Monodispersed Pd-nanoparticles on carbon fiber fabrics as structured catalyst for selective hydrogenation

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Abstract

Monodispersed Pd-nanoparticles (~ 8 nm) prepared via a modified microemulsion method were deposited on active carbon fibers (ACF) fabrics and studied in a semi-batch 1-hexyne liquid-phase hydrogenation. The catalyst Pd(0.45 wt%)/ACF demonstrated > 96% selectivity to 1-hexene up to 90% of conversion. Initial activity at 303 K, 1.3 MPa pressure, in n-heptane as a solvent was 0.14 \( \text{kmol}_\text{H}_2 \text{ kg}^{-1} \text{Pd} \text{ s}^{-1} \). Assuming a Langmuir–Hinshelwood kinetics with a weak hydrogen adsorption a kinetic model was developed. It was shown to be consistent with the experimental data and allowed determining the main kinetic parameters.

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1. Introduction

Catalytic hydrogenation is one of the key processes in fine chemicals production. The performance of the hydrogenation process and product distribution are strongly influenced by the catalyst activity and selectivity, the interaction of chemical kinetics and mass transfer, as well as the reactor design. To avoid internal and external mass transfer limitations and to attain high product selectivity catalyst particles of small diameter are required. In technical applications the minimal size, however, is limited due to the catalyst handling.

One approach to overcome these problems is the use of filamentous catalytic materials (Kiwi-Minsker, 2002). The diameters of the filaments are in the order of several micrometers and correspond to the diameter of the traditional suspension catalysts. Therefore, internal mass transfer limitations could be minimized. Platinum-group metals were deposited on filamentous woven cloths and demonstrated high efficiency in various liquid-phase hydrogenations (Höller et al., 2000; Macias Peres et al., 1997).

Among the structured supports, activated carbon fiber (ACF) fabrics gained special attention due to high specific surface area of 600–3000 \( \text{m}^2 \text{ g}^{-1} \), easy handling and metal recovery, low resistance to the passage of fluid, and high fluid permeability. Pd/ACF catalysts showed high activity and selectivity in 2-butyne-1,4-diol selective hydrogenation both in the stirred tank reactor (Joannet et al., 2002) and a loop reactor with an integrated bubble column staged by the catalyst layers (Kiwi-Minsker et al., 2004). However, conventional catalyst preparation by ion-exchange does not result in the formation of monodispersed Pd nanoparticles. Active metal size control is an important issue for the structure-sensitive reactions, like alkynes hydrogenation. The highest activity in 1-butyne hydrogenation was observed with Pd dispersions < 20% (Boitiaux et al., 1983). To achieve Pd nanoparticles monodispersion on ACF support, we prepared Pd/ACF catalysts (Semagina et al., 2006) with monodispersed particles of ~ 8 nm diameter via a modified reverse microemulsion technique (Eriksson et al., 2004). The present paper reports on the kinetics of 1-hexyne liquid phase hydrogenation over the novel microemulsion-derived Pd/ACF catalysts. The reaction kinetics was studied in a semi-batch reactor; a kinetic model was developed and the main kinetic parameters were determined.
2. Experimental

2.1. The preparation method

Pd/ACF catalysts were prepared via a procedure described by Semagina et al. (2006). KOH mex® ACF Fabrics AW-1101 (BET specific surface area of 880 m² g⁻¹, average pore diameter of 2 nm) were purchased from Taiwan Carbon Technology Co., Ltd. and used as a support after pretreatment in a boiling aqueous solution of 6.5 wt% HNO₃ for 1 h. The surfactant AOT (sodium di-2-ethylhexylsulfosuccinate) was vacuum-dried for 24 h at 333 K directly before use. Dried isooctane (max. 0.005% water) was used for the microemulsion.

For the catalyst preparation 0.05 M Pd(NH₃)₄Cl₂ solution of pH 8.5 was used as a metal precursor, and 1 M hydrazine hydrate as a reducing agent. Nanoparticle-containing microemulsion water/AOT/isoctane with the water-to-surfactant molar ratio of 3 was prepared according to (Chen et al., 1999). A 0.35 M solution of AOT in 200 mL of isooctane was divided in half. The 1.88 mL of the palladium precursor and reductant solutions were injected separately to AOT/isoctane and stirred until transparent microemulsions were obtained, which were mixed immediately. The reverse microemulsion was stirred at room temperature for 1 h, and then placed into a rotary evaporator at 323 K for 20 min. Methanol was added to the residuals at room temperature to dissolve AOT and to flocculate the Pd nanoparticles. After centrifugation at 8000 rpm (20 min), the supernatant was decanted and the washing was repeated. The precipitate was redispersed in 12 mL of water by ultrasonic treatment for 20 min. This macroscopically homogeneous black suspension was used immediately to impregnate 0.5 g of ACF. The impregnated support was air dried at 393 K for 40 min, followed by washing in heptane and subsequent impregnation step. Finally, the catalyst was air-dried overnight at 393 K.

The method allows retaining the nanoparticles monodispersity by avoiding the calcination step. High-resolution transmission electron microscopy analysis confirmed fcc crystalline structure of Pd nanoparticles of 8 nm size and their monodispersity (< ±15%).

2.2. Hydrogenation experiments

Hydrogenations were carried out in a semi-batch reactor as described previously (Joannet et al., 2002). The structured Pd/ACF catalyst (typically, 2 pieces of 1 × 2.5 cm) was placed between two metal gauzes (2 × 4 cm) fixed on the self-gassing hollow shaft stirrer. For the reaction with the powdered Lindlar catalyst, 8-blade disk turbine impeller was used. A typical experiment was performed at 303 K, 1.3 MPa H₂ pressure, 1500 rpm. n-Heptane was used as a reaction medium containing 0.5 kmol m⁻³ of 1-hexyne in 100 mL. The substrate-to-palladium molar ratio was between 20 000–30 000. The reaction kinetics was studied at 293–323 K and pressure between 0.4–1.7 MPa. For the reuse experiments, the catalyst was air-dried at room temperature between the reaction runs.

The samples of the reaction mixtures were periodically withdrawn from the reactor. The GC analysis was performed using AutoSystem XL (Perkin Elmer) equipped with a 100 m Petrocol DH 0.25 mm capillary column with a 0.5 μm coating at the oven temperature of 333 K and the carrier gas (He) pressure of 280 kPa. Injector and FID temperature were 493 K. n-Octane was used as the internal standard.

The initial reaction rate, \( r_0 \) [kmol H₂ kg⁻¹ Pd⁻¹ s⁻¹], was used as a characteristic of catalytic activity. Selectivity to 1-hexene was calculated as the ratio of its concentration to the total concentration of all products in the reaction mixture. As by-products, \( n \)-hexane, cis- and trans-2-hexenes were found. Kinetic modeling was performed using Berkley Madonna™ software (Macey and Oster, 1997–2001).

3. Results and discussion

Kinetic modeling was performed based on the simplified reaction scheme (Fig. 1), which has been reported for liquid-phase alkyne hydrogenation over Pd catalysts (Boitiaux et al., 1983). In this approach direct alkyne hydrogenation to alkane is neglected, and transformations of 2-cis- and 2-trans-hexenes are assumed to be identical without a reverse isomerisation to 1-hexene.

To ensure that the reaction kinetics is not influenced by diffusion, several catalysts with different Pd loading (0.45 wt%, 0.6 wt%, 1.2 wt%) and the same dispersion were synthesized. They showed an identical initial activity of 0.140 ± 0.004 kmol H₂ kg⁻¹ Pd⁻¹ s⁻¹ at 303 K and 1.3 MPa H₂. Selectivity to 1-hexene was 97.1 ± 0.4% up to 80% conversion, and 95.9 ± 0.4% at 90% conversion.

The kinetics of 1-hexyne hydrogenation was studied over Pd(0.45 wt%)/ACF catalyst. The initial reaction rate as a function of hydrogen pressure is presented in Fig. 2. A first order towards H₂ was observed being in agreement with the reported data on 1-butyne liquid-phase hydrogenation (Boitiaux et al., 1983).

Typical concentration–time profiles are presented in Fig. 3 showing the experimental and simulated curves. A negative apparent order towards 1-hexyne can be explained on the base of a Langmuir–Hinshelwood kinetic model assuming competitive adsorption of the reactants with weak non-dissociative adsorption of H₂ and a bimolecular reaction of the adsorbed species. The transformation rate of 1-hexyne can be expressed as follows:

\[
K_{H₂}C_{H₂}K_YC_Y \left(1 + K_YC_Y + K_{H₂}C_{H₂} + K_{1E}C_{1E} + K_{2E}C_{2E}\right)^{-2}
\]

As the adsorption equilibrium constants of the olefinic products are small compared to the adsorption constant of the acetylenic reactant, it can be assumed that \( K_E \cong K_{1E} \cong K_{2E} \), thus reducing the number of adjustable model parameters. Taking also into consideration weak hydrogen adsorption on Pt group metals \( K_{H₂} \ll 1 \) (Singh and Vannice, 2000) that is consistent with the observed first order to H₂, Eq. (1) may be
For other reactions presented in Fig. 1, the expressions can be developed:

\[ r_2 = k_2 \frac{K_{H_2}C_{H_2}K_EC_{1E}}{(1 + K_YC_Y + K_EC_{1E} + C_{2E}))^2}, \]  
\[ r_3 = k_3 \frac{K_EC_{1E}}{(1 + K_YC_Y + K_EC_{1E} + C_{2E}))^2}, \]  
\[ r_4 = k_4 \frac{K_{H_2}C_{H_2}K_EC_{2E}}{(1 + K_YC_Y + K_EC_{1E} + C_{2E}))^2}. \]  

The mass balances for 1-hexyne and the reaction products are given by the following differential equations:

\[ \frac{dC_Y}{dt} = -\frac{m_{\text{cat}}}{V_L} r_1, \]  
\[ \frac{dC_{1E}}{dt} = \frac{m_{\text{cat}}}{V_L} (r_1 - r_2 - r_3), \]  
\[ \frac{dC_{2E}}{dt} = \frac{m_{\text{cat}}}{V_L} (r_3 - r_4), \]  
\[ \frac{dC_A}{dt} = \frac{m_{\text{cat}}}{V_L} (r_2 + r_4), \]  

where \( m_{\text{cat}} \) is the catalyst mass and \( V_L \) is a volume of liquid phase in the reactor.

Eqs. (6)–(9) were solved numerically with a Rosenbrock method. Hydrogen concentration under the reaction conditions (303 K, 1.3 MPa) is 0.105 kmol m\(^{-3}\) (Brunner, 1985). The model parameters were estimated by fitting the simulated curves to the experimental data (Fig. 3). The square of the Pearson product moment correlation coefficient between the experimental and simulated data was never less than 0.9. The adsorption equilibrium constant of 1-hexyne was found to be two orders of magnitude higher than for olefinic products \( K_Y/K_E = 111 \), while the rate constant of 1-hexene hydrogenation, \( k_2 \) was 2.5-fold higher than \( k_1 \). This is in agreement with the reaction thermodynamics if high selectivity to 1-alkene is due to the stronger adsorption of alkyne compared to alkene and not to the higher hydrogenation rate constant (Molnar et al., 2001). The ratio \( K_Y/K_{H_2} \) was found to be 511 being close to the reported value of 400 for acetylene hydrogenation over Pd/Al\(_2\)O\(_3\) (Bos et al., 1993). This confirms weak hydrogen adsorption assumed.
A series of kinetic experiments was performed at constant pressure of 1.3 MPa and temperature variation from 293 to 323 K. Kinetic modelling allowed determining the intrinsic rate constants at each temperature. Arrhenius plots for each reaction are presented in Fig. 4a. The activation energies were found to be $E_1 = 50$ kJ mol$^{-1}$, $E_2 = 65$ kJ mol$^{-1}$, $E_3 = 61$ kJ mol$^{-1}$, $E_4 = 42$ kJ mol$^{-1}$ and the pre-exponential factors characterizing the number of active sites were calculated as $k_{o(1)} = 2 \times 10^{12}$ kmol kg$_\text{Pd}$$^{-1}$ s$^{-1}$, $k_{o(2)} = 2 \times 10^{15}$ kmol kg$_\text{Pd}$$^{-1}$ s$^{-1}$, $k_{o(3)} = 3 \times 10^{11}$ kmol kg$_\text{Pd}$$^{-1}$ s$^{-1}$, $k_{o(4)} = 5 \times 10^{8}$ kmol kg$_\text{Pd}$$^{-1}$ s$^{-1}$. The enthalpy of adsorption of 1-hexyne, hexenes and hydrogen were calculated from the temperature dependencies of the adsorption equilibrium constants (Fig. 4b) and found to be $-\Delta H_F = 30$ kJ mol$^{-1}$, $-\Delta H_E = 21$ kJ mol$^{-1}$, $-\Delta H_H = 28$ kJ mol$^{-1}$. These values are in fair agreement with the reported for liquid- and gas-phase hydrogenations over Pd-group catalysts (Singh and Vannice, 1999; Vattuone et al., 2000; Vincent and Gonzalez, 2001; Zea et al., 2005).

Tests on the catalyst stability in the six repeated runs revealed negligible Pd leaching: the initial reaction rate of $0.085 \pm 0.008$ kmol kg$_\text{Pd}$ s$^{-1}$ remained constant from the second run. No changes in selectivity were observed at reuse (Semagina et al., 2006).

4. Conclusions

- Monodispersed Pd-nanoparticles (∼ 8 nm) were prepared via modified microemulsion method and deposited on active carbon fibers (ACF) fabrics.
- The catalyst Pd(0.45 wt%)/ACF was tested in a semi-batch 1-hexyne liquid-phase hydrogenation and showed the initial activity of $0.14$ kmol kg$_\text{Pd}$ s$^{-1}$ (303 K, 1.3 MPa, in $n$-heptane). The selectivity to 1-hexene of > 96% up to 90% conversion was observed.
- Assuming Langmuir–Hinshelwood kinetics with a weak hydrogen adsorption, a kinetic model was developed being consistent with the experimental data. The main kinetic parameters like reaction orders, enthalpy of adsorption and activation energy were determined.
- The developed Pd/ACF catalyst is suitable for performing multiphase reactions in the reactors with structured catalytic beds.

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References


