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Aquivion[®]-carbon composites *via* hydrothermal carbonization: Amphiphilic catalysts for solvent-free biphasic acetalization†‡

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One-pot hydrothermal carbonization of polysaccharides (i.e. guar gum or cellulose) with Aquivion[®] perfluorosulfonic superacid at 180 °C produced new amphiphilic Aquivion[®]-carbon composites. The materials stabilized dodecyl aldehyde/ethyleneglycol Pickering emulsions, and thus catalyzed efficiently the solvent-free biphasic acetalization reaction under moderate conditions with excellent reusability.

Organic solvents are commonly used in organic synthesis for enhancing the solubility/miscibility and conditioning the reactivity of reagents.¹ However, solvents (including water) increase artificially the complexity of a reaction system and require further extraction/purification steps for recovery and recycling, hampering the green footprint of the process. Phase-transfer catalysts and surfactant-combined catalysts can be used for boosting the contact and transfer between immiscible reagents, but offering poor recyclability.²

Pickering interfacial catalysts (PIC) can provide an elegant solution for conducting solvent-free biphasic reactions in the presence of emulsions.³ In this concept, the particle assembly at the liquid/liquid interface increases not only the interfacial area between the reagents, but also alleviates external mass transfer limitations. Despite these potential benefits, developing advanced PIC systems remains still a great challenge.⁴ Among the catalysts available, composite materials combining hydrophobic carbons with hydrophilic particles play a central role. Resasco and co-workers pioneered the synthesis of amphiphilic nanohybrids combining single-walled carbon nanotubes (SWCNTs) and silica bearing

catalytic sites (i.e. Pd nanoparticles and alkali moieties).⁵ The materials catalyzed efficiently the aldol condensation/hydrogenation reaction of 5-methylfurfural and acetone in water/oil emulsions with controllable phase selectivity. The same team further developed multi-walled CNTs grown on alumina and 'onion-like' carbon on silica for hydrogenation and partial oxidation reactions.⁶ Additional examples of amphiphilic carbon catalysts for biofuel upgrading include Au@ PHCS (PHCS = porous hollow carbonaceous spheres), Ru@pristine-CNT, Pd@CN (CN = N-doped mesoporous carbon), iron oxide/CNT, TiO₂/CNT and Ag/graphene oxide.⁷

In the current progress to novel PIC catalysts, it would be highly desirable to design materials with versatile hydrophilic/hydrophobic properties for target reactions. Herein, we prepared for the first time amphiphilic Aquivion[®]-carbon composites as novel interfacial acid catalysts. Aquivion[®] represents a new class of perfluorosulfonic superacid resin (H₀~12) constituted by a tetrafluoroethylene backbone and sulfonyl fluoride vinyl ether side chains (Fig. S1).

The Aquivion[®]-carbon composites were prepared from the one-pot hydrothermal carbonization (HTC) of guar gum or cellulose.⁸ Briefly, 1 g of Aquivion[®] (Aq-PW98-S, acid loading = 1.0 mmol/g) was added into 20 mL of deionized water and the solution was stirred at 50 °C for 2 h. Then, 1 g of either guar gum or cellulose was added slowly into the Aquivion[®] water dispersion under vigorous stirring. Noteworthy, in the presence of guar gum, the Aquivion[®] solution generated a light yellow viscous gel within few minutes, which was not observed in the presence of cellulose. Then the mixture was sealed in a Teflon[®]-lined autoclave (50 mL) and submitted to hydrothermal synthesis at 180 °C for 24 h. After this period, the autoclave was quenched to room temperature and the resulting solid was filtered, washed with deionized water until neutral pH, and dried at 100 °C overnight under vacuum. These materials are hereinafter termed as Aq-guar and Aq-cell, respectively. For comparison, two reference carbons (i.e. C-guar and C-cell) were prepared using the same protocol (see SI). The carbon yields for Aq-guar and Aq-cell were 36% and 41%, respectively, whereas the yields for C-guar and C-cell were about 20%.

The composite materials were first inspected by XRD (Fig. S2). Two broad reflections centered at 16° and 39° could be observed for Aq-PW98-S, which in analogy to Nafion[®]-carbon composite films

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can be attributed to the perfluorocarbon backbone of the polymer.⁹ A similar pattern was observed for the Aq-carbon composites, but the reflection at 39° decreased largely for Aq-guar and even vanished for Aq-cell. A shoulder was visualized in the range 20-30° for the composites, which can be attributed to graphitic (002) planes.¹⁰ Overall, the XRD patterns confirm the fixation of Aquivion® into the carbon matrix, this being composed of carbon sheets arranged in a random fashion.

The surface composition of the Aq-guar and Aq-cell was further inspected by FT-IR spectroscopy (Fig. 1). The composites showed additive peak positions found in Aquivion® and the pristine carbon. The IR signature of Aquivion® could be easily found in the range 500-1400 cm⁻¹. Characteristic bands appeared at 515 and 634 cm⁻¹ for Aquivion® and Aq-guar that by analogy with trifluoromethane sulfonates can be assigned to C-S and S-OH deformation modes of CF₂-SO₃ and SO₃H groups in the resin, respectively.¹¹ A band also appeared at 970 cm⁻¹ that can be attributed to combined symmetric stretching modes of C-F and C-O-C species.¹² Additional bands were also visible that can be assigned to symmetric stretching modes of SO₃⁻ groups (1057 cm⁻¹),^{12b,13} combined asymmetric stretching modes of C-O-C and SO₃⁻ groups and stretching vibrations involving C-F bonds (1154 cm⁻¹),^{12b-c,14} and combined symmetric and asymmetric stretching modes of CF₂ and SO₃⁻ groups (1220 cm⁻¹ and 1300 cm⁻¹, respectively) as previously reported on hydrated Nafion®.^{12b-c,13} Finally, the band appearing at 1420 cm⁻¹ for Aq-char can be ascribed to symmetric stretching modes of S=O bonds belonging to undissociated SO₃H groups.^{12b}

In addition to these bands, the Aq-carbon composites exhibited bands associated to the carbon material appearing mostly in the range 1500-3000 cm⁻¹. In particular, two typical bands were visible at 1700 cm⁻¹ and 1616 cm⁻¹ that can be assigned to asymmetric stretching vibrations of C=O and C=C groups in the aromatic rings, respectively.^{10b,15} Noticeably, Aq-guar showed two bands centered at 2928 cm⁻¹ and 2858 cm⁻¹ that can be ascribed to aliphatic C-H stretching vibrations, but which could be hardly observed on Aq-cell.¹⁶ Finally, the distinctive band appearing at 3480 cm⁻¹ for Aq-guar attributed to the stretching vibration modes of -OH groups reflects an enhanced hydrophilic behavior for this sample.

Besides FT-IR, the different samples were characterized by ¹⁹F and ¹³C-NMR MAS (Fig. 2). In agreement with the liquid ¹⁹F-NMR spectra (Fig. S3), the ¹⁹F-NMR MAS spectrum of the pristine Aq-PW98-S exhibited four characteristic resonance regions (Fig. 2A):^{14,17} (1) a signal at -76 ppm that can be attributed to O-CF₂ groups belonging to the side chain of Aquivion®; (2) two sharp signals at -118 ppm and -122 ppm that can be assigned to CF₂-S and CF₂ groups in the side chains and in the backbone of the resin, respectively; and (3) a small signal at -131 ppm that can be assigned to CF groups in the backbone of Aquivion®. This pattern was kept almost unchanged for Aq-guar and Aq-cell composites, reflecting the incorporation of Aquivion® into the carbon matrix. Interestingly, the signal belonging to CF₂-S groups (-118 ppm) was still visible in the composites, but at a much lower intensity. This observation suggests a preferential interaction of SO₃H/SO₃⁻ groups in the side chains of Aquivion® with the carbon matrix (probably with phenolic OH groups driven by presence of moisture), limiting the motion of CF₂-S bonds.¹⁸ Finally, the absence of band at 48 ppm indicates the absence of SO₂F moieties in both the polymer and the composites.

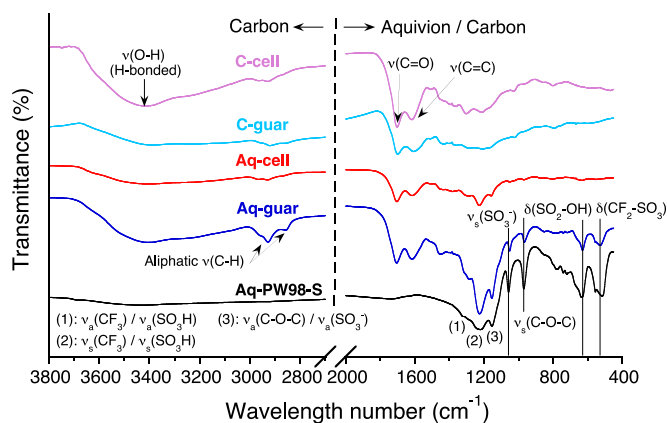


Fig. 1 FT-IR spectra of Aq-PW98-S, Aq-carbon composites and pristine carbon materials.

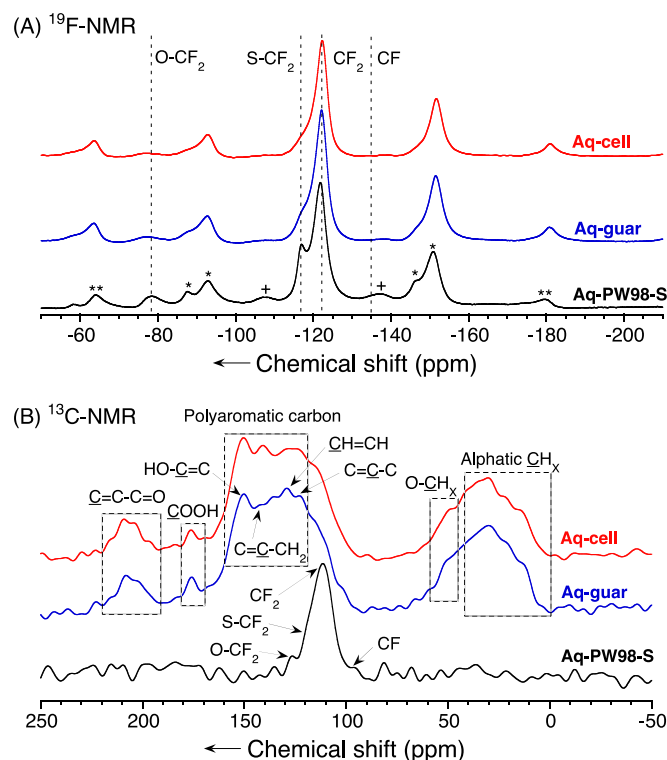


Fig. 2 (A) ¹⁹F-NMR MAS and (B) ¹³C-NMR MAS spectra measured on Aq-PW98-S and Aq-carbon composites. The asterisks and crosses in the ¹⁹F CP-MAS NMR spectrum denote first and second-order spinning sidebands. For comparison, liquid ¹⁹F-NMR and ¹³C-NMR spectra on Aq-PW98-S (suspension) can be found in the ESI (Fig. S3, S4).

The ¹³C-NMR MAS spectrum of Aq-PW98-S displayed a broad band centered at 110 ppm revealing the presence of CF₂ and CF₂-S groups (Fig. 2B). The liquid ¹³C-NMR spectrum measured on the same sample but without decoupling displayed a triplet due to the coupling with adjacent fluorine atoms ($J=276.8$ Hz, Fig. S4). Two additional signals were also apparent at 105 ppm and 125 ppm that can be assigned to CF and CF₂-O groups belonging to the backbone and side chains of the resin, respectively. Turning now our attention into Aq-guar and Aq-cell, the ¹³C-NMR spectra of both composites presented four main resonance regions (Fig. 2B): (1) signals in the range 11-50 ppm that can be attributed to methylene or aliphatic CH_x groups (sp³-carbon);¹⁹ (2) broad band in the range 110-160 ppm

that can be associated to Aquivion® combined with polycyclic aromatic carbon atoms (sp^2 -carbon),^{8a,19c-d} and (3) signals at 176 ppm and in the range 197-210 ppm that can be assigned to COOH and C=O groups bonded to the polycyclic aromatic rings, respectively.^{19c-d,20} In particular, in the second region, the signals appearing at 139 ppm and 150 ppm can be assigned to aromatic carbon atoms bonded to methylene groups and oxygenated carbons (*e.g.*, phenolic -OH), respectively.^{19c-d,20} Aq-guar exhibited a higher degree of aromatization than Aq-cell, which is consistent with the black color of Aq-guar compared to the brown color shown by Aq-cell (Fig. S5). Overall, these results confirm the incorporation of Aquivion® into the carbon matrix, this being constituted by polycyclic aromatic carbon sheets decorated with OH, C=O and COOH groups and with methylene linkage between the sheets.

XPS was used to gain further insight into the nature of surface groups in the Aq-carbon composites (Fig. S6). A single S2p peak was observed at 168.5 eV on both composites, which is very similar to that found on the pristine Aq-PW98-S (168.8 eV), confirming the presence of SO_3H groups.^{20b} A second S2p band also appeared for Aq-PW98-S at 169.5 eV, but vanished after carbonization, which can be attributed to free sulfate species issued from the synthesis of the resin.¹⁰ The C1s BE appeared at 290.6 eV on both the pristine Aq-PW98-S and both composites, which can be interpreted as a superposition of signals from CF_2 , CF-O and CF_2 -O groups in the polymer chain.²¹ Moreover, new carbon species were detected in the composites, which can be assigned to polyaromatic (284.4 eV) and aromatic and/or aliphatic hydrocarbons (285.0 eV), as well as phenolic hydroxyl (286.2 eV) and carboxyl groups (288.8 eV).²²

The acid density in Aq-guar and Aq-cell was quantified by acid-base titration using NaOH and compared to the value measured on the pristine Aq-PW98-S (Table 1). In the latter case, the acid density was in excellent agreement with the sulfur content of the sample (1.0 mmol/g), suggesting the sole presence of SO_3H centers. In contrast, the acid density measured on both composites was slightly higher than the sulfur content, which can be explained by the presence of COOH groups at a level of 30 and 20 $\mu\text{mol/g}$ for Aq-guar and Aq-cell, respectively. Overall, Aq-guar exhibited a higher density of strong SO_3H groups than Aq-cell (0.29 vs. 0.09 mmol/g), reflecting an Aquivion® loading *ca.* 3 times higher for the former sample. These results point out the relevant influence of the starting polysaccharide material for defining the Aquivion® loading during hydrothermal carbonization and in turn the acidity of the composites. Notwithstanding this fact, as inferred from TGA analysis, the polysaccharide did not exert an observable effect on the thermal stability of the composites (Fig. S7).

The textural properties of the Aq-carbon composites were assessed from N_2 adsorption/desorption isotherms at 77 K. Both Aq-guar and Aq-cell exhibited Type IV isotherms with capillary condensation steps in the P/P_0 range 0.7-0.8 and 0.85-0.98 revealing the presence of large mesopores and macropores (Fig. S8). A large H2-type hysteresis loop was observed for Aq-guar, suggesting the presence of a 3D caged porous structure with a small entrance (<4 nm).²³ Aq-guar displayed a much higher BET surface area than Aq-cell (82 vs. 13 m^2/g), but with a lower pore volume (0.10 vs. 0.20 cm^3/g) and a smaller mean pore size (9 vs. 32 nm, BJH) (Table 1). Furthermore, the C_{BET} constant fitted from the BET isotherm showed a value of 56 and 73 for Aq-guar and Aq-cell, respectively. Noteworthy, these constants values are much lower than those commonly found on untreated silicas (*e.g.*, 276 for Aerosil® 200), but remain comparable to the values measured on polystyrene-grafted silicas with 6-58% sulfonation degree.^{4h}

The Aq-carbon composites were composed of two families of particles: (1) small particles (mean particle size <1 μm), and (2) large particles (mean particle size >50 μm) as revealed by combined particle size distribution (PSD) measurements (Fig. S9) and optical/SEM microscopy (not shown). Aq-guar showed a larger amount of particles in the range 100-300 nm, whereas Aq-cell showed larger particles in the range 1-3 μm . The mean particle size decreased in the sense Aq-cell (780 nm) > Aq-PW98-S (660 nm) > Aq-guar (520 nm) (Table 1).

The catalytic performance of the Aq-carbon composites was assessed in the biphasic acetalization reaction of fatty dodecyl aldehyde (C_{12} -aldehyde) with ethyleneglycol (EG) towards the cyclic acetal (C_{12} -G) at 45 °C for 1 h. A series of benchmark catalysts were also tested, including homogeneous p-toluenesulfonic acid (PTSA) and heterogeneous HZSM-5 and H-resin (Fig. 3A-left). A first series of experiments was conducted at equal number of acid equivalents (10 μmolH^+ based on C_{12} -aldehyde). Among the different catalysts, Aq-guar displayed the highest productivity to C_{12} -G (903), whereas Aq-cell exhibited a productivity of 507. Noticeably, both samples showed a higher activity than HZSM-5 (298) and H-resin (343), which was also better than the value measured on the Aquivion®-silica composite reported in a previous study (AqSi-1, 440).²⁴ Finally, Aq-PW98-S and PTSA were also tested, revealing a lower productivity than that of Aq-guar (696 and 649, respectively). The macroscopic appearance of the C_{12} -aldehyde/EG system in the presence of Aq-guar, Aq-cell and Aq-PW-98-S showed in all cases the genesis of emulsions, but with variable stability. For comparison, no emulsion was formed either in the absence of particles, or in the presence of HZSM-5, H-resin and PTSA, showing preferential dispersion in EG with rapid phase separation after shearing.

Table 1 Acid, textural and emulsification properties of Aq-PW98-S and Aq-carbon composites.

Samples	Acid density (mmol/g) ^a	Aq. loading (wt.%) ^b	Mean particle size (nm) ^c	Textural properties ^d				Emulsification properties (DA/EG) ^e	
				S_{BET} (m^2/g)	V_{p} (cm^3/g)	D_{p} (nm)	C_{BET} (-)	Emulsion volume (%)	Droplet size (μm)
Aq-PW98-S	1.0 (1.0)	-	660	<0.1	-	-	-	76	15 (81)
Aq-guar	0.29 (0.32)	29%	520	82	0.1	9	56	54	9 (-)
Aq-cell	0.09 (0.11)	9%	780	13	0.2	32	73	68	55 (19)

^a Calculated from the sulfur content as measured by ICP-AES; in parentheses, values determined by acid-base titration using NaOH. ^b Measured from the sulfur content. ^c Supernatant values measured on a Malvern Mastersizer 3000. ^d Measured from N_2 adsorption/desorption at 77 K. ^e Measured just after homogenization; in parentheses, values measured after 1 h.

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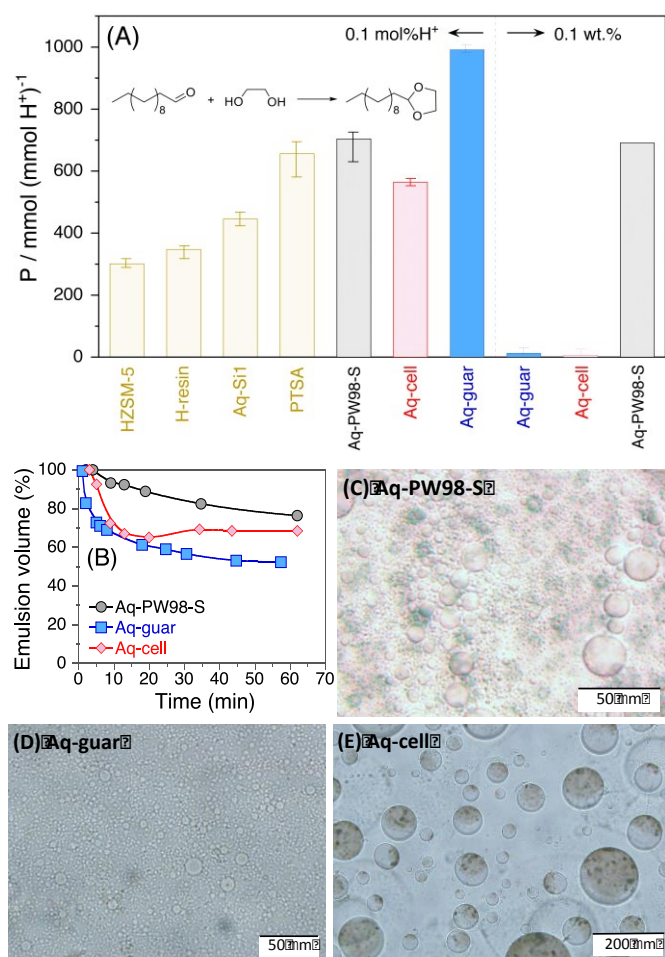


Fig. 3. (A) C₁₂-G yield per total amount of acid equivalent in the acetalization reaction of C₁₂-aldehyde with EG over Aq-PW98-S, Aq-carbon composites and benchmark catalysts (HZSM-5, H-resin, PTSA); (B) Time-evolution of the emulsion volume for the C₁₂-aldehyde/EG system stabilized by Aq-PW98-S, Aq-guar and Aq-cell; (C-E) optical images of initial C₁₂-aldehyde/EG emulsions stabilized by Aq-PW98-S, Aq-guar and Aq-cell. **Reaction conditions:** 45 °C, 1 h, C₁₂-aldehyde (10 mmol), EG (20 mmol), catalyst amount adjusted to afford the same number of H⁺ equivalents (10 μmol H⁺) or weight loading (0.1 wt.%), homogenization at 45 °C for 5 min at 13,000 rpm. Additional optical images for emulsions stabilized by Aq-PW98-S are available in Fig. S12.

To further assess the capacity of Aq-PW98-S, Aq-guar and Aq-cell for generating Pickering emulsions, a series of emulsification tests were carried out by homogenizing the different solids (10 μmolH⁺ with respect to C₁₂-aldehyde) with C₁₂-aldehyde and EG (1:2 C₁₂-aldehyde/EG molar ratio) at 45 °C for 5 min at 13,000 rpm. Aq-PW98-S showed a higher ability for stabilizing emulsions than the Aq-carbon composites. As a matter of fact, the emulsion volume only decreased by ca. 7% for Aq-PW98-S during the first 10 min, whereas a decline of ca. 30% was observed for both composites (Fig. 3B, Fig. S10, S11). The emulsion volume decreased gradually to 76% and 54% of the initial value after 1 h for Aq-PW98-S and Aq-guar,

respectively. In contrast, the emulsion volume remained relatively constant for Aq-cell at ca. 70%. For comparison, C-guar and C-cell were unable to stabilize emulsions, showing a fast decline of the emulsion volume during the first 10 min. This body of results point out the amphiphilic properties of Aq-PW98-S for the C₁₂-aldehyde/EG system, affording the stabilization of Pickering emulsions. This property was preserved after immobilization into carbon, suggesting that the emulsification capacity of Aq-guar and Aq-cell emerges primarily from the hosted Aquivion® resin rather than from the surface properties of carbon particles (including COOH, CO and OH groups).

The visualization of the emulsions just after shearing revealed the genesis of very small and fine droplets for Aq-guar with a mean size of 9 μm (Table 1, Fig. 3D). Aq-PW98-S was able to generate droplets with a mean size of 15 μm, whereas Aq-cell formed much larger droplets (55 μm) (Fig. 3C,E). Larger particles could also be observed for Aq-guar and Aq-cell, but far from the C₁₂-aldehyde/EG interface. The droplets vanished after 30 min for Aq-guar, while Aq-cell and Aq-PW98-S still stabilized droplets after 1 h with a mean size of 19 and 81 μm, respectively (Table 1). Despite the poorer emulsion stability exhibited by Aq-guar, the generation of small C₁₂-aldehyde/EG droplets at the beginning of the reaction might be at the origin of the higher catalytic activity offered by this sample. Moreover, Aq-guar could be reused up to 10 times after centrifugation (Fig. 4), stabilizing emulsions in the consecutive recycling tests with quite stable performance. In contrast, AqSi-1 suffered from fast deactivation due to Aquivion® leaching within the EG phase, whereas the pristine Aq-PW98-S could not be recycled.

To further ascertain the interfacial catalytic properties of the Aq-carbon composites, a second series of catalytic tests was carried out at the very same conditions, but keeping the catalyst loading constant and at a low value (0.1 wt.% based on C₁₂-aldehyde, Fig. 3A-right). Interestingly, Aq-guar and Aq-cell exhibited an extremely low productivity to C₁₂-G (12 and 5, respectively), whereas Aq-PW98-S displayed almost the same productivity as that obtained in the first series of catalytic tests (i.e. 10 μmolH⁺ based on C₁₂-aldehyde). Under such conditions, Aq-guar and Aq-cell were unable to stabilize Pickering emulsions (Fig. S13), whereas Aq-PW98-S could generate emulsions with a mean droplet size of 15 μm. In light of these results, the enhanced catalytic activity of Aq-guar in the first series of catalytic tests (i.e. 10 μmolH⁺) appears to be ascribed to the higher capacity of this sample for stabilizing emulsions. Note that under such conditions, the catalyst loading was about 0.32 wt.%, 1.1 wt.% and 3.6 wt.% for Aq-PW98-S, Aq-guar and Aq-cell, respectively, which are far beyond the values required for stabilizing C₁₂-aldehyde/EG emulsions with amphiphilic organosilicas.^{4f}

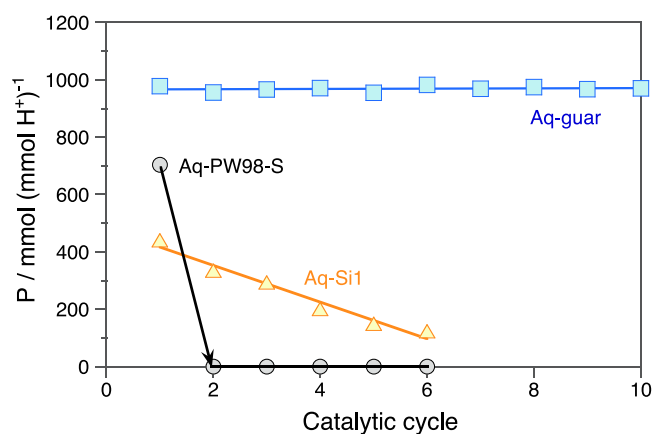


Fig. 4 Evolution of the catalytic activity of Aq-guar, AqSi-1 and Aq-PW98-S in the acetalization reaction of C₁₂-aldehyde with EG in 6-10 consecutive runs. Reaction conditions: 45 °C, 1 h, C₁₂-aldehyde (10 mmol), EG (20 mmol), 10 μmolH⁺ catalyst.

Conclusions

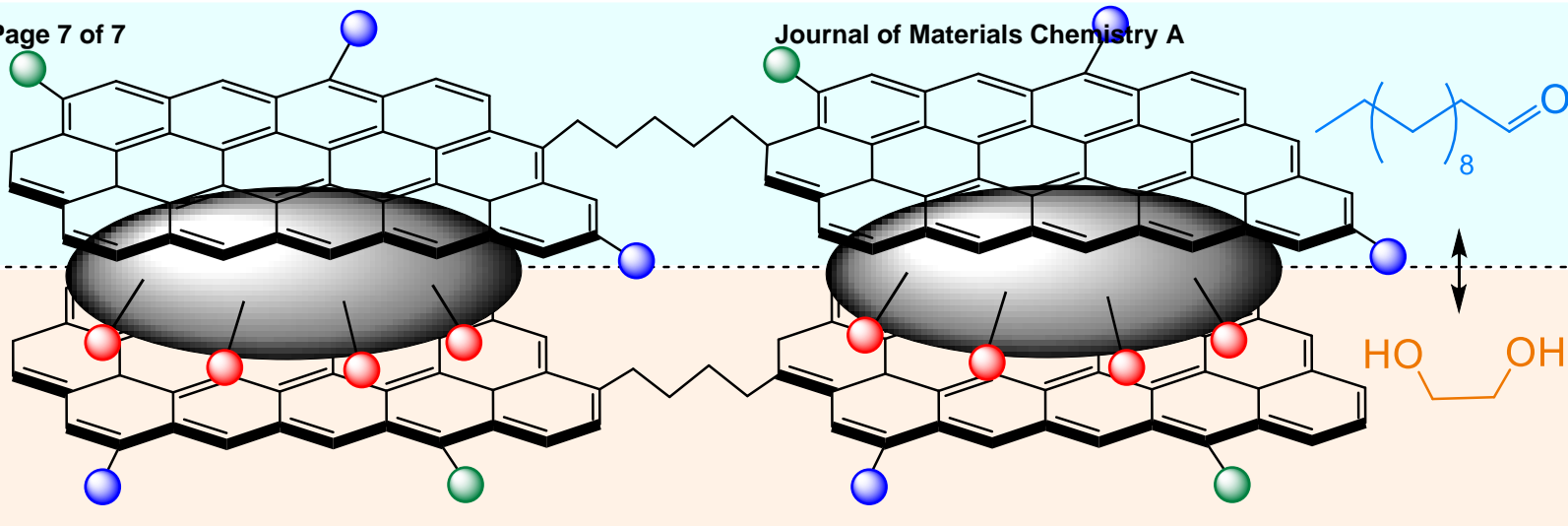
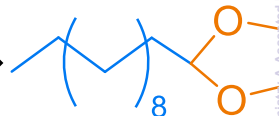
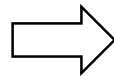
We developed new Aquivion[®]-carbon composites as solid acid catalysts from a facile one-pot hydrothermal carbonization of polysaccharides (guar gum or cellulose) with Aquivion[®] resin at 180 °C. The as-synthesized polycyclic amphiphilic composites efficiently realized the solvent-free acetalization reaction between immiscible fatty dodecyl aldehyde and ethyleneglycol at 45 °C due to the genesis of Pickering emulsions at short reaction times. Very small aldehyde/EG droplets could be formed with the Aquivion[®]-guar composite at high dispersion volumes, implying the generation of interfacial surface and in turn a mitigation of the external mass transfer resistance towards the acid centers. The catalyst could be recovered after reaction by centrifugation and reused with no appreciable deactivation.

Notes and references

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● $-\text{SO}_3\text{H}$ ● $-\text{OH}$ ● $-\text{COOH}$