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Magnetic solid sulfonic acid-enabled direct catalytic production of biomass-derived N-substituted pyrroles

Keping Wang^a, Mei Wu^b, Yixuan Liu^a, Ying Yang^a, Hu Li*^a

Five-membered nitrogen heterocyclic pyrroles have extremely high physiological activity and are widely used in medicine, agriculture, material chemistry, industry, and supramolecular chemistry. Developing a mild and eco-friendly way to synthesize functionalized pyrroles from biologically derived materials is desirable. In this study, biomass-derived 2,5-dimethylfuran can react with a series of aromatic amines to synthesize 2,5-dimethyl-*N*-arylpyrroles through acid-enabled ring-opening and Paal-Knorr condensation in one pot. Among the tested acid catalytic materials, a new magnetic biocarbon-based sulfonic acid solid catalyst (WK-SO₃H) showed excellent catalytic performance in the synthesis of N-substituted pyrroles (up to ca. 90% yield) and was easy to be separated and recovered by an external magnetic field. The ring-opening of furan proved to be the rate-determining step of the above one-pot multi-step conversion process, and 2,5-hexanedione is a key intermediate for cascade reactions, while the addition of water could significantly enhance the above-mentioned ring-opening reaction. Furthermore, multiple characterization methods (e.g., FT-IR, TGA, XRD, NH₃-TPD, and XPS) confirmed that (WK-SO₃H) has good stability in the aqueous reaction system.

1. Introduction

In the past, non-renewable oil is regarded as a major source of chemical raw materials and energy, while excessive exploitation and utilization of fossil energy not only meet the development of human society but also lead to environmental pollution and the greenhouse effect.¹ To alleviate the undue dependence on non-renewable energy, more and more researches focus on the development of green sustainable resources, especially organic carbon.² It is estimated that the total amount of biomass produced by photosynthesis is about 160 billion tons per year, which contains about 10 times the world's total energy consumption, of which carbohydrate reserves account for about 75%.³ Biomass is considered to be the best choice to produce fine chemicals and liquid fuels because of its rich organic carbon resources, wide sources, and easy availability.^{4,5}

Under the action of the suitable acid, alkali, and/or metal catalysts, biomass can be converted into oxygen-containing compounds (e.g., alcohols, organic acids, furan derivatives, and phenols) through a series of chemical or biological catalytic

^a State Key Laboratory Breeding Base of Green Pesticide & Agricultural Bioengineering, Key Laboratory of Green Pesticide & Agricultural Bioengineering, Ministry of Education, State-Local Joint Laboratory for Comprehensive Utilization of Biomass, Center for R&D conversion pathways.⁶ It is worth noting that nitrogen-containing biomass materials such as chitin, chitosan, and protein can be degraded in series and coupled with amination to synthesize nitrogen-containing compounds, such as acrylamide, 1,4-butanediamine, *N*-methylpyrrolidone, amino acids, and other nitrogen-containing high-value compounds.⁷⁻⁹ Among many nitrogen-containing compounds, *N*-heterocyclic compounds often exhibit good biological activities.¹⁰ In particular, pyrrole derivatives, as an important five-member nitrogen-containing heterocyclic skeleton, are widely present in a series of commercial drug molecules (e.g., aloracetam for the treatment of Alzheimer's disease and atorvastatin for the prevention of cardiovascular diseases).¹¹ In addition, they are also widely used in polymers, catalysts, dyes, food, pesticides, and other fields.¹²

Generally, the synthesis of *N*-heterocyclic compounds involves the formation of C–C and C–N bonds (e.g., amination, cycloaddition, and condensation), the synthesis methods or processes are often more complex than those of nitrogen-containing straight-chain molecules.¹³⁻¹⁵ Using petroleum-based chemicals as raw materials, pyrrole derivatives can be prepared by Paal-Knorr, Barton-Zard, multicomponent condensation, and cycloaddition reactions.^{16,17} Yan et al. reported the direct catalytic synthesis of pyrrole derivatives from chitin, shrimp shell, bagasse, and other biomass materials. However, the yield is quite low (< 20%) and the reaction temperature is high ($300 - 600 \,^\circ$ C).¹⁸⁻²¹ Cao et al. successively used biomass platform small molecules such as 2,5-hexanedione^{22,23}, 2,5dimethoxytetrahydrofuran^{24,25} or 2,5-dimethylfuran²⁶ as raw materials, which could furnish high catalytic amination activity under mild conditions (> 80% yield). Catalytic conversion of biomass

sugars via 5-hydroxymethylfurfural to 2,5-dimethylfuran has been extensively reported, which ensures that the source of 2,5dimethylfuran and relevant furanic compounds is sustainable.²⁷⁻²⁹ It is worth noting that the catalysts required for the above conversion system are mostly supported noble metal (Ru) or heterogeneous metal materials (H-Y), and the subsequent catalyst recovery steps (centrifuge or filter) are cumbersome, which limits its application in practical processes. In contrast, non-noble metals have high reserves, low cost and easy availability, and have more development potential in the catalytic synthesis of biomass-based pyrrole derivatives.³⁰ With the advancement of nanomaterials, the smaller particle size shows better mass transfer but also leads to more difficult catalyst recovery (passing through filter paper or complicated operation).³¹ Fe₃O₄ nanomaterial has great development potential in overcoming the cumbersome catalyst separation process from the system due to its magnetic properties and the economy of raw materials.³²

To overcome the shortcomings of the above catalytic system, a new type of magnetic carbon-based sulfonic acid material was designed and prepared in this paper, it was successfully applied to catalyze the synthesis of a series of N-substituted pyrrole derivatives from biomass-based 2,5-dimethylfuran and amine compounds via one-pot multi-step reaction. Especially, the catalytic reaction system showed the characteristics of easy separation and recovery, green synthesis process, and sustainability.

2. Experimental

2.1 Materials

2,5-Dimethylfuran (99%), chitosan (95%), ammonia (AR, 25.0-28.0%), glutaraldehyde (50 wt% aqueous solution), tetraethyl orthosilicate (99%), aniline (99%), FeCl₃· GH_2O (98%), and FeSO₄· TH_2O (98%) were all purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD.

2.2 Preparation of catalysts

The detailed procedures for the preparation of renewable magnetic mesoporous biocarbon-based acid catalysts are as follows.

2.2.1 Preparation of magnetic Fe₃O₄

First, 5.40 g FeCl₃·6H₂O, 2.78 g FeSO₄·7H₂O, and 80 mL deionized water were added to a 250 mL round-bottomed flask and quickly stirred at room temperature until the solids are completely dissolved. Subsequently, the pH of the mixture was adjusted to alkalinity (pH = 10) with ammonia water, and the reaction system was transferred to an oil bath. The heating temperature and time were set at 80 °C and 1.5 h, respectively. After the reaction was finished and cooled to room temperature, the magnetic solid precipitate was adsorbed by a magnet to separate from the liquid solution, and the resulting solid was dried in an oven at 80 °C for 6 h to obtain magnetic Fe₃O₄.

2.2.2 Preparation of magnetic Fe₃O₄@SiO₂

1.0 g above prepared Fe₃O₄, 20 mL deionized water, 80 mL ethanol, and 1 mL ammonia were added into a 250 mL round-bottom flask, and the reaction system was magnetically stirred for 10 min to make the particles evenly dispersed. Then, 1 mL tetraethyl orthosilicate was added to the mixture and stirred for 6 h.

The solid in the round-bottom flask was separated by a magnet. The obtained solid was washed with deionized water 1-2 times, and then washed with anhydrous ethanol 2-3 times, which was subsequently dried at 80 °C for 6 h in a vacuum drying oven to obtain Fe₃O₄@SiO₂.

2.2.3 Preparation of Fe₃O₄@SiO₂@CS-SO₃H

0.5 g chitosan (CS) was added to 50 mL 1% acetic acid aqueous solution and stirred for 24 h to dissolve the chitosan at room temperature. Then 1.0 g $Fe_3O_4@SiO_2$ was added into the above mixture and stirred with the magnetic force for 10 min to make it evenly dispersed. Subsequently, 5.7 g p-toluene sulfonic acid was added and stirred for 10 min. Afterward, 1 mL glutaraldehyde (50 wt% aqueous solution) was added slowly and stirred for 3 h to obtain a gel-like solid at 25 °C. Then, the solid was separated and placed in a vacuum dryer at 80 °C for 6 h, followed y grinding into small particles and washing with anhydrous ethanol 3-4 times till to neutral. The catalyst obtained after drying was $Fe_3O_4@SiO_2@CS-SO_3H$, and named WK-SO_3H.

2.3 Characterization

The XRD pattern of the sample was recorded by Tongda TD-3500 X-ray diffractometer (CuK α radiation λ = 0.154056 nm), and the range of 20 was 5-80°. The infrared spectrum of the sample was obtained by KBr 360 Nicolet infrared spectrometer. The background was scanned automatically every time. The sample was scanned 32 times after KBr tableting, and the range was 400-4000 cm⁻¹. Thermal gravimetric analysis (TGA, Mettler-TGA/DSC1) was used to determine the mass loss of the sample at 25-800 °C in a nitrogen atmosphere, and the heating rate was 10 °C/min. The morphology of the catalyst was observed by scanning electron microscope (SEM, JSM-6700 F, 5 kV). The samples were analyzed by X-ray photoelectron spectroscopy (XPS) using Thermo ESCALAB 250 equipment (Al-K α anode, h = 1253.6 eV). The structural parameters of the catalytic materials were determined by the Bruner-Emmett-Teller (BET) method using N₂ adsorption-desorption apparatus (ASAP 2460 Micromeritics Equipments Co., Ltd.) at -196 °C. The sample was degassed at 120 °C for 3 h before testing. The specific surface area, pore size and pore volume were determined from the N₂ adsorption-desorption isotherms. The analysis of the sample specific surface area and pore size distribution adopted the BET method and Barrett-Joiner-Halenda (BJH) model, respectively, and the sample pore volume was calculated from the relative gas pressure and the amount of N₂ adsorption.

2.4 Reaction process

In a general procedure, 1 mmol 2,5-dimethylfuran, 1 mmol aniline, and 4 mg naphthalene (internal standard) were added into a 10 mL sealed reactor. Then the reactor was placed into a constant temperature oil bath with a magnetic stirring device and reacted for 1-3 h. After the reaction, the reactor was removed from the oil bath and immediately placed in tap water, and quickly cooled to room temperature. The obtained product was diluted with anhydrous methanol, which was then quantitatively analyzed by GC (Agilent 7890B) with an HP-5 column (30 m × 0.25 mm × 0.25 μ m) and a flame ionization detector, and qualitatively identified by GC-MS equipped with 5973 MS mass spectrometer (Agilent 6890-5973).

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3. Results and discussion

3.1 Structure characterization of catalyst

The XRD curves are shown in Fig. 1(a). The diffraction peaks at 20 of 30.2°, 35.6°, 43.3°, 57.3°, and 62.9° are respectively classified into the (220), (311), (400), (511) and (440) crystal planes of Fe₃O₄, which are in perfect agreement with those of the standard Fe₃O₄ (JCPDS database, 190629)^{33,34} and γ -Fe₂O₃ (JCPDS database,

895894).³⁵⁻⁴⁰ The XPS spectra showed that iron, oxygen, carbon, nitrogen, sulfur, and silicon are the main elements of the WK-SO₃H catalyst (Fig. 1(b)). The narrow Fe 2p XPS spectrum of catalyst WK-SO₃H (Fig. 1(c)) also confirms the presence of Fe₃O₄, where Fe 2p_{3/2} (at 710.9 eV) and Fe 2p_{1/2} (at 724.3 eV) are characteristic peaks of Fe₃O₄. The signal peak of Fe²⁺ is located at 714.5 eV. These results further prove that Fe species are composed of Fe²⁺ and Fe³⁺, and the prepared catalyst is magnetic.



Fig. 1 (a) XRD pattern, (b) XPS of full spectrum, (c) XPS of Fe 2p spectrum, (d) FT-IR spectrum, (e) TGA curve, and (f) NH₃-TPD profile of the catalyst WK-SO₃H.

Fig. 1(d) is the FT-IR spectrum of catalyst WK-SO₃H. The absorption peak at wavenumber 569 cm⁻¹ is caused by the vibration of Fe–O bond of Fe₃O₄,⁴¹ and the absorption peaks at 1531 cm⁻¹ and 1379 cm⁻¹ are the vibration peaks of N–H and C–O bonds. The peak at 3378 cm⁻¹ is the stretching vibration peak of the O–H bond.³⁵ The above FT-IR results confirmed that CS was successfully wrapped on Fe₃O₄ nanospheres, in agreement with the structure illustrated in Fig. 2(b). In addition, the characteristic absorption peaks of –SO₃H appeared at 1180 cm⁻¹ and 1068 cm⁻¹,³⁶ indicating that the sulfonic

acid groups were successfully loaded onto $Fe_3O_4@SiO_2$. The FT-IR spectrum (Fig. S1) of the reused catalyst WK-SO₃H is similar to that in Fig. 1(d), and there is no loss of functional groups before and after the reaction, further indicating that the catalyst is successfully prepared and highly stable.

TGA curve is shown in Fig. 1(e). Weight loss and decomposition of the WK-SO₃H catalyst occurred in the temperature range of 0-800 °C, which can be divided into three stages. Firstly, in the temperature range of 0-200 °C, the mass of the catalyst decreased

by 5.37 %, which could be attributed to the loss of residual water in the sample and the hydroxyl group on chitosan.⁴¹ Secondly, in the temperature range of 200-500 °C, the weight loss was 43.61 %, which was ascribed to the decomposition of organic components.⁴² Finally, in the temperature range of 500-800 °C, the weight loss was 5.7 %, mainly due to the decomposition of some Fe₃O₄ at a high temperature. Since the reaction temperature required for the catalytic synthesis of pyrrole derivatives is not higher than 170 °C, the WK-SO₃H catalyst can maintain good stability under corresponding reaction conditions.

It can be seen from NH₃-TPD spectra (Fig. 1(f)) that three groups of peaks appeared at the desorption temperatures of 100-200 °C, 200-350 °C and 350-550 °C for WK-SO₃H catalyst, corresponding to weak, medium and strong acid sites, respectively, and the total acid content was 3.474 mmol/g. These acid sites of the catalyst should be sufficient to open the ring of 2,5-dimethylfuran and catalyze the subsequent reaction of amination. From the SEM images of WK-SO₃H (Figs. 2(a)), it was observed that the surface of WK-SO₃H was relatively porous and distributed in the block. The TEM shows that the catalyst exists in the core-shell structure (Figs. 2(b) & S2), in which the core center marked by the red line is Fe₃O₄ nanoparticles and the edge part marked by the blue line is the CS shell. The porous surface of the WK-SO₃H observed by SEM was also demonstrated by N₂ adsorption-desorption. The relevant data (S_{BET} = 59.1 m²/g and V_{Total} = 0.22 cm³/g) are summarized in Fig. 3(a), and the reused catalyst still has excellent parameters ($S_{BET} = 34.7 \text{ m}^2/\text{g}$ and $V_{Total} = 0.21 \text{ cm}^3/\text{g}$). The pore size of the reused catalyst was slightly reduced from 23.5 nm to 15.6 nm (Fig. 3(b)), showing the adsorption of organic species during the reaction process. The large S_{BET} and pore size are conducive to better contact between the catalyst and the substrate.

The elemental mappings of the catalyst WK-SO₃H are presented in Fig. 4(a). The distribution of the S element on the surface of the WK-SO₃H catalyst was uniform and the active sites were fully exposed, indicating that the catalyst was successfully prepared. The elemental composition distribution of WK-SO₃H in the catalyst shows that the proportion of S atoms is 6% (Fig. 4(b)), proving the successful loading of -SO₃H species, which is consistent with the results of NH₃-TPD. Related to the acid loading reduces the S_{BET}, V_{Total} and pore volume of SiO₂ (Fig. S3). In addition, the Fe element is evenly dispersed in the catalyst, indicating that the magnetic distribution of the catalyst is uniform, which is beneficial to its separation from the reaction system. The conversion of 2,5dimethylfuran and the reusability of the catalyst were tested at 130 °C for 1 h. As can be seen from Fig. 4(c), WK-SO₃H is magnetic and can be quickly adsorbed and separated from the system by a magnet. The recycled catalyst was washed 3 times with deionized water and ethanol, respectively. After drying, the catalyst was used for the next reaction. The recovered catalyst can be reused 4 times almost constant and remains activity (Fig. 4(d)).



Fig. 2 (a) SEM and (b) TEM images of the WK-SO₃H catalyst.



Fig. 3 (a) N₂ adsorption-desorption isotherms, and (b) pore size distribution of WK-SO₃H (Red line is fresh, the Black line is reused).



Fig. 4 (a) elemental mappings, (b) elemental composition distribution, (c) magnetic separation image, and (d) reusability of WK-SO₃H catalyst.

3.2 Optimization of reaction conditions

3.2.1 Reaction time

The reaction time was optimized for 6 time periods with 0.5 h as the interval at 170 °C. As shown in Fig. 5(a), the yield of 2,5dimethyl-N-phenylpyrrole increased from 64% to 89% with the extension of time from 1 h to 2.5 h. Since the reaction process of acid-catalyzed ring-opening of 2,5-dimethylfuran to 2,5hexadienone is reversible, it can be promoted by WK-SO₃H to occur in the positive reaction direction by appropriately extending the reaction time and adding water. It is worth noting that the yield of 2,5-dimethyl-N-phenylpyrrole was 77% after the continuous extension of reaction time to 3 h, which was slightly lower than that of 2.5 h. The possible reason is that the pyrrole derivative is unstable under acidic conditions and is easily converted into other nitrogen-containing compounds.43 In addition to the formation of the dominant product a (2,5dimethyl-N-phenylpyrrole), 6.5% of b (N-(5-(phenylimino)hexan-2yl)aniline), 7.2% of **c** (N^2 , N^5 -diphenylhexane-2,5-diimine) and a trace amount of unknown products were mainly produced for 3 h. The GC-MS spectra of the target products and side-products are illustrated in Fig. S4. By comparing the reaction results obtained after 2.5 h and 3.0 h, the optimum reaction time was 2.5 h.

3.2.2 Reaction temperature

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Fig. 5(b) shows that in the presence of WK-SO₃H, 2,5dimethylfuran can react with aniline at 110 °C for 2.5 h to give 2,5dimethyl-*N*-phenylpyrrole in a yield of 24%. When the temperature rose to 130 °C, the yield reached 76%. This indicates that the cascade reaction is sensitive to temperature. It is speculated that the conversion process can be divided into ringopening, ring-closure, dehydration, and other multi-step reactions, and the increase of temperature is especially conducive to the ring-opening and dehydration of the reaction system.^{44,45} Furthermore, when the reaction temperature increased from 130 °C to 170 °C, the yield also increased 13%. Given the subsequent little increase, 170 °C was selected as the suitable temperature for further optimization.

3.2.3 Catalyst amount

Considering that the cost of catalyst preparation is generally high, low dosage and better catalytic activity are important indicators to measure whether a catalyst can be applied to the reaction system. In the experiment of optimizing the amount of catalyst (5-20 wt%), it was found that the number of active sites increased with the increase of the amount of catalyst, and the catalytic efficiency also increased significantly. Fig. 5(c) shows that with the increase of the catalyst dosage to 15 wt% (14.4 mg), the yield of 2,5-dimethyl-*N*-phenylpyrrole reached the highest (89%). However, the yield decreased slightly with increasing the amount of WK-SO₃H catalyst (yield of 77% at 20 wt%). The reason may be that excessive catalyst sulfonic acid sites can induce further

ARTICLE

conversion or degradation of the target product,^{46,47} thereby reducing its yield. Therefore, the amount of 14.4 mg catalyst is more suitable for the subsequent optimization of this reaction system.



Fig. 5 Single-factor optimization of aniline reacting with 2,5-dimethylfuran to yield 2,5-dimethyl-*N*-phenylpyrrole: (a) time, (B) temperature, (c) catalyst amount, and (d) water content.

3.2.4 Water content

When anhydrous methanol is used as the reaction solvent, it is difficult to start the reaction. After adding 50 μ L of deionized water as an additive, the yield of 2,5-dimethyl-*N*-phenylpyrrole increased significantly (67%), further explaining that it is very necessary to optimize the water content. Fig. 5(d) shows that the target yield gradually increases (67-89%) with the increase of water content (0-200 μ L). However, when the amount of water added exceeded 200 μ L, the yield of 2,5-dimethyl-*N*-phenylpyrrole decreased. This result well reflects that the conversion process of 2,5-dimethylfuran to 2,5-hexanedione is reversible. As a result, water is involved in the ring-opening process as a reactant and inhibits the dehydration process as a product. Obviously, although excess water promoted the formation of 2,5-hexanedione, it inhibited the downstream

Paal–Knorr reaction. Therefore, it is crucial to select an appropriate water content for improving the yield of 2,5-dimethyl-*N*-phenylpyrrole. Accordingly, 200 µL deionized water is most appropriate

3.2.5 Comparison of catalytic performance of different types of acid catalysts

The effect of different carriers on the reaction activity was explored (Table S1). Renewable CS used as an acid carrier with glutaraldehyde as a cross-linking agent to load Brønsted acid (– SO_3H) could achieve the high activity, which can not only more effectively protect Fe_3O_4 from reacting with the introduced acid species (with enhanced catalyst stability), but also increase the loading of the acid species (due to the presence of more —OH species on the biocarbon).³¹ In order to explore the role of Brønsted

acid and Lewis acid in the reaction system, a series of typical acidic catalysts (e.g., AlCl₃, ZrCl₄, ZrO₂, Ru/Al₂O₃, H-Y Amberlyst-15, and HCOOH) were selected to carry out control experiments. The results are illustrated in Table 1. Under the reaction conditions of 170 °C and 2.5 h, Brønsted acid was found to be more suitable for catalyzing the reaction system. The higher the catalyst acidity (acidity: WK-SO₃H > Amberlyst-15 > HCOOH), the higher the corresponding catalytic efficiency can be obtained (WK-SO₃H; entries 1-3). However, for Lewis acids (AlCl₃, $ZrCl_4$, ZrO_2 , Ru/Al_2O_3 and H-Y), the yield of 2,5-dimethyl-N-phenylpyrrole is not high regardless of high acidity (entries 4-8). The above results show that Lewis acid sites are not suitable for this catalytic system, and Brønsted acid is an indispensable active site for promoting condensation and other reactions. In particular, the strong Brønsted acid site is necessary to ensure the high catalytic activity of WK-SO₃H because it can directly provide a large amount of H⁺ to open the furan ring for the subsequent reaction steps.^{54,55} Conversely, Lewis acid cannot efficiently promote this reaction, to some extent.

 Table 1
 Comparison of catalytic activities of aniline with 2,5dimethylfuran using different acid catalysts.

Entry	Catalyst	Conv. (%)	Yield (%)	Ref.
1	WK-SO₃H	96	89	This work
2	Amberlyst-15	85	47	[48]
3	НСООН	57	5	[49]
4	AICI ₃	95	63	[50]
5	ZrCl ₄	96	42	[51]
6	ZrO ₂	77	9	[52]
7	Ru/Al_2O_3	83	36	[53]
8	H-Y	79	27	[26]

(Reaction conditions: 1 mmol 2,5-dimethylfuran, 1 mmol aniline, 2 mL methanol, 200 μ L H₂O, 14.4 mg WK-SO₃H catalyst, 170 °C, 2.5 h, and 4 mg naphthalene as internal standard.)

Table 2 Effect of solvent types on the reaction of aniline with 2,5dimethylfuran.

Entry	Solvent	Conv. (%)	Yield (%)
1	Methanol	96	89
2	Ethanol	80	53
3	1-Propanol	96	63
4	1-Butanol	96	86
5	Isopropyl alcohol	92	78
6	N,N-Dimethylformamide	60	1
7	Dichloromethane	96	2
8	Tetrahydrofuran	94	74
9	Cyclohexane	72	12

(Reaction conditions: 1 mmol 2,5-dimethylfuran, 1 mmol aniline, 2 mL methanol, 200 μ L H₂O, 14.4 mg WK-SO₃H catalyst, 170 °C, 2.5 h, and 4 mg naphthalene as internal standard.)

3.2.6 Solvent type

Considering the importance of solvent in the synthesis reaction, the effect of nine organic solvents on the reaction of 2,5-dimethylfuran with aniline was studied. As tabulated in Table 2, the highest yield

ARTICLE

of 2,5-dimethyl-*N*-phenylpyrrole catalyzed by WK-SO₃H was only 12% in aprotic polar or low-polar organic solvents such as *N*,*N*-dimethylformamide, dichloromethane, and cyclohexane. On the contrary, the yield of 2,5-dimethyl-*N*-phenylpyrrole was 78%-89% in protic solvents such as methanol, *n*-butanol, and isopropyl alcohol. At the same time, the effect of proton organic solvents on the system is that the stronger the polarity, the higher the yield of the target product is. Presumably, for the Paal-Knorr reaction, the strong polar proton solvent is more conducive to the transport of protonic acid in the catalytic system, which greatly promotes the reaction. Therefore, methanol was selected as the best organic solvent.

3.3 Reaction mechanism

Under the catalysis of the Brønsted acid catalyst WK-SO $_3$ H, 2,5hexanedione can react with an organic amine to synthesize pyrrole derivatives via Paal-Knorr reaction, and it is found that 2,5hexanedione is the key intermediate of the reaction.²⁶ However, 2,5-hexanedione was not detected in the existing reaction process. In order to verify the reaction mechanism, the original model reaction was divided into two steps under the same conditions. One was the ring-opening of 2,5-dimethylfuran to generate 2,5hexanedione, and the other was the direct reaction of 2,5hexanedione with aniline to generate pyrrole. It was found that in the presence of aniline, the in situ generated 2,5-hexanedione reacted immediately to form pyrrole derivatives, and the yield of pyrrole derivatives from 2,5-hexanedione instead of furan was high (> 99%). In addition, it was found that even if the reaction time was prolonged, 2,5-dimethylfuran could be only converted to 2,5hexanedione in a small amount (< 5% yield) due to the difficulty of occurring the furan ring-opening reaction under anhydrous conditions. When an appropriate amount of water was added, the yield of 2,5-hexanedione gradually increased.



Fig. 6 Possible mechanism for the synthesis of 2,5-dimethyl-*N*-phenylpyrrole from aniline and 2,5-dimethylfuran.

The above results show that 2,5-hexanedione is still the intermediate of the reaction, which is consistent with previous reports.²⁶ However, in this catalytic system, the ring-opening process of furan was slow, which was the decisive step of the reaction, while the downstream Paal–Knorr process was fast. On this basis, a possible reaction mechanism is speculated, and shown in Fig. 6. First, in the presence of water, a strong Brønsted acid provides H⁺ to attack the furan ring, causing it to open the furan ring to form 2,5-hexanedione. Then, 2,5-hexanedione and aniline

undergo amination, ring closure, dehydration, and other processes to produce the corresponding pyrrole derivatives.

3.4 The substrate scope expansion

Under the above optimal reaction conditions, a range of 2,5dimethyl-N-arylpyrroles were also attempted to be prepared by condensation of equimolar 2,5-dimethylfuran with anilines containing different structures (including ortho-, meta- and parasubstituted aniline). As shown in Fig. 7, aniline bearing ---CH3 substituent can efficiently react with 2,5-dimethylfuran to selectively give methyl-substituted pyrroles (ortho-78% and meta-83%) in both ortho- and meta- positions of aniline. Likewise, -OCH₃, $-NO_2$ and -F substituents at the meta- and para-positions of aniline undergoing reaction with 2,5-dimethylfuran can also be converted into corresponding pyrrole derivatives (57-79% yields). The results showed that the catalytic conversion process was not only suitable for the synthesis of 2,5-dimethyl-*N*-phenylpyrrole, but also appropriate for the preparation of other *N*-substituted pyrrole derivatives under suitable reaction conditions. In addition, other interesting bio-derived furans (including furan and 2-methylfuran) were also investigated, which could also provide corresponding pyrroles in considerable yields of 68% and 76% yield under the optimal reaction conditions, respectively.



Fig. 7 Cascade reaction of bio-derived furans and anilines bearing different substituents to yield pyrroles.

(Reaction conditions: 1 mmol bio-derived furan, 1 mmol arylamine, 2 mL methanol, 200 μL H_2O, 14.4 mg WK-SO_3H catalyst, 170 °C, and 4 mg naphthalene as internal standard)

4. Conclusions

In this work, a novel biocarbon-derived magnetic -SO₃H catalyst (WK-SO₃H) with good stability was prepared, which could effectively catalyze the reaction of biomass-based 2,5dimethylfuran and substituted aniline to prepare a series of 2,5dimethyl-N-arylpyrroles. The catalyst WK-SO₃H was easy to be separated and recovered from the reaction system by an applied magnetic field. The control experiment confirmed that the ringopening of 2,5-dimethylfuran was the decisive step of the cascade reaction, and 2,5-hexanedione was the key intermediate of the reaction. Under the action of Brønsted acid sites of WK-SO $_3H$ catalyst, the addition of water can significantly promote the ringopening reaction, and thus the target product 2,5-dimethyl-Narylpyrrole can be efficiently synthesized with high selectivity (up to >90%). The preparation process of magnetic carbon-based sulfonic acid catalyst is simple and sustainable, which overcomes the problems of the cumbersome recovery process and high preparation cost of traditional catalytic materials.

Author Contributions

Keping Wang: Investigation, verification, experiment, summary, writing, data collation, editing, review. Mei Wu: Mapping, data analysis, resource management, investigation. Yixuan Liu: Writing review. Ying Yang: Data representation, writing review, data summary, resources. Hu Li: Resources, funding, summary, writing, editing, reviewing.

Conflicts of interest

There is no conflict to declare.

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