Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Improving Hydrodesulfurization Performance of Sulfur-resistant Intermetallic Ni_2Si Based on MOF-derived Route

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Table of Contents

Experimental

Reagents and Equipment: 2, 5-Dihydroxyterephthalic acid (H_4DOT) (98.0% Aladdin), nickel nitrate hexahydrate (99.0% Kermel), cobalt nitrate hexahydrate (98.0% Kermel), dimethyldichlorosilane (96.0% Aladdin), NaOH (96.0% Kermel), N, N-dimethylformamide (DMF) (99.7% Kermel), methanol (MeOH) (99.5% Kermel), ethanol (EtOH) (99.7%, Kermel), dibenzothiophene (98.0% J&K Chemicals), decalin (98.0% Sinopharm), Octane (98% Guangfu) were purchased and used without further purification. Argon (99.999%), hydrogen (99.999%) and nitrogen (99.999%) were purchased from dalian Institute of Chemical Physics. DI water was lab-synthesized. A domestic microwave oven (WBFY-201) operated at 2.45GHz with a power of 800 W was used for synthesis.

Synthesis of MOF-74: In a typical synthesis, H_4DOT (0.15 g), nickel nitrate hexahydrate or cobalt nitrate hexahydrate (0.66 g) were treated in ultrasonic and dissolved in 50 mL DMF, 3 mL EtOH, and 3 mL H_2O in a 100-mL beaker. This beaker was sealed tightly and placed in an isothermal oven at 120 ^oC for 20 h for the completion of the solvothermal reaction. The resulting MOF-74 precipitates were washed with H_2O and MeOH for three times, and finally dried under vacuum at 80 ^oC for 24 h.[1]

Synthesis of M/C (M=Ni and Co) samples: The M/C was prepared by thermolysis of MOF-74. 0.5 g of MOF-74 was pyrolysis at 600 ^oC for 4 h under argon atmosphere. The temperature was raised from room temperature to the target temperature at a heating rate of 5 ^oC/min.

Synthesis of M_2Si/C (M=Ni and Co) catalysts: The M_2Si/C (M=Ni and Co) was synthesized by microwave-assisted method. An amount of M/C (M=Ni and Co) precursors were loaded in the quartz tube and kept in argon atmosphere to exclude the air. Subsequently organosilane ($Cl_2Si(CH_3)_2$) was introduced to the reaction by using argon (40 sccm) as the carrier gas that flowed through a bubbler containing organosilane and maintained at 0 ^{o}C. After 30 minutes for the deposition of $Cl_2Si(CH_3)_2$, the tube was microwave processed for 5 minutes. The M_2Si/C (M=Ni and Co) was prepared after processed three-time cycles.

Characterization: The prepared samples were dissolved in aqua regia and the chemical compositions (Co, Ni, and Si) were determined by inductively coupled plasma optical emission spectroscopy (ICP-OES) and the contents of C, H, and N were measured by elemental analysis with a vario EL III. Thermogravimetric/derivative thermogravimetric (TG/DTG) experiments were performed on a Mettler Toledo TGA/SDTA851 thermogravimetric analyzer. XRD patterns were recorded on a Rigaku D/Max-RB diffractometer with a Cu Kα monochromatized radiation source, operated at 40 KV and 100 mA and Raman measurements were carried out on a micro-Raman spectrometer (Renishaw England) with a 532 nm Ar laser. SEM was performed using a JEOL JSM-5600LV SEM from FEI Company, equipped with an energy-dispersive X-ray (EDX) analyzer and TEM images of $Ni_2Si@C$ were obtained was performed using a T2-Tecnai F30 transmission electron microscope (accelerating voltage 200 kV) using high-resolution imaging. The X-ray photoelectron spectra (XPS) were obtained on an ESCALAB250 (Thermo VG, USA) spectrometer with Al Kα (1486.6 eV) radiation with a power of 150 W. Nitrogen physisorption was implemented for obtaining the BET surface areas, pore volumes, and pore size distributions of the catalysts (approximately 0.1 g sample) at liquid N_2 temperature with an autosorb iQ automated gas sorption analyzer.

Catalytic evaluation： The as-prepared catalysts were treated by 5.0 mol/L NaOH solution at 50 °C for 5 h to etch the presumable SiO_x passivation layer.[2] The HDS of DBT was performed in a conventional fixed-bed reactor with at a total pressure of 3.0 MPa H_2. 200 mg catalyst mixed well with 5.0 mL quartz sands (60-80 mesh) was placed into the center of the reactor and was reduced in situ with a H_2 flow of 40 mL/min at 400 °C for 2 h. After the reduction, the reactor was adjusted to the test temperature and the feedstock was fed into the reaction system by a high-pressure pump at a certain flow rate. The liquid reactant was composed of 0.5 wt.% octane (as internal standard), 0.3 wt.% DBT reactant, and decalin as solvent. The temperature and contact time was varied for achieved the catalytic activity. The products during a sampling period were collected and analyzed by a gas chromatograph (Agilent 7890F) and a SE-54/52 capillary column. The selectivity to BP is used as the benchmark to present the selectivity to the DDS pathway over the catalysts, and ($1\text{-}Sel_{BP}$) is used to calculate selectivity to the HYD pathway.

The space velocity (SV) was evaluated by the formula as: SV = $Q\rho/m$

where Q is the flow of liquid reactant, ρ is the density of the liquid reactant, m is the weight of catalyst (0.2 g).

The contact time (τ) was evaluated by the formula as: $\tau = 1/SV$

Table S1 The element content of as-prepared Ni_2Si/C and Co_2Si/C samples.

Sample	Elements composition (at.%)					
	C[a]	H[a]	N[a]	Co[b]	Ni[b]	Si[b]
Ni_2Si/C	35.82	20.30	2.14	-	18.69	23.05
Co_2Si/C	32.65	18.66	1.41	21.19	-	26.09

[a] Measured by elementary analysis. [b] As determined by the ICP-OES.

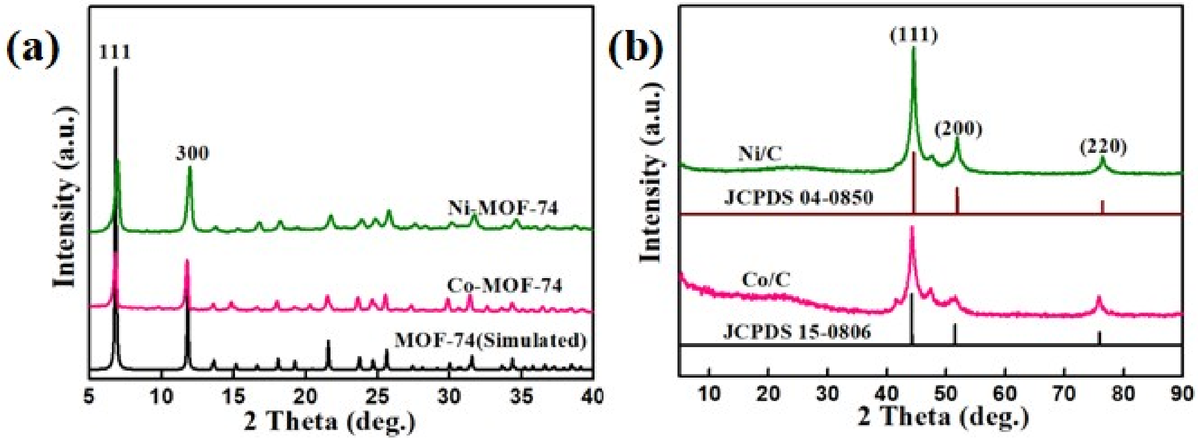

Fig. S1 XRD patterns of M-MOF-74 (a) and M/C (b) (M=Ni/Co).

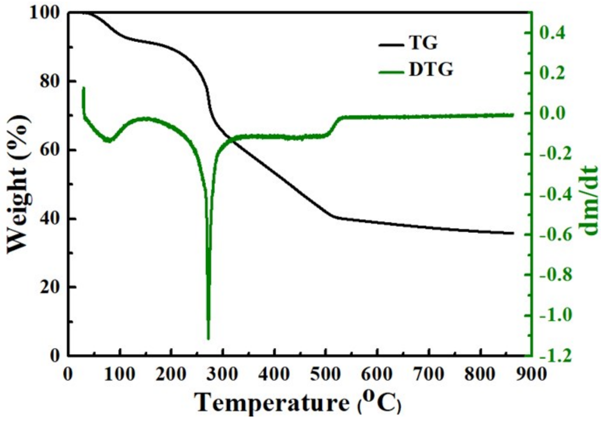

Fig. S2 TG-DTG curves of Ni-MOF-74.

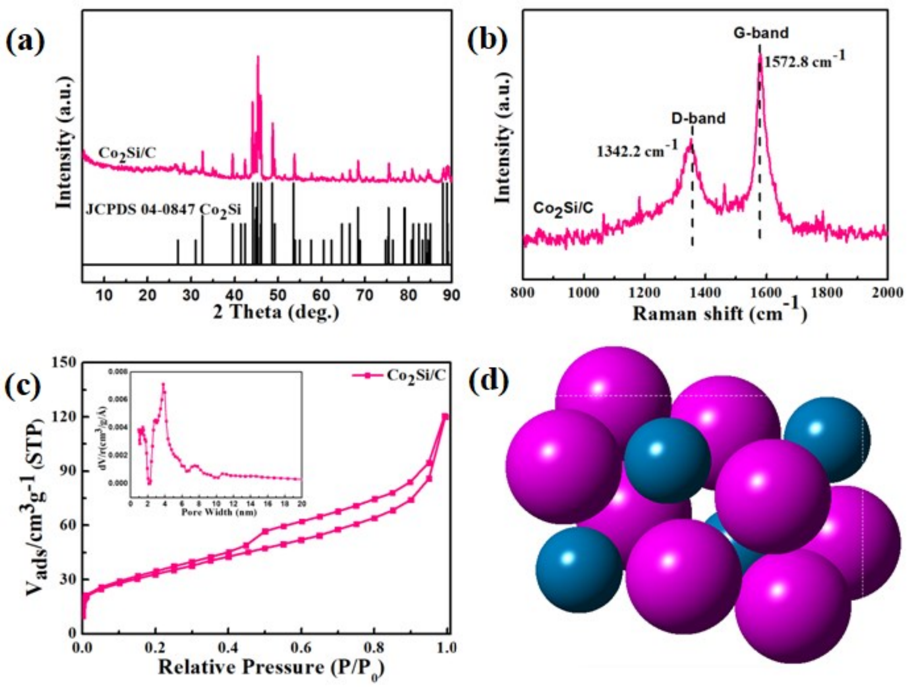

Fig. S3 (a) XRD pattern, (b) Raman spectrum, (c) Nitrogen adsorption-desorption isotherms at 77 K and corresponding pore size distribution curves inserted in (c), and (d) crystal structure of Co$_2$Si/C sample.

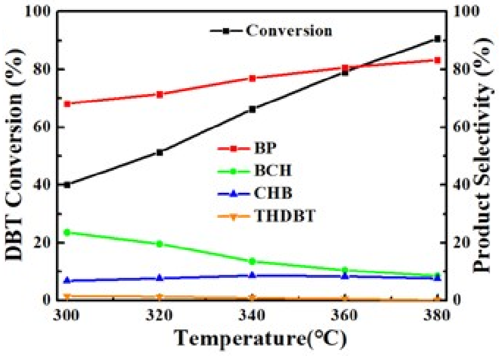

Fig. S4 DBT conversion and product selectivity versus temperature over Ni_2Si/C catalysts (reaction conditions: 0.2 g catalysts, 3 MPa H_2, contact time 2.84 min)

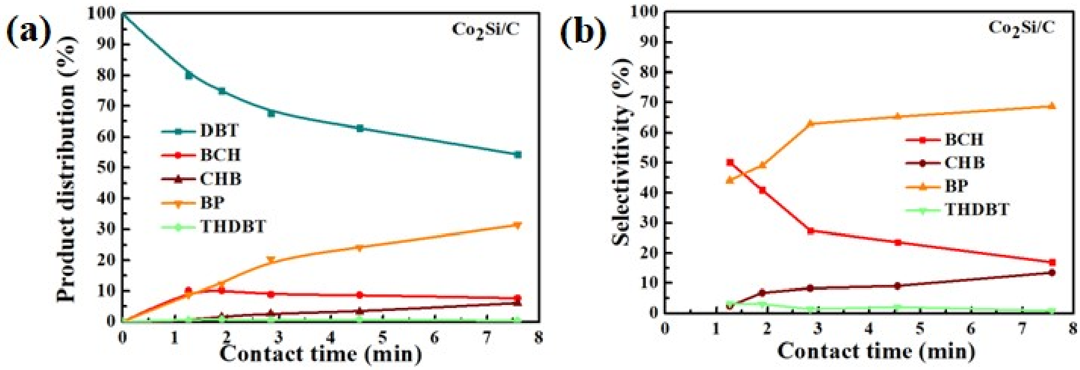

Fig. S5 Product distribution and selectivity of the HDS of DBT versus the contact time at 3 MPa H_2 and 340 °C over the Co_2Si/C catalyst.

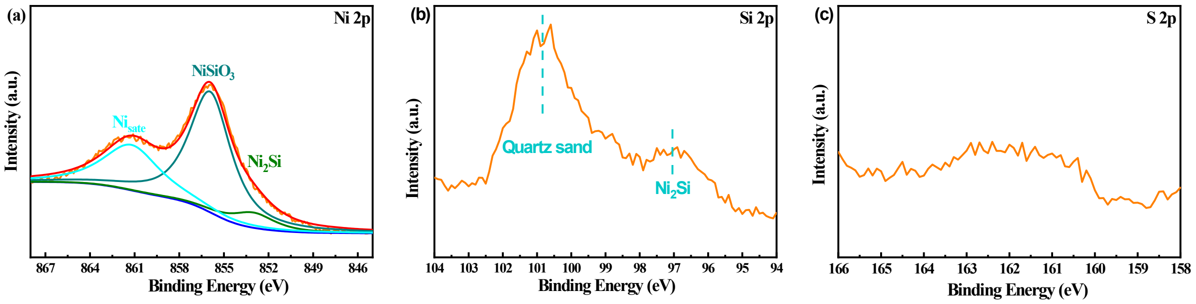

Fig. S6 XPS spectra for the spent Ni_2Si/C catalyst after 120 h: (a) Ni 2p core level spectra, (b) Si 2p core level spectra, (c) S 2p core level spectra.

References

1 L. Wang, H. Deng, H. Furukawa, F. Gándara, K. Cordova, D. Peri, and O. Yaghi, *Inorg. Chem.*, 2014, **53**, 5881-5883.

2 K. Yang, X. Chen, L. Wang, L. Zhang, S. Jin, and C. Liang, *ChemCatChem*, 2017, **9**, 1337-1342.