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Reuseable Monolithic Nanoporous Graphite-Supported Nanocatalysts (Fe, Au, Pt, Pd, Ni, and Rh) from Pyrolysis and Galvanic Transmetalation of Ferrocene-Based Polyamide Aerogels

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Supporting Information

ABSTRACT: Polyamide aerogels with ferrocene as a monomer repeat unit were prepared in one step from ferrocene dicarboxylic acid and tris(4-isocyanatophenyl)methane. Pyrolysis at \geq 800 °C yielded nanoporous carbons doped throughout with crystallites of α -Fe (about 50 nm in diameter), which in turn were shrouded in graphitic ribbons (<30 graphene layers thick). Transmetalation was carried out with aqueous solutions of Au, Pt, Pd, Rh, and Ni salts, via a path akin to galvanic corrosion, whereas graphitic ribbons separated anodes (α -Fe particles) from cathodes (defects along the ribbons). The new metallic phases formed clusters of smaller crystallites (10-20 nm in diameter) on the graphitic ribbons, leaving behind empty cage-like formations previously occupied by the Fe(0) nanoparticles. All metal-doped carbons were monolithic and over 85% porous. Catalytic activity was demonstrated with the oxidation of benzyl alcohol to benzaldehyde catalyzed with carbon-supported Au or Pt, the reduction of nitrobenzene by hydrazine to aniline catalyzed with carbon-supported Fe, and two Heck coupling reactions of iodobenzene with styrene or butyl acrylate, catalyzed with carbon-supported



Pd. The distinguishing feature of those catalysts was that they could be just picked up, for example, with a pair of tweezers, and redeployed in a new reaction mixture immediately, thus bypassing less efficient recovery processes like filtration.

1. INTRODUCTION

Heterogeneous catalysis is a surface phenomenon,^{1,2} thereby heterogeneous catalysts consist of high surface-to-volume catalytic particles on inert supports. The latter include mostly oxides, carbides, nitrides, and activated carbon.^{3,4} Supports, typically in particulate/coarse-powder form, provide high surface area for the smaller catalytic particles to latch on and pack in a way that ensures low mass transfer resistance to and from the catalytic sites. Recovery of the catalyst at the end of a catalytic cycle is typically carried out by filtration,⁵ which is time-consuming and may lead to catalyst loss. At the other extreme, industrial, continuously recyclable heterogeneous catalysts, like those employed in fuel cells⁶ or in catalytic converters,^{7,8} operate with gas-phase reagents and are threelevel structures, in which the two lower levels incorporate the general principles set forth above, while, out of engineering necessity, the top level adds their key macroscopic feature: monolithicity. Transferring that feature to any other system is conceptually and practically equivalent to having monolithic catalysts that could be picked up and redeployed immediately in any suitable situation. Clearly, such catalysts will have to be based on porous supports, and in that regard oxide or ceramic aerogels^{9,10} doped with metallic nanoparticles¹¹ could comprise a reasonable option. However, in general those types of aerogels are delicate materials that would not survive harsh reaction environments. Thus, we opted for sturdier carbon aerogels,¹²⁻¹⁵ and at that point our attention shifted toward a better dispersion of the metallic nanoparticles in the carbon matrix. For this, a sensible approach is to incorporate a precursor of metallic nanoparticles into every monomer repeat unit of a carbonizable polymer. In that regard, we chose ferrocene, a known precursor of iron nanoparticles.¹⁶

At the implementation level, that system design was carried out with a hyperbranched polyamide aerogel prepared from ferrocene dicarboxylic acid $(Fc(COOH)_2)$ and tris(4isocyanatophenyl)methane (TIPM) as shown in Scheme 1. TIPM is an inexpensive monomer, and it was chosen because it is also a known precursor of several carbonizable polymeric aerogels,^{17,18} including polyamides.¹⁹

Indeed, pyrolysis of ferrocene-based polyamide aerogels gave monolithic carbon aerogels bearing Fe(0) nanoparticles dispersed throughout their volume. Apart from their own catalytic activity, those materials were transmetalated with selected metal ions, replacing Fe(0) nanoparticles with Au, Pt, Pd, Ni, and Rh. All materials were characterized along all processing steps in terms of their chemical composition and their micro-/nanomorphology. Catalytic activity was demon-

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Scheme 1. Reaction of a Triisocyanate (TIPM) with Ferrocene Dicarboxylic Acid Toward a Polyamide (atom labeling is used for NMR peak assignment)



strated with selected reactions catalyzed by the corresponding metal nanoparticles.

2. RESULTS AND DISCUSSION

This section moves from the synthesis and characterization of ferrocene-based polyamide aerogels (Section 2.1) to their pyrolytic conversion to Fe(0)-doped carbon (Section 2.2), to transmetalation (Section 2.3), and finally to a demonstration of catalytic activity as set forth above (Section 2.4). Emphasis is placed on the metal content, particle size, and pore structure.

2.1. Synthesis and Characterization of Ferrocene-Based Polyamide Aerogels (FcPA-xx). The reaction of Scheme 1 was implemented according to Scheme 2. Fc-





 $(COOH)_2$ was prepared following literature procedures²⁰⁻²² and was codissolved at room temperature in a 1.5:1 mol/mol ratio with TIPM in variable amounts of DMF/ethyl acetate (see Experimental Section). All formulations are provided in Table S.1 of Appendix I in Supporting Information. Gelation was carried out at 90 °C, and gelation times (included in Table S.1) varied from 95 min to approximately 3 h, depending on the monomer concentration. Wet-gels were aged in their molds at 90 °C for 24 h, solvent-exchanged with acetone, dried with liquid CO2, and vented off at the end as a supercritical fluid (SCF). The resulting aerogels were sturdy monoliths and are referred to as FcPA-xx, where xx stands for the total weight percent concentration of the monomers in the sol, and was varied in the range $05 \le xx \le 25$. Materials characterization data for all xx are summarized in Table S.2 of Appendix II in Supporting Information. A typical monolith is shown in Figure 1, along with materials from further processing.



Figure 1. Photograph of samples after different stages of processing as shown. For relevant data refer to Table 1.

In brief, FcPA-xx shrunk 35-41% in linear dimensions relative to the molds and in reverse order with xx. Skeletal densities (ρ_s) did not vary in any systematic way that could imply closed porosity. Bulk densities ($\rho_{\rm b}$) and porosities (Π = $100 \times (\rho_{\rm s} - \rho_{\rm h})/\rho_{\rm s}$) varied from 0.12 g cm⁻³ and 92% (v/v) (xx = 05) to 0.49 g cm⁻³ and 63% (v/v) (xx = 25). The porous structure was probed with N₂-sorption porosimetry (Appendix III in Supporting Information). Isotherms started off (at $\mathbf{x}\mathbf{x} =$ 05) with very narrow hysteresis loops, becoming wider at higher densities with well-defined saturation plateaus at xx >15. Accordingly, lower-density samples were dominated by larger macropores, shifting to smaller macropores and mesopores as density increased (volume ratio, $V_{>300 \text{ nm}}$ / $V_{1.7-300_{\text{nm}}} = 4.2$ for FcPA-05, versus 0.8 for FcPA-25—see Table S.2). BET surface areas, σ , were in the 460–260 m² g⁻¹ range, in descending order with xx. Microscopically, the skeletal framework of all FcPA-xx consisted of random assemblies of nanoparticles (Figure 2A). Particle radii calculated from N₂sorption data via $r = 3/(\rho_s \times \sigma)$ were in the 4.5–8.7 nm range and agreed well with primary particle radii calculated from small-angle X-ray scattering data (SAXS: 2.9-6.5 nm-see Appendix IV in Supporting Information). SAXS further showed that primary particles aggregated into surface fractal secondary particles with diameters in the range of 35-60 nm (white circles in Figure 2A).

Solid-state CPMAS ¹³C NMR spectra (Figure 3) showed the aliphatic carbon from TIPM at 55 ppm, the cyclopentadienyl carbons from Fc(COOH)₂ as a broad resonance centered at 71 ppm, and the aromatic carbons of TIPM in the 110–140 ppm range. The peak at 167 ppm was assigned to the amide \underline{C} ==O, and the peak at 154 ppm was assigned to the \underline{C} ==O resonance of TIPM-derived polyurea. The latter has been prepared independently by reacting TIPM either with water¹⁸ or with boric acid²³ and its spectrum is included in Figure 3 as reference.



Figure 2. Scanning electron microscopy (SEM) of representative samples along processing. White circles in FcPA-15 denote secondary particles as identified via SAXS (see Appendix IV in Supporting Information).

The reaction of a carboxylic acid with an isocyanate toward an amide starts with a condensation step to a mixed carbamiccarboxylic anhydride (-NH-CO-O-CO-), which either rearranges intramolecularly to the amide $(+CO_2)$ or reacts intermolecularly with another molecule of carbamic-carboxylic anhydride toward urea and anhydride;^{24,25} the latter two products may also react with one another toward the same amide obtained via the intramolecular route.²⁶ As confirmed from FTIR (Figure S.6 of Appendix V in Supporting Information), the FcPA-xx does not include an anhydride. On the other hand, based on ¹³C NMR data obtained during gelation, the solution in the pores of freshly made wet-gels contains a soluble product, which is also observed by adding P_2O_5 (as a dehydrating agent) in a solution of $Fc(COOH)_2$ in DMSO- d_6 . The ¹³C NMR spectrum of that product was consistent with the strained intramolecular anhydride $(FcCO)_2O_2$, which, however, was unstable and could not be isolated easily for further characterization. Thus, it is speculated that owing to the favorable topology of the second -COOH group of $Fc(COOH)_2$ relative to the primary condensation product (the carbamic-carboxylic anhydride), the two groups (-COOH and -NH-CO-O-CO-) react intramolecularly expelling $Fc(CO)_2O_2$, a free amine, and CO_2 . In other words, the isocyanate acts as a dehydrating agent of $Fc(COOH)_2$. The free amine reacts with yet unreacted -NCO groups toward urea. At any rate, TIPM-derived polyurea is a high-yield (56%



Figure 3. Solid-state CPMAS ¹³C NMR of **FcPA-xx** (top) and of TIPM-derived polyurea (second from top). Liquid state ¹³C NMR of $Fc(COOH)_2$ in DMSO- d_6 (third from the top) and of TIPM in CDCl₃ (bottom two spectra—for peak assignment refer to Scheme 1) The APT (Attached Proton Test) spectrum of TIPM confirms that C-4 and C-6 overlap. (S: solvent peak).

(w/w) carbonizable polymer in its own right¹⁸ and thereby is expected to contribute toward the carbon matrix.

Integration of the two <u>C</u>=O resonances in the solid-state ¹³C NMR spectra of **FcPA-xx** gives a ratio of ferrocene-based polyamide and TIPM-derived polyurea equal to 1:1 mol/mol. Based on (a) that mol ratio, (b) application twice (once for the polyamide and once for the polyurea) of eq 1 that gives the

$$G_n = T - 3(1 - 2^n)(D + T) + 3 \times 2^n \times (end-cap)$$
(1)

molecular mass (G_n) of hyperbranched polymers from di- (D)and tri- (T) functional building blocks ($n \ge 0$: the generation number of the hyperbranched polymer),²⁷ (c) assuming one bidentate $Fc(CO-)_2$ end-cap for every two tips of the hyperbranched polyamide (see also Section 2.2b below), and (d) considering the limit of eq 1 for $n \to \infty$, the expected iron content in FcPA-xx was 8.7% (w/w). (It is noted in passing that if FcPA-xx consisted exclusively of ferrocene-derived polyamide, the expected iron content would have been 13.0% (w/w).) The expected iron content in **FcPA-xx** agrees well with the experimental value $(9.5 \pm 1.1\% (w/w))$ that was calculated from data obtained with thermogravimetric analysis (TGA) in O_2 (Figure 4). In that regard, the TGA residue of FcPA-xx at 1000 °C was identified by using powder X-ray diffraction (PXRD) as Fe₂O₃, and it was found equal to $13._6 \pm 1._5 \%$ (w/ w) (average of 8 samples from different batches). Then, the weight percent of iron in FcPA-xx was calculated via eq 2:

Fe % (w/w) =
$$[2 \times MW_{Fe}/MW_{Fe2O3}] \times$$

(TGA Residue % (w/w) at 1000 °C) (2)

2.2. Pyrolytic Conversion of FcPA-xx to Fe(0)-Doped Carbon. 2.2a. Pilot Runs. Our first objective was to find out



Figure 4. Representative thermogravimetric analysis (TGA) data under O₂ at 5 °C min⁻¹ of samples as shown. (TGA was repeated several times with samples from different batches, and results were used to derive the metal content of various samples as shown in Table 1). The dashed lines and arrow point to the first step of mass loss by FcPA-15 (about 16% (w/w) at around 310 °C). (Via eq 1, bidentate Fc(CO-)₂ end-caps contribute 14.3% (w/w) to the total mass of FcPA-15.).

whether and under what conditions **FcPA-xx** could be converted to carbon-supported Fe(0). For this, mid-density **FcPA-15** samples ($\rho_b = 0.34$ g cm⁻³) were pyrolyzed under flowing H₂ at various temperatures in the range of 400 to 1400 °C. Samples shrunk uniformly, e.g., 68% at 800 °C and up to 86% at 1400 °C, but remained monolithic. Relevant material properties at various pyrolytic temperatures are given in Table S.3 of Appendix II in Supporting Information. Screening for metallic iron was carried out with powder X-ray diffraction (PXRD—Figure 5). Scheme 3 summarizes the results in terms of chemical composition of the products and their behavior toward transmetalation (refer to Section 2.3 below).

It is noted that our initial attempts focused on producing Fe(0)-doped carbons carbothermally,^{28–31} and accordingly pyrolysis was carried out under flowing Ar. However, the only crystalline phase that was observed at ≤ 1100 °C was Fe₃C; some α -Fe was noted only at 1200 °C. Under H₂, on the other hand, the main crystalline phase was always α -Fe. In fact, at 400/500 °C α -Fe was the only crystalline phase obtained. Some cementite (Fe₃C) started showing up at ≥ 600 °C, along with some martensite (Fe_{1.91} $C_{0.09}$) at 1400 °C (Figure 5). By putting those pieces of information together, it is reasonable to speculate that under H₂, carbides were produced in a parallel carbothermal process. As summarized in Scheme 3, at ≥800 $^{\circ}C/H_2$ samples were electrically conducting, Fe(0) became chemically accessible (e.g., they would react with ions in solution filling the pores-see Figure S.7 of Appendix VI in Supporting Information), and PXRD included the (002) reflection of graphite at $2\theta = 26.44^{\circ}$ (Figure 5), consistent with iron being a low-temperature graphitization catalyst.^{32–34} At ≥ 1000 °C the (002) reflection of graphite dominated the PXRD spectra. Samples at the onset of those properties, namely, those obtained at 800 °C, comprised the basis for further study and are referred to as Fe@C.

2.2b. Characterization of Fe@C and Chemical Accessibility of Fe(0). The pyrolytic (char) yield of FcPA-15 to Fe@C was $37_{.3} \pm 1_{.9} \%$ (w/w). Material properties of Fe@C and its derivatives from further processing (transmetalation) are compared with those of FcPA-15 in Table 1. As shown in Figure 1, Fe@C shrunk (49%) relative to their parent FcPA-15,



Figure 5. Powder X-ray diffraction (PXRD) data after pyrolysis of **FcPA-15** at different temperatures. The (002) reflection of graphite at $2\theta = 26.44^{\circ}$ first shows up after pyrolysis at 800 °C and dominates the diffraction pattern above 1000 °C. (Line spectra are included at the bottom for identification.)

Scheme 3. Properties at a Glance: Chemical Composition, Electrical Conductivity (+), and Ability for Transmetalation via Reaction with Metal Ions, $[M]^{n+}$, of the Product from Pyrolysis of FcPA-15 at Different Temperatures



for a 68% of total linear shrinkage relative to the molds. Evidently, however, mass loss compensated for additional shrinkage, and Fe@C monoliths were less dense (0.286 ± 0.004 g cm $^{-3}$ versus 0.340 \pm 0.004 g cm $^{-3})$ and more porous (88% (v/v) versus 74% (v/v)) than FcPA-15 (Table 1.) Microscopically, the framework of Fe@C consisted of finer, fused-together-like particles (Figure 2B). N₂-sorption porosimetry (Appendix III in Supporting Information) showed that the balance of pores shifted to larger macropores relative to FcPA-15 $(V_{>300 \text{ nm}}/V_{1.7-300 \text{ nm}} = 3.4$, vs 1.2 in FcPA-15). In short, despite that Fe@C were significantly smaller in size than FcPA-15, they had a higher percentage of internal empty space, and their pores were larger than those of the latter. The BET surface area of Fe@C (about 370 m² g⁻¹) was also somewhat higher than that of FcPA-15 (about 310 m² g⁻¹), but the distinguishing feature here was that a significant portion of the total BET surface area (175 m² g⁻¹, 48%) was assigned (via *t*-plot analysis, Harkins and Jura Model³⁵) to newly formed

	metal % (w/w)	punoj	9.5 ± 1.1	$11_{.5} \pm 2_{.1}$	ı	$33{6} \pm 8{8}$	34.5 ± 0.8	$19_{\cdot8}\pm1_{\cdot8}$	$(): \Pi = 100 \times$	$-V_{1.7-300m}$	to numbers is,
		expected ^k	8.7	255 ± 32		$31{4} \pm 4{4}$	$31_{\cdot 2} \pm 4_{\cdot 4}$	$19_{.9} \pm 2.1$	empty space	$\sum_{i=1}^{20} \frac{1}{V} = V_{Total}$	tween the tw
		particle radius $(nm), t'$	7.31	3.38	6.24	15.2	16.0	11.4	prosity (percent of	ion method. ${}^{g}V_{>3}$	the discrepancy be
		av. pore diameter $(nm), 4V/\sigma^{i}$	14 [29]	9 [33]	9 [45]	14 [188]	11 [188]	16 [124]	0 measurements. ^d Po	and the BJH desorpt	$(1/\rho_{\rm s})$. (The greater
		BET surface area, σ $(m^2 g^{-1})^h$	308 (10.6)	369 (176)	282 (113)	101(14.7)	100(1.94)	133 (4.55)	e sample, average of 5	m N ₂ -sorption data : 1 Iura Model ³⁵) ⁱ For	1 to $V_{\text{Total}} = (1/\rho_{\text{h}}) - 1$
	$cm^{3} g^{-1}$)	$V_{>300 \text{ nm}}^{g}$	1.214	2.375	2.452	4.399	4.417	3.591	leter). ^c Singl	300 nm fro Harbins and	s taken equa
	ore volume	$V_{1.7-300_\mathrm{nm}}^{}f$	0.983	0.705	0.769	0.354	0.284	0.533	(mold diam	een 1.7 and d using the	u usurg urc ckets], V wa
2	specific 1	$V_{ m Total}{}^e$	2.191	3.080	3.221	4.753	4.701	4.124	iameter)/	res betw Calculate	er in [bra
		Π^{q}	74	88	85	90	89	89	ample d	ie of pc	e numb
c		skeletal density, $\rho_{\rm s}$ (g cm ⁻³) ^c	1.333 ± 0.005	2.400 ± 0.004	1.704 ± 0.006	$1.96_4 \pm 0.03_8$	$1.87_5 \pm 0.01_6$	$1.98_1 \pm 0.01_8$	(mold diameter – s). ^f Cumulative volum a allocated to micro	at $P/P_0 \rightarrow 1.0$; for th
		bulk density, $\rho_{\rm b}$ (g cm ⁻³) ^a	0.340 ± 0.004	0.286 ± 0.004	$0.26_3 \pm 0.01_0$	0.190 ± 0.003	0.191 ± 0.004	0.216 ± 0.008	ır shrinkage =100 ×	$\mu_{\rm l} = (1/\rho_{\rm b}) - (1/\rho_{\rm s})$	along the isotherm
		linear shrinkage (%) ^{a,b}	38.11 ± 0.03	$68.2_4 \pm 0.5_0$	$68.3_3 \pm 0.1_6$	69.10 ± 0.02	70.04 ± 0.02	70.13 ± 0.05	ree samples. ^b Line	Calculated via V _{Tota}	me of N, absorbed
		sample	FcPA-15	Fe@C	Fe@C HCl	<i>tm-</i> Au@C	tm-Pt@C	tm-Pd@C	^a Average of thu	$(\rho_{\rm s}-\rho_{\rm b})/\rho_{\rm s}$. ^e C	maximum volu

Table 1. Materials Characterization Data after Various Stages of Processing

he more macroporous the material.) \overline{f} Particle radius, $r = 3/(\rho_s \times \sigma)$. ^kFor *tm*-M@C (M: Au, Pt, Pd,) expected values were calculated based on replacement of Fe at 11.5% (w/w).

maximum volume of N_2 absorbed along the isotherm at $P/P_0 \rightarrow 1.0$; for the number in [brackets], V was taken equal to $V_{Total} = (1/\rho_b) - (1/\rho_s)$. (The greater the discrepancy between the two numbers is,

(open) micropores. The apparent particle radius in Fe@C (based on gas sorption data) was smaller (3.4 nm) than that of FcPA-xx (7.3 nm). However, owing to the lack of well-defined nanoparticles (refer to the network morphology in Figure 2B), this value for the particle radius in Fe@C should be taken only as an estimator of the overall feature size we are dealing with. The iron content of Fe@C (11.5 \pm 2.1% (w/w), via TGA in

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 O_2 —Figure 4) was 40–50% (w/w) of the expected value (25.5 \pm 3.2%) had all iron in FePA-15 (9.5 \pm 1.1 % (w/w)) had been retained. That loss of iron is consistent with an early loss of the $Fc(CO-)_2$ end-caps of the ferrocene-based polyamide during pyrolysis: indeed, based on eq 1, those end-caps contribute 14.3% (w/w) to the mass of FcPA-xx, which in turn is consistent with the mass loss of about 16% at 310 °C noted in TGA (Figure 4).

The skeletal density of Fe@C ($\rho_s = 2.4 \text{ g cm}^{-3}$) was the exact weighted average of iron (7.86 g cm⁻³ at 11.5% (w/w)—the TGA-derived value from above) and the experimental skeletal density of the matrix (1.7 g cm^{-3}) after removing Fe with HCl. (The matrix comprised 88.5% (w/w) of the total mass of Fe@C.) Despite graphitization, the skeletal density of Fe@C was lower even than the density of sp²-rich amorphous carbon $(1.8-2.0 \text{ g cm}^{-3})$,³⁶ suggesting that the skeletal framework included closed pores; this is very likely considering that, along the newly formed open micropores, some may have been actually closed. (Assuming that all closed pores were confined within the matrix (carbon), the volumetric percent of closed pores on the skeletal backbone varied in the 5-15% (v/v) range-depending on the density of the skeletal carbon-in the 1.8-2.0 g cm⁻³ range.)

A closer topological view of Fe(0) within Fe@C, which turns out to be important for rationalizing the transmetalation process (Scheme 3 and Section 2.3), was obtained with TEM (Figure 6 and S.10 of Appendix VII in Supporting Information). Fe(0) particles were embedded evenly throughout the surrounding matrix (Figure 6A). Their size distribution was broad with a maximum at 52 nm and fwhm = 31 nm. The average crystallite size (via the Scherrer equation applied to the (110) peak of Fe(0)—see Figure 5 above) was also equal to 52 \pm 1 nm. Under higher magnification (Figure 6B), Fe(0) particles were shrouded in layered ribbons fading away into the surrounding matrix, presumably amorphous carbon. As ribbons faded away, they swirled around occasionally forming pockets similar to those encapsulating Fe(0) (see Figure S.10); however, the key observation was that Fe(0) particles were always encased in layered ribbons. The ribbon around the particle of Figure 6B is 9.48 nm thick and consists of 28 graphene layers, giving an interlayer spacing of 3.39 Å, which is close to that of graphite (3.35 Å).³⁷ That graphene layer stack height is consistent with the value ($L_a = 16.9$ nm) calculated from Raman data using Knight's empirical formula³⁸ and the ratio of the areas under the characteristic D and G bands of disordered graphite (at 1326 and 1592 cm⁻¹, respectively; $I_{\rm D}/I_{\rm G}$ = 2.27-see Figure S.11 of Appendix VIII in Supporting Information). The agreement between the graphene layer stuck height via TEM and Raman renders graphitic ribbons and cages like those in Figure 6B a general structural property of the entire sample.

Graphitic ribbons are a rather common occurrence in lowtemperature Fe(0)-catalyzed graphitization.^{39–41} In many cases, shrouding Fe(0) particles in such ribbons (as in Figure 6B) isolates the metal from its environment.^{42,43} In Fe@C, however, Fe(0) particles were chemically accessible and were



Figure 6. Transmission electron microscopy (TEM). A, B: Fe@C at two different magnifications. Inset in A: Patricle size distribution. C: Fe@C after HCl-treatment. D: *tm*-Pt@C. Arrows point at empty graphitic cages after removing Fe(0). (Additional TEM data are shown in Appendix VII in Supporting Information.)

removed quantitatively with concentrated aqueous HCl (see Experimental Section), as confirmed by Figure S.8 of Appendix VI that compares PXRD spectra of Fe@C before and after HCl treatment. In addition, general inspection with TEM of HCl-treated samples (Figure S.10) shows an absence of Fe(0) particles, while cage-like structures like those previously shrouding Fe(0) particles abound (Figure 6C). Macroscopically, HCl treatment caused no further shrinkage, but BET surface areas were somewhat compromised (about 280 vs 370 m² g⁻¹ before HCl-treatment); yet, 40% of that area (about 110 m² g⁻¹) was still assigned to open micropores. (Material properties of HCl-treated samples are included in Table 1.)

2.3. Transmetalation of Fe@C to *tm*-M@C. The chemical accessibility of Fe(0) in Fe@C, as magnifested by our ability to dissolve Fe(0) away with aq. HCl, made it possible to replace Fe(0) with Au, Pt, or Pd (M) via reaction with ions of the corresponding metals, $[M]^{n+,44,45}$ according to eq 3. In all three

$$n Fe(0) + 2[M]^{n+} \rightarrow n Fe^{2+} + 2M(0)$$
 (3)

cases, the corresponding reactions are highly exothermic with standard redox potentials of over 1.0 V. Experimentally, Fe@C monoliths, right after they came out of the pyrolysis furnace, were infiltrated quickly with aqueous solutions of $[M]^{n+}$ using capillary action under reduced pressure. Transmetalated monoliths (referred to as tm-M@C) were washed with water and acetone and were dried under ambient pressure without noticeable changes in their size relative to their Fe@C precursors (Figure 1). Microscopically, tm-M@C appeared very similar to Fe@C, although voids seemed to be larger (Figure 2C). Quantitative materials characterization data of the three tm-M@C are included in Table 1. Thus, porosities (86–90% (v/v)) remained in the same range as those of Fe@C (88% (v/v)), but pore sizes shifted to even larger macropores

(the $V_{>300_nm}/V_{1.7-300_nm}$ ratio moved from 3.4 in Fe@C up to 6.7 in *tm*-Pd@C, 12.4 in *tm*-Au@C, and 15.6 in *tm*-Pt@C). The BET surface areas were reduced from about 370 m² g⁻¹ in Fe@C (and 282 m² g⁻¹ in HCl-treated Fe@C) to 100-130 m² g^{-1} in *tm*-M@C, with an even greater reduction in the surface area assigned to micropores (from about 170 $m^2 \ g^{-1}$ in Fe@C and about 110 m² g⁻¹ in HCl-treated Fe@C, to $5-15 \text{ m}^2 \text{ g}^{-1}$ in tm-M@C). According to the pore volume data, surface-tensiondriven nanoscopic contraction cannot be ruled out as a mechanism for the observed changes in the pore structure. On the other hand, however, surface area data suggest that transmetalation, as opposed to removing Fe(0) with HCl, blocked access to micropores. That would increase closed porosity and would decrease the apparent skeletal densities. Indeed, the skeletal densities of all three *tm*-samples were found lower than that of Fe@C, despite quantitative replacement of Fe(0) with heavier metals; as summarized in Table 1, the skeletal densities of the three *tm*-M@C were in the 1.88–1.98 g cm⁻³ range, versus $\rho_s = 2.40$ g cm⁻³ for Fe@C.

The PXRD spectra of tm-M@C were dominated by the new metallic phases (Figure 7). No residual Fe(0) was detected in



Figure 7. Powder X-ray diffraction (PXRD) data of Fe@C samples transmetalated with Au, Pt, and Pd, as shown. The PXRD spectrum of Fe@C is included for comparison. All samples retain the small amount of Fe_3C present in the original Fe@C.

any of the transmetalated samples, and minor additional reflections were assigned to Fe₃C. TGA-in-O₂ (Figure 4) supported quantitative replacement of Fe(0) by M; that is, starting with $11._5 \pm 2.1\%$ (w/w) of Fe(0) in the parent Fe@C, the expected/found values of M were (% (w/w)): Au, $31._4 \pm 4.4/33._6 \pm 8._8$; Pt, $31._2 \pm 4._4/34._5 \pm 0.._8$; and Pd, $19._9 \pm 2._1/19._8 \pm 1._8$ (Table 1). The average crystallite sizes (via the Scherer equation applied to the (111) reflections) were Au, 15.2 ± 0.5 nm; Pt, 20.9 ± 0.7 nm; Pd, 21.4 ± 0.7 nm), namely, significantly smaller than those of Fe(0) in Fe@C (52 ± 1 nm). According to TEM (Figure 6D), the graphitic pockets

shrouding the parent iron particles in Fe@C were now empty (like after treatment with HCl—compare with Figure 6C), and the new metallic particles clustered on the graphitic ribbons. In no occasion (see also Figure S.10) new metallic nanoparticles were formed inside cages previously occupied by Fe(0). Macroscopically, bulk iron dipped in gold plating solutions is passivated by a layer of Au(0).⁴⁶ Microscopically, redox transmetalation typically yields core—shell⁴⁵ or hollow particles.⁴⁷ Here, complete consumption of Fe(0) nanoparticles, together with (a) the location of the new metallic particles (on the ribbons rather than in the pockets) and (b) their smaller size relative to the parent Fe(0) points to a galvanic corrosion mechanism (Scheme 4),⁴⁸ in which graphitic

Scheme 4. Galvanic Transmetalation Mechanism of Fe@C to tm-M@C (e.g., M = Au)



ribbons separated physically and connected electrically anodes and cathodes. The former were the Fe(0) nanoparticles; the latter were end-points and defects on ribbons serving as concentrators of the electric field, accelerating electrode kinetics. Statistically, there are more such defects than Fe(0)particles; therefore, we expect clusters of smaller Au, Pt, or Pd crystallites than those of the parent Fe(0), as observed. This galvanic mechanism also explains the curious formation of a yellow gold layer on the outer geometric surface of all tm-Au@ C monoliths (see Figure 1): while reduction of ions infiltrated quickly within the monolith still goes on, namely, while there is still unreacted Fe(0), ions diffusing from the surrounding solution toward the monolith get reduced at the point of their first encounter with the conducting carbon network. In further support of the galvanic reduction mechanism, initial transmetalation attempts of Fe@C with nickel were unsuccessful, despite that the standard redox potential of the reaction Ni^{2+} + $Fe(0) \rightarrow Ni(0) + Fe^{2+}$ is positive (but low: 0.183 V). Meanwhile, Raman (Figure S.11) on one hand shows that at higher processing temperatures the grapheme layer stack high does not change much (L_{α} = 21 nm at 1400 °C, versus L_{α} = 17 nm in Fe@C), but PXRD on the other hand (Figure 5) shows that higher-temperature samples contain more graphite. Reasoning that the internal ohmic drop along the skeletal framework in samples with higher graphite content would be lower, FcPA-15 processed at 1200 °C were transmetalated successfully with Ni²⁺ and also with another precious metal, Rh, in which case the crystallite size was found even smaller (9 ± 1) nm) than that of all other metals in *tm*-M@C. (For PXRD data of tm-Rh@C and tm-Ni@C see Figure S.9 of Appendix VI in Supporting Information.) The ability of galvanic transmetalation to step particle size down is particularly relevant to catalysis as, for example, only nanosized Au is catalytic.⁴⁹⁻⁵¹

2.4. Evaluation of Fe@C and tm-M@C as Catalysts. Fe@C and tm-M@C monoliths similar to those shown in Figure 1 were dipped under vigorous magnetic stirring in reaction mixtures that could be catalyzed by the respective metals.⁵²⁻⁵⁴ Reactions, run times, and results are summarized in Table 2. Based on the weight of each monolith and its metal

Table 2. Use of Fe@C and tm-M@C (M: Au, Pt, I	Pd) in
Catalysis: Yields as a Function of Catalytic Cycle ((yield %
mol/mol) ^a	

		catalytic cycle						
		yield % mol/mol						
catalyst	RXN $(t)^{b}$	1st	2nd	3rd	4th	5th		
Fe@C	1 (24 h)	89	84	75	83	86		
tm-Au@C	2 (24 h)	98	89	75	71	70		
tm-Pt@C	2 (24 h)	85	84	79	80	71		
tm-Pd@C	3 (24 h)	98	84	74	62	75		
tm-Pd@C	4 (2 h)	91	92	79	73	71		

^{*a*}In all cases (catalytic metal):(limiting reagent) = 5% mol/mol—see Experimental Section; for the raw data and data analysis see Appendix IX in Supporting Information). ^{*b*}RXN (*t*): Reaction (run time). 1. nitrobenzene + hydrazine \rightarrow aniline. 2. benzyl alcohol + O₂ \rightarrow benzaldehyde. 3. iodobenzene + styrene \rightarrow *cis*- + *trans*-stilbene. 4. iodobenzene + butyl acrylate \rightarrow butyl cinnamate

content (Table 1), the metal-to-limiting reagent ratio was adjusted at 5% mol/mol. Aliquots were taken in regular intervals and were analyzed using gas chromatography (GCsee Experimental Section; for the raw data see Appendix IX in Supporting Information). Reactions were stopped by removing the catalyst shortly after their limiting reagents had disappeared from the GC traces (see Figures S.12-S.20; typically 24 h, except Heck coupling of iodobenzene with butyl acrylate that proceeded much faster-Table 2). In order to remove them, catalytic monoliths were picked up with a pair of tweezers, were rinsed briefly with the reaction solvent, and were transferred immediately into new reaction mixtures to continue catalysis. The procedure was repeated five times with each catalyst. All monoliths were robust and survived the prolonged "beating" by the magnetic stirrer. Yields remained \geq 70% for all catalysts, all cycles (Table 2). No product was observed in any of the controls that included swapping tm-M@C with Fe@C or with Fe@C monoliths after HCl-treatment. In the case of tm-Au@ C, catalysis was also attempted with a 1 in.² gold foil left in the reaction mixture for several days-no reaction was observed. Optimization of catalytic activity, e.g., in terms of turn over numbers (TON), was beyond the scope of this work. Nevertheless, TON were found in the range of 70-100 and compare favorably with C-supported catalysts in powder form.⁵³ Oxidation of benzyl alcohol with either *tm*-Au@C or tm-Pt@C gave practically identical results, pointing to the effectiveness of galvanic replacement to furnish catalytically active nanosized Au.

Finally, because of the way the catalytic experiments were designed and executed, namely, (a) in all catalytic runs the (metal inside the catalyst):(limiting regent) ratio was fixed at 5% mol/mol and (b) all reactions were monitored and stopped shortly after the limiting reagent had been consumed, it was deemed reasonable to average the yields of the five reactions after each catalytic cycle and plot them against the latter (Figure 8). According to Figure 8, all catalysts in the family of catalysts of this report behave similarly, namely, independent of



Figure 8. Cumulative graph of % Yield versus Catalytic cycle for all catalysts used in this study (data from Table 2). The solid black line connects the average % yields after each cycle. Error bars are one standard deviation from the average % yields.

reaction and catalytic metal. Therefore, the common catalyst "fatigue" observed in Figure 8 is attributed to the matrix, which, owing to its open porous structure, may have allowed for catalyst loss. This subject goes beyond the immediate scope of this report but certainly warrants further investigation.

3. CONCLUSION

Although it is known that pyrolysis of mixtures of carbon or carbon precursors with iron salts yields similar nanostructures to those described here,^{39–43} the key feature of this work is that macroscopically the resulting porous materials are robust monoliths, a key requirement for easily redeployable catalysts. The conceptual point of departure for this configuration was the structure of catalytic converters. In that regard, it is conceivably possible to transfer back and apply our findings to our point of departure, but that requires supports inert toward O_2 at high temperatures (e.g., SiC aerogels⁵⁵). With regards to the C-supported catalysts at hand, it is rather straightforward to expand the present approach to other metallocenes. However, loss of ferrocene at two stages during processing (i.e., during gelation and during the early stages of pyrolysis) renders that route less attractive for expensive metals. On the other hand, galvanic replacement is atom-efficient, steps-down the particle size, and is a room-temperature process, which removes any possibility for sintering. Our current attention is focusing on carbide-free materials, like those obtained at 400/500 °C, and in order to render Fe(0) nanoparticles accessible, we are exploring how to deconvolute reduction and carbonization via, for example, stepwise pyrolysis.

4. EXPERIMENTAL SECTION

4.1. Materials. All reagents and solvents were used as received, unless noted otherwise. Ferrocene, aluminum chloride, acetyl chloride, lithium aluminum hydride, sodium hydroxide, dichloromethane, hexane, anhydrous *N*,*N*-dimethylformamide (DMF), butyl acrylate, styrene (inhibitor was removed by extraction with 5 M solution of NaOH followed by drying with anhydrous sodium sulfate), acetophenone, hexadecane, benzaldehyde, iodobenzene, benzyl alcohol, butyl cinnamate, triethyl amine, *cis-* and *trans*-stilbene, chloroplatinic acid hydrate, palladium chloride, nickel(II) chloride hexahydrate, and concentrated HCl (12.1 N) were purchased from Sigma-Aldrich Chemical Co. A gold plating solution (catalog number: 42307) and rhodium(III) chloride trihydrate were purchased from Alfa Aesar. Tris(4-isocyanatophenyl)methane (TIPM) was donated from

Covestro LLC as a 27% (w/w) solution in dry ethyl acetate under the trade name of Desmodur RE. Desmodur RE was also purchased independently from M.F. Cachat (Lakewood, OH, www.mfcachat. com). Deuterated DMSO (DMSO- d_6) and CDCl₃ were obtained from Cambridge Isotope Laboratories Inc. Argon (99.99999%) and H₂ (99.9999%) were purchased from Ozark Gas (Rolla, MO).

1,1'-Ferrocene Dicarboxylic Acid (Fc(COOH)₂). (Fc(COOH)₂) was prepared in two steps from ferrocene according to literature procedures (Scheme 5).²⁰⁻²² Yield: 63%; mp >250 °C. ¹H NMR

Scheme 5. Synthesis of 1,1'-Ferrocene Dicarboxylic Acid (Fc(COOH)₂)



(400 MHz, DMSO- d_6) δ 4.47 (d, 4H), 4.72 (d, 4H), 12.34 (s, 2H). ¹³C NMR (400 MHz, DMSO- d_6) δ 171, 73, 72, 71. IR (KBr) 3429, 1687, 1495, 1301, 514 cm⁻¹. Elemental Analysis, (CHN): Theoretical % (w/w) for C₁₂H₁₀O₄Fe: C, 52.55; H, 4.38. Found: C, 51.83; H, 4.13.

Synthesis of Ferrocene Polyamide Aerogels (FcPA-xx). In a typical procedure, Fc(COOH)₂ (4.11 g, 0.015 mol) was dissolved in anhydrous DMF, and the solution was added to 13.6 g of Desmodur RE (containing 3.67 g, 0.01 mol of TIPM). The resulting sol was stirred at room temperature under N2 for 20 min, and was poured in molds (Wheaton 4 mL Polypropylene Omni-Vials 1.04 cm in inner diameter, Fisher part No. 225402), which were then sealed and left for gelation at 90 $\,^\circ \! \hat{C}.$ The total weight percent of monomers (TIPM + $Fc(COOH)_2$) in the sol was varied by varying the amount of solvent (DMF) and is denoted by extension -xx in the sample names. All formulations and gelation times are summarized in Table S.1 of Appendix I in Supporting Information. Gels were aged for 24 h at 90 °C in their molds. Subsequently, wet gels were removed from their molds, washed with DMF ($3\times$, 8 h each time), acetone ($4\times$, 8 h each time, using $4 \times$ the volume of the gel for each wash) and were dried in an autoclave with liquid CO2, which was taken out at the end as a supercritical fluid (SCF). Elemental Analysis, (CHN): Found % (w/ w): C, 64.34; H, 4.86; N, 8.57.

Preparation of Fe(0)-Doped Nanoporous Carbons. FcPA-15 aerogel monoliths were transferred into a MTI GSL1600X-80 tube furnace (alumina 99.8% pure, 72/80 mm inner/outer diameters, 457 mm heating zone). The temperature of the furnace was raised to the desired temperature (400-1400 °C) at 5 °C min⁻¹ under flowing H₂ (150 mL min⁻¹). Samples were heated at the prescribed temperature for 5 h. At the end of the heating period the temperature returned to room temperature at 5 °C min⁻¹ under constant flow of H₂. FcPA-15 samples processed at 800 °C/H₂ comprised the basis for further study and are referred to as Fe@C. For control purposes, FcPA-15 samples were also treated at 800 and 1200 °C under flowing Ar (150 mL min⁻¹) for 5 h. Fe(0) was leached out of Fe@C by dipping monoliths in concentrated HCl under vacuum for 24 h. The HCl solution was changed every 6 h, and after the second wash it was noted that it remained colorless. Subsequently, samples were washed with water and acetone (2× with each solvent, 6 h each time) and were air-dried.

Transmetalation of Fe@C to Noble-Metal (M)-Doped Nanoporous Carbons (tm-M@C). Fe@C monoliths were transmetalated with noble metals (tm-M@C, M: Au, Pt, Pd) by dipping in the corresponding metal ion solutions ($[Au^{3+}] = 0.018$ M; $[H_2PtCl_6] =$ 0.035 M; $[PdCl_2] = 0.035$ M) under reduced pressure, right after they came out of the furnace. The volume of each precious metal solution was adjusted based on the expected amount of Fe(0) in each Fe@C monolith ($11.5 \pm 2.1\%$ (w/w)); in general, in all cases the (volume of metal ion solution):(volume of the Fe@C monolith) ratio was equal to about 80. After 5 h in the respective transmetalation bath, monoliths were placed in a water bath and were heated at around 50 °C for 5 h still under reduced pressure. Subsequently, they were washed with water (2 \times , 8 h each time) followed by acetone (2 \times , 8 h each time) and were vacuum-dried overnight at 80 °C.

4.2. Methods. Drying Procedure. Drying of wet-gels with supercritical fluid (SCF) CO_2 was carried out in an autoclave (SPIDRY Jumbo Supercritical Point Dryer, SPI Supplies, Inc. West Chester, PA, or in a Spe-edSFE system, Applied Separations, Allentown, PA). Samples were loaded into the autoclave and acetone was added until all samples were submerged. The pressure vessel was closed and liquid CO_2 was allowed in at room temperature. Acetone was drained out from the pressure vessel as it was being displaced by liquid CO_2 . Subsequently, more liquid CO_2 was allowed into the vessel and was drained out several more times until all acetone was extracted out of the pores of the samples. The criterion for that was that vented-out CO_2 started forming dry ice. Subsequently, the temperature of the autoclave was raised to 40 °C, and SCF CO_2 was vented off as a gas.

Physical Characterization. Bulk densities (ρ_b) were calculated from the weight and the physical dimensions of the samples. Skeletal densities (ρ_s) were determined with helium pycnometry using a Micromeritics AccuPyc II 1340 instrument. Porosities, Π , as percent of open empty space were calculated from ρ_b and ρ_s via $\Pi = 100 \times [\rho_s - \rho_b]/\rho_{s}$.

Chemical Characterization. Elemental analysis (CHN) was conducted with a PerkinElmer elemental analyzer (Model 2400 CHN).

Infrared (IR) spectra were obtained in KBr pellets, using a Nicolet-FTIR Model 750 spectrometer. Raman spectroscopy of carbon samples was conducted with a Jobin-Yvon micro-Raman spectrometer with a 632.8 nm He–Ne laser as the excitation source.

Liquid ¹H and ¹³C NMR spectra were recorded in deuterated solvents using a 400 MHz Varian Unity Inova NMR instrument (100 MHz carbon frequency). Solid-state ¹³C NMR spectra were obtained with samples ground into fine powders on a Bruker Avance III 400 MHz spectrometer with a carbon frequency of 100 MHz, using magic-angle spinning (at 5 kHz) with broadband proton suppression and the CPMAS TOSS pulse sequence for spin sideband suppression. Solid-state ¹³C NMR spectra were referenced externally to glycine (<u>C</u>=O: 176.03 ppm).

Powder X-ray diffraction (PXRD) was conducted with a PANalytical X'Pert Pro multipurpose diffractometer (MPD) with Cu $K\alpha$ radiation ($\lambda = 1.54$ Å) and a proportional counter detector equipped with a flat graphite monochromator. Phase composition was estimated via Rietveld refinement of the X-ray diffraction patterns utilizing RIQAS software (Materials Data, Inc., version 4.0.0.26). Structural information for crystalline phases was obtained from the ICSD database version 2.01. Crystallite sizes were calculated using the Scherrer equation and the fwhm of the lowest-angle diffractions. A Gaussian correction was applied utilizing NIST SRM 660a LaB₆ to determine the instrumental broadening.

Thermogravimetric analysis (TGA) was conducted under O₂ at 5 $^{\circ}$ C min⁻¹ using a TA Instruments Model TGA Q50 thermogravimetric analyzer. The residue from Fe@C after TGA analysis was collected and was analyzed with XRD. The only crystalline phase found was Fe₂O₃.

Gas chromatography (GC) was carried out with a Hewlett-Packard 5890 Series II gas chromatograph equipped with a DB-5 capillary column (30 m/0.25 mm) and a flame ionization detector (FID).

Characterization of the Porous Structure. Brunauer–Emmett– Teller (BET) surface areas, pore volumes, and pore size distributions for pores in the 1.7–300 nm range were determined with N_2 -sorption porosimetry at 77 K using a Micromeritics ASAP 2020 surface area and porosity analyzer. Pore size distributions were calculated by applying the Barrett–Joyner–Halenda (BJH) equation to the desorption branch of the isotherms.

Characterization of the Skeletal Framework. Scanning electron microscopy (SEM) was conducted with Au-coated samples on a Hitachi Model S-4700 field-emission microscope. Transmission electron microscopy (TEM) was conducted with an FEI Tecnai F20 instrument employing a Schottky field emission filament operating at a 200 kV accelerating voltage. The samples were finely ground by hand in a mortar with a pestle, and the powder was mixed with isopropanol

in 5 mL glass vials, which were ultrasonicated for 20 min to disperse the smallest particles in the solvent. Immediately afterward, and just before particle settling was complete, a single drop was taken and placed on a 200 mesh copper grid bearing a lacey Formvar/carbon film. The grid was allowed to air-dry overnight before microscopy. At least six different areas/particles were examined to ensure that the results were uniform over the entire sample.

The fundamental building blocks of the FcPA-xx aerogels were also probed with small-angle X-ray scattering (SAXS), using ~2 mm thick disks cut dry with a diamond saw. SAXS analysis was carried out with the same PANalytical X'Pert Pro multipurpose diffractometer (MPD) described above configured for scattering, using a 1/32° SAXS slit, a $1/16^\circ$ antiscatter slit on the incident beam side, and a 0.1 mm antiscatter slit together with a Ni 0.125 mm automatic beam attenuator on the scattered beam side. Samples were placed in circular holders between thin Mylar sheets, and scattering intensities were measured by running 2θ scans from -0.1° to 5° with a point detector in the transmission geometry. All scattering data were reported in arbitrary units as a function of Q, the momentum transferred during a scattering event. Data analysis was conducted using the Beaucage Unified $\mathsf{Model}^{\mathsf{56},\mathsf{57}}$ applied with the Irena SAS tool for modeling and analysis of small angle scattering within the Igor Pro application (a commercial scientific graphing, image processing, and data analysis software from Wave Metrics, Portland, OR).

Evaluation of Fe@C and tm-M@C as Catalysts. All four catalysts (Fe@C, tm-Au@C, tm-Pt@C, tm-Pd@C) were used at a 5% mol/mol ratio relative to the limiting reagent in the corresponding reaction mixture. Starting materials and products were quantified using gas chromatography and internal standards. Response factors were equal to the slopes of calibration curves that were constructed with a series of samples containing known concentrations of each reactant, product, and internal standard.

Reduction of nitrobenzene⁵² was catalyzed with Fe@C and was carried out in a thick-jacketed round-bottom pressure flask with a Teflon screw-cap. Nitrobenzene (0.984 g, 8 mmol) was dissolved in THF (50 mL). Hydrazine hydrate (0.641 g, 20 mmol) was added as a reducing agent and hexadecane (1000 μ L, 3 mmol) as an internal standard. The flask was sealed and the reaction mixture was stirred for 24 h at 100 °C. Aliquots (100 μ L) were taken every 2 h by cooling the flask temporarily to 40 °C and were analyzed immediately with GC. After 24 h the reaction mixture was cooled down to room temperature, and the Fe@C monolith was picked up with a pair of tweezers, rinsed briefly with THF, and transferred immediately to a new reaction mixture for the next cycle. The whole process was repeated five times.

mixture for the next cycle. The whole process was repeated five times. Oxidation of benzyl alcohol⁵³ was catalyzed either with *tm*-Au@C or *tm*-Pt@C. Benzyl alcohol (0.864 g, 8 mmol) was dissolved in distilled water (50 mL), and acetophenone (1000 μ L, 8 mmol) was added as an internal standard. The reaction mixture was heated with an oil bath to 60 °C under constant bubbling of oxygen and vigorous magnetic stirring. Aliquots (100 μ L) were taken every 2 h, extracted with diethyl ether (2 mL), and analyzed immediately with GC. After 24 h the reaction mixture was cooled down to room temperature, and the *tm*-Au@C and *tm*-Pt@C monoliths were harvested out as above, rinsed briefly with water, and transferred to new reaction mixture for the next cycle. The whole process was repeated five times. Heck coupling reactions⁵⁴ were catalyzed with *tm*-Pd@C at 80 °C,

Heck coupling reactions⁵⁴ were catalyzed with *tm*-Pd@C at 80 °C, with constant magnetic stirring under N₂ in DMF (5 mL) using a mixture of iodobenzene (1.632 g, 8 mmol), triethyl amine (0.809 g, 8 mmol), and butyl acrylate (1.28 g, 10 mmol) or styrene (1.04 g, 10 mmol). In both cases, hexadecane was added as an internal standard (1000 μ L, 3 mmol). The same protocol as above was observed for GC analysis and recycling of the catalyst.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemma-ter.6b02364.

Appendix I: Formulations of FcPA-xx aerogels. Appendix II: Materials characterization data for FcPA-xx, Fe@C, and *tm-M*@C. Appendix III: N₂-sorption data. Appendix IV: Small-angle X-ray scattering (SAXS) data for FcPAxx. Appendix V: FTIR of FcPA-xx. Appendix VI: Additional PXRD data related to transmetalation and removal of Fe(0) with HCl. Appendix VII: Additional TEM of Fe@C and *tm-M*@C. Appendix VIII: Raman data for FcPA-15 after pyrolysis at different temperatures. Appendix IX: Data from catalysis using Fe@C and *tm-M*@C as catalysts (PDF)

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Notes

The authors declare no competing financial interest.

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