Electronic Supplementary Material (ESI) for RSC Advances

Supporting Informations

"New generation biofuels: γ-valerolactone into valeric esters in one pot"

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1. Experimental section

Materials - SiO_2-ZrO_2 A (4 wt.% ZrO_2, SSA = 455 m^2g^{-1}, PV = 0.71 mLg^{-1}), SiO_2-ZrO_2 B (4.7 wt.% ZrO_2, SSA = 304 m^2g^{-1}, PV = 1.62 mLg^{-1}); SiO_2-Al_2O_3 (13 wt% Al_2O_3, SSA = 485 m^2g^{-1} ; PV = 0.79 mL g^{-1}); ZSM-5 (5.67 wt% Al_2O_3, SSA = 426 m^2g^{-1}) were supplied by Grace Davison. γ-valerolactone (99%), EtOH (≥99%) were purchased from Sigma Aldrich and used without any further purification.

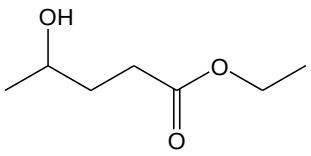
Catalyst preparation - Cu/SiZr A and B, Cu/SiAl and Cu/ZSM-5 were prepared by chemisorption hydrolysis as reported elsewhere.[14a] The support was added to a solution containing $[Cu(NH_3)_4]^{2+}$ and the slurry was slowly diluted with water. The solid was later separated by filtration, washed with water and dried overnight at 120 °C to finally being calcined in air at 350 °C for 4 h.

Prior to catalytic tests, the catalysts were activated *ex-situ*: calcined and treated under vacuo at 270 °C for both 30 min; and finally were reduced in batch mode under H_2.

Recycling experiments of the solid acid catalyst were carried out by removing the liquid part of the mixture and loading with a fresh mixture of EtOH and GVL.

TEM specimens were prepared by gently crushing the powder catalyst in an agate mortar. The milled powder was suspended in isopropanol, sonicated in an ultrasonic bath and a drop of the suspension was then deposited on a holey carbon film supported copper TEM grid. TEM and STEM analysis were performed after solvent evaporation overnight with a ZEISS LIBRA200 EFTEM. Statistic distribution was calculated over 500 particles.

2. NMR identification



^{1}HNMR (400 MHz, $CDCl_3$): δ = 1.20 (d, J = 6.29 Hz), δ = 1.25 (t, J = 7.1 Hz), δ = 1.74 (m, J = 5.9 Hz), δ = 2.43 (t, 2 H, J = 7.28 Hz), δ = 3.83 (qd, 1 H, J_1 = 6.3 Hz, J_2 = 5.9 Hz), δ = 4.13 (q, 2H, J = 7.14 Hz).

^{13}CNMR (75 MHz, $CDCl_3$): δ = 14.18, 23.49, 30.79, 33.86, 60.42, 67.29, 174.1

3. Recycling test

Number runs	Conversion %	S_{EV}	$S_{4hydroxy\ ethyl\ pentanoate}$	$S_{ethyl4\text{-}ethoxypentanoate}$
Run1	69.3	59.2	7.4	30.9
Run2	62.7	64.0	0.7	35.2
Run3	59.9	67.9	0.7	31.4
Run4	58.2	70.0	0.6	28.1
Run5	57.1	71.4	0.6	28.0
Run6	53.7	74.1	0	25.9
Run7	53.9	68.1	0	31.9
Run8	55.2	60.3	0	36.5
Run9	54.1	59.2	0	37.5

Table S1: Conversion and selectivity on recycling of 8 wt. % Cu on SiO_2-ZrO_2 4.7 wt.% at 250 °C and 10 bars H_2, 700 rpm, 20 hours. GVL/Catalyst = 10/1 wt.%, GVL/EtOH = 1/10 mol.

4. ICP results

	Concentration in ppb
R1	47
R4	61
R9	88

Table S2: Concentration in ppb of Cu detected in solution, after 20 h of reaction during the recycling test.

5. TPR analysis

TPR analysis was performed with a modified version of the Micromeritics Pulse Chemisorb 2700 apparatus. Catalysts (25 mg) were diluted with an equal amount of quartz, calcined at 500°C under O_2 (40 mL/min), and then reduced at 8 °C/min under a flow (15 mL/min) of a 8% H_2/Ar mixture.

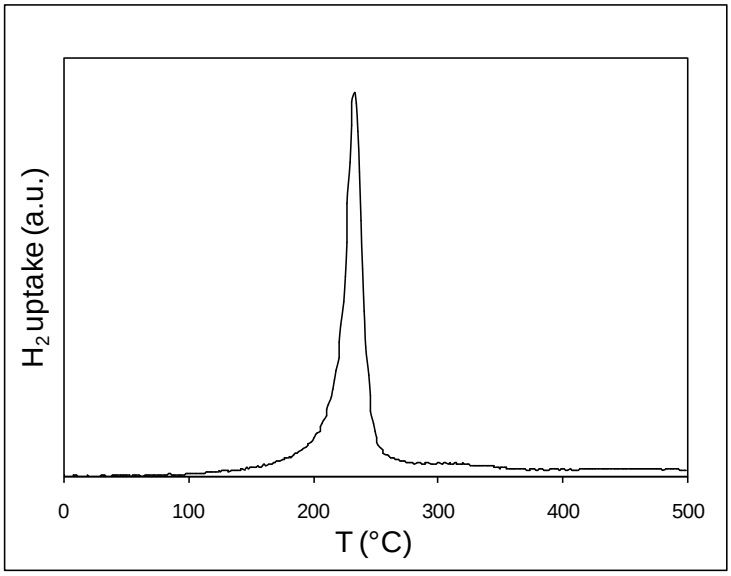


Figure S1- TPR profile of 8% Cu/SiZr B

6. TEM and STEM Micrographs

TEM (Fig.S2A) and STEM (Fig.S2B/C) micrographs of fresh catalyst showed a good distribution of particle on the catalyst of crystalline and well shaped NPs, whereas for the catalyst after first (Fig. S3) and ninth (Fig.S4) bigger particles are shown. In details, after the first cycle STEM micrographs (Fig.S3B) highlight bigger aggregation of particles next to the little dispersed ones (Fig.S3A). After 9 cycles the big particles are more crystalline and well shaped (Fig.S4A-C)

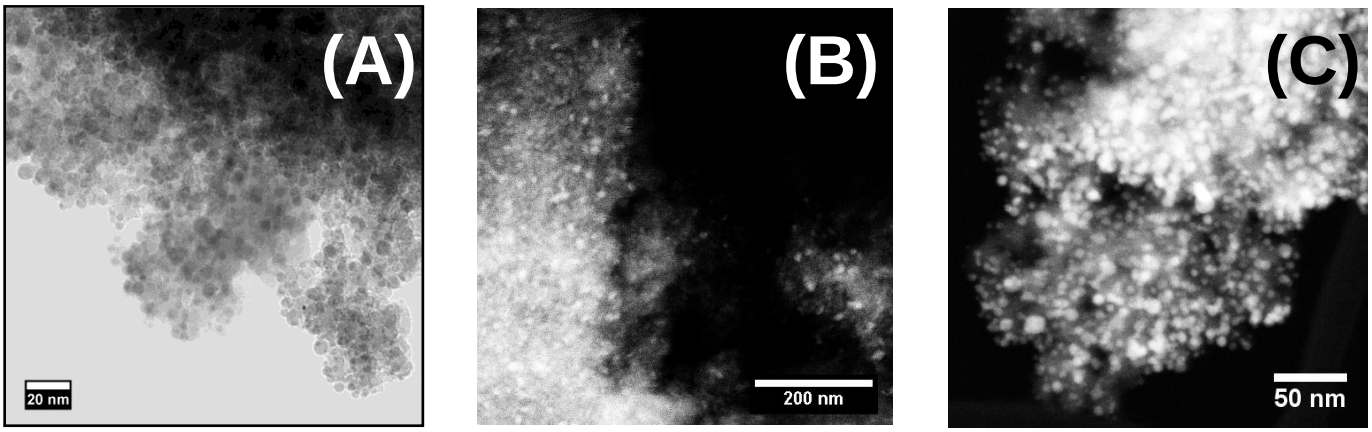


Figure S2: TEM and STEM micrographs of fresh catalyst Cu/SiZr

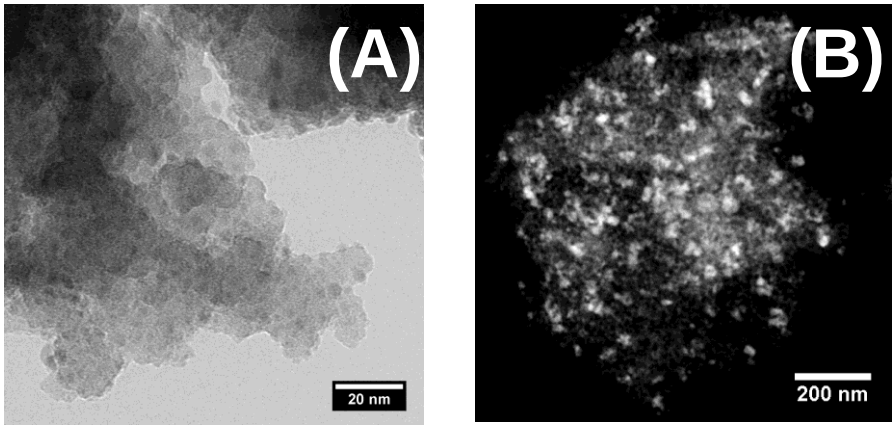


Figure S3: TEM and STEM micrographs of Cu/SiZr catalyst after the first catalytic cycle

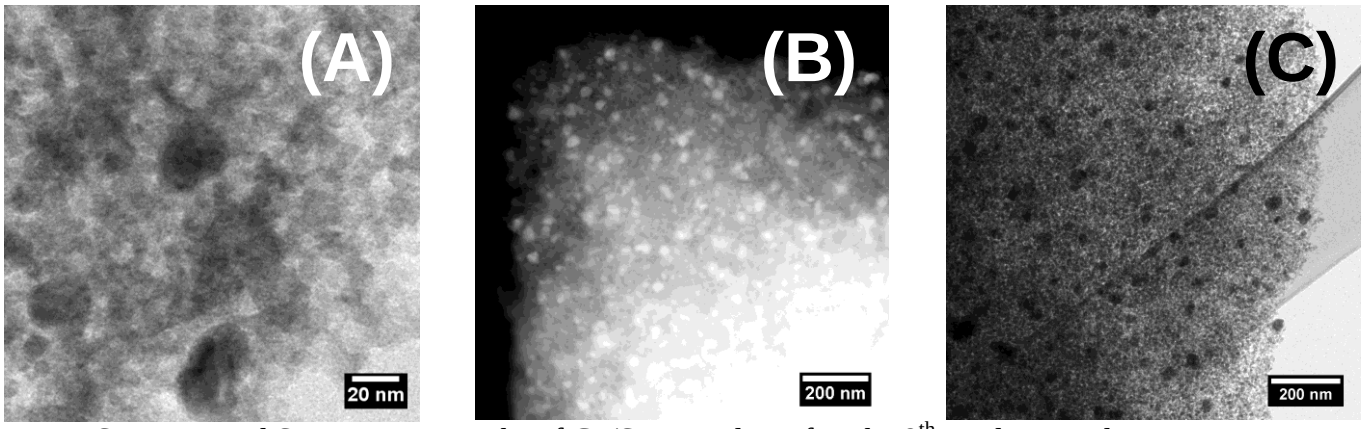


Figure S4: TEM and STEM micrographs of Cu/SiZr catalyst after the 9th catalytic cycle