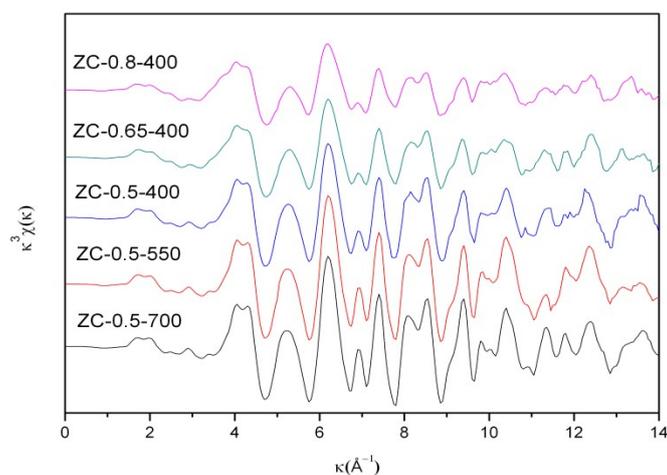


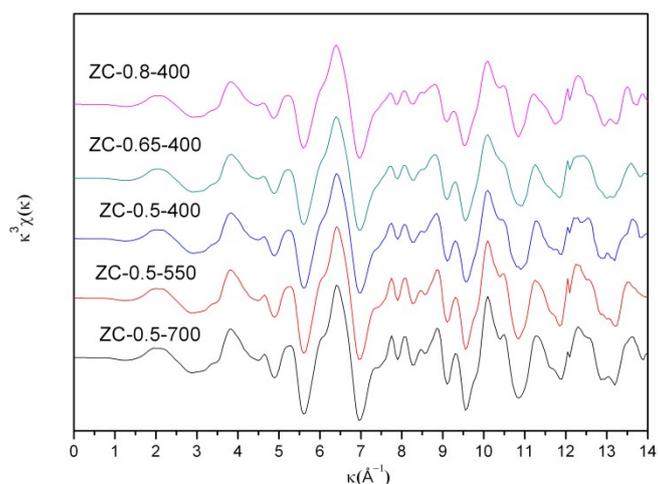
## The real active sites over Zn-Cr catalysts for direct synthesis of isobutanol from syngas: Structure-Activity relationship

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The EXAFS signals of the Zn and Cr K edge with  $k^3$ -weight were compared in Fig. S1-1 and Fig. S1-2. The oscillations were similar among samples ZC-0.5-700, ZC-0.5-550, ZC-0.5-400, ZC-0.65-400 and ZC-0.8-400, implying that these catalysts had a very similar structure around Zn and Cr. The intensity of peak became weaker with decreasing annealing temperature and increasing Zn/Cr molar ratios implying that the cation disorder distribution became more serious.

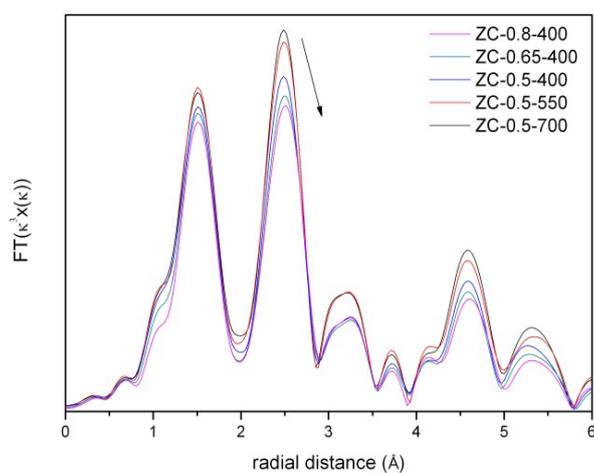


**Fig. S1-1.** The  $k^3$ -weighted EXAFS signals for the Zn K-edge.



**Fig. S1-2.** The  $K^3$ -weighted EXAFS signals for the Cr K-edge.

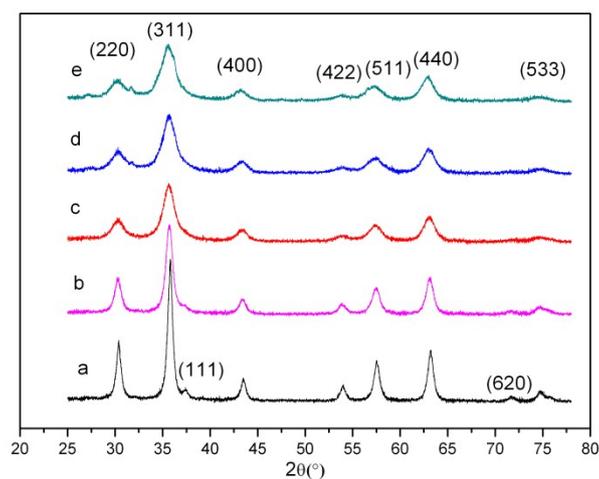
For the Cr K-edge, as showed in Fig. S2, the distance between the central atom and the second coordinated shell peak became longer with decreasing annealing temperature and increasing Zn/Cr molar ratios. This behavior should also be explained by the cation disorder distribution. A similar effect can be found in coprecipitated  $ZnFe_2O_4$ . [1] As Cr atoms substitute to tetrahedral sites from octahedral sites, the coordination number of Cr/Zn centered at about 3.45 Å increases, while the coordination number of Cr/Zn centered at about 2.94 Å decreases. As a result, the second coordinated shell atoms became more distant.



**Fig. S2.** The Fourier transform EXAFS signals for the Cr K-edge

**Table. S1.** O species surface composition of different catalysts

catalysts	$O_{\text{ads}} / (O_{\text{latt}} + O_{\text{ads}} + O_{\text{OH}^-})$	$O_{\text{OH}^-} / (O_{\text{latt}} + O_{\text{ads}} + O_{\text{OH}^-})$
ZC-0.5-700	0.26	0.07
ZC-0.5-550	0.27	0.15
ZC-0.5-400	0.27	0.16
ZC-0.65-400	0.32	0.19
ZC-0.8-400	0.32	0.20



**Fig. S3.** The XRD patterns of catalysts, a) ZC-0.5-700, b) ZC-0.5-550, c) ZC-0.5-400, d) ZC-0.65-400, e) ZC-0.8-400

The powder XRD patterns of various Zn/Cr molar ratio samples after calcination

at different temperature are shown in Fig. S3. The main reflections are consistent with the crystalline  $\text{ZnCr}_2\text{O}_4$  (JCPDS cards 22-1107), indicating that the Zn-Cr oxides have a spinel structure with cubic (f c c) cells. The diffraction intensity of samples becomes stronger with increasing the calcination temperature, illustrating larger particle size and better crystallinity had been gotten when samples were calcined at higher temperature. The particle size calculated by Scherrer equation with XRD signals is from 17.8 nm to 5.9 nm with decreasing annealed temperature from 700°C to 400°C and keeps no change regardless of the Zn/Cr molar ratios.

It is worth noting that no additional peaks of ZnO are observed in all of the patterns of the samples, even though the samples of molar ratio of Zn/Cr is greater than 0.5 which is the value of Zn/Cr molar ratio in an ideal spinel. The undetected ZnO phase maybe result from amorphous or highly divided ZnO phases at the surface of spinel or the excessive ZnO may be inside the spinel structure to form non-stoichiometry.

**Table. S2.** Texture parameters of catalysts

catalysts	$S_{\text{BET}}(\text{m}^2\text{g}^{-1})$	$V_p(\text{cm}^3\text{g}^{-1})$	$r_p(\text{nm})$
ZC-0.5-700	32.99	0.1366	13.22
ZC-0.5-550	54.32	0.1632	12.02
ZC-0.5-400	89.41	0.2305	9.189
ZC-0.65-400	95.36	0.3043	11.65
ZC-0.8-400	100.2	0.3711	13.01

Texture parameters of catalysts are showed in Table. S2. The average crystallite size of  $\text{ZnCr}_2\text{O}_4$  calculated by XRD patterns shows a decrease in the crystallite size of  $\text{ZnCr}_2\text{O}_4$  at low calcination temperature. That could probably explain the increase of

BET surface areas at low calcination temperature. The enhancement of pore volumes and decrease of sample radii at low calcination temperature should be due to the same reason.

No decrease but slightly increase of the BET surface areas is found with increasing the ratios of Zn to Cr. It may be due to the formation of non-stoichiometry and the conclusion has been further demonstrated by some former researchers. Massimo Bertoldi [2] et al believed that even a small excess of zinc inside the spinel phase increased the surface area, whereas the presence of a ZnO phase appeared to lower it. That is consistent with our results.

## Reference

- [1] B. Jeyadevan, K. Tohji, K. Nakatsuka, *J. Appl. Phys.* . 76 (1994) 6325-6327.
- [2] M. Bertoldi, B. Fubini, E. Giamello, G. Busca, F. Trifirò, A. Vaccari, *J. Chem. Soc., Fara. Trans.* 84 (1988) 1405.