Surveying Iron–Organic Framework TAL-1-Derived Materials in Ligandless Heterogeneous Oxidative Catalytic Transformations of Alkylarenes

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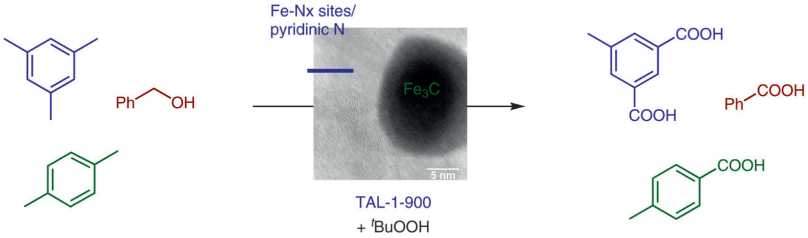

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Abstract The use of carbonized materials derived from metal–organic frameworks (MOFs) in catalytic organic transformations is less well explored than is the use of MOFs. Here, we survey the oxidative performance of heterogeneous catalyst materials derived from the polycrystalline iron–organic framework TAL-1.

Key words iron catalysis, oxidation, sustainable chemistry, metal–organic framework, alkyl arenes, carboxylic acids

Pavel Starkov was born in Tallinn, Estonia. He obtained his BSc *cum laude* in natural sciences from the University of Tartu, Estonia; his MRes in biomolecular science from Imperial College, London (research project with Professor Alan Armstrong and Dr David Mann); and, in 2011, his Ph.D. in chemistry from University College London, under the guidance of Professor Tom Sheppard. Before completing his Ph.D., he joined Professor Ulrike Eggert at Harvard Medical School and later relocated to Israel for a research stay with Professor Rafal Klajn at the Weizmann Institute of Science and Professor Ilan Marek at Technion–Israel Institute of Technology. Pavel joined Tallinn University of Technology as a senior research scientist (independent PI) in 2016.

Besides their many other noteworthy applications,[1–3] metal–organic frameworks (MOFs) are an established platform for chemocatalysis.[2–5] However, much less is known about the chemical performance of the carbonized materials derived from the corresponding MOFs containing metal–ligand and/or purely N-based sites.[6–8] We recently showed that, by altering the structure of the underlying fused hybrid carbon-rich organic linkers,[9] one can achieve substantial gains in the electrochemical performance of single-precursor-derived MOF-based electrocatalyst materials in oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs).[10,11] Here, we assess the best-performing electrocatalyst from the ORR/OER series, TAL-1-900, and its precursor TAL-1 (Scheme 1) in various catalytic oxidative transformations.[12]

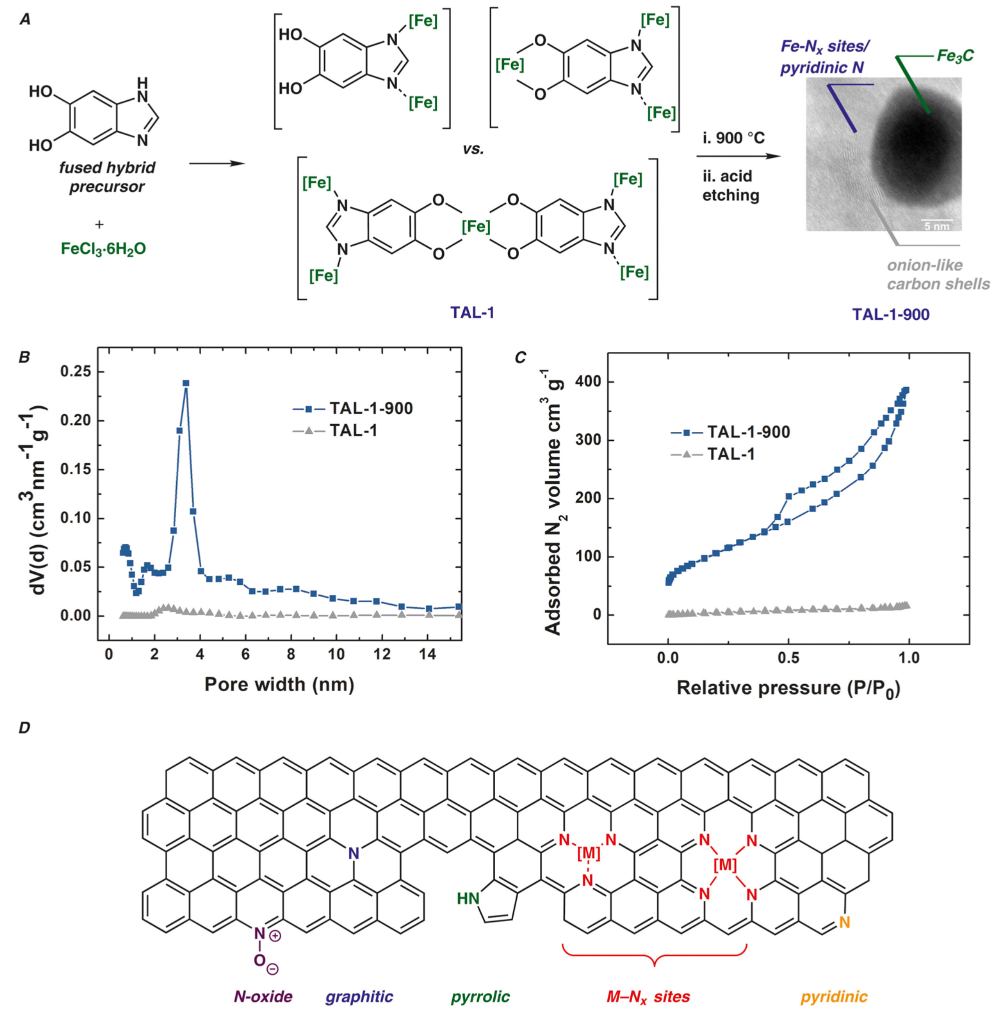
In 1964, Jasinski reported[13] cobalt phthalocyanine as the first ORR electrocatalyst material not based on a platinum-group metal.[14–16] Its performance was originally assessed (along with the Fe, Ni and Cu-based systems) in oxidative organic transformations.[13] In the present work, we intended to take a reciprocal approach by examining the performance of the recently developed electrocatalyst TAL-1-900 and its direct precursor in oxidative reactions.[11]

Whereas TAL-1 is a nonporous polycrystalline MOF, TAL-1-900 is a porous material (Scheme 1b and 1c) obtained from TAL-1 by carbonization at 900 °C and subsequent acid leaching. The latter procedure removes iron oxides from the surface of the material and decreases the amount of α-Fe in the carbon onion-shell-embedded α-Fe/Fe_3C nanocrystals. This results in a final catalyst material, TAL-1-900, that has a significantly higher porosity than

TAL-1. Moreover, TAL-1-900 can be utilized in metal-catalyzed transformations in a ligand-free manner, as the Fe–N_x and other sites with potential catalytic activity (e.g., pyridinic, pyrrolic, or graphitic nitrogens) are preassembled during the carbonization step (Scheme 1d) and subsequently made accessible by acid etching.[11] For instance, the presence and precise distribution of these active sites is known to be essential for the overall performance of the bifunctional electrocatalyst materials in electrochemical OER/ORR reactions.[15–18]

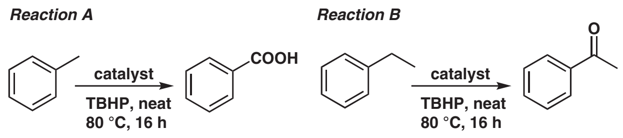
One challenge that we wished to address by using our newly developed materials was the practical, laboratory-bench conversion of alkylarenes[19] into the corresponding arylcarboxylic acids or ketones. To this end, the classical approach relies on the stoichiometric use of a strong oxidant, typically, $KMnO_4$.[20] In 2007, Nakanishi and Bolm introduced an iron chloride-catalyzed oxidation conducted in pyridine with *tert*-butyl hydroperoxide (TBHP) as the terminal oxidant.[21] Given the fact that our bifunctional ORR/OER electrocatalyst TAL-1-900 and its MOF precursor TAL-1 incorporated ligated iron centers,[11] we wished to investigate their performance in similar transformations.

We have screened the iron-based TAL-1 and TAL-1-900 systems in two classical transformations in order to determine which of the two is the more robust catalyst (Table 1).[22] We used a 70% aqueous solution of TBHP as the terminal oxidant. In our hands, TAL-1 caused rapid decomposition of TBHP and **should be handled with extreme care**. With regard to the oxidation of toluene, TAL-1 showed low activity (up to a 14% isolated yield of benzoic acid), whereas TAL-1 exhibited much greater activity in the oxidation of ethylbenzene to acetophenone. Gratifyingly, TAL-1-900 showed a more-consistent performance in converting toluene into benzoic acid (Reaction A) and ethylbenzene into acetophenone (Reaction B) (entries 4–7).



Scheme 1 (a) Preparation of TAL-1 and TAL-1-900. (b) Pore sizes in TAL-1 and TAL-1-900 catalysts. (c) Dinitrogen adsorption/desorption by TAL-1 and TAL-1-900. (d) Diversity of the potential nitrogen (N) catalytic sites in carbonized TAL-1-900 catalyst, in addition to the matrix-embedded metal carbide nanocrystals.

Table 1 Optimization of the Reaction Conditions for the Oxidation of Toluene (Reaction A) and Ethylbenzene (Reaction B)[a]



Entry	Catalyst[b]	TBHP (equiv)	Isolated yield (%)	
			Reaction A	Reaction B
1	TAL-1	3	11	9
2	TAL-1	6	11	34
3	TAL-1	10	14	50
4	TAL-1-900	3	28	24
5	**TAL-1-900**	**6**	**34**	**44**
6	TAL-1-900[c]	6	34	67
7	TAL-1-900	10	35	45

[a] Reaction conditions: 70% aq. TBHP, neat, 80 °C, 16 h.
[b] Catalyst loading: 5 mg/mmol of substrate, except entry 6.
[c] Catalyst loading: 10 mg/mmol of substrate.

Table 2 TAL-1-900-Catalyzed Oxidations[a]

Entry	Substrate	Major product	TBHP (equiv)	Isolated yield (%)
1	toluene	benzoic acid	6	37
2	BnOH	benzoic acid	3	84
3	$PhCH_2CO_2H$	benzoic acid	3	49
4			6	70
5	*m*-xylene	isophthalic acid	12	32
6	*p*-xylene	4-$MeC_6H_4CO_2H$	12	34
7	mesitylene	uritic acid	18	38
8	PhEt	PhCOMe	3	50
9			6	54
10	Ph_2CH_2	Ph_2CO	3	47
11			6	94

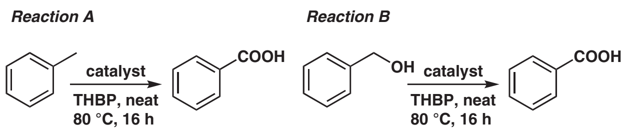
[a] Reaction conditions: TAL-1-900 (5 mg/mmol of substrate), 70% aq TBHP, neat, 80 °C, 24 h.

The robust performance of TAL-1-900 was enhanced by its stability and by its potential to serve as a recoverable and recyclable catalyst. The surface of porous TAL-1-900 is covered with catalytically active Fe–N_x sites (pyridinic, pyrrolic, and graphitic nitrogen), as shown by X-ray photoelectron spectroscopy.[11] The use of highly organized materials as catalysts can often reduce the need for complimentary ligands and bases, and can ensure that low levels of metal leaching occur, potentially rendering the heterogeneous catalyst material recyclable.

Next, we wished to investigate the catalytic performance of TAL-1-900 in converting various alkylarenes into the corresponding carboxylic acids or ketones (Table 2).[19,22] Toluene, benzyl alcohol, and phenylacetic acid were converted into benzoic acid (entries 1–3). It is likely that phenylacetic acid is initially oxidized to phenylglyoxylic acid, which then undergoes decarboxylation by the TBHP radical.[23,24] In the case of polymethylated arenes, the major isolated products are shown in Table 2 (entries 4–6). *m*-Xylene gave isophthalic acid (entry 4), *p*-xylene gave *p*-toluic acid (entry 5), and mesitylene was converted into 5-methylisophthalic acid in 38% yield (entry 6). Ethylbenzene (entries 8 and 9) and diphenylmethane (entries 10 and 11) were converted into the corresponding ketones; increasing the number of equivalents of TBHP from three to six increased the isolated yield of benzophenone (entry 11).

Finally, we showed that the TAL-1-900 catalyst could be reused several times (Table 3).

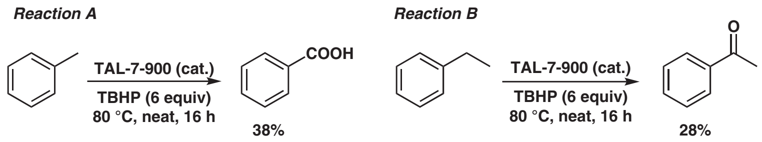
Table 3 Recycling Experiments[a]



Cycle	Yield[b] (%)	
	Reaction A	Reaction B
1	35	89
2	35	90
3	40	91

[a] Reaction conditions: 70% aq. TBHP, neat, 80 °C, 16 h; catalyst loading: 5 mg/mmol of substrate.
[b] Determined by NMR with 1,3,5-trimethoxybenzene as internal standard.

We then tested a related catalyst material obtained from TAL-7. This was prepared from 5,6-dimethoxy-1*H*-benzo[*d*]imidazole, a methyl-protected version of the TAL-1 organic precursor 1*H*-benzo[*d*]imidazole-5,6-diol.[10] Interest-



Scheme 2 TAL-7-900-catalyzed oxidations (catalyst loading: 5 mg/mmol of substrate).

ingly, catalyst TAL-7-900 performed similarly to TAL-1-900 in the oxidation of toluene (Scheme 2; isolated yield 38% vs. 34%); however, the yield from the oxidation of ethylbenzene was significantly less (28% vs. 44%).

We have previously shown by microwave plasma atomic-emission spectroscopy that the total amount of iron in TAL-1-900 (0.896 ± 0.006 wt%) differs from that in TAL-7-900 (3.603 ± 0.035 wt%).[11] Despite the fact that TAL-7-900 contains about four times as much iron as TAL-1-900, we found that TAL-1-900 performed as well as or slightly better than TAL-7-900 in oxidative transformations (Reactions A and B; Table 1 and Scheme 2). Notably, whereas the two benzimidazole-based organic linkers used to prepare TAL-1- and TAL-7-derived catalysts both contain electron-donating groups (OH and OMe, respectively), only the unprotected catechol had the propensity to form bis- and triscatecholato complexes with iron.[25] Hence, the precise nature of the iron complexes formed at the surface of the catalyst material following carbonization might contribute to the overall catalytic performance of our heterogeneous catalysts. In practice, one would seek to employ additional porous carbon supports,[26] which might increase the accessible specific surface area of the final catalyst material.

In summary, we have shown that iron-based TAL-1-900 is a reliable catalyst for the oxidation of alkylarenes to the corresponding carboxylic acids or ketones. Because the total iron content in this heterogeneous catalyst is very low (≤1%), its performance as a catalyst is promising. The long-term advantages of using metal-doped carbonized materials as catalysts for organic transformations include their recyclability, low metal leaching, and no requirement for additional ligands.

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Supporting Information

Supporting information for this article is available online at https://doi.org/10.1055/s-0037-1611877.

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(22) **5-Methylisophthalic Acid (Table 2, Entry 7): Typical Procedure**
A mixture of mesitylene (100 mg, 0.832 mmol, 1.0 equiv), 70% aq TBHP (2.05 mL, 14.98 mmol, 18.0 equiv), and TAL-1–900 (4.2

mg) was stirred at 80 °C for 24 h. It was then filtered through a Celite pad with MeOH. The resulting solution was concentrated under reduced pressure then purified by flash chromatography [silica gel, EtOAc–PE (1:20 to 1:10)] to give a colorless solid; yield: 57.2 mg (0.317 mmol, 38%); mp 296–297 °C.
^{1}H NMR (400 MHz, DMSO-d_6): δ = 13.18 (s, 2 H), 8.28 (s, 1 H), 7.98 (s, 2 H), 2.43 (s, 3 H). ^{13}C NMR (100 MHz, DMSO-d_6): δ = 166.7, 138.8, 133.9, 131.2, 127.3, 20.6. HRMS (ESI): *m/z* [M + H]$^+$ calcd. for $C_9H_9O_4$: 181.0495; found: 181.0496.

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