Supplementary Information

Aerobic oxidation of alcohols catalyzed by a new ZnO supported copper oxide nanocatalyst in green media

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General

Chemicals were purchased from Merck chemical company. All products were identified by comparison of their spectroscopic data (NMR, IR) and physical data with authentic samples. The IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer. All the NMR spectra were recorded on a Bruker Advance 400 MHz. The Bruker AXS D8 advanced diffractometer carries out the X-ray diffraction (XRD) analysis to determination of structural properties of the catalyst. The sample was scanned over the range of $2\theta=10-80^\circ$ at a rate of $0.05^\circ/\text{s}$ using Cu $K\alpha$ radiation ($\lambda = 1.5406^\circ\text{\AA}$). The specific surface area of samples determined by nitrogen adsorption-desorption using BET method. BET tests were carried out using an automated gas adsorption analyzer (Tristar 3020, Micromeritics). Prior to BET tests the samples were degassed under vacuum at 150°C for 2 h. The morphology of the catalyst was investigated comprehensively by field emission scanning electron microscopy (SEM)

and high resolution transmission electron microscopy (HRTEM) techniques using a HITACHI S-4160 instrument, and JEOL JEM-2100 (200 kV) microscope. Yields refer to isolated pure products.

Catalyst Preparation

The 20 wt% CuO supported on ZnO catalyst was prepared via a co-precipitation method, by adding 0.5 M $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ solution drop-wise into a mixture of 0.03 M $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ solutions under continuous mixing. The obtained suspension was aged at pH=8.5 for 15 min at 65 °C, then filtered and washed with warm deionized water. The precipitates were dried 12h at 100 °C followed by calcination at 300 °C for 3h. In addition, a batch of ZnO support was prepared under this condition for the supplementary tests. The prepared catalyst is entitled as 20CuO/ZnO, where 20 is the amount of CuO weight percent in the catalyst.

General Procedure

A mixture of alcohol (1 mmol), Cs_2CO_3 (0.5 mmol) and CuO/ZnO nanocatalyst (0.07 g) in water was stirred under oxygen atmosphere in a slurry reactor reflux condition. After reaction completion, catalyst was recovered by filtration, then washed with hot acetone (2×5 mL), and dried for consecutive reaction runs. The filtrate was quenched with 2 M HCl aqueous solution, extracted with EtOAc three times and dried over anhydrous MgSO_4 . Evaporation of the solvent followed by column chromatography on silica gel afforded the pure products.

Figure 1. XRD patterns of (a) ZnO, and (b) 20CuO/ZnO nanocatalyst.

Figure 2. (a) N_2 adsorption/desorption isotherms, and (b) pore size distributions, of ZnO and 20CuO/ZnO samples.

Figure 3. SEM micrographs of (a,b) ZnO, and (c,d) 20CuO-ZnO samples.

Figure 4. TEM image and particle size distribution of 20CuO/ZnO nanocatalyst.

NAME Azad-Gachsearan UN
EXPNO 254
PROCNO 1
Date_ 20140305
Time_ 16.36
INSTRUM Spect
PROBHD 5 mm PABEO BBO
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 24
DS 0
SMH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 181
DM 62.400 usec
DE 6.50 usec
TE 287.0 K
D1 6.00000000 sec
TD0 1

CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 0.00 dB
PR1 11.8635200 MHz
SFO1 400.2230200 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

Current Data Parameters
 NAME A-M
 EXPNO 102
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20140218
 Time 7.50
 INSTRUM spect
 PROBHD 5 mm GNP 1H/1
 PULPROG zg
 TO 32768
 SOLVENT CDC13
 NS 10
 DS 0
 SMH 11950.407 Hz
 FIDRES 0.365918 Hz
 AQ 1.3664756 sec
 RG 161.3
 DM 41.700 usec
 DE 6.00 usec
 TE 300.0 K
 D1 15.00000000 sec

===== CHANNEL f1 =====
 NUC1 1H
 P1 11.00 usec
 PL1 -1.00 dB
 SF01 400.1324710 MHz

F2 - Processing parameters
 SI 32768
 SF 400.1258704 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

1D NMR plot parameters
 CX 20.00 cm
 F1P 43.969 ppm
 F1 5569.50 Hz
 F2P -1.597 ppm
 F2 -635.11 Hz
 PPMCM 0.77782 ppm/cm
 HZCM 311.23056 Hz/cm

7.4193
 7.3988
 7.0854
 7.0649

11.3092

ppm

2.3502
 2.0092

1.0000

Integrals

NAME Azad-Gachasan UN
EXPNO 388
PROCNO 1
Date_ 20140814
Time 12.43
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 24
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 2030
EW 62.400 usec
DE 1.450 usec
TE 296.8 K
D1 6.00000000 sec
D1 1
TD0 1

===== CHANNEL f1 =====
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NAME Azad-Gachasan UN
 EXPNO 462
 PROCNO 1
 Date_ 20140329
 Time 12.24
 INSTRUM spect
 PROBHD 5 mm PABBO BB
 PULPROG zgpg30
 TD 65536
 SOLVENT DMSO
 NS 24
 DS 0
 SWH 8012.820 Hz
 FIDRES 0.122266 Hz
 AQ 4.0894966 sec
 RG 1440
 DW 62.400 usec
 DE 6.50 usec
 TE 294.6 K
 D1 6.00000000 sec
 TDO 1

===== CHANNEL f1 =====
 NUC1 1H
 P1 14.00 usec
 PL1 -2.00 dB
 PL1W 11.86359406 W
 SFO1 400.2236020 MHz
 SI 32768
 SF 400.2200000 MHz
 WDW EM
 SSB 0
 RB 0.30 Hz
 GB 0
 PC 1.00

7.731
 7.711
 7.474
 7.455
 7.436
 7.365
 7.344

8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 ppm

4.10
 4.15
 2.14

NAME Azad-Gachasan UN
 EXPNO 463
 PROCNO 1
 Date_ 20140329
 Time 12.29
 INSTRUM spect
 PROBHD 5 mm PABBO BB-
 PULPROG zgpg30
 TD 65536
 SFO1 100.626135 MHz
 NS 500
 DS 0
 SMH 25252.525 Hz
 FIDRES 0.385323 Hz
 AQ 1.2976629 sec
 RG 256
 KW 19.800 usec
 DE 6.50 usec
 TE 294.6 K
 D1 2.00000000 sec
 D11 0.03000000 sec
 TD0 1

===== CHANNEL f1 =====
 NUC1 13C
 P1 9.00 usec
 PL1 -0.90 dB
 PL12 14.16 dB
 PL13 17.90 dB
 PL14 14.16 dB
 PL15 14.16 dB
 PL16 14.16 dB
 PL17 14.16 dB
 PL18 14.16 dB
 PL19 14.16 dB
 PL20 14.16 dB
 PL21 14.16 dB
 PL22 14.16 dB
 PL23 14.16 dB
 PL24 14.16 dB
 PL25 14.16 dB
 PL26 14.16 dB
 PL27 14.16 dB
 PL28 14.16 dB
 PL29 14.16 dB
 PL30 14.16 dB
 PL31 14.16 dB
 PL32 14.16 dB
 PL33 14.16 dB
 PL34 14.16 dB
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 PL48 14.16 dB
 PL49 14.16 dB
 PL50 14.16 dB
 PL51 14.16 dB
 PL52 14.16 dB
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 PL56 14.16 dB
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 PL62 14.16 dB
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 PL73 14.16 dB
 PL74 14.16 dB
 PL75 14.16 dB
 PL76 14.16 dB
 PL77 14.16 dB
 PL78 14.16 dB
 PL79 14.16 dB
 PL80 14.16 dB
 PL81 14.16 dB
 PL82 14.16 dB
 PL83 14.16 dB
 PL84 14.16 dB
 PL85 14.16 dB
 PL86 14.16 dB
 PL87 14.16 dB
 PL88 14.16 dB
 PL89 14.16 dB
 PL90 14.16 dB
 PL91 14.16 dB
 PL92 14.16 dB
 PL93 14.16 dB
 PL94 14.16 dB
 PL95 14.16 dB
 PL96 14.16 dB
 PL97 14.16 dB
 PL98 14.16 dB
 PL99 14.16 dB
 PL100 14.16 dB

===== CHANNEL f2 =====
 CPDPRG2 waltz16
 NUC2 1H
 P2 9.00 usec
 PL2 -0.90 dB
 PL22 14.16 dB
 PL23 17.90 dB
 PL24 14.16 dB
 PL25 14.16 dB
 PL26 14.16 dB
 PL27 14.16 dB
 PL28 14.16 dB
 PL29 14.16 dB
 PL30 14.16 dB
 PL31 14.16 dB
 PL32 14.16 dB
 PL33 14.16 dB
 PL34 14.16 dB
 PL35 14.16 dB
 PL36 14.16 dB
 PL37 14.16 dB
 PL38 14.16 dB
 PL39 14.16 dB
 PL40 14.16 dB
 PL41 14.16 dB
 PL42 14.16 dB
 PL43 14.16 dB
 PL44 14.16 dB
 PL45 14.16 dB
 PL46 14.16 dB
 PL47 14.16 dB
 PL48 14.16 dB
 PL49 14.16 dB
 PL50 14.16 dB
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 PL62 14.16 dB
 PL63 14.16 dB
 PL64 14.16 dB
 PL65 14.16 dB
 PL66 14.16 dB
 PL67 14.16 dB
 PL68 14.16 dB
 PL69 14.16 dB
 PL70 14.16 dB
 PL71 14.16 dB
 PL72 14.16 dB
 PL73 14.16 dB
 PL74 14.16 dB
 PL75 14.16 dB
 PL76 14.16 dB
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 PL95 14.16 dB
 PL96 14.16 dB
 PL97 14.16 dB
 PL98 14.16 dB
 PL99 14.16 dB
 PL100 14.16 dB

7.292
2.156
2.111
2.098
2.053
1.906
1.865
1.844
1.803
1.685
1.667
1.630
1.613

NAME Azad-Gachasan UN
EXPNO 416
PROCNO 1
Date_ 20140724
Time_ 7.24
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 65536
SOLVENT CDCl3
NS 23
DS 0
SWH 8012.820 Hz
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 1440
DW 62.400 usec
DE 8.500 usec
TE 295.0 K
D1 6.00000000 sec
TD0 1
CHANNEL f1
NUC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.2236020 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

NAME Azad-Gachasan UN
EXPNO 416
PROCNO 1
Date_ 20140701
Time 7:49
INSTRUM spect
PROBHD 5 mm PABBO BB-
PULPROG zg
TD 65536
FIDRES 0.122266 Hz
AQ 4.0894966 sec
RG 1440
DW 62.400 usec
DE 6.50 usec
TE 295.0 K
D0 6.00000000 sec
DO 1
CHANNEL f1
UC1 1H
P1 14.00 usec
PL1 -2.00 dB
PL1W 11.86359406 W
SFO1 400.223720 MHz
SI 32768
SF 400.2200000 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00