Electronic Supplementary Material (ESI) for Green Chemistry

Catalytic conversion of cellulose to hexitols with mesoporous carbon supported Ni-based bimetallic catalysts

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Supplemental Materials

1. Preparation of catalysts

MC was synthesized by a nanocasting method with silica fume as the hard template. In detail, 1.0 g silica fume was impregnated with 1.25 g sucrose, 0.14 g concentrated H_2SO_4, and 5 g H_2O. The resultant mixture was left at ambient temperature overnight, and dried at 100 °C for 6 h and 160 °C for 6 h. The above impregnation procedure was repeated once again with 80 % amounts of the sucrose and concentrated sulfuric acid that were used in the first impregnation. The final solid was carbonized at 800 °C in N_2 for 6 h. The silica was removed by etching with 5 wt% HF solution for 3 times. After filtration, washing, and drying at 80 °C overnight, the MC was obtained.

The Ni-based bimetallic catalysts were prepared with an incipient wetness impregnation method. In a typical preparation, 1.0 g MC was impregnated with an aqueous solution containing 0.44 g H_2IrCl_6 solution (6.22 wt% Ir) and 0.26 g nickel nitrate, followed with drying at 120 °C for 12 h and reduction in H_2 flow at 450 °C for 1 h. The resulting catalyst is denoted as 1%Ir-5%Ni/MC. Other Ni-based bimetallic catalysts, including 1%Ru-5%Ni/MC, 1%Pt-5%Ni/MC, 1%Pd-5%Ni/MC, and 1%Rh-5%Ni/MC were also prepared with a similar method. For comparison, activated carbon (AC, Norit) supported bimetallic catalysts were also prepared with a similar method.

2. Catalyst characterizations

X-ray diffraction (XRD) patterns of catalysts were collected on a PW3040/60 X'

Pert PRO (PANalytical) diffractometer equipped with a Cu Kα radiation source (λ = 0.15432 nm), operated at 40 kV and 40 mA. A continuous mode was used for collecting data at a scanning speed of 5 ^{o}/min.

The specific surface areas and pore size distribution of carbon supports and catalysts were tested by N_2 adsorption at -196 ^{o}C with a Micromeritics ASAP 2010 Instrument. Prior to the measurements, the samples were degassed at 300 ^{o}C for 5 h. The specific surface areas were calculated with BET equation and the average pore diameters were estimated with desorption branches based on BJH model.

The TEM images of the catalysts were obtained on a transmission electron microscope (Tecnai G^2 Spirit FEI Transmission Electron Microscope and a JEOL 2000EX electronic micoroscope) operated at 120 kV. HAADF-STEM images were recorded on a JEOL2010F instrument by using an electron probe (0.5 nm diameter) at a diffraction camera length of 10 cm. HRTEM images were recorded on the same microscope with 0.19 nm spatial resolution.

The measurement of glucose and cellobiose adsorption on the carbon materials were conducted by a static adsorption method. For each measurement, 0.05 g sample was put into 5 ml aqueous solution of glucose or cellobiose (0.2 wt%) and stirred at room temperature for 24 h. The glucose or cellobiose uptake was determined based on the difference of sugars concentration before and after the adsorption, which was analyzed with HPLC (High performance liquid chromatography, Agilent 1200).

3. Reaction test

The catalytic conversion of cellulose (Merck, microcrystalline) was carried out in a stainless-steel autoclave (Parr Instrument Company, 100 ml) at 6 MPa H_2 pressure (measured at RT) and 245 °C for 30 min. For each run, 0.5 g cellulose, 0.15 g catalyst and 50 mL water were put into the reactor, and stirred at 1000 rpm/min. After the reaction, the liquid-phase products were analyzed by HPLC and TOC (Total organic carbon, Vario EL III, Element, Germany). The gas products were analyzed by GC (gas chromatograph, Agilent 6890N). Cellulose conversions were determined by the change of cellulose weight before and after the reaction. The yields of polyols were calculated by the equation: yield (%) = (mole of carbon in each polyol product)/ (mole of carbon in cellulose which was determined by CHNS) ×100%.

4. Results

Table S1 Textural properties of carbon materials and the carbon-supported catalysts

Samples	S_{BET}[a] /m^2g^{-1}	S_{micro}[b] / m^2g^{-1}	V_{meso}[c] /cm^3g^{-1}	V_{micro}[b] /cm^3g^{-1}	D_p[c] /nm
AC	702	420	--	0.19	--
MC	983	385	1.48	0.14	9.4
20%Ni/AC	687	252	--	0.11	--
20%Ni/MC	700	252	1.26	0.08	10.1
1%Ir/MC	938	304	2.13	0.13	12.6
5%Ni/MC	1024	205	3.40	0.08	13.9
1%Ir-5%Ni/MC	1051	211	3.21	0.09	13.4
1%Rh-5%Ni/MC	1037	210	3.15	0.10	14.2
1%Pd-5%Ni/MC	1038	227	3.12	0.09	14.7
1%Pt-5%Ni/MC	1068	201	3.05	0.08	13.5
1%Ru-5%Ni/MC	1054	266	2.28	0.11	12.4
1%Ir-5%Ni/AC	710	399	--	0.18	--
4%Ir-4%Ni/MC	1106	211	3.51	0.09	14.8

[a]S_{BET} is the surface area calculated by the Brunauer–Emmett–Teller (BET) method. [b] Micropore area (S_{micro}) and micropore volume (V_{micro}) were determined according to the *t*-plot method. [c] Mesopore volume (V_{meso}) and the average pore diameter (Dp) were derived from the desorption branches of the isotherms using the Barrett–Joyner–Halenda (BJH) method.

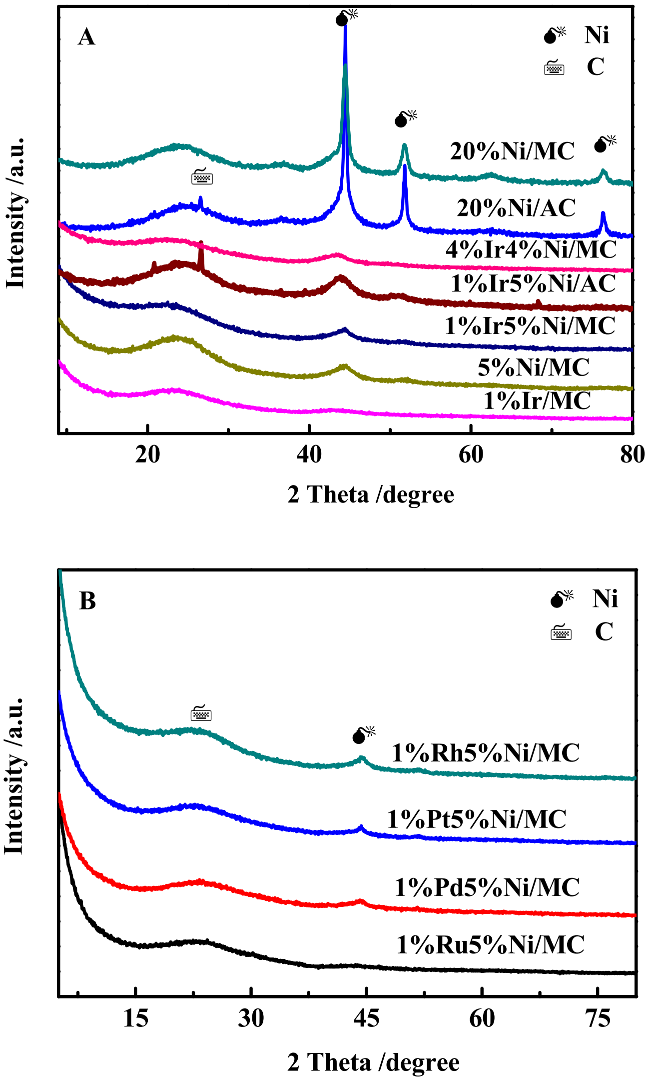
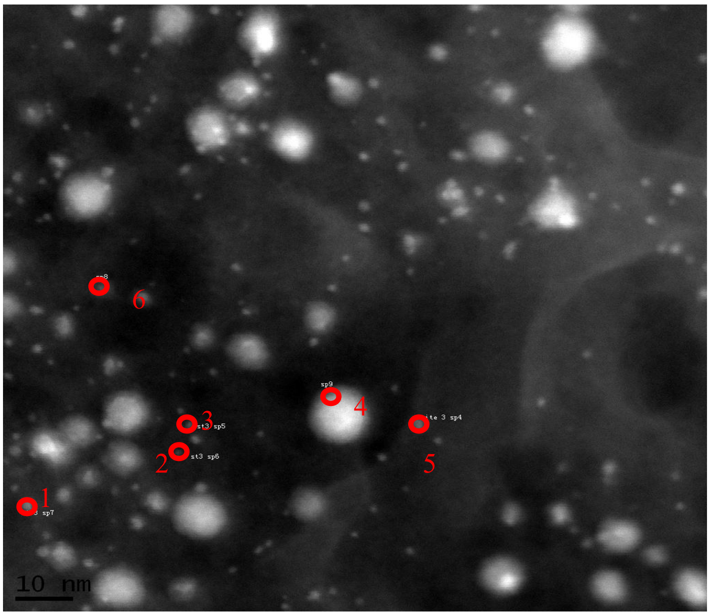


Figure S1. The XRD patterns of Ir-promoted (A) and other noble metal-promoted (B) Ni-based catalysts. The broader peaks of the 20%Ni/MC in comparison to 20%Ni/AC indicate that the Ni particles are better dispersed on the MC. For the Ir-Ni bimetallic catalysts, the iridium addition broadens the diffraction peaks of Ni, but no peaks corresponding to Ir is present. Meanwhile, the Ni peaks shift to lower angles with the increase of the Ir content, indicating that nickel and iridium interact intimately and form alloys.



Particle	1	2	3	4	5	6
Ir/Ni (atomic ratio)	20:80	14:86	0:100	4:96	100:0	23:77

Figure S2 HAADF-STEM image and EDX analysis of 1%Ir-5%Ni/MC catalyst.

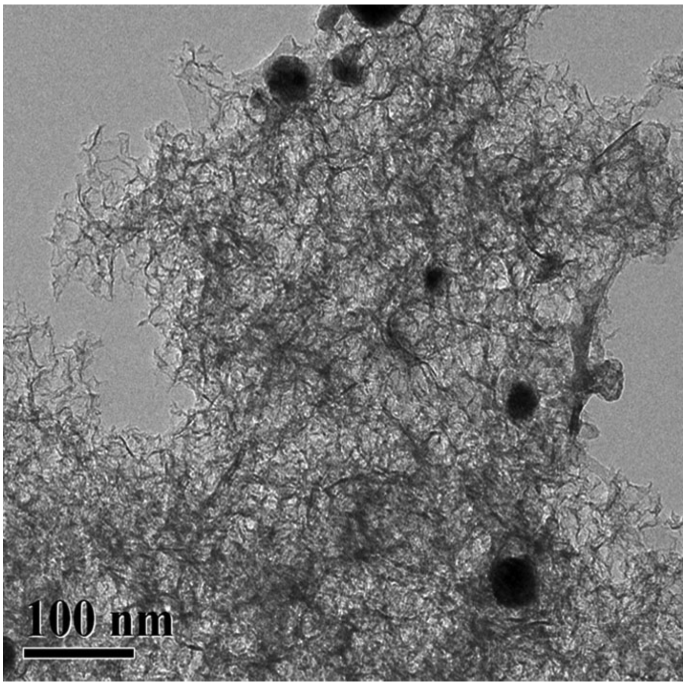


Figure S3 TEM image of 20%Ni/MC after 5 repetitive runs.

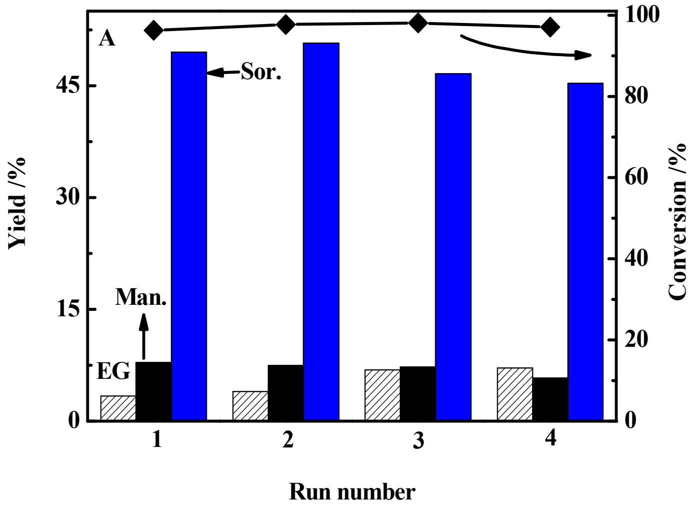


Figure S4 The reusability of 1%Ir-5%Ni/MC catalyst in cellulose conversion. (245 ^{o}C, 30 min, 6 Mpa H_2, microcrystalline cellulose)

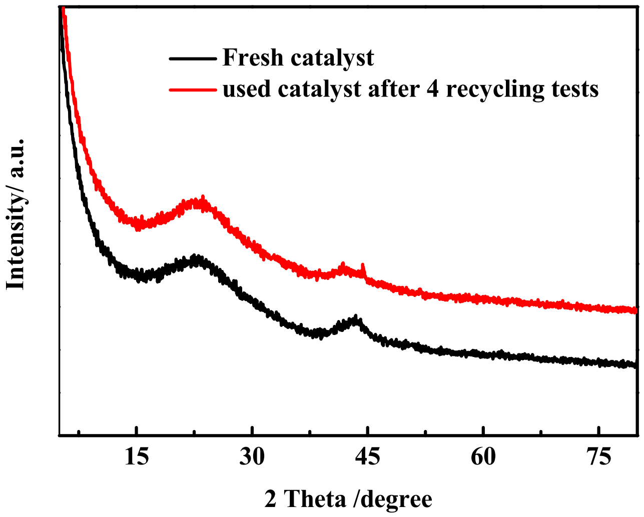


Figure S5 XRD patterns of 4%Ir-4%Ni/MC before and after the reaction

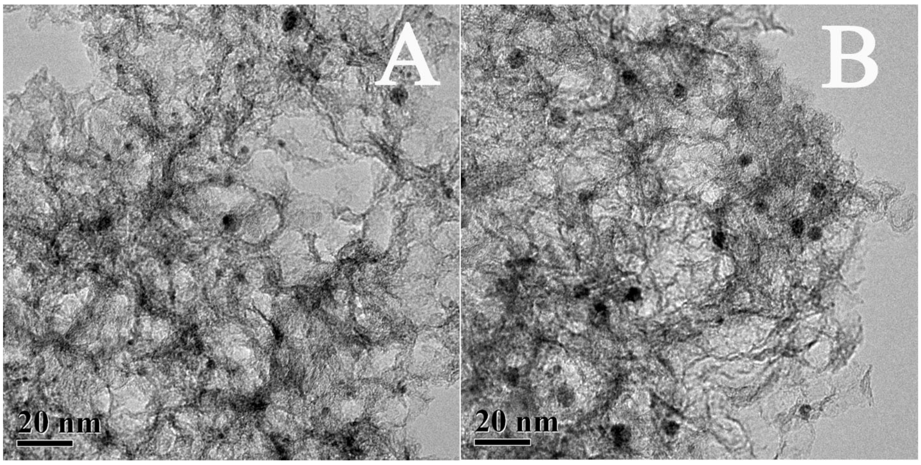


Figure S6 TEM images of 4%Ir-4%Ni/MC before and after the reaction (A: fresh catalyst, B: the used catalyst after 4 recycling tests)

Table S2 The results of glucose hydrogenation over various catalysts[a]

Catalyst	Yield /%					
	Gly.	EG	PG	Man.	HA	Sor.
1%Ir/AC	---	1.1	5.4	4.3	5.0	16.3
5%Ni/AC	1.8	11.7	9.3	1.4	18.3	3.3
1%Ir5%Ni/AC	0.4	1.1	8.5	6.7	3.4	11.4
1%Ir/MC	1.6	10.7	5.7	2.7	11.2	9.5
5%Ni/MC	1.0	6.2	3.9	1.2	3.1	13.4
1%Ir5%Ni/MC	2.2	12.1	4.8	8.1	6.5	40.3

[a] 0.15 g catalyst and 30 ml water were charged in autoclave and heated to 245 ^{o}C, and then glucose solution (1 wt%) was injected into the autoclave with a high pressure pump at a speed of 2 ml/min for 10 min and then kept at 245 ^{o}C for 10 min; Gly., EG, PG, Man., HA, Sor. represent glycerol, ethylene glycol, 1,2-propylene glycol, mannitol, hydroxyacetone and sorbitol, respectively.