

Continuous Catalytic Hydrogenolysis of Polyaromatic Hydrocarbon (PAH) Compounds in Hydrogen-Supercritical Carbon Dioxide (ScCO₂)

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Introduction

Polycyclic aromatic hydrocarbons (PAHs) are the class of hydrocarbons consisting of molecules of two or more fused benzene rings. They are found in higher concentrations at industrial sites associated with petroleum, coal-tar, gas production and wood preservative industries. Because certain members of this class have been demonstrated to be both carcinogenic and mutagenic, PAHs are considered as environmental priority pollutants (US EPA).¹ They are recalcitrant in soils with half-lives in soil are similar to the more highly chlorinated polychlorinated biphenyl (PCB) compounds.^{2,3}

Hydrogenation over transition metal catalyst to reduce PAHs has been broadly investigated by several researchers.^{4,5,6,7,8} Typically, these hydrogenation reactions have been carried out under high temperature and high H₂ pressure. The product distribution of PAHs hydrogenation is highly dependent on catalyst type, temperature, pressure and solvent. Previous research on catalytic hydrogenation of PAHs over palladium supported on gamma-alumina in batch reaction system indicated that PAHs underwent efficient hydrogenation under mild conditions. Because the ScCO₂ is totally miscible with H₂, it is possible to increase the efficiency of PAHs hydrogenation with continuous hydrogenation by using ScCO₂ as a transportation and reaction medium.

The objectives of the current study were to devise and optimize a device to continuously hydrogenate selected 3-5 fused ring PAHs over Pd/g-Al₂O₃ under mild conditions of temperature and pressure. All the PAHs were efficiently transformed to highly saturated products providing an alternative remediation technique for PAH contaminated soil.

Material and Methods

Chemicals: Anthracene, phenanthrene, chrysene, and benzo(α)pyrene; Pd°/g-Al₂O₃ (5%, w/w) and organic solvents were purchased from Aldrich Chemical Co., Oakville, ON and were used as received. Molecular hydrogen and carbon dioxide were purchased from MEGS, Saint Laurent, QC.

Reactor and Operation: The reactor consisted of a 25x1 cm column containing palladium supported on gamma alumina (Pd°/γAl₂O₃) that was terminated with a capillary restrictor. (25 cm x0.05 mm inner diameter) In operation, substrate was injected (2.5mg) as a plug or pumped continuously (0.05 mg/min) for up to 3 hours into the reactor, that had pre-equilibrated to the desired operating pressure/temperature. Mixtures of hydrogen and carbon dioxide (~5%, 16% and 30% H₂, v/v) were passed through the reactor maintained at the desired pressure. The reaction products were collected in an organic trapping solvent positioned at the exit of the restrictor. Samples were collected in every 10 or 15 min during the running of the experiment up to 210 min. The reactions were monitored by gas chromatography with mass spectrometric or flame ionization detection (FID).

Results and Discussion

The influences of the reaction pressure (2300-3500 psi) and solvent amount were evaluated for the hydrogenation of 2.5mg anthracene over Pd°/g-Al₂O₃ during 60 minutes. The substrate was injected into the reactor and 6 samples were collected in every 10 minutes subsequently. The residue of substrate and products in the reactor was also collected. At 90 °C and with the pressure of 2300 psi, 2600 psi 3000 psi and 3500 psi of ScCO₂ (~4ml/min) respectively, anthracene was hydrogenated into octahydroanthracenes and tetradecahydroanthracenes. With the

condition of 3000psi and 3500psi, more than 80% of products were eluted out in 20 minutes and almost all the products can be transferred out of the column reactor by scCO_2 in 1 hour. While with 2600 psi and 2300 psi, the transfer rate of products were only around 50% and 15% in 20 minutes and reached to 80% in 1 hour. This suggested the higher pressure of scCO_2 , the higher transfer rate of the products and the more efficient of hydrogenation process. Under the condition of 90°C and 3500 psi of ScCO_2 , 0.1 ml/min, 0.5 ml/min, 1.0 ml/min and 1.5 ml/min hexane was flushed with ScCO_2 respectively. The mass transfer of the anthracene hydrogenation with 1.5 ml/min hexane seemed better than those of 0.1 ml/min, 0.5 ml/min and 1.0 ml/min (See Figure 1). But the hydrogenation of anthracene with 0.1ml/min hexane adding in the ScCO_2 has the highest the tetradecahydroanthracenes to octahydroanthracenes ratio than those of 0.5 ml/min, 1.0 ml/min and 1.5 ml/min. This may due to the more solvent with the ScCO_2 , the less concentration of H_2 in the fluid. Too much solvent like 1.5 ml/min in the ScCO_2 sometimes caused the phase of the fluid not being homogeneous and blocked the flow system. So adding small amount of hexane in the ScCO_2 can help the mass transfer of the anthracene hydrogenation process.

The hydrogenation of phenanthrene (1 mg/min continuously pumped into the reactor) with different concentration of H_2 of approximately 5%, 16% and 30% (v/v) in the ScCO_2 (~4 ml/min) at 90°C and 3000 psi were also investigated (see Table 1). The main products of the phenanthrene hydrogenation were tetradecahydrophenanthrenes (perhydrophenanthrenes) and octahydrophenanthrenes, and small amount of biphenyl in the case of with 30% H_2 in ScCO_2 . The higher amount of H_2 in the ScCO_2 , the more efficient of phenanthrene hydrogenation with higher perhydrophenanthrene ratio in the products. The reaction with 5% H_2 in ScCO_2 had octahydrophenanthrene as the main products. But the high concentration of H_2 in ScCO_2 causes the decrease of solubility of the substrate and products in ScCO_2 and may block the flow reaction system with long time running.

With 3000 psi, ~10 ml/min ScCO_2 (~16% H_2) and 150 °C, hydrogenation of anthracene, phenanthrene, chrysene and benzo(a)pyrene (see Figure 2) in continuous reactions were tested respectively. The rate of substrate of anthracene, and phenanthrene into the reactor was 0.1 mg/min, while the rate of chrysene and benzo(a)pyrene were 0.05 mg/min. The samples of hydrogenation products were collected in every 15 minutes up to 3.5 hours. After 30 min, the processes of the hydrogenation of anthracene and phenanthrene became stable and anthracene and phenanthrene were hydrogenated to fully saturated tetradecahydroanthracenes (6 detected isomers) and tetradecahydrophenanthrenes (5 detected isomers), with a small amount of bicyclohexane (no more than 1% and 4% respectively). Chrysene was hydrogenated into fully saturated octadecahydrochrysenes (8 detected isomers) after 60 min and the process became stable. Benzo(a)pyrene hydrogenation process got stable also after 75 minutes with fully saturated eicosahydrobenzo(a)pyrenes (7 detected isomers) as the product. Hydrogenation of benzo(a)pyrene at the temperatures of 200 °C and 250 °C respectively under 3000 psi and ~10 ml/min of ScCO_2 were also investigated (Figure 3). At higher temperatures, the products of the benzo(a)pyrene hydrogenation were as the same as that at 150 °C. No cracking of the aromatic ring was observed. But the distribution of the isomers varied with the temperature of the reaction. High reaction temperature favors the early elute isomers on GC chromatograph (the first isomer), while the low temperature favors the 4th and 6th isomers peaks in the GC chromatograph.

Conclusion

In summary, the efficiency of the hydrogenation of PAHs increases with the H_2 concentration, temperature and pressure and flow rate of ScCO_2 , small amount of solvent was observed with no or little effect on the hydrogenation of PAHs. The hydrogenation of PAHs can be achieved to the fully saturated hydrogenation products with ring structure remained.

References

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Figures and Table

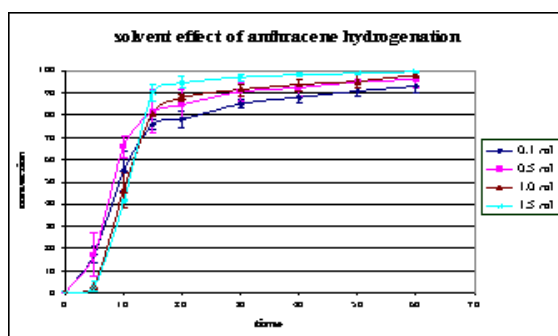


Figure 1. The effect of Hexane on anthracene hydrogenation mass transfer rate through the reactor at 90°C and 3500 psi ScCO₂ within 1 hour.

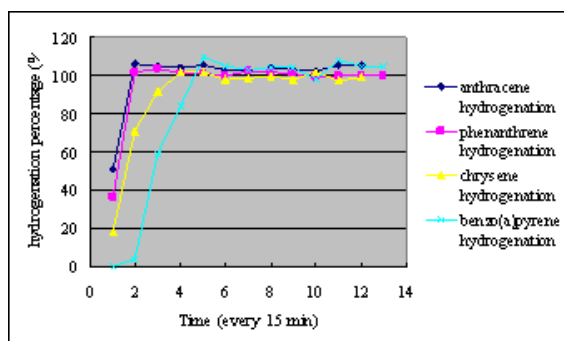


Figure 2. Hydrogenation percentage of anthracene, phenanthrene, chrysene and benzo(a)pyrene hydrogenation with time at 3000 psi and 150 °C.

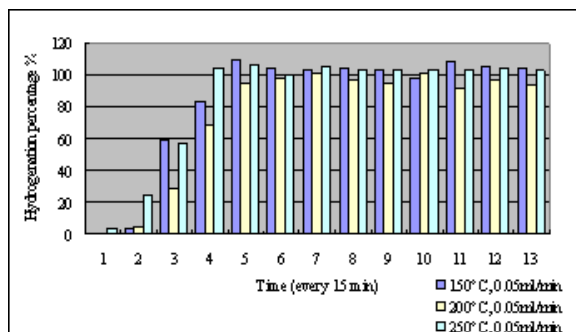


Figure 3. Hydrogenation percentage of benzo(a)pyrene hydrogenation with time at 3000 psi and 150 °C, 200 °C and 250 °C respectively.

Table 1. Mass balance of phenanthrene hydrogenation at 3000psi, 90 °C, 1 mg/min substrate with different H₂ concentration in ScCO₂ (flow rate ~4 ml/min).

H ₂	Products	1	2	3	4	5	6	7	8
~5% H ₂	octahydrophenanthrene	0	13±34	60±14	77±9	77±10	78±2	79±5	81±4
	perhydrophenanthrene	0	25±8	26±6	27±12	27±8	26±2	26±2	25±4
	sum	0	38±7	86±8	104±4	104±5	103±1	105±3	106±4
~16% H ₂	octahydrophenanthrene	0	7±41	28±4	33±28	31±44	13±2	9±8	9±7
	perhydrophenanthrene	0	26±9	56±4	61±1	70±9	55±4	52±0	61±2
	sum	0	33±24	84±7	94±11	100±1	95±5	88±1	97±3
	biphenyl	0	0	5±2	5±1	5±1	5±3	5±1	5±3
~30% H ₂	octahydroanthracene	0	4±3	4±2	4±3	5±4	5±3	5±6	5±6
	perhydroanthracene	0	13±43	22±7	34±15	68±10	95±7	102±5	108±4
	sum	0	17±31	31±5	44±12	77±9	105±7	111±5	117±3