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The carbon material functionalized with NH₂⁺ and SO₃H groups catalyzed esterification with high activity and selectivity[†]

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A novel carbon-based solid acid was conveniently prepared by heating a mixture of D-glucose, *p*-toluenesulfonic acid and diphenylammonium tosylate. Its structure was measured by XRD, FT-IR, XPS, ¹³C MAS NMR and EA to illustrate that the carbon material has been functionalized with NH_2^+ and SO_3H groups and has a strong "hydrophobic effect". It can be used to catalyze the esterification reaction of carboxylic acids with equimolar amounts of sterically demanding and acid-sensitive alcohols with high reactivity (yield up to 90%) and selectivity (up to 95%) in heptane at 80 °C. It could be easily recovered and reused more than ten times without loss of activity.

Generally, the esterification reaction between carboxylic acids and alcohols is catalyzed with Brønsted acids such as H₂SO₄, p-toluenesulfonic acid, etc.^{1,2} Although these catalysts show good activity for esterification reaction, too strong acidity often leads to low selectivity for some acid-sensitive alcohols, such as secondary alcohols which can be converted to alkenes in the presence of a strong acid.³ In 2000, Tanabe et al. developed a new type of esterification catalyst diphenylammonium triflate $([Ph_2NH_2]^+[OTf]^-)$, which has a weaker acidity and can be used to catalyze esterification of carboxylic acids with equimolar amounts of secondary alcohols in high yields. Subsequently, Ishihara's group reported that bulky diarylammonium pentafluorobenzenesulfonates ([Ar₂NH₂]⁺[O₃SC₆F₅]⁻) were more efficient than [Ph₂NH₂]⁺[OTf]⁻ in catalytic activity and selectivity.^{3,5-7} They assumed that it is the dimeric cyclic ion pairs composed of two diarylammonium cations ([Ar₂NH₂]⁺) and two pentafluorobenzenesulfonate anions ($[O_3SC_6F_5]^-$) which could form a "hydrophobic wall" to promote the esterification reactions. Also their steric hindrance could effectively



Scheme 1 Proposed strategy to improve the catalytic activity and selectivity by a synergistic effect of Ishihara's and Hara's catalysts.

suppress the dehydrative elimination of secondary alcohols to produce alkenes (Scheme 1).⁶ In order to reuse these catalysts, several groups had tried to immobilize these types of ammonium salts on the polymer, but complex synthetic process and instability of the polymer at high temperatures limited their application.^{7–9}

In 2005, Hara's group found a new carbon-based solid sulfonic acid, which was prepared by incompletely carbonizing glucose at high temperatures (over 300 °C) to form a carbonbased material first, and then sulfonating it with a large amount of concentrated sulfuric acid.¹⁰ Successive research optimized this preparation method,^{11–16} including using aryl sulfonic acid as the resource of sulfonic acid groups to avoid harsh reaction conditions.^{17–19} This method is a convenient and efficient way to immobilize the sulfonic acid groups on the carbon-based material, and the recyclable catalyst showed good activity for esterification of simple carboxylic acids (such as acetic acid, oleic acid, *etc.*) and alcohols (such as methanol, ethanol, *etc.*).^{20–24} Strong hydrophobic polycyclic aromatic carbon sheets formed by incomplete carbonizing of organic matter is the key issue, which can prevent the produced water

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from gaining access to the active site of the catalysts and thus inhibiting the inactivation of the catalyst by water (Scheme 1). 24,25

Based on that, we assume using polycyclic aromatic carbon sheets in amorphous carbon to replace the bulky diarylamine and pentafluorophenyl groups as a "hydrophobic wall", and the less bulky diphenylaminium tosylate ($[Ph_2NH_2]^+[OTs]^-$) as an active site, the new carbon-based solid acid should have similar catalytic reactivity and selectivity to Ishihara's (Scheme 1). Moreover, the salt is embedded into the matrix of the carbon-based material, so that it can be reused in catalytic esterification reaction.

Here, we report a novel carbon-based solid acid prepared by introducing $[Ph_2NH_2]^{\dagger}[OTs]^{-}$ into the carbon-based material during the process of one-step incomplete carbonization of glucose and *p*-toluenesulfonic acid. This carbon-based solid acid showed high activity and selectivity in the catalytic ester condensation, and was recycled ten times without losing the catalytic activity.

The carbon-based solid acid can be readily prepared by heating a mixture of glucose, *p*-toluenesulfonic acid and $[Ph_2NH_2]^+[OTs]^-$ at 180 °C for 5 hours under a flow of nitrogen (Scheme 2). After cooling down to room temperature, the reaction product was washed with hot toluene to remove and recover the unreacted raw materials, and then the glucose-diphenylaminium tosylate-derived carbon solid acid (GDTCSA) was obtained as a black powder.

The X-ray diffraction (XRD) pattern of the sample GDTCSA exhibits two diffraction peaks at 2θ angle of 20° and 45° (see ESI†), which is typical of amorphous carbon consisting of disordered polycyclic aromatic carbon sheets²⁶ with a flat structure. The absorption spectrum of Fourier transform infrared spectroscopy (FT-IR) for the GDTCSA at 1040 cm⁻¹, 1167 cm⁻¹ and 1495 cm⁻¹, 1507 cm⁻¹ confirms the existence of $[Ph_2NH_2]^+[OTs]^-$ (see ref. 7) and SO₃H groups²³ (see ESI†). The X-ray photoelectron spectroscopy (XPS) spectra of the GDTCSA reveal a single S 2p peak at 168 eV and a single N 1s peak at 401 eV (Fig. 1), which are attributable to sulfur in the SO_3H groups²⁷ and nitrogen in the diphenylammonium (Ph₂NH₂⁺)²⁸ respectively. The ¹³C magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectrum of the GDTCSA is shown in Fig. 2. The peak at 20 ppm is assigned to CH₃ groups on the polycyclic aromatic rings; 130 ppm is the signal peak of polycyclic aromatic carbon atoms. There are three peaks at 139, 140 and 141 ppm, which are attributable to polycyclic aromatic



Fig. 1 XPS spectra of the GDTCSA.



Fig. 2 ¹³C MAS NMR spectrum of the GDTCSA.

carbon sheets with SO₃H groups,²⁹ [Ph₂NH₂]⁺ (see ref. 7) and *p*-toluenesulfonate anions (TsO⁻).⁸ In addition, the GDTCSA also contains phenolic OH (150 ppm) and COOH (180 ppm) groups. These results show that the carbon-based material is a polycyclic aromatic plane structure loaded with active Brønsted acids of [Ph₂NH₂]⁺[OTs]⁻ and SO₃H groups.

Table 1 summarizes the structural parameters of the GDTCSA, including the nominal composition, the acid amount of $[Ph_2NH_2]^+[OTs]^-$ and SO₃H groups. The nominal composition of the GDTCSA suggests that the sulfur component is more than nitrogen, which indicates that sulfur not only existed in the form of *p*-TsOH to form a salt with diphenylamine, but there is also about 1/4 sulfur attached to the polycyclic aromatic carbon sheets in the form of SO₃H groups. The amount of GDTCSA as a catalyst for the esterification reaction is based on the acid amount of $[Ph_2NH_2]^+[OTs]^-$ and SO₃H groups. GDTCSA was treated with dilute aqueous NaOH (Scheme 3). The reactant was filtered, the filtered aqueous



Scheme 2 Preparation of the GDTCSA.

Table 1 Structural parameters of the GDTCSA and the GDCSA

Catalysts	Composition ^{<i>a</i>}	Acid amount ^b (mmol g^{-1})	
GDTCSA GDCSA	$\begin{array}{c} CH_{0.89}O_{0.2}N_{0.03}S_{0.04}\\ CH_{0.88}O_{0.17}N_{0.03}S_{0.01} \end{array}$	2.43 0.61	

^{*a*} The nominal sample composition was determined by elemental analysis. ^{*b*} The acid amount of $[Ph_2NH_2]^+[OTs]^-$ and SO₃H groups was estimated by sulfur elemental analysis.



Scheme 3 GDTCSA was reacted with dilute aqueous NaOH.

phase was concentrated and then recrystallized by EtOH to give a white solid (32 wt%), which was confirmed as sodium p-toluene sulfonate by ¹H NMR analysis and melting point measurement.³⁰ For the black filter residue GDCSA (67 wt%), the FT-IR absorption spectrum (see ESI†) and the component (Table 1) show that TsO⁻ was lost from GDTCSA, but diphenylamine groups were still immobilized on the matrix of the carbon-based material, and there were also small number of SO₃H groups connected with it.

These results illustrate that *p*-toluenesulfonic acid participated in the process of incompletely carbonized glucose and provided the SO₃H groups for the polycyclic aromatic carbon sheets of a flat structure. Meanwhile, most of the $[Ph_2NH_2]^+[OTs]^-$ were introduced to the carbonaceous material and the diphenylamine groups were embedded in the carbon sheets to provide the NH_2^+ groups.

According to the Ishihara's method,^{3,7} 4-phenylbutyric acid was condensed with an equimolar amount of cyclododecanol in heating heptane using 5 mol% [Ph₂NH₂]⁺[OTs]⁻,⁸ dimesitylammonium pentafluorobenzenesulfonate ([Mes₂NH₂]⁺-[O₃SC₆F₅]⁻),³¹ the glucose-TsOH-derived carbon solid acid (GTCSA),¹⁷ and GDTCSA as catalysts respectively to examine their catalytic activities and selectivities in this reaction by ¹H NMR analysis (Fig. 3). First, a homogeneous catalyst $[Ph_2NH_2]^+[OTs]^-$ was used, cyclododecyl 4-phenylbutyrate (graph A red line) and cyclododecene (graph A black line) were produced at 80 °C, and latter conversion was up to 15%, while the bulky homogeneous catalyst [Mes₂NH₂]⁺[O₃SC₆F₅]⁻ showed higher catalytic activity (graph B red line) and selectivity (graph B black line) than [Ph2NH2]⁺[OTs]⁻; these results were similar to the Ishihara's report.^{3,7} The dehydration rate from cyclododecanol to cyclododecene decreased to 3% (graph C black line), but the esterification rate also decreased to 54% (graph C red line) even at heptane reflux (98 °C) with the heterogeneous catalyst GTCSA. When the novel carbon-based solid acid GDTCSA was used, the catalytic rate was slower initially than the two homogeneous catalysts indicated above. This might be due to physical diffusion barriers of the heterogeneous catalyst.^{32,33} As the reaction progressed, both external and internal diffusion limitations did not affect the overall reaction rate,³² so the maximum conversion of the ester increased to more than 95% (graph D red line) and the cyclododecene was suppressed to less than 5% (graph D black line) at 80 °C. These experimental results showed that GDTCSA



Fig. 3 Esterification of 4-phenylbutyric acid with cyclododecanol catalyzed by various catalysts $[Ph_2NH_2]^+[OTS]^-$ (graph A), $[Mes_2NH_2]^+[O_3SC_6F_5]^-$ (graph B), GTCSA (graph C), and GDTCSA (graph D). The ratio of cyclododecanol (blue line), cyclododecyl 4-phenylbutyrate (red line) and cyclododecene (black line) in the reaction mixture over time was evaluated by ¹H NMR analysis. Catalytic activity: $[Mes_2NH_2]^+[O_3SC_6F_5]^- \ge [Ph_2NH_2]^+[OTS]^- \ge GDTCSA > GTCSA.$ Selectivity: $GTCSA \ge GDTCSA \ge [Mes_2NH_2]^+[O_3SC_6F_5]^- > [Ph_2NH_2]^+[OTS]^-.$

immobilized with both NH_2^+ and SO_3H groups was more active than GTCSA containing only SO_3H groups in the catalytic condensation reaction. The strong "hydrophobic effect" due to polycyclic aromatic carbon sheets of the carbon solid acid could effectively suppress the dehydrative elimination of secondary alcohols to produce alkene by comparison between GDTCSA and the less bulky $[Ph_2NH_2]^+[OTS]^-$.

To explore the generality and scope of the selective esterification catalyzed by GDTCSA (2 mol%) in heptane at 80 °C, the condensation was examined with an equimolar mixture of various structurally diverse carboxylic acids and alcohols (Table 2). Straight-chain carboxylic acids and alcohols were easily condensed to produce the corresponding esters (entries 1-6). Sterically demanding pivalic acid and 3-cyclopentene-1carboxylic acid were apt to be condensed to obtain the corresponding esters (entries 7–9). Benzoic acid and α , β -unsaturated carboxylic acids were also transformed into the relevant esters (entries 10-12). Allylic alcohol and propargylic alcohol were similarly converted into the appropriate esters (entries 13 and 14). In particular, GDTCSA could be used for acid-sensitive and sterically demanding alcohols such as cyclododecanol, cyclohexanol and menthol to give the desired esters in good yields with high selectivity (entries 15-20). The citric acid and glycerol could also be esterified completely with the corresponding alcohol and carboxylic acid respectively (entries 21 and 22).

Table 2	Esterification reaction between an	equimolar mixture of	carboxylic acids and alcoho	ls catalyzed by GDTCSA ^a
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		PLCO U	LOP ²	GDTCSA (2 mol%)	-1			
		$K^{*}CO_{2}n$ + HOK*		heptane, 80 °C	\rightarrow R ¹ CO ₂ R ²			
Entry	$R^1CO_2R^2$	Time (h)	$\operatorname{Yield}^{b}(\%)$	Entry	$R^1CO_2R^2$	Time (h)	$\operatorname{Yield}^{b}(\%)$	
1	PhCH ₂ CO ₂ C ₁₂ H ₂₅	1	94	13	PhCH ₂ CO ₂	3	97	
2	PhCH ₂ CO ₂ Bn	1	99	14	PhCH ₂ CO ₂	24	90	
3 4 5 6 7 8 9	$\begin{array}{c} Ph(CH_2)_3CO_2C_6H_{13}\\ Ph(CH_2)_3CO_2C_8H_{17}\\ C_{11}H_{23}CO_2C_6H_{13}\\ C_{17}H_{33}CO_2C_6H_{13}\\ t\text{-BuCO}_2C_6H_{13}\\ t\text{-BuCO}_2C_8H_{17}\\ \hline \hline -\text{Co}_2C_6H_{13}\\ \end{array}$	1 1 4 7 6 6 5	99 98 93 94 94 94 94	15 16 17 18 19 20 21	$\begin{array}{c} PhCH_{2}CO_{2}C_{12}H_{23}{}^{c} \\ Ph(CH_{2})_{3}CO_{2}C_{12}H_{23}{}^{c} \\ PhCH_{2}CO_{2}C_{6}H_{11}{}^{d} \\ C_{11}H_{23}CO_{2}C_{6}H_{11}{}^{d} \\ PhCH_{2}CO_{2}C_{10}H_{19}{}^{e} \\ Ph(CH_{2})_{3}CO_{2}C_{10}H_{19}{}^{e} \\ Ho + C_{0,Bu} \end{array}$	10 10 7 11 8 10 24	97 (98) 95 (98) 97 (99) 91 (99) 92 f (99) 94 g (99) 95	
10	PhCO ₂ C ₆ H ₁₃	24	93	22	$ \begin{array}{c} \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \ \$	18	93	
11	Ph CO ₂ C ₆ H ₁₃	24	95					
12	CO2C6H13	24	92					

^{*a*} Unless otherwise noted, a solution of carboxylic acid (2 mmol) and alcohol (2 mmol) in heptane (4 mL) was heated at 80 °C in the presence of GDTCSA (2 mol%). ^{*b*} Isolated yield of ester. Selectivity in parentheses. ^{*c*} Cyclododecanol (C₁₂H₂₃OH) was used. ^{*d*} Cyclohexanol (C₆H₁₁OH) was used. ^{*e*} (–)-Menthol (C₁₀H₁₉OH) was used. ^{*f*} [*a*]²⁵_D – 65.8° (*c* 1.38, CH₂Cl₂). ^{*g*} [*a*]²⁵_D – 59.2° (*c* 1.38, CH₂Cl₂).

 Table 3
 The cycling experiment of catalytic activity^a

Ph(CH ₂) ₃ CO ₂ H		+ HOC ₆ H ₁₃		GDTCSA (5 mol%)				Ph(CH ₂) ₃ CO ₂ C ₆ H ₁₃		
				he	heptane, 80 °C, 1 h					
Run	1	2	3	4	5	6	7	8	9	10
Conv.(%)	99	99	99	98	98	98	98	98	97	97

 a The conversion of hexanyl 4-phenyl butyrate based on hexanol over time was evaluated by $^1{\rm H}$ NMR analysis.

The reusability of the carbonaceous material GDTCSA was measured. After the reaction, the 'used' catalyst was recovered by centrifugation and reused. It was confirmed that the activity and selectivity remained unchanged, even after the GDTCSA had been recycled ten times (Table 3).

Conclusions

Using polycyclic aromatic carbon sheets formed by incompletely carbonized glucose as a "hydrophobic wall", along with simple and inexpensive diphenylaminium tosylate as an active site, the novel carbon-based material functionalized with NH₂⁺ and SO₃H groups has been achieved with one step synthesis by heating the mixture of *D*-glucose, *p*-toluenesulfonic acid and diphenylammonium tosylate together. And its structure has been illustrated by a series of tests such as XRD, FT-IR, XPS, ¹³C MAS NMR and EA. It not only could be used to catalyze the ester condensation reaction of carboxylic acids with equimolar amounts of sterically demanding and acid-sensitive alcohols with high reactivity and selectivity under mild conditions, but also could be easily recovered and reused more than ten times without loss of activity, which indicated that the novel material holds great potential for the green chemical processes.

Experimental section

In a typical synthesis, 3.6 g glucose (20.0 mmol) and 1.9 g *p*-toluenesulfonic acid monohydrate (10.0 mmol) were mixed in toluene, then 3.41 g diphenylammonium tosylate⁸ (10.0 mmol) prepared in advance was added to the mixture, under a flow of nitrogen. The water formed during the reaction and the toluene were distilled off while heating to 180 °C slowly, after reacting for 5 hours. The product was washed with hot toluene for 5×25 mL (toluene and 1.3 g *p*-toluenesulfonic acid were recovered) to obtain a black powder GDTCSA (5.7 g). The nominal sample composition was determined by elemental analysis to be $CH_{0.89}O_{0.2}N_{0.03}S_{0.04}$, and the acid amount of SO_3H groups and $[Ph_2NH_2]^+[OTs]^-$ was 2.43 mmol g^{-1} (see Scheme 2).

The reaction mixture, carboxylic acid (2.0 mmol), alcohol (2.0 mmol), 2 mol% of GDTCSA (2.43 mmol NH_2^+ and SO_3H g⁻¹; 16 mg, 0.04 mmol), and heptane (4 mL), was stirred at 80 °C. Then separation of GDTCSA by filtration and evaporation of heptane *in vacuo* gave the crude material, which was purified by column chromatography to give the desired carboxylic ester as colorless oil.

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