

Support information

Enhancing the Activity of Pd/Zn-Al-O Catalysts for CO Esterification to Dimethyl Oxalate via Increasing Oxygen Defects by Tuning Zn/Al Ratio

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Catalytic Activity Evaluation

The catalytic activity evaluation of the catalysts for the CO direct esterification reaction to DMO were performed under atmospheric pressure and 130 °C using a fixed-bed quartz tubular reactor and the weight of the fresh catalyst was 0.2 g. In the experiment, the reactant gases (28% CO, 20% CH₃ONO, 4% Ar and N₂ balance) were passed via the reactor at a weight hourly space velocity (WHSV) about 3000 h⁻¹. The resulting mixture was introduced into an on-line Shimadzu GC-2014 gas chromatograph equipped with TCD and FID to monitor for testing the composition of the reactant gases and reaction products. Catalytic activities were mainly indicated by the conversion of CO and the selectivity to DMO.

These parameters were calculated according to the following equations:

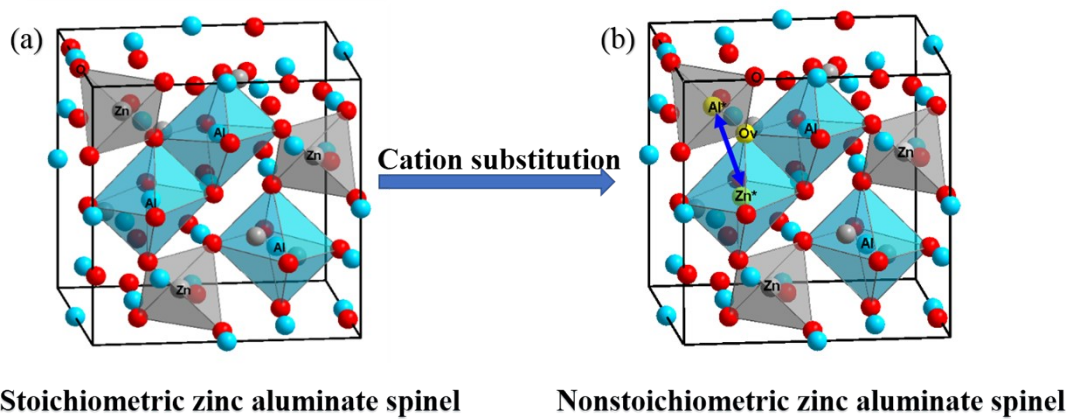
$$\text{Conversion of CO (\%)} = \frac{[CO]_{in}/[Ar]_{in} - [CO]_{out}/[Ar]_{out}}{[CO]_{in}/[Ar]_{in}} * 100\%$$

$$\text{Selectivity of DMO (\%)} = \frac{S_{DMO} * F_{DMO}}{S_{DMO} * F_{DMO} + S_{DMC} * F_{DMC}} * 100\%$$

$$\text{WTY of DMO (g Kg}_{cat}^{-1} \text{ h}^{-1})$$

$$= \frac{\text{conversion of CO} * \text{selectivity to DMO} * \text{WHSV of CO} * 118.09 \text{ g} \cdot \text{mol}^{-1}}{2 * 22.4 \text{ L} \cdot \text{mol}^{-1}}$$

where [Ar]_{in} and [Ar]_{out} are the concentrations of Ar at the inlet and outlet, [CO]_{in} and [CO]_{out} are the concentrations of CO at the inlet and outlet, respectively, S_{DMO} and S_{DMC} are the peak areas of dimethyl oxalate and dimethyl carbonate and F_{DMO} and F_{DMC} are the relative correction factors of dimethyl oxalate and dimethyl carbonate, respectively.



Scheme S1 Lattice structure of (a) stoichiometric and (b) nonstoichiometric zinc aluminate spinel.

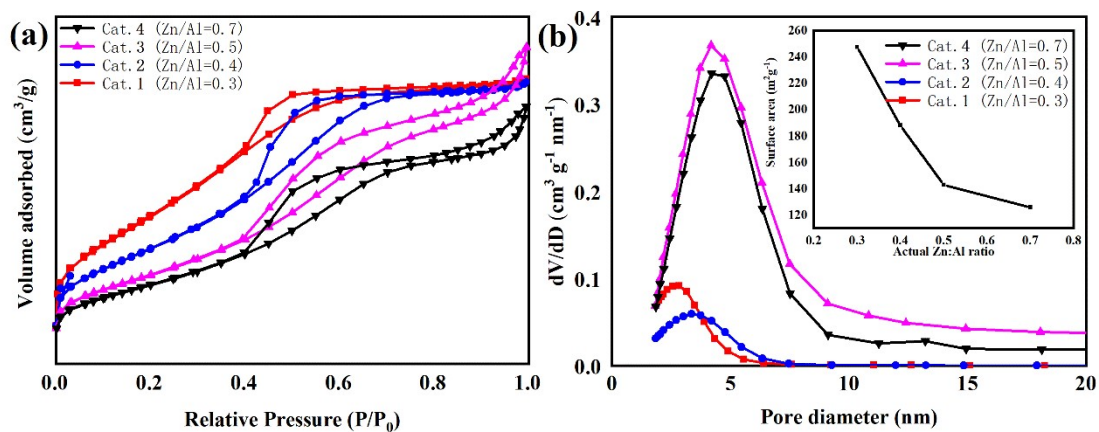


Fig. S1 N₂ sorption isotherms (a) and pore size distribution (b) of Cat. 1 (Zn/Al=0.3), Cat. 2 (Zn/Al=0.4), Cat. 3 (Zn/Al=0.5) and Cat. 4 (Zn/Al=0.7). (Inset: the change of surface areas as the increase of actual Zn/Al ratio).