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Integration of Methanation into the Hydrogenation Process of Benzoic Acid

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The traditional industrial process for hydrogenation of benzoic acid to cyclohexanecarboxylic acid (CCA) has drawbacks of low-activity and fast deactivation of the Pd/C catalyst due to the poisoning of CO arising from the decarboxylation of CCA. A novel rapidly quenched skeletal NiCrFe promoter (RQ NiCrFe) is developed for the methanation of CO to harmless CH_4. Evaluations in bench-scale autoclave and in traditional industrial equipment verified that RQ NiCrFe was very effective in promoting the activity of the Pd/C catalyst in the hydrogenation of benzoic acid. In order to solve the catalyst recycle and separation problem introduced by RQ NiCrFe, the industrial process was modified by incorporating a hydraulic cyclone and a magnetic separator to the separation unit. The modified process showed merits of lower costs of catalyst and operation, higher productivity, and better product purity than the traditional process.
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Introduction

As an excellent catalyst for liquid-phase hydrogenations, the Pd/C catalyst has been widely used in petrochemical, pharmaceutical, and agrochemical industries.[1–3] In particular, a large quantity of Pd/C has been used in chemical fiber industry for ε-caprolactam manufacture,[4] and in polyester industry for the refinery of terephthalic acid.[5]

The commercial synthetic process for ε-caprolactam from toluene, the Snia Viscosa process,[6] mainly involves oxidation of toluene to benzoic acid, hydrogenation of benzoic acid to cyclohexanecarboxylic acid (CCA), and amidation of CCA to ε-caprolactam. In this process, hydrogenation of benzoic acid is carried out in a cascade of continuously stirred-tank reactors at about 443 K under H_2 pressure of 1–2 MPa on a 5% Pd/C catalyst.[6–8] After every catalytic run, the Pd/C catalyst is recycled as slurry (termed as recycled Pd/C catalyst) by centrifuging the liquid stream, then mixed with benzoic acid and additional fresh Pd/C catalyst to compensate for the deactivated Pd/C catalyst. The product is flash distilled *in vacuo* to retrieve quantitatively the residual Pd/C catalyst which is followed by recovery.[9]

However, the traditional process for hydrogenation of benzoic acid suffers from a number of limitations that lead to the lack of efficiency of the equipment and the excessive consumption of the Pd/C catalyst. The recycled Pd/C catalyst only exhibits an activity 1/6–1/5 of that of the fresh 5% Pd/C catalyst. Moreover, in order to maintain this activity, it necessitates the frequent addition of fresh Pd/C catalyst and recovery of Pd, which drastically increases the possibility of

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the loss of noble Pd metal. The low activity of the recycled Pd/C catalyst constitutes not only the central problem in this industrial process for hydrogenation of benzoic acid, but also the bottle-neck in ε-caprolactam manufacture.

Among factors that result in the deactivation of the Pd/C catalyst, CO arising from the decarboxylation of CCA is regarded as one of the most important reasons, because trace amount of CO is sufficient to deactivate the Pd/C catalyst.[10] When trying to improve the performance of the Pt/C catalyst in the hydrogenation of benzoic acid, we noticed that the surface science study has demonstrated that the adsorption strengths of CO on Pd and Ni are comparable,[11] implying that introduction of Ni may alleviate the deactivation of Pd by competitively adsorbing CO on Ni. Moreover, Ni is known as an excellent methanation catalyst that readily transforms CO to CH_4, which is harmless to Pd,[12] thus, offering an opportunity to sustain the antipoisoning function of Ni and improve the activity of the Pd/C catalyst. Fortunately, the formation of the poisonous and volatile nickel-carbonyl complex is thermodynamically not favored under the reaction temperature for hydrogenation of benzoic acid.[13]

Following this concept, we made basic and applied research in improving the performance of the Pd/C catalyst in the hydrogenation of benzoic acid, and certain preliminary results have been reported elsewhere.[4,9,14] In this article, we reported systematically the modification of the industrial process for hydrogenation of benzoic acid by the inclusion of a novel skeletal Ni-based promoter prepared by the rapid quenching technique. In order to solve the catalyst recycle and separation problem caused by the presence of the skeletal Ni-based promoter, a hydraulic cyclone and a novel magnetic separator were implemented in the industrial unit. It is found that the activity of the Pd/C catalyst was substantially enhanced and stabilized after such modification, which remarkably improved the economics of the industrial process for hydrogenation of benzoic acid.

Experimental

Preparation of Ni-based promoters

Three skeletal Ni-based promoters were screened to find out the promoter which is more effective in enhancing the catalytic activity of the recycled 5% Pd/C catalyst in the hydrogenation of benzoic acid. The promoters were the conventional Raney Ni (Degussa), skeletal Ni (RQ Ni) leached by alkali from a rapidly quenched $Ni_{48}Al_{52}$ alloy (Ni/Al, w/w), and skeletal NiCrFe (RQ NiCrFe) leached by alkali from a rapidly quenched $Ni_{48}Cr_{2.5}Fe_{1.5}Al_{48}$ alloy. Cr can enhance the acid-resistance of the skeletal Ni promoter, as the reaction mixture was acidic, and Fe can enhance the magnetic susceptibility of the promoter so as to meet the demand of the magnetic separation technique.

The preparation of the RQ NiCrFe promoter is described as an example. 48 g of metallic Ni, 48 g of metallic Al, 2.5 g of metallic Cr, and 1.5 g of metallic Fe were mixed and melted at 1,773 K in an induction furnace sufficiently for a long time to ensure the homogeneity of the melt. The melt was sprayed through a nozzle to a water-cooled copper roller with a spinning rate of 800 rpm to fabricate ribbons. The cooling rate was estimated to be about 10^7 K/s. The ternary $Ni_{48}Cr_{2.5}Fe_{1.5}Al_{48}$ alloy (RQ NiAlCrFe) was subsequently ground to about 40 μm, and slowly added to 500 mL of 20 wt % NaOH aqueous solution at 373 K under gentle stirring. After the addition, the mixture was kept on stirring at 373 K for 1 h for further alkali leaching. The black powder was then washed to neutrality with distilled water of 353 K, and stored in water for further use. Since these promoters are pyrophoric, they were weighed in a graduated tube with the protection of water.

The 5% Pd/C catalyst was prepared by wetness impregnation of a commercially available coconut active carbon with a $PdCl_2$ aqueous solution, followed by reduction with H_2 at 313 K.[15] A uniform distribution of Pd on active carbon was favored for hydrogenation of benzoic acid.[3]

Bench-scale test

The activity of the recycled 5% Pd/C catalyst from an industrial unit of Sinopec without or with the addition of the skeletal Ni-based promoters in hydrogenation of benzoic acid was examined in a bench-scale stainless steel shaking autoclave of 500 mL capacity. 200 g of benzoic acid, 2 g of recycled Pd/C catalyst, and a certain amount of skeletal Ni-based promoter were loaded in the autoclave. After being flushed with N_2, the autoclave was filled with N_2 to 2.0 MPa, heated to 423 K, and pressurized with H_2 to 11.0 MPa. The shaking rate is 50 times per min. When the system pressure dropped to 9.0 MPa due to the uptake of H_2, the autoclave was charged immediately to restore the pressure to 11.0 MPa. The activity of the Pd/C 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 fresh 5% Pd/C catalyst, Z_0 is usually around 1.0–1.2, while for recycled 5% Pd/C catalyst, Z_0 is only about 0.2. Control experiments demonstrated that compared with the Pd/C catalyst, skeletal Ni-based promoters showed negligible activity in hydrogenation of benzoic acid.

Industrial-scale test

A schematic diagram of the traditional industrial unit for hydrogenation of benzoic acid is illustrated as Figure 1. The four-tank reactors have the same volume of 45 m^3 each, in which 5.4 t of the 5% Pd/C catalyst was loaded. The operation temperature was 443–453 K, the pressure was 1.2–1.35 MPa, and the stirring rate was 156 rpm. The conversion of benzoic acid was determined with a WZS-1 Abbe refractometer at 315 K. During hydrogenation, the reaction mixture overflowed from the top of one reactor to the successive reactor. The content of benzoic acid leaving the fourth reactor was less than 1%. Every day about 200 kg of spent Pd/C catalyst was unloaded from the unit, followed by incineration to recover Pd. Meanwhile, the same quantity of fresh Pd/C catalyst was added to maintain the productivity of the unit.

Results and Discussion

Bench-scale evaluation of the skeletal Ni-based promoters

We first studied the effect of the amount of CO purposely added in the autoclave on the activity of recycled 5% Pd/C catalyst in the hydrogenation of benzoic acid. It is found that

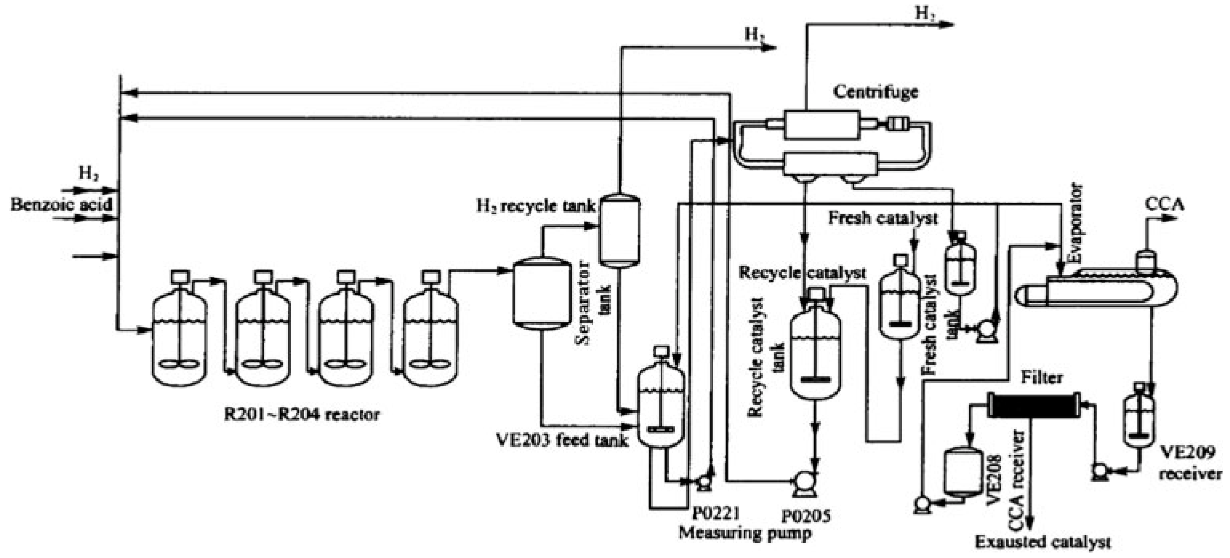

Figure 1. Schematic diagram of the traditional industrial process for hydrogenation of benzoic acid.

at the presence of 200 ppm of CO, the activity of recycled Pd/C catalyst drastically dropped from 0.25 to 0.08. The presence of 400 ppm of CO essentially led to the complete deactivation of recycled Pd/C catalyst. This experiment clearly confirms the vital poisoning effect of CO on the Pd/C catalyst in hydrogenation of benzoic acid.

Table 1 summarizes the activity of recycled 5% Pd/C catalyst with or without the addition of skeletal Ni-based promoters. With the aid of Raney Ni, the activity of recycled Pd/C catalyst increased substantially from 0.25 to 0.41, validating our assumption that Ni can effectively eliminate CO, which is poisonous to the Pd/C catalyst. More interestingly, by integration of the rapid quenching technique with the preparation of the skeletal Ni promoter, RQ Ni with a similar bulk composition to Raney Ni displayed a superior promoting effect, as shown in Table 1. In previous works, Hu et al. have identified that rapid quenching can lead to lattice expansion of RQ Ni relative to Raney Ni, which is leached by alkali from the naturally solidified NiAl alloy.[16,17] Experimental and theoretical works have demonstrated that CO dissociation on Ni is the rate-determining step for the methanation reaction, $CO + 3H_2 \rightarrow CH_4 + H_2O$.[18,19] Based on the self-consistent density functional calculations, Mavrikakis et al. revealed that when the lattice constant parallel to the surface of Ru(0001) is increased or the coordination number is smaller, the *d* bands have to move up in energy, which leads to stronger interaction with CO, and lowers the dissociation barrier of CO.[20] Moreover, the correlation between the interaction strength and the *d*-band center can be generalized to other adsorbates and metals. Since the lattice of RQ Ni is expanded relative to Raney Ni, it can be deduced that the dissociation probability of CO on RQ Ni is increased, which further improves the methanation activity, and, consequently, enhances the activity of recycled Pd/C catalyst.

Table 1. The Effect of the Skeletal Ni-Based Promoters on the Activity of Recycled 5% Pd/C Catalyst in Bench-Scale Hydrogenation of Benzoic Acid

Promoter	Bulk Composition (Weight Ratio)	Promoter : Pd/C (wt%)	Z_0
None	–	0	0.25
Raney Ni	$Ni_{88}Al_{12}$	2.5	0.41
RQ Ni	$Ni_{88}Al_{12}$	2.5	0.47
RQ NiCrFe	$Ni_{88}Al_9Cr_2Fe_1$	2.5	0.50

Noticeably, Table 1 demonstrates that addition of only a small amount of Cr and Fe can further increase the antipoisoning ability of RQ Ni. The Z_0 value of recycled 5% Pd/C catalyst was increased to 0.50 when using RQ NiCrFe as the promoter, which is two times more active than the Pd/C catalyst alone, showing promising prospect for its application in hydrogenation of benzoic acid. So we mainly focused on the RQ NiCrFe promoter in the following studies.

Figure 2 shows the effect of the amount of RQ NiCrFe on the activity of recycled 5% Pd/C catalyst in hydrogenation of

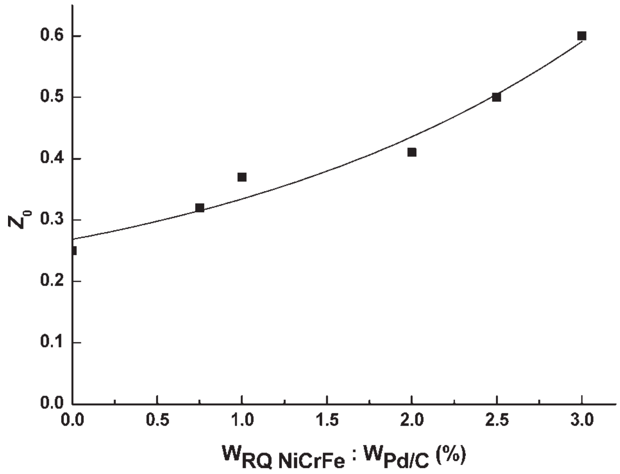

Figure 2. Effect of the amount of the RQ NiCrFe promoter on the activity of recycled 5% Pd/C in bench-scale hydrogenation of benzoic acid.

Table 2. The Effect of the Amount of the RQ NiCrFe Promoter on the Catalytic Performance of Recycled 5% Pd/C Catalyst in the Traditional Industrial Process for Hydrogenation of Benzoic Acid

RQ NiCrFe : Pd/C (wt%)	Z_0	Productivity (t_{CCA}/kg Pd)	Fresh Pd/C Added (kg/d)	Ni in the Spent Pd/C Catalyst (ppm)
0	0.20	35.0	150	–
0.2	0.21	37.0	120	200
0.5	0.25	46.9	100	500
0.8	0.29	50.0	80	800

benzoic acid. It is found that the Z_0 value of recycled Pd/C catalyst was increased steadily to 0.60, with the RQ NiCrFe to Pd/C ratio increasing to 3.0 wt %. Moreover, it is revealed that using recycled 5% Pd/C catalyst alone, the concentration of CO in the autoclave was 33 ppm. After the addition of RQ NiCrFe, the concentration of CO dropped substantially to <10 ppm, corroborating well with our expectation that Ni can enhance the activity of the Pd/C catalyst by eliminating CO from the reaction system. Although an even higher RQ NiCrFe to Pd/C ratio showed better promoting effect, it should be emphasized that the presence of RQ NiCrFe would complicate the recycle and recovery of the Pd/C catalyst. So in the industrial unit, the amount of RQ NiCrFe added was restricted.

Verification of the promoting effect of RQ NiCrFe in the traditional industrial process

Industrial operation proved the feasibility of using RQ NiCrFe to improve the catalytic performance of the Pd/C catalyst in hydrogenation of benzoic acid. In the traditional industrial unit outlined in Figure 1, the RQ NiCrFe promoter was loaded in tank VE203 first, then pump P0221 was started to circulate the RQ NiCrFe promoter and the 5% Pd/C catalyst in the four reactor tanks until their homogeneous distribution. Similar to the bench-scale results, after the addition of the RQ NiCrFe promoter the concentration of CO in the reaction system was reduced from ~300 ppm to ~100 ppm. In Table 2, it is identified that increasing the amount of RQ NiCrFe enhanced steadily the activity of recycled Pd/C catalyst. As a result, the amount of CCA produced by per kg Pd was increased from 35.0 t, using recycled Pd/C catalyst alone to 50.0 t, using a combination of 0.8 wt % of RQ NiCrFe and recycled Pd/C catalyst. The consumption of fresh 5% Pd/C catalyst to sustain the hydrogenation activity was reduced by 46%. The lower activities in Table 2 than those in bench-scale studies are attributed to the different hydrogenation conditions.

Since the centrifuge separator was originally designed for the separation of the Pd/C catalyst, and the RQ NiCrFe promoter is much denser than the Pd/C catalyst, we found that the industrial separation unit was not sufficient to recycle the RQ NiCrFe promoter. As listed in Table 2, there were several hundred ppms of Ni left in the spent Pd/C catalyst, which prolonged the incineration period of the spent Pd/C catalyst to two weeks, thus, greatly increasing the cost for the spare fresh Pd/C catalyst. It is obvious that process improvement was necessary to solve the recycle and separation problem caused by introduction of the RQ NiCrFe promoter to the traditional industrial process for hydrogenation of benzoic acid.

Modification of the industrial process

In order to fully utilize the beneficial promoting effect of RQ NiCrFe on the industrial process, we modified the existing catalyst separation unit by implementing a hydraulic cyclone after reactor R204, and a novel magnetic separator after the evaporator. The modified industrial process for hydrogenation of benzoic acid is outlined in Figure 3. In the modified process, the hydraulic cyclone can recycle the majority of RQ NiCrFe and Pd/C to tank VE203, which lightened the burden on the centrifuge separator. A comparison

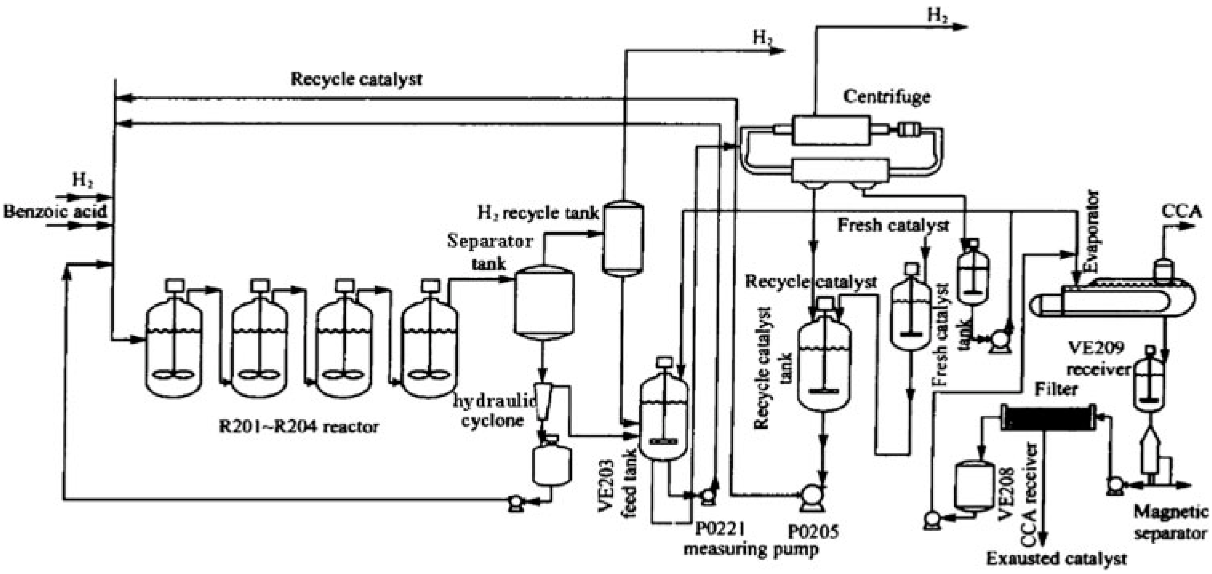

Figure 3. Schematic diagram of the modified industrial process for hydrogenation of benzoic acid.

Table 3. The Effect of the Amount of the RQ NiCrFe Promoter on the Catalytic Performance of Recycled 5% Pd/C Catalyst in the Modified Industrial Process for Hydrogenation of Benzoic Acid

Hydraulic Cyclone	Magnetic Separator	RQ NiCrFe : Pd/C (wt%)	Productivity (t_{CCA}/kg Pd)	Fresh Pd/C Added (kg/d)	Ni in the Spent Pd/C Catalyst (ppm)
Yes	No	0.2	46.0	100	20
Yes	No	0.5	49.0	80	50
Yes	No	0.8	52.6	65	80
Yes	Yes	0.2	53.0	90	5
Yes	Yes	0.5	56.4	70	15
Yes	Yes	0.8	59.8	60	30

between Table 2 and Table 3 shows that when the hydraulic cyclone was implemented in the separation unit, the residual Ni in the spent Pd/C catalyst was markedly reduced to 10% of that without the hydraulic cyclone. The incineration period of the spent Pd/C catalyst was shortened to 7–8 days accordingly.

The permanent magnet-[14] or the electromagnet-based magnetic separator operated in the magnetic condensation mode[13,21] can further isolate the RQ NiCrFe promoter from the deactivated Pd/C catalyst. The novel magnetic separator was designed on the basis that the RQ NiCrFe promoter is ferromagnetic (Figure 4), whereas the Pd/C catalyst is not magnetizable. In the modified process as shown in Figure 3, after evaporation of most CCA, the RQ NiCrFe promoter and the Pd/C catalyst escaping from the centrifuge were concentrated in receiver VE209. The effluent from VE209 then passed through the magnetic separator, in which the promoter and the Pd/C catalyst underwent separation. Table 3 shows that the concentration of Ni remaining in the spent Pd/C catalyst using this three-step separation strategy was only 1/4–1/3 of that using a combination of the hydraulic cyclone and the centrifuge separator. The incineration period of the spent Pd/C catalyst was further shortened to 4–5 days, which is close to that without the addition of RQ NiCrFe.

At present, the industrialized magnetic separator is based on the permanent magnet; its configuration is illustrated in Figure 5. The working mechanism of the magnetic separator is described as follows. The unsettled RQ NiCrFe and Pd/C with CCA flowed upward in the outer container of the magnetic separator. At the beginning, the magnet was on the bottom of the inner container, so RQ NiCrFe was mainly attracted on the outside of the bottom of the inner container, where the magnetic field was the strongest. After a certain period of magnetic attraction, the magnet was moved up by a motor, the attracted RQ NiCrFe on the bottom of the inner container automatically dropped in the collector due to the action of gravity, and the loss of the magnetic field.

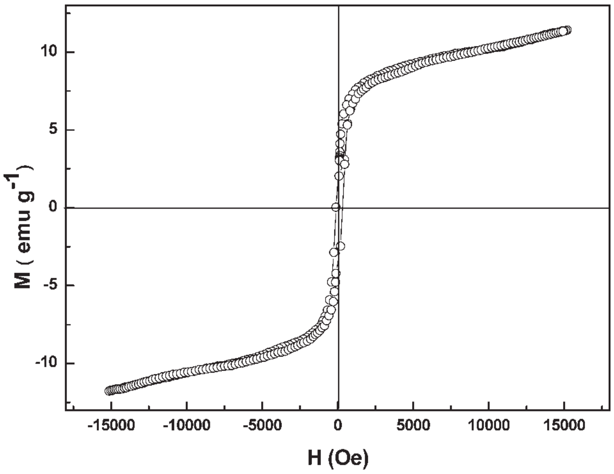

Figure 4. Magnetic hysteresis loop of the RQ NiCrFe promoter.

Table 3 shows that because of the much thorough recycle of the RQ NiCrFe promoter, the amount of CCA produced by per kg Pd was increased by $\sim$20%, as compared to that using the centrifuge separator alone. The consumption of fresh 5% Pd/C catalyst was reduced by $\sim$50%. Meanwhile, the purity of CCA was increased by 0.5%, demonstrating the superiority of the modified process with a combination of the RQ NiCrFe promoter and the three-step separation strategy for hydrogenation of benzoic acid. Moreover, it is found that the operation ranges of temperature and pressure were stabilized on the modified industrial unit, thus, less adjustment was needed, which simplified the operation procedure. Also, the prolonged lifetime of the Pd/C catalyst called for less frequent recovery of the spent Pd/C catalyst. The RQ NiCrFe promoter and the modified separation unit have been successfully applied in a commercial unit of Sinopec for hydrogenation of benzoic acid. Only the expenditure for fresh 5% Pd/C catalyst could be saved by $2 million annually after such process improvement.

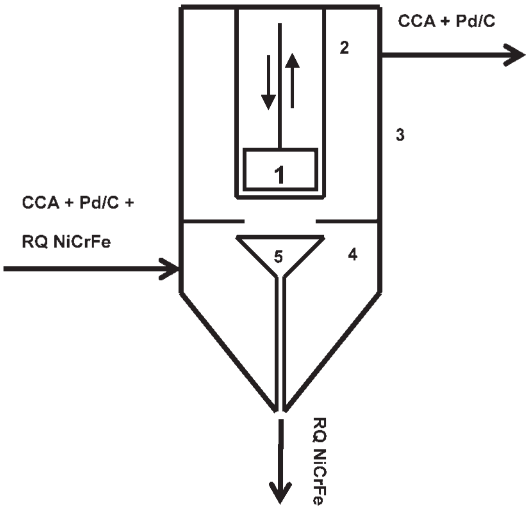

Figure 5. Process concept for the permanent magnet separator.

(1) Movable permanent magnet driven by a motor, (2) inner container, (3) outer container, (4) baffle, and (5) catalyst collector.

It should be noted that the concept of using the methanation reaction to retard the deactivation of noble metal catalysts is not confined to the hydrogenation of benzoic acid on the Pd/C catalyst. The concept is also valid in hydrogenation of substituted benzoic acids on other noble metal catalysts. For example, in bench-scale hydrogenation of p-ethyl benzoic acid on a 5%Ru/C catalyst and p-isopropyl benzoic acid on a PtO_2 catalyst, we found that after the introduction of the RQ NiCrFe promoter to the reaction system, the hydrogenation activity was increased by 66 and 75%, respectively. These works strongly indicate that this concept and separation strategy present opportunity for the improvement of other industrial hydrogenation processes, which are also interfered with CO poisoning.

Conclusions

Bench- and industrial-scale evaluations showed that the novel RQ NiCrFe promoter was very efficient in alleviating CO poisoning on the Pd/C catalyst in hydrogenation of benzoic acid. By incorporating the hydraulic cyclone and the novel magnetic separator to the traditional industrial process, the catalyst recycle and recovery problem caused by the presence of the RQ NiCrFe promoter was satisfactorily settled. As compared to the traditional process, the modified industrial process for hydrogenation of benzoic acid displayed advantages of enhanced catalytic activity, reduced catalyst consumption, simplified operation procedure, improved product purity, and, consequently, the improved overall economics of the process. This work demonstrates that the concept from surface science study and technical innovation are beneficial for the improvement of traditional industrial processes or for the establishment of new industrial processes. Surface chemistry and kinetic studies are being planned to further elucidate the mechanism of the modification effect of the RQ NiCrFe promoter on the Pd/C catalyst and the kinetics of the reaction system in these laboratories.

Acknowledgments

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