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Sulfonated Ordered Mesoporous Carbon as a Stable and Highly Active Protonic Acid Catalyst

Xiqing Wang,[†] Rui Liu,[†] Mahesh M. Waje,[‡]
Zhongwei Chen,[‡] Yushan Yan,[‡]
Krassimir N. Bozhilov,[§] and Pingyun Feng*[,†]

Department of Chemistry, Department of Chemical and Environmental Engineering, and Central Facility for Advanced Microscopy and Microanalysis, University of California, Riverside, California 92521

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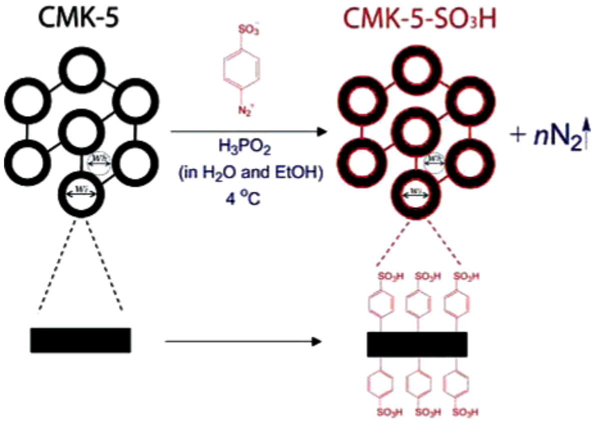
The principles of green chemistry and increasing concerns about environmental issues have stimulated the search for recyclable strong solid acids to replace of conventional toxic and corrosive acid catalysts, such as sulfuric acid.[1] Integration of acidic functional groups (e.g., $-SO_3H$) into ordered mesoporous silicas (OMSs) has been explored to produce promising solid acids.[2−8] Sulfonated OMSs were usually synthesized through attachment of sulfur-containing (e.g., −SH and −S−S−) organic silanes on the silica surface by grafting or co-condensation methods and subsequent oxidation of sulfur to generate sulfonic acid groups.[2−8] Efforts on incorporation of a high density of functional groups led to the formation of porous materials at the expense of mesostructural order.[3] In addition, harsh oxidation conditions caused a degradation of structural uniformity, and incomplete oxidation of thio groups at high sulfur loadings (e.g., >1.5 mmol/g) resulted in the formation of disulfides.[4b]

In addition to sulfonated OMSs, carbon-based solid acids have been recently reported.[9−11] For example, by sulfonation of incompletely carbonized sugars, Hara et al. obtained a series of carbon-based catalysts with acid densities ranging from 0.37 to 1.34 mmol H^+/g.[10] Similarly, Budarin et al. synthesized a mesoporous sulfonated Starbon-400 with 0.5 mmol/g SO_3H loading.[11] These materials have shown higher stability than sulfonated OMSs. However, such materials were non-ordered[11] or nonporous[10] and exhibited low surface area, which may limit the accessibility to active sites. Recently, ordered mesoporous carbons (OMCs) have been synthesized through the nanocasting technique using OMSs as templates[12] or via self-assembly of phenolic resins and block copolymers.[13] These materials exhibit high surface area, narrow pore size distribution, and large pore volume. Thus functionalization of OMCs with sulfonic acid groups is expected to allow high densities of functional groups and ensure good accessibility to active sites. Early efforts on functionalization of OMCs by oxidation with nitric acid indicate that harsh oxidation conditions led to degradation of the meso-structural order.[14] In addition to acid treatment,[9−11,14] many other efficient modification methods on the carbon surface, such as grafting through electrochemical[15] or chemical[16] reduction of aryl diazoniums and reductive alkylation or arylation,[17] have been developed and can be applied for functionalization of OMCs. Very recently, Dai and co-workers have showed the efficiency of chemical reduction of aryl diazonium for covalent attachment of ortho-substituted aryl groups (Ar−R, R = Cl, $COOCH_3$, $C(CH_3)_3$,

Scheme 1. Functionalization of CMK-5 with Sulfonic Acid Groups



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* Corresponding author. E-mail: pingyun.feng@ucr.edu.
[†] Department of Chemistry.
[‡] Department of Chemical and Environmental Engineering.
[§] Central Facility for Advanced Microscopy and Microanalysis.

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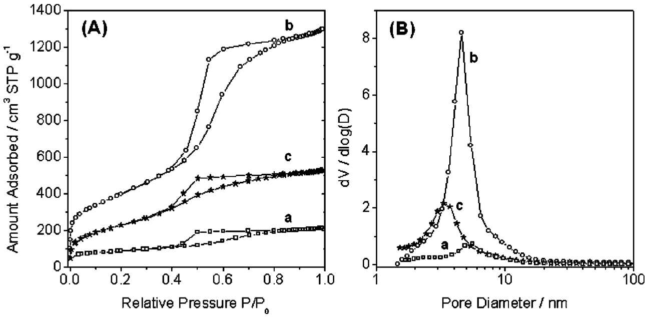


Figure 1. (A) N_2 sorption isotherms and (B) BJH pore size distribution plots of (a) C/SBA-15 composite, (b) CMK-5, and (c) CMK-5-SO_3H.

$(CH_2)_3CH_3$) on the surface of OMCs.[18] However, there is so far no report on functionalization of OMCs with sulfonic acid groups and on the use of such materials as solid acid catalysts.

Here, we report the functionalization of OMC by covalent attachment of sulfonic acid-containing aryl radicals, which can be produced by homogeneous reduction of diazonium salt by hypophosphorous acid,[16] on the carbon surface under mild conditions (see Scheme 1). Through the combination of the advantages of carbon-based catalysts (e.g., excellent stability) and the unique features of OMCs (e.g., large surface area), the resulting material shows high activity for acid-catalyzed reactions, such as esterification and condensation. It also exhibits high stability and can be used for at least five cycles without obvious loss of activity.

Hexagonal tube-like CMK-5[12c] was chosen as the substrate because CMK-5 exhibits mesoporosity both inside nanopipes and between nanopipes (see Scheme 1), which is readily available for modification with sulfonic acid groups. CMK-5 was synthesized using Al-SBA-15 as the hard template and furfuryl alcohol (FA) as the carbon precursor (see Supporting Information). As shown in Figure 1, before removal of silica template, Al-SBA-15/carbon composite exhibits a type IV isotherm with a considerable amount of N_2 uptake, indicating incomplete filling of FA due to surface-templated polymerization. After dissolving the silica template by HF, CMK-5 shows a uniform pore size distribution, centered at 4.6 nm, suggesting an overlapping of the pore diameter between nanopipes (w_b) and the internal pipe pore size (w_i). Functionalization of CMK-5 was carried out by reacting with 4-benzene-diazoniumsulfonate in the presence of hypophosphorous acid. After sulfonation (denoted as CMK-5-SO_3H), pore diameters decrease by about 1.3 nm, giving a pore size distribution with a center at 3.3 nm. Consequently, surface area and pore volume decrease from 1436 m^2/g and 2.0 cm^3/g to 843 m^2/g and 0.82 cm^3/g, respectively. The X-ray diffraction (XRD) pattern of CMK-5 (Figure S1, Supporting Information) shows four well-resolved peaks, which can be indexed as 100, 110, 200, and 210 reflections from the hexagonal *p*6*m* symmetry. The relatively high intensity of the 110 peak is the characteristic of tube-type CMK-5.[12c] After modification, CMK-5-SO_3H retains the hexagonal structure, as also confirmed by scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images

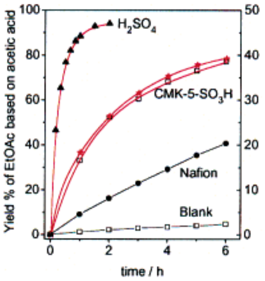
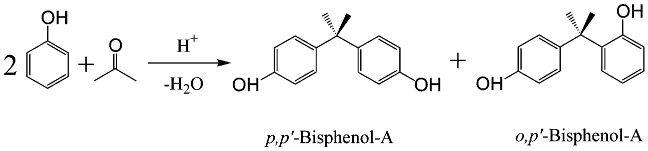


Figure 2. Acid catalyzed (100 mg of catalyst) esterification of acetic acid (0.05 mol) with ethanol (0.5 mol) at 70 °C to generate ethyl acetate (EtOAc). Yield of EtOAc was based on acetic acid. In the case of CMK-5-SO_3H, results of two individual runs are shown.

Scheme 2. Acid-Catalyzed Formation of Bisphenol-A



(Figure S2, Supporting Information), but the intensity of XRD peaks decreases and the 100 peak becomes invisible (Figure S1, Supporting Information). The decrease in intensity of XRD peaks is due to the decreased scattering contrast between walls and channels after modification, which has been observed for OMSs after surface functionalization.[19] The acid exchange capacity of CMK-5-SO_3H was determined to be 1.93 ± 0.08 mmol H^+/g by potentiometric titration, which is higher than most of the other sulfonic acid functionalized mesoporous materials reported so far.[2−8]

CMK-5 is hydrophobic even though it contains some oxygen residues after pyrolysis and carbonization of FA. As shown in a digital graph (Figure S3, Supporting Information), CMK-5 does not exhibit a good wettability in water, while CMK-5-SO_3H can form a homogeneous suspension in water, suggesting the modified sample exhibits hydrophilic property. Therefore, CMK-5-SO_3H can be viewed as a material with a hydrophobic substrate and hydrophilic functional groups. Such amphiphilic properties would allow CMK-5-SO_3H to be an efficient solid catalyst in both hydrophobic and hydrophilic environments. Thermal gravimetric analysis (TGA) results (under flowing N_2) also confirm the hydrophilic property of CMK-5-SO_3H (Figure S4, Supporting Information). The weight loss of CMK-5-SO_3H below 150 °C (ca. 5.2 wt %) can be attributed to physically adsorbed water, while there is negligible weight loss for unmodified CMK-5 in the same temperature range. Further weight loss of CMK-5-SO_3H at higher temperature accounts for loss of the SO_3H segment and pyrolysis of hydrocarbons. At 800 °C, the total weight loss reaches about 28%.

The catalytic performance of CMK-5-SO_3H was investigated by esterification of acetic acid with ethanol at 70 °C. Figure 2 shows the conversion of acetic acid over the reaction time. For comparison, results for the same amount of concentrated sulfuric acid (98%, acid capacity 20.4 mmol/g) and protonated Nafion (NR50, Aldrich, acid capacity 0.8 mmol/g) are also shown. Ethyl acetate was the only product

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Table 1. Acid-Catalyzed Formation of Bisphenol-A[a]

catalyst	acid amount, mmol H^+/g	conversion,[b] %	selectivity,[c] %	TON[d]
none		0		
CMK-5-SO_3H	1.93	8.9 ± 0.4[e]	84.0 ± 0.8[e]	23.0 ± 1.1[e]
EPMO-propyl-SO_3H[f]	1.72	1.58	75.6	4.6
SBA-15-CH_2CH_2aryl-SO_3H[g]	0.26	1.23	75	13

[a] Condensation of phenol (70 mmol) with acetone (10 mmol) in the presence of 70 mg of catalyst at 85 °C for 24 h. [b] The maximum conversion of phenol is 28.6%. [c] Selectivity to *p,p′*-bisphenol A is based on molar fraction. [d] TON is defined as mmol of bisphenol A per mmol of active site. [e] The reaction was performed in duplicate. [f] Reference 6a. EPMO-propyl-SO_3H, sulfonated ethylene-bridged periodic mesoporous organosilica by the co-condensation method. [g] Reference 5. SBA-15-CH_2CH_2aryl-SO_3H, sulfonated SBA-15 by the co-condensation method, 0.033 mmol of H^+ catalyst used.

detected by gas chromatography (GC) for all systems studied. In the absence of acid catalyst, the conversion of acetic acid was only 4.7% after 6 h of reaction. In comparison, CMK-5-SO_3H gave ca. 80% yield of ethyl acetate (based on acetic acid). Under identical conditions, the yield of ethyl acetate was only 41% for Nafion after 6 h. Sulfuric acid, as a homogeneous acid catalyst, has higher activity at 94% after 2 h of reaction, but it lacks the advantages of heterogeneous solid catalysts, such as CMK-5-SO_3H reported here.

The stability of CMK-5-SO_3H was investigated by reuse of the catalyst for esterification of acetic acid with ethanol. After each use, the catalyst was recycled by simple filtration or centrifugation, followed by washing with distilled water and drying in an oven at 100 °C overnight. As shown in Figure S5 (Supporting Information), the identical high catalytic activity remained even for a fourth recycle. The results indicate that CMK-5-SO_3H is more stable than sulfonic acid functionalized mesoporous silicas that showed obvious loss of catalytic activity after even the first recycle. The low stability of the latter is due to the weak attachment of functional groups on the silica surface through unstable Si−O−Si−R siloxane bonds, which are susceptible to hydrolysis especially at low pH values.[20] The good recycleability of CMK-5-SO_3H can be attributed to high stability of ordered mesoporous CMK-5 and tight attachment of aryl sulfonic acid group on the substrate through the stable C−C bond.

CMK-5-SO_3H has also been used to catalyze the formation of bisphenol A (Scheme 2 and Table 1) because bisphenol A is a very important raw material for preparation of polymers and resins. Condensation of phenol with acetone leads to two isomers, *p,p′*-bisphenol A and *o,p′*-bisphenol A. CMK-5-SO_3H showed a phenol conversion of 8.9% (28.6% maximum) with high selectivity of 84.0% to *p,p′*-bisphenol A. Both conversion and selectivity for CMK-5-SO_3H are much better than those obtained by sulfonated ethylene-bridged periodic mesoporous organosilica (EPMO-propyl-SO_3H) and sulfonated SBA-15 (SBA-15-CH_2CH_2aryl-SO_3H) under identical conditions (Table 1). Among these three catalysts, CMK-5-SO_3H exhibits the highest acid amount, but the largest amount of active sites may not be the only reason for the best performance. Therefore, TON, which represents yield of product per active site (mmol of product/mmol of active site), is used to compare the activity of these catalysts. CMK-5-SO_3H exhibits the highest TON. Recent studies indicate that catalysts containing hydrophobic groups can provide positive effects on catalysis.[7,21] Accordingly, hydrophobic substrate of CMK-5-SO_3H likely contributes to the superior performance on catalyzed formation of bisphenol A. The effect of hydrophobicity of CMK-5-SO_3H on catalytic properties will be investigated in detail.

In addition to being a highly active acid catalyst, CMK-5-SO_3H may also be a desirable support for electrocatalysts used in polymer electrolyte fuel cells because of its ability to conduct simultaneously electrons and protons. Note that current carbon black based fuel cell catalyst supports do not possess proton conductivity, and thus the proton conductivity within the catalyst layer has to be realized by addition of an ionomer, for example, Nafion, making the catalyst layer structure complex. The proton conductivity of CMK-5-SO_3H was measured at room temperature and 100% relative humidity using two-electrode impedance spectroscopy (see details in Supporting Information).[22] A proton conductivity of 0.009 S/cm was obtained, and this conductivity is expected to be able to offer significant enhancement in fuel cell performance over carbon black.

In summary, we report a stable and highly active solid acid based on sulfonic acid functionalized OMC with high surface area and uniform pore size. Another unique feature of sulfonated CMK-5 is the integration of hydrophobicity and hydrophilicity into the same material, which may provide synergistic effects on catalysis. In addition to reactions of esterification and condensation, CMK-5-SO_3H may also find applications in other acid-catalyzed reactions, such as the production of biodiesel.[10a,23] Moreover, the method described here can be extended for attachment of other functional groups on the surface of OMCs to generate diverse functionalized OMCs for different applications.

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Supporting Information Available: Experimental details. XRD patterns, SEM and TEM images, digital graph, TGA profiles, and Nyquist plots (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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