Electronic Supplementary Material (ESI) for RSC Advances. This journal is © The Royal Society of Chemistry 2015

Supplementary Material to

$Comparison \ of four \ different \ synthetic \ routes \ of \ Ni_2P/TiO_2-Al_2O_3 \ catalysts \ for$ $hydrode sulfurization \ of \ dibenzothiophene$

Ruchao Wei, Qingqing Zhu, Fei Han, Qingxin Guan, Wei Li*

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), Collaborative

Innovation Center of Chemical Science and Engineering (Tianjin), College of Chemistry,

Nankai University, Tianjin, 300071, China

^{*} Corresponding Author. Tel: +86-22-23508662; fax: +86-22-23508662. E-mail address: weili@nankai.edu.cn (W. Li).

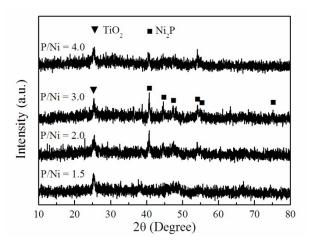


Fig. S1 XRD patterns of Ni-P/TiO₂-Al₂O₃ catalysts with different P/Ni ratios prepared by method II (Ni₂P loading = 30 wt%).

 $\label{eq:catalysts} \textbf{Table S1} \ \ \text{Textural properties and superficial P/Ni mole ratios of Ni-P/TiO_2-Al_2O_3}$ $\ \ \ \text{catalysts prepared by method II (Ni_2P \ loading = 30 \ wt\%)}$

Catalyst	S_{BET} (m^2/g)	Average pore size (nm)	Pore volume (cm ³ /g)	Superficial atomic ratio P/Ni
Ni-P/Ti/Al-II-1.5	31	3.8	0.05	2.96
Ni-P/Ti/Al-II-2.0	4	4.8	0.01	-
Ni-P/Ti/Al-II-3.0	3	4.8	0.01	3.18
Ni-P/Ti/Al-II-4.0	2	4.8	0.01	-

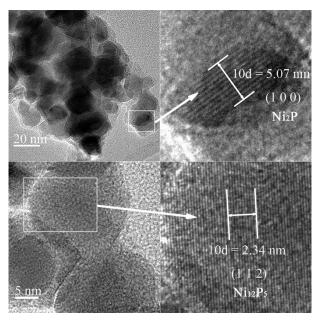


Fig. S2 High resolution TEM micrographs of the Ni-P/Ti/Al-II-1.5 catalyst.

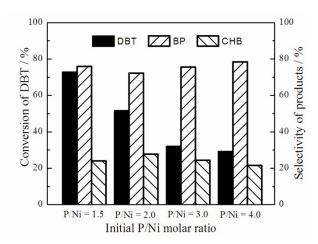


Fig. S3 HDS performance of Ni-P/TiO₂-Al₂O₃ catalysts with different P/Ni mole ratios prepared by method II (Ni₂P loading = 30 wt%). Reaction conditions: 583 K, 3.0 MPa, WHSV = $6 \, h^{-1}$, H₂/oil = $600/1 \, (v/v)$.

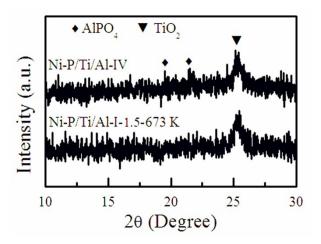


Fig. S4 Comparison of XRD patterns of the Ni-P/Ti/Al-I-1.5-673 K catalyst and Ni-P/Ti/Al-IV catalyst.

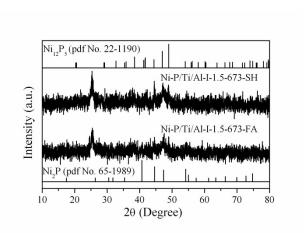


Fig. S5 XRD patterns of Ni-P/TiO₂-Al₂O₃ catalysts prepared using NiCl₂•6H₂O and NH₄H₂PO₂ as precursor with an initial P/Ni mole ratio of 1.5. Ni-P/Ti/Al-I-1.5-673-SH: prepared in static H₂, Ni-P/Ti/Al-I-1.5-673-FA: prepared in flowing Ar.

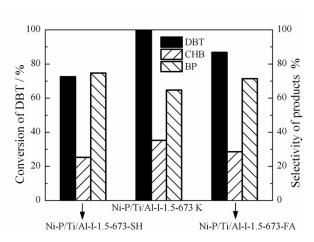


Fig. S6 Effect of preparation methods on the HDS performance of Ni-P/TiO₂-Al₂O₃ catalysts prepared using NiCl₂•6H₂O and NH₄H₂PO₂ as precursor with an initial P/Ni mole ratio of 1.5. Ni-P/Ti/Al-I-1.5-673-SH: prepared in static H₂, Ni-P/Ti/Al-I-1.5-673-FA: prepared in flowing Ar. Reaction conditions: 583 K, 3.0 MPa, WHSV = 6 h⁻¹, H₂/oil = 600/1 (v/v).

Table S2 Effects of Ni-P loadings and supports on the textural properties of various supported Ni-P catalysts prepared by method II (P/Ni mole ratio = 1.5)

Catalysts	S _{BET} (m ² /g)	Average pore size(nm)	Pore volume
Ni-P/Ti/Al-II-10%	123	3.8	$\frac{\text{(cm}^3/\text{g})}{0.17}$
Ni-P/Ti/Al-II-20%	93	3.8	0.12
Ni-P/Ti/Al-II-30%	31	3.8	0.05
Ni-P/Al ₂ O ₃ -II-30%	45	3.8	0.04

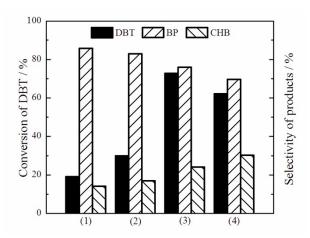


Fig. S7 HDS performance of various supported nickel phosphide catalysts prepared by method II (P/Ni = 1.5): (1) Ni-P/TiO₂-Al₂O₃, 10 wt%; (2) Ni-P/TiO₂-Al₂O₃, 20 wt%; (3) Ni-P/TiO₂-Al₂O₃, 30 wt%; (4) Ni-P/Al₂O₃, 30 wt%. Reaction conditions: 583 K, 3.0 MPa, WHSV = 6 h⁻¹, H₂/oil = 600/1 (v/v).