APPENDIX C - Publications, Conference Papers, and Presentations based on this work

Publications

Refereed

Postula, W.S., Z. Feng, C.V. Philip, A. Akgerman, and R.G. Anthony, "Conversion of Synthesis Gas to Isobutylene over Zirconium Dioxide Based Catalysts," *J. Catal.* **145,** 126 1994.

Postula, W.S., A. Akgerman, and R.G. Anthony, "The Effect of Hydrogen Sulfide on Isosynthesis over 7% (wt) Cerium Zirconia Catalyst," *Applied Catalysis* A:General **112,** 175-185 (1994).

Feng, Z., W.S. Postula, C. Erkey, C.V. Philip, A. Akgerman, and R.G. Anthony, "Selective Formation of Isobutane and Isobutene from Synthesis Gas over Zirconia Catalysts Prepared by a Modified Sol Gel Method," *J. Catal.* **148,** 84-90 (1994).

Feng, Z., W.S. Postula, A. Akgerman, and R.G. Anthony, "Synthesis and Characterization of Zirconia Based Catalysts Prepared by Precipitation, Calcination, and Modified Sol-Gel Methods," to be submitted to *I&EC Research (Kinetics and Catalysis).*

Feng, Z., A. Akgerman, and R.G. Anthony, "Selective Formation of Isobutane and Isobutene from Synthesis over Calcium Promoted Zirconias," to be submitted to *Appl. Catal. A.*

Erkey, C., J. Wang, W.S. Postula, Z. Feng, C.V. Philip, A. Akgerman, and R.G. Anthony, "Isobutylene Production from Synthesis Gas over Zirconia in a Slurry Reactor," to be submitted to *I&EC Research (Kinetics and Catalysis).*

Papers for Technical Conferences

Anthony, R.G., A. Akgerman, C. Erkey, Z. Feng, W. Postula, and C.V. Philip, "Catalyst and Process Development for Synthesis Gas Conversion to Isobutylene," *Proceedings of DOE Liquefaction Contractors' Review Meeting*, Pittsburgh, PA, September 3-5, 1991.

Anthony, R.G., W. Postula, Z. Feng, and A. Akgerman, "Use of Zirconia in the Conversion of Hydrogen Lean Synthesis Gas to Isobutylene," Preprint Paper-*Am. Chem. Soc., Div. Fuel Chem.*, **37,** 247-53 (1992). Preprints of Symposium on Coal Liquefaction at the Spring ACS National Meeting in San Francisco, CA, April 1992.

Anthony, R.G., A. Akgerman, W.S. Postula, Z. Feng, C.V. Philip, and C. Erkey, "Catalyst and Process Development for Synthesis Gas Conversion to Isobutylene," *Proceedings of DOE Liquefaction Contractors' Review Meeting*, Pittsburgh, PA, September 22-24, 1992.

Anthony, R.G., W.S. Postula, Z. Feng, C.V. Philip, and A. Akgerman, "Isobutylene Synthesis Using Zirconia and Modified Zirconia," *Proceedings of the Ninth Annual International Pittsburgh Coal Conference*, Pittsburgh, PA, October 12-16, 1992.

Anthony, R.G., A. Akgerman, W.S. Postula, Z. Feng, C.V. Philip, and C. Erkey, "Catalyst and Process Development for Synthesis Gas Conversion to Isobutylene," *Proceedings of DOE Liquefaction Contractors' Review Meeting*, Pittsburgh, PA, September 27-29, 1993.

Also, monthly and quarterly reports were filed at the appropriate times with DOE.

Presentations

Anthony, R.G., "Catalyst and Process Development for Synthesis Gas Conversion to Isobutylene," DOE Liquefaction Contractors' Review Meeting, Pittsburgh, PA, September 3-5, 1991.

Postula, W.S., "Conversion of SynGas to Isobutylene over Zirconium Dioxide Catalyst," Second Annual Chemical Engineering Graduate Research Symposium, Texas A&M University, College Station, Texas, January 9, 1992.

Anthony, R.G., "Use of Zirconia in the Conversion of Hydrogen Lean Synthesis Gas to Isobutylene," Symposium on Coal Liquefaction at the Spring ACS National Meeting in San Francisco, CA, April 1992.

Anthony, R.G., "Catalyst and Process Development for Synthesis Gas Conversion to Isobutylene," DOE Liquefaction Contractors' Review Meeting, Pittsburgh, PA, September 22-24, 1992.

Anthony, R.G., "Isobutylene Synthesis Using Zirconia and Modified Zirconia," Ninth Annual International Pittsburgh Coal Conference, Pittsburgh, PA, October 12-16, 1992.

Anthony, R.G., "Catalyst and Process Development for Synthesis Gas Conversion to Isobutylene," DOE Liquefaction Contractors' Review Meeting, Pittsburgh, PA, September 27-29, 1993.

Postula, W.S., "Isobutylene Synthesis Over Zirconia-Based Catalysts," 49th American Chemical Society Southwest Regional Meeting, Hyatt Regency Hotel, Austin, Texas, October 27, 1993.

APPENDIX D - TABLES

List of Tables 1.1 - 3.35 on pages viii-x

TABLE 1.1. Conversions and product distributions[a] of CO/H_2 reactions at equilibrium

Pressure (atm)	50		70	
Temperature (K)	653	723	653	723
CO	0.000339	0.001660	0.000295	0.001401
H_2	0.000886	0.001936	0.000750	0.001639
CO_2	0.338798	0.360891	0.338427	0.360205
H_2O	0.331568	0.312950	0.331927	0.313742
C	0.223619	0.214070	0.223464	0.213770
CH_4	0.104789	0.108471	0.105138	0.109227
C_2H_6	0	0.000016	0.000016	0.000016
CO conversion	0.999636	0.998214	0.999732	0.998675
H_2 conversion	0.986799	0.97117	0.990141	0.97848

[a] Distributions are on a weight basis, 1/1 CO/H_2 in the feed.

TABLE 2.1. Chemicals utilized in precipitated, hydrothermal, and calcination catalyst preparation

Compound	Purity	Main impurities (ppm)
$ZrO(NO_3)_2 \cdot 5H_2O$	tech	Hf-3700, Fe-400, Si-250
NaOH	97%	Na_2CO_3-10000, K-2000
$LiNO_3$	99.99%	Cs-16, Ca-7, K-1, Na-0.8
$Ba(NO_3)_2$	99.98%	Sr-100, Si-25, Ni-10
$Cu(NO_3)_2 \cdot 3H_2O$	99.999%	None detected
$Mg(NO_3)_2 \cdot 6H_2O$	99.995+%	Na-9, Mn-1, Zn-1
$Mn(NO_3)_2 \cdot 6H_2O$	98%	No analysis
$Al(NO_3)_3 \cdot 9H_2O$	99.997%	Si-2, Na-1
$Ce(NO_3)_3 \cdot 6H_2O$	99%	La-2000, Ca-65, Si-25
$Dy(NO_3)_3 \cdot 5H_2O$	99.9%	Si-100, Er-35, Ca-4
$TiCl_3$	99%	No analysis
$Y(NO_3)_3 \cdot 5H_2O$	99.9%	Si-25, La-10, Ca,Mg<0.2
$Th(NO_3)_4 \cdot 4H_2O$	98%	La<2000, Ti-100, Fe-20
TaF_5	98%	No analysis
$(CH_3)_4NOH$ (25 wt% in MeOH)		No analysis
$(C_4H_9)_4NBr$	99%	No analysis
$Ti(i\text{-}OC_3H_7)_4$	97%	No analysis
$Zr(OC_3H_7)_4$ (70 wt% in $1\text{-}C_3H_7OH$)		No analysis

TABLE 2.2. Chemicals used in modified sol gel catalyst preparation

Chemical	Formula	Manufacturer	Purity and State
Tetraisopropyl titanate	$Ti(OC_3H_7)_4$	Aldrich	97%, liquid
Tetraorthoethyl silicate	$Si(OC_2H_5)_4$	Aldrich	97%, liquid
Zirconium isopropoxide	$Zr(OC_3H_7)_4$	Aldrich	70% in C_3H_7OH
Aluminum *tri sec* butoxide	$Al(C_4H_9O)_3$	Aldrich	97%, liquid
Zirconyl chloride	$ZrOCl_2 \cdot 8H_2O$	Aldrich	98%, solid
Sodium hydroxide	NaOH	Aldrich	97%, solid
Potassium hydroxide	KOH	Aldrich	87.1%, solid
Methanol	CH_3OH	Mallinckrodt	99.9%, liquid
Acetone	CH_3COCH_3	Mallinckrodt	99.8%, liquid
Hydrochloric acid	HCl	Baker	37.3%, liquid
Sulfuric acid	H_2SO_4	Baker	95.9%, liquid
Nitric acid	HNO_3	Mallinckrodt	70.3%, liquid
Ammonium hydroxide	NH_4OH	Baker	30%, liquid
Tetramethylammonium hydroxide	$(CH_3)_4NOH$	Aldrich	25% in MeOH
Rubidium hydroxide	RbOH	Aldrich	50% in H_2O
Lithium hydroxide	LiOH	Aldrich	98%, solid
Cesium hydroxide	CsOH	Aldrich	50% in H_2O
Barium hydroxide	$Ba(OH)_2$	Aldrich	98%, solid
Calcium nitrate	$Ca(NO_3)_2 \cdot xH_2O$	Aldrich	83.5%, solid
Magnesium nitrate	$Mg(NO_3)_2 \cdot 6H_2O$	Aldrich	99%, solid

TABLE 3.1. Effect of calcination time on properties of zirconia

Calcination time (min)	N_2 BET surface area (m^2/g)	Crystal phase[a]
5	87	C
30	80	C/M
180	61	M/C

[a] C: cubic, M: monoclinic, predominant phase listed first

TABLE 3.2. d spacings and relative intensities of peaks in zirconia XRD patterns

Monoclinic (#36-420)[a]		Tetragonal (#24-1164)		Cubic (#27-997)	
d (Å)	Intensity	d (Å)	Intensity	d (Å)	Intensity
3.694	18	2.995	100	2.93	100
3.636	12	2.635	10	2.55	25
3.163	100	2.574	13	1.801	50
2.839	64	1.8412	23	1.534	20
2.620	22	1.820	13		
2.605	12	1.5821	8		
2.540	14	1.5553	15		
2.2131	12				
1.8480	16				
1.8186	18				
1.8032	12				
1.6567	12				

[a] The number given is the catalog number in the Powder Diffraction File (*37*).

TABLE 3.3. Effect of calcination temperature on properties of zirconia

Calcination conditions		N_2 BET surface area (m^2/g)	Crystal phase[a]	Bulk density (g/cm^3)
T (K)	Time (hr)			
383	24	270	A	1.64
723	2½	89	C/M	2.14
1273	2½[b]	0.36	M	3.57

[a] A: amorphous, C: cubic, M: monoclinic, predominant phase listed first
[b] 5 K/min heat-up from 348 K and 5 K/min cool-down to 348 K

TABLE 3.4. Changes in catalyst properties with preparation method

Method	Pore volume (cm^3/g)	Pore diameter (Å)	Bulk density (g/cm^3)
Precipitation	0.10	30-40	2.2
Hydrothermal	0.28	150-200	1.0
Calcining	0.20	30-40, 150-200	1.7

TABLE 3.5. Properties of isobutylene synthesis catalysts

Batch #	Precipitated catalysts[a]	N_2 BET Surface area[b] (m^2/g)			Crystal phase[c]	Bulk density (g/cm^3)
		B.R.	A.R.	R.C.		
1	ZrO_2	55	42		M	1.65
2	ZrO_2	52	35	40	M	1.88
3	1.6% Na, ZrO_2	58	45	49	M/C	2.11
4	3.2% Ti, 2% Th, ZrO_2	49	14	46	C/M	2.62
5	2% Mn, ZrO_2	35	0.4		C	2.82
6	7% Ce, ZrO_2	103	49		C	2.28
7	7% Ce, ZrO_2	93	55		C	2.39
8	7% Ce, ZrO_2	98	42	79	C	2.32
9	ZrO_2	89	35	84	C/M	2.14
10	0.22% Li, ZrO_2	98	41	87	C/M	2.18
11	0.34% Li, ZrO_2	99	40	85	C/M	2.10
12	0.67% Li, ZrO_2	101	36	83	C/M	2.13
13	0.79% Mg, ZrO_2	86	29	79	C/M	2.18
14	1.16% Mg, ZrO_2	98	45	86	C/M	2.18
15	1.72% Mg, ZrO_2	85	46	79	C/M	2.19

[a] Catalyst composition is wt%

[b] B.R.-after calcination but before reaction, A.R.-after reaction, R.C.-recalcined

[c] C-cubic, T-tetragonal, M-monoclinic, A-amorphous, predominant phase listed first

TABLE 3.5. Continued

Batch #	Precipitated catalysts[a]	N_2 BET Surface area[b] (m^2/g)			Crystal phase[c]	Bulk density (g/cm^3)
		B.R.	A.R.	R.C.		
16	2.28% Mg, ZrO_2	99	36	84	C/M	2.20
17	0.86% Al, ZrO_2	115	38	100	C	2.00
18	2.50% Al, ZrO_2	133	51	109	C	1.93
19	4.97% Dy, ZrO_2	96	46	80	C	2.32
20	13.39% Dy, ZrO_2	92	33	86	C	2.55
21	5.48% Ta, ZrO_2	35	34		C/M	1.93
22	24.64% Ta, ZrO_2	38	36		M/C	1.60
23	1.30% Y, 4.03% Ba, 2.80% Cu, ZrO_2	85	79	84	C	2.32
24	1.30% Y, 4.03% Ba, 2.80% Cu, ZrO_2	92	70	81	C	2.29
25	ZrO_2	82	55	79	C/M	2.05
26	ZrO_2	93	57	82	C/M	2.14
27	ZrO_2	99	18	83	C/M	2.32
28	7% Ce, ZrO_2	88	71	84	C	2.18
	Hydrothermal catalysts[a]					
29	1.6% Na, 10.3% Ti, ZrO_2	70	68	70	C	0.94

[a] Catalyst composition is wt%
[b] B.R.-after calcination but before reaction, A.R.-after reaction, R.C.-recalcined
[c] C-cubic, T-tetragonal, M-monoclinic, A-amorphous, predominant phase listed first

TABLE 3.5. Continued

Batch #	Hydrothermal catalysts[a]	N_2 BET Surface area[b] (m^2/g) B.R.	A.R.	R.C.	Crystal phase[c]	Bulk density (g/cm^3)
30	0.6% Na, 2% Ti, 2% Th, ZrO_2	53	50	53	C/M	1.08
	Calcination of zirconyl nitrate					
31	ZrO_2	39	36	39	C/M	1.71
	Commercial zirconia					
32	ZrO_2 (H-0304)	35			M	2.4
	Sol gel catalysts[a]					
33	2.2% Al, ZrO_2 (CSG)	13			T/M	0.71
34	ZrO_2 (MSG)	24			T	2.2
35	5.8% Si, ZrO_2 (MSG)	24			A	2.3
36	4.0% Al, ZrO_2 (MSG)	51			T	2.0
37	0.41% Li, ZrO_2 (MSG)	10			M	2.0
38	0.48% Na, ZrO_2 (MSG)	18			T	2.3
39	0.52% K, ZrO_2 (MSG)	32			T	2.3
40	0.44% Rb, ZrO_2 (MSG)	27			M	2.0
41	0.93% Cs, ZrO_2 (MSG)	22			T	2.4

[a] Catalyst composition is wt%
[b] B.R.-after calcination but before reaction, A.R.-after reaction, R.C.-recalcined
[c] C-cubic, T- tetragonal, M-monoclinic, A-amorphous, predominant phase listed first

TABLE 3.5. Continued

Batch #	Sol gel catalysts[a]	N_2 BET Surface area[b] (m^2/g)			Crystal phase[c]	Bulk density (g/cm^3)
		B.R.	A.R.	R.C.		
42	0.46% Mg, ZrO_2 (MSG)	25			T	2.4
43	0.53% Ca, ZrO_2 (MSG)	26			T	2.3
44	1.8% Ca, ZrO_2 (MSG)	34			T	2.3
45	0.54% Ba, ZrO_2 (MSG)	22			T	2.3
46	7.0% Si, ZrO_2 (MSG) (using NaOH)	99			T	1.5

[a] Catalyst composition is wt%
[b] B.R.-after calcination but before reaction, A.R.-after reaction, R.C.-recalcined
[c] C-cubic, T- tetragonal, M-monoclinic, A-amorphous, predominant phase listed first

TABLE 3.6. Ionic radii for 8 coordinated cations

Cation[a]	Ionic Radius (Å)	Cation	Ionic Radius (Å)
Li^{+}	0.700	Ho^{+3}	0.917
Na^{+}	0.979	Lu^{+3}	0.876
Ba^{+2}	1.39	Nd^{+3}	1.03
Ca^{+2}	1.02	Sc^{+3}	0.834
Cu^{+2}	0.989	Sm^{+3}	0.989
Mg^{+2}	0.670	Y^{+3}	0.956
Al^{+3}	0.515	Yb^{+3}	0.886
Dy^{+3}	0.937	Zr^{+4}	0.814
Gd^{+3}	0.968	Ta^{+5}	0.721

[a] Cations used in this study are indicated in outline type.

TABLE 3.7. Details of vacancies created by various dopants

Molar Ratio (M/100 Zr)	Vacancies/100 Zr[a]						Zr defects/100 Zr sites					
	Li	Mg	Al	Dy	Ta	YBaCu[b]	Li	Mg	Al	Dy	Ta	YBaCu
4	6	4	2	2	1	-	4	4	4	4	4	-
6	9	6	-	-	-	-	6	6	-	-	-	-
9	-	9	-	-	-	-	-	9	-	-	-	-
12	18	12	6	6	-	11	12	12	12	12	-	12
24	-	-	-	-	6	-	-	-	-	-	24	-

[a] Refers to oxygen vacancies in the cases of lower valence dopants and zirconium vacancies in the case of higher valence dopants.

[b] Molar ratio refers to total (Y+Ba+Cu)/Zr molar ratio.

TABLE 3.8. Typical coke deposition on catalysts under reaction conditions

Batch #	Precipitated catalysts	Time used[a] (hr)	g_{coke}/g_{cat}
2	ZrO_2	264	0.0374
3	1.6% Na, ZrO_2	1848	0.0378
8	7% Ce, ZrO_2	308	0.0640
11	0.34% Li, ZrO_2	26	0.0740
20	13.39% Dy, ZrO_2	26	0.0395
	Hydrothermal catalyst		
28	1.6% Na, 10.3% Ti, ZrO_2	768	0.0415
	Calcination catalyst		
31	ZrO_2	36	0.0060

[a] Refers to time spent at reaction conditions.

TABLE 3.9. Comparison of hydrocarbon distribution for precipitated, calcination, and hydrothermal catalysts at 673 K, 50 atm, and 1/1 CO/H_2 ratio

	Space time[a]	CO conv.	Hydrocarbon distribution (wt%)					
Precipitated catalysts	(sec)	(%)	C_1	C_2	C_3	C_4	C_5+	$i\text{-}C_4/\Sigma C_4$
ZrO_2[b]	45	12.8	10.2	2.6	2.0	21.2	64.0	70.7
1.6% Na, ZrO_2	30	11.6	6.6	3.0	1.5	18.4	70.5	76.7
3.2% Ti, 2% Th, ZrO_2	30	12.4	31.1	8.5	5.8	27.3	27.3	74.2
7% Ce, ZrO_2	30	13.1	27.8	9.6	8.0	30.7	23.9	63.2
Calcination catalyst								
ZrO_2	60	11.6	27.9	7.5	5.1	33.5	26.0	66.5
Hydrothermal catalysts								
1.6% Na, 10.3% Ti, ZrO_2	90	11.4	35.6	3.4	6.1	29.6	25.4	99.3
0.6% Na, 2% Ti, 2% Th, ZrO_2	90	11.7	27.5	2.8	2.4	14.9	52.4	100

[a] Space time (τ) is defined as V_{bed}/υ_o (υ_o is inlet volumetric flow rate at reaction P and T).
[b] Reaction pressure is 95 atm in this case.

TABLE 3.10. Comparison of activity and selectivity of commercial, modified sol gel, and precipitated zirconias at 70 atm and 1/1 CO/H_2 ratio

Catalyst	ZrO_2 (H-0304)	ZrO_2 (MSG)	ZrO_2 (ppt.)
Temperature (K)	723	723	673
Space time (sec)	80	80	45
CO conversion (%)	11.8	17.0	13.2
Hydrocarbon distribution (wt%)			
C_1	11.8	22.5	15.3
C_2	3.60	3.71	2.9
C_3	2.91	2.14	2.3
C_4	9.01	15.63	25.3
C_5+	72.68	56.02	54.2
C_4 distribution (wt%)			
isobutane	30.10	25.20	9.1
n-butane	6.14	2.48	2.0
1-butene	3.26	2.98	9.1
isobutylene	47.60	63.90	67.6
trans-2-butene	7.23	2.07	5.5
cis-2-butene	5.66	3.36	6.7

TABLE 3.11. A summary of time on stream experiments over Th-ZrO_2 (HT) at 723 K, 50 atm, 1/1 CO/H_2 ratio, and 40 second space time

Experiment	A	B	C	D
Time on stream, hr	4	20	55	88
CO conversion, %	18.1	17.8	18.7	19.5
CH_4/iso-C_4's, wt/wt	0.827	0.804	0.872	1.36

TABLE 3.12. Comparison of activity and selectivity between iron and aluminum CO cylinders at 673 K, 50 atm, and 1/1 CO/H_2 ratio over 7% $Ce\text{-}ZrO_2$

	Iron cylinder			Aluminum cylinder		
Space time (sec)	60	90	120	60	90	120
CO conversion (%)	20.0	26.7	30.6	23.1	29.2	34.0
Hydrocarbon distribution (wt%)						
C_1	29.5	30.8	32.6	36.1	44.7	47.7
C_2	8.3	7.5	6.6	9.4	8.8	8.5
C_3	7.1	5.3	4.6	8.5	5.0	4.4
C_4	29.0	29.4	28.8	19.8	19.5	20.1
C_5+	26.2	27.0	27.4	26.4	22.0	19.3

TABLE 3.13. Comparison of activity and selectivity at 673 K, 50 atm, and 1/1 CO/H_2 [or $CO/(H_2+H_2S)$] ratio

	without H_2S				with H_2S		
Space time (sec)	60[a]	60	90	120	60	90	120
CO conv (%)	23.56	23.12	29.23	33.96	23.55	27.93	33.07
Hydrocarbon distribution (wt%)							
C_1	29.61	36.05	44.65	47.66	26.46	29.40	32.33
C_2's + C_3's	20.23	17.83	13.81	12.87	10.75	8.26	8.20
C_4's	28.84	19.75	19.54	20.14	22.71	24.51	26.91
C_5+'s	21.23	26.37	22.00	19.33	39.09	37.83	32.57
Oxy/HC[b]	1.6	0.7	1.1	0.8	2.1	2.3	1.6
C_4 distribution (wt%)							
isobutane	10.12	12.30	21.90	29.00	13.97	22.60	30.98
n-butane	3.13	6.03	5.73	6.55	3.03	3.64	4.53
1-butene	8.36	7.75	6.81	6.45	7.26	6.72	6.23
isobutylene	52.11	49.52	43.55	37.29	53.20	46.10	38.70
trans-2-butene	15.82	14.38	13.00	12.26	13.41	12.41	11.57
cis-2-butene	10.47	10.03	9.01	8.44	9.15	8.54	7.99

[a] Run performed as an activity check on second batch of catalyst before feeding H_2S.
[b] Oxygenate produced/hydrocarbon produced (g/100 g)

TABLE 3.14. Effect of hydrogen sulfide on C_5 selectivity at 673 K, 50 atm, and 1/1 CO/H_2 [or $CO/(H_2+H_2S)$] ratio

	without H_2S	with H_2S
Space time (sec)	60	60
CO conversion (%)	23.6	23.6
C_5 distribution (wt%)		
3-m[a]-1-$C_4^=$	4.0	73.0
2-m C_4, 1-$C_5^=$, 2-m-1-$C_4^=$	32.5	8.5
n-C_5, *trans*-2-$C_5^=$, *cis*-2-$C_5^=$, 2-m-2-$C_4^=$	63.5	18.5

[a] m=methyl

TABLE 3.15. Gibbs free energy of formation at 700 K for C_5 alkanes and alkenes

C_5 hydrocarbon	$\Delta G_f°$ (kcal/mol)
3-methyl-1-butene	53.96
2-methyl butane	45.18
1-pentene	54.20
2-methyl-1-butene	51.55
n-pentane	46.19
trans-2-pentene	52.60
cis-2-pentene	52.71
2-methyl-2-butene	50.47

TABLE 3.16. Changes in activity and selectivity with temperature at 50 atm, 1/1 $CO/(H_2+H_2S)$ ratio, and 90 second space time

T (K)	CO conv. (%)	Hydrocarbon distribution (wt%)						C_4 distribution (wt%)					
		C_1	C_{2+3}[a]	C_4	C_5	C_6+	O/HC[b]	*i*-C_4	*n*-C_4	1-$C_4^=$	*i*-$C_4^=$	*t*-2-$C_4^=$	*c*-2-$C_4^=$
648	14.42	33.55	3.56	20.64	22.04	20.21	26.1	18.57	1.64	6.36	59.83	6.78	6.83
673	27.93	29.40	8.26	24.51	16.17	21.66	2.3	22.60	3.64	6.72	46.10	12.41	8.54
698	38.96	37.21	8.57	27.14	12.24	14.84	0.2	45.43	7.38	5.14	26.73	9.09	6.22
723	52.08	50.68	8.97	25.70	7.42	7.22	0.0	66.93	12.2	2.82	10.22	4.75	3.12

		C_5 distribution (wt%)		
		3-m[c]-1-$C_4^=$	2-m C_4, 1-$C_5^=$, 2-m-1-$C_4^=$	*n*-C_5, *t*-2-$C_5^=$, *c*-2-$C_5^=$, 2-m-2-$C_4^=$
648	14.42	93.95	0.55	5.49
673	27.93	67.59	12.26	20.15
698	38.96	50.55	30.30	19.15
723	52.08	25.17	60.47	14.36

[a] C_2 plus C_3 hydrocarbons
[b] Oxygenate produced/hydrocarbon produced (g/100 g)
[c] m=methyl

TABLE 3.17. Comparison of activity and selectivity at 673 K, 50 atm, and 1/1 $CO/(H_2+H_2S)$ ratio over 7% $Ce\text{-}ZrO_2$ without and with presulfiding

	without presulfiding		with presulfiding
Space time (sec)	60	90	90
CO conversion (%)	23.55	27.93	21.22
Hydrocarbon distribution (wt%)			
C_1	26.46	29.40	31.52
C_2	5.93	4.83	5.49
C_3	5.82	3.43	3.18
C_4	22.71	24.51	22.51
C_5	20.46	16.17	23.98
C_6+	18.63	21.66	13.31
C_4 distribution (wt%)			
isobutane	13.97	22.60	11.14
n-butane	3.03	3.64	2.77
1-butene	7.26	6.72	5.55
isobutylene	53.20	46.10	65.75
trans-2-butene	13.41	12.41	8.02
cis-2-butene	9.15	8.54	6.77
C_5 distribution (wt%)			
3-m-1-$C_4^=$	73.1	67.6	82.6
2-m C_4, 1-$C_5^=$, 2-m-1-$C_4^=$	8.5	12.3	4.8
n-C_5, *trans*-2-$C_5^=$, *cis*-2-$C_5^=$, 2-m-2-$C_4^=$	18.4	20.1	12.6
Oxygenate/HC (g/100 g)	2.1	2.3	1.9

TABLE 3.18. Comparison of activity and selectivity for vacancy theory isosynthesis at 673 K, 50 atm, 1/1 CO/H_2 [or $CO/(H_2+H_2S)$] ratio, and 90 second space time

Run	CO conv.	Hydrocarbon distribution (wt%)						C_4 distribution (wt%)					
	(%)	C_1	C_2	C_3	C_4	C_5+	O/HC[a]	*i*-C_4	*n*-C_4	1-$C_4^=$	*i*-$C_4^=$	*t*-2-$C_4^=$	*c*-2-$C_4^=$
PurZ	23.59	32.71	7.65	5.07	23.80	30.77	1.4	19.02	4.08	6.78	49.29	12.31	8.52
LiZ04	25.63	34.09	8.12	5.06	25.36	27.38	1.5	17.99	3.49	6.74	51.63	11.96	8.19
LiZ06	23.47	33.96	8.16	5.09	24.05	28.75	1.5	18.72	3.67	6.30	51.43	11.85	8.03
LiZ12	23.71	33.89	8.23	5.01	24.70	28.17	1.4	17.99	3.84	6.52	51.77	11.75	8.13
MgZ04	22.25	36.13	8.42	5.20	23.64	26.62	1.4	19.96	4.14	6.85	48.37	12.37	8.31
MgZ06	25.55	34.65	8.27	4.99	26.25	25.83	1.4	24.71	2.79	5.97	47.56	11.26	7.71
MgZ09	29.13	31.95	7.95	4.96	29.11	26.02	1.9	18.60	4.52	6.47	51.25	11.33	7.83
MgZ12	25.96	34.21	7.94	5.04	25.49	27.32	1.6	18.05	2.88	6.72	52.82	11.74	7.79
AlZ04	22.89	35.79	8.45	5.50	25.10	25.16	2.2	23.77	3.03	6.52	45.92	12.46	8.31
AlZ12	21.16	38.58	9.17	5.76	24.66	21.84	2.3	17.42	3.73	7.06	49.89	13.15	8.76
DyZ04	24.10	34.50	8.44	6.18	27.53	23.35	2.6	17.52	5.20	7.60	46.77	13.73	9.19
DyZ12	22.44	31.60	8.31	4.99	27.66	27.44	5.5	13.12	5.27	8.01	50.09	13.99	9.50

[a] Oxygenate produced/hydrocarbon produced (g/100 g)

TABLE 3.18. Continued

Run	CO conv. (%)	Hydrocarbon distribution (wt%)						C_4 distribution (wt%)					
		C_1	C_2	C_3	C_4	C_5+	O/HC[a]	*i*-C_4	*n*-C_4	1-$C_4^=$	*i*-$C_4^=$	*t*-2-$C_4^=$	*c*-2-$C_4^=$
TaZ04	4.55	40.53	16.70	10.89	11.62	20.26	0.0	9.40	0.00	13.78	27.87	29.27	19.68
TaZ24	1.10	46.79	29.37	13.79	3.62	6.43	0.0	24.28	0.00	9.71	18.82	33.52	13.67
YBCZ	33.64	51.77	5.53	3.38	17.78	21.53	0.6	31.52	4.65	6.64	36.04	12.93	8.22
YBCZS	44.85	73.54	3.21	2.36	9.52	11.37	0.0	54.92	4.24	2.55	30.97	4.23	3.09

[a] Oxygenate produced/hydrocarbon produced (g/100 g)

TABLE 3.19. Effect of temperature cycles and H_2S on activity and selectivity over 7% Ce-ZrO_2 at 673 K, 50 atm, and 1/1 CO/H_2 [or $CO/(H_2+H_2S)$] ratio

	Fresh		Cycled	Reheat	Reheat w/H_2S
Space time (sec)	60	90	90	60	60
CO conversion (%)	19.98	26.52	24.77	16.24	15.20
Hydrocarbon distribution (wt%)					
C_1	29.46	30.83	57.96	46.45	24.42
C_2's	8.29	7.48	8.04	15.24	6.43
C_3's	7.05	5.29	4.09	11.41	6.96
C_4's	29.00	29.38	18.40	12.54	17.35
C_5+'s	26.21	27.02	11.51	14.35	44.83
Oxy/HC	1.6	1.6	2.0	0.2	0.5
C_4 distribution (wt%)					
isobutane	13.28	23.35	35.05	11.41	13.24
n-butane	4.66	5.28	7.61	14.94	2.48
1-butene	7.31	6.77	5.33	9.31	8.54
isobutylene	51.66	42.89	35.71	33.24	48.70
trans-2-butene	13.62	12.83	9.40	18.51	16.15
cis-2-butene	9.48	8.88	6.90	12.60	10.90

TABLE 3.20. Variation of CO conversion with time on stream at 673 K, 60 atm, 1050/hr, and 2/1 CO/H_2 over ZrO_2 (ppt.)

Time on stream (hr)	2	11	14	17
CO conversion (%)	12.4	13.2	13.3	13.5

TABLE 3.21. Comparison of fixed bed and slurry reactors at 673 K and 1/1 CO/H_2 over ZrO_2 (ppt.)

	CO conversion (%)	wt% C_1	wt% C_2	wt% C_3	wt% C_4	wt% C_5+
Slurry (60 atm, 1050/hr)	13.0	13.6	15.4	16.5	38.8	15.7
Fixed bed (50 atm, 900/hr)	25.0	31.8	7.9	5.4	28.0	26.8

TABLE 3.22. Comparison of C_4 distribution in slurry and fixed bed reactors at 673 K and 1/1 CO/H_2 over ZrO_2 (ppt.)

weight %	isobutane	*n*-butane	1-butene	isobutylene	*trans*-2-butene	*cis*-2-butene
Slurry (60 atm, 1050/hr)	5.3	6.3	10.2	57.1	12.3	8.9
Fixed bed (50 atm, 900/hr)	14.5	3.4	6.1	58.7	10.2	7.1

TABLE 3.23. Comparison of hydrocarbon distribution at different CO/H_2 ratios in the slurry reactor at 679 K, 60 atm, and 400/hr over commercial zirconia

	CO conversion (%)	wt% C_1	wt% C_2	wt% C_3	wt% C_4	wt% C_5+
2/1 CO/H_2	10.0	28.9	11.8	16.3	22.4	20.6
3/2 CO/H_2	11.0	30.2	12.1	19.1	22.5	16.1
1/1 CO/H_2	11.0	31.8	11.6	28.5	14.0	14.0

TABLE 3.24. Comparison of C_4 distribution at different CO/H_2 ratios in the slurry reactor at 679 K, 60 atm, and 400/hr over commercial zirconia

weight %	isobutane	*n*-butane	1-butene	isobutylene	*trans*-2-butene	*cis*-2-butene
2/1 CO/H_2	7.2	5.6	11.4	59.8	9.0	7.1
3/2 CO/H_2	7.8	4.9	11.0	57.7	10.3	8.9
1/1 CO/H_2	6.7	5.1	13.6	62.8	11.0	8.0

TABLE 3.25. Product distributions for the slurry reactor at 673 K, 60 atm, and 1050/hr over ZrO_2 (ppt.)

	CO conversion (%)	wt% C_1	wt% C_2	wt% C_3	wt% C_4	wt% C_5+
2/1 CO/H_2	13.3	25.7	19.7	12.0	30.1	12.4
1/1 CO/H_2	13.0	13.6	15.4	16.5	38.8	15.7

TABLE 3.26. Rate constants and CO_2 adsorption equilibrium constants obtained from SimuSolv® at 673 K, 50 atm, and 1/1 CO/H_2 ratio

Catalyst	$k_p \times 10^6$ $\left(\frac{mol}{kg_{cat}\, atm^{1.5}\, sec}\right)$	K_{CO_2} (atm^{-1})	$\rho_b k_p \times 10^6$ $\left(\frac{mmol}{cm^3\, atm^{1.5}\, sec}\right)$	Rank	
				Model	Exp.
7% Ce-ZrO_2 (ppt., Al CO cyl.)	11.52	0.504	26.23	1	1
7% Ce-ZrO_2 (ppt., H_2S, Al CO cyl.)	10.97	0.503	25.45	2	2
1.6% Na-ZrO_2 (ppt.)	11.55	1.001	24.37	3	5
7% Ce-ZrO_2 (ppt., Iron CO cyl.)[a]	10.52 ± 0.79	0.596 ± 0.039	23.99	4	3
3.2% Ti, 2% Th -ZrO_2 (ppt.)	8.79	0.641	23.06	5	4
ZrO_2 (ppt.)	6.90	0.330	14.77	6	6
ZrO_2 (CAL.)	5.79	0.643	9.90	7	7
1.6% Na, 10.3% Ti -ZrO_2 (HT)	8.18	0.736	7.65	8	8
0.6% Na, 2% Ti, 2% Th -ZrO_2 (HT)	6.83	0.642	7.36	9	9

[a] Errors given in this case are representative of those obtained for other simulations.

TABLE 3.27. Rate constants and CO_2 adsorption equilibrium constants for other reaction conditions obtained from SimuSolv®

Catalyst	T(K)	P (atm)	CO/H_2 or $[CO/(H_2+H_2S)]$	$k_p \times 10^6$ $\left(\frac{mol}{kg_{cat}\, atm^{1.5}\, sec}\right)$	K_{CO_2} (atm^{-1})
7% Ce-ZrO_2 (ppt., H_2S, Al CO cyl.)	648	50	1/1	4.73	0.804
	698	50	1/1	14.85	0.350
	723	50	1/1	20.55	0.255
1.6% Na-ZrO_2 (ppt.)	673	95	2/1	11.55	0.601
7% Ce-ZrO_2 (ppt., Iron CO cyl.)	698	50	1/1	14.27	0.430
	723	50	1/1	15.38	0.235
ZrO_2 (ppt.)	673	95	2/1	6.12	0.202
	673	95	1/1	6.12	0.306
	673	95	1/3	6.12	0.459
1.6% Na, 10.3% Ti -ZrO_2 (HT)	648	50	1/1	4.55	1.001
	698	50	1/1	12.11	0.508
ZrO_2 (MSG)	723	70	1/1	5.88	0.331

TABLE 3.28. Activation energies and CO_2 heats of adsorption found using SimuSolv® rate parameters

Catalyst	E_a *(kcal/mol)*[a]	ΔH_{ads} CO_2 *(kcal/mol)*
7% Ce-ZrO_2 (ppt.) [H_2S, Al CO cyl.]	12.14 ± 0.50	14.22 ± 0.58
7% Ce-ZrO_2 (ppt.) [Iron CO cyl.]	7.39 ± 2.42	17.91 ± 3.48
1.6% Na, 10.3% Ti, ZrO_2 (HT)	17.64 ± 1.65	12.15 ± 0.92

[a] To convert to *kJ/mol* multiply by 4.184

TABLE 3.29. Gamma values at 673 K, 50 atm, and 1/1 CO/H_2 ratio

	7% Ce, ZrO_2 (ppt.)		1.6% Na, ZrO_2 (ppt.)		3.2% Ti, 2% Th, ZrO_2 (ppt.)	
i	$\gamma_i \times 10^3$	$\gamma_{ci} \times 10^3$	$\gamma_i \times 10^3$	$\gamma_{ci} \times 10^3$	$\gamma_i \times 10^3$	$\gamma_{ci} \times 10^3$
1	137.1 ± 1.4	274.2 ± 2.8	38.30 ± 0.87	76.60 ± 1.7	198.3 ± 3.4	396.6 ± 6.8
2	17.86 ± 1.0	71.44 ± 4.0	8.87 ± 0.25	35.48 ± 1.0	17.99 ± 1.0	71.96 ± 4.0
3	9.33 ± 0.72	55.98 ± 4.3	2.96 ± 0.06	17.76 ± 0.36	8.00 ± 0.46	48.00 ± 2.8
4	39.14 ± 0.38	313.1 ± 3.0	31.27 ± 0.59	250.2 ± 4.7	36.98 ± 1.3	296 ± 10
5+	28.54 ± 0.44	285.4 ± 4.4	62.00 ± 0.58	620.0 ± 5.8	18.77 ± 2.9	188 ± 29

TABLE 3.30. Parameters in the semi-empirical kinetic model

Catalyst	α	κ
ZrO_2 (H-0304)	0.333±0.043	3.80±0.08
ZrO_2 (MSG)	0.508±0.060	2.26±0.34
Li-ZrO_2 (MSG)	0.232	1.76
K-ZrO_2 (MSG)	0.464	3.98
Mg-ZrO_2 (MSG)	0.408	4.49
Ca-ZrO_2 (MSG)	0.480	5.17

TABLE 3.31. Kinetic parameters for the two catalysts used in slurry modeling

	Precipitated catalyst	Commercial catalyst
k_p, $\times 10^6$ mol/(kg_{cat} $atm^{1.5}$ s)	6.12	6.397
K_{CO2}, atm^{-1}	0.306	1.694

TABLE 3.32. Phase equilibrium constants used in the slurry modeling

	CH_4	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}
K_i values	4.0	3.0	2.2	1.5	1.15

TABLE 3.33. Slurry modeling results for the precipitated catalyst at 673 K, 60 atm, 1/1 CO/H_2 ratio, GHSV 1050 1/hr, liquid mass rate 0.08 g/sec, and W_{cat}=20 g

	CH_4	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}
γ_i used in the modeling	0.06167	0.03828	0.02743	0.05115	0.01497
weight percentage, %	13.86	15.05	16.17	40.20	14.71

TABLE 3.34. Slurry modeling results for the commercial catalyst at 679 K, 60 atm, 1/1 CO/H_2 ratio, GHSV 419 1/hr, liquid mass rate 0.04 g/sec, and W_{cat}=15.9 g

	CH_4	C_2H_4	C_3H_6	C_4H_8	C_5H_{10}
γ_i used in the modeling	0.1462	0.03095	0.04838	0.01852	0.01452
weight percentage, %	32.10	11.88	27.86	14.22	13.94

TABLE 3.35. Predicted synthesis conversions for precipitated and commercial catalyst

H_2/CO	Conversion, %			
	Precipitated catalyst		Commercial catalyst	
	CO	H_2	CO	H_2
1.0	12.30	6.91	13.53	8.74
1.5			12.11	11.74
2.0	10.41	11.69	11.16	14.43