## Supporting Information

## Efficient upgrade of polystyrene plastics to nitriles through a catalytic

## oxidative amination process

Chengyang Sun, Xiaohui Liu, Yong Guo, Yanqin Wang\*

Shanghai Key Laboratory of Functional Materials Chemistry, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Shanghai 200237,

P. R. China.

E-mail: wangyanqin@ecust.edu.cn



Fig. S1 Alkaline promoting the oxidation activity. Reaction conditions: 0.2 g PS, 0.1 g  $NiO/TiO_2$ , 5 g H<sub>2</sub>O, 1 MPa Air, 200°C. \*: introduction of 0.3 g NaOH.



**Fig. S2** Activity evaluation using different nitrogen sources. Reaction conditions: 0.2 g PS pellets, 0.1 g NiO/CeO<sub>2</sub>, 5 g CH<sub>3</sub>CN, 0.5 MPa NH<sub>3</sub> or equimolar nitrogen of other nitrogen sources, the CO<sub>2</sub> and AcOH are also equimolar to the NH<sub>3</sub>, 2.5 MPa Air, 220°C, 2 h.



Fig. S3 Gas phase analysis by GC using TCD and FID (with a methane reformer).



**Fig. S4** Catalysts screening of benzamide dehydration reaction. Reaction conditions: 0.2 g benzamide, 0.1 g catalyst, 5 g CH<sub>3</sub>CN, 2 MPa N<sub>2</sub>, 220°C, 4 h. \*Introduction of 0.5 MPa NH<sub>3</sub>.



Fig. S5 Methods to move out the dissolved  $NH_3$  from the solution. The reflux was conducted under 80°C for 8 h. The evaporation was conducted using rotary evaporator to move out the CH<sub>3</sub>CN solvent then add new solvent in. Reaction conditions of the dehydration: the sample after the NH<sub>3</sub> removal treatment, 0.1 g NbOPO<sub>4</sub>, 2 MPa N<sub>2</sub>, 220°C, 4 h.



Fig. S6 GC/MS chromatogram of dehydration products. Reaction conditions: 0.2 g benzamide, 0.1 g NiO/CeO<sub>2</sub>, 0.1 g H<sub>2</sub>O, 2 MPa N<sub>2</sub>, 280°C, 4 h.



Fig. S7 Molecular weight distribution of the polystyrene samples measured by GPC.



**Fig. S8** Stability test of the NiO/CeO<sub>2</sub> catalyst. The catalyst was washed and dried before the next cycle. The refresh of catalyst was conducted under calcination at 500°C in air for 4 h. Reaction conditions: Step 1: 0.2 g PS pellets, 0.1 g NiO/CeO<sub>2</sub>, 5 g CH<sub>3</sub>CN, 0.5 MPa NH<sub>3</sub>, 2.5 MPa Air, 220°C, 2 h; Step 2: 2 MPa N<sub>2</sub>, 280°C, 4 h.



Fig. S9 TG curve of the used catalyst.



**Fig. S10** The partly over-oxidation of benzaldehyde to  $CO_2$ , analyzed by GC/MS and HPLC. Reaction conditions: 0.2 g benzaldehyde, 0.1 g NiO/TiO<sub>2</sub>, 5 g H<sub>2</sub>O, 1 MPa Air, 200°C, 2 h.



**Fig. S11** The amination product of benzaldehyde under a non-oxidative atmosphere, analyzed by GC/MS. Reaction conditions: 0.2 g benzaldehyde, 0.1 g NiO/CeO<sub>2</sub>, 5 g CH<sub>3</sub>CN, 0.5 MPa NH<sub>3</sub>, 2.5 MPa N<sub>2</sub>, 220°C, 2 h.



Fig. S12 GC/MS chromatogram of amination oxidation products.



Fig. S13 XRD patterns of the mentioned Ni-based catalysts.

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Entry	Sample	M <sub>w</sub> (Da)	PDI	
1	PS pellets	177873	2.05	
2	Culture dish	239342	2.35	
3	Weighing dish	228416	2.35	
4	PS foam	217162	2.22	

Table S1 Weight-average molecular weight  $(M_w)$  and polymer dispersity index (PDI) of polystyrene samples obtained by GPC measurements.

Table S2 Elementary composition of PS samples determined by Elemental analyzer.

Entry	Sample	C (wt%)	H (wt%)
1	PS-C <sub>8</sub> H <sub>8</sub> (Theoretical)	92.3	7.7
2	PS pellets	92.6	8.1
3	Culture dish	92.7	7.9
4	Weighing dish	88.6	7.9
5	PS foam	91.3	7.6