

**Effect of Alkali Metal Addition on Catalytic Performance of Ag/ZrO₂/SBA-16 Catalyst for
Single-Step Conversion of Ethanol to Butadiene**

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Reactivity

Table S1. Reactivity performance for ethanol conversion over 4Ag-4ZrO₂/SBA-16 at varied ethanol WHSV (hr⁻¹).

WHSV (hr ⁻¹)	Conversion (%)	Selectivity									Butadiene Productivity (hr ⁻¹)
		Ethylene	DEE	Acetaldehyde	Propylene	Butenes	Butadiene	Pentenes	C2-C5 Alkanes	Other Oxygenates	
0.23	96.3	9.1	7.0	0.4	2.9	14.6	62.4	1.0	0.8	0.9	0.08
0.45	95.3	8.2	4.0	4.7	2.1	9.4	66.7	1.0	0.5	3.0	0.17
0.68	94.9	4.5	2.4	4.7	1.9	9.9	70.9	1.3	0.4	3.6	0.27
1.01	89.4	8.4	3.7	7.4	1.7	7.4	67.4	0.4	0.3	3.0	0.40
1.99	42.9	8.1	8.7	11.0	1.1	4.1	60.8	0.4	0.4	5.6	0.34
3.97	34.2	8.2	22.0	26.6	0.7	1.7	34.4	0.3	1.4	4.4	0.30
7.94	20.6	12.3	18.9	40.4	1.4	1.0	19.6	0.4	2.5	2.8	0.20

Catalyst 4Ag/4ZrO₂/SBA-16. T = 325°C, P = 1 atmosphere, P_{Ethanol} = 24.3% ethanol/balance N₂. TOS = 6 hr. Other oxygenates: ethyl acetate, butanol, acetone, crotonaldehyde, crotyl alcohol. Butadiene productivity reported as g butadiene/g ethanol hr⁻¹.

XRD

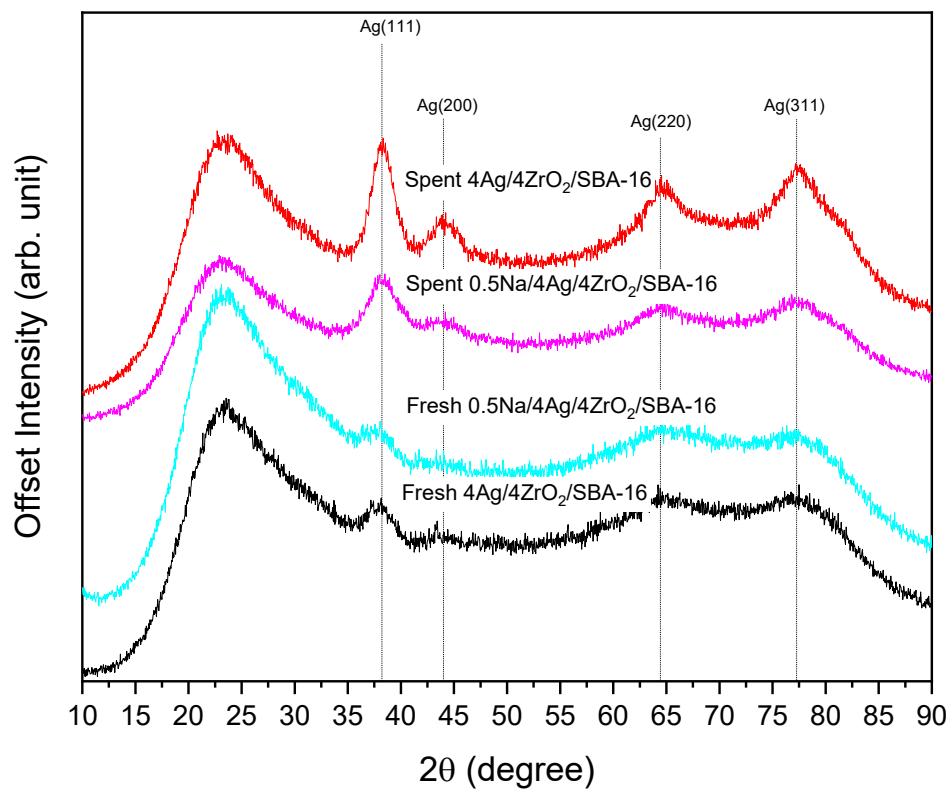


Figure S1. XRD diffractograms of fresh catalysts after reduction in 5% H₂/N₂ balance at 325°C and spent 72hr lifetime test catalysts for 4Ag/4ZrO₂/SBA-16 (Baseline) and the Na doped Baseline.

TEM

TEM Images of 4Ag/4ZrO₂/SBA-16 Baseline Catalyst post reduction in 5% H₂/N₂ at 325°C

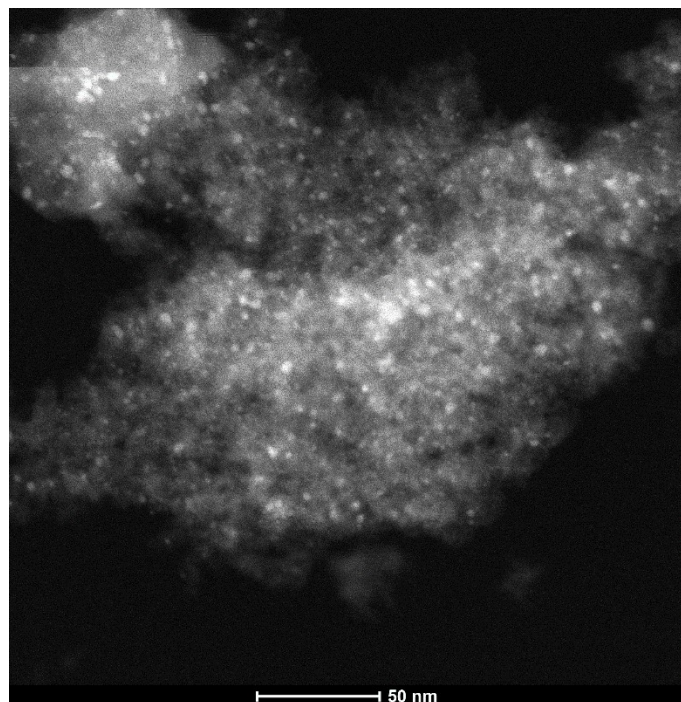


Figure S2. TEM Image of 4Ag/4ZrO₂/SBA-16 Baseline Catalyst.

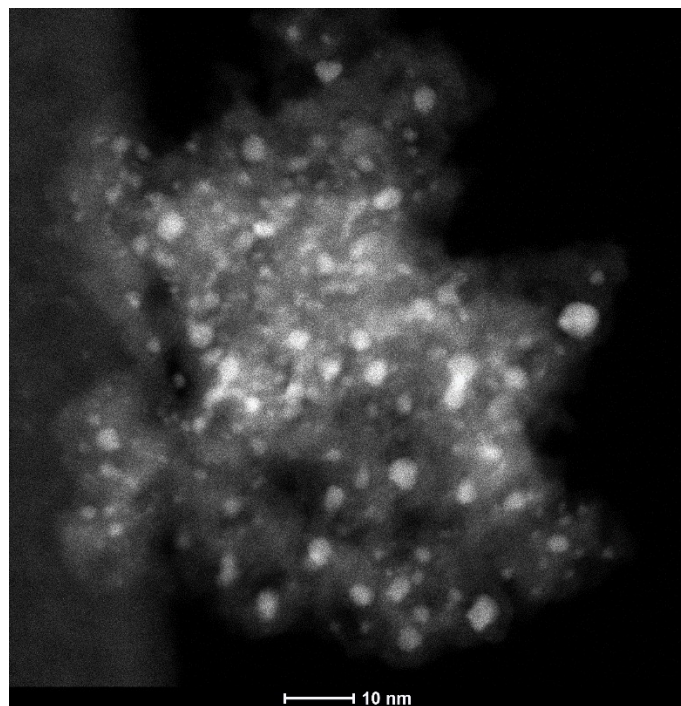


Figure S3. TEM Image of 4Ag/4ZrO₂/SBA-16 Baseline Catalyst.

TEM Images of 0.5K/4Ag/4ZrO₂/SBA-16 Catalyst post reduction in 5% H₂/N₂ at 325°C

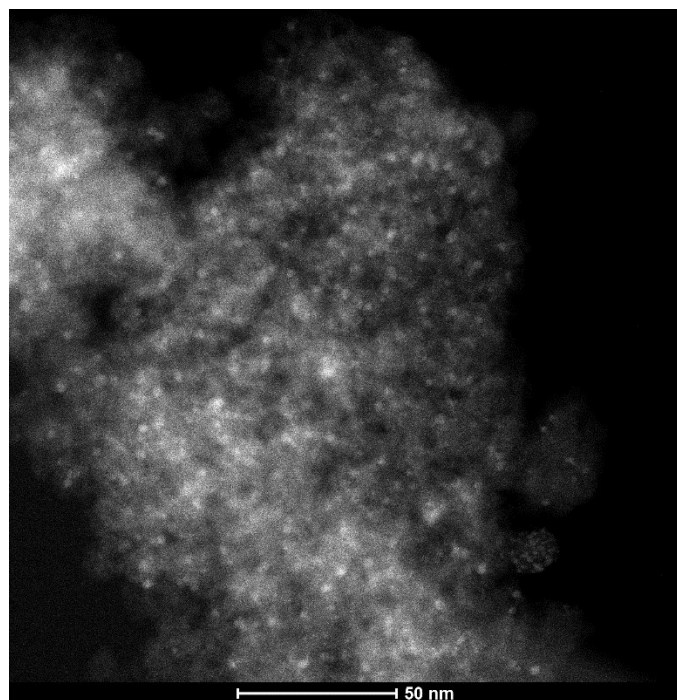


Figure S4. TEM Image of 0.5K/4Ag/4ZrO₂/SBA-16 Catalyst

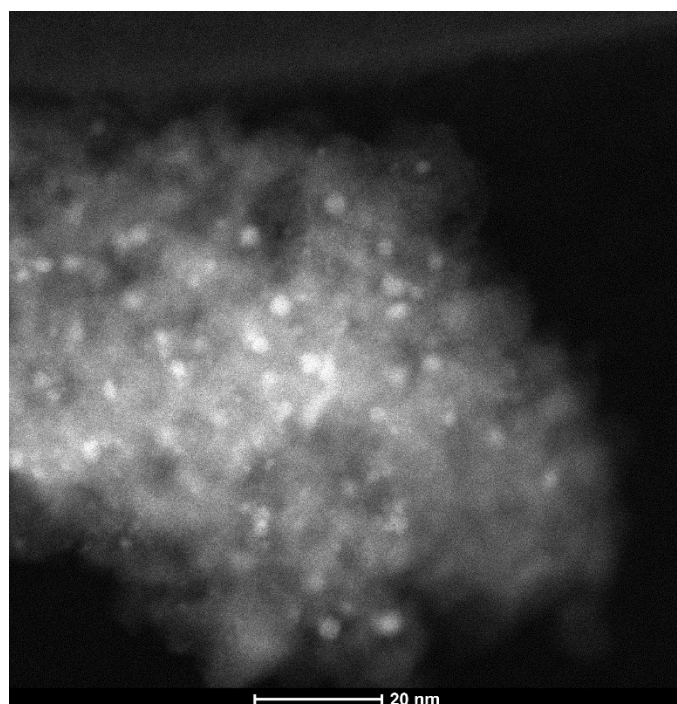


Figure S5. TEM Image of 0.5K/4Ag/4ZrO₂/SBA-16 Catalyst

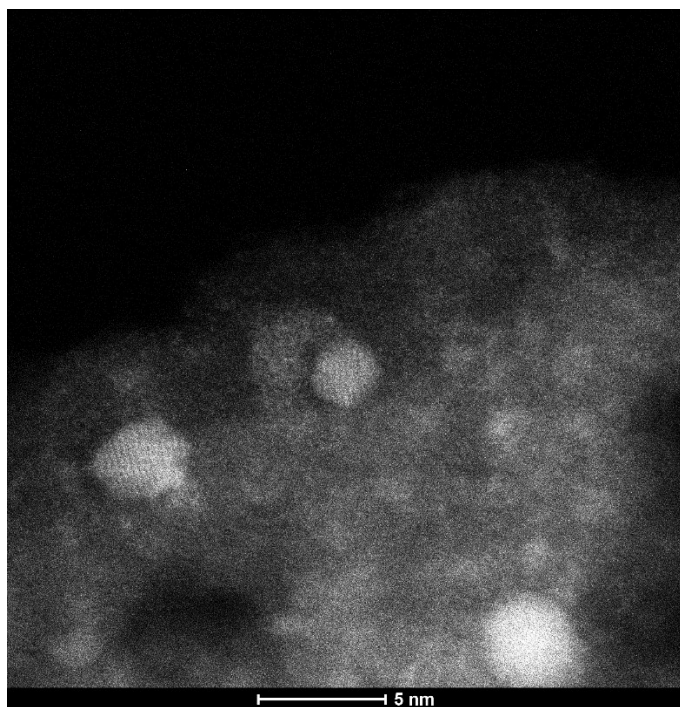


Figure S6. TEM Image of 0.5K/4Ag/4ZrO₂/SBA-16 Catalyst

TEM Images of 0.5Na/4Ag/4ZrO₂/SBA-16 Catalyst post reduction in 5% H₂/N₂ at 325°C

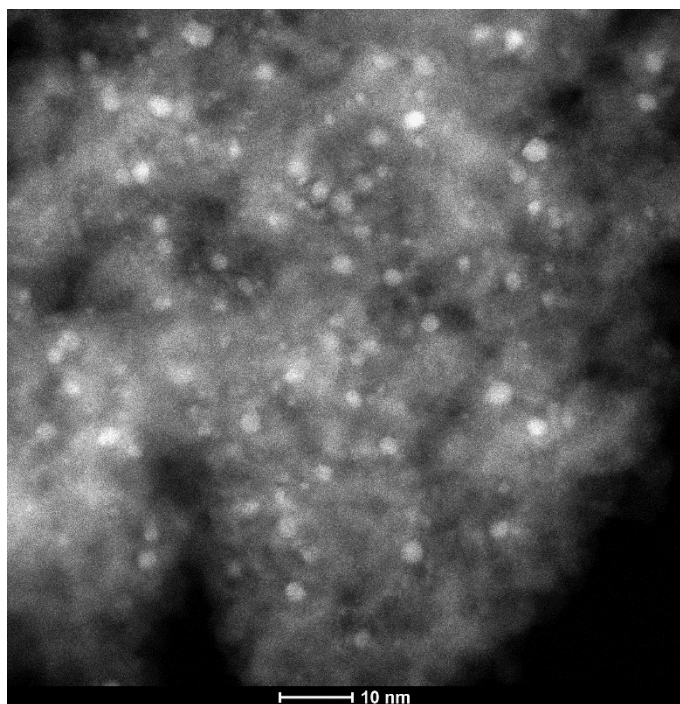


Figure S7. TEM Image of 0.5Na/4Ag/4ZrO₂/SBA-16.

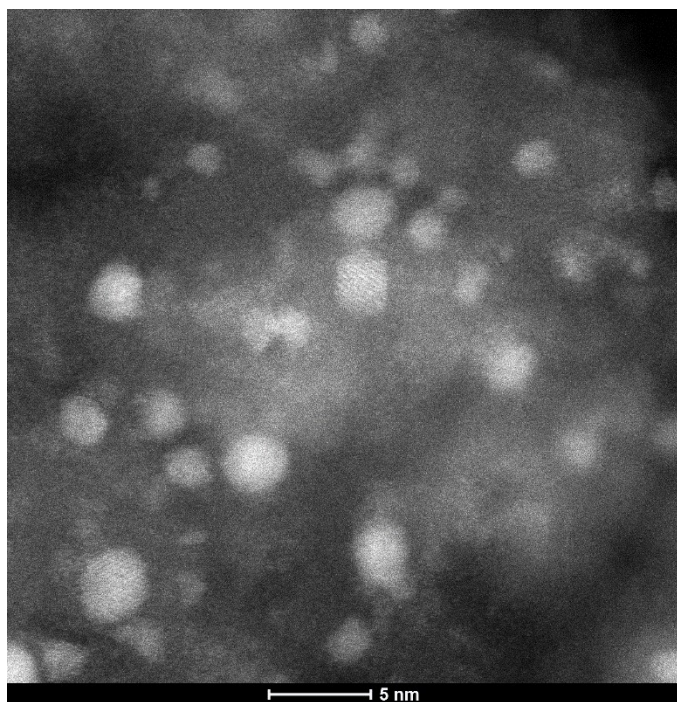


Figure S8. TEM Image of 0.5Na/4Ag/4ZrO₂/SBA-16.

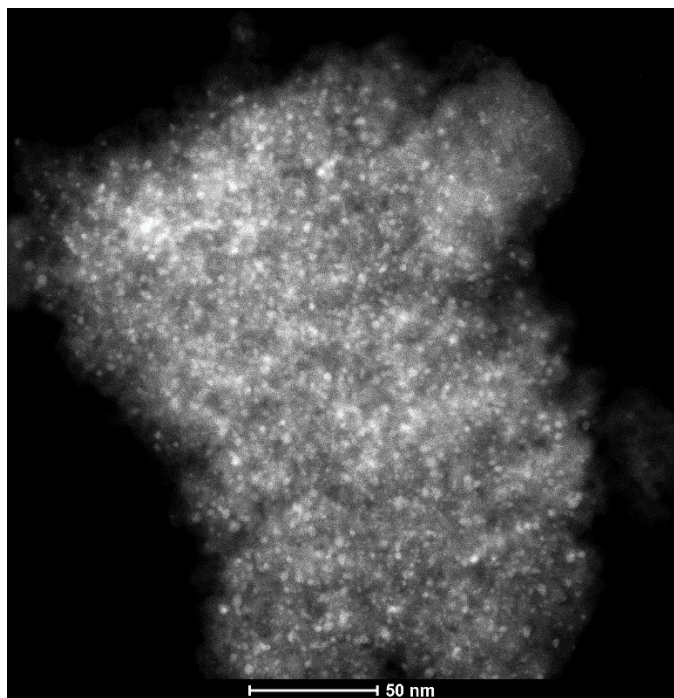


Figure S9. TEM Image of 0.5Na/4Ag/4ZrO₂/SBA-16.

TEM Images of Spent 4Ag/4ZrO₂/SBA-16 after 72h lifetime study presented in Figure 4

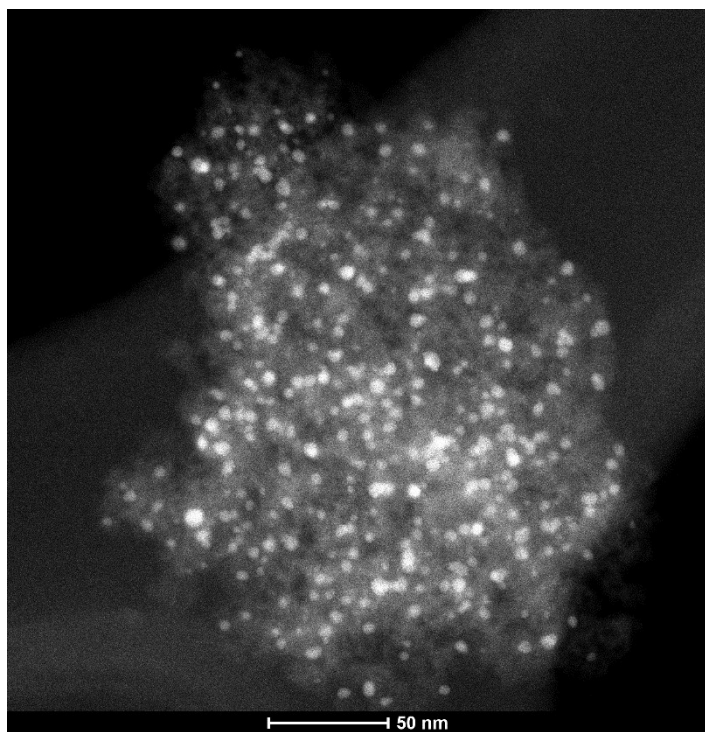


Figure S10. TEM Image of the spent 4Ag/4ZrO₂/SBA-16.

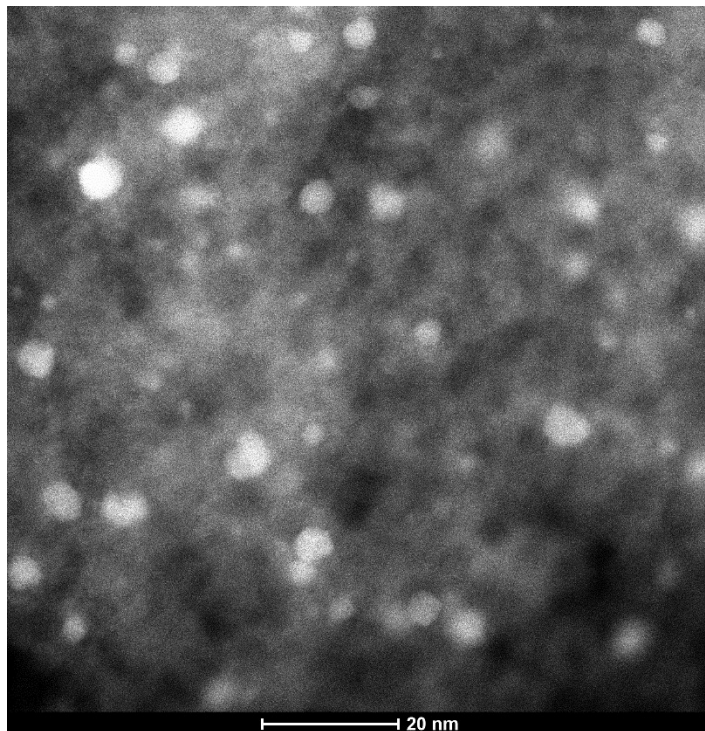


Figure S11. TEM Image of the spent 4Ag/4ZrO₂/SBA-16.

TEM Images of Spent 0.5Na/4Ag/4ZrO₂/SBA-16 after 72h lifetime study presented in Figure 4

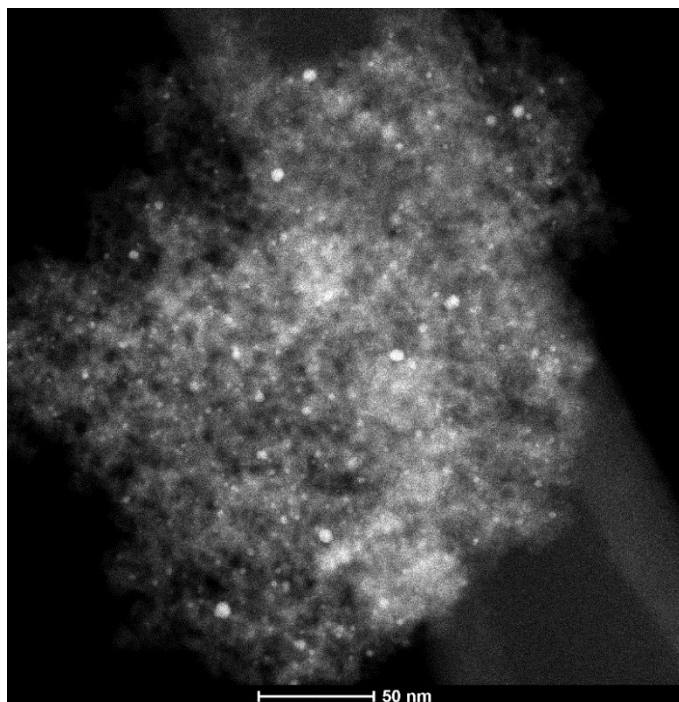


Figure S12. TEM Image of the spent 0.5%Na/ 4Ag/4ZrO₂/SBA-16.

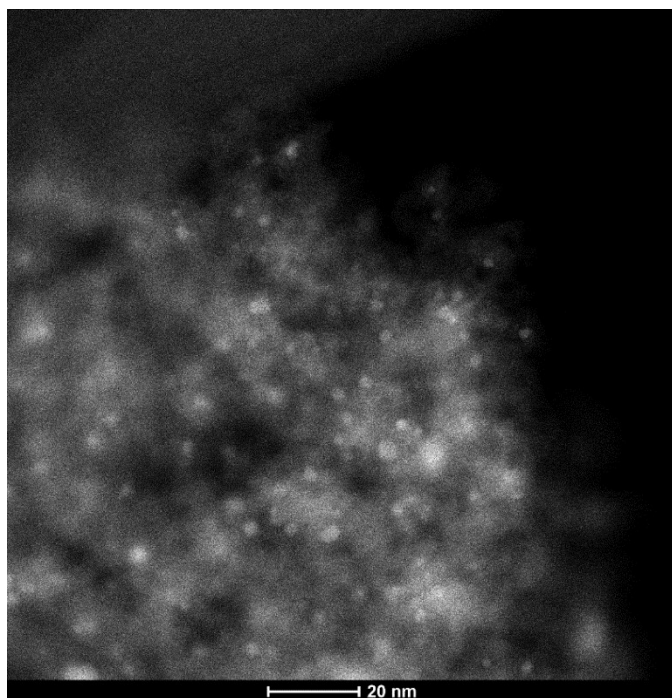


Figure S13. TEM Image of the spent 0.5%Na/ 4Ag/4ZrO₂/SBA-16.

Ag Particle Size Distributions from TEM Images

4Ag/4ZrO₂/SBA-16

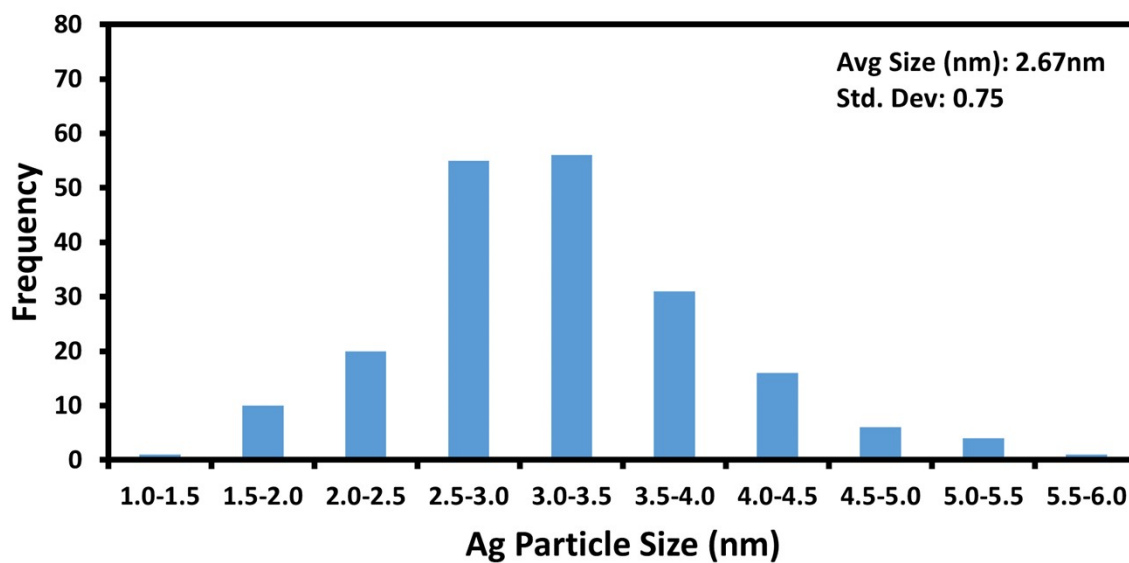


Figure S14. Ag Particle Size Distribution from sampling of TEM images collected of reduced 4Ag/4ZrO₂/SBA-16

0.5K/4Ag/4ZrO₂/SBA-16

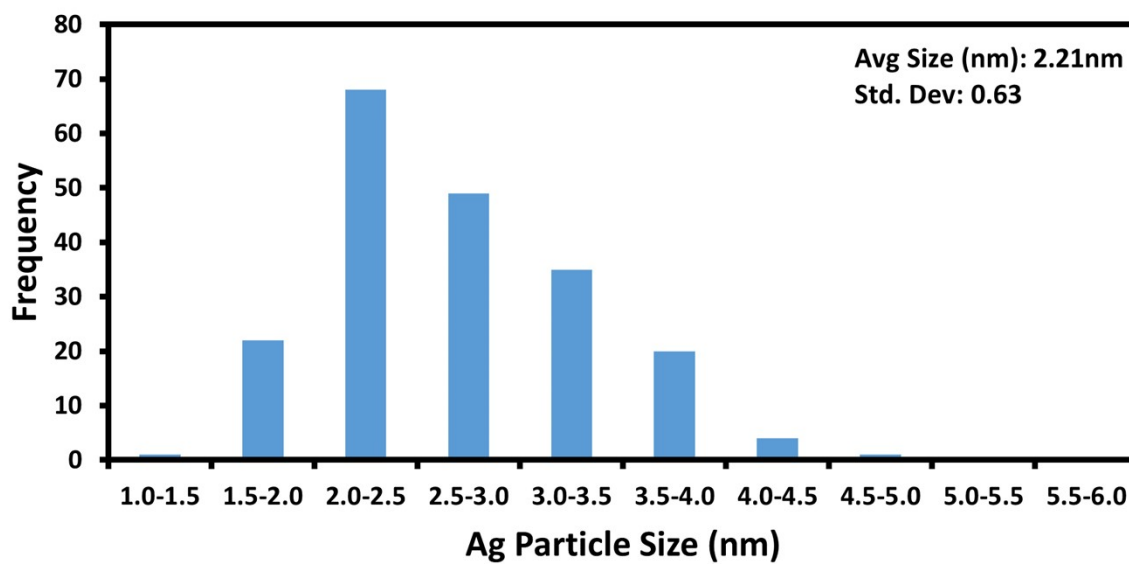


Figure S15. Ag Particle Size Distribution from sampling of TEM images collected of reduced 0.5K/4Ag/4ZrO₂/SBA-16

0.5Na/4Ag/4ZrO₂/SBA-16

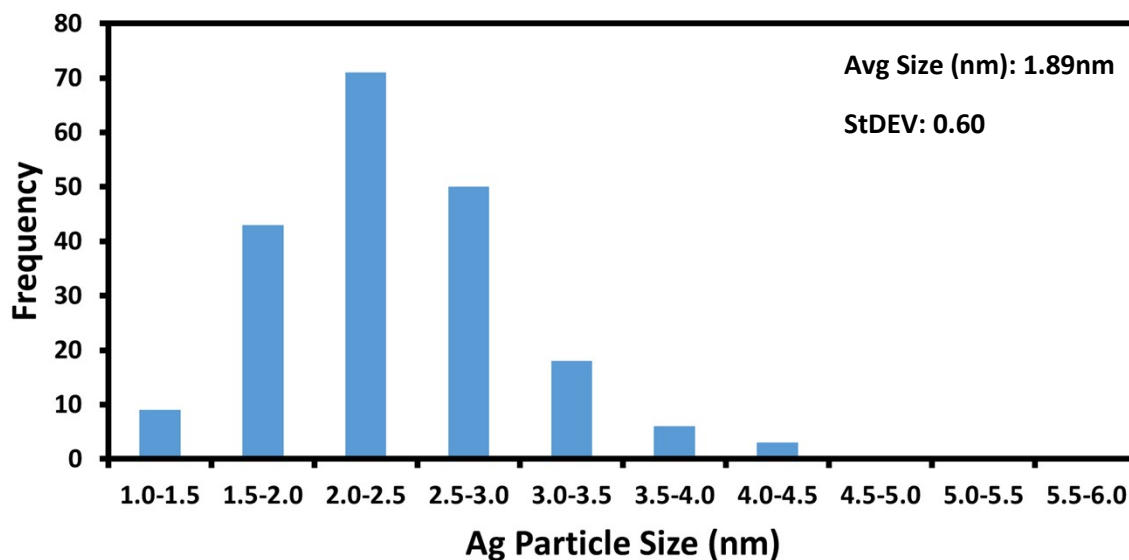


Figure S16. Ag Particle Size Distribution from sampling of TEM images collected of reduced 4Ag/4ZrO₂/SBA-16

4Ag/4ZrO₂/SBA-16 after 72 hr lifetime study presented in Figure 4

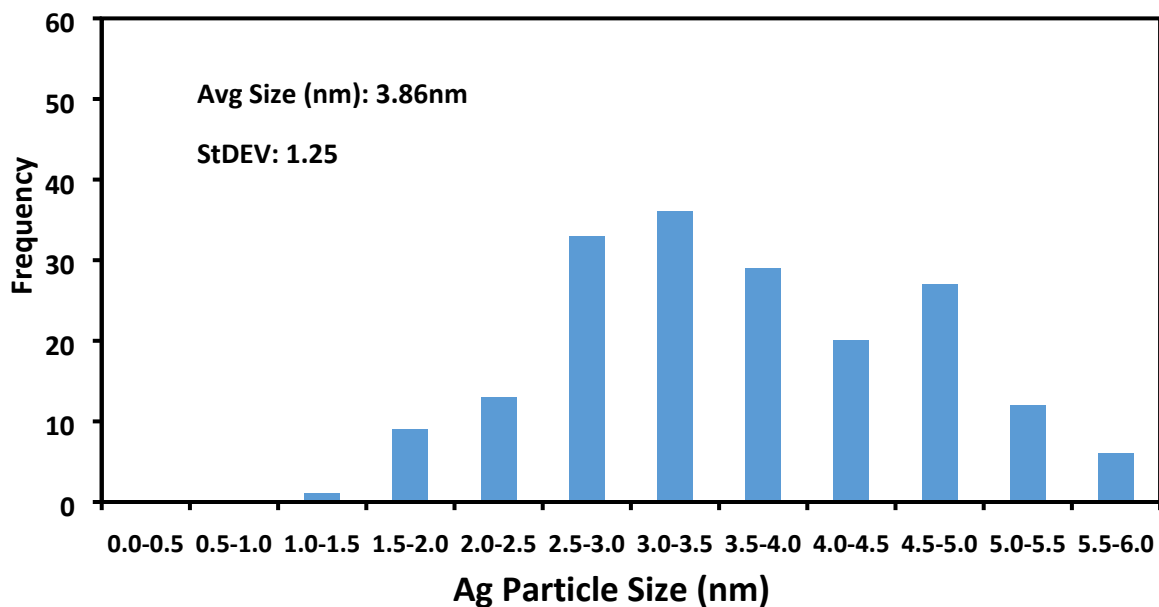


Figure S17. Ag Particle Size Distribution from sampling of TEM images collected for the spent 4Ag/4ZrO₂/SBA-16 after 72 hr lifetime study

0.5Na/4Ag/4ZrO₂/SBA-16 after 72 hr lifetime study presented in Figure 4

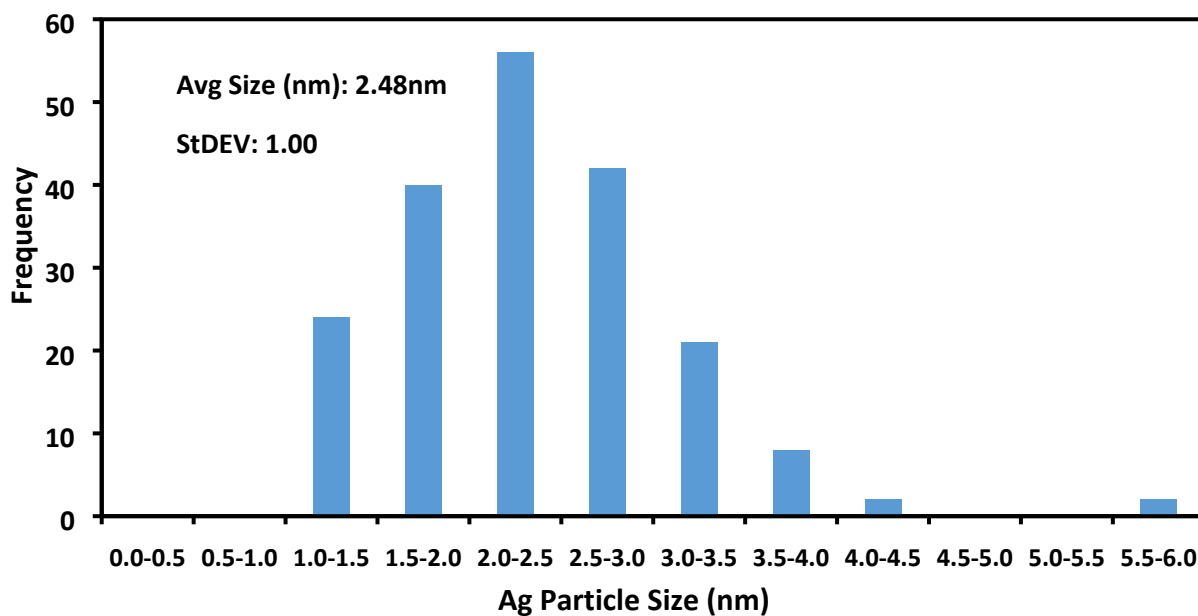


Figure S18. Ag Particle Size Distribution from sampling of TEM images collected for the spent 0.5Na/4Ag/4ZrO₂/SBA-16 after 72 hr lifetime study

Total Carbon Analysis

Table S2. Total carbon analysis for each 72 h catalyst lifetime study. $WHSV_{EtOH} = 0.23h^{-1}$. $P_{EtOH}=11\%$ in N₂. $P = 0$ psig. $T = 325^{\circ}C$. Results from the average of three analysis runs.

CATALYST	TOTAL CARBON (%)
4Ag/4ZrO ₂ /SBA-16	5.54
0.5Na/4Ag/4ZrO ₂ /SBA-16	6.64

Lifetime Activity Data

Table S3. Lifetime activity data for 4Ag/4ZrO₂/SBA-16

TOS (hour)	Conversion (%)	Selectivity (%)							Butadiene Yield (%)	Butadiene Productivity (hr ⁻¹)
		Butadiene	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	DEE	Acetaldehyde	Other Oxygenates		
6	95.8	67.9	8.3	1.7	7.9	7.5	2.5	2.3	65.1	0.090
12	86.6	65.0	9.1	1.5	6.9	9.8	3.2	2.7	55.8	0.077
18	80.3	62.4	10.1	1.5	6.6	11.0	3.7	3.0	49.6	0.069
24	72.0	60.0	10.7	1.3	6.5	12.2	4.2	3.4	41.5	0.058
30	70.3	58.6	11.4	1.3	6.5	12.9	4.4	3.2	40.2	0.056
36	67.8	54.9	11.5	1.2	9.6	13.4	4.6	3.2	36.0	0.050
42	61.4	55.5	12.4	1.2	6.4	14.4	5.1	3.5	32.1	0.045
48	59.5	54.4	12.8	1.2	6.4	15.0	5.3	3.3	30.8	0.043
54	59.8	53.4	13.3	1.2	6.3	15.6	5.3	3.4	31.1	0.043
60	56.2	52.4	13.6	1.1	6.2	16.0	5.6	3.5	27.6	0.038
66	55.9	51.6	13.9	1.1	6.2	16.4	5.7	3.4	27.5	0.038
72	53.4	50.4	14.2	1.1	6.1	16.7	6.0	3.6	24.9	0.035

WHSV_{EtOH} = 0.23hr⁻¹. P_{EtOH} = 11% in N₂. P = 1 atmosphere. T = 325°C. Other oxygenates: ethyl acetate, butanol, acetone, crotonaldehyde, crotyl alcohol.

Table S4. Lifetime activity data for 0.5Na/4Ag/4ZrO₂/SBA-16 with 100% ethanol feed.

TOS (hour)	Conversion (%)	Selectivity (%)							Butadiene Yield (%)	Butadiene Productivity (hr ⁻¹)
		Butadiene	C ₂ ⁼	C ₃ ⁼	C ₄ ⁼	DEE	Acetaldehyde	Other Oxygenates		
6	89.8	75.1	3.3	1.8	10.2	1.8	2.1	3.2	70.0	0.097
12	75.1	71.4	3.2	1.8	9.0	2.0	4.6	5.6	57.6	0.080
18	66.2	68.7	3.2	1.6	8.2	2.1	6.3	7.5	49.0	0.068
24	62.4	68.7	3.4	1.6	7.8	2.2	6.8	7.0	47.8	0.066
30	56.8	66.5	3.3	1.6	7.4	2.1	8.0	7.8	41.9	0.058
36	53.6	65.8	3.4	1.6	7.1	2.2	8.6	7.8	39.1	0.054
42	51.0	65.5	3.5	1.6	7.0	2.2	9.1	8.1	37.3	0.052
48	48.5	64.9	3.6	1.6	6.8	2.3	9.7	8.0	35.8	0.050
54	48.3	62.9	3.4	1.5	8.3	2.2	9.8	8.1	33.6	0.046
60	44.3	60.9	3.5	3.9	6.4	2.3	11.1	9.0	29.2	0.040
66	42.9	62.4	3.7	1.5	6.4	2.4	11.4	8.9	30.4	0.042
72	41.0	61.6	3.8	1.5	6.3	2.4	11.9	9.2	28.6	0.040

WHSV_{EtOH} = 0.23hr⁻¹. P_{EtOH} = 11% in N₂. P = 1 atmosphere. T = 325°C. Other oxygenates: ethyl acetate, butanol, acetone, crotonaldehyde, crotyl alcohol.