# **Supplementary Information**

A mild route for one pot synthesis of 5,6-unsubstituted 1,4dihyropyridines catalyzed Sulphated mixed metal oxides

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## 1. Experimental

#### a) Catalyst preparation:

All chemicals were of analytical grade and were used without any further purification. The  $SO_4^{2-}/Ce_xZr_{1-x}O_2$  were prepared by the method described by Lee et al.<sup>1-2</sup> Precipitate of  $Zr(OH)_4$  was obtained by adding aqueous ammonia into an 0.25 M solution of zirconium oxychloride at room temperature with vigorous stirring until the pH of the mother liquor reached at 8. The preparation of catalyst doped with Ce and modified with sulphate simultaneously was carried out by adding an acidic aqueous solution of cerium sulphate (Ce(SO<sub>4</sub>)<sub>2</sub>.4H<sub>2</sub>O) to the Zr(OH)<sub>4</sub> followed by drying at 110 °C for 24 h and calcined at 650°C for 2 h. The series of catalysts were prepared by varying mol % of cerium (0.02-0.15) added in the catalyst.

#### b) Typical experimental procedure:

A 10 mL round-bottomed flask was charged with suitable amine (2 mmol) and  $\beta$ keto ester (2 mmol), SO<sub>4</sub><sup>2-</sup>/Ce<sub>0.07</sub>Zr<sub>0.93</sub>O<sub>2</sub> (20 wt%) along with acetonitrile (4 mL) and the solution was stirred at room temperature for 30 minutes. To this solution was then added a  $\alpha,\beta$ -unsaturated aldehyde (2.2 mmol) with ethanol (2 mmol). The reaction mixture was further stirred at room temperature for 1 h, catalysts was separated by simple filtration and filtrate dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and concentrated to dryness. The progress of the reaction was monitored by TLC and GC. All the products obtained and discussed in this work have been previously reported and representative products were characterized by suitable techniques such as <sup>1</sup>H NMR (Varian 300 MHz) and GC-MS (Shimadzu QP 2010) analysis.

#### 2. BET surface area and acidity of catalyst

Catalyst	BET Surface area	Acidity	<i>E</i> :( <b>mV</b> ) <sup>c</sup>	
Catalyst	$(m^2.g^{-1})$	(mmol/g) <sup>b</sup>	L1(mv)	
$SO_4^{2-}/Ce_{0.02}Zr_{0.98}O_2$	22	3.17	440	
SO <sub>4</sub> <sup>2-</sup> /Ce <sub>0.07</sub> Zr <sub>0.93</sub> O <sub>2</sub>	53	4.23	560	
$SO_4^{2-}/Ce_{0.10}Zr_{0.90}O_2$	28	3.52	450	
$SO_4^{2-}/Ce_{0.15}Zr_{0.85}O_2$	14	3.50	460	

 Table 1. BET surface area and number and relative strength of acid sites by

 potentiometric method<sup>a</sup>

<sup>a</sup>All the catalysts are calcined at 650 °C for 2 h, <sup>b</sup>Total number of acid sites determined by n-butylamine potentiometric titration, <sup>c</sup> $E_i$ - Inital electrode potential (mV)

BET surface areas of the as synthesized  $SO_4^{2-}/Ce_xZr_{1-x}O_2$  (X=0.02-0.15) catalysts were determined (**Table 1**). The results indicate that both the surface area and acidity (**Figure 4**) are dependent on Ce: Zr ratio of the catalyst.  $SO_4^{2-}/Ce_{0.07}Zr_{0.93}O_2$  has the highest surface area as compared to other compositions.

### 3. Characterization data of compounds:

## GC-MS Spectra of the 1, 4 Dihydropyridines compounds:



Figure 1: Mass spectra of compound 7a (Table 4, entry 1)



Figure 2: Mass spectra of compound 7b (Table 4, entry 3)



Figure 3: Mass spectra of compound 7c (Table 4, entry 4).



Figure 4: Mass spectra of compound 7d (Table 4, entry 5)



Figure 5: Mass spectra of compound 7e (Table 4, entry 6)



Figure 6: Mass spectra of compound 7f (Table 4, entry 8)



Figure 7: Mass spectra of compound 7g (Table 4, entry 9)



Figure 8: Mass spectra of compound 7h (Table 4, entry 10)



Figure 9: Mass spectra of compound 7i (Table 4, entry 11)



Figure 10: Mass spectra of compound 7j (Table 4, entry 12)



Figure 11: Mass spectra of compound 7k (Table 4, entry 13).



Figure 12: Mass spectra of compound 7l (Table 4, entry 14).



Figure 13: Mass spectra of compound 7m (Table 4, entry 15).



Figure 14: Mass spectra of compound 7n (Table 4, entry 16).



Figure 15: Mass spectra of compound 70 (Table 4, entry 17).



Figure 16: Mass spectra of compound 7p (Table 4, entry 18).

#### **References:**

- Sohn, J.R.; Lee, S. H.; Lim, J. S. New solid superacid catalyst prepared by doping ZrO<sub>2</sub> with Ce and modifying with sulfate and its catalytic activity for acid catalysis. *Catalysis Today* 2006, *116*,143–150.
- Sohn, J. R.; Lim, J. S.; Lee, S. H. A New Solid Superacid Catalyst Prepared by doping ZrO<sub>2</sub> with Ce and Modifying with Sulfate Simultaneously. *Chemistry Letters* 2004, 33, 1490-1491