

Revisiting the reaction kinetics of selective hydrogenation of phenylacetylene over an egg-shell catalyst in excess styrene



Zhiming Zhou^{a,*}, Jiawei Hu^a, Rui Zhang^b, Li Li^c, Zhenmin Cheng^a

^a State Key Laboratory of Chemical Engineering, East China University of Science and Technology, Shanghai 200237, China

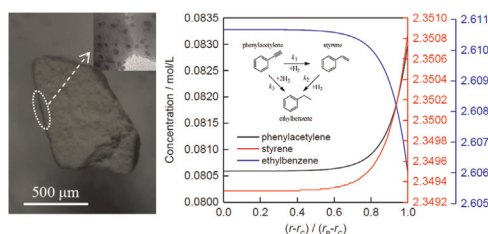
^b Engineering Research Center of Large Scale Reactor Engineering and Technology, Ministry of Education, East China University of Science and Technology, Shanghai 200237, China

^c Chemical Engineering Research Center, East China University of Science and Technology, Shanghai 200237, China

HIGHLIGHTS

- The kinetics of phenylacetylene hydrogenation in excess styrene was studied.
- A reactor model combining kinetics and mass transfer processes was developed.
- The liquid-phase residence time distribution was determined by tracer pulse method.
- The kinetic parameters were estimated by nonlinear least-squares regression.
- The internal diffusion limitations in the egg-shell catalyst were non-negligible.

GRAPHICAL ABSTRACT



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ABSTRACT

Selective hydrogenation of phenylacetylene is an important reaction for the removal of a small amount of phenylacetylene from styrene monomer. In this work, the kinetics of phenylacetylene hydrogenation over an egg-shell Pd/Al₂O₃ catalyst in the presence of excess styrene was investigated by using a laboratory-scale fixed-bed reactor. The liquid-phase residence time distribution (RTD) in the reactor under different operating conditions was measured by tracer pulse method, and the Peclet number was determined based on the experimental data and the RTD model. The kinetic experiments showed that an increase in temperature and pressure or a decrease in the liquid hourly space velocity gave rise to increased conversion of phenylacetylene and decreased concentration of styrene. A rigorous mathematical model combining reaction kinetics, external mass transfer, intraparticle diffusion as well as axial dispersion of the liquid phase was developed to describe the selective hydrogenation of phenylacetylene in the reactor, and the kinetic and adsorption parameters involved in the kinetic model were estimated by minimization of the sum of squares of relative residuals between observed and model-derived concentrations of different components. The kinetic model can describe the phenylacetylene hydrogenation over the Pd/Al₂O₃ catalyst very well, and the activation energies for the hydrogenation reactions of phenylacetylene to styrene, styrene to ethylbenzene and phenylacetylene to ethylbenzene were 48.6, 52.2 and 57.9 kJ/mol, respectively.

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* Corresponding author. Tel.: +86 21 64252230; fax: +86 21 64253528.

E-mail address: zmzhou@ecust.edu.cn (Z. Zhou).

1. Introduction

Styrene, an important monomer for the production of polystyrene and several synthetic polymers in the petrochemical industry, is nowadays mainly produced by the dehydrogenation of ethylbenzene (Cavani and Trifirò, 1995). In recent years, recovery of styrene from pyrolysis gasoline (pygas, a by-product of steam cracking of naphtha) by extractive distillation has attracted much interest in both academic and industrial communities (Lee et al., 1999), because a plant with an annual production capacity of 1 million tons of ethylene can produce around 24–42 kilo tons of styrene (Li et al., 2010). Whatever the method employed, a small amount of phenylacetylene is present in the styrene-containing feedstock, which has adverse effects on the cost and process control of the polymerization as well as on the quality of the resulting polystyrene (Merrill, 2004).

It is difficult to separate phenylacetylene from styrene by distillation owing to their similar properties, and the most effective way to remove phenylacetylene, at present, is the hydrogenation of phenylacetylene, with the goal of achieving complete conversion of phenylacetylene while minimizing loss of styrene. The selective hydrogenation of dienes and alkynes is usually carried out by using supported metal catalysts (Arnold et al., 2008), e.g., Pd/C (Domínguez-Domínguez et al., 2008), Pd/Al₂O₃ (Zhou et al., 2010a), Pd/SiO₂-Al₂O₃ (Shao et al., 2010), Pt/CNTs (Li et al., 2012a, b), Mo₂C/Al₂O₃ (Pang et al., 2015), etc. Considering the relatively high reaction rate and therefore the significant effect of mass transfer on the selectivity, egg-shell catalysts with a very thin active layer (a few tenths of micrometer thickness) are used in practice (Arnold et al., 2008; Pang et al., 2015). Nevertheless, the influence of internal diffusion limitations is still non-negligible. In a previous study on the kinetics of selective hydrogenation of pygas over a commercial egg-shell catalyst (Zhou et al., 2010b), it was found that the effect of internal diffusion limitations was noticeable although the thickness of the active layer was only 60 μm.

To date, a few studies have been devoted to the kinetics of selective hydrogenation of phenylacetylene (Chaudhari et al., 1986; Jackson and Shaw, 1996; Wilhite et al., 2002; Berenblyum et al., 2015), and the activation energies reported in the literature vary greatly, being 9.7–54.6 kJ/mol for the hydrogenation of phenylacetylene to styrene and 23.2–53.6 kJ/mol for the hydrogenation of styrene to ethylbenzene. Despite the fact that different types of catalysts may have different activation energies, the contribution of the effect of mass transfer processes should not be overlooked, especially for the selective hydrogenation reactions that have high reaction rates (Vergunst et al., 2001). In fact, even though the same type of catalysts was used, e.g., Pd/C, the activation energy for the hydrogenation of phenylacetylene to styrene was reported of 51.5 kJ/mol by Chaudhari et al. (1986), but only 26 ± 2 kJ/mol by Jackson and Shaw (1996). Another shortcoming in earlier work is that the kinetic experiments were conducted in the absence of styrene in the feedstock, which is different from the real situation where excess styrene is present. Taking into account the well-known competitive adsorption of phenylacetylene and styrene on the active sites of the catalyst (Jackson and Shaw, 1996; Wilhite et al., 2002), the kinetic data obtained in excess styrene are probably different from those in the absence of styrene, which in turn affects the kinetic parameters involved in the rate expression.

Very recently, we have developed a two-step method to prepare nano-Pd/Al₂O₃ catalysts (Hu et al., 2014), which display good activity, selectivity and stability in the selective hydrogenation of phenylacetylene. Different from the previous work where fine powder catalysts (about 40 μm) were used to explore the structure–performance relationship of the Pd/Al₂O₃ catalyst (Hu et al.,

2014), a more practical mm-sized egg-shell catalyst (20–40 mesh) is employed here to study the reaction kinetics of selective hydrogenation of phenylacetylene in the presence of excess styrene, with the aim of obtaining the intrinsic kinetic parameters and probing the influence of internal diffusion limitations. The experiments are carried out in a laboratory-scale fixed-bed reactor by using a model C₈ fraction of pygas, and a rigorous reactor model including kinetics and mass transfer processes is developed. The kinetic and adsorption parameters in the rate expression are estimated by fitting the model to the observed concentrations of different components by nonlinear least-squares regression.

2. Experimental section

2.1. Catalyst preparation

The Pd/Al₂O₃ egg-shell catalyst was prepared by a two-step technique, formation of colloidal Pd nanoparticles (NPs) followed by impregnation of Pd NPs into sub-millimeter-sized Al₂O₃ (Hu et al., 2014). In the first step, about 0.42 g of polyvinylpyrrolidone (PVP) was added into a mixture of 56 mL of C₂H₅OH and 14 mL of H₂O with vigorous stirring at room temperature. After PVP was dissolved, 24 mL of H₂PdCl₄ solution (2 mmol/L) was added and stirred for 3 min. Finally 4 mL of NaBH₄ solution (25 mmol/L) was added and stirred for 3 h. In the second step, 1 g of α-Al₂O₃ powder with an average particle size of 0.68 mm (20–40 mesh) was added into the above-prepared colloidal solution at room temperature and stirred for 2 days, after which the particles were filtered, successively washed with C₂H₅OH and H₂O for several times, dried at 110 °C for 12 h, and finally calcined in air at 450 °C for 3 h with a heating rate of 2 °C/min. The resulting Pd/Al₂O₃ catalyst had a Pd loading of around 0.5 wt%. The α-Al₂O₃ support was obtained as follows: 1/8 in. γ-Al₂O₃ pellet (Alfa Aesar 43855) was first crushed and sieved to 20–40 mesh powder, and then calcined at 1200 °C for 3 h.

2.2. Selective hydrogenation of phenylacetylene

Selective hydrogenation of phenylacetylene over the Pd/Al₂O₃ catalyst was performed in a cocurrent gas–liquid downflow fixed-bed reactor with an inner diameter of 1 cm and a height of 20 cm. 1.5 g of Pd/Al₂O₃ was loaded at the middle of the reactor (catalyst bed height: 2 cm), and the upper and lower parts of the reactor were filled with glass beads. The particle sizes of catalyst and glass bead were the same. Before test, the catalyst was reduced in situ in a 50% H₂/N₂ flow at 400 °C for 2 h. A schematic diagram of the experimental setup is shown in Fig. 1. The reactor temperature, monitored by a thermocouple located at the center of the catalyst bed, was maintained at the desired value by adjusting the temperature of the water circulating through the reactor jacket. The liquid feedstock was composed of phenylacetylene (2 wt%), styrene (28 wt%), ethylbenzene (30 wt%) and xylene (40 wt%), the composition of which was similar to that of commercial C₈ fraction of pygas (Li et al., 2010). The kinetic experiments were conducted over a temperature range of 30–70 °C and a pressure range of 2–8 bar. The liquid flow rate was accurately controlled by a metering pump, varying from 2 to 5 mL/min, while H₂ was introduced through a mass flow controller with a flow rate between 16 and 39 NmL/min. In each run, the molar flow rate ratio of H₂ to phenylacetylene in the feed was fixed to be 2.

During the kinetic experiments, each run was stabilized for 1 h before sample collection and analysis. The product composition was analyzed by a gas chromatograph (HP 6890) equipped with a flame ionization detector and a DB-Wax capillary column (30 m × 0.32 mm × 0.5 μm). The column oven temperature program was as

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