Reactivation of Spent Pd/AC Catalyst by Supercritical CO_2 Fluid Extraction

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In this article, we reported a nondestructive and environmentally friendly method for the reactivation of a spent Pd/AC catalyst for the hydrogenation of benzoic acid by using supercritical CO_2 ($scCO_2$) fluid extraction. The effects of reactivation conditions, such as extraction temperature, pressure, CO_2 flow rate, and time, on the activity of the reactivated Pd/AC catalyst, were presented. The catalyst was characterized by N_2 physisorption, laser particle size analysis, and transmission electron spectroscopy, and the liquid extract was analyzed by GC-MS. It is found that $scCO_2$ fluid extraction was very efficient in eliminating organic substances blocking the pores of the catalyst, while did not affect noticeably the granule size of the catalyst and the particle size of Pd. The reactivated Pd/AC catalyst regained more than 70% of the activity of the fresh 5.0 wt % Pd/AC catalyst, and has been successfully used in an industrial unit for the hydrogenation of benzoic acid. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2382–2388, 2009

Keywords: Pd/AC, supercritical CO_2 fluid, reactivation, benzoic acid, hydrogenation

Introduction

The Pd/activated carbon catalyst (Pd/AC) has been widely used in petrochemical, pharmaceutical, and agrochemical industries because of its excellent catalytic performance in reactions including liquid phase hydrogenations.[1–3] For example, the catalytic hydrogenation of benzoic acid to cyclohexanecarboxylic acid (CCA) over the Pd/AC catalyst constitutes an essential stage in the commercial manufacture of caprolactam from toluene (SNIA process).[4] In this process, benzoic acid is hydrogenated over 5.4 t of 5.0 wt % Pd/AC catalyst in a cascade of four continuously operated and stirred tank reactors at ca. 443 K under H_2 pressure of 2.0 MPa.[4–6] However, this process is impaired by the fast deactivation of the expensive Pd/AC catalyst. To maintain the required activity level, about 80 kg of the used Pd/AC catalyst is unloaded from the reactor (termed as the spent catalyst), which is replaced by the same amount of the fresh Pd/AC catalyst even on a daily basis. Although the noble Pd metal on the spent Pd/AC catalyst can be recovered by incineration and acid dissolution, such traditional recovery process is environmentally and atomically unfriendly due to the consumption of AC and acid, emission of CO_2, and the pollution of the waste acid. Moreover, these factors all serve to significantly increase capital and operating costs of the process. Thus, it is highly desirable to develop a mild and environmentally friendlier alternative to the recovery of the spent Pd/AC catalyst in its entirety rather than to the recovery of Pd alone.

In general, the reasons for catalyst deactivation can be categorized as (1) poisoning, (2) carbonaceous species deposition, or (3) sintering or restructuring.[7] In our preceding

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Correspondence concerning this article should be addressed to B. Zong at zongbn@ripp-sinopec.com work, we have demonstrated that deactivation of the Pd/AC catalyst by CO poisoning arising from the decarboxylation of CCA can be amended by introducing a novel Ni-based promoter for the methanation of CO to harmless CH_4.[8] However, deactivation, although less prominent than that before the process improvement, still occurs. Characterizations of the spent Pd/AC catalyst by X-ray diffraction and transmission electron microscopy (TEM) revealed no obvious growth of the Pd particles, strongly suggesting that the deposition of the carbonaceous species such as impurities in benzoic acid or as byproducts formed during the hydrogenation process is the principal factor underlying the loss of the activity. It is noted that removal of carbonaceous species from activated carbon by supercritical CO_2 ($scCO_2$) fluid extraction has long been adopted in food industry and waste water treatment.[9] It is well known that gas-like and liquid-like properties are combined for supercritical fluid, rendering its diffusivities gas-like and densities/dissolving power more liquid-like.[10,11] This will result in an enhancement of the diffusivity and solubility of heavy organic compounds adsorbed on porous catalysts.

As to the application of supercritical fluid to the regeneration of deactivated catalysts, while most works have been focused on the removal of oligomers on solid acid catalysts,[12–16] less attention has been received by the reactivation of metal catalysts for hydrogenation reactions by this technique. Available examples include $scCO_2$ reactivation of a Pd/Al_2O_3 catalyst for cyclododecatriene hydrogenation,[17] and $scCO_2$ regeneration of a spent Pd/AC catalyst used in the hydrogenation of a variety of organic compounds.[18,19] Provided that the carbonaceous species on the spent Pd/AC catalyst for the hydrogenation of benzoic acid can be eliminated by $scCO_2$, the environmental impact and cost for the regeneration of the spent Pd/AC catalyst can be substantially reduced. Moreover, commercialization of the supercritical fluid-based reactivation method for the spent catalyst has not been reported so far.

Based on the above concept and considerations, we have made preliminary studies on the reactivation of the spent Pd/AC catalyst for the hydrogenation of benzoic acid by $scCO_2$ fluid extraction, and some results have been reported elsewhere.[20,21] In the present contribution, we reported systematically the effects of the parameters of $scCO_2$ fluid extraction including temperature, pressure, CO_2 flow rate, and time on the hydrogenation activity of the reactivated Pd/AC catalyst. The efficiency of $scCO_2$ fluid extraction was compared with other nondestructive reactivation methods such as washing by hot NaOH aqueous solution or by toluene. Our first practice in the industrial utilization of $scCO_2$ fluid extraction to reactivate the spent Pd/AC catalyst was also presented in this article.

Experimental

Reactivation of the spent Pd/AC catalyst by $scCO_2$ fluid extraction

A schematic diagram of the bench-scale apparatus for $scCO_2$ fluid extraction of the spent Pd/AC catalyst is depicted in Figure 1. The extractor is a jacketed AISI 316 stainless steel vessel with a volume of 1 L (i.d. 6.6 cm, height 30 cm). In a typical run, 500 g of the spent Pd/AC catalyst from an industrial unit at Shijiazhuang Chemical Fibre, Sinopec, were loaded in the extractor. Food-grade liquid CO_2 (Beijing LingYun Chemicals) was pumped from a CO_2 cylinder or a liquid CO_2 reservoir to the extractor. The extractor was then heated and pressurized to attain the supercritical conditions of CO_2. After $scCO_2$ fluid extraction, $scCO_2$ with the dissolved carbonaceous species entered the separators, in which the carbonaceous species was precipitated and $scCO_2$ became gaseous. Gaseous CO_2 was recovered by condensation before returning to the liquid CO_2 reservoir. The reactivated Pd/AC catalyst was characterized by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Elemental IRIS Intrepid), N_2 physisorption (Micromeritics TriStar3000), laser particle size distribution (Malvern Mastersizer E), and TEM (FEI TECNAI F20), while the liquid extract was analyzed by a Finnigan Voyagen GC-MS equipped with an FFAP capillary column.

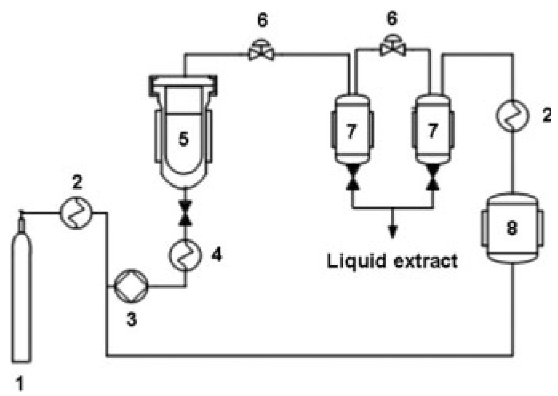

Figure 1. Schematic illustration of the $scCO_2$ fluid extraction apparatus for reactivating the spent Pd/AC catalyst.

(1) CO_2 cylinder; (2) cooler; (3) pump; (4) heat exchanger; (5) extractor; (6) back pressure regulator; (7) separator; (8) CO_2 reservoir.

Activity test

The activity of the reactivated Pd/AC catalyst in the hydrogenation of benzoic acid was examined in a bench-scale stainless steel shaking autoclave of 500 mL capacity. Two hundred grams of benzoic acid and 2.0 g of the reactivated Pd/AC catalyst (1 wt % with respect to benzoic acid) were loaded in the autoclave. After being flushed with N_2 for several times, the autoclave was filled with H_2 to 2.0 MPa, heated to 423 K, and pressurized with H_2 to 11.0 MPa. The shaking rate of the stirrer was 50 rpm. When the system pressure dropped to 9.0 MPa due to the uptake of H_2, the autoclave was charged with H_2 immediately to restore the pressure to 11.0 MPa. The activity of the Pd/AC catalyst is expressed as $Z_0 = r_0/4$, where r_0 is the H_2 pressure dropped per min at the beginning of the reaction. For the fresh 5 wt % Pd/AC catalyst, Z_0 was usually around 1.0–1.1 due to the fluctuation of the quality of different batches, while for the spent Pd/AC catalyst, Z_0 was below 0.2.

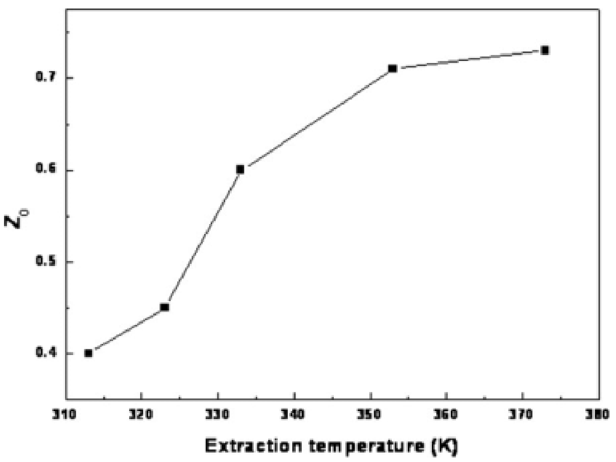

Figure 2. Effect of extraction temperature on the activity of the reactivated Pd/AC catalyst in hydrogenation of benzoic acid.

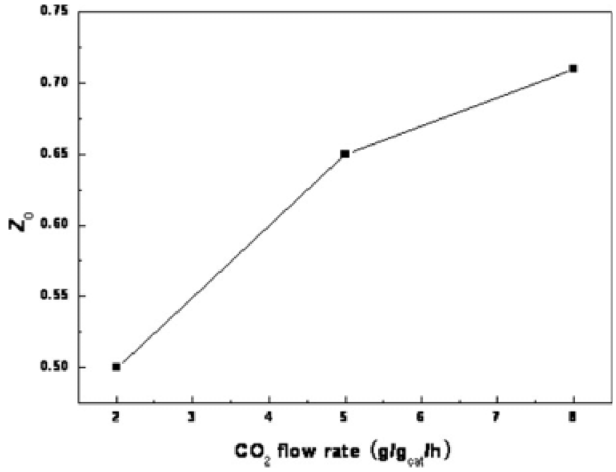

Figure 4. Effect of CO_2 flow rate on the activity of the reactivated Pd/AC catalyst in hydrogenation of benzoic acid.

Results and Discussion

Bench-scale $scCO_2$ fluid extraction of the spent Pd/AC catalyst

Figure 2 shows the evolution of the activity of the reactivated Pd/AC catalyst in the hydrogenation of benzoic acid with the extraction temperature. Other extraction parameters were fixed as extraction pressure of 15 MPa, CO_2 flow rate of 8 g/(g_{cat}·h), and extraction time of 8 h. It is found that Z_0 of the reactivated Pd/AC catalyst increased continuously from 0.40 to 0.73 when the extraction temperature was elevated from 313 to 373 K. According to Grajek,[9] high extraction temperature not only accelerates the desorption of the adsorbate from the adsorbent but also increases the solubility of the adsorbate in the $scCO_2$ fluid, which are both advantageous to the extraction of the carbonaceous species adsorbed on the spent Pd/AC catalyst.

Figure 3 plots the activity of the reactivated Pd/AC catalyst in the hydrogenation of benzoic acid against the extraction pressure. Other extraction parameters were fixed as extraction temperature of 353 K, CO_2 flow rate of 8 g/(g_{cat}·h), and extraction time of 8 h. It can be seen that the activity of the reactivated Pd/AC catalyst increased with the extraction pressure, which can be explained by the higher density of the $scCO_2$ fluid at higher pressure. To a first approximation, the solvating power of the supercritical fluid is proportional to its density,[9] so the solubility of the adsorbate was increased and more carbonaceous species were dissolved from the spent Pd/AC catalyst at higher extraction pressure. On the other hand, according to the Peng-Robinson equation of state,[22] the increment of the density of the $scCO_2$ fluid is more pronounced in the pressure range of 5–25 MPa. It can be seen from Figure 3 that Z_0 increased only by 0.02 when the extraction pressure was increased from 20 to 30 MPa.

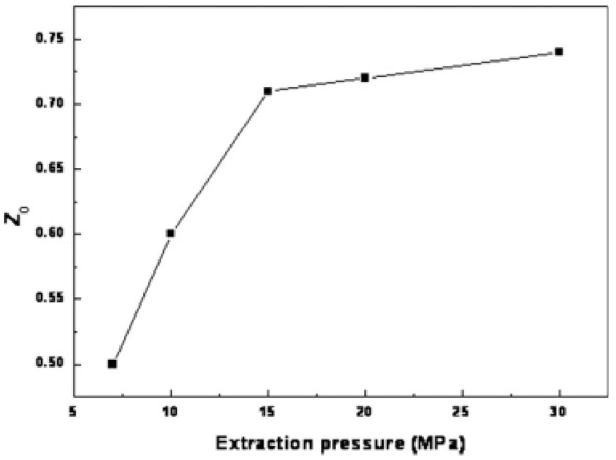

Figure 3. Effect of extraction pressure on the activity of the reactivated Pd/AC catalyst in hydrogenation of benzoic acid.

Figure 4 presents the effect of the flow rate of the $scCO_2$ fluid on the activity of the reactivated Pd/AC catalyst in the hydrogenation of benzoic acid. Other extraction parameters were fixed as extraction temperature of 353 K, extraction pressure of 15 MPa, and extraction time of 8 h. As expected, the faster the flow rate of the $scCO_2$ fluid, the higher was the activity of the reactivated Pd/AC catalyst. At CO_2 flow rate of 8 g/(g_{cat}·h), Z_0 of the reactivated Pd/AC catalyst was 0.71 as compared to 0.19 of the spent Pd/AC catalyst and 1.0 of the fresh 5 wt % Pd/AC catalyst (Table 1).

Table 1. Textural and Catalytic Properties of the Fresh, the Spent, and the Reactivated Pd/AC Catalysts

Catalyst	S_{BET} (m^2/g)	V_{pore}[*] (cm^3/g)	d_{pore} (nm)	Z_0
Fresh	995	0.605 (0.409)	1.82	1.00
Spent	373	0.230 (0.148)	2.03	0.19
Reactivated by $scCO_2$	724	0.521 (0.350)	1.87	0.71
Reactivated by hot NaOH aqueous solutio[†]	560	0.350 (0.190)	2.00	0.40
Reactivated by toluene[‡]	612	0.371 (0.230)	1.90	0.59

[*] Micropore volumes are given in parenthesis.

[†] Reactivation conditions: 10 wt % NaOH aqueous solution, NaOH/catalyst = 1 (weight ratio), temperature = 323–333 K, time = 2 h.

[‡] Reactivation conditions: toluene/catalyst = 4 (weight ratio), temperature = 298 K, time = 2 h.

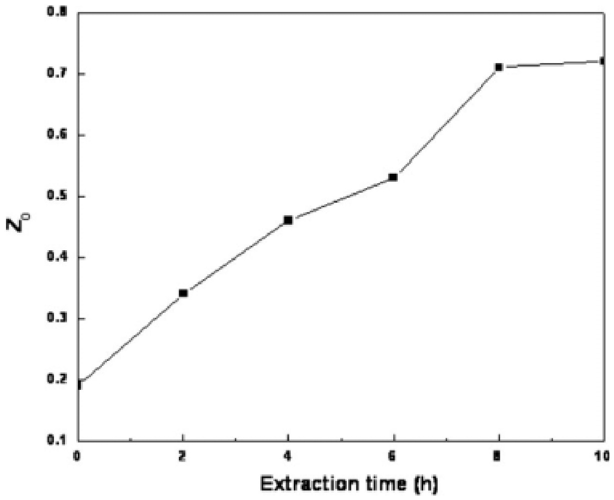

Figure 5. Effect of extraction time on the activity of the reactivated Pd/AC catalyst in hydrogenation of benzoic acid.

Figure 5 demonstrates the effect of the extraction time on the activity of the reactivated Pd/AC catalyst. Other extraction parameters were fixed as extraction temperature of 353 K, extraction pressure of 15 MPa, and CO_2 flow rate of 8 g/(g_{cat}·h). According to the figure, Z_0 of the reactivated Pd/AC catalyst increased steadily from 0.34 to 0.71 when the extraction time was prolonged from 2 to 8 h, and increased slightly when further prolonged to 10 h, suggesting the presence of some strongly bounded organic species on the spent Pd/AC catalyst, as will be confirmed by the textural analysis shown below.

Pilot-scale $scCO_2$ fluid extraction of the spent Pd/AC catalyst

The bench-scale results verified that the $scCO_2$ fluid extraction method is highly efficient in reactivating the spent Pd/AC catalyst. At proper extraction conditions, the spent Pd/AC catalyst regained more than 70% of the activity of the fresh 5 wt % Pd/AC catalyst in the hydrogenation of benzoic acid. This result is sufficiently encouraging for us to extend the supercritical fluid extraction method to pilot-scale evaluation. The pilot-scale $scCO_2$ fluid extraction experiments were performed on an apparatus containing a 24 L extractor (i.d. 19 cm, height 100 cm). The extraction conditions were 10 kg of the spent Pd/AC catalyst, extraction temperature of 353 K, extraction pressure of 25 MPa, CO_2 flow rate of 8 g/(g_{cat}·h), and extraction time of 8 h.

Table 1 summarizes the textural properties and activities of the fresh, the spent, and the reactivated Pd/AC catalysts for the hydrogenation of benzoic acid. For the fresh 5.0 wt % Pd/AC catalyst, the BET surface area, pore volume, and average pore diameter were 995 m^2/g, 0.605 cm^3/g, and 1.82 nm, respectively. For the spent Pd/AC catalyst, the BET surface area and pore volume drastically were decreased to 373 m^2/g and 0.230 cm^3/g, respectively, while the average pore diameter was enlarged to 2.03 nm, signifying the occurrence of pore blockage. After $scCO_2$ fluid extraction, the BET surface area, pore volume, and average pore diameter were increased to 724 m^2/g, 0.521 cm^3/g, and 1.87 nm, respectively. In Table 1, it is also found that other nondestructive reactivation methods based on washing by hot NaOH aqueous solution and by toluene were less effective in recovering the textural properties of the spent Pd/AC catalyst. It should be mentioned that the reactivation times of these two methods have been optimized, and prolonging the reactivation time did not lead to improved performance of the reactivated catalysts. Consequently, the spent Pd/AC catalyst reactivated by $scCO_2$ fluid extraction exhibited the highest activity, verifying that $scCO_2$ fluid extraction is efficient in eliminating pore blocking species from the spent Pd/AC catalyst. Moreover, unlike the Pd/AC catalyst reactivated by NaOH or toluene, additional cleaning and drying steps were unnecessary for the Pd/AC catalyst reactivated by $scCO_2$ fluid extraction, as $scCO_2$ readily vaporized and left the catalyst when the extractor was depressurized.

As $scCO_2$ extraction was conducted under relatively high pressure, it might cause the pulverization of the Pd/AC catalyst and thus, incompatible with the original industrial catalyst separation procedure. Our preliminary studies have revealed that under the extraction conditions used here, no changes in the average granule sizes of SiO_2, AC, and the fresh Pd/AC catalyst occurred. Figure 6 shows that the average granule sizes were 37.9 and 35.6 μm for the fresh and the reactivated Pd/AC catalyst, respectively, suggesting that mechanical attrition rather than $scCO_2$ fluid extraction is responsible for the slight reduction of the granule size of the reactivated catalyst. In addition, TEM observations of the fresh and the reactivated Pd/AC catalysts disclosed that the most probable particle size of Pd increased slightly from 4 to 5 nm (Figure 7), which can be attributed to the growth of the Pd nanoparticles during the hydrogenation process, as it is expected that the mild extraction temperature is insufficient to evoke sintering of Pd nanoparticles.

The kind and amount of the carbonaceous species extracted by $scCO_2$ fluid were analyzed by GC-MS; the results are presented in Table 2. Besides the feedstock benzoic acid and the product CCA left on the spent Pd/AC catalyst, there were more than 50 kinds of organic compounds in the liquid extract such as 1,1′-bicyclohexyl, cis-2-methyl-1,1′-bicyclohexyl, 4,4′-dimethyl-1,1′-bicyclohexyl, benzyl

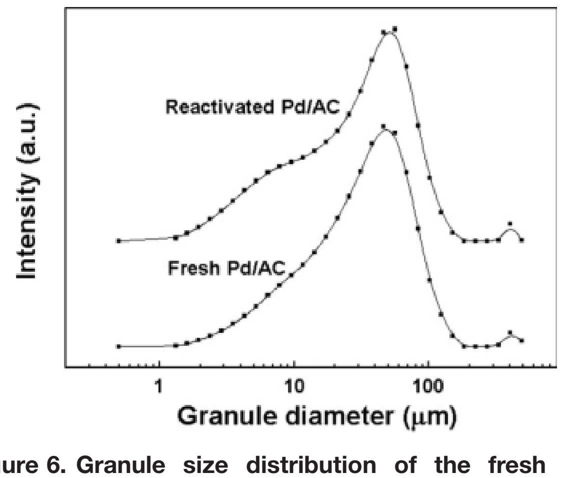

Figure 6. Granule size distribution of the fresh and reactivated Pd/AC catalysts.

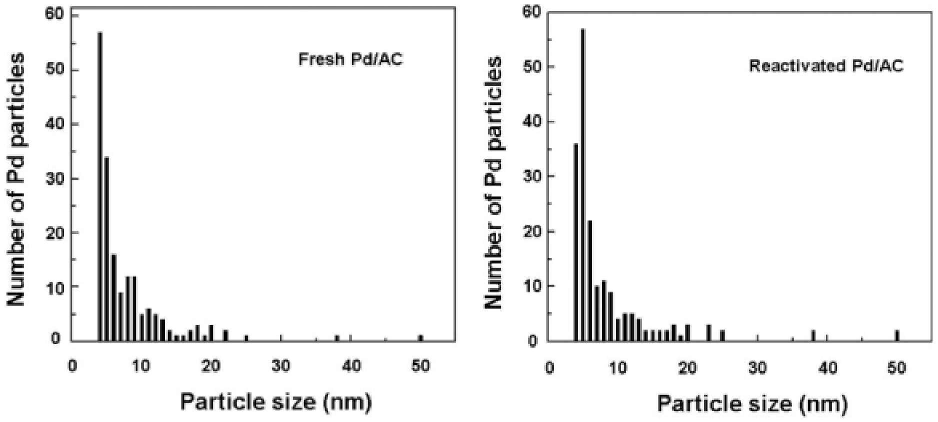

Figure 7. Particle size distribution of Pd on the fresh and reactivated Pd/AC catalysts.

benzoate, and cyclohexenecarboxylic acid, which are byproducts during the hydrogenation of benzoic acid and impurities in benzoic acid prepared via toluene oxidation. Removal of these organic compounds could account for the substantial recovery of the textural properties and activity of the spent Pd/AC catalyst after $scCO_2$ fluid extraction, although Table 1 indicates that there were still a portion of organic compounds retaining on the reactivated Pd/AC catalyst, which are most likely tightly trapped in the micropores of the catalyst. On the other hand, leaching of Pd from the Pd/AC catalyst due to mechanical attrition during the hydrogenation process can be another important factor for the incomplete reactivation of the spent Pd/AC catalyst. ICP-AES analysis showed that the Pd loading on the spent and the reactivated Pd/AC catalysts from different batches was 4.2–4.7 wt % as compared to 5.0 wt % on the fresh Pd/AC catalyst. Besides, the change in the particle size of Pd and the possible change in the surface chemical states of Pd may also contribute to the incomplete reactivation of the spent Pd/AC catalyst, which deserves detailed further research. However, it is interesting to note that the lifetime of the reactivated Pd/AC catalyst was close to that of the fresh catalyst, presumably due to the reconstruction of Pd nanoparticles during the hydrogenation process.

Table 2. The Kind and Amount of Organic Compounds in the Liquid Extract

Compound	Mass Fraction (%)
Cyclohexanone	0.011
Methyl cyclohexanecarboxylic acid	0.122
1,1′-Bicyclohexyl	0.451
cis-2-Methyl-1,1′-bicyclohexyl	0.393
Dodecahydro-1H-fluorene	0.291
Benzaldehyde	0.021
1-Cyclohexylmethyl-cyclohexane	0.009
4,4′-Dimethyl-1,1′-bicyclohexyl	0.245
Dimepheptanol	0.100
Cyclohexenecarboxylic acid	0.188
4-Methyl-1,1′-biphenyl	0.045
Benzyl benzoate	0.210
Others excluding benzoic acid and cyclohexanecarboxylic acid	1.376

Industrial scale application of $scCO_2$ fluid extraction to reactivate the spent Pd/AC catalyst

Based on the above bench- and pilot-scale results, an industrial scale $scCO_2$ fluid extraction unit for the reactivation of the spent Pd/AC catalyst in the hydrogenation of benzoic acid was established and commercialized, as shown schematically in Figure 8. The industrial scale $scCO_2$ fluid extraction unit hosts two 500 L extractor vessels (i.d. 53 cm, height 240 cm) in parallel with operation limits of 373 K and 50 MPa. The unit also contains a CO_2 recycling subunit to recover the large volume of CO_2 used in the extraction process. The commercial unit was run periodically for about six times per month. To gain a better extraction result, we optimized the extraction parameters on the commercial extraction unit further. The typical extraction conditions on the commercial unit were extraction temperature of 343–353 K, extraction pressure of 25 MPa, CO_2 flow rate of 1500 kg/h, and extraction time of 9–12 h. The activity of the reactivated Pd/AC catalyst sampled from the commercial extraction unit was tested in a bench-scale autoclave under benchmark conditions. Representative catalytic data of the Pd/AC catalyst reactivated on the commercial extraction unit in the year of 2005 are presented in Table 3, which clearly shows

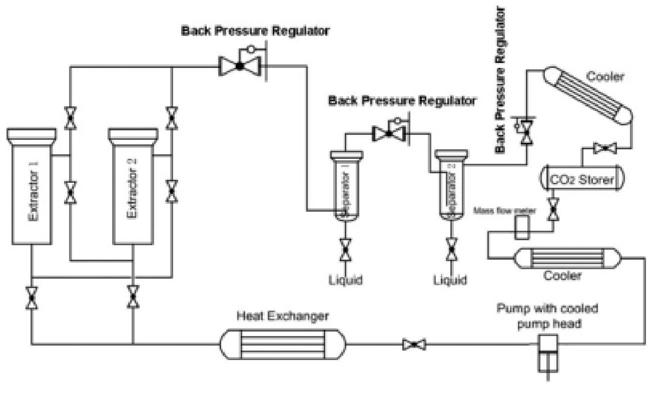

Figure 8. Schematic representation of an industrial plant used for $scCO_2$ extraction consisting of 2 × 500 L extractors and two separators.

Table 3. Catalytic Performance of the Pd/AC Catalyst Reactivated on an Industrial Scale scCO$_2$ Fluid Extraction Unit

Run	Weight of the Spent Pd/AC Catalyst Reactivated (kg)	Extraction Time (h)	Z_0
1	410	11	0.89
2	303	10	0.98
3	408	11	1.02
4	413	10	0.84
5	441	12	0.75
6	384	10	0.98
7	320	9	0.83
8	419	10	0.91
9	323	10	0.91
10	411	12	0.99
11	366	10	1.02
12	345	10	0.95
Average in year	366	10.2	0.88

that the reactivated Pd/AC catalyst regained 80% of the activity of the fresh 5.0 wt % Pd/AC catalyst after scCO$_2$ fluid extraction. It should be mentioned that Z_0 of the fresh Pd/AC catalyst of this batch was 1.1, and Z_0 of the spent catalyst was 0.14. Taking into account of the lower Pd content on the reactivated Pd/AC catalyst, such catalytic performance indicates that the spent Pd/AC catalyst subjected to scCO$_2$ fluid extraction has been reactivated satisfactorily on the industrial scale scCO$_2$ extraction unit.

The reactivated Pd/AC catalyst was used in the industrial unit for the hydrogenation of benzoic acid. In a traditional 60 kt/a industrial unit for the hydrogenation of benzoic acid, the daily feed rates of benzoic acid and the fresh 5.0 wt % Pd/AC catalyst were about 216 t/d and 80 kg/d, respectively. After the industrialization of the scCO$_2$ fluid extraction process, because more Pd/AC catalyst became usable, the throughput of the industrial hydrogenation unit was improved to 70 kt/a. When without using the reactivated Pd/AC catalyst, ca. 93 kg/d of the spent Pd/AC catalyst was unloaded and replaced by the same amount of the fresh 5.0 wt % Pd/AC catalyst. When using a combination of the fresh 5.0 wt % Pd/AC catalyst and the reactivated Pd/AC catalyst, we unloaded 100 kg of the spent Pd/AC catalyst daily, and replenished with 60 kg of the fresh 5.0 wt % Pd/AC catalyst and 40 kg of the reactivated Pd/AC catalyst, as the activity of the latter was equivalent to that of 93 kg of the fresh 5.0 wt % Pd/AC catalyst. So, the quantity of the fresh 5.0 wt % Pd/AC catalyst added was reduced by about 25% averaged in 1 year, and only the capital cost for the fresh 5.0 wt % Pd/AC catalyst was reduced by \$1 million annually by using the scCO$_2$ fluid extraction method.

It should be noted that reactivation of the spent catalyst by scCO$_2$ fluid extraction is not limited to the Pd/AC catalyst used for the hydrogenation of benzoic acid. Preliminary experiments showed that the technique is also suitable for the reactivation of the spent 0.5 wt % Pd/AC catalyst for the hydrorefinery of terephthalic acid and the spent 1.0 wt % Pd/γ-Al$_2$O$_3$ for the hydrogenation of 2-ethyl anthraquinone. These findings strongly indicate that the scCO$_2$ fluid extraction technique presents a new opportunity for the reactivation of spent metallic catalysts for other industrial hydrogenation processes in which pore blockage by carbonaceous species resulted in the deactivation of the catalysts.

Conclusions

Reactivation of the spent Pd/AC catalyst by scCO$_2$ fluid extraction can restore more than 70% of the activity of the fresh 5.0 wt % Pd/AC catalyst for the hydrogenation of benzoic acid. Characterization of the reactivated Pd/AC catalyst revealed that such activity recovery is mainly resulted from the removal of the carbonaceous species blocking the pores of the catalyst by scCO$_2$ fluid. No pulverization of the granule size of the catalyst and sintering of the Pd nanoparticles were found after scCO$_2$ fluid extraction, demonstrating that scCO$_2$ fluid extraction is an excellent nondestructive, atomically economical, and environmentally friendly technique for the reactivation of the spent Pd/AC catalyst.

Acknowledgements

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