Supplementary information for

Selective Ethylbenzene Dehydrogenation to Styrene at Lewis Acid-Base Site Pairs on Zirconia Surfaces

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1. Results and discussions

1.1. De Donder relations for catalytic sequences

Ethylbenzene dehydrogenation on Zr-O LAB pairs involves a sequence of elementary steps initiating with the molecular adsorption of gaseous molecules onto an LAB site pair. Ethylbenzene then undergoes two H-abstraction events and ultimately desorbs as styrene and dihydrogen to preserve reaction stoichiometry. Because each elementary step of this sequence is reversible, the whole sequence is also reversible, and the reversed sequence reflects styrene hydrogenation pathway. A priori, each elementary step occurs in both forward and reverse direction with rates that must also obey the law of mass action in each direction. The difference between forward $\vec{r}_i$ and reverse $\overleftarrow{r}_i$ rates for elementary step reflects the net rate r_i .

$$r_i = \vec{r}_i - \overleftarrow{r}_i \quad \text{(S1)}$$

According to De Donder relations[1], the ratio of forward and reverse rates of an elementary step is related to the chemical affinities (A_i) for this step, defined as $A_i = -(\frac{\partial G}{\partial \xi_i})_{T,P}$ where G denotes Gibbs free energy and ξ is the extent of reaction i:

$$\frac{\vec{r}_i}{\overleftarrow{r}_i} = e^{\frac{A_i}{RT}} \quad \text{(S2)}$$

For elementary step chemical affinity is defined as

$$A_i = RT \cdot ln(K_i \cdot \prod_i a_j^{-v_j}) \quad \text{(S3)}$$

where a_j and v_j reflect the thermodynamic activity and molecularity of the species j involved in step i, (v_j is positive for products and negative for reactants). The ratio of forward ($\vec{k}_i$) and reverse ($\overleftarrow{k}_i$) kinetic constants for any elementary step reflects equilibrium constant of this step,

$$\frac{\vec{k}_i}{\overleftarrow{k}_i} = K_i \quad \text{(S4)}$$

For any sequence of elementary steps, including catalytic reaction on surfaces, the net rate of overall reaction is related to the rates of each elementary step as follows:

$$r = \frac{r_i}{\sigma_i} \quad \text{(S5)}$$

here σ_i is the stoichiometric number for Step i, defined as the number of times it must occur to complete catalytic sequence. The overall forward and reverse rates are related as follows[2–4]:

$$\frac{\vec{r}}{\overleftarrow{r}} = \frac{\prod_i \vec{r}_i}{\prod_i \overleftarrow{r}_i} = \prod_i e^{\frac{A_i}{RT}} = e^{\frac{\sum_i A_i}{RT}} = e^{\frac{A}{\bar{\sigma} RT}} \quad \text{(S6)}$$

Where $A = \sum_i \sigma_i A_i$ represents chemical affinity of overall catalytic sequence and $\bar{\sigma} = \frac{\sum_i \sigma_i A_i}{\sum_i A_i}$ is affinity-averaged stoichiometric number for the overall reaction. Because each elementary step occurs in both forward and reverse directions, the whole catalytic sequence must proceed in both forward and reverse direction with respective rates related by Equation S2 at a given set of reaction conditions defined by temperature, and partial pressures of each component. In fact, the sign of chemical affinity defines the direction of the process at a given set of reaction conditions:

if overall chemical affinity (reflecting decreasing Gibbs free energy as forward reaction proceeds), then forward rate is higher than reverse rate.

Importantly, at a given set of reaction conditions the ratio of kinetic constants for the forward and reverse reactions is related to equilibrium constant (K) for the overall reaction by[2]:

$$\frac{\vec{k}}{\overleftarrow{k}} = K^{\frac{1}{\sigma}} \qquad \text{(S7)}$$

If all elementary steps in catalytic sequence have stoichiometric numbers of unity, Equation S7 becomes mathematically indistinguishable from Equation 10 derived for a single elementary step. However, Equation S7 can only be applied for a given set of reaction conditions, while Equation S4 is valid under any conditions because elementary reactions must always obey the law of mass action.

For catalytic reaction sequences on surfaces the rates of elementary steps which involve surface species are determined not only by partial pressures of reactants in the gas phase, but also by surface coverages if reactants are surface species. Combining equations 9 and 12, for catalytic sequence[2–4]::

$$\frac{\vec{r}}{\overleftarrow{r}} = \frac{\prod_i \vec{r}_i}{\prod_i \overleftarrow{r}_i} = \frac{\prod_i (\vec{k}_i)}{\prod_i (\overleftarrow{k}_i)} \prod_i \prod_j (a_j^{-v_j}) \text{ (S8)}$$

where some (a_j) terms correspond to activity of gaseous species and others reflect activity of surface species. For gaseous species activity can be expressed as their partial pressures. Under the given set of reaction conditions activities of all surface species are identical. Because sum of all elementary steps must represent a stoichiometric equation each intermediate appearing as a product in one elementary step is a reactant in other elementary step, and therefore these terms cancel in overall Equation 14 leading to:

$$\frac{\vec{r}}{\overleftarrow{r}} = \frac{\prod_i (\vec{k}_i)}{\prod_i (\overleftarrow{k}_i)} \prod_r a_r^{-v_r} = K \cdot \frac{(C_8H_{10})}{(C_8H_8)\cdot(H_2)} \text{ (S9)}$$

where a_r and v_r correspond to activity and molecularity of gas-phase reactants and products of overall reaction (C_8H_{10}, C_8H_8 and H_2 for ethylbenzene dehydrogenation). Importantly, this is applicable only under given set of reaction conditions where surface coverages of all species are identical, and therefore corresponding terms cancel each other. However, under specific conditions, relations between forward and reverse reaction rates which are mathematically identical to Equation S9 can be observed even when these rates are measured under different reaction conditions. This would require that both forward and reverse reaction sequences have the same kinetically-relevant elementary step (m) with surface intermediate(s) s participating in this step as reactant or product, and all other steps are quasi-equilibrated, then ratio of forward to reverse rates can be expressed as follows:

$$\frac{\vec{r}}{\overleftarrow{r}} = \frac{\prod_i \vec{r}_i}{\prod_i \overleftarrow{r}_i} = \prod_{i \neq m} K_i \cdot \frac{\vec{k}_m}{\overleftarrow{k}_m} \cdot \prod_s (a_s^{-v_s}) \cdot \prod_r a_r^{-v_r} = K \cdot \frac{(C_8H_{10})}{(C_8H_8)\cdot(H_2)} \cdot \prod_s (a_s^{-v_s})$$

(S10)

where a_s and v_s correspond to activity of surface intermediates participating in rate-limiting step m. If activity of surface intermediates involved in the kinetically-relevant step is identical under different reaction conditions, then Equation S10 transforms to one mathematically equal to Equation 9, which is true for reactions occurring on bare catalytic surfaces. The only surface

intermediates which have identical activity at different reaction conditions are bare sites, which require that surfaces remain essentially free from adsorbed reactants, products or intermediates under wide range of conditions where both forward and reverse reaction rates are measured. Additionally, forward and reverse catalytic sequences must have kinetically-relevant step mediated by identical transition state.
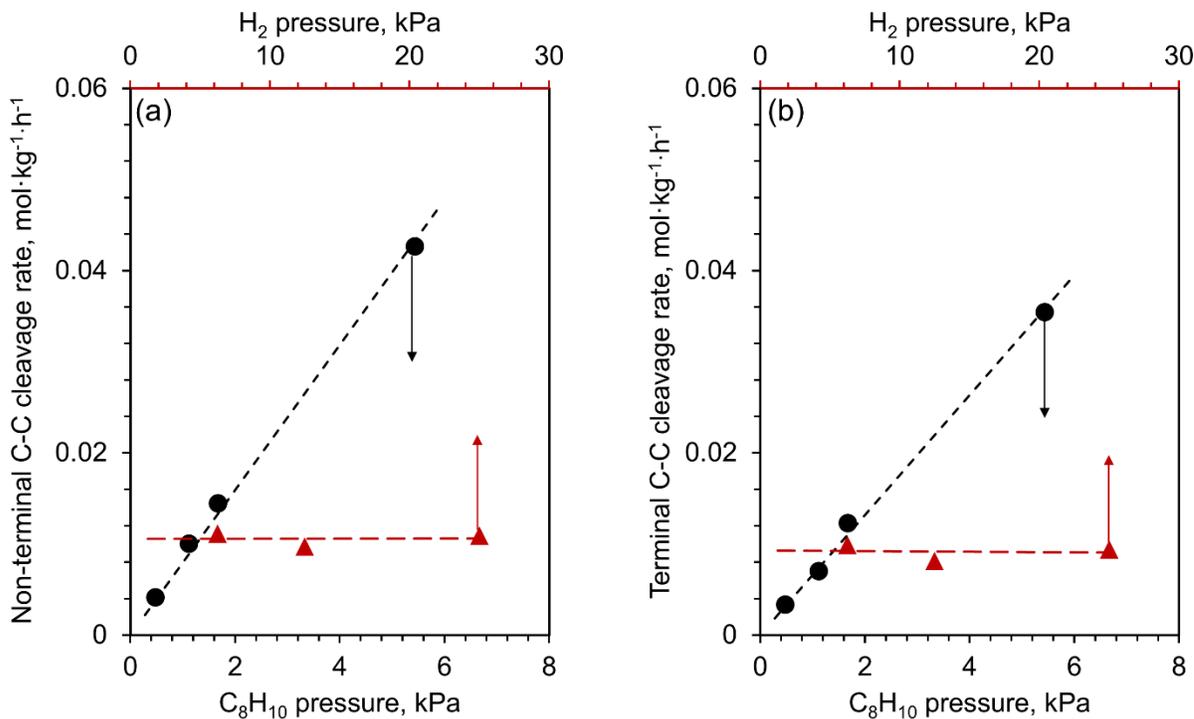
1.2. Rates of terminal and non-terminal C-C cleavage

Figure S1. a) Rates (per mass) of non-terminal C-C cleavage calculated as rates of benzene formation (a) and terminal C-C cleavage calculated as rates of toluene formation (b) on DME-treated (at 723 K, 1.5 kPa DME, 0.9 ks) m-ZrO_2 as a function of C_8H_{10} pressure (bottom axis, black; 13.5 kPa H_2) and H_2 pressure (top axis, red; 1.3 kPa C_8H_{10}) at 723 K. Dashed lines are to guide the eye.
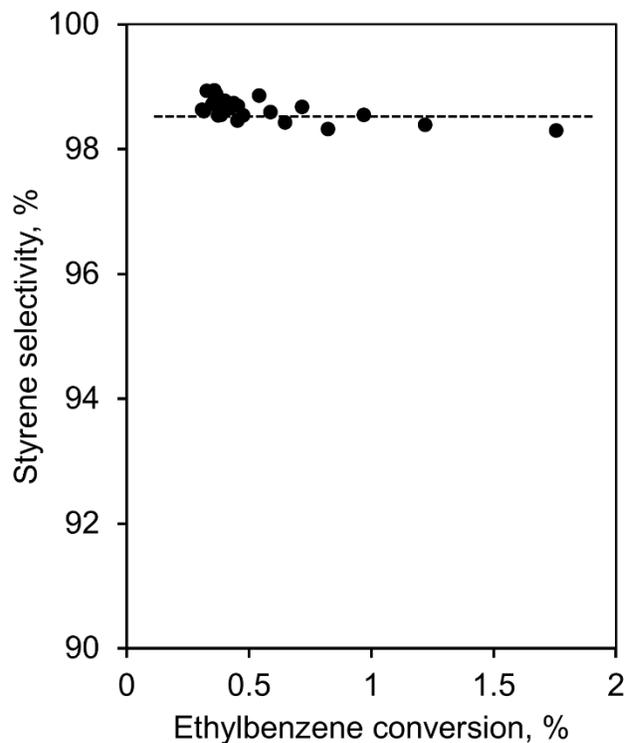
Figure S2. Selectivity to styrene at different ethylbenzene conversions on DME-treated m-ZrO$_2$, 1.8 kPa C$_8$H$_{10}$, 12 kPa H$_2$, 723 K.
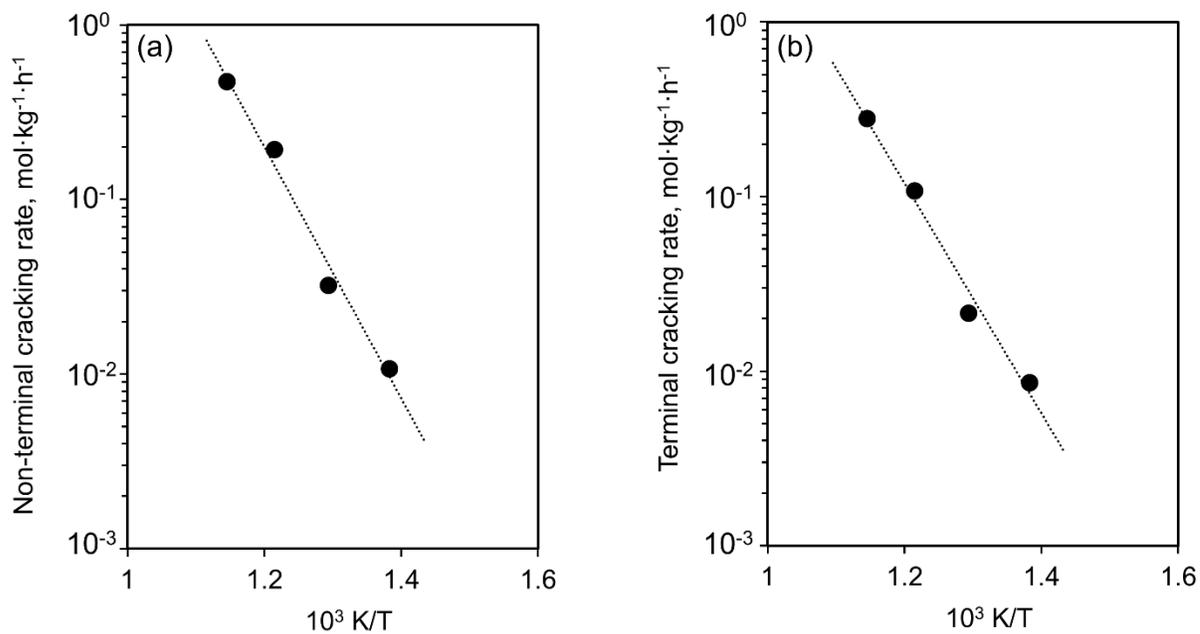

Figure S3. First-order rate constants for non-terminal (a) and terminal (b) C-C cleavage on DME-treated (723 K) m-ZrO$_2$ plotted in Arrhenius-type form. Dashed lines from exponential regression.

1.3. Estimations of H₂O titrants concentrations in the inlet streams

In experiments 20 mg of m-ZrO$_2$ catalyst were used. Given BET surface area of 130 m^2·g^{-1} and site density of 0.56 sites·nm^{-2}, this corresponds to 2.4·10^{-6} mol of LAB pairs sites. For DME treated samples the extrapolation of linear decay for as-supplied ethylbenzene shows that catalyst would be fully deactivated after 1.7 ks and for purified EtBz around 5.9 ks (Figure S4). Total gas flow of 50 ml·min^{-1} (298 K, 101.325 kPa) correspond to 3.4·10^{-2} mol·ks^{-1}. For feed with as-supplied ethylbenzene titrants levels are 2.4·10^{-6}/(3.4·10^{-2} 1.5)= 40 ppm
For dried ethylbenzene levels are 2.4·10^{-6}/(3.4·10^{-2} 5.9)=10 ppm.

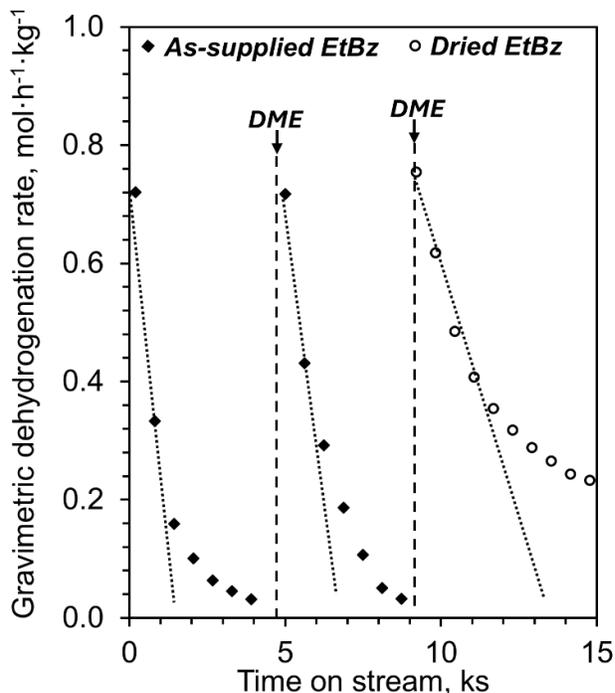### 1.4. Effect of stream purities on deactivation of DME-treated *m-*ZrO$_2$.

Figure S4. a) Ethylbenzene dehydrogenation rates on DME-treated (723 K, 1.5 kPa, 0.9 ks) *m*-ZrO$_2$ at 723 K (1 kPa C$_8$H$_{10}$, 12.5 kPa H$_2$) as a function of time on stream using as-supplied (filled diamonds) and purified (open circles) ethylbenzene reactants. Black arrow and the dashed line indicate DME treatment for catalyst reactivation, dotted lines represent linear fit during the initial deactivation period
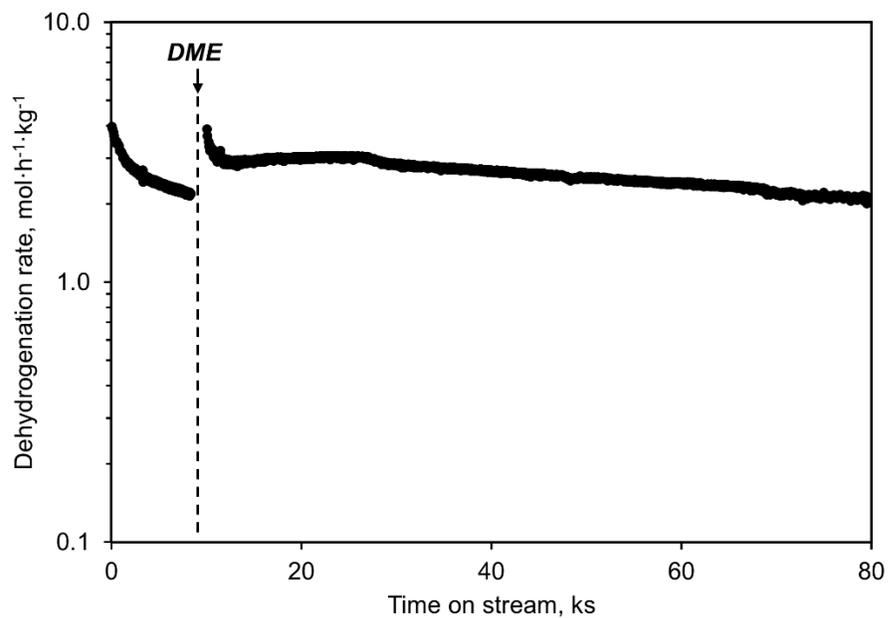
Figure S5. Ethylbenzene dehydrogenation rates on DME-treated (723 K, 1.5 kPa DME, 0.9 ks) m-ZrO$_2$ at 773 K (1.5 kPa C$_8$H$_{10}$, 12 kPa H$_2$, balance He) using rigorously purified ethylbenzene reactants. Black arrow and the dashed line indicate DME treatment for catalyst reactivation.

1.5. Space velocity effects during ethylbenzene dehydrogenation on *m*-ZrO₂.
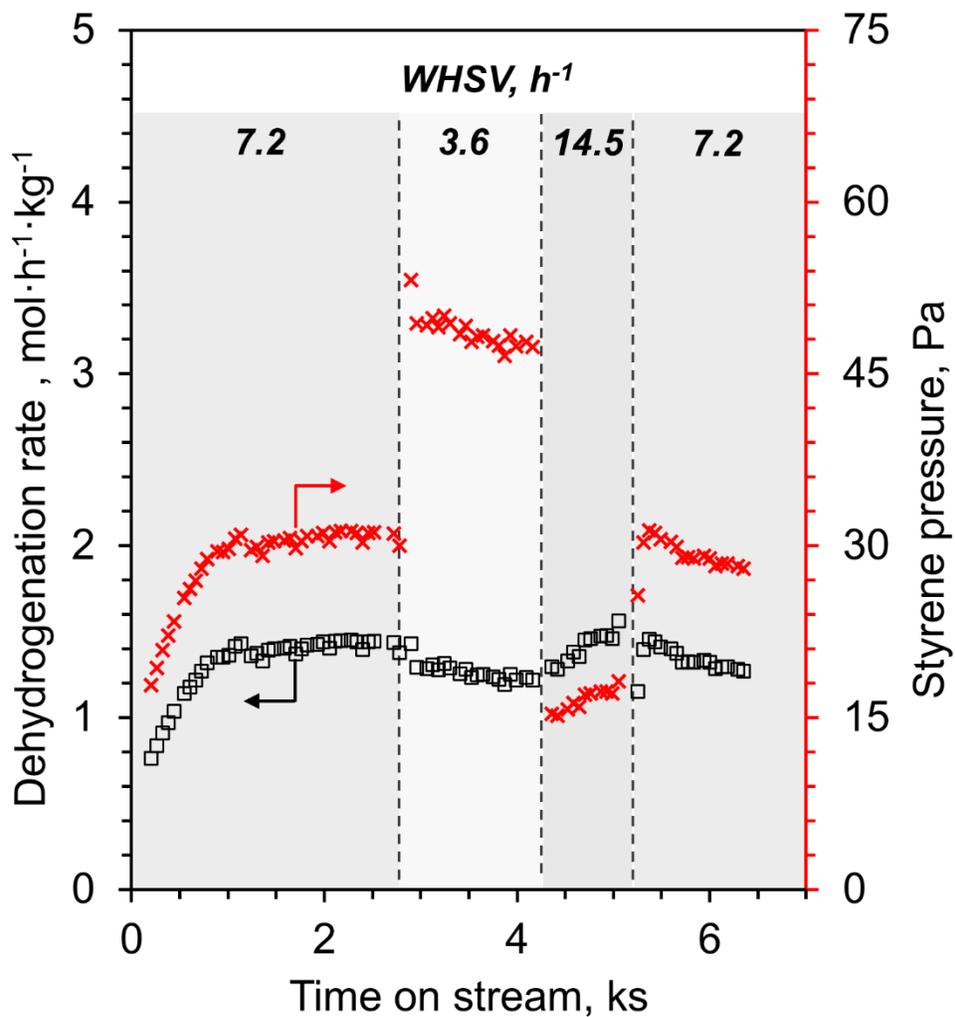

Figure S6. Ethylbenzene dehydrogenation rates (open squares, black, left axis) and averaged styrene pressures (crosses, red, right axis) on He-treated (773 K, 1.8 ks, open squares) *m*-ZrO₂ plotted versus time on stream at different space velocities indicated on top of the graph. Vertical dashed lines indicate change of hourly space velocities.

1.6. Comparison of ethylbenzene dehydrogenation rates with reported catalyst.

Table S1. Reported ethylbenzene gravimetric dehydrogenation rates, styrene selectivities and reaction conditions on various catalysts (alkali-promoted Fe-based catalysts, Fe-containing zeolites, Ca, Sr and Ba zirconates, activated carbon materials, and dispersed MoO_3 domains) compared to expected dehydrogenation rates and selectivities on DME-treated m-ZrO_2 using the rate relations shown in Equation 1 and Figures 1 and 2.

| Catalyst	C_8H_{10} pressure, kPa	Temperature (K)	Dehydrogenation rates, mol kg^{-1} h^{-1}	C_8H_8 selectivity, %	Dehydrogenation rates on m-ZrO_2[a], mol kg^{-1} h^{-1}	C_8H_8 selectivity on m-ZrO_2[b], %
FeO$_x$/K[5]	7	873	14.9	96	125	96
FeO$_x$/Al[6]	9	803	0.6	94	36	97
FeO$_x$/K[7]	19	912	2.6	89	671	95
FeO$_x$/K[7]	20	867	2.2	94	314	96
FeO$_x$/K/Ce[8]	12	893	25	93	298	95
FeO$_x$/K/Ce[9]	13	883	9.3	95	272	95
FeO$_x$/K/Ce[10]	12	893	38	89	298	95
FeO$_x$/K/Ce/Mo[10]			36	93		
C[11]	3	773	3	97.3	5.3	98
CaZrO$_3$[12]	6	848	1.08	-	66	96
SrZrO$_3$[12]			3.6	-		
BaZrO$_3$[12]			36	97		
FeZSM-5[13]	9	803	0.35	100	36	97
FeMCM-41[13]			0.18	52		
MoO$_3$/ZrO$_2$[14]	90	853	3.24	97.5	1043	96

[a] from extrapolation of measured rates in Figures 1 and 2 to the conditions of those reported for each catalyst in previous studies using the functional form of Equation 1

[b] from extrapolation of measured selectivities in Figures 3 to the conditions of those reported for each catalyst in previous studies
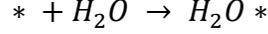
1.7. Plug-flow reactor model

For the kinetic model in plug-flow reactor the following chemical reactions were considered:

1. Ethylbenzene (EtBz) dehydrogenation to styrene (STY) and H_2 on titrant-free LAB sites (denoted as *)

$$* + EtBz \rightarrow STY + H_2 + *$$
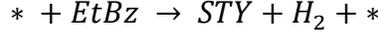
2. Adsorption of H_2O on free LAB sites forming H_2O-titrated LAB sites ($H_2O *$) which are catalytically inactive

$$* + H_2O \rightarrow H_2O *$$

3. Reaction of H_2O-titrated LAB site with cleaning agent (CA, nature is discussed *vide infra*) leading to titrant-free site and product(s) of reaction (X) which are irrelevant for any further transformations

$$H_2O * + CA \rightarrow * + X$$

The rates of each corresponding reaction can be expressed as follows:

$$r_{dehyd} = k_{dehyd} \cdot [EtBz] \cdot \theta \cdot n_s \qquad \text{(S11)}$$

$$r_{titr} = k_{titr} \cdot [H_2O] \cdot \theta \cdot n_s \qquad \text{(S12)}$$

$$r_{clean} = k_{clean} \cdot [EtBz] \cdot (1 - \theta) \cdot n_s \qquad \text{(S13)}$$

Where r_i are rates of corresponding reaction per mass of catalyst (mol^{-1}·kg$_{cat}^{-1}$·s^{-1}), k_i are rate constants per catalytic site (kg$_{cat}$·mol sites^{-1}·s^{-1}), $[X]_{x=EtBz \ or \ H_2O}$ is concentration in gas phase (mol·l^{-1}), n_s is density of Zr-O LAB pairs acting as catalytic sites in the material (mol sites·kg^{-1}) and θ corresponds to the fraction of titrant-free sites.

As it was demonstrated that cleaning agent is ethylbenzene, equation 11 can be rewritten as

$$r_{clean} = k_{clean} \cdot [EtBz] \cdot (1 - \theta) \cdot n_s \qquad \text{(S14)}$$

The following assumptions were made:

1) Chemical reactions do not change gas flow velocity or catalyst density: u and ρ are constants and do not depend on time or position along the bed of catalyst.

2) Ethylbenzene is not significantly depleted along the reactor (evidenced by low conversion <3 %):

$$r_{dehyd} = k_{dehyd} \cdot [EtBz] \cdot \theta \cdot n_s \approx k_{dehyd} \cdot EtBz_0 \cdot \theta \cdot n_s \qquad \text{(S15)}$$

3) Ethylbenzene consumption by reaction 3 is negligible.

Material balance equations are as follows:

$$\frac{\partial [EtBz]}{\partial t} = -u \frac{\partial [EtBz]}{\partial x} - k_{dehyd} \cdot EtBz_0 \cdot \theta \cdot n_s \cdot \rho \qquad \text{(S16)}$$

$$\frac{\partial [H_2O]}{\partial t} = -u \frac{\partial [H_2O]}{\partial x} - k_{titr} \cdot [H_2O] \cdot \theta \cdot n_s \cdot \rho \qquad \text{(S17)}$$

$$n_s \frac{\partial [\theta]}{\partial t} = \rho (k_{clean} \cdot EtBz_0 \cdot (1 - \theta) \cdot n_s - k_{titr} \cdot [H_2O] \cdot \theta \cdot n_s) \qquad \text{(S18)}$$

where u is the gas flow rate, x is bed axial position and ρ is density of catalyst bed.

The following non-dimensionalizing manipulations have been performed:

- Defining axial coordinate (ξ) as $\xi = \dfrac{x}{l_{bed}}$

- Defining the bed residence time (τ_{bed}) as $\tau_{bed} = \dfrac{l_{bed}}{u}$

- Defining the conversion of EtBz and H$_2$O $X_{EtBz} = \dfrac{EtBz_0 - [EtBz]}{EtBz_0}$, $X_{H_2O} = \dfrac{H_2O_0 - [H_2O]}{H_2O_0}$, where $EtBz_0$ and H_2O_0 are inlet concentrations of ethylbenzene and H$_2$O, respectively, and $[EtBz]$, $[H_2O]$ are corresponding concentrations in gas phase.

- Defining a characteristic times for the ethylbenzene dehydrogenation reaction (τ_{dehyd}) as $\tau_{dehyd} = (k_{dehyd} \cdot n_s \cdot \rho)^{-1}$, H$_2$O binding reaction $\tau_{titr} = (k_{titr} \cdot n_s \cdot \rho)^{-1}$ and H$_2$O* scavenging reaction $\tau_{clean} = (k_{clean} \cdot n_s \cdot \rho)^{-1}$

- Defining a Damkohler numbers $\text{Da}_{EtBz} = \dfrac{l_{bed}/u}{(k_{dehyd} \cdot n_s \cdot \rho)^{-1}}$ and $\text{Da}_{H_2O} = \dfrac{l_{bed}/u_0}{(k_{titr} \cdot n_s \cdot \rho)^{-1}}$

Then material balance for ethylbenzene can be simplified to

$$\tau_{bed} \frac{\partial X_{EtBz}}{\partial t} = -\frac{\partial X_{EtBz}}{\partial \xi} + \text{Da}_{EtBz} \cdot \theta \qquad \text{(S19)}$$

Under experimental conditions the time scale over which reaction rate changes is much longer than a residence time:

$$t \gg \tau_{bed}$$

$$\frac{\partial X_{EtBz}}{\partial \xi} = \text{Da}_{EtBz} \cdot \theta$$

Same treatment for H$_2$O balance equation gives

$$\frac{\partial X_{H_2O}}{\partial \xi} = \text{Da}_{H_2O} \cdot \theta \, (1 - X_{H_2O})$$

For site balance

$$\frac{\partial [\theta]}{\partial t} = \rho (k_{clean} \cdot EtBz_0 \cdot (1 - \theta) - k_{titr} \cdot [H_2O] \cdot \theta)$$

$$\frac{1}{\rho \cdot k_{clean} \cdot EtBz_0} \cdot \frac{\partial [\theta]}{\partial t} = (1 - \theta) - \frac{k_{titr} \cdot [H_2O]}{k_{clean} \cdot EtBz_0} \cdot \theta$$

Using these assumptions, the equations can be simplified as follows:

$$\frac{\partial X_{EtBz}}{\partial \xi} = \text{Da}_{EtBz} \cdot \theta \qquad \text{(S20)}$$

$$\frac{\partial X_{H_2O}}{\partial \xi} = \text{Da}_{H_2O} \cdot (1 - X_{H_2O}) \cdot \theta \qquad \text{(S21)}$$

$$\frac{\partial \theta}{\partial t'} = (1 - \theta) - \chi' \cdot (1 - X_{H_2O}) \cdot \theta \qquad \text{(S22)}$$

11

Where X_{EtBz} and X_{H_2O} correspond to conversion of ethylbenzene and water, and $Da_{EtBz} = \frac{l_{bed}/u}{(k_{dehy} \cdot n_s \cdot \rho)^{-1}}$ and $Da_{H_2O} = \frac{l_{bed}/u_0}{(k_{titr} \cdot n_s \cdot \rho)^{-1}}$ are Damköhler numbers for ethylbenzene and water for reactions 1 and 2, respectively, and $\chi = \frac{k_{titr} \cdot H_2O_0}{k_{clean} \cdot EtBz_0}$

with initial and boundary conditions:

$X_{EtBz}(t, 0) = 0$

$X_{H_2O}(t, 0) = 0$

$X_A(0, x) = \theta_0$

1.8. Strategy for integrating the system of equations:

1. Integrate Equations S12 and S13 at $t^* = 0$ using the initial condition $\theta(t^* = 0) = \theta_0$ to get $X_{EtBz}(t^* = 0, \xi)$ and $X_{H_2O}(t^* = 0, \xi)$
2. Use these dependencies to integrate Equation S14 at each $\xi \in [0, 1]$ from $t^* = 0$ to a later time $t^* = 1 \cdot \delta t$, where δt is a small interval, to get $\theta(t^* = 1 \cdot \delta t, \xi)$
3. Use this dependency to integrate Equations S12 and S13 with initial $\theta(t^* = 1 \cdot \delta t) = \theta_0$ to get $X_{EtBz}(t^* = 1 \cdot \delta t, \xi)$ and $X_{H_2O}(t^* = 1 \cdot \delta t, \xi)$
4. Use these dependencies to integrate Equation S14 at each $\xi \in [0, 1]$ from $t^* = 1 \cdot \delta t$ to a later time $t^* = 2 \cdot \delta t$, where δt is a small interval, to get $\theta(t^* = 2 \cdot \delta t, \xi)$
5. Iterate steps 3 and 4 until t^* reaches 1.

For the numerical simulation, Matlab software has been used. Grid of 1000 time steps for δt and 100 spatial steps for ξ has been employed.
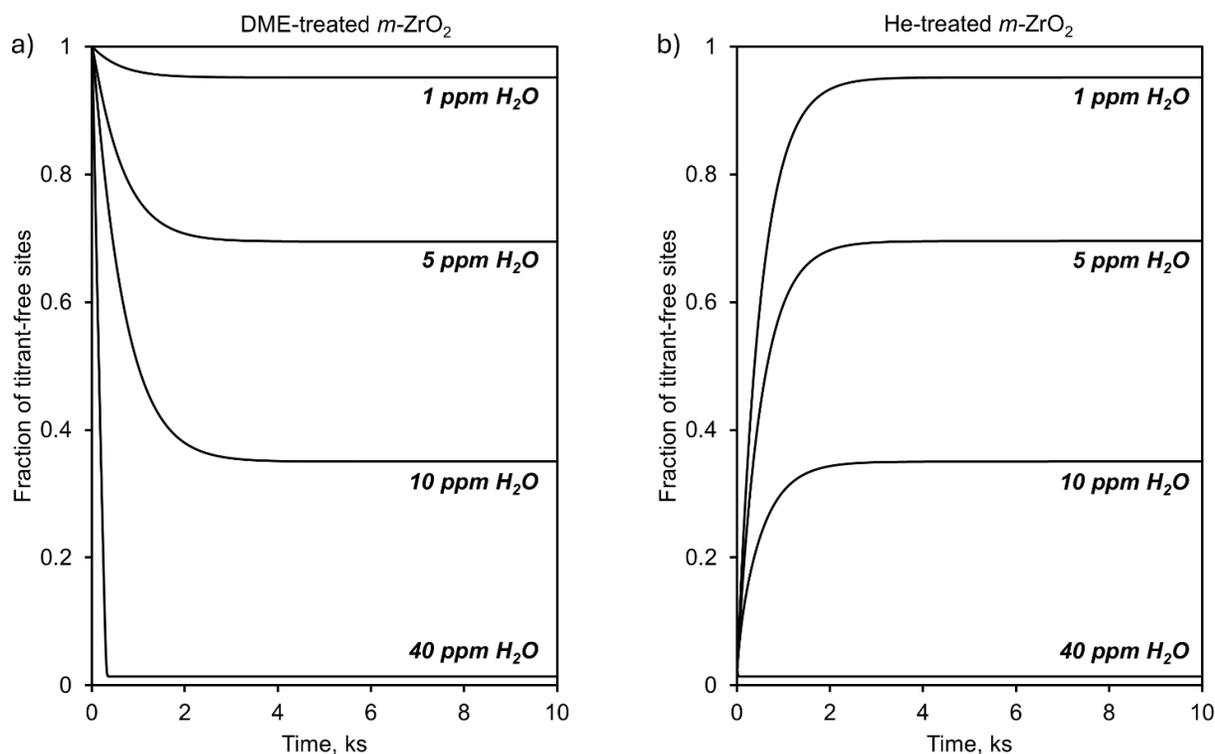
Figure S7. Predicted fraction of titrant-free sites as a function of reaction time during ethylbenzene dehydrogenation on DME-treated (a) and He-treated (b) m-ZrO$_2$ at reaction conditions identical to described at Figure 5 (1 kPa C$_8$H$_{10}$, 12.5 kPa H$_2$ balanced with He, 773 K) for various H$_2$O inlet levels.

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