

Electronic Supplementary Information

Direct SVUV-PIMS Identification of Unstable Oxygenated Intermediates in Ethanol to Butadiene Reaction

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Catalysts synthesis:

Preparation of the MgO-SiO₂ (4:1 MgO/SiO₂ molar ratio) catalyst was shown as an example. First, 25.6 g of Mg(NO)₃•6H₂O was dissolved in 50 g of ethanol with continuously stirring, and then 1.5 g of silica gel was added into the aforesaid solution. The mixture was stirred at 60 °C until ethanol was totally evaporated and a semitransparent gel was formed. It was then calcined in a muffle furnace at a temperature of 500 °C for 3 h at a rate of 5 °C/min. The same procedure was used to prepare the single component catalyst. All chemicals were purchased from Aladdin and used as received without further purification.

Catalyst characterization:

The basicity of the catalyst was determined by CO₂-temperature-programmed desorption (CO₂-TPD) on a Micromeritics Autochem II 2920 apparatus. 120 mg catalyst was charged in a U-shaped fixed-bed quartz microreactor. First pre-treatment under He at 300 °C for 2 h, then cooled to room temperature, pre-adsorption for 1 h at 10% CO₂/He, switching to He gas for removing physically absorption CO₂ for 1 h, and finally raising the temperature to 700 °C to induce desorption of CO₂.

X-ray diffraction (XRD) was carried out using a Rigaku Ultima IV X-ray diffractometer with Cu K_α radiation at 40kV. The data was recorded from 5° to 90° with a scanning speed of 10°/min.

The morphology of the prepared catalysts was obtained via scanning electron microscope (SEM) (HITACHI S-4700). Transmission electron microscope (TEM) (FEI Tecnai G2 F30) with energy-dispersive X-ray spectroscopy was also employed for imaging and elemental mapping.

Reaction studies:

All experiments were performed in a quartz reactor. 1 g 20-40 mesh catalyst was charged into the quartz reactor, heated under 10 standard cubic centimeter per minute (SCCM) nitrogen flow at 10 °C/min to 400 °C for 1 h on the stream. Then cooled to room temperature.

To protect the analytical system, most of the product gas was removed through a pump. So, the reaction pressure was less than atmospheric pressure. A very small amount of the product gas was ionized by vacuum ultraviolet light in the ionization chamber and entered the time-of-flight mass spectrum. The rest was pumped out of the reaction system. The vacuum ultraviolet was set as 11.0 eV if no extra mention, which was greater than the ionization energy of the main product and intermediate molecules, but less than that of the carrier gas (CO₂ and N₂). Spectra were collected every 60 seconds. The detected substances were determined by molecular weight and ionization energy. Molecular weight was

calculated by time of flight and corrected by certain substances. In the photoionization efficiency (PIE) experiment, when the light energy exceeded the ionization energy (IE) of the object to be detected, the signal strength would have a sharp inflection point. The database was obtained from the Center for NSRL Photoionization Mass Spectrometry.

For converting ethanol, the MgO-SiO₂ catalyst was employed. After the catalyst was pretreated, ethanol was introduced into the reactor by bubbling at room temperature. The carrier gas was nitrogen, at a flow rate of 10 SCCM. After the bubble was stabilized, the temperature was set at a constant temperature. After the system was stable, the mass spectrum signal was recorded.

CO₂ gas was employed to poison the active sites of the MgO-SiO₂ catalyst. An ethanol conversion experiment was carried out under the above conditions at a constant temperature. When stabilization, carrier gas was changed from N₂ to CO₂ with the same flow rate (10 SCCM). After lasting more than 30 minutes, CO₂ was replaced by N₂. Data were recorded throughout the whole proceeding.

When acetaldehyde was feeding, bubbling was in an ice bath. The carrier gas was nitrogen, at a flow rate of 10 SCCM. After the bubble was stabilized, the temperature was programmed to rise at a rate of 5 °C/min from 50 °C. The MgO-SiO₂ catalyst, single component MgO, and SiO₂ were employed as a contrast.

Photoionization efficiency (PIE) experiment was carried out as follows. After the MgO-SiO₂ catalyst was pretreated according to the above method, the reaction temperature was maintained at a constant temperature. Acetaldehyde was introduced into the reactor by bubbling in an ice bath. The carrier gas was nitrogen, at a flow rate of 10 SCCM. After the bubble and temperature were stabilized, the energy of SVUV was set to increase at a certain step (0.01eV) per minute from 9.58 eV to 9.78 eV.

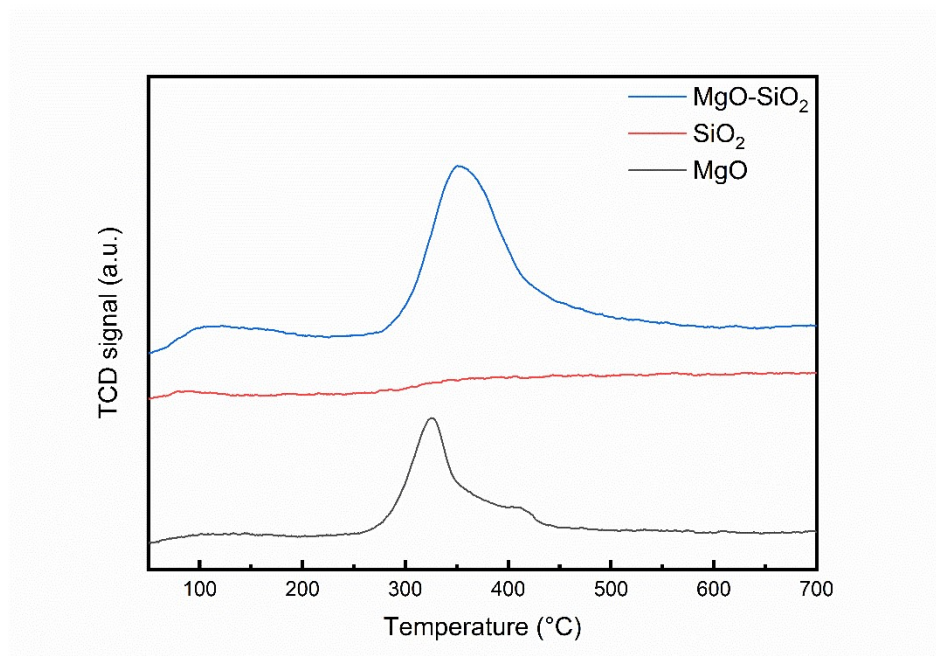


Figure S1. CO₂-TPD profiles for different catalysts.

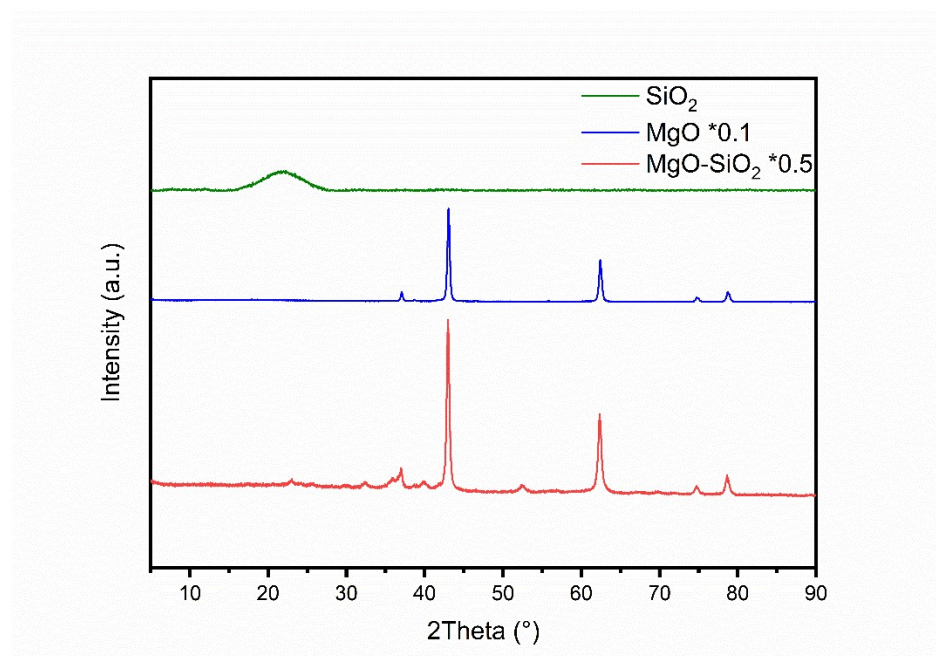


Figure S2. XRD patterns of different catalysts.

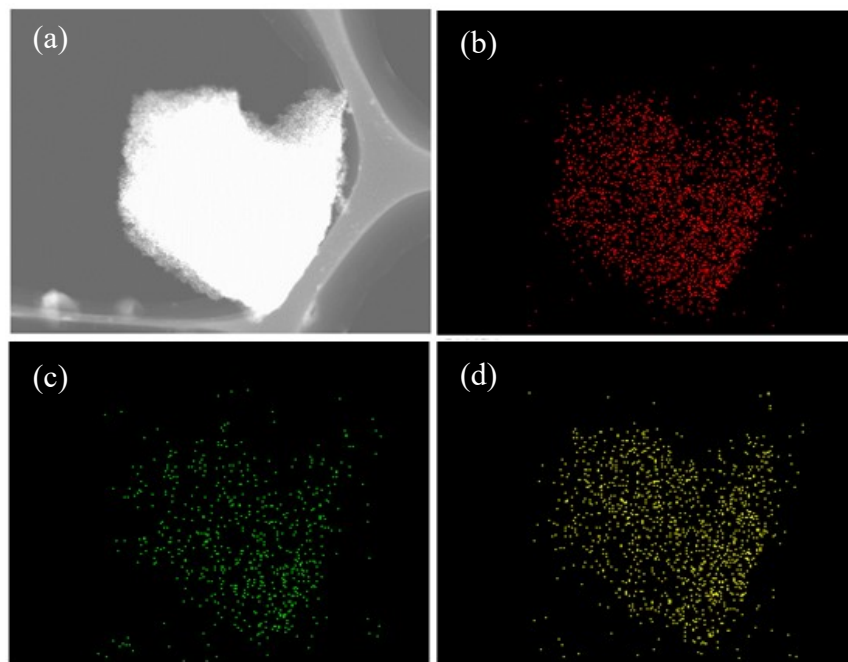


Figure S3. Images of MgO-SiO₂ (3:7 MgO/SiO₂ molar ratio) catalyst: (a) TEM; (b) EDX mapping -Si channel; (c) EDX mapping -Mg channel; (d) EDX mapping -O channel.



Figure S4. SEM image of MgO-SiO₂ catalyst.

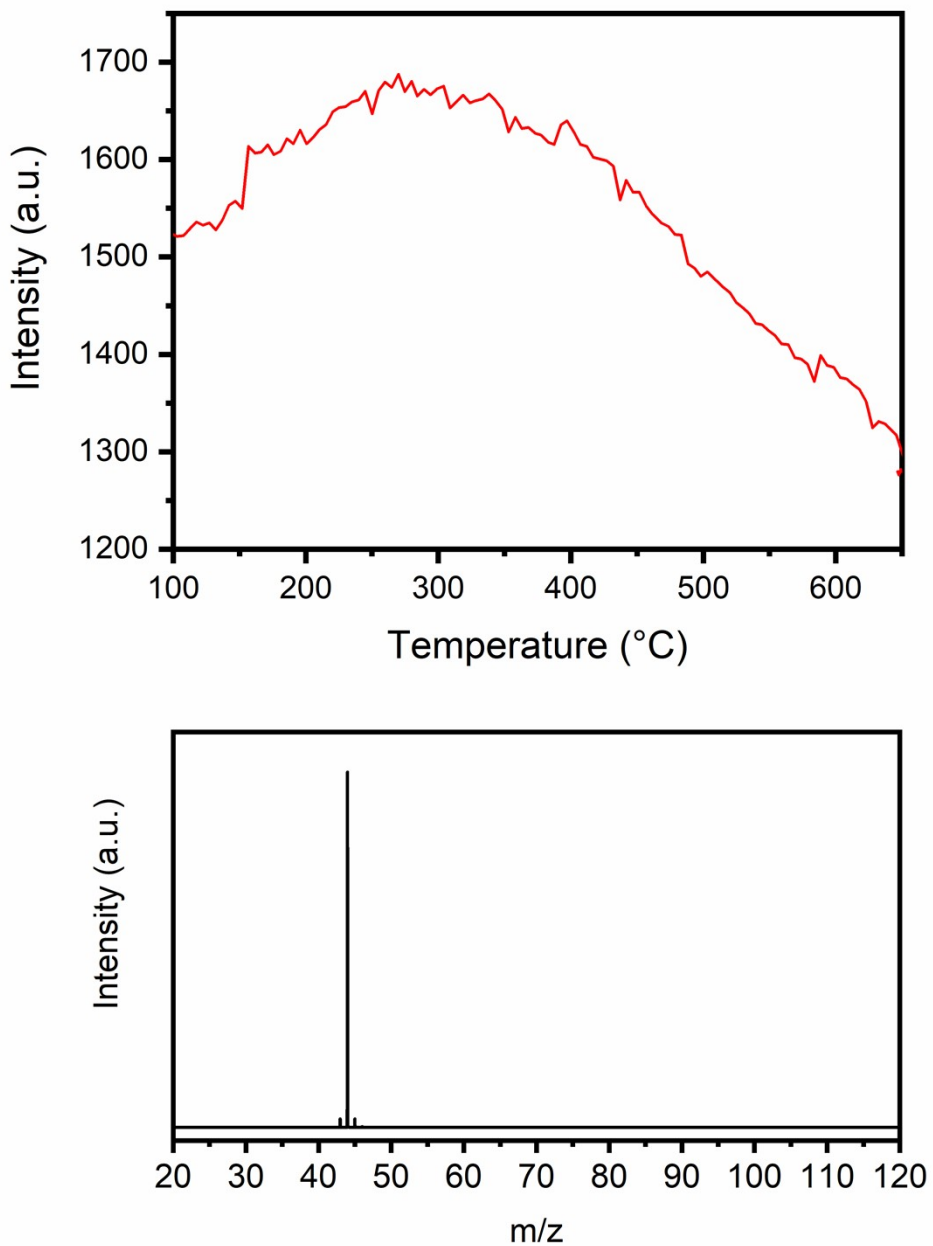


Figure S5. (a): Temperature-programmed reaction profiles of converting acetaldehyde in the absence of catalysts. Reaction conditions: bubbling in an ice bath, 10 SCCM N₂ as the carrier gas, a heating rate of 10 °C/min. (b): Single mass spectrum at 450°C in the absence of catalysts. Reaction conditions: bubbling at ice bath, 10 SCCM N₂ as carrier gas.

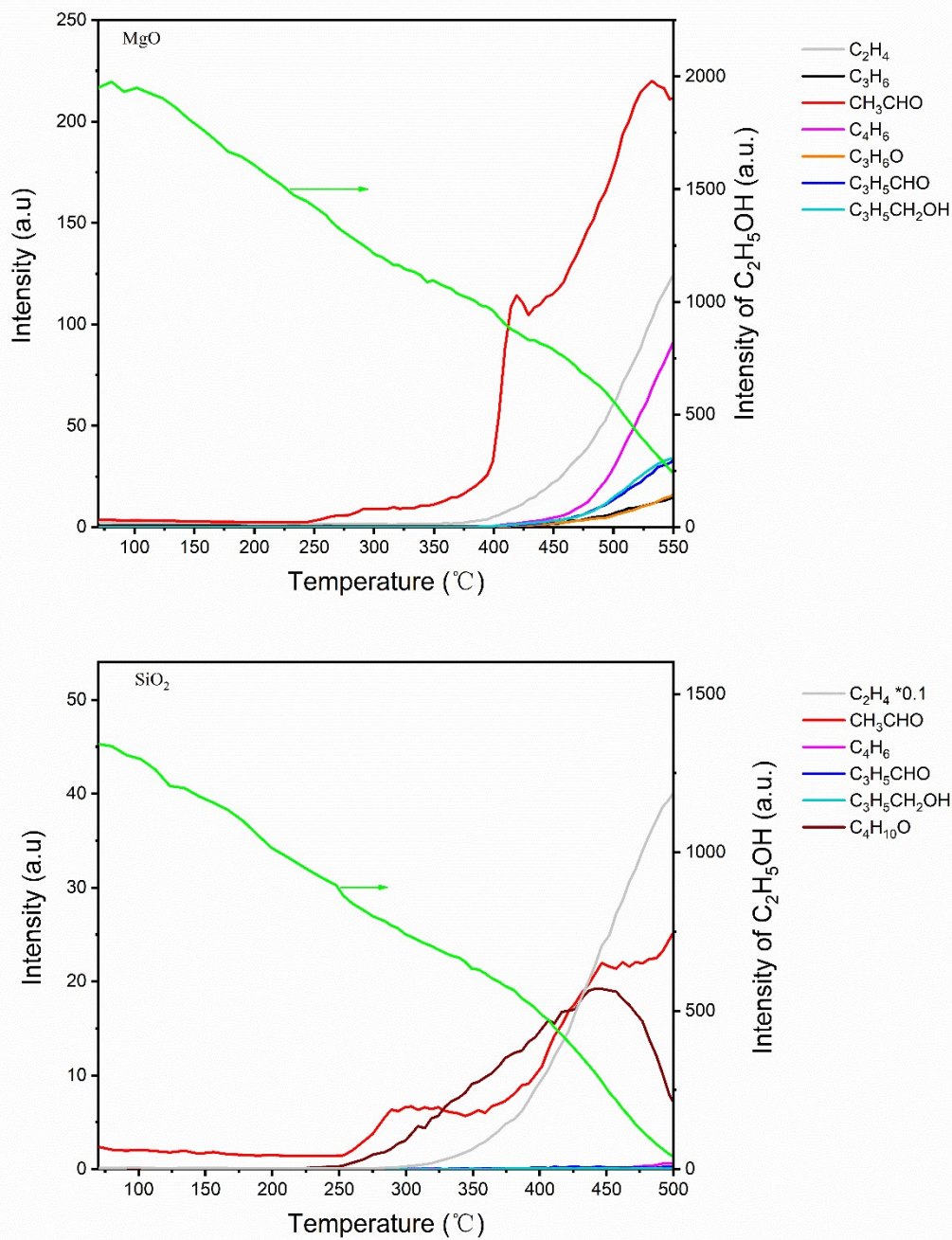
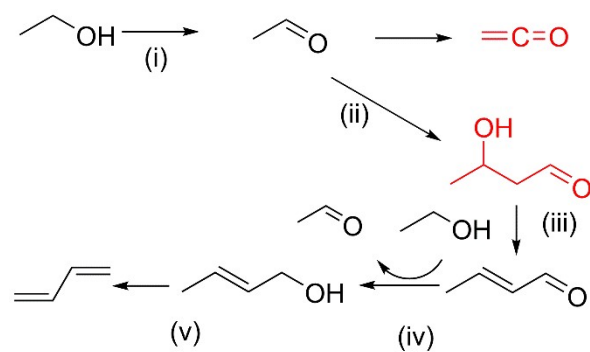


Figure S6. Temperature-programmed reaction profiles of converting ethanol over MgO and SiO₂ catalysts. Reaction conditions: bubbling at room temperature, 10 SCCM N₂ as a carrier gas, a heating rate of 10 °C/min.

Table S1. Main intermediates and products of converting acetaldehyde over MgO-SiO₂ catalyst. Reaction conditions: 450 °C, bubbling in an ice bath, 10 SCCM N₂ as carrier gas.

Formula	Molecular weight	
	Calculated value	Theoretical value
C₂H₄	28.029	28.031
C₂H₆O	46.039	46.041
C₃H₆O	58.035	58.041
C₂H₄O₂	60.006	60.020
C₄H₆O	70.041	70.041
C₄H₈O	72.058	72.056
C₆H₆	78.049	78.046
C₄H₈O₂	88.076	88.052
C₇H₈	92.075	92.062
C₆H₈O	96.079	96.057
C₈H₁₄	110.091	110.109
C₉H₁₂	120.091	120.093
C₈H₁₀O	122.096	122.073

Scheme S1: The generally accepted reaction mechanism of the ethanol to butadiene



conversion and ketene intermediate.