Supplementary Materials: Facile, One-Pot, Two-Step, Strategy for the Production of Potential Bio-Diesel Candidates from Fructose

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1. Characterization of SiO_2-HNO_3

The BET surface area and average pore diameter remain stable under acid modification, but the total acid sites of SiO_2-HNO_3 increased significantly (Table S1), possibly due to the activation of the Si-O bond, forming more silicon hydroxyl groups after the acid treatment. The XRD and ^{29}Si NMR analysis were also performed and no distinct differences were observed between the original silica gel and the acid-modified one, confirming that the structure of silica gel was maintained after acidification (Figures S1 and S2).

Table S1. Characterization of the catalysts based on silica gel.

Catalyst	Untreated silica gel	SiO_2-HNO_3
BET surface area (m^2/g)	372	376
Average pore diameter (nm)	12.3	12.1
Total acid sites (nmol/g)[a]	0.009	0.037

[a] Determined by NH_3-TPD analysis.

Table S2. Characterization of the reused catalysts SiO_2-HNO_3.

Run	BET surface area (m^2/g)	Average pore diameter (nm)	Total acid sites (nmol/g)[a]
Fresh	376	12.1	0.037
1	372	11.9	0.033
2	370	11.6	0.032
3	365	11.0	0.029
4	362	10.9	0.026
5	357	10.4	0.023

[a] Determined by NH_3-TPD analysis.

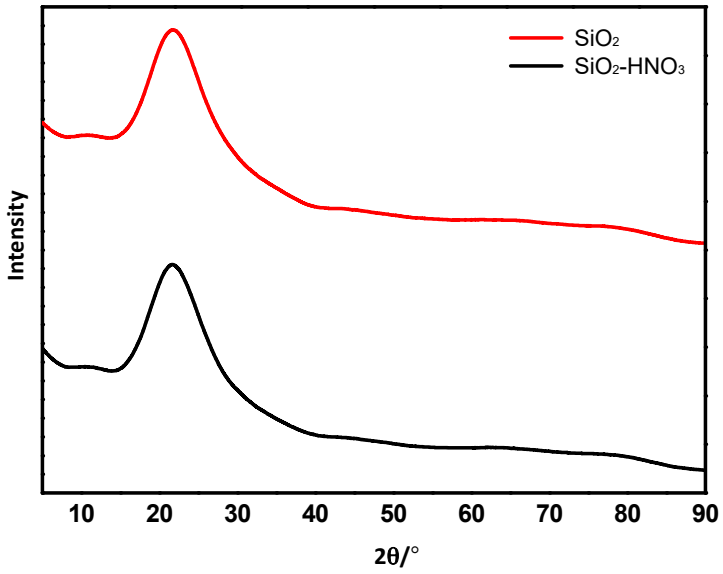

Figure S1. XRD analysis of SiO_2-HNO_3.

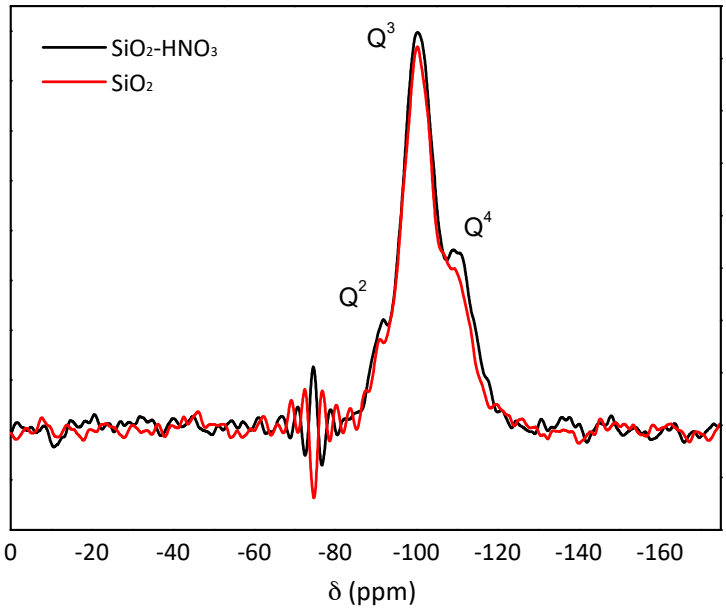

Figure S2. ^{29}Si NMR analysis of SiO_2-HNO_3.

The FTIR spectra of SiO_2-HNO_3 exhibits characteristic bands at 1105, 804 and 470 cm^{-1} corresponds to asymmetric stretching, symmetric stretching and bending vibrations modes of Si-O-Si bonds, respectively (Figure S3) [1,2]. The bands at 3437 and 1633 cm^{-1} could be attributed to the stretching and bending O-H vibrations in Si-OH groups, respectively [3,4]. The sharp band at 1343 cm^{-1} was ascribed to the N-O symmetric stretch, indicating the existence of residual NO^{3-}.

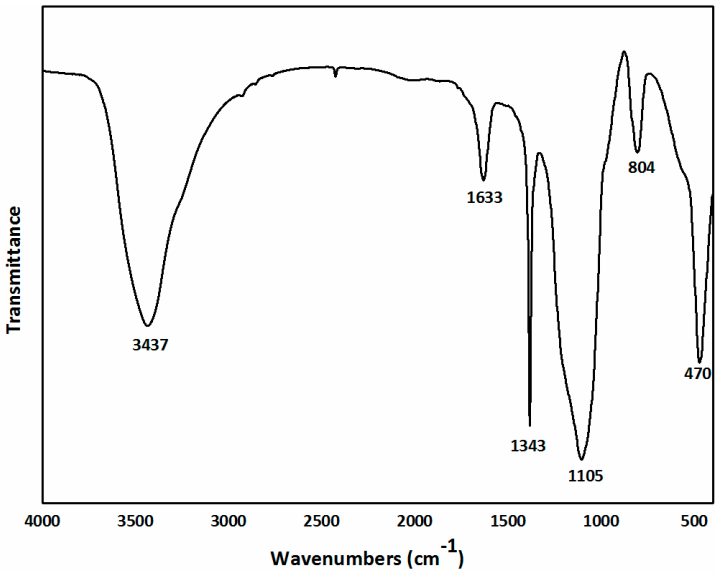

Figure S3. FTIR spectra of SiO_2-HNO_3.

2. Spectral Data of HDMF, MMF, and DMMF

HDMF. ^{1}H NMR (600 MHz, DMSO) δ 6.62 (dd, J = 20.4, 5.9 Hz, 2H), 6.54 – 6.31 (m, 29H), 6.25 (t, J = 4.2 Hz, 19H), 5.68 – 5.51 (m, 5H), 5.49 – 5.38 (m, 20H), 5.33 – 5.17 (m, 21H), 4.67 – 4.36 (m, 33H), 4.36 (s, 22H), 3.33 (s, 68H), 3.31 – 3.20 (m, 144H), 3.20 – 3.07 (m, 4H), 2.59 – 2.43 (m, 26H), 2.17 (s, 2H), 1.32 – 1.09 (m, 7H), 1.21 – 1.09 (m, 4H), 1.21 – 1.07 (m, 4H).

MMF. ^{1}H NMR (600 MHz, DMSO) δ 9.58 (s, 45H), 7.51 (d, J = 3.5 Hz, 50H), 6.73 (d, J = 3.5 Hz, 50H), 4.47 (s, 122H), 3.57 (s, 24H), 3.48 – 3.10 (m, 378H), 2.71 (t, J = 6.5 Hz, 16H), 2.58 – 2.27 (m, 133H), 2.27 – 2.14 (m, 6H), 2.10 (s, 23H).

DMMF. ^{1}H NMR (600 MHz, DMSO) δ 6.43 – 6.39 (m, 4H), 6.38 (s, 2H), 5.42 (d, J = 6.2 Hz, 3H), 4.32 (s, 7H), 3.26 (t, J = 30.0 Hz, 35H), 2.50 (dt, J = 3.5, 1.7 Hz, 2H).

3. The catalytic performance of the untreated silica gel in the two-step process.

The catalytic effectiveness of the untreated silica gel was investigated for the reaction of the produced 5-HMF from fructose and methanol into HDMF in DMSO. Contrastive profiles of the substrate and products with the untreated silica gel or SiO_2-HNO_3 after 2 h are shown in Figure S4. Completed conversions of fructose were obtained when either catalysts were used, indicating that silica gel could efficiently promote the dehydration of the fructose to 5-HMF. However, when catalyzed by untreated silica gel, an optimum HDMF yield of 20% was obtained, while the SiO_2-HNO_3 possessed a HDMF yield of 70%, which was attributed to the lower acid sites on the untreated silica gel. Therefore, the acid-treatment silica gel was more effective than the untreated silica gel for the production of HDMF from fructose.

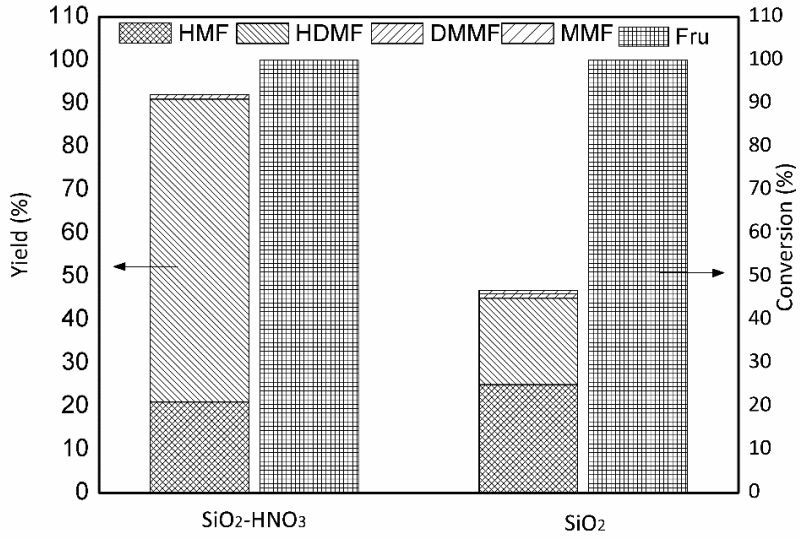

Figure S4. Effect of acid-treatment on the activity of the silica gel in the two-step reaction. Reaction conditions: 1.37 mmol fructose in 4.0 mL DMSO at 150 °C with 50 mg SiO_2-HNO_3 or SiO_2; after 2 h, 9.3 mL methanol was added and the reaction time was extended to 3 h at 100 °C.

4. A kinetic analysis of the various involved reactions depending on the reaction medium

Kinetic analyses of both the 5-HMF conversion in the methanol and fructose conversion over SiO_2-HNO_3 in the DMSO/methanol system were performed (Table S3–S6). Both conversions were identified as first-order reactions. The value of the pseudo-first-order rate constant (k) was obtained by plotting the values of ln (1−x) (where x is the conversion of 5-HMF or fructose) against the reaction time (t). In Table S3 and S5, the value of k increases with increasing the temperature, indicating that a higher reaction temperature accelerated the 5-HMF and fructose conversion reaction rates. The kinetic parameters for the SiO_2-HNO_3-catalyzed 5-HMF conversion in the methanol and fructose conversion in the DMSO/methanol system are summarized in Tables S3 and S5, respectively. The apparent activation energy of 5-HMF conversion was 63.3 kJ·mol^{-1}, which was lower than that of fructose in the DMSO/methanol system; a possible explaination was that 5-HMF itself was an intermediate product in the conversion of fructose and the protic solvent (methanol) interfered the fructose conversion in the DMSO/methanol system.

Table S3. Rate constants (k) of 5-HMF conversion with methanol at different reaction temperatures[a]

Entry	Temperature (K)	k (min^{-1})	Correlation coefficient
1	393	0.0277	0.9923
2	403	0.0437	0.9941
3	413	0.0791	0.9945
4	423	0.1043	0.9982

[a] Conditions: 0.77 mmol 5-HMF in 4.0 mL of methanol with 26 mg of SiO_2-HNO_3, 30 min.

Table S4. Kinetic parameters of 5-HMF conversion with methanol

Parameter	Value
reaction order, n	1
activation energy, *E*a (kJ·mol^{-1})	63.3
pre-exponential factor, *A* (min^{-1})	7.2×10^{6}
correlation coefficient	0.99

Table S5. Rate constants (k) of fructose conversion at different reaction temperatures in the DMSO/methanol system [a]

Entry	Temperature (K)	*k* (min^{-1})	Correlation coefficient
1	393	0.0167	0.9964
2	403	0.036	0.9925
3	413	0.0771	0.9971
4	423	0.1137	0.9956

[a] Conditions: 1.37 mmol fructose, 50 mg SiO_2-HNO_3, 4.0 mL solvent (DMSO/methanol 30/70 v/v), 30 min.

Table S6. Kinetic parameters of the fructose conversion in the DMSO/methanol system

Parameter	Value
reaction order, n	1
activation energy, *E*a (kJ·mol^{-1})	90.28
pre-exponential factor, *A* (min^{-1})	1.77×10^{10}
correlation coefficient	0.9854

References

1. Timin, A.S.; Solomonov, A.V.; Musabirov, I.I.; Sergeev, S.N.; Ivanov, S.P.; Rumyantsev, E.V.; Goncharenko, A. Immobilization of bovine serum albumin onto porous poly (vinylpyrrolidone)-modified silicas. *Ind. Eng. Chem. Res.* **2014**, *53*, 13699–13710.
2. Lenza, R.F.S.; Nunes, E.H.M.; Vasconcelos, D.C.L.; Vasconcelos, W.L. Preparation of sol-gel silica samples modified with drying control chemical additives. *J. Non-Cryst. Solids* **2015**, *423–424*, 35–40.
3. Sanjini, N.S.; Velmathi, S. CuO Impregnated mesoporous silica KIT-6: A simple and efficient catalyst for benzene hydroxylation by C-H activation and styrene epoxidation reactions. *J. Porous Mater.* **2016**, *23*, 1527–1535.
4. Meeks, N.D.; Smuleac, V.; Stevens, C.; Bhattacharyya, D. Iron-based nanoparticles for toxic organic degradation: Silica platform and green synthesis. *Ind. Eng. Chem. Res.* **2012**, *51*, 9581–9590.