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Rational Engineering of Brønsted Acid Sites for Product-Specific and Accelerated Furfurylamine Formation

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Chemicals

Ruthenium (III) trichloride hydrate, furfural, furfurylamine, naphthalene, 7N NH_3 in methanol, aqueous NH_3, methanol, potassium thiocyanate, and 2,6-lutidine were purchased from TCI chemicals. All the chemicals were used as received. NH_4^+-ZSM-5 (40) was purchased from Zeolyst International and calcined at 550 °C for 6 h to obtain H-ZSM-5 (40).

Catalyst preparation

The zeolite support was prepared by controlled desilication of H-ZSM-5(40). In a typical procedure, 1 g of H-ZSM-5(40) and 20 g of 2.35 M NH_3 solution (28% in water) were taken in an Ace pressure round-bottom flask (50 mL). The flask was then placed in a preheated oil bath (80 °C) on a hot plate with a magnetic stirrer, and the mixture was stirred at 600 rpm for 1, 3 and 5 h. The slurry was then immediately filtered by vacuum filtration, thoroughly washed until the supernatant was neutral, dried at 80 °C overnight, and ground to a powder to obtain desilicated H-ZSM-5 zeolite support, denoted as DZ-1, DZ and DZ-5, respectively. Likewise, H-ZSM-5 was subjected to alkaline treatment as follows. 1 g of HZSM-5 (Si/Al = 40) and 10 mL of 1 M aqueous NaOH solution were placed in a 50 mL Ace pressure tube. The tube was then kept in a preheated oil bath at 80 °C on a magnetic stirrer with a hot plate and stirred for 1 and 3 h. After the treatment, the supernatant was decanted by vacuum filtration, and the solid residue was washed several times with excess water until the pH was neutral. The resulting solid was then dried in an oven at 80 °C overnight. Subsequently, it was treated with a 1 M aqueous NH_4Cl solution at 65 °C for 3 hours to remove any Na^+ ions that had been exchanged during the desilication process. The slurry was then filtered, thoroughly washed with ample water, and dried again in an oven at 80 °C overnight to obtain the modified HZSM-5, denoted as DZ-Na1 and DZ-Na3.

The as-synthesised materials were used as a support for Ru metal loading via hydrothermal treatment. The slurry containing the required amount of DZ-1, DZ, DZ-5, DZ-Na1 and DZ-Na3 (500 mg) in 15 g of water was transferred to a round-bottom flask, to which a prepared aqueous solution of ruthenium(III) trichloride hydrate (corresponding to 1 wt% Ru) in 6 g of water was slowly added while stirring. Then, the flask was placed in a preheated oil bath (80 °C) on a hot plate with a magnetic stirrer for 2 h at 600 rpm, then aged and dried overnight at 80 °C in an oven, and ground into powder. The obtained materials were finally reduced at 450 °C with a heating rate of 2 °/min for 3 h in a tubular furnace under 5% H_2/N_2 and were labelled as Ru/DZ-1, Ru/DZ, Ru/DZ-5, Ru/DZ-Na1 and Ru/DZ-Na3. Similarly, $Ru_{0.5}$/DZ (0.5 wt% Ru) and $Ru_{1.5}$/DZ (1 wt% Ru) were also prepared. 1 wt% Ru supported on parent H-ZSM-5 (40) (Ru/HZ) was also prepared using the same procedure described above.

Catalyst Characterisation

X-ray diffractograms were collected using a Rigaku diffractometer (Smart LAB SE) between a 2θ range of 10-80° and a 2° min^{-1} scan rate by utilising a Cu-Kα radiation source at 40 kV and 50 mA. The surface area and total pore volume of the catalysts were measured using a Quantachrome AutosorbiQ physisorption analyser. All samples were degassed at 150 °C for 3 h prior to analysis. The amount of N_2 adsorbed at a relative pressure of around 0.99 was used to obtain the sorption isotherms as well as the Brunauer-Emmett-Teller (BET) surface area and total pore volume. The pore diameter was obtained from the desorption branch using the Barrett-Joyner-Halenda (BJH) method. The t-plot method was used to measure micropore volume and micropore surface area. The oxidation states and chemical environments of different elements were investigated using X-ray photoelectron spectroscopy

with a Thermoscientific NEXA Surface analyser, equipped with an Al Kα monochromatic X-ray source. For calibration, the C 1s binding energy of 284.6 eV was employed.

The microscopic images of the samples were collected using a Thermo Scientific Apreo 2 field-emission scanning electron microscope (FESEM) with gold coating prior to analysis. The high resolution transmission electron microscopy (HRTEM) images were captured using an FEI Tecnai G2 (Germany) at an operating voltage of 200 kV with a charge-coupled device (CCD) detector. Before capturing the images, the samples were dispersed well in an ethanolic solution under sonication and then placed on a copper grid, which was vacuum-dried. The elemental mapping and compositional analysis were performed using an energy dispersive spectrophotometer (EDS) attached to the same instrument.

Temperature-programmed desorption (TPD) with NH_3 as a probe molecule was conducted to investigate the type and quantity of acidic sites on the catalyst surface using a BELCAT II equipped with a TCD detector. In a typical process, 50 mg of the catalyst was placed in a quartz tube and pre-treated for 1 hour at 350 °C under He gas flow (30 ml min^{-1}). After cooling to 50 °C, the sample was exposed to 5% NH_3 in He at a flow rate of 50 ml min^{-1} for 30 min. The physisorbed NH_3 was removed by flushing with He gas for 30 min at a flow rate of 30 ml min^{-1}. The NH_3 desorption profile was collected between 50 and 500 °C at a ramp rate of 10 °C min^{-1}. During NH_3-TPD tests, the NaOH trap was used to remove any moisture present.

In situ pyridine- and N-FFA- diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy studies were performed using a Brucker (invenio-S) instrument coupled with a Harrick high-temperature cell, and spectra were collected between 600 and 4000 cm^{-1} with 128 scans at a resolution of 4 cm^{-1}. An appropriate amount of Ru/DZ (or Ru/HZ) taken in the sample holder was first treated at 300 °C for 1 h under an N_2 atmosphere, and the background

spectra were recorded at 50 °C. Pyridine adsorption was performed with a pyridine-saturated N_2 flow using a custom-made accessory at 50 °C for 30 min, followed by N_2 purging for 30 min to eliminate any physisorbed pyridine. The temperature was then raised to 100 °C, and the spectra were collected.

The following formula was used to estimate the semi-quantitative concentrations of Brønsted and Lewis acid sites for both Ru/DZ and Ru/HZ, primarily for comparative purposes.

$$C_L \text{ (mmol/g)} = (1.42 * IA_L * R^2)/W$$

$$C_B \text{ (mmol/g)} = (1.88 * IA_B * R^2)/W$$

Where IA_L and IA_B represent the peak absorbance area of Brønsted acid sites (1450 cm^{-1}) and Lewis acid sites (1540 cm^{-1}), respectively. R refers to the radius of the cell; w is the sample weight.

In the case of in situ N-FFA-DRIFTS studies, a fine drop of a methanolic N-FFA solution was drop-casted at 50 °C onto the samples, flushed with N_2 for 15 min, and the spectra were recorded at 60 °C.

Reductive amination of furfural

The reductive amination of FUR was performed in a 50 mL high-pressure Parr reactor. An appropriate amount of FUR, 7N NH_3 in methanol, naphthalene (internal standard), catalyst, and methanol as solvent were placed in a 50 ml stainless steel vessel. The reactor was then carefully and tightly closed and pressurised to the required H_2 pressure. The reaction mixture was heated to the desired temperature and stirred at 400 rpm for the specified period. The reaction was then quenched with ice water, an aliquot of the reaction mixture was filtered through a 0.2 μm filter, and analysed by gas chromatography with a flame ionisation detector (FID) (Agilent 7693A) using a DB-HeavyWAX column (30 m ×

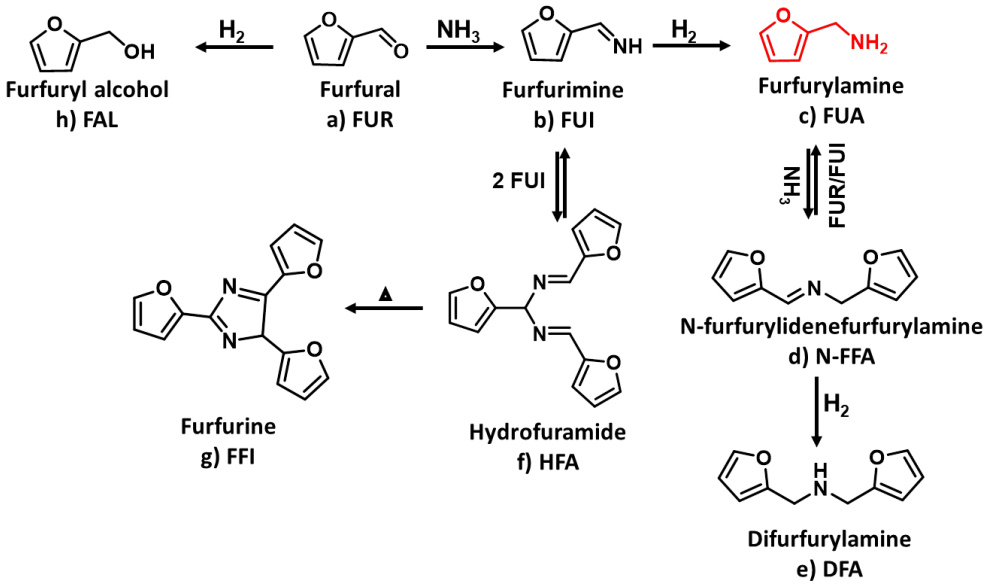
0.320 mm × 0.25 μm). The substrate conversion, product yield, and selectivity were quantified by calibration against a series of individual standards. The yield of N-FFA was calculated assuming a maximum of 0.5 mmol of N-FFA could be obtained from 1 mmol of FUR. As HFA was not commercially available, N-FFA was used as the calibration standard. The obtained yields were corrected by a factor of 2/3 to account for the difference in carbon number between HFA (C15) and N-FFA (C10) (Figures S1). The products (FUA) and byproducts (N-FFA and HFA) were confirmed using gas chromatography-mass spectrometry (GC-MS) (Figures S2 and S3) (ThermoScientific Trace 1300; HP-5 column: 30 m × 0.320 mm × 0.25 μm).

Synthesis of N-furfurylidenefurfurylamine (N-FFA)

1 mmol of FUR, 1 mmol of FUA, and 10 g of MeOH were taken in a round-bottom flask and stirred at 60 °C for 30 min. The formation of N-FFA was confirmed by GC and GC-MS analyses (Figure S4). The GC chromatogram indicated near-complete conversion of the substrates. The known concentration of N-FFA was used as a standard for quantifying N-FFA and for N-FFA DRIFT studies.

Pre-adsorption of N-FFA over Ru/DZ and Ru/HZ and its conversion towards FUA formation

Equimolar quantities of FUR and FUA (1 mmol each) were individually mixed in methanol (10 mL) in two separate round-bottomed flasks, and then 80 mg of Ru/HZ and Ru/DZ were added to each one. The mixtures were stirred at 60 °C for 30 min to form the intermediate N-furfurylidenefurfurylamine (N-FFA). The aliquots of the reaction mixture were injected into a GC-MS analysis, which indicated the formation of only N-FFA in both cases. The reaction mixture was then transferred to a high-pressure reactor preloaded with the appropriate amount of Ru/DZ (or Ru/HZ), charged with NH_3 in MeOH and H_2, and subjected to the desired reaction conditions, as described in Table S3, using N-FFA as the substrate.



Scheme S1. The plausible pathway for the product formation during the reductive amination of FUR to FUA.

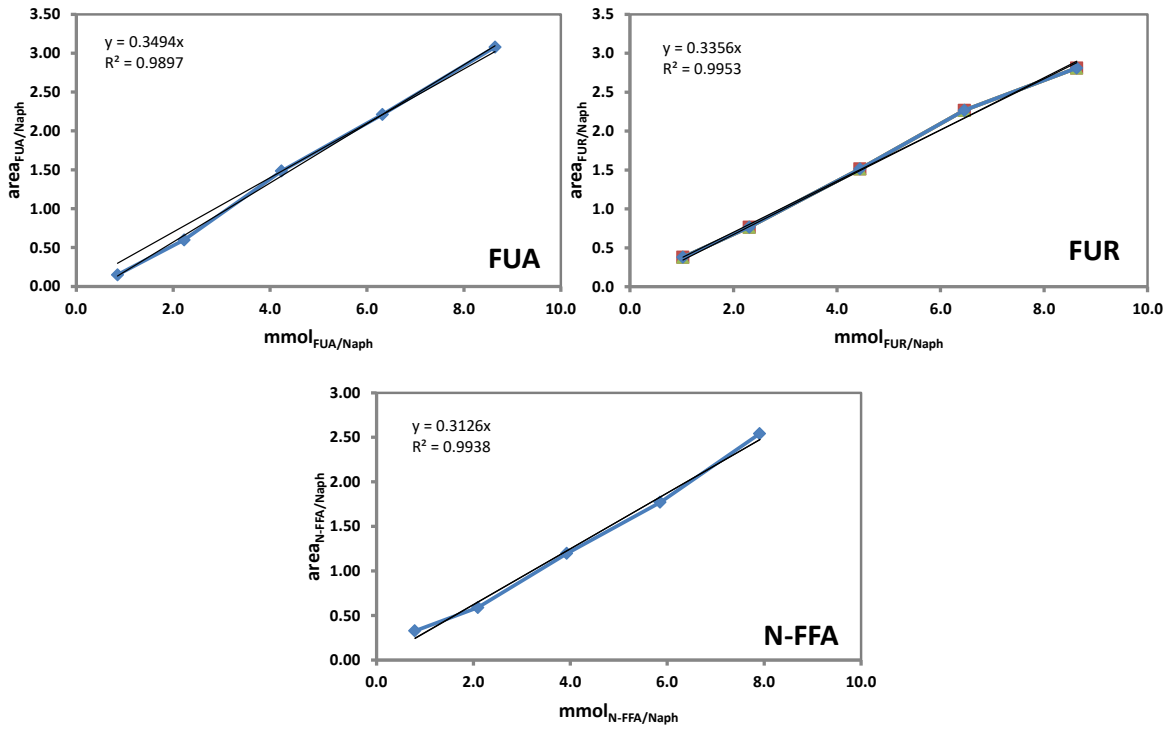


Figure S1. Calibration curves of (a) FUA, (b) FUR, and (c) N-FFA, constructed using a series of individual standard solutions.

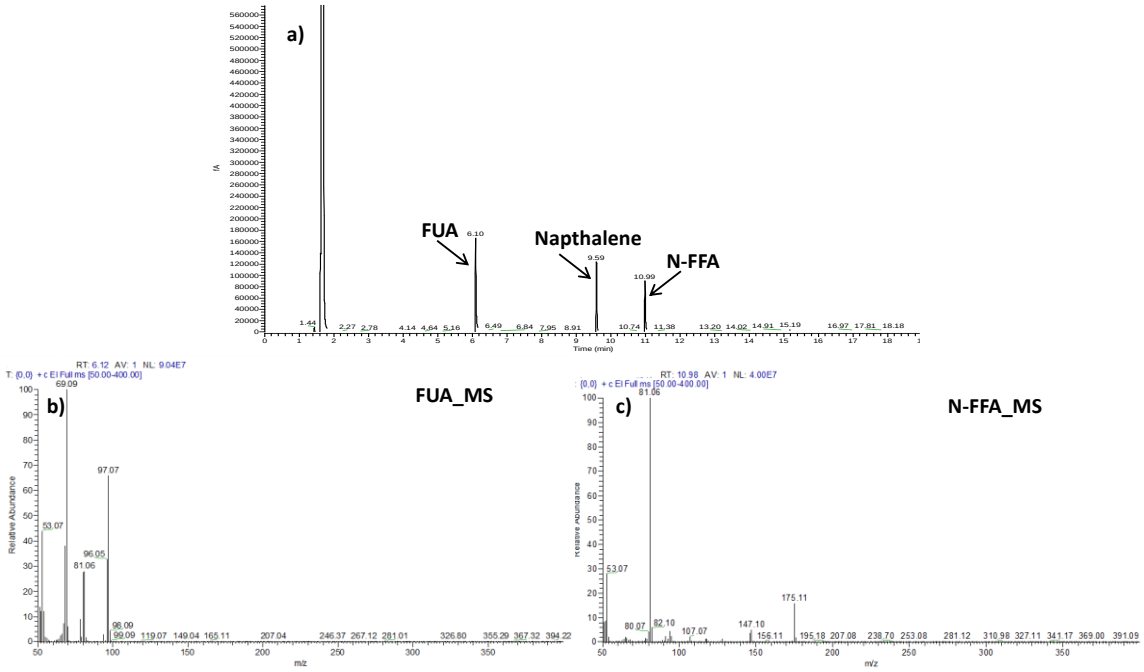


Figure S2. a) GC Chromatogram of the reaction mixture using Ru/DZ as catalyst; MS fragmentation patterns of b) FUA and c) N-FFA.

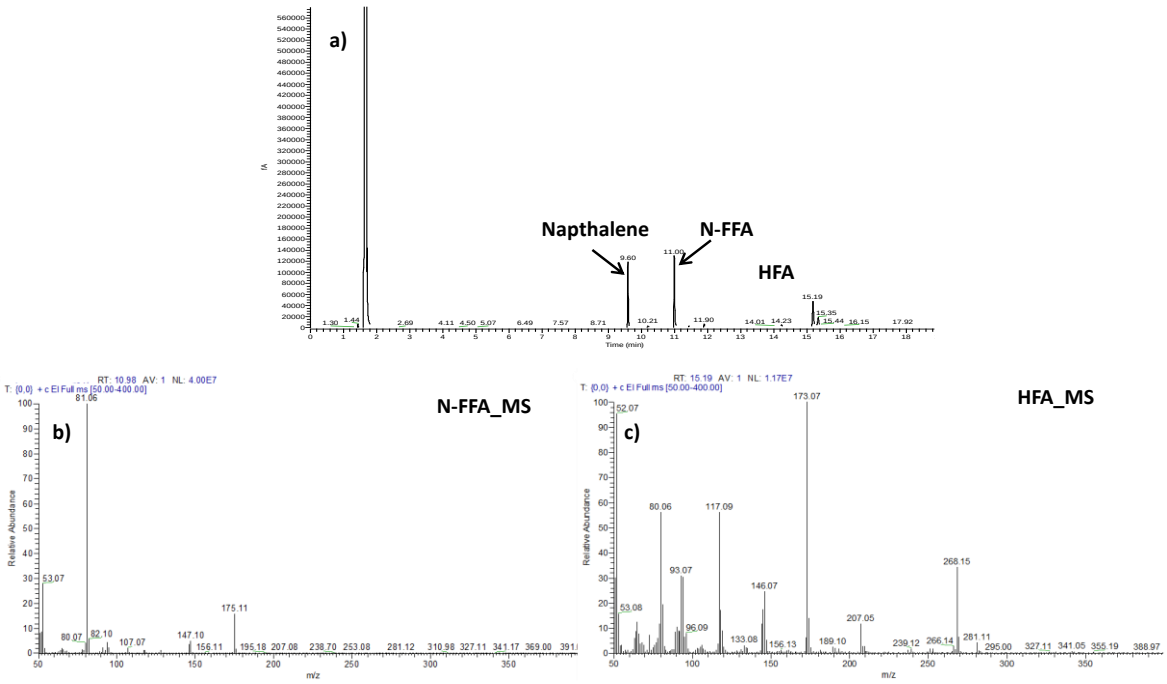


Figure S3. a) GC Chromatogram of the reaction mixture using Ru/HZ as catalyst; MS fragmentation patterns of b) N-FFA and c) HFA.

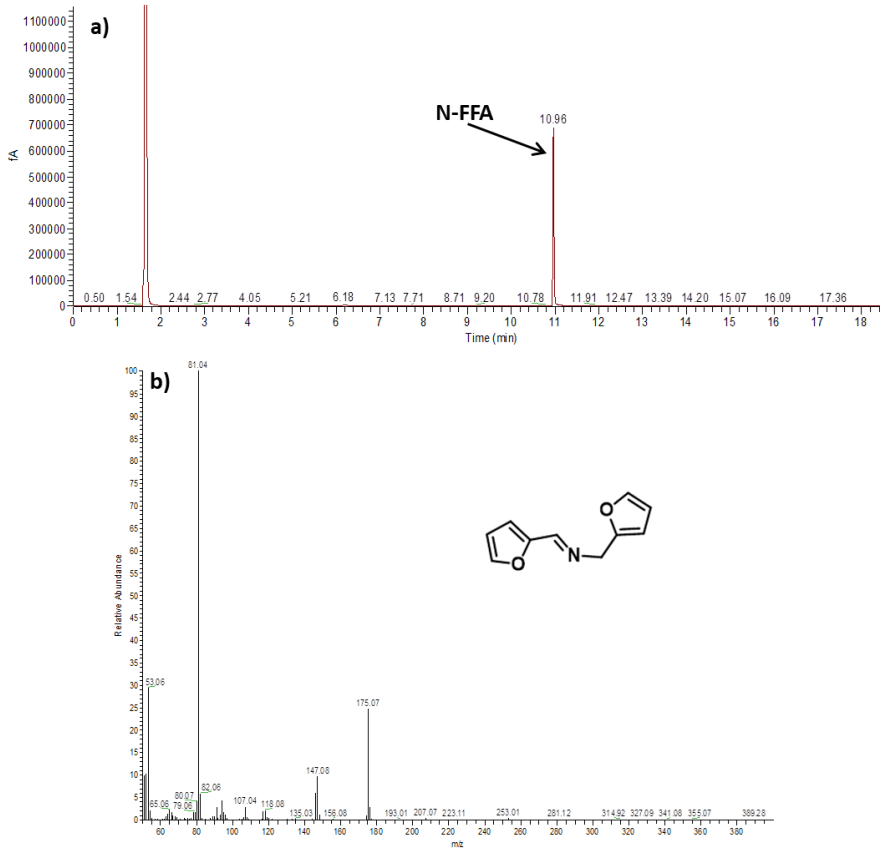


Figure S4. a) GC chromatogram and b) GC-MS spectra of N-FFA.

Note: N-FFA was prepared as mentioned in the experimental section above.

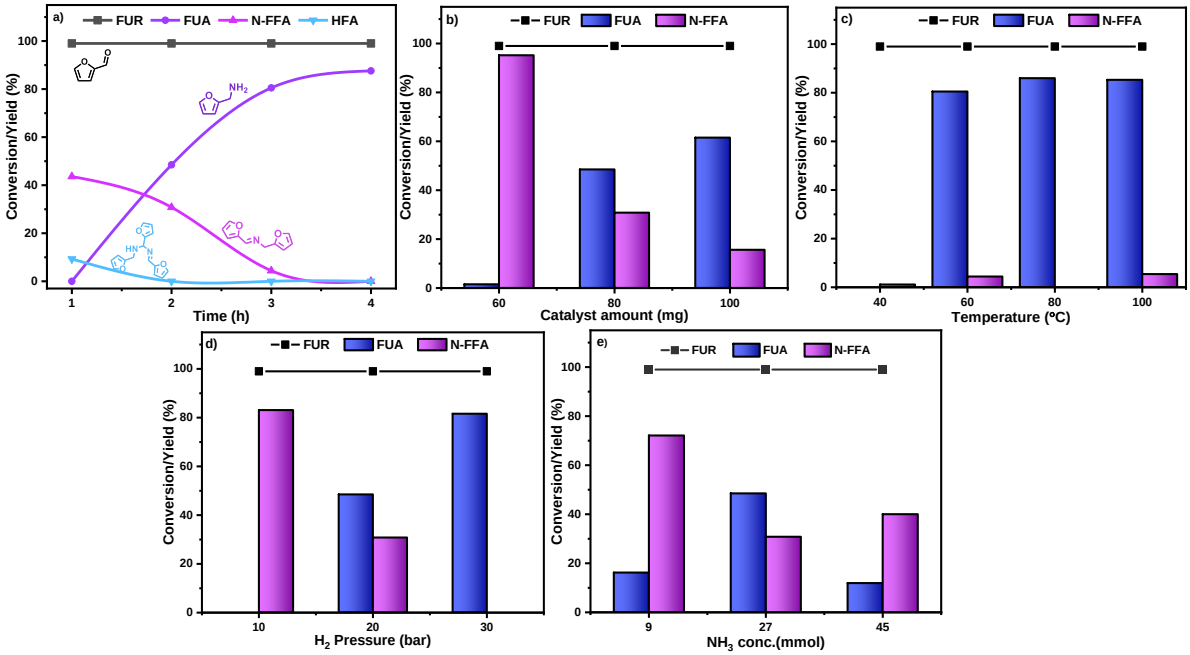


Figure S5. Optimisation of reaction parameters. a) time course study (reaction conditions: 1 mmol FUR, 27 mmol NH_3, 12 g MeOH, 60 °C, 80 mg Ru/DZ, 20 bar H_2), b) catalyst loading (reaction conditions: 1 mmol FUR, 27 mmol NH_3, 12 g MeOH, 60 °C, 2h, 20 bar H_2), c) temperature (reaction conditions: 1 mmol FUR, 27 mmol NH_3, 12 g MeOH, 3h, 80mg Ru/DZ, 20 bar H_2), d) H_2 pressure (reaction conditions: 1 mmol FUR, 27 mmol NH_3, 12 g MeOH, 60 °C, 2h, 80 mg Ru/DZ) and e) ammonia concentration (reaction conditions: 1 mmol FUR, 12 g MeOH, 60 °C, 2h, 80mg Ru/DZ, 20 bar H_2).

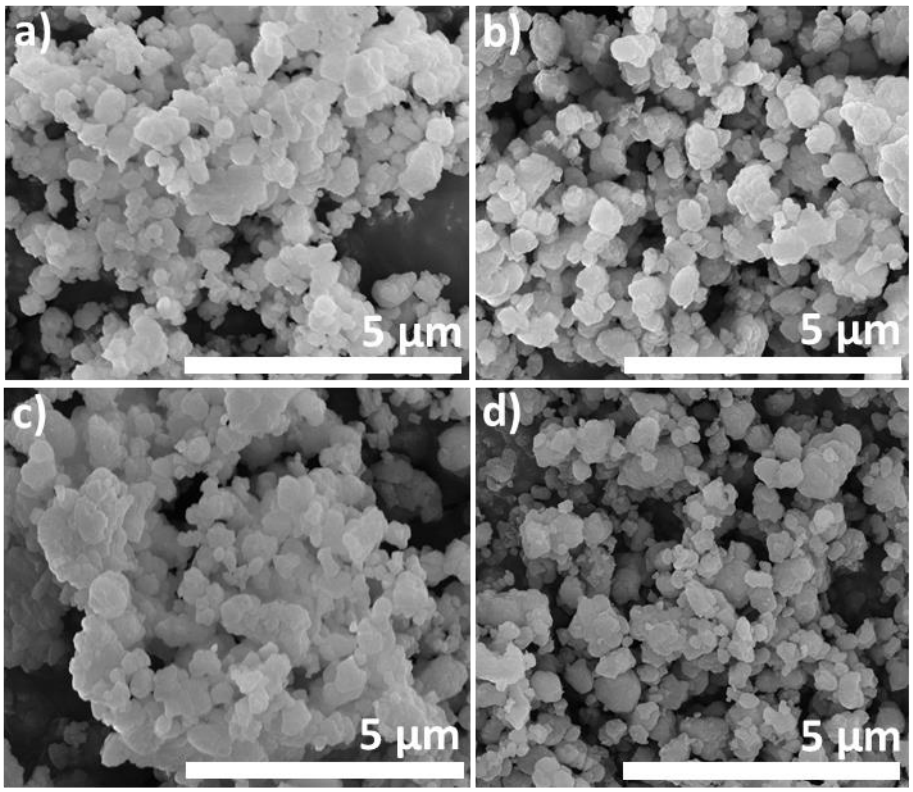


Figure S6. a) FE-SEM images of a) HZ, b) DZ, c) Ru/HZ and d) Ru/DZ.

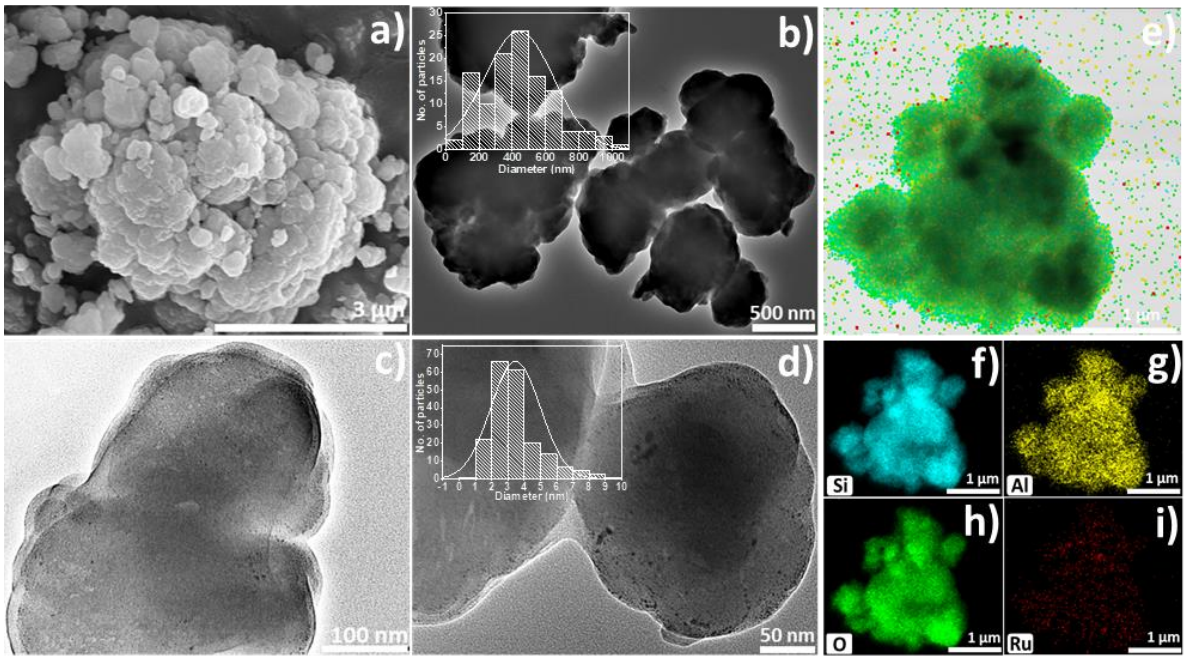


Figure S7. a) FE-SEM image, b-d) HRTEM images (Ru and HZ particle size (inset b and d)) and e-i) EDX mapping of Ru/HZ.

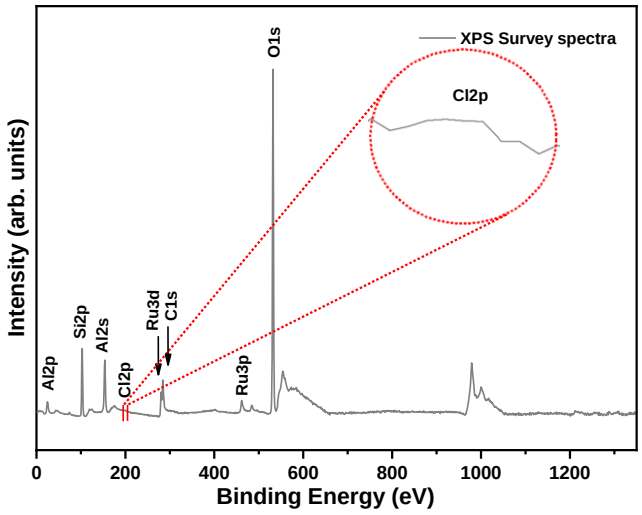


Figure S8. *XPS survey scan spectrum of Ru/DZ [1].*

Note: The XPS survey spectrum of Ru/DZ exhibits a negligible Cl 2p signal, suggesting that chlorine has a negligible contribution to the catalytic activity.

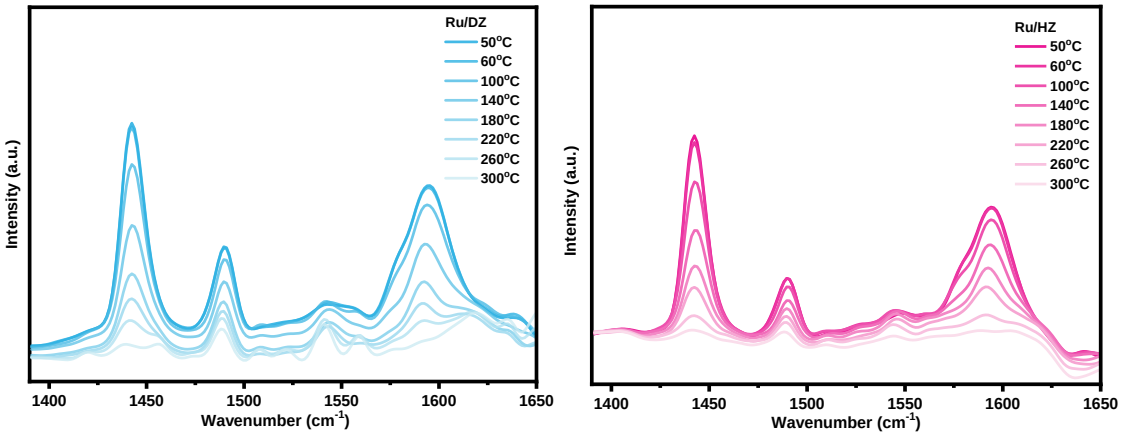


Figure S9. Pyridine DRIFT spectra of a) Ru/DZ and b) Ru/HZ catalysts.

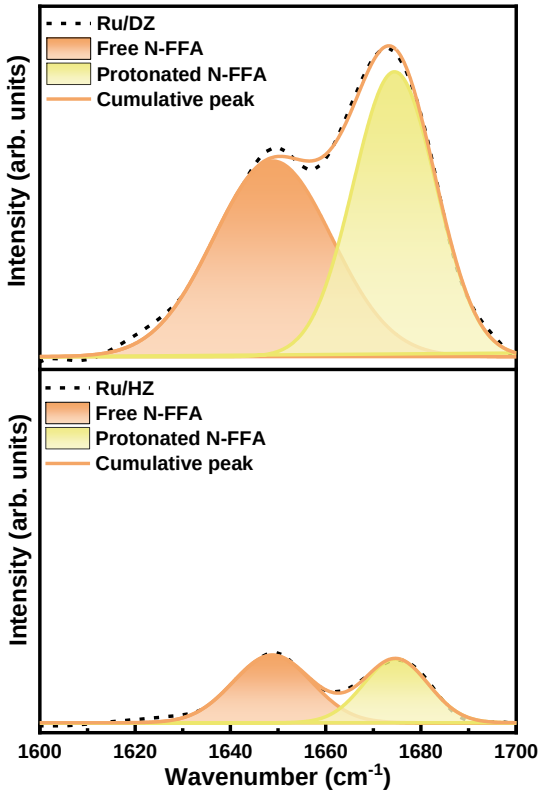


Figure S10. Deconvoluted DRIFT spectra of N-FFA adsorbed on Ru/DZ and Ru/HZ, derived from Figure 3c.

Pre-poisoning Ru/DZ with NH_3 and testing its catalytic activity

The pre-poisoning experiment was carried out by adding an appropriate amount of Ru/DZ and NH_3 in methanol (as described in the reaction procedure) in an Ace pressure tube. The mixture was kept in an oil bath maintained at 60 °C and stirred for 1 hour using a magnetic stirrer. It was then cooled in an ice bath, and a portion of the mixture was collected, filtered, washed with MeOH, and dried at 80 °C overnight. The obtained solid (Ru/DZ-A) was mixed with KBr in a 1:1 ratio, ground thoroughly, and its DRIFT spectrum was recorded. The remaining mixture, corresponding to the optimised reaction conditions, was then subjected to reductive amination. An aliquot of the reaction mixture was collected and analysed using GC. The NH_3-pre-poisoned Ru/DZ (Ru/DZ-A) and the catalyst recovered after the reductive amination reaction (Ru/DZ-AAR) were analysed using DRIFT for comparison (Figure S11).

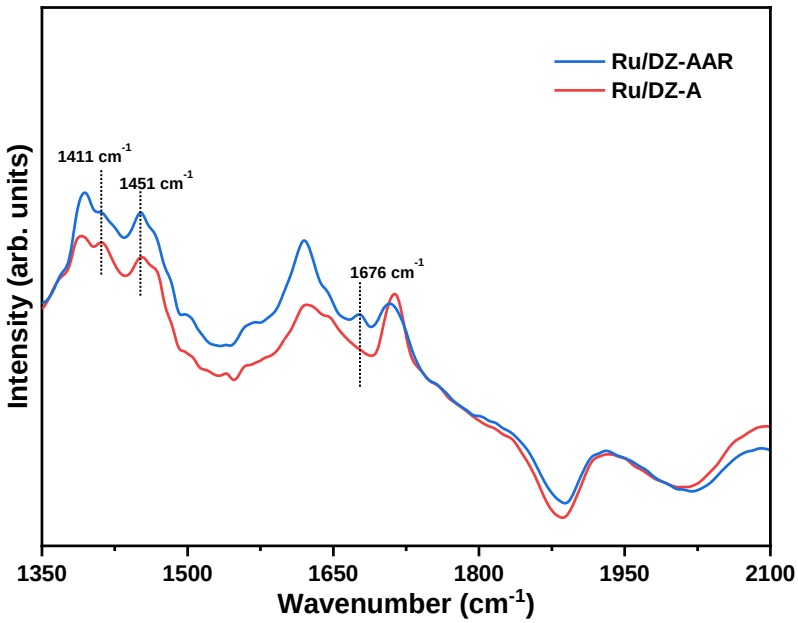


Figure S11. DRIFT spectra of Ru/DZ pre-poisoned with NH_3 before (Ru/DZ-A) and after (Ru/DZ-AAR) the reductive amination reaction.

Note: To determine whether NH_3 poisons the Brønsted acid sites of Ru/DZ and prevents the transformation of N-FFA to FUA, pre-poisoning experiments were performed by treating Ru/DZ with NH_3 in methanol (Ru/DZ-A) prior to the reaction under identical conditions. Ru/DZ-A produced 71.5% N-FFA and 5.1% HFA, with no FUA, confirming effective site poisoning. DRIFT analysis of Ru/DZ-A and the post-reaction catalyst (Ru/DZ-AAR) showed characteristic NH_4^+ bending peaks at 1411 and 1452 cm^{-1} [2], which persisted after the reaction, along with a small peak attributed to protonated N-FFA (Figure S10), indicating suppressed protonation and conversion to FUA. Under the reaction conditions used in this study, however, NH_3 does not block Brønsted acid sites, possibly due to competitive adsorption, allowing selective N-FFA protonation and subsequent facile conversion to FUA.

Table S1. *Influence of varied desilication time with Ru/DZ catalysts on the yield of FUA.*

Entry	Catalysts	FUR Conv. (%)	Yield (%)		
			FUA	N-FFA	HFA
1.	Ru/DZ-1	>99		71.6	5.9
2.	Ru/DZ	>99	48.5	30.8	-
3.	Ru/DZ-5	>99	-	34.9	18.1
4.	Ru/DZ-Na1	>99	-	43.4	18.8
5.	Ru/DZ-Na3	>99	2.2	82.7	11.9

Reaction conditions: 1 mmol FUR, 12 g MeOH, 60 ˚C, 27 mmol NH_3 in MeOH, 20 bar H_2, 2 h, 80 mg Ru/DZ.

Table S2. *Influence of Ru loading over DZ on the yield of FUA.*

Entry	Catalyst	FUR Conv. (%)	Yield (%)		
			FUA	N-FFA	HFA
1.	$Ru_{0.5}$/DZ	>99	-	29.2	17.2
2.	Ru/DZ	>99	48.5	30.8	-
3.	$Ru_{1.5}$/DZ	>99	28.3	21.7	-

Reaction conditions: 1 mmol FUR, 12g MeOH, 60 ˚C, 27 mmol NH_3 in MeOH, 20 bar H_2, 2h, 80 mg Ru/DZ.

Table S3. *Time-course study with Ru/HZ on the product formation.*

Entry	Time (h)	FUR Conv. (%)	Yield (%)		
			FUA	N-FFA	HFA
1.	1	>99	-	4.9	34.3
2.	2	>99	-	35.4	9.2
3.	3	>99	-	74.9	6.7
4.	4	>99	-	80.1	4.0

Reaction conditions: 1 mmol FUR, 12g MeOH, 60 ˚C, 27 mmol NH_3 in MeOH, 20 bar H_2, 2h, 80 mg Ru/HZ.

Table S4. Physicochemical properties of with and without Ru supported on parent and modified HZ.

S. No.	Catalyst	S_{micro} ($m^2 g^{-1}$)	S_{BET} ($m^2 g^{-1}$)	V_{micro} ($cm^3 g^{-1}$)	V_{mes} ($cm^3 g^{-1}$)	V_{total} ($cm^3 g^{-1}$)
1.	HZ	359	437	0.150	0.093	0.267
2.	DZ	340	415	0.144	0.119	0.271
3.	Ru/HZ	327	405	0.139	0.103	0.265
4.	Ru/DZ	317	390	0.131	0.129	0.266

Table S5. The number of acidic sites for with and without Ru support on the parent and modified HZ, obtained from the corresponding NH_3-TPD profiles.

Entry	Catalyst	Acidity ($\mu mol\ g^{-1}$)		
		Weak	Medium/ strong	Total
1.	HZ	419	238	657
2.	DZ	374	266	640
3.	Ru/HZ	386	172	558
4.	Ru/DZ	439	286	725

Table S6. Amount of Brønsted and Lewis acid sites calculated from the corresponding pyridine DRIFT spectra

S.No.	Cat	Lewis acid sites (µmol/g)	Brønsted acid sites (µmol/g)	Lewis/Brønsted sites (µmol/g)
1.	Ru/HZ	32.3	1.47	21.9
2.	Ru/DZ	41.6	3.27	12.7

Table S7. Conversion of N-FFA to FUA with Ru/HZ and Ru/DZ.

S.No.	Catalyst	N-FFA Conv. (%)	FAM Yield.(%)
1.	Ru/HZ	14.1	3.2
2.	Ru/DZ	20.9	11.4

Reaction conditions: 1 mmol N-FFA, 12 g MeOH, 60 ˚C, 20 bar H_2, 27 mmol NH_3, 80 mg catalyst, 2h.

Table S8. Influence of additives towards the catalytic activity of Ru/DZ for the reductive amination of FUR

Entry	Catalyst	FUR Conv. (%)	FUA Yield. (%)	N-FFA Yield (%)
1.	KSCN	>99	-	-
2.	Ru/DZ+KSCN	>99	-	0.9
3.	Luitidine	>99	-	2.0
4.	Ru/DZ+luitidine	>99	-	37.6

Reaction conditions: 1 mmol FUR, 1 mmol of KSCN/0.1 mmol of luitidine additive, 27 mmol NH_3 in MeOH, 12 g MeOH, 60 °C, 2h, 80 mg catalyst, 20 bar H_2.

References

1. Shi B, Zhao C, Ji Y, Shi J, Yang H, Applied Surface Science, 2020, 508, 145298.
2. Perra D, Drenchev N, Chakarova K, Cutrufello MG, Hadjiivanov K, RSC advances, 2014, 4(99) 56183-7.