

Supplementary Information

Screening of Ni based catalysts supported on metal oxides for liquid-phase hydrogenation of furfural to furfuryl alcohol

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Materials

Al₂O₃ (99.99% metals basis, γ phase, 20 nm) was purchased from Aladdin Industrial Corporation, SiO₂ (99%, 20 nm), ZrO₂ (>99%, 20-40 nm), TiO₂ (99%, 15-25 nm) and MgO (98%, 20 nm) were purchased by XFNANO, Inc. Ni(NO₃)₂·6H₂O (AR, \geq 98.0%), FAL (AR, \geq 99.0%) and isopropanol (AR, \geq 99.7%) were supplied from Sinopharm Chemical Reagent Co., Ltd. All chemicals were used without purification.

Catalyst characterization

The mass losses and the physicochemical changes of the precursors after impregnation in heat treatment were identified by Thermogravimetry-differential thermal analysis (TG-DTA) experiments using a HENVEN HCT-1 instrument. For each test, about 10 mg of the sample was placed in an alumina crucible and then introduced inside the furnace. All the samples were analyzed in the temperature interval 40-800°C, with a nominal heating rate of 10°C/min.

The crystal structures of the catalysts were analyzed by using a X-ray diffractometer (Rigaku Ultima IV, Cu K α target, λ =1.5406 Å) at 40 kV/100 mA on a spinner in the range of 2θ =5-80° with a step size of 0.02°.

X-ray photoelectron spectroscopy (XPS) spectra were recorded using a Thermo ESCALAB 250XI spectrometer with Al-K α radiation ($h\nu$ =1486.6 eV). Binding energies were determined with the adventitious carbon (C 1s at 284.8 eV) as the reference.

Transmission electron microscopy (TEM) images and energy dispersive X-ray spectroscopy (EDS) mapping were taken by a FEI Tecnai G2 F20. Prior to the measurement, the samples were prepared by depositing a drop of an ultra-sonicated methanol suspension of the solid material onto a carbon-coated Cu grid for TEM measurement.

N₂ adsorption-desorption isotherms were recorded at 77 K using a Micromeritics ASAP-2010 instrument. Before the adsorption of N₂, the catalysts were outgassed at 200°C for 2 h to remove moisture and some gases physically adsorbed on/in the porous structure and surface of the catalyst. Specific surface areas of the sample were calculated according to the Brunauer-Emmett-Teller (BET) method. The t-plot was applied to evaluate the external surface area and micropore volume. Pore size distributions and mesoporous volume were estimated by the Barrett-Joyner-Halenda (BJH) and micropore (MP) methods.

H₂-temperature programmed reduction (H₂-TPR) patterns of the catalysts after calcination were recorded by employing Vodo VDSorb-91i instrument. The fresh catalysts after calcination (ca. 50 mg but precisely weighted) were loaded in a U-shaped quartz reactor, and the sample was held by using quartz wool. After that, the sample was heated from room temperature to 850 °C (heating rate of 10 °C/min) under a 10 vol% H₂/Ar with a flow rate of 15 mL/min. The final signal (hydrogen consumption) was recorded by a thermal conductivity detector (TCD).

CO₂-temperature-programmed desorption (CO₂-TPD) was carried out to determine the basicity of catalysts using Vodo VDSorb-91i instrument. Approximately 50 mg of sample was pretreated in He flow (20 mL/min) at 500 °C for 1 h (10 °C/min). The reaction temperature was lowered to 50 °C and a pure CO₂ stream (20 mL/min) was subsequently introduced into the reactor for 2 h. The CO₂-TPD was conducted between 50 and 900 °C, under a He flow (10 °C/min and 20 mL/min) and the amount of CO₂ evolved was analyzed using a thermal conductivity reaction (TCD).

H₂ pulse chemisorption measurements was also conducted in Vodo VDSorb-91i instrument. First, Approximately 100 mg of the sample was loaded in a quartz tube and reduced at corresponding temperature under the flow of 10 vol.% H₂/Ar (20 mL/min) for 5 h. The gas flow was then switched over to pure Ar (20 mL/min) for 1 h to remove traces of hydrogen from the catalyst and entire flow path and then the sample was cooled down to 40 °C. Pulses of 0.4 mL 10 vol.% H₂/Ar were injected by quantitative loop connected with the six-way valve till saturation (three consecutive H₂ peaks were similar). The area of peaks was used to calculate the total volume of H₂ chemisorbed; which was further used to calculate Ni metal dispersion based on the assumption that H₂/Ni stoichiometry is equal to 2.

Figures

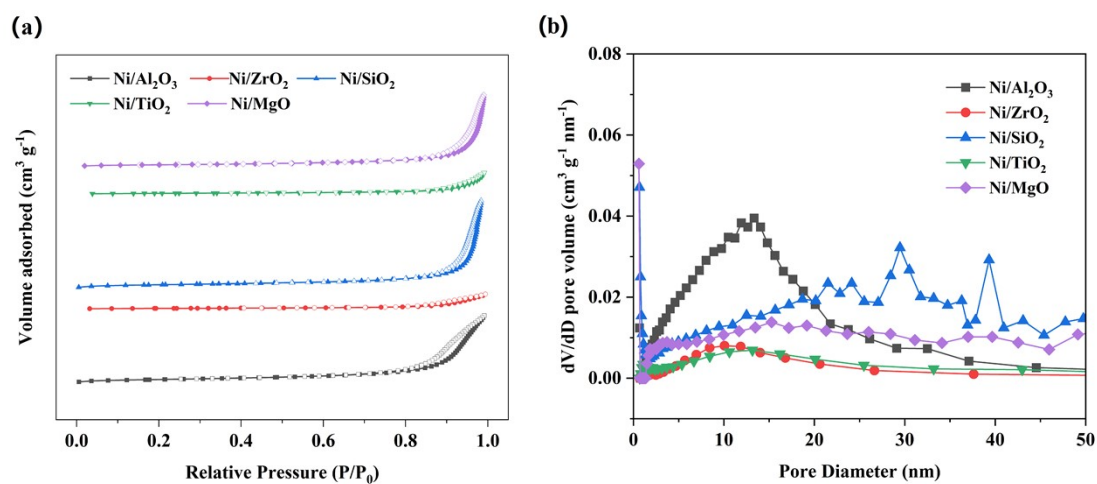


Fig. S1 The results of N₂ adsorption-desorption on the catalysts at 77 K, (a) N₂ adsorption-desorption isotherms and (b) pore-size distributions.

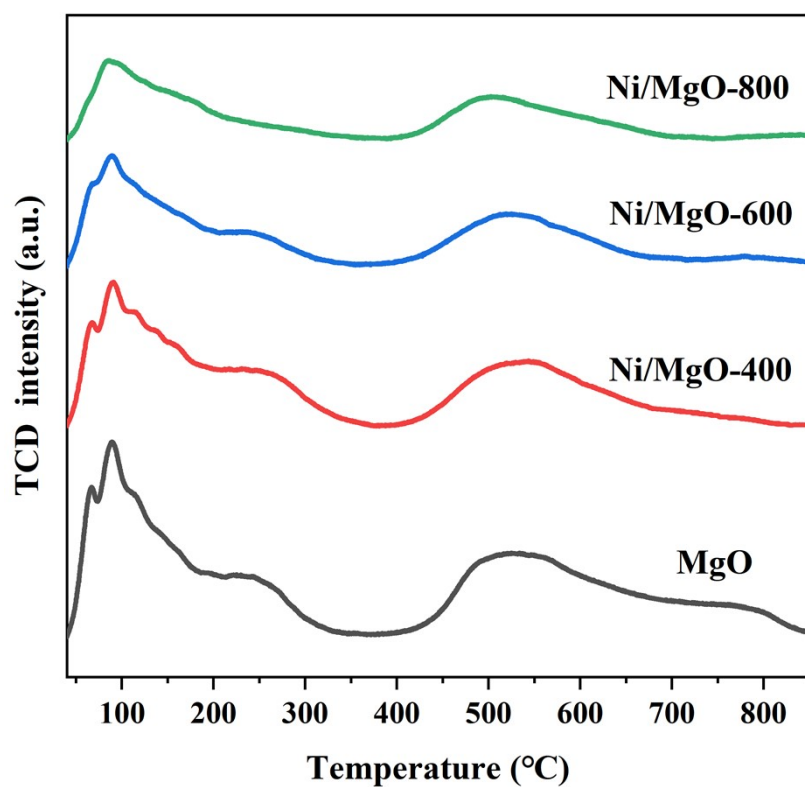


Fig. S2 CO₂-TPD profiles of MgO and Ni/MgO catalysts reduced by H₂ at different temperature.

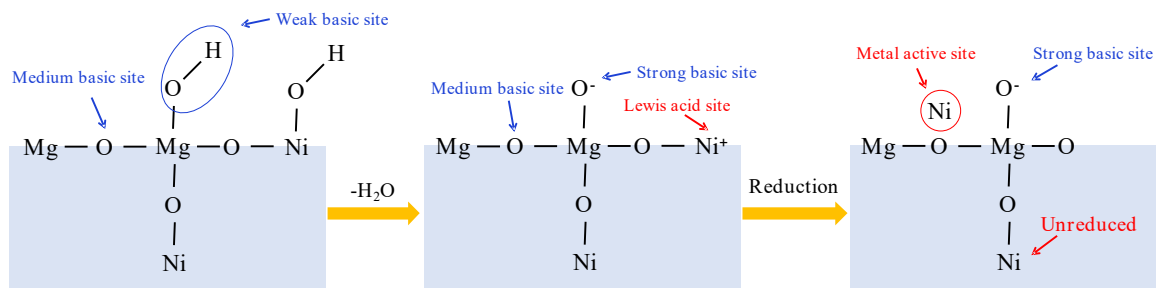


Fig. S3 The proposed changing mechanisms of structural properties for the Ni/MgO catalyst during preparation process.

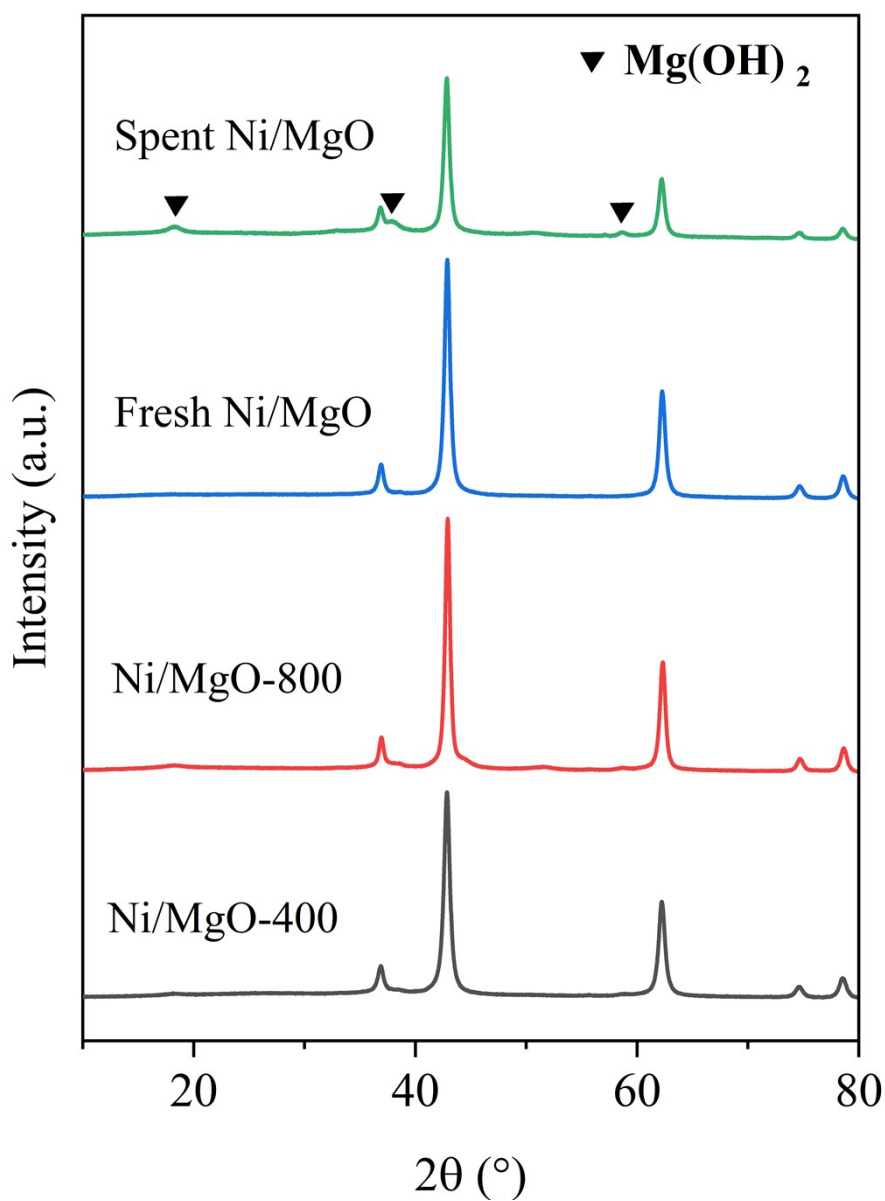


Fig. S4 XRD patterns of the Ni/MgO catalysts.



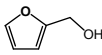
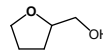
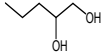
Table

Table S1 XPS Data for Ni/MgO Catalysts reduced by H₂ at different temperature.

RT (°C)	Binding energy (eV)/Atomic concentration (%)							Atomic ratio Ni/Mg
	C 1s		O 1s		Mg 1s	Ni 2p		
400	284.9 (15.15%)	288.7 (4.23%)	529.4 (25.18%)	530.9 (30.94%)	1303.3 (26.67%)	854.8 (0.76%)	859.8 (1.03%)	0.067
600	284.9 (14.24%)	288.7 (3.07%)	529.4 (15.82%)	530.9 (36.39%)	1303.2 (27.91%)	854.8 (1.52%)	859.8 (1.05%)	0.092
800	284.9 (15.02%)	288.7 (2.28%)	529.4 (15.57%)	530.9 (36.27%)	1303.2 (27.92%)	854.8 (1.71%)	859.8 (1.23%)	0.105

RT: Reduction temperature

Table S2 The reaction results of FAL hydrogenation to FOL over Ni/MgO with different using amount^a.

Entry	Catalyst amount (g)	Conversion (%)	Selectivity of products (%)					
								others ^b
1	0.05	59.2	0	1.9	97.3	0.3	0.1	0.4
2	0.1	74.1	0	1.5	96.1	2.0	0.1	0.3
3	0.2	97.7	0	0.9	94.7	4.1	0.1	0.2

^a Reaction conditions: 1 mL FAL, 40 mL isopropanol, 2 MPa H₂, 200°C, 2 h, stirred at 700 rpm.

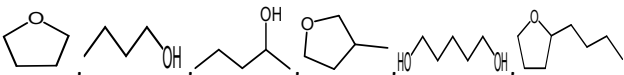





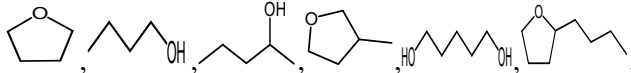
^b others contain 

Table S3 The reaction results of FAL hydrogenation to FOL over Ni/MgO reduced at different temperature^a.

Entry	reduction temperature (°C)	Conversion (%)	Selectivity of products (%)					
								others ^b
1	400	70.5	0	0.8	95.7	3.0	0.2	0.3
2	600	97.7	0	0.9	94.7	4.1	0.1	0.2
3	800	76.8	0	0.8	88.1	10.6	0.1	0.4

^a Reaction conditions: 1 mL FAL, 0.2 g catalyst, 40 mL isopropanol, 2 MPa H₂, 200°C, 2 h, stirred at 700 rpm.

^b others contain .