

**Low-temperature, highly selective, highly stable Nb<sub>2</sub>O<sub>5</sub>-NiO/Ni-foam  
catalyst for the oxidative dehydrogenation of ethane**

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## Part I. Supplementary characterization and catalytic experimental results.

**Table S1.** EDX results of the Nb<sub>2</sub>O<sub>5</sub>-NiO/Ni-foam and Nb<sub>2</sub>O<sub>5</sub>-NiO/Ni-foam-A in Fig.2.

Catalyst	Region	Weight/%			Atomic/%		
		Ni K	Nb L	O K	Ni K	Nb L	O K
Nb <sub>2</sub> O <sub>5</sub> -NiO/Ni-foam	A1	94.09	2.39	3.52	86.76	1.47	11.77
Nb <sub>2</sub> O <sub>5</sub> -NiO/Ni-foam	A2	9.65	44.22	46.13	4.66	13.51	81.83
Nb <sub>2</sub> O <sub>5</sub> -NiO/Ni-foam-A	A3	56.02	6.67	37.31	28.41	2.14	69.45

**Table S2.** Catalytic performance of Nb<sub>2</sub>O<sub>5</sub>-NiO/Ni-foam catalysts with different Nb<sub>2</sub>O<sub>5</sub> loadings.<sup>a</sup>

Nb <sub>2</sub> O <sub>5</sub> content (wt%)	Conv. (%)	Select. (%)		Productivity (g <sub>Ethylene</sub> g <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup> )
		C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	
0.0	43.4	44.0	56.0	0.20
1.0	51.8	56.0	44.0	0.30
3.0	57.6	64.9	35.1	0.39
5.0	59.6	68.0	32.0	0.43
7.0	58.5	68.9	31.1	0.42

<sup>a</sup> Reaction conditions: T = 410 °C, C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub>/N<sub>2</sub> = 1/1/8, GHSV = 9000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>.

**Table S3.** H<sub>2</sub> consumption of Ni-foam structured catalysts.

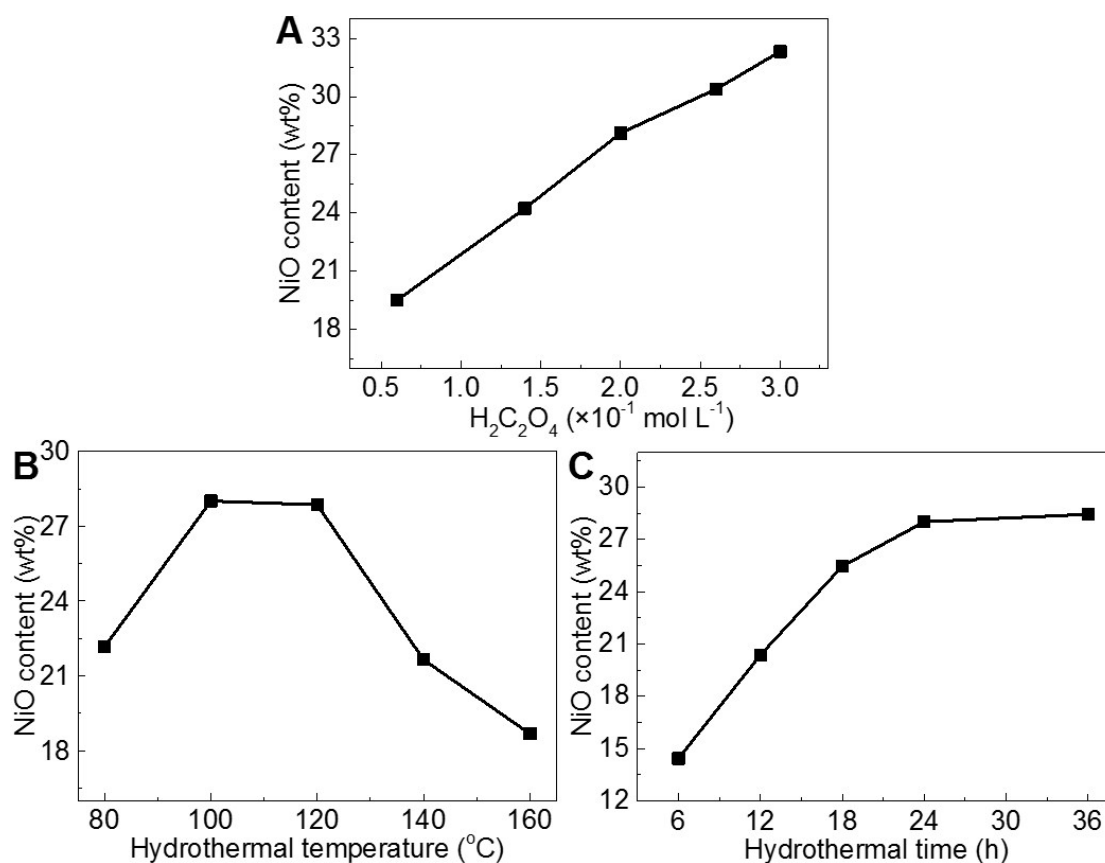
Catalyst	H <sub>2</sub> consumption (mmol g <sup>-1</sup> ) <sup>a</sup>
NiO/Ni-foam-A	3.75
Nb <sub>2</sub> O <sub>5</sub> -NiO/Ni-foam-A	3.68
Nb <sub>2</sub> O <sub>5</sub> -NiO/Ni-foam	3.67

<sup>a</sup> Measured by H<sub>2</sub> pulse experiment.

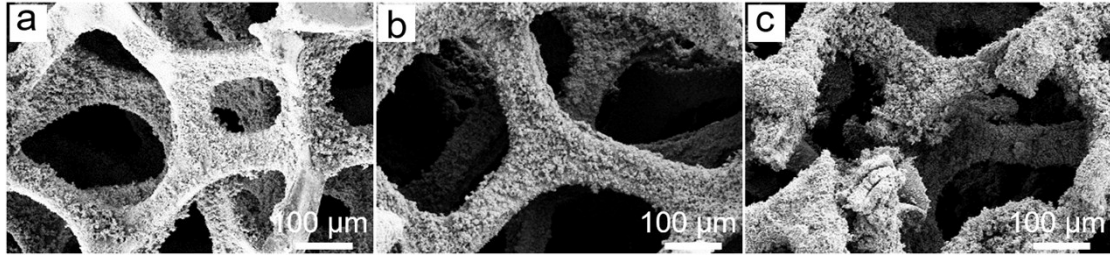
**Table S4.** Catalytic performance of Ni-foam structured and particulate catalysts as a function of ODE reaction temperature.<sup>a</sup>

Catalyst	Temperature (°C)		Conv. (%)	Select. (%)		Productivity ( $\text{g}_{\text{C}_2\text{H}_4} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$ )
	Furnace	Bed		C <sub>2</sub> H <sub>4</sub>	CO <sub>2</sub>	
Nb <sub>2</sub> O <sub>5</sub> /NiO (5/28, wt/wt)	340	352	20.8	79.8	20.2	0.17
	350	384	44.7	67.1	32.9	0.31
	360	399	50.5	66.9	33.1	0.35
	370	412	52.3	65.9	34.1	0.36
	380	422	52.5	64.5	35.5	0.35
Nb <sub>2</sub> O <sub>5</sub> -NiO/Ni-foam	350	355	22.6	76.1	23.9	0.18
	375	384	39.1	72.7	27.3	0.30
	400	411	55.0	69.6	30.4	0.40
	410	424	59.6	68.1	31.9	0.43
	425	438	57.1	67.3	32.7	0.40

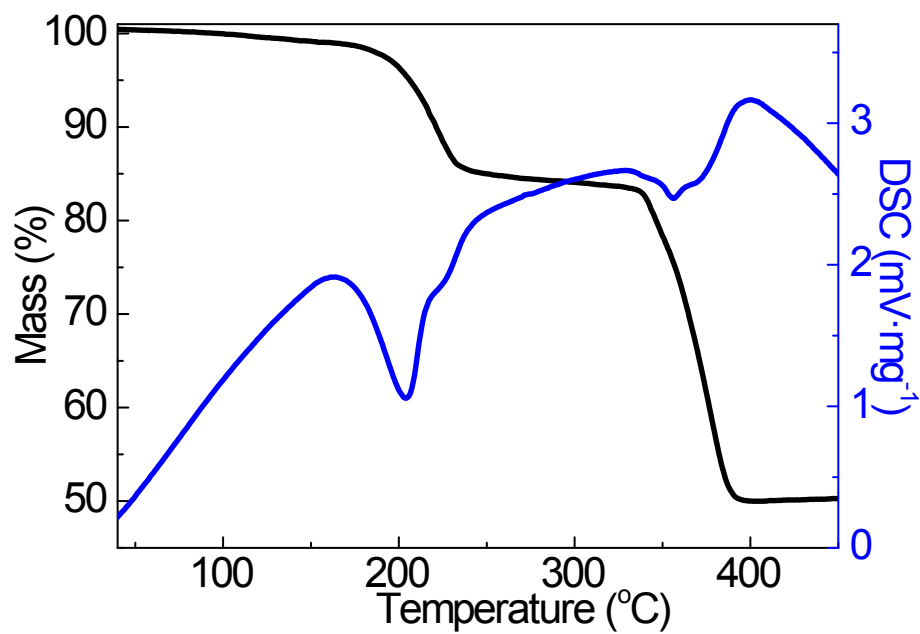
<sup>a</sup> Reaction conditions: C<sub>2</sub>H<sub>6</sub>/O<sub>2</sub>/N<sub>2</sub> = 1/1/8, GHSV = 9000 cm<sup>3</sup> g<sup>-1</sup> h<sup>-1</sup>.



**Fig. S1** NiO loading of NiO/Ni-foam-A prepared under varied hydrothermal conditions. (A) Effect of oxalic acid concentration with a fixed hydrothermal time of 24 h and hydrothermal temperature of 100 °C. (B) Effect of hydrothermal temperature with a fixed hydrothermal time of 24 h and oxalic acid concentration of 0.2 mol L<sup>-1</sup>. (C) Effect of hydrothermal time with a fixed hydrothermal temperature of 100 °C and oxalic acid concentration of 0.2 mol L<sup>-1</sup>.

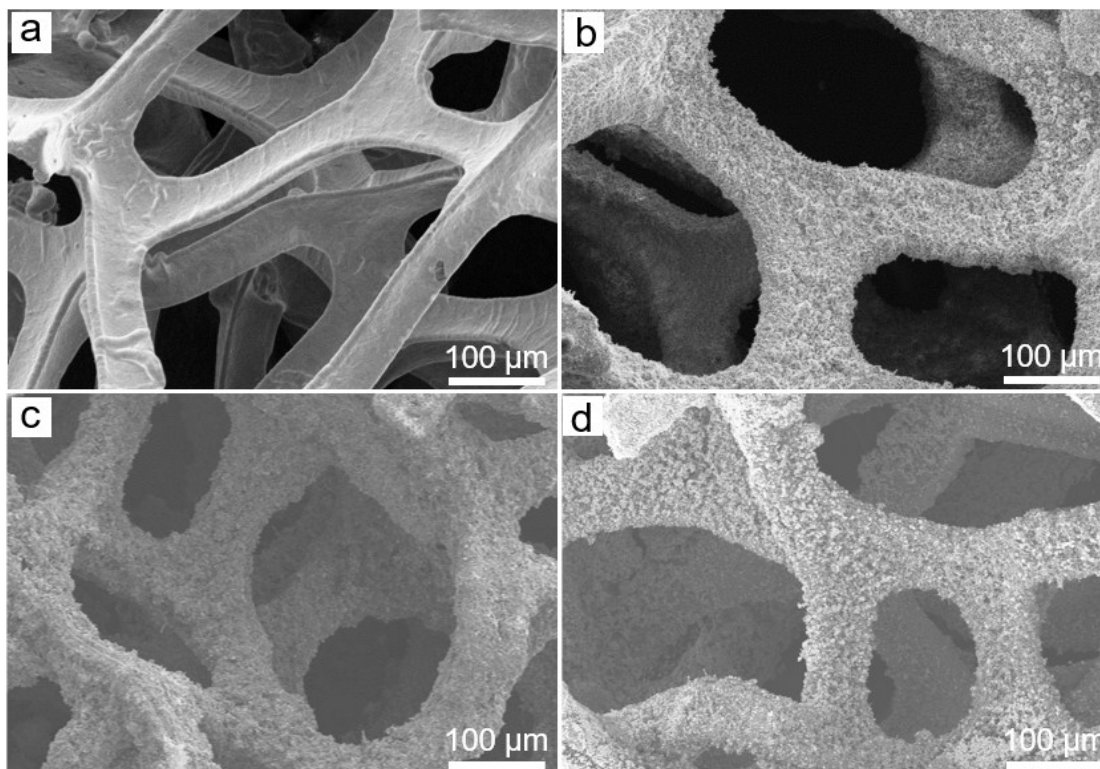


**Fig. S2** Low-magnification SEM images of NiO/Ni-foam-A prepared by hydrothermal treatment for 24 h at 100 °C, using different oxalic acid concentrations of (a) 0.06 mol L<sup>-1</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, (b) 0.1 mol L<sup>-1</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> and (c) 0.26 mol L<sup>-1</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>.

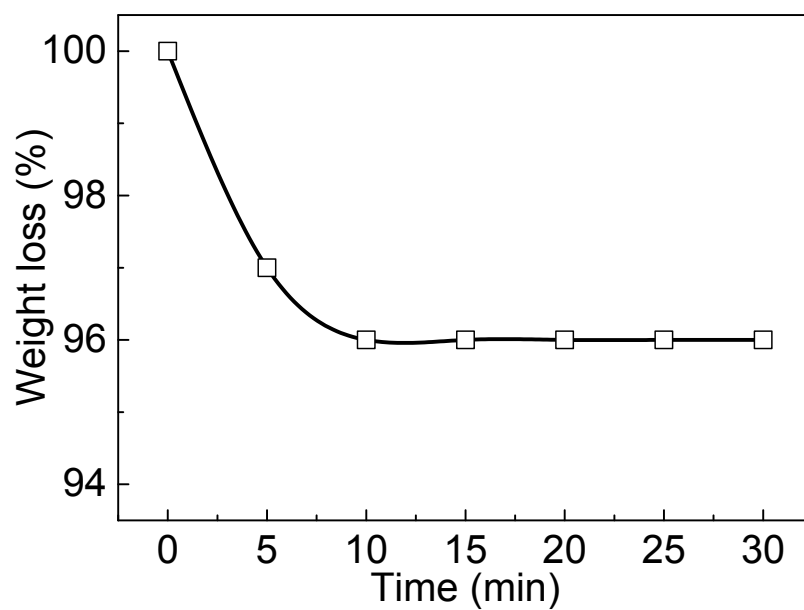


**Fig. S3** TG-DTA curve of the  $\text{NiC}_2\text{O}_4/\text{Ni-foam}$  sample.

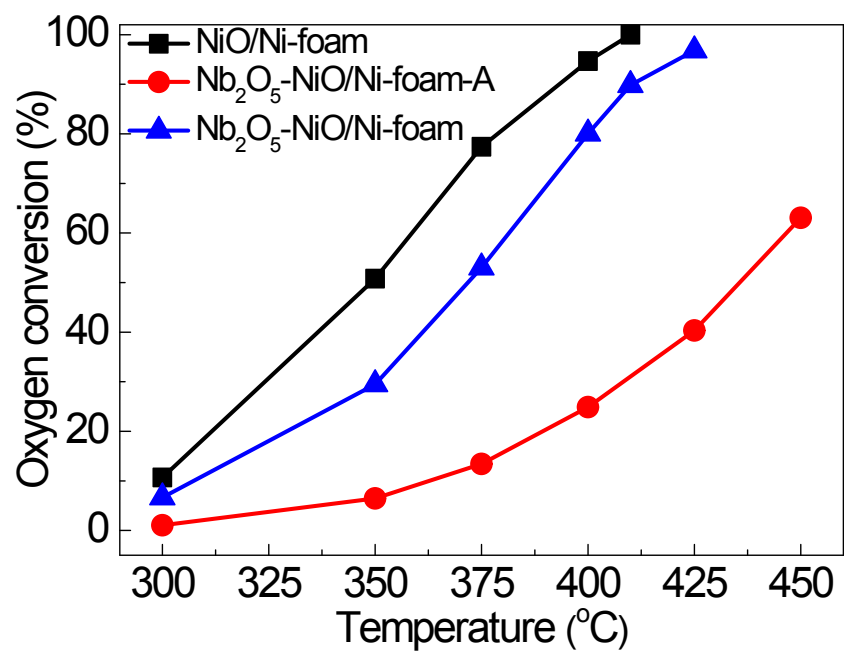




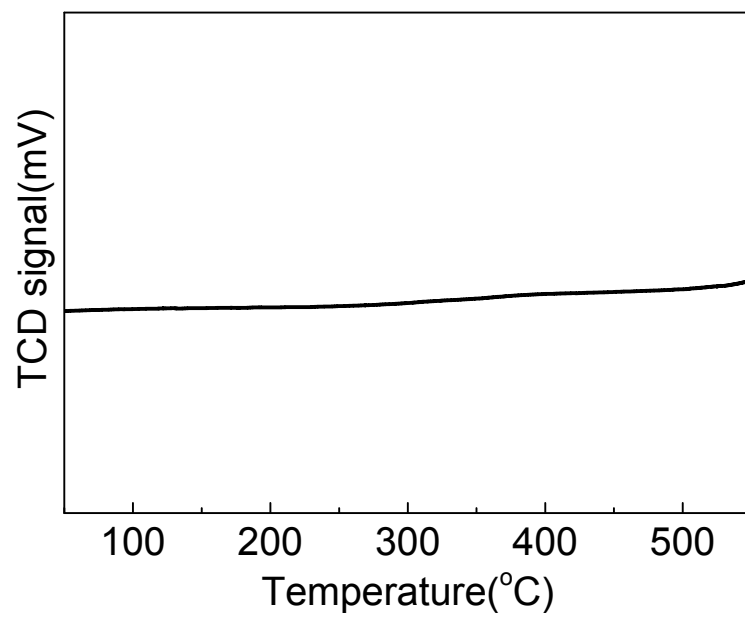
**Fig. S4** Low-magnification SEM images of (a) Ni-foam, (b)  $\text{NiC}_2\text{O}_4/\text{foam}$ , (c)  $\text{Nb}_2\text{O}_5\text{-NiO/Ni-foam}$  and (d)  $\text{Nb}_2\text{O}_5\text{-NiO/Ni-foam-A}$ .



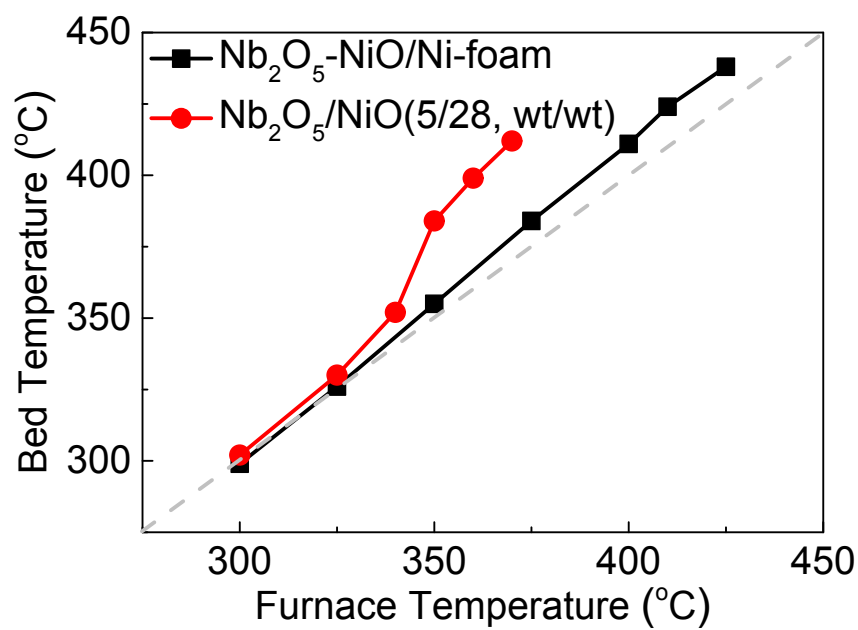
**Fig. S5** Adherence test of the  $\text{NiC}_2\text{O}_4/\text{Ni}$ -foam sample.



**Fig. S6** Oxygen conversion of the as-prepared catalysts. Reaction conditions:  $C_2H_6/O_2/N_2 = 1/1/8$ , GHSV =  $9000 \text{ cm}^3 \text{ g}^{-1} \text{ h}^{-1}$ .



**Fig. S7** H<sub>2</sub>-TPR profiles of the Nb<sub>2</sub>O<sub>5</sub>.



**Fig. S8** Temperature-rising of the Ni-foam structured catalyst  $\text{Nb}_2\text{O}_5\text{-NiO/Ni-foam}$  and the particulate counterpart  $\text{Nb}_2\text{O}_5\text{/NiO}$  (5/28, wt/wt).

## Part II. Additional discussion.

### 2.1. Effects of hydrothermal conditions on NiC<sub>2</sub>O<sub>4</sub> loading

To gain the optimal NiC<sub>2</sub>O<sub>4</sub> loading, a series of control experiments with varied hydrothermal temperature, hydrothermal time and oxalic acid concentrations were performed. The morphology and NiO loading were studied by SEM and TPR measurements, respectively. In order to easily determine the NiC<sub>2</sub>O<sub>4</sub> loading on Ni-foam, all the NiC<sub>2</sub>O<sub>4</sub>/Ni-foam samples were first calcined to transform into NiO/Ni-foam-A, of which NiO loading could be easily measured by H<sub>2</sub>-TPR.<sup>S1-S3</sup>

Fig. S1A shows that the NiO loading displays a volcano-shaped evolution behavior with the hydrothermal temperature and reaches a maximum NiO loading of 28 wt% at 100 °C, when fixing oxalic acid concentration at 0.2 mol L<sup>-1</sup> and hydrothermal time at 24 h. This observation indicates that 100-120 °C is beneficial for the growth of NiC<sub>2</sub>O<sub>4</sub>. Additionally, the NiO loading presents a pronounced increase with the oxalic acid concentration at the hydrothermal temperature of 100 °C and hydrothermal time of 24 h (Fig. S1B). However, when the oxalic acid concentration was further increased to 0.26 mol L<sup>-1</sup>, the Ni-foam framework is seriously etched and collapses (Fig. S2). Besides, the effect of hydrothermal time (6, 12, 18, 24 and 36 h) on the NiC<sub>2</sub>O<sub>4</sub> loading was investigated by fixing oxalic acid concentration at 0.2 mol L<sup>-1</sup> and hydrothermal temperature at 100 °C, but no higher NiO loading than that at the hydrothermal time of 24 h could be obtained owing to the limitation of the Ni-foam surface area (Fig. S1C). Therefore, the NiC<sub>2</sub>O<sub>4</sub>/Ni-foam sample with the highest NiC<sub>2</sub>O<sub>4</sub> loading and preferable Ni-foam framework could be prepared readily at an optimal

temperature of 100 °C in 0.2 mol L<sup>-1</sup> H<sub>2</sub>C<sub>2</sub>O<sub>4</sub> solution for 24 h.

## **2.2. Enhanced heat/mass transfer: Ni-foam-structured catalyst vs. powdered catalyst**

Table S4 shows the ODE reaction results catalyzed by the structured Nb<sub>2</sub>O<sub>5</sub>-NiO/Ni-foam and powdered Nb<sub>2</sub>O<sub>5</sub>/NiO (5/28, wt/wt) catalysts. Clearly, the Nb<sub>2</sub>O<sub>5</sub>-NiO/Ni-foam catalyst achieves higher ethylene productivity than the powdered counterpart (Table S4). Besides, the structured catalyst bed shows much lower temperature-rising (i.e., temperature difference between catalyst bed and reactor wall) than the powdered catalyst bed (Fig. S8). On the one hand, Ni-foam with enhanced thermal conductivity is essential to rapidly dissipate the great release of reaction heat, which favors a big reduction of “hotspot” temperature (Fig. S8). In our previous studies concerning the CO and/or CO<sub>2</sub> methanation reactions that are strongly exothermic, both experimental and CFD calculation results revealed that the Ni-foam structured catalysts also deliver much lower temperature-rising and more homogeneous temperature distribution than the powdered catalysts.<sup>S1-S3</sup> On the other hand, the unique flow pattern and enhanced mass transfer in the Ni-foam-structured catalyst bed are also central to the notion of increasing the activity, selectivity and productivity. Thus, it is not surprising that our Ni-foam-structured catalyst yields better ODE performance than the powdered counterpart.<sup>S1-S5</sup>

## References

- S1 Y. K. Li, Q. F. Zhang, R. J. Chai, G. F. Zhao, F. H. Cao, Y. Liu and Y. Lu, *Appl. Catal. A*, 2016, **510**, 216.
- S2 Y. K. Li, Q. F. Zhang, R. J. Chai, G. F. Zhao, Y. Liu and Y. Lu, *ChemCatChem.*, 2015, **7**, 1427.
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- S4 Z. Q. Zhang, J. Ding, R. J. Chai, G. F. Zhao, Y. Liu and Y. Lu, *Appl. Catal. A*, 2018, **550**, 151.
- S5 Z. Q. Zhang, L. P. Han, Q. F. Zhang, R. J. Chai, Y. K. Li, G. F. Zhao, Y. Liu and Y. Lu, *Catal. Commun.*, 2017, **88**, 90.