Supplementary Materials

Effect of C3-Alcohols Impurities on Alumina-Catalyzed Dehydration of Bioethanol to Ethylene. Experimental Study and Reactor Modeling

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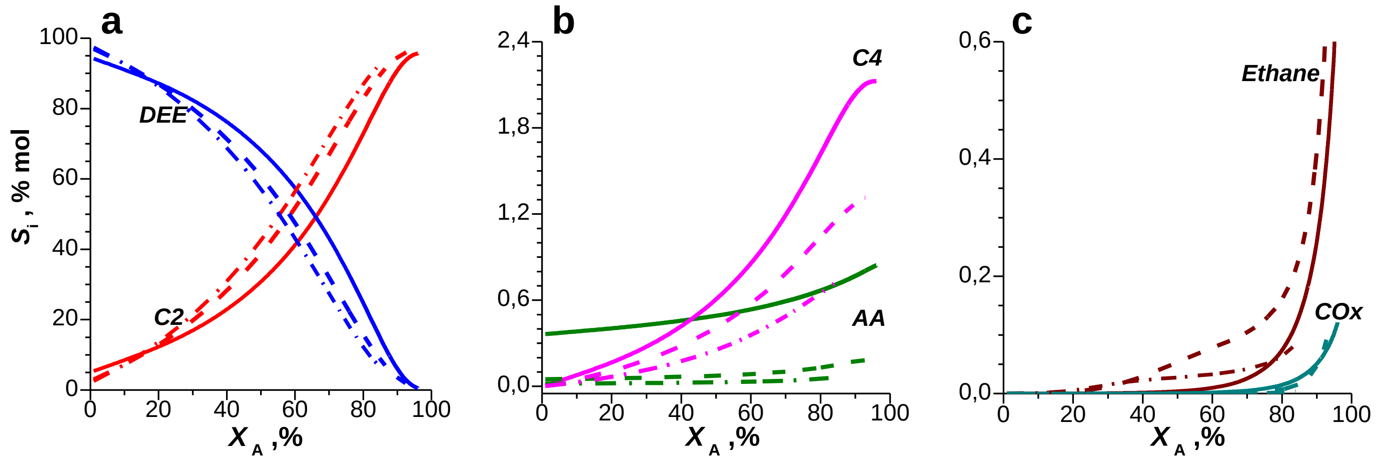

Figure S1. The calculated selectivity to *C2* and *DEE* **(a)**, *C4* and *AA* (**b)**, ethane and *COx* **(c)**, *vs*. ethanol conversion X_A in *PFR*.

Conditions: 400°C, 0.726 g catalyst, 21.05 g/h solution of 92%wt *EtOH* and C3-alcohol impurities of 0.001 (solid), 0.15 (dash) and 0.3%mol (dash-dot).

Mathematical model of tubular reactor

Quasi-homogeneous 2D model [34, 35] describes heat and mass transfer in axial and radial directions. This model also takes into account the changes of effective radial conductivity value λ_R from the conductivity in the core bed to the gas phase conductivity in the wall region [36]. For a more accurate representation of hydrodynamic and exchange processes when reacting gas flows through the layer of particles of complex geometric shapes, this model takes into account the different interstitial gas velocities around the particles (u_{out}) and inside their holes (u_{hole}) (*Figure S2*). The model adequately describes behavior of a multitubular fixed-bed reactor (*MTR*) and appropriately predicts the performance of heterogeneous catalytic processes [25, 34-35, 37, 38-40]. The *MTR* simulation assumes that all the wall-heated tubes were identical in behavior.

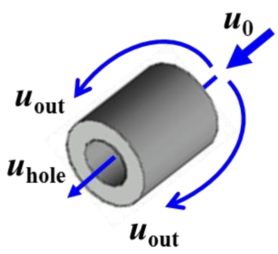

Figure S2. A sketch of "gas flow sharing" in a holed cylinder

Quasi-homogeneous 2D model of a wall-heated tubular reactor [25,34] accounts for material and heat transfer in radial and axial directions of tube with fixed-bed catalyst:

$$\frac{P_0}{RT_0}\frac{\partial(\overline{u_l}y_i)}{\partial l}+\frac{1}{r}\frac{P_0}{RT_0}\frac{\partial}{\partial r}(r\overline{u_r}y_i)-\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{P}{RT}D_R\frac{\partial y_i}{\partial r}\right)=-\sum_j^9(1-\varepsilon)\xi_{ij}\varpi_j\;;\; i=\overline{1{,}11}\;;$$
$$\frac{P_0}{RT_0}\overline{u_l}c_p\frac{\partial T}{\partial l}+\frac{P_0}{RT_0}\overline{u_r}c_p\frac{\partial T}{\partial r}-\sum_i c_{pi}\left(\frac{\partial T}{\partial r}\right)\frac{P}{RT}D_R\frac{\partial y_i}{\partial r}-\frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda_R\frac{\partial T}{\partial r}\right)=-(1-\varepsilon)\sum_j^9\Delta H_j\varpi_j\;; \qquad (S1)$$

Here

l and r are tube length and radius coordinates, respectively;
y_i is molar fraction of i^{th} component;
ξ_{ij} is stoichiometric coefficient of i^{th} component in j^{th} reaction;
ϖ_j is apparent rate of j^{th} reaction in a catalyst grain,
ε is a bed void fraction,
$\varepsilon=\varepsilon_{bed}+\varepsilon_{hole}(1-\varepsilon_{bed})$;
ε_{bed} is a void fraction for solid pellets,
$\varepsilon_{bed}=0.36+0.1\,d_{eq.sph}/ID+0.7\left(d_{eq.sph}/ID\right)^2$;
ε_{hole} is a void fraction of a single pellet, $\varepsilon_{hole}=\frac{N_{hole}}{D}$;
$d_{eq.sph}$ is diameter of equivalent-volume sphere, $d_{eq.sph}=D\sqrt[3]{1.5\,h/D}$;
ID is inner tube diameter;
D is outer diameter of the pellet;
h is height of the pellet;
$D_{R\,i}$ is effective radial diffusivity;

$$D_{R\,i}=D^0_{R\,i}+\frac{\nu}{K}\left[\varepsilon_{bed}Re_{out}+\varepsilon_{hole}(1-\varepsilon_{bed})Re_{hole}\right],\; K=\frac{8}{1.78}\left[2-\left(1-\frac{2}{\frac{ID}{d_{eq.sph}}}\right)^2\right]; \qquad (S2)$$

ν is gas viscosity, m²/s;
ΔH_j is enthalpy of j^{th} reaction;
λ_R is effective radial thermal conductivity in a fixed bed defined as a sum of conductivity without flow and convective constituent

$$\lambda_R^{conv},\lambda_R^{conv}=\frac{\lambda_{gas}}{K}\left[\varepsilon_{bed}Re_{out}+\varepsilon_{hole}(1-\varepsilon_{bed})Re_{hole}\right]Pr\;; \qquad (S3)$$

Pr is Prandtl number;
Re_{out} and Re_{hole} are Reynolds numbers expressed in terms of corresponding velocities and mixing length,
$Re_{out}=d_{eq.sph}\,u_{out}/\nu$,
$Re_{out}=d_{hole}\,u_{hole}/\nu$,
$d_{hole}=2\langle\cos\theta\rangle h$;
c_p is total gas heat capacity;
P is pressure;
P_0 is pressure under normal conditions;
R is universal gas constant;
T is temperature;
T_0 is temperature under normal conditions;
u_l is superficial axial gas velocity;
$\overline{u_l}$ is superficial axial gas velocities at standard temperature and pressure (STP);
$\overline{u_r}$ is radial gas velocities at STP;

$$\frac{\partial\overline{u_l}}{\partial l}=\frac{2RT_0}{\frac{ID^2}{4}P_0}\int_0^{\frac{ID}{2}}\sum_i\sum_j^9 r(1-\varepsilon)\xi_{ij}\varpi_j dr\;; \qquad (S4)$$

$$\overline{u_r} = -\frac{RT}{P_0 r}\int_r^{\frac{ID}{2}}(1-\varepsilon)r\sum_i \sum_j^9 \xi_{ij}\varpi_j dr + \frac{1}{r}\frac{\partial \overline{u_l}}{\partial l}\left(\frac{ID^2}{4}-\frac{r^2}{2}\right) \;;$$

Boundary conditions:

$$0 \le r \le \tfrac{ID}{2} \quad l = 0 : \overline{u_l}(0,r) = \overline{u_0} \;,\quad T(0,r) = T_{in} \,,\, y_i(0,r) = y_{in} \quad, i = \overline{1{,}11};$$

$$0 \le l \le L \quad r = 0 : \; \frac{\partial y_i(l,0)}{\partial r} = 0 \,, \frac{\partial T(l,0)}{\partial r} = 0 \;; \qquad (S5)$$

$$r = \tfrac{ID}{2}: \quad \frac{\mathrm{d}y_i(l,ID/2)}{\mathrm{d}r} = 0,\, i = \overline{1{,}11} \;;\; \overline{u_r}(l,ID/2) = 0 \;;\; \lambda_R\frac{\partial T}{\partial r} = \alpha\,(T_w - T);$$

Here

$y_{i\,\mathrm{in}}$ is an inlet molar fraction of i^{th} component;
$\overline{u_0}$ is superficial inlet gas velocity at STP;
L is tube length;
T_W is tube wall temperature;
α is wall heat transfer coefficient,
$\alpha = \frac{\lambda_R}{D_{\mathrm{H.EQ}}[\ln(\lambda_R/\lambda_{gas})-1]}$;
$D_{\mathrm{H.EQ}}$ is equivalent diameter of a pore channel;

A dusty gas model described diffusion in a porous isothermal particle:

$$\frac{\partial}{\partial\rho}\left(D_{ri}^*\frac{\partial C_i}{\partial\rho}\right) - \frac{RT}{P}\frac{\partial}{\partial\rho}(V_i^* C_i) = \sum_{j=1}^9 \xi_{ij}\omega_j \,,\, i = \overline{1{,}11}; \qquad (S6)$$

Boundary conditions:

$$\rho = 0 : \;,\; \frac{\partial C_i}{\partial\rho} = 0 \,,\quad i = \overline{1{,}11}; \qquad (S7)$$

$$\rho = \rho_{grain} : \;,\; C_i^{surf} = 0 \,,\quad i = \overline{1{,}12};$$

Here

D_{ri}^* is a generalized diffusivity coefficient or Wilke diffusion coefficient of i^{th} component;
V_i^* is so-called hydrodynamic velocity of i^{th} component [34, 41];
C_i is molar concentration of i^{th} component;
C_i^{surf} is concentration of the i^{th} component on the surface
$\varpi_j = \frac{1}{\rho_{grain}}\int_0^{\rho_{grain}}\omega_j(\rho)d\rho$;
ρ_{grain} is an equivalent particle size, that is the ratio of the pellet geometric volume to the pellet external geometric surface area;
ω_j is a rate of j^{th} reaction under kinetics controlled conditions.

The Wilke diffusion coefficient D_{ri}^* and hydrodynamic velocity V_i^* [34, 41] depend on the effective binary diffusion coefficient $D_{ik}^* = \Pi D_{ik}$ and on the effective Knudsen diffusion coefficient $D_i^{*kn} = \Pi D_i^{kn}$, where D_{ik} is binary diffusion coefficient, D_i^{kn} is Knudsen diffusion coefficient, Π is the empirical permeability coefficient; Π accounts for the physical behavior of the porous structure.

Pressure drop per the bed length unit, that is, specific hydraulic resistance $\Delta P/L$ was calculated for the catalyst of arbitrary shape according to the approach set forth in [34, 36]:

$$\begin{cases} u_l = \varepsilon_{bed}u_{out} + (1-\varepsilon_{bed})\varepsilon_{hole}u_{hole} \\ g_1 u_{hole} + g_2 u_{hole}^2 = \dfrac{\Delta P}{\langle cos\theta\rangle h} = f_1 u_{out} + f_2 u_{out}^2 \end{cases} \qquad (S8)$$

Here

ΔP is the pressure drop over the distance $\langle cos\theta\rangle h$;
$g_1 = \frac{16\pi\mu}{d^2}$; $g_2 = \frac{1.75\pi\rho_{gas}}{4h}\left(1-\frac{\varepsilon_{hole}}{N_{hole}}\right)$;
$f_1 = \frac{150\mu}{d_{\mathrm{eq.sph}}^2}\left(\frac{1-\varepsilon_{bed}}{\varepsilon_{bed}}\right)^2$; $f_2 = \frac{1.75\rho_{gas}}{d_{\mathrm{eq.sph}}}\frac{1-\varepsilon_{bed}}{\varepsilon_{bed}}$;
d is inner diameter of the pellet;
μ is gas viscosity,
N_{hole} is holes number;
ρ_{gas} is gas density.

Analytic expression which provides to determine pressure gradient in the bed was published in [37].

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