

Electronic Supplementary Information

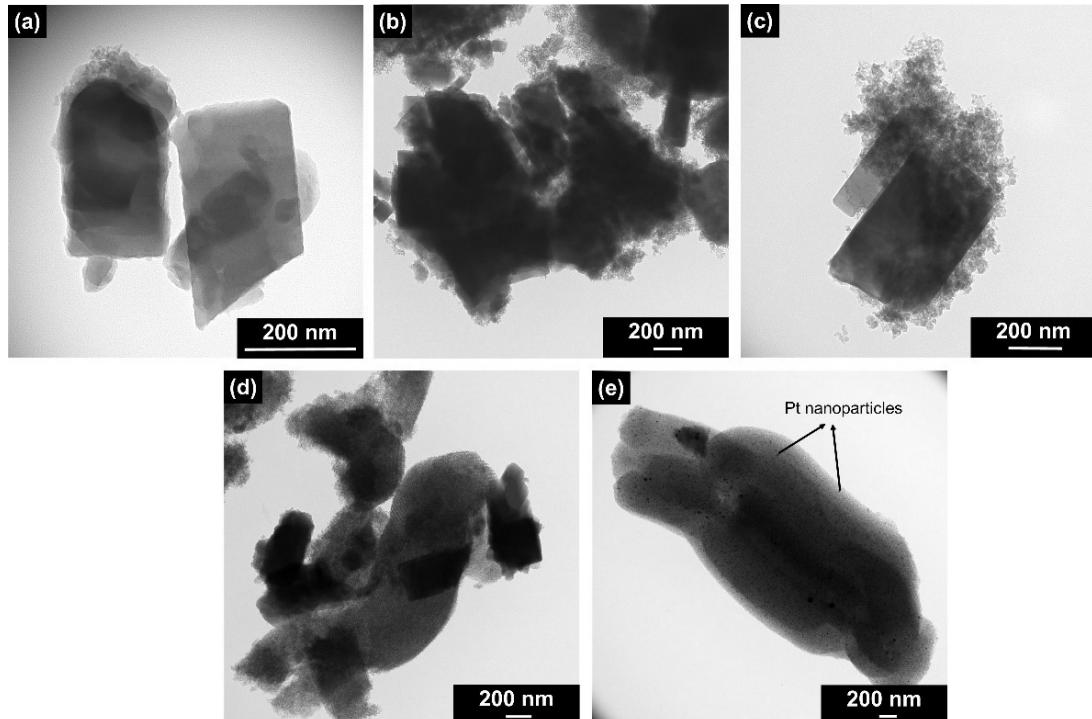


Fig. S1. TEM images of the commercial and modified ZSM-5 catalysts (a) ZSM-comm, (b) meso-ZSM, (c) Mg/meso-ZSM, (d) Mg-Ni/meso-ZSM, and (e) Mg-Pt/meso-ZSM.

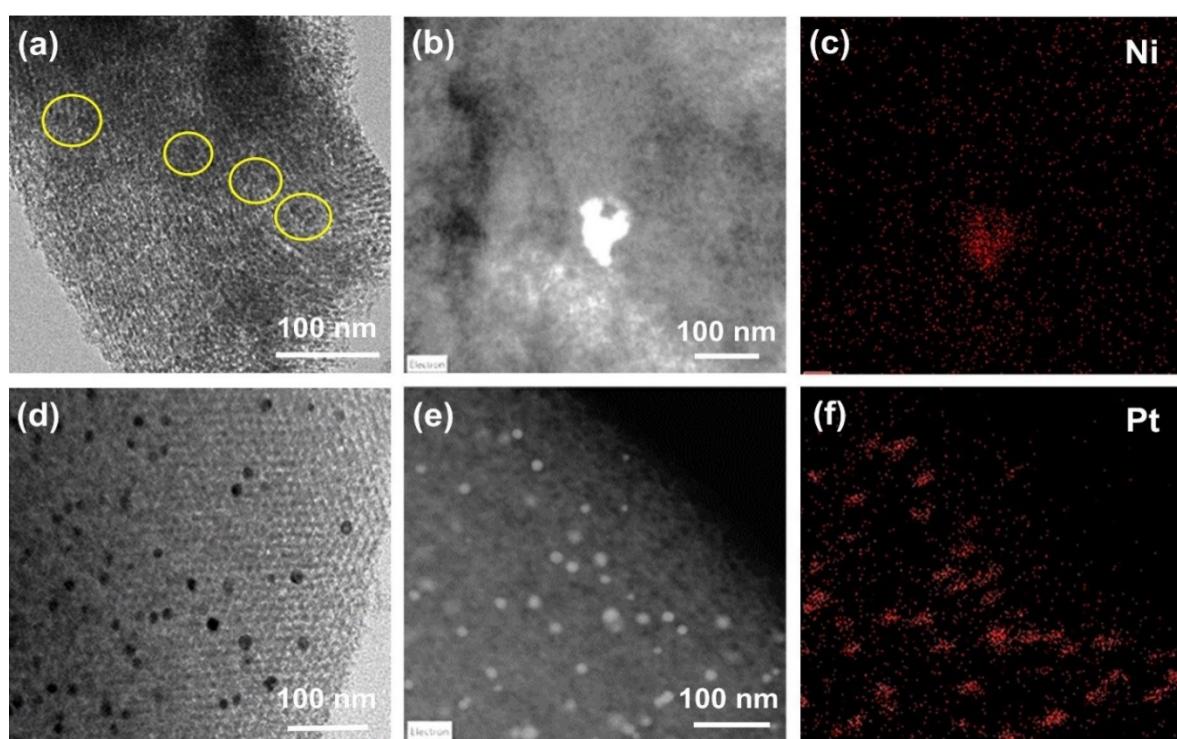


Fig. S2. (a) HRTEM and (b) STEM images, and (c) elemental mapping of Mg-Ni/meso-ZSM for Ni. (d) HRTEM and (e) STEM images, and (f) elemental mapping of Mg-Pt/meso-ZSM for Pt.

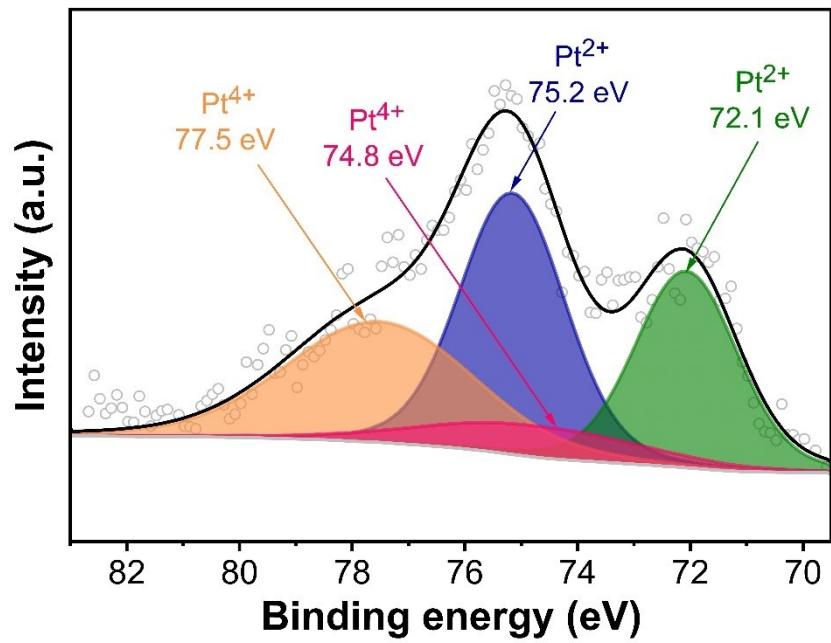


Fig. S3. High-resolution Pt 4f XPS spectrum of Mg/Pt-meso-ZSM.

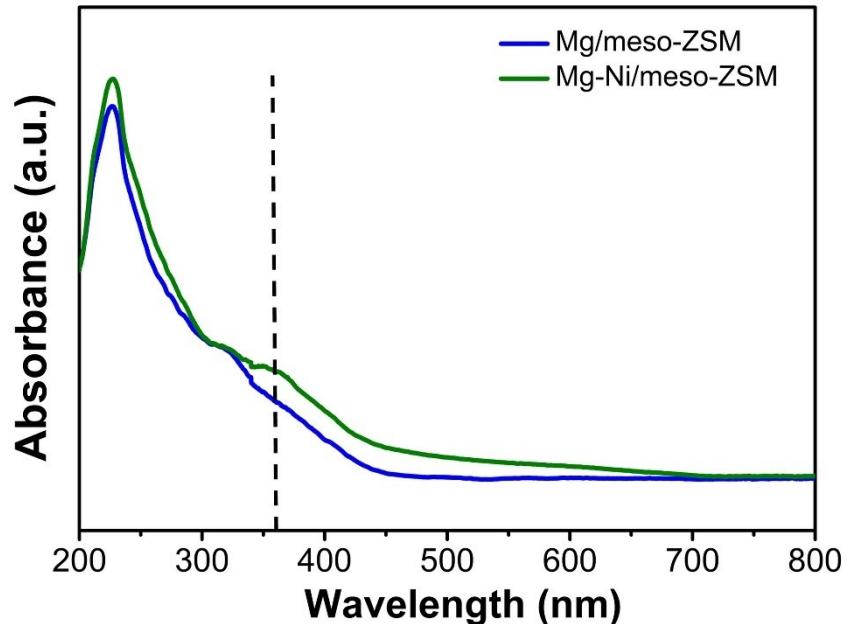


Fig. S4. UV-vis diffuse reflectance spectrum of Mg/Ni-meso-ZSM.

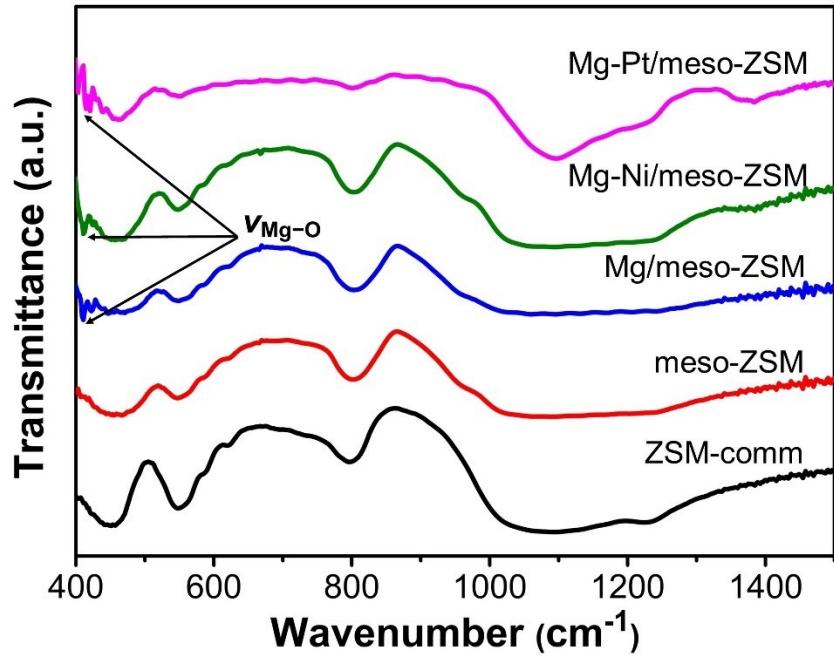


Fig. S5. FTIR spectra of commercial and modified ZSM-5 catalysts.

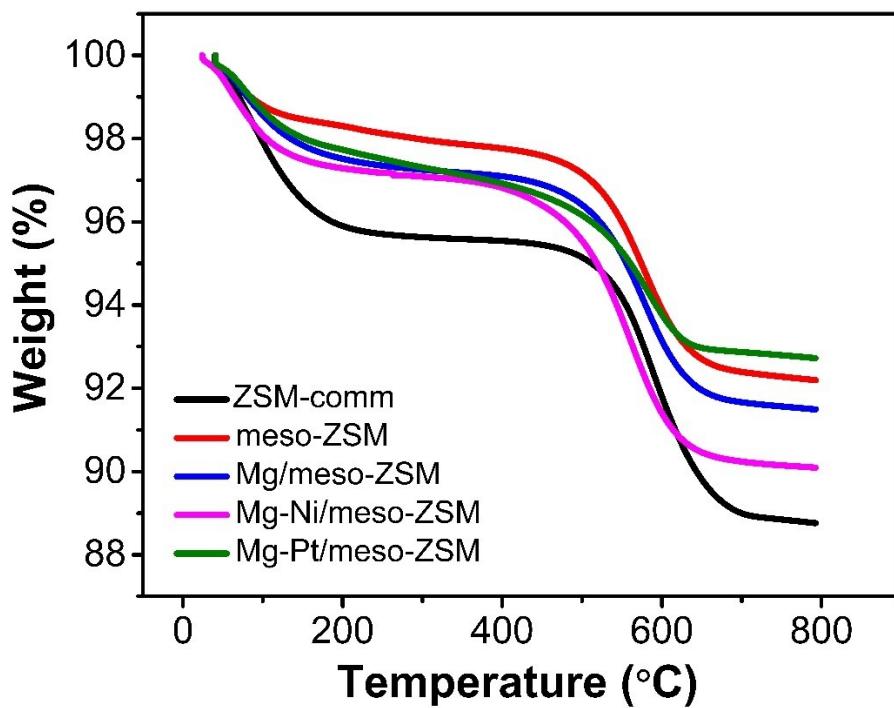


Fig. S6. TG curves of spent catalysts regenerated under air.

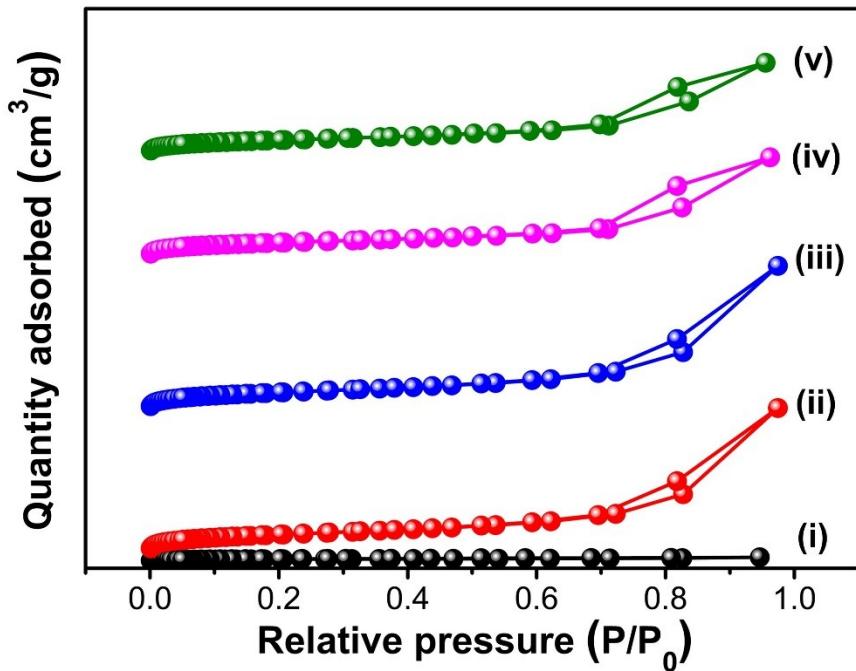


Fig. S7. Nitrogen adsorption-desorption isotherms of the spent catalysts: (i) spent ZSM-comm, (ii) spent meso-ZSM, (iii) spent Mg/meso-ZSM, (iv) spent Mg-Ni/meso-ZSM, and (v) spent Mg-Pt/meso-ZSM.

Table S1. BET surface area and coke loading of spent catalysts.

Catalyst	S_{BET} (m^2/g)	Coke loading (%)
Comm-ZSM	21.70	6.8
meso-ZSM	132.2	5.9
Mg/meso-ZSM	253.2	5.9
Mg-Ni/meso-ZSM	123.7	7.0
Mg-Pt/meso-ZSM	134.9	4.8

Table S2. Bio-oil product selectivity based on GC-MS peak areas.Non-cat:

Compounds	GC – MS Area (%)	Compounds	GC –MS Area (%)
Alcohol	0.9	Phenols	39.5
3-Buten-2-ol, 3-methyl-	0.2	Phenol, 2-methyl-	0.4
2-Heptanol, 6-methyl-	0.8	Phenol, 3-methyl-	1.3
Acids & esters	13.3	Phenol, 2-methoxy-	4.2
Propanoic acid, 2-oxo-, methyl est	4.2	1,4-Benzenediol, 2,6-dimethyl-	0.4
Malic Acid	0.3	Creosol	5.1
Propanoic acid, 2-oxo-, ethyl este	1.5	Catechol	3.3
2-Propenoic acid, 2-methyl	0.4	Catechol	0.9
2-Hexenoic acid	0.2	1,2-Benzenediol, 3-methyl-	0.6
Acetoacetic acid, 1-thio-, S-allyl	0.5	Phenol, 4-ethyl-2-methoxy-	1.7
2-Hexanone, 4-methyl-	0.2	1,2-Benzenediol, 4-methyl-	3.9
Butanoic acid, 2-oxo-	0.3	2-Methoxy-4-vinylphenol	4.9
2-Pentenoic acid, 4-methyl-, methy	1.1	Eugenol	0.9
Homovanillic acid	1.6	Phenol, 2-methoxy-4-propyl-	0.2
Benzoic acid, 4-(methylthio)-, eth	0.2	Vanillin	2.1
Homovanillic acid	2.5	trans-Isoeugenol	3.1
Dehydroabietic acid	0.3	Apocynin	6.4
Ketones & aldehydes	12.9	Furans	16.1
Succindialdehyde	0.4	Furfural	3.2
2-Pentanone, 4-hydroxy-4-methyl	0.5	2-Furanmethanol	3.0
2-Cyclopenten-1-one, 2-hydroxy-	6.9	2-Furanmethanol	0.3
2(5H)-Furanone, 5-methyl-	0.3	2(5H)-Furanone	2.2
Cyclohexanone	0.2	2-Furancarboxaldehyde, 5-methyl	0.6
2,3-Pentanedione	0.4	2-Furanmethanol	0.3
1,2-Cyclopentanedione, 3-methyl-	2.6	Furan	0.7
Cyclopentanone, 2-methyl-	1.6	2-Furanmethanol, tetrahydro-5-meth	0.3
Sugars	17.3	5-Hydroxymethylfurfural	5.6
1,4:3,6-Dianhydro-.alpha.-d-glucop	1.2		
.beta.-D-Glucopyranose, 1,6-anhydr	15.6		
L-Mannose	0.4		

ZSM-comm:

Compounds	GC -MS Area (%)	GC -MS Area (%)	
Alcohols	4.4	Phenols	10.8
1-Pentanol, 2-methyl	2.78	Creosol	3.73
1-Heptanol, 2-propyl-	1.26	Mequinol	2.87
2-Hexyl-1-octanol	0.43	2-Methoxy-4-vinylphenol	1.71
Aromatics	67.5	trans-Isoeugenol	1.39
Toluene	19.19	Phenol, 4-ethyl-2-methoxy-	0.89
o-Xylene	14.69	Phenol, 3-methyl-	0.24
Benzene	7.74	Furans	0.4
Naphthalene, 2-methyl-	6.49	Furan, 2,5-dimethyl-	0.26
Naphthalene	4.13	2(3H)-Furanone, 5-methyl-	0.14
Naphthalene, 1,4-dimethyl-	2.82	Alkanes & alkenes	7.6
Benzene, 1-ethyl-3-methyl-	2.16	2-Hexene, 3-methyl-, (Z)-	1.81
Benzene, 1,3-dimethyl-	2.08	Hexane, 3-methyl-	1.02
Ethylbenzene	1.67	2-Hexene, (E)-	0.76
Benzene, 1,2,3-trimethyl-	1.36	Nonane, 2-methyl-5-propyl-	0.62
Phenanthrene	1.06	Cyclohexene, 1-methyl-	0.45
Anthracene, 9-methyl-	0.92	2-Methyl-2-heptene	0.38
Benzene, 1-propynyl-	0.71	2-Octene, (E)-	0.35
Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	0.65	2-Hexene, 3-methyl-, (Z)-	0.38
Indane	0.52	2-Heptene	0.27
2-Methylindene	0.36	Cyclopentane, 1,2-dimethyl-, cis-	0.26
Naphthalene, 1-methyl-	0.36	Cyclopropane, pentyl-	0.24
1,4-Dihydronaphthalene	0.32	Cyclobutene, 3,3-dimethyl-	0.18
1H-Indene, 2,3-dihydro-4-methyl-	0.29	1-Decene	0.17
Acids & esters	3.2	Undecane	0.17
Propanoic acid, 2-oxo-, methyl ester	1.09	1,3,5-Hexatriene, (Z)-	0.14
Acetic acid, (acetoxy)-	0.87	Heptane, 3-methylene-	0.14
Acetic acid, methyl ester	0.73	3-Hexadecene, (Z)-	0.14
3-Cyclopentylpropionic acid, 2-phenylethyl ester	0.53	Cyclopropane, 1-hexyl-2-methyl-	0.11
Ketones & aldehydes	6.0		
2-Propanone, 1-hydroxy-	2.34		
Nonanal	1.35		
2-Cyclopenten-1-one	0.59		
Levoglucosenone	0.55		
2-Cyclohexen-1-one, 4-hydroxy-	0.48		
Succindialdehyde	0.35		
Ethanone, 1-cyclopropyl-	0.32		

meso-ZSM:

Compounds	GC -MS Area (%)	Compounds	GC -MS Area (%)
Alcohols	2.9	Phenols	23.6
2-Nonen-1-ol	1.36	Creosol	5.33
1,3-Pentanediol, 4-methyl-2-nitro-	0.59	Mequinol	3.92
1-Heptanol, 2-propyl-	0.48	trans-Isoeugenol	3.02
1,2-Ethanediol, diacetate	0.48	2-Methoxy-4-vinylphenol	2.50
Aromatics	19.0	Phenol, 4-ethyl-2-methoxy-	2.48
Toluene	7.82	Vanillin	0.92
o-Xylene	4.54	Apocynin	0.90
Benzene	3.25	Phenol, 2-methoxy-4-propyl-	0.78
Naphthalene	1.08	Eugenol	0.77
Naphthalene, 2-methyl-	0.68	trans-Isoeugenol	0.75
Ethylbenzene	0.62	Phenol, 2-methoxy-4-propyl-	0.66
Benzene, 1-ethyl-2-methyl-	0.42	trans-Isoeugenol	0.60
Naphthalene, 2,3-dimethyl-	0.29	4-(1-Hydroxyallyl)-2-methoxyphenol	0.54
Styrene	0.28	Phenol, 3-methyl-	0.40
Acids & esters	15.4	Furans	8.7
Acetic acid	6.22	Furfural	3.64
Propanoic acid, 2-oxo-, methyl ester	3.40	2(5H)-Furanone	2.28
Acetic acid	1.99	2-Furancarboxaldehyde, 5-methyl-	1.19
Acetic acid, (acetoxy)-	1.38	3(2H)-Furanone, dihydro-5-methyl-	0.71
Acetic acid, methyl ester	1.19	2(3H)-Furanone, 5-methyl-6-Methoxy-3-methylbenzofuran	0.56
Benzoic acid, cyclohexylmethyl ester	0.46		0.31
6,7-Dioxabicyclo[3.2.2]nonane	0.44	Alkanes & alkenes	3.2
Cyclopentanecarboxylic acid, 3-phenyl-2-propenyl ester	0.32	2-Pentene, 3-ethyl-	0.63
Ketones & aldehydes	27.3	3-Hexene, (Z)-	0.57
2-Propanone, 1-hydroxy-	4.39	2-Hexene, 2-methyl-	0.54
Propanal, 2,3-dihydroxy	3.91	Decane, 1-chloro-	0.46
1,2-Cyclopentanedione	3.42	Hexane, 3-methyl-	0.38
2-Butanone, 3-methyl-	2.28	3-Penten-1-yne, (Z)-	0.34
Nonanal	2.05	1,3,5-Hexatriene, (Z)-	0.27
2-Pyrrolidinone, 5-(cyclohexylmethyl)-	1.93		
3-Cyclobutene-1,2-dione, 3,4-dihydroxy	1.66	Ketones & aldehydes	
Levoglucosenone	1.61	Ethanone, 1-cyclopropyl-	0.45
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.38	2-Azaquinuclidone-3	0.35
Cyclohexanone, 4-methylidene	1.02	2-Cyclopenten-1-one, 2-methyl-	0.28
Propan-2-one, 1-(4-isopropoxy-3-methoxyphenyl)-	0.96	6-Iodohexanal	0.28
1,3-Cyclopentanedione	0.79		
2-Butanone, 4-hydroxy-3-methyl-	0.52		

Mg/meso-ZSM:

Compounds	GC -MS Area (%)	Compounds	GC -MS Area (%)
Alcohols	2.7	Phenols	22.8
1-Heptanol, 2-propyl-	1.16	Creosol	5.79
Glycrin	0.97	Mequinol	4.05
1,2:5,6-Dianhydrogalactitol	0.57	Phenol, 4-ethyl-2-methoxy-	2.58
Aromatics	20.1	trans-Isoeugenol	2.53
Toluene	7.71	2-Methoxy-4-vinylphenol	1.98
o-Xylene	4.82	Vanillin	0.85
Benzene	3.56	Eugenol	0.76
Naphthalene	1.03	Phenol, 2-methoxy-4-propyl-	0.68
Naphthalene, 2-methyl-	0.75	Phenol, 3-methyl-	0.67
Tridemorph	0.71	Phenol, 2-methoxy-4-propyl-	0.65
Ethylbenzene	0.66	Phenol, 3-methyl-	0.52
Benzene, 1-ethyl-2-methyl-	0.46	trans-Isoeugenol	0.52
Naphthalene, 2,3-dimethyl-	0.37	trans-Isoeugenol	0.46
Acids & esters	14.0	4-(1-Hydroxyallyl)-2-methoxyphenol	0.46
Acetic acid	4.44	2-Methoxy-5-methylphenol	0.27
Propanoic acid, 2-oxo-, methyl ester	3.54	Furans	9.0
Acetic acid, (acetoxy)-	2.53	Furfural	2.94
Acetic acid, methyl ester	1.44	2(5H)-Furanone	1.92
1,4-Dioxin, 2,3-dihydro-	0.94	5-Hydroxymethyl-2[5H]-furanone	1.71
3-Cyclopentylpropionic acid, 2-phenylethyl ester	0.46	2-Furancarboxaldehyde, 5-methyl-	1.03
Benzoic acid, cyclohexylmethyl ester	0.39	2(3H)-Furanone, 5-methyl-	0.58
Hexanoic acid, oct-3-en-2-yl ester	0.25	Furan, 2,5-dimethyl-	0.44
Ketones & aldehydes	24.4	Furan, 2,3-dihydro-	0.35
2-Propanone, 1-hydroxy-	5.93	Alkanes & alkenes	7.1
2-Butanone, 3-methyl-	3.66	2-Hexene, 2-methyl-	1.19
Nonanal	2.67	2-Hexene, (E)-	1.00
Pentanal	2.02	Hexane, 3-methyl-	0.96
Cyclobutene-1,2-dione, 3,4-dihydroxy	1.62	Tetradecane, 1-chloro-	0.65
Levoglucosenone	1.43	1,3-Cyclopentadiene	0.44
2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	1.09	2-Octene, (E)-	0.38
Cyclohexanone, 4-methylidene	0.97	2-Heptene, (E)-	0.37
Propan-2-one, 1-(4-isopropoxy-3-methoxyphenyl)-	0.89	Cyclohexene, 1-methyl-	0.36
6-Oxa-bicyclo[3.1.0]hexan-3-one	0.70	2-Methyl-2-heptene	0.32
Ethanone, 1-cyclopropyl-	1.34	Cyclobutane, 1,2,3,4-tetramethyl-	0.28
Succindialdehyde	0.64	2-Hexene, 3-methyl-, (Z)-	0.28
7-Oxabicyclo[2.2.1]heptan-2-one	0.61	Dodecane	0.26
2-Cyclopenten-1-one, 2-methyl-	0.33	Heptadecane	0.25
1,2-Cyclooctanedione	0.29	Cyclopentene	0.21
2,3-Pentanedione	0.25	2-Heptene, 3-methyl-	0.15

Mg-Ni/meso-ZSM:

Compounds	GC - MS Area (%)	Compounds	GC - MS Area (%)
Alcohols & ethers	3.1	Phenols	16.5
Hexyl octyl ether	1.73	Phenol, 2-methoxy-	3.94
4-Hepten-1-ol	0.83	Creosol	3.91
2,6-Cyclooctadien-1-ol	0.51	Phenol, 4-ethyl-2-methoxy-	1.65
Aromatics	23.5	trans-Isoeugenol	1.35
Toluene	9.96	2-Methoxy-4-vinylphenol	0.79
o-Xylene	5.85	Phenol, 3-methyl-	0.78
Benzene	4.78	1,2:5,6-Dianhydrogalactitol	0.77
Ethylbenzene	0.87	Vanillin	0.64
Benzene, 1-ethyl-3-methyl-	0.58	Propan-2-one, 1-(4-isopropoxy-3-methoxyphenyl)-	0.63
Azulene	0.53	Apocynin	0.59
Naphthalene, 1,2,3,4-tetrahydro-1,1,6-trimethyl-	0.25	Phenol, 2-methoxy-4-propyl-	0.45
Naphthalene, 2-methyl-	0.7	Phenol, 2-methoxy-3-(2-propenyl)-	0.36
Acids & esters	7.0	Phenol, 2-methoxy-4-propyl-	0.34
Butyl 2-(2-(2-ethoxyethoxy)ethoxy)acetate	2.07	Phenol, 3-methyl-	0.33
Acetic acid	1.78	Furans	3.9
1,2-Propanediol, 1-acetate	1.62	2(5H)-Furanone	1.28
3-Cyclopentylpropionic acid, 2-phenylethyl ester	0.82	Furan, 2,3-dihydro-5-methyl-	0.98
Acetic acid, methyl ester	0.35	2-Furancarboxaldehyde, 5-methyl-	0.91
2-Propenoic acid, 2-methoxyethyl ester	0.34	3,4-Furandiol, tetrahydro-, cis-	0.58
Ketones & aldehydes	19.6	2-Vinylfuran	0.18
3-Cyclopentene-1-acetaldehyde, 2-oxo-	3.76	Alkanes & alkenes	26.3
Methyl vinyl ketone	3.41	2-Hexene, 3-methyl-, (Z)-	5.1
1,2-Cyclopentanedione	2.67	Dodecane	2.72
Cyclohexanone, 4-methylidene	1.83	Hexane, 3-methyl-	1.91
2-Butanone, 4-hydroxy-3-methyl-	1.51	Hexane, 2,2,3,3-tetramethyl-	1.14
1,2-Cyclopentanedione, 3-methyl-	1.32	Heptane, 3-methylene-	1.09
Nonanal	1.25	1-Butene, 2,3-dimethyl-	0.85
2-Butanone, 4-hydroxy-3-methyl	0.99	Heptane, 4-chloro-	0.81
Levoglucosenone	0.79	Heptadecane, 2,6,10,15-tetramethyl-	0.81
3-Buten-2-one, 3-methyl-	0.49	2-Hexene, 3-methyl-, (Z)-	0.77
2-Butanone, 4-hydroxy-3-methyl-	0.45	Pentadecane	0.74
2-Cyclopenten-1-one, 2-methyl-	0.43	Heptadecane	0.71
2-Cyclopenten-1-one, 3-methyl-	0.41	Tetradecane	1.24
1,2-Cyclopentanedione	0.32	Eicosane	1.83
		2,4-Dimethyl-3-hexene(c,t)	0.62
		Undecane, 4,7-dimethyl-	0.61
		Cyclopentane, ethylidene	0.53
		Undecane	0.53
		1,3-Pentadiene, (E)-	0.5
		1-Hexene, 2-methyl-	0.49

2-Heptene	0.47
Cyclopentene, 3-ethyl-	0.44
3-Undecene, 6-methyl-, (E)-	0.44
2-Hexene, 5-methyl-, (E)-	0.4
2-Methyl-2-heptene	0.4
3-Methyl-3-hexene	0.28
Cyclopropane, 2-methylene-1-propionyl-	0.28
2-Octene, (E)-	0.25
2-Octene, (Z)-	0.23

Mg-Pt/meso-ZSM:

Compounds	GC – MS Area (%)	Compounds	GC – MS Area (%)
Alcohols & ethers	4.4	Alkanes & alkenes	19.6
1,2-Propanediol, 1-acetate	1.64	2-Hexene, 3-methyl-, (Z)-	3.96
Hexyl octyl ether	1.64	Hexane, 3-methyl-	1.64
1,2:5,6-Dianhydrogalactitol	0.73	Tetradecane, 1-chloro-	1.19
1-Heptadec-1-ynyl-cyclopentanol	0.43	Cyclopentane, 1,2-dimethyl-, cis-	0.83
Aromatics	28.2	Heptadecane, 2,6,10,15-tetramethyl-	0.75
Toluene	11.79	Pentadecane	0.69
o-Xylene	6.98	2-Hexene, 3-methyl-, (Z)-	0.63
Benzene	5.71	Tetradecane	0.60
Azulene	1.08	Heptadecane	0.60
Ethylbenzene	1.07	Tetradecane	0.59
Naphthalene, 2-methyl-	0.91	Undecane	0.57
Benzene, 1-ethyl-3-methyl-	0.62	Heneicosane	0.52
Acids & esters	5.6	Eicosane	0.50
Butyl 2-(2-(2-ethoxyethoxy)ethoxy)acetate	2.25	2-Pentene, 3-ethyl-2-methyl-	0.48
3-Cyclopentylpropionic acid, 2-phenylethyl ester	1.03	2-Methyl-2-heptene	0.44
Butanoic acid, 3-methyl-	0.89	Eicosane	0.44
Propanoic acid, ethyl ester	0.69	2-Heptene	0.42
Acetic acid, methyl ester	0.46	Methane, (methylsulfinyl)(methylthio)-	0.41
Formic acid	0.30	2-Decene, 5-methyl-, (Z)-	0.40
Ketones & aldehydes	14.0	1-Hexene, 2-methyl-	0.38
1,2-Cyclopentanedione	2.67	2-Octene, (Z)-	0.16
Nonanal	2.12	1,3-Cyclohexadiene	0.14
Methyl vinyl ketone	1.53	3-Methylenecyclohexene	0.12
Cyclohexanone, 4-methylidene	1.38	2-Nonene, (E)-	0.12
1,2-Cyclopentanedione, 3-methyl-	1.26	1-Decene	0.11
Levoglucosenone	1.14	2-Decene, 5-methyl-, (Z)-	0.40
Heptanal, 2-methyl-	0.92	1-Hexene, 2-methyl-	0.38
2-Hexanone oxime	0.60	2-Octene, (E)-	0.34
3-Buten-2-one, 3-methyl-	0.51	Cyclopentene, 3-ethyl-	0.33
Coniferyl aldehyde	0.45	Heptane, 3-methylene-	0.28
2-Butenal	0.42	1-Heptene, 2-methyl-	0.27
2-Cyclopenten-1-one, 2-methyl-	0.38	Cyclopropane, 2-methylene-1-propionyl-	0.24
2-Cyclopenten-1-one, 3-methyl-	0.35	1,3-Pentadiene, (E)-	0.23
1,2-Cyclopentanedione	0.32	5-Undecene	0.22
Phenols	0.00	Cyclopropane, 1,1,2-trimethyl-	0.20
Phenol, 2-methoxy-	5.49		
Creosol	5.45		
trans-Isoeugenol	2.06		
2-Methoxy-4-vinylphenol	1.82		
Phenol, 4-ethyl-2-methoxy-	1.77		
Vanillin	1.13		

Apocynin	0.90
Phenol, 3-methyl-	0.62
Phenol, 2-methoxy-4-propyl-	0.59
Phenol, 2-methoxy-3-(2-propenyl)-	0.38
Phenol, 3-methyl-	0.28
Furans	7.7
Furan, 2,5-dimethyl	3.58
2(5H)-Furanone	1.40
2-Furancarboxaldehyde, 5-methyl-	0.97
Furan, 2,5-dibutyl-	0.90
Furan, 2,3-dihydro-5-methyl	0.85