Supporting information

Amorphous Phosphorus Oxynitride as a Robust Catalyst for Steam-free Direct Dehydrogenation of Ethylbenzene to Styrene: Effect of Calcination Temperature

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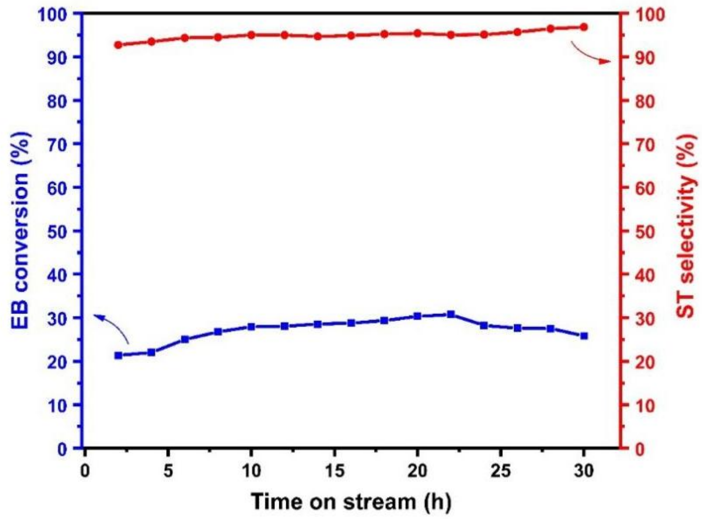

Fig. S1 The plots of x_{EB} and S_{ST} *vs.* time on stream of PNO-700 for the DDH reaction of ethylbenzene to styrene. Reaction conditions: 50 mg catalyst, 600 °C, 2.8 vol% ethylbenzene in N_2, 20 mL min^{-1}.

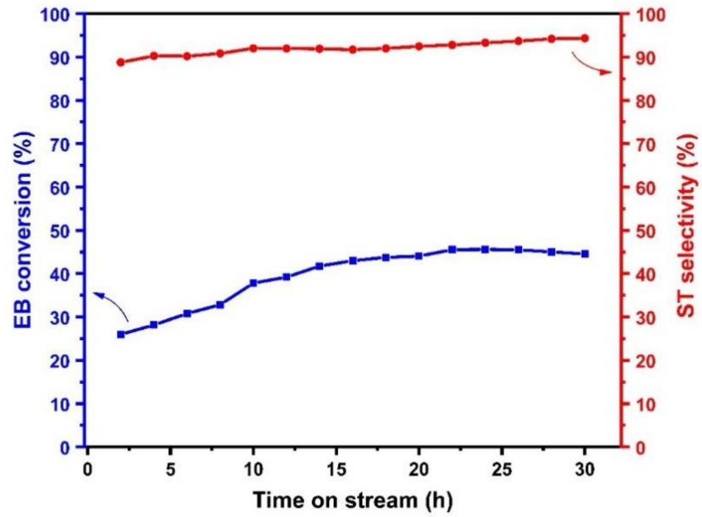

Fig. S2 The plots of x_{EB} and S_{ST} *vs.* time on stream of PNO-900 for the DDH reaction of ethylbenzene to styrene. Reaction conditions: 50 mg catalyst, 600 °C, 2.8 vol% ethylbenzene in N_2, 20 mL min^{-1}.

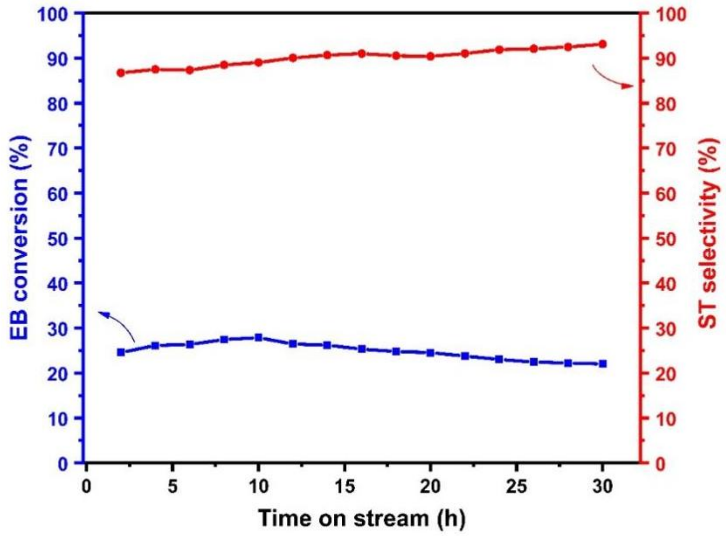

Fig. S3 The plots of x_{EB} and S_{ST} *vs.* time on stream of PNO-1000 for the DDH reaction of ethylbenzene to styrene. Reaction conditions: 50 mg catalyst, 600 °C, 2.8 vol% ethylbenzene in N_2, 20 mL min^{-1}.

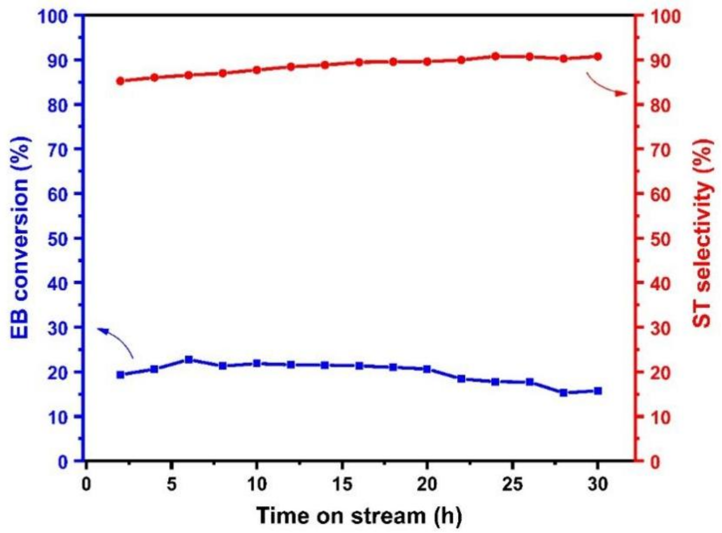

Fig. S4 The plots of x_{EB} and S_{ST} *vs.* time on stream of the commercial P_3N_5 for the DDH reaction of ethylbenzene to styrene. Reaction conditions: 50 mg catalyst, 600 °C, 2.8 vol% ethylbenzene in N_2, 20 mL min^{-1}.

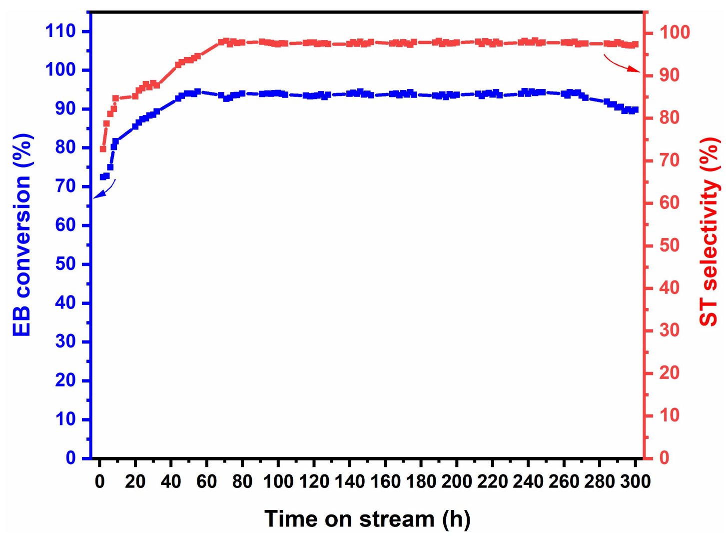

Fig. S5 The plots of x_{EB} and S_{ST} *vs.* time on stream of PNO-800/Al_2O_3 catalyst. Reaction conditions: 2.0g catalyst (40-60 mesh A.S.T.M), 600 °C, 2.8 vol% ethylbenzene in N_2, 20 mL min^{-1}.

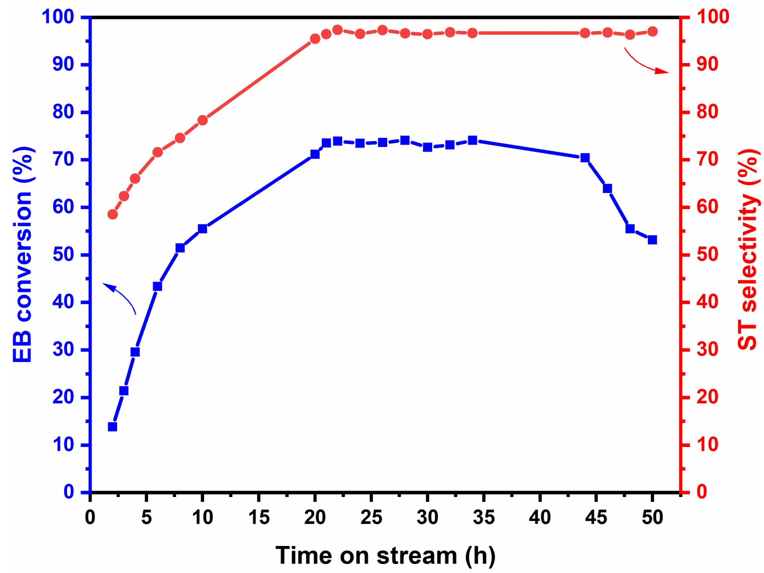

Fig. S6 The plots of x_{EB} and S_{ST} *vs.* time on stream of PNO-800/SiO_2 catalyst. Reaction conditions: 2.0g catalyst (40-60 mesh A.S.T.M), 600 °C, 2.8 vol% ethylbenzene in N_2, 20 mL min^{-1}.

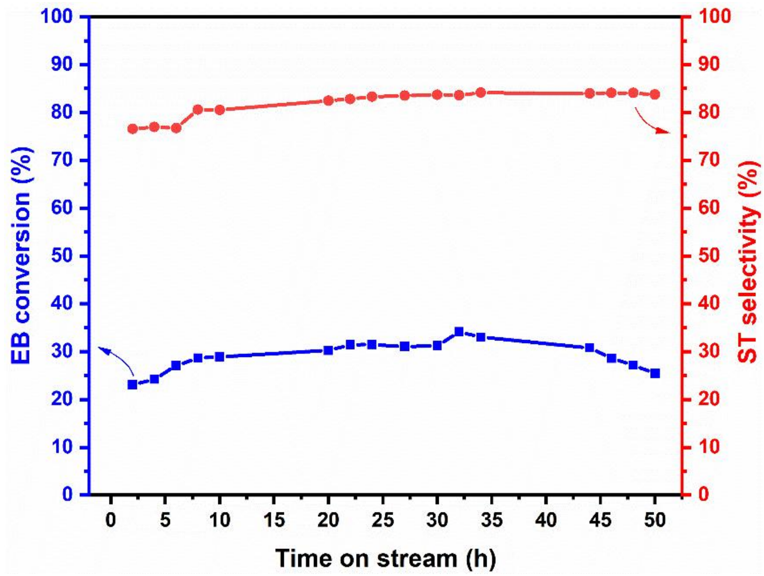

Fig. S7 The plots of x_{EB} and S_{ST} *vs.* time on stream of PNO-800/$AlPO_4$ catalyst. Reaction conditions: 2.0g catalyst (40-60 mesh A.S.T.M), 600 °C, 2.8 vol% ethylbenzene in N_2, 20 mL min^{-1}.

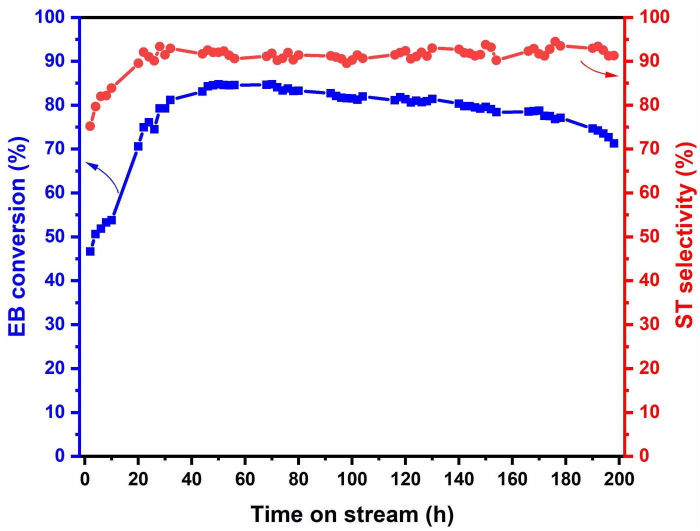

Fig. S8 The plots of x_{EB} and S_{ST} *vs.* time on stream of PNO-800/AlN catalyst. Reaction conditions: 2.0g catalyst (40-60 mesh A.S.T.M), 600 °C, 2.8 vol% ethylbenzene in N_2, 20 mL min^{-1}.

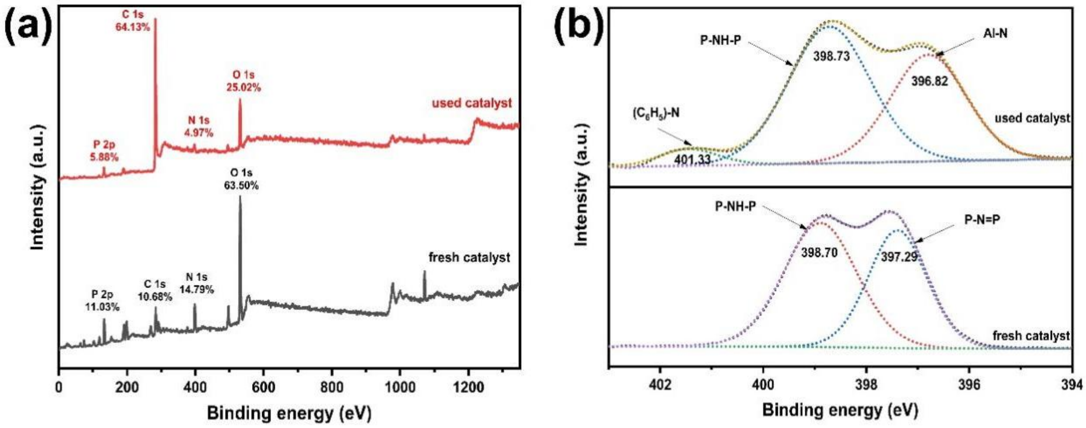

Fig. S9 XPS survey spectra (a), N 1s spectra (b) of PNO-800/Al_2O_3 before and after 300 h reaction.

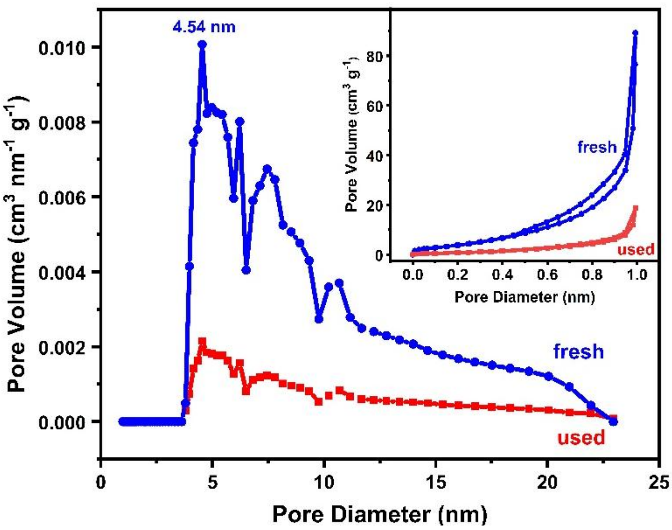

Fig. S10 N_2 adsorption-desorption isotherms and BJH pore-size distribution curves of PNO-800/Al_2O_3 before and after 300 h reaction.

Table S1 Comparison of various metal-free catalysts for DDH of ethylbenzene.

Catalyst	Reaction Condition	Catalytic Performance			Reference
		x_{EB} (%)	S_{ST} (%)	ST Yield (mmol g^{-1} h^{-1})	
PNO-800	50 mg cat, 600 °C, 2.8 vol% EB in 20 mL min^{-1} N_2	52.86	98.24	15.59	---
PBN-1.2	50 mg cat, 600 °C, 2.8 vol% EB in 20 mL min^{-1} N_2	61.85	93.5	17.45	Ref.11
N-CNT-AC	25 mg cat, 550 °C, 2.8 vol% EB in 10 mL min^{-1} Ar	---	94.7	2.46	Ref.29
H-ND	25 mg cat, 550 °C, 2.8 vol% EB in 10 mL min^{-1} Ar	---	95.8	4.8	Ref.30
ND-CN	25 mg cat, 550 °C, 2.8 vol% EB in 10 mL min^{-1} Ar	---	99.3	5.61	Ref.6
ND@NMC-700	150 mg cat, 550 °C, 2.8 vol% EB in 30 mL min^{-1} He	37.7	99.6	5.8	Ref.31
ND/CNT–SiC-ms-HN	30 mg cat, 550 °C, 2.8 vol% EB in 10 mL min^{-1} Ar	---	98.4	5.49	Ref.32
ND–CNT–SDS/SiC	25 mg cat, 550 °C, 2.8 vol% EB in 10 mL min^{-1} Ar	---	99.5	6.25	Ref.33
ND/CN-ms-o	25 mg cat, 550 °C, 2.8 vol% EB in 10 mL min^{-1} He	---	>98.2	7.06	Ref.34
ND@NMC/SiC	300 mg cat, 600 °C, 10.0 vol% EB in 30 mL min^{-1} He	38.3	96.7	9.9	Ref.35
NMCS-4-800	100 mg cat, 550 °C, 2.8 vol% EB in 10 mL min^{-1} He	---	90	2.0	Ref.36

Reference for Table S1:

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Table. S2 S_{BET} and pore structure analysis of fresh and used PNO-800/Al_2O_3.

Catalysts	S_{BET} (m^2 g^{-1})	Micropore volume (cm^3 g^{-1})	Mesoporous volume (cm^3 g^{-1})	Total pore volume (cm^3 g^{-1})
fresh PNO-800/Al_2O_3	15.139	0	0.142	0.142
used PNO-800/Al_2O_3	3.291	0	0.030	0.030