Supporting Information for

Reaction kinetics analysis of ethanol dehydrogenation catalyzed by MgO-SiO₂

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1. Butadiene Production



Figure S1. Butadiene production over 0.08% MgO/SBA-15. (a) Linearized data used to obtain the initial selectivity, (b) Selectivity to butadiene at 100% ethanol conversion, showing extrapolation to zero-time. Reaction conditions: 0.5g of catalyst, 698 K, WHSV = 0.017 hr⁻¹, ethanol partial pressure 2.27 kPa, and total pressure 101 kPa.

2. Catalyst Deactivation

The production rates of ethylene and acetaldehyde exhibited continuous deactivation with respect to the time on stream as shown in Figures S2 and S3. Time zero in Figure S3 corresponds to the completion of the 8 hours aging process described in Section 2.2 of the main text. We hypothesize that this deactivation is due to blocking of the active sites on the surface of catalyst coupled with eventual blocking of the catalyst pores.



Figure S2. Catalyst deactivation during acetaldehyde (\blacktriangle) and ethylene (\bullet) production. Reaction conditions: 0.0067g catalyst, WHSV 0.16-0.55 min⁻¹, ethanol partial pressure 3.92-5.25 kPa, 723 K, total pressure 101 kPa.



Figure S3. Catalyst deactivation during acetaldehyde (\blacktriangle) and ethylene (\bullet) production. Reaction conditions: 0.0067g catalyst, WHSV 0.41-0.55 min⁻¹, ethanol partial pressure 3.93-5.25 kPa, 723 K, total pressure 101 kPa.

3. Deactivation Correction

The observed ethylene and acetaldehyde production rates were corrected for deactivation. The data shown in Figure S4 were fit by assuming two parallel first-order deactivation processes. We hypothesize that these correspond to deposition of carbon on the catalyst surface and eventual blocking of the catalyst pores. Attempts to fit the data to either a single first-order or second-order deactivation process were unsuccessful.



Figure S4. Correction of the deactivation for acetaldehyde (a) and ethylene (b) production rates (red \blacktriangle is the observed rate, blue line is the predicted rate, and black \blacktriangle is the corrected rate) Reaction conditions: 0.0067g catalyst, WHSV 0.41-0.55 min⁻¹, ethanol partial pressure 3.93 kPa, 723 K, total pressure 101 kPa.

4. Catalyst Characterization Data



Figure S5. Pore size distributions for 0.08 wt% MgO/SBA-15 (\bullet), calcined SBA-15 (\blacktriangle), and non-calcined SBA-15 (\bullet) catalysts based on the adsorption branch of N₂ adsorption isotherms collected at 77 K (see Section 2.3 in the main text).



Figure S6. X-ray diffractogram for 0.08% MgO/SBA-15. No reflections corresponding to MgO were observed.

5. Operando FTIR spectroscopy

To identify the surface species during ethanol conversion under reaction conditions, we performed the reaction at elevated temperatures by feeding Ar/ethanol to the Harrick Praying Mantis environmental chamber and collecting spectra referenced to the clean surface of MgO/SBA-15. Prior to the reaction, the catalyst surface was pretreated at 673 K, 623 K and 573 K under dry Ar flow for 2 hours at each temperature. Several single beam spectra were collected at each temperature. During the reaction 50 SCCM flow of Ar/ethanol stream was generated by pass Ar through a gas washing bottle filled with absolute ethanol at 296 K, and this stream was fed to the environmental chamber. The temperature was then heated stepwise to 573 K, 623 K and 673 K and held for several hours until a steady state condition was confirmed by comparison of two spectra recorded at least one hour apart.

Figure S7 shows a summary of the DRIFTS spectra collected at steady state during reaction of the MgO/SBA-15 with a continuous flow of Ar/ethanol at the indicated temperatures. The spectra, referenced to the clean surface at each temperature, show interaction of ethanol with the silanol groups of SBA-15, resulting in a strong negative-going band at 3745 cm⁻¹. The \Box (CH) bands of ethanol, which are stronger in the presence of gas phase ethanol than in the stepwise temperature programmed desorption spectra of Figure 7 (main text), make identification of ethoxide species more difficult, even at the highest reaction temperature of 673 K. However, the presence of a weak peak at 3680 cm⁻¹, shown in the inset at the frequency observed by Taifan, *et al.*,¹ and assigned to the hydroxyl group on magnesium silicates, suggests that the model catalyst prepared here may have sites similar to those present on MgO-SiO₂ catalysts synthesized by wet kneading. This peak is not present on pure MgO or bare SBA-15.

The spectra shown in Figure S7B confirm the production of acetaldehyde which desorbs and is observed in the gas phase, with the P, Q, and R branches centered at 1775, 1750, and 1725 cm⁻¹, whose relative intensities suggest that the molecules are rotationally hot. The bands between 1350 and 1500 cm⁻¹ have contributions from both ethanol and acetaldehyde. The production of acetaldehyde indicates that the operando measurements reveal catalytic behavior consistent with that of the catalyst under our flow reactor conditions where detailed kinetic information has been obtained. Unfortunately, further experiments were not possible at this time due to closing of the laboratory during the COVID-19 pandemic.



Figure S7. *operando* DRIFT spectra during continuous feed of Ar/ethanol to the environmental chamber at a) 573 K, b) 623 K and c) 673 K, referenced to the clean MgO/SBA-15 surface at the same temperature. A) Hydroxyl and \Box (CH) stretching regions showing the interaction of ethanol with silanol groups, and a weak positive-going peak at 3680 cm⁻¹ (shown in the inset) that may correspond to formation of hydroxyls on magnesium-silicates under reaction conditions. B) Spectra in the 1350 – 1800 cm⁻¹ range are dominated by gas phase acetaldehyde and molecularly adsorbed ethanol.

6. References:

1. Taifan, W. E. & Baltrusaitis, J. In Situ Spectroscopic Insights on the Molecular Structure of the MgO/SiO2 Catalytic Active Sites during Ethanol Conversion to 1,3-Butadiene. *J. Phys. Chem. C* 122, 20894–20906 (2018).