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Catalyst preparation and deactivation issues for nitrobenzene hydrogenation in a microstructured falling film reactor

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Abstract

Hydrogenation of nitrobenzene to aniline in ethanol was performed continuously in a microstructured falling film reactor at 60 °C, 1–4 bar hydrogen pressure and residence time 9–17 s. Palladium catalyst was deposited as films or particles via sputtering, UV-decomposition of palladium acetate, incipient wetness or impregnation. Deactivation was observed and was particularly pronounced for the sputtered and UV-decomposed catalysts. Catalysts prepared through incipient wetness or impregnation were more stable and activity could be recovered by oxidation at 130 °C. The main causes of deactivation were determined to be deposition of organic compounds and palladium loss.

Keywords: Microstructured reactor; Falling film; Hydrogenation; Palladium; Nitrobenzene

1. Introduction

Falling film reactors employ thin liquid films that are created by a liquid feed falling under gravitational pull. The liquid film is in contact with a solid support, which is usually either a thin wall or stack of pipes. Due to the presence of the thin films, heat and mass transfer is rapid. Therefore, these systems are used for extraction, evaporation and highly exothermic processes. Examples include air dehumidification [1], absorption chillers [2], carbon dioxide absorption [3], sulfur dioxide adsorption [4], ammonia absorption [5], sulfonation reactions [6,7] and evaporation [8].

Conventional falling film systems generate films with thickness of the order of 0.5–3 mm [9,10]. A microstructured falling film reactor (μ-FFR) developed by the Institut für Mikrotechnik Mainz (IMM) can generate films less than 100 μm thick. This reactor offers excellent heat removal capabilities and has been used safely in the direct fluorination of aromatics [11,12]. Our research aims to evaluate the performance of the μ-FFR in solid catalysed gas–liquid hydrogenations, using as a model system the hydrogenation of nitrobenzene to aniline over a palladium catalyst with ethanol as solvent. For this purpose, a suitable catalyst incorporation method had to be developed that also provided a stable catalyst for continuous operation.

In general, palladium [13–16], platinum [17] or nickel [18–21] are used as catalysts. The precious metal catalysts are usually supported on carbon but other supports such as glass fibre [17], gels [13] and silica [14] have also been used. Industrially, Du Pont utilises a palladium–platinum catalyst supported on carbon [22]. Various examples of microreactor technology involve the use of unsupported metallic catalysts deposited through sputtering [23]. Where greater catalytic surface area is required, anodisation of metals (typically aluminium) has been used, since a variety of surface morphologies and porous

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layer thicknesses can be made in a controlled fashion [24]. Supports have also been prepared using sol–gel techniques [25–27] and by growing zeolites [28,29]. Fixed bed microreactors have also been produced [30]. More examples of catalyst incorporation in microreactors can be found in [31].

2. Microstructured falling film reactor

The most crucial part of the reactor is the stainless steel plate where the falling film is generated. Sixty four straight, parallel channels (300 μm wide, 100 μm deep, 78 mm long separated by 100 μm wide walls) were fabricated using electrodischarge machining or wet chemical etching. At both ends of the channels, a slot was cut through the plate to form the inlet and exit ports. The entire plate measured 89 mm × 46 mm. It was housed in a stainless steel enclosure shown in Fig. 1. Liquid was fed to and removed from the back of the plate. A structured heat exchanger copper plate was inserted into a cavity beneath the falling film plate. A Viton O-ring was used to prevent leakage of the heat transfer fluid. Teflon and stainless steel gaskets were placed on top of the plate. Their geometry was such that the whole length of the channels were exposed with the exception of the first and last 5 mm which helped to distribute the liquid across the plate. The top part of the housing contained the gas inlet and outlet. It also had a view port (covered by a thick piece of glass) that showed the entire channel section of the falling film plate. When both top and bottom parts of the housing were placed together, a cavity would be created above the plate through which the gas would flow. The housing was held together by screws placed around the edge of the reactor. A Viton O-ring was used to prevent leakage.

3. Reaction

The hydrogenation of nitrobenzene to aniline is a highly exothermic reaction (545 kJ/mol). It can proceed along different reaction pathways and involves several intermediates which can also react with each other (see Fig. 2) [17]. Good temperature control is essential to avoid violent decomposition of nitrobenzene or partially hydrogenated intermediates, particularly phenylhydroxylamine [32]. Experiments with palladium catalyst in batch reactors showed that almost complete conversion to aniline could be obtained after long reaction times but intermediates were observed at short reaction times [17]. Due to the short residence time of the μ-FFR, it is possible that some of the intermediates would be present in the product. In addition, aniline can also further react (on nickel)

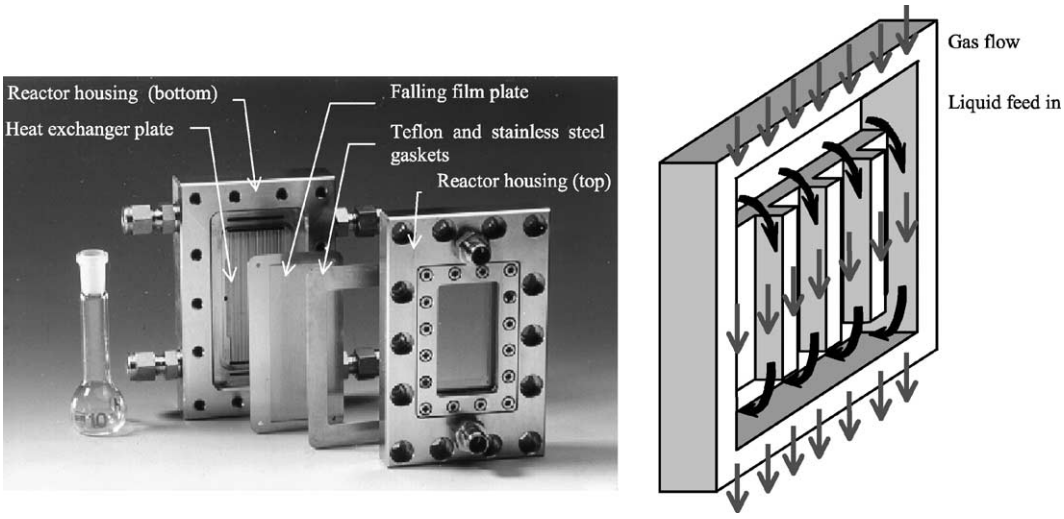

Fig. 1. Components and schematic of the microstructured falling film reactor.

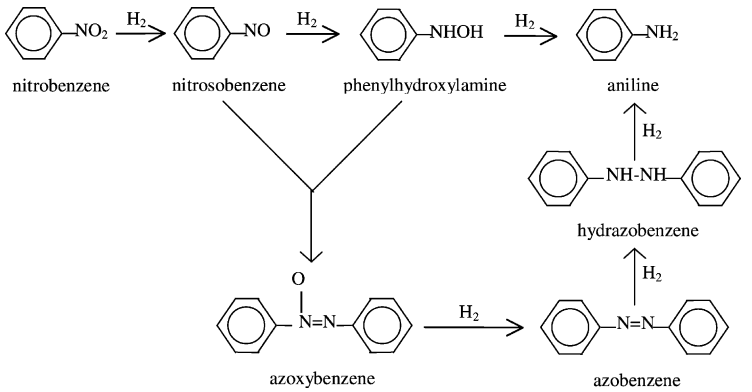

Fig. 2. Reaction scheme for nitrobenzene hydrogenation to aniline [17].

to produce several side products such as cyclohexanol, *N*-ethyl aniline, toluidine, cyclohexyl amine and diaminobenzene [21].

4. Catalyst preparation

Four different methods of preparing the catalyst were employed: sputtering, UV-decomposition of palladium acetate, wet impregnation and incipient wetness. The sputtering and UV-decomposition methods did not require modification of the surface of the falling film plate, while the other two methods involved prior deposition of a γ-alumina layer. The various methods are briefly described below.

4.1. Sputtering of palladium (SP)

The entire reaction side of the plate was coated with a 100 nm thick layer of palladium using the sputtering process, a conventional thin film technology. In this process, which is performed under vacuum conditions, the substrate (falling film plate) is operated as the anode, whereas the coating material (palladium) is operated as the cathode which emits atoms to the substrate.

4.2. UV-decomposition of palladium acetate (UV)

The reaction channels were covered with a solution of palladium acetate which was then irradiated using a UV lamp for 30 min. This served to decompose the organic part of the palladium acetate molecule, leaving behind elemental palladium on the surface of the channels.

4.3. Wet impregnation (IP)

A γ-alumina layer was deposited using the slurry/washcoating process. First, the area surrounding the channels was covered with tape. The channels were subsequently covered with an aqueous suspension of γ-alumina powder (20% solids content, average particle size 3 μm), binder (PVA) and acid (acetic acid or nitric acid). Excess suspension was wiped off and the plate was calcined at 700 °C for 2 h. This resulted in a 10 μm thick film, with pore size of about 20 nm and surface area of 58 m^2/g [27]. A solution of palladium(II) nitrate (Aldrich, Pd 12–16% w/w) with ca. 1.3 wt.% palladium was prepared. The channel area was covered in 10 ml of this solution for 2 h, after which the remaining solution was removed and the plate left to dry in air for 2 h. The plate was then heated at 120 °C for 30 min to drive off all moisture before being calcined in air at 400 °C for 3 h. It was then rinsed with distilled water and ethanol.

4.4. Incipient wetness (IW)

The γ-alumina layer was prepared as above. An amount of 10 ml of the same palladium(II) nitrate solution was used to cover the channels and left to dry in a fume cabinet. The plate was then calcined in air at

400 °C for 3 h and subsequently rinsed with distilled water and ethanol.

5. Experimental apparatus and procedure

A HPLC pump (Knauer K-120, 50 ml pump head) was used to feed the reaction mixture via a three-way valve. Prior to entering the reactor, the feed was passed through a heating bath (Grant W14) to bring it close to the reaction temperature. A syringe pump (Razel A-99) was connected to the other end of the three-way valve. It was used to clean the system with ethanol prior to shutdown. Hydrogen flow through the system was controlled using a pressure regulator. The gas line was connected to the top gas port of the reactor while the bottom gas port was blocked to maintain high pressure in the reactor. A needle valve was used to control the outlet flowrate. A nitrogen line was used for purging, while water was used as heat exchange fluid.

Experiments were conducted at 1–4 bar pressure, 60 °C and flowrates of 0.2–0.5 ml/min nitrobenzene solution (99.5%, Fluka, diluted in ethanol). Reaction conditions for the experiments are presented in Table 1. Product analysis was performed using an Agilent 6890 GC with an auto-sampler. Blank experiments carried out to test the catalytic activity of stainless steel concluded that no discernible reactions took place.

Nitrobenzene conversion, X, and aniline selectivity, S, were calculated by

$$X = \frac{\text{moles of nitrobenzene reacted}}{\text{moles of nitrobenzene entering}}$$

Table 1
Experimental conditions for the various catalysts (SP: sputtered palladium, UV: UV-decomposed palladium, IP: wet impregnation, IW: incipient wetness)[a]

Catalyst	Nitrobenzene concentration (mol/l)	Hydrogen pressure (bar)	Flowrate (ml/min)	Residence time (s)
SP	0.4	4	0.2	17
UV	0.04	4	0.2	17
IP	0.04	4 (1 bar after reactivation)	0.35	12
IW	0.1	1	0.5	9

[a] Reaction temperature 60 °C.

$$S = \frac{\text{moles of aniline produced}}{\text{moles of nitrobenzene reacted}}$$

6. Results and discussion

6.1. Sputtered palladium (SP) catalyst

In preliminary experiments, low conversion and eventually complete deactivation were observed. In addition, side products were detected after several hours of operation. Cleaning the plate with ethanol and acetone did not lead to recovery of reactivity. The catalyst plate was then oxidised in air at 450 °C for 4 h and reduced in pure hydrogen at 350 °C for 4 h. Some activity was recovered and the change in nitrobenzene conversion with time is shown in Fig. 3. There was rapid initial deactivation followed by a slower, steady deactivation. Initially, no side products were detected. The conversion irregularities shown in the figure (at 9, 17 and 31 h of operation) are associated with interruptions of the experiment. Reactivating the catalyst after 36 h through another oxidation–reduction cycle showed no significant recovery in conversion. After 43 h, conversion of nitrobenzene to aniline was negligible.

Selectivity was erratic (refer to Fig. 3). However, it seemed to follow the trend of conversion. After the reactivation at 36 h, only aniline was observed. However, this was followed by a sharp decrease in selectivity, i.e. side products were produced when the catalyst was not fresh. Subjecting the catalyst to another oxidation–reduction cycle failed to recover aniline production.

Analysis of the side products showed the presence of all intermediates, except phenylhydroxylamine. However, the presence of azoxybenzene (main side product), azobenzene and hydrazobenzene suggested that phenylhydroxylamine had been produced. Azoxybenzene continued to be produced even when aniline production became negligible. This suggested that phenylhydroxylamine preferentially reacted with nitrosobenzene and the pathway from azoxybenzene to aniline was either blocked or required longer residence time. Hydrazobenzene concentration was much larger than that of azobenzene, therefore it appears that the hydrogenation of hydrazobenzene was inhibited. These observations agree with Blaser et al.

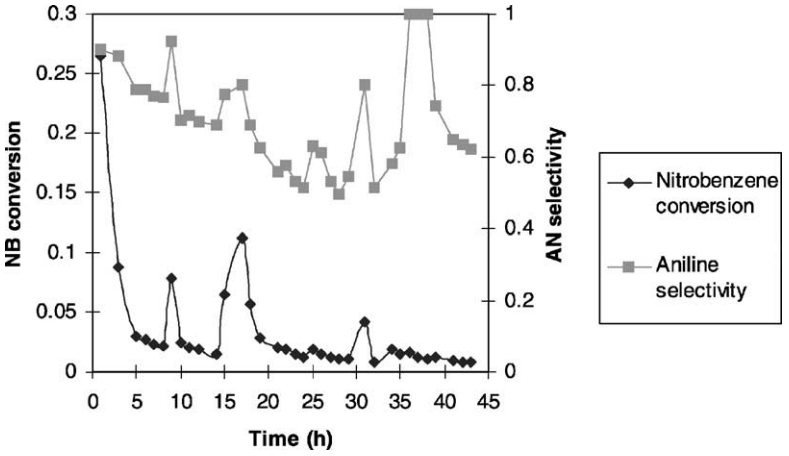

Fig. 3. Nitrobenzene conversion and aniline selectivity as a function of reaction time for the sputtered palladium catalyst (0.4 mol nitrobenzene/l, 60 °C, 4 bar, 0.2 ml/min).

[32] who reported that nitroso, azo and azoxy intermediates adsorb strongly, and the reduction of the hydrazo compound is slow, requiring elevated temperatures and pressures. It also seems plausible that the reaction between nitrosobenzene and phenylhydroxylamine was favoured by the continuous palladium layer where active sites were densely packed.

Another possible cause for deactivation was the high reactivation temperature. van Gelder et al. [33] used a temperature of only 130 °C for reactivating their catalyst in air and did not employ a reduction cycle. The high temperatures used in our experiments (450 °C) may have adversely affected the structure of the catalyst. Examination of the catalyst after reaction revealed a cracked and flaky surface (see Fig. 4).

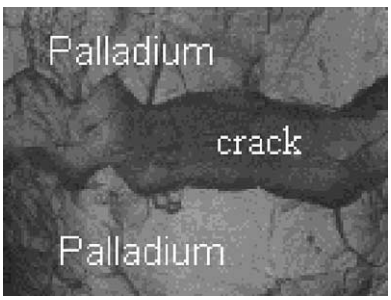

Fig. 4. Image of sputtered palladium plate after reaction (magnification: 200×).

Therefore, van Gelder et al.'s reactivating procedure [33] was used for the rest of the experiments.

6.2. UV-decomposed palladium acetate (UV) catalyst

The plate was heated in air at 130 °C for 4 h before performing experiments. Nitrobenzene conversion as a function of time is shown in Fig. 5 for lower nitrobenzene concentration than used for the SP plate (0.04 mol nitrobenzene/l). A stepped trend in conversion was observed. Each step occurred after the reactor was shut down. Aniline selectivity followed the same trend as conversion. The same side products as for the sputtered palladium plate were detected. The plate was reactivated after 33 h by oxidation in air at 130 °C for 4 h. Activity was recovered but short-lived.

It appeared that deactivation occurred when the reactor was left idle. The plate was analysed using Raman spectroscopy and the presence of carbon was detected. This showed that carbon-containing compounds were forming on the catalyst surface and that heat treatment was required to remove them. This catalyst remained active for a longer period than the sputtered one. This could be due to several reasons: lower nitrobenzene concentration, higher palladium amount and a different catalyst structure due to the different preparation method.

The used plate was examined using SEM (Hitachi S-570) (Fig. 6) revealing a rough, uneven and cracked

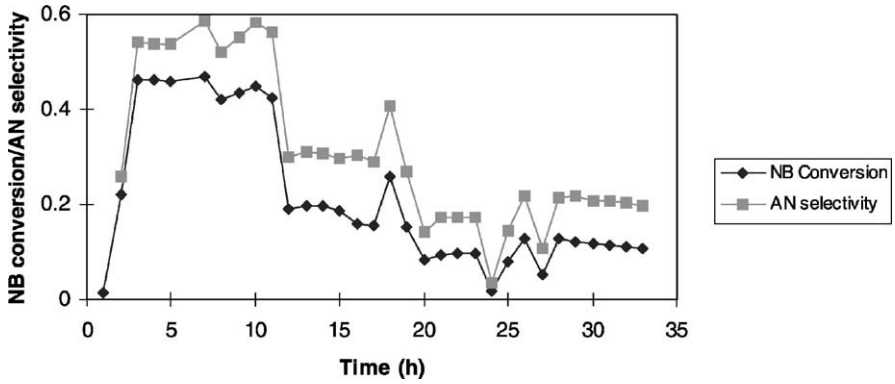

Fig. 5. Nitrobenzene conversion and aniline selectivity as a function of reaction time for the UV-decomposed palladium acetate catalyst (0.04 mol nitrobenzene/l, 60 °C, 4 bar, 0.2 ml/min).

surface. The void regions are probably areas where palladium crystallites have detached. This observation led to the conclusion that one of the causes of deactivation was palladium loss. This would exacerbate deactivation due to deposition of carbonaceous species.

6.3. Impregnated palladium (IP) catalyst

Complete conversion was achieved and maintained for 6 h, far longer than for the previous catalysts (see Fig. 7). Selectivity to aniline decreased with time but, as with conversion, this catalyst retained high selectivity for a longer period. It was clear that this catalyst was a significant improvement over the SP and UV catalysts. No side products were detected but deactivation remained a problem.

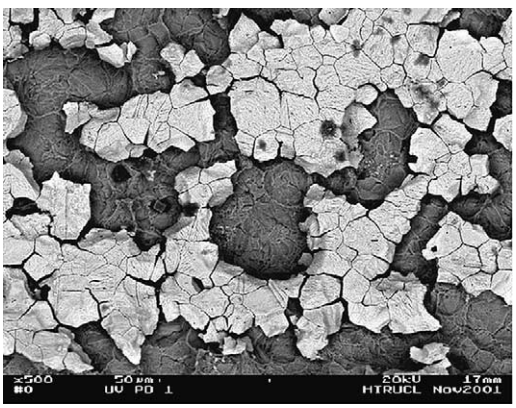

Fig. 6. SEM image of UV-deposited palladium plate after reaction (magnification: 500×).

For the first reactivation attempt, the plate was cleaned in dichloromethane and heated in air at 130 °C for 4 h. Fig. 8 (series IPA) shows that activity was recovered (note that 1 bar pressure was used after the first 3.5 h). Compared to the initial deactivation rate (refer to Fig. 7), the reactivated catalyst lost its activity more quickly. The next reactivation attempt was by cleaning in dichloromethane only. The plate was tested at the same conditions as before, except that the pressure was 1 bar (to prevent complete conversion so that recovery of activity could be more accurately gauged). As Fig. 8 shows (series IPB), there was initial recovery of activity but this was followed by rapid deactivation. For the third reactivation, the catalyst was once again washed using dichloromethane. Initial activity was recovered, but deactivation was even more rapid this time (Fig. 8, series IPC). Note that GC analysis of the wash liquid produced no other peaks besides that of dichloromethane. However, the recovery of activity following the wash indicates that deactivating compound(s) has been removed from the surface of the catalyst. The fact that nothing else was detected yet activity recovered suggests that the removed compound(s) was either sparingly soluble in dichloromethane and/or had been present on the catalyst in very small amounts.

The catalyst was then reactivated by heating in air at 130 °C for 4 h. As shown in Fig. 8 (series IPD), complete conversion was obtained initially, i.e.

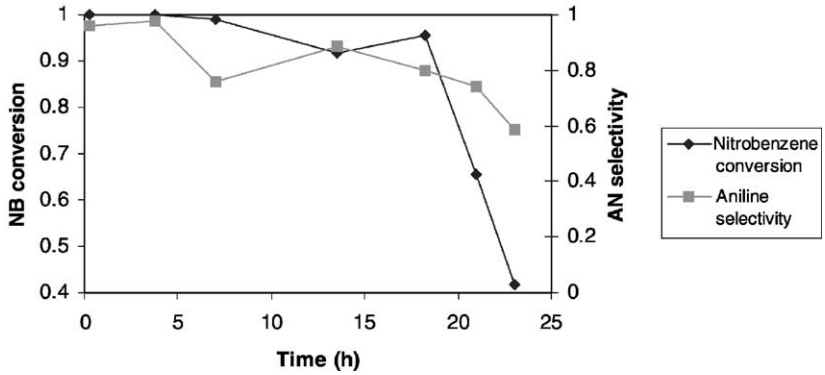

Fig. 7. Nitrobenzene conversion and aniline selectivity as a function of reaction time for the impregnated palladium catalyst (0.04 mol nitrobenzene/l, 60 °C, 4 bar, 0.35 ml/min).

the recovery of activity was better than when using dichloromethane alone. The activity remained stable for much longer as well. Successive reactivations at the same conditions all brought about recovery of activity, but the retention of activity was shorter each time. However, after the fifth reactivation by oxidation, reproducible behaviour was achieved. As shown in Fig. 9, nitrobenzene conversion immediately after each reactivation was the same and the deactivation rate seems to have levelled off (series IPH–IPJ).

These findings point out two factors at work:

(a) Deposition of organic material had occurred during the reaction thus reducing activity. The deposits could be removed by either dichloromethane washing or oxidation, the latter being more effective.
(b) Since catalyst activity decreased more quickly after each reactivation, it seems that changes to palladium had occurred, either structural changes or

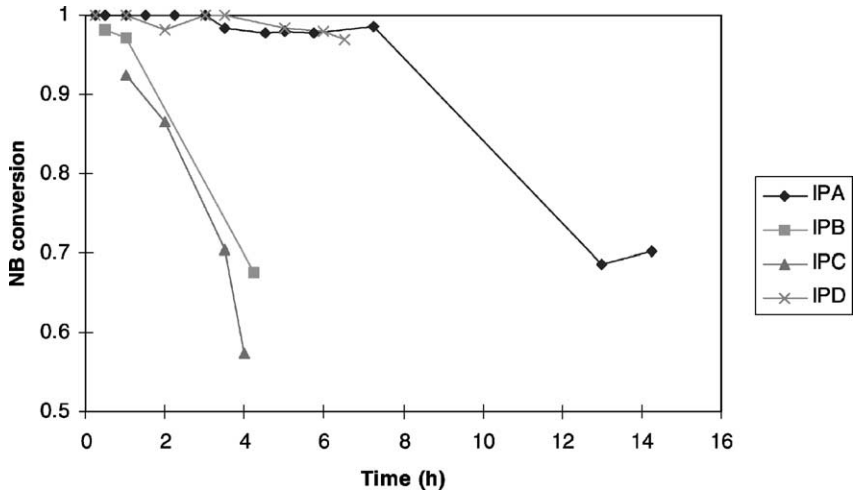

Fig. 8. Nitrobenzene conversion as a function of reaction time for the impregnated palladium catalyst after different reactivation procedures (0.04 mol nitrobenzene/l, 60 °C, 1 bar, 0.35 ml/min): IPA—dichloromethane wash and oxidation (note: 4 bar pressure used for first 3.5 h); IPB—dichloromethane wash; IPC—dichloromethane wash; IPD—oxidation.

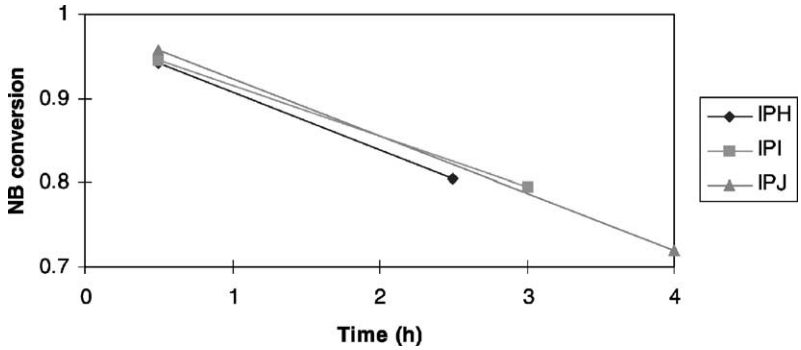

Fig. 9. Nitrobenzene conversion as a function of reaction time for the impregnated palladium catalyst after five successive reactivations by oxidation (0.1 mol nitrobenzene/l, 60 °C, 1 bar, 0.5 ml/min). IPH, IPI and IPJ correspond to data after the fifth, sixth and seventh reactivations, respectively.

leaching. This led to overall decreased but eventually stable activity.

6.4. Incipient wetness (IW) catalyst

The results for this catalyst are shown in Fig. 10. Initial conversion was high, but this settled down to about 82% and remained at that level for almost 9 h. This catalyst retained stable activity for a much longer period than any of the other catalysts. After 28 h, conversion was still at 75%. Aniline selectivity was more erratic, but had an average value of 80%. As with the IP catalyst, no side products were detected.

When the plate was removed from the reactor, several observations were evident:

(a) The shiny metallic palladium coating had become duller.
(b) There seemed to be less palladium as the channels were noticeably deeper.
(c) Black particles were found at the exit end of the plate.

The particles were analysed using XPS, confirming that they were carbon-based compounds. It is possible that these particles had formed when the catalyst was hydrogen-starved, which could have led to formation of high molecular weight carbonaceous species. Palladium was detected in the particles as well demonstrating that catalyst had been lost during the experiments. Further experimentation after reactivation brought the

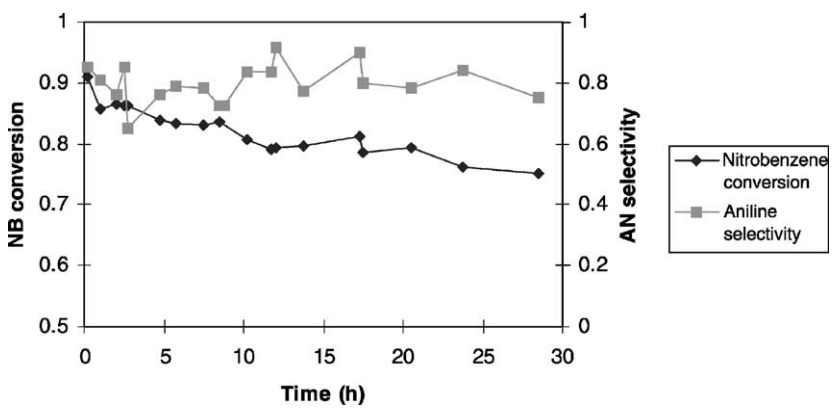

Fig. 10. Nitrobenzene conversion and aniline selectivity as a function of reaction time for the incipient wetness catalyst (0.1 mol nitrobenzene/l, 60 °C, 1 bar, 0.5 ml/min).

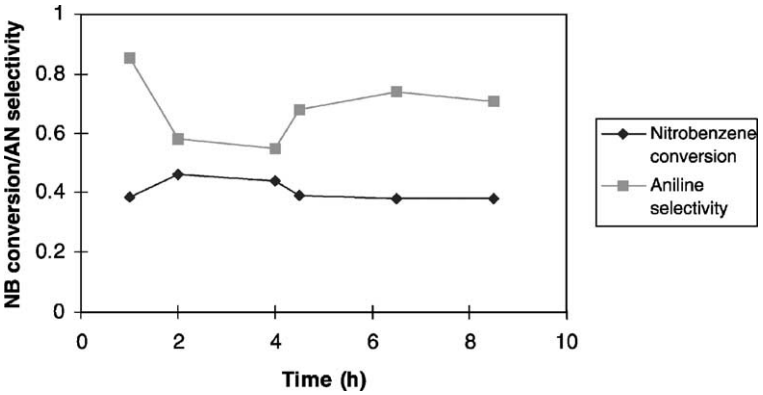

Fig. 11. Nitrobenzene conversion and aniline selectivity as a function of reaction time for the incipient wetness catalyst (1 mol nitrobenzene/l, 60 °C, 1 bar, 0.5 ml/min).

catalyst back to its original level of activity, suggesting that there was still sufficient palladium present to sustain activity.

To determine whether higher concentrations of nitrobenzene had any deleterious effects on the catalyst, a set of experiments was performed using a higher concentration of nitrobenzene (1 mol/l), keeping all other conditions the same. The results are shown in Fig. 11 (the catalyst was heated in air at 130 °C prior to these experiments to return it to its initial level of activity). There appeared to be negligible change in activity with time. The catalyst surface was noticeably darker after 8.5 h of operation and black particles were again found. Both conversion and selectivity were lower with average values of 41 and 68%, respectively.

7. Comparison of catalysts and deactivation issues

The IW plate is estimated to contain 140 mg of palladium. The IP plate contained a smaller amount of palladium since not all the palladium present in the impregnation solution was allowed to deposit. Both IP and IW plates had larger catalytic surface areas than the SP and UV plates due to the presence of the γ-alumina layer. From visual observations, the UV plate is expected to have a larger amount of palladium than the SP plate, which has a 100 nm thick layer of palladium (4.7 mg).

Catalyst longevity appeared to be dependent on palladium loading, the greater the loading, the longer the active lifespan (operation time before reactivation was required). This was likely due to the larger number of active sites, thus lessening the effect of their blockage by heavy nitrogen-containing carbon compounds. Catalyst lifespan shown in Fig. 12 (experimental conditions as noted in Table 1) follows the order: IW > IP > UV > SP. The IW catalyst was superior to the other catalysts, both in terms of longevity and activity. The IP catalyst had similar initial performance but demonstrated fairly drastic reduction in activity after several hours. The UV catalyst demonstrated high activity after a start-up period but which decreased to a more stable conversion of 18%. The SP catalyst was the least active of all, with a very short-lived period of high activity before settling down to a conversion of about 1%.

The selectivity of the catalysts towards aniline followed a similar trend. The IW catalyst had the best selectivity (average 80%). The IP catalyst had an initial selectivity of 96% but it eventually decreased to 58%. The selectivity of the UV catalyst followed the same trend as its conversion with a maximum observed at 60%. The SP catalyst showed better selectivity than the UV catalyst (between 50 and 90%).

The selectivity data vary significantly, well beyond experimental and sampling error. In addition, another incongruity was present: the carbon balance could not be closed, sometimes by as much as 20%. In general, when side products were detected, they were found in

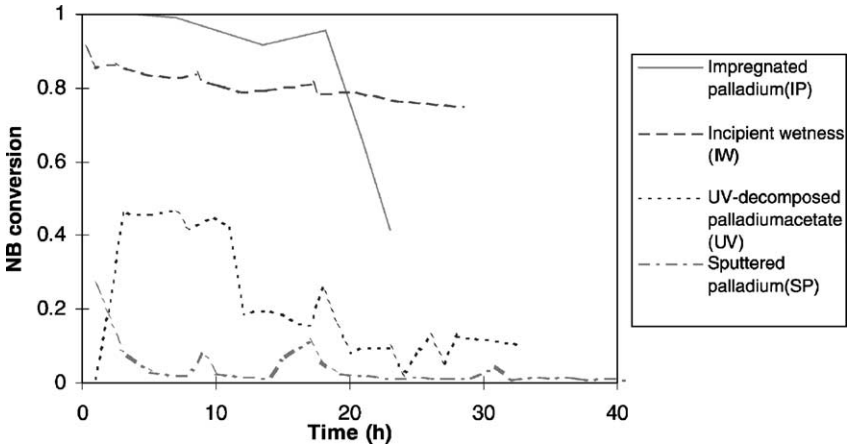

Fig. 12. Comparison of the deactivation behaviour of the various catalysts (refer to Table 1 for experimental conditions).

small quantities which could not account for the missing carbon. As mentioned before, it is possible that this carbon was in the form of heavier organic compounds which either remained on the surface of the catalyst or could not be detected using the GC. To determine the likelihood of the second possibility, a sample from the IW series operated at high nitrobenzene concentration (1 mol nitrobenzene/l, 60 °C, 1 bar, 0.5 ml/min) was analysed using thin layer chromatography (TLC). This particular sample had been chosen as it had the lowest selectivity (55%) and the carbon balance was off by 20%. The results of this analysis showed no evidence of any compounds which had not been detected using the GC. This lent credence to the postulate that the missing carbon had in fact adhered to the surface of the catalyst or reactor.

While the exact cause(s) of deactivation have not been pinpointed with complete confidence, the evidence so far suggest that two main factors are involved:

(a) High molecular weight organic deposits are likely to be forming but can be removed by heating the catalyst to 130 °C. This agrees with the observations of van Gelder et al. [33] for the hydrogenation of 2,4,6-trinitrotoluene. Given the constant rate of deactivation obtained for the IP catalyst and the formation of carbon-containing particles on the IW catalyst, this seems to be the leading cause of deactivation.

(b) The inability to return the catalysts to their initial activity, the quicker deactivation after successive reactivations, observation of missing/flaking palladium and the detection of palladium in the carbonaceous particles all point to the fact that palladium loss had occurred. However, since the deactivation rate for the IP catalyst eventually became constant after several reactivations, it seems likely that the rate of palladium loss gradually decreases for the IP and IW catalysts. While organic deposits are responsible for short-term deactivation, palladium loss leads to irrecoverable long-term loss of activity. According to Blaser et al. [32], metal leaching can become pronounced under hydrogen-starved conditions. This could be happening in this system since hydrogen was the limiting reactant, and the catalyst was always in contact with liquid during reaction.

8. Conclusions

It has been demonstrated that the hydrogenation of nitrobenzene over palladium catalyst in a microstructured falling film reactor is feasible, provided that suitable catalyst incorporation methods are employed. Deactivation took place most likely through the formation of organic compounds on the catalyst surface and palladium loss. The former was addressed by oxidation in air at 130 °C for 4 h, leading to recovery of

activity. The latter could not be halted but the effects were hindered by increased catalyst amount. A reasonably robust catalyst (γ-alumina supported palladium prepared through incipient wetness) has been developed to surmount these problems. At nitrobenzene concentration 0.1 mol/l, flowrate 0.5 ml/min, temperature 60 °C, pressure 1 bar, the microstructured falling film reactor can produce 394 kmol aniline/m^3 reactor daily while a batch reactor of 3 m^3 volume, operating at 20 bar, 125 °C, initial nitrobenzene concentration 0.4 mol/l, 5% Pd/C catalyst (0.0001 kg catalyst/kg reaction mixture) [15] would have a daily production rate of 204 kmol aniline/m^3 reactor (assuming no downtime between batches).

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