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Synthesis of Sulfonated Carbon Nanocage and Its Performance as Solid Acid Catalyst

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Abstract A carbon nanocage material (CKT) was first successfully sulfonated by introducing sulfophenyl groups on the surface of pore channels through benzenesulfonic acid-containing aryl radical in situ generated from the reaction of 4-aminobenzenesulfonic acid and isoamyl nitrite in water. The sulfonated carbon nanocage material (S-CKT) was characterized by Fourier transform infrared spectroscopy, transmission electron microscopy, powder small-angle X-ray diffraction and nitrogen sorption measurements. The results showed that the S-CKT still possess the high specific surface area (787 m^2/g) and uniform mesoporous (pore diameter 4.7 nm) structures, although the structure of S-CKT is slightly disorder, compared with its unsulfonated precursor. S-CKT, as a carbon-based solid acid catalyst, showed good catalytic performance and reusability in the cross-Aldol condensation of ketones with aromatic aldehydes under solvent-free condition.

Keywords Carbon nanocage · Mesoporous carbon · Sulfonated carbon material · Solid acid catalyst · Cross-Aldol condensation

1 Introduction

The principles of green chemistry and increasing concerns about environmental issues have stimulated the search for recyclable strong solid acids to replace conventional toxic and corrosive acid catalysts, such as sulfuric acid [1]. In the past few years, various types of solid acids have been developed, such as sulfonated ordered mesoporous silicas (OMSs) [2–8] and sulfonated silica/carbon nanocomposites [9]. In 2010, Jacobs' group reported that the sulphonation of carbon–silica hybrid materials and its use in the hydrolysis of cellulose into high yields of glucose in mild conditions [9]. In addition to sulfonated OMSs and sulfonated silica/carbon hybrids, carbon-based solid acids have been recently reported [10–13]. For example, by sulfonation of incompletely carbonized sugars, Hara et al. obtained a series of carbon-based solid acid catalysts with acid densities ranging from 0.37 to 1.34 mmol/g [11, 12]. However, these materials were non-ordered [13] or non-porous [11, 12] and exhibited low surface area, which lead to modest catalysis activity. Recently, ordered mesoporous carbons (OMCs) have been synthesized through the nanocasting technique using OMSs as templates [14–16] or via self-assembly of phenolic resins and block copolymers [17–19]. These carbon materials exhibit high surface area, narrow pore size distribution (PSD) and large pore volume. Thus the functionalization of OMCs with sulfonic acid groups is expected to allow high densities of functional groups and ensure good accessibility to active sites.

Significant efforts have been devoted to the sulfonation of OMCs [20–23], and their potential applications in catalysis have been reported [24, 25]. But those sulfonation processes were reported with two-dimensional hexagonal carbon as precursor. In 2005, Vinu and co-workers reported a series of three-dimensional cage type mesoporous

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carbons (CKTs) using face centered cubic *Fm3m* mesoporous silicas (KITs) as inorganic templates synthesized from Pluronic F127 ($EO_{106}PO_{70}EO_{106}$) as a structure-directing agent [26]. These materials possess a well ordered pore structure, high specific pore volume, specific surface area and tunable pore diameter, and have been using in adsorptions for biomolecules such as proteins, vitamins, amino acids etc. [27, 28] and separation of tea components such as catechin and tannic acid [29]. However, the hydrophobic and inert nature of mesoporous carbons can be unfavorable for direct applications. In addition, the three-dimensional carbon nanocages, as new mesoporous carbon materials, are made up of connected cage of each other. The connected structure of pore walls make for mass transport in chemical reaction, and each cage is like a micro-reactor. Surface sulfonation of carbon nanocage materials may not only change the character of materials from hydrophobicity to hydrophilicity, but also enable them available as a good Brønsted acid catalyst. Considering these, herein we report the preparation of sulfonated carbon nanocages through benzenesulfonic acid-containing aryl radical in situ generated from the reaction of 4-aminobenzenesulfonic acid and isoamyl nitrite to introduce sulfophenyl groups on the surface of pore channels. The structure of sulfonated carbon nanocages were investigated with electron microscopic and spectroscopic method etc. Furthermore the catalytic performance, as a carbon-based solid acid catalyst, was evaluated through cross-Aldol condensation of ketones with aromatic aldehydes.

2 Experiment Procedures

2.1 Measurement Instrument and Chemicals

The IR spectra of samples were collected on an Avatar360E.S.P.FTIR spectrometer using KBr pellets. The powder small-angle X-ray diffraction (SAXD) patterns of samples were recorded by a Rigalcu (D/Max2550VB) diffractometer with Ni-filtered Cu Kα radiation (40 kV, 40 mA). The step width was 0.02° at an acquisition time of 8 s per step. N_2 adsorption isotherms were measured using a Micromeritics ASAP 2020 M adsorption analyzer under liquid N_2 temperature. Prior to the measurements, the samples were degassed for 6 h in the degas port of the adsorption apparatus at 200 °C. The specific surface areas (S_{BET}) were calculated using the Brunauer–Emmett–Teller (BET) method based on adsorption data in the relative pressure (P/P_0) range 0.05–0.35, the total pore volumes (V_t) were determined based on the amount of the N_2 adsorbed at a relative pressure of 0.992 (P/P_0), and the PSDs were derived from the desorption branches of isotherms by using the Barrett–Joyner–Halenda (BJH) model. The transmission electron microscopy (TEM) experiments were conducted on a JEM-2100 electron microscope operated at 200 kV. The samples for TEM measurements were suspended in ethanol and supported onto a holey carbon film on a Cu grid. The ^1H NMR spectra were collected on Super-conducting Fourier Digital NMR spectrometer (AVANCE 300 MHz) with TMS as the internal reference. The melting points of compounds were measured by X-5 microscopic melting point apparatus. The acid capacity of sample was determined by ZD-2 automatic potentiometric titrator. All chemicals used were of analytical grade.

2.2 The preparation and Sulfonation of Carbon Nanocage Material

The carbon nanocage material, CKT-3(A), was synthesized with cage type mesoporous silica KIT-5-150 (where 150 denote the synthesis temperature of the silica material) as inorganic template and sucrose as the carbon source using literature method [26]. In the typical sulfonation process of carbon material, 0.12 g of CKT-3(A) was mixed with 15 mL deionized water in a glass flask. The contents were homogenized under vigorous stirring. The reaction flask was heated to 80 °C in an oil bath. 0.48 g of 4-aminobenzenesulfonic acid and 400 μL isoamyl nitrite were then added, and a condenser was attached. The mixture was stirred vigorously for 12 h at 80 °C. Then the contents were allowed to cool to room temperature and filtered on a Teflon filter (0.45 μm). The filter cake was repeatedly washed with NaOH (1 M) and absolute alcohol to remove any remaining unreacted organic matters, and then neutralized to excessive NaOH with HCl (1 M), and dried at 40 °C overnight in a vacuum oven. The obtained sample was denoted as S-CKT. Acid capacity of sulfonated sample was determined by titration with NaOH aqueous solution [30]. Briefly, 50 mg of S-CKT was dispersed in 15 g of aqueous solution of NaCl (2 M) with stirring at room temperature overnight. The dispersion was then titrated potentiometrically with 0.1 M NaOH. Titration was repeated for 3 times and the average number was reported.

2.3 General Procedure for Cross-Aldol Condensation of Ketones with Aromatic Aldehydes

1 mmol of Ketone, 2 mmol (or 1 mmol) of aromatic aldehyde, and certain amount of S-CKT were mixed thoroughly, placed in a glass flask equipped with a magnetic stirrer and a reflux condenser. The mixture was heated at 70 °C with stirring for 30–120 min until aromatic aldehyde was exhausted (monitored with TLC). After the mixture was cooled to room temperature, dichloromethane was added and heated for few minutes to sufficiently

dissolve the products. The catalyst (S-CKT) was removed by filtration, and can be recycled after washing with dichloromethane and drying. The filtrate was concentrated in normal pressure to recycle the dichloromethane, and the solid residue was recrystallized from acetone or ethanol to give pure target product.

2,6-Dibenzylidenecyclohexanone: mp 116–117 °C (lit. 116–117 °C) [31]. ^{1}H NMR (300 MHz, DMSO-d$_6$)δ 1.81–1.85 (t, $J = 6.4$ Hz, 2H, CH$_2$), 2.94–2.98 (t, $J = 6.4$ Hz, 4H, 2CH$_2$), 7.34–7.59 (m, 10H, Ar–H), 7.83 (s, 2H, =CH).

2,6-Di(4-nitrobenzylidene)cyclohexanone: mp 159–160 °C (lit. 159 °C) [31]. ^{1}H NMR (300 MHz, CDCl$_3$)δ 1.84–1.88 (t, $J = 6.2$ Hz, 2H, CH$_2$), 2.93–2.95 (t, $J = 6.2$ Hz, 4H, 2CH$_2$), 7.59–7.61 (d, $J = 8.2$ Hz, 4H, Ar–H), 7.81 (s, 2H, =CH), 8.26–8.29 (d, $J = 8.2$ Hz, 4H, Ar–H).

2,6-Di(4-methoxybenzylidene)cyclohexanone: mp 202–203 °C (lit. 203–204 °C) [31]. ^{1}H NMR (300 MHz, CDCl$_3$)δ 1.80–1.83 (t, $J = 6.0$ Hz, 2H, CH$_2$), 2.92 (t, $J = 6.0$ Hz, 4H, 2CH$_2$), 3.84 (s, 6H, 2OCH$_3$), 6.92–6.95 (d, $J = 8.1$ Hz, 4H, Ar–H), 7.44–7.47 (d, $J = 8.1$ Hz, 4H, Ar–H), 7.76 (s, 2H, =CH).

2,6-Di(4-hydroxybenzylidene)cyclohexanone: mp 294–295 °C (lit. 294–295 °C) [31].^{1}H NMR (300 MHz, CDCl$_3$) δ 1.71 (t, $J = 6.2$ Hz, 2H, CH$_2$), 2.85 (t, $J = 6.2$ Hz, 4H, 2CH$_2$), 6.82–6.85 (d, $J = 8.1$ Hz, 4H, Ar–H), 7.39–7.42 (d, $J = 8.1$ Hz, 4H, Ar–H), 7.54 (s, 2H, =CH), 9.93 (s, 2H, 2OH).

2,6-Di(3,5-dimethoxybenzylidene)cyclohexanone: mp 136–137 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.71 (t, J=6.2 Hz, 2H, CH$_2$), 2.89 (t, $J = 6.2$ Hz, 4H, 2CH$_2$), 3.77 (s, 12H, 4OCH$_3$), 6.54 (s, 2H, Ar–H), 6.67 (s, 4H, Ar–H), 7.55 (s, 2H, =CH); ^{13}C NMR (300 MHz, DMSO-d6) δ 22.8, 28.3, 55.7, 101.4, 108.6, 136.3, 137.2, 137.6, 160.8, 189.5.

2,6-Di(3,4,5-trimethoxybenzylidene)cyclohexanone: mp 211–213 °C (lit. 208–210 °C) [32]. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.84 (t, J=6.2 Hz, 2H, CH$_2$), 2.97 (t, J=6.2 Hz, 4H, 2CH$_2$), 3.89 (s, 18H, 6OCH$_3$), 6.72 (s, 2H, Ar–H), 7.74 (s, 2H, =CH).

2,6-Di[4-(dimethylamino)benzylidene]cyclohexanone: mp 250–252 °C (lit. 250–252 °C) [31]. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.79 (t, J=5.4 Hz, 2H, CH$_2$), 2.93 (t, J=5.4 Hz, 4H, CH$_2$), 3.02 (s, 12H, 4CH$_3$), 6.71–7.44 (m, 8H, Ar–H), 7.75 (s, 2H, =CH).

Chalcone: mp 55–57 °C (lit 57–58 °C) [33]. ^{1}H NMR 300 MHz, CDCl$_3$)δ 6.12 (d, $J = 16.0$ Hz, 1H, =CH), 7.26 (d, $J = 16.0$ Hz, 1H, =CH), 7.10–7.32 (m, 5H, Ar–H), 7.42–7.92 (m, 5H, Ar–H).

4-Methoxychalcone: mp 74–75 °C (lit. 75–77 °C) [33]. ^{1}H NMR (300 MHz, CDCl$_3$)δ 3.86 (s, 3H, OCH$_3$), 6.92–6.95(d, $J = 8.2$ Hz, 2H, Ar–H), 7.38–7.44 (d, $J = 15.6$ Hz, 1H, =CH), 7.49–7.52 (d, $J = 7.1$ Hz, 2H, Ar–H), 7.59 (m, 3H, Ar–H), 7.76–7.81 (d, $J = 15.6$ Hz, 1H, = CH), 7.99–8.02 (d, $J = 7.1$ Hz, 2H, Ar–H).

4-Nitrochalcone: mp 157–158 °C (lit. 158–160 °C) [33]. ^{1}H NMR (300 MHz, CDCl$_3$)δ 7.54–7.61 (m, 5H, Ar–H), 7.62–7.67 (d, $J = 15.6$ Hz, 1H), 7.80–7.85 (d, $J = 15.6$ Hz, 1H), 8.03–8.05 (d, $J = 6.6$ Hz, 2H, Ar–H), 8.27–8.29 (d, $J = 6.6$ Hz, 2H, Ar–H).

3 Results and Discussion

3.1 Materials Characteristics

Sulfonated carbon materials, such as sulfonated hexagonal tube-like mesoporous carbon [23, 26], sulfonated carbon nanotubes [34, 35] and sulfonated amorphous carbon material [11] etc., have attracted considerable attention due to their applications in catalysis as Brønsted acid catalysts, and fuel cells [35]. We attempted to explore the functionalization of carbon nanocage CKT-3(A) with sulfophenyl group and its catalysis effect as solid Brønsted acid. Sulfonation of CKT-3(A) was carried out using the method reported by Tour's group for sulfonating carbon nanotubes [22], this method generates benzenesulfonic acid-containing aryl radicals in situ from the reaction of 4-aminobenzenesulfonic acid and isoamyl nitrite in water. In order to check the structural change of carbon material after sulfonation treatment, the CKT-3(A) and S-CKT were characterized by nitrogen isothermal adsorption, TEM images, SAXD and IR spectra. Nitrogen gas adsorption–desorption isotherm tests were conducted to investigate the pore-structural character for the carbon materials (Fig. 1). According to the International Union of Pure and Applied Chemistry (IUPAC) classification [36], the samples of

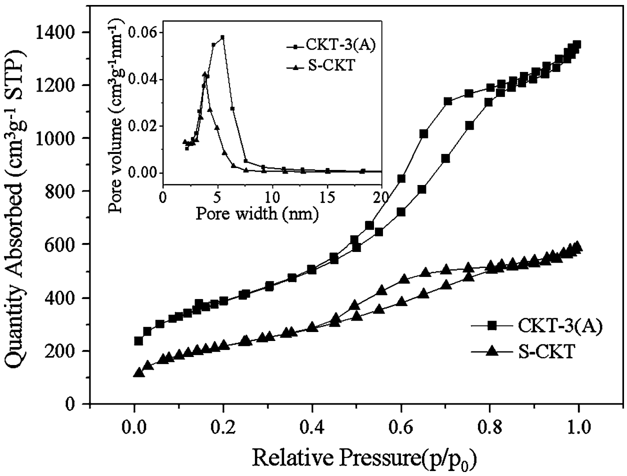


Fig. 1 Nitrogen absorption isotherms and pore size distribution of CKT-3(A) and S-CKT

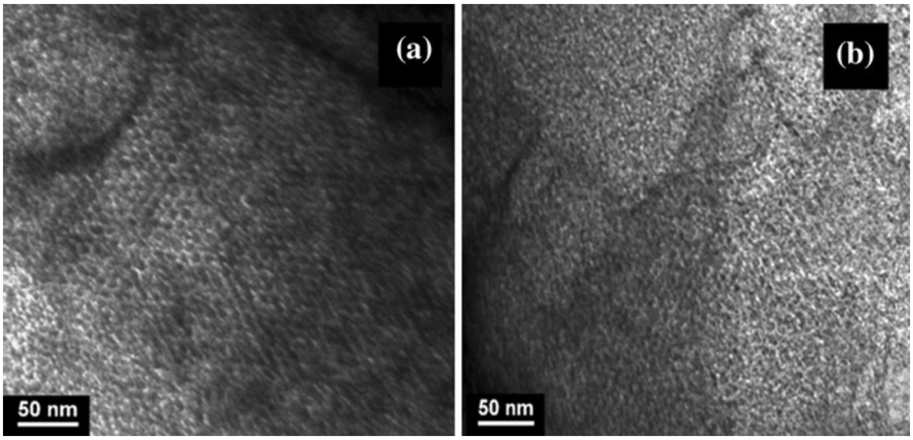


Fig. 2 TEM images of CKT-3(A) (**a**) and S-CKT (**b**)

CKT-3(A) and S-CKT present type IV isotherms with quite significant H2-type hysteresis loops, which is a characteristic of mesoporous materials with "ink-bottle" type pores [36], and the PSD curves (inserted in Fig. 1) exhibit sharp peaks centered at 5.1 and 4.7 nm, respectively. These data indicated that S-CKT holds the mesoporous characteristics of CKT-3(A), except for a slight decrease of the pore diameter. The specific surface area (787 m^2/g) and pore volume (0.91 cm^3/g) of S-CKT present obviously decrease compared with that of CKT-3(A) (1368 m^2/g and 2.10 cm^3/g). These results showed that the sulfonation process obviously changes the textural parameters of carbon material, which may be attributed to some block of pore by the introduced sulfophenyl groups on the surface of pore channels, and structural destruction and collapse partially in the sulfonation reaction. These changes of structure can be also observed from TEM images (Fig. 2). The collapse and disorder of some pore structure appear in the TEM image of S-CKT (Fig. 2b), although the periodical pore structure of CKT-3(A) is represented in Fig. 2a. However, S-CKT still possesses higher specific surface area (787 m^2/g), and the mesoporous structure of CKT-3(A) is mainly kept in S-CKT deduced from the similarity of the SAXD patterns between CKT-3(A) and S-CKT as shown in Fig. 3.

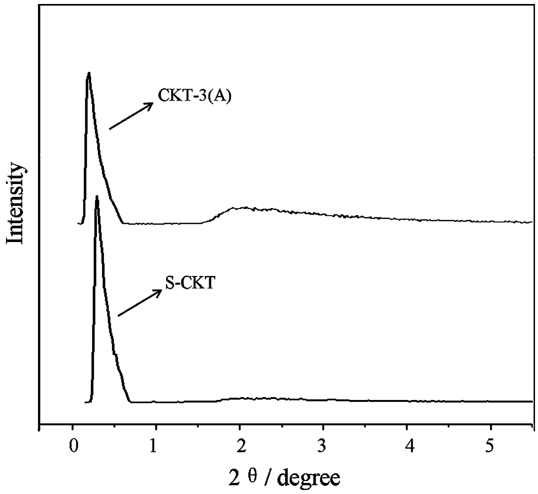


Fig. 3 SAXD patterns of CKT-3(A) and S-CKT

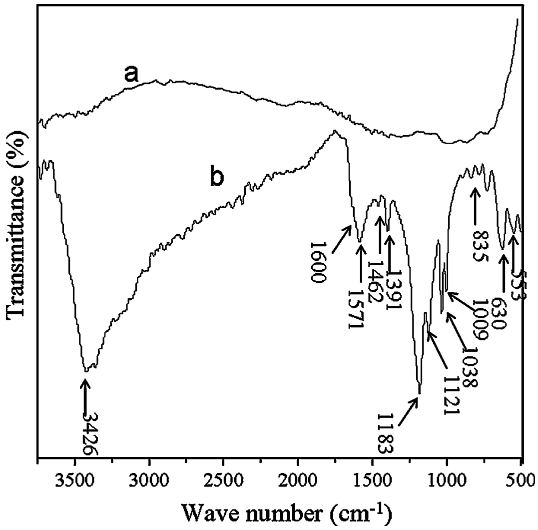


Fig. 4 FTIR spectra of CKT-3(A) (*a*) and S-CKT (*b*)

The introduction of sulfophenyl group on the surface of the pore of S-CKT was successful. It was proved by the significant difference between the FTIR spectra of CKT-3(A) and S-CKT (Fig. 4). Nearly no absorption peak was observed in the FTIR spectrum of CKT-3(A), in contrast the peaks appear obviously in the FTIR spectrum of S-CKT. The $–SO_2OH$ groups can be identified by the peak at 3426 (–OH, and –OH from adsorptive water, stretching vibration), 1391 and 1183 cm^{-1} ($–SO_2$-asymmetric and symmetric stretching modes). When adsorptive water combines with the sulfonic acid group, the asymmetric and symmetric stretching modes shift to 1121 and 1038 cm^{-1}. The peak at 630 cm^{-1} also indicate the S=O stretching mode of $–SO_3H$ [37]. The absorption peaks of phenyl group present at 1600, 1571 and 1462 cm^{-1} (aromatic C=C), 1009 cm^{-1} (=CH), and 835 cm^{-1} (C–H para-aromatic out-of-plane vibration)

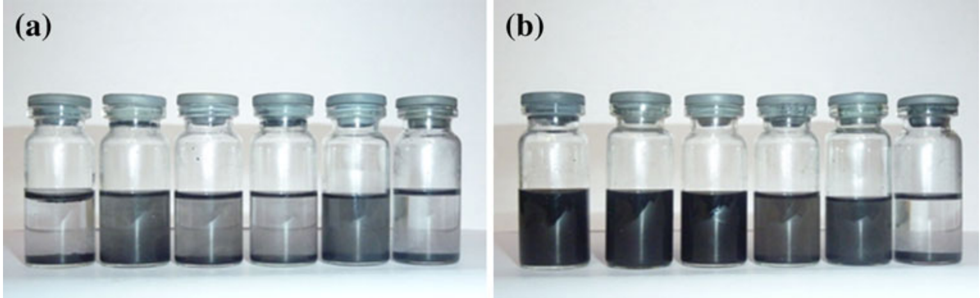


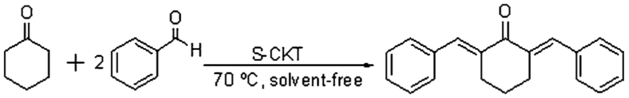
Fig. 5 Dispersibility of CKT-3(A) (**a**) and S-CKT (**b**) in H_2O, DMF, EtOH, $CHCl_3$, CH_3COCH_3 and $C_6H_5CH_3$ (from left to right) after disperse by vibration and standing for 24 h

[35]. In low frequency range, the peak at 553 cm^{-1} was assigned to C–S stretching mode, suggesting the existence of covalent sulfonic acid groups. These representative absorption peaks indicate that sulfophenyl groups were successfully modified on the surface of cage type mesoporous carbon S-CKT.

The density of the SO_3H group was measured using NaOH (0.10 mol/L) as titrant by acid-base potentiometric titration [30]. The amount of SO_3H loaded to the S-CKT was 1.53 ± 0.09 mmol/g. The sulfonation process has changed the surface property of the carbon materials. As shown in digital graph (Fig. 5a), CKT-3(A) does not exhibit a good suspension in water and various organic solvents after vibration, while S-CKT (Fig. 5b) can form a homogeneous suspension in solvents, especially in water and highly polar solvents (EtOH, DMF), and these homogeneous suspension systems were retained even after 6 months. The S-CKT exhibits hydrophobic and hydrophilic properties because it possesses a hydrophobic substrate and hydrophilic functional groups. This amphiphilic material may allow S-CKT to be an efficient solid catalyst in both hydrophobic and hydrophilic environments.

3.2 Catalytic Effect of S-CKT as Solid Acid on Aldol Condensation Reaction

The Aldol condensation reaction is recognized to be one of the most important carbon–carbon bond-forming processes in organic synthesis [38, 39]. It is well known that Aldol condensation can be catalyzed not only by base, but also by acid. In order to explore the catalytic properties of this sulfonated carbon material as a solid acid, herein, the cross-Aldol condensation of cyclohexanone and benzaldehyde was used as a model reaction under solvent-free condition (Scheme 1). Initially, 0.75 g of S-CKT was used to catalyze the reaction of cyclohexanone (1 mmol) and benzaldehyde (2 mmol) at 70 °C. The reaction could be over in 30 min resulting from the TLC tracking, and gave a target compound in 88.5% yield (entry 1 in Table 1). Decreasing the catalyst amount from 0.75 to 0.10 g/mmol of cyclohexanone, the time of reaction completion, yield and formation rate of target product were not changed obviously, but the turnover frequency (TOF) at acid sites increased from 0.026 to 0.195 (from entry 1 to entry 4 in Table 1). When the catalyst amount was further decreased to 0.05 g/mmol of cyclohexanone, the time of reaction completion was increased to 60 min, the yield was reduced dramatically to 68.6% and TOF was decreased to 0.149 (entry 5 in Table 1). These results indicated the amount of catalyst at 0.10 g/mmol of cyclohexanone is minimum dose in the reaction. *p*-$CH_3C_6H_4SO_3H$ is used as Brønsted acid catalyst in high frequency. When 0.05 g (0.29 mmol) of *p*-$CH_3C_6H_4SO_3H$ instead of SCKT was used to catalyze this reaction, the reaction could complete in 20 min, but the yield of target product was only in 70.0%, and the reaction exhibited lower selectivity compared to the reaction catalyzed by S-CKT. It is noteworthiness the recovery of *p*-$CH_3C_6H_4SO_3H$ from the reaction mixture is tedious and difficult. Though sulfonic acid supported on solid materials such as non-mesoporous carbon [40], nanoporous silica [41] and polystyrene [42] have been applied to catalyze the cross-Aldol condensation of cyclohexanone and benzaldehyde, they needed longer reaction time, larger amount of catalyst or noxious solvent. Herein S-CKT exhibited a higher efficiency to catalyze this reaction under solvent-free condition.



Scheme 1 The cross-Aldol condensation of cyclohexanone and benzaldehyde

The recycling of catalyst is very important. The S-CKT can stably suspend in water and highly polar solvents

Table 1 Condensation of cyclohexanone and benzaldehyde under different catalyst loading

Entry	Sample	Catalyst loading (g/mmol)[a,b]	Time of reaction completion (min)	Yield (%)[c]	Formation rate of product (μmol/min)	TOF (min^{-1})[d]
1	S-CKT	0.75	30	88.5	29.5	0.026
2		0.35	30	87.2	29.1	0.054
3		0.20	30	90.8	30.3	0.099
4		0.10	30	89.7	29.9	0.195
5		0.05	60	68.6	11.4	0.149
6	*p*-$CH_3C_6H_4SO_3H$	0.05	20	70.0	35.0	0.121

[a] Catalyst loading is the amount of S-CKT used in the reaction to 1 mmol of cyclohexanone

[b] The density of $–SO_3H$ on the S-CKT was 1.53 ± 0.09 mmol/g

[c] The isolated yield of target compound

[d] TOF = moles product formed per mole of acid site per minute

Table 2 Reusability of catalyst on condensations of cyclohexanone and benzaldehyde[a]

No. of run	Time of reaction completion (min)	Yield (%)[b]
1	30	89.7
2	30	84.6
3	30	82.2
4	30	83.8
5	30	77.0
6	30	77.4
7	40	70.0

[a] The amount of catalyst used was 0.2 g/mmol of cyclohexanone

[b] The isolated yield of target compound

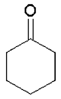
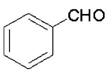
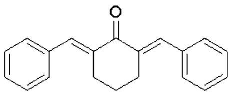
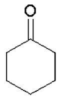
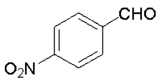
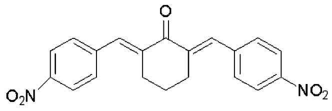
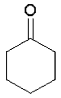
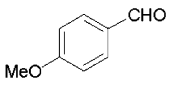
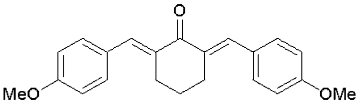
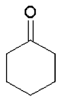
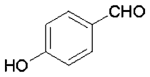
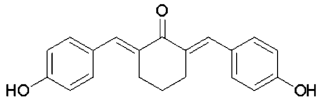
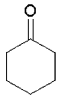
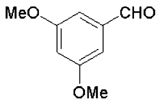
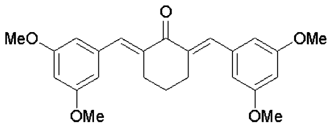
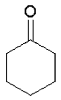
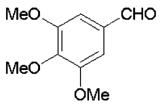
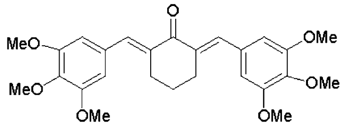
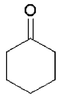
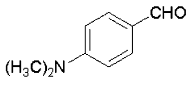
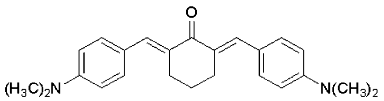
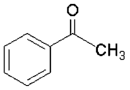
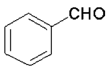
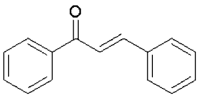
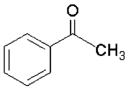
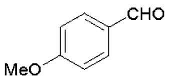
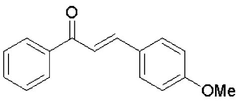
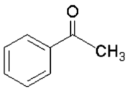
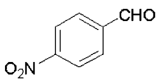
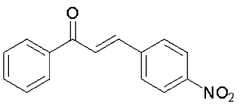
(EtOH, DMF), but it can still be recovered easily from the solution of dichloromethane by a simple filtration. After reaction, dichloromethane was added to the reaction mixture and heated for few minutes to sufficiently dissolve the mixture. Then, the catalyst was recovered by reduced pressure filtration, washed with dichloromethane and drying in vacuum for recycling. Table 2 shows the catalyst after being recycled six times still present a high catalytic activity for this Aldol condensation reaction, this run could give yields of 77.4% within the same reaction time. As we can see in Table 2, the yields after recycling are gradually decrease, it may be attributed to the loss of catalyst during recycling and the loss of active sites. Considering unfunctionalized carbon material can be also used as a catalyst in some reactions itself [43, 44], when we used the same amount of unfunctionalized carbon CKT-3(A) instead of S-CKT to test whether the condensation reaction of cyclohexanone and benzaldehyde occurred under the same conditions, no target compound was found in the reaction mixture. This result indicated the $–SO_3H$ group of S-CKT plays an important role in the cross-Aldol condensation of cyclohexanone and benzaldehyde.

This sulfonated carbon material should also be able to catalyze the Aldol condensation of other compounds. We expanded reaction to the condensation of various substituted aromatic aldehydes with ketones in the same condition. The results shown in Table 3 indicate that the key advantages of this catalyst are shorter reaction times, higher yield and simple workup. The catalytic activity of S-CKT may be attributed to its large surface area and cage-type mesoporous besides higher density of the SO_3H groups. The catalyst with cage type mesoporous is benefit to mass transport of molecules in reaction [45], and may act as numerous connected micro-reactors to help the reaction to proceed in a short time.

4 Conclusions

In summary, a nanocage carbon bearing benzene sulfonic acid, S-CKT, is prepared by contacting the CKT parent material with an aqueous solution of sulfophenyl radicals, which are easily generated by reacting 4-aminobenzenesulfonic acid with isoamyl nitrite in water. The sulfonated nanocage carbon material possesses higher surface area (787 m^2/g), narrower PSD and higher density of the SO_3H group (1.53 mmol/g). S-CKT presents good suspension in various solvents, especially in some highly polar solvents such as water, EtOH and DMF. These homogeneous suspension systems were maintained even after 6 months. When using S-CKT to the cross-Aldol condensations of ketones and aromatic aldehydes, it exhibited good catalytic activity under solvent-free condition. We believe this new carbon-based Brønsted

Table 3 Cross-Aldol condensation of ketones with aromatic aldehydes in the presence of S-CKT[a]

Entry	Ketone	Aldehyde	Product	Time of reaction completion (min)	Yield (%) [b]
1				30	90.8
2				40	84.4
3				40	83.2
4				50	84.4
5				40	92.3
6				35	72.2
7				60	80.5
8				100	81.2
9				90	76.4
10				120	75.6

[a] Reaction condition: the mixture of 1 mmol of ketone, 2 mmol (entry 1–7) or 1 mmol (entry 8–10) of aromatic aldehyde and 0.2 g of S-CKT was heated at 70 °C with stirring

[b] The isolated yield of product

acid catalyst can be also used extensively to catalyze other reaction because of its numerous potential benefits, such as high efficiency, easy recovery and reuse, and low environmental impact.

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