Recent Advances in Carbon-Based Sulfonated Catalyst: Preparation and Application

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Abstract – *Carbon-based sulfonated catalyst (CBSC) becomes a research hot-spot in recent years. In this paper, the preparation and application of CBSC are reviewed. In the preparation of CBSC, various carbon raw materials, various sulfonating agents, and various carbonization operation conditions have been developed. Biomass derived CBSC would be promising as biomass is renewable, abundant, low-cost, and easy for preparation. CBSC was widely studied and showed high catalytic activities in many chemical reactions, including hydrolysis, dehydration, esterification, alkylation, condensation, oxathioketalization, dimerization, benzylation and trimethylsilylation, etc. CBSC is a high potential solid acid catalyst due to its high catalytic activities and extensive applications. However, further works on economic study, improvement of catalytic stability, and mechanical strength should be conducted.* ***Copyright © 2013 Praise Worthy Prize S.r.l. - All rights reserved.***

Keywords: *Sulfonated Catalyst, Solid Acid, Biomass, Carbonization, Catalytic Activity*

I. Introduction

Acid-catalyzed reaction is very important in chemical processes, and acid catalysts are studied and developed all along the recent decades. The acid catalysts can be classified into homogeneous and heterogeneous acid catalysts according to their existing states in the reactions. H_2SO_4, HF etc. are widely used as liquid homogeneous acid catalysts, which can show effective catalytic performance even at some low temperatures, because they often participate in reactions in their molecular state. However, there are some problems in using these liquid acid catalysts, e.g. massive waste liquors would be produced, process equipment would be eroded, separation of catalyst with raw materials and products is not convenient, and successive reaction operation is hard to be conducted, etc. In order to overcome these problems that the liquid acid catalyst brought into the reactions, study of eco-friendly and easy reusable heterogeneous solid acid catalysts become meaningful. A series of solid acid catalysts are developed, including metal oxide (e.g. Al_2O_3), metal sulfide (e.g. CdS), zeolite molecular sieve (e.g. H-ZSM-5), heteropoly acid (e.g. $H_3PW_{12}O_{40}$), immobilized liquid acid (e.g. $HF/AlCl_3$), cation exchange resin (e.g. Nafion-H), natural clay (e.g. bentonite), and solid superacid (SO_4^{2-}/ZrO_2) etc. However, none of the above solid acids is perfect among all of the acid-catalyzed reactions. For example, studies dealing with the use of the solid acid catalysts for biodiesel synthesis were somewhat limited due to restricted reaction rates and unfavorable side reactions [1], [2].

SO_4/ZrO_2 deactivates due to sulfate leaching [3]-[5]. Internal mass transfer limitation has severely limited the performance of microporous heterogeneous acid catalysts, such as zeolite Hb [6]. Tungstated zirconia can be deactivated as a result of the formation of carbonaceous deposits on Brønsted acid sites [7].

In recent years, carbon material has become a hot research area, and carbon-based sulfonated catalysts (CBSCs) are developing rapidly. All of the CBSCs own the carbon skeleton and $-SO_3H$ group, and the carbon skeleton is stable and insoluble in most acidic/basic conditions as well as organic solvents.

The carbon based catalyst can be easily separated from reaction system, which is very convenient for recovery and reuse. For biomass derived CBSC, the body is often amorphous and owns aromatic structure. Moreover, the biomass derived CBSC possesses a high density of nearly neutral phenolic -OH in addition to Brønsted acid sites ($-SO_3H$ and $-COOH$), which is distinct from conventional solid acids bearing single functional groups. The possible structural model of the biomass derived CBSC is shown in Fig. 1.
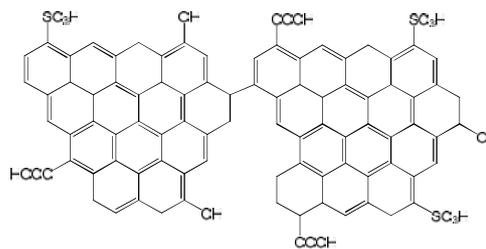

Fig. 1. Proposed structural model of the biomass derived CBSC

The contents of -SO₃H, -OH, -COOH groups on CBSC are usually among 0.1-4.9, 0-0.9, 0-7.8 mmol/g, respectively [8]-[34].

Though -SO₃H groups are considered as the key active acidic site, [35] the existence of -OH and -COOH groups would provide hydrophilic reactants accessing to the -SO₃H groups, which would be in favor of effective catalytic performance.

However, as we known, specialized information on summary and comment on this fast developing CBSC was lacking. In this review, we focus on the preparation and application studies of CBSC in the recent decade.

II. Preparation Methods

The method for preparation of the high catalytic activity and stability CBSC has been an important and attractive work. Various carbon based raw materials (e.g. biomass, aromatic compounds, carbon nanotube, activated carbon, etc.), various sulfonating agents (e.g. concentrated/ fuming H_2SO_4, hydroxyethylsulfonic acid, etc.), and various carbonization operation conditions (e.g. hydrothermal conversion, pyrolysis, etc.) have been developed.

The concrete preparation methods are summarized, classified, and discussed as below.

II.1. Directly Incomplete H_2SO_4 Carbonization

The directly incomplete H_2SO_4 carbonization method is shown in Fig. 2. Hara, et al.[17], and Fu, et al.[36] found that CBSC synthesized from naphthaline by directly incomplete H_2SO_4 carbonization showed high catalytic activities in esterification, hydrolysis reactions. However, when various low polycyclic aromatic hydrocarbons (e.g. naphthaline, anthracene, etc.) were used as the raw materials, these kinds of CBSCs showed leaching of -SO₃H groups at somewhat high temperatures [17]. Guo et al. [37] obtained a lignin-derived CBSC by directly incomplete H_2SO_4 carbonization, and they found this catalyst displayed high catalytic activity in esterification of acidified soybean soapstock with methanol. However, there was also a little decline in -SO₃H content during the recycling. There was no added preprocess (e.g. hydrothermal carbonization, pyrolysis, etc.) for carbon materials production for this preparation method, so it simplify the process and reduce the cost.
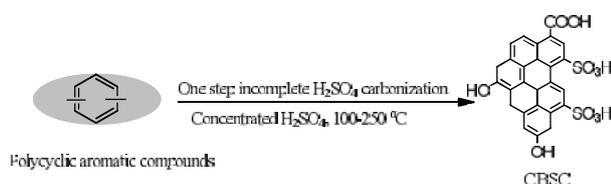

Fig. 2. CBSC preparation by directly incomplete H_2SO_4 carbonization

However, further studies on improvement of -SO₃H group stability on the carbon surface would be necessary before this preparation method could be considered in industry.

II.2. Sulfonation of Biomass Carbonization Products

Biochars can be obtained by carbonization of biomass or biomass derived products.

The carbonization methods include pyrolysis, gasification, flash carbonization, and hydrothermal carbonization, etc.[38]. Recently, sulfonation of biochars from pyrolysis for catalyst preparation is widely studied, [13], [39]-[46], and the preparation process is shown in Fig. 3.

The pyrolysis temperature is often between 250-650 °C. High temperature would result in a "rigid" carbon material, which would be adverse to the formation of -SO₃H group during the sulfonation process, resulting low acid density. [41], [44]. Moreover, the "rigid" carbon material would have no function for certain neutral/ polar molecules to reach the -SO₃H groups, resulting in a limited catalysis.

Samorì et al. reported that lower pyrolysis temperatures at longer time favored thermal-resistant carbon materials more prone to be sulfonated to a high degree.[45] Kastner et al. found that biochars synthesized at a lower temperature and sulfonated at a lower temperature (400°C for pyrolysis, 100 °C for sulfonation) had the highest activity [29]. Compared with pyrolysis, hydrothermal carbonization temperature is somewhat low, and the biochar produced by hydrothermal carbonization (hydrochar) possess more surface oxygen containing groups [47], [48]. Sulfonation of hydrochar has also been developed [49], [50].

Concentrated and fuming H_2SO_4 are used as the sulfonating agents, and the CBSC prepared with fuming H_2SO_4 resulted in a much higher catalytic activity [13], [29].

However, the use of fuming H_2SO_4 would bring excess safety and operation problem as compared with that of concentrated H_2SO_4, so the application of fuming H_2SO_4 as sulfonating agent is not advocated.

Both catalyst surface area and total acid density are important parameters in the catalytic reactions. The Brunauer-Emmett-Teller (BET) area of the biochar produced by direct carbonization is often low (< 30 m^2/g), and sulfonation process seems having no effects on the improvement of BET area [21], [51]. In order to get high surface area of CBSC, as shown in Fig. 3, the biochar can be activated to become porous carbon material followed by sulfonation to form activated carbon-based sulfonated catalysts (ACBSCs) [16], [19], [52], [53].

In Kitano's work, the specific surface area of ACBSC could get a maximum of 1560 m^2g^{-1} [44].
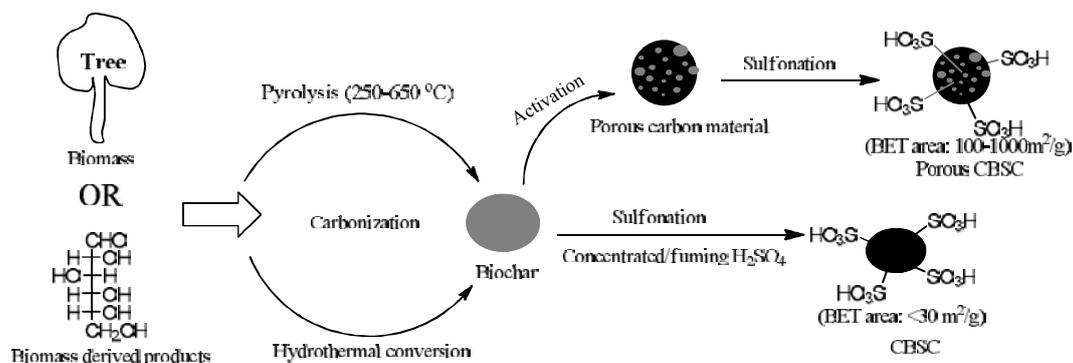
Fig. 3. CBSC preparation by sulfonation of biomass carbonization products
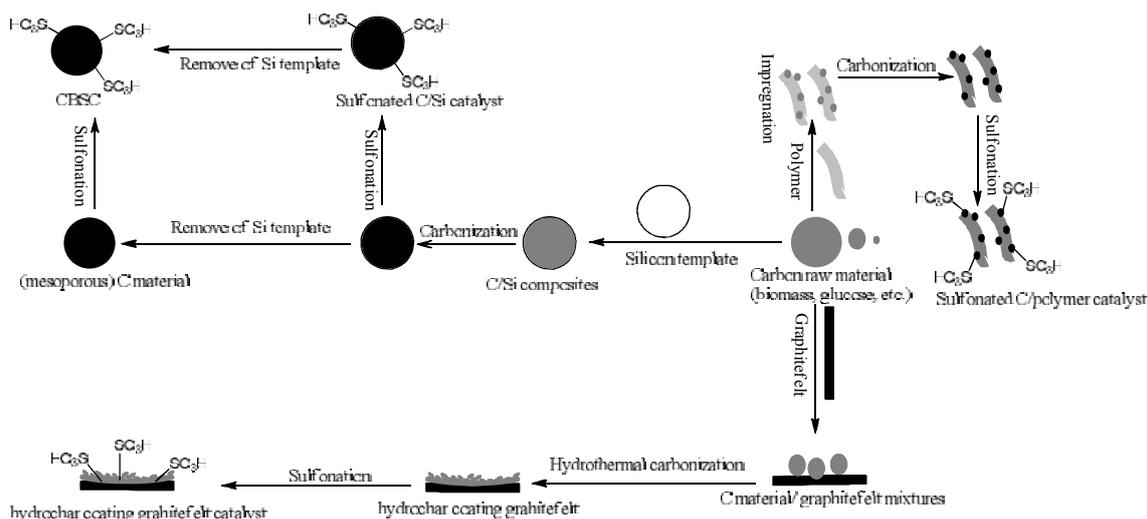

Fig. 4. Preparation of special structure CBSC

Dehkhoda et al. [13] have got high surface area carbon catalyst (BET area reach 207 m^2/g) through the carbonization, activation, and then sulfonation processes, and their results showed that the catalyst with the higher surface area has higher catalytic activity for the production of biodiesel.

It was also reported that the carbon catalyst with high surface area showed improved catalytic activity in the reactions of large molecule, e.g. esterification of aliphatic acids with longer carbon chains and benzylation of toluene [16], [19].

However, the catalytic activity for some small molecule reactions (e.g. esterification of acetic acid with ethanol) was found to be independent of the specific surface area, but related to acid density of the carbon catalyst [19].

Some other carbon materials, such as single-walled carbon nanotubes (SWCNTs) were treated with H_2SO_4 to synthesize sulfonated SWCNTs, and more -SO_3H groups can be introduced onto the surfaces of SWCNTs compared with activated carbon [54]. One advantage of the sulfonated SWCNTs is that it can be uniformly dispersed in water and organic solvents as a result of the hydrophilic sidewalls formed by high degree surface sulfonation [54].

II.3. Special Structure CBSC Preparation

Various substrates/templates were used in the preparation of special structure CBSC, and synthesis of some special structure CBSC is shown in Fig. 4.

Grahitefelt [55] and polymer [27] were used as substrate in the carbon flat and carbon club catalysts respectively. The use of grahitefelt as precursor would result in highly hydrophilic, and thickness tunable catalyst. While in the use of polymer, the mechanical strength and stability of the catalyst would be improved.

Moreover, silicon template was used in the synthesis of sulfonated C/Si composites catalyst, the acid density increased firstly and decreased latterly while the BET surface area decreased as the C content increased in the C/Si composites [56]. The Si template can be removed for ordered mesoporous CBSC preparation by two ways.

(1) Remove of silica template by HF after the sulfonation of silica template/carbon composite, which can retain most of the initial BET surface area of the composites, but resulted in low -SO_3H content [57].

(2) Sulfonation of ordered mesoporous carbon, while the ordered mesoporous carbon is formed by removing of silica template firstly. Sulfonation after removing of silica template can cause destruction of internal pores,

resulting in low BET surface area [57]. Al$_2$O$_3$ was also used as template for ordered mesoporous CBSC preparation [58], [59].

The catalysts synthesized by sulfonating carbon-coated alumina prior to alumina removal showed better catalyst dispersion for biodiesel production than the catalyst whose alumina template was removed prior to sulfonation [58]. Howerver, in the esterification reaction, the sulfonated carbon-silica composites show a higher acetic acid conversion than the sulfonated mesoporous carbons [60]. And Valle-Vigón et al. reported that the silica–carbon composites contain ~30 wt% of carbonaceous matter with a high density of acidic groups attached to the deposited carbon [61].

Three-dimensional sulfonated nanocages were prepared as new ordered mesoporous carbon catalysts, one of the significant interesting is that the nanocages are connected of each other, and each cage is like a micro-reactor [26]. Preparation of ordered mesoporous CBSC is meaningful due to its tunable porosity and high surface area, further work on the development of high acidity ordered mesoporous CBSC seems promising. Some other functional carbon catalysts can be prepared by their special original carbon structure, such as sulfonated graphene, which was reported almost having no limitation of mass transfer in the reaction [31].
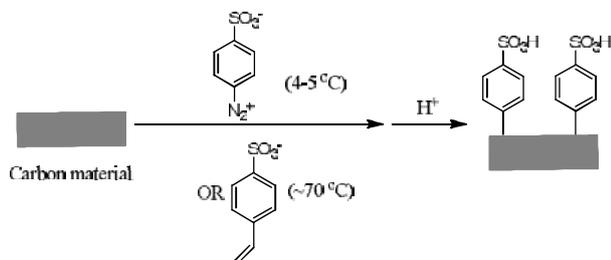

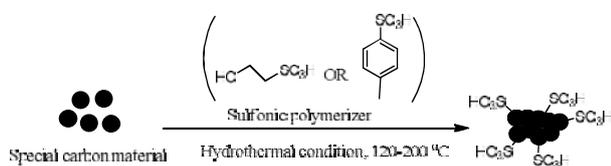Fig. 5. 4-Benzenediazoniumsulfonate and p-styrenesulfonic acid used as sulfonating agents

Fig. 6. P-toluenesulfonic acid and hydroxyethylsulfonic acid used as the sulfonating agents

II.4. CBSC Synthesis by Special Sulfonating Agents

Some "rigid" carbon materials, e.g. carbon nanotubes, graphene, ordered mesoporous carbon, et al. are hard to be sulfonated by concentrated/ fuming H$_2$SO$_4$. However, as shown in Fig. 5, these "rigid" carbon materials can be sulfonated by some special sulfonating agents, including 4-benzenediazoniumsulfonate [20], [21], [62], p-styrenesulfonic acid [63], [64], and ClSO$_3$H [33], [65], [66].

Moreover, Aldana-Pérez et al.[65] reported that ClSO$_3$H /H$_2$SO$_4$ mixture is a suitable agent for the sulfonation of Starbons-300. One advantage in using 4-benzenediazoniumsulfonate and p-styrenesulfonic acid is that the sulfonation temperature is very low, so it can maintain the original skeleton structure of the used carbon materials. CBSCs were also synthesized by adapting p-toluenesulfonic acid (TsOH) [9], [67]-[68], hydroxyethylsulfonic acid [70]-[71] as the sulfonating agents at the aid of hydrothermal conditions (Fig. 6).

This method has attracted much attention because of moderate reaction temperature (usually lower than 200 ^{o}C), simple operation approach, and easy separation process (compared with the concentrated H$_2$SO$_4$ as sulfonating agent, as the separation of the carbon material from concentrated H$_2$SO$_4$ was a tedious work).

However, all of these above special sulfonating agents are expensive, which would increase the cost of CBSC preparation. Furthermore, the use of p-toluenesulfonic acid (TsOH) and hydroxyethylsulfonic acid should be limited to some special carbon material which can be polymerized in hydrothermal conditions. These special carbon materials are mainly hydroxyl compounds and aldehydes. Zhang et al. [9] used the glucose/resorcinol/TsOH mixtures as raw materials in the polymerization, and got monolithic carbons with sulfonic groups. Xiao et al. [69] found furaldehyde is a good polymerizing material with TsOH to form CBSC. Xiao et al. [10] also found the CBSC produced by glucose/citric acid/hydroxyethylsulfonic acid mixtures hydrothermal carbonization showed high stability, high activity, and reusability. Liang et al. [71] synthesized CBSC via hydrothermal carbonization of polyvinyl alcohol and hydroxyethylsulfuric acid.

II.5. Synthesis of Resin/PVC Derived CBSC

Resin can be a polymeric carbon source, and sulfonation of carbonized resin would result in special polymeric structure CBSC[11], [22], [72].
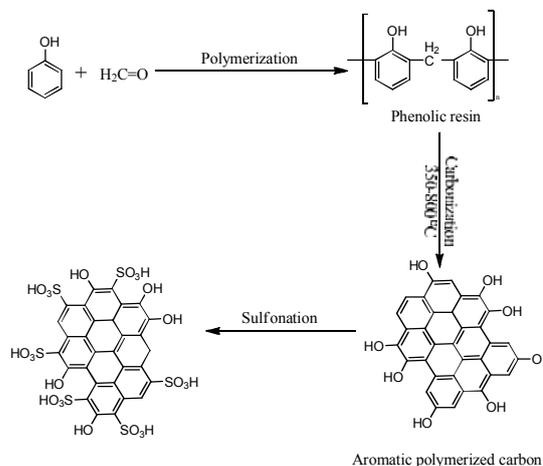

Fig. 7. Synthesis of resin derived CBSC

Tian et al. [72] have prepared CBSC from phenolic resin, and the synthesis method is shown in Fig. 7. This phenolic resin derived CBSC owned higher recyclability than the traditional nafion resin catalyst, and higher density of attached -SO$_3$H groups than other sulfonated carbon framework catalyst.

Suganuma et al. [11] prepared mesoporous CSBC from resorcinol–formaldehyde resin with similar process, and Suganuma et al. found that their catalyst showed remarkable catalytic performance for the selective dimerization of a-methylstyrene by preventing intramolecular Friedel–Crafts alkylation.

Polyvinyl chloride (PVC) was also studied as the raw material to produce CBSC. The PVC derived CBSC facilitated the diffusion of reactants and enhanced the reactivity of SO$_3$H groups bonded to the carbon sheets, which resulted in much higher catalytic performance than conventional CBSC [73].

II.6. CBSC Preparation by Thermolysis of Polymer

CBSC can be prepared by thermolysis of ammonia sulfate loaded on carbon materials and some other copolymers containing sulfonic precursor. The ammonia sulfate can be decomposed to SO$_3$ ((NH_4)$_2$SO$_4 \rightarrow$ 2NH_3+H_2O+SO_3), which can then reacts with the H on the surface of carbon to form -SO$_3$H groups. Load and thermolysis of ammonia sulfate is a simple process, one adverse factor is that there would produce environmental unfriendly gas (NH_3).

Li et al. [74] have prepared sulfonated block copolymer poly(acrylic acid)-block-poly(styrene sulfonic acid) (PAA-b-PSSH) catalyst by direct thermolysis of the precursor copolymers poly (tert-butylacrylate) -block-poly (neopentyl styrenesulfonate) (the concise preparation step is shown in Fig. 8), and it was found the PAA-b-PSSH showed high catalytic activity in hydrolysis of starch. Preparation of copolymer thermolysis derived sulfonated carbon catalyst is not encouraged, because the synthesis of precursor copolymers is often complicated and costly.

II.7. Preparation of Special Ingredient Loaded CBSC

Carbon is widely used as a carrier material in the synthesis of noble/heavy metal catalyst.

Some metal (e.g. Pt, Pd, Fe, etc.) containing sulfonated carbon catalysts are exploited by two different processes (Fig. 9): (1) heavy metal was loaded on the sulfonated carbon catalyst; (2) metal containing carbon was sulfonated.

The two preparation processes (1, 2) were used in the synthesis of Pt containing sulfonated carbon catalyst and Pd containing sulfonated carbon catalyst, respectively. Both the sulfonated carbon catalyst showed improved catalytic activity compared with these carbon catalyst containing Pt and Pd without sulfonation [75]-[77].
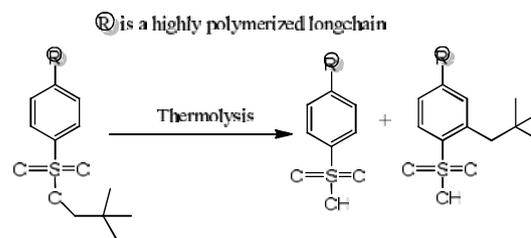
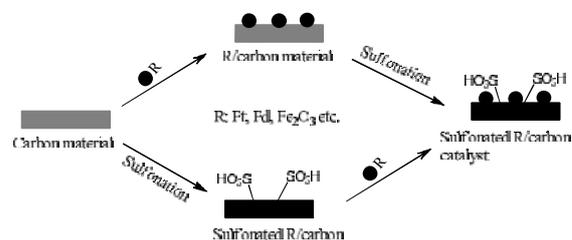

Fig. 8. CBSC preparation by thermolysis of polymer

Fig. 9. Preparation of CBSC loaded with special ingredients

Magnetic CBSC (Fe/CBSC) was prepared by the pyrolysis of cellulose and subsequent sulfonation, and results showed that Fe exists in the carbon body in the form of γ-Fe_2O_3 and the Fe/CBSC has superparamagnetic properties [78]. Magnetically active and SO$_3$H-functionalized ordered mesoporous carbon can also be prepared by high-temperature hydrothermal synthesis from resol, copolymer surfactant, and iron cations, followed by sulfonation.[79] Moreover, Zhang et al. prepared a core–shell Fe_3O_4@C-SO$_3$H nanoparticle with a magnetic Fe_3O_4 core encapsulated in a sulfonated carbon shell [80]. Lewis acids $AlCl_3$, $SbCl_3$, Bi(NO)$_3$, $ZnCl_2$, $FeCl_3$ were reported loading on the sulfonated carbon, forming a difunctional acid catalyst which contains both Lewis acid and Brønsted acid sites [81]. Furthermore, as reported by Hung et al., Nafion®-based self-humidifying composite membrane (N-SHCM) with sulfonated carbon nanofiber-supported Pt (s-Pt/CNF) catalyst, N-s-Pt/CNF, was prepared using the solution-casting method [82].

These above discussion indicates that these sulfonated carbon material can be further treated with special loaded ingredients, further research for difunctional or multifunctional catalyst production would be promising.

III. Application of CBSC

III.1. Catalytic Hydrolysis

Crystalline pure cellulose is not hydrolyzed by conventional strong solid Brønsted acid catalysts such as niobic acid, H-mordenite, Nafion and Amberlyst-15, whereas CBSC bearing -SO$_3$H, -COOH, and -OH function was an efficient catalyst for the reaction, as shown in Scheme 1. Furthermore, a lot of work have been published on catalytic conversion of cellulose with various CBSCs[14], [32], [42], [51], [73], [80], [83]-[85].
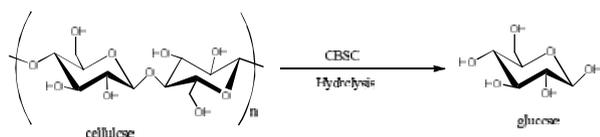
Scheme 1. Catalytic hydrolysis of cellulose
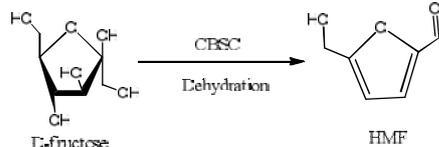
Scheme 2. Catalytic dehydration of D-fructose to HMF

Suganuma et al. [14] indicated that the high catalytic activity for cellulose hydrolysis reaction can be attributed to the ability to adsorb β-1,4 glucan, the large effective surface area in water, and -SO$_3$H groups tolerable to hydration in the carbon material. The effect of catalytic hydrolys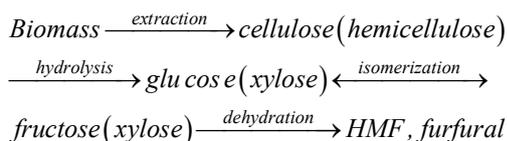is of cellulose using CBSC depends largely on the amount of water, and the glucose yield by the heterogeneous catalytic reaction reaches a maximum with an amount of water comparable to the solid catalyst weight [85]. The hydrolysis efficiency of cellulose increases with increasing reaction temperature firstly, however, too much high temperature (>363 K) would result in degradation of the cellulose surface, which prevents efficient hydrolysis of cellulose [85]. ACBSC showed high activity and remarkably high selectivity for the glucose production from cellulose, resulted in glucose yields of about 40 C-% and the product selectivity of about 90 C-% [51].

Besides the effect of promoting hydrolysis from cellulose to glucose, the CBSC is found catalytic activity for hydrolysis from hemicellulose to xylose and glucose, as well as the dehydration from xylose to furfural, and dehydration from fructose to furfural and hydroxymethylfurfural (HMF, as shown in Scheme 2). [50], [43], [86], [87] HMF and furfural are important industrial chemicals, it was reported that the yield of HMF was amount to 91.2% form fructose [86], and the yield of furfural reached 66% from xylose [87]. It is promising to get HMF and furfural from biomass considering the following steps:

$$Biomass \xrightarrow{extraction} cellulose\,(hemicellulose)$$
$$\xrightarrow{hydrolysis} glu\cos e\,(xylose) \xleftarrow{isomerization}$$
$$fructose\,(xylose) \xrightarrow{dehydration} HMF, furfural$$

However, glucose is somewhat hard to produce HMF and furfural through dehydration, and isomerization from glucose to fructose was not affected by the use of CBSC [88]. Further works on extraction of cellulose (hemicellulose) from biomass and isomerization from glucose to fructose seem meaningful.
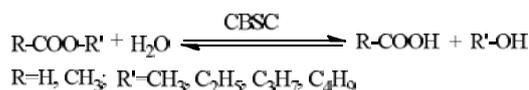
Scheme 3. Hydrolysis of different carboxylic acid esters

A series of carboxylic acid esters were well hydrolyzed by carbon-based solid acid (Scheme. 3), and the CBSC showed higher conversions than the typical Amberlyst-15 resin, Nafion catalysts [25], [36].

The catalytic activities for methyl acetate hydrolysis were closely related to the acid density, and the conversion ratio of hydrolysis decreased with the length increase of carbon chain of carboxylic acid esters [36].
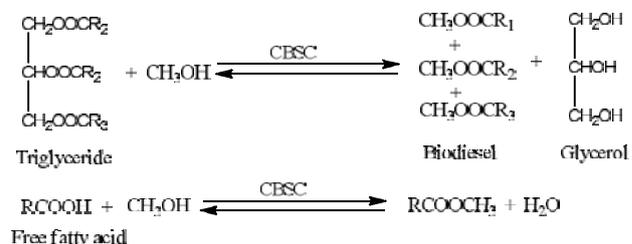
III.2. Catalytic Production of Biodiesel

Biodiesel can be prepared from the transesterification of triglycerides or the esterification of free fatty acid (FFA) with methanol, and the preparation process is completed by forward and reverse reactions (Scheme 4).

A large number of CBSCs have been studied in the catalytic synthetisis of Biodiesel. [13], [24], [27], [32], [58], [89] -[92].

During the CBSC catalytic reaction, all of the forward and reverse reactions follow second order kinetics [8]. In the production of biodiesel from canola oil, the CBSC catalyst with highest surface area and acid density showed the highest catalytic activity [13]. And good dispersion of mesoporous CBSC leads to a high efficiency for the esterification of oleic acid with methanol.

Moreover, in the transesterification of triglycerides, the CBSC may catalyze hydrolysis of triglycerides forming free fatty acids, which would accelerate the fatty acid methyl ester production, due to catalytic esterification of free fatty acid is usually easier than transesterification of triglycerides. Glycerol is a main byproduct in biodiesel production, and crude glycerol is usually low-cost.

Scheme 4. Catalytic production of biodiesel
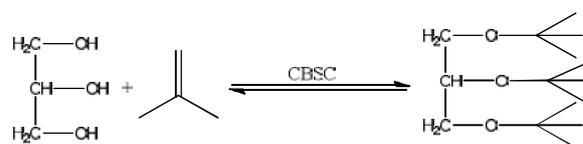
Scheme 5. Catalytic etherification of glycerol with isobutylene

Zhao et al. [93] found that CBSC also showed high catalytic activity in glycerol etherification with isobutylene (Scheme 5), with a high selectivity (92.1%) toward the sum of the desired glycerol ethers (mono-tert-butylglycerols and di-tert-butylglycerols).

It was reported that the cloud point and viscosity can be reduced when 20% of glycerol ethers are blended with biodiesel, while the glycerol ethers and biodiesel mixed fuel showed burning characteristics similar to that of petroleum-based diesel [93], [94].

The above results indicated that CBSC would be a promising catalyst in biodiesel production without an excess separation of glycerol. By the way, CBSC could be used for esterification of glycerol with acetic acid, and the results showed that glycerol was completely transformed into a mixture of glycerol esters, including a high selectivity of about 50% to triacetylglycerol [40].

III.3. Catalytic Michael-Type Friedel–Crafts and Alkylation Reactions

CBSC was used in Michael-type Friedel–Crafts (F-C) reactions of indoles with a,b-unsaturated carbonyl compounds in water (Scheme 6), one advantage of the catalytic system is that protection of the indole NH functional group is unnecessary [95]. The reaction of indole and its derivatives with methyl vinyl ketone proceeded smoothly at ambient temperature in the presence of 5 mol% of CBSC, giving 85–96% yield of isolated product without side reactions [95].

2-tert-butylhydroquinone (2-TBHQ) is widely used as antioxidant, which can be prepared by alkylation of hydroquinone with tert-butanol. Sulfonated carbon nanotube was used as a solid acid catalyst in the alkylation of hydroquinone with tert-butanol for 2-TBHQ production (Scheme 7), with 73.3% of conversion ratio and 53.7% of 2-TBHQ yield [64]. In the CBSC catalytic alkylation reaction for thymol production, a complete conversion of m-cresol was obtained within a contact time of 3 min at 1:5 molar ratio of m-cresol to iso-propyl alcohol [96].
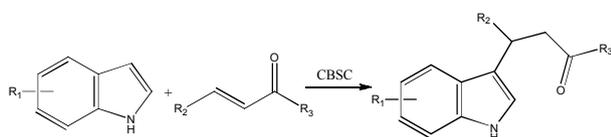
Scheme 6. Catalytic Michael-type Friedel–Crafts of indoles with a,b-unsaturated carbonyl compounds

Scheme 7. Catalytic alkylation of hydroquinone with tert-butanol

III.4. Catalytic Condensation/ Oxathioketalization/ Dimerization Reactions

The Aldol condensation reaction is an important carbon–carbon bond-forming process in organic synthesis. Sulfonated carbon nanocage showed good catalytic performance and reusability in the cross-Aldol condensation of ketones with aromatic aldehydes (Scheme 8) under solvent-free condition [26].

The key advantages of sulfonated carbon nanocage in Aldol condensation reactions are shorter reaction times, higher yield, and simple workup. Besides, acetalization of benzaldehyde with methanol can also be catalyzed by CBSC, and the results showed that the CBSC catalyst own high activity and reusability [9].

Moreover, the CBSC has shown very high catalytic ability in the oxathioketalization reaction (Scheme 9), and the catalytic activity of CBSC was much better than the traditional solid acid catalysts (e.g. zeolite (HY), Amberlyst-15), and almost the same as concentrated sulfuric acid [10], [70], [71].

Bisphenol A is a very important raw material for preparation of polymers and resins, mesoporous (CMK-5) CBSC has been used to catalyze the formation of bisphenol A (Scheme 10). With the addition of mesoporous CBSC, both conversion and selectivity are much better than those obtained by adding sulfonated ethylene-bridged periodic mesoporous organosilica and sulfonated SBA-15 under identical conditions [20].

Sulfonated mesoporous C/Si composite catalyst showed remarkable catalytic performance for the dimerization of methylstyrene (Scheme 11). [11], [97]

Moreover, the composite catalysts prevent intramolecular Friedel-Crafts alkylation, and it showed a high selectivity (exceeds 98%) for unsaturated dimmers [11], [97].
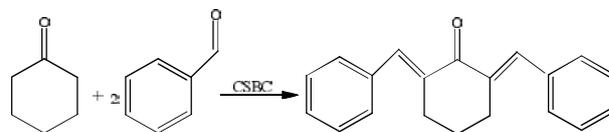
Scheme 8. Catalytic cross-Aldol condensation
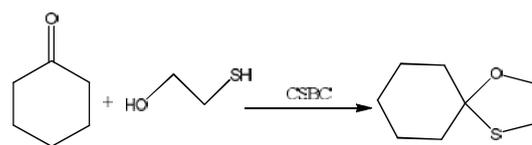
Scheme 9. Catalytic oxathioketalization reaction

Scheme 10. Catalytic preparation of bisphenol A

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Scheme 11. Catalytic dimerization of methylstyrene

Scheme 12. Reversible catalytic reaction of 1,3-propanediol with acetaldehyde

III.5. Reversible Catalytic Reactions

CBSC was found effective for both forward and reverse reactions in reversible reactions, which can be applied in some applications, e.g. separation of special compounds. CBSC was effective for acet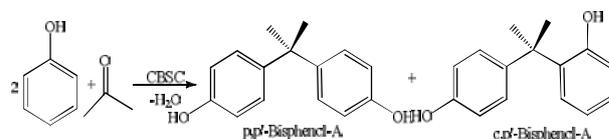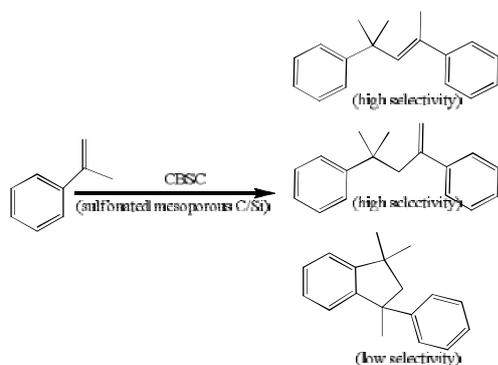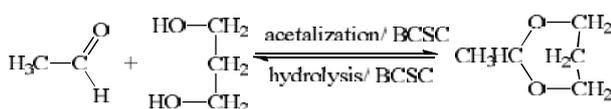alization of 1, 3-propanediol (1,3-PDO) with acetaldehyde, and also effective for hydrolysis of 2-methyl-1,3-dioxane (Scheme 12). The conversion of acetalization of 1, 3-PDO with acetaldehyde reached 92%, while the conversion of the hydrolysis reached 99% [98]. Based the high reversible catalytic effects, CBSC was feasible for reactive extraction recovery of 1, 3-propanediol from a model solution of 1,3-propanediol biologically derived from glycerol [98]. Devi et al. [99] reported CBSC catalytic methodology for effective tetrahydropyranylation of alcohols and phenols, and their deprotection (Scheme 13) by changing solvent medium.

In the present of CBSC, tetrahydropyranylation of alcohols and phenols in dichloromethane (DCM) medium resulted in excellent yields (80–98%). In presence of methanol, this CBSC was also efficient in using 3, 4-Dihydro-2H-pyran ethers to provide the corresponding free alcohols in consistently excellent yields (95–99%).

Scheme 13. Reversible catalytic reaction of alcohols (phenols) with 3,4-Dihydro-2H-pyran
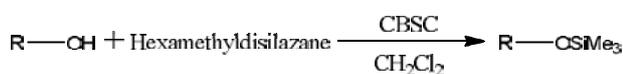
Scheme 14. Trimethylsilylations of alcohols and phenols with hexamethyldisilazane

III.6. Catalytic Benzylation and Trimethylsilylation

Porous CBSC exhibited high catalytic activity for benzylation of toluene, and the activity for the reaction is dependent on both the specific surface area and the acid density, however, non-porous sulfonated carbon has very limited activity for benzylation of toluene reaction [19].

Trimethylsilylations of alcohols and phenols with hexamethyldisilazane were successfully carried out over sulfonated mesoporous carbon catalyst in CH_2Cl_2 at ambient temperature, with excellent conversion ratios (Scheme 14) [62]. Moreover, primary, bulky secondary, tertiary, and phenolic hydroxylfunctional groups were protected in good to excellent yields in the mesoporous CBSC catalytic trimethylsilylation reaction [62].

III.7. Oxidation and Electrochemical Reaction

ACBSC was used in catalytic wet peroxide oxidation of the acid dye Chromotrope 2R, and the enhanced affinity between the reactant and the catalyst surface was due to the presence of surface groups containing sulphur [100], [102].

Metal/ carbon-nanotube based sulfonated catalyst (CNBSC) was reported an effective electrochemical catalyst for oxidation of ethanol and ethylene glycol in alkaline medium. [102][103] Pt/CNBSC was used in the polymer electrolyte fuel cells, and the results showed that the electrodes with the Pt/CNBSC exhibited better performance than those counterparts without sulfonation [77].

Similarly, Pd/CNBSC showed higher catalytic activity, higher CO tolerance, and better stable life than those counterparts without sulfonation [75].

III.8. Other Catalytic Aplications

Peckmann reaction of resorcinol with ethyl acetoacetate and hydration of propylene oxide were well catalyzed by sulfonated graphene catalyst [31]. Pd/CSBC was used to decompose lignin model compound 4-phenixyphenol, and the catalyst with largest acidity showed the highest conversion of 4-phenixyphenol.[76] Through the dehydration reaction, CBSC was effective to convert 1-phenylethanol to styrene .[104]

From the above discussion, CBSC is becoming a popular solid acid catalyst. As we known, CBSC catalytic hydrolysis of cellulose and synthesis of biodiesel are two of the mostly studied fields. However, for some of these CBSC catalytic reactions, e.g. catalytic dimerization, alkylation, etherification reactions, etc., though a few papers were published, further work on the expanded application studies seems meaningful and necessary. Besides, there are some drawbacks in using these CBSCs. The CBSC can be deactivated by leaching of sulfonated species [9], [16]-[18], [29], [51], formation of sulfonic esters [105]. Leaching of sulfonated species would

further lead to waste fluids and water soluble by-products.

Abrasion of the CBSC would occur as the mechanical strength of CBSC framework is not high enough during the agitation. Moreover, for some porous carbon materials, the BET surface area and pore volume after reaction would be reduced [29]. According to the preparation temperature and thermal stability of CBSC, the catalytic temperature should be lower than 250°C.

Thus, further works on improvement of catalytic stability and mechanical strength of CSBC should be conducted.

IV. Conclusion

A number of preparation methods and applications on CBSC have been critically reviewed in this paper. An outlook on both fields is discussed:

For the preparation methods, considering that biomass is renewable, abundant, and low-cost, CBSC produced directly from biomass would own potential advantage. Besides, high surface area and porous carbon material would increase the contact of reactant with catalytic active sites, while CBSC with a limited pore diameter would improve the catalytic selectivity, further works on high surface area and controllable porous CBSC would be promising.

For the applications of the CBSC, CBSC has shown high catalytic effects in many chemical reactions, and it is becoming a popular solid acid catalyst. However, further studies on improvement of catalytic stability and mechanical strength are necessary. Moreover, an overall economic study and comparison with the traditional solid acid catalyst are required before this kind of catalyst can be considered on an industrial scale.

Acknowledgements

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