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Preferential synthesis of ethanol from syngas via dimethyl oxalate hydrogenation over an integrated catalyst

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1. Experimental

1.1 Preparation of precursor of Fe_5C_2

Iron oxide was synthesized by our earlier reported simple precipitation method.[1] In a typical preparation, firstly, $Fe(NO)_3 \cdot 9H_2O$ was dissolved in distilled water and the resulted solution was heated to 343 K. Secondly, an aqueous solution of sodium carbonate (1M) was added into iron nitrate solution under continuous stirring at 343 K until pH of about 7.0 was reached. The resulted suspension was then filtered and washed with distilled water several times to removing excess ions. The precipitate was dried at 383 K for 12 and calcined at 673 K for 6h, then pressed, crushed and sieved to desired size.

1.2 Preparation of precursor of Cu-SiO_2 and CuZnO-SiO_2

The Cu-SiO_2 and CuZnO-SiO_2 (Cu/Zn molar ratio=9:1) was prepared by the same hydrolytic precipitation method as described in our previous work.[2] An appropriate amount of copper (Ⅱ) nitrate and zinc (Ⅱ) nitrate was added into distilled water to form the salt solution A. A required amount of TEOS (tetraethyl orthosilicate) was added into ethanol to form the organic solution B. Then the above solution was mixed well to form mixture C. To precipitate the metal and silica support, $(NH_4)_2CO_3$ solution (0.25 M) and the mixture C were dropped into distilled water at 353 K under stirring. The pH of solution is maintained at 7-7.5 during this process. After that, the suspension was aged for 18 h at 353 K. Then, the precipitate was obtained after filtration and washing with 800 ml water. After drying at 353 K in vacuum oven, the solid was calcinated at 673 K for 4 hours.

1.3 Catalytic performance test

The catalytic performances of the catalysts in gas-phase catalytic hydrogenation of dimethyl oxalate (DMO) were examined in a stainless-steel fixed-bed reactor with an internal diameter of 8 mm.

For the preparation of Fe_5C_2, the samples of the calcined catalyst (40-60 mesh) was first placed in the center of the reactor and both sides of the catalyst bed were packed with quartz powder (20-40 mesh) and reduced by H_2 in situ (99.999%, 653 K, 2.50 MPa) for 4 h. Then, the reduced samples were carbonized at 2.50 MPa and 533 K by a methanol-H_2 mixture (ratio of methanol/H_2 = 20:1) for 24 h. The catalyst was passivated by 1% O_2/Ar at room temperature after carbonization or catalytic performance test.

For the preparation of Cu-SiO_2 and CuZnO-SiO_2, the samples of the calcined catalyst (40-60 mesh) was first placed in the center of the reactor and both sides of the catalyst bed were packed with quartz powder (20-40 mesh) and reduced by H_2 (99.999%, 653 K, 2.50 MPa) for 4 h.

For the integrated catalysts with dual-bed configuration, both the catalysts were ex-situ prepared. Fe_5C_2 was got by the ex-situ carbonization of the reduced bulk Fe_2O_3 in a methanol/H_2 flow. While the CuZnO-SiO_2 was reduced ex-situ before packed into the tube reactor. Then, the integrated catalyst bed was made by sequentially packing the two components into the reactor. The first layer and the second layer were divided by an inert quartz sand layer with thickness of about 0.5 cm.

For the granular mixture, the samples (40-60 mesh) of as-prepared Fe_5C_2 catalyst and Cu-based catalyst were mixed and well distributed with quartz sand. The samples (total mass is about 0.7 g for each integrated catalyst) were weighed according to the given mass ratio of the two components.

During the reaction, the reactant was injected from the top of the reactor using a high-pressure pump at a system pressure of 2.50 MPa. Catalytic performance was tested at different temperature from 513 to 573 K and the DMO weight liquid hourly space velocity (WLHSV) varied from 0.2 to 2.0 h^{-1}. The mole ratio of H_2/DMO was 180. As for the hydrogenation of MA, EG and MG, the catalytic performance was tested at varying temperature from 503 to 533 K. The feed is 98% MA and 20 wt.% methanol solution for DMO, EG and MG.

For separated system, the DMO feed was first introduced to the Fe_5C_2 catalyst bed and the liquid products were collected in a 263 K cold trap. Then, the liquid products were injected into the reactor with CuZnO-SiO_2 catalyst bed and the final liquid products were collected and analyzed. The reaction conditions were set to be the same as that with integrated system.

The reaction products collected in the condenser were analyzed using a gas chromatography (BEIFEN 3420A) with an HP-INNOWAX capillary column (30 m × 0.25 mm ×0.25 μm) equipped with a flame ionization detector (FID). More than three samples were taken under the same experimental conditions and the results were averaged to ensure repeatability.

DMO conversions were determined by carbon balance based on compounds in the liquid phase (equation 1). The selectivity of ethylene glycol (EG), methyl acetate (MA), ethanol (EtOH) and C3-C4OH (involving (iso-) propanol, (iso-)butanol, 1,2-propanediol and 1,2-butanediol) were calculated by the following equation (equation 2).

$$\mathit{Conversion}\ (\%) = \frac{\mathit{mol\ of\ DMO\ put\ into\ the\ reactor} - \mathit{mol\ of\ DMO\ in\ the\ product}}{\mathit{mol\ of\ DMO\ put\ into\ the\ reactor}} \times 100\% \qquad (1)$$

$$\mathit{Selectivity}\ \ (\%) = \frac{\mathit{mol\ of\ EG, MA, EtOH\ or\ C}3 - \mathit{C}4\mathit{OH\ in\ the\ product}}{\mathit{mol\ of\ DMO\ put\ into\ the\ reactor} - \mathit{mol\ of\ DMO\ in\ the\ product}} \times 100\% \qquad (2)$$

The reaction rate of hydrogenation of MA, EG and MG was calculated by the following equation (equation 3).

$$\mathit{Reaction\ rate}$$
$$= \frac{\mathit{mol\ of\ MA, EG\ and\ MG\ put\ into\ the\ reactor} - \mathit{mol\ of\ MA, EG\ and\ MG\ in\ the\ prod}}{\mathit{mass\ of\ catalyst}\ \times \mathit{reaction\ time}}$$

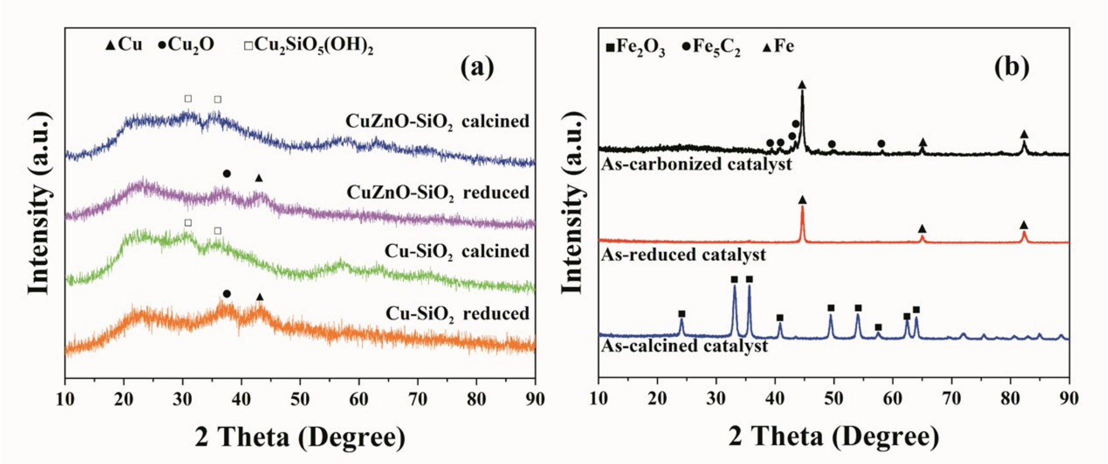
1.4 Catalyst characterization

X-ray photoelectron spectroscopy (XRD) measurements were carried out using a Rigaku C/max-2500 diffractometer, employing the graphite-filtered Cu Ka radiation (λ = 1.5406 Å) at room temperature. The particle size of catalysts was calculated with the X-ray-broadening technique using the Scherrer’s equation. Data points were acquired by step scanning with a rate of 8°/min from 2theta = 10° to 90°.

Transmission electron microscopy (TEM) was conducted on a JEOL JEM-2100F system electron microscope to observe the morphology and structure of the samples. Before the experiments, the samples were ground into powder and then dispersed in ethanol with the assistance of ultrasound. After that, the suspension was allowed to stand a while and then the supernatant was dropped onto the ultrathin carbon film.

CO_2-TPD was performed to study the basicity of the catalysts by using a Micromeritics Autochem II 2920. First, 100 mg catalyst sample was introduced into the U-shaped tube and reduced at 573 K in pure hydrogen flow. After being cooled to 323 K in helium, the sample was pretreated by 10% CO_2/ He for 1 h to ensure the basic sites were occupied sufficiently. After that, the samples were heated to 873 K with a ramping rate of 10 K/min in the pure He flow. The quantity of CO_2 was detected by TCD. And the desorption gas was analyzed by Mass Spectrum (HIDEN HPR-20) for Fe_5C_2.

NH_3-TPD was measured on PCA-1200 chemical adsorption instrument. First, about 50 mg catalyst sample was introduced into the U-shaped tube and reduced at 573 K in 1% H_2/He hydrogen flow. Then, the sample was cooled to 373 K in helium, followed by an expose to 10% NH_3/He flow for 30 min. Until the baseline of the TCD signal was stable in the purging gas He, the TPD program started from 373 K to 973 K with a ramping rate of 10 K/min in the pure He flow. The quantity of NH_3 was detected by TCD.



. **Fig. S1** XRD patterns of catalysts. (a) Cu-based catalysts. (b) Fe-based catalysts.

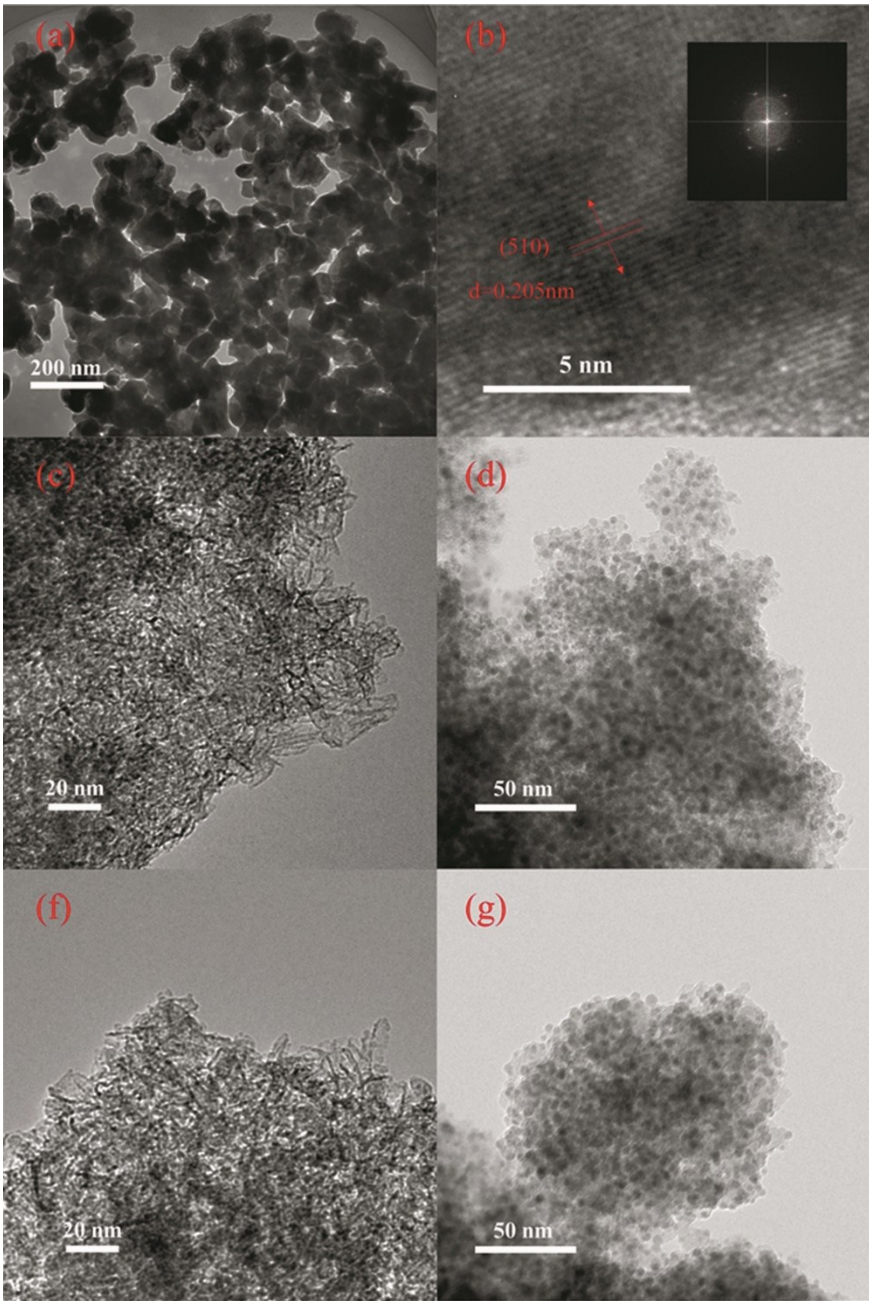


Fig. S2 TEM images of catalysts. (a) and (b) TEM and HRTEM of carbonized Fe-based catalyst. (c) calcined Cu-SiO_2. (d) reduced Cu-SiO_2. (f) calcined CuZnO-SiO_2. (g) reduced CuZnO-SiO_2.

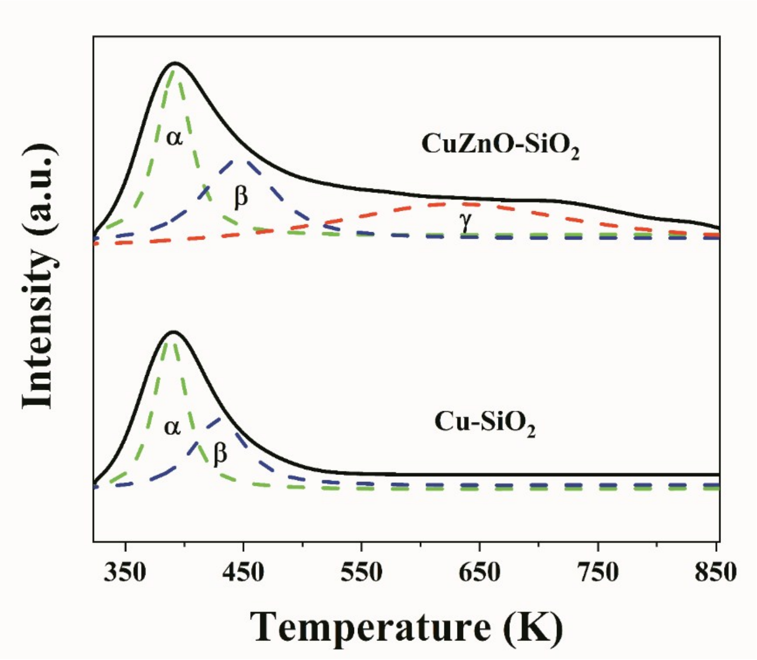


Fig. S3 CO_2-TPD patterns of reduced Cu-SiO_2 and CuZnO-SiO_2.

The profile of Cu−SiO_2 can be divided into two Gauss peaks, the weak peak (α peak) was assigned to the silicon hydroxyl, and another peak (β peak) could be ascribed to the moderately basic sites provided by the metal−oxygen pairs. However, a stronger peak (γ peak) appears in the catalysts after the modification of the zinc species, which could be ascribed to the strongly basic sites provided by low coordination oxygen atoms.[3] The presence of the strong basic sites led to the formation of more C3-4OH on CuZnO-SiO_2 catalyst.

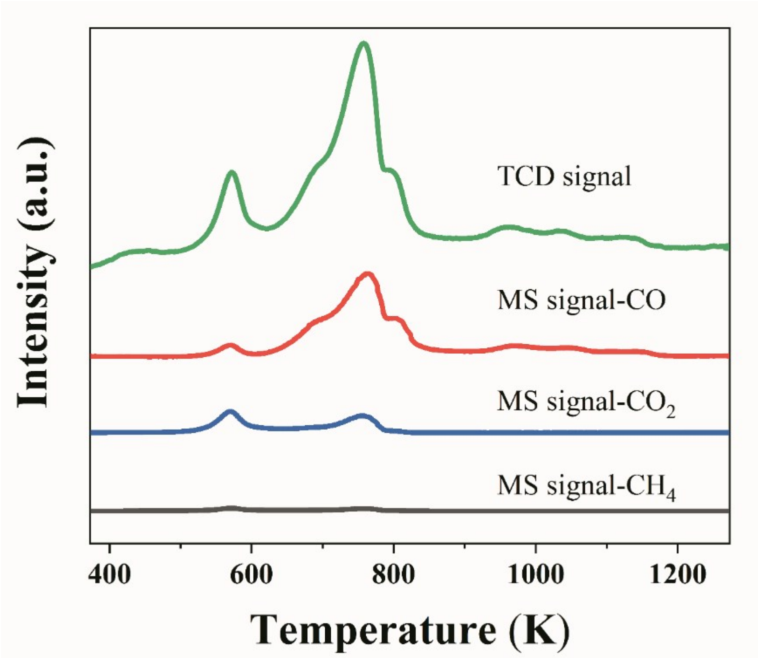


Fig. S4 CO_2-TPD-MS patterns of Fe_5C_2

There is a desorption peak at 570 K and several broad desorption peaks from 610 K to 840 K in the TCD patterns. However, according to the MS results, these peaks should be ascribed to the concurrent desorption of CO and CO_2. Obviously, there might be a chemical reaction between the adsorbed CO_2 and carbon species on Fe_5C_2 catalyst in this system, which lead to the generation of CO (as shown in equation 1). Therefore, CO_2-TPD is not a suitable method to evaluate basic sites on Fe_5C_2.

$$C + CO_2 \leftrightarrow 2CO \tag{1}$$

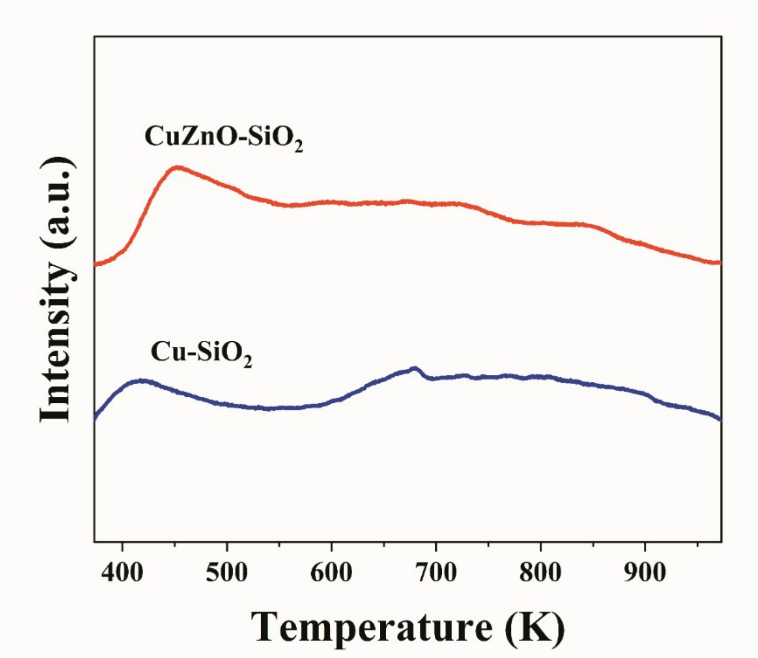


Fig. S5 NH_3-TPD patterns of reduced Cu-SiO_2 and CuZnO-SiO_2.

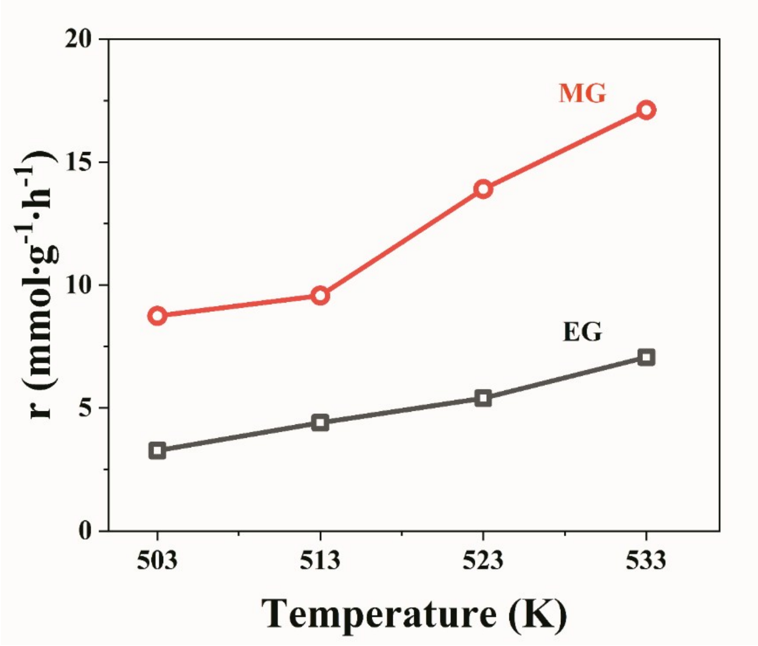


Fig. S6 The reaction rate on Fe_5C_2 for hydrogenation of MG and EG. Reaction conditions: H_2/feed (mole) =30, WLHSV=2.0 h^{-1}, P=2.5 MPa.

Compared with conversion of MG, the reaction rate of EG is much slower (about 1/3 that of MG conversion rate). We speculated that the C=O in the MG molecule might facilitate the adsorption of MG on Fe_5C_2 as it did on Cu-based-catalyst. These experimental data are well corresponded with our catalytic activity results in Fig. 1 and 3, which indicated that it was much more difficult for the conversion of EG to ethanol on Fe_5C_2.

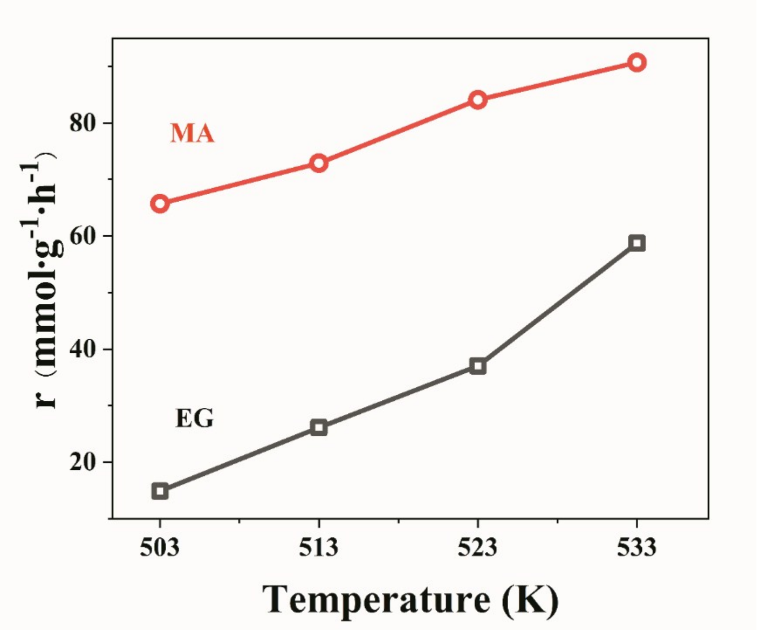


Fig. S7 The reaction rate on CuZnO-SiO_2 for hydrogenation of MG and EG. Reaction conditions: H_2/feed (mole) =30, WLHSV=10.0 h^{-1} for MA and 8.0 h^{-1} for EG. P=2.5 MPa.

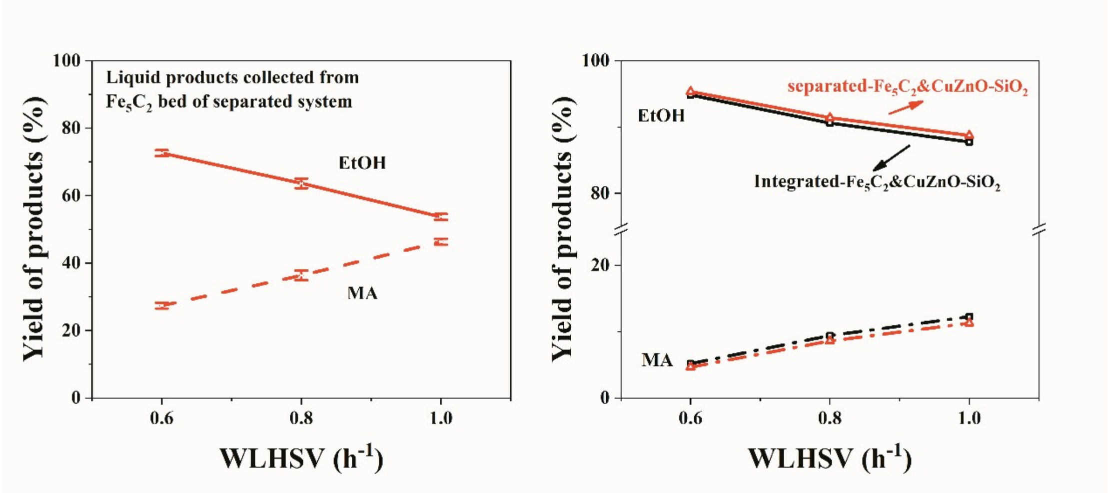


Fig. S8 Yield of products on integrated system and separated system.

Compared with integrated catalysts, the separated- Fe_5C_2&CuZnO-SiO_2 presented a similar overall selectivity to ethanol which indicated that the separated system had a similar effect as integrated system on selective synthesis of ethanol via DMO hydrogenation.

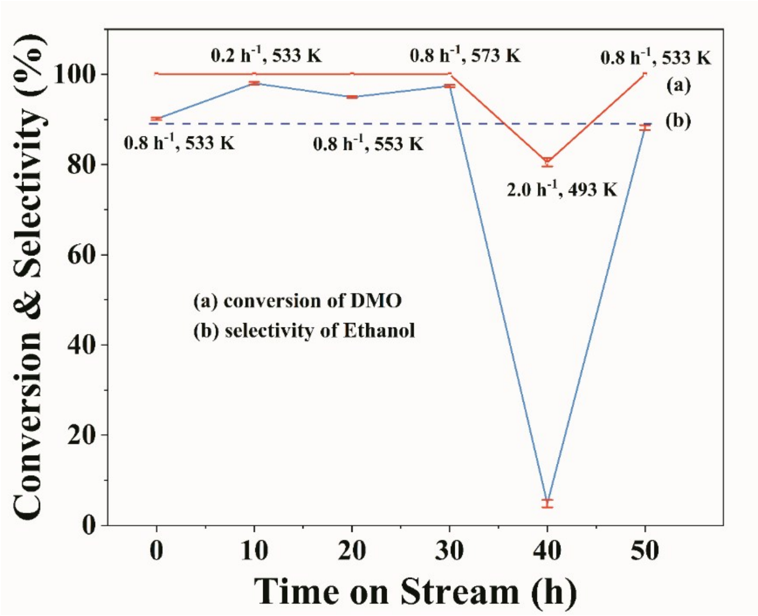


Fig. S9 Stability data of Fe_5C_2&CuZnO-SiO_2 catalyst. Reaction condition: P = 2.5 MPa, H_2/DMO= 180.

References

1. J. He, Y. Zhao, Y. Wang, J. Wang, J. Zheng, H. Zhang, G. Zhou, C. Wang, S. Wang and X. Ma, *Chem Commun (Camb)*, 2017, **53**, 5376-5379.

2. Y. Zhao, B. Shan, Y. Wang, J. Zhou, S. Wang and X. Ma, *Industrial & Engineering Chemistry Research*, 2018, **57**, 4526-4534.

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