Supporting Information

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

^{*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 of Fine Chemicals, Guizhou University, Guiyang 550025, Guizhou, China

^b College of Biology and Engineering, Guizhou Medical University, Guiyang 550025, China

*Corresponding author: E-mail: hli13@gzu.edu.cn (Hu Li)

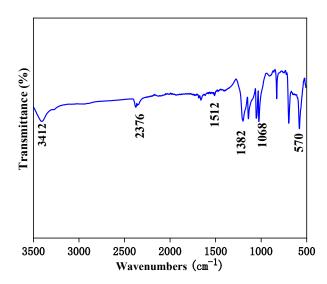


Fig. S1 FT-IR spectrum of the reused WK-SO₃H.

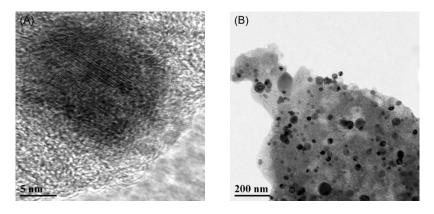


Fig. S2 (A) HR-TEM and (B) TEM images of WK-SO₃H.

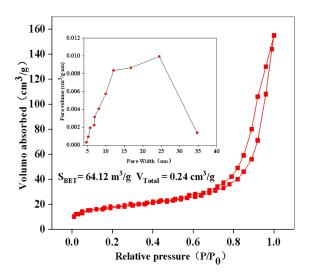
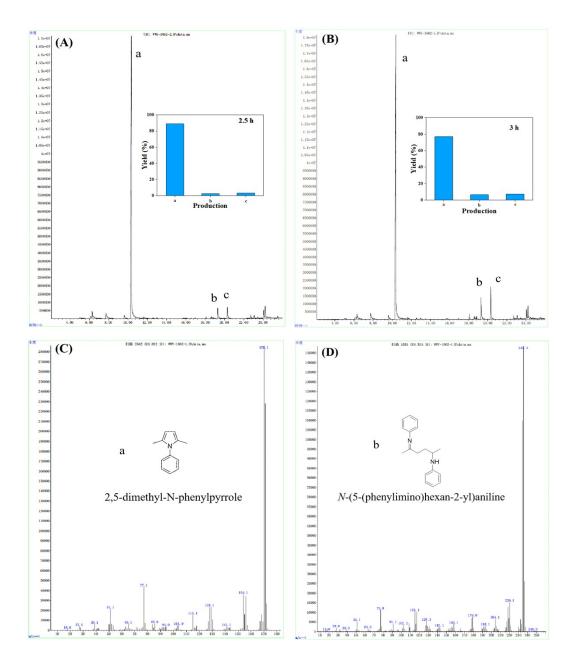


Fig. S3 N_2 adsorption-desorption isotherm of Fe₃O₄@SiO₂ (the insert is pore size distribution).

In addition to the formation of the dominant product **a** (2,5-dimethyl-N-phenylpyrrole), 6.5% of **b** (*N*-(5-(phenylimino)hexan-2-yl)aniline), 7.2% of **c** (N^2 , N^5 -diphenylhexane-2,5-diimine) and a trace amount of unknown products were mainly produced for 2.5 h. The GC-MS spectra of the target products and side-products have been illustrated in Fig. S2. After extending the reaction time to 3 h, the yields of products **b** and **c** increase (**b**-6.5%, **c**-7.2%) appropriately. By comparing the reaction results obtained after 2.5 h and 3.0 h, it can found that the difference between conversion and yield is indeed due to the conversion or degradation of the target product.



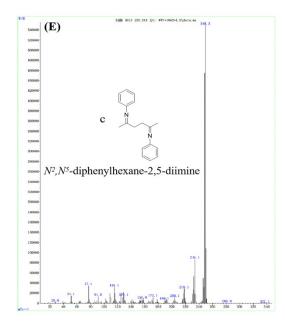


Fig. S4 (A) Product distribution diagram after 2.5 h; (B) Product distribution diagram after 3 h; MS diagrams of (C) Product **a**, (D) Product **b**, and (E) Product **c**.

Control experiments show that the yield of **a** (2,5-dimethyl-N-phenylpyrrole) is 3.1% when pure Fe₃O₄ is used, and 5.4% is obtained as SiO₂ is used as carrier (Table S1, entries 1 & 2). The catalytic activity of the carbonaceous material without — SO₃H is extremely low (entries 2 & 4). Directly encapsulating CS on Fe₃O₄ and loading sulfonic acid on CS provided 27% yield (entry 3). Only WK-SO₃H can provide high yield (89%). This can be attributed to the SiO₂ can protect Fe₃O₄ from reacting with the introduced acid species. In addition, the acid loading reduces the specific surface area, pore volume and pore volume of SiO₂ (Figs. 3 & S3).

Entry	Catalysts	Yield (%)
1	Fe ₃ O ₄	3.1%
2	Fe ₃ O ₄ @SiO ₂	5.4%
3	Fe ₃ O ₄ @CS-SO ₃ H	27%
4	Fe ₃ O ₄ @SiO ₂ @CS	7.1%
5	Fe ₃ O ₄ @SiO ₂ @CS-SO ₃ H (WK-SO ₃ H)	89%

 Table S1 Reactivity of different catalysts in reaction of aniline and 2,5-dimethylfuran to 2,5-dimethyl-N-phenylpyrrole (a).