

## Electronic Supplementary Information

# Fe<sub>5</sub>C<sub>2</sub> Nanocatalyst for the Preferential Synthesis of Ethanol from Dimethyl Oxalate Hydrogenation

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### 1. Experimental

#### 1.1 Catalyst preparation

Iron oxide was prepared by a simple precipitation method. In a typical preparation, firstly, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Kermel, 98%) were dissolved in distilled water and the resulting solution was heated to 70 °C and an aqueous solution of sodium carbonate (1.0 M) was added to mixed nitrate solution under continuous stirring at a rate of 2–3 ml/min at 70 °C until pH 7.0 was achieved. The resulting precipitate was aged at pH of 7 for 2 h and then filtered and washed with warm distilled water several times for removing excess ions. The precipitate was then dried in air at 110 °C for 12h. The as-prepared support was calcined at 400 °C in air atmosphere for 6 h with a ramp rate of 3 °C/min.

#### 1.2 Catalytic performance test

Activity and selectivity measurements in gas-phase catalytic hydrogenation of dimethyl oxalate (DMO) were carried out in continuous flow mode in a stainless-steel fixed-bed reactor with an internal diameter of 8 mm. About 0.67 g (40-60mesh) sample of the calcined catalyst was first reduced by H<sub>2</sub> in situ (96 mL/min H<sub>2</sub>, 380 °C, 25 atm) for 4 h. Then the reduced samples were carbonized at 25 atm by a methanol-H<sub>2</sub> mixture (ratio of methanol/H<sub>2</sub> = 20:1) for 24 h. The final sample was designed as xK-Fe where x denotes different carbonization temperature. During the reaction, the reactant (10wt.% DMO in methanol solution) was injected from the top of the reactor using a high-pressure pump at a system pressure of 25 atm. Catalytic performance was tested at different temperature varied from 200 to 280 °C and the DMO weight liquid hourly space velocity (WLHSV) varied from 0.2 to 1.0 h<sup>-1</sup>. The reaction products collected in the condenser were analyzed using a gas chromatography (Agilent Micro GC 6820) with an HP-INNOWAX capillary column (Hewlett-Packard Company, 30 m × 0.32 mm × 0.50 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 the change of DMO weight before and after the reaction (equation 1). The

selectivity of methyl glycolate (MG), methyl acetate (MA) and ethanol (EtOH) were calculated using the following equation (equation 2).

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

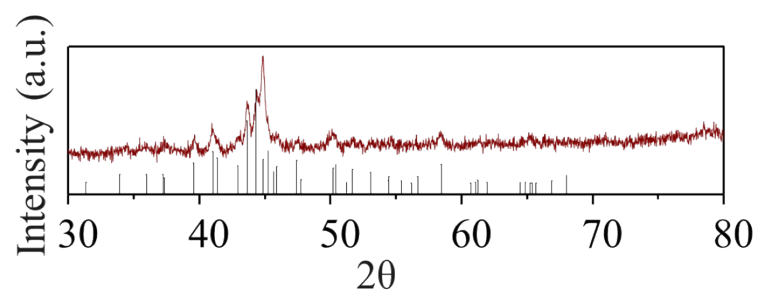
$$\text{Selectivity (\%)} = \frac{\text{mol of MG, MA or EtOH in the product}}{\text{mol of DMO put into the reactor} - \text{mol of DMO in the product}} \times 100\% \quad (2)$$

### 1.3 Catalyst characterization

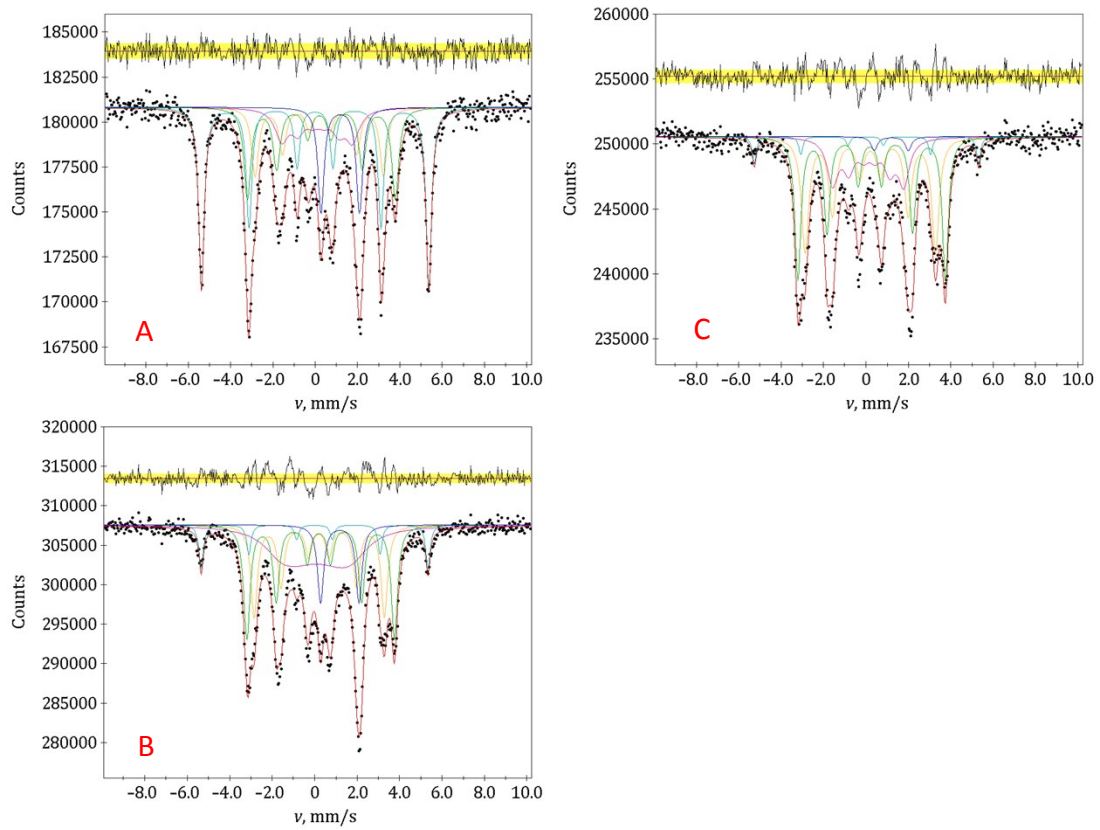
X-ray photoelectron spectroscopy (XRD) measurements were carried out using a Rigaku C/max-2500 diffractometer, employing the graphite-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ) at room temperature. The particle size of iron carbide was calculated with the X-ray-broadening technique using the Scherrer's equation. Data points were acquired by step scanning with a rate of  $8^\circ/\text{min}$  from  $2\theta = 10^\circ$  to  $2\theta = 90^\circ$

Transmission electron microscope (TEM) was conducted using a Philips TECNAI G2 F20 system electron microscope at 100 kV equipped with a field emission gun. The sample powder was dispersed in ethanol under ultrasonic and drops of the suspension were applied on a micro grid, followed by drying in air. About 200 particles were counted to evaluate the particle size distribution.

The room temperature  $^{57}\text{Fe}$  Mössbauer spectra were recorded under various simulated conditions by using a Topologic 500A spectrometer and a proportional counter. A  $^{57}\text{Co}(\text{Rh})$ , moving with a constant acceleration mode, was used as the  $\gamma$ -ray radioactive source. The velocity was calibrated by a standard  $\alpha$ -iron foil. The spectra were fitted with the appropriate superpositions of Lorentzian lines using the MössWinn 3.0i computer program.



**Fig. S1** XRD pattern of 260K-Fe (JCPDS no. 36-1248).



**Fig.S2** Mössbauer spectra of the Carbonized Catalysts: (A) 513K-Fe; (B) 533K-Fe; (C) 553K-Fe.

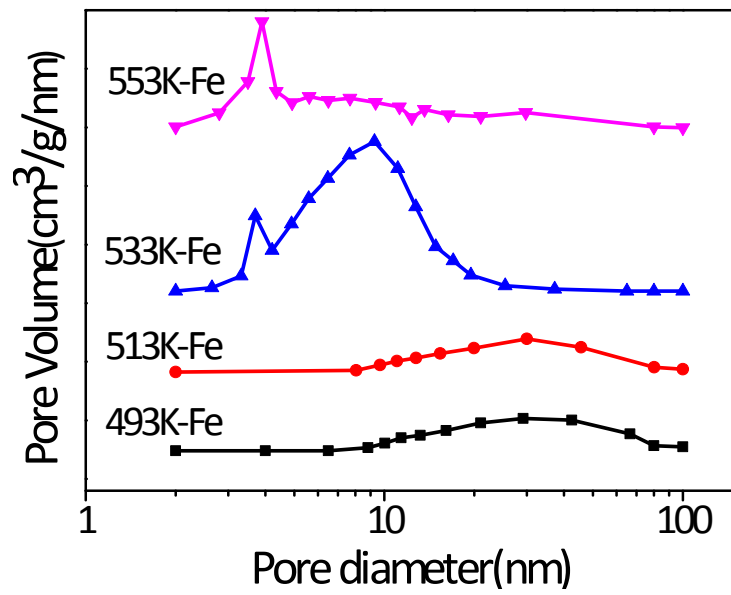


Fig.S3 BJH pore size distribution spectrum of various catalysts carbonized at different temperatures.