

Supporting Information

**Ni@C Catalyzed Hydrogenation of Acetophenone to
Phenylethanol under Industrial Mild Conditions in Flow Reactor**

Shanshan Lin^{a,c}, Jianguo Liu^{b*}, Longlong Ma^{b*}

^a CAS Key Laboratory of Renewable Energy, Guangdong Provincial Key Laboratory of New and Renewable Energy Research and Development, Guangzhou Institute of Energy Conversion, Chinese Academy of Sciences, Guangzhou 510640, P. R. China.

^b Key Laboratory of Energy Thermal Conversion and Control of Ministry of Education, School of Energy and Environment, Southeast University, Nanjing 210096, PR China.

^c University of Chinese Academy of Sciences, Beijing 100049, P. R. China.

* Corresponding author: liujg@seu.edu.cn; mall@seu.edu.cn

Content

S1. Methods and materials	2
S2. Preparation of Ni@C catalyst	2
S3. Procedure for the synthesis of phenylethanol	3
S3.1. General procedure for hydrogenation of acetophenone in a batch reactor	3
S3.2. General procedure for hydrogenation of acetophenone in a flow reactor	3
S4. TEM spectra of Ni@C-700-EtOH and Ni@C-700-EtOH (recycled) catalyst.	3
S5. XRD spectra of Ni@C-700-EtOH and Ni@C-700-EtOH (recycled) catalyst.	4
S6. XPS spectra of Ni@C-700- EtOH catalyst	5
S7. EDS element of Ni@C-700- EtOH Ni@C-700-EtOH (recycled) catalyst.....	6
S8. BET spectra of Ni@C-700-EtOH	7
S9. GC and GC-MS spectra	7

S1. Methods and materials

1,3,5-trimethoxybenzene was purchased from Sigma Aldrich Co., Ltd.; Ni(NO₃)₂•6 H₂O (AR, 98%), anhydrous citric acid (AR, ≥99.5%), commercial single ruthenium atom nitrogen-doped carbon catalyst were obtained from Shanghai Macklin Biochemical Co., Ltd.; H₂SO₄ (GR, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd.; acetophenone (AR, ≥99.0%), ethanol (AR, 99.7%), commercial single palladium atom nitrogen-doped carbon catalyst, Raney nickel catalyst (20~40 meshes) were purchased from Aladdin (Shanghai) Chemical Technology Co., Ltd.; (+/-)1-phenylethanol (AR,98.0%) was purchased from Tokyo Chemical Industry Co., Ltd.; Deionized water ($\sigma < 5 \mu\text{S/m}$) was self-made in the laboratory. Before using, the purity of acetophenone and phenylethanol has been checked.

S2. Preparation of Ni@C catalyst

Nickel(II) nitrate hexahydrate (Ni(NO₃)₂•6 H₂O, 0.03 mol) and citric acid (C₆H₈O₇, 0.03 mol) were dissolved in 20 mL of absolute ethanol, and then the mixture was stirred at 70°C (300 rpm) Aging for 4-8 hours until a bubble-like green gel is obtained. Place it in a drying oven at 100 °C for 24 to 72 hours to remove excess water. Then the green solid obtained was calcined in a fixed bed at 700 °C under 40 mL min⁻¹ of high-purity N₂ (99.999%) atmosphere for 3 h, and the heating rate was controlled at 2 °C min⁻¹. The resulting black solid was treated in a 1M H₂SO₄ aqueous solution at 70 °C until the solution became colorless to remove unsafe and uncovered Ni particles. Then, the black solid was washed thoroughly with deionized water until the pH value of the waste liquid was 7. Finally, the black solid was dried in a freeze dryer at -48 °C for 12 h to obtain Ni@C-700-EtOH catalyst.

S3. Procedure for the synthesis of phenylethanol

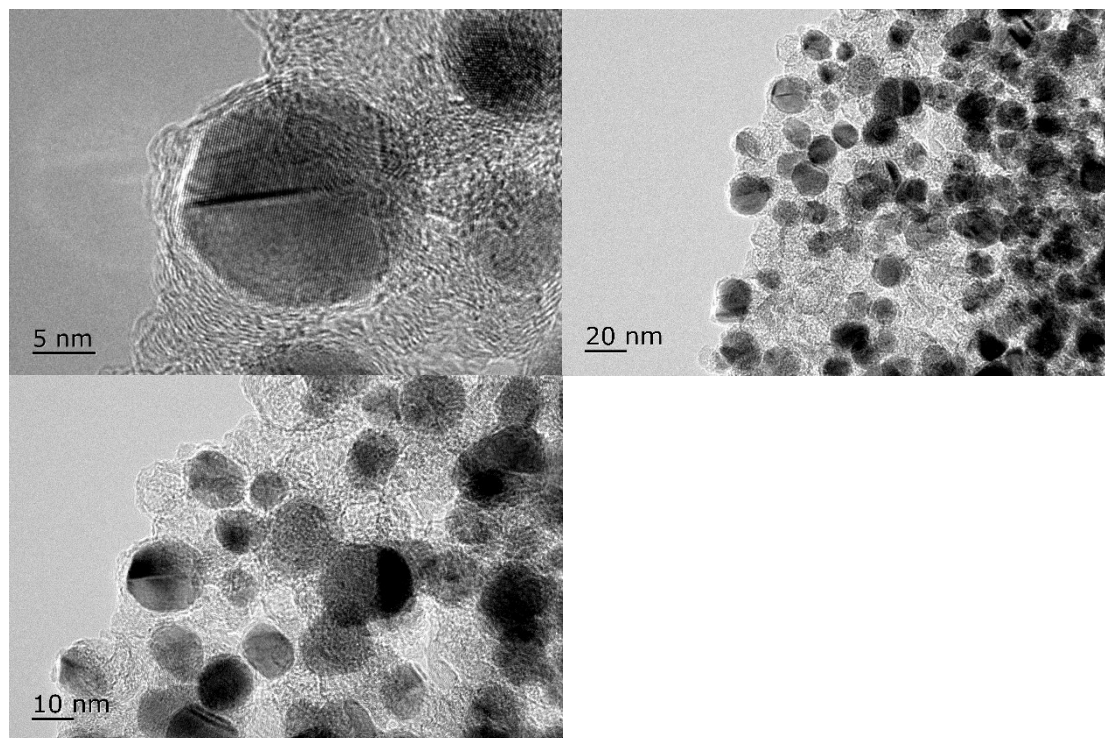
S3.1. General procedure for hydrogenation of acetophenone in a batch reactor

The reaction is carried out in a stainless-steel autoclave (Shanghai Yanzheng Instrument Co., Ltd.), which has a 10 mL well, a thermocouple, and a circulating water-cooling device. A glass lining is placed in the well, which contains a 10 mm magnetic stir bar, 0.5 mmol acetophenone, 10 mg catalyst, and 6 mL solvent. Then, the autoclave was sealed and purged with H₂ 3 times under a pressure of 1MPa, and pressurized with the set target H₂ pressure. Put the autoclave into the heating mantle and set the stirring speed to 300 rpm. The autoclave is preheated from room temperature to the target temperature (the internal temperature detected by the thermocouple) at a rate of 2 °C·min⁻¹. The target temperature is used as the reaction temperature. The reaction is carried out at the reaction temperature for the required time. After the reaction, the autoclave was cooled to room temperature and the remaining gas was discharged. The reaction solution was collected with a dropper and filtered. The catalyst was fixed on a magnetic stir bar and washed thoroughly with ethanol and water. Then use a freeze dryer to dry the catalyst (together with a magnetic stir bar) under vacuum at -48 °C for 12 hours. The reaction product was identified by GC, and the yield of the reaction product was determined by GC, using 1,3,5-trimethoxybenzene as the internal standard.

S3.2. General procedure for hydrogenation of acetophenone in a flow reactor

The reaction is carried out in a flow reactor (Ou Shisheng (Beijing) Technology Co., Ltd.). First, the flow reactor reaction tube is filled with magnets that can adsorb 100 mg of catalyst, and the reaction tube is maintained at a specific reaction temperature and H₂ pressure. Then, the acetophenone reaction raw material with a concentration of 0.083 mol/L is replaced with gas. The mixed liquid is pumped into the reaction tube at a flow rate of 0.4ml/min, and the reacted mixed liquid flows through the gas-liquid separator at a constant flow rate and enters the product collection device for gas phase and nuclear magnetic measurement. The reaction product was identified by GC, and the yield of the reaction product was determined by GC, using 1,3,5-trimethoxybenzene as the internal standard.

S4. TEM spectra of Ni@C-700-EtOH and Ni@C-700-EtOH (recycled)



catalyst

Figure S1 TEM images of Ni@C-700-EtOH

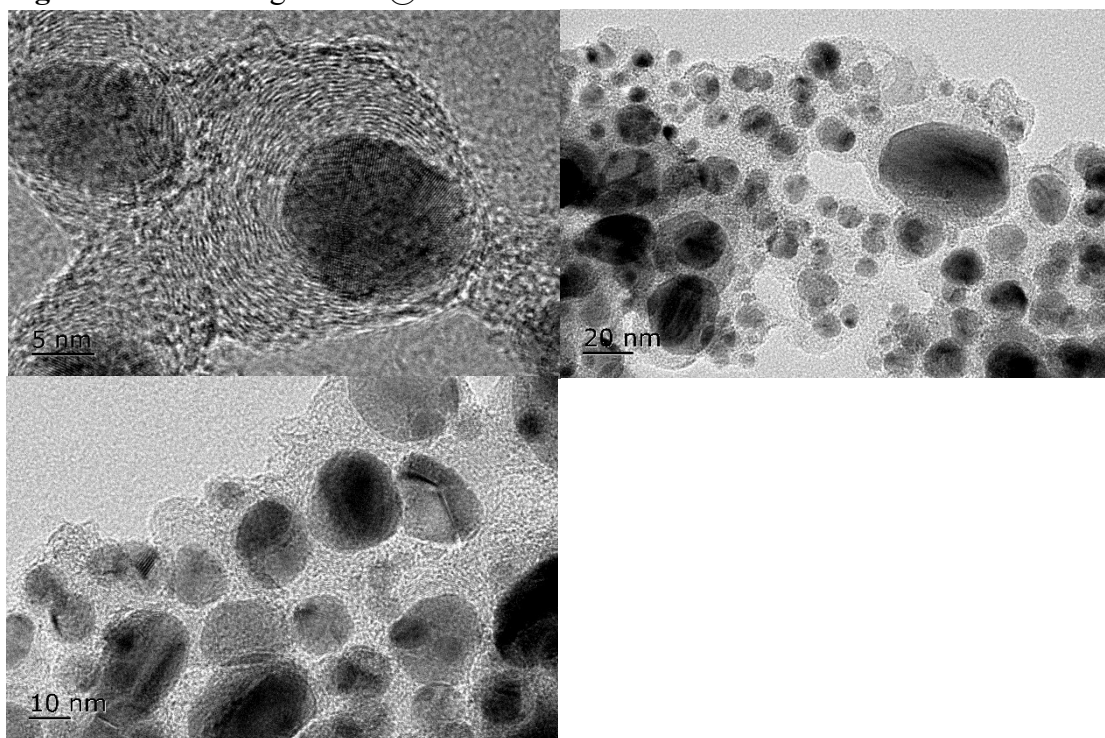


Figure S2 TEM images of Ni@C-700-EtOH (recycled)

S5. XRD spectra of Ni@C-700-EtOH and Ni@C-700-EtOH (recycled) catalyst

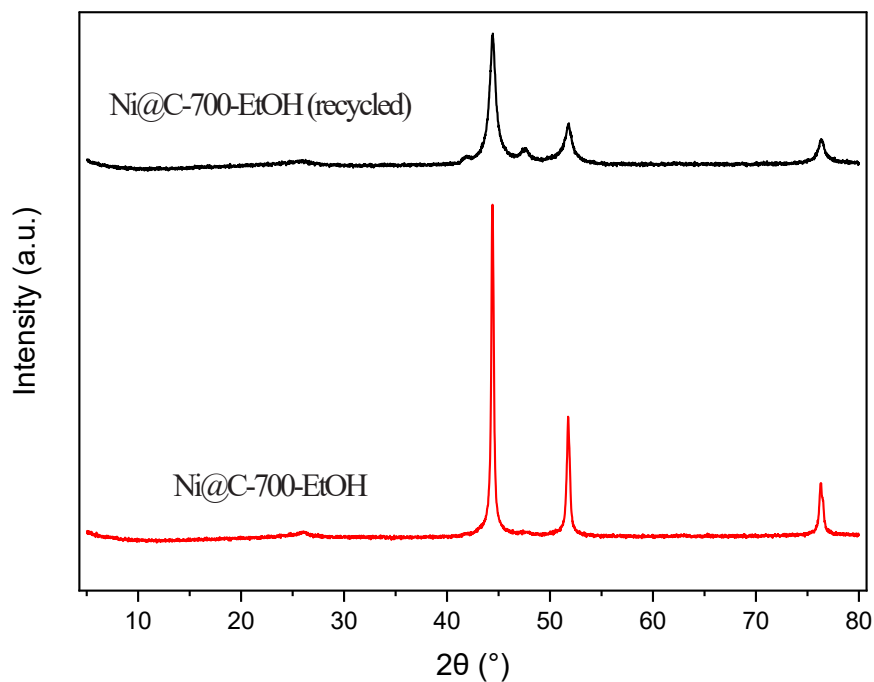


Figure S3 XRD patterns of Ni@C-700-EtOH and Ni@C-700-EtOH (recycled)

S6. XPS spectra of Ni@C-700- EtOH catalyst

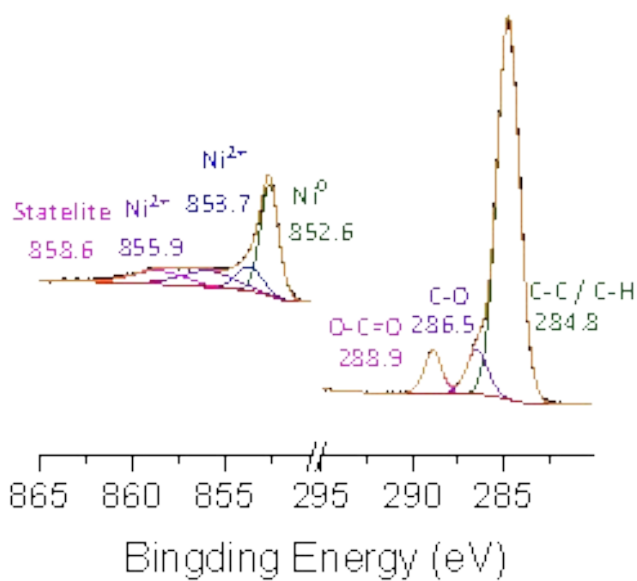
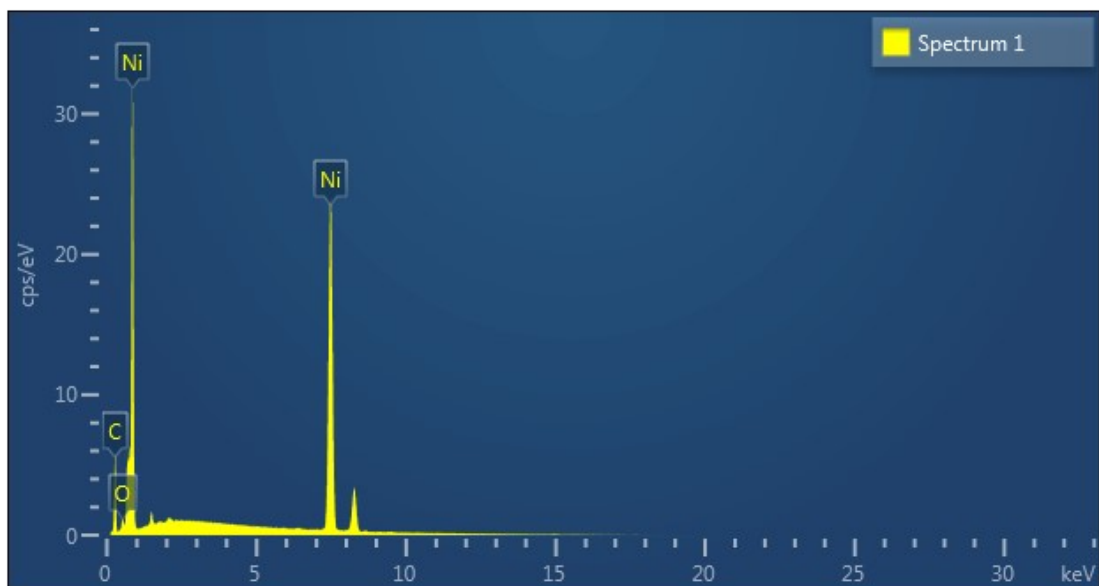


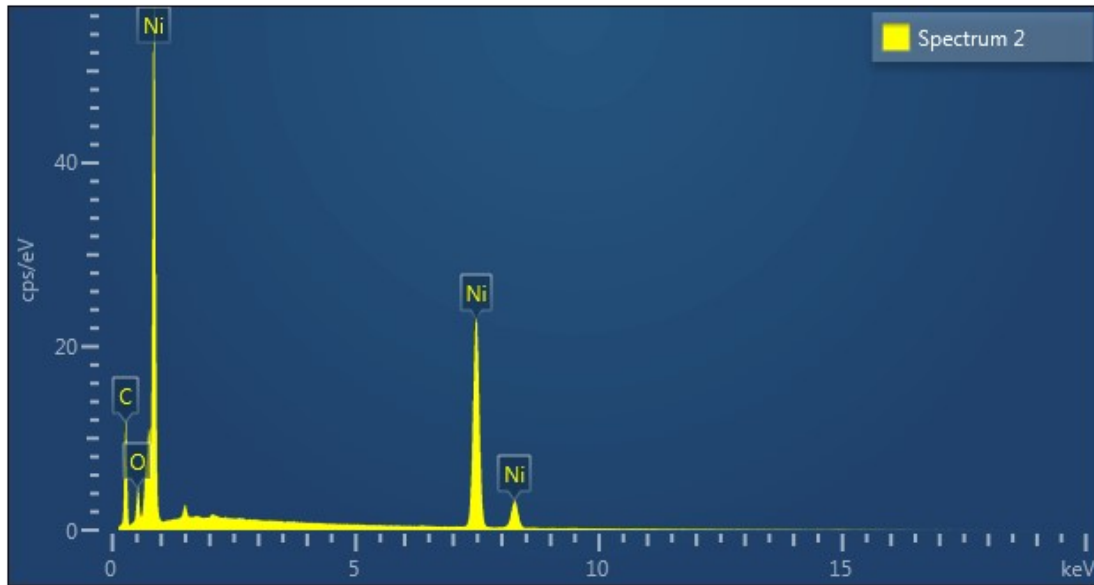
Figure S4 XPS image of Ni@C-700-EtOH

S7. EDS element of Ni@C-700-EtOH and Ni@C-700-EtOH (recycled)



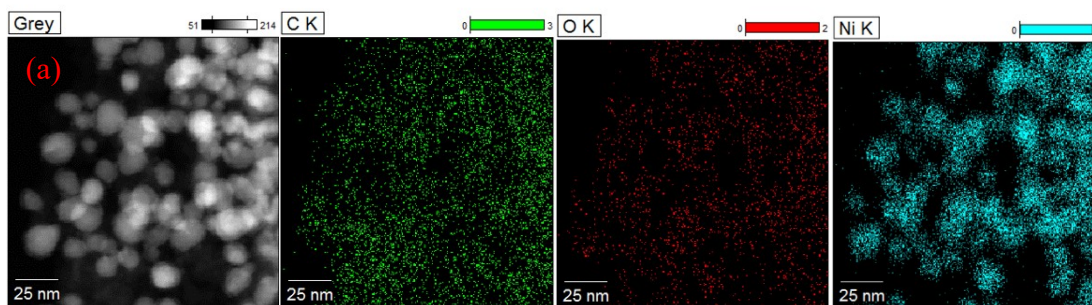
Element	Line Type	Apparent Concentration	k Ratio	Wt %	Wt % Sigma	Atomic %	Standard Label	Factor Standard	Standard Calibration Date
C	K series	5.20	0.05204	25.15	0.26	60.92	C Vit	Yes	
O	K series	1.36	0.00459	1.50	0.07	2.72	SiO2	Yes	
Ni	K series	81.40	0.81395	73.36	0.26	36.36	Ni	Yes	
Total:				100.00		100.00			

Figure S5 EDX pattern of Ni@C-700-EtOH



Element	Line Type	Apparent Concentration	k Ratio	Wt %	Wt % Sigma	Atomic %	Standard Label	Factor	Standard	Standard Calibration Date
C	K series	11.20	0.11200	36.13	0.23	68.67	C Vit	Yes		
O	K series	6.31	0.02122	6.27	0.11	8.94	SiO2	Yes		
Ni	K series	78.98	0.78982	57.60	0.22	22.39	Ni	Yes		
Total:				100.00		100.00				

Figure S6 EDX pattern of Ni@C-700-EtOH (recycled)



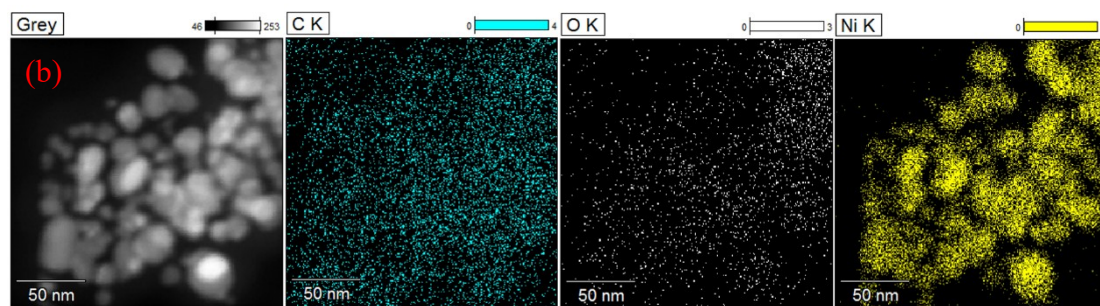


Figure S7 EDS mapping of (a) Ni@C-700-EtOH and (b) Ni@C-700-EtOH (recycled)

S8. BET spectra of Ni@C-700-EtOH

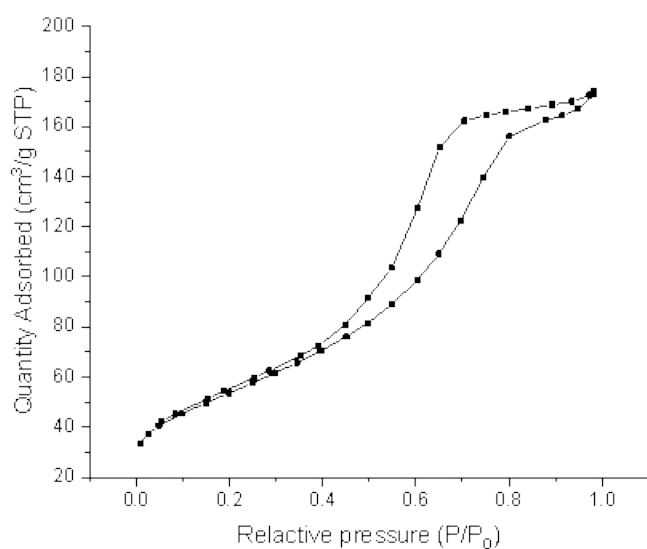
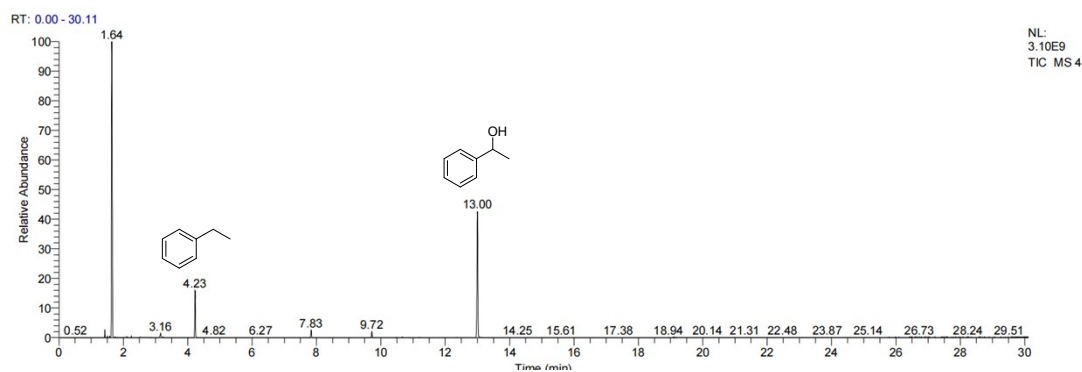
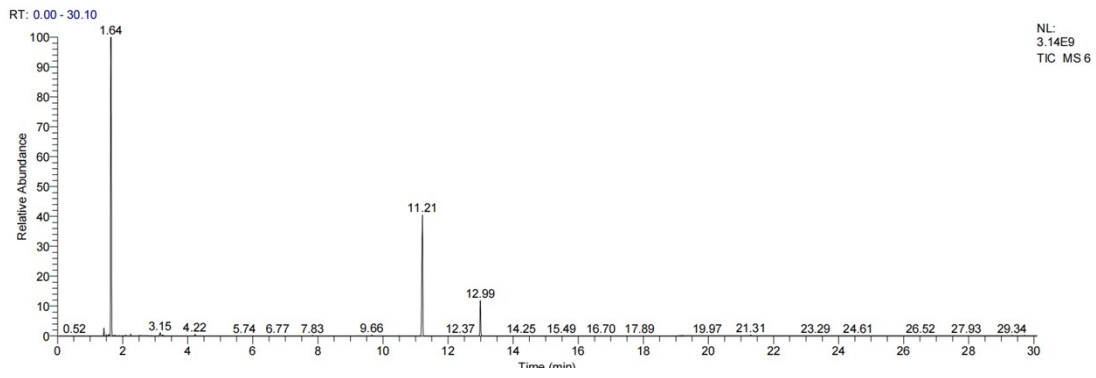
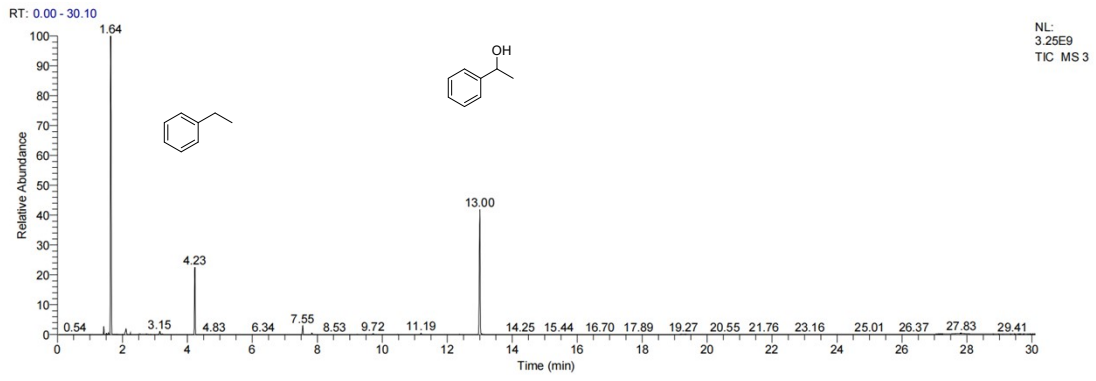
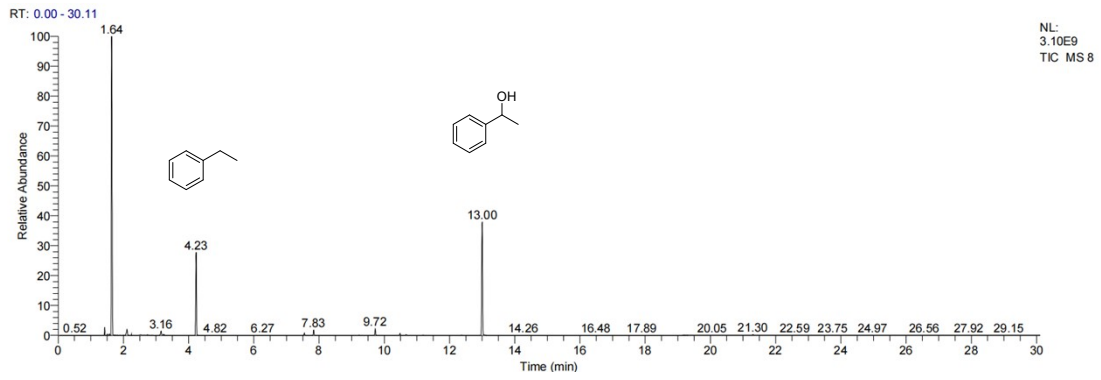
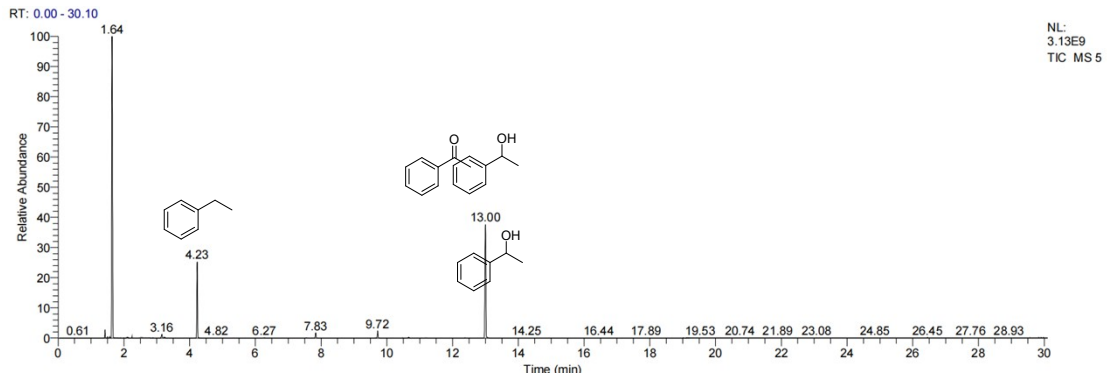
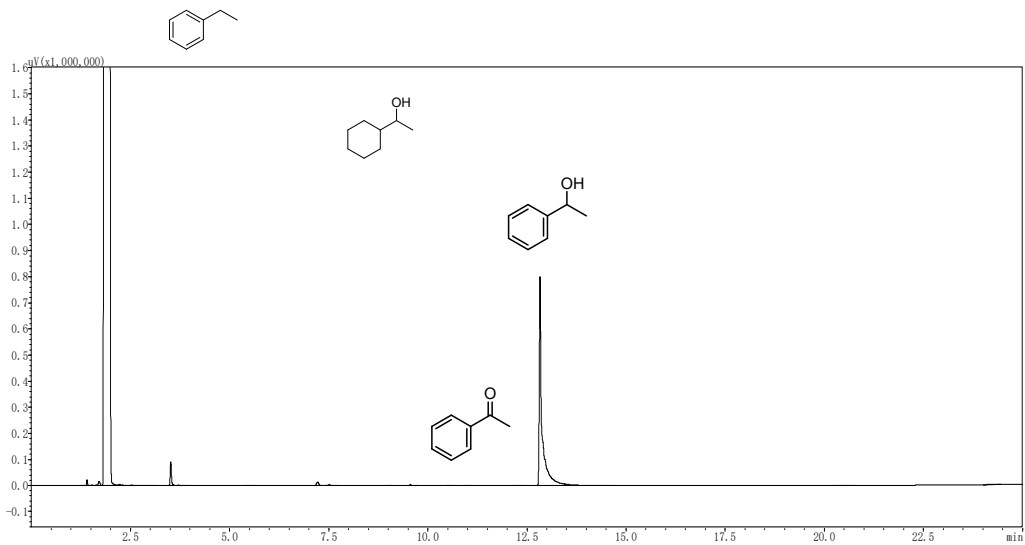
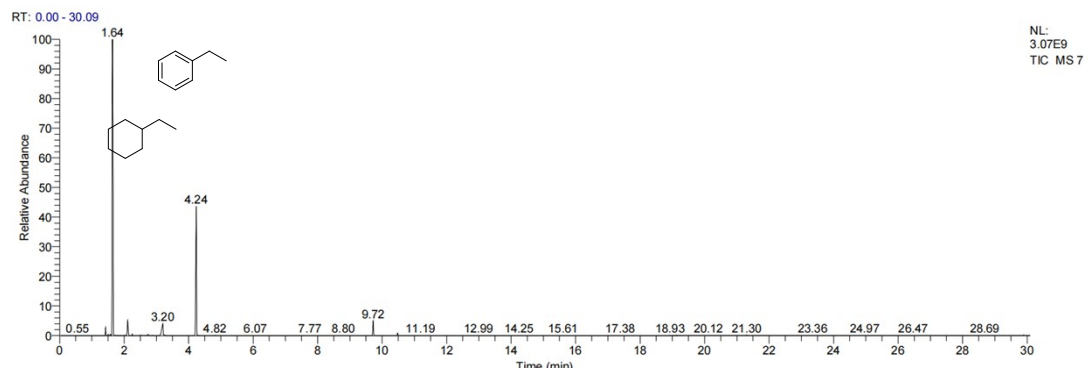
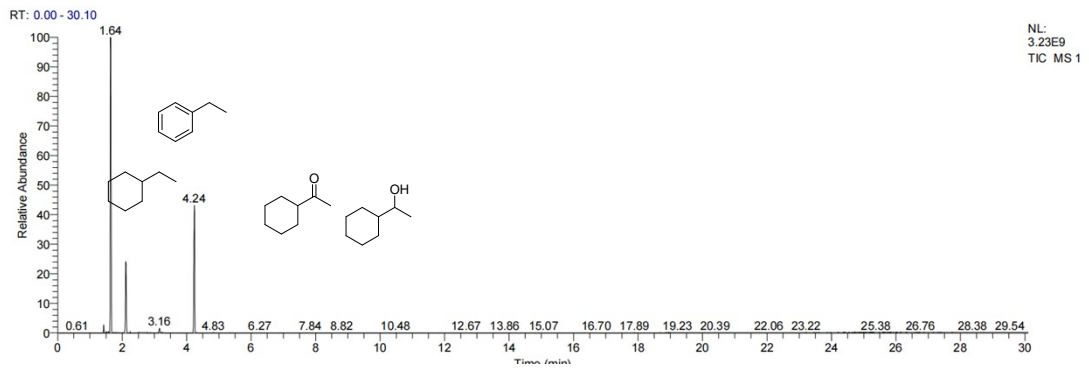
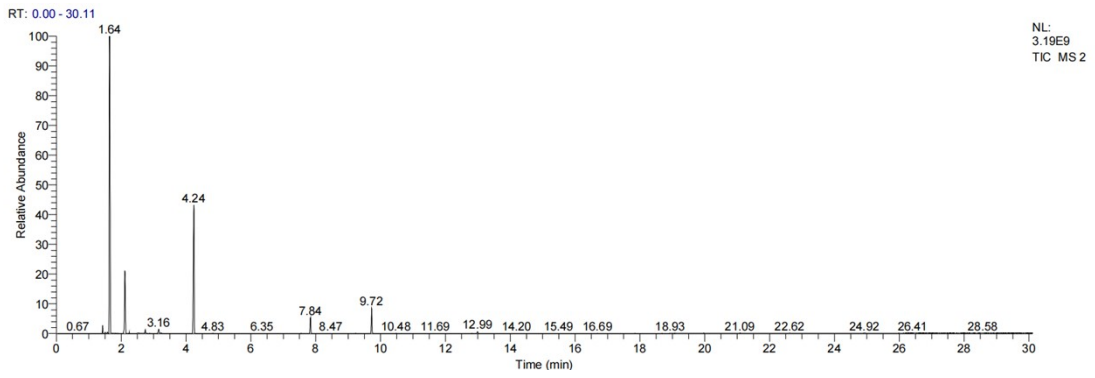


Figure S8 Nitrogen adsorption-desorption isotherms of Ni@C-700-EtOH

S9. GC and GC-MS spectra







The first 8 graphs are GC-MS graphs of the hydrogenation of acetophenone by catalysts A to I in a batch reactor.

The last graph represent the GC graph of the hydrogenation of acetophenone under optimization conditions in flow reactor.