Supporting Information

Cobalt–graphene nanomaterial as an efficient catalyst for selective hydrogenation of 5-hydroxymethylfurfural into 2,5-dimethylfuran

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Experimental

Materials

5-Hydroxymethyl-2-furaldehyde (HMF) (98%) was obtained from Fluorochem Ltd., UK. Ethanol absolute ($\geq$99.7%) was purchased from Tianjin Damao Chemical Reagent Factory (China). 2,5-Dimethylfuran (DMF) (99%) were purchased from J&K Chemical Reagent Co., Ltd. (China). 5-Methylfuran-2-yl)methanol (MFA) (98%) was purchased from Yuanye Bio-Technique Co. Ltd (Shanghai, China). 2,5-Bihydroxymethylfuran (BHMF) (98%) was purchased from Dibo Chemical Reagent Co., Ltd (Shanghai, China). $Fe(NO_3)_3 \cdot 9H_2O$ ($\geq$98.0%), $Co(NO_3)_2 \cdot 6H_2O$ ($\geq$98.5%), $Ni(NO_3)_2 \cdot 6H_2O$ ($\geq$98.0%), KNO_3 ($\geq$99.0%), $KMnO_4$ ($\geq$99.0%) and H_2SO_4 (95~98%) were supplied by Tianjin Kermel Chemical Reagent Co., Ltd. (China). Graphite (99.95% metals basis, $\geq$325 mesh) and tetradecane (99%) were purchased from Aladdin Chemical Reagent Co., Ltd. (China). Hydrazine hydrate (80% in water) was purchased from Sinopharm Chemical Reagent Co., Ltd.(China). All aforementioned chemicals were used without further purification.

Activated carbon (AC, vacuum drying at 105 ℃ for 10h before use) was obtained from Beijing Jindawei Activated Carbon Co., Ltd. (China).

Catalyst preparation

Reduced graphene oxide (rGO) was prepared following the method we used before.[S1] Briefly, the graphene oxide (GO) was prepared following a modified Hummers' method.[S2] The obtained GO suspension was reduced with hydrazine hydrate (80% in water) followed by filtering and washing with deionized water. The yielded filter cake was dried with freeze-drying method to get a reduced graphene oxide (rGO). The hydrogen-treated rGO (HrGO) was obtained by calcination of rGO in H_2 at 700 ℃ for 1h.

The catalysts were prepared by impregnation-calcination method. Taking Co-carried rGO as an example, the first step was to support the cobaltnitrate on the rGO surface by incipient wetness impregnation method.[26] The solution used to dissolve cobaltnitrate was 20 wt% of ethanol water solution. The impregnation mixture was vacuum dried at 50 ℃ for 12 h. The second step was to calcinate the impregnation mixture at 500 ℃ under N_2 flow in a tube furnace for 2 h (heating rate: 10 ℃/min). The preparation methods of the Co-carried HrGO and AC were the same as above. The catalysts prepared were designated as Co_x/support, in which x represent the amount of Co metal loaded on per gram support (mmol/g). For example, $Cu_{1.0}$/rGO is a catalyst with 1.0 mmol Co loaded on 1.0 g of rGO. The catalysts after the calcinations were used in reactions directly. The BET specific surface areas of $Co_{1.0}$/rGO, $Co_{1.0}$/HrGO and $Co_{1.0}$/AC are 476 m^2 g^{-1}, 357 m^2 g^{-1} and 716 m^2 g^{-1}, respectively. For comparative analysis, cobalt oxide was obtained by calcining cobalt nitrate at 500 ℃ in a muffle furnace.

Catalyst characterization

High resolution transmission electron microscopy (HRTEM) images were carried out on a Tecnai G2 F30 microscope. High-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were obtained on a JEOL JEM-ARM200F STEM/TEM equipped with a CEOS probe corrector, with a guaranteed resolution of 0.08 nm. To prepare samples for the image study, graphene derived samples were dispersed in ethanol, and deposited onto copper grids coated with a thin holey carbon film. Temperature programmed reduction (TPR) of the catalysts were analyzed by self-assembly instrument. For each test, 20 mg of the sample was dried in nitrogen at 200 ℃ for 1 h and then reduced in 5 vol.% H_2/Ar gas mixture (30 mL/min) at a linear heating rate of 10 ℃/min in the temperature range from 50 ℃ to 850 ℃. The exhaust gas after removal of moisture was first monitored by a TCD detector for testing the H_2 consumption amount, followed by component analysis with a gas chromatography (Agient 7820 with a TCD detector and a FID detector). Surface area measurement with nitrogen adsorption was performed with a Micromeritics ASAP 2020. The specific surface area (S_{BET}) was determined by the BET equation (P/P^0 = 0.05–0.3). Mass spectroscopy was performed on a GC–MS system (HP Agilent 6890N-5973N) for compound structure analysis. X-ray powder diffraction (XRD) patterns were recorded at room temperature on a Rigaku SmartLab 9kW (M/s. Rigaku Corporation, Japan) X-ray diffractometer using Cu Kα radiation (λ = 1.5406 Å) with a scan range of 2-80° at 40 kV and 30 mA. The contents of C, H, O and N in graphene materials were obtained with Elemental Analyzer vario EL cube.

Catalytic performance measurement

HMF hydrogenation was carried out in an autocontrol batch-reactor system consisting of stainless steel autoclaves (50 mL) under mechanical stirring (Beijing Century Senlang Experimental Apparatus Co., Ltd.). In a typical run, 500 mg of HMF, 50 mg of catalyst (without pre-reduction treatment), 20 mL of ethanol and a given amount of tetradecane as an inert internal standard were loaded into the autoclave and sealed. After purged five times with H_2, the reactor was pressurized with H_2 to 2 MPa at room temperature. Then, the reactor was heated to 200 ℃ and maintained for 1 hour at 500 rpm. When the time is due, the reaction was quenched immediately with cold water. The liquid mixture obtained was filtered using a 0.2 mm syringe filter to remove the catalyst for compositional analysis by GC. The recycle studies were carried out as follows. After each catalytic run, the spent catalyst was recovered from the reaction mixture by centrifuge and washed with ethanol two times by dispersing and centrifuging to removal of the supernatant liquid. Finally, the catalyst residue was used for the next run without drying and calcination.

The products were analyzed by a gas chromatograph (GC HP7820) with flame ionization detector (FID) using a SE-30 capillary column (made by Dalian Zhonghuida Scientific Instrument Co., Ltd, China) and H_2 as a carrier gas. The results were quantified as HMF conversion, product selectivity and yield in molar percentage on the basis of initial molar amount of HMF. Repeated runs showed that data variation was in the range of ± 2% (relative value). Overall carbon balance in the products was > 98.5%.
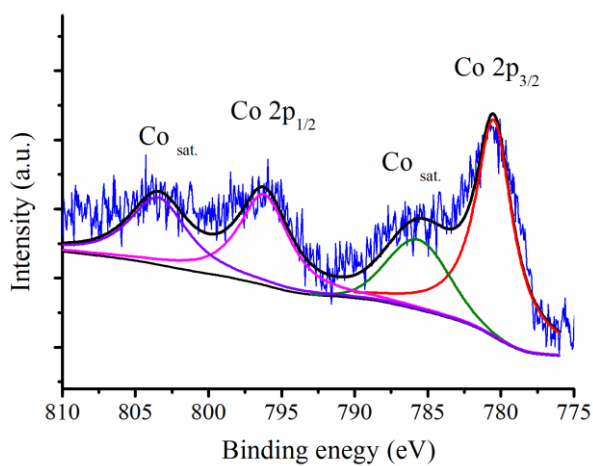
References
S1   J. Zhou, Y. Wang, X. Guo, J. Mao and S. Zhang, *Green Chem.*, 2014, **16 (11)**, 4669 - 4679.
S2   N. I. Kovtyukhova, P. J. Ollivier, B. R. Martin, T. E. Mallouk, S. A. Chizhik, E. V. Buzaneva and A. D. Gorchinskiy, *Chem. Mater.*, 1999, **11**, 771–778.
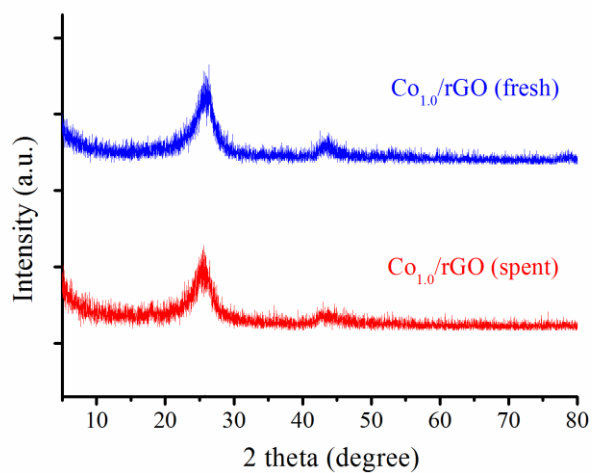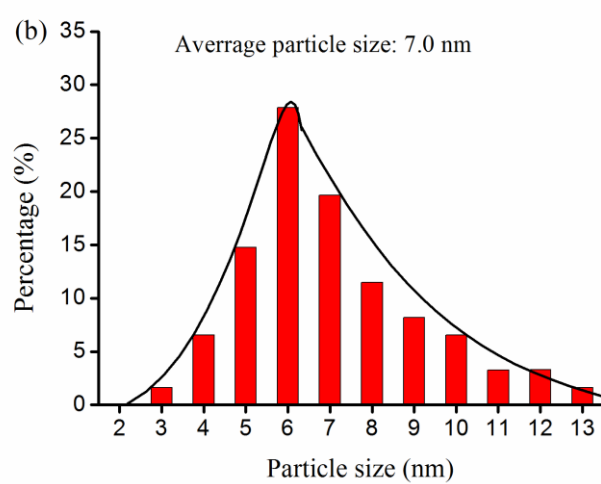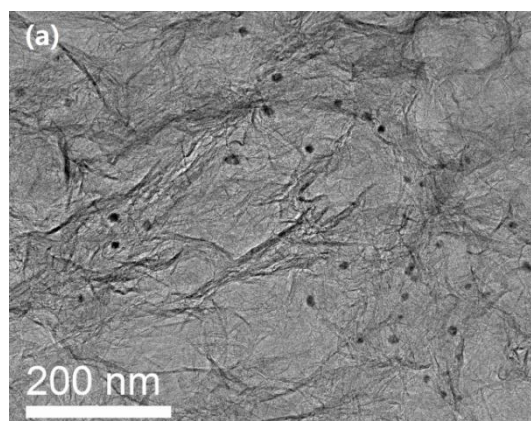
Figures
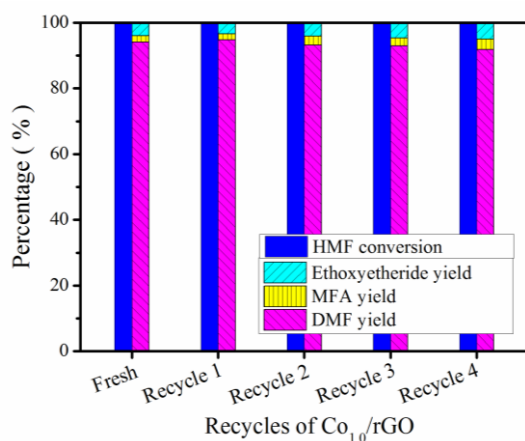
Fig. S1. Reuse of $Co_{1.0}$/rGOcatalyst (reaction conditions: 500 mg of HMF in 20 mL of ethanol solvent, catalyst loading = 50 mg, 200 °C, 2MPa H_2, and 1 h).

Fig. S2. XPS spectra in the binding energy range of Co $2p$ of $Co_{1.0}$/rGO.

Fig. S3. XRD patterns of the fresh and spent $Co_{1.0}$/rGO catalysts.

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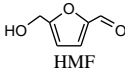Fig. S4. (a) TEM image and (b) Particle size distribution of the spent $Co_{1.0}/rGO$ catalyst.
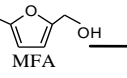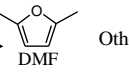
Tables

Table S1. Direct hydrogenation of HMF into DMF over transition metal catalysts.

Entry	Catalyst	Pre-reduction (^{o}C)	Solvent	T (^{o}C)	H$_2$ (MPa)	t (h)	Cat.(wt%)[a]	Con.$_{HMF}$(%)	Yield$_{DMF}$(%)	Stability of the catalyst	Ref.[b]
1	Ni/Al$_2$O$_3$	Reduced by H$_2$ at 500 ^{o}C	1,4-dioxane	180	1.2	4	6.7	100	91.5	Deactivated during recycling due to Ni oxidation and polymerization.	7
2	Ni/C	Reduced by H$_2$ at 400 ^{o}C	THF	180	4.5	17	5	100	67	The catalyst is deactivated during recycling even if reduced each time.	8
3	Ni/phyllosilicate	Reduced by H2 at 500 ^{o}C	1,4-dioxane	150	1.5	3	5.3	100	DMF:64.1 DMTHF:26.1	Not mentioned.	9
4	Cu/ZnO	Reduced by H$_2$ at 220 ^{o}C	1,4-dioxane	220	1.5	5	33.3	100	91.8	A sharp decrease of HMF conversion and DMF selectivity was observed due to deposition of carbonaceous species	10
5	Fe/AC	Reduced by C while pyrolyzed under Ar	n-butanol	240	4	5	158.6	100	86.2	The catalytic activity was maintained well during five recycles.	11
6	Co-CoO$_x$	Reduced by H$_2$ at 400 ^{o}C	1,4-dioxane	170	1	12	20	100	83.3	After the sixth run for furfural hydrogenation, the hexagonal catalyst vanished and aggregated into larger blocks.	12
7	Ni-Co/C	Reduced by H$_2$ at 400 ^{o}C	THF	130	1.0	24	80	100	95.0	Maintain the activity after five successive runs.	13
8	CuCo/Al$_2$O$_3$	Reduced by H$_2$ at 280 ^{o}C	THF	220	3	8	158.6	100	78	Deactivity of the catalyst due to sintering and carbon deposition	14
9	CuNi/TiO$_2$	Reduced by H$_2$ at 450 ^{o}C	1,4-dioxane	200	2.5	8	60	99	84.3	Reactivity was gradually degradated during recycles	15
10	Cu-Ni/γ-Al$_2$O$_3$	Reduced by H$_2$ at 300 ^{o}C	THF	200	3	6	250	99	56	NiO and CuO were appeared in the spent catalyst	16
11	CuZn alloy	The drying and calcination atmosphere is not clear	CPME	200	2	6	20	100	DMF:80.8 DMTHF: 16.2	The DMF+DMTHF yield decreased to 66% after the 6th cycle, and 3% product yield was observed in the 7th cycle.	17
12	NiZn alloy	Reduced by H$_2$ at 500 ^{o}C	1,4-dioxane	180	1.5	15	10	100	93.6	After 4 runs, HMF conversion and DMF yield exhibited a great decrease, indicating the deactivation of the catalyst.	18
13	Ni/ N-rich carbon	Reduced by H$_2$ at 700 ^{o}C	H$_2$O	200	3	6	19.8	>99.9	98.7	After reaction, metallic Ni species interact with H$_2$O to form NiO species and the catalyst need to be reduced before the repeated reaction	19
14	CuCo/NGr/α-Al$_2$O$_3$	Reduced by H$_2$ at 400 ^{o}C	THF	180	2	16	79.4	>99	>99	The catalytic performance decreased after being reused five times due to the decrease of the content of pyrrolic-N in the catalyst.	20
15	C-coated CuCo nanoparticles	Reduced by polyethene glycol at 800 ^{o}C	Ethanol	180	5	8	8	100	99.4	Oxidation of active metallic species due to the loss of carbon layer	21

[a] Catalyst loading (wt%) is corresponding to the mass of HMF; [b] The reference numbers are corresponding to the numbers in the reference citations of the main text.

Table S2. Results of the hydrodeoxygenation of HMF over various catalysts.[a]

Entry	Catalyst	Temp. (℃)	Pressu. (MPa)	Time (h)	Conversion (%) HMF →	Yield (%) BHMF	MFA	DMF	Others[b]
1	$Co_{1.0}$/rGO	180	2	2	100.0	0.0	3.0	94.3	2.7
2		150	2	16	100.0	0.0	4.4	90.7	4.9
3[c]		140	2	20	100.0	0.0	0.0	94.7	5.3
4		200	3	15	100.0	0.0	0.0	97.6	2.4
5		220	4	1	100.0	0.0	0.0	>99.0	<1.0
6	$Co_{1.0}$/HrGO +Co_3O_4[d]	200	2	1	100.0	0.0	0.0	97.1	2.9
7	$Fe_{1.0}$/rGO	200	2	1	24.2	24.2	-	-	-
8	$Ni_{1.0}$/rGO	200	2	1	58.4	43.8	6.2	3.6	4.6

[a] Reaction conditions: 500 mg of HMF in 20 mL of ethanol, catalyst loading = 50 mg (10 wt.% with respect to HMF); [b] Ethoxyetherides from etherification of ethanol with HMF and its derivatives; [c] Catalyst loading = 100 mg (20 wt.% with respect to HMF); [d] Catalyst loading = 50 mg of $Co_{1.0}$/HrGO + 50mg of Co_3O_4.