Supporting Information

Nickel-embedded zeolite subcrystal catalyst: Rapid enhancement of activity and metal impurity resistance in hydrodesulfurization of 4,6-dimethyldibenzothiophene

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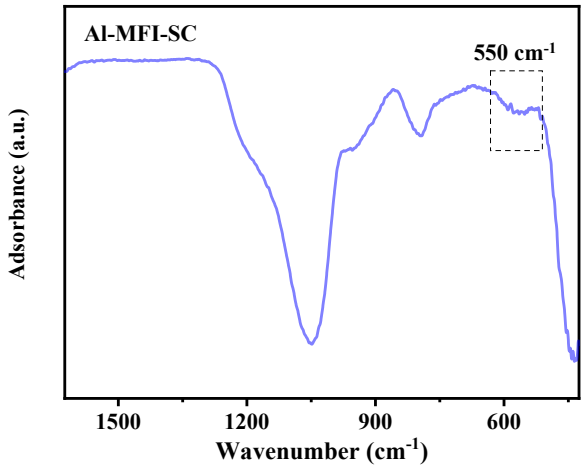


Figure S1 Fourier transform infrared (FT-IR) spectrum of Al-MFI-SC.

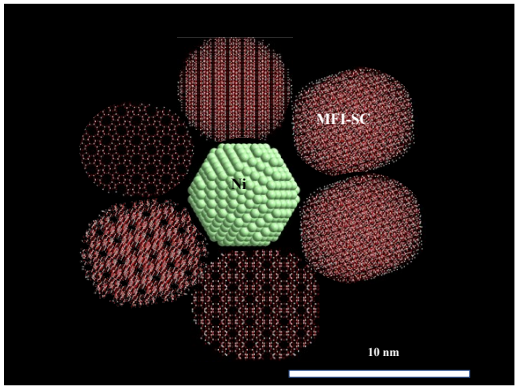


Figure S2 Diagram of Ni embedded in the zeolite subcrystal matrix.

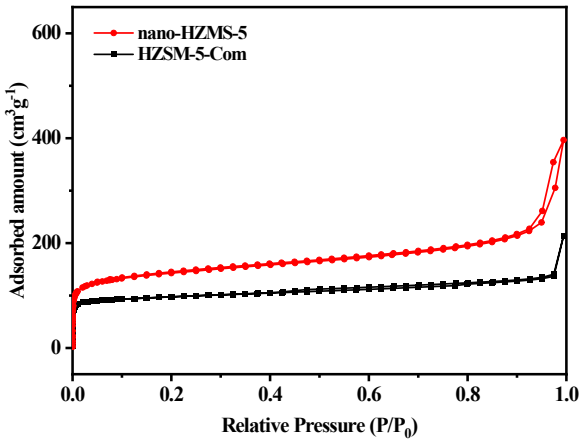


Figure S3 Ar sorption-desorption isotherms of nano-HZSM-5 and HZSM-5-Com.

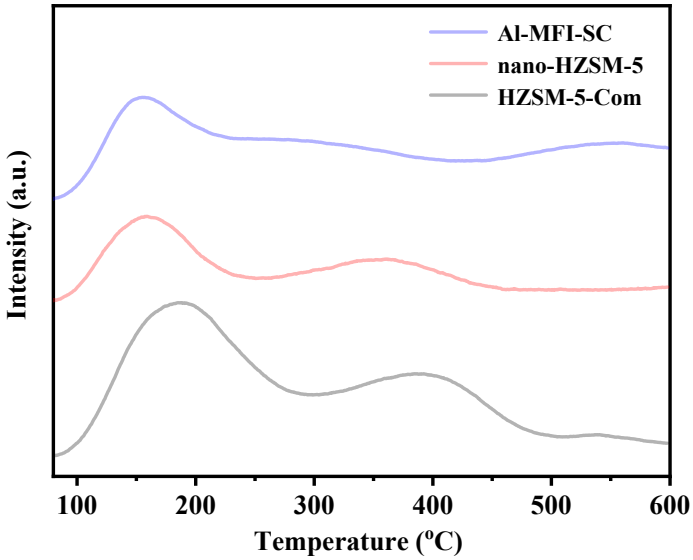


Figure S4 NH_3-TPD profiles of Al-MFI-SC, nano-HZMS-5, HZSM-5-Com.

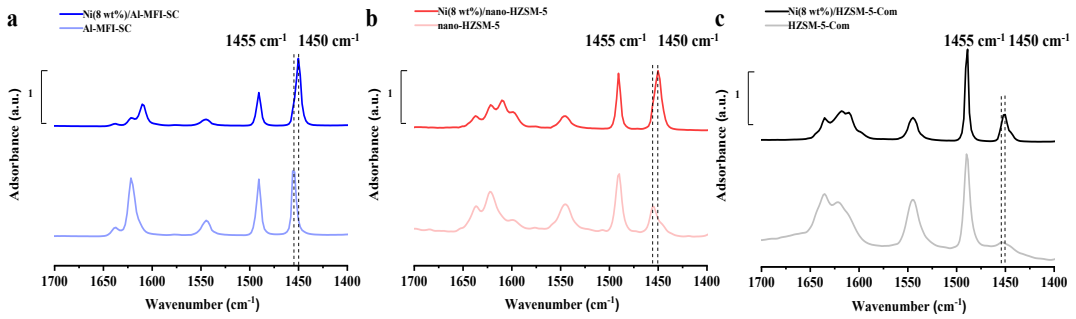


Figure S5 Pyridine adsorbed FT-IR spectra of Al-MFI-SC, Ni(8 wt%)/Al-MFI-SC (a), nano-HZSM-5, Ni(8 wt%)/nano-HZSM-5 (b) and HZSM-5-Com, Ni(8 wt%)/HZSM-5-Com (c) after evacuation at 300 ℃.

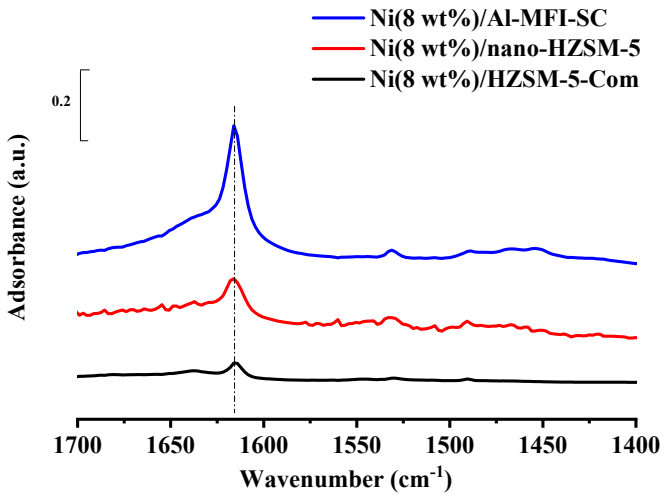


Figure S6 2,6-ditertbutyl-pyridine adsorbed FT-IR spectra of three catalysts after evacuation at 300 ℃.

When 2,6-ditertbutyl-pyridine (kinetic diameter: 0.79 nm) is used to probe the accessible surface acid sites of three catalysts, Ni(8 wt%)/Al-MFI-SC shows remarkly higher adsorption of 2,6-ditertbutyl-pyridine (peak around 1615 cm^{-1}) than Ni(8 wt%)/nano-HZSM-5 and Ni(8 wt%)/HZSM-5-Com.

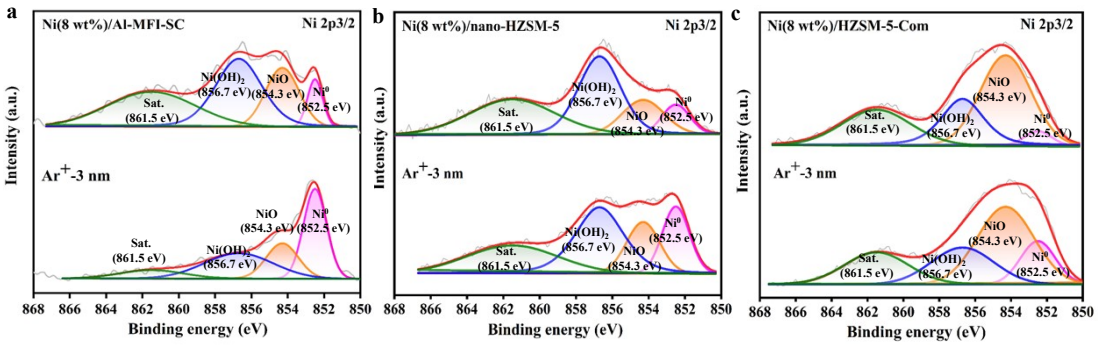


Figure S7 XPS spectra of Ni(8 wt%)/Al-MFI-SC (a), Ni(8 wt%)/nano-HZSM-5 (b) and Ni(8 wt%)/HZSM-5-Com (c) catalysts before and after Ar ion beam.

The comparison of XPS results at different depths using the argon ion beam (removing a depth of 3 nm from the surface) in Figure S7 confirms this observation. Hence, we can conclude that oxidic Ni species derive from the oxidation of Ni^0 in the air. To further clearly express this, the detailed relative amount of different Ni species before and after Ar ion beam was listed in Table S1. Obviously, Ni^0 percentage of three catalysts have increased substantially after Ar ion beam.

Table S1 Relative amounts of different Ni species before and after Ar ion beam of XPS analyses.

Catalysts	Relative amount of Ni (%)[a]		
	Ni^0/Ni_{total}	NiO/Ni_{total}	$Ni(OH)_2/Ni_{total}$
Ni(8 wt%)/Al-MFI-SC	11.6 (42.0)	31.9 (22.8)	56.5 (35.2)
Ni(8wt%)/nano-HZSM-5	14.1 (24.7)	24.7 (23.2)	61.2 (52.1)
Ni(8 wt%)/HZSM-5-Com	5.4 (18.5)	62.5 (53.5)	32.1 (28.0)

[a]The data in parentheses represent XPS analysis results after Ar ion sputtering treatment.

Table S2 TOF of 4,6-DMDBT conversion and desulfurization over three catalysts.

	Conversion (%)	TOF (h^{-1})	Desulfurization (%)	TOF (h^{-1})
Ni(8 wt%)/Al-MFI-SC	27.6	1.67	28.8	0.87
Ni(8 wt%)/nano-HZSM-5	30.8	0.16	28.3	0.14
Ni(8 wt%)/HZSM-5-Com	26.6	0.13	25.6	0.086

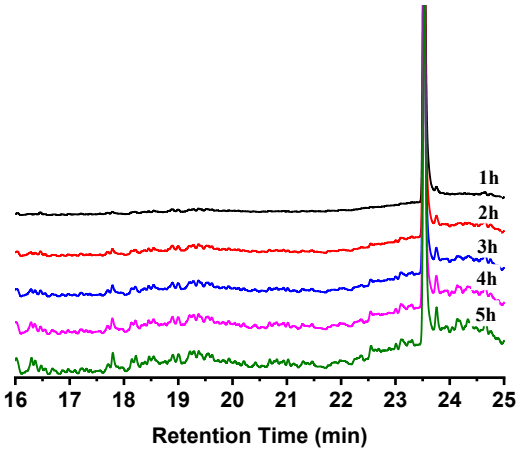


Figure S8 GC spectra of reaction solution catalyzed by Al-MFI-SC at the different reaction time during the conversion of 4,6-DMDBT.

There are not any desulfurization product peaks in GC spectra, and only a spot of isomerization product appears around 23.8 min.

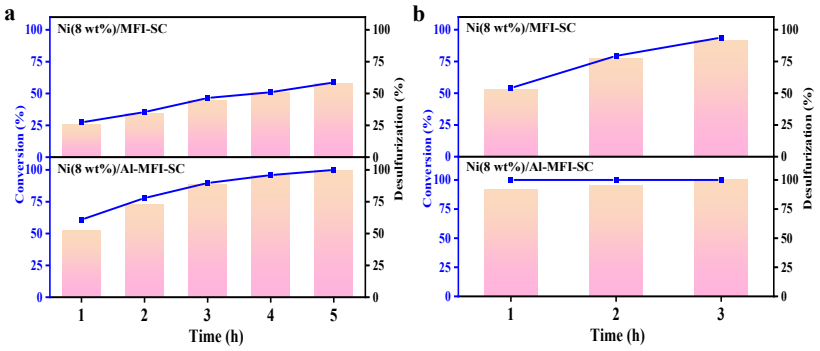
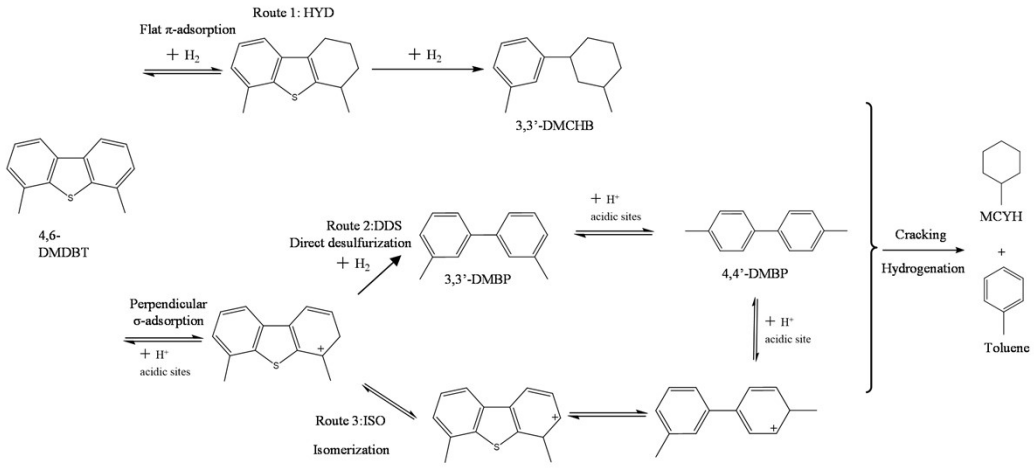


Figure S9 HDS performances of DBT (a) and thiophene (b) on Ni(8 wt%)/MFI-SC and Ni(8 wt%)/Al-MFI-SC catalysts.



Scheme S1 The conversion routes of 4,6-DMDBT in the presence of Ni/Al-MFI-SC catalyst. Route 1: HYD; Route 2: DDS; Route 3: ISO. 4,6-THDMDBT: 4,6-tetrahydro-dimethyl-dibenzothiophene; 3,3′-DMCHB: 3,3′-dimethyl-cyclohexyl-benzene; 3,3′-DMBCH: 3,3′-dimethyl-bicyclohexyl; 3,3′-DMBP: 3,3′-dimethyl-biphenyl; 4,4′-DMBP: 4,4′-dimethyl-biphenyl.

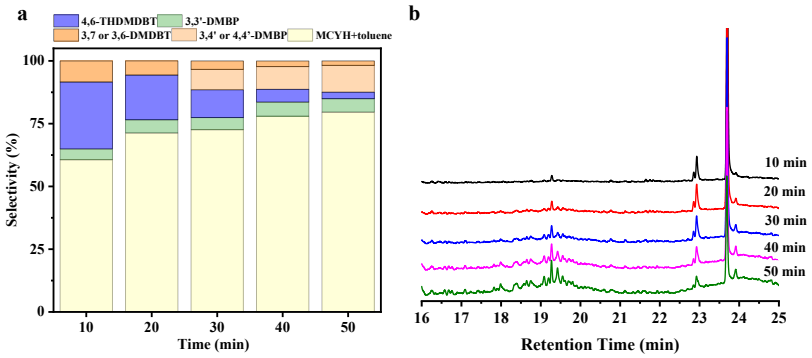


Figure S10 Product selectivity (a) and GC spectra (b) of the reaction solution over Ni(8 wt%)/Al-MFI-SC at the beginning of the 4,6-DMDBT conversion. 4,6-THDMDBT: 4,6-tetrahydro-dimethyl-dibenzothiophene; 3,3′-DMBP: 3,3′-dimethyl-biphenyl; 3,7-DMDBT: 3,7-dimethyl-dibenzothiophene; 3,6-DMDBT: 3,6-dimethyl-dibenzothiophene; 3,4′-DMBP: 3,4′-dimethyl-biphenyl; 4,4′-DMBP: 4,4′-dimethyl-biphenyl; MCYH: methyl-cyclohexane.