

REFERENCES

- Abello,M.C., Gomez,M.F. and Cadus,L.E. Ind. Eng. Chem. Res. **35**, 2137-2143 (1996).
- Armendariz,H., Aguilar-Rios,G., Salas,P., Valenzuela,M.A. and Schifter,I. Appl. Catal. **92**, 29-38 (1992).
- Au,C.T., Zhang,W.D. and Wan,H.L. Catal. Lett. **37**, 241-256 (1995).
- Bettahar,M.M., Costentin,G., Savary,L. and Lavalle,J.C. Appl. Catal. **145**, 1-48 (1996).
- Bhattacharyya,D., Bej,S.K. and Rao,M.S. Appl. Catal. **87**, 29-43 (1992).
- Blanchard,M. and Louguet,G. Kinetics and Catalysis (U.S.S.R.) **14**,20 (1973).
- Boisdrone,N., Monnier,A., Jalowlecki-Duhamel,L. and Barbaux,Y. J. Chem. Soc. Faraday Trans. **91**(17), 2899-2905 (1995).
- Burch,R. and Crabb, E.M. and Tsang,S.C. Appl. Catal. **65**, 259 (1990).
- Burch,R. and Swarnakar,R. Appl. Catal. **70**, 129-148 (1991).
- Burch,R. and Crabb, E.M. Appl. Catal. **100**, 111-130 (1993).
- Busca,G., Ricchiardi,G., Sam,D.S.H. and Volta,J.C. J. Chem. Soc. Faraday Trans. **90**(8), 1161-1170(1994).
- Cadus,L.E., Abello,M.C., Gomez,M.F. and Rivarola,J.B. Ind. Eng. Chem. Res. **35**, 14-18 (1996).
- Caldararu,M., Popa,V.T., Sprinceana,D. and Ionescu,N.I. Appl. Catal. **125**, 247-256 (1995).
- Carrazan, S.R.G., Peres,C., Bernard,J.P., Ruwet,M., Ruiz,P. and Delmon, B. J. Catal. **158**, 452-476 (1996).
- Castiglioni,J., Poix,P. and Kieffer,R. Proceedings of the 10th International Congress on Catalysis 1924 July, Budapest, Hungary, 2309-2312 (1993).
- Cavani,F. and Trifiro,F. Catalysis R. Soc. Chem. Cambridge, 11,246 (1994).
- Cavani,F. and Trifiro,F. Catalysis Today **24**, 307-313 (1995).
- Cavani,F. and Trifiro,F. Catalysis Today **36**,431-439 (1997).
- Centi,G. Catal. Lett. **22**, 53-66 (1993).

- Chaar,M.A., Patel,D., Kung,M.C. and Kung,H.H. J. Catal. **105**, 483-498 (1987).
- Chaar,M.A., Patel,D. and Kung,H.H. J. Catal. **109**, 463-467 (1988).
- Chang, Y., Somarjai,G.A. and Heinemann,H. Appl.Catal. **96**,305 (1993).
- Cherrak,A., Hubaut,R., Barbaux,Y. and Mairesse,G. Catal. Lett. **15**, 377-383 (1992).
- Choudary,V.R. and Rane,V.H. J.Catal. **135**, 310 (1992).
- Concepcion,P., Lopez Nieto,J.M. and Perez-Pariente,J. Catal. Lett. **19**, 333-337 (1993).
- Concepcion,P., Lopez Nieto,J.M. and Perez-Pariente,J. Catal. Lett. **28**, 9-15 (1994).
- Conway,S.J. and Lundford, J.H. J.Catal. **131**,513(1991).
- Corma,A., Nieto,J.M.L. and Paredes,N. Appl. Catal. **97**, 159-175 (1993a).
- Corma,A., Nieto,J.M.L. and Paredes,N. Appl.Catal. **104**, 161-174 (1993b).
- Corma,A., Nieto,J.M.L. and Paredes,N. J.Catal. **144**, 425-435 (1993c).
- Courcot,D., Grzybowska,B., Barbaux,Y., Rigole,M., Ponchel,A. and Creaser,D. and Andersson,B. Appl. Catal. **141**, 131-152 (1996).
- Desponds,O., Keiski,R.L. and Somorjai,G.A. Catal. Lett. **19**, 17-32 (1993).
- Ducarme,V. and Martin , G.A. Catal.Lett. **23**, 97-101 (1994).
- Eastman,A.D. and Kolts.J.H.,US.Patent 4370259 (1983).
- Finocchio,E., Busca,G., Lorenzelli,V. and Escribano,V.S. J.Chem.Soc. Faraday Trans. **92**(9), 1587-1593 (1996a).
- Finocchio,E., Ramis,G., Busca,G., Lorenzelli,V. and Willey, R.J. Catalyst Today **28**, 381-389 (1996b).
- Gao,X., Ruiz,P., Xin,Q., Guo,X. and Delmon,B.Catal. Lett. **23**, 321-337 (1994a).
- Gao,X., Ruiz,P., Xin,Q., Guo,X. and Delmon,B.J.Catal. **148**,56-67 (1994b).
- Gelbshtein, A.I., Mishchenko, Y.A., Nechiporuk, P.P., and Goldstein, N.P. J. Phys. Chem. **217**, 642(1974).
- Golodets, G.I. Heterogeneous catalytic reaction Elsevier, Amsterdam, (1983).
- Grabowski,R.,Grzybowska,B.,Samson,K.,Slolzinski,J.,Stoch,J. and Weislo,K. Appl.Catal. **125**,129 (1995).

- Guelton,M. J. Chem. Soc., Faraday Trans. **92**(9), 1609-1617 (1996).
- Guerrero-Ruiz,A., Ramos,I.R., Freno, J.L.G., Soenen,V., Herrmann,J.M. and Volta, J.C. Stud. in Surf. Sci. and Catal. Elsevier, Amsterdam, **72**,203 (1992).
- Guerrero-Ruiz,A., Ramos,I.R., Ferreira-Aparicio,P. and Volta,J.C. Catal.Lett. **45**, 113-118 (1997).
- Hayakawa,T., Andersen,A.G., Orita,H., Shimizu,M. and Takehira,K. Catal. Lett. **16**, 373-387 (1992).
- Ji,L.,Liu,J.,Chen,X. and Li,M. Catal.Lett. **39**, 247-252 (1996).
- Jones,C.A.,Leonard,J.J. and Sofranko,J.A.,US.Patent4737595 (1998).
- Kazanskii, V.B. Kinetics and Catalysis (U.S.S.R.) **14**, 72(1973).
- Kemball,C. Catalysis Volume I London : Billing Press (1977).
- Keulks, G.W., and Kenzde, L.D. 6th Internat. Congress Catalysis London, Chemical Society, London, Vol.2 in press (1976).
- Kim,Y-C, Ueda,W and Moro-oka,Y. Appl. Catal. **70**, 175-187 (1991).
- Korili,S.A. and Delmon,P.R.B. Catalyst Today **32**, 229-235(1996).
- Krishnammachari,N. and Calvo,C. Canadian Journal of Chemistry **49**, 1629-1637 (1971).
- Kryrov, O.V. Kinetics and Catalysis (U.S.S.R.) **14**,24 (1973).
- Kung,M.C. and Kung,H.H. J. Catal. **128**, 287-291 (1991).
- Kung,M.C. and Kung,H.H. J. Catal. **134**, 668-677 (1992).
- Landau,M.U.,Kaliya,M.L.,Herskowitz,M.,Oosterkamp,P.F.V.D. and Bocque, P.S.G. Chemtech**26**(2), 24 (1996).
- Lars,S. and Andersson,T. Appl. Catal. **112**, 209-218 (1994).
- Lavalley, J.C. Catalysis Today**27**, 377-401 (1996).
- Lindblad,T., Rebenstorf,B., Yan,Z. and Andersson,S.L.T. Appl. Catal. **112**, 187-208 (1994).
- Marales,E. and Lundford,J.H. J.Catal. **118**, 255 (1989).
- Matsuura, I., and Schuit, G.C.A. J. Catal. **20**, 19(1972).
- Matsuura,S. and Kimura,N. Stud.Surf.Sci.Catal. **82**, 271 (1994).

- Mazzocchia,C., Aboumrad,C., Diagne,C., Tempesti,E., Herrmann,J.M. and Thomas,G. Catal. Lett. **10**, 181-192 (1991).
- Michalakos,P.M., Kung, M.C., Jahan, I. and Kung ,H.H. J.Catal. **140**, 226-242 (1993).
- Morales,E. and Lundsford, J.H. J.Catal. **118**,255 (1989).
- Moro-oka, Y., and Takita, Y. Proc. 5th Internat. Congress Catalysis Miami Beach, North Holland, Amsterdam, Vol.2,1025 (1972).
- Morrison, S.R. J. Catal. **34**, 462 (1974).
- Ng,H.N. and Calvo,C. Can. J. of Chem. **50**, 3619-3624 (1972).
- Nguyen,K.T. and Kung, H.H. J. Catal. **122**,415 (1990).
- Nguyen,K.T. and Kung, H.H.Ind.Eng.Chem.Res. **30**, 352-361 (1991).
- Novakova, J., and Jira, P. J. Catal. **27**, 155 (1972).
- Oganowski,W., Hanuza,J., Macalik,L. and Mista,W.Bulletin of the Polish Academy of Sciences Chemistry **42** No.4, 525-541 (1994).
- Oganowski,W., Hanuza,J., Drulis, H., Macalik,L. and Mista,W. Appl.Catal. **136**, 143-159 (1996).
- Okuhara,T., Inumaru,K., Misono,M., Matsubayashi,N., Shimada,H. and Nishijima,A.Catal. Lett. **20**, 73-79 (1993).
- Otsubo, T., Miura, H., Morikawa, Y., and Shirasaki, T. J. Catal. **36**, 240 (1975).
- Otsuka,K., Ando,T., Suprapto,S., Wang,Y. and Ebitani,K.Catalysis Today **24**, 315-320 (1995).
- Oyama, S.T. and Somorjai, G.A. J. Phys.Chem. **94**,5022 (1990).
- Pantazidis,A.,Auroux,A.,Herrmann,J.M. and Mirodatos, C. Catalysis Today **32**, 81-88 (1996a).
- Pantazidis,A. and Mirodatos,C. Studies in surface science and catalysis **101**, 1029-1068 (1996b).
- Parmaliana,A., Sokolovskii,V., Miceli,D. and Giordano,N. Appl. Catal. **135**, L1-L5 (1996a).

- Patel,D. and Kung,H.N. In Proc.9th Int. Congr. Catalysis Calgary, vol.4,1553 (1988).
- Pendleton, P., and Taylor, D. J.C.S. Faraday I 72, pp. 1114, 1976
- Peng,X.D. and Barreau,M.A. Catal. Lett. 12, 245-254 (1992).
- Puglisi,M., Arena,F., Frusteri,F. Sokolovskii,V. and Parmaliana,A. Catal. Lett. 41, 41-43 (1996).
- Qiu,F.Y., Weng,L.T., Sham,E., Ruiz,P. and Delmon,B. Appl. Catal. 51, 235-253 (1989).
- Sam,D.S.H., Soenen,V. and Volta,J.C. J. Catal. 123, 417-435 (1990).
- Sancier, K.M., Wentzcek, P.R., and Wise, H. J. Catal. 39,22 (1975).
- Satterfield,C.N. Heterogeneous Catalysis in Practice McGraw-Hill book, (1980).
- Schulz, I.W., and Scheve, J. Proceedings of the Symposium on the Mechanisms of Hydrocarbon Reactions Elsevier, Amsterdam, 283 (1975).
- Smits,R.H.H., Seshan,K. and Ross,J.R.H. J. Chem. Soc., Chem. Commun. 558-559 (1991).
- Soenen,V., Herrmann,J.M. and Volta,J.C. J.Catal. 159, 410-417 (1996).
- Sokolovskii,V.D. Catal.Rev.Sci.Eng. 32 (1&2), 1-49 (1990).
- Sokolovskii,V.D. Catal. Today 24, 377-381 (1995).
- Sulikowski,B., Krysciak,J., Valenzuela,R.X. and Cartes-Corberan,V. Stud.Surf.Sci.Catal. 82 ,133 (1994).
- Tellez,C., Menendez,M. and Santamaria,J. AIChE J. 43(3), 777-784 (1997).
- Thammanonkul,H. Master of Engineering thesis Chulalongkorn University, (1996).
- Vedrine,J.C., Millet,J.M.M. and Volta,J.C. Catalyst Today 32, 115-123 (1996).
- Vedrine,J.C. 3rd World Congress on Oxidation Catalysis 1997 Elsevier Science B.V., 61-76 (1997).
- Vuurman,M.A., Stufkens,D.J., Oskam,A., Deo,G. and Wachs,I.E. J. Chem. Soc., Faraday Trans. 92(17), 3259-3265 (1996).
- Wang,R. Xie,M. and Li,P. Catal. Lett. 24, 67-77 (1994).

- Watling, T.C., Deo, G., Seshan, K., Wachs, I.C.E. and Lercher, J.A. Catalysis Today **28**, 139-145 (1996).
- Wragg, R.D., Ashmore, P.G., and Hockey, J.A. J. Catal. **22**, 49(1971).
- Wragg, R.D., Ashmore, P.G., and Hockey, J.A. J. Catal. **28**, pp. 337, 1973.
- Yokoyama, C. Catal. Lett. **38**, 181-188, (1996).
- Yoon, Y.S., Fujikawa, N., Ueda, W. and Moro-oka, Y. Chemistry Letter 1635-1636 (1994).
- Yoon, Y.S., Ueda, W. and Moro-oka, Y. Catal. Lett. **35**, 57, (1995).
- Zhang, W., Zhou, X., Tang, D., Wan, H. and Tsai, K. Catal. Lett. **23**, 103-106 (1994).
- Zhaorigetu, B., Kieffer, R. and Hindermann, J. Studied in Surface Science vol. 101 part B 1049-1058 (1996).

APPENDIX A

CALCULATION OF CATALYST PREPARATION

A.1 Calculation for the preparation of the unpromoted 28V-Mg-O catalyst.

The vanadia aqueous solution used in catalyst preparation consists of NH_4VO_3 0.5 wt.% and NH_3OH 1.0 wt. %. If the volume of this solution is designed to be 100 ml., hence NH_4VO_3 , NH_3OH and H_2O are weighted for 0.5, 1.0, and 98.5 gram, respectively.

The amount of MgO powder for 28 wt.% vanadia in V-Mg-O catalyst is calculated as follows :

If the weight of catalyst is 100 gram, 28V-Mg-O would compose of vanadia 28 g. and MgO 72 g. Therefore, in this system (compose of vanadia 0.5 g.),

$$\begin{aligned} \text{the amount of MgO} &= 72/28 * 0.5 \\ &\approx 1.2857 \text{ g.} \end{aligned}$$

Therefore, there is vanadia on MgO support = $0.5/(0.5+1.2857) * 100$

$$= 28 \text{ wt.\%}$$

A.2 Calculation for the preparation of alkali loaded 28V-Mg-O catalyst.

The calculation method in this section is similar to the above calculation, except the calculation of alkali loading. For 1wt. % alkali loading in 28 V-Mg-O,

$$\begin{aligned} \text{the amount of alkali} &= (0.5+1.2857) * 1/100 \\ &\approx 0.0179 \text{ g.} \end{aligned}$$

Hence, the amount of alkali 2wt.% and 3wt.% which is loaded in 28V-Mg-O equal 0.0357 g. and 0.1071 g., respectively.

APPENDIX B

CALCULATION OF REACTANT FLOW RATE

B.1 Calculation of the flow rate of C_3H_8 , air and argon in the ratio of 4:8:88

The sample of calculation shown below is for feed composition of 4 vol.% propane, 8 vol.% oxygen and the balance argon,

total flow rate = 100 ml./min.

flow rate of 21% O_2 in air is assumed to be X ml./min.

flow rate of 20% C_3H_8 in N_2 is assumed to be Y ml./min.

if the feed contains 8 vol.% oxygen,

$$\text{then there is } O_2 \text{ in flow of } O_2 \text{ in air} = 21X/100 = 8$$

$$\text{also there is } C_3H_8 \text{ in flow of } C_3H_8 \text{ in } N_2 = 20Y/100 = 4$$

$$\text{therefore } X = 38.09 \text{ ml./min.}$$

$$Y = 20 \text{ ml./min.}$$

Argon is used as balance gas, hence its flow is equal to $100 - 38.09 - 20$

$$= 41.91 \text{ ml./min.}$$

B.2 Calculation of checking explosive limit of propane in air.

The explosive limit of propane in air is shown below :

	lower limit in air	upper limit in air
propane	2.37 %	9.5 %

Therefore, the amount of propane in the feed must not be in the range of this explosive limit (between 2.37-9.5 % in air).

Calculation for the condition of feed stream 4:8:88,

flow rate C_3H_8 used in this study is fixed to 4 ml./min.

flow rate of air is 38.09 ml./min.

hence, there is propane in air = $4/38.09 * 100$

$$= 10.50\% \text{ (this value is O.K.)}$$

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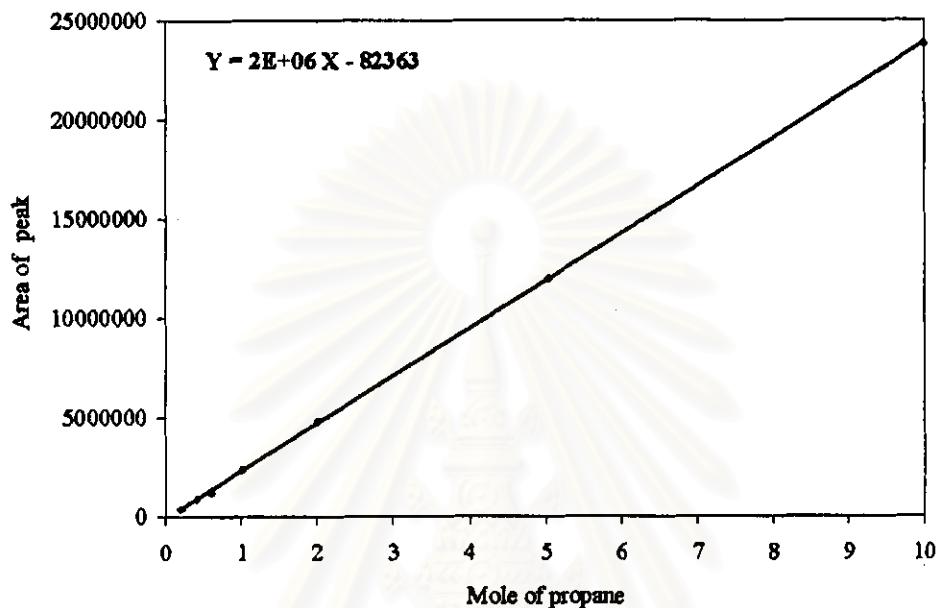
APPENDIX C**CALIBRATION CURVE**

Figure C1 The calibration curve of propane

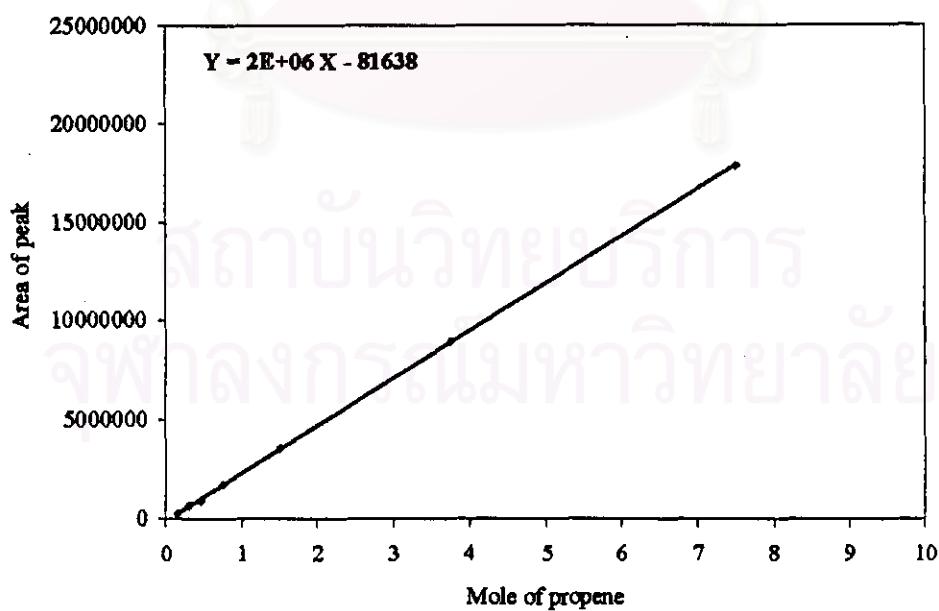


Figure C2 The calibration curve of propene

APPENDIX D

DATA OF EXPERIMENTS

D1 Data of TPD experiment

Table D1 Data of figure 5.34

T (°C)	area of O ₂	area of H ₂ O	T(°C)	area of O ₂	area of H ₂ O
30	0	0	299	21	1480
32	15	0	326	20	1430
76	15	0	352	18	1414
88	14	1236	381	23	1562
115	15	1713	407	23	1361
139	13	2669	434	24	1206
166	20	3623	489	22	920
192	21	2163	517	22	861
221	19	1854	543	24	784
247	18	1674	569	24	725
273	20	1446	600	22	639

Table D2 Data of figure 5.35

T (°C)	area of O ₂	area of H ₂ O	T(°C)	area of O ₂	area of H ₂ O
29	0	0	342	12	3110
64	0	0	368	18	3211
77	0	282	394	21	2799
105	0	1277	420	26	2431
130	0	3081	476	31	1555
155	0	3455	502	25	1379
182	0	3227	528	30	1157
210	0	2756	551	32	1179
235	0	2607	577	33	966
288	3	2818	600	46	910
316	9	2901			

Table D3 Data of figure 5.36

T (°C)	area of O ₂	area of H ₂ O	T(°C)	area of O ₂	area of H ₂ O
31	27	0	301	3	986
42	13	0	327	7	1140
77	21	0	354	21	1164
90	15	0	380	20	1175
119	13	1120	458	21	0
143	14	1502	484	24	0
169	11	1492	511	18	0
196	11	1266	536	8	0
224	10	1048	563	814	0
253	11	833	590	14	0
278	5	937	600	23	0

Table D4 Data of figure 5.37

T (°C)	area of O ₂	area of H ₂ O	T(°C)	area of O ₂	area of H ₂ O
32	64	0	337	27	1481
50	77	0	363	54	1592
80	47	478	405	11	1252
109	43	931	432	28	840
136	42	1290	458	50	697
166	42	1227	484	22	421
194	39	1217	510	6	310
222	60	111	536	38	0
246	38	974	560	9	0
273	23	1074	587	24	0
303	41	1208	600	36	0

Table D5 Data of figure 5.38

T (°C)	area of O ₂	area of H ₂ O	T (°C)	area of O ₂	area of H ₂ O
31	0	0	312	17	2684
35	0	0	338	22	2800
79	0	1296	364	25	2734
104	1	1829	390	33	2516
129	7	2532	417	36	2255
156	9	2775	44	44	2042
181	8	2756	471	45	1640
208	11	2562	498	46	1568
233	11	2477	524	48	1265
260	13	2380	550	53	1124
286	15	2639	600	60	903

Table D6 Data of figure 5.39

T (°C)	area of O ₂	area of H ₂ O	T (°C)	area of O ₂	area of H ₂ O
31	0	0	321	290	5137
41	26	0	345	321	6412
77	86	0	370	365	7377
88	95	0	394	394	6544
117	123	1694	418	427	4545
141	139	2982	442	452	3567
167	163	2867	467	487	2927
193	187	2533	490	521	2414
220	208	2216	514	539	1988
245	231	2253	537	551	1916
273	255	2882	563	568	1398
298	270	4015	600	589	1184

Table D7 Data of figure 5.40

T (°C)	area of O ₂	area of H ₂ O	T(°C)	area of O ₂	area of H ₂ O
30	0	0	316	7	7481
63	0	0	343	6	8946
78	2	805	369	8	8713
103	3	1827	395	4	5662
129	3	3411	422	8	3873
156	5	3379	449	6	3170
183	8	3001	475	2	2143
209	7	2736	502	4	1747
236	6	2874	528	6	1296
262	5	3547	555	7	965
290	4	4987	600	5	609

Table D8 Data of figure 5.41

T (°C)	area of O ₂	area of H ₂ O	T(°C)	area of O ₂	area of H ₂ O
30	0	0	307	18	3640
61	2	0	333	28	3727
77	8	833	360	27	3859
99	6	2180	386	26	3478
126	4	4395	407	24	3303
150	7	4711	438	18	2521
176	9	4349	465	18	2015
203	23	3887	490	30	1477
228	24	3330	541	43	1305
255	19	2987	566	48	1158
281	21	3289	600	57	988

Table D9 Data of figure 5.42

T (°C)	area of O ₂	area of H ₂ O	T (°C)	area of O ₂	area of H ₂ O
44	8	0	297	14	2499
48	6	0	321	17	3064
71	4	0	345	11	3718
95	4	810	369	11	3713
128	0	2323	394	10	2866
151	0	2793	418	11	2197
175	2	2547	442	14	1847
200	1	2196	467	11	1482
224	15	1883	491	9	1170
248	15	1854	516	10	918
273	13	2089	600	19	0

Table D10 Data of figure 5.43

T (°C)	area of O ₂	area of H ₂ O	T (°C)	area of O ₂	area of H ₂ O
37	44	0	317	19	2230
52	25	0	347	18	2644
91	36	0	373	21	2449
102	30	1638	405	16	1926
129	18	2424	430	17	1537
161	29	2897	457	11	1165
188	31	2567	484	20	997
214	26	2016	510	20	604
239	28	1811	541	12	420
266	25	1868	568	22	0
292	18	2086	600	12	0

D2 The data of catalytic reaction test

Table D11 Data of figure 5.44

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	4	19	0.8
350	9	17	1.5
400	10	20	2
450	38	12	4.6
500	82	8	6.6
550	99	1	1
600	99	1	1

Table D12 Data of figure 5.45

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0	6	0
350	1	5	0
400	1	3	0
450	4	2	0
500	10	1	0.1
550	23	1	0.23
600	45	1	0.45

Table D13 Data of figure 5.46

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	2	36	0.7
400	4	24	0.9
450	7	18	1.3
500	16	14	2.2
550	34	13	4.4
600	68	8	5.4

Table D14 Data of figure 5.47

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	1	65	0.7
400	4	28	1.1
450	9	20	1.8
500	17	16	2.7
550	35	19	6.7
600	84	13	10.9

Table D15 Data of figure 5.48

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	8	8	0.6
350	8	9	0.7
400	10	10	1
450	11	12	1.3
500	18	14	2.5
550	37	16	5.9
600	48	5	2.4

Table D16 Data of figure 5.49

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1	7	0.1
350	5	6	0.3
400	32	3	1
450	52	2	1
500	62	2	1.2
550	59	2	1.2
600	45	2	1

Table D17 Data of figure 5.50

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	13	6	0.8
350	11	7	0.8
400	24	3	0.7
450	50	2	1
500	77	1	0.8
550	76	1	0.8
600	58	2	1.2

Table D18 Data of figure 5.51

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	3	19	0.6
400	6	14	0.8
450	8	13	1
500	15	12	1.8
550	40	11	4.4
600	48	4	1.9

Table D19 Data of figure 5.52

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	4	13	0.5
400	4	13	0.5
450	7	10	0.7
500	11	7	0.8
550	14	8	1.1
600	36	6	2.2

Table D20 Data of figure 5.53

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	4	18	0.7
400	4	19	0.8
450	5	20	1
500	10	11	1.1
550	18	7	1.3
600	32	6	1.9

Table D21 Data of figure 5.54

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1	51	0.5
350	1	51	0.5
400	4	25	1
450	10	13	1.3
500	43	3	1.3
550	99	1	1
600	99	1	1

Table D22 Data of figure 5.55

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	4	15	0.6
350	3	19	0.6
400	10	7	0.7
450	34	2	0.7
500	48	8	3.8
550	61	16	9.8
600	65	13	8.5

Table D23 Data of figure 5.56

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	2	57	1.1
400	6	29	1.7
450	14	12	1.7
500	38	6	2.3
550	64	6	3.8
600	94	2	1.9

Table D24 Data of figure 5.57

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1		
350	1	71	0.7
400	4	30	1.2
450	13	14	1.8
500	40	11	4.4
550	66	9	5.9
600	98	1	1

Table D25 Data of figure 5.58

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	2	32	0.6
350	5	13	0.7
400	13	5	0.7
450	31	3	0.9
500	39	18	7
550	45	23	10
600	47	16	7.5

Table D26 Data of figure 5.59

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	1	63	0.6
400	2	33	0.7
450	6	19	1.1
500	14	12	1.7
550	29	12	3.5
600	35	15	5.3

Table D27 Data of figure 5.60

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	2	69	1.4
400	3	30	0.9
450	5	19	1
500	10	18	1.8
550	17	17	2.9
600	23	14	3.2

Table D28 Data of figure 5.61

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1	51	0.5
350	2	33	0.7
400	8	15	1.2
450	13	16	2.1
500	27	14	3.8
550	61	5	3.1
600	98	1	1

Table D29 Data of figure 5.62

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1	71	0.7
350	2	42	0.8
400	3	26	0.8
450	5	20	1
500	9	16	1.4
550	31	6	1.9
600	96	2	1.9

Table D30 Data of figure 5.63

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1		
350	1	73	0.7
400	2	58	1.2
450	8	23	1.8
500	14	9	1.3
550	46	3	1.4
600	98	1	1

Table D31 Data of figure 5.64

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	3	23	0.7
350	4	22	0.9
400	7	15	1
450	17	10	1.7
500	49	7	3.4
550	97	1	1
600	99	1	1

Table D32 Data of figure 5.65

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1	51	0.5
350	2	48	1
400	3	26	0.8
450	7	17	1.2
500	28	14	3.9
550	99	1	1
600	99	1	1

Table D33 Data of figure 5.66

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	4	15	0.6
350	8	8	0.6
400	21	3	0.6
450	47	2	0.9
500	66	4	2.6
550	71	7	5
600	70	3	2.1

Table D34 Data of figure 5.67

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	4	13	0.5
350	1	12	0.1
400	3	10	0.3
450	11	9	1
500	52	3	1.6
550	69	6	4.1
600	73	6	4.4

Table D35 Data of figure 5.68

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	3	13	0.4
350	1	13	0.1
400	5	11	0.6
450	10	12	1.2
500	39	2	0.8
550	66	5	3.3
600	70	5	3.5

Table D36 Data of figure 5.69

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1	12	0.1
350	0	10	0
400	2	7	0.1
450	11	6	0.7
500	29	4	1.2
550	41	5	2
600	66	3	2

Table D37 Data of figure 5.70

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	3		
350	7	20	1.4
400	32	3	1
450	45	2	0.9
500	56	1	0.6
550	56	2	1.1
600	41	3	1.2

Table D38 Data of figure 5.71

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	1		
350	5	16	0.8
400	34	2	0.7
450	36	2	0.7
500	38	2	0.8
550	38	3	1.1
600	39	3	1.2

Table D39 Data of figure 5.72

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	4	22	0.9
400	33	3	1
450	35	3	1.1
500	36	3	1.1
550	37	3	1.1
600	39	3	1.2

Table D40 Data of figure 5.73

T(°C)	% C ₃ H ₈ conversion	% C ₃ H ₆ selectivity	%yield
300	0		
350	4	21	0.8
400	33	3	1
450	35	2	0.7
500	34	32	1
550	36	3	1.1
600	38	3	1.1

APPENDIX E**PUBLISHED PAPER**

This published paper emerged during this study was presented at Academic Conference, 7th ,Chiangmai University, 23-25 October 1997.



Oxidative dehydrogenation of propane on V-Mg-O catalyst : Effect of pretreatment gas

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ABSTRACT

Pretreatment of a V-Mg-O catalyst with oxidising or non-oxidising atmosphere at an elevated temperature (*e.g.* 500°C) affects surface structure and, thus, catalytic property of the V-Mg-O catalyst used for the oxidative dehydrogenation of propane to propene. The catalysts pretreated in air and in an inert atmosphere show the same propane conversion but different propene selectivity. The catalyst pretreated in the inert atmosphere exhibits higher propene selectivity than the catalyst pretreated in air in low reaction temperature region but approaching the same value when the reaction temperature is further increased. IR spectra reveal that the catalyst pretreated in the inert atmosphere lost some of its V-O-V structure from its surface, thus, leading to different propene selectivity.

Introduction

Oxidative dehydrogenation (ODH) of alkane is of widely considerable industrial and academic interest, due to this reaction has possibility to upgrade a low value alkane to its higher value corresponding alkene at a relatively low temperature. Furthermore, any effects from catalyst deactivation by coking is also minimised.

The oxidation of propane to propene is an ODH reaction being studied by several research groups [*e.g.* 1-11]. Any catalyst used in this reaction must active enough to activate the quite inert propane without the activation of the more active propene. Among several catalyst systems investigated the V-Mg-O system was found to be a system that can balance between propane conversion and propene selectivity [9]. Despite the fact that the V-Mg-O system was investigated by several researchers, the functional groups responsible for alkane activation and alkene selectivity have yet to be agreed. However, many researchers believe that the structures of V-Mg-O catalyst which involves in the ODH reaction are Mg₃V₂O₈, α -Mg₂V₂O₇ and β -MgV₂O₆ phase [3,12].

At present, it has been emerged that the catalytic properties of the V-Mg-O catalyst depend on the ability of the catalyst to supply its lattice oxygen ions to the adsorbed hydrocarbon *i.e.* the reducibility of the catalyst by a hydrocarbon [13]. The reducibility of the catalyst relates to the structure of the surface lattice oxygen ion. Two main structures can be categorise *i.e.* M-O-M or M=O where M is metal atom and O is oxygen atom.

In this paper, we present the relationship between the structure of the surface lattice oxygen and catalytic property of the V-Mg-O catalyst by performing catalyst treatment in different atmosphere.

Experiment

An 28V-Mg-O catalyst (28%V as V_2O_5) was prepared by the conventional wet impregnation method. An appropriate amount of MgO powder is added to the solution containing NH_4VO_3 and NH_4OH . The obtained slurry was evaporated to dryness until white fine powder was obtained. After grinding the powder, the resulting solid was calcined at 550 °C for 6 hours.

To study the catalytic property of the obtained catalyst, 0.1 gram of the obtained catalyst was packed in a quartz microreactor. Two treatment conditions were performed before the ODH reaction. The first condition was heating the catalyst at 500 °C in air atmosphere for 1 hour before cooling down to 300°C. This condition is to kept the catalyst surface in fully oxidised state. (This catalyst will be called 28V-Mg-O/Air.) The second condition was similar to the first condition but Ar was used in stead of air. This condition was intended to partially reduced the catalyst surface to an extent. (This catalyst will be called 28V-Mg-O/Ar.)

The catalyst surface after each treatment was also characterised by FT-IR using Nicolet model Impact 400. Each sample was prepared by mixing an appropriate amount of the catalyst with KBr to form a thin wafer for IR characterisation. The crystal structure was characterised by XRD using SIEMENS D5000 diffractrometer with $CuK\alpha$ radiation. The reactant used in the reaction contained 4 vol% C_3H_8 , 8 vol% O_2 and balance Ar. Further details of the experimental system was already described elsewhere [13].

Results and Discussion

1. X-ray diffraction

X-ray diffraction patterns of the catalyst pretreated in Air and Ar are presented in figures 1 and 2 respectively. Only diffraction lines of MgO can be observed. The results can be interpreted that the structure of vanadium on magnesium does not form a large enough crystal to be detected by this technique. In reality it is accepted that vanadium does not form vanadium oxide on MgO surface but form a new compound containing V-Mg-O. The structure of the new oxide compound depends on vanadium loading and preparation technique. However, some research group had report reported that for a V-Mg-O catalyst with vanadium content over 35 wt%V (calculate as V_2O_5) the catalyst can exhibit the diffraction lines of $Mg_3V_2O_8$.

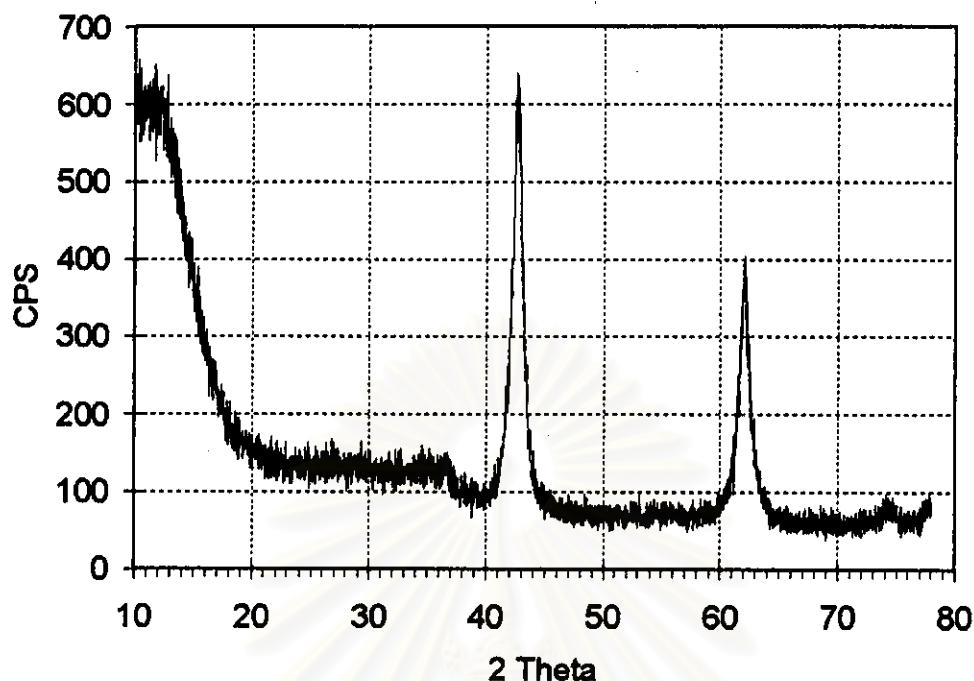


Figure 1 X-ray diffraction pattern of 28V-Mg-O/Air catalyst

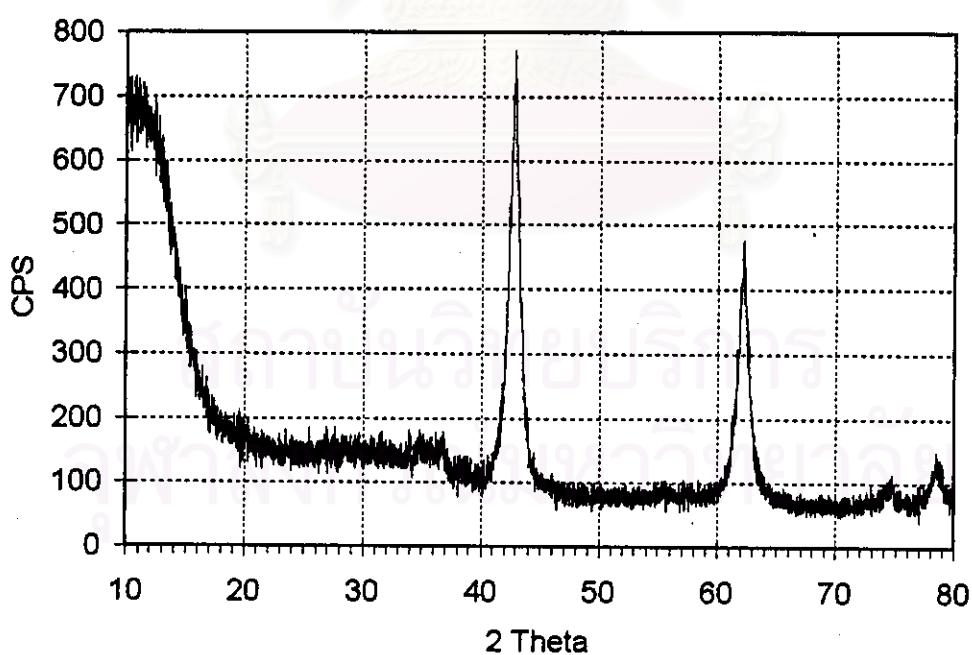


Figure 2 X-ray diffraction pattern of 28V-Mg-O/Ar catalyst

2. Infrared spectroscopy

The IR spectra of 28V-Mg-O/Air and 28V-Mg-O/Ar are exhibited in figures 3 and 4 respectively. The peak at around 860 cm^{-1} can be assigned to VO_3 unit and the shoulder around 660 cm^{-1} can be assigned to V-O-V structure [14]. The main difference between both spectra is at the intensity of the shoulder at 660 cm^{-1} . The IR spectrum of the 28V-Mg-O/Air catalyst shows clearer shoulder than the spectrum of the 28V-Mg-O/Ar catalyst which means that the catalyst can lost some oxygen from the V-O-V structure during the pretreatment in Ar. It has been shown before that the 28V-Mg-O catalyst can lost some of its lattice oxygen by heating in a non-oxidising atmosphere.

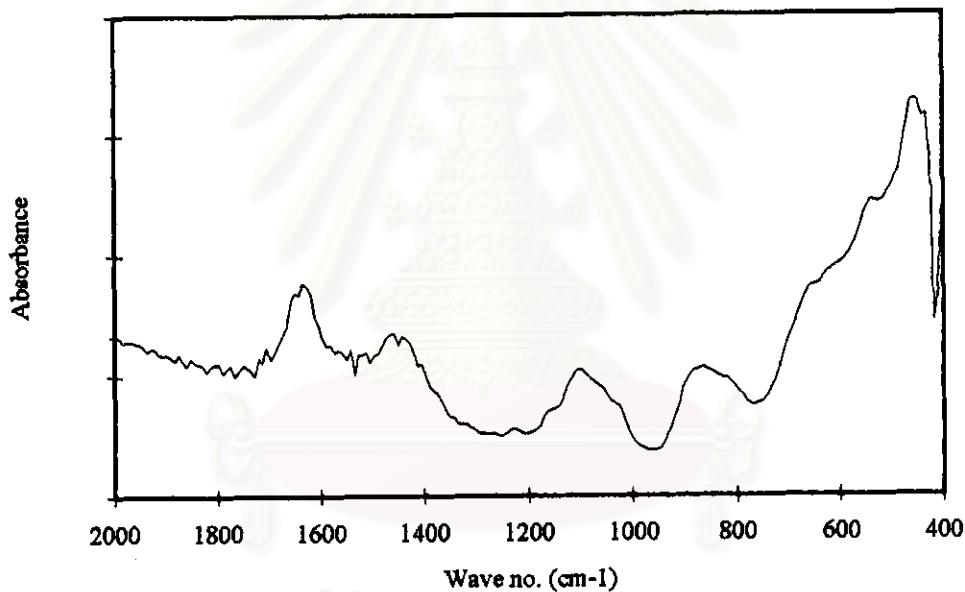


Figure 3 IR spectrum of 28V-Mg-O/Air catalyst.

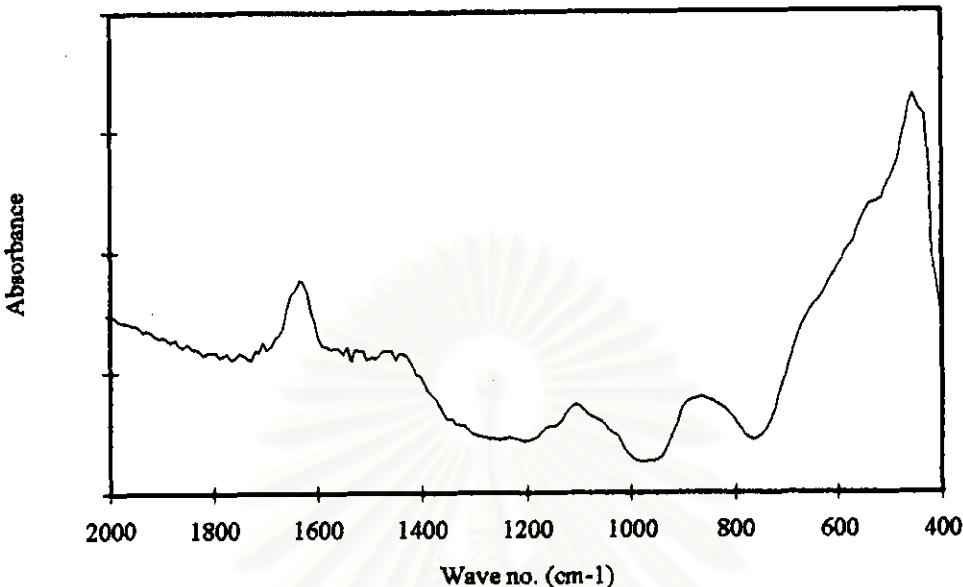


Figure 4 IR spectrum of 28V-Mg-O/Ar catalyst.

3. Oxidative dehydrogenation of propane to propene

The catalytic property of the 28V-Mg-O/Air catalyst is illustrated in figure 5. The figure shows that the activity of the catalyst increases rapidly when the reaction temperature is higher than 400°C, while the selectivity to propene gradually decreases to nearly zero at 550°C. Propane conversion of the 28V-Mg-O/Ar catalyst, figure 6, also shows the same trend as the catalyst pretreated in air. Propene selectivity of the 28V-Mg-O/Ar, however, is about twice times higher in the reaction temperature region below 500°C but approaching zero when the reaction temperature is further increased.

From the reaction study which shows that both catalysts exhibit the same propane conversions but different propene selectivity, and from the IR results (figures 3 and 4) which show that only some V-O-V species disappears from the catalyst surface we may postulate that the V-O-V structure and VO₃ species play different role in the ODH of propane. The VO₃ structure acts as propane activation and the V-O-V species involves in the propene selectivity. In the temperature region below 500°C the gas phase oxygen may not be effective in the reoxidation of the catalyst surface. But in the temperature region higher than 500°C the gaseous oxygen can oxidise the reduced surface of the 28V-Mg-O/Ar catalyst back to its oxidised form, the same form as of the 28V-Mg-O/Air catalyst. Therefore, both catalysts have the same surface structure and the same catalytic properties.

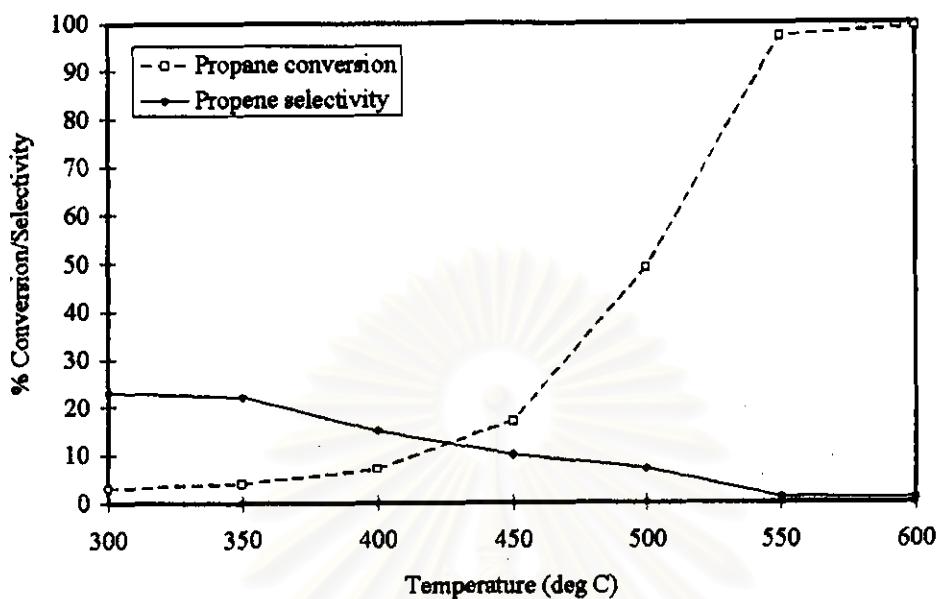


Figure 5 Propane conversion and propene selectivity of 28V-Mg-O/Air catalyst.

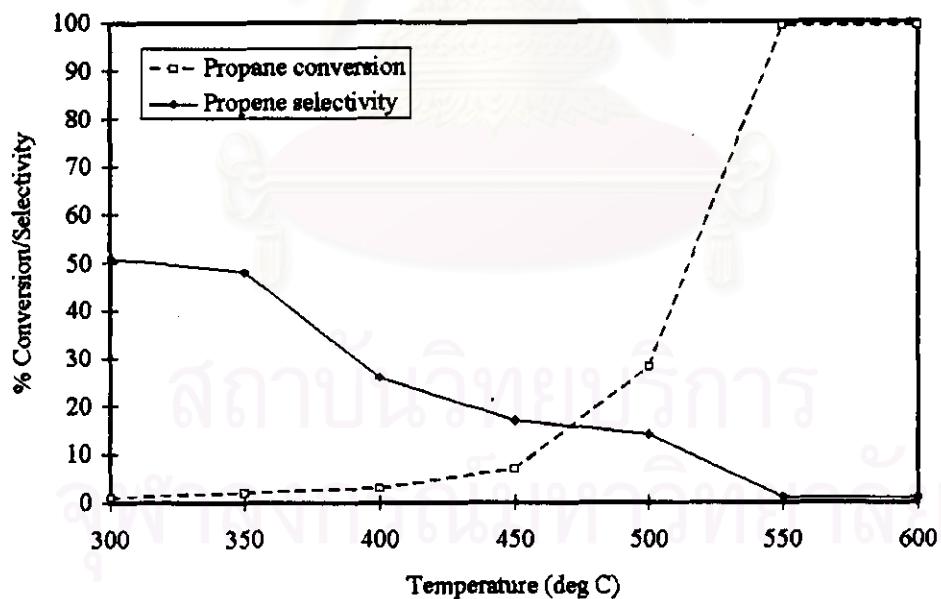


Figure 6 Propane conversion and propene selectivity of 28V-Mg-O/Ar catalyst.

Acknowledgements

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References

- [1] Chaar,M.A., Patel,D. Kung,M.C. and Kung,H.H., "Selective oxidative dehydrogenation of butane over V-Mg-O catalysts", *J. Catal.*, 105,483-498 (1987).
- [2] Chaar,M.A., Patel,D. and Kung,H.H., "Selective oxidative dehydrogenation of propane over V-Mg-O catalysts", *J. Catal.*, 109,463-467 (1988).
- [3] Kung,M.C. and Kung,H.H., "The effect of potassium in the preparation of magnesium orthovanadate and pyrovanadate on the oxidative dehydrogenation of propane to butene", *J. Catal.*, 134,668-677 (1992).
- [4] Owen,O.S., Kung,M.C. and Kung, H.H., "The effect of oxide structure and cation reduction potential of vanadates on the selective oxidative dehydrogenation of butane and propane", *Catal. Lett.*, 12,45-50 (1992).
- [5] Burch,R. and Crabb,E.M., "Homogeneous and heterogeneous contributions to the catalytic oxidative dehydrogenation of ethane", *Appl. Catal.*, 97,49-65 (1993).
- [6] Gao,X., Ruiz,P., Xin,Q., Guo,X. and Delmon,B., "Preparation and characterization of three pure magnesium vanadate phases as catalysts for selective oxidation of propane to propene", *Catal. Lett.*, 23,321-337 (1994).
- [7] Oganowski,W., Hanuza,J., Macalik,L. and Mišta,W., *Bulletin of the Polish Academy of Sciences*, 42 No.4,525-541 (1994).
- [8] Wang,R. Xie,M. and Li,P., "Catalytic and electrocatalytic oxidation of propane on V-Mg-O and V-Mg-O(Ag) catalysts", *Catal. Lett.*, 24,67-77 (1994).
- [9] Carvani,F. and Trifirò,F., "The oxidative dehydrogenation of ethane and propane as an alternative way for the production of light olefins", *Catalysis Today*, 24,307-313 (1995).
- [10] Creaser,D. and Andersson,B., "Oxidative dehydrogenation of propane over V-Mg-O : kinetic investigation by nonlinear regression analysis", *Appl. Catal.*, 141,131-152 (1996).
- [11] Pantazidis,A. and Mirodatos,C., "Mechanistic approach of the oxidative dehydrogenation of propane over V-Mg-O catalysts by *in situ* spectroscopic and kinetic techniques", *Studies in surface science and catalysis*, 101,1029-1068 (1996).
- [12] Corma,A., López Nieto,J.M. and Paredes,N., "Oxidative dehydrogenation of propane on vanadium supported on magnesium silicates", *Appl. Catal.*, 97,159-175 (1993).
- [13] Hongsuda Thammanonkul, "Oxidative Dehydrogenation of Propane over V-Mg-O catalyst", M.Eng.Thesis, Chulalongkorn University, 1996.
- [14] Busca,G., Ricchiardi,G., Siew Hew Sam,D. and Volta,J., "Spectroscopic characterisation of magnesium vanadate catalysts : Part 1 - Vibrational characterisation of $Mg_3(VO_4)_2$, $Mg_2V_2O_7$ and MgV_2O_6 powders", *J. Chem. Soc. Faraday Trans.*, 90(8), 1161-1170 (1994).

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