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Supporting Information

Modulation of supported Ni catalysts with phosphorus for the hydrogenation of diethyl oxalate to ethyl glycolate

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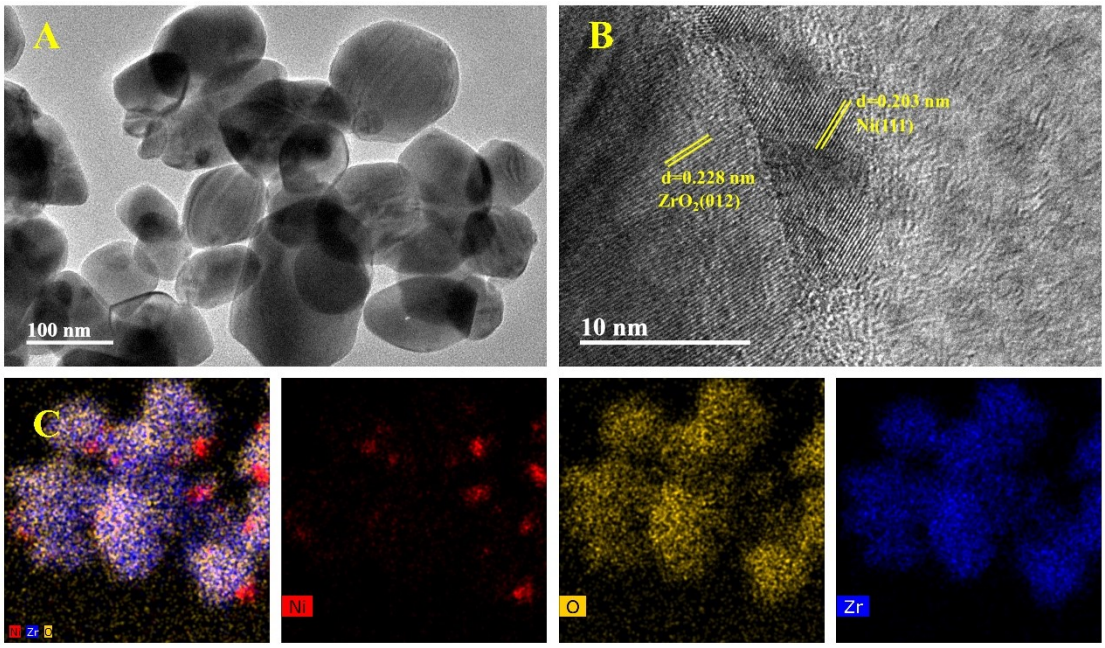

Fig.S1. TEM image and EDS mapping of 13-Ni/ZrO_2.

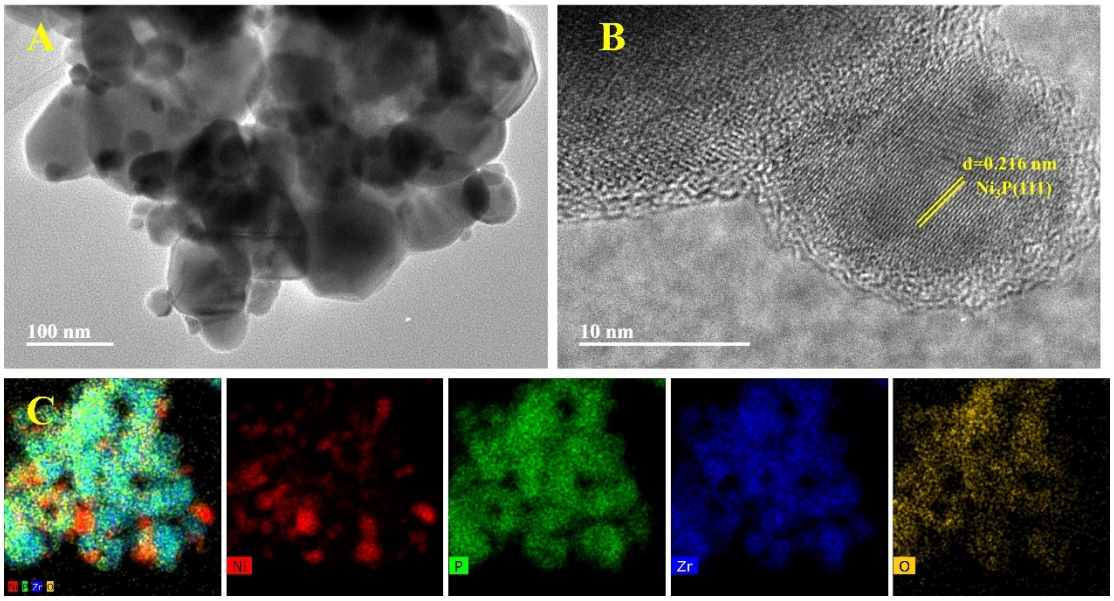

Fig.S2. TEM image and EDS mapping of 13-Ni_3P/ZrO_2.

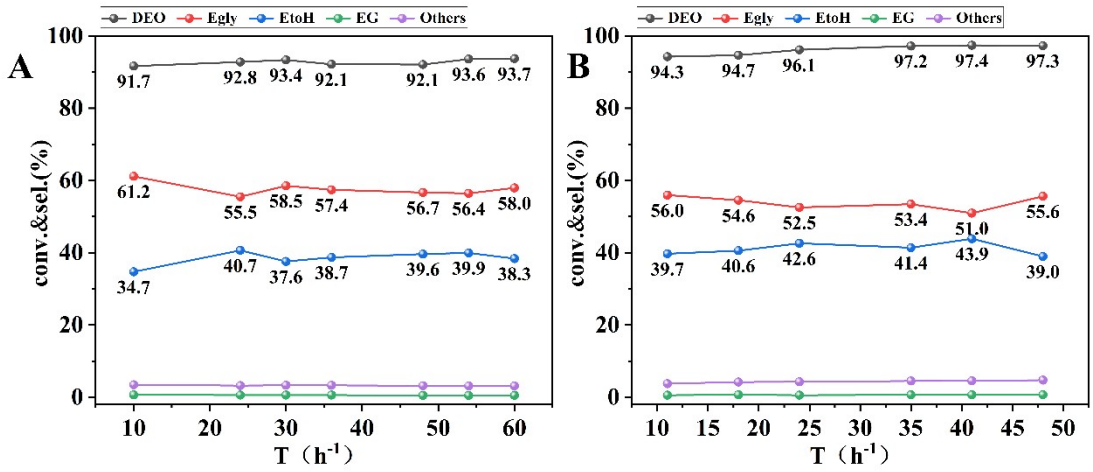

Fig.S3. DEO conversion and Egly selectivity versus time on stream over the 13-Ni_3P/ZrO_2 catalyst. (A) reaction temperature 210℃, (B) reaction temperature 230℃(P=2.5MPa, H_2/DEO molar ratio=120, WHSV= 1 h^{-1})

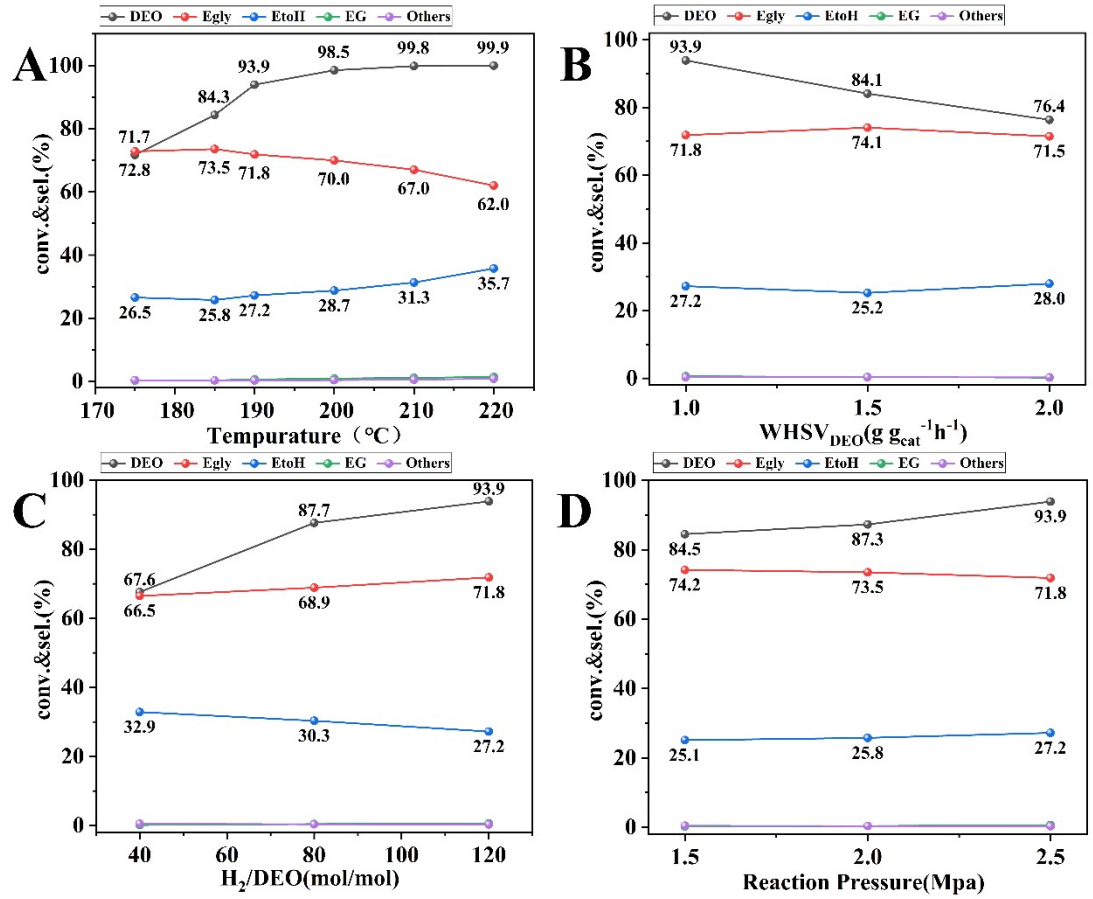

Fig. S4. Conversion and selectivity of the 13-Ni_3P/SiO_2 catalyst under different reaction conditions. (A) reaction temperature (P=2.5MPa, H_2/DEO molar ratio=120, WHSV= 1 h^{-1}), (B) WHSV (T=190℃, P=2.5MPa, H_2/DEO molar ratio=120), (C) H_2/DEO molar ratio (T=190℃, P=2.5MPa, WHSV= 1 h^{-1}), (D) reaction pressure (T=190℃, WHSV= 1 h^{-1}, H_2/DEO molar ratio=120).

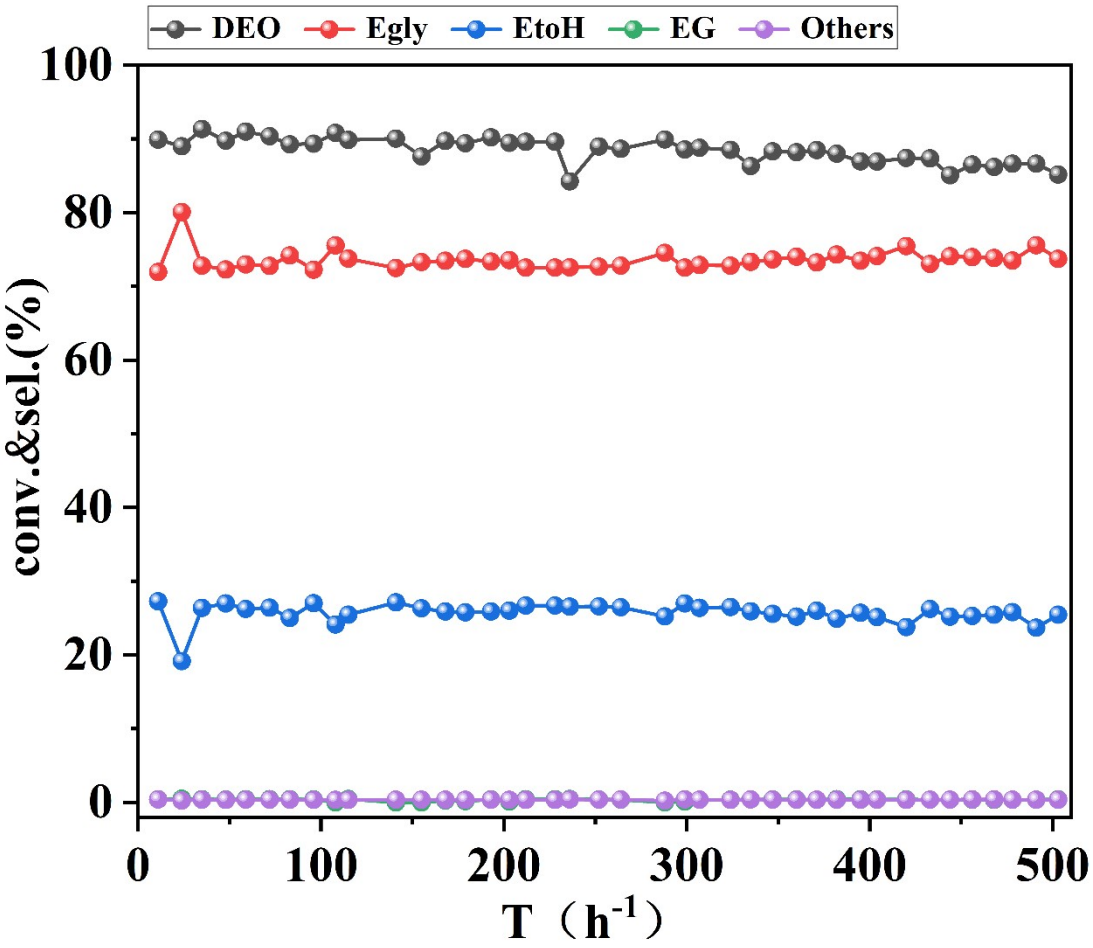

Fig. S5. Long-term performance of DEO hydrogenation over 13-Ni_3P/SiO_2 catalyst. Reaction conditions: P=2.5MPa, T=190°C, H_2/DEO molar ratio=120, WHSV= 1 h^{-1}

The stability of the catalyst was also tested. As shown in Fig. S5, no significant loss of activity and selectivity was observed during the 500 h continuous test.

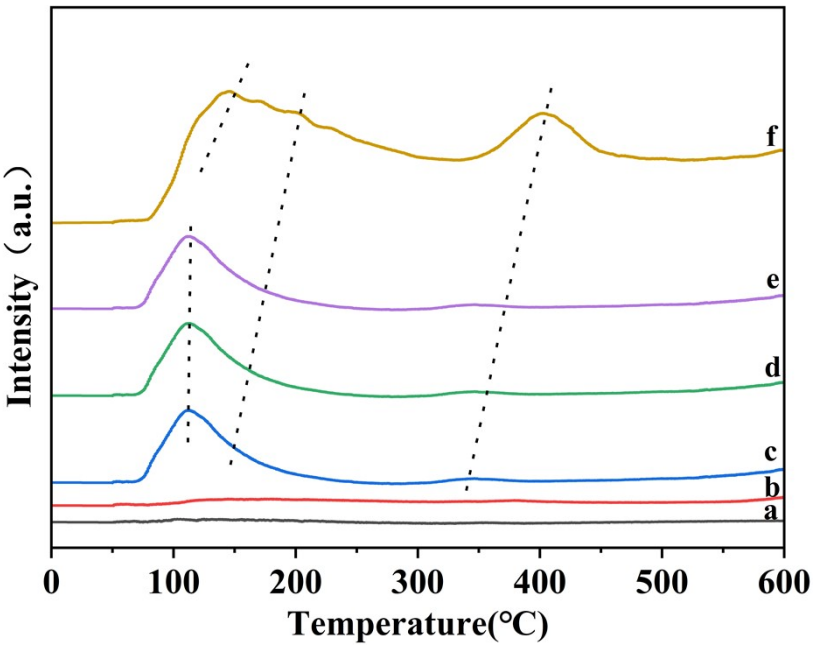

Fig. S6. NH_3-TPD profiles of the (a)13-Ni/ZrO_2, (b) 13-Ni_3P/ZrO_2, (c) 6-Ni_3P/SiO_2, (d) 13-Ni/SiO_2, (e) 13-Ni_3P/SiO_2, (f) 25-Ni_3P/SiO_2.

Fig. S6. shows the NH_3-TPD profiles of the nickel-based catalyst. The low-temperature peak centered at 120°C observed in the spectra is attributed to the adsorption peak of the SiO_2 carrier itself[1]. The NH_3 desorption peak appearing as a shoulder at about 170°C is attributed to the adsorption at the weak acid sites. In addition, the weak adsorption peak at about 390°C is attributed to the adsorption of NH_3 on the medium-strength acid sites on the surface (Fig. S6.c-f)[2]. The ZrO_2-loaded nickel-based catalysts did not show NH_3 desorption peaks (Fig. S6. a, b).

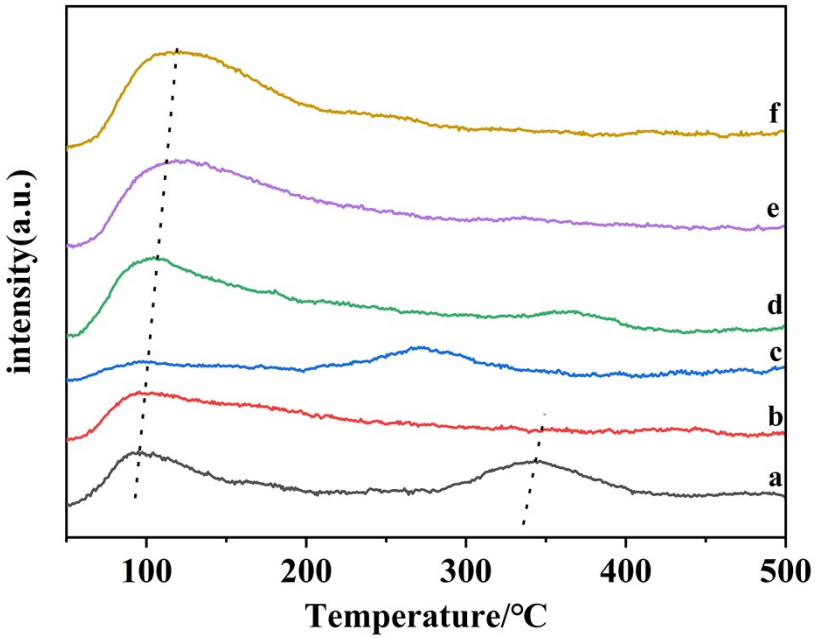

Fig. S7. CO_2-TPD profiles of the (a)13-Ni/ZrO_2, (b) 13-Ni_3P/ZrO_2, (c) 6-Ni_3P/SiO_2, (d) 13-Ni/SiO_2, (e) 13-Ni_3P/SiO_2, (f) 25-Ni_3P/SiO_2.

CO_2-TPD profiles (Fig. S7.) showed that the desorption peaks located at low temperatures (~100°C) were weakly basic sites, and the desorption peaks around 300°C were attributed to moderately strong basic sites[3]. As shown in Fig.S7.a,b and c-f, the moderate intensity basicity peak site is weakened after phosphorylation. Taking into account that the actual reaction temperature is around 200 °C, the medium-strength basicity plays a major role in DEO hydrogenation. However, the medium-strength basicity almost disappeared after phosphatization, indicating that the surface basicity has a relatively small effect on the catalyst reaction performance.

Table S1. Comparison of the 13-Ni_3P/SiO_2 catalyst with the reported ones for the DMO/DEO-to-MG/Egly reaction.

Catalyst	T (°C)	P (Mpa)	H_2/DMO (mol/mol)	WHSV ($gg_{cat}^{-1}h^{-1}$)	DMO/DEO Conv.(%)	MG/Egly Sel.%	Lifetime (h)	Ref
Ni_2P/TiO_2	230	3.0	300	0.1	100	76	3600	[4]
Ni_3P/Ni-Foam	230	2.5	180	0.44	99.5	97	1000	[5]
Ni_3P/RB-MSN	190	2.5	90	0.44	100	86	500	[1]
13-Ni_3P/SiO_2	210	2.5	120	1.0	100	67	No data	This
13-Ni_3P/SiO_2	190	2.5	120	1.0	94	72	500	work

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[3] F. Han, H. Liu, W. Cheng, Q. Xu, *Rsc Advances* **2020**, *10*, 33620-33627.

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