CERTIFICATE of Appreciation

This is to certify that

Dr. Hendrik Oktendy Lintang

contributed as

Oral Presenter

in Ma Chung International Conference on Chromatography

9 - 11 October 2017, Malang, Indonesia

Organized by:

UNIVERSITAS MA CHUNG

Ma Chung Research Center for Photosynthetic Pigments

SHIMADZU Excellence in Science

HKI Himpunan Kimia Indonesia

Dr. Leny Yuliati
Organizing Committe Chair
MIC-Chroma

Tatas H.P. Brotosudarmo, Ph.D.
Director of Ma Chung Research Center
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Dr.Eng. Leny Yuliati, S.Si., M.Eng.
Ketua Panitia
NIP. 20160018

UNIVERSITAS
MA CHUNG

LETTER OF ASSIGNMENT

No: 309B/MACHUNG/ST/X/2017

The Rector of Universitas Ma Chung hereby assigns:

Name	:	Dr.Eng. Hendrik Oktendy Lintang, S.Si., M.Eng.
Employee's Number	:	20160017
Position	:	Principal Investigator of MRCPP

to participate in the **Ma Chung International Conference on Chromatography (MIC-Chroma) as Oral Presenter** with abstract entitled **"Porous Kaolin-Phosphotungstic Acid Composites as Heterogeneous Catalyst for Friedel-Crafts Acylation of Anisole"** hosted by MRCPP Universitas Ma Chung which is held on 9-11 Oktober 2017 in Ijen Suites Resort and Convention, Malang.

He has to submit an official report when returns to work.

Please be informed.

Malang, 9 October 2017

Rector

MA CHUNG

Dr. Chatief Kunjaya

Acknowledged by,

Ma Chung International Conference on Chromatography
MIC-Chroma

(Name)

CC:
1. Vice Rector
2. Ma Chung Research Center for Photosynthetic Pigments (MRCPP)
3. Human Resource Management

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Ma Chung Research Center
for Photosynthetic Pigments

MIC-Chroma

Ma Chung International Conference on Chromatography

Abstracts & Program

9 - 11 October 2017

Malang, Indonesia

In collaboration with :

SHIMADZU
Excellence in Science

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Kimia
Indonesia

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GENERAL SCHEDULE

Tuesday, 10 October 2017

Time	Ballroom	Classroom
08:00 - 09:15	Registration	
09:15 - 09:25	Opening remark	
09:25 - 10:15	Plenary lecture (PL-01): **Prof. Dr. Hian Kee Lee** *"Miniaturized and Green Sample Preparation Procedures in Combination with Chromatographic Analysis"* Moderator: Tatas H.P. Brotosudarmo, Ph.D.	
10:15 - 10:30	Coffee break	
10:30 - 11:05	Keynote lecture (KL-01): **Prof. Dr. Mohd Marsin Sanagi** "*Recent Advances in Solid Phase Microextraction Techniques towards Green Chemical Analysis*" Moderator: Dr. Leny Yuliati	
11:05 - 11:40	Keynote lecture (KL-02): **Assoc. Prof. Dr. Koichiro Awai, Ph.D.** "*Chromatography on Lipid Analysis: From Traditional Methods to Advanced Technologies*" Moderator: Dr. Hendrik Oktendy Lintang	
11:40 - 12:00	Group photo	
12:00 - 13:00	Lunch break	
13:00 - 14:30	Poster session	
14:30 - 14:55	Invited speaker (IS-01): **Dr. Zhaoqi Zhan** "*The Shimadzu MRM Method Package Tool For Rapid Method Development on LC/MS/MS for Various Applications*" Moderator: Dr. Hendrik Oktendy Lintang	Invited speaker (IS-02): **Wangsa Tirta Ismaya, Ph.D.** "*Development of HPLC Analysis of Protein Based Therapeutic Drug Product*" Moderator: Rehmadanta Sitepu, S.Farm, M.Si., Apt.

14:55 - 15:20	Invited speaker (IS-03): **Dr. rer.nat Rino R. Mukti** "*Recent Advances in the Syntheses of Zeolites and Their Emerging Applications*" Moderator: Dr. Yuyun Yuniati	Invited speaker (IS-04): **Tatas H.P. Brotosudarmo, Dipl.Chem., Ph.D., MRSC.** "*Analysis of Major Photosynthetic Pigment from Marine Brown Alga*" Moderator: Monika Prihastyanti, M.Nat.Sc.
15:20 - 15:35	Coffee break	
15:35 - 16:35	Oral presentation Moderator: 1. Dr. Hendrik Oktendy Lintang 2. Dr. Yuyun Yuniati	Oral presentation Moderator: 1. Rehmadanta Sitepu, S.Farm., M.Si., Apt. 2. Monika Prihastyanti, M.Nat.Sc.
18:00	Gala dinner	

Wednesday, 11 October 2017

Time	Ballroom	Classroom
08:00 - 09:00	Registration	
09:00 - 09:25	Invited speaker (IS-05): **Prof. Dr.rer.nat. Gunawan Indrayanto** "*Validation of Chromatographic Methods of Analysis: Application for Herbal Drugs*" Moderator: Dion Notario, S.Farm., M.Sc., Apt.	Invited speaker (IS-06): **Prof. Dr. Suppa Hannongbua** "*Determination of Absolute Configuration of Natural Products by Computational Approaches*" Moderator: Rokiy Alfanaar, S.Si., M.Si.
09:25 - 09:50	Invited speaker (IS-07): **Assoc. Prof. Dr. Chua Lee Suan** "*LC-MS/MS Based Phytochemical Profiling Integrated with Chemometrics for Quality Assurance of Herbal Plants*" Moderator: Ruth Febriana Kesuma, S.Si., M.Si.	Invited speaker (IS-08): **Assoc. Prof. Dr.Sc. Akhmad Sabaruddin, S.Si., M.Sc.** "*Development of Organic Polymer-based Monoliths: Application to Analytical and Bioanalytical Chemistry by Liquid Chromatography*" Moderator: Eva Monica, S.Farm., M.Sc., Apt.
09:50 - 10:05	Coffee break	

10:05 - 11:50	Oral presentation Moderator: 1. Dion Notario, S.Farm, M.Sc., Apt. 2. Ruth Febriana Kesuma, S.Si., M.Si.	Oral presentation Moderator: 1. Rokiy Alfanaar, S.Si., M.Si. 2. Eva Monica, S.Farm., M.Sc., Apt.
11:50 - 13:00	Lunch break	
13:00 - 14:15	Oral presentation Moderator: 1. Heriyanto, S.Si., M.Si., M.Sc. 2. Martanty Aditya, M.Farm-Klin., Apt.	Oral presentation Moderator: 1. Rollando, S.Farm., M.Sc., Apt. 2. Renny Indrawati, .S.TP., M.Nat.Sc.
14:15 - 14:30	Coffee break	
14:30 - 16:30	ABP session : **Prof. Dr. Reiko Motohashi** **Dr. Shin Usuki** Moderator: Tatas H.P. Brotosudarmo, Ph.D.	
16:30	Closing ceremony	

SCHEDULE OF ORAL PRESENTATIONS

Tuesday, 10 October 2017

Time	Ballroom	Classroom
15.35 – 15.50	**Faisal Hussin (OP-01)** *"Highly Efficient Zinc Oxide-Carbon Nitride Hybrid Photocatalysts for Degradation of Phenol under UV and Visible Light Irradiation"*	**Siti Maryam Jasman (OP-05)** *"Photocatalytic Oxidation of Nitrite Ion over Carbon Nitride"*
15:50 – 16:05	**Bactiar R.P. Ihsan (OP-02)** *"Validation Method HPLC for analysis Andrographolide in Ethyl Acetate Fractions of 70% Ethanol Extracts Andrographis paniculata"*	**Darius Greenidge (OP-06)** *"Investigations of Color Center Phenomena in Cinnabar and Metacinnabar through Electron Spin Resonance"*
16:05 – 16:20	**Nurul Istiqomah (OP-03)** *"Potential Fraction Cytotoxicity of Sisik Naga (Pyrrosia piloselloides [L.] M.G. Price.) Steril Fronds, Fertile Fronds, and Rhizome on Breast Cancer Cell T47D and Colon WiDr"*	**Suci Amalia (OP-07)** *"Preparation of Monolithic Nanobiocatalyst Microreactor for Fast Protein Digestion and Their Peptide Identification by Liquid Chromatography"*
16:20 – 16.35	**Moh. Mualliful Ilmi (OP-04)** *"Isothermal Adsorption Study of Congo Red Dye with ZSM-5 Directly Synthesized from Bangka Kaolin without Organic Template"*	**Renny Indrawati (OP-08)** *"Re-Evaluation on Multi-Chromatogram Approach of 3D-Chromatographic Data"*
Moderator	**1. Dr. Hendrik O. Lintang** **2. Dr. Yuyun Yuniati**	**1. Rehmadanta Sitepu, M.Si., Apt.** **2. Monika Prihastyanti, M.Nat.Sc.**

Wednesday, 11 October 2017

Time	Ballroom	Classroom
10:05 – 10:20	**Septi F. Raeni (OP-09)** *"Development of Ti^{4+}-Immobilized Nanoporous Monolithic Polymer for Selective Separation and Detection of Phosphopeptides"*	***Delianis Pringgenies (OP-17)*** *"Optimal Concentration of Magrove (Rhizopora Mucronata) Leaf and Propagule Based Natural Dye"*
10:20 – 10:35	**Nurul Husna Sabran (OP-10)** *"Significant Contribution of Copper(I) Pyrazolate Complex in Improving Activity of Anatase Titania"*	***Mohamad Azani Jalani (OP-18)*** *"Size-Exclusion Liquid Chromatography for Effective Purification of Amphiphilic Trinuclear Gold(I) Pyrazolate Complex"*
10:35 – 10:50	**Nurliana Ruslan (OP-11)** *"Gas Chromatography with Flame Ionization and Mass Spectrometer Detectors for Evaluation of Trimethylphenol Oxidation using Heterogeneous Catalyst Nanocomposite"*	***Mohd Hayrie Mohd Hatta (OP-19)*** *"Synthesis of Highly Active Crystalline Carbon Nitride Prepared in Various Salt Melts for Photocatalytic Degradation of Phenol"*
10:50 – 11:05	**Mohamad Rafi (OP-12)** *"Chromatographic Fingerprint Analysis for Quality Control of Medicinal Plant"*	***Agung Bagus Pambudi (OP-20)*** *"Direct Synthesis of ZSM-5 from Kaolin without Organic Template: Part 2. Effect of Type Seeding"*
11:05 – 11:20	**Yohanes Martono (OP-13)** *"Degradation Study Of Stevioside using*	***Florentinus D.O. Riswanto (OP-21)*** *"Analytical Method Validation and*

	HPLC and ESI-MS/MS"	*Determination of Daidzein and Genistein in Ethanolic Extract of Tempeh Using RP-HPLC"*
11:20 – 11:35	**Rahmat Budiarto (OP-14)** *"Gas Chromatography Mass Spectrometry to Profile Leaf Metabolites of Two Popular Citrus Rootstocks in Indonesia"*	***Edi Setiyono (OP-22)*** *"Identification of Carotenoids from Marine Bacterium Erythrobacter sp. KJ5 by Liquid Chromatography-Mass Spectrometry"*
11:35 – 11:50	**Leny Yuliati (OP-15)** *"Optimization of Reaction Condition for Phenol Degradation over Platinum/Titanium Dioxide Photocatalyst"*	***Bimo B. Santoso (OP-23)*** *"Two antimicrobial compounds drimane sesquiterpene polygodial and 11 Hydroxydrim-8-en-7-one from the stem bark of Drimys arfakensis Gibbs."*
11:50 – 12:05	**Hermin Pancasakti Kusumaningrum (OP-16)** *"Comparison of Patchouli Oil Quality from Several Place in Batang Region, Indonesia: Attempt in Improvement of Essensial Oil Quality using GC-MS Methods"*	***Mochammad Junus (OP-24)*** *"The Effect of Dairy Cattle Unit Sludge on the Nutrient of Rice Straw Composite"*
Moderator	1. Dion Notario, M.Sc.Apt. 2. Ruth Febriana Kesuma, S.Si., M.Si.	1. Rokiy Alfanaar, S.Si., M.Sc. 2. Eva Monica,S.Farm., M.Sc., Apt.

Wednesday, 11 October 2017

Time	Ballroom	Classroom
13:00 – 13:15	**Atiqa Rahmawati (OP-25)** *"Fermentation and Purification Study of Food Grade Bioethanol from Sugar Palm Sap (Arenga Pinnata)"*	**Sri Widarti (OP-30)** *"The Influence of Metal Ions; Calcium, Sodium and Copper in Activating a-Amylase with Respect to β-Cyclodextrin Grafted to Polystyrene−Diaminopropane as Stationary Phase in Affinity Chromatography"*
13:15 – 13:30	**Cheer Haan Lau (OP-26)** *"Influence of Concentrating Method on The Quality of Orthosiphon stamineus Extract"*	**Changi Wong (OP-31)** *"Screening of Bioactive compounds from Nepenthes ampullaria and Nepenthes rafflesiana"*
13:30 – 13:45	**Julius Pontoh (OP-27)** *"Gas Chromatographic Analysis of Fatty Acid Composition in the Fresh Water Fishes in North Sulawesi"*	**Rinaldi Idroes (OP-32)** *"The Effect of Column and Temperature Variation on the Determination of Dead Time in Chromatographic System using Mathematical Method"*
13:45 – 14.00	**Dewi Setyaningsih (OP-28)** *"Development and Validation of Thin Layer Chromatography Method for Estimation of Curcumin in Dissolution Samples Containing Mixture of Curcuminoids"*	**Randi Abdur Rohman (OP-33)** *"Role of Phenolic Acids as a Defense System in Oil Palm Infected by Ganoderma boninense"*
14:00 – 14:15	**Hendrik O. Lintang (OP-29)** *"Porous Kaolin-Phosphotungstic Acid Composites as Heterogeneous Catalyst for Friedel-Crafts Acylation of Anisole"*	**Rosita Dwi Chandra (OP-34)** *"Study on Pro-vitamin A and Metabolite Compounds Changes during Ripening Stages in Banana Agung Semeru (Musa paradisiaca formatypica)"*
Moderator	1. Heriyanto, S.Si., M.Si., M.Sc. 2. Martanty Aditya., M.Farm-Klin., Apt.	1. Rollando, S.Farm., M.Sc., Apt. 2. Renny Indrawati, S.TP., M.Nat.Sc.

OP-29

Porous Kaolin-Phosphotungstic Acid Composites as Heterogeneous Catalyst for Friedel-Crafts Acylation of Anisole

Hendrik O. Lintang[1-3]*, Norsahika Mohd Basir[4] and Salasiah Endud[4]

[1]*Ma Chung Research Center for Photosynthetic Pigments (MRCPP), Universitas Ma Chung, Villa Puncak Tidar N-01, Malang 65151, East Java, Indonesia*
[2]*Department of Chemistry, Faculty of Science and Technology, Universitas Ma Chung, Villa Puncak Tidar N-01, Malang 65151, East Java, Indonesia*
[3]*Centre for Sustainable Nanomaterials, IbnuSina Institute for Scientific and Industrial Research, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*
[4]*Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, 81310 UTM Johor Bahru, Johor, Malaysia*

*Corresponding author: hendrik.lintang@machung.ac.id

Keywords: acylation, anisole, gas chromatography, porous kaolin, phosphotungstic acid

Friedel-Crafts acylations are of great importance in industry and are typically carried out by using significant amount of homogeneous acid catalysts [1]. However, the process has produced a large amount of hazardous waste, undesirable products and difficulty in separation [2]. In this work, we reported phosphotungstic acid (HPW) supported onto porous kaolin (PK) as heterogeneous catalysis PK/HPW for the acylation of anisole with propionic anhydride as an acylating agent. A series of PK/xHPW catalysts were successfully prepared with concentration of 10–40 wt% (x is the concentration of HPW) using wet impregnation method. By using pyridine adsorption-FTIR spectroscopy, acidity studies showed that porous kaolin possessed strong Lewis acid sites. In contrast, the surface acidity of the PK/HPW catalysts increased and almost comprised of strong Brönsted acid sites. The catalytic activity was evaluated using gas chromatography with flame ionization detector (GC-FID) consisting of HP-5 column (100% dimethylpolysiloxane, 25 x 0.20 mm I.D). Moreover, analysis of a product as *p*-methoxypropiophenone was carried out using GC with mass spectrometer (GC-MS) detector equipped with the same column. After 3 hours at 100 ^{o}C, the PK/30HPW catalyst (70 mg under solvent-free condition) in the mixture of anisole (30 mmol) and propionic anhydride (30 mmol) showed excellent catalytic activity with 86% conversion and high selectivity in 95% toward *p*-methoxypropiophenone. This result indicates the importance of Brönsted acid sites of well-dispersed HPW onto porous materials with balance of total pore volume and hierarchical factor value (ratio of mesoporosity to microporosity).

References:
[1] Spagnol, M., Gilbert, L. & Alby, D. 1996. In: J. R. Desmurs, S. Rattoy (Eds.). The Roots of Organic Development. Amsterdam: Elsevier.
[2] Olah, G. A. 1973. Friedel-Crafts Chemistry. New York: John Wiley and Sons.

Ma Chung Research Center for Photosynthetic Pigments

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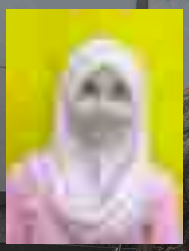
OP-29

Porous Kaolin-Phosphotungstic Acid Composites as Heterogeneous Catalyst for Friedel-Crafts Acylation of Anisole



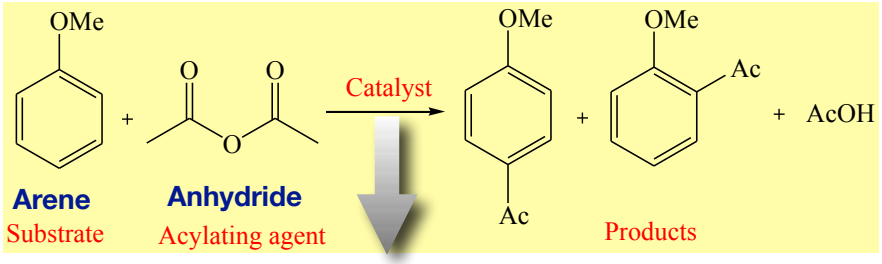
Hendrik. O. Lintang,[1,2,3]
Norsahika Mohd Basir[4], and Salasiah Endud[4]

[1]Ma Chung Research Center for Photosynthetic Pigments (MRCPP), [2]Department of Chemistry, Faculty of Science and Technology, Universitas Ma Chung, INDONESIA
[3]Centre for Sustainable Nanomaterials, [4]Department of Chemistry, Faculty of Science, Universiti Teknologi Malaysia, MALAYSIA

1

Friedel-Crafts Acylation

Electrophilic Aromatic Substitution Reaction between Arenes (Aromatic Rings) and Acyl Chlorides or Anhydrides using a Strong Lewis Acid Catalyst to Produce Monoacylated (Polyalkylated) Products



Intermediates for Fine Chemical and Pharmaceutical Industries or as Precursors for Functional Polymer

Homogeneous Catalyst

Lewis Acid Catalysts ($FeCl_3$, $ZnCl_2$, $AlCl_3$ and BF_3)

Drawbacks

- Significant Hazardous Acids
- High Toxicity
- Corrosion
- Difficult to Separate
- Destroy the Catalysts

Spagnol, M., *et al*., **1996**, *Book; The Roots of Organic Development*

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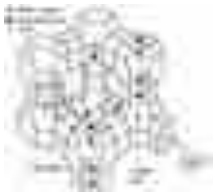
Heterogeneous Acid Catalysts

Example of Heterogeneous Acid Catalysts



Zeolite

Mesoporous Silica

Clay

Heteropoly Acids

Examples

- **UDCat-5;** **99% Selectivity** **57% Conversion**
- **Mordenite Zeolite;** **99% Selectivity** **45% Conversion**

Low Percentage of Conversion

Advantages

- High Surface Area and Pore Volume
- Strong Acidity from Lewis Acid Sites
- Micro- and Mesoporous Structure Balance
- Easy to Separate and Recycle
- Cheaper Precursors

Sartori, G and Maggi, R., *Chemical Review* **2006**, *106*, 1077

Yadav, G.D. and George, G., *Microporous and Mesoporous Materials* **2006**, *96*, 36

Bhadauria, J., *et al*., Journal of Chemical and Pharmaceutical Research, **2011**, 3, 245

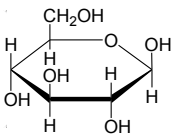
Porous Clay Heterostructures (PCHs)

Functionalization and or Modification of Clays for Increasing Porous Structures

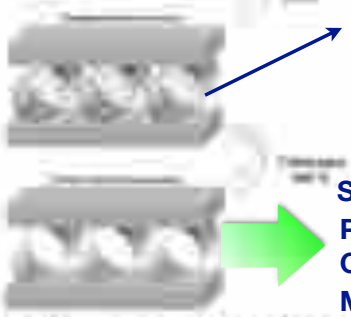
Clay

- Cationic surfactant templates
- Neutral amines co-templates

Biological Template such as Modified Starch (Glucose)



- **Expensive**
- **Difficult to remove**



Silica pillars for high thermal stability

Porous structure with high surface area

Combination of micro- and mesoporoosity

Modification of surface acidity (Brönsted and Lewis Acid Sites)

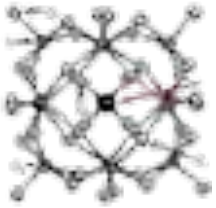
Galarneau, A., *et al*., *Nature* **1995**, *374*, 239

Heteropoly Acids

A Class of Acids from the Combination of Hydrogen and Oxygen with Certain Metals and Non-Metals

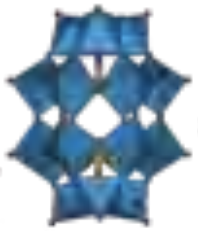
Examples: Phosphotungstic acid (HPW)

Keggin structure ($XM_{12}O_{40}^{n}$)



$H_3PW_{12}O_{40}$

- Strong Brönsted acidity (pK 1.6)
- Problems in bulk form
  - Low surface area
  - Rapid deactivation
  - Thermally less stable (> 200 °C)



Dawson structure ($X_2M_{18}O_{62}^{n}$)

X = P or Si

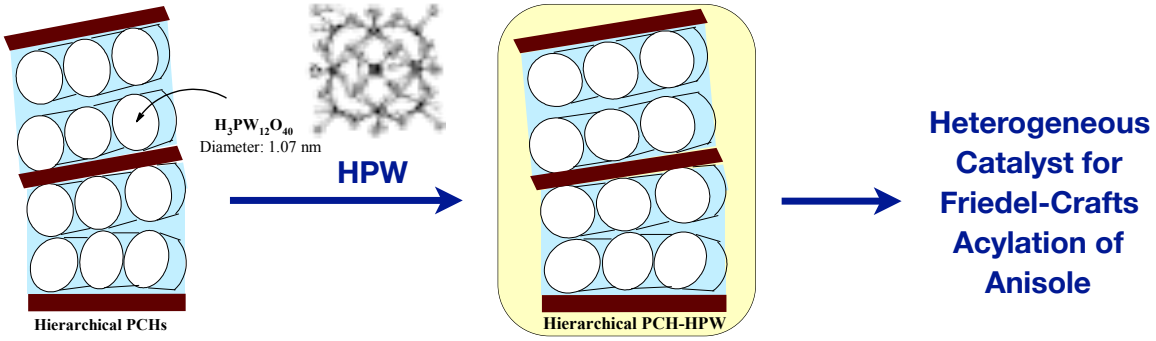
M = Mo, W or V

PCH-HPW Composites as Heterogeneous Catalyst

- Good Surface Area
- Good Porosity
- Hierarchical Structure
- Acidity Properties

Campbell, K.A., *et al*., *Langmuit* **2002**, *21*, 4738
Parida, et al., *Langmuit* **2010**, *21*, 4738

Research Objectives



Porouc Clay Heterostructures (PCHs)

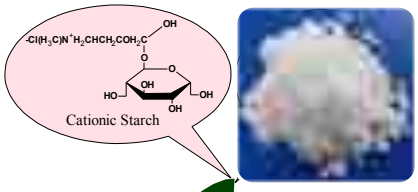
PCH-HPW Composites

Heterogeneous Catalyst for Friedel-Crafts Acylation of Anisole

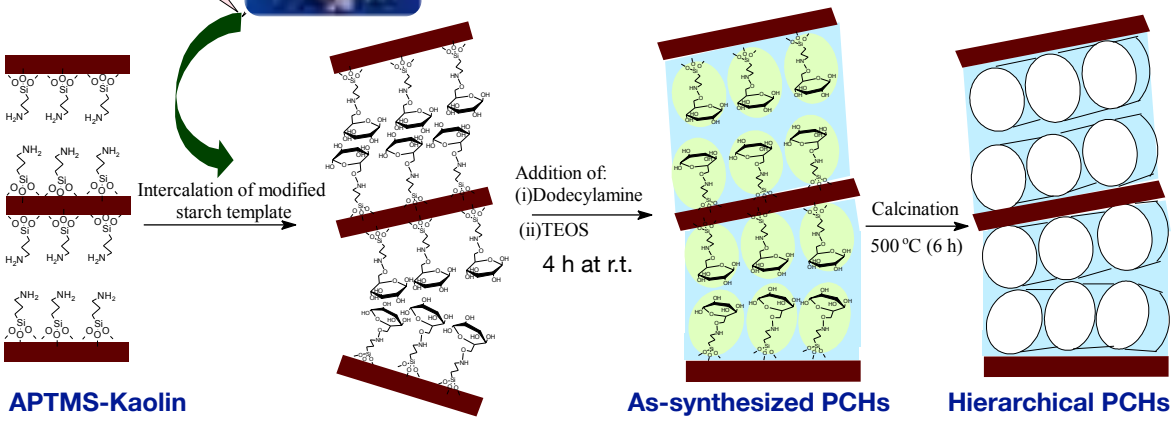
Porous Clay Heterostructures-Phosphotungstic Acid Composites as Heterogeneous Catalyst for Friedel-Crafts Acylation of Anisole

- **Synthesis of Hierarchical Porous Clay Heterostructures (PCHs)**
- **Synthesis of PCHs-Phosphotungstic Acid (HPW) Composites**
- **Friedel-Crafts Acylation of Anisole using PCH-HPW Composites**

Synthesis of Porous Clay Heterostructures (PCHs)



Modification of Potato Starch (PS) as Cationic Starch (CS) in 15 g/200 mL DMSO at 80 °C using NaOH (0.5 g) in water (20 mL) containing N-(3-chloro-2-hydroxypropropyl)trimethylammonium chloride (12.35 mL) at 60 °C



APTMS-Kaolin | **As-synthesized PCHs** | **Hierarchical PCHs (Porous Kaolin = PK)**

modified clay/dodecylamine/TEOS = 1/ 10/ 75

APTMS = 3-aminopropyltrimethoxysilane

Galarneau, A., *et al*., *Nature* **1995**, *374*, 239

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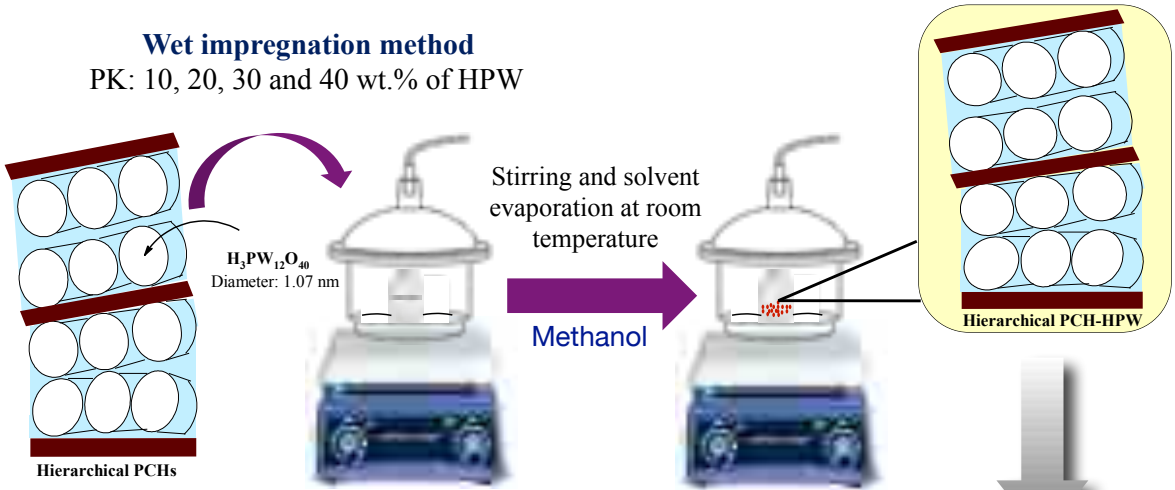
Synthesis of PCH-HPW Composites

Wet impregnation method

PK: 10, 20, 30 and 40 wt.% of HPW



PK/*y*HPW

y = loading amount of HPW ranging 10-40 wt%

Galarneau, A., *et al*., *Nature* **1995**, *374*, 239

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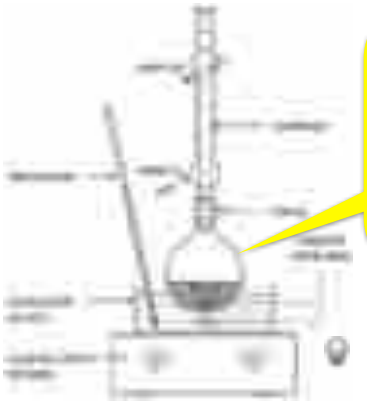
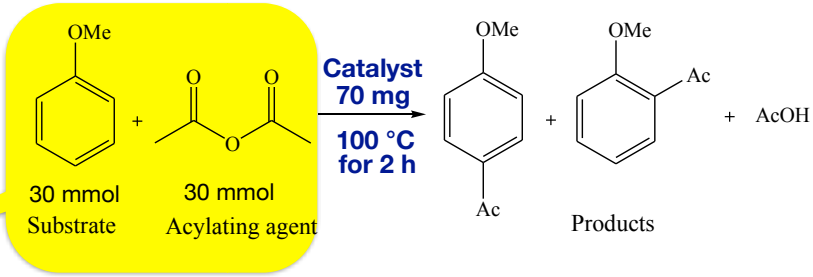
Friedel-Crafts Acylation of Anisole





Analysis of Reaction Products:

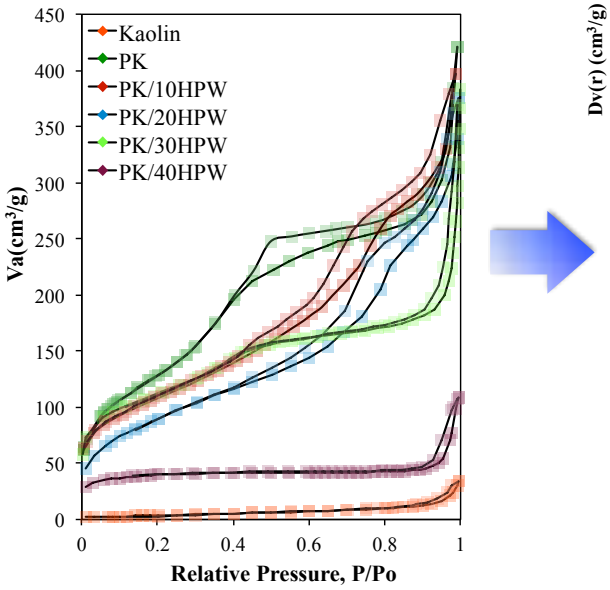
Gas Chromatography - Flame Ionization Detector (GC-FID)

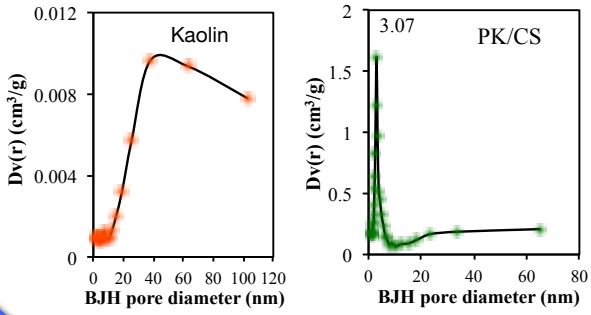
- Hewlett Packard 5890 series II GC instrument
- HP-5 (100% dimethylpolysiloxane, 25 x 0.20 mm I.D) column
- Oven Temp. Program: initial temperature 50 °C (8 mins), rate of temperature 15 °C/min until 200 °C (5 mins).

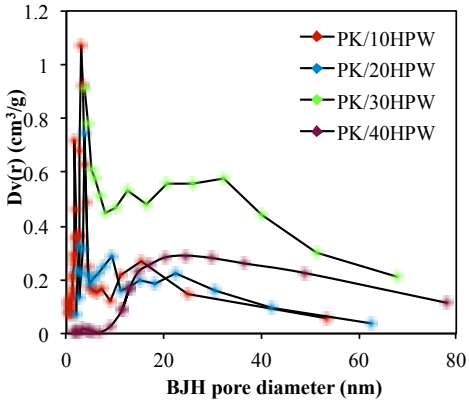
Gas Chromatography - Mass Spectrometry (GC-MS)

- Agilent 6890N-5973 Mass Spectrometry
- HP-5MS column (30 m x 0.251 mm x 0.25 μm)
- Oven Temp. Program: 50 °C (8 mins) to 200 °C (10 mins) with the rate of 15 °C/min.

Nitrogen Absorption-Desorption of Composites







Textural Parameters of Composites

Sample	S_{BET} (m^2g^{-1})	S_{micro} (m^2g^{-1})	S_{meso} (m^2g^{-1})	V_{pores} (cm^3g^{-1})	V_{micro} (cm^3g^{-1})	V_{meso} (cm^3g^{-1})	D (nm)	HF
Kaolin	15	-	23	0.034	-	0.031	6.96, 38.18	-
PK/CS	897	248	282	0.653	0.107	0.546	3.07	0.0872
PK/10HPW	439	183	256	0.486	0.138	0.348	1.71, 3.03	0.1655
PK/20HPW	417	169	248	0.423	0.149	0.274	3.90, 9.26	0.2098
PK/30HPW	389	145	244	0.330	0.132	0.198	3.23	0.2509
PK/40HPW	184	68	116	0.167	0.052	0.115	7.80	0.1963

- Reduction of Surface Area from the Blocking of Pore Channels
- Reduction of Pore Volume from Dispersion of HPW on Surface of Mesoporous Channels
- Increasing of HF Value from High Amount of the HPW Incorporated into the Pore Structure for Reduction of Mesopore Characteristics

The hierarchy factor (HF) = $(V_{micro}/V_{pores}) \times (S_{meso}/S_{BET})$
V_{micro} is obtained from the t–plot method

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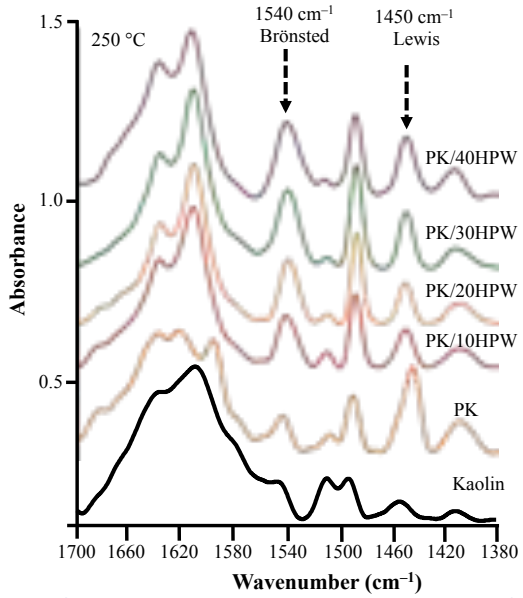
Pyridine Absorption of Composites using FT-IR

NH Banding of pyridinium ions

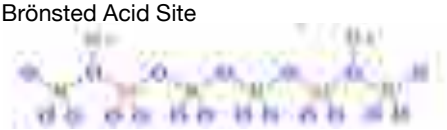


Concentration of Brönsted and Lewis Acid Sites with Evacuation at 250 °C

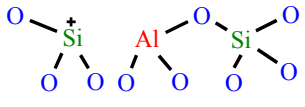
Catalyst	Acidity (μmol g^{-1})		B/L	Total Acidity
	BAS	LAS		
Kaolin	5.32	14.48	0.4	19.80
PK	13.32	89.39	0.2	102.71
PK/10HPW	55.90	34.22	1.6	90.12
PK/20HPW	80.79	30.78	2.6	111.57
PK/30HPW	109.16	23.08	4.7	132.24
PK/40HPW	90.25	26.42	3.4	116.67

PK/30HPW showed the best B/L and total acidity

BAS = Brönsted Acid Site



LAS = Lewis Acid Site



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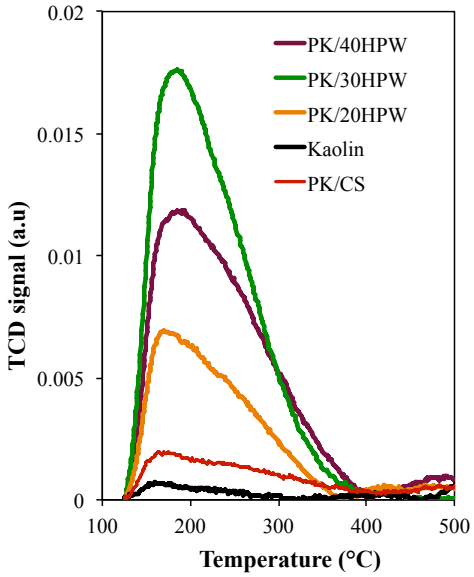
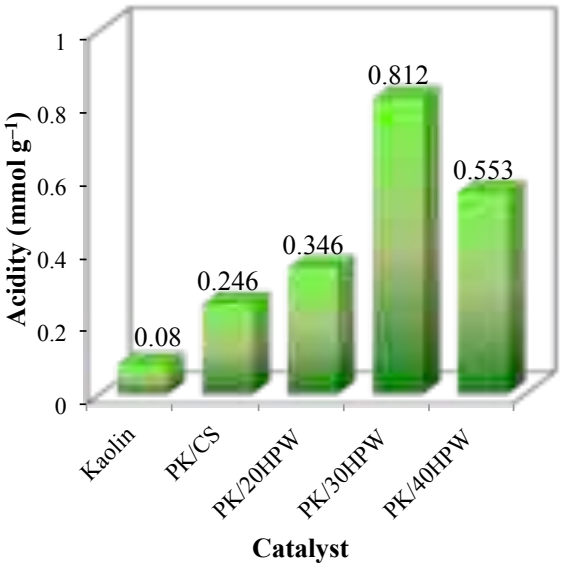
Ammonia Desorption of Composites using TPD

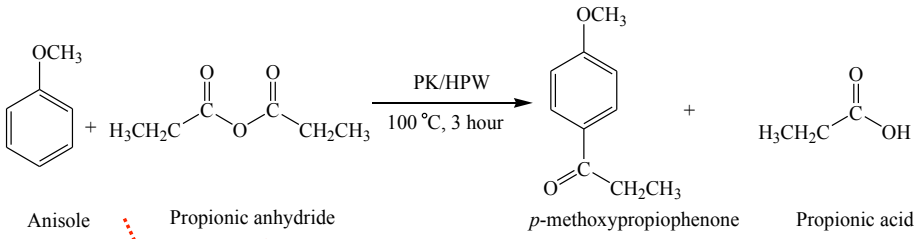




PK/30HPW showed highest acidity from the formation of monolayer coverage of HPW on the hierarchical support

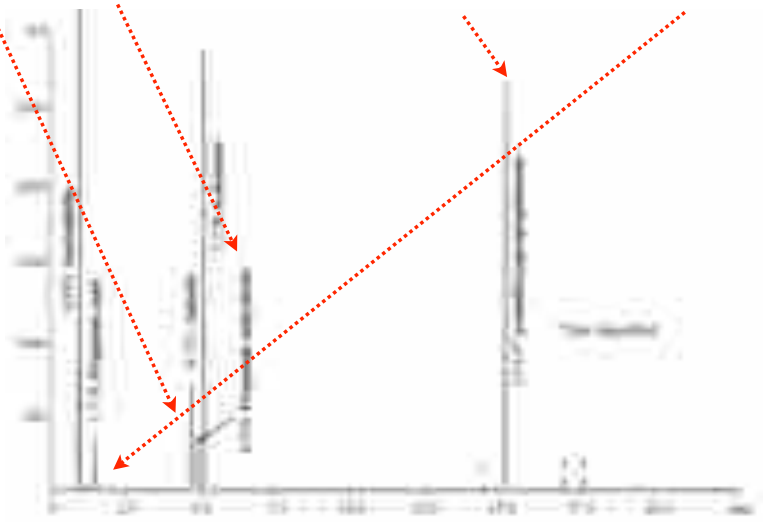
Acidity = total acid sites per unit surface area

Catalytic Activity of Composites in the Acylation

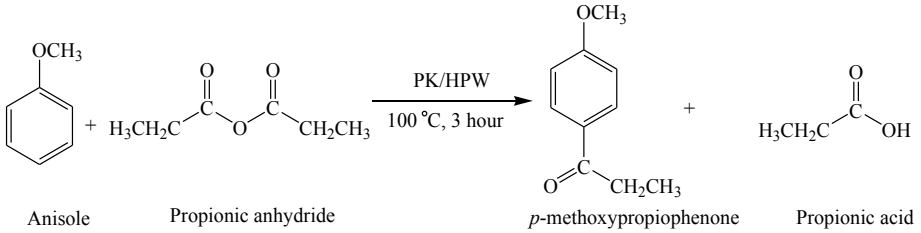


GC-FID Chromatogram

acylation of anisole using PK/30HPW



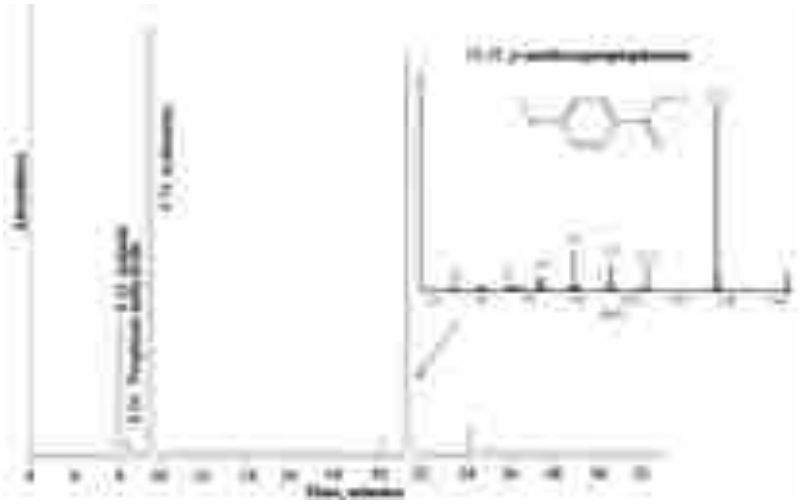
Catalytic Activity of Composites in the Acylation



Anisole | Propionic anhydride | *p*-methoxypropiophenone | Propionic acid

GC-MS Spectrum

acylation of anisole using PK/30HPW



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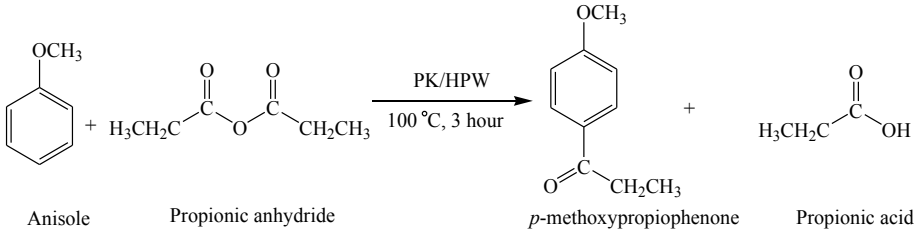
Catalytic Activity of Composites in the Acylation



Anisole | Propionic anhydride | *p*-methoxypropiophenone | Propionic acid

p-MPP | PA

Catalyst	Conversion (%)	Yield of product (mmol)	Selectivity (%)		
			p-MPP	PA	Other products
HPW	35.98	10.66	74.99	17.48	7.53
Kaolin	15.15	4.54	62.34	37.66	0
PK	28.14	8.44	71.95	27.04	1.01
PK/10HPW	68.31	20.02	81.99	15.44	2.57
PK/20HPW	76.17	22.40	88.98	8.47	2.55
PK/30HPW	86.30	25.89	95.39	3.81	0.8
PK/40HPW	80.28	23.51	91.16	7.22	1.62

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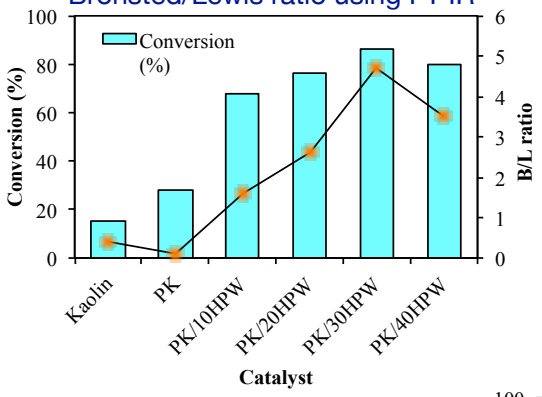
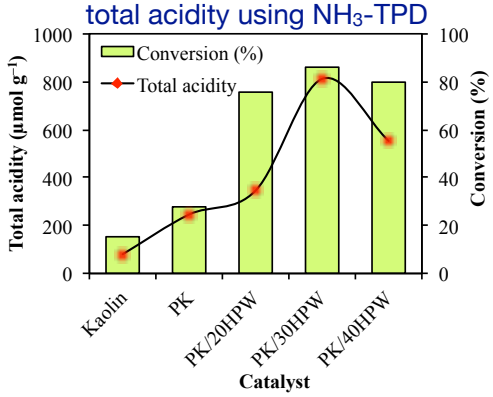
Activity-Acidity Relationship

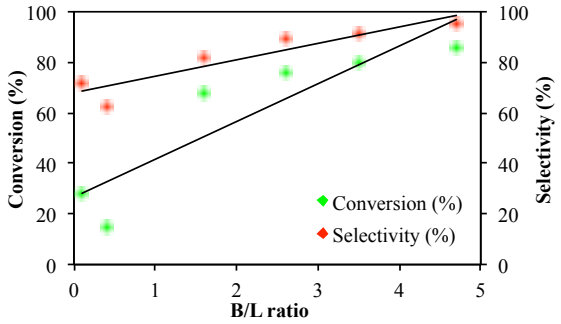
relationship of activity on the Brönsted/Lewis ratio using FT-IR



relationship of activity on the total acidity using NH_3-TPD



relationship of conversion and selectivity on the Brönsted/Lewis ratio using different catalysts



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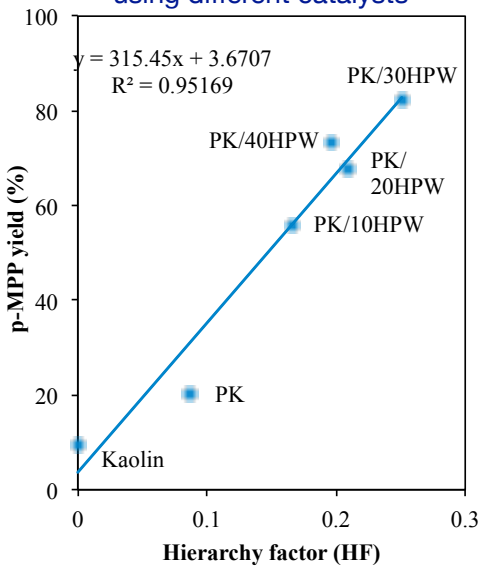
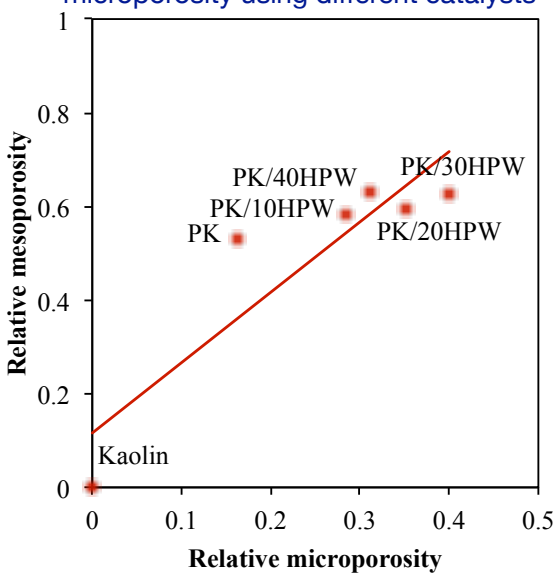
Activity-Hierarchical Factor (HF) Relationship

relationship of activity and HF using different catalysts

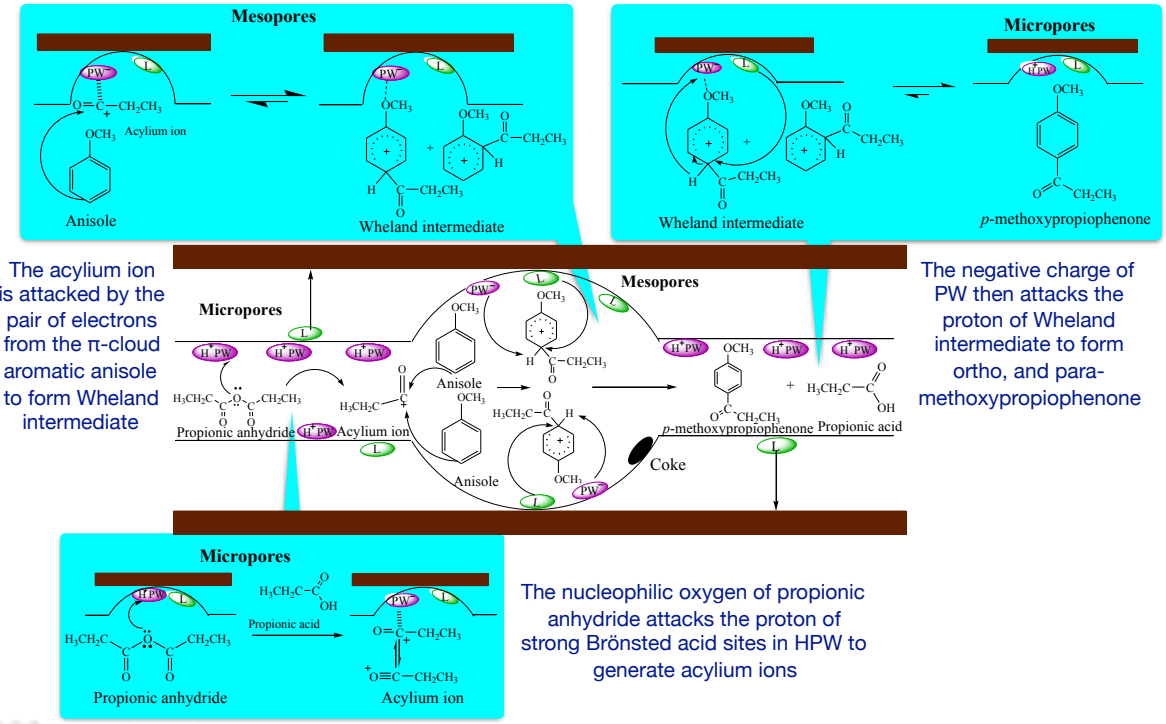


relationship of mesoporosity and microporosity using different catalysts



The best catalyst (PK/30HPW) to give high yield of *p*-MPP has the highest HF and the relative microporosity/mesoporosity ratio

Proposed Mechanism of the Acylation of Anisole



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Conclusions

1. High concentration Brönsted acid sites can be generated in HPW-supported hierarchical Porous Kaolin (PK) for application as Friedel-Crafts acylation heterogeneous catalyst.

2. The 30 wt.% of HPW loading supported on hierarchical PK (PK/30HPW) was the most active catalyst in Friedel-Crafts acylation of anisole.

3. The structure-properties-catalytic activity relationship involved high concentration of strong Brönsted acid sites and hierarchical factor index of heterogeneous catalysts.

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Acknowledgements

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