**KINETICS OF THE CONVERSION OF ETHANOL AND ACETALDEHYDE INTO 1,3-BUTADIENE OVER A TA2O5/SBA15 CATALYST.**

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**Highlights**

* The reaction network including main and by-products was experimentally determined.
* A kinetic model was developed for the second-step of the ethanol to butadiene process.
* The experimental observations were explained through the model parameters.

**1. Introduction**

1,3-Butadiene is a valuable conjugated diene which is industrially produced as a co-product of naphtha steam cracking. It is used primarily as a chemical intermediate and as a monomer in the manufacture of synthetic rubbers, most of which are destined to the automobile industry. The onset of the US shale gas has impacted the 1,3-butadiene market as the change in feedstock for steam cracking to ethene have resulted in a lower 1,3-butadiene production. Therefore, while the 1,3-butadiene market shrank, the global 1,3-butadiene demand continued to grow. In that context, the conversion of bioethanol to 1,3-butadiene arises as an interesting and environmentally friendly alternative in a highly competitive and unstable marketplace.

In the literature we can find very few kinetic studies of the ethanol to 1,3-butadiene conversion, and none of these studies includes the effect of co-feeding water among with the feedstock. That way, we aim to develop a formal kinetic model describing the main reactions pathway that can predict the catalyst performance in a range of operating conditions close to the optimum.

**2. Methods**

 The catalyst was prepared following the methodology reported in the work of Chae et al. [1]. Catalytic tests were carried out in a continuous flow fixed-bed reactor at 300-350 ºC, 0.22-1.63h-1, 0-7.5% w/w water in the feedstock, ethanol/acetaldehyde mole rate between 1.7 and 2.7, ethanol partial pressure of 0.13 bar and atmospheric pressure. The bed was divided into three sections. The top section was a SiC bed, the middle one comprised a bed of catalyst (0.3-0.5 mm) diluted in the necessary amount of SiC to obtain a bed length of 13 cm, and the bottom section was also a SiC bed. All sections were separated by a glass wool plug. The ethanol was fed with an HPLC-pump and N2 was used as carrier gas. The reactor output line was electrically traced and insulated to avoid product condensations before analysis by an Agilent 7890A on-line gas chromatograph (GC) equipped with two flame ionization detectors (FID) and a thermal conductivity detector (TCD).

**3. Results and discussion**

Making use of the tests carried out in the laboratory-scale reactor, a kinetic model was developed. The reaction scheme considered for the calculation of the balance is a simplification of the most accepted reaction pathway nowadays, lumping some products like olefins and the major lump “others” that includes a huge amount of compounds with little contribution such as acetone, propanal, butanal, methanol, and so on. The differential mole balance equations were solved obtaining an initial guess of the kinetic parameters assuming constant molar flow along the reactor and solving the algebraic system. These rough parameters were used as initial guess values for solving the differential mole balance equations along the reactor.

* Main reaction: C2H5OH +C2H4O 🡪 C4H6 + 2H2O
* Ethanol dehydration: 2 C2H5OH 🡪 (C2H5)2O + H2O

 C2H5OH 🡪 C2H4 + H2O

* Butenes formation: 2 C2H5OH 🡪 C4H8 + 2H2O
* Tishenko reaction: 2C2H4O 🡪 CH3COOC2H5
* Etilacetate to “other compounds” lump (Butanal): 2 CH3COOC2H5 + C4H8O2 🡪 2C4H8O + 2H2O
* “Other compounds” lump formation: C2H5OH +C2H4O 🡪 C4H8O + H2O
* Heavy compounds formation (Diethoxyethane): 3 C2H5OH +1.5C2H4O 🡪 1.5C6H14O2 + 1.5H2O

 **4. Conclusions**

The main products observed while co-feeding ethanol and acetaldehyde over a TA2O5/SBA15 catalyst were 1,3-butadiene, ethene, diethyl ether, ethyl-acetate, butenes and heavy compounds. The developed kinetic model may be used to design and optimize an industrial facility. The proposed model fitting concurs with the experimental results.

**References**

1. H. Chae, T. Kim, Y. Moon, H. Kim, K. Jeong, C. Kim, S. Jeong, App Catal B, 150-151 (2014) 596-604.