

## The role of non-stoichiometric spinel for iso-butanol formation from biomass syngas over Zn-Cr based catalysts

**Table S1** Typical catalytic performance of ZnCr-c catalyst under different GHSV

| GHSV (h <sup>-1</sup> ) | CO conversion (%) | Alcohol selectivity (%) | Total alcohol rate (g/ml h) | Alcohol distribution /wt% |         |          |             |                         |
|-------------------------|-------------------|-------------------------|-----------------------------|---------------------------|---------|----------|-------------|-------------------------|
|                         |                   |                         |                             | Methanol                  | Ethanol | Propanol | Iso-butanol | C <sub>5+</sub> alcohol |
| 1000                    | 35.4              | 30.7                    | 0.043                       | 75.9                      | 1.34    | 1.98     | 18.9        | 3.78                    |
| 3000                    | 30.4              | 49.6                    | 0.091                       | 74.4                      | 1.56    | 2.91     | 20.2        | 1.21                    |
| 5000                    | 18.7              | 59.8                    | 0.15                        | 77.9                      | 1.72    | 2.75     | 17.1        | 1.56                    |
| 8000                    | 13.4              | 73.6                    | 0.22                        | 78.4                      | 1.77    | 2.03     | 15.8        | 1.27                    |

**Reaction conditions:** Temperature =400°C, Pressure=10 Mpa.

**Table S2** Typical catalytic performance of ZnCr-c catalyst at different reaction temperature

| Temperature (°C) | CO conversion (%) | Alcohol selectivity (%) | Total alcohol rate (g/ml h) | Alcohol distribution /wt% |         |          |             |                         |
|------------------|-------------------|-------------------------|-----------------------------|---------------------------|---------|----------|-------------|-------------------------|
|                  |                   |                         |                             | Methanol                  | Ethanol | Propanol | Iso-butanol | C <sub>5+</sub> alcohol |
| 360              | 24.2              | 52.9                    | 0.13                        | 78.7                      | 2.27    | 1.04     | 8.84        | 2.11                    |
| 380              | 28.7              | 50.5                    | 0.099                       | 77.8                      | 2.48    | 2.32     | 15.4        | 1.63                    |
| 400              | 30.4              | 49.7                    | 0.091                       | 74.4                      | 1.56    | 2.91     | 20.2        | 1.21                    |
| 420              | 36.0              | 29.9                    | 0.057                       | 70.0                      | 5.31    | 1.85     | 20.2        | 2.07                    |

**Reaction conditions:** GHSV=3000 h<sup>-1</sup>, Pressure=10 Mpa.

**Table S3** Typical catalytic performance of ZnCr-c catalyst under different pressure

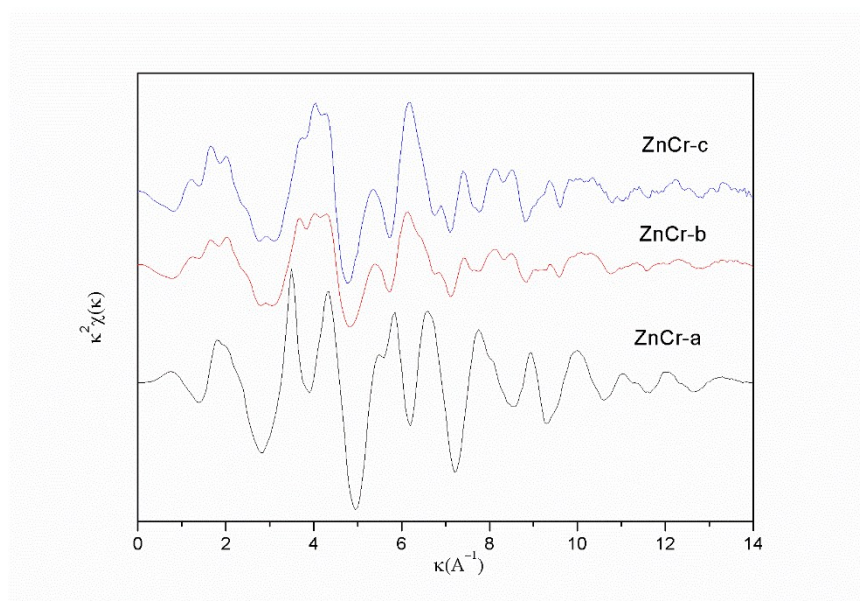
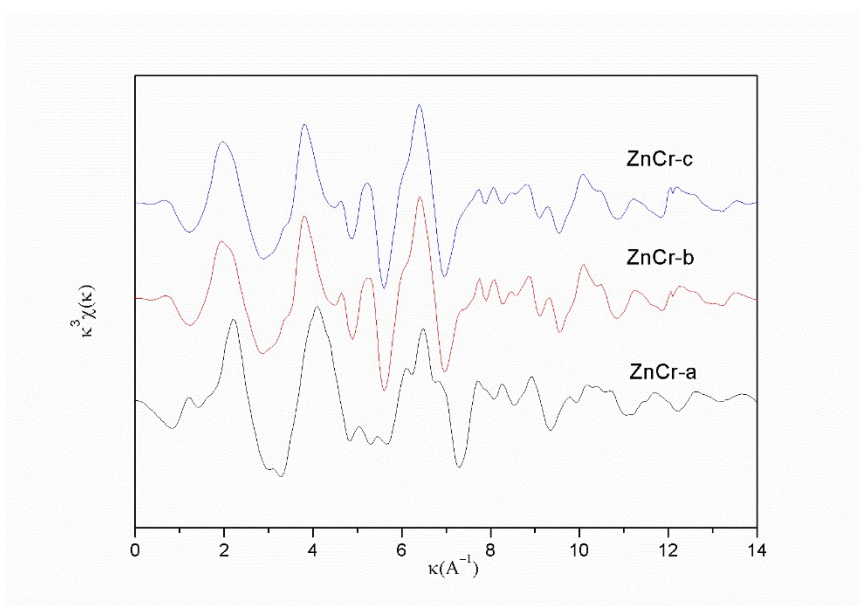
| Pressure (Mpa) | CO conversion (%) | Alcohol selectivity (%) | Total alcohol rate (g/ml h) | Alcohol distribution /wt% |         |          |             |                         |
|----------------|-------------------|-------------------------|-----------------------------|---------------------------|---------|----------|-------------|-------------------------|
|                |                   |                         |                             | Methanol                  | Ethanol | Propanol | Iso-butanol | C <sub>5+</sub> alcohol |
| 3              | 12.8              | 33.1                    | 0.028                       | 72.8                      | 2.82    | 1.10     | 20.8        | 1.17                    |
| 6              | 19.8              | 40.5                    | 0.059                       | 75.9                      | 2.41    | 1.08     | 19.5        | 1.31                    |
| 8              | 24.4              | 46.7                    | 0.079                       | 76.8                      | 2.09    | 1.32     | 20.8        | 0.93                    |
| 10             | 30.4              | 49.7                    | 0.091                       | 74.4                      | 1.56    | 2.91     | 20.2        | 1.21                    |

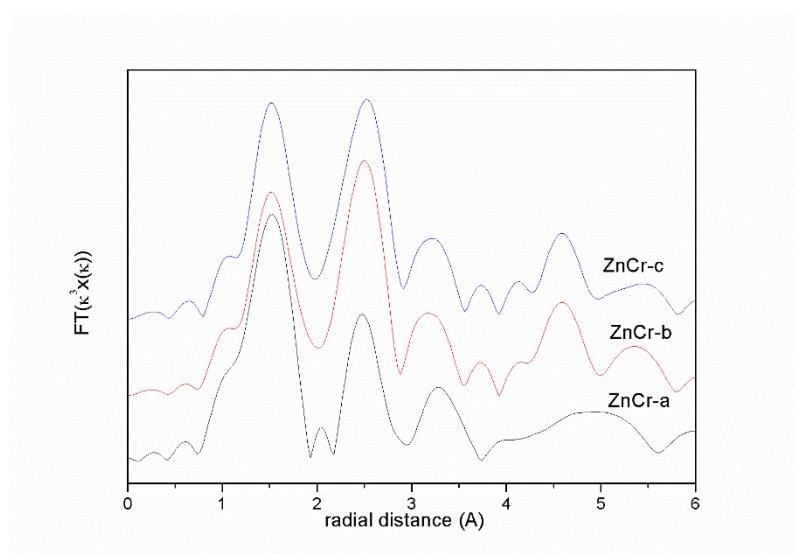
**Reaction conditions:** GHSV=3000 h<sup>-1</sup>, Temperature=400 °C.

**Table S4** Typical catalytic performance of ZnCr-c catalyst under different H<sub>2</sub>/CO molar ratios

| H <sub>2</sub> /CO | CO conversion (%) | Alcohol selectivity (%) | Total alcohol rate (g/ml h) | Alcohol distribution /wt% |         |          |             |                          |
|--------------------|-------------------|-------------------------|-----------------------------|---------------------------|---------|----------|-------------|--------------------------|
|                    |                   |                         |                             | Methanol                  | Ethanol | Propanol | Iso-butanol | C <sub>5</sub> + alcohol |
| 1                  | 15.2              | 54.1                    | 0.072                       | 75.7                      | 2.34    | 1.01     | 20.5        | 2.37                     |
| 1.5                | 16.3              | 52.2                    | 0.083                       | 75.2                      | 2.51    | 1.80     | 19.7        | 2.21                     |
| 2                  | 22.5              | 50.3                    | 0.086                       | 74.8                      | 2.13    | 1.32     | 19.8        | 1.93                     |
| 2.6                | 30.4              | 49.7                    | 0.091                       | 74.4                      | 1.56    | 2.91     | 20.2        | 1.21                     |

**Reaction conditions:** Temperature=400 °C, Pressure=10 Mpa, GHSV=3000 h<sup>-1</sup>

**Figure S1.** The K<sup>3</sup>-weighted EXAFS signals for the Zn atom in catalysts.**Figure S2.** The K<sup>3</sup>-weighted EXAFS signals for the Cr atom in catalysts.



**Figure S3** Fourier transform EXAFS signals for Cr atom in catalysts.