

## APPENDIX B

CO HYDROGENATION ON RU/ZEOLITE CATALYSTS  
DECOMPOSED UNDER VACUUM

Table B-1 Catalytic Properties of RuHY for CO Hydrogenation

Temperature (K)	493	503	513	524	533	543	553	563
CO Conversion (%)	2.7	4.5	6.5	8.3	9.4	11.0	12.1	14.0
Activity ( $\mu\text{mol/h.g.cat.}$ )	5.4	9.1	12.9	16.6	18.8	21.9	24.2	27.9
TOF x 1000 (1/sec)	13.0	22.1	31.5	40.4	45.8	53.5	59.0	67.9
SELECTIVITY (wt%)								
C1	22.7	23.4	27.5	34.3	40.0	48.0	56.1	63.5
C2	11.0	10.9	12.0	13.7	14.7	16.0	16.7	16.6
C3	16.8	16.9	18.0	19.1	18.6	17.2	14.8	11.7
C4	21.6	20.8	19.8	17.1	14.3	11.4	8.2	5.6
C5	19.6	18.8	16.5	12.2	9.3	6.1	3.6	2.3
C6+	8.3	9.2	6.3	3.5	3.1	1.3	0.5	0.3
% C4 in C4-fraction								
Isobutane	55.2	58.2	57.4	53.0	47.9	40.1	33.4	26.8
N-Butane	9.7	10.3	12.7	17.1	21.7	28.2	35.6	42.4
1-Butene	14.1	9.7	8.7	8.7	9.8	10.9	12.7	14.0
Trans-2-Butene	13.7	13.7	13.1	13.0	12.7	12.6	11.6	10.5
Cis-2-Butene	7.4	8.1	8.1	8.1	7.8	8.2	6.8	6.3
Propylene/Propane Ratio	2.9	2.3	1.6	1.1	0.8	0.6	0.4	0.3
Cis/Trans Ratio	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.6

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.

Table B-2 Catalytic Properties of RuLiY for CO Hydrogenation

Temperature (K)	493	503	512	523	533	543	553	563
CO Conversion (%)	1.1	1.8	2.5	3.4	4.5	5.5	6.7	8.3
Activity ( $\mu\text{mol/h.g.cat.}$ )	2.2	3.5	4.9	6.9	9.1	10.9	13.3	16.6
TOF x 1000 (1/sec)	3.4	5.5	7.7	10.7	14.2	17.1	20.8	25.9
SELECTIVITY (wt%)								
C1	28.2	28.0	28.3	33.4	38.3	44.6	51.6	58.6
C2	12.9	13.0	13.0	14.3	15.1	15.9	16.4	16.5
C3	22.2	21.5	21.3	21.8	21.1	20.0	17.8	14.6
C4	19.4	19.5	20.0	17.6	15.1	12.3	9.6	6.9
C5	12.7	14.8	13.4	11.8	9.2	6.3	4.0	2.9
C6+	4.6	3.1	4.1	1.1	1.2	0.8	0.6	0.4
% C4 in C4-Fraction								
Isobutane	20.5	26.1	28.3	27.3	23.5	18.6	13.6	10.7
N-Butane	12.1	11.5	12.8	13.2	16.9	21.4	27.5	32.9
1-Butene	27.3	24.9	23.5	22.2	22.1	22.4	23.3	22.1
Trans-2-Butene	26.1	23.3	22.3	23.0	23.1	22.9	22.1	20.4
Cis-2-Butene	14.0	14.1	13.1	14.3	14.5	14.7	13.4	13.9
Propylene/Propane Ratio								
	4.2	4.0	3.8	2.8	2.0	1.5	1.1	0.8
Cis/Trans Ratio								
	0.5	0.6	0.6	0.6	0.6	0.6	0.6	0.7

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.

Table B-3 Catalytic Properties of RuNaY for CO Hydrogenation

Temperature (K)	493	503	513	523	533	543	548	565
CO Conversion (%)	1.3	1.6	2.2	3.1	4.0	5.0	6.6	48.4
Activity ( $\mu\text{mol/h.g.cat.}$ )	2.6	3.1	4.4	6.2	8.0	9.9	13.2	96.7
TOF x 1000 (1/sec)	2.8	3.5	4.8	6.8	8.8	10.9	14.5	106.6
SELECTIVITY (wt%)								
C1	28.8	27.0	29.0	32.7	38.4	45.3	51.6	97.2
C2	12.9	12.4	13.2	14.0	14.8	15.5	16.9	1.7
C3	23.4	21.5	21.6	21.5	20.6	19.6	17.5	0.8
C4	18.9	20.1	19.4	17.1	14.3	11.8	8.8	0.2
C5	13.7	14.3	13.8	10.9	8.5	6.0	4.2	.0
C6+	2.2	4.7	3.0	3.9	3.5	1.8	1.0	.0
% C4 in C4-Fraction								
Isobutane	17.5	19.5	21.9	20.2	16.2	13.6	9.5	6.9
N-Butane	15.6	8.6	8.6	10.2	12.9	17.1	35.4	52.7
1-Butene	28.1	29.7	27.2	27.0	27.0	26.7	22.7	17.6
Trans-2-Butene	24.8	27.2	26.2	26.4	26.6	26.2	19.8	13.7
Cis-2-Butene	13.9	15.0	16.1	16.3	17.2	16.3	12.7	9.2
Propylene/Propane Ratio	3.1	6.1	5.5	4.2	3.0	2.1	0.8	0.3
Cis/Trans Ratio	0.6	0.6	0.6	0.6	0.6	0.6	0.6	0.7

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.

Table B-4 Catalytic Properties of RuKY for CO Hydrogenation

Temperature (K)	493	503	513	523	533	543	553	563
CO Conversion (%)	0.5	0.9	1.6	2.3	3.4	4.5	5.9	7.7
Activity ( $\mu\text{mol/h.g.cat.}$ )	0.9	1.9	3.3	4.6	6.7	9.0	11.8	15.4
TOF x 1000 (1/sec)	1.6	3.2	5.6	7.9	11.6	15.4	20.2	26.4
SELECTIVITY (wt%)								
C1	32.2	29.8	28.8	30.7	31.8	35.3	39.7	46.8
C2	10.7	12.8	13.0	13.7	14.0	14.5	15.2	15.5
C3	26.8	26.8	23.9	23.5	22.0	21.5	20.7	18.8
C4	16.9	16.0	16.3	15.8	15.1	14.0	12.5	10.3
C5	9.3	8.9	11.5	11.0	10.5	9.2	7.9	6.2
C6+	4.1	5.8	6.5	5.2	6.8	5.6	4.1	2.3
% C4 in C4-Fraction								
Isobutane	1.0	0.5	0.9	1.7	2.2	2.2	2.0	1.6
N-Butane	17.0	14.4	12.0	11.5	11.8	13.1	15.2	20.5
1-Butene	14.0	17.6	20.4	24.2	26.4	26.9	26.0	24.1
Trans-2-Butene	44.0	44.4	41.4	38.6	36.9	35.3	34.7	32.6
Cis-2-Butene	24.0	23.0	25.2	24.0	22.6	22.5	22.2	21.2
Propylene/Propane Ratio								
	6.0	7.7	7.3	6.4	5.4	4.3	3.1	2.1
Cis/Trans Ratio								
	0.5	0.5	0.6	0.6	0.6	0.6	0.6	0.6

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.

Table B-5 Catalytic Properties of RuRbY for C0 Hydrogenation

Temperature (K)	493	502	513	523	534	544	553	568
C0 Conversion (%)	1.0	1.8	3.0	4.4	6.8	9.1	10.6	62.9
Activity ( $\mu\text{mol/h.g.cat.}$ )	2.0	3.5	5.9	8.8	13.5	18.2	21.1	125.5
TOF x 1000 (1/sec)	3.2	5.6	9.5	14.0	21.6	29.0	33.6	200.4
SELECTIVITY (wt%)								
C1	28.4	30.3	32.4	33.6	40.7	46.5	54.4	99.2
C2	12.1	13.7	14.2	14.4	15.0	15.2	15.4	0.7
C3	24.0	24.1	22.7	22.0	20.7	18.6	16.1	0.1
C4	16.3	15.7	15.1	15.3	12.4	10.4	8.3	0
C5	11.7	11.6	9.5	9.7	7.5	6.2	4.2	0.0
C6+	7.5	4.5	6.1	5.1	3.8	3.2	1.6	0.0
Z C4 in C4-Fraction								
Isobutane	0.5	0.6	1.1	1.0	0.9	1.0	1.0	0.0
N-Butane	14.2	12.1	11.0	11.3	15.8	20.4	25.1	35.0
1-Butene	18.6	21.6	25.8	27.0	26.0	24.6	23.9	35.0
Trans-2-Butene	39.7	40.5	38.3	36.4	35.0	32.3	29.9	20.0
Cis-2-Butene	27.0	25.3	23.8	24.4	22.3	21.6	20.1	10.0
Propylene/Propane Ratio	6.4	7.5	6.5	5.7	3.2	2.2	1.6	0.8
Cis/Trans Ratio	0.7	0.6	0.6	0.7	0.6	0.7	0.7	0.5

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.

Table B-6 Catalytic Properties of RuCSY for CO Hydrogenation

Temperature (K)	493	503	513	523	531	541	553	568
CO Conversion (%)	1.0	1.9	3.1	4.5	6.8	8.8	11.4	17.1
Activity ( $\mu\text{mol/h.g.cat.}$ )	2.0	3.9	6.1	9.1	13.5	17.7	22.7	34.2
TOF x 1000 (1/sec)	2.7	5.3	8.3	12.4	18.4	24.0	30.9	46.6
SELECTIVITY (wt%)								
C1	30.3	29.5	32.0	36.1	41.2	49.4	60.5	76.5
C2	12.1	12.5	12.7	13.2	13.4	13.8	13.9	12.5
C3	25.8	22.7	22.2	21.6	19.7	17.6	13.5	6.9
C4	18.0	17.8	17.1	15.1	12.8	10.2	6.9	2.7
C5	10.2	12.3	11.5	9.8	8.1	6.0	3.5	1.2
C6+	3.7	5.3	4.5	4.2	4.8	3.0	1.5	0.1
% C4 in C4-Fraction								
Isobutane	0.4	0.7	1.1	1.2	1.0	1.0	0.9	1.9
N-Butane	12.9	11.2	10.2	10.4	13.0	17.7	25.0	36.1
1-Butene	18.2	24.9	26.8	28.1	26.8	26.1	24.3	24.6
Trans-2-Butene	41.8	38.4	37.8	37.1	35.9	33.3	29.9	22.6
Cis-2-Butene	26.7	24.9	24.2	23.3	23.2	21.9	19.9	14.9
Propylene/Propane Ratio	7.1	7.8	7.6	6.1	4.1	2.7	1.6	0.8
Cis/Trans Ratio	0.6	0.6	0.6	0.6	0.6	0.7	0.7	0.7

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.

Table B-7 Catalytic Properties of Ru/SiO<sub>2</sub> for CO Hydrogenation

Temperature (K)	488	503	513	522	533	543
CO Conversion (%)	0.25	0.61	0.87	1.53	2.18	3.67
Activity ( $\mu\text{mol/h.g.cat.}$ )	0.5	1.2	1.7	3.1	4.4	7.3
TOF x 1000 (1/sec)	1.43	3.52	5.01	8.86	12.60	21.19
SELECTIVITY (wt%)						
C1	37.1	41.8	47.9	52.9	67.0	75.0
C2	29.4	19.0	17.9	15.4	16.2	14.2
C3	18.6	16.8	14.7	12.4	10.2	7.0
C4	14.9	12.1	11.8	7.6	5.6	3.3
C5	0.0	8.5	5.0	6.1	1.1	0.5
C6+	0.0	1.8	2.8	6.2	0.0	0.0
2 C4 in C4-Fraction						
Isobutene	0.0	0.0	0.0	0.0	0.0	0.0
N-Butane	13.0	25.0	24.2	33.6	40.8	48.4
1-Butene	39.1	26.1	20.3	19.9	19.7	17.0
Trans-2-Butene	19.6	26.1	35.2	24.7	23.0	22.9
Cis-2-Butene	28.3	22.8	20.3	21.9	16.4	11.8
Propylene/Propane Ratio	4.5	1.9	1.3	0.8	0.4	0.2
Cis/Trans Ratio	1.4	0.9	0.6	0.9	0.7	0.5

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Reaction Time = 5 min.



Table B-8 Catalytic Properties of RuNaX for CO Hydrogenation

Temperature (K)	493	513	523	533	543	553	563
CO Conversion (%)	0.1	0.7	1.7	2.7	3.6	5.1	6.2
Activity ( $\mu\text{mol/h}\cdot\text{g}\cdot\text{cat.}$ )	0.3	1.4	3.3	5.5	7.3	10.3	12.4
TOF $\times 1000$ (1/sec)	0.5	2.5	5.8	9.6	12.8	18.0	21.9
SELECTIVITY (wt%)							
C1	31.5	20.1	17.3	18.4	21.7	27.2	33.9
C2	8.0	10.1	11.7	12.9	13.9	14.7	15.3
C3	25.0	26.6	24.9	25.0	25.1	25.3	24.6
C4	22.0	20.2	19.4	18.3	17.5	16.2	14.3
C5	13.4	14.3	15.1	14.6	12.8	10.1	7.1
C6+	0.0	8.7	11.6	10.9	9.0	6.4	4.7
% C4 in C4-Fraction							
Isobutane	0.0	0.0	0.0	0.0	0.1	0.1	0.2
N-Butane	27.0	12.2	8.2	6.7	6.3	6.3	7.8
1-Butene	18.9	19.9	20.9	22.9	23.4	24.4	24.3
Trans-2-Butene	32.4	39.2	40.5	40.8	40.7	39.6	39.4
Cis-2-Butene	21.6	28.7	30.3	29.6	29.5	29.6	28.4
Propylene/Propane Ratio							
	1.9	7.9	13.6	17.7	16.1	11.7	8.8
Cis/Trans Ratio							
	0.7	0.7	0.7	0.7	0.7	0.7	0.7

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.

Table 8-9 Catalytic Properties of RuKL for CO Hydrogenation

Temperature (K)	493	503	513	523	533	543	553	563
CO Conversion (%)	0.3	0.6	0.8	1.6	2.5	3.8	5.5	9.0
Activity ( $\mu\text{mol/h.g.cat.}$ )	0.7	1.2	1.6	3.2	5.0	7.6	10.9	18.0
TOF $\times 1000$ (1/sec)	1.7	3.1	4.2	8.4	13.2	19.8	28.7	47.3
SELECTIVITY (wt%)								
C1	31.3	33.5	48.8	49.4	55.4	66.0	73.7	84.4
C2	11.2	10.7	14.0	12.3	12.4	13.0	12.3	9.1
C3	21.7	19.9	8.3	17.8	14.9	11.7	7.8	4.0
C4	19.7	15.6	16.4	11.7	9.4	6.6	3.9	1.6
C5	9.8	13.9	8.7	6.1	5.8	2.2	2.0	0.6
C6+	6.3	6.4	3.7	2.6	2.0	0.5	0.3	0.3
Z C4 in C4-Fraction								
Isobutane	11.3	12.0	11.5	12.3	11.8	9.1	8.6	7.0
N-Butane	13.8	12.0	11.5	13.1	15.9	17.8	29.2	35.5
1-Butene	12.5	13.7	14.5	16.5	19.3	18.3	24.7	23.0
Trans-2-Butene	41.3	40.2	38.8	36.0	32.1	22.5	22.8	16.5
Cis-2-Butene	21.3	22.2	23.6	22.0	20.9	14.1	14.6	10.5
Propylene/Propane Ratio								
	6.4	6.7	1.5	3.8	2.4	1.4	0.8	0.5
Cis/Trans Ratio								
	0.5	0.6	0.6	0.6	0.7	0.6	0.6	0.6

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.

Table B-10 Catalytic Properties of RuNaM for CO Hydrogenation

Temperature (K)	493	503	513	523	533	543	553	563
CO Conversion (%)	0.2	0.3	0.6	1.1	1.8	2.8	4.3	6.5
Activity ( $\mu\text{mol/h.g.cat.}$ )	0.3	0.7	1.2	2.3	3.6	5.7	8.6	13.0
TOF $\times 1000$ (1/sec)	1.2	2.4	4.4	8.2	12.9	20.2	30.5	46.2
SELECTIVITY (wt%)								
C1	35.2	46.8	51.5	55.1	62.8	70.0	75.1	81.2
C2	13.5	14.4	16.3	16.4	16.4	15.6	14.5	12.3
C3	15.5	13.8	13.6	12.1	10.8	8.7	6.7	4.2
C4	15.9	9.9	6.7	6.1	4.6	3.2	2.1	1.3
C5	19.9	13.6	10.3	6.9	4.8	2.2	1.5	0.7
C6+	0.0	1.4	1.6	3.3	0.6	0.3	0.1	0.3
% C4 in C4-Fraction								
Isobutane	24.2	26.2	28.8	27.3	25.0	24.8	27.2	29.5
N-Butane	27.3	31.0	40.4	42.0	51.0	53.1	49.1	53.3
1-Butene	12.1	16.7	3.8	5.7	3.8	4.4	6.1	4.8
Trans-2-Butene	21.2	16.7	17.3	15.9	13.5	10.6	10.5	6.7
Cis-2-Butene	15.2	9.5	9.6	9.1	6.7	7.1	7.0	5.7
Propylene/Propane Ratio								
	0.7	0.6	0.5	0.5	0.4	0.3	0.2	0.2
Cis/Trans Ratio								
	0.7	0.6	0.6	0.6	0.5	0.7	0.7	0.9

Reaction Conditions: 1 atm, CO/H<sub>2</sub> = 1, Reactants Flow Rate = 2.4 l/hr,  
Catalyst Charge = 0.250 g, Reaction Time = 5 min.