Conversion of isobutylene to octane-booster compounds after MTBE phaseout: The role of heterogeneous catalysis

Hilman Ibnu Mahdi[1], Oki Muraza[1*]

[1]Chemical Engineering Department and Center of Research Excellence in Nanotechnology, King Fahd University of Petroleum & Minerals, Dhahran 30261, Saudi Arabia

*Corresponding author. Tel.:+966 13 860 7612; e-mail address: omuraza@kfupm.edu.sa

Table S1. Dimerization, trimerization, and oligomerization of isobutylene over different catalysts.

Method	Phase	Temp [^oC]	Time [h]	X [%]	Sel [%]	Catalyst	Modification	Ref.
Dimerization	G	25	-	0.7	0.98	Ni-Y zeolite	Modified over $NiCO_3$–$2Ni(OH)_2.4H_2O$	1
Dimerization	L	50 – 100	1 – 4	91 – 100	46 – 66	Indion-125 resin	Macroporous acidic catalysts	2
Dimerization	L	50 – 100	1 – 4	78 – 98	53 – 60	Indion-130 resin	Macroporous acidic catalysts	2
Trimerization	-	60	16	69	10	Nickel	Aluminum alkyl-treated nickel (1.5 mol%)	3
Trimerization	L	40 – 100	Up to 25	100	~ 60	Beta (25) zeolite	Dehydration at 300 ^oC for 10 h using N_2	4
Trimerization	L	40 – 100	Up to 25	100 – 90	~ 40	USY zeolite	Dehydration at 300 ^oC for 10 h using N_2	4
Trimerization	L	40 – 100	Up to 25	90 – 20	~ 10	Mordenite zeolite	Dehydration at 300 ^oC for 10 h using N_2	4
Trimerization	L	40 – 100	1 – 11	60 – 40	~ 15	ZSM-5 zeolite	Calcination at 550 ^oC for 8 h to form a proton	5
Trimerization	L	40 – 100	1 – 12	90 – 20	10	Mordenite zeolite	Dehydration at 300 ^oC for 10 h using N_2	5
Trimerization	L	30 – 110	10	< 5	36	Amberlyst 31 resin	Ion exchanged over ethanol to remove water	6
Trimerization	L	30 – 110	10	90	64	Amberlyst 15 resin	Ion exchanged over ethanol to remove water	6
Trimerization	L	30 – 110	10	71	50	Amberlyst DT resin	Ion exchanged over ethanol to remove water	6
Trimerization	L	30 – 110	10	70	16	Mordenite zeolite	Calcination at 550 ^oC for 8 h to form a proton	6
Trimerization	-	140	-	100	54	Sulfated titania	Synthesized over titanium alkoxide	7
Trimerization	-	40 – 100	-	85.6	40	Amberlyst 15 resin	SO_3H as a functional structure	8
Trimerization	G – L	50 – 110	2	> 90	80	Amberlyst 15 resin	Cleaning using acetone for 70 h	9
Oligomerization	-	140	-	100	39	Sulfated titania	Synthesized over titanium alkoxide	7
Oligomerization	L	40	< 4	70	-	Amberlyst 15 resin	Heating at 107 ^oC for 75 min to remove water	10
Oligomerization	L	40	< 2	< 10	-	Dowex 50 WX8	Heating at 107 ^oC for 75 min to remove water	10
Oligomerization	L	40	< 5	60 – 95	-	β, Y, ZSM-5 zeolites	Calcination in dry air to the H-form at 500 ^oC	10
Oligomerization	-	40 – 100	-	85.6	5.8	Amberlyst 15 resin	SO_3H as a functional structure	8

L = liquid; G = gas; X = Conversion; Sel = Selectivity.

Table S2. Dimerization of isobutylene to isooctene over different catalysts.

Catalyst	System	Selectivity enhancer	Solvent	Temp [°C]	Pressure [atm]	Time [h]	Conversion and Selectivity [%]	Ref.
Tulsion T-63	Continuous RD	-	Isooctane	-	-	-	X = 73; S = 93	[11]
Beta – 10 zeolite	-	-	-	-	-	-	X = 87; S = 60	[12]
Beta – 50 zeolite	-	-	-	-	-	-	X = 96; S = 58	[12]
Beta – 150 zeolite	-	-	-	-	-	-	X = 96; S = 55	[12]
Amberlyst 35	CSTR	TBA	Isopentane	70 – 110	15 – 18	-	X = 30 – 70; S = 95	[13]
Amberlite IR-118	FBR and BR	-	Organic	60	6 – 7	1 – 4	X = < 20; S = > 90	[14]
ZSM-5 zeolite	FBR and BR	-	Organic	70	6 – 7	1 – 6	X = 1.3; S = 90	[14]
Y zeolite (CBV 760)	FBR and BR	-	Organic	70	6 – 7	1 – 6	X = 48.4; S = 60	[14]
Amberlyst 15	BR	-	Organic	60	6 – 7	5	X = 90; S = ~ 60	[14]
Ion exchange resin	CSTR	MeOH and TBA	Isopentane	60 – 100	14.8	-	X = 53 – 89; S = 48 – 86	[15]
Amberlyst 15	-	TBA	C_3-C_4 alkanes	10 – 100	3 – 34	-	S = 90	[16]
Amberlyst 35	-	Methanol, ethanol, and isopropanol	-	40 – 50	-	3	X = 40 – 75; S = 79 – 95	[8]
Amberlyst 15	TR	Methanol	-	72 – 74	-	-	X = 79 – 88; S = 79 – 93	[17]

Note : S = selectivity; X = conversion; TBA = *tert*-butyl alcohol; MeOH = methanol; MTBE = methyl *tert*-butyl ether; CBV-760 = zeolite H-sdusy powder; RD = reactive distillation; FBR = Fixed bed reactor; BR = batch reactor; CSTR = continuous stirred tank reactor; TR = tubular reactor.

Table S3. Physical properties of catalysts used in dimerization of isobutylene [96-98, 118, 124, 126, 128, 130, 135-138].

Properties	ZSM-5-Z	Mor-Z	β-Z	FER-Z	A-16	A-35	P-CT I75
cross-linking (%)	-	-	-	-	M	H	H
exchange capacity (eq H^+/kg)	-	-	-	-	4.8	5.3	4.98
porosity (cm^3/g)	-	-	-	-	-	0.35	-
specific surface area (m^2/g)	402 – 418	500	650	400	30 – 149	44 – 166	157
pore diameter (nm)	-	3.62	8.75	50–150	25 – 30	30 – 33	66
temperature stability (^{o}C)	-	-	-	-	130	150	145
particle size (mm)	-	-	-	-	0.6 – 0.8	0.51 – 1.25	0.94
acidity (mequiv H^+/g.dry)	-	0.82	0.37	-	-	5.32	4.98
Si/Al ratio	140 – 230	45	9–75	10 – 27	-	-	-
Na_2O (%)	0.03 – 0.05	-	-	-	-	-	-
moisture content (%)	-	-	-	-	-	55.4	-
apparent density (g/cm^3)	-	-	-	-	-	0.82	-
pore volume (cm^3/g)	-	0.01	0.89	0.14	0.013	0.21	0.5 – 0.8

Z = zeolite; A = amberlyst; P = purolite; Mor = mordenite; FER = ferrierite; β = beta; H = high; M = medium.

Table S5. Dimerization over zeolite based catalysts.

Zeolite	Topology	MR	D	Si/Al	Phase	Surface area [m^2/g]	Solvent	Temp [^oC]	Time [h]	Results [%]	Ref.
NH_4-ZSM-5	MFI	10	3	16 – 17	-	358	-	150 – 450	2	AE = 48.3 – 267 kJ/mol	18
ZSM-5	MFI	10	3	23.8	Gas-Liquid	370	Propane and CO_2	100	120 – 200	X = 32 – 56	19
ZSM-23	MTT	10	1	19.7	Gas-Liquid	110	Propane and CO_2	100	120 – 200	X = 32 – 56	19
MSU-S/S_{BEA}	BEA	12	3	45	Gas	529	-	60	30	X = 51 – 32; S = 70 – 79	20
Al-USY	FAU	12	3	30	Liquid	745	*n*-butane	70	20	X = 99.2; S = 21	21
HY	FAU	12	3	1.4	Liquid	722	*n*-butane	70	6	X = 83.1; S = 32.5	22
HY-500	FAU	12	3	1.4	Liquid	660	*n*-butane	70	6	X = 91; S = 26.3	22
HY-600	FAU	12	3	1.4	Liquid	617	*n*-butane	70	6	X = 98.4; S = 16	22
USY	FAU	12	3	30	Liquid	720	*n*-butane	40 – 100	Up to 25	X = 100 – 90; S = > 30	4
Beta-25	BEA	12	3	12.5	Liquid	680	*n*-butane	40 – 100	Up to 25	X = 100; S = ~ 10	4
Ferrierite	FER	10	2	10	Liquid	400	*n*-butane	40 – 100	1 – 12	X = 100; S = ~ 10	5
Ni-Y	FAU	12	3	2.6	Gas	404	-	25	-	X = 0.7; S = 0.98	1
Ni-Beta	BEA	12	3	75	Gas	438	-	25	-	-	1
Ni-mordenite	MOR	12	1	45	Gas	394	-	25	-	-	1
ZSM-5	MFI	10	3	15 – 25	Liquid	-	*n*-butane	30 – 70	Up to 2	X = 64 – 0	10
Mordenite	MOR	12	1	-	Liquid	-	*n*-butane	30 – 70	Up to 2	X = 68 – 0	10
Mordenite	MOR	12	1	-	Liquid	500	*n*-pentane	40 – 140	-	S = 90; r = first order	23
H-Y	FAU	12	3	-	Liquid	-	*n*-butane	30 – 70	Up to 5	X = 94 – < 10	10
Mordenite	MOR	12	1	12.5	Liquid	500	*n*-butane	40 – 100	1 – 12	X = 90 – 20; S = ~ 90	5
Beta	BEA	12	3	-	Liquid	-	*n*-butane	30 – 70	Up to 5	X = 88 – < 10	10

MR = member ring; D = dimension; AE = activation energy; X = conversion; S = selectivity; MSU-S/S_{BEA} = non-meso structured aluminosilicates of beta seed; r = the reaction order.

Reference

1. Yaocíhuatl, M. G.; Martín, H. L.; Jorge, A. C., Dimerization of isobutene over nickel modified zeolites to obtain isooctene. *Catalysis letters* **2006,** 110, (1-2), 107-113.
2. Grover, G.; Chaudhari, R., Selective dimerization of isobutene using a cation exchange resin catalyst. *Recent Developments in catalysis-Theory and Practice, Narosa Publishing House, New Delhi* **1991**, 345.
3. Behr, A.; Rentmeister, N.; Seidensticker, T.; Vosberg, J.; Peitz, S.; Maschmeyer, D., Highly Selective Dimerization and Trimerization of Isobutene to Linearly Linked Products by Using Nickel Catalysts. *Chemistry–An Asian Journal* **2014,** 9, (2), 596-601.
4. Yoon, J. W.; Chang, J.-S.; Lee, H.-D.; Kim, T.-J.; Jhung, S. H., Trimerization of isobutene over a zeolite beta catalyst. *Journal of Catalysis* **2007,** 245, (1), 253-256.
5. Yoon, J. W.; Lee, J. H.; Chang, J.-S.; Choo, D. H.; Lee, S. J.; Jhung, S. H., Trimerization of isobutene over zeolite catalysts: Remarkable performance over a ferrierite zeolite. *Catalysis Communications* **2007,** 8, (6), 967-970.
6. Yoon, J. W.; Chang, J.-S.; Lee, H.-D.; Kim, T.-J.; Jhung, S. H., Trimerization of isobutene over cation exchange resins: Effect of physical properties of the resins and reaction conditions. *Journal of Molecular Catalysis A: Chemical* **2006,** 260, (1), 181-186.
7. Mantilla, A.; Tzompantzi, F.; Ferrat, G.; Lopez-Ortega, A.; Alfaro, S.; Gomez, R.; Torres, M., Oligomerization of isobutene on sulfated titania: Effect of reaction conditions on selectivity. *Catalysis today* **2005,** 107, 707-712.
8. Di Girolamo, M.; Marchionna, M., Acidic and basic ion exchange resins for industrial applications. *Journal of molecular catalysis A: chemical* **2001,** 177, (1), 33-40.
9. Alcántara, R.; Alcántara, E.; Canoira, L.; Franco, M. a. J.; Herrera, M.; Navarro, A., Trimerization of isobutene over Amberlyst-15 catalyst. *Reactive and functional polymers* **2000,** 45, (1), 19-27.
10. Hauge, K.; Bergene, E.; Chen, D.; Fredriksen, G. R.; Holmen, A., Oligomerization of isobutene over solid acid catalysts. *Catalysis today* **2005,** 100, (3), 463-466.
11. Talwalkar, S.; Mankar, S.; Katariya, A.; Aghalayam, P.; Ivanova, M.; Sundmacher, K.; Mahajani, S., Selectivity engineering with reactive distillation for dimerization of C4 olefins: experimental and theoretical studies. *Industrial & engineering chemistry research* **2007,** 46, (10), 3024-3034.
12. Dakka, J. M.; Geelen, M. O. J.; Mathys, G. M.; Allen, P. W., Process for the selective dimerization of isobutene. In Google Patents: 2005.
13. Honkela, M. L.; Root, A.; Lindblad, M.; Krause, A. O. I., Comparison of ion-exchange resin catalysts in the dimerisation of isobutene. *Applied Catalysis A: General* **2005,** 295, (2), 216-223.
14. Huang, Y.-J.; Sun, Y.-M.; Chang, F.-L.; Hung, A. Y.; Wang, C.-T., The Feasibility Study of the Octane-Enhancing Process: Isobutylene Dimerization Using C4 Mixture. *Journal of Environmental Science and Health, Part A* **2003,** 38, (11), 2661-2678.
15. Honkela, M.; Krause, A., Influence of polar components in the dimerization of isobutene. *Catalysis letters* **2003,** 87, (3-4), 113-119.
16. Evans, T. I.; Karas, L. J.; Rameswaran, R., Selective olefin oligomerization. In Google Patents: 2002.
17. Di Girolamo, M.; Lami, M.; Marchionna, M.; Pescarollo, E.; Tagliabue, L.; Ancillotti, F., Liquid-phase etherification/dimerization of isobutene over sulfonic acid resins. *Industrial & engineering chemistry research* **1997,** 36, (11), 4452-4458.
18. Brown, T. C.; Miron, D. J.; Alanazi, A. K.; Le Minh, C., Rate Parameter Distributions for Isobutane Dehydrogenation and Isobutene Dimerization and Desorption over HZSM-5. *Catalysts* **2013,** 3, (4), 922-941.
19. Koskinen, R.; Turunen, H.; Tiitta, M.; Keiski, R. L., Extended activity of zeolite catalysts with CO 2 as reaction medium. *Chemical engineering journal* **2012,** 213, 235-244.

20. Park, D. H.; Kim, S.-S.; Pinnavaia, T. J.; Tzompantzi, F.; Prince, J.; Valente, J. S., Selective isobutene oligomerization by mesoporous MSU-SBEA catalysts. *The Journal of Physical Chemistry C* **2011,** 115, (13), 5809-5816.
21. Yoon, J. W.; Lee, J. S.; Jhung, S. H.; Lee, K.-Y.; Chang, J.-S., Oligomerization of isobutene over aluminum chloride-loaded USY zeolite catalysts. *Journal of Porous Materials* **2009,** 16, (6), 631-634.
22. Yoon, J. W.; Jhung, S. H.; Choo, D. H.; Lee, S. J.; Lee, K.-Y.; Chang, J.-S., Oligomerization of isobutene over dealuminated Y zeolite catalysts. *Applied Catalysis A: General* **2008,** 337, (1), 73-77.
23. Ngandjui, L. T.; Thyrion, F., Kinetic study of the oligomerization of isobutene over H-mordenite. *Chemical Engineering and Processing: Process Intensification* **1992,** 31, (1), 1-6.