

# Selective Hydrogenation of C<sub>8</sub> Aromatics in Pyrolysis Gasoline (PYGAS) on Ni<sub>3</sub>CuSn<sub>0.3</sub>/SiO<sub>2</sub> Catalyst: Reaction Kinetics and Reactor Modeling

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## Highlights

- A cost-effective and highly selective Ni<sub>3</sub>CuSn<sub>0.3</sub>/SiO<sub>2</sub> catalyst was developed.
- A kinetic model was established for selective hydrogenation of C<sub>8</sub> aromatics in PYGAS.
- A mathematical model was developed to depict the hydrogenation process in a fixed-bed reactor.

## 1. Introduction

Styrene is an important chemical monomer, which is extensively utilized in the production of plastics and synthetic rubbers, such as polystyrene, acrylonitrile-butadiene-styrene resin, and styrene-butadiene rubber. With the development of the ethylene industry and the expansion of facilities, there has been significant interest in recovering styrene from pyrolysis gasoline (PYGA), a byproduct of steam cracking of naphtha. The recovery process primarily involves three units: distillation to achieve C<sub>8</sub> aromatics fraction, selective hydrogenation to eliminate phenylacetylene, and extraction to obtain high-purity styrene. The C<sub>8</sub> aromatics fraction entering the selective hydrogenation unit is characterized by a minority of phenylacetylene in excess of styrene, making it crucial to convert phenylacetylene while minimizing hydrogenation losses of styrene. Currently, the selective hydrogenation of phenylacetylene primarily utilizes Pd-based catalysts [1], known for their high activity and low initiation temperature. However, the styrene selectivity of Pd-based catalysts is generally not high, especially when phenylacetylene is completely converted; typically, the styrene selectivity is lower than 80%. Moreover, Pd metal is expensive, leading to higher catalyst costs. Very recently, we have developed a non-noble metal Ni<sub>3</sub>CuSn<sub>0.3</sub>/SiO<sub>2</sub> catalyst, exhibiting excellent performance in the selective hydrogenation of phenylacetylene [2]. When phenylacetylene is completely converted, the styrene selectivity is as high as 93.3%. Herein, the reaction kinetics of selective hydrogenation of C<sub>8</sub> aromatics over Ni<sub>3</sub>CuSn<sub>0.3</sub>/SiO<sub>2</sub> was studied; furthermore, the selective hydrogenation process in a fixed-bed reactor was investigated experimentally and theoretically. The main objective of this research is to assess the practical application potential of Ni<sub>3</sub>CuSn<sub>0.3</sub>/SiO<sub>2</sub>, analyze the selective hydrogenation process of C<sub>8</sub> aromatics in a fixed-bed reactor, and offer theoretical insights for the recovery of styrene from PYGAS.

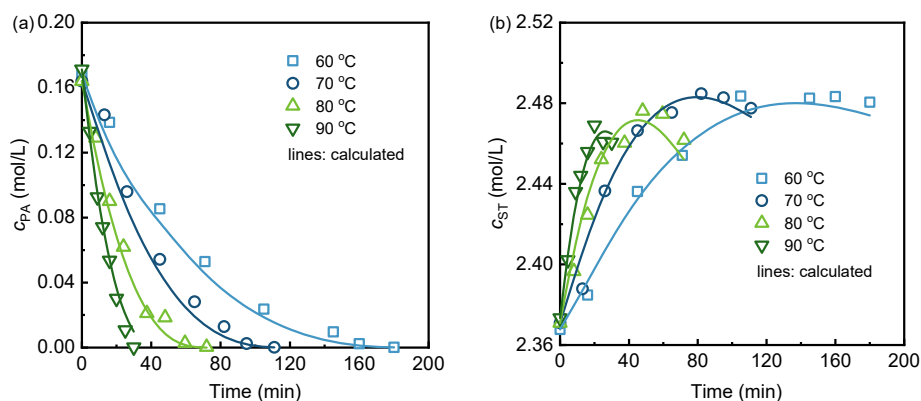
## 2. Methods

The reaction kinetics experiments were conducted using an autoclave. First, the internal and external diffusion limitations were eliminated by reducing the catalyst particle size and increasing the stirring speed, respectively. Next, intrinsic kinetic experiments for the selective hydrogenation of C<sub>8</sub> aromatics were carried out under conditions of 60-90 °C and 0.2-1.0 MPa. Unless otherwise specified, the feedstock was composed of phenylacetylene (PA, 2 wt.%), styrene (ST, 28 wt.%), ethylbenzene (EB, 30 wt.%) and meta-xylene (MX, 40 wt.%). The fixed-bed reactor used was a jacketed stainless-steel reactor (inner diameter 1 cm, height 25 cm). Catalyst particles (average diameter 0.64 mm, 1 g) were placed at the center of the reactor (catalyst bed height 2 cm), with the remaining space filled with quartz sand (0.64 mm). The reaction temperature was controlled using an external circulating water bath.

## 3. Results and discussion

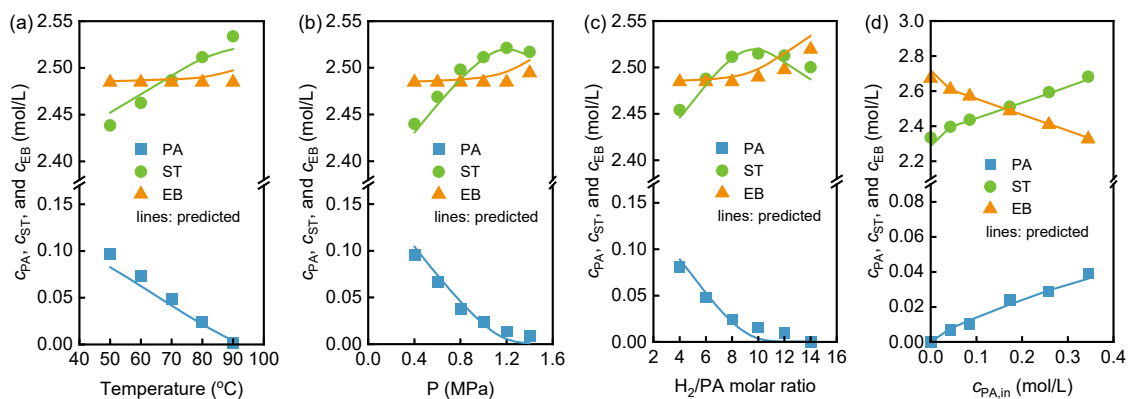
Figure 1 illustrates the typical variation in PA and ST concentrations with varying reaction temperatures. With an increase in temperature, the reaction rates of both PA and ST increase, leading to a reduction in the time required for complete PA conversion. Moreover, the maximum concentration of ST decreases as the temperature rises. A power-law kinetic model was developed based on the experimental data,

with activation energies for the PA→ST and ST→EB reactions being 46.33 and 68.95 kJ/mol, respectively. As shown in Figure 1, the calculated values of PA and ST concentrations from the kinetic model closely match the experimental values.



**Figure 1.** Concentration variation of (a) PA and (b) ST with reaction time at different temperatures (symbols: experimental data; lines: calculated from the kinetic model).

Figure 2 shows the effect of reaction temperature, pressure, H<sub>2</sub>/PA molar ratio, and PA concentration in the feedstock on the selective hydrogenation of C<sub>8</sub> aromatics in the fixed-bed reactor. Generally, an increase in temperature, pressure, and H<sub>2</sub>/PA molar ratio is beneficial for PA conversion, while an appropriate increment in these variables can enhance ST yield. Worthy of mention is that when the feedstock does not contain PA (the zero point in Figure 2d), the ST concentration experiences a marginal decrease from 2.365 mol/L in the feedstock to 2.334 mol/L in the product, resulting in a mere 1.3% loss. This indicates that Ni<sub>3</sub>CuSn<sub>0.3</sub>/SiO<sub>2</sub> exhibits lower activity for the ST→EB reaction. Subsequently, a one-dimensional model accounting for interfacial and intraparticle gradients is established. As presented in Figure 2, the mathematical model accurately depicts the selective hydrogenation process in the fixed-bed reactor and can serve as guidance for future reactor design and operational optimization.



**Figure 2.** Variation in outlet concentrations of PA, ST, and EB with (a) temperature, (b) pressure, (c) H<sub>2</sub>/PA molar ratio, and (d) feedstock PA concentration in the fixed-bed reactor (symbols: experimental data; lines: model prediction).

#### 4. Conclusions

This study conducted experimental and theoretical research on the selective hydrogenation of C<sub>8</sub> aromatics in PYGAS using Ni<sub>3</sub>CuSn<sub>0.3</sub>/SiO<sub>2</sub> catalyst. The reaction kinetic model and fixed-bed reactor mathematical model were established to accurately describe the hydrogenation process.

#### References

- [1] J. Hu, Z. Zhou, R. Zhang, L. Li, Z. Cheng, *J. Mol. Catal. A: Chem.* 381 (2014) 61–69
- [2] W. Chen, H. Xu, X. Ma, L. Qi, Z. Zhou, *Chem. Eng. J.* 455 (2023) 140565

#### Keywords

Selective hydrogenation; Ni-based catalyst; reaction kinetics; reactor modeling.