Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information

High Sulfur Tolerance of Ni-Si Intermetallics as Hydrodesulfurization Catalysts

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Computational Details

In this work, the adsorption of H_2S and electronic structure of Ni (111) and $NiSi_2$(111) surfaces were studied by first-principles based calculations using the Vienna ab initio Simulation Package (VASP).[S1-S4] During the calculations, the ion cores were described in projector-augmented wave (PAW) scheme.[S5] Spin-polarized Perdew-Burke-Ernzerhof (PBE) functional within the formulation of gradient approximation (GGA) was used to handle the exchange and correlations.[S6] A kinetic energy cutoff of 300 eV was used to study the clean Ni(111), $NiSi_2$(111), and H_2S absorbed structures. The integration of the Brillouin zone was conducted with a $4 \times 4 \times 1$ Monkhorst-Pack grid centered at Γ-point.[S7] For the structures reported in this work, all atoms were fully relaxed until the forces were reduced below 1×10^{-2} eV/Å.

The bulk lattice parameters of Ni and $NiSi_2$ are obtained as 3.52 Å and 5.44 Å, respectively. These results are comparable with the experimental values of a=3.52 Å for Ni and a=5.43 Å for $NiSi_2$, and previous DFT results.[S8-S9] Based on these, hexagonal surface slabs are constructed to mimic the surface chemistry of Ni and $NiSi_2$ surfaces. The Ni (111) surface was represented by a 7-layer slab with periodic boundary conditions in the two directions parallel to the surface. In order to ensure the decoupling of the consecutive slabs, a 15 Å thick vacuum region was employed. A (3×3) surface unit cell with 9 atoms in each layer was used to study the adsorption of H_2S, HS, S and H at the coverage of 1/9 monolayer (ML). The $NiSi_2$ (111) surface was simulated by a 10-layer periodic slab model, and the slab was separated from its periodic image in z-dimension by a 15 Å thick vacuum region. A (2×2) surface unit cell with 4 atoms in each layer was used for the study adsorption at 1/4 ML coverage.

For the study concerning adsorption of H_2S, HS, S and H, the adsorption energy is calculated as the energy difference between the species absorbed surface slab and the gas phase species plus the clean surface slab, following Equation (1). Both the top two atomic layer of the surface slab and the adsorbed species were fully optimized until the forces were reduced below 1×10^{-2} eV/Å.

$$E_{ads} = E_{surface+Species} - \left(E_{Species} + E_{Surface} \right) \quad (1)$$

The $E_{Species}$ is the energy of species in gas phase, and is calculated by fully optimization of the specie in a $25.0 \times 25.1 \times 25.2$ Å^3 orthogonal cell with Γ only k-point sampling. Bader analysis is employed to get a quantitative description of the interfacial charge transfer upon gas adsorption.[S10]

Characterization

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. Diffraction data were collected between 5° and 90° (2θ) with a resolution of 0.02°.

Surface compositions were investigated by X-ray photoelectron spectroscopy (XPS) employing an ESCALAB250 (Thermo VG, USA) spectrometer with Al KR (1486.6 eV) radiation with a power of 150 W. Survey and individual high-resolution spectra were recorded with a pass energy of 50 eV. Ni 2p, Si 2p, and S 2p lines were monitored. All core-level spectra were referenced as the C1s neutral carbon peak at 284.6 eV and were deconvoluted into Gaussian component peaks.

Nitrogen adsorption and desorption isotherms were constructed using the multipoint method at -196 ℃ and were measured using a Micrometrics 2020. Prior to the measurements, all samples were degassed completely at 200 ℃ in a vacuum of 10^{-3} Torr for at least 4 h. Surface areas were calculated from the linear part of the Brunauer-Emmet-Teller (BET) plot.

In a Micromeritics ASAP 2010 apparatus, CO chemisorptions analyses were performed under static volumetric conditions. Prior to measurement, samples were reduced *in situ* in H_2 at 400 ℃ for 2 h. The chemisorption isotherm was obtained by measuring the amount of CO adsorbed for pressures varying from 10 to 600 mmHg at 40 ℃. After completing the initial analysis, the reversibly adsorbed gas was evacuated and the analysis repeated to determine the chemisorbed molecules alone.

References

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Table S1 Adsorption Properties of H_2S, HS, S and H on Ni(111) and $NiSi_2$(111) Surfaces.

Absorbate/Substrate		E_{ads} [a] (eV)	$D_{M\text{-}S/H}$ [b] (Å)	$D_{S\text{-}H}$ [c] (Å)	Configuration [d]
Ni(111)	H_2S	-0.86	2.21	1.37	atop
	HS	-3.27	2.17	1.52	bridge
	S	-5.22	2.14	--	fcc
	H	-2.80	1.71	--	fcc
$NiSi_2$(111)	H_2S	-0.68	2.30	1.36	atop
	HS	-2.82	2.35	1.37	bridge
	S	-4.67	2.31	--	h2
	H	-2.02	1.61	--	bridge

[a] The Eads is calculated as the energy difference between the species absorbed surface slab and the gas phase species plus the clean surface slab. [b] For adsorption of H_2S, HS and S, DM-S/H is the minimum distance between surface Ni and S atoms. And for adsorption of H, DM-S/H is the minimum distance between surface Ni and H atoms. [c] DS-H is the S-H distance in the adsorption structures. [d] The corresponding adsorption configuration as the follow description: The atop sites where the absorbate stands on top of a single surface Ni atom; The bridge site where the absorbate sits at the middle of two adjacent Ni atoms; The hcp site where the absorbate is on top of a Ni atom of the second layer; The fcc site where the absorbate is interacting with 3 surface Ni atoms and right on the top of a 3rd layer Ni atom; The h1 site stands on top of a 2nd layer Si atom; The h2 site stands on top of a 5th layer Si atom.

Table S2 Textural and Properties of the Ni-Si Intermetallics.

Sample	BET surface area (m^2 g^{-1})	Pore volume (cm^3/g)	Pore diameter (nm)	CO uptake (μmol g^{-1})
Ni	69	0.22	2.50	83.2
Ni_2Si	14	0.06	2.48	15.9
NiSi	12	0.07	2.24	3.0
$NiSi_2$	20	0.09	3.85	2.9

Table S3 Spectral Parameters Obtained by XPS Analysis.

Sample	Condation	Bingding energy (eV)						
		Ni $2p_{3/2}$		Si $2p_{3/2}$			S 2p	
		$NiSi_x$	NiS	$NiSi_x$	SiO_x	SiO_2	Sulphates	NiS
Ni_2Si	Fresh	852.6		98.9	103.1			
	Spent	852.6	855.6			103.3	168.9	161.5
NiSi	Fresh	852.9		98.4	102.6			
	Spent	852.9		98.4		103.3	168.5	
$NiSi_2$	Fresh	853.4		98.3	102.2			
	Spent	853.4		98.3		103.3	168.5	

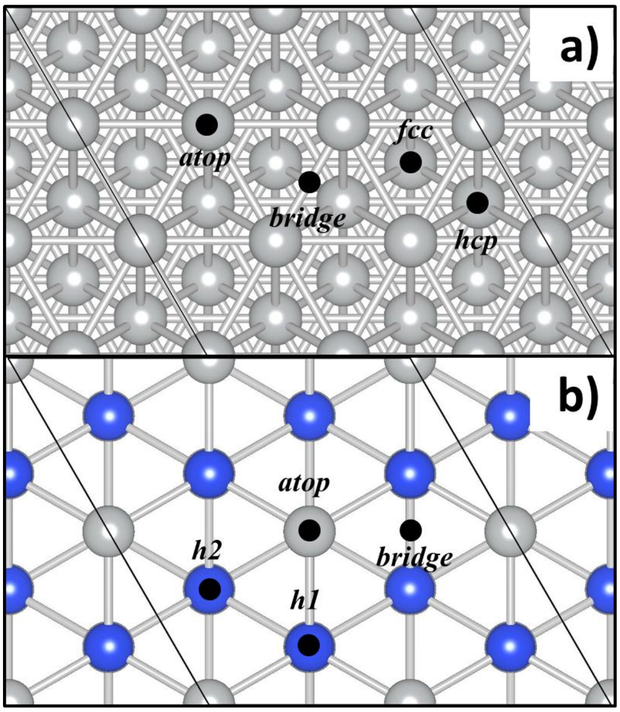

Fig. S1 Top view of the atomic structures and possible adsorption sites on Ni (111) (a) and $NiSi_2$ (111) (b). The adsorption sites are marked with filled black circles. Ni atoms are presented with gray spheres and Si atoms are in blue spheres.

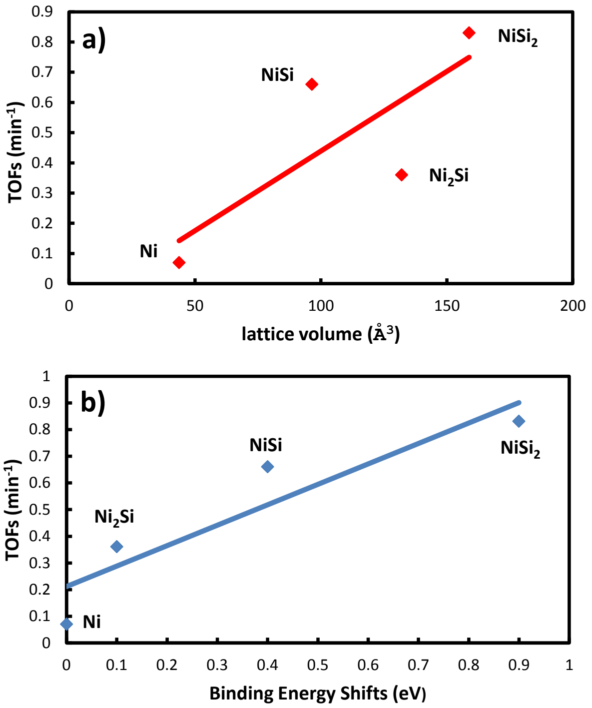

Fig. S2 TOFs of DBT during the HDS versus a) the lattice volume and b) the Ni 2p binding energy shifts over the Ni-Si intermetallics in comparison with metallic Ni catalyst at 340 °C.

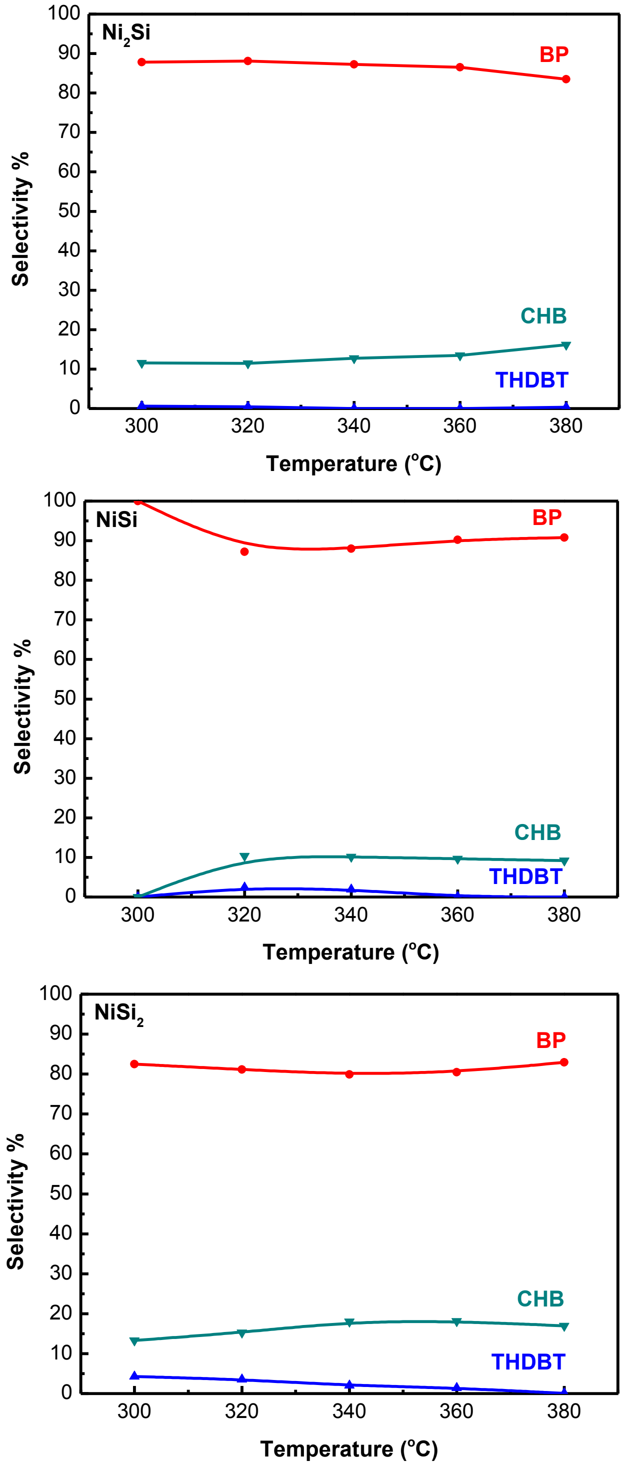

Fig. S3 Product selectivities of HDS of DBT at different reaction temperature over the Ni-Si intermetallics.

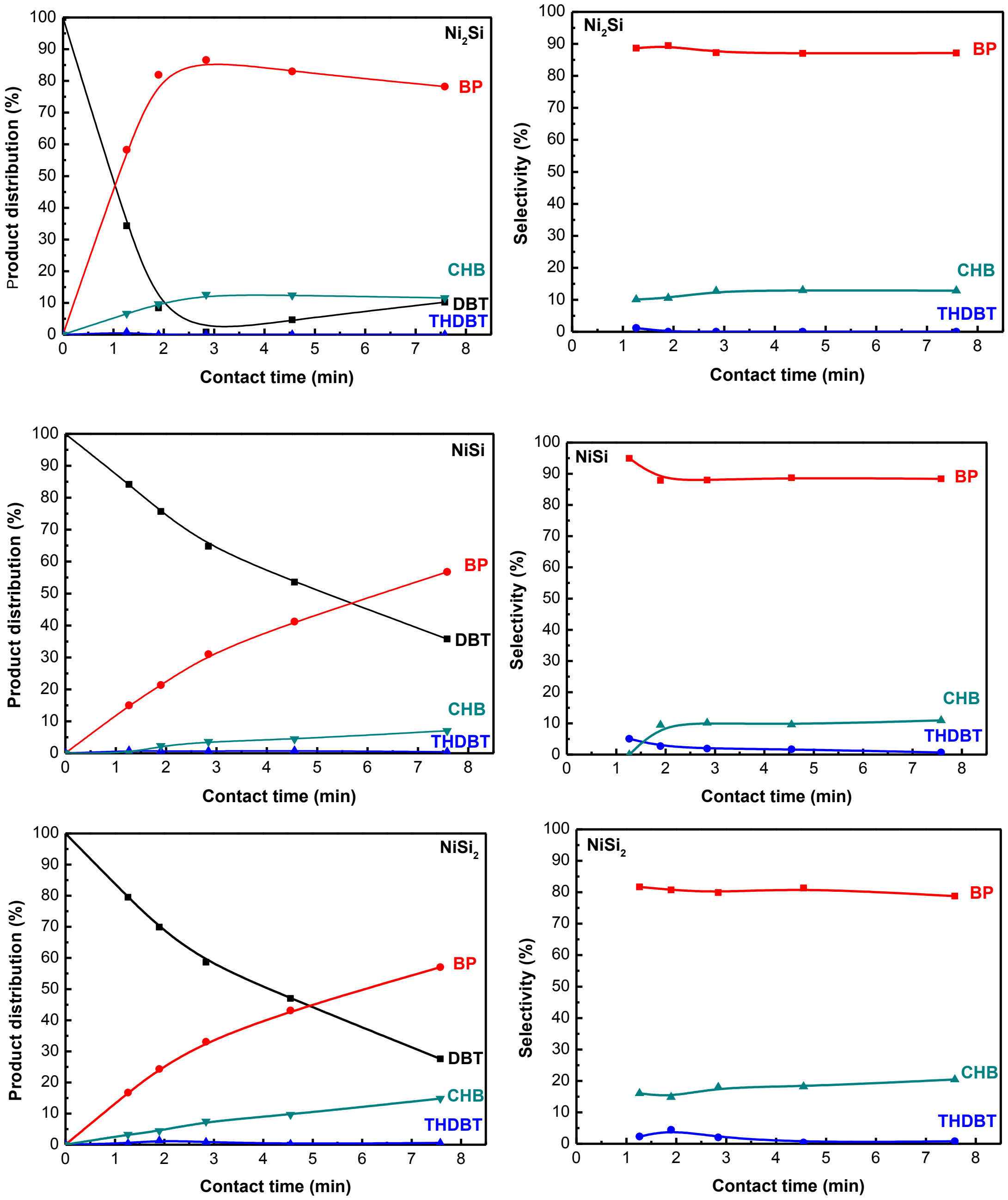

Fig. S4 Reactant and product distribution and selectivities to products in the HDS reaction at different contact time over the Ni_2Si, NiSi, and $NiSi_2$ intermetallics.

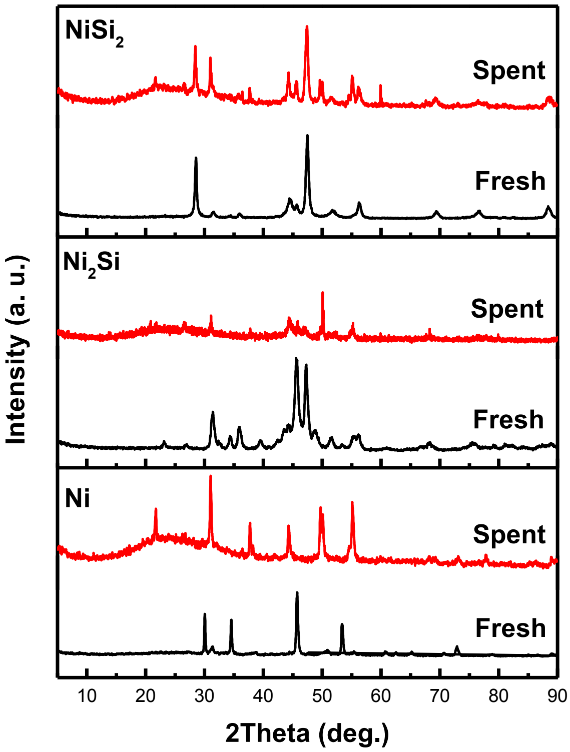

Fig. S5 Comparison of XRD patterns for the fresh and spent catalysts performed for 50 h in HDS of DBT, a) Ni, b) Ni_2Si, and c) $NiSi_2$.