## Supporting Information for

## Preparation of supported hydrodesulfurization catalysts with enhanced performance using Mo-based inorganic-organic hybrid nanocrystals as a superior precursor

Wei Han<sup>a,b</sup>, Pei Yuan<sup>a\*</sup>, Yu Fan<sup>a</sup>, Gang Shi<sup>b</sup>, Haiyan Liu<sup>a,b</sup>, Danjiang Bai<sup>c</sup>, Xiaojun Bao<sup>b\*</sup>
<sup>a</sup>State Key Laboratory of Heavy Oil Processing, China University of Petroleum, No. 18 Fuxue Rd., Changping, Beijing 102249, P. R. China
<sup>b</sup>The Key Laboratory of Catalysis, China National Petroleum Corporation, China University of Petroleum, No. 18 Fuxue Rd., Changping, Beijing 102249, P. R. China
<sup>c</sup> Jinao (Hubei) Science & Technology Chemical Industry Co., Ltd., Zhanghua Beilu, Qianjiang City, Hubei 433132, P. R. China

<sup>&</sup>lt;sup>\*</sup> Corresponding authors. E-mail: yuanpei@cup.edu.cn, baoxj@cup.edu.cn; Tel.: +86(0) 10 89732338, +86(0) 10 89734836; Fax: +86(0) 10 89734979.



*Fig. S1.* (a) XRD patterns of Mo/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalysts with different MoO<sub>3</sub> loadings prepared via the HNC-assisted method and (b) the change of the surface areas of the catalysts prepared via the different methods as a function of MoO<sub>3</sub> loading. 1, the HNC-assisted method; 2, the conventional impregnation method. From Fig. S1a, we can conclude that the HNC-assisted method not only facilitates the dispersion of MoO<sub>3</sub> on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> but also increases MoO<sub>3</sub> loading, endowing the resulting catalysts with a plenty of potential active sites to reactants. From Fig. S1b, we can clearly see that HA-CATs prepared via the HNC-assisted method have much higher surface areas than IM-CATs with the MoO<sub>3</sub> loading ranging from 0 to 30 wt.%. Meanwhile, with the increasing MoO<sub>3</sub> loading in HA-CATs, the decreases in the surface areas of the resulting catalysts prepared via the HNC-assisted method and MoO<sub>3</sub> loading the resulting catalysts are very small, distinctly different from those of IM-CATs, indicating that the catalysts prepared via the HNC-assisted method possess higher dispersion, more open pore channels and higher accessibility to reactants.



*Fig. S2.* HRTEM images of the catalysts Ni-HA-CAT (a) and Ni-IM-CAT (b) after 300 h hydrotreating reaction using the real coking diesel as feedstock; average length and average stacking number layer of  $MoS_2$  (c) on the two sulfided catalysts after 300 h hydrotreating reaction. Compared with the conventional bimetallic catalyst Ni-IM-CAT, the HNC-derived catalyst Ni-HA-CAT after reaction still kept much shorter slabs, higher stacking layer numbers and thereby possessed better dispersion of  $MoS_2$  nanoparticles and more exposed active sites to reactant molecules.

Electronic Supplementary Material (ESI) for Journal of Materials Chemistry This journal is O The Royal Society of Chemistry 2012



*Fig. S3.* The DBT HDS activity of Ni-HA-CAT (a) and Ni-IM-CAT (b) at the LHSVs of 5, 10, 15, 20, 25  $h^{-1}$ . Compared with the conventional bimetallic catalyst Ni-IM-CAT, the HNC-derived catalyst Ni-HA-CAT possesses much better stability in its catalytic activity with the increasing LHSV up to 25  $h^{-1}$ .