

Supporting information

Zinc hydroxystannate: A promising solid acid–base bifunctional catalyst

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1. Carbonylation of glycerol with urea

Table S1. Basicity measurement of all the catalysts by Hammett indicator method.

Fig. S1. FT-IR spectrum of ZHS catalyst.

Fig. S2. XRD pattern of recycled catalyst.

2. Transesterification of glycerol with dimethyl carbonate

2.1. Experimental Procedure

2.2. Table S2

3. Carbonylation of glycerol with urea

Table S1. Basicity measurement of all catalyst by Hammett indicator method

Catalyst	Colour change		Total (mmol/g)	
	Nile Blue ($pK_{BH^+} = 10.1-11.1$)	Phenolphthalein ($pK_{BH^+} = 8.0-9.6$)	Nile Blue	Phenolphthalein
ZnSn(OH) ₆	Blue - Pink	No colour change	0.3	-
ZnSn(OH) ₆ calcined @ 600 °C	Blue-Pink	Colourless – Pink	0.2	0.03
CaSn(OH) ₆	Blue-Pink	Colourless – Pink	0.07	0.2
MgSn(OH) ₆	Blue-Pink	Colourless – Pink	0.2	0.1
ZnO	No colour change	Colourless – Pink	-	0.10
SnO ₂	No colour change			
Sn(OH) ₄	No colour change	Colourless – Pink	-	0.03
MgO	No colour change	Colourless – Pink	-	0.13
CaO	No colour change	Colourless – Pink	-	0.18
HTc (Mg/Al)	No colour change	Colourless – Pink	-	0.26
HTc (Zn/Al)	No colour change	Colourless – Pink	-	0.18

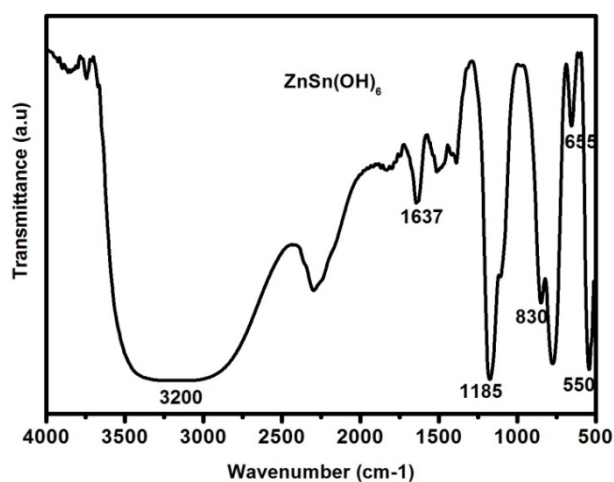


Fig.S1. FT-IR spectrum of ZHS catalyst

FTIR spectrum was recorded from 500-4000 cm^{-1} for ZHS catalyst. IR bands of Zn–O, Sn–O, Zn–OH, Sn–OH and OH were identified. The peaks at 550 and 655 cm^{-1} correspond to Sn–O and O–Sn–O stretching vibrations. The IR peak around 1637 cm^{-1} indicates the formation of the metal

oxide (M-O) whereas 830 and 1185 cm^{-1} , and 3200 cm^{-1} correspond to O-H bending and stretching vibrations respectively.

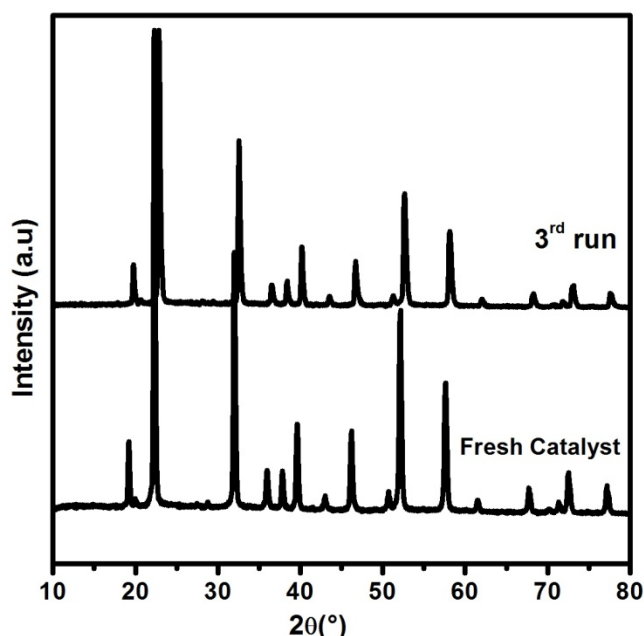


Fig S2. XRD pattern of recycled catalyst.

4. Transesterification of glycerol with dimethyl carbonate

Reaction procedure:

Transesterification reaction of glycerol with dimethyl carbonate (DMC) was carried out in a glass reactor equipped with a magnetic stirring bar, a Liebig condenser, and a thermometer. The required amounts of glycerol and DMC were taken in the reactor and 5 wt% of preactivated catalyst was added into it along with the diluent DMF. The reaction was performed under stirring at 75 °C. After the reaction, the mixture was taken out and centrifuged for 10 min to separate the catalyst from the liquid phase. The thus obtained product was analyzed in gas chromatography (Shimadzu, GC-2014) with flame ionization detector (FID) equipped with a capillary column (0.25 mm I.D and 30 m length, Stabilwax, Restek). All the products were confirmed by gas chromatography with mass spectroscopy (Shimadzu, GCMS QP 2010).

Table S2 Catalytic activity of different solid base catalysts for transesterification of glycerol with dimethyl carbonate

Catalyst	Calcination temperature (°C)	Conversion of glycerol (mol %)	Yield of glycerol carbonate (mol %)
CaSn(OH) ₆	150	92.6	90.7
MgSn(OH) ₆	150	88.2	88.0
ZnSn(OH) ₆	150	52.8	52.6
KF/ Al ₂ O ₃	600	96.0	94.8
CaO	850	70.8	70.5
MgO	850	68.4	68.0
HTc (Mg/Al)	120	94.2	94.0

Reaction conditions: Glycerol: DMC: DMF mole ratio = 1: 2: 0.5, catalyst weight= 5 wt% of total reactant weight, temp = 75 °C, time = 2 h.