Supplemental Information

Contrasting Effects of Potassium Addition on M_3O_4 (M = Co, Fe, Mn) Oxides during Direct NO Decomposition Catalysis

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Catalytic Activity

Table S1. NO Decomposition Catalytic Performance at 400 °C

Sample	NO Conversion (%)	NO_2 Selectivity (%)	N_2O Selectivity (%)	N_2 Selectivity (%)	Activity (µmol NO to N_2/g/s)
Co_3O_4	4.5	97.4	0.0	2.6	4.8E-04**
0.9K Co_3O_4	4.4	99.3	0.0	0.7	1.3E-04**
2K Co_3O_4	4.5	95.3	0.0	4.7	8.7E-04**
3K Co_3O_4	4.6	87.8	0.0	12.2	2.3E-03
Fe_3O_4	2.9	≤100.0*	0.0	0.0	0.0E+00
0.9K Fe_3O_4	2.5	98.8	1.2	0.0	0.0E+00
2K Fe_3O_4	2.4	98.9	1.1	0.0	0.0E+00
3K Fe_3O_4	2.0	96.9	0.0	3.1	2.6E-04
Mn_3O_4	2.7	≤100.0	0.0	0.0	0.0E+00
0.9K Mn_3O_4	1.8	99.5	0.5	0.0	0.0E+00
2K Mn_3O_4	1.7	96.9	3.1	0.0	0.0E+00
3K Mn_3O_4	0.9	95.5	4.5	0.0	0.0E+00

* Unreliable selectivity calculation due to low NO Conversion (i.e. ≤ 3.0%)

** Unreliable activity calculation (i.e. ≤ 2.0E-03 µmol NO to N_2/g/s)

Table S2. NO Decomposition Catalytic Performance at 450 °C

Sample	NO Conversion (%)	NO_2 Selectivity (%)	N_2O Selectivity (%)	N_2 Selectivity (%)	Activity (μmol NO to N_2/g/s)
Co_3O_4	3.5	82.1	0	17.9	2.6E-03
0.9K Co_3O_4	4.6	70.5	0	29.5	5.6E-03
2K Co_3O_4	5.5	58.5	0	41.5	9.4E-03
3K Co_3O_4	4.9	57.9	0	42.1	8.6E-03
Fe_3O_4	2.5	≤100	0	0	0
0.9K Fe_3O_4	2.5	98.1	1.9	0	0
2K Fe_3O_4	2.4	98.6	1.4	0	0
3K Fe_3O_4	2.4	98.8	1.2	0	0
Mn_3O_4	2.4	≤100	0	0	0
0.9K Mn_3O_4	2.2	99.5	0.5	0	0
2K Mn_3O_4	2.3	99.2	0.8	0	0
3K Mn_3O_4	1.8	96	4	0	0

Table S3. NO Decomposition Catalytic Performance at 550 °C

Sample	NO Conversion (%)	NO_2 Selectivity (%)	N_2O Selectivity (%)	N_2 Selectivity (%)	Activity (μmol NO to N_2/g/s)
Co_3O_4	2.8	44.3	0	55.7	6.4E-03
0.9K Co_3O_4	24.1	10.5	0	89.5	8.9E-02
2K Co_3O_4	23.3	10.6	0	89.4	8.6E-02
3K Co_3O_4	18.8	10.9	0	89.1	6.9E-02
Fe_3O_4	0.9	≤100	0	0	0
0.9K Fe_3O_4	1.1	91.3	5.5	3.2	1.4E-04
2K Fe_3O_4	0.8	93.6	6.4	0	0
3K Fe_3O_4	0.5	87.6	12.4	0	0
Mn_3O_4	0.6	≤100	0	0	0
0.9K Mn_3O_4	0.9	≤100	0	0	0
2K Mn_3O_4	0.6	98.3	1.7	0	0
3K Mn_3O_4	0.3	≤100	0	0	0

Table S4. NO Decomposition Catalytic Performance at 650 °C

Sample	NO Conversion (%)	NO_2 Selectivity (%)	N_2O Selectivity (%)	N_2 Selectivity (%)	Activity (µmol NO to N_2/g/s)
Co_3O_4	1.7	30.7	0	69.3	4.9E-03
0.9K Co_3O_4	59.2	1.1	0	98.9	2.4E-01*
2K Co_3O_4	62.5	0.9	0	99.1	2.5E-01*
3K Co_3O_4	44.3	2.9	0	97.1	1.72E-01
Fe_3O_4	0.2	100	0	0	0
0.9K Fe_3O_4	1.3	40.7	0	59.3	3.15E-03
2K Fe_3O_4	1.5	44.4	0	55.6	3.33E-03
3K Fe_3O_4	1	49.3	0	50.7	2.08E-03
Mn_3O_4	0.1	≤100	0	0	0
0.9K Mn_3O_4	0.5	93.1	0	6.9	1.38E-04
2K Mn_3O_4	0.7	91.3	0	8.7	2.45E-04
3K Mn_3O_4	0.3	≤100	0	0	0

* NO Conversion percentage is above differential conditions, activity calculation is not comparable

Table S5. NO Decomposition at 650 °C 0.9K Co_3O_4, 2K Co_3O_4, and 3K Co_3O_4 Under Differential Conditions

Sample	NO Conversion (%)	Activity (µmol NO to N_2/g/s)
0.9K Co_3O_4	7.8	1.8E-1
2K Co_3O_4	6.2	1.4E-1
3K Co_3O_4	0.5	1.3E-2

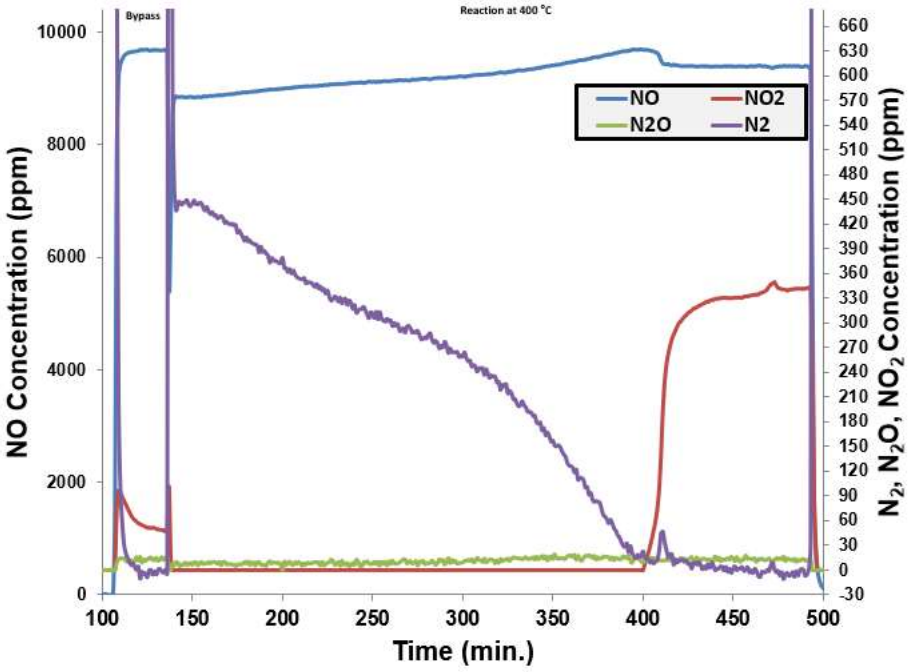

Figure S1. NO Decomposition over Fe_3O_4 as a function of time at 400 °C

XRD

Table S6. Crystallite Size from X-Ray Diffraction Patterns as Calculated Via Scherrer Equation

Sample	Calculated Crystallite Size (nm)
Co_3O_4 Fresh	22
Co_3O_4 Spent	65
0.9K Co_3O_4 Fresh	25
0.9K Co_3O_4 Spent	31
2K Co_3O_4 Fresh	25
2K Co_3O_4 Spent	30
3K Co_3O_4 Fresh	25
3K Co_3O_4Spent	28
Mn_3O_4 Fresh	86
Mn_3O_4 Spent	101
0.9K Mn_3O_4 Fresh	78
0.9K Mn_3O_4 Spent	81
2K Mn_3O_4 Fresh	70
2K Mn_3O_4 Spent	86
3K Mn_3O_4 Fresh	54
3K Mn_3O_4 Spent	70
Fe_3O_4 Fresh	53
Fe_3O_4 Spent	47
0.9K Fe_3O_4 Fresh	53
0.9K Fe_3O_4 Spent	55
2K Fe_3O_4 Fresh	57
2K Fe_3O_4 Spent	52
3K Fe_3O_4 Fresh	51
3K Fe_3O_4 Spent	52

Note: For all materials, assumed 0.89 for shape factor in Scherrer equation, and λ = 1.5418 Å
For Co_3O_4 Samples, utilized FWHM of (103) peak at ~ 36.8°
For Mn_3O_4 samples, utilized FWHM of hausmannite (103) peak at ~32.3°
For Fe_3O_4 samples (sans spent Fe_3O_4), utilized FWHM of magnetite (220) peak at ~30.2°
For Spent Fe3O4, utilized FWHM of hematite (104) peak at ~33.1°

X-Ray Photoelectron Spectroscopy

Table S7. XPS Peak Position Summary of Cobalt *2p3/2* Curve Fits

Sample	Peak 1 Position (eV)	Peak 2 Position (eV)	Peak 3 Position (eV)	Peak 4 Position (eV)	Peak 5 Position (eV)
Co_3O_4 (ref[42])	779.6	780.9	782.2	785.2	789.5
Co_3O_4 Fresh	779.4	780.5	782.7	786.2	789.3
Co_3O_4 Spent	779.3	780.4	781.7	785.4	789.4
0.9K Co_3O_4 Fresh	778.8	779.9	781.6	785.1	788.9
2K Co_3O_4 Fresh	778.7	779.9	781.6	785.1	788.7
3K Co_3O_4 Fresh	778.6	779.8	781.6	785.1	788.5
0.9K Co_3O_4 Spent	778.7	779.8	781.6	785.1	788.8
2K Co_3O_4 Spent	778.6	779.8	781.6	785.1	788.5
3K Co_3O_4 Spent	778.7	779.8	781.6	785.7	789.0

Table S8. XPS Peak Area Percentage Summary of Cobalt *2p3/2* Curve Fits

Sample	Peak 1 Area (%)	Peak 2 Area (%)	Peak 3 Area (%)	Peak 4 Area (%)	Peak 5 Area (%)
Co_3O_4 (ref[42])	40.5	29.1	15.2	8.1	7.2
Co_3O_4 Fresh	17.6	60.8	13.0	3.3	5.3
Co_3O_4 Spent	20.1	29.4	39.0	5.9	5.5
0.9K Co_3O_4 Fresh	26.6	42.8	16.3	6.5	7.8
2K Co_3O_4 Fresh	30.0	44.7	14.3	5.0	6.0
3K Co_3O_4 Fresh	27.3	48.4	14.6	3.4	6.3
0.9K Co_3O_4 Spent	18.2	54.1	16.7	5.3	5.8
2K Co_3O_4 Spent	25.5	51.5	15.2	2.4	5.4
3K Co_3O_4 Spent	24.4	52.3	13.6	4.8	4.9

Table S9. XPS Peak Position Summary of Manganese *2p3/2* Curve Fits

Sample	Peak 1 Position (eV)	Peak 2 Position (eV)	Peak 3 Position (eV)	Peak 4 Position (eV)	Peak 5 Position (eV)	Peak 6 Position (eV)	Peak 7 Position (eV)
Mn^{2+} (ref[42])	640.3	641.5	642.3	643.2	645	647.5	
Mn^{3+} (ref[42])	641.2	641.9	642.7	643.7	645.1		
Mn^{4+} (ref[42])	641.9	642.7	643.4	644.2	645.2	646.2	
Mn_3O_4 Fresh	640.7	642	643.7	646.2	649.1	653.4	656.2
Mn_3O_4 Spent	640.2	641.4	643.2	646	649.1	652.8	655.6
0.9K Mn_3O_4 Fresh	640.6	641.9	643.2	645.8	649.9	653.6	656.3
2K Mn_3O_4 Fresh	640.4	641.9	643.2	646.1	649.8	653.7	656.4
3K Mn_3O_4 Fresh	640.5	641.9	643.2	646.4	650.8	653.7	656.2
0.9K Mn_3O_4 Spent	640.2	641.7	643.2	645.8	649.1	653.3	655.2
2K Mn_3O_4 Spent	640.4	641.9	643.2	645.8	649.1	653.7	656.3
3K Mn_3O_4 Spent	640.7	642.1	643.2	645.8	649.1	653.8	656.5

Table S10. XPS Peak Area Percentage Summary of Manganese *2p3/2* Curve Fits

Sample	Peak 1 Area (%)	Peak 2 Area (%)	Peak 3 Area (%)	Peak 4 Area (%)	Peak 5 Area (%)	Peak 6 Area (%)	Peak 7 Area (%)
Mn^{2+} (ref[42])	24	27.8	22.1	12.5	4.7	9.1	
Mn^{3+} (ref[42])	24	24	27.8	17.5	6.7		
Mn^{4+} (ref[42])	41.7	26.5	15.5	9.1	4.9	2.5	
Mn_3O_4 Fresh	13.3	30.3	15.9	5.2	4.0	29.2	2.2
Mn_3O_4 Spent	10.5	31.2	17.0	5.0	2.8	29.6	3.9
0.9K Mn_3O_4 Fresh	7.9	23.9	23.6	6.8	4.8	30.3	2.8
2K Mn_3O_4 Fresh	3.4	27.4	26.9	5.2	4.8	30.3	1.9
3K Mn_3O_4 Fresh	4.2	28.1	27.2	5.0	4.8	27.8	3.0
0.9K Mn_3O_4 Spent	6.6	30.5	20.4	4.5	2.7	32.7	2.5
2K Mn_3O_4 Spent	3.8	30.0	23.1	4.5	3.4	34.4	0.8
3K Mn_3O_4 Spent	9.3	12.9	28.8	5.0	4.7	38.0	1.3

Table S11. XPS Peak Position Summary of Iron *2p3/2* Curve Fits

Sample	Peak 1 Position (eV)	Peak 2 Position (eV)	Peak 3 Position (eV)	Peak 4 Position (eV)	Peak 5 Position (eV)	Peak 6 Position (eV)	Peak 7 Position (eV)
Fe^0 (ref[42])	706.6	N/A	N/A	N/A	N/A	N/A	N/A
FeO (ref[42])	708.4	709.7	710.9	712.1	715.4		
hematite Fe_2O_3 (ref[42])	709.8	710.7	711.4	713.3	713.3	719.3	
maghemite Fe_2O_3 (ref[31])	709.8	710.8	711.8	713	714.1	719.3	
Fe_3O_4 Fe^{2+} Peaks (ref[42])	708.4	709.2	N/A	N/A	N/A		
Fe_3O_4 Fe^{3+} Peaks (ref[42])	710.2	711.2	712.3	713.4	714.5		
Fe_3O_4 Fresh	709.8	711	712.8	715.3	718.7	723.8	725.5
Fe_3O_4 Spent	710.5	712.1	713.2	714.3	718.9	723.9	
0.9K Fe_3O_4 Fresh	709.2	710.4	712.8	715.1	718.3	723.3	725.6
2K Fe_3O_4 Fresh	709	710.1	711.9	714.5	718.1	723.1	725.2
3K Fe_3O_4 Fresh	709.1	710.2	711.9	714.5	718.1	723.1	725.3
0.9K Fe_3O_4 Spent	709.4	710.3	711.9	714.5	718.3	723.3	725.3
2K Fe_3O_4 Spent	709.3	710.2	711.9	714.5	718.2	723.2	725.5
3K Fe_3O_4 Spent	709.4	710.4	711.9	714.4	718.2	723.4	725.4

Table S12. XPS Peak Area Percentage Summary of Iron *2p3/2* Curve Fits

Sample	Peak 1 Area (%)	Peak 2 Area (%)	Peak 3 Area (%)	Peak 4 Area (%)	Peak 5 Area (%)	Peak 6 Area (%)	Peak 7 Area (%)
Fe^0 (ref[42])	100	N/A	N/A	N/A	N/A	N/A	N/A
FeO (ref[42])	24.2	30.1	14.5	25.6	5.6		
hematite Fe_2O_3 (ref[42])	26.1	22	17.4	25.9	8.6		
maghemite Fe_2O_3 (ref[42])	27.4	27.4	20.3	9.1	9.3		
Fe_3O_4 Fe^{2+} Peaks (ref[42])	16.6	14.8	N/A	N/A	N/A		
Fe_3O_4 Fe^{3+} Peaks (ref[42])	23.7	17.8	12.2	5.7	9.1		
Fe_3O_4 Fresh	13.0	22.6	19.8	6.8	13.1	17.4	7.5
Fe_3O_4 Spent	51.0	6.9	6.3	5.6	6.7	23.4	0.0
0.9K Fe_3O_4 Fresh	9.6	33.2	13.2	5.4	13.5	19.0	6.1
2K Fe_3O_4 Fresh	10.1	25.2	18.6	7.0	12.8	19.3	6.8
3K Fe_3O_4 Fresh	10.4	24.3	18.6	7.7	14.4	19.6	5.0
0.9K Fe_3O_4 Spent	9.8	22.6	19.9	8.2	13.5	18.7	7.3
2K Fe_3O_4 Spent	9.6	25.9	20.6	8.8	14.9	14.9	5.2
3K Fe_3O_4 Spent	10.1	21.6	19.2	8.4	14.3	19.3	7.0

EDX and BET

Table S13. Summary of Potassium Weight Loading on Fresh and Spent Catalysts

Sample	K Loading Fresh Catalyst (wt.%)	K Loading Spent Catalyst (wt.%)
Co_3O_4	0	0
0.9K Co_3O_4	1.0	0.9
2K Co_3O_4	2.0	1.9
3K Co_3O_4	3.3	3.0
Fe_3O_4	0	0
0.9K Fe_3O_4	0.8	0.9
2K Fe_3O_4	2.2	2.1
3K Fe_3O_4	3.0	2.7
Mn_3O_4	0	0
0.9K Mn_3O_4	1.0	0.9
2K Mn_3O_4	2.0	2.0
3K Mn_3O_4	2.7	2.7

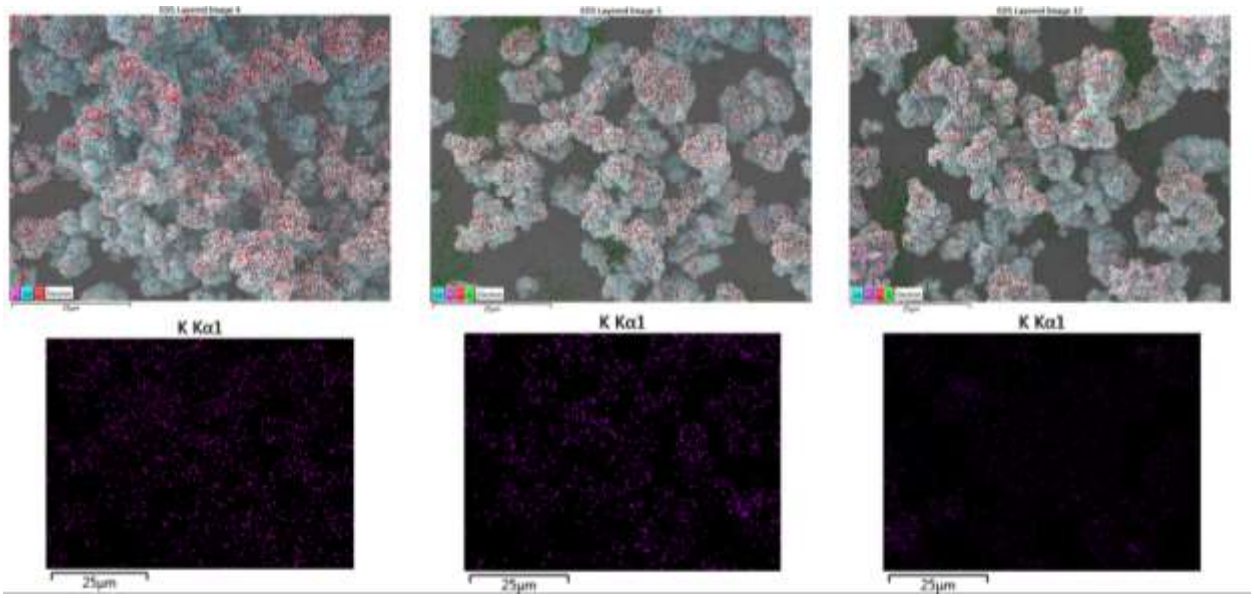

Figure S2. EDX map of K distribution on 0.9K Co_3O_4 (left), 2K Co_3O_4 (middle), and 3K Co_3O_4 (right).

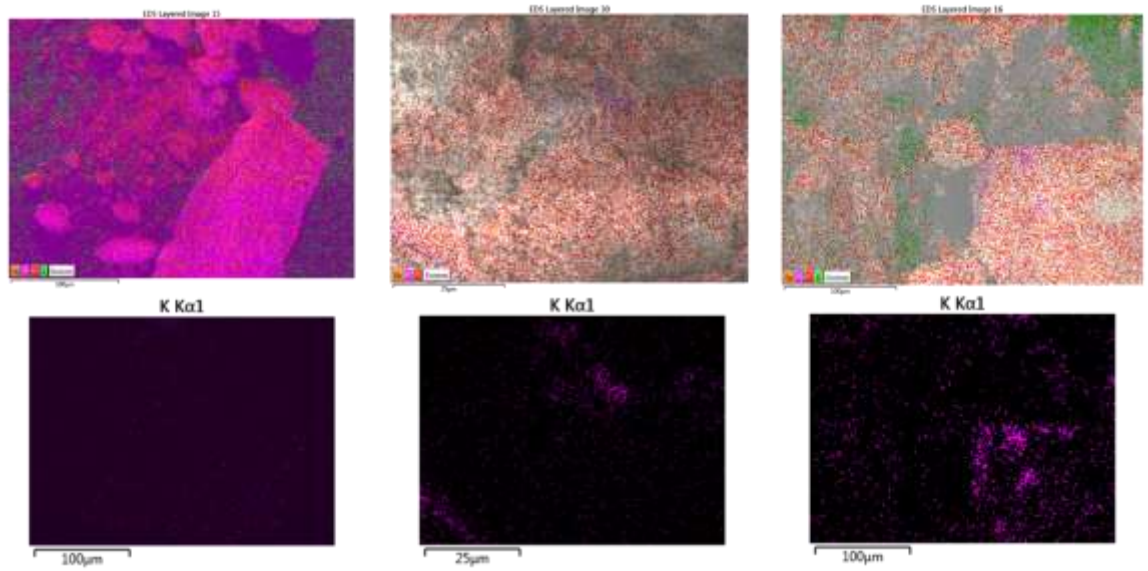

Figure S3. EDX map of K distribution on 0.9K Fe_3O_4 (left), 2K Fe_3O_4 (middle), and 3K Fe_3O_4 (right).

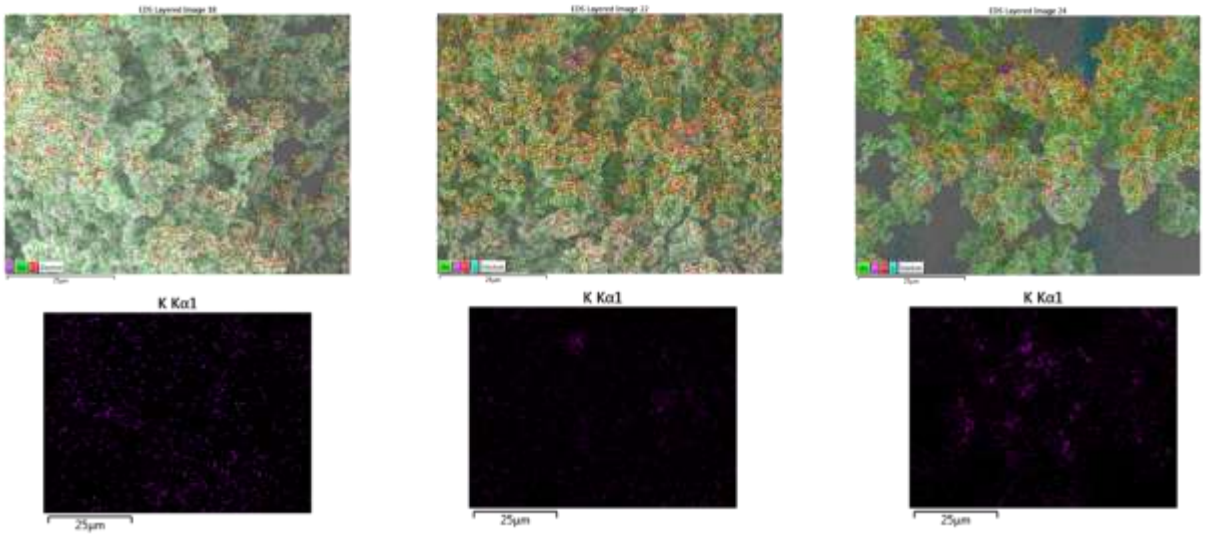

Figure S4. EDX map of K distribution on 0.9K Mn_3O_4 (left), 2K Mn_3O_4 (middle), and 3K Mn_3O_4 (right).

Table S14. BET Specific Surface Area

Sample	BET Specific Surface Area (m^2/g)
Co_3O_4	36
0.9K Co_3O_4	33
2K Co_3O_4	33
3K Co_3O_4	32
Fe_3O_4	9
0.9K Fe_3O_4	7
2K Fe_3O_4	6
3K Fe_3O_4	10
Mn_3O_4	2
0.9K Mn_3O_4	2
2K Mn_3O_4	2
3K Mn_3O_4	1