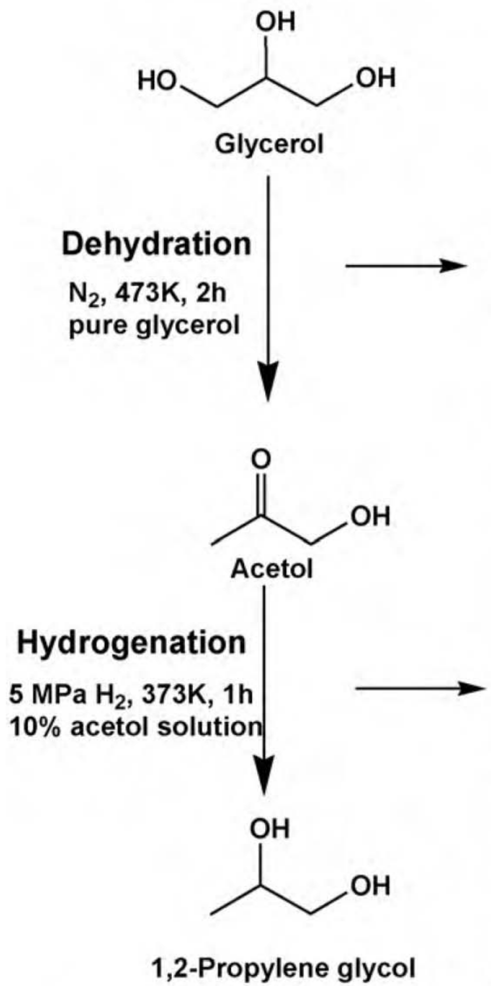


双中心（脱水和氧化）嵌入式催化剂

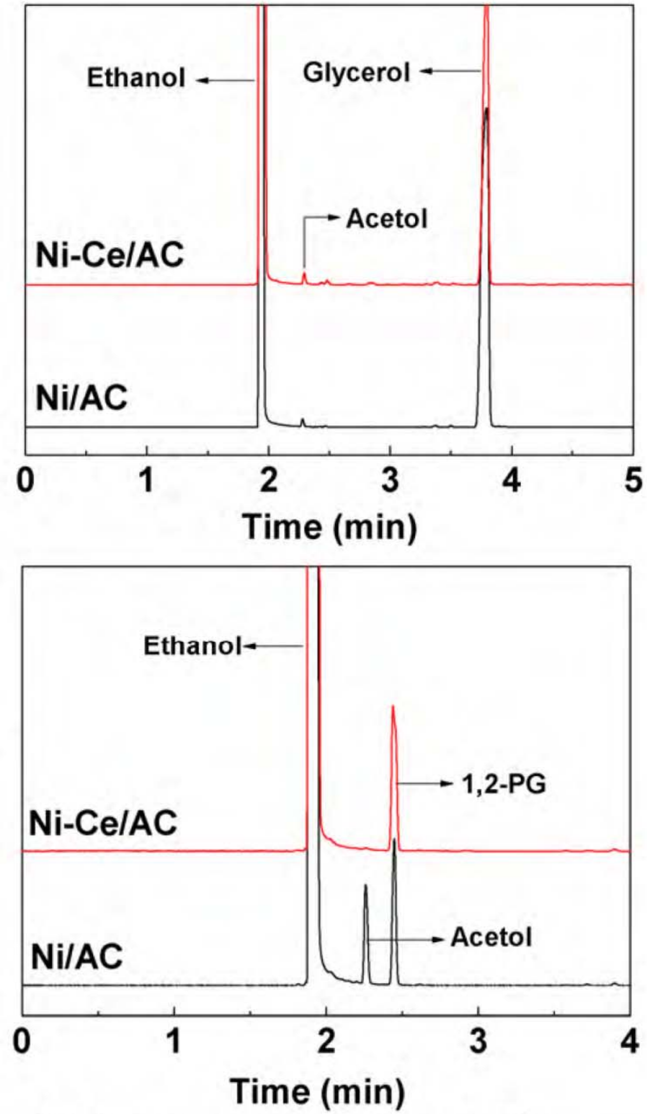
催化加氢丙三醇制备1,2-丙二醇



Weiqiang Yu, Jie Xu, et al
Appl. Catal. A 383(2010) 73–78



Cotrolled reaction process



GC traces of the reaction mixtures

催化加氢丙三醇制备1,2-丙二醇

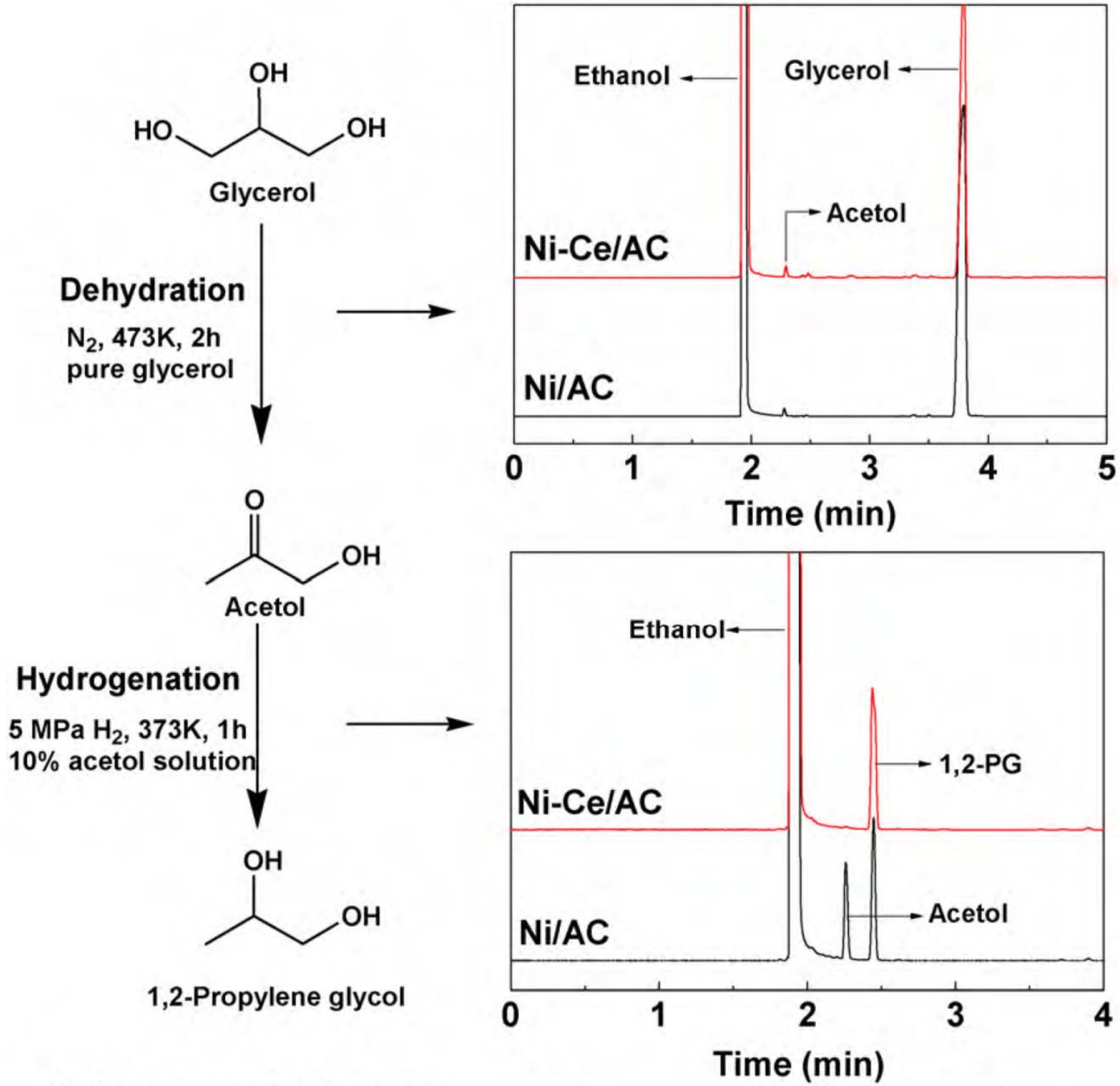
Supported nickel-Ce catalysts

Conversion of glycerol: 90.4%

Selectivity 1,2-propylene glycol 65.7%

Selectivity ethylene glycol 10.7%

Weiqiang Yu, Jie Xu, et al
Appl. Catal. A 383(2010) 73–78



Cotrolled reaction process

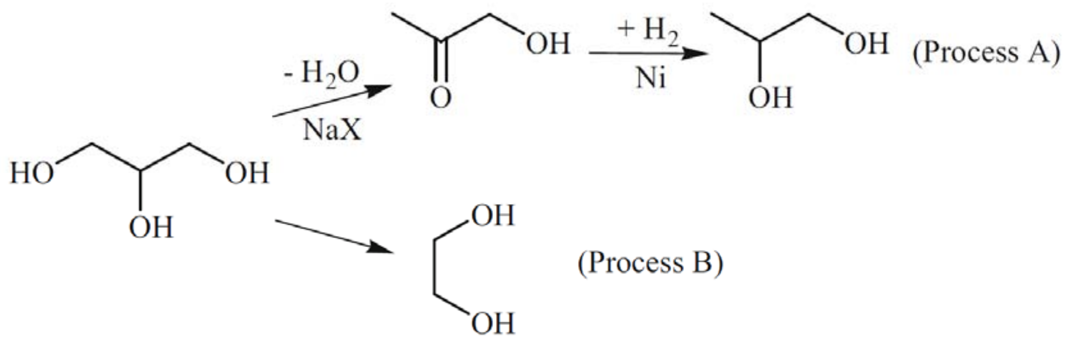
GC traces of the reaction mixtures

催化加氢丙三醇制备1,2-丙二醇

Entry	Catalyst	S_{Ni} (m^2/g)	Conversion (%)	Selectivity (%) 1,2-PG	EG	Others[a]
1	Ni/NaMOR	21.2	14.0	56.7	13.3	30.0
2	Ni/NaZSM-5	9.8	47.8	9.4	13.0	77.6
3	Ni/NaA	10.4	65.3	46.8	14.1	39.1
4	Ni/NaX	25.5	94.5	72.1	11.1	16.8
5	Ni/SiO_2	27.9	56.9	44.4	8.8	46.8
6	$Ni/\gamma\text{-}Al_2O_3$	22.2	97.1	44.2	7.5	48.3

Reaction conditions: 160 g 25 wt% glycerol aqueous solution, 2.0 g catalyst (metal-based), 200 °C, 6.0 MPa H_2, 10 h, stirring speed: 500 rpm

[a] Others: ethanol, *n*-propanol, acetol, CO, CO_2 and CH_4



Jing Zhao, Jie Xu, et al
Catal Lett 134 (2010) 184–189

结论

- 丙三醇氧化脱水反应，减少积碳；采用嵌入式催化剂，丙烯酸收率提高到26%
- 丙三醇加氢反应，镍基催化剂，铂碳加氢制备1,2-丙二醇收率68%

展望

- 丙三醇制备丙烯酸：双中心催化剂
- 丙三醇仲碳选择加氢制备1,3-丙二醇

谢谢大家！