

**CATALYTIC ESTERIFICATION OF BENZYL ALCOHOL WITH ACETIC
ACID BY ZIRCONIA -LOADED ON MESOPOROUS MATERIAL**

MEHDI ERFANI JAZI

UNIVERSITI TEKNOLOGI MALAYSIA

**CATALYTIC ESTERIFICATION OF BENZYL ALCOHOL WITH ACETIC
ACID BY ZIRCONIA-LOADED ON MESOPOROUS MATERIAL**

MEHDI ERFANI JAZI

A Dissertation Submitted To The Faculty Of Science In Partial Fulfillment Of The
Requirement For The Award Of The Degree In Masters of Science (Chemistry)

Faculty of Science
Universiti Teknologi Malaysia

MARCH 2010

ABSTRACT

This research focuses on the synthesis and characterization of metal-containing mesoporous silica for catalytic esterification of benzyl alcohol with acetic acid. In this study Zr-containing MCM-41 (Zr-MCM-41) with different molar ratios were synthesized successfully, and the influence of the Si/Zr molar ratio on the crystalline structure, textural properties, morphological features and surface acidity of Zr-MCM-41 mesoporous molecular sieves was investigated by X-ray diffraction (XRD), N₂ adsorption-desorption measurement, SEM and FTIR (Fourier transform infrared) Spectroscopy, UV-Vis diffuse reflectance (UV-Vis DR), spectroscopy and single point BET. It is observed that the structural ordering of Zr-MCM-41 varies with the Si/Zr ratio, and highly ordered mesoporous molecular sieves could be earned for a Si/Zr molar ratio larger than 5. Calcination may significantly improve the structural regularity. After impregnation with 15 wt % of H₃PW₁₂O₄₀ (denoted as HWP hereafter), in esterification reaction of benzyl alcohol with acetic acid, the benzyl alcohol conversion over all the HPW/Zr-MCM-41 catalysts linearly increases with increasing the reaction temperature, and selectivity to benzyl acetate was 100 %. The molar ratios of reactants also were investigated for final product yield; the molar ratio of acetic acid to benzyl alcohol can be 2:1 for high yield. The presence of zirconium in tetrahedral coordination was indicated by UV-Vis DR spectra, which shows an absorption band around 220 nm in Zr-MCM41. The catalyst had more active sites than pure Si-MCM-41 due to enhanced hydrophobicity properties and the presence of framework zirconium species as Lewis active sites. Kinetics studies have shown that the esterification reaction follows the Eley-Rideal mechanism. The energy of activation for the reaction follows the order: HPW/Zr-MCM-41(Si/Zr=5) > Zr-MCM-41(Si/Zr=10) > Zr-MCM-41(Si/Zr=20).

ABSTRAK

Penyelidikan ini adalah terfokus pada sintesis dan pencirian silika mesolias yang mengandungi logam bagi pemangkinan pengesteran benzil alkohol dengan asid asetik. Dalam kajian ini MCM-41 yang mengandungi Zr dengan nisbah molar yang berbeza-beza telah berjaya disintesis, dan pengaruh nisbah molar Si/Zr terhadap struktur hablur, ciri-ciri tekstur, morfologi dan keasidan permukaan penapis molekul mesolias Zr-MCM-41 mesoporous telah dikaji menggunakan pembelauan sinar-X (XRD), penjerapan-penyahjerapan N_2 , SEM, spektroskopi FTIR (inframerah Fourier-transform), spektroskopi ultra-lembayung nampak pemantulan difusi (UV-Vis DR), dan analisis BET titik tunggal. Didapati bahawa keteraturan struktur Zr-MCM-41 berubah mengikut nisbah Si/Zr, dan penapis molekul mesolias bertertib julat jauh dapat dihasilkan bagi sampel yang bernisbah molar Si/Zr lebih besar daripada 5. Proses pengkalsinan secara jelas boleh meningkatkan keteraturan struktur. Setelah pengisitepuan dengan $H_3PW_{12}O_{40}$ 15 wt% (diwakili sebagai HWP), dalam tindak balas pengesteran benzil alkohol dengan asid asetik, penukaran benzil alkohol bermangkinkan kesemua HPW/Zr-MCM-41 meningkat secara linear dengan peningkatan suhu tindak balas, dan peratus pemilihan terhadap benzil asetat adalah 100%. Nisbah molar reaktan juga dikaji terhadap penghasilan produk tindak balas, di mana nisbah molar asid asetik kepada benzil alkohol 2:1 telah menunjukkan peratusan hasil paling tinggi. Kehadiran zirkonium dalam koordinatan tetrahedral telah ditunjukkan oleh jalur serapan pada sekitar 220 nm dalam spektrum UV-Vis DR bagi Zr-MCM-41. Mangkin tersebut adalah lebih aktif berbanding Si-MCM-41 tulen kerana peningkatan sifat hidrofobik dan kehadiran spesies zirkonium bingkai sebagai tapak aktif Lewis. Kajian kinetik telah menunjukkan bahawa tindak balas pengesteran benzil alkohol dengan asid asetik berlaku menurut mekanisme Eley-Rideal. Tenaga pengaktifan bagi tindak balas tersebut adalah mengikut tertib: HPW/Zr-MCM-41 (Si/Zr = 5) > Zr-MCM-41 (Si/Zr = 10) > Zr-MCM-41 (Si/Zr = 20).

TABLE OF CONTENTS

CHAPTER	TITLE	PAGE
	DECLARATION	ii
	DEDICATION	iii
	ACKNOWLEDGEMENT	iv
	ABSTRACT	v
	ABSTRAK	vi
	TABLE OF CONTENTS	vii
	LIST OF TABLES	viii
	LIST OF FIGURES	xi
	LIST OF ABBREVIATIONS	xii
	LIST OF APPENDICES	xv
1	INTRODUCTION	
	1.1 Research Background	1
	1.2 Objectives of the study	2
	1.3 Scope of research	3
	1.4 Outline of research	4
2	LITERATURE REVIEW	
	2.1 Porous Materials	5
	2.2 Mesoporous MCM-41	8
	2.3 Synthesis of Mesoporous MCM-41	9

2.4	Characterization of MCM-41	11
2.5	Mechanism of Formation of Mesoporous MCM-41	12
2.5.1	Liquid Crystal Templating Mechanism	13
2.5.2	Silicate Rod Assembly	13
2.5.3	Folded Sheet Mechanism	15
2.5.4	Mechanism of Transformation from Lamellar to Hexagonal Phase	15
2.6	Incorporation of Zirconia into MCM-41	15
2.7	Zirconia as acid catalyst	17
2.8	Heteropoly acids as impregnated to the mesoporous materials	18
2.9	Esterification of benzyl alcohol with acetic acid	18
3	METHODOLOGY	
3.1	Introduction	22
3.2	Chemical	22
3.3	Catalyst Synthesis	23
3.3.1	Synthesis of Zr-MCM-41 Supports	23
3.3.2	Preparation of H ₃ PW ₁₂ O ₄ supported Zr-MCM-41(HPW/Zr-MCM-41)	24
3.4	Characterization of HPW/Zr-MCM-41	25
3.4.1	Powder X-Ray Diffraction (XRD)	26
3.4.2	Fourier Transform Infrared Spectroscopy	26
3.4.3	Ultraviolet-Visible Diffuse Reflectance Spectroscopy (UV-Vis DR)	27
3.4.4	Scanning Electron Microscopy (SEM)	28
3.4.5	N ₂ adsorption Analysis	28
3.5	Catalytic testing	28
3.5.1	Esterification of benzyl alcohol with acetic acid in presence of HPW/Zr-MCM-41	29
3.5.2	Analysis of the Reaction Products	30



4	RESULT AND DISCUSSION	
4.1	Synthesis of Zirconia containing MCM-41 (Zr-MCM-41)	32
4.2	Characterization of Zr-MCM-41 support	33
4.2.1	XRD Analysis	33
4.2.2	Textural properties	36
4.2.3	Morphology features	38
4.2.4	UV-Vis DR analysis	40
4.3	H ₃ PW ₁₂ O ₄₀ /Zr-MCM-41 catalyst	42
4.3.1	FTIR Studies	42
4.4	Catalytic Test	45
4.4.1	Influence of molar ratio of the reactants	46
4.4.2	Influence of the catalyst concentration	48
4.4.3	Influence of the temperature	50
4.4.4	Influence of the reaction time	52
4.4.5	Kinetics of esterification of benzyl alcohol with acetic acid	54
4.4.6	Mechanism	58
5	CONCLUSION AND RECOMMENDATION	
5.1	Conclusion	63
5.2	Recommendation	64
	REFERENCES	65
	APPENDICES	71



LIST OF TABLES

TABLE NO.	TITLE	PAGE
2.1	Classification of porous materials	5
2.2	Examples of zeolites and molecular sieves	7
2.3	Different molar ratios of surfactant /silica for mesoporous synthesis and the typical phases formed	10
2.4	Routes for synthesis mesoporous materials	11
3.1	List of chemical used in synthesis of catalyst	23
3.2	Sample codes for different Si/Zr ratio of the materials	24
3.3	GC-FID oven-programmed set up for identifying benzyl acetate	30
3.4	GC-MSD oven-programmed set up for verifying benzyl acetate	31
4.1	Reaction rate constants (10^{-3}) and energy of activation (kJ mol^{-1})	55

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
1.1	Esterification of benzyl alcohol with acetic acid	2
1.2	Outline of research	4
2.1	The mesoporous M41S family	9
2.2	The structure of mesoporous MCM-41 material	9
2.3	(1) Liquid crystal phase initiated and (2) silicate anion initiated	14
3.1	Scheme for generation of Brønsted and Lewis acid sites	25
4.1	XRD patterns of the as-made and calcined Zr-MCM-41(Si/Zr=20)	34
4.2	XRD patterns of the calcined Zr-MCM-41(Si/Zr=10)	35
4.3	XRD patterns of the calcined Zr-MCM-41(Si/Zr=5)	35
4.4	(a) Pore diameter distribution of the sample calcined at 600°C. (b) The N ₂ adsorption-desorption isotherm of the sample (Si/Zr=20)	37
4.5	(a) Pore diameter distribution of the sample calcined at 600°C. (b) N ₂ adsorption-desorption isotherm of the sample (Si/Zr=10)	37
4.6	(a) Pore diameter distribution of the sample calcined at 600°C. (b) N ₂ adsorption-desorption isotherm of the sample (Si/Zr=5)	38
4.7	SEM images of MCM-41	39
4.8	SEM images of Zr-MCM-41(Si/Zr=20)	39

4.9	SEM images of Zr-MCM-41(Si/Zr=10)	40
4.10	UV-Visible Spectra for MCM – 41 and Zr-MCM-41(Si/Zr=20 and 5)	41
4.11	FTIR Spectrum of HPW/Zr-MCM-41	43
4.12	FTIR Spectrum of Zr-MCM-41 and MCM-41	44
4.13	Esterification of BA with AA	45
4.14	Esterification of benzyl alcohol with acetic acid: effect of catalyst type. Acetic acid(AA):benzyl Alcohol(BA), 2:1(mol/mol); reaction time 1 h; catalyst weight 0.5 g ; reaction temperature, 383 K. Conversion (purple); Selectivity (light yellow), ester	46
4.15	Esterification of benzyl alcohol with acetic acid: effect of AA:BA molar ratio (mol/mol); reaction time 1 h; catalyst weight, 0.5 g; reaction temperature, 383 K. Conversion (purple); Selectivity (light yellow), ester (Si/Zr=10)	47
4.16	Esterification of benzyl alcohol with acetic acid: effect of AA:BA molar ratio (mol/mol); reaction time 1 h; catalyst weight, 0.5 g ; reaction temperature, 383 K. Conversion (purple); Selectivity (light yellow), ester (Si/Zr=20)	48
4.17	Esterification of benzyl alcohol with acetic acid: effect of catalyst weight. AA:BA 2:1(mol/mol); reaction time 1 h; catalyst weight, 0.5 g; reaction temperature= 383 K. Conversion (purple); Selectivity (light yellow), ester	49
4.18	Esterification of benzyl alcohol with acetic acid: effect of catalyst weight. AA:BA 2:1(mol/mol); reaction time 1 h; catalyst weight, 0.5 g; reaction temperature= 383 K. Conversion (purple); Selectivity (light yellow), ester	49
4.19	Esterification of benzyl alcohol with acetic acid: effect of reaction temperature AA:BA 2:1(mol/mol); reaction time 1 h; catalyst weight, 0.5 g; reaction temperature, 383 K. Conversion (); Selectivity (), (ester)	51
4.20	Esterification of benzyl alcohol with acetic acid: effect of reaction time AA: BA 2:1(mol/mol); catalyst weight, 0.5 g; reaction temperature, 383 K.	

	Conversion (); Selectivity (), (ester)	53
4.21	Reaction pathway for the esterification of BA with AA	54
4.22	Effect of catalyst weight on reaction rate	56
4.23	Plot of first-order rate equation for esterification of BA with AA over Si/Zr=20 at 403K, 393K and 383K respectively from above	56
4.24	Plot of first-order rate equation for esterification of BA with AA over Si/Zr=10 at 403K, 393K and 383K respectively from above	57
4.25	Plot of first-order rate equation for esterification of BA with AA over Si/Zr=5 at 403K, 393K and 383K respectively from above	57
4.26	Plot of first-order rate equation for esterification of benzyl alcohol with acetic acid in absence of any catalyst at 403 K, 393 K and 383K from above	58
4.27	Esterification of BA with AA: effect of acetic acid concentration on the initial reaction rate. Concentration of benzyl alcohol, 8.1 mol; reaction temperature, 383 K; catalyst weight, 0.5g	59
4.28	Esterification of BA with AA: effect of acetic acid concentration on the initial reaction rate. Concentration of benzyl alcohol, 8.1 mol; reaction temperature, 383 K; catalyst weight, 0.5g	60
4.29	Possible reaction mechanism for the esterification of BA with AA over mesoporous materials	61
4.30	Plot of C_B/r_E vs C_B/C_A for esterification reaction of BA with AA. Reaction temperature, 383 K, catalyst weight 0.5g	62

LIST OF ABBREVIATIONS

AAS	-	Atomic absorption spectroscopy
AA	-	Acetic acid
BA	-	Benzyl alcohol
CTABr	-	Cetyltrimethylammonium bromide
ER	-	Eley-Ridel
FTIR	-	Fourier transformer infrared spectroscopy
HPW	-	Tungsten phosphoric acid
KBr	-	Potassium bromide
LH	-	Langmuir-hinshelwood
MCM	-	Mobil composition of matter
RHA	-	Rice husk ash
SI – MCM – 41	-	Purely siliceous MCM-41
TEOS	-	Tetraethylorthosilicate
DR UV – Vis	-	Diffuse reflectance ultraviolet-visible Spectroscopy
XRD	-	X-ray diffraction
Zr – MCM - 41	-	Zirconia containing MCM-41

LIST OF APPENDICES

APPENDIX	TITLE	PAGE
A	Quantitative analysis of gas chromatography	73
B	Reaction rate versus acetic acid concentration	74
C	Reaction rate versus type of catalyst	75
D	First order equation reaction versus time	75
E	Rate versus acetic acid concentration	76

Solid acid catalysts as zeolites are convenient alternatives to such conventional acids which have been used as catalysts since 1960s in petrochemicals manufacture, further expanding into areas of speciality and fine chemical synthesis [6]. But zeolites are microporous materials and meet with diffusional resistance both for reactants and products as well as applicable only for smaller molecular organic compound.

Mesoporous silica possesses high specific surface areas, tunable pore channels from 16 to 100 and high specific pore volumes, which show that mesoporous silica is considerable to overcome the limitation of zeolites. Since, mesoporous materials do not have efficient catalytic properties due to absence of catalytically active sites, so MCM-41 is often modified by incorporating certain active materials such as metal oxides, metal complexes and others. therefore, the research is conducted in order to synthesize the zirconia loaded MCM-41 and the resulting material tested in the esterification of benzyl alcohol with acetic acid. Figure 1.1 gives the reaction scheme for esterification of benzyl alcohol with acetic acid.

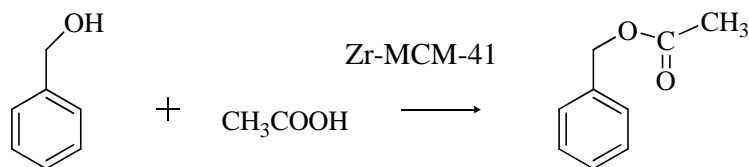


Figure 1.1 Esterification of benzyl alcohol with acetic acid

1.2 Objectives of Study

The research objectives are listed as below:

- (a) To synthesize high quality zirconia loaded on MCM-41

- (b) To characterize the physicochemical properties of the catalyst by, Fourier-Transform Infrared (FTIR) spectroscopy, Diffuse reflectance UV-Visible (DRUV-Vis) spectroscopy, X-ray diffraction (XRD), and nitrogen adsorption desorption measurement.
- (c) To investigate the catalytic properties of Zr-MCM-41 in the esterification of benzyl alcohol with acetic acid
- (d) To study the chemical kinetics of the esterification of benzyl alcohol with acetic acid.

1.3 Scopes of Research

The scopes of the research are listed as below:

- (a) Direct synthesis of zirconia loaded on MCM-41(Zr-MCM-41) with various content of zirconium.
- (b) Characterization of physicochemical properties of Zr-MCM-41 using XRD, nitrogen on adsorption desorption isotherm, DR UV-Vis and FTIR spectroscopies.
- (c) Optimization of the reaction parameters such as temperature, reaction time and molar ratio of reactants.
- (d) Investigation on the chemical kinetic of reaction of benzyl alcohol with acetic acid.

REFERENCES

1. Junzo, O. and Joji, N. (2010). *Reaction with Carboxylic Acids*. In Junzo, O. (Ed.) *Esterification: Methods, Reactions, and Applications*. (pp. 250-300). New York: Wiley-VCH.
2. Marchetti, J.M. and Errazu, A.F. (2008). Esterification of free fatty acids using sulphuric acid as catalyst in the presence of triglycerides. *Short Communication*. **32**. 892-895.
3. Trissa, J., Suman, S. and Halligudi, S. B. (2005). Heterogeneous catalysis in esterification reactions: Preparation of phenethyl acetate and cyclohexyl acetate by using a variety of solid acidic catalyst. *Industrial and Engineering Chemistry Research*. **33**. 2198-2208.
4. Hiroshi, U., Hideo, H. and Toshiharu, M. (1975). Mechanism of esterification of alcohols with surface silanols and hydrolysis of surface esters on silica gels *Journal of Colloid and Interface Science*. **50**. 154-161.
5. Johanna, L., Johan, W., Tapio, S., Lars, J., Pettersson, J., Henrik, G., Mats, R. and Dmitry, Y. (2005). Esterification of propanoic acid with ethanol, 1-propanol and butanol over a heterogeneous fiber catalyst. *Chemical Engineering Journal*. **115**. 1-12.
6. Martina, B., Dana, P. and Jiri, C. (2009). Acylation reactions over zeolites and mesoporous catalysts. *Journal of Chemistry and Sustainability*. **2**. 486-499.

7. I.U.P.A.C. (1972). *Manual of Symbols & Terminology*. Washington, DC: Pure and Applied Chemistry.
8. Borislav, D.Z., Jiří, J., Martin, Š. and Josef, J. (2007). Pore classification in the characterization of porous materials: A perspective. *Central European Journal of Chemistry*. **5**. Number 2.
9. Masakazu, I. (1994). Zeolites in Environmental Catalysis. *Studies in Surface Science and Catalysis*. **84**. 1395-1410.
10. Kulkarni, S. J. (1998). Recent trends in the applications of zeolites and molecular sieves for the synthesis of speciality and fine chemicals. *Studies in Surface Science and Catalysis*. **113**. 151-161.
11. Peiddong, Y., Tao, D., Dongyuan, Z., Pingyum, F., David, P., Bradlyf, C., George, M., White, S. and Galen, D. (1998). Hierarchically ordered oxide. *Science*. **282**. 2244-2246.
12. Avelino, C. (1997). From microporous to mesoporous molecular sieves materials and their use in catalysis. *Chem Rev*. **97(6)**. 2373-2420.
13. Ying, M., Hua, Z. and Steven, L. S. (2000). A review of zeolite-like porous materials. *Microporous and Mesoporous Materials*. **37**. 243-252.
14. Chengdu, L., Zuojiang, Li. and Sheng, D. (2008). Mesoporous Carbon Materials: Synthesis and Modification. *Angewandte Chemie International Edition*. **47**. 3696-3717.
15. Sonia, A. and Antonio, B.F. (2004). Template synthesis of mesoporous carbons with tailorable pore size and porosity. *Carbon*. **42**. 433-436.
16. Kresge, C.T., Leonowicz, M.E., Roth, W.J., Vartuli, J.C. and Beck, J.S. (1992). Ordered mesoporous molecular sieves synthesized by a liquid-crystal template mechanism. *Nature*. **359**. 710-712.

17. Yong-Ming, L., Zhao-Yin, D. and Xia-Ming, Z. (2007). Synthesis and Characterization of Ordered Mesoporous Aluminasilicate Molecular sieves with high stability in High-Temperature Steam. *Chinese Journal of Chemistry*. **25**. 635-639.
18. Patarin, J., Lebeau, B. and Zana, R. (2002). Recent advances in the formation mechanisms of organized mesoporous materials. *Current Opinion in Colloid & Interface Science*. **7**. 107-115.
19. Tatiana, K., Mario, C. and Jorge, R. (2003). Ni and Mo interaction with Al-containing MCM-41 support and its effect on the catalytic behaviour in DBT hydrodesulfurization. *Applied Catalysis A: General*. **240**. 29-40.
20. Kazu, O., Kyoichi, N. and Miki, N. (2001). Prominent catalytic activity of Ga-containing MCM-41 in the Friedel–Crafts alkylation. *Microporous and Mesoporous Materials*. **45**. 509-516.
21. Xiaozhong, W., Wenhui, L., Guangshan, Z., Shilun, Q., Dongyuan, Z. and Bing, Z. (2004). Effects of ammonia/silica molar ratio on the synthesis and structure of bimodal mesopore silica xerogel. *Microporous and Mesoporous Materials*. **71**. 87-97.
22. Yu-De, W., Chun-Lai, M., Xiao-Dan, S. and Heng-De, Li. (2002). Neutral templating route to mesoporous structured TiO₂. *Materials Letters*. **54**. 359-363.
23. Lefevre, B., Saugey, A., Barrat, J., Bocquet, L., Charlaix, E., Gobin, P. F. and Vigier, G. (2004). Intrusion and extrusion of water in highly hydrophobic mesoporous materials: effect of the pore texture. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*. **241**. 261-272.
24. Cong-Yan, C., Hong-Xin, L. and Mark, E.D. (1993). Studies on mesoporous materials: I. Synthesis and characterization of MCM-41. *Microporous Materials*. **2**. 18-26.

25. González, F., Pesquera, C., Perdigón, A. and Blanco, C. (2009). Synthesis, characterization and catalytic performance of Al-MCM-41 mesoporous materials. *Applied Surface Science*. **255**. 7825-7830.
26. Lorette, S., Jörn, F., Michel, S., Bénédicte, L., Joël, P., Tim, D., Raoul, Z. and Frédéric, K. (2001). Investigations by fluorescence techniques of the mechanism of formation of silica- and alumina-based MCM-41-type materials. *Microporous and Mesoporous Material*. **45**. 25-31.
27. Akinori, N., Aya, W., Kenjirou, H., Yuichi, T., Kunikazu, M. and Keiji, Y. (2009). Molecular states of prednisolone dispersed in folded sheet mesoporous silica (FSM-16). *International Journal of Pharmaceutics*. **378**. 17-22.
28. Ryosuke, S., Kaori, T., Masaki, G., Nobutake, T., Hitoshi, M. and Shoji, K. (2006). Barotropic phase transition between the lamellar liquid crystal phase and the inverted hexagonal phase of dioleoylphosphatidylethanolamine. *Colloids and Surfaces B: Biointerfaces*. **50**. 85-88.
29. Zhaohua, L., Chi-Feng, C., Wuzong, Z. and Jacek, K. (1995). Mesopore Molecular Sieve MCM-41 Containing Framework Aluminum. *J. Phys. Chem.* **99**. 1018-1024.
30. Woojin, C., Jin-woo, P. and Chang-Sik, H. (2004). Direct synthesis of titanium-modified hybrid periodic mesoporous organosilicas from 1,2-bis(triethoxysilyl)ethane and titanium isopropoxide. *Materials Letters*. **58**. 3551-3554.
31. Mark, S.M. and Galen, D.S. (1999). Isomorphic Substitution and Post synthesis Incorporation of Zirconium into MCM-48 Mesoporous Silica. *J. Phys. Chem. B*. **103**. 2037-2041.
32. Liu, S-H. and Paul, W. H. (2002). Photocatalytic generation of hydrogen on Zr-MCM-41. *International Journal of Hydrogen Energy*. **27**. 859-862.

33. Yongzhong, Z.S., Jaenicke, G. and Chuah, K. (2003). Supported zirconium propoxide—a versatile heterogeneous catalyst for the Meerwein–Ponndorf–Verley reduction. *Journal of Catalysis*. **218**. 396-404.
34. Biju, M.D., Lefebvre, F., Walter, B., Jack, F. and Halligudi, S.B. (2005). Synthesis of linear alkyl benzenes over zirconia-supported 12-molybdophosphoric acid catalysts. *Journal of Molecular Catalysis A: Chemical*. **236**. 162-167.
35. Wang, J.A., Zhou, X.L., Chen, L.F., Noreña, L.E., Yu, G.X. and Li, C.L. (2009). Hydroisomerization of n-heptane on the Pt/H₃PW₁₂O₄₀/Zr-MCM-41 catalysts. *Journal of Molecular Catalysis A: Chemical*. **299**. 156-160
36. Halligudi, S. B. (2007). Tungstophosphoric acid and zirconia supported on mesoporous silica catalyst in veratrole acetylation. *Journal of Molecular Catalysis A: Chemical*. **170**. 1325-1330.
37. Bhattachary, K. A., Mamadou, A., Diallo, K. and Ganesh, N. (2008). SbCl₃ as a Highly Efficient Catalyst for the Acetylation of Alcohols, Phenols, and Amines under Solvent-Free Conditions. **38**. 1518-1526.
38. Sharath, R., Kirumakki, N., Nagaraju, K., Chary, V.R. and Sankarasubbier, N. (2003). Kinetics of esterification of aromatic carboxylic acids over zeolites H and HZSM5 using dimethyl carbonate. *Applied Catalysis A: General*. **247**. 161-167.
39. Ali, S.H. and Sabiha, M. Q. S. (2006). Kinetics of the esterification of acetic acid with 2-propanol: Impact of different acidic cation exchange resins on reaction mechanism. *International Journal of Chemical Kinetics*. **38**. 593-612.

40. Adam, M. and Halina, S. (2004). Esterification Kinetics of Glycerol with Fatty Acids in the Presence of Zinc Carboxylates: Preparation of Modified Acylglycerol Emulsifiers. *Ind. Eng. Chem. Res.* **43**. 7744-7753.
41. Wen-Tzong, L. and Chung-Sung, T. (2001). Liquid-Phase Esterification of Propionic Acid with *n*-Butanol . *Ind. Eng. Chem. Res.***40**. 3281–3286.
42. Chen, L. F., Zhou, X. L., Noreña, L.E., Wang, J. A., Navarrete, J. P., Montoya, A., Del Angel, P. and Llanos, M. E. (2006). Comparative studies of Zr-based MCM-41 and MCM-48 mesoporous molecular sieves: Synthesis and physicochemical properties. *Applied Surface Science.* **253**. 2443-2451.