

**Supplementary Information**

**Direct Catalytic Co-conversion of Cellulose and Methane to  
Renewable Petrochemicals**

Aiguo Wang<sup>1</sup>, Danielle Austin<sup>1</sup>, Peng He<sup>1</sup>, Xiaohui Mao<sup>2</sup>, Hongbo Zeng<sup>2</sup>, Hua Song<sup>1\*</sup>

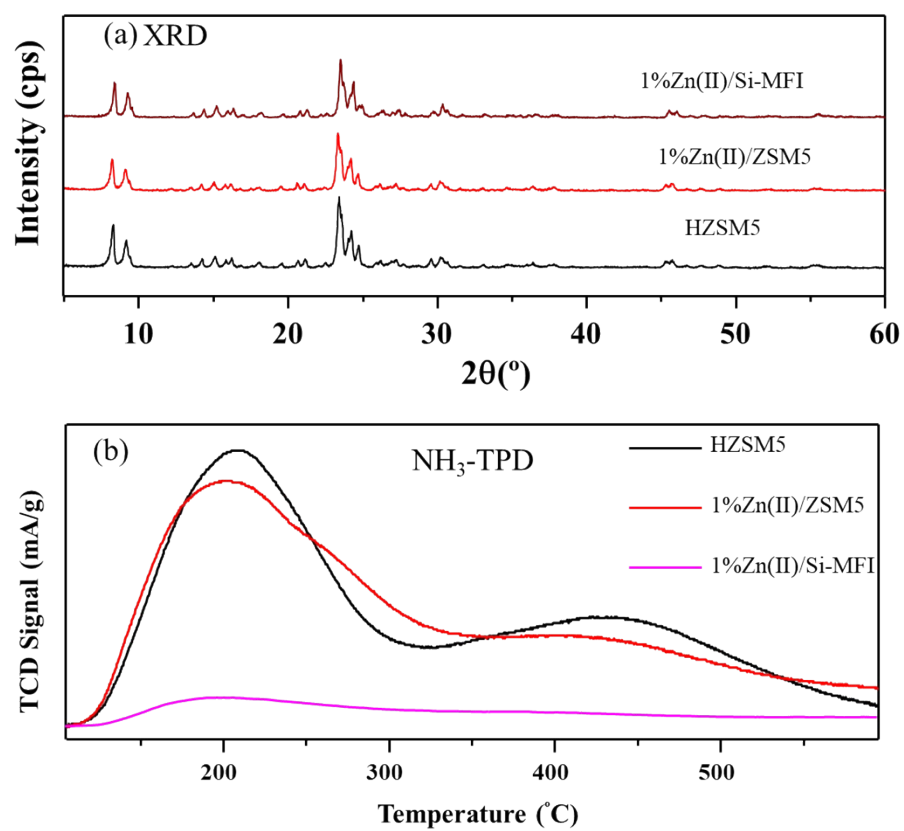
<sup>1</sup>Department of Chemical and Petroleum Engineering, University of Calgary  
2500 University Drive, NW, Calgary, Alberta T2N 1N4, Canada

<sup>2</sup>Department of Chemical and Materials Engineering, University of Alberta  
9211-116 Street NW, Edmonton, Alberta T6G 1H9, Canada

\*Corresponding author.

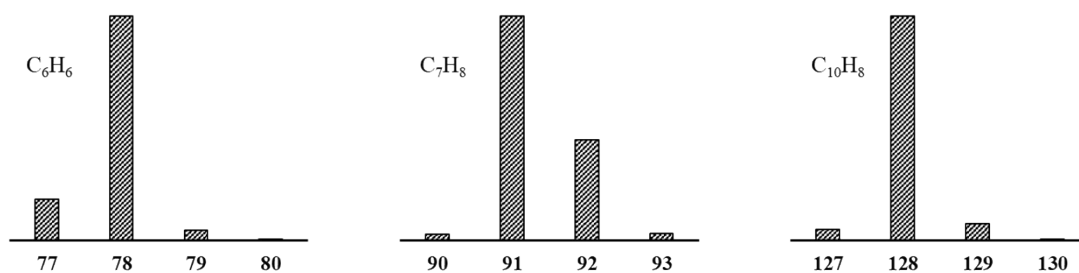
Fax: +1 (403) 284-4852; Tel: +1 (403) 220-3792;

E-mail: [sonh@ucalgary.ca](mailto:sonh@ucalgary.ca)

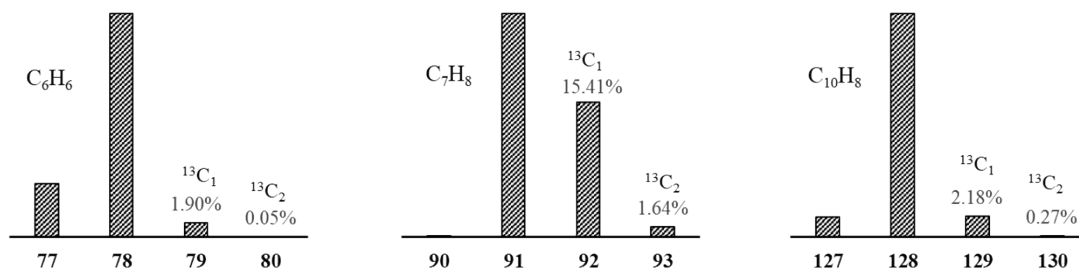


**Figure S1.** XRD (a) patterns and  $\text{NH}_3$ -TPD (b) profile of the catalysts HZSM5, 1%Zn( II )/ZSM5 and 1%Zn( II )/Si-MFI.

(a) Products from cellulose + CH<sub>4</sub>



(b) Products from cellulose + <sup>13</sup>CH<sub>4</sub>



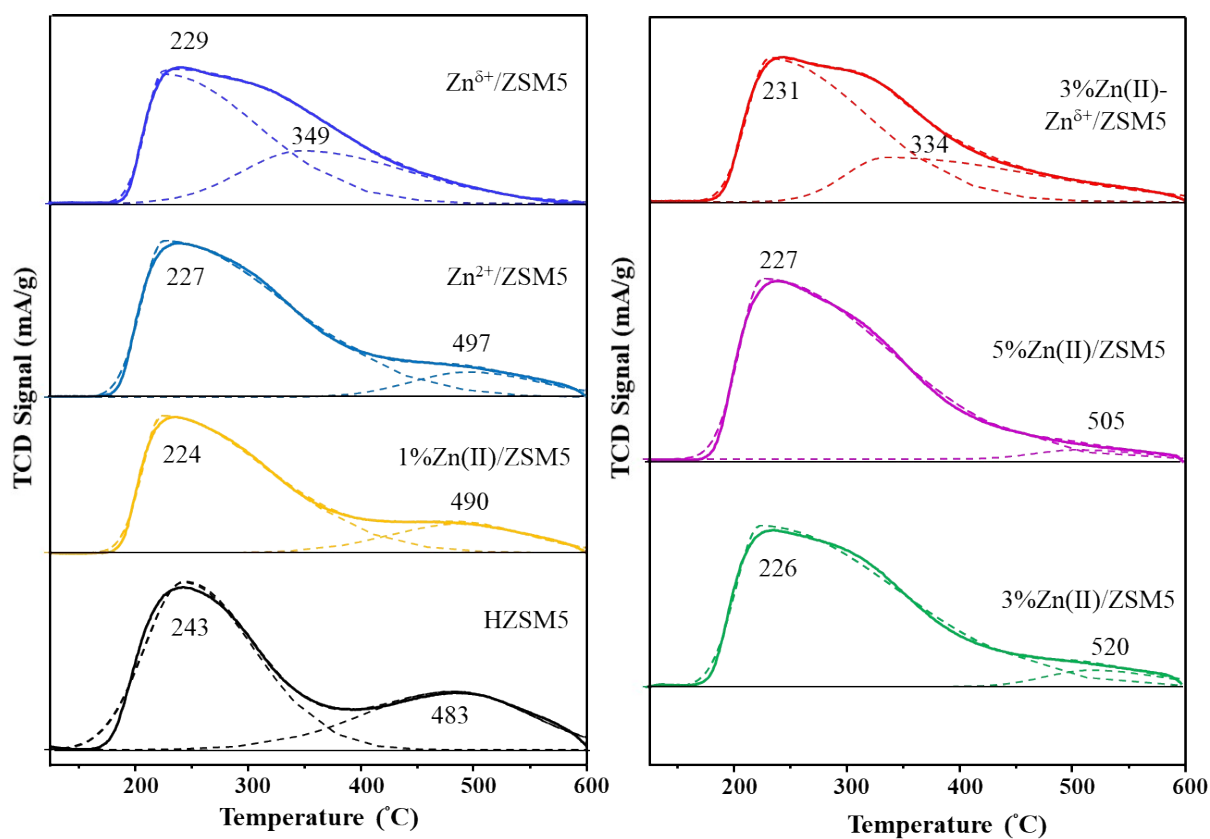
**Figure S2.** Mass spectra of major products (C<sub>6</sub>H<sub>6</sub>, C<sub>7</sub>H<sub>8</sub>, and C<sub>10</sub>H<sub>8</sub>): (a) with the natural abundance of <sup>13</sup>C and (b) formed from <sup>13</sup>CH<sub>4</sub> and cellulose over 3%Zn-Zn/ZSM5 with the estimated isotopic composition (mol%)

**Table S1.** <sup>13</sup>C liquid NMR peak area ratio with respect to CDCl<sub>3</sub> of the products from cellulose conversion under <sup>13</sup>CH<sub>4</sub> and CH<sub>4</sub> environments

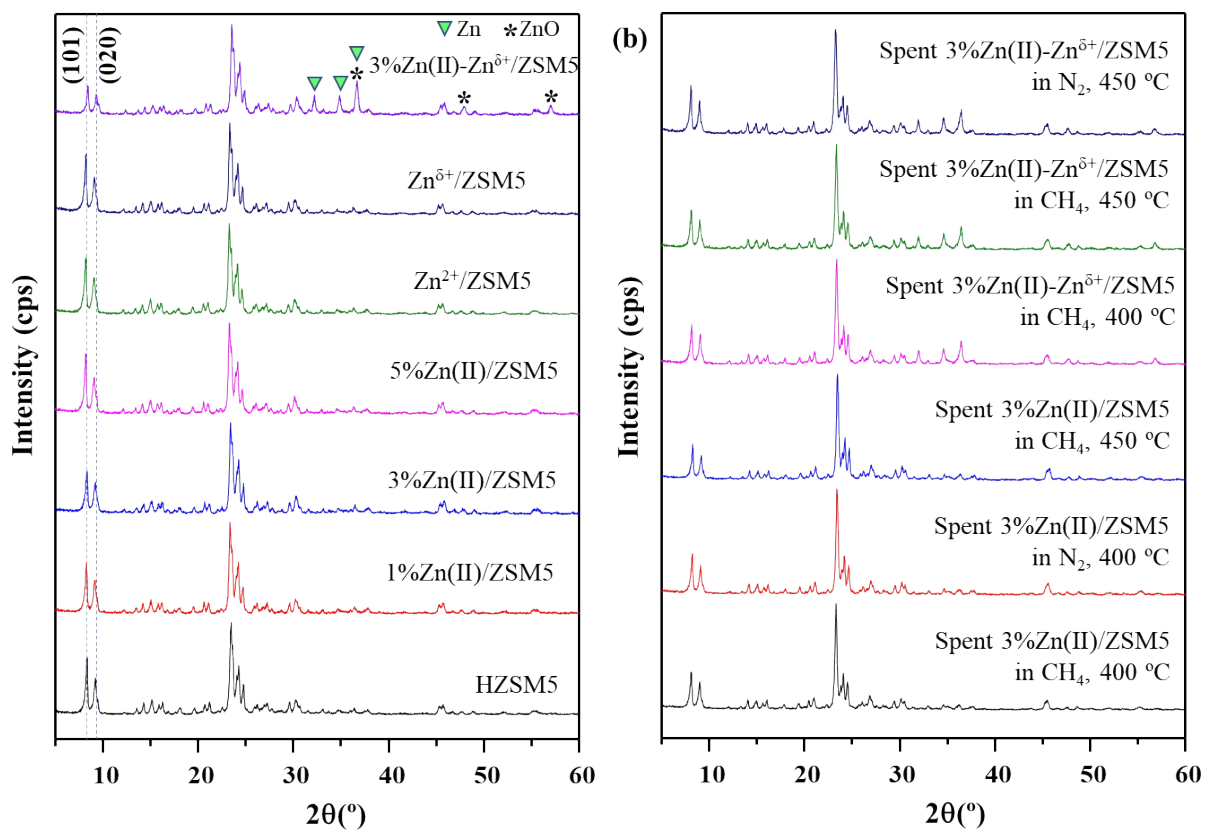
Chemical shift/ppm	Peaks assigned	<sup>13</sup> CH <sub>4</sub>	CH <sub>4</sub>	Increased by / %
129.05	Ortho positions of the alkyl substituted phenyl ring	0.107	0.067	60.3
128.34	Benzene ring /meta positions of the alkyl substituted phenyl ring	0.205	0.192	6.4
125.42	Para positions of the alkyl substituted phenyl ring	0.037	0.021	74.3
21.72	Benzylic carbon	0.060	0.046	30.7

**Table S2.**  $^1\text{H}$  liquids NMR peak area ratio with respect to  $\text{CDCl}_3$  of the products from the reactions between cellulose and  $\text{CH}_4/\text{CD}_4$

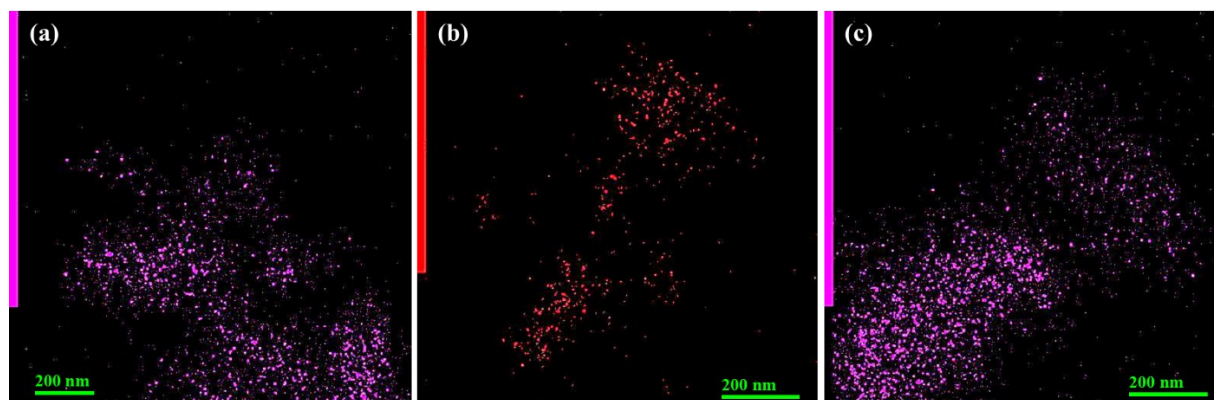
The type of proton	Chemical Shifts /ppm	cellulose+ $\text{CH}_4$	cellulose+ $\text{CD}_4$
<b>aromatic</b>	7.0-7.8	3.98	1.25
<b>benzylic</b>	2.0-2.8	0.99	0.30
<b>Alkyl</b>	0.6-1.4	4.53	4.51



**Figure S3.** NH<sub>3</sub>-TPD profiles and Bigaussian deconvoluted peaks of various fresh catalysts.



**Figure S4.** Powder XRD patterns of (a) various fresh catalysts, and (b) spent 3%Zn( II )-Zn<sup>δ+</sup>/ZSM5 and 3%Zn( II )-Zn<sup>δ+</sup>/ZSM5 catalysts under different environments



**Figure S5.** TEM-EDS mapping analysis of Zn species on the fresh 3%Zn( II )-Zn<sup>δ+</sup>/ZSM5 catalyst (a), spent 3%Zn( II )-Zn<sup>δ+</sup>/ZSM5 catalysts collected under environments of CH<sub>4</sub> (b) and N<sub>2</sub> (c).