

# Microkinetic modelling of isosynthesis over monoclinic zirconia catalyst

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## Highlights

- Isosynthesis is a selective reaction to isobutylene being important jet fuel intermediate
- Reaction mechanism for isosynthesis was determined using DFT calculations and operando spectroscopy
- Microkinetic model was determined using the mechanism and generated kinetic data

## 1. Introduction

Aviation is responsible for 2 % of global greenhouse gas emissions and these emissions are expected to grow steadily if no actions are taken. [1] On the other hand, it is expected that liquid fuels will be the main energy source for the aviation still for decades and therefore, sustainable aviation fuels are urgently needed. According to ReFuelEU Aviation initiative, 70 % of aviation fuels consumed in EU should be sustainable aviation fuels (SAF) by 2050 comprising electrofuels and sustainable biofuels. [2]

Current routes to synthetic aviation fuels are quite unselective for jet fuel range hydrocarbons. Isosynthesis is a reaction to produce isobutylene selectively from sustainably produced syngas typically catalyzed by metal oxide catalysts. [3] Through oligomerization and hydrogenation, jet fuel range hydrocarbons can be produced with high selectivity from the isobutylene.

In this study, reaction mechanism for the isosynthesis on the surface of monoclinic zirconia catalyst was determined applying density functional theory (DFT) calculations and operando spectroscopy (DRIFTS). The mechanism was used to determine the rate equations of a microkinetic model for the isosynthesis and the kinetic parameter estimation was performed using kinetic data created in a gas phase fixed bed laboratory scale reactor.

## 2. Methods

Altogether 25 kinetic experiments were performed using an Inconel-625 tubular reactor. The effluent was analyzed with an on-line gas chromatograph equipped with TCD and FID detectors. The catalyst was a monoclinic ZrO<sub>2</sub> with a particle size of 150–200 μm. The reaction condition ranges of the experiments were T=400–500°C, GHSV=1000–2000 1/h, P=35–50 bar and H<sub>2</sub>/CO=0.8–1.2.

The vdW-corrected (Tkatchenko–Scheffler correction) DFT calculations were carried out using the GPAW 21.1.0 code [4]. The exchange and correlation effects were described by the Hubbard-corrected Perdew–Burke–Ernzerhof (PBE+U) functional together with PAW setups to treat the core electrons of elements within the frozen core approximation.

DRIFTS measurements were performed at Utrecht University department of Inorganic Chemistry and Catalysis. The FTIR spectroscope, Bruker Tensor 37 with praying mantis module, was equipped with Harrick reaction chamber and mass flow controllers for He, CO, and H<sub>2</sub>.

Estimation of kinetic parameters was performed using least square problem optimizers included in MATLAB. It was evaluated that internal and external mass transfer limitations were negligible and therefore, the reactor was described applying a pseudo-homogeneous plug flow model. The formed set of ordinary differential equation (ODEs) was solved in MATLAB using ode15s solver.

### 3. Results and discussion

DFT calculations focused on the isosynthesis mechanisms proposed in the literature [1] for the formation of isobutene from syngas over stepped *m*-ZrO<sub>2</sub>( $\bar{2}12$ ) surface. In the proposed mechanisms, C<sub>2</sub> intermediate (acetaldehyde/ethenolate) formed via carbonylation of the methyl or methylene species is transformed into C<sub>3</sub> intermediate by the aldol condensation with formaldehyde. Isobutene is formed by the aldol condensation between the formed C<sub>3</sub> intermediate and formaldehyde. DRIFTS measurements were performed to confirm the derived reaction mechanism, i.e., to detect the surface species on the monoclinic zirconia expected to participate the reaction mechanism. With syngas feed at atmospheric pressure and 400 °C distinct formate peaks appeared, and hydroxide peaks diminished. Methoxy was also tentatively assigned, but the peaks were minor and overlapped with formate peaks.

The reaction network included in the kinetic model was determined based on the performed kinetic experiments. In addition to the formation of isobutylene, isobutylene can be hydrogenated to isobutane. Furthermore, linear C<sub>2</sub> – C<sub>5</sub> alkenes and methane are formed as side reactions and all these alkenes can be hydrogenated to corresponding alkanes.

All reactions yielding hydrocarbons from syngas were assumed to follow the same basic mechanism with a hydrocarbon (an alkene or methane) and CO<sub>2</sub> as the products. These side reactions were modelled using power law rate equations whereas hydrogenation reactions of alkenes were assumed to follow LH-kinetics with dissociative competitive adsorption of hydrogen. The rate equation of the main reaction was derived based on the developed mechanism using quasi-equilibrium hypothesis. Kinetic parameters were estimated for the reaction system of 11 reactions including 27 parameters to be estimated.

### 4. Conclusions

The mechanistic model was compared to simple power law models and it was concluded that the best fit of the model was obtained using the mechanistic model. Identifiability of the parameters in the model was reasonable.

### References

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### Keywords

Isosynthesis, DFT, operando spectroscopy, microkinetics