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Heterogeneously-catalyzed competitive hydroarylation/hydromination of norbornene with aniline in the presence of Aquivion® ionomer

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Abstract: The hydroarylation of alkenes with aniline is a reaction of high interest, in particular for the manufacture of polyurethanes. This reaction has been mostly investigated in the presence of homogeneous catalysts. So far, heterogeneous catalysts have been scarcely reported for this reaction, mainly due to their inherent low activity and deactivation during the course of the reaction. Here we report the catalytic performance of Aquivion® ionomer, a perfluorinated solid acid polymer, in the hydroarylation of norbornene with aniline. We show that Aquivion® ionomer was robust and can be recycled for at least 6 runs without any decrease of its catalytic performances. Our results also highlight that Aquivion® ionomer improves the propensity of aniline to react through its aromatic ring, thus yielding a higher proportion of hydroarylation products as compared to other tested homogeneous and heterogeneous catalysts.

Keywords: Heterogeneous catalysis, Acid catalysis, Hydroarylation, Hydroamination, Aniline

Abbreviations: HFIP (Hexafluoroisopropanol); PFSA (Perfluorosulfonic acid); TfOH (Triflic acid); PW (Powder); TGA (Thermogravimetric analysis)

1. Introduction

Aniline is industrially produced at more than 8 million tons per year and at a very competitive price (around 1 €/kg).[1] Hence, aniline is a chemical of considerable interest in the chemical industry, in particular for the synthesis of polymer foams. In this context, the hydroarylation of alkenes with aniline is a reaction of high interest, as it provides a 100% atom economical access to organic building blocks for bioactive chemicals[2] and, more importantly, polyurethanes, the largest market share of aniline. Indeed, aniline-derived hydroarylation products are dimerized on large scale with formaldehyde to yield a diamine, which serve as a monomer in the fabrication of polyurethanes. Compared to the well-documented hydroarylation of alkenes with aromatics,[3, 4] the reaction of alkenes with aniline is more challenging, since the hydroarylation competes with the hydroamination reaction, leading to a mixture of products.[5, 6] As a result, one of the main challenges is to optimize the formation of hydroarylation products for applications in the field of polyurethanes.

The catalytic hydroarylation of alkenes with aniline derivatives has been extensively investigated. This reaction is generally catalyzed by acids [7-11], transition metals such as Rh[12, 13], Ir [14-19], Ta [20], Ti [21], Au [22], Y [23], Ru [24], Sc [25], Co [26] or frustrated Lewis pair [27]. However reports studying the non-functionalized aniline are rare. In the reported examples, transition metal complexes or Lewis/Brønsted acids were investigated, leading to different ratios of hydroamination and hydroarylation products, depending on the reaction conditions.[28-32] In an industrial context, the utilization of solid catalysts for this reaction is highly desirable to facilitate the separation of hydroarylation / hydroamination products, and/or the recycling of

catalysts after the reaction. Most of the studies reported so far have focused on the homogeneously-catalysed hydroarylation of alkenes with aniline derivatives.[3] To our knowledge, the heterogeneously-catalyzed hydroarylation of alkenes with non-functionalized aniline has only been reported sporadically by Burgoyne (using 13% $\text{Al}_2\text{O}_3/\text{SiO}_2$)[33] and Shi (using USY zeolite).[34] Both solid acid catalysts afforded hydroarylation products with good-to-excellent selectivity (70-95%). This high selectivity towards hydroarylation products was ascribed to a Hofmann-Martius rearrangement of hydroamination products back to hydroarylation products, a reaction that typically occurs over Lewis acid sites at high temperatures. Despite these promising results, under the working conditions, solid acid catalysts unfortunately suffer from coking due to uncontrolled polymerization of the alkene, leading to their deactivation. So far, there is a lack of stable solid acid catalysts capable of promoting the hydroarylation of alkenes with aniline.

In recent years, we, among other authors, have reported the performance of Aquivion[®] PFSA, a perfluorinated sulfonic acid (PFSA) ionomer, in acid-catalyzed organic reactions.[35-42] Due to the presence of perfluorinated chains, Aquivion[®] PFSA is regarded as a solid superacid with a Hammett acidity (H_0) of -12, which is similar to that of H_2SO_4 and higher than that of other commercial sulfonated cation exchange resins such as Amberlyst[®]-15 ($H_0 = -2$) for instance (Fig. S1). As a result, Aquivion[®] PFSA is active at lower temperatures than common solid acid catalysts, thus limiting the formation of coke and subsequent deactivation. Furthermore, the mechanical and chemical integrity of Aquivion[®] PFSA is preserved at temperatures up to 150-180 °C, which is a positive aspect regarding its long-term recyclability.

Recently, through combined experimental-theoretical studies, we and others [43-45] have reported that the hydroarylation of aniline can be performed at close to ambient

temperatures, using hexafluoroisopropanol (HFIP) as a protic fluorinated solvent, in the presence of Brønsted-acidic catalysts such as trifluoromethanesulfonic acid (TfOH). We proposed that the origin of the enormously increased activity of the catalyst in HFIP compared to other solvents resulted from stabilizing H-bond interactions between HFIP and the acid catalyst in the rate-limiting transition state.[43] Altogether, these results prompted us to investigate in more detail the possible use of Aquivion® PFSA as a perfluorinated solid acid catalyst for this reaction.

Here we investigate the catalytic performance of Aquivion® PFSA as a solid acid catalyst in the hydroarylation of norbornene with non-functionalized aniline. A comparison with commonly used homogeneous and heterogeneous catalysts was also included to shed light on the unique benefits of Aquivion® PFSA for the hydroarylation/hydroamination of alkenes with aniline.

2. Experimental

A Parr-reactor was charged with norbornene (188 mg, 2 mmol, 1 equiv.), aniline (931 mg, 10 mmol, 5 equiv.) and toluene (15 mL). Then, the given catalyst (10 mol% H⁺) was added at room temperature, and the reaction mixture was stirred under a N₂ atmosphere at the desired temperature. Note that for heterogeneous catalysts, the mass of introduced Aquivion PFSA samples, sulfonated carbon and Amberlyt-36 were calculated so that the amount of introduced H⁺ into the reactor correspond to 10 mol% of norbornene. After completion of the reaction, the reactor was cooled down to room temperature and the heterogeneous catalyst was removed by filtration, and the reaction mixture was analyzed using an Agilent 7890 GC equipped with an HP-5 MS capillary column bearing 5 wt% phenyl groups (length 30 m; inner diameter 0.25 mm) and a FID detector, as described in ref 43. The heating ramp of the oven was slightly

adjusted for products listed in Table 2 as they differ in terms of molecular weight and polarity. In all the methods, the injector temperature was set at 250 °C, the FID detector temperature was 300 °C and the sample injection volume was 1 µL. The calibrations were performed using dodecane as an internal standard (see representative chromatogram in Fig. S2a-b). The TOF of the reaction provided at 140 and 170°C for Aquivion PW98 was measured at the initial stage of the reaction, typically at a conversion below 25%.

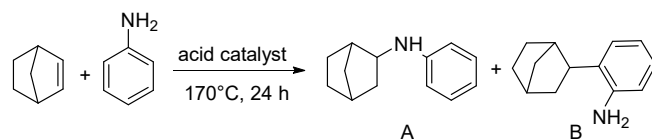
3. Results and discussion

The hydroarylation of norbornene with aniline was selected as a model reaction to assess the catalytic performance of Aquivion® PFSA. In a typical experiment, norbornene was mixed with a 5-fold excess of aniline and heated in toluene at 170 °C (in an autoclave) for 24 h in the presence of 10 mol% of H⁺. Note that for heterogeneous catalysts described below (Aquivion PFSA, sulfonated carbon and Amberlyt-36, see proton loading in Table 1), the masses of catalyst were calculated so that the amount of introduced H⁺ into the reactor correspond to 10 mol% of norbornene. An excess of aniline was employed to prevent the successive addition of two norbornene moieties on one aniline molecule, as shown elsewhere.[5] The reaction (conversion, yield, selectivity, Table 1) was monitored by gas chromatography (Fig. S2-S4). Note that in the absence of a catalyst, no reaction occurred, indicating that a catalyst was mandatory to activate the reaction (Table 1, entry 1).

In the presence of HCl or H₂SO₄ (10 mol % H⁺), no appreciable conversion of norbornene was observed (Table 1, entries 2, 3). In contrast, with triflic acid (TfOH), 86% norbornene was converted, indicating that very strong Brønsted acid sites are required to catalyze the reaction (Table 1, entry 4). Analysis of the reaction products

by $^1\text{H}/^{13}\text{C}$ NMR and gas chromatography revealed the formation of the hydroamination (A) and hydroarylation (B) products with yields of 41% and 14%, respectively. It corresponds to an A/B molar ratio of 75/25. Note that the hydroarylation reaction exclusively furnished the *ortho* isomer (see NMR in the SI), in line with previous reports. Other products formed were mostly di- and trihydroarylation products and isomerization products, as described elsewhere.[32]

With these results in hand, strong solid acids such as HZSM-5 zeolite, a cation exchange resin (Amberlyst[®] 36) and a sulfonated carbon (Carbon-SO₃H), were then tested. HZSM-5 was poorly active, leading to a norbornene conversion of only 7% after 24h of reaction, presumably due to the reaction temperature which was too low for such solid catalyst (Table 1, entry 5). Amberlyst[®] 36 and the sulfonated carbon led to moderate norbornene conversions of 21% and 25%, respectively (Table 1, entries 6, 7). The selectivity to hydroamination / hydroarylation products was similar to that observed with TfOH (A/B ratio ~ 70/30).

Table 1 Hydroamination of norbornene with aniline catalyzed by different catalysts.^[a]

Entry	Catalyst	Conv./ %	Yield A (%)	Yield B (%)	A/B ratio	Other (%) ^[b]
1	-	0	-	-	-	-
2	HCl	<5	-	-	-	-
3	H ₂ SO ₄	<5	-	-	-	-
4	TfOH	86	41	14	75/25	31
5 ^[c]	HZSM-5	7	-	-	-	-
6 ^[d]	Amberlite 36	21	8	3	73/27	10
7	Carbon-SO ₃ H ^[e]	25	14	6	70/30	5
8	PW87 ^[f]	55	26	21	55/45	8
9	PW66 ^[g]	61	30	25	55/45	6
10	PW98 ^[h]	52	28	20	58/42	4
11 ^[i]	PW98	85	43	29	60/40	13

^[a] 2 mmol norbornene, 10 mmol aniline, 15 mL toluene, [H⁺] 10mol%, 170 °C, N₂ atmosphere; ^[b] Other products formed were mainly di- and trihydroarylation products and isomerization products; ^[c] 0.2 g HZSM-5 (Si/Al = 25, acid site density = 0.9 mmol/g); ^[d] proton exchange capacity = 5.4 mmol H⁺/g; ^[e] proton loading = 0.54 mmol/g; ^[f] proton loading = 1.15 mmol/g; ^[g] proton loading = 1.45 mmol/g; ^[h] proton loading = 1.0 mmol/g; ^[i] collected after 55 h of reaction.

To our delight, in the presence of strongly acid Aquivion[®] PW87 (PW = powder form, the number referring to the proton loading, see Table 1, entries 8-10), 55% of norbornene was converted, affording the hydroarylation and hydroamination products in 21 and 26% yield, respectively (Table 1, entry 8). A change of the -SO₃H loading on Aquivion[®] PFSA from 1.0 to 1.46 mmol/g, while keeping 10 mol % of H⁺ relative to norbornene, did not significantly increase the yields of A and B, as well as the norbornene conversion. This result suggests that, within this -SO₃H loading range, the density of acid sites on Aquivion[®] PFSA does not impact its catalytic performance, which could have been expected with a change of the hydrophilic-lipophilic balance of the catalytic surface, or cooperativity between -SO₃H groups (Table 1, entries 8-10). Interestingly, compared to the other catalysts listed in Table 1, the hydroarylation product was formed in a higher proportion when using Aquivion[®] PFSA catalysts, as inferred by the decrease of the A/B ratio from 75/25 to 55-58/45-42. To monitor the selectivity along the reaction, over Aquivion[®] PW98, we plotted the yield of hydroarylation (B) and hydroamination (A) products, as well as the A/B ratio, as a function of the norbornene conversion (Figure 1). This plot revealed an almost constant A/B molar ratio of ~60:40, irrespective of the norbornene conversion. In the case of the homogeneous TfOH catalyst, we noticed the same behaviour, albeit at the aforementioned higher A/B molar ratio of ~75:25 (Fig. S5), further corroborating the higher selectivity of Aquivion[®] PFSA towards hydroarylation products.

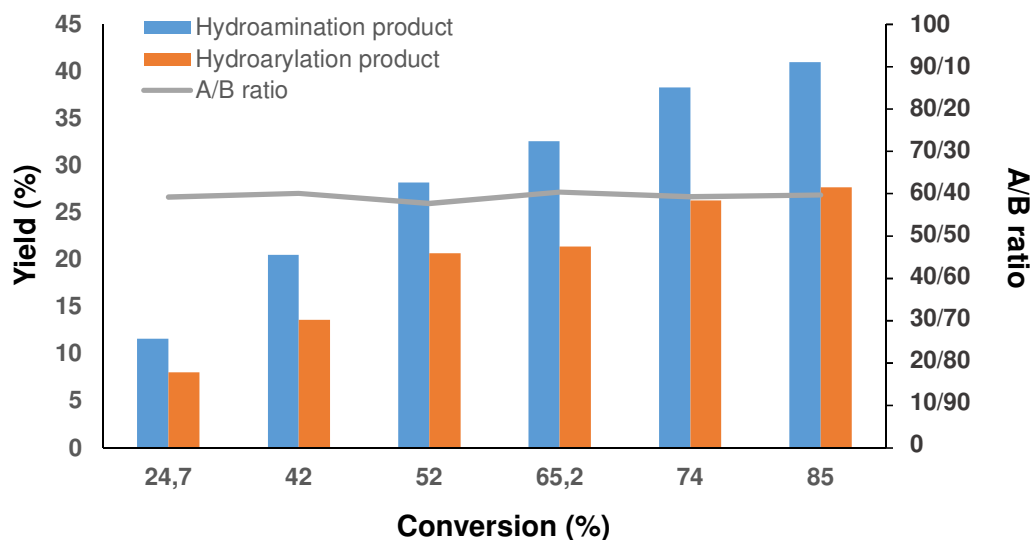


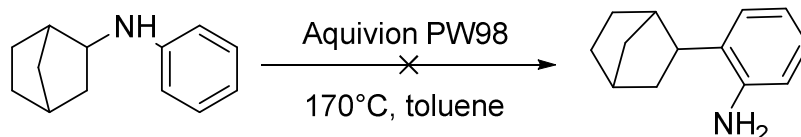
Fig. 1. Plot of the A and B yields, and A/B ratio, as a function of the norbornene conversion (2 mmol norbornene, 10 mmol aniline, 15 mL toluene, $[H^+]$ 10 mol% (Aquivion® PW98), 170 °C, N_2 atmosphere).

Varying the catalyst amount from 1 to 10 mol% obviously impacted the norbornene conversion rate, but did not alter the A/B ratio, confirming that the high amount of hydroarylation product is not a result of diffusion limitations, but is indeed controlled by the Aquivion® PFSA catalyst (Fig. S6). Extending the reaction time from 24 to 55 h increased the norbornene conversion from 52 to 85% (Table 1, entry 11). At 85% conversion, the hydroamination and hydroarylation products were formed in 43 and 29% yield, respectively (60/40 ratio), with the *ortho* isomer as the only hydroarylation product. At high conversion (85%), the amount of “other products” increased steadily from 4% to 13%, mostly due to subsequent di- and trihydroarylation of aniline (Table 1, entries 10, 11).

Note that reducing the temperature from 170 to 140 °C resulted in a strong decrease of the Aquivion® PW98 activity (TOF from 0.6 to 0.1 h^{-1}) (Fig. S7, S8), but without significant impact on the hydroarylation/hydroamination selectivity (Table 1, entries 1,

2). A further reduction of the temperature below 140°C unfortunately led to unacceptable reaction rates. More information on the impact of the reaction temperature on the selectivity of the reaction is discussed at the end of the manuscript.

In an attempt to understand the reasons behind the slightly higher selectivity of Aquivion® PFSA towards hydroarylation products, compared to other catalysts, additional experiments were conducted. As discussed in the introduction, at 140-170°C, an acid-catalyzed Hofmann–Martius rearrangement of A to B cannot be ruled out, which could explain the highest selectivity of Aquivion® PFSA towards the hydroarylation product. To this end, the hydroamination product A was isolated and subjected to the reaction conditions listed in Table 1. No formation of the hydroarylation product was observed, ruling out this rearrangement in the presence of Aquivion® PFSA (Scheme 1).



Scheme 1 Hofmann-Martius rearrangement of A to B.

Instead, we suspect that the fluorine environment on the surface of Aquivion® PFSA could be responsible for the slightly higher selectivity towards the hydroarylation product. This hypothesis is inspired by a previous work of Lekta who demonstrated that C-F bonds, when positioned over the π cloud of aromatic rings, can drastically increase the reactivity of aromatic rings towards electrophiles (up to 1500 fold increase in reactivity),^[46] which may explain the highest propensity of Aquivion® PFSA to form the hydroarylation product.

To further demonstrate how the electron density on the aromatic ring may influence the hydroamination / hydroarylation ratio, various aniline derivatives bearing electron-donating or withdrawing groups were tested in the presence of Aquivion® PW98. In these experiments, the concentration of reactants was increased by a factor of 5, while keeping constant the concentration of H⁺ at 10 mol%, to speed up the reaction (reduction of the reaction time from 24 to 2 h).

As shown in Table 2, the functionalization of aniline exerted a significant effect on the hydroamination / hydroarylation selectivity. For instance, *para* substitution of aniline by a -OMe electron-donating group favoured the hydroarylation reaction (Table 2, entry 2). With halogen substituents, the hydroamination reaction became dominant (Table 2, entries 3, 4), and it was the exclusive reaction when aniline was functionalized with strong electron-attracting groups such as -CF₃ or -NO₂. (Table 2, entries 5, 6).

Table 2 Effect of aniline substituents on the yield and selectivity^[a]

Entry	R	Conv. (%)	Yield A (%)	Yield B (%)	A/B ratio
1	H	85	43	29	60/40
2	4-OMe	31	9	18	33/66
3	4-Cl	83	43	12	78/20
4	2-Cl	100	82	17	83/17
5	3,5-CF ₃	100	94	0	100/0
6	2-NO ₂	100	99	0	100/0

^[a] 10 mmol norbornene, 50 mmol aniline, 10 mL toluene, 10 mol% -SO₃H on Aquivion®, 170 °C.

As a general trend, the selectivity to the hydroarylation product correlates with the basicity of the aniline derivatives (Fig. 2): the higher the basicity of aniline derivatives, the higher the selectivity to hydroarylation products. This can be easily rationalized in terms of electron density on the aromatic ring of aniline. Electron-donating substituents such as -OMe increase the electron density of the aromatic ring, while electron-withdrawing substituents lower the electron density, hence increasing or reducing the propensity of aniline to react through the -NH or =C-H bond.[5, 12] The change of A/B molar ratio as a function of the electron density on the aromatic ring of aniline also supports our hypothesis of an electronic enrichment of the aromatic ring of aniline by Aquivion® PFSA.

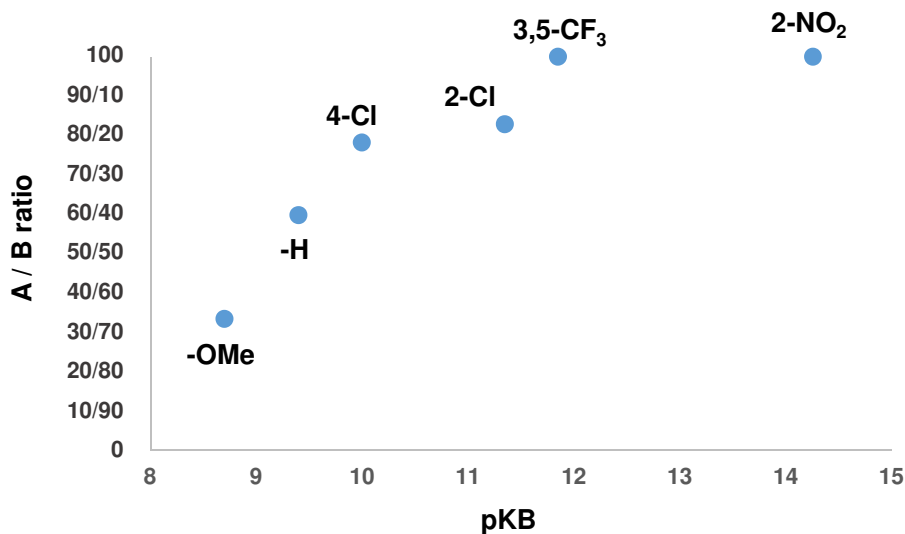


Fig. 2. A/ B ratio as a function of the pK_b of aniline derivatives.

Recycling is one of the advantages of heterogeneous catalysis over homogeneous catalysis. To this end, the recyclability of Aquivion® PW98 was assessed at 170 °C for 2 h of reaction. After the first catalytic run, Aquivion® PW98 was recovered by filtration, washed with water and ethanol, and reused without any further purification. Gratifyingly, Aquivion® PW98 could be successfully recycled for at least 6 times without appreciable decrease of conversion, yield and A/B ratio, further confirming the robustness of this catalyst in the acid-catalyzed Hydroarylation / hydroamination of norbornene with aniline (Fig. 3).

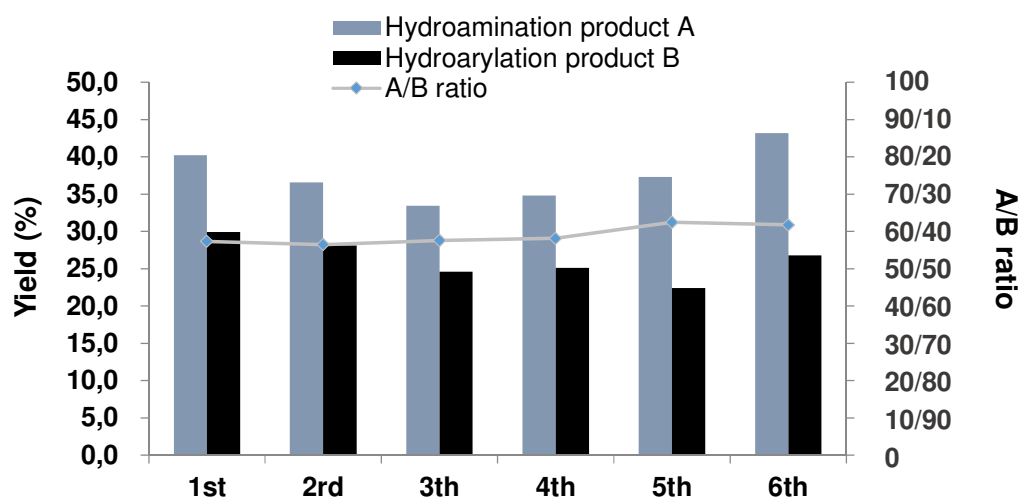


Fig. 3. Recycling experiments (10 mmol norbornene, 50 mmol aniline, 10 mL toluene, 10 mol% $\text{-SO}_3\text{H}$ on Aquivion®, 170 °C, 2 h).

Titration of fresh Aquivion® PW98 confirmed the presence of $\text{-SO}_3\text{H}$ with a concentration of 1 mmol/g, matching the theoretical value (see procedure in SI). After the first catalytic run, the $\text{-SO}_3\text{H}$ concentration dropped to 0.82 mmol/g, which can be attributed to either (i) the reaction of $\text{-SO}_3\text{H}$ with aniline leading to a gain in mass and, as a result, to partial dilution of $\text{-SO}_3\text{H}$ sites, or (ii) the deposition of poly-oligomeric material on the Aquivion® PW98 surface. In contrast to fresh Aquivion® PW98, TGA of spent Aquivion® PFSA revealed an additional mass loss of 11% at 370 °C (Fig. S9). Treatment of Aquivion® PW98 with aniline in toluene (*i.e.* without norbornene), followed by thorough washing with ethanol and water, led to a similar TGA profile, strongly supporting the reactivity of Aquivion® PW98 with aniline (Fig. S10). Assuming complete reaction of $\text{-SO}_3\text{H}$ groups with aniline (acid-base reaction), a theoretical mass gain of ~ 10% would be expected, which is close to the additional mass loss observed by TGA on the spent Aquivion® PFSA. Besides reaction with aniline, we cannot rule out a slight coking of Aquivion® PFSA, as corroborated by a change of colour of Aquivion® PW98 during the reaction from transparent to brown (Fig. S11). Our TGA

analyses revealed, however, that carbon deposition was very low and did not affect significantly the long-term recycling of Aquivion® PW98. This was further confirmed by titration of Aquivion® PW98 after two catalytic cycles which revealed a -SO₃H concentration stable at 0.80 mmol/g. Furthermore, by means of ¹⁹F NMR, no trace of fluorine was detected in the solution, at least within the detection limit, further confirming the chemical stability of Aquivion® PW98 under our working conditions (Fig. S12).

4. Conclusions

In this work, we investigated the catalytic performances of Aquivion® PFSA, a perfluorinated solid acid polymer, in the hydroarylation / hydroamination of norbornene with aniline. This reaction has been scarcely investigated in the presence of solid catalysts, mainly due to the difficulty of avoiding a rapid catalyst deactivation. We report here that Aquivion® PFSA, in its powder form, is a recyclable solid acid catalyst capable of promoting the hydroarylation of norbornene with neat aniline. Our results also suggest that the fluorine environment on Aquivion® PFSA impacts, to some extent, the competition between the hydroamination and hydroarylation reactions. In particular, Aquivion® PFSA increases the propensity of aniline to react through the aromatic ring, leading to a higher proportion of hydroarylation products, compared to all other tested catalysts.

At the stage of our investigations, the precise reason for the higher selectivity of Aquivion® PFSA compared to the other tested catalysts remains unclear. In this context, DFT calculations are now the topic of current investigations in our groups to assess the interaction of fluorine atoms of Aquivion® PFSA with the aromatic ring of aniline.

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