Supporting information for

Selective conversion of microcrystalline cellulose into hexitols on nickel particles encapsulated within ZSM-5 zeolite

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Materials

Microcrystalline cellulose (relative crystallinity of about 74%) was purchased from Alfa Aesar. $Ni(NO_3)_2$ 9 H_2O (AR) was purchased from Sinopharm Chemical Reagent, SiO_2 (Sigma-Aldrich), TiO_2 (Sigma-Aldrich), γ-Al_2O_3, bentonite and kieselguhr (Sinopharm Chemical Reagent) were used as received. ZSM-5 (NKF-5, H type, Si/Al=25) was purchased from the Catalyst Plant of Nankai University.

The properties of ZSM-5 are as follows: Crystallinity: >=95%, Pore size: 5Å, Framework Density: 1.81 (determined in isooctane), Thermal stability: The differential thermal analyst (DTA) curve shows that the crystal exhibits no major structural change up to temperature of about 1200℃. Hydro-thermal stability: The binder-additive catalyst could retain its crystallinity when treated under 100% steam at a temperature of 700℃ for 12 h. It was cited from the site of The Catalyst Plant of Nankai University http://www.nkcatalyst.com/en/productshow.asp?id=2284&t=&pp=.

Catalyst preparation

The modified incipient impregnation method: A serious of supports (Al_2O_3, SiO_2, ZSM-5, bentonite, kieselguhr and TiO_2) were immersed in an aqueous $Ni(NO_3)_2$ 9 H_2O solution with a certain concentration at room temperature. After ultrasonic treatment for 1 h, the mixture was dried at 343 K with strongly stirring. During this process, water was slowly evaporated and the Ni^{2+} could immerse into the ZSM5 channels. This process will take about 6 h, after that the mixture was vacuum dried at 333 K for 12 h. All the samples were calcined under Ar atmosphere at 723 K for 2 h with heating rate of 5 K/min.

Table S1 The reduction temperature of the Ni catalysts.

Catalyst	Ni/Al_2O_3	Ni/SiO_2	Ni/ZSM-5	Ni/ZSM-5-DP	Ni/bentonite	Ni/kieselguhr	Ni/TiO_2
T/℃	450	400	360	300	400	350	450

The deposition-precipitation method: The supports were put into a certain concentration of $Ni(NO_3)_2$ 9 H_2O solution and dispersed by ultrasonic treatment for 1h. After being heated to 313 K with stirring, a certain concentration Na_2CO_3 solution was dropwise added into the mixture. Then the mixture was aged at 313 K for 2 h and filtrated by air pump filtration. The obtained solid was vacuum dried at 333 K for 12 h. The subsequent treatment of the samples is the same to that of the modified incipient impregnation method.

Hydrogenation experiments

Cellulose hydrogenation

All the catalysts were pre-reduced by H_2 for 2h at appropriate temperatures with heating rate of 5 K/min before being tested in cellulose hydrogenation. The reduction temperatures of the Ni catalyst are shown in Table S1.

In a standard experiment, the reduced catalyst was transferred from the quartz tube to a 50 ml teflon-lined stainless steel autoclave with 10 ml water by a glass catheter and then the substrate was loaded into the reactor. The reactor was flushed with H_2 for three times and then pressurized with 4 MPa H_2 (RT). After being heated to the desired temperature with stirring at a low agitating rate, the reaction was started with stirring at a rate of 1300 rpm. After reaction the products were centrifuged to separate the solid. The solid was dried at 353 K overnight and weighted. The conversion was calculated by weight difference of solid before and after reaction. Quantification of the products was conducted by using HPLC. The yield of each product was calculated as follows: yield (%) = (moles of carbon in each product)/(moles of carbon in cellulose)×100%.

Table S2 Hydrolytic hydrogenation of cellulose on Ni/ZSM-5 catalysts [a]

Catalyst	Conversion/ %	Yield $_{Hexitols}$/ %	Sel [b].$_{Hexitols}$ /%
--	NA	Not detected	Not detected
5% Ni/ZSM-5	86.2	27.2	31.5
17% Ni/ZSM-5	85.9	58.2	67.7
40% Ni/ZSM-5	85.5	48.6	56.8
17% Ni/ZSM-5 [c]	48.9	44.6	91.2
17% Ni/ZSM-5-DP [d]	81.7	16.8	20.6

[a] Reaction conditions:513 K, H_2 4.0 MPa (RT), microcrystalline cellulose 0.2 g, H_2O 10 ml, 4 h, catalyst 100 mg. [b] The selectivity of the product = the yield of product calculated based on calibration curves/the conversion of the cellulose. [c]503 K, 6 h. [d]The catalyst was prepared by deposition-precipitation method. For the blank experiment, we found that the color of the unreacted cellulose changed from white to black, which indicated the humins was formed on the surface of the cellulose through a sequence of degradation, dehydration and polymerization reaction under the reaction conditions. The hexitols and other hydrogenation products were not found, and the thermal conversion of cellulose was not calculated since it is impossible to separate the solid humins and the unreacted cellulose (The conversion of the cellulose was usually calculated by the weight difference of the solid before and after the reaction).

Sorbitol hydrogenolysis

The experiments were conducted at the identical conditions as used for cellulose.

Product analysis

The products were analyzed by a HPLC system (Shimadzu LC-20AB) equipped with RI detector (Shimadzu RID-10A), and a Aminex HPX-87H column (Bio-Rad, 300× 7.8 mm), using 0.5 mM H_2SO_4 as eluent at a flow rate of 0.7 ml/min at 313 K. The content of the each polyol was determined by external standard method.

Table S3 Hydrogenolysis of sorbitol on Ni/ZSM-5 catalysts [a]

Catalyst	Conversion/%	Yield/%			
		Glucose	Glycerol	1,2-PDO	EG
5% Ni/ZSM-5	2.6	1.3	0.8	<0.5	<0.5
17% Ni/ZSM-5	7.8	1.8	1.9	1.3	1.8
40% Ni/ZSM-5	8.6	2.0	1.7	1.2	1.9
17% Ni/ZSM-5 [b]	14.1	2.4	3.0	1.5	2.1

[a] Reaction conditions:503K, H_2 4.0 MPa (RT), microcrystalline cellulose 0.2g, H_2O 10 ml, 6h, catalyst 100 mg. [b] 513K, 4h.

Catalyst characterization

HRTEM

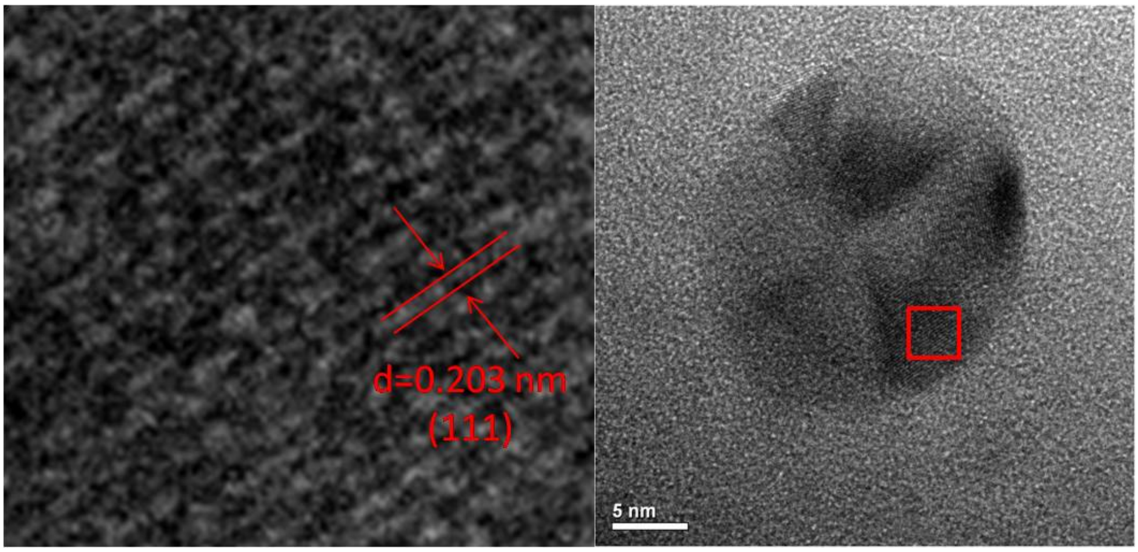

Figure S1 High-magnification TEM images of nickel particles on 17% Ni/ZSM-5