Destruction and Preservation of Nonstoichiometric ZnCr Oxide Catalyst from Machine-Learning Simulation

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Method

Deactivation barrier estimation:

(1) The reaction rate of methanol yield (r_r) is approximately 200 g kg_{cat}^{-1} h^{-1} at 673 K (*J. Chem. Soc., Chem. Commun.* ***1984****, 10, 656*).

(2) The selectivity of syngas-to-alcohol decreases over time from 80 wt% to 60 wt% after 1000 hours (*Fuel Process. Technol.* **2019,** *193*, 53).

(3) Based on (1) and (2), we can estimate the deactivation rate (r_d) is 0.04 g kg_{cat}^{-1} h^{-1} (200 * (80-60)/ 100 / 1000 = 0.04)

(4) The ratio of deactivation rate to reaction rate (r_d/r_r) is approximately 1:10000, that is

$$\frac{r_d}{r_r} = \frac{A_d * e^{-E_{a,d}/RT}}{A_r * e^{-E_{a,r}/RT}} = 1/10000$$

(5) We assume the pre-exponential factor of deactivation (A_d) is equal to the pre-exponential factor of reaction (A_r). Because the apparent experimental reaction barrier for syngas-to-methanol ($E_{a,r}$) is ~1.20 eV (113±5 kJ mol^{-1}, *Catal. Lett.* **1989,** *3*, 65), the energy barrier of deactivation ($E_{a,d}$) is therefore 1.73 eV.

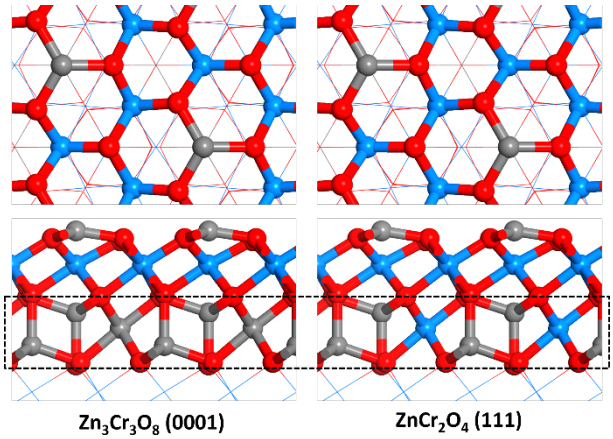

Figure S1. The structures of $ZnCr_2O_4$ (111) and $Zn_3Cr_3O_8$ (0001) surfaces.

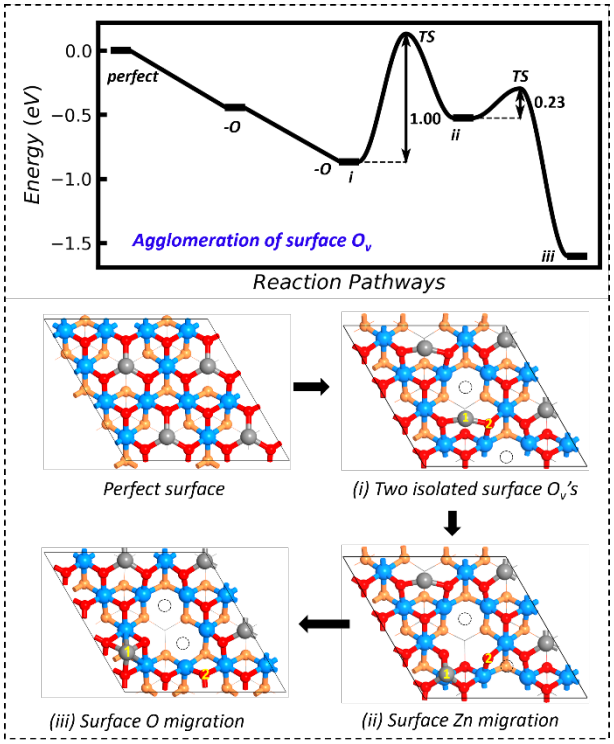

Figure S2. The energy profile of surface O_v agglomeration.

Starting from the perfect $Zn_3Cr_3O_8$ (0001) surface, two surface O atoms can be readily removed by reacting with H_2 that releases the energy of 0.44 and 0.36 eV. The resulted two O_vs are separated by a surface O[2] atom (state ***i***). The Zn[1] atom can migrate to the top of surface Cr atom with the formation of Zn-O-Zn structural pattern (state ***ii***). This Zn migration needs to overcome the energy barrier of 1.00 eV and the reaction energy is 0.34 eV. Then, the separator O[2] atom migrates to fill O_v, exposing four interconnected [CrO_5] structural pattern (state ***iii***). The migration barrier and reaction energy are 0.23 eV and -1.08 eV. The final obtained surface structure with O_v agglomeration is 0.74 eV more stable than that with isolated O_v's, indicating the thermodynamic preference of O_v agglomeration.

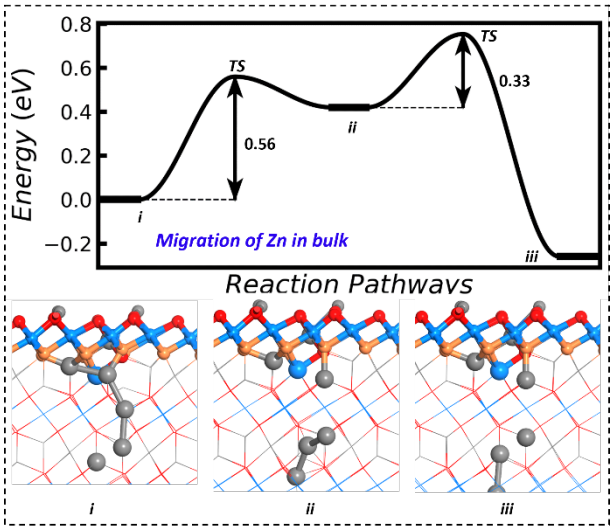

Figure S3. The energy profile of bulk Zn migration. The green, dark blue and red represent the Zn, Cr and O atoms, respectively.

The Zn migration in bulk is much easier with the migration barrier of only 0.75 eV.

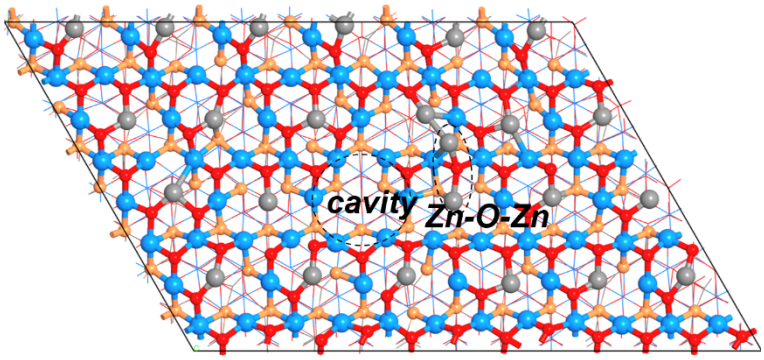

Figure S4. The surface structure after 2 ns MD-NN simulation at 673 K.

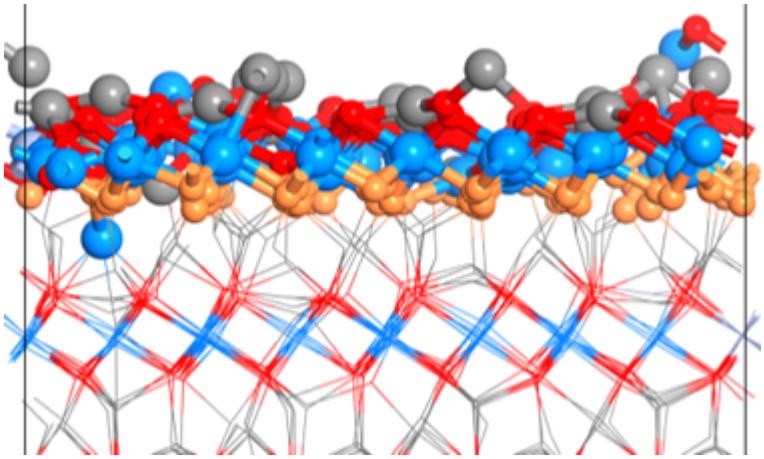

Figure S5. The structure after 2 ns MD-NN simulation at 873 K from side view.