1 Supporting Information

Dynamic Reconstructing Sulfur Vacancies-Rich Ni_3S_2 Interfaces for Highly Selective Silane-Alcohol Dehydrogenation Coupling

Yahui Zhu[1], Senqun Liu[1], Wenbo Ye[3], Jiayao Chen[1], Shengjun Deng[1], Rong Zeng[2], Shunmin Ding[1*], Chao Chen[1]

1. Key Laboratory of Jiangxi Province for Environment and Energy Catalysis, School of Chemistry and Chemical Engineering, Nanchang University, Jiangxi 330031, P.R. China
2. School of Chemistry and Materials Science, East China University of Technology, Nanchang 330013, P.R. China
3. Dongguan City Betterly New Materials Co., Ltd, Dongguan, 523145, P.R. China.
E-mail: Shunmin Ding sding@ncu.edu.cn

Table of Contents

1. Experimental section

1.1 Analysis of the products

At the end of the reaction, the catalyst was separated by filtration and the reaction solution was further filtered using a 0.22 μm filter membrane. The filtered solution was passed through an Agilent 19091S-433 capillary column (HP-5MS, 30 m × 250 μm × 0.25 μm) for analysis and the products were determined using a gas chromatography-mass spectrometry (GC-MS) coupled with a gas chromatography-mass spectrometer (Agilent 7890B-5977A MS). Based on the nuclear magnetic resonance (NMR) and MS characterization data that have been obtained in the previous stage, the products were only validated by GC-MS analysis in this study.[1] Changes in the composition of the reaction solution with reaction time were analyzed at constant temperature. All experimental data were obtained by three independent repeated measurements. The conversion (Conv.), selectivity (Sel.), and yield data for the reaction were calculated using the following formulas:

$$Conversion\ (\%) = \left(1 - \frac{moles\ of\ residual\ silane}{moles\ of\ initial\ silane}\right) * 100\%$$

$$Selectivity\ (\%) = \frac{moles\ of\ product}{moles\ of\ reacted\ silane} * 100\%$$

$$Yield\ (\%) = （Conversion\ (\%) * Selectivity\ (\%)） * 100\%$$

1.2 Filtering experiment

The filtering experiment was carried out under the same conditions. After the reaction lasted for 15 min, the catalyst was separated from the reaction system by filtration. The filtrate was kept at reaction temperature for another 25 min.

1.3 Catalyst recyclability testing

In the dehydrogenative coupling cycle experiments of dimethylphenylsilane with ethanol using CNS-Ni-600 catalyst, the reaction was carried out in a 50 mL two-necked

round-bottomed flask equipped with a reflux condenser and a magnetic stirrer. 5 mL of ethanol and 5 mmol of silane were added to the reaction system and the reaction was carried out under optimal conditions (30 min, 80 °C, 30 mg catalyst). After each cycle, we separated the catalyst by centrifugation, and the recovered catalyst was washed with a large amount of ethanol and then vacuum dried at 80 °C for 12 h. Finally, the recovered catalyst was used for the next cycle.

1.4 Calculation of TOF Values

The TOFs were calculated based on the conversion, selectivity of silanes and total loading of Ni.

TOF = [Mol(substrate)*(conversion*selectivity)]/[Mol(Ni)*dispersity*reaction time (hour)]

2. Figure

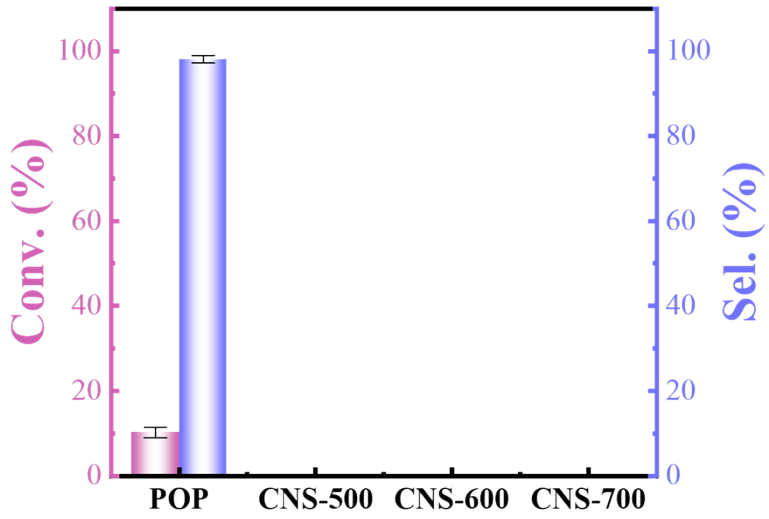


Fig. S1 Conversion and selectivity of POP, CNS-500, CNS-600 and CNS-700 catalyzed dimethylphenylsilane coupling reactions with alcohol dehydrogenation.

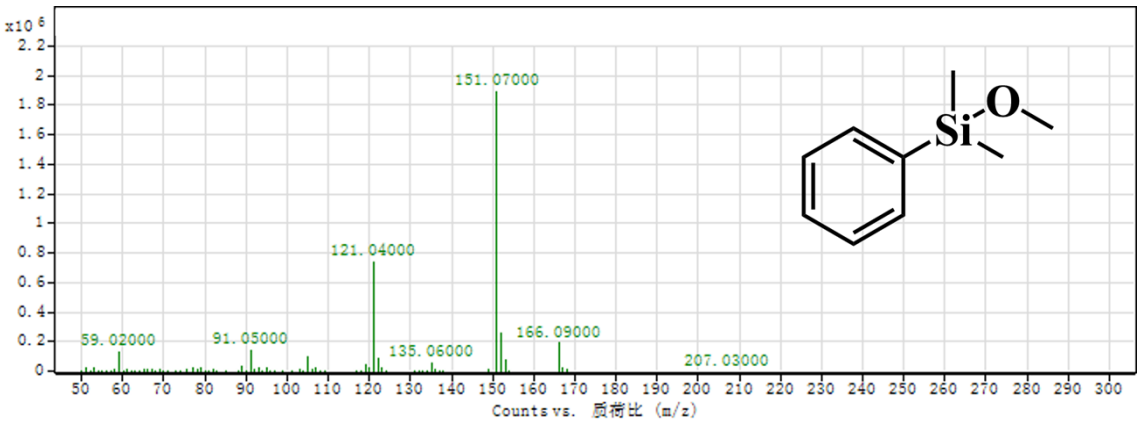


Fig. S2 Substrate expansion 1a mass spectrum.

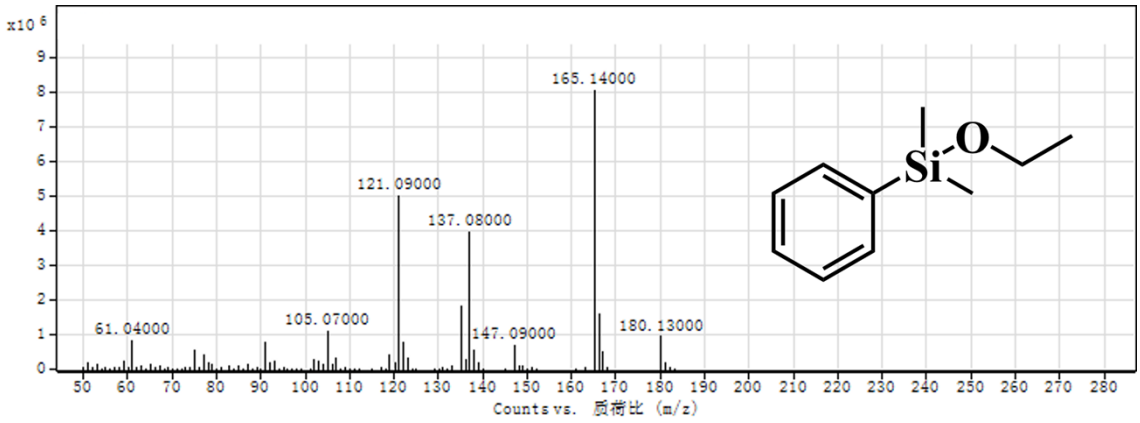


Fig. S3 Substrate expansion 1b mass spectrum.

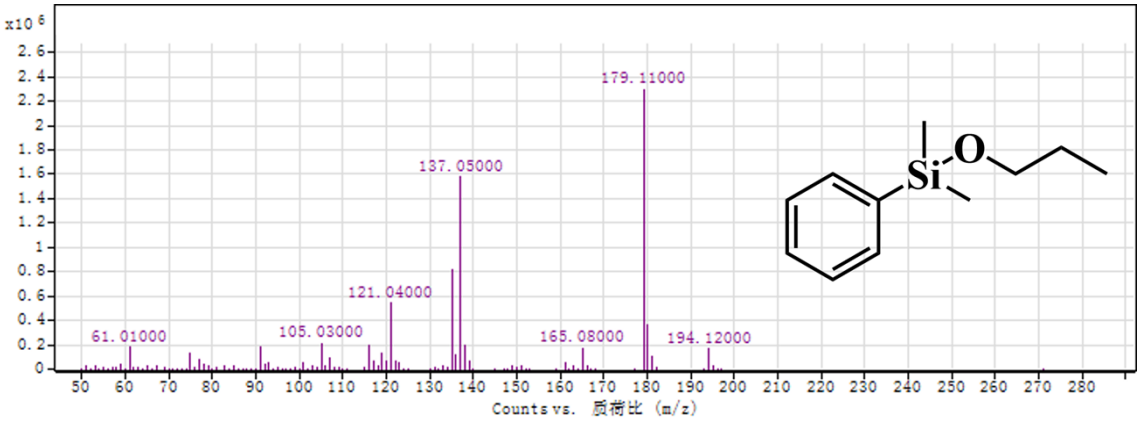


Fig. S4 Substrate expansion 1c mass spectrum.

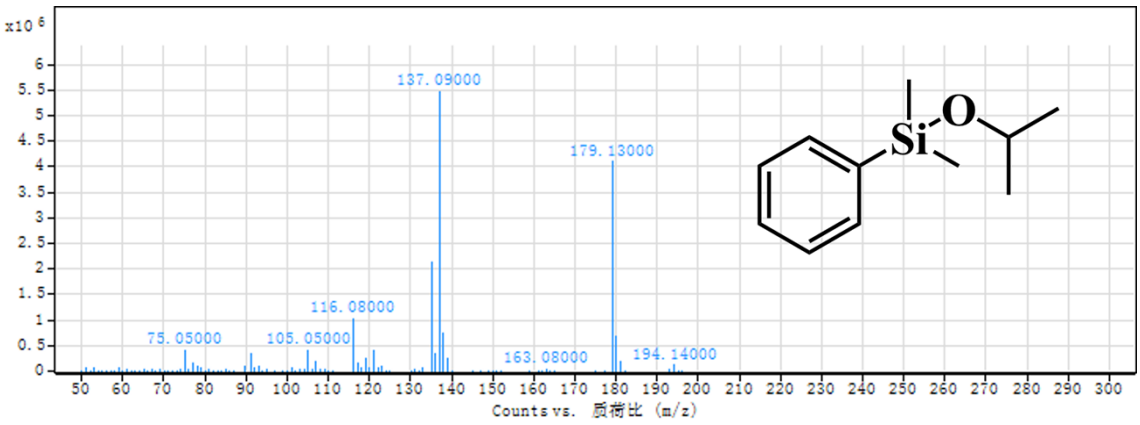


Fig. S5 Substrate expansion 1d mass spectrum.

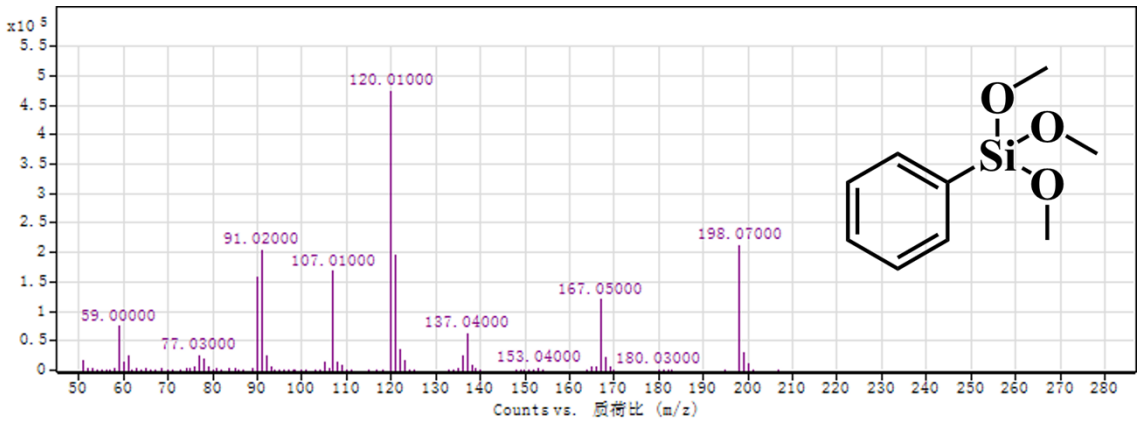


Fig. S6 Substrate expansion 1e mass spectrum.

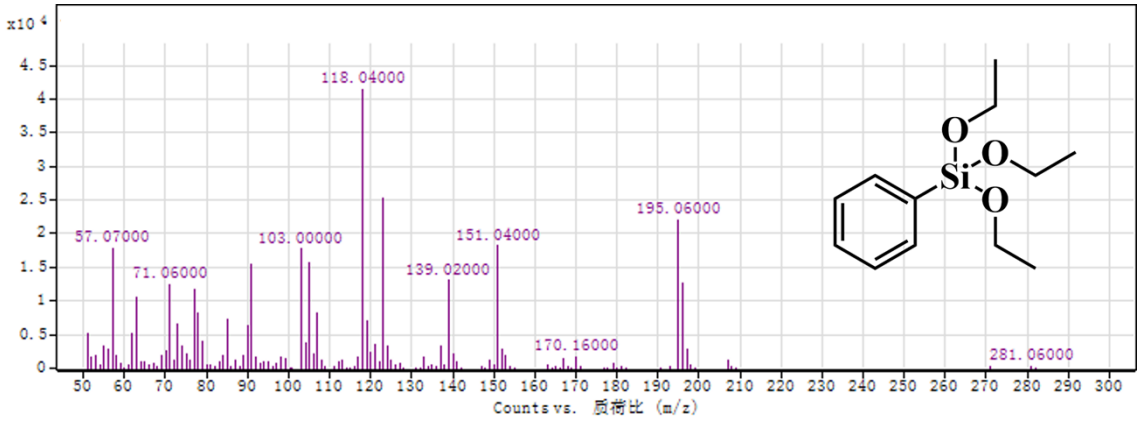


Fig. S7 Substrate expansion 1f mass spectrum.

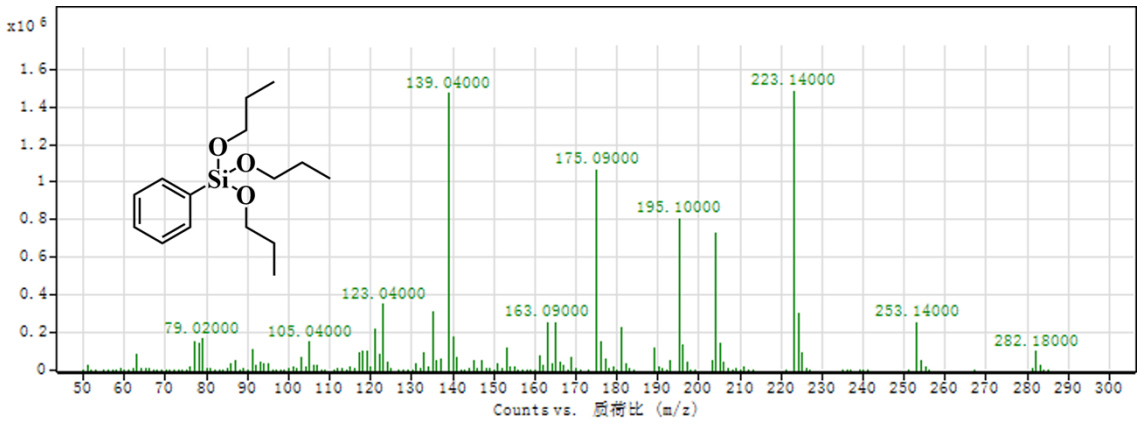


Fig. S8 Substrate expansion 1g mass spectrum.

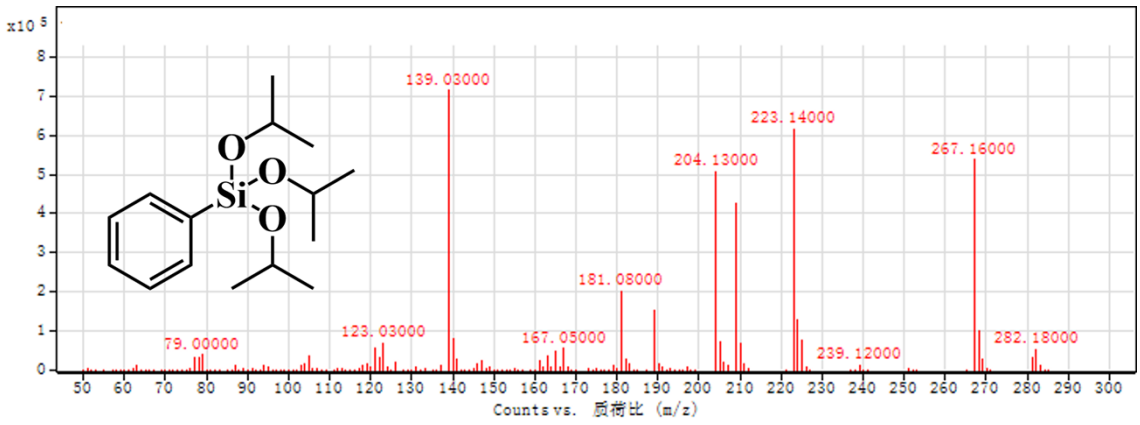


Fig. S9 Substrate expansion 1h mass spectrum.

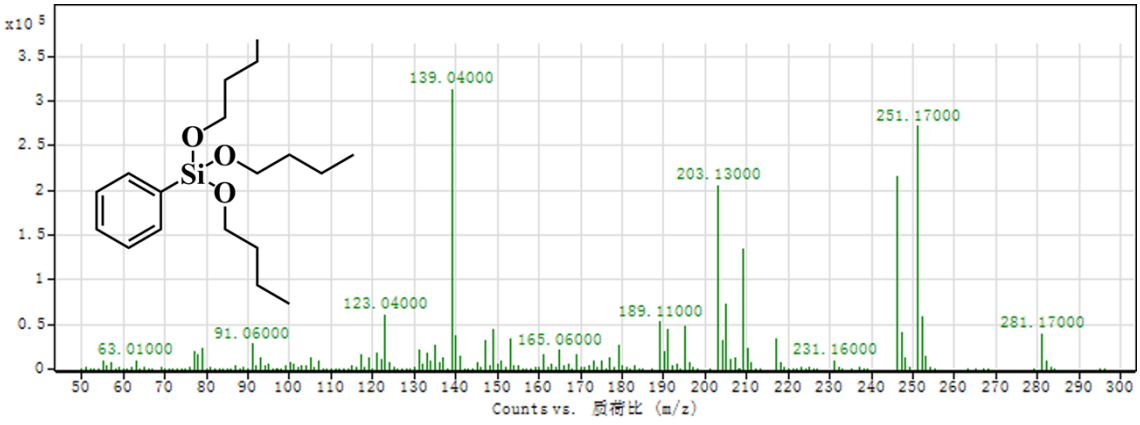


Fig. S10 Substrate expansion 1i mass spectrum.

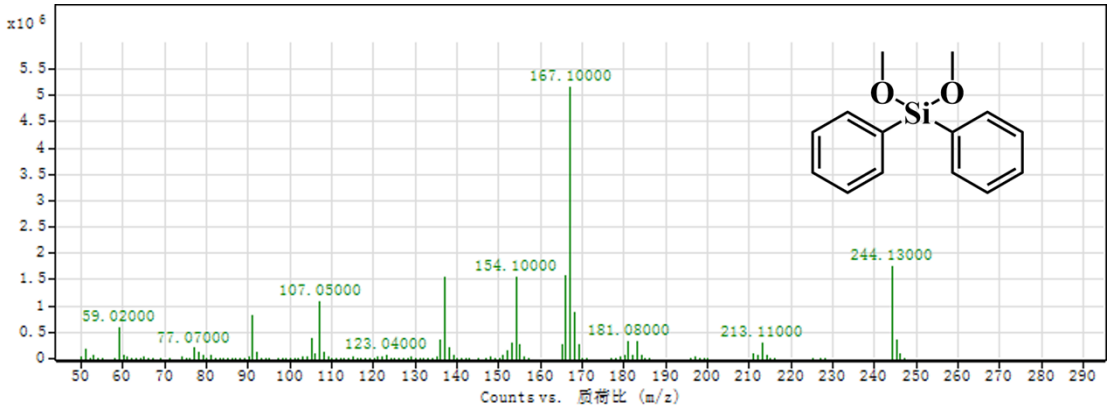


Fig. S11 Substrate expansion 1j mass spectrum.

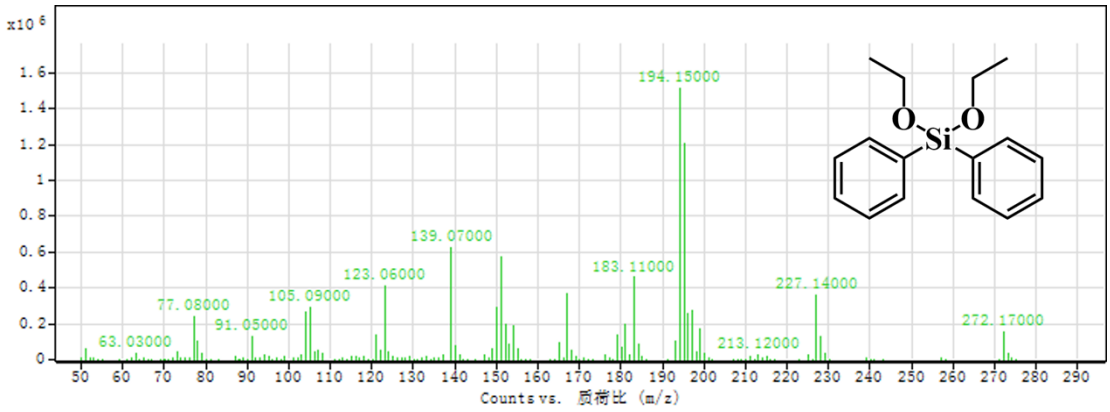
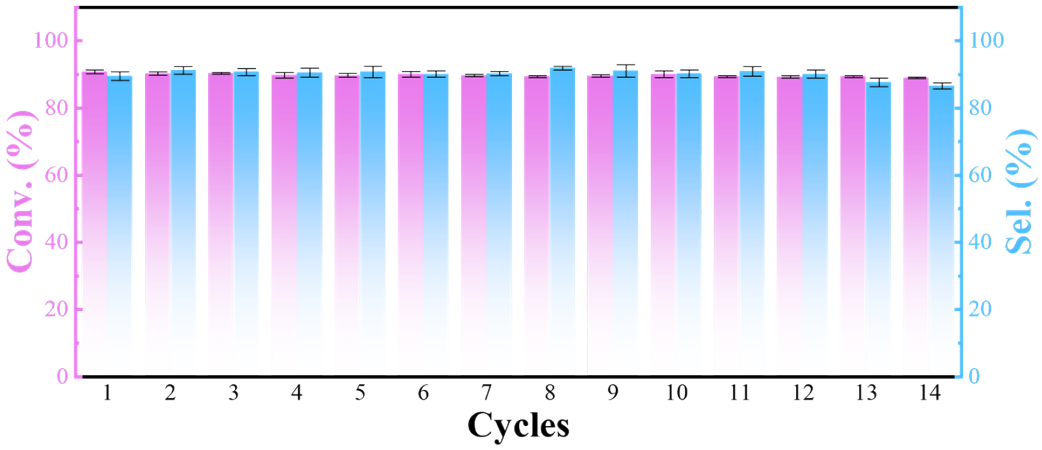


Fig. S12 Substrate expansion 1k mass spectrum.



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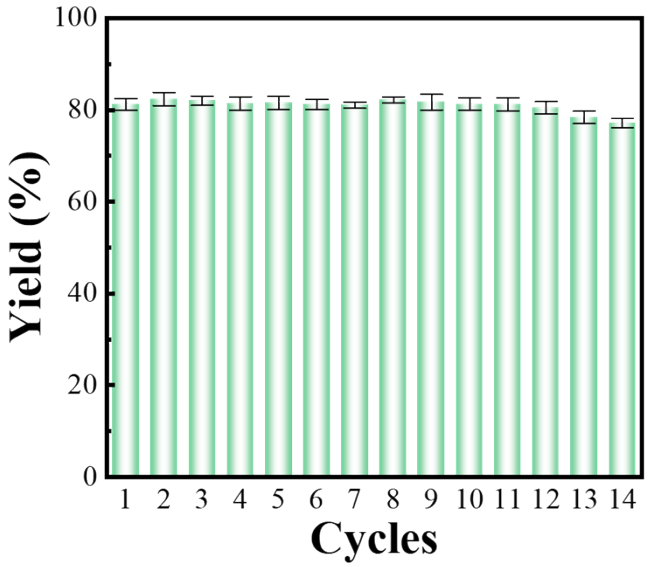

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3 **Fig. S13** Cyclic stability experiments with fivefold expansion of the reaction substrate.

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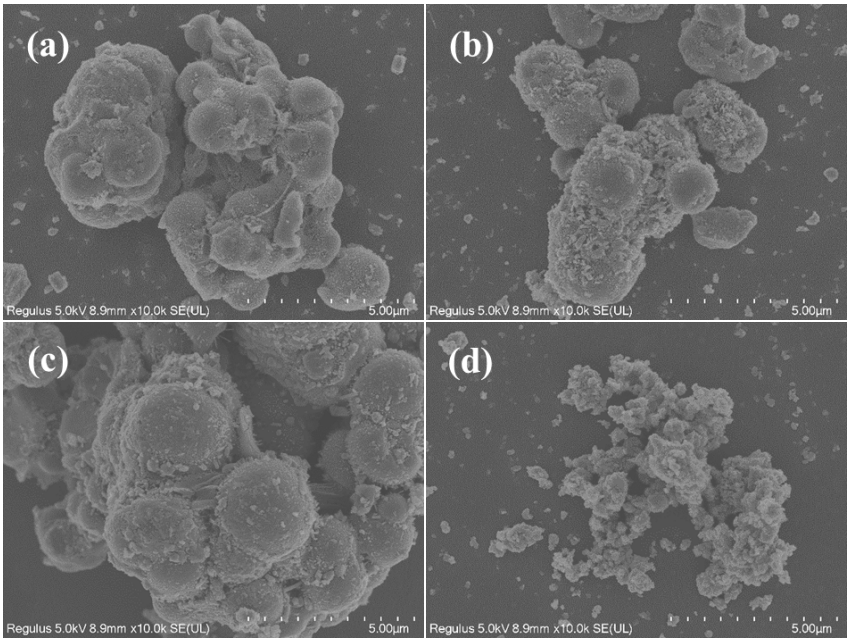
1 

2 **Fig. S14** SEM images of CNS-Ni-500-used (a), CNS-Ni-600-used (b), CNS-Ni-700-used (c),

3 CNS-Ni-600-14runs (d).

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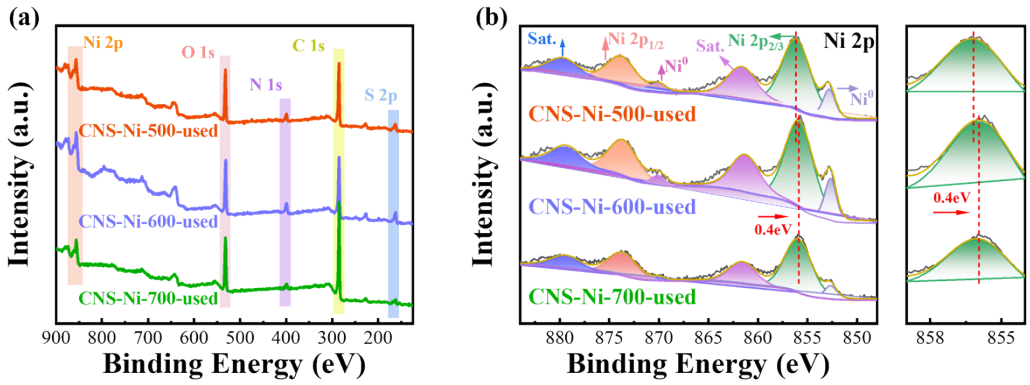


Figure S15. (a)XPS wide spectra and (b) Ni 2p core-level spectrum of CNS-Ni-T-used (T=500, 600, 700).

3. Tables

Table S1. CNS-Ni-T catalyst of Surface Area and Pore Structure Parameters

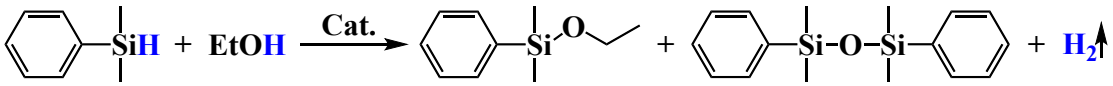
Sample	S_{BET} [a] (m^2/g)	V_p [b] (cm^3/g)	D_p [c] (nm)
CNS-Ni-500	225	0.26	4.66
CNS-Ni-600	396	0.28	2.85
CNS-Ni-700	446	0.31	2.80

[a] Caculated by Brunauer-Emmett-Teller (BET) methods.

[b] Total pore volume.

[c] Average pore diameter.

Table S2. Dehydrogenative coupling of dimethylphenylsilane (1a) with ethanol over the catalysts under different conditions[a].



1a **1b** **1c**

Entry	Catalysts	t/min	Conv./%[b]	Sel./% (1c)[b]
1	none	1440	-	-
2	POP	1440	10	98
3	CNS-500	1440	-	-
4	CNS-600	1440	-	-
5	CNS-700	1440	-	-
6	CNS-Ni-600	30	＞99	＞99
7	CNS-Ni-500	30	59	＞99
8	CNS-Ni-700	30	31	＞99
9[c]	CNS-Ni-600	30	59	＞99
10[d]	CNS-Ni-600	30	＞99	＞99
11[e]	CNS-Ni-600	30	69	＞99
12[f]	CNS-Ni-600	30	＞99	＞99

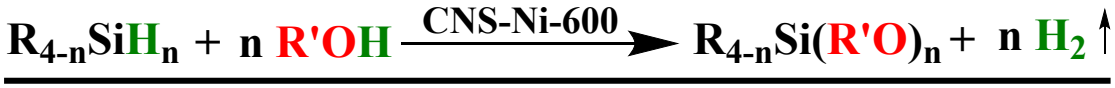
[a]Reaction conditions: 1a (5 mmol), ethanol (5 mL), catalysts (30 mg) and 80 °C.[b]Determined by GC using n-dodecane as an internal standard.[c]70 °C. [d]90 °C. [e]CNS-Ni-600 (20 mg). [f]CNS-Ni-600 (40 mg).

Table S3. Comparison of different catalysts in the dehydrogenation coupling reaction of silanes and alcohols.

Catalysts	Cat. (mg)	Silanes (mmol)	Time	Atmosphere	Yield (%)	TOF (h^{-1})	Cycle	Ref.
CNS-Ni-600	**30 mg (19.4 wt % Ni)**	**5 mmol**	**30min**	**Air**	**99**	**1410**	**15**	**This Work**
AgCr@CN-800	15 mg (Ag + Cr 13.7-18.0 wt %)	1 mmol	20min	Air	97	327	4	[2]
$Cu_3(BTC)_2$	50 mg (Co 0.9ppm)	1 mmol	15min	Ar	99	266	3	[3]
Cu(B)G	0.5 mol %	5 mmol	48h	Ar	99	4.16	3	[4]
Au/HAP_{nano}	0.5 mol %	2 mmol	1h	Air	99	128	4	[5]
Co SAs/2D NC	5.34 mg (Co 0.15 wt%)	1 mmol	2h	Ar	97.5	3858	5	[6]
KCC-1-APTS/Au	1 mg (0.05 wt % Au)	1.5 mmol	24h	Air	99	21625	10	[7]
[Au]-SMAP-Rh (75000)	Me_2PhSiH/Rh 75 000：1	12 mmol	16h	Air	80	3750	4	[8]
G(CN)-Au	10 mg (0.6 wt % Au)	1 mmol	5min	Air	99	139494	4	[9]
10Dod-AuNP	2.7×1011 mL^{-1}	150 μmol	1h	Air	82.8	55000	3	[10]

Reaction substrate: Me_2PhSiH

Table S4. Dehydrogenative coupling of silanes and alcohols catalyzed by CNS-Ni-600[a].



Entry	silane	alcohol	Conv./%[b]	Sel./%[b]
1	$Ph(Me)_2SiH$	MeOH	99	99
2	$Ph(Me)_2SiH$	EtOH	99	99
3	$Ph(Me)_2SiH$	*n*-PrOH	99	96
4	$Ph(Me)_2SiH$	*i*-PrOH	97	93
5	$PhSiH_3$	MeOH	99	99
6	$PhSiH_3$	EtOH	99	96
7	$PhSiH_3$	*n*-PrOH	99	90
8	$PhSiH_3$	*i*-PrOH	99	73
9	$PhSiH_3$	*n*-BuOH	99	87
10	$(Ph)_2SiH_2$	MeOH	99	68
11	$(Ph)_2SiH_2$	EtOH	99	54

[a]Reaction conditions: silane (5 mmol), alcohol (5 mL), CNS-Ni-600 (30 mg), and time 30 min. [b]Determined by GC using dodecane as internal standard.

Table S5. CNS-Ni-T-used the content of different elements on the surface of the sample.

Samples	Composition (wt%)			
	Ni[a]	C	N	S
CNS-Ni-500	18.9	58.9	5.3	16.8
CNS-Ni-500-used	18.2	59.3	5.5	15.7
CNS-Ni-600	19.4	56.8	7.2	16.5
CNS-Ni-600-used	19.1	56.6	7.0	14.9
CNS-Ni-700	22.4	59.4	3.8	14.3
CNS-Ni-700-used	21.8	60.5	3.7	13.9

[a]Ni content by ICP-OES. [b]*C* 、*N* 、S content by Elemental analysis.

Table S6. Peak positions of XPS spectra in Ni $2p_{3/2}$ and S $2p_{1/2}$ in CNS-Ni-T-used (T=500, 600,700 ℃).

Catalyst	Ni $2p_{3/2}$ (eV)	S $2p_{1/2}$ (eV)
CNS-Ni-500-used	856.19	163.36
CNS-Ni-600-used	855.80	163.20
CNS-Ni-700-used	855.95	163.51

Table S7. The surface chemical compositions of the CNS-Ni-T-used[a].

Samples	CNS-Ni-600-used	CNS-Ni-500-used	CNS-Ni-700-used
Ni^0/Ni^{2+} (%)	17.73	16.43	8.33
S $2p_{1/2}$/S 2p (%)	46.81	38.27	32.43

[a]Data were obtained from XPS analysis.

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