

KINETIC MODEL FOR THE TRANSFORMATION OF BIO-ETHANOL INTO OLEFINS OVER A HZSM-5 ZEOLITE TREATED WITH ALKALI

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Summary

A kinetic model has been developed for the transformation of bio-ethanol into hydrocarbons upon a catalyst with low deactivation by coke deposition (based on a HZSM-5 zeolite treated with alkali in order to moderate its acidic strength). Kinetic data have been obtained in isothermal fixed bed reactor (300-375 °C range, with water content in the feed up to 75 wt %). The kinetic model describes the distribution of product lumps (ethylene, olefins C₃-C₄, gasoline or C₅-C₁₂, and paraffins C₂-C₃) by including an autocatalytic step for olefin production. The attenuating effect of water upon the steps of kinetic scheme is quantified with an exponential function.

Keywords

Reaction Path Analysis, Green CRE, Chemical feedstocks from biomass, Biomass processing technologies.

Introduction

Apart from its use as fuel, mixed with gasoline or Diesel,¹ bioethanol has great interest for catalytic transformation in order to obtain hydrogen² or for obtaining raw materials of growing demand, such as propylene and butanes and BTXE monoaromatics.^{3,4} The catalytic transformation of bioethanol into hydrocarbons upon acidic catalysts, such as HZSM-5 zeolite, has the advantage that it avoids the costly elimination of water required for obtaining pure ethanol.⁴

In order to obtain a high yield of light olefins in the transformation of bioethanol upon HZSM-5 zeolite catalyst (BTO process), high reaction temperature is required (above 400 °C) to enhance the cracking of higher hydrocarbons, but it has the inconvenience of causing irreversible deactivation of the catalyst by dealumination of the zeolite in the presence of high temperature steam.⁴ In a previous paper,⁵ it has been proven that a moderate alkaline treatment (10 min with a diluted solution of NaOH) is an efficient method for moderating the acidic strength of the HZSM-5 zeolite in order to increase light olefins selectivity at moderate temperature (as it restricts the steps of transformation of light olefins into heavier hydrocarbons) and it also contributes to attenuating deactivation by coke deposition.

In order to progress in the technological development of the transformation of bioethanol into C₃-C₄ olefins or BTXE aromatics, a kinetic model is required which quantifies the effect of the operating conditions upon the concentration of product lumps at the reactor outlet. This

paper addresses this objective in the 300-375 °C range, since above this temperature the catalyst irreversible deactivation takes place for water content of 5 wt %.

Experimental

The zeolite modified by alkaline treatment has been prepared according to the method of Ogura et al.⁶, by mixing the zeolite ammonium ZSM-5 with 0.2 M NaOH solution at 80 °C (during 10 min), followed by fast cooling, filtration, drying, exchange with NH₄NO₃ and calcination at 550 °C for 16 h. Final catalyst has been prepared by agglomerating the active phase (zeolite, 25 wt %) with a binder (bentonite, 30 wt %) and an inert solid (alumina, 45 wt %), in order to confer upon the final catalyst sufficient thermal and mechanical resistance for its use in the reactor. Prior to use, the catalyst is calcined at 575 °C for 2 h.

The kinetic runs have been carried out in an automated reaction equipment provided with an isothermal fixed bed connected on-line to a gas chromatograph (HP-6890-II) for products analysis.⁷ The initial composition of the reaction products has been obtained by extrapolating at zero time on stream the kinetic data obtained at constant temperature in the 300-375 °C range, with space time up to 1.52 g_{catalyst}h/g EtOH and water content in the feed up to 75 wt %.

Results and discussion

Based on the observed kinetic behaviour, the reaction products are grouped into four lumps of components: ethylene (E, the true reactant for the formation of hydrocarbons, since ethanol dehydration occurs instantly in all conditions studied); light olefins (O= C₃-C₄), which are intermediate products in the kinetic scheme, since its composition passes through a maximum with the space time; light paraffins (P= C₂-C₃), whose composition is very low in the conditions studied and increases continuously with space time and gasoline or C₅-C₁₂ lump (G), which are the main products for a high value of space time.

Different kinetic schemes have been proposed, based on that proposed by Gayubo et al³ for the BTG process (bioethanol to gasoline). The kinetic equations have been established assuming elementary steps and expressing the composition as mass fraction referred to the organic components. The decrease of the conversion due to the presence of water in the reaction medium is taken into account by multiplying each kinetic constant by a function, $\theta(X_w)$, dependent on water content:

$$\theta(X_w) = \exp(-k_w X_w) \quad (1)$$

where X_w is the mass fraction of water referred to organic compounds. The discrimination of models and calculation of kinetic parameters were carried out using a Matlab program, which fits to the experimental values, by multiple non-linear regression, the values of composition calculated by solving the conservation equations of each lump in the kinetic scheme

Figure 1 shows the kinetic model of best fit, which includes an autocatalytic step of olefin formation and the formation of gasoline by reaction between ethylene and olefins. This kinetic scheme predicts the unusual evolution of composition with space time at low temperature and high water content (Figure 2), conditions for which the rates of ethylene disappearance and gasoline lump formation goes through a maximum.

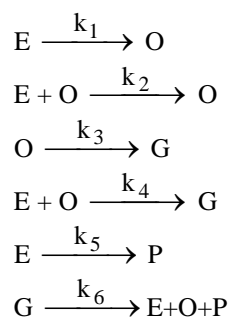


Figure 1. BTO process kinetic scheme.

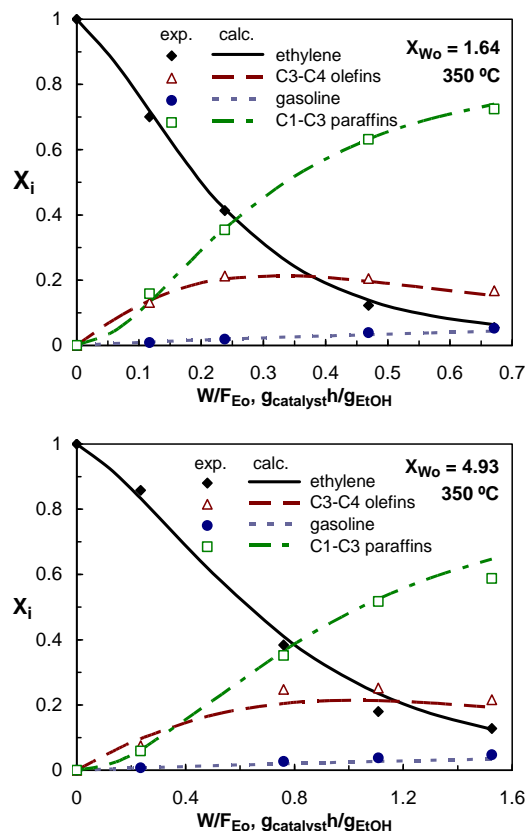


Figure 2. Comparison of the experimental (points) and calculated (lines) values of composition of product lumps at 350 °C for different water contents in the feed.

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