

## Supporting Information

# Hydrodeoxygenation of guaiacol to phenol using endogenous hydrogen induced by chemo-splitting of water over a versatile nano-porous Ni catalyst

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## Materials

Nickel, Iron, Cobalt, Copper and Aluminum metal powders of high purity and superfine were purchased from Nangong Xinshi Alloy Welding Material Spraying Co., Ltd.  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  was purchased from Tianjin Damao Chemical Reagent Factory and used as a nickel precursor.  $(\text{NH}_4)_2\text{CO}_3$  was purchased Guangdong Guanghua Sci-Tech Co., Ltd. Support materials ( $\text{Ni}/\text{MgO}$ ,  $\text{Ni}/\text{Al}_2\text{O}_3$ ,  $\text{Ni}/\text{SiO}_2$ ,  $\text{Ni}/\text{HZSM-5}$ ,  $\text{Ni}/\text{TiO}_2$ ) were purchased from Wuxi Zehui Chemical Co., LTD.  $\text{Pt}/\text{C}$ ,  $\text{Pd}/\text{C}$ ,  $\text{Ru}/\text{C}$  were purchased from Xi'an Catalyst Chemical Co., LTD. Methanol was purchased from Tianjin Fuyu Fine Chemical Co., Ltd.  $\text{NaOH}$  was purchased from Guangdong Xilong Chemical Co., Ltd. Guaiacol, 2-amyl alcohol, cyclohexane, isopropanol and phenol were purchased from Sinopharm Chemical Reagent Co., Ltd. 4-methyl-guaiacol, 4-ethyl-guaiacol and 4-propyl – guaiacol were purchased from Aladdin Reagent Co., LTD. Nitrogen and hydrogen were supplied by Air Liquide company. Deionized water was obtained from a Millipore system. All chemicals were analytical grade and used as received without further purification.

## Preparation of catalyst

### Preparation of nano-porous metal catalysts

The alloy powder was prepared by a microplanetary high energy ball mill (LUVERISETTE7). First, pure nickel(iron,cobalt and copper) powder , aluminum powder and modified metal powder with a certain quality were weighed and added into the ball milling tank made of zirconia. In the mechanical alloying process, the cold welding between metal powders would affect the mechanical alloying, so 0.4 mL ethanol was added as the process control agent. The air in the ball mill tank was replaced with argon gas for 6 times, and the planetary ball mill was run at room temperature. The

grinding ball used in the experiment was a zirconia ball with a diameter of 3 mm. The total mass of the metal powder was kept at 4 g, and the mass ratio of the grinding ball to the metal powder was 15. When the ball mill is running at the set time, open it in a glove box filled with N<sub>2</sub> (to avoid spontaneous combustion) and oxidize it fully in the air, then remove the alloy powder and put it into the sample tube.

The programmed heat treatment is carried out in a self-made tubular furnace to make the metal components in the alloy powder form stable intermetallic compounds. 1 g of alloy powder prepared by mechanical alloying was weighed in a small quartz boat, and then the boat was placed in the middle part of the tube furnace for programmed heating in a nitrogen atmosphere. The temperature was heated to 600 °C at a rate of 10 °C•min<sup>-1</sup> and held for 2 h. After cooling slowly to room temperature in the tubular furnace, the alloy powder is taken out and ground in a mortar, then loaded into the sample tube and stored in the dryer.

2.224 g of NaOH was weighed in a 25 mL beaker and 10.8 mL of deionized water was added to prepare an alkaline solution with a mass concentration of 17 wt.%. Then, 0.5 g of alloy powder was weighed and slowly added into the NaOH aqueous solution at 50 °C for several times. Then, the alloy was dealloyed at 90 °C for 1 h. After the dealloying process is completed, the beaker is cooled in a bath of ice water and the catalyst is washed several times with a large amount of deionized water until the aqueous solution is neutral.

### **Preparation of different nickle-based catalysts**

The supported nickel catalysts were prepared according to the deposition–precipitation (DP) method and the experimental procedure is as follows. Firstly, the support was added into an aqueous

solution containing nickel salt. Then the suspension was heated to 50 °C in constant stirring for 1 h and a little silica sol was added into the suspension for another 1 h. The precipitant solution was dripped into the above mixture. After a given time of deposition–precipitation, the suspension was cooled to 25 °C and then filtered. The sample was washed with distilled water and ethanol to remove the possible adsorbed ions and dried at 60 C for 24 h. The dried precursor was heated to 500 °C at a heating rate of 7.5 °C min<sup>-1</sup> under N<sub>2</sub> and reduced for 4 h in 20 mL• min<sup>-1</sup> of H<sub>2</sub>. The catalyst was cooled to room temperature under N<sub>2</sub> and gradually exposed to air in 10 min for further usage.

**Table S1** Activity performance tests of different catalysts.

Cat.	Atmosphere	Conv.(% )	Sel. (%)			
			Cyclohexanone	Cyclohexanol	2-methoxy cyclohexanol	Phenol
Blank	N <sub>2</sub>	0	0	0	0	0
NP-Cu <sup>b</sup>	N <sub>2</sub>	0	0	0	0	0
	H <sub>2</sub>	69.2	1.0	70.3	18.6	10.1
NP-Fe <sup>b</sup>	N <sub>2</sub>	1.9	0	0	0	100
	H <sub>2</sub>	34.9	6.4	42.0	0	51.6
NP-Co <sup>b</sup>	N <sub>2</sub>	1.6	0	0	0	100
	H <sub>2</sub>	52.2	11.8	46.8	7.2	34.2
NP-Ni <sup>a</sup>	N <sub>2</sub>	47.2	13.3	17.3	0	69.4
NP-Ni <sup>b</sup>	N <sub>2</sub>	41.5	0	0	0	100
	H <sub>2</sub>	95.2	3.1	81.8	14.2	0.9
Spent NP-Ni	N <sub>2</sub>	3.5	0	0	0	100
Spent NP-Ni	H <sub>2</sub>	90.3	0.8	94.0	1.0	4.2
Commercial Raney Ni <sup>a</sup>	N <sub>2</sub>	33.5	12.2	20.5	0	67.3
Commercial Raney Ni <sup>b</sup>	N <sub>2</sub>	28.2	0	0	0	100
Ni/MgO	N <sub>2</sub>	24.3	0	0	0	100
	H <sub>2</sub>	73.5	0	39.7	0	60.3
Ni/HZSM-5	N <sub>2</sub>	4.8	0	0	0	100
	H <sub>2</sub>	27.6	4.9	7.1	0	88
Ni/SiO <sub>2</sub>	N <sub>2</sub>	6.6	0	0	0	100
	H <sub>2</sub>	31.0	9.7	33.3	0	57.0
Ni/Al <sub>2</sub> O <sub>3</sub>	N <sub>2</sub>	4.2	0	0	0	100
	H <sub>2</sub>	31.8	12.4	29.5	0	58.1
Ni/TiO <sub>2</sub>	N <sub>2</sub>	1.6	0	0	0	100
	H <sub>2</sub>	31.1	9.1	13.6	0	77.3
Pt/C	N <sub>2</sub>	0	0	0	0	0
Pd/C	N <sub>2</sub>	0	0	0	0	0
Pd/C	H <sub>2</sub>	55.5	2.1	4.4	92.2	1.3
Au/C	N <sub>2</sub>	0	0	0	0	0
Ru/C	N <sub>2</sub>	0	0	0	0	0

Reaction conditions: 2 mmol guaiacol, 15 mL H<sub>2</sub>O, (a:200 mg wet Cat., b:200 mg dry cat.), 160 °C, initial 0.5 MPa (N<sub>2</sub> or H<sub>2</sub>), 2 h.

**Table S2** ICP-AES analysis results

Catalyst	Ni loading amount /wt%
Ni/MgO	37.3
Ni/Al <sub>2</sub> O <sub>3</sub>	40.6
Ni/SiO <sub>2</sub>	35.8
Ni/HZSM-5	40.1
Ni/TiO <sub>2</sub>	36.2

**Table S3** Comparison of different solvents.

Solvent	Time (h)	Conv. (%)	Sel.(%)		
			Cyclohexanone	Cyclohexanol	Phenol
THF	2	0			
	6	0			
THF&H <sub>2</sub> O	2	26.3	0	0	100
THF&IPA	2	89.6	1.2	75.1	23.7

Reaction conditions: 2 mmol guaiacol, 15 mL mixed solvent, 200 mg Cat., 160 °C, initial 0.5 MPa N<sub>2</sub>, 2 h.

**Table S4** Performance of nano-porous nickel for hydrodeoxygenation of different substrates.

Sbustrate.	Conv.(% )	Productivity (mmol <sub>H<sub>2</sub></sub> ·g <sub>cat</sub> <sup>-1</sup> ·h <sup>-1</sup> )	Sel.(%)		
			Cyclohexanone	Cyclohexanol	Phenol
Guaiacol	41.5	2.10	0	0	100
Catechol	0	0	0	0	0
Phenol	5.1	0.51	100	0	-

Reaction conditions: 2 mmol Substrate, 15 mL H<sub>2</sub>O, 200 mg Cat., 160 °C initial 0.5 MPa N<sub>2</sub>, 2 h.



**Table S5** Effect of hydrogen pressure on guaiacol hydrodeoxygenation

Entry	Conv.(%)	P(MPa)	Productivity( $\text{mmol}_{\text{phenol}} \cdot \text{g}_{\text{cat.}}^{-1} \cdot \text{h}^{-1}$ )	Sel.(%)		
				Cyclohexanone	Cyclohexanol	Phenol
1	41.5	0.5(N <sub>2</sub> )	2.07	0	0	100
2	18.1	1/625(H <sub>2</sub> )	0.86	1.9	2.5	95.6
3	32.1	1/25(H <sub>2</sub> )	1.45	5.1	4.1	90.8

Reaction conditions: 2 mmol guaiacol , 15 mL H<sub>2</sub>O, 200 mg Cat., 160 °C ,2 h

**Table S6** Effect of methanol content on guaiacol hydrodeoxygenation

n.(mmol)	Conv.(%)	Productivity( $\text{mmol}_{\text{phenol}} \cdot \text{g}_{\text{cat.}}^{-1} \cdot \text{h}^{-1}$ )	Sel.(%)		
			Cyclohexanone	Cyclohexanol	Phenol
0	41.5	2.07	0	0	100
0.5	28.7	1.21	9.8	6.3	84.0
1	24.6	1.06	8.9	5.3	85.8
4	18.5	0.56	13.5	26.5	60.0
8	9.2	0.26	10.9	33.7	55.4

Reaction conditions: 2 mmol guaiacol, 15 mL H<sub>2</sub>O, 200 mg Cat., 160 °C, initial 0.5 MPa N<sub>2</sub>, 2 h

**Table S7** Effect of temperature on hydrodeoxygenation of guaiacol.

T.(°C)	Conv.(%)	Productivity (mmol <sub>phenol</sub> ·g <sub>cat</sub> <sup>-1</sup> ·h <sup>-1</sup> )	Sel.(%)		
			Cyclohexanone	Cyclohexanol	Phenol
120	6.5	0.33	-	-	100
140	11.5	0.29	-	-	100
160	41.5	2.07	-	-	100
180	79.3	3.56	5.3	4.9	89.8
200	90.9	3.58	12.7	8.5	78.8

Reaction conditions: 2 mmol guaiacol, 15 mL H<sub>2</sub>O, 200 mg Cat., initial 0.5 MPa N<sub>2</sub>, 2 h.

**Table S8** Effect of reaction time hydrodeoxygenatio of guaiacol.

Time (h)	Conv. (%)	Productivity ( $\text{mmol}_{\text{phenol}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ )	Sel.(%)		
			Cyclohexanone	Cyclohexanol	Phenol
0	0	0.00	0	0	0
0.5	7.5	1.50	0	0	100
1	13.8	1.38	0	0	100
2	41.5	2.07	0	0	100
4	49.6	1.07	7.6	5.8	86.6
6	50.8	0.69	9.9	8.7	81.4
8	51.1	0.48	12.7	12.7	74.6
10	53.7	0.41	12.4	12.4	75.6
12	53.4	0.32	14.0	14.8	71.2

Reaction conditions: 2 mmol guaiacol, 15 mL H<sub>2</sub>O, 200 mg Cat., 160 °C, initial 0.5 MPa N<sub>2</sub>.

**Table S9** Effect of amount of catalyst on hydrodeoxygenatio of guaiacol.

Catalyst/Sbstrate	Conv.(%)	Productivity ( $\text{mmol}_{\text{phenol}} \cdot \text{g}_{\text{cat}}^{-1} \cdot \text{h}^{-1}$ )	Sel.(%)		
			Cyclohexanone	Cyclohexanol	Phenol
0.5:1	7.5	0.75	0	0	100
1:1	41.5	2.07	0	0	100
2:1	27.2	0.68	0	0	100
3:1	22.3	0.37	0	0	100

Reaction conditions: 2 mmol guaiacol, 15 mL H<sub>2</sub>O, 160 °C, initial 0.5 MPa N<sub>2</sub>, 2 h.

**Table S10** Results for the hydrodeoxygenation of guaiacol under different conditions.

Entry	Conv.(%)	Tem. (°C)	Time (h)	Sel. (%)		
				Cyclohexanone	Cyclohexanol	Phenol
1	41.5	160	2	0	0	100
2	49.6	160	4	7.6	5.8	86.6
3 <sup>a</sup>	6.2	180	4	69.4	30.6	-
4 <sup>a</sup>	7.6	190	3	67.1	32.9	-
5 <sup>b</sup>	31.8	160	2	44.3	55.7	-
6	43.3	180	1	4.2	3.0	92.8
7	79.3	180	2	5.3	4.9	89.8
8	94.5	180	4	10.6	8.5	80.9
9 <sup>c</sup>	57.3	180	2	2.9	2.2	94.9
10 <sup>c</sup>	88.9	180	4	7.2	5.2	87.6
11	96.3	190	3	11.7	10.4	77.9
12 <sup>c</sup>	90.5	190	3	5.0	4.7	90.3
13	90.9	200	2	12.7	8.5	78.8

Reaction Conditions: unless otherwise specified, 2 mmol guaiacol, 15 mL H<sub>2</sub>O, initial 0.5 MPa N<sub>2</sub>.

- The substrate is 2 mmol phenol.
- The substrate is a mixture of 2 mmol phenol and 2 mmol methanol.
- Methanol is separated during the reaction by opening the relief valves.

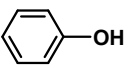

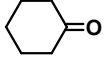
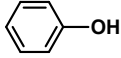
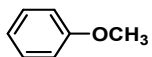
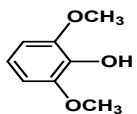
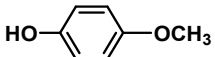
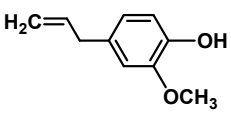
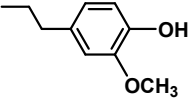
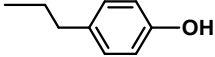
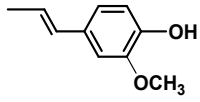
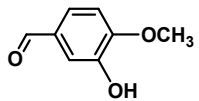
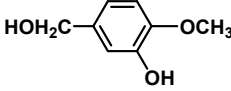
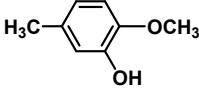
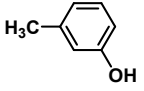
**Table S11** Ni/Al ratio of fresh catalyst and waste catalyst obtained by ICP analysis.

Cat.	Ni(mg/L)	Al(mg/L)	Ni/Al	Al(mg)
Fresh catalyst	1012	115.7	8.8	20.4
Spent catalyst	722.5	59.9	12.1	15.3

Fresh catalyst:200 mg

Spent catalyst:200 mg

**Table S12** *In-situ* HDO of phenolic monomers over nano-porous Ni in water.

Entry	Sbustrate	Conv.(%)	Sel.(%)		
1		5.1		 100	
2		1.2	100		
3		3.9			50.5
4		4.6			100
5		50.7	 77.7	 16.8	 5.5
6		39.5	 51.8	 38.8	 9.4

Reaction conditions: 2 mmol sbustrate, 15 mL H<sub>2</sub>O, 200 mg Cat., 160 °C, initial 0.5 MPa N<sub>2</sub>, 2 h.

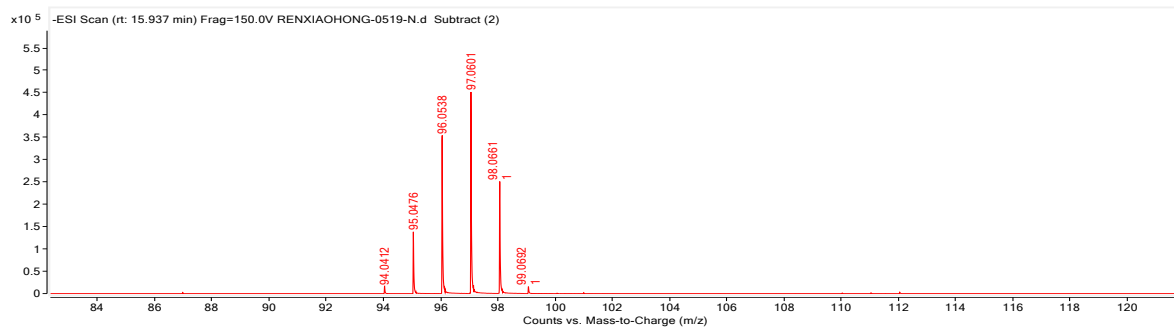


**Table S13** Comparison of different catalytic systems for HDO of guaiacol and other lignin monomers to phenolics.

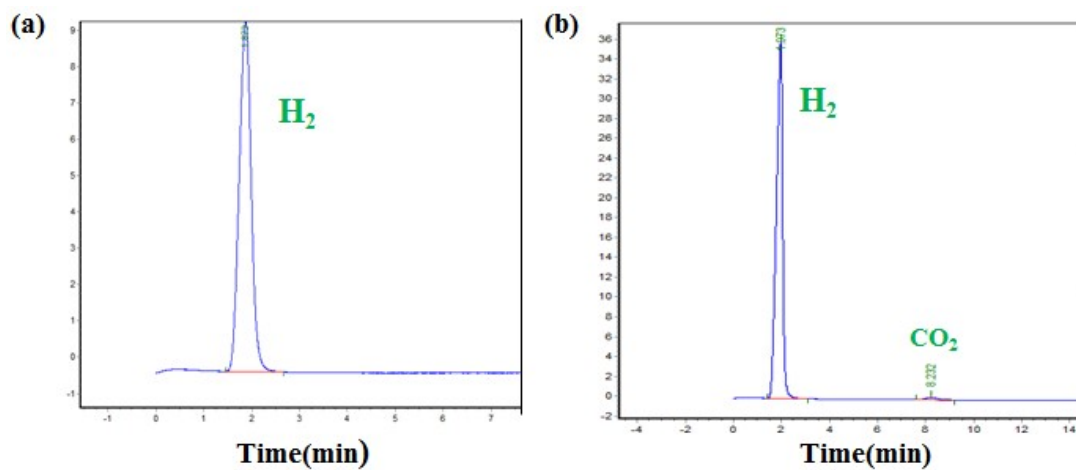
Entry	Catalyst	Reactor	Tem (°C)	H <sub>2</sub> Pre. (bar)	Solvent	Substrate	Conv (%)	Product (Sel. %)	Ref.
1	MoN/SBA15	Batch	300	50	Decalin	Guaiacol	44	Phenol (26)	1
2	MoN-A	Batch	300	50	Decalin	Guaiacol	95	Phenol (90)	2
3	1Mo/C	Fixed-bed	350	40	No Solvent	Guaiacol	74.1	Phenol (78.5)	3
4	NiMo/Al <sub>2</sub> O <sub>3</sub>	Packed- bed	450	20.7	No Solvent	4- propylguaiacol	~95	4-propylphenol (~70)	4
5	$\alpha$ -MoC <sub>1-x</sub> /AC	Batch	340	-	Tetralin <sup>a</sup>	Guaiacol	53	Phenol (84)	5
6	MoWBO <sub>x</sub> /AC	Fixed-bed	400	40	Methanol	Vanillic acid + Syringic acid	100	p- hydroxybenzoic acid (71.6)	6
7	MoC <sub>x</sub> /C	Batch	300	5	Hexane	Guaiacol	99	Phenol (76)	7
8	MoC <sub>x</sub> /C	Batch	300	5	Hexane	Syringol	91	Phenol (37)	7
9	Re/ZrO <sub>2</sub>	Batch	300	50	Decalin	Guaiacol	~50	Phenol (~35)	8
10	WP/SiO <sub>2</sub>	Packed bed	300	50	No Solvent	Guaiacol	60	Phenol (100)	9
11	Fe/CeO <sub>2</sub>	Fixed-bed	400	1	No Solvent	Guaiacol	61.6	Phenol (57.6)	10
12	Au/TiO <sub>2</sub>	Batch	300	65	Toluene	Guaiacol	100	Phenol (49.6)	11
13	Ru/TiO <sub>2</sub>	Batch	240	4	Water	Guaiacol	83.6	Phenol (70.4)	12
14	Ni/CeO <sub>2</sub> -C	Batch	250	-	Water	Guaiacol	22	Catechol (20)	13
15	Ru/C	Batch	250	-	Water	Guaiacol	25.1	Catechol (12)	14
16	$\alpha$ -2Mo1Sn	Batch	300	4	n-hexane	Guaiacol	100	Phenol (92.5%)	15
17 <sup>a</sup>	NP-Ni	Batch	160	-	Water	Guaiacol	41.5	Phenol (100)	This work
18 <sup>a</sup>	NP-Ni	Batch	180	-	Water	Guaiacol	79.3	Phenol (89.8)	This work
19 <sup>b</sup>	NP-Ni	Batch	180	-	Water	Guaiacol	88.9	Phenol (87.6)	This work
20 <sup>b</sup>	NP-Ni	Batch	190	-	Water	Guaiacol	90.5	Phenol (90.3)	This work
21 <sup>b</sup>	NP-Ni	Batch	200	-	Water	4-propyl -guaiacol	75.8	4-propyl – phenol ( 87.1 )	This work

a. Unless otherwise specified, the reaction condition is: 2 mmol guaiacol, 15 mL H<sub>2</sub>O, initial 0.5 MPa N<sub>2</sub>.

b. Methanol is separated during the reaction by opening the relief valves.



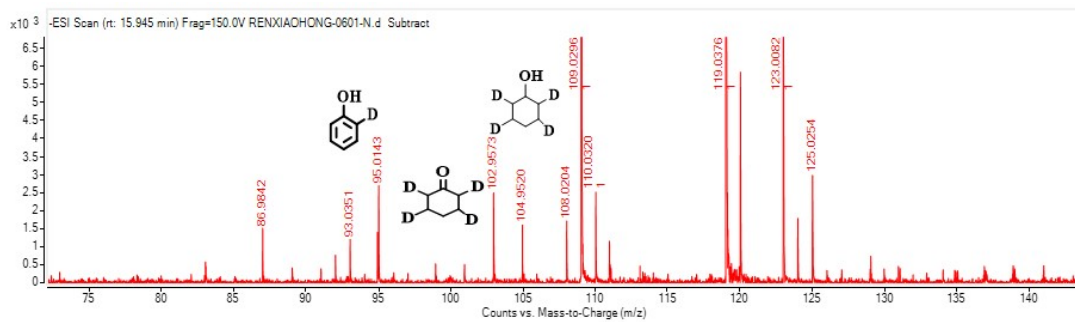
**Fig. S1** Mass spectrogram of the products after reaction in D<sub>2</sub>O.



**Fig. S2** (a) Gas chromatograms of  $H_2$  (b) Gas chromatograms of  $H_2$  and  $CO_2$ .

Reaction conditions: (a) 15 mL  $H_2O$ , 160 °C, initial 0.5 MPa  $N_2$ , 2 h.

Reaction conditions: (b) 2 mmol methanol, 15 mL  $H_2O$ , 160 °C, initial 0.5 MPa  $N_2$ , 2 h.



**Fig. S3** Liquid mass spectrometry of hydrodeoxygenation products of guaiacol.

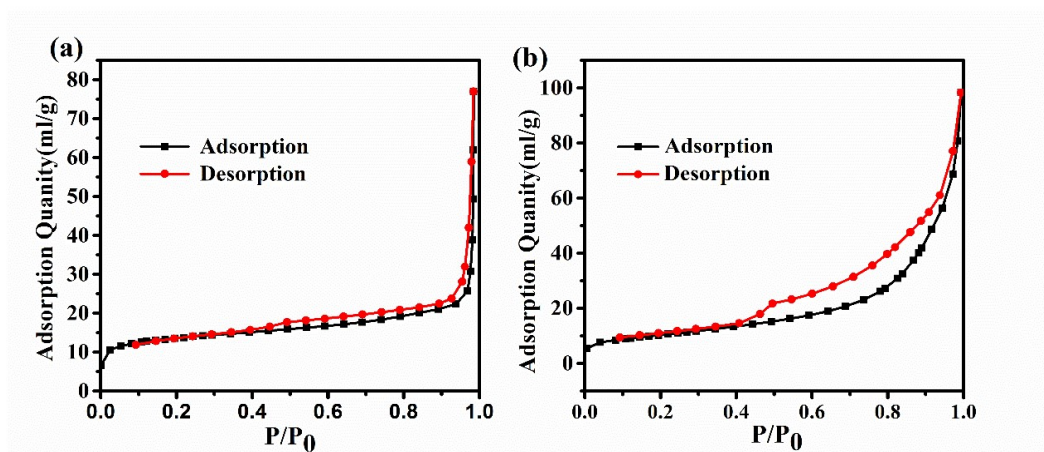


Fig. S4 (a)  $N_2$  adsorption-desorption of fresh catalyst, (b)  $N_2$  adsorption-desorption of spent catalyst.

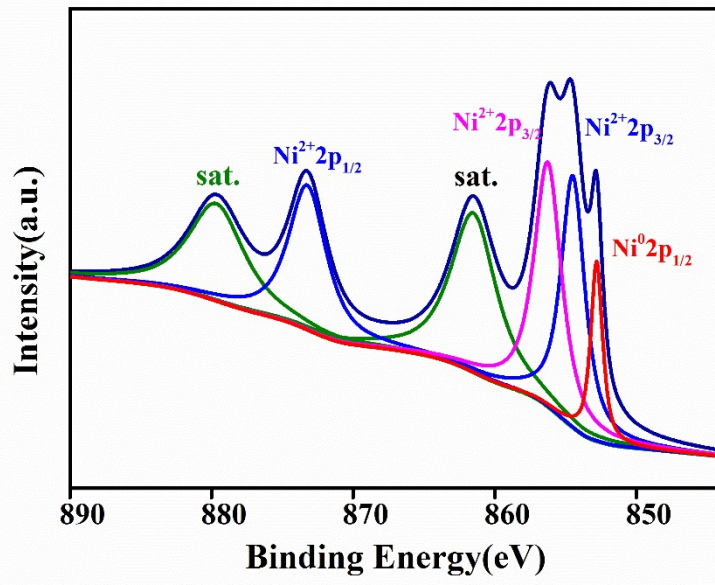


Fig. S5 XPS spectra of the regenerative catalyst.

## References:

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