

Efficient metal borate catalysts for oxidative dehydrogenation of propane

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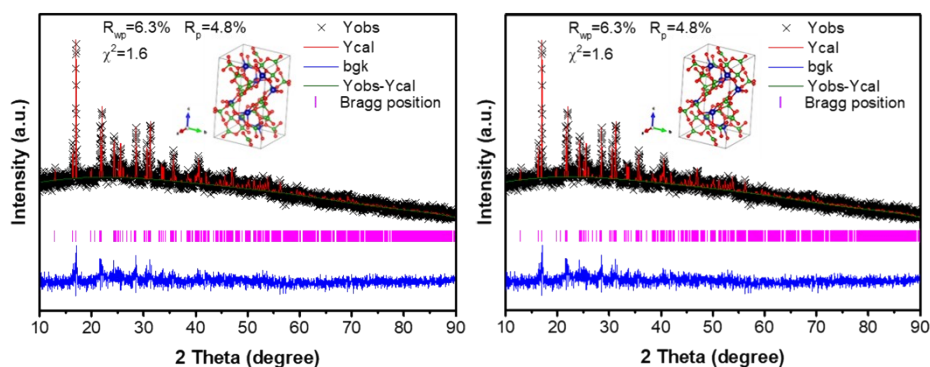


Figure S1. Rietveld fitting diagram of XRD of the catalysts: (a) CoB_4O_7 , (b) $\text{Ni}_3\text{B}_2\text{O}_6$.

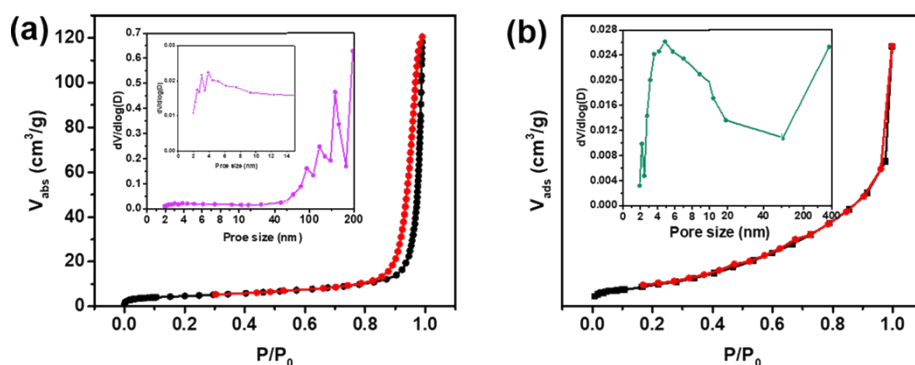


Figure S2. N_2 adsorption-desorption isotherms and pore size distribution of CoB_4O_7 and $\text{Ni}_3\text{B}_2\text{O}_6$ catalysts: (a) CoB_4O_7 , (b) $\text{Ni}_3\text{B}_2\text{O}_6$.

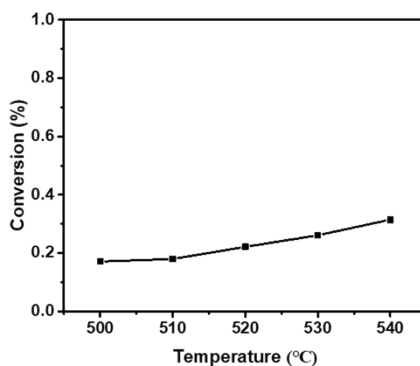


Figure S3. Influence of temperature on the ODHP conversion of propane over quartz; Reaction conditions: temperature, 490 °C; quartz weight, 600 mg; gas feed $\text{C}_3\text{H}_8/\text{O}_2/\text{N}_2$ with 2.5:1:4 volume ratio; flow rate, 30 mL min^{-1} .

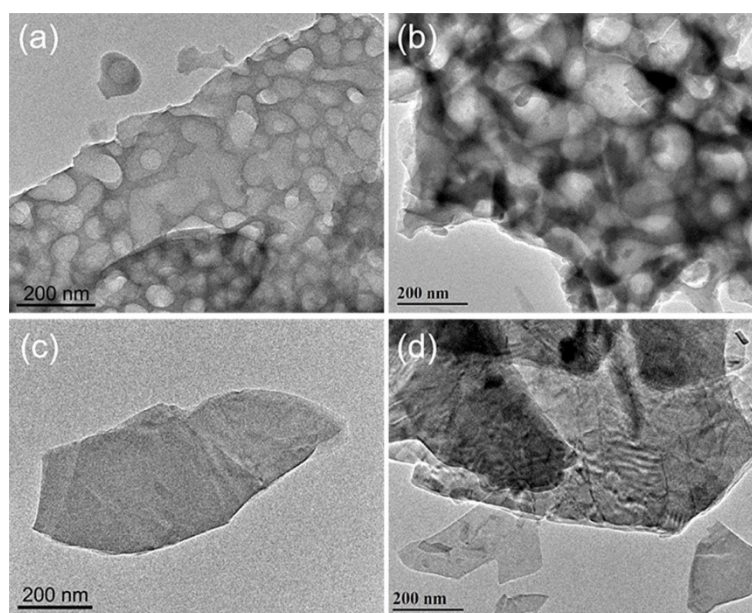


Figure S4. TEM images of CoB_4O_7 and $\text{Ni}_3\text{B}_2\text{O}_6$ catalysts: (a) fresh CoB_4O_7 , (b) spent CoB_4O_7 , (c) fresh $\text{Ni}_3\text{B}_2\text{O}_6$, (d) spent $\text{Ni}_3\text{B}_2\text{O}_6$.

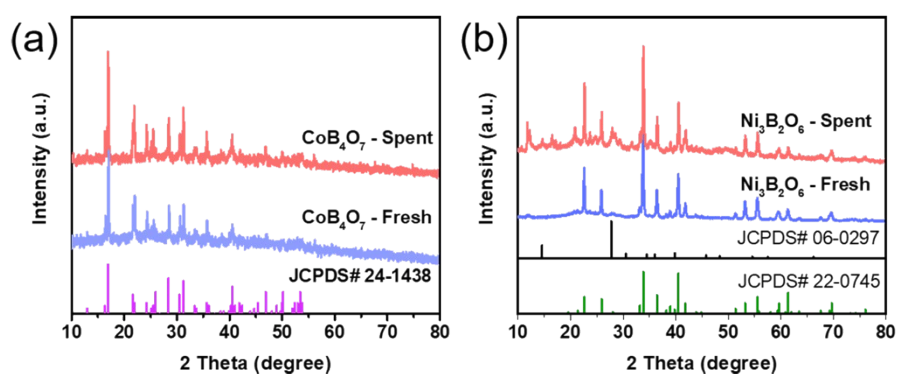


Figure S5. XRD patterns of fresh and spent catalysts: (a) CoB_4O_7 , (b) $\text{Ni}_3\text{B}_2\text{O}_6$.

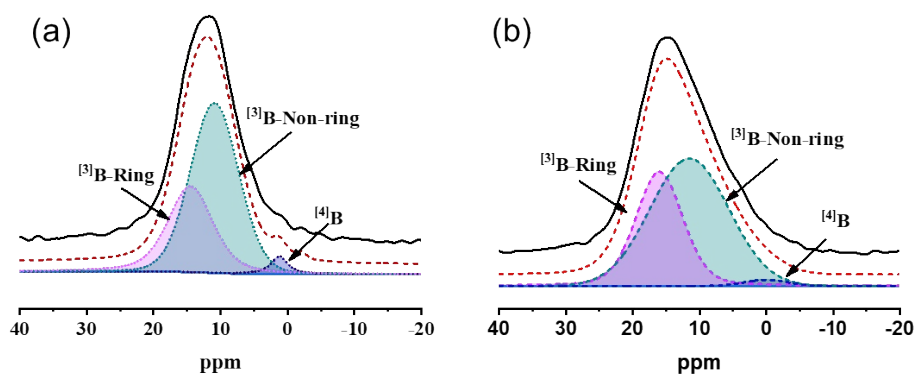


Figure S6. ^{11}B MAS-NMR spectra (14.1 T) of the borate catalysts: (a) CoB_4O_7 -Fresh, (b) CoB_4O_7 -Spent.

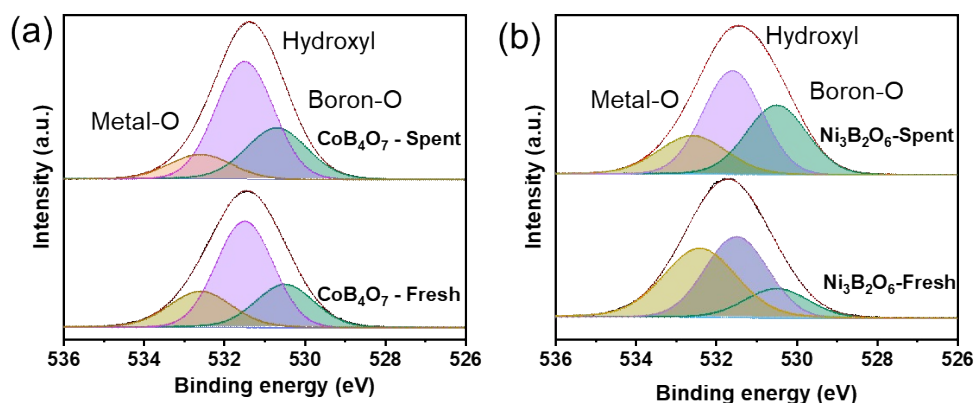


Figure S7. B 1s XPS spectra of fresh and spent catalysts: (a) CoB_4O_7 , (b) $\text{Ni}_3\text{B}_2\text{O}_6$.

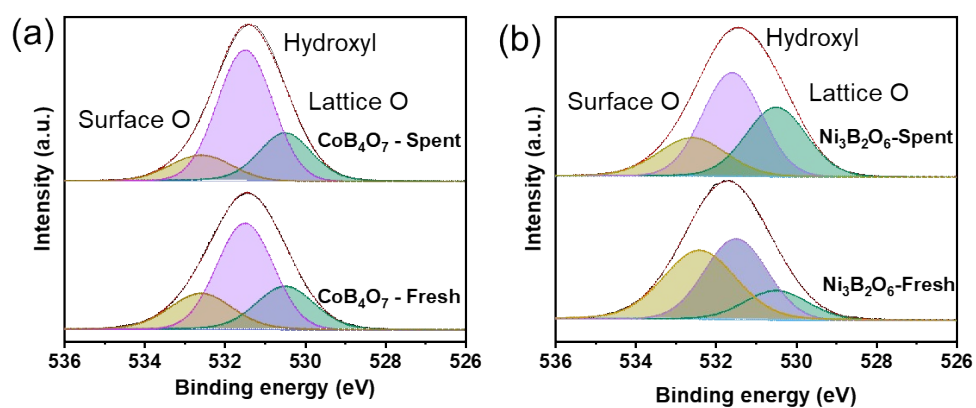


Figure S8. O 1s XPS spectra of fresh and spent catalysts: (a) CoB_4O_7 , (b) $\text{Ni}_3\text{B}_2\text{O}_6$.

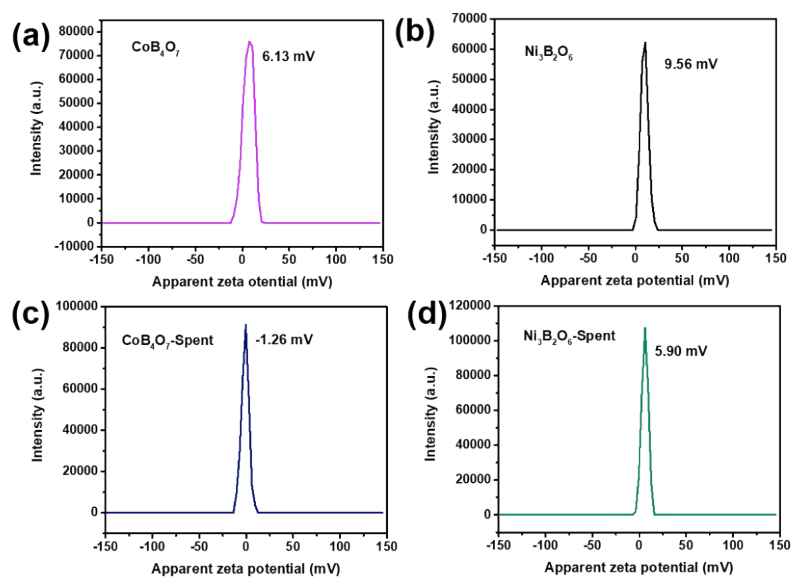


Figure S9. Zeta potentials of the catalysts.

Table S1 Catalytic performance of the CoB₄O₇ and Ni₃B₂O₆ catalyst in comparison with representative ODHP catalysts in the literatures.

Num.	Catalysts	Temp (°C)	WHSV (g _{C₃H₈} g _{cat} ⁻¹ h ⁻¹)	Conversion (%)	Selectivity (%)						Yield (%)	Ref.
				C ₃ H ₆	C ₃ H ₈	C ₂ H ₄	CH ₄	CO	CO ₂	Olefins	C ₃ H ₆	
1	h-BN	490	3.96	14.0	79.0	12.0	-	-	-	91.0	11.1	1
2	h-BN	560	-	11.3	71.8	20.0				91.8	8.1	2
3	B	490	90.0	16	77.9	10.0	1.4	6.6	3.6	87.9	12.4	3
4	NiB	490	8.04	6.1	85.4	9.3	2.0	2.2	0.3	94.7	5.2	3
5	Co ₂ B/Co ₃ B	490	6.92	3.2	87.9	7.9	1.8	1.5	0.2	95.7	2.8	3
6	BOS-10	500	9.4	31.5	64.0	19.1	0	14.8	2.1	87.4	20.1	4
8	BPO ₄ (bulk)	550	9.4	15.3	79.8	11.2	-	-	-	91.0	12.2	5
9	BPO ₄ (OM)	515	9.4	14.3	82.5	9.0	-	-	-	91.5	11.8	5
10	Boronhyperdoped silicon	450	28.2	10.6	64.1	7.2	-	9.7	2.5	71.3	6.8	6
15	Ni ₃ B ₂ O ₆	510	5.9	6.3	81.9	12.0	2.3	3.3	0.5	91.9	5.2	This work
16	Ni ₃ B ₂ O ₆ -200 h	510	5.9	13.2	77.4	16.4	3.1	2.4	0.5	93.7	10.2	This work
18	CoB ₄ O ₇	490	5.9	9.1	81.7	11.7	1.5	4.4	0.7	93.4	7.4	This work
19	CoB ₄ O ₇ -200 h	490	5.9	17.3	74.3	17.1	1.8	6.2	0.6	89.5	12.8	This work

Table S2 The content of three types of boron species in fresh and spent catalysts measured at 14.1 T

Samples		Ratio of boron species (%)		
		^[3] B-ring	^[3] B non-ring	^[4] B
CoB ₄ O ₇	Fresh	33.1	63.6	3.3
	Spent	36.5	58.7	4.8
Ni ₃ B ₂ O ₆	Fresh	32.1	63.8	4.1
	Spent	35.9	62.5	1.7

Table S3 Summary of XPS data for the CoB₄O₇ and Ni₃B₂O₆ catalysts

Samples		Content (%)			
		Co	Ni	O	B
CoB ₄ O ₇	Fresh	5.0	-	53.3	41.6
	Spent	5.0	-	53.5	41.5
Ni ₃ B ₂ O ₆	Fresh	-	4.3	53.6	42.1
	Spent	-	10.0	50.0	40.0

Table S4 Summary of B 1s and O 1s XPS spectra data for the CoB₄O₇ and Ni₃B₂O₆ catalysts

Sample	Boron species (%)	Oxygen species (%)
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		M-B-O	B-O	M-O	OH	B-O
CoB ₄ O ₇	Fresh	70.3	29.7	29.2	50.9	19.9
	Spent	73.1	26.9	28.2	58.7	13.1
Ni ₃ B ₂ O ₆	Fresh	60.1	39.9	15.1	41.8	43.1
	Spent	70.7	29.3	32.9	46.2	20.9

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