Understanding the kinetics of 2,3-butanediol dehydration into 1,3-butadiene *via* kinetic modeling

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The selective dehydration of 2,3-butanediol (BDO) is currently being investigated as a potential renewable route for green 1,3-butadiene (BD) production [1]. The BDO conversion towards BD comprises of two consecutive dehydrations, with 3-buten-2-ol (3B2OL) as intermediate. Due to side products, such as methylethylketone, formation, the 1st dehydration is more challenging [2]. Consequently, optimizing the first step is critical for maximal BD formation. ZrO_2 is a unique metal oxide that has the essential acid-base concerted sites to catalyze the formation of 3B2OL via 1,2-elimination [1]. Using the so-called hydrothermal synthesis method, it is possible to maximize the acid-base concerted sites on a ZrO_2 surface, resulting in a high 3B2OL selectivity up to 42% (mol/mol). A fundamental understanding of the reactions occurring over the acid-based concerted sites of the ZrO_2 catalyst surface *via* kinetic modeling will allow better catalyst design and identifying optimal operating conditions.

A systematic set of experiments were performed in a wide range of operating conditions in absence of transport limitation in a Berty reactor, allowing to determine the effect of temperature (300 - 375°C), space time (28 - 1130 kg.s/mol), inert-to-feed ratio (1 - 8 mol/mol) at a total pressure of 10 bar in an isolated manner. The parameters constituting the Langmuir-Hinshelwood Hougen-Watson type kinetic model are determined *via* regression to the experimental data using the commercially available Athena Visual Studio software.

The model is globally significant, with an *F*-value exceeding a 1000, greatly exceeding the tabulated one of 4; all the parameters are statistically significant, and the multiple correlation coefficient, R squared amounted to 0.99. The kinetic model construction resulted in a clear understanding of the reaction network, in particular with respect to the adsorption on the acid-base concerted sites. The adsorption configuration of 2,3-BDO on the active sites for the formation of MEK and 3B2OL was represented by an equilibrium adsorption enthalpy amounting to -123 kJ/mol and -174 kJ/mol respectively, which indicates the critical need to tune the adsorption properties of the catalyst. Furthermore, the model reproduces the experimental data well, capturing important trends such as the increase in selectivity towards 3B2OL as the reaction temperature is reduced and as the space-time is increased. This is attributed to the enhancement of adsorption on those acid-base concerted sites facilitating the formation of 3B2OL.

References

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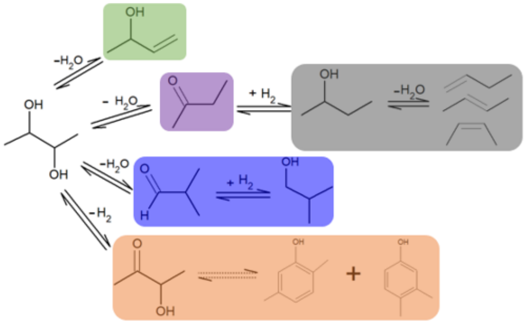
OH
$-H_2O$
OH
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$- H_2O$
O
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O
H
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OH
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O
OH
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+
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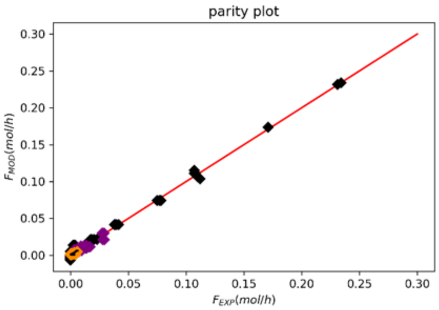
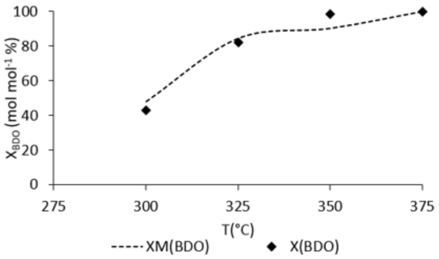
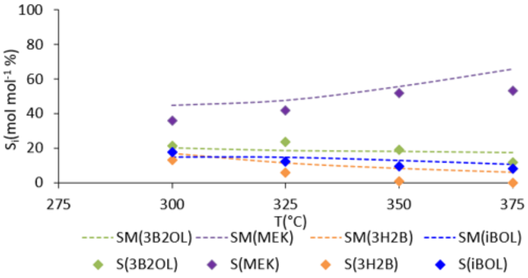

parity plot
$F_{MOD}(mol/h)$
$F_{EXP}(mol/h)$
0.00
0.05
0.10
0.15
0.20
0.25
0.30
0.00
0.05
0.10
0.15
0.20
0.25
0.30


X_{BDO} (mol mol^{-1} %)
100
80
60
40
20
0
275
300
325
350
375
T(°C)
XM(BDO)
X(BDO)


S_i(mol mol^{-1} %)
100
80
60
40
20
0
275
300
325
350
375
T(°C)
SM(3B2OL)
SM(MEK)
SM(3H2B)
SM(iBOL)
S(3B2OL)
S(MEK)
S(3H2B)
S(iBOL)