Electronic Supplementary Information

Carbon heterogeneous surface modification on mesoporous TiO_2-supported catalyst and its enhanced hydrodesulfurization performance

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Materials

Ammonium heptamolybdate ($(NH_4)_6Mo_7O_{24}$•$4H_2O$, Sinopharm Chemical Reagent Co., Ltd), nickel nitrate ($Ni(NO_3)_2$•$6H_2O$, Sinopharm Chemical Reagent Co., Ltd), dichloromethane (CH_2Cl_2, Shanghai Linfeng Chemical Reagent Co., Ltd), phenyl-phosphonic acid ($C_6H_7O_2P$, Aldrich), actone (C_3H_6O, Suzhou Henghuixiang Chemical), hydrochloric acid (HCl, Wuhan Gehua Co., Ltd), decalin ($C_{10}H_{18}$, Sinopharm Chemical Reagent Co., Ltd), carbon bisulfide (CS_2, Sinopharm Chemical Reagent Co., Ltd), dibenzothiophene ($C_{10}H_8S$, Acros Organics). All chemicals were used as received.

Mesoporous TiO_2 was prepared from potassium titanate ($K_2Ti_2O_5$) according to our previous work.[1] In short, $K_2Ti_2O_5$ was ion exchanged with HCl aqueous solution (0.1 M) to be hydrated titanate ($H_2Ti_2O_5$). Then, the calcinations of $H_2Ti_2O_5$ were performed in a muffle oven at 550 ^oC to obtain mesoporous TiO_2. The structural data of mesoporous TiO_2 were showed in Table 1.

Preparations

1. Supports

The surface modified TiO_2 support was prepared in two main steps. In the first step, 1.131 g of phenyl-phosphonic acid (PPA) was dissolved in 60 mL of CH_2Cl_2, and 3 g of TiO_2 was added in this solution under vigorous stirring at room temperature. After stirring for 24 h, the precipitation was filtered and washed with 500 mL of water/acetone (50/50 by volume) solution, and then dried in oven (100 ^oC, 12 h). The as-synthesized sample was denoted as PPA/TiO_2. In the second step, the PPA/TiO_2 was thermally treated at 500 ^oC for 8 h under N_2 atmosphere. The obtained powder was denoted as C/TiO_2.

2．Catalysts

The obtained supports were used to prepare MoNi catalysts with 6 wt% MoO_3 and 1.56 wt% NiO by typical incipient wetness impregnation using an aqueous solution of $(NH_4)_6Mo_7O_{24}\bullet 4H_2O$ and $Ni(NO_3)_2\bullet 6H_2O$. The impregnated power were dried (100 ^oC, 12 h), and calcined (500 ^oC, 2 h) under N_2 atmosphere to obtain the MoNi catalysts. The unmodified catalyst was denoted as MoNi/TiO_2, and MoNi/C/TiO_2 represented the catalyst with surface modification.

3．Preparation of control samples

In comparison with MoNi/TiO_2 and MoNi/C/TiO_2, we also prepared three control samples. Corresponding preparations of these samples were described as follows:

1) MoNi/P/TiO_2: the corresponding support of catalyst, P/TiO_2, was obtained by thermal treatment of PPA/TiO_2 in flowing air at 500 ^oC for 4 h to remove the carbon species of modifier. Other preparation steps of MoNi/P/TiO_2 catalyst were the same as those of MoNi/C/TiO_2.

2) MoNi/C(hi)/TiO_2: the degree of surface modification of MoNi/C(hi)/TiO_2 catalyst was higher than that of MoNi/C/TiO_2 catalyst. PPA solution was mixed with TiO_2 in a high-pressure vessel of 100 mL for solvothermal treatment at 150 ^oC for 24 h. FT-IR results (not shown) of this PPA/TiO_2 sample didn't show the bands corresponding to adsorbed water in the profile. It indicated that most of TiO_2 surface were occupied by PPA molecules. Calcinations process was also carried out under N_2 atmosphere at 500 ^oC for 8 h. Other not-mentioned preparation procedures of MoNi/C(hi)/TiO_2 catalyst were in accordance with that of MoNi/C/TiO_2.

3) MoNi(hi)/TiO_2: Except for MoO_3 and NiO content, the preparation procedure of MoNi(hi)/TiO_2 catalyst was identical to that of unmodified catalyst MoNi/TiO_2. The load of

MoO_3 and NiO of this catalyst was 11 wt% and 2.86 wt%, respectively, which was close to that of industrial catalysts.[2] There were no characteristic peaks ascribed to MoO_3 and NiO observed in XRD pattern (not shown), suggesting both MoO_3 and NiO were also dispersed well in MoNi(hi)/TiO_2 catalyst.

To figure out the difference of catalysts, some characteristics of catalysts were summarized in following **Table S1**.

Table S1 Chemical properties of all catalysts

Samples	Modification situation	Content of MoO_3, NiO	Modification species $^{\alpha}$	others
$MoNi/C/TiO_2$	Modified	6 wt%, 1.56 wt%	C, P	/
$MoNi/TiO_2$	unmodified	6 wt%, 1.56 wt%	/	/
$MoNi/P/TiO_2$	Modified	6 wt%, 1.56 wt%	P	/
$MoNi(hi)/TiO_2$	unmodified	11 wt%, 2.86 wt%	/	/
$MoNi/C(hi)/TiO_2$	Modified	6 wt%, 1.56 wt%	C, P	Higher degree of modification

α: C represents the modification species containing carbon elements, and P suggests the phosphorous modification species.

Characterizations

Thermo-gravimetric (TG) analysis was performed on a Model SDT 2960 (TA, America) instrument. The measure was conducted with the temperature of 35~950 °C at a rate of 10 °C/min under air atmosphere.

Raman Spectra were obtained using a Horiba HR 800 spectrometer, equipped with a CCD camera detector. As a source of excitation the 514 nm line of a Spectra Physics 2018 Argon/Krypton Ion Laser system were focused through an Olympus BX41 microscope equipped with a 50 magnification objective. The laser power never exceeded 5 mW for each sample.

X-ray Photoelectron Spectroscopy (XPS) analysis was performed in an ESCALAB 250 spectrometer (ThermoFisher Scientific, USA) equipped with Al Kα radiation operated at 300 W. The shift of binding energy was corrected using the C 1s level at 284.9 eV as an internal standard.

The content of phosphorus in terms of the corresponding oxides in the samples was determined on an ADVANT'XP X-ray fluorescence (XRF) analyzer (ARL Co., Switzerland).

Nitrogen adsorption/desorption at -196 °C were performed by using the TriStarII 3020M system (Micromeritics, USA). Surface area was calculated by BET method (S_{BET}), pore volume (V_P) was determined by nitrogen adsorption at a relative pressure of 0.99. Pore size distribution was found from adsorption isotherms by Barrett-Joyner-Halenda (BJH) method.

X-ray diffraction (XRD) patterns of the samples were collected on a D8 diffractometer (Bruker, Switzerland) equipped with a Cu Kα radiation (λ = 1.5406 Å). The diffractograms were recorded for 2θ values between 5^o and 60^o at a rate of 0.2 s $step^{-1}$. Phase identification was carried out by comparison with the JCPDS database.

H_2S-temperature-programmed desorption (H_2S-TPD) tests were carried out on a BELCAT-A apparatus (Ankersmid, Netherlands). As-made (dried) samples were put in a quartz reactor. First, each sample, about 0.333 g of material with 20~40 mesh, was pretreated from room temperature to 300 °C at a rate of 10 °C min^{-1} and then cooled down to room temperature in a pure He flow. Then, H_2S was adsorbed at 35 °C for 2 h using a mixture gas of 5 vol% H_2S/He, and subsequently the sample was purged by a flowing pure He stream to remove excessive and weakly adsorbed H_2S. Finally, the sample was heated to 600 °C at a rate of 10 °C min^{-1} in a pure He flow and desorption pattern was recorded.

Temperature-programmed reduction (TPR) experiments were conducted by using the TP-5000 equipment (Tianjin Xianquan Co., Ltd., China). The test temperature was increased up to 600 °C at a rate of 10 °C/min, and the gas mixture of 10 vol. % H_2/Ar was introduced at 20 mL/min into the quartz reactor and was also used as a reference gas.

The morphology of the active phases on sulfided catalysts was characterized by high-resolution transmission electron microscopy (HRTEM) conducted on a JEM-2010 UHR

(JEOL Co., Japan) at 200 kV. The catalysts to be measured were ultrasonically dispersed in ethanol and testing samples were prepared by dropping the dispersed suspensions on carbon-coated copper grids.

Catalyst evaluation

HDS performance of catalysts was evaluated in a continuous flow, fixed bed Micro-reactor. The catalyst was placed in the middle of the reactor while the rest empty volume was filled with quartz sand. Before the reaction, the catalyst was submitted to in situ sulphidation, using a solution of 3 vol% CS_2/decalin. After 10 h of sulphidation, the pump system was changed to inject a decalin solution of 1 wt% Dibenzothiophene (DBT) into the reactor. Reaction temperature, pressure, feed WHSV and H_2/feed ratio were 300 ^{o}C, 2 MPa, 6 h^{-1} and 600 Nm^3 m^{-3}, respectively. During each run, products were sampled periodically every hour and identified by a gas chromatography equipped with a flame ionization detector and a 30 m OV-101 capillary column.

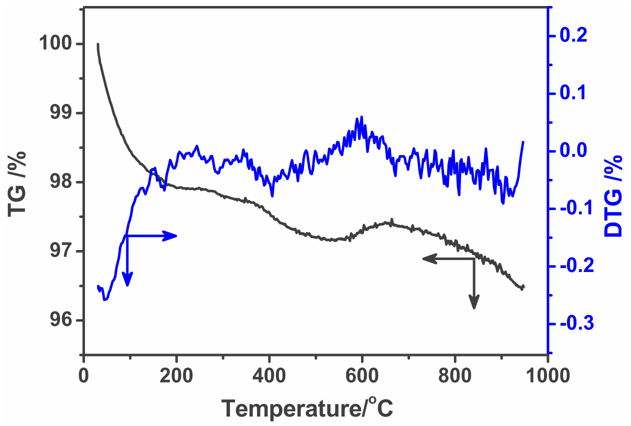

Fig. S1 TG and DTG curves of C/TiO_2

As shown in Fig. S1, there are many overlapped peaks observed in the DTG curve, which are assigned to the mass changes of various species. The process of mass change of C/TiO_2 contains evaporation of physical-absorbed H_2O, desorption of hydroxyl groups, oxidation of phosphorus species, oxidation of carbon species, volatilization of phosphorus oxide, and so on. These processes may occur simultaneously at one certain temperature range. Thus, it is difficult to confirm the accurate mass loss of carbon species. Generally, the oxidation of carbon species occurs at 400~600 °C.[3] As shown in the TG curve of Fig S1, the mass loss at 400~600 °C is less than 1 wt%. Thus, we can qualitatively confirm the content of carbon species of C/TiO_2 is less than 1 wt%.

Table S2 The P_2O_5 content characterized by XRF

Sample	*Content of P_2O_5 (wt%)*
PPA/TiO_2	**1.10**
C/TiO_2	**1.09**

According to the XRF results, we can estimate the extent of surface modification over C/TiO_2. Table S2 shows that the P_2O_5 content of C/TiO_2 is 1.09%, which is similar to that of PPA/TiO_2. This indicates the phosphorus element can't be lost by way of evaporation during the thermal process. Therefore, we could indirectly know how many surface area of C/TiO_2 are modified according to the content of phosphorus element. Occupied area of a PPA molecule has been assumed to 0.24 nm^2 as reported in the literature.[4] As following formula, we can calculate that 29% of TiO_2 surface are occupied by the modified species:

$$\text{Degree of modification} = N_P \times N_A \times S_{PPA} / S_{C/TiO_2} \times 100\%$$

$$= \frac{(m \times w_{P_2O_5} \div M_{P_2O_5} \times 2) \times N_A \times S_{PPA}}{S_{C/TiO_2} \times m} \times 100\%$$

(Three new parameters m, $w_{P_2O_5}$ and $M_{P_2O_5}$ in the formula represent the mass of C/TiO_2, the weight percent of P_2O_5 and the molar mass of P_2O_5.)

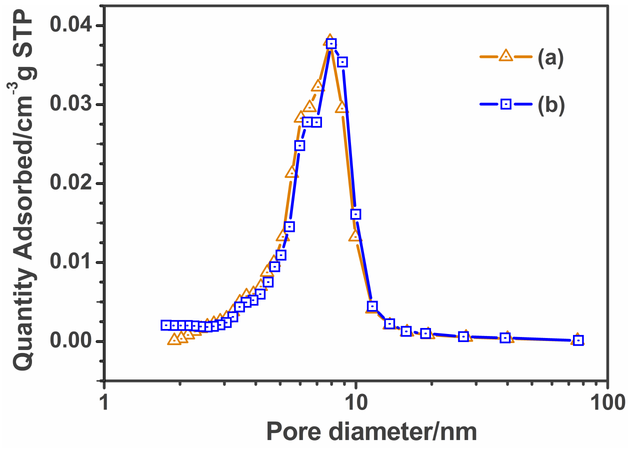

Fig. S2 Pore size distribution of C/TiO_2 (a) and TiO_2 (b)

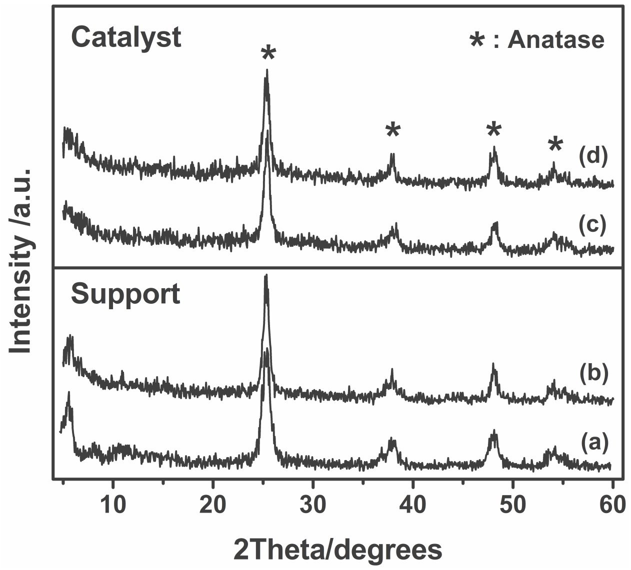

Fig. S3 XRD patterns of C/TiO_2 (a), TiO_2 (b), $MoNi/C/TiO_2$ (c) and $MoNi/TiO_2$ (d)

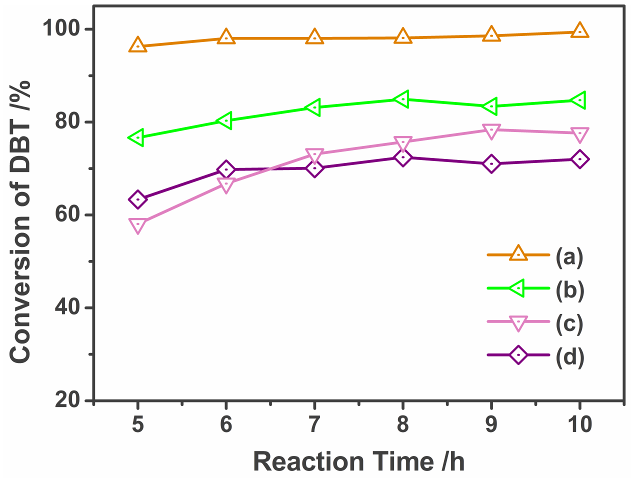

Fig. S4 HDS performance over various catalysts

(a) MoNi/C/TiO_2, (b) MoNi(hi)/TiO_2, (c) MoNi/C(hi)/TiO_2, (d) MoNi/P/TiO_2

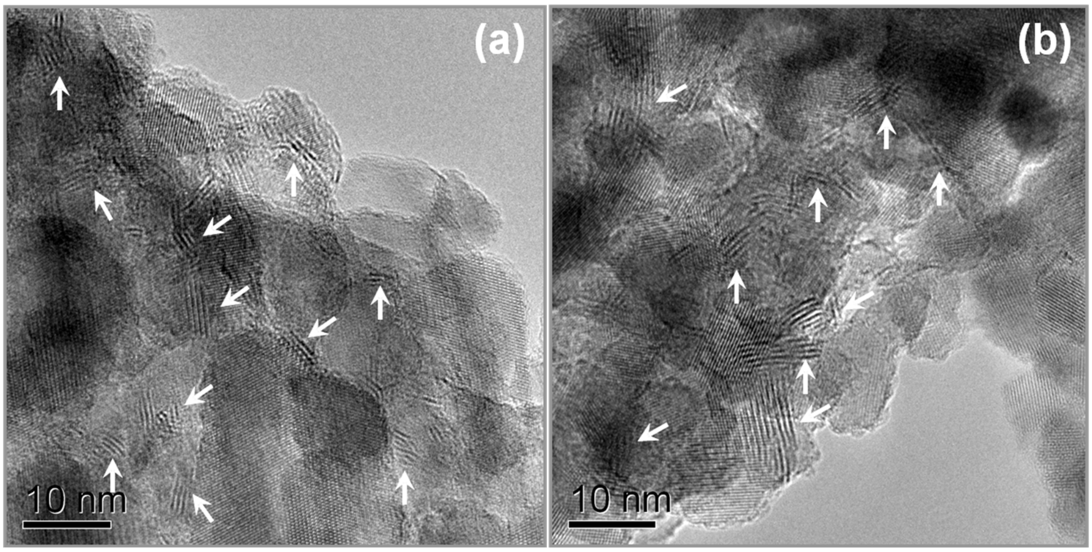

Fig. S5 HRTEM images of sulfide catalyst

(a) Modified catalyst MoNi/C/TiO_2; (b) Unmodified catalyst MoNi/TiO_2

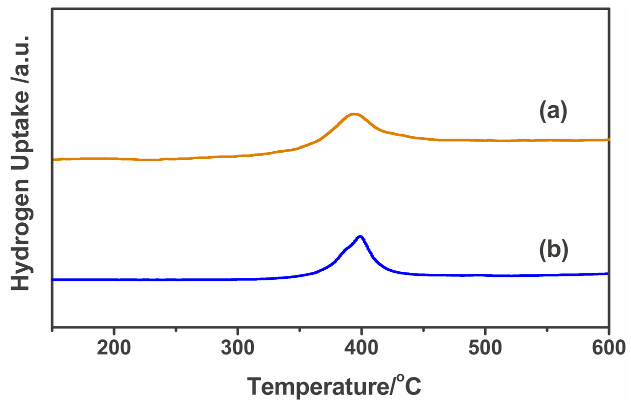

Fig. S6 TPR patterns of various catalysts

(a) modified catalyst $MoNi/C/TiO_2$; (b) unmodified catalyst $MoNi/TiO_2$

There is one obvious reduction peak at around 400 °C observed in the pattern of $MoNi/C/TiO_2$ and $MoNi/TiO_2$, respectively, which is assigned to the reduction of Mo^{6+} to Mo^{4+}.[5] The temperature of of reduction peak of $MoNi/C/TiO_2$ is similar to that of $MoNi/TiO_2$, which indicates that both of them have a similar interaction between active species and support.

References

1. M. He, X. H. Lu, X. Feng, L. Yu and Z. H. Yang, *Chem. Commun.*, 2004, 2202.
2. J. A. Toledo-Antonio, M. A. Cortes-Jacome, C. Angeles-Chavez and J. Escobar, *Appl. Catal. B-Environ.*, 2009, **90**, 213.
3. L. Lu, Y. Zhu, F. Li, W. Zhuang, K. Y. Chan and X. Lu, *J. Mater. Chem.*, 2010, **20**, 7645.
4. U. Lafont, L. Simonin, M. Gaberscek and E. M. Kelder, *J. Power Sources*, 2007, **174**, 1104.
5. J. A. Mendoza-Nieto, I. Puente-Lee, C. Salcedo-Luna and T. Klimova, *Fuel*, 2012, **100**, 100.