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APPENDICES

Appendix A Calibration Curves for Methane and Gas Product

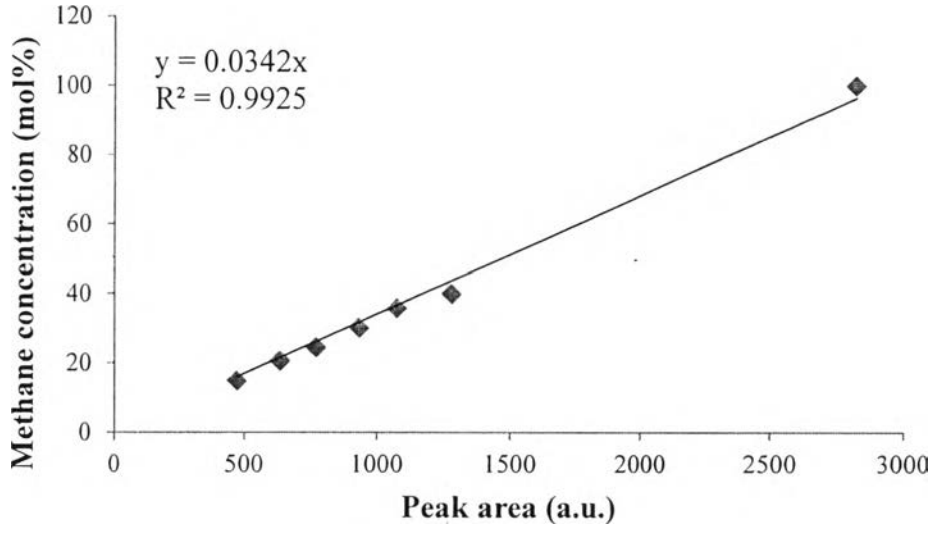

Figure A1 The relationship between amount of methane (CH_4) and peak area.

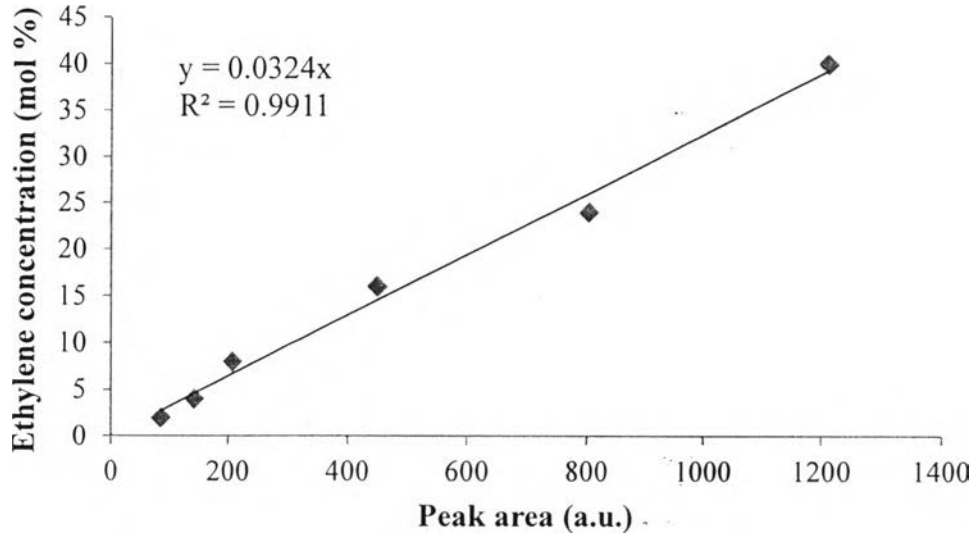

Figure A2 The relationship between amount of ethylene (C_2H_4) and peak area.

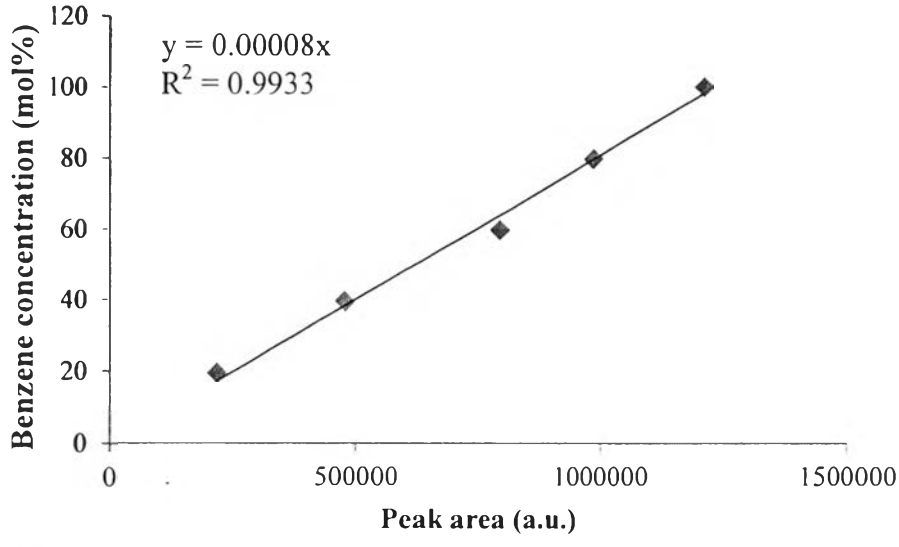

Figure A3 The relationship between amount of toluene (C_7H_8) and peak area.

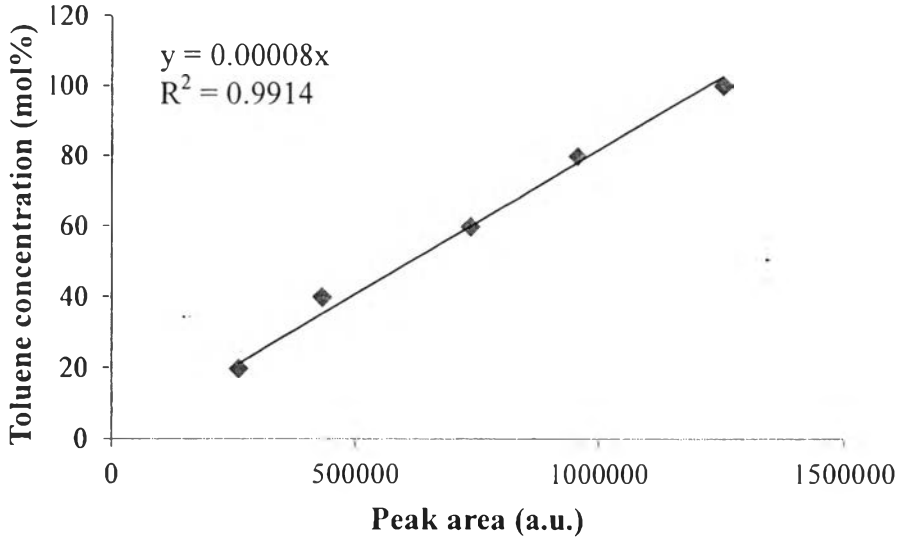

Figure A4 The relationship between amount of toluene (C_7H_8) and peak area.

Appendix B Calibration Curves for Flow Meter

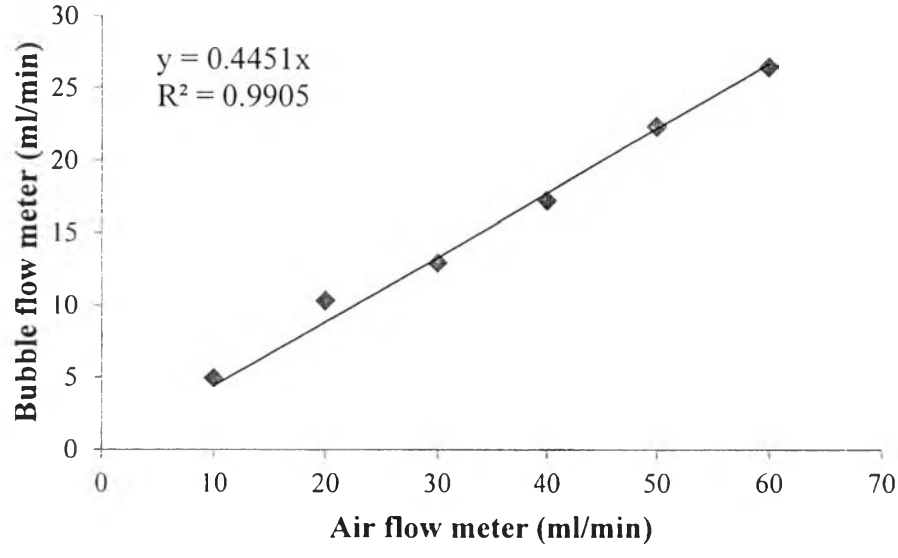

Figure B1 The relationship between bubble flow meter and methane air flow meter.

Appendix C Calculation of Metal Dispersion

The metal dispersion was calculated following Equation 1.

$$\text{Metal Dispersion} = V_m \times A_w \times 10^4 / (W\% \times S_f) \quad (1)$$

V_m is the monolayer volume (moles of gas per gram of sample)

A_w is the metal atomic weight (gram of metal per mole)

W% is the metal percentage in sample

S_f is a stoichiometric factor (molecule of gas per metal atom)

Table C1 Stoichiometric factors for different types of reaction (Fadoni *et al.*)

Method	Reaction	Stoichiometry (Sf)
Hydrogen chemisorption	$M + 1/2H_2 = M\text{-}H$	0.5
Carbonmonoxide chemisorption	$M + CO = M\text{-}CO$	1
	$2M + CO = M\text{-}CO\text{-}M$	0.5
Hydrogen/Oxygen titration	$M\text{-}O + 3/2H_2 = M\text{-}H + H_2O$	1.5
Oxygen/Hydrogen titration	$M\text{-}H + 3/4\ O_2 = M\text{-}O + 1/2H_2O$	0.75
Nitrous oxide reaction	$2M + N_2O = M\text{-}O\text{-}M + N_2$	0.5

M is accessible metal atom

For monometallic 3%Ni/HZSM-5 catalyst, the monolayer volume was determined by H_2-TPR Technique. Atomic weight of Ni is 58.69.

$V_m = 11.348 \times 10^{-6}$ mol H_2/g catalyst

$A_w = 58.69$ g metal/ mol metal

W% = 3 wt%

So

$$\text{Metal dispersion} = 11.348 \times 10^{-6} \times 10^4 \times 58.69 / 3 / 0.5$$

$$= 4.44\ \%$$

For monometallic 3%Mo/HZSM-5 catalyst, the monolayer volume was determined by H_2-TPR Technique. Atomic weight of Mo is 95.95.

$$V_m = 7.379 \times 10^{-6} \text{ mol } H_2/\text{g catalyst}$$

$$A_w = 95.95 \text{ g metal/ mol metal}$$

$$W\% = 3 \text{ wt\%}$$

So

$$\text{Metal dispersion} = 7.379 \times 10^{-6} \times 10^{4} \times 95.95 / 3 / 0.5$$

$$= 4.72 \%$$

For bimetallic 0.5%Ni-3%Mo/HZSM-5 catalyst

From H_2-TPR

$$V_m = 9.41 \times 10^{-6} \text{ mol } H_2/\text{g catalyst}$$

Atomic weight of Ni and Mo is 58.69 and 95.95 g metal/ mol metal.

The fraction of metal loaded on catalyst is calculated as follows:

$$\text{Fraction of Ni} = \frac{\text{wt\% of Ni}}{\text{Total wt\% of metal}}$$

$$= \frac{0.5}{3.5} = 0.14$$

So $$\text{Fraction of Mo} = 1 - 0.14 = 0.86$$

Therefore $$A_w = (0.14 \times 58.69) + (0.86 \times 95.95) = 90.73 \text{ g metal/ mol metal}$$

$$\text{Metal dispersion} = 9.41 \times 10^{-6} \times 10^{4} \times 90.73 / 3.5 / 0.5$$

$$= 4.88 \%$$

For bimetallic 1%Ni-3%Mo/HZSM-5 catalyst

From H_2-TPR

$$V_m = 10.018 \times 10^{-6} \text{ mol } H_2/\text{g catalyst}$$

Atomic weight of Ni and Mo is 58.69 and 95.95 g metal/ mol metal.

The fraction of metal loaded on catalyst is calculated as follows:

$$\text{Fraction of Ni} = \frac{\text{wt\% of Ni}}{\text{Total wt\% of metal}}$$

$$= \frac{1}{4} = 0.25$$

So $$\text{Fraction of Mo} = 1 - 0.25 = 0.75$$

Therefore $A_w = (0.25 \times 58.69) + (0.75 \times 95.95) = 86.64$ g metal/ mol metal

Metal dispersion $= 10.018 \times 10^{-6} \times 10^4 \times 86.64 / 4 / 0.5$

$= 4.34$ %

For bimetallic 2%Ni-3%Mo/HZSM-5 catalyst

From H_2-TPR

$V_m = 12.215 \times 10^{-6}$ mol H_2/g catalyst

Atomic weight of Ni and Mo is 58.69 and 95.95 g metal/ mol metal.

The fraction of metal loaded on catalyst is calculated as follows:

$$\text{Fraction of Ni} = \frac{\text{wt\% of Ni}}{\text{Total wt\% of metal}}$$

$$= \frac{2}{5} = 0.4$$

So Fraction of Mo $= 1 - 0.4 = 0.6$

Therefore $A_w = (0.4 \times 58.69) + (0.6 \times 95.95) = 81.05$ g metal/ mol metal

Metal dispersion $= 12.215 \times 10^{-6} \times 10^4 \times 81.05 / 5 / 0.5$

$= 3.96$ %

For bimetallic 3%Ni-3%Mo/HZSM-5 catalyst

From H_2-TPR

$V_m = 11.213 \times 10^{-6}$ mol H_2/g catalyst

Atomic weight of Ni and Mo is 58.69 and 95.95 g metal/ mol metal.

The fraction of metal loaded on catalyst is calculated as follows:

$$\text{Fraction of Ni} = \frac{\text{wt\% of Ni}}{\text{Total wt\% of metal}}$$

$$= \frac{3}{6} = 0.5$$

So Fraction of Mo $= 1 - 0.4 = 0.5$

Therefore $A_w = (0.5 \times 58.69) + (0.5 \times 95.95) = 77.32$ g metal/ mol metal

Metal dispersion $= 11.213 \times 10^{-6} \times 10^4 \times 77.32 / 6 / 0.5$

$= 2.89$ %

Appendix D Experimental Data of Catalytic Activity Tests for Methane Dehydrogenation and Coupling to Olefins and Aromatics

Table D1 Catalytic activity test of 3%Mo/HZSM-5 catalyst using 20 % methane as a feed at reaction temperature 750 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	5.92	89.65	7.17	3.18
30	7.86	87.97	8.58	3.45
60	5.79	88.70	8.08	3.22
90	5.98	75.98	20.69	3.33
120	8.78	84.23	11.05	4.72
150	7.24	86.76	9.42	3.82
180	3.14	90.61	6.68	2.71

Table D2 Catalytic activity test of 3%Ni/HZSM-5 catalyst using 20 % methane as a feed at reaction temperature 750 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	5.92	89.65	7.17	3.18
30	7.86	87.97	8.58	3.45
60	5.79	88.70	8.08	3.22
90	5.98	75.98	20.69	3.33
120	8.78	84.23	11.05	4.72
150	7.24	86.76	9.42	3.82
180	3.14	90.61	6.68	2.71

Table D3 Catalytic activity test of 0.5%Ni-3%Mo/HZSM-5 catalyst using 20 % methane as a feed at reaction temperature 750 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	7.44	76.02	2.86	21.12
30	6.12	82.06	2.45	15.49
60	13.00	86.76	1.44	11.79
90	6.38	82.01	0.88	17.11
120	5.38	86.97	0.73	12.30
150	1.87	88.46	0.53	11.01
180	1.94	88.37	0.49	11.14

Table D4 Catalytic activity test of 1%Ni-3%Mo/HZSM-5 catalyst using 20 % methane as a feed at reaction temperature 750 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	4.58	84.20	2.88	12.92
30	10.59	93.48	1.78	4.73
60	11.97	92.63	1.38	5.99
90	8.31	92.56	1.09	6.35
120	6.45	93.08	0.96	5.97
150	5.41	94.14	0.66	5.20
180	3.62	95.19	0.49	4.31

Table D5 Catalytic activity test of 2%Ni-3%Mo/HZSM-5 catalyst using 20 % methane as a feed at reaction temperature 750 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	7.92	83.96	1.81	14.23
30	7.68	90.52	1.20	8.28
60	8.81	91.52	0.84	7.64
90	14.91	90.14	0.46	9.40
120	6.95	91.92	0.43	7.65
150	3.22	93.20	0.28	6.52
180	2.73	93.38	0.27	6.34

Table D6 Catalytic activity test of 3%Ni-3%Mo/HZSM-5 catalyst using 20 % methane as a feed at reaction temperature 750 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	9.20	92.55	0.52	6.93
30	6.10	94.26	0.30	5.44
60	7.40	92.41	0.19	7.40
90	9.26	90.49	0.17	9.34
120	15.34	93.56	0.10	6.34
150	8.82	93.94	0.08	5.98
180	3.97	95.62	0.07	4.31

Table D7 Catalytic activity test of 2%Ni-3%Mo/HZSM-5 catalyst using 20 % methane as a feed at reaction temperature 800 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	2.80	90.42	0.82	8.75
30	7.57	91.20	0.37	8.43
60	10.22	92.25	0.22	7.52
90	11.33	88.90	0.19	10.91
120	15.99	92.13	0.19	7.69
150	12.97	93.82	0.08	6.10
180	3.23	94.02	0.10	5.88

Table D8 Catalytic activity test of 2%Ni-3%Mo/HZSM-5 catalyst using 40 % methane as a feed at reaction temperature 750 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	6.26	86.74	2.24	11.03
30	6.89	91.29	1.34	7.37
60	7.95	91.61	1.19	7.20
90	4.97	91.78	0.80	7.43
120	8.87	94.58	0.58	4.84
150	16.96	92.75	1.01	6.24
180	3.96	93.99	0.86	5.16

Table D9 Catalytic activity test of 2%Ni-3%Mo/HZSM-5 catalyst using 40 % methane as a feed at reaction temperature 800 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	11.42	95.99	0.94	3.06
30	4.26	97.84	0.47	1.69
60	6.56	97.84	0.27	1.89
90	8.31	98.05	0.17	1.79
120	17.11	97.50	0.14	2.36
150	13.87	96.32	0.13	3.56
180	6.77	95.71	0.10	4.19

Table D10 Catalytic activity test of 3%Ni-3%Mo/HZSM-5 catalyst using 20 % methane as a feed at reaction temperature 800 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	9.43	90.11	0.50	9.38
30	10.90	91.68	0.29	8.03
60	8.46	92.05	0.18	7.78
90	17.90	93.88	0.17	5.95
120	11.30	94.35	0.09	5.55
150	5.81	95.01	0.07	4.92
180	5.01	95.06	0.08	4.86

Table D11 Catalytic activity test of 3%Ni-3%Mo/HZSM-5 catalyst using 40 % methane as a feed at reaction temperature 800 °C, with GHSV 1,500 ml/g/h under atmospheric pressure

TOS (min)	CH_4 Conversion (mol%)	Ethylene Selectivity (%)	Benzene Selectivity (%)	Toluene Selectivity (%)
15	5.94	94.16	0.21	5.63
30	8.84	94.06	0.13	5.81
60	10.43	96.49	0.08	3.43
90	18.53	96.96	0.09	2.95
120	11.57	97.32	0.06	2.61
150	9.12	97.59	0.08	2.33
180	4.52	97.38	0.08	2.54

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