Rational Approach Towards

Novel Catalysts for Biomass Conversion and Upgrading

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Outline

1. Introduction
2. Overview of Activities
3. Adsorption and Reaction of Oxygenates on Oxides
4. Conclusion and Outlook

Challenges in Biomass to Fuels Conversion

Starting Point: Switchgrass (Alamo)

	C	*H*	*N*	*O*
Mass%	48	5.4	0.42	41.7
Atom%	33.2	44.9	0.2	21.7

Goal: Transportation Fuels

Gasoline (US): Hydrocarbons (15% C4–C8 straight-chain alkanes, 25 to 40% C4–C10 branched alkanes, 10% cycloalkanes, less than 25% aromatics, and 10% straight-chain and cyclic alkenes)

Diesel: Hydrocarbons (alkanes, cycloalkanes, aromatics)

Challenges

Need to remove O while producing right ratio of C:H (e.g. alkanes: C_nH_{2n+2})

"Switchgrass as an energy crop for biofuel production: A review of its ligno-cellulosic chemical properties", Kasi David and Arthur J. Ragauskas, Energy Environ. Sci., 2010, 3, 1182–1190

Steve Ritter "Gasoline", Chemical & Engineering News 2005, Volume 83, Number 8, p. 37

Approaches to Biomass Conversion

Overview of conversion routes of plant materials to biofuels

Plant material	Conversion route	Primarily product	Treatment	Products
Ligno-cellulosic biomass	Flash pyrolysis	Bio-oil	Hydrotreating and refining	C_xH_x, diesel fuel, chemicals, oxygenates, hydrogen
	Gasification	Syngas	Water gas shift + separation	Hydrogen
			Catalyzed synthesis	Methanol, dimethyl ether, FT diesel, C_xH_x, SNG (CH_4)
	Hydrolysis	Sugar	Fermentation	Bioethanol
	Hydrothermal liquefaction	Bio-oil	Hydrotreating and refining	C_xH_x, diesel fuel, chemicals
	Anaerobic digestion	Biogas	Purification	SNG (CH_4)
Sugar and starch crops	Milling and hydrolysis	Sugar	Fermentation	Bioethanol
Oil plants	Pressing or extraction	Vegetable oil	Esterification	Biodiesel
			Pyrolysis	Bio-oil, diesel fuel, gasoline

Friederike Jentoft, Lance Lobban, Richard Mallinson, Daniel Resasco, (Roberto Galiasso), Rolf Jentoft

Demirbas, A.(2010) 'Biorefinery Technologies for Biomass Upgrading', Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 32: 16, 1547 — 1558, http://dx.doi.org/10.1080/15567030902780394

Pyrolysis Products

Pine sawdust		Switchgrass	
Gases	19± 3	Gases	11
Pyrolysis (bio) oil	66 ± 11	Water + organics	62
Char	12	Char + ash	20
(Water)	21		

Nokkosmaki MI, Kuoppala ET, Leppamaki EA, Krause AOI , Catalytic conversion of biomass pyrolysis vapours with zinc oxide, JOURNAL OF ANALYTICAL AND APPLIED PYROLYSIS 55 (2000) 119-131

F. A. Agblevor, S. Besler, A. E. Wiselogel, “Fast Pyrolysis of Stored Biomass Feedstocks” Energy Fuels, 1995, 9 (4), pp 635–640, DOI: 10.1021/ef00052a010

Pyrolysis Oil Constituents

Compound	Weight %
Acetic acid	2.94
Glyoxal	Trace
Furfural	0.62
Furfuryl alcohol	-
2-methyl-2cyclopenten-1-one	0.16
3-methyl-2cyclopenten-1-one	0.34
Hydroxy acetaldehyde	2.40
4-hydroxy-4-methyl-2-pentanone	0.05
Acetol	2.75
Levoglucosan	6.38
Guaiacol	0.18
2-methoxy-4-methylphenol	0.07
Isoeugenol	0.45
2,6-dimethoxyphenol	0.20
Phenol	0.66
O-cresol	0.19
2,5-dimethyl phenol	0.01
p-cresol	0.27
m-cresol	0.20
2,4-dimethylphenol	0.10
3,5-dimethylphenol	0.05
4-ethylphenol	0.22
3-ethylphenol	0.04
2-ethylphenol	0.03

Oxygenates:

Alcohols R-OH

Ethers R-O-R

Ketones R-CO-R

Aldehydes R-CHO

Acids R-COOH

Many molecules with more than one functional group

Small molecules

Not separable by distillation

“Chemical Composition of Bio-oils Produced by Fast Pyrolysis of Two Energy Crops”, Charles A. Mullen and Akwasi A. Boateng, Energy & Fuels 2008, 22, 2104–2109

Transformations for Pyrolysis Oil Upgrading

Starting Point: Switchgrass (Alamo)

	C	*H*	*N*	*O*
Mass%	48	5.4	0.42	41.7
Atom%	33.2	44.9	0.2	21.7

Intermediate: Pyrolysis oil

Mixture of small oxygenates

Transformations to obtain fuel molecules (hydrocarbons)

Additions (increase of chain length)

Deoxygenations: removal of O
- as CO or CO_2 (“loss” of C)
- as H_2O (requires additional H)

Pyrolysis Oil Upgrading – Catalyst Needs

Catalysts

Solid Acids and Bases: Alkylations, aldol addition, Michael addition...

(Supported) Metals: Selectively cleave C-O or C-C bonds

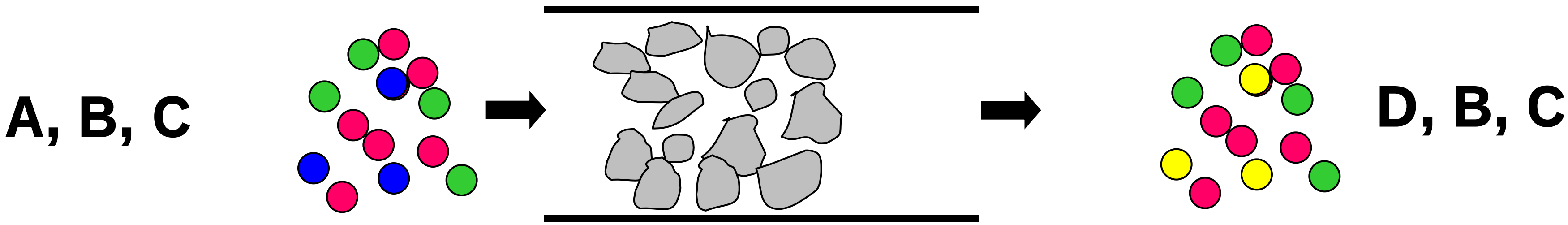
Can we use known catalysts?

Transformations to obtain fuel molecules (hydrocarbons)

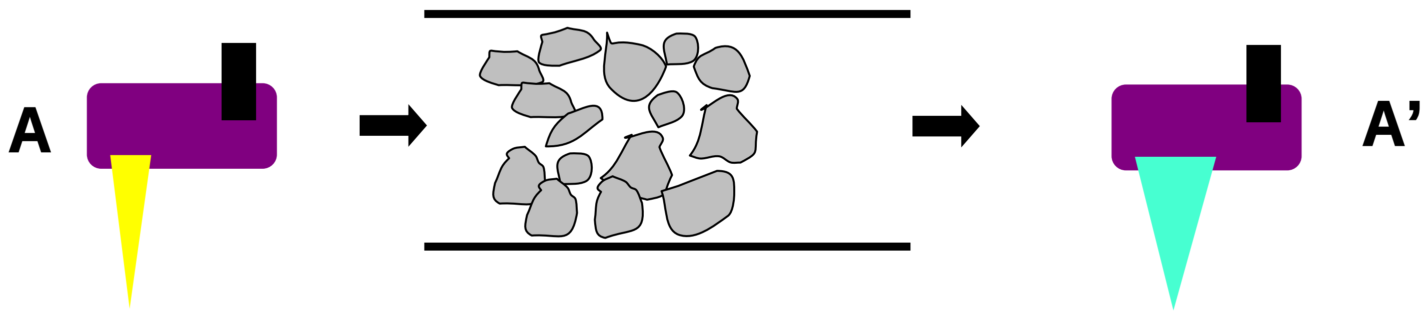
Additions (increase of chain length)

Deoxygenations: removal of O
- as CO or CO_2 (“loss” of C)
- as H_2O (requires additional H)

Selectivity Challenges in Pyrolysis Oil Conversion

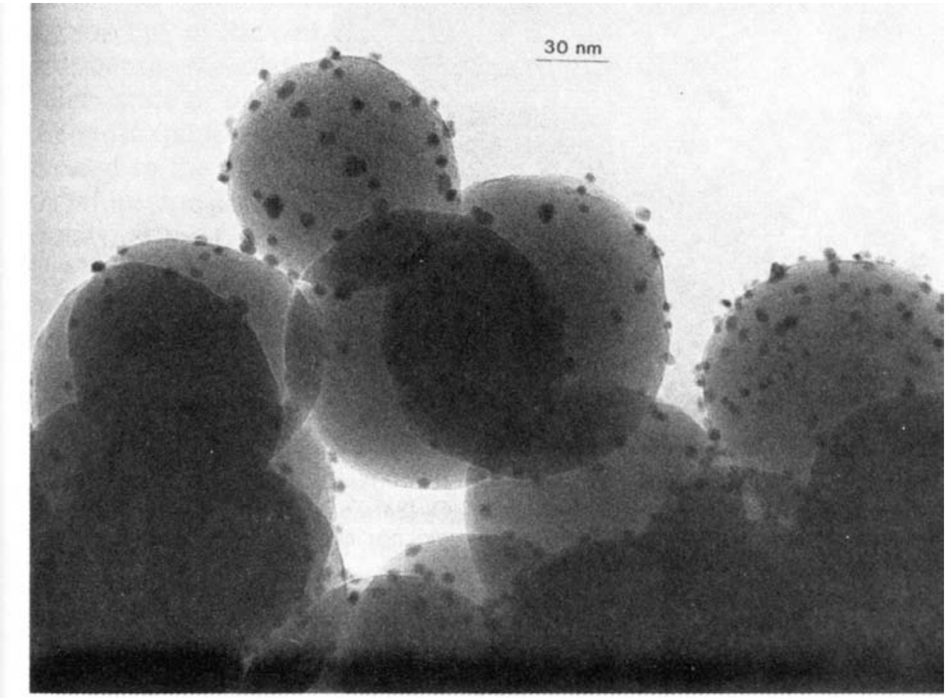


May want to convert individual molecules in a mixture



May want to convert one functional group in a molecule but not another

Supported Metal Catalysts



transmission electron microscopy: Rh/SiO_2

Why support metal particles?

- Maximize surface area (cost), prevent sintering

- Change in reactivity

Role of support?

- Supports are typically oxides (sometimes carbon materials)
- In many applications, interaction of reactant with metal much stronger than with support
- Oxygenates will interact with hydrophilic support (such as oxide)

Image from B.C. Gates, Catalytic Chemistry, John Wiley, 1992

Current Research Projects

Novel Solid Acids and Bases as Catalysts and Supports

Christian P. Scherer (Oct. 09 - May 10)

Katlin D. Robinson (Fall 2010)

News Methods for Surface Characterization

ThuHuong (Kassie) Ngo

(Aug. 2008 - present)

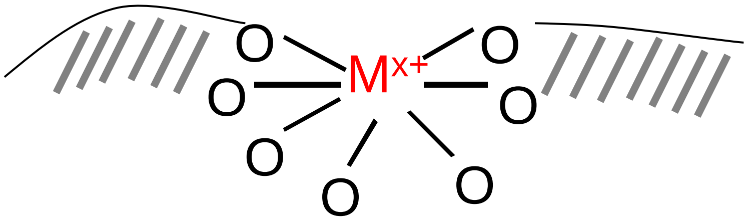
Understanding Catalyst Deactivation

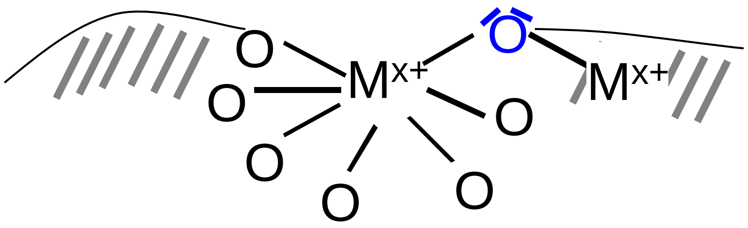
Matthew J. Wulfers
(Aug. 2008 - present)

Adsorption and Reaction of Small Oxygenates

Chandramouli Vaddepalli
(Jan. 2010 – present)

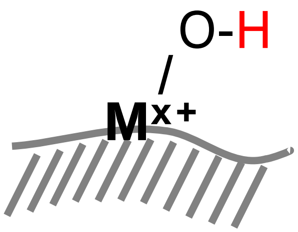
Solid Acids and Bases: Oxide Surfaces



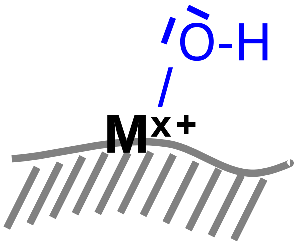


Lewis acid sites
coordinatively unsaturated (cus) metal cations (acidic, electron pair acceptors)

Lewis basic sites
oxygen anions (basic, electron pair donors)



Brønsted acid sites
proton donor



Brønsted basic sites
proton acceptor

Variation of anions: Nitrides, carbides

Variation of cations: Main group metals, transition metals, rare earths

Questions and Strategy

Questions regarding adsorption of oxygenates on catalysts and supports

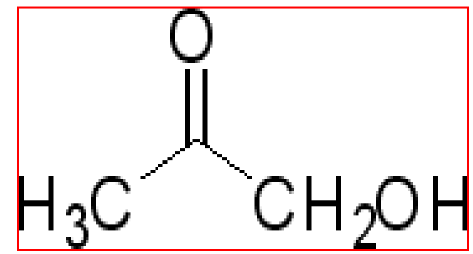
- Adsorption sites?
- Strength of interaction?
- Competitive adsorption of molecules with various functional groups?
- Dominating interaction with surface in molecules with more than one functional group?

Strategy

- Select one bifunctional relevant molecule and its monofunctional counterparts
- Investigate adsorption and reaction on various common catalysts and supports using spectroscopic methods and calorimetry

Pyrolysis Oil Constituents

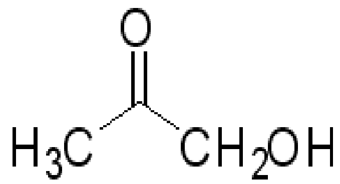
Compounds	Weight %
Hydroxyacetaldehyde	7.34
Furfural	1.44
Acetic acid	7.55
Propanoic acid	0.78
Hydroxyacetone (Acetol)	2.63
1-Hydroxy-2-butanone	1.21
1,2-Ethanediol	0.23
Furfuryl alcohol	0.029
Diethoxymethyl acetate	0.34
Phenol	0.41
1,2-Benzenediol	0.42
Levoglucosan	1.61



Major components of oil from switch grass pyrolysis at 500 C

“Influence of pyrolysis condition on switchgrass bio-oil yield and physicochemical properties”, R. He, X. P. Ye, B. C. English J. A. Satrio, Bioresource Technology 100 (2009) 5305–5311

Reactant Molecules and Catalysts (Supports)



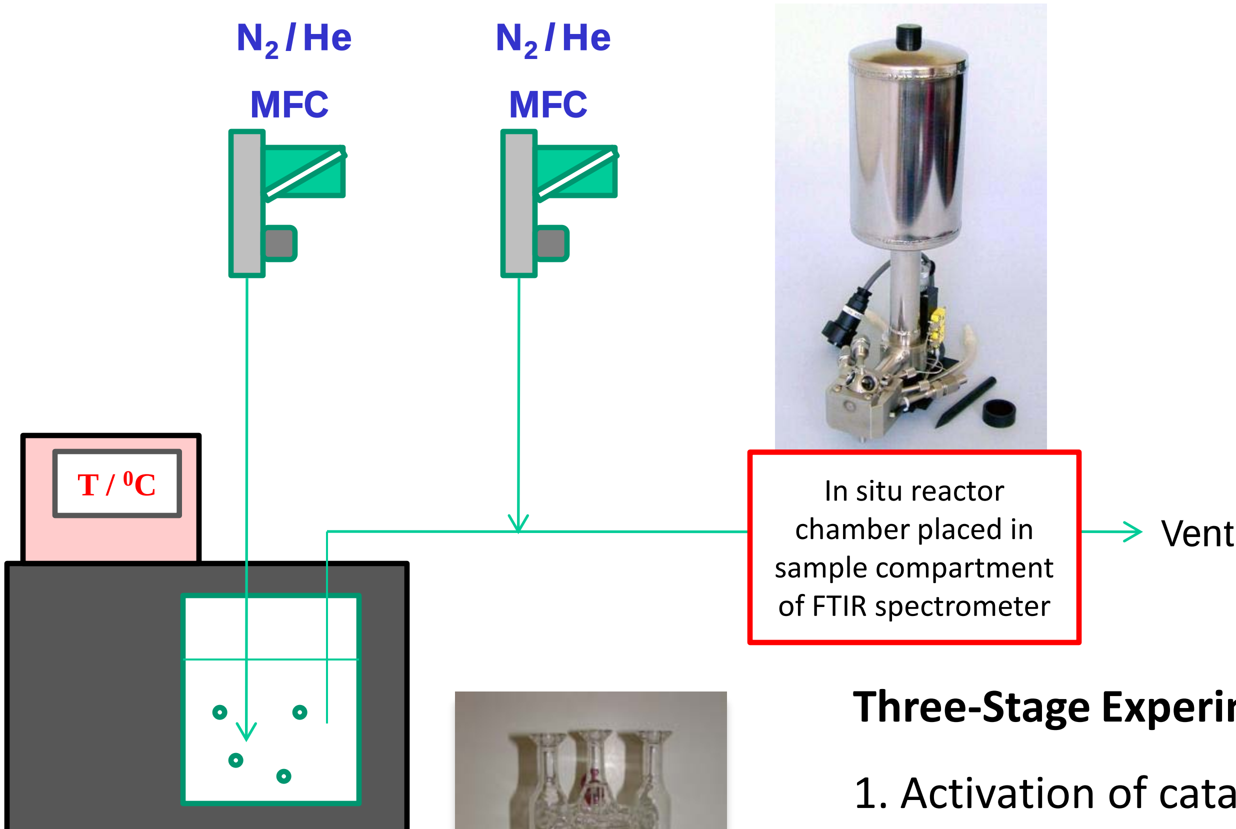
Hydroxy acetone (ketone + alcohol)

n-Propanol (alcohol only)

Acetone (ketone only)

Catalyst	BET surface area in m^2/g
Silica (Hisil, PPG Industries)	190
γ-Alumina (Alfa)	80 - 120
Titania anatase (Alfa)	7 – 14
Ceria (Alfa)	70 0.3
Zirconia (Mel)	150 0.8

Experiment



Hydroxy acetone

Partial Pressure 559 Pa

Temperature of bath 25^{0}C

Acetone

Partial Pressure 1658 Pa

Temperature of bath -18^{0}C

Propanol

Partial Pressure 557 Pa

Temperature of bath 3^{0}C

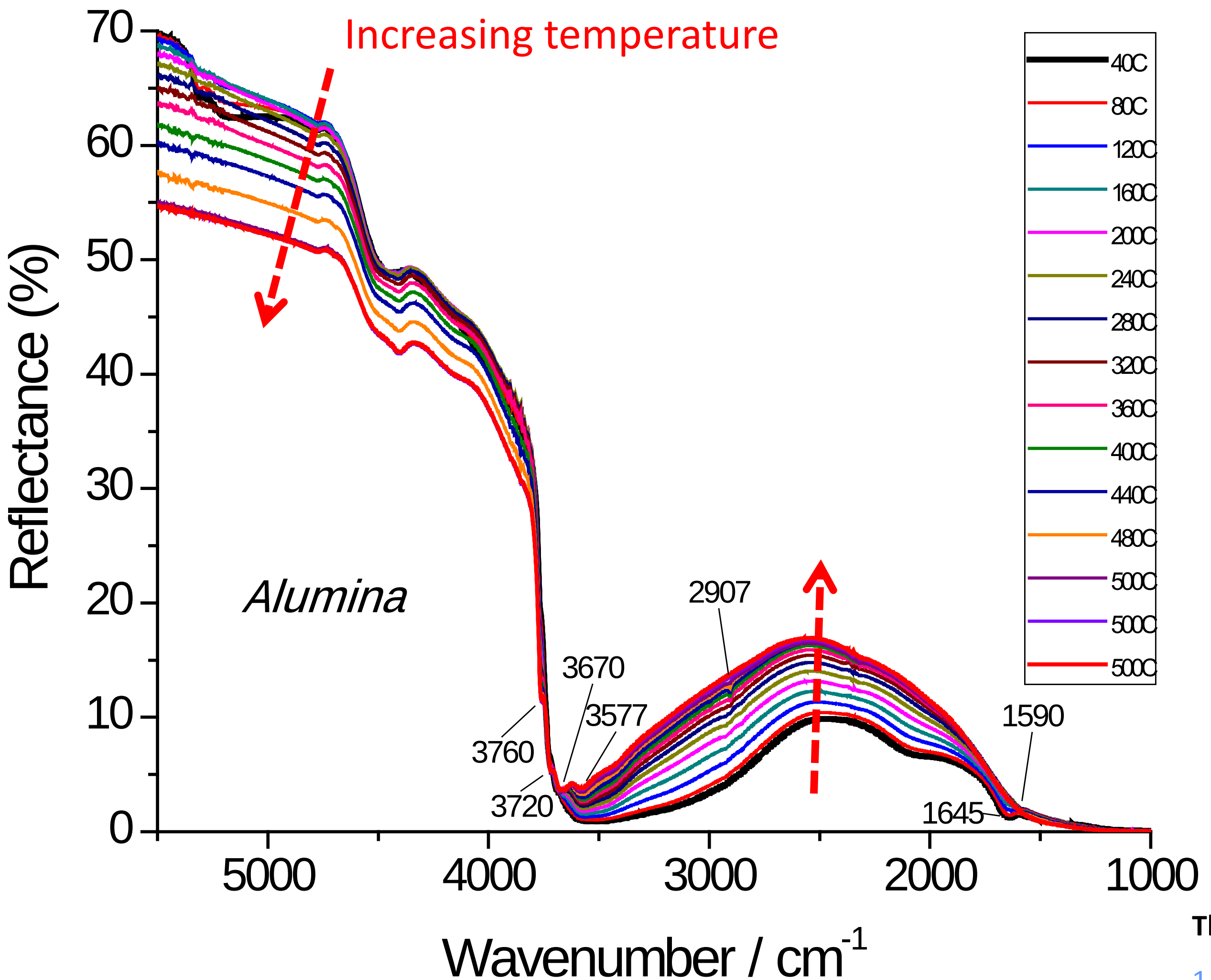
Three-Stage Experiment

1. Activation of catalyst

2. Adsorption of reactant at 40°C
(removal of physisorbed species by purge)

3. Desorption (reaction) through heating

Results: Activation



H_2O ads. desorbs:

Bands above 5000 cm^{-1} and at 1645 cm^{-1} disappear

Broad band from H-bonding at 3700 cm^{-1} and below weakens

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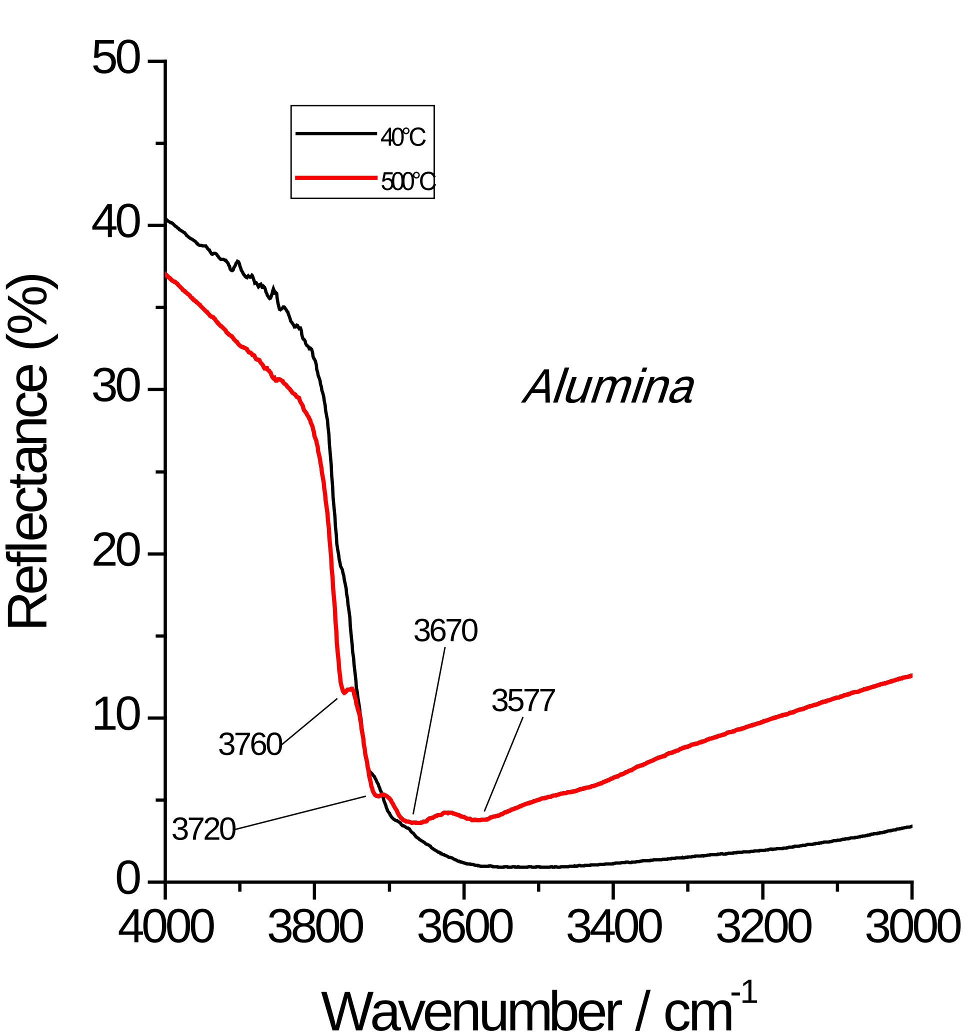
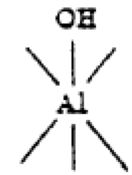
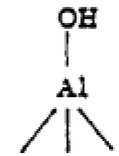
Results: Activation



Type Ib 

3785-3800

Type Ia 

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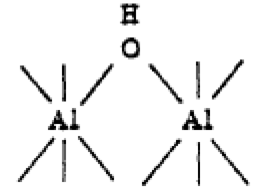
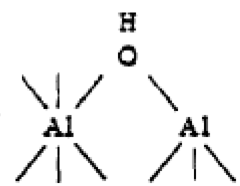
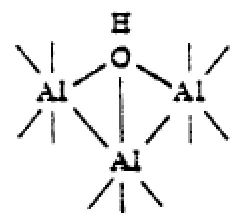
Type IIb 

3740-3745

Type IIa 

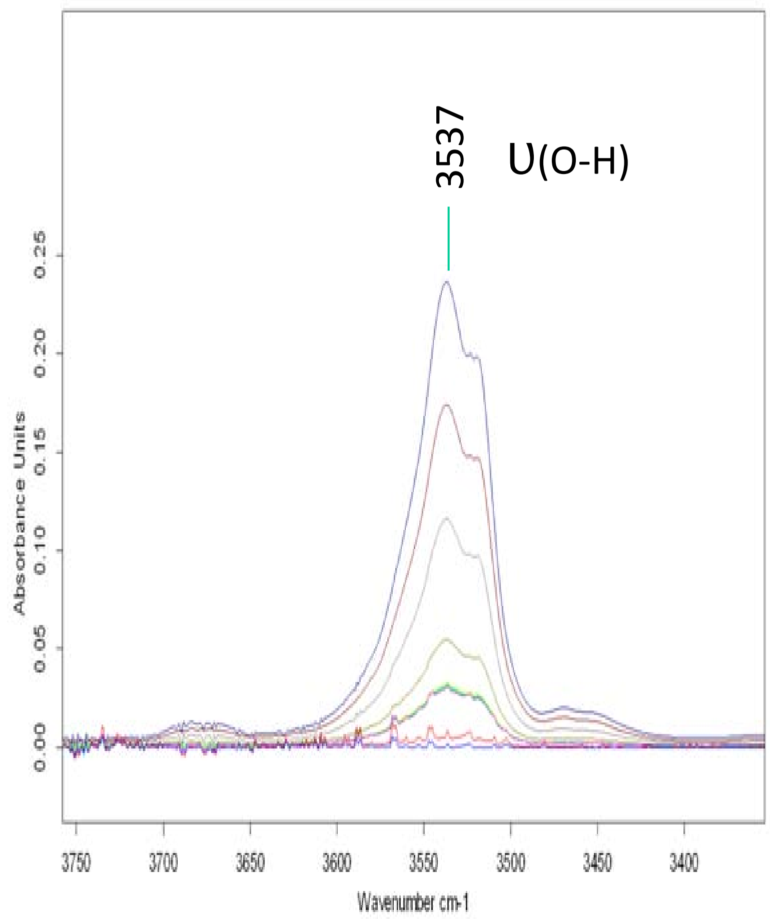
3730-3735

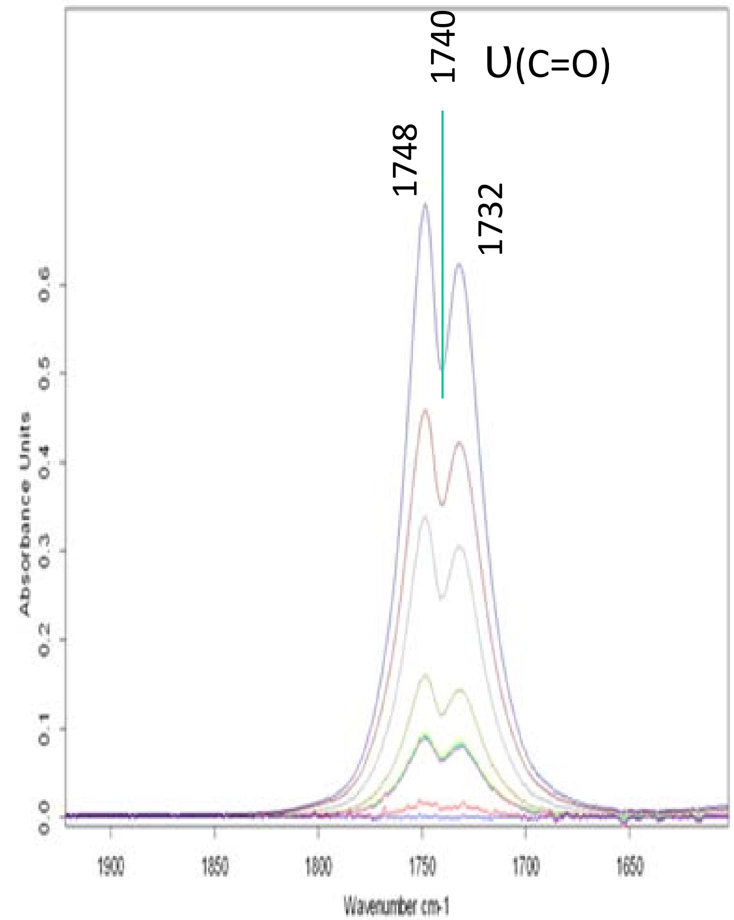
Type III 

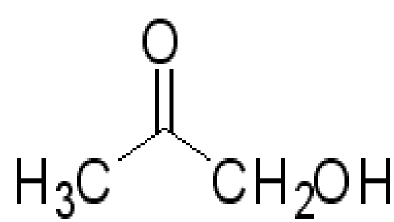
3700-3710

Knözinger, H., Ratnaswamy, P.: Catal. Rev. Sci. Eng. 17,31 (1978)

Hydroxy Acetone Gas Phase Spectrum

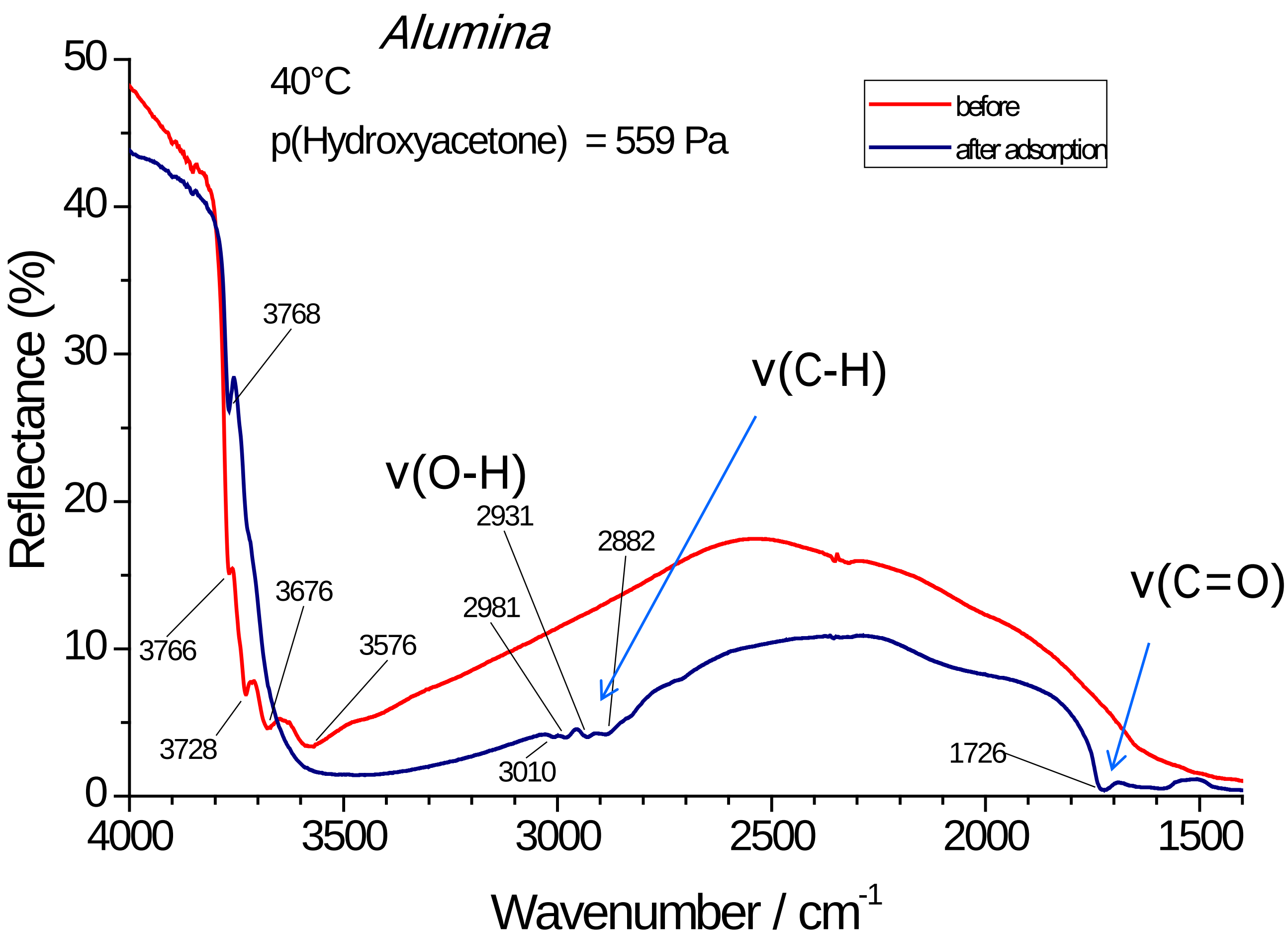




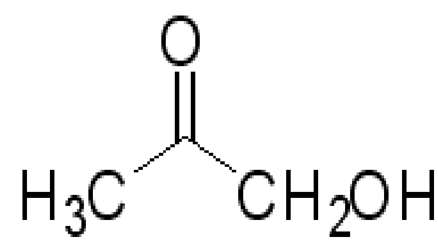


Parameter: partial pressure

Example: Hydroxy Acetone Adsorption



- v(O-H) of adsorbed hydroxy acetone never detectable
- Carbonyl vibration slightly red-shifted relative to gas phase
- Not all OH-groups on alumina surface interact



Three-Stage Experiment

1. Activation of catalyst

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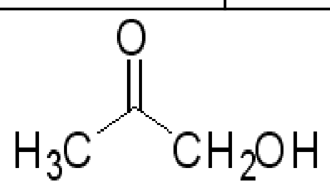
(removal of physisorbed species by purge)

3. Desorption (reaction) through heating

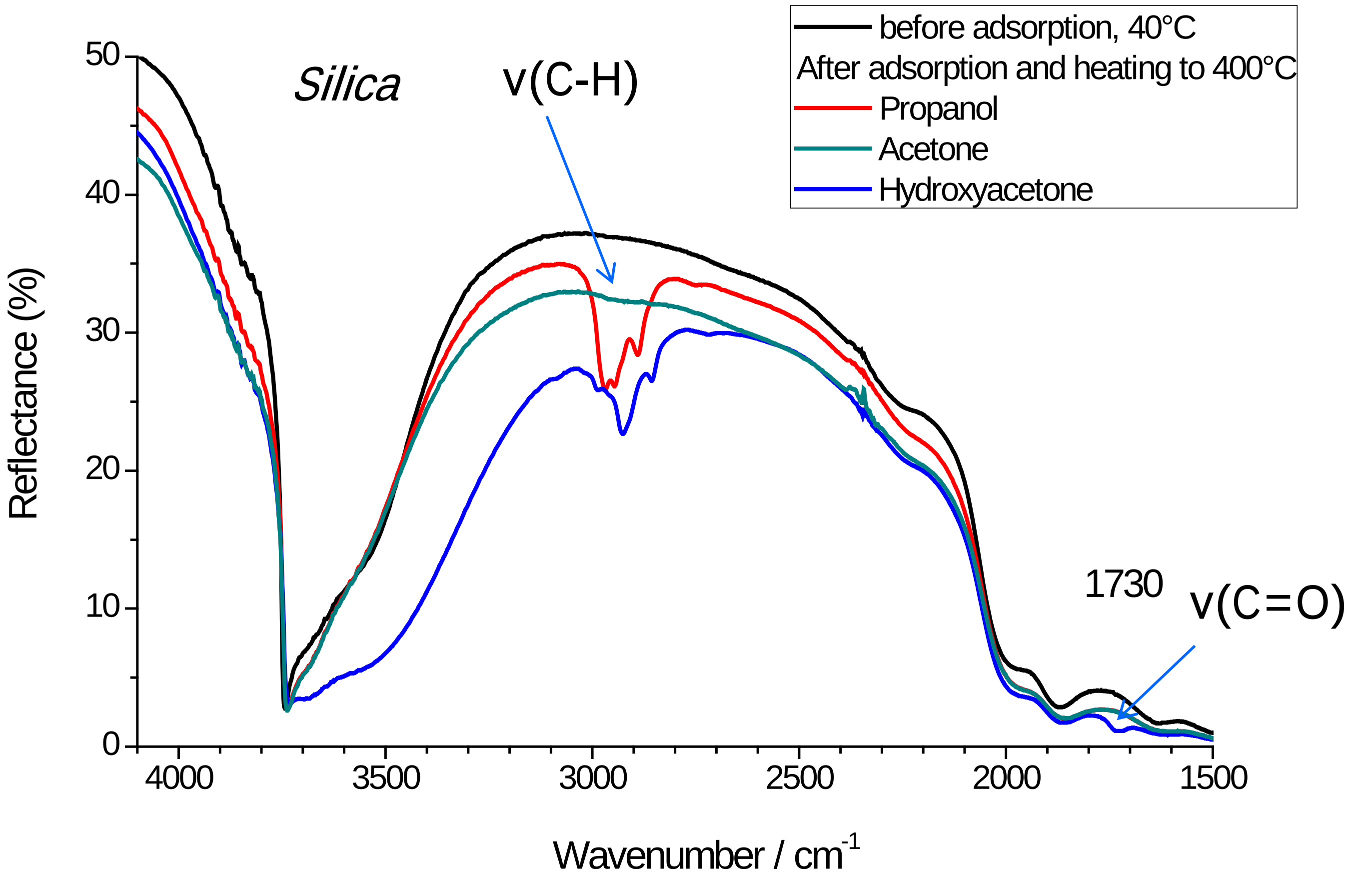
Carbonyl Vibrations (in cm^{-1})

Reactant →	Hydroxy Acetone		Acetone	
Gas Phase	*1740*		*1731**	
Oxide ↓	Position	Shift	Position	Shift
Hisil	1730	-10	1709	-22
Alumina	1726	-14	1702	-29
Titania	1731	-9	1709	-22
Zirconia	1720	-20	1703	-28
Ceria	1710	-30	1697	-34



*"Vibrational spectra and assignment of acetone, ααα-acetone-d3 and acetone-d6", DELLEPIA.G, OVEREND J , SPECTROCHIMICA ACTA 22 (1966) 593

Desorption (and Reaction)



- ν(C-H) indicated remnants of reactant on surface

Three-Stage Experiment

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Preliminary Overview: Desorption (and Reaction)

Reactant → Catalyst ↓	Propanol	Acetone	Hydroxy Acetone
Silica	Stable surface species (alkoxides?)	Complete desorption	Stable surface species
Alumina	Complete desorption	Stable surface species	Stable surface species
Titania	Complete desorption	Desorption Reduction of titania	Stable surface species OH- groups of titania consumed
Zirconia	Stable surface species	Stable surface species (unsaturated)	Stable surface species (unsaturated) High- frequency OH- groups of zirconia consumed
Ceria	Almost complete desorption	Stable surface species (unsaturated)	Stable surface species (unsaturated)

To be complemented by analysis of evolved gases during desorption

Summary and Outlook

Summary

- Strong interactions of oxygenates with the hydrophilic surfaces of common oxides
- Controlled conversion of pyrolysis oil may prove difficult

Outlook

- Complement data with adsorption calorimetric measurements
- Consider other supports

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