Supplementary Information

Vapor phase coupling of n-butanol over the mixed catalyst system PdZn/SiO_2+TiO_2

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Table S1: Conversions and product selectivities from n-butanol coupling reactions over mixtures of TiO_2 and $PdZn/SiO_2$

TiO2:PdZn/SiO2	0.5			1			2		
Contact Time (min)	2.3	4.7	9.4	2.3	4.7	9.4	2.3	4.7	9.4
Conversion (%)	51 ± 3	64 ± 3	76 ± 4	48 ± 2	64 ± 3	82 ± 4	41 ± 2	66 ± 3	81 ± 4
Selectivity (%)									
Butanal	60 ± 6	33 ± 3	19 ± 2	52 ± 5	33 ± 3	14 ± 1	54 ± 5	24 ± 2	13 ± 1
C8 Oxygenates	30 ± 3	48 ± 5	52 ± 5	37 ± 4	50 ± 5	57 ± 6	37 ± 4	57 ± 6	59 ± 6
C7 Hydrocarbons	1 ± 0.2	3 ± 0.5	5 ± 0.8	2 ± 0.3	2 ± 0.3	3 ± 0.5	1 ± 0.2	2 ± 0.3	3 ± 0.5
C8 Hydrocarbons	3 ± 0.5	6 ± 0.9	9 ± 1.4	5 ± 0.8	6 ± 0.9	11 ± 1.7	3 ± 0.5	7 ± 1.1	11 ± 1.7
C12 Hydrocarbons	2 ± 0.3	3 ± 0.5	8 ± 1.2	2 ± 0.3	4 ± 0.6	11 ± 1.7	2 ± 0.3	6 ± 0.9	11 ± 1.7
Dehydration	1 ± 0.2	2 ± 0.3	2 ± 0.3	1 ± 0.2	1 ± 0.2	1 ± 0.2	1 ± 0.2	1 ± 0.2	2 ± 0.3
Others	3 ± 0.5	5 ± 0.8	5 ± 0.8	1 ± 0.2	3 ± 0.5	3 ± 0.5	2 ± 0.3	3 ± 0.5	1 ± 0.2

Table S2: Summary of reactions performed using individual catalysts and different feeds

Catalyst	**Reactant**	**Conversion (%)**	**Products (Selectivity)**
TiO_2	n-Butanol	0.5	Butenes
TiO_2	Butanal	53	2-Ethylhexenal
TiO_2	80% n-Butanol/20% Butanal	10*	2-Ethylhexenal (55%) 2-Ethylhexanal (25%) 2-Ethylhexanol (20%)
$PdZn/SiO_2$	2-Ethylhexanol	60	2-Ethylhexanal (97%) C_7 Hydrocarbons (1%) C_8 Hydrocarbons (2%)
TiO_2	2-Ethylhexanol	20	C_8 Olefins
K-TiO_2	n-Butanol	0.3	Butenes
W-TiO_2	n-Butanol	2	Butenes

* Total conversion of C_4 oxygenates in feed

Table S3: Approach to equilibrium for n-butanol dehydrogenation during coupling reactions with mixed catalysts beds

Catalyst Mixture	Contact Time (min)	Approach to Equilibrium (η)
$0.5TiO_2$:PdZn/SiO_2	2.3	1.0
	4.7	1.0
	9.4	1.0
$1.0TiO_2$:PdZn/SiO_2	2.3	0.8
	4.7	1.0
	9.4	1.0
$2.0TiO_2$:PdZn/SiO_2	2.3	0.6
	4.7	0.8
	9.4	0.9
2.0K-TiO_2:PdZn/SiO_2	4.7	1.0
2.0W-TiO_2:PdZn/SiO_2	9.4	0.7

$$\eta = \frac{1}{K_{Dehydrogenation}} * \frac{P_{Butanal} P_{H_2}}{P_{Butanol}}$$

Where η is the approach to equilibrium, $K_{Dehydrogenation}$ is the equilibrium constant for butanol dehydrogenation, and $P_{Butanal}$, P_{H2}, and $P_{Butanol}$ are the partial pressures of butanal, hydrogen, and butanol, respectively. An η = 1.0 indicates the dehydrogenation reaction is at equilibrium. The equilibrium constant was calculated from data available in:

D.R. Stull, E.F. Westrum, G.C. Sinke, "The Chemical Thermodynamics of Organic Compounds," John Wiley and Sons, Inc. New York, 1969

Table S4: Summary of K-TiO_2 catalysts synthesized by the modified liquid phase grafting procedure

Potassium Salt	Solvent	Salt Concentration (mol/L)	Potassium Loading (wt%)
N/A	Water	N/A	0.02
KOH	Water	0.05	1.22
KOH	Water	0.1	1.54
KOH	Water	0.25	2.12
KOH	Water	0.5	3.10
KOH	Water	1.0	5.54
KOH	Water	1.5	7.85
KOH	Water	2.0	10.34
K_2CO_3	Water	0.01	0.14
K_2CO_3	Water	0.05	0.50
K_2CO_3	Water	0.1	0.61
KCH_3CO_2	Ethanol	0.01	0.34
KCH_3CO_2	Ethanol	0.05	0.78
KCH_3CO_2	Ethanol	0.1	1.03

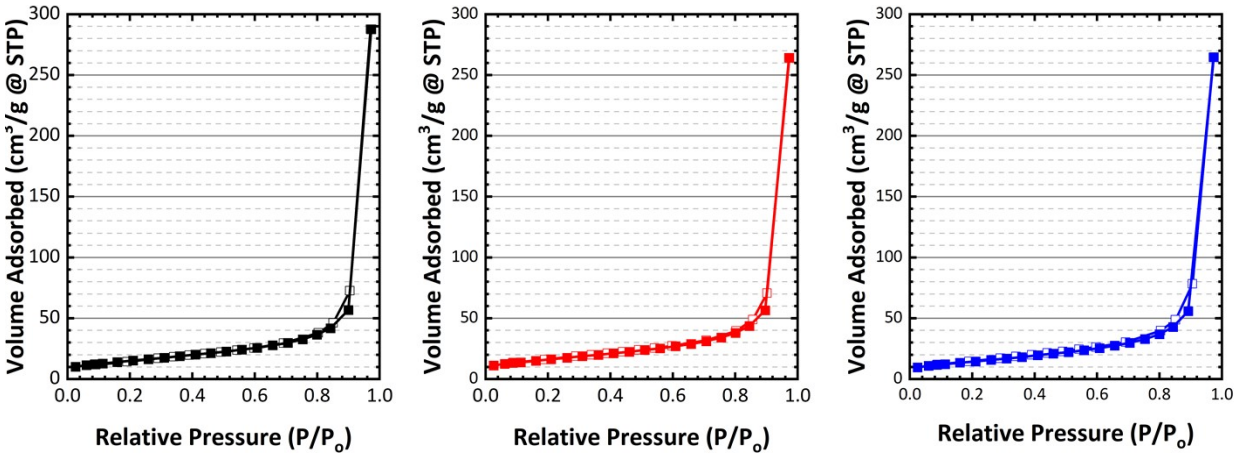

Figure S1: N_2 adsorption (solid symbols) and desorption (open symbols) isotherms collected at 77K. Left panel – TiO_2, center panel – K-TiO_2, and right panel – W-TiO_2.

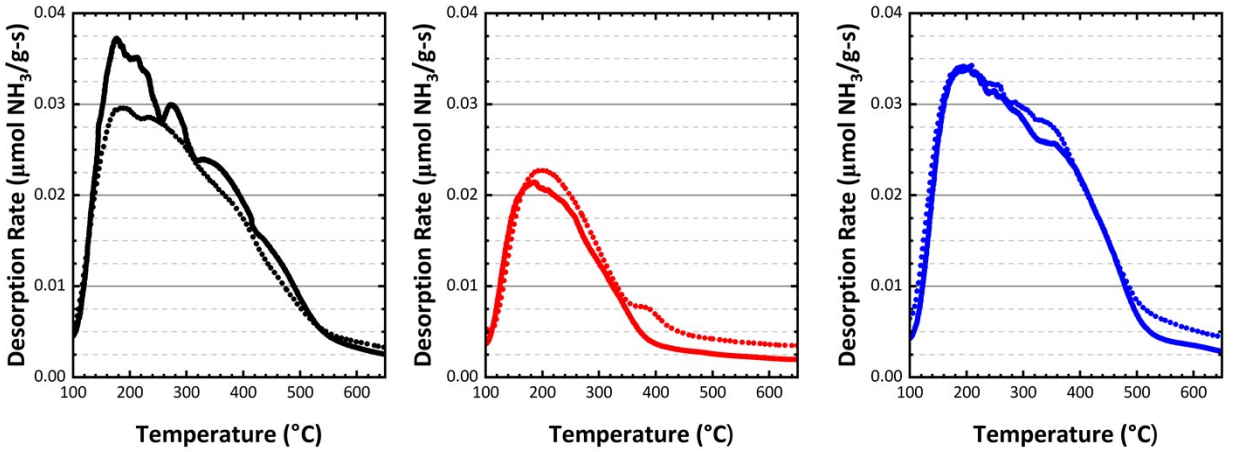

Figure S2: Normalized NH_3 desorption profile measured during temperature programmed desorption of ammonia. Left panel – TiO_2, center panel – K-TiO_2, and right panel – W-TiO_2. Solid profiles – He pretreatment and Dashed profiles – 10% H_2/Ar pretreatment

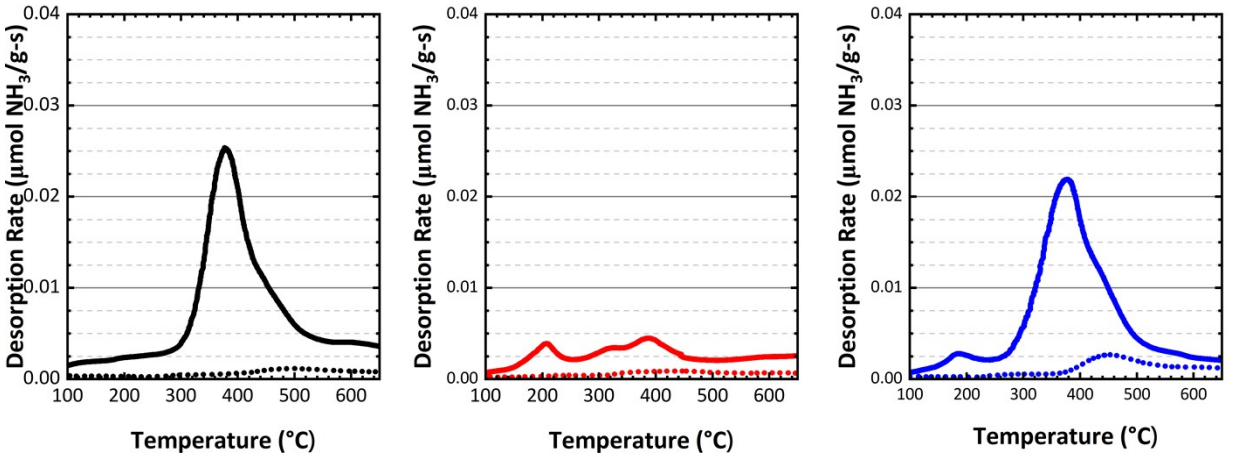

Figure S3: Normalized NH_3 desorption profile measured during temperature programmed desorption of propylamine. Left panel – TiO_2, center panel – K-TiO_2, and right panel – W-TiO_2. Solid profiles – He pretreatment and Dashed profiles – 10% H_2/Ar pretreatment

Table S5: Conversions and product selectivities from n-butanol coupling reactions over mixtures of modified TiO_2 and $PdZn/SiO_2$

Catalyst	K-TiO_2 + $PdZn/SiO_2$	W-TiO_2 + $PdZn/SiO_2$
Contact Time (min)	9.4	4.7
Conversion (%)	66 ± 3	60 ± 3
Coupling Yield (%)	39	36
Selectivity (%)		
Butanal	35 ± 4	28 ± 3
C8 Oxygenates	48 ± 5	39 ± 4
C7 Hydrocarbons	2 ± 0.3	1 ± 0.2
C8 Hydrocarbons	6 ± 0.9	16 ± 2
C12 Hydrocarbons	3 ± 0.5	4 ± 0.6
Dehydration	1 ± 0.2	9 ± 1.4
Others	4 ± 0.6	2 ± 0.3